"AN EXPERIMENTAL INVESTIGATION ON REMOVAL AND RECOVERY OF PHOSPHORUS USING SLUDGE CONDITIONED WITH SKELETON MATERIAL"

Thesis

submitted in partial fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

by

RASHMI H R

(177115CV010)

Under the Guidance of
Dr. C P DEVATHA

DEPARTMENT OF CIVIL ENGINEERING

NATIONAL INSTITUTE OF TECHNOLOGY KARNATAKA

SURATHKAL, MANGALORE-575025

OCT, 2021

D E C L A R A T I O N

I hereby declare that the Research Thesis entitled **AN EXPERIMENTAL INVESTIGATION ON REMOVAL AND RECOVERY OF PHOSPHORUS USING SLUDGE CONDITIONED WITH SKELETON MATERIAL** which is being submitted to the **National Institute of Technology Karnataka, Surathkal** in partial fulfillment of the requirements for the award of the degree of **Doctor of Philosophy** in **Civil Engineering,** is a bonafide report of the research work carried out by me. The material contained in this Research Thesis has not been submitted to any University or Institution for the award of any degree.

……………………………………………

(177115CV010, Rashmi H R)

Department of Civil Engineering

Place: NITK, Surathkal

Date: 07/10/2021

C E R T I F I C A T E

This is to certify that the Research Thesis entitled **AN EXPERIMENTAL INVESTIGATION ON REMOVAL AND RECOVERY OF PHOSPHORUS USING SLUDGE CONDITIONED WITH SKELETON MATERIAL,** submitted by **Mr. RASHMI H R, (**Register Number:**177115CV010),** as the record of the research work carried out by her, is accepted as the Research Thesis submission in partial fulfillment of the requirements for the award of the degree of **Doctor of Philosophy.**

(Dr. C P Devatha)
Associate Professor and Research Guide,
Department of Civil Engineering,
NITK, Surathkal

Chairman – DRPC
Department of Civil Engineering
NITK, Surathkal

Date: 07/10/2021

Acknowledgment

With my deepest gratitude, I would like to thank my supervisor, Dr. C P Devatha, Associate professor, Department of Civil Engineering for giving me the opportunity to undertake this research project under her supervision and guidance. I would not be the researcher I am today without her support, suggestions, valuable discussions and continuous provisions that benefited me much in completion and success of this study.

I would like to thank Dr. B R Jayalekshmi, Professor and Head, Department of Civil Engineering, NITK Surathkal for providing necessary facilities. I would like to thank all the faculty of Civil Engineering Department. I would like to thank Mr. Manohar K.Shanbhogue, Senior Technical assistant for his help and contribution towards completing my Laboratory works. I would like to thank Dr. Arun Kumar Thalla, Associate Professor, for his help during my PhD journey.

Finally, special thanks to my dearest and most precious father (H Ramachandra), mother (S Sowbhagya), father-in-law (Ramaiah), Mather-in-law (Venkatalakshmi), sister (Sheela H R), brother-in-law (Basavaraju), Brother (Balakrishna H R) and Sister-in-law (Kavya B C), Shakunthala, Mahadevu, Karthik M, Koushik M, Surya M, Shivashankar, Tanuja, Srihan Krishna and Dhuthikrishna for their support, encouragement and love. My greatest thanks go to my husband (Manjunath R), my daughter (Gritha M) and my son (Rishith Raman M) who make everything and every moment in my life shine brighter, and for their continuous support and prayers and love; my life has no meaning without you since you are the largest part of it. Thank you very much.

I would like to express my greatest appreciation to all those who have contributed in no small means for the completion of this thesis. This is an indication of what your help and support has calumniated in.

Thank you

ABSTRACT

The production of excess sludge in wastewater treatment processes has been a serious issue for the operation of wastewater treatment plants (WWTPs) on both economic and environmental perspective. The disposal of sludge is a challenging task as it increases the handling and transportation cost. Therefore, sludge dewatering is the prominent to overcome the mentioned limitation. Dewatering using low-cost skeleton materials is a promising technique due to its efficiency, economic and environmental point of view. Further, it is a resource of nutrients like phosphorus and nitrates in not only in sludge but as well as in wastewater. However, phosphorus in the waste water leads to eutrophication of water bodies and result in algal blooms. As effluent discharge limits become more stringent, there is continued interest in removing phosphorus from wastewater. To prevent the receiving waters from eutrophication, the Enhanced Biological Phosphorus Removal (EBPR) process is a cost-effective and environmentally-friendly process for phosphorus removal in wastewater treatment systems. Phosphorus recovery from wastewater can help alleviate reliance on imported phosphate and reduce vulnerability to fluctuating prices.

Hence in the present study, objectives have been framed in three phases. First phase deals with dewatering of sludge using the skeleton materials and its characterization. Second phase investigated on phosphorus removal using dewatered sludge by EBPR process and Finally recovery was carried out by crystallization. Reducing the moisture content in secondary sludge is a key factor in reducing the capital costs, operational costs, and transportation costs in wastewater management. In the present study, an attempt has been made to utilize granulated blast furnace slag and modified coconut shell biochar for sludge dewatering.

In first phase, experimental work includes the initial characterization of the sludge and granulated blast furnace slag and evaluation of the dewatering ability of the treated sludge (capillary suction time, moisture content, turbidity, zeta potential, and heavy metal and biopolymer contents). Optimization using the Box-Behnken design was carried out with various operational parameters, and the best performance was

found to be at a pH of 10, a dose of 0.34 g/g dry solids, and a contact time of 14 min. Characterization study was carried out by scanning electron microscopy in conjunction with energy dispersive X-ray spectroscopy, X-ray diffractometry, and Fourier transform infrared spectroscopy to confirm the structural features (dense), elemental composition, and the presence of different functional groups.

Coconut shell is a bio waste and its availability is high as a waste in the coastal region of Karnataka, India. It is modified with ferric chloride to enhance the sludge dewaterability and it is evaluated experimentally (Capillary suction time, moisture content, settleability, zeta potential, heavy metals, and phosphate). Further, scanning electron microscopy, Fourier transformation infrared spectroscopy, and X-ray diffraction characterization were carried out to identify the structure change. A significant reduction in capillary suction time(56sec) and the moisture content (96.5%) of the dewatered sludge cake was obtained. Sludge dewatering using coconut shell biochar modified with ferric chloride was optimized by a Box Behnken method with three main factors including dosage, rapid mixing time, and slow mixing time. Optimum capillary suction time (55.8 sec) was achieved at coconut shell biochar modified with ferric chloride dosage (41% dry solids), rapid mixing time (10min), and slow mixing time (19min). The significant structural change in sludge particles was confirmed through characterization studies. During the dewatering process, the removal of heavy metal (cadmium, chromium, lead, and nickel) and phosphate (50.6%) was evident.

For the second phase, an attempt was made to propose an anaerobic-aerobic process by EBPR induced with crystallization for the removal and recovery of phosphorus using dewatered sludge. An experimental investigation was carried out with the setup (anaerobic-aerobic process) and was stably operated for 125 days. A sequential batch reactor of 4 liters was set up for the alternative anaerobic-aerobic operation fitted with rectangular peddle mechanical stirrer and a air diffuser. Effect of pH on EBPR was studies for one complete cycle in a batch mode. Metabolism of PAOs takes place in anaerobic-aerobic process that is in anaerobic process PAOs releases phosphorus and in aerobic process phosphorus uptake takes place. The phosphorus removal efficiency was achieved in this process as 84%.

Finally, recovery of phosphorus in terms of struvite was performed by crystallization using $MgCl_2$. The recovery efficiency by crystallization was achieved to be 72%. The obtained crystals of struvite were characterized by scanning electron microscope equipped energy dispersive spectroscopy and Fourier transform infrared spectroscopy. The result indicates that the proposed process achieves not only good phosphorus removal but also significant phosphorus recovery. It is compared with the adsorption process using granulated blast furnace slag as an adsorbent for removal of phosphorus and achieved as 86%.

Hence, this study concluded that the use of both quicklime with granulated blast furnace slag and coconut shell biochar modified with ferric chloride as a skeleton material is suitable for conditioning during sludge dewatering. It is an economical and promising option for sludge dewatering. Also, the present investigation proves that proposed enhanced biological phosphorus removal process to be an advantageous prospective substitute for the removal and recovery of phosphorus. Adsorption studies were carried out using GBFS for the comparative study and found to be good adsorbent with the maximum removal of phosphorus.

CONTENTS

List of Tables

List of Figures

LIST OF ABBREVIATIONS

AAT	Anaerobic/Anoxic Tank
ADS	Anaerobically Digested Sludge
AEDS	Aerobically Digested Sludge
ANOVA	Analysis of Variance
ATP	Adenosine tri phosphate
BBD	Box-Behnken Design
BIS	Bureau of Indian Standards
BOD	Biochemical Oxygen Demand
COD	Chemical Oxygen Demand
CSB	Coconut shell biochar
CST	Capillary Suction Time
DD	Disintegration Degree
DGGE	Denaturing Gradient Gel Electrophoresis
DNA	Deoxyribonucleic acid
DO	Dissolved Oxygen
DS	Dry Solids
EC	Electrical conductivity
EBPR	Enhanced Biological Phosphorus Removal
EPS	Extracellular Polymeric Substances
FISH	Fluorescence insitu hybridization
FTIR	Fourier transform infrared spectroscopy

GBFS	Granulated blast furnace slag
GAOs	Glucose accumulating organisms
HAP	Hydroxyapatite
HRT	Hydraulic Retention Time
MAP	Magnesium ammonium phosphate
MBBR	Moving bed biofilm reactor
MBR	Membrane Bioreactors
MCSB	Modified coconut shell biochar
MLSS	Mixed Liquor Suspended Solids
MLVSS	Mixed Liquor Volatile Suspended Solids
P/Ac	Phosphorus/Acetate
PAOs	Polyphosphate Accumulating Organisms
PHAs	Polyhydroxyalkanoates
PHB	Poly hydroxyl butyrate
PPM	Part per million
PRESS	Prediction sum of squares
PRT	Phosphorus Recovery Tank
rbCOD	readily biodegradable chemical oxygen
RNA	Ribonucleic acid
RPM	Revolution Per Minute
RSM	Response Surface Methodology
SBR	Sequential Batch Reactor

SCOD	Soluble Chemical Oxygen Demand
SEM-EDS	Scanning electron microscopy with X-ray microanalysis
SRF	Specific Resistance to Filtration
SRT	Sludge Retention Time
SS	Suspended Solids
TDS	Total dissolved solids
TS	Total Solids
TTF	Time to filter
TSS	Total Suspended Solids
VFA	Volatile Fatty Acid
VOC	Volatile Organic Compound
VS	Volatile Solids
WAS	Waste Activated Sludge
WWTP	Waste Water Treatment Plant
XRD	Powder X-ray diffraction
ZP	Zeta Potential

NOMENCLATURES

Symbol	Description	Unit
Al^{3+}	Aluminum (III) ion	
As	Arsenic	
BOD_5	Biochemical oxygen demand after 5 days	mg/L
Ca^{2+}	Calcium ion	
$CaCO_3$	Calcium carbonate	
CaO	Calcium oxide	
$Ca(OH)_2$	Calcium hydroxide	
$Ca_3(PO_4)_2$	Tricalcium phosphate	
Cd	Cadmium	
CO_2	Carbon dioxide	
COD	Chemical oxygen demand	mg/L
CO_3^{2-}	Carbonate ion	
EDTA	Ethylene diamine tetra acetic acid	
Fe^{2+}	Iron (II) ion	
g/L	Gram per liter	
HCl	Hydrochloric acid	
HNO_3	Nitric acid	
H_3PO_4	Phosphoric acid	
H_2PO_4	Di hydrogen phosphate ion	
H_2SO_4	Sulfuric acid	

KCl	Potassium chloride	
m	Mass of dry adsorbent	g
m^2/g	Square meter per gram	
m^3	Cubic meter	
m^3/d	Cubic meter per day	
kg/d	Kilogram per day	
km^3	Cubic kilometer	
Mg^{2+}	Magnesium ion	
$MgCl_2$	Magnesium chloride	
$MgCl_2.6H_2O$	Magnesium chloride hexahydrate	
$MgNH_4PO_4.6H_2O$	Magnesium ammonium phosphate hexahydrate	
MgO	Magnesium oxide	
$Mg(OH)_2$	Magnesium hydroxide	
mg/L	Milligram per liter	
min	Minute	
mL/min	Milliliter per minute	
N	Nitrogen	
NaOH	Sodium hydroxide	
NH^{4+}	Ammonium ion	
NH_4Cl	Ammonium chloride	
NO^{2-}	Nitrite ion	
NO^{3-}	Nitrate ion	

P	Phosphorus
Pb^{2+}	Lead ion
PO_4^{3-}	Phosphate ion

CHAPTER –1

INTRODUCTION

1.1 General

Rapid population growth and industrialization are depleting natural resources and causing significant environmental issues such as water contamination and soil pollution, among others. wastewater with a wide range of characteristics which when directly disposed into the natural water systems would directly or indirectly affect the surrounding environment, aquatic lives, and human health thus demanding a reliable treatment technology which is sustainable and techno-economically viable.

1.2 Theory

Sewage sludge is a waste product generated by wastewater treatment plants, and processing and disposing of it contributes significant costs to the operation of these facilities. Sludge used to be incinerated, compost, and landfilling before disposal, but as it is not economic and environmentally friendly investigations are carried out on sludge dewatering process which is sustainable technologies so that sludge can be converted to semi-solid which will be easy to handle and transport. Dewatering is a vital step in the treatment and disposal of sludge. Some sludge is used to produce biogas, organic matter, and also a source of energy (Wei et al., 2018). Hence, numerous approaches have been implemented to determine optimal environmental and economical solutions for sludge treatment.

Sludge consists of a various matrix of inorganic particles like contaminants, dirt and microorganisms, fibrous matters, organic particles, and extracellular polymeric substances (EPS) which are bounded with various lipids, proteins, organic acids, and polysaccharides. Improper disposal of sludge results in human health and environmental effects such as odour, pathogenic microorganisms, heavy metal leaching, groundwater contamination, etc. Hence it is very much necessary to dispose of the sludge in a safe, effective, and cost-efficient way (Manu et al.,2017). Composting, incineration, anaerobic digestion, sludge dewatering, landfilling, gasification is the various methods used for sludge processing and handling.

Sewage sludge consists of organic matter in its colloidal form, and it is very difficult to dewater compared to industrially produced sludge. As the particles in the sludge are strongly bonded to each other, settling is prevented and offers resistance to compression and filtration. When the sludge particles are subjected to high compression, deformation of the particles occurs, forming a sludge cake with no voids. In a sludge cake, the voids are usually closed and lead to low filterability and impermeable layers in the filter channel (Chunhong et al., 2019). To overcome this, sludge dewatering has been adopted by utilizing physical/chemical or both conditioners.

Chemical conditioners promote particle agglomeration in the sludge, which forms particles of a larger diameter. The involved mechanism in the charge neutralization of anionic particles with the addition of cationic compounds (Duan and Gregory, 2003). Ferric chloride, ferrous sulphate, ferric chloride sulphate, aluminium sulphate, poly-aluminium chloride, lime, and cationic polyacrylamide are some of the utilized chemical conditioners (Amokrane et al., 1997). The major limitation of using chemical conditioners is the low compressibility of the sludge, which may eventually lead to low filtration.

Physical conditioners are also implemented as filter aids or skeleton builders. Physical conditioners are normally used to improve the mechanical strength and permeability of sludge solids during compression to reduce the compressibility of sludge. These conditioners remain porous when subjected to relatively high pressures and form a stringent and permeable structure during mechanical dewatering (Zall and Galil, 2015). A wide range of carbonaceous materials are usually utilized as skeletal materials, such as rice husks, wheat dregs, wood chips, bagasse, sawdust, and other wastes are also utilized, such as slag, construction, and demolition waste, fly ash, cement kiln dust, lignite, rice husk biochar, cement and tannery sludge incineration ash (Zhu et al., 2018).

The use of physical/chemical conditioners alone cannot enhance sludge dewatering capacity. Mazaheri et al., (2018) examined sludge conditioning using moringa peregrina and ferric chloride individually and using a mixture of Moringa peregrina and a small quantity of ferric chloride. The application of both Moringa peregrina and ferric chloride exhibited a synergistic effect and increased the permeability of dewatered sludge. Several investigations on sludge dewatering using both physical and chemical conditioners have been carried out, which, in turn, enhanced sludge dewatering performance by achieving better settleability, the release of trapped water, accelerated sludge filterability, and decreased sludge compressibility (Smollen and Kafaar 1997). Hence, it has been inferred that adopting physical and chemical conditioners in combination produces better sludge dewaterability than when implemented individually. Nevertheless, convenient and effective implementation depends upon several factors, including pH, dosage, contact time, time to filter, rapid mixing time, slow mixing time, and speed.

Zhao et al., (2002) stated that sludge conditioning should not only include efficiency in sludge dewatering but also the compressibility of cake. To fulfill this skeleton builder or physical conditioner can be added to the sludge. As the particles in the sludge are strongly bonded to each other so that settling is prevented and also offers resistance to the compression and filtration. The designs of filtration machines were most important in sludge dewatering. Capillary suction time (CST), decanter centrifuge, belt filters, membrane plate press, specific resistance to filtration (SRF) are the most widely considered experiments for sludge dewatering. CST is the method used for assessing sludge dewaterability. This method is a simple way to measure but alone cannot be considered for assessing the dewatering of sludge. It is measured with respect to time. The CST test is taken up using a cylindrical column, filter paper, and a timer. A whatman filter paper is used to check the movement of water in the sludge with respect to time to find the efficiency of sludge dewatering. SRF is used to measure the rate of filtration for sludge dewatering under constant pressure. For enhancing the sludge dewatering performance, optimization processes are carried out.

Optimization is a real-time control system that makes efficient use of various parameters. The Box-Behnken design (BBD) of response surface methodology (RSM) is a widely used tool for the design of experiments assessing the effects of influencing factors within a system. This tool allows for building a model in a time-efficient way and for achieving the optimum conditions for the desired responses.

The convenient implementation of this approach accounts for how accurately pH, dosage, and contact time are selected (Hansdah et al., 2018). Therefore, trial and error is the most convenient approach for optimizing these variables. The experiments were carried out by changing one factor at a time and the remaining factors will be unchanged for the appropriate set of experiments (Swamy et al., 2014). RSM is a technique used for the design of internal experiments that allows researchers to determine the effects of significant variables, develop their models, and minimize the number of experiments. Analysis of variance (ANOVA) offers tests and statistical data for diagnostic control and empowers researchers to determine the capability of the models and the effect of operating parameters on the optimized condition are described using 3D plots.

Due to the pressure on limited freshwater resources, the wastewater treatment plants end up with polluted wastewater from human and animal waste, infiltrated groundwater, household waste, inflows from surface water, and industrial waste. This wastewater provides essential nutrients for aquatic health, such as phosphorus, nitrogen, and carbon, but they pose a threat in large amounts.

Phosphorus is an important nutrient for our life and the growth of the aquatic plants in the ecosystem. Phosphorus content in the effluents which come out from the industries, household domestic wastewater is affecting the water bodies(Mithra et al., 2017). The excessive phosphorus content causes aquatic plants or algae to overgrow, which in turn decreases the dissolved oxygen content of water bodies and contributes to eutrophication. As a result, phosphorous needs to be eliminated as soon as possible to protect water sources from contamination (Hamming et al., 2016).

Phosphorus is in high demand since 90% of the phosphates available on the earth are used for fertilizers. According to existing data, whatever phosphate minerals are currently present in the world will be depleted in the next 100 years (Nancharaiah, 2016).Increase in algae growth, reduction of dissolved oxygen, and deaths of fishes in the water bodies are mainly due to eutrophication. Due to the abundance of phosphorus and nitrogen content in the water sources, eutrophication is induced, so the elimination of phosphorus in the wastewater is necessary to avoid eutrophication.

The hindrance of eutrophication can be effectively done by phosphorus removal in the wastewater using a closed water system. If phosphorus is high, it leads to different water quality problems like recreation values will be low, the possibility of algal effects, loss in live-stock, and treatment cost will be increased (Arun et al., 2011). Generally, the removal of phosphate from the wastewater is attained by chemical precipitation. Chemical precipitation is costly and also results in increase sludge production but the main advantage of this method is its relatively mere process. During this process, the sludge increase was up to 30% of volume, and also the sludge was contaminated with a high range of heavy metals. As a result, chemical precipitation as an alternative for phosphorus removal is necessary.

The physical and chemical method of treatment involves the usage of high energy, pressure, and chemicals and finally may lead to the release of toxic by-products. Out of all the methods, the biological method is one of the economic, environmentally friendly, as well as oxidized sludge, is produced that is converted as a fertilizer. However, because of the lack of low carbon sources, the biological method of phosphorous removal has a drawback. This limitation can be fixed by using an improved biological phosphorous removal method, which is a relatively new technology.

The sequential batch reactor (SBR) is also termed a fill and draw-type reactor, wherein a single reactor, operating conditions can be separated. When compared to a continuous flows system, the SBR is different as it can be easily suitable for various biological reactions, flow rates can be easily changed, reduction in the cost, and also lower operational management. Therefore for a small wastewater treatment plant, the SBR technique is very much effective.

One such established approach used for phosphorus elimination is enhanced biological phosphorus removal (EBPR). The primary advantages of EBPR in the eradication of chemicals and also a reduction in the sludge during the processes. Biological phosphate removal is one method that has distinct benefits when compared to chemical phosphorus removal. The sludge obtained after the biological phosphorus removal processes has a high agricultural value because phosphates availability is high in the sludge and also a shortfall of other objectionable chemicals. If the phosphorus content is removed by chemical precipitation using aluminium salts or iron salts, the phosphates usually remain in the metals by binding to it after anaerobic treatment (Parsons et al., 2008).

EBPR is an activated sludge process that involves bacteria removing the phosphorus from the wastewater. The biochemical models explain the behaviour of polyphosphate accumulating organisms (PAOs) in the EBPR process. The PAOs metabolism takes place in an anaerobic and aerobic process. During the anaerobic process, PAOs use acetate or propionate which are volatile fatty acids formed due to the fermentative bacteria in the anaerobic process or the VFAs present in the influent to form carbon storage compounds also called polyhydroxyalkanoates (PHAs). The obtained PHAs depend on the type of volatile fatty acids utilized by PAOs (Yadav et al., 2017). Adenosinetriphosphate (ATP) is the energy carrier used for PHAs synthesis. ATPs are generally utilized for the hydrolysis of the polyphosphate and also from glycogen degradation. During the hydrolysis, orthophosphate is released into the liquid phase. The stored glycogen is degraded to get reducing power in terms of $NADH_2$ for the synthesis of PHA. Full or partial tricarboxylic acid will oxidize the VFAs which can also act as a reducing power (Zhou et al., 2010).

In the aerobic process, by utilizing oxygen or nitrate as an electron acceptor, PHAs are oxidized to CO_2. The energy released is used for the formation of growth of new cells, polyphosphate, and glycogen (Oehmen et al., 2007). Various factors affect the EBPR system. In particular, the degradation of the EBPR is due to conflict that arises between PAOs and glycogen accumulating organisms (GAO's). The competition between PAOs and GAOs is influenced by the major parameters; pH, temperature, and carbon source. Microorganisms are one of the responsible factors for the effective functioning of the EBPR system. Studies were carried out to understand and identify the different types of microorganisms present in the EBPR process. Microorganisms like *Acinetobacter, Accumulibacter, Tetrasphaera*, etc., are present in EBPR for metabolism.

On the other hand, phosphorus is one of the key elements which is essential for the growth of the plant and also harmful. Phosphorus is used in major industries like fertilizers, beverages, paints, pharmaceuticals, detergents, and corrosion inhibitors. Phosphorus plays a significant role in our day-to-day life and also it is a non-renewable resource (Tu et al., 2015). Due to the high usage of phosphorus in various fields, there is a complete reduction in the available phosphate such that within 50-100 years there may be the complete exhaust of global phosphate (Eljamal et al., 2013). Hence researchers are developing new technologies for combined removal of phosphorus with recovery options from wastewater.

Other than phosphorous removal and recovery, it has shown good results for the removal of chemical oxygen demand (COD). A denitrifying phosphorous accumulating organism is used in EBPR which acts as the main role by saving carbon source and helps in phosphorus removal. Various methods like induced crystallization, precipitation, adsorption, and membrane technology are coupled with EBPR which yields better results for the recovery of phosphorous.

Phosphorus can be recovered by various means like EBPR, constructed wetland system, precipitation, and struvite crystallization. However, recovering phosphorus as magnesium ammonium phosphate (MAP) through crystallisation has the added benefit of recovering both nitrogen and phosphorus at the very same time. Struvite is also called a MAP as it consists of magnesium, ammonium, and phosphorus in equimolar concentration (Muster et al., 2013). Struvite is a white crystalline, an environmentally friendly substance that can be used as a fertilizer as it contains a low concentration of heavy metals and low nutrient release rate when compared to phosphate rocks (Bing et al., 2019). The two main factors responsible for the struvite precipitation are pH and molar ratio of Mg: NH_4: P. Equation 1 can be expressed as the basic chemical equation of the struvite.

$Mg_2^+ + NH_4^+ + PO_4^{3-} + 6H_2O \rightarrow Mg\ NH_4\ PO_4 .\ 6H_2O$ ……………………….... 1.1

With this background, a thorough literature survey was done in line with the above discussion, objectives were derived from the gaps identified in the area and addressed appropriately.

1.3 Objectives

Based on the research gaps, the following research objectives have been formulated for the present research.

- To investigate the suitability of skeleton material (Granulated blast furnace slag and coconut shell biochar) for sludge dewaterability.
- To investigate the potential for phosphorus removal using dewatered sludge by enhanced biological phosphorus removal and assess the effect of pH.
- To investigate the phosphorus recovery through crystallization as a struvite.

1.4 Thesis outline

The thesis has been organized into six chapters as under

Chapter 1 is a general introduction and addresses the objectives and outline of the thesis.

Chapter 2 Literature review on sludge dewatering, EBPR, and crystallization.

Chapter 3 presents the materials and methodology used for the experimental studies on sludge dewatering, EBPR, and crystallization.

Chapter 4 presents the results and discussion for experimental investigation on sludge dewatering using GBFS and MCSB- $FeCl_3$ as skeleton material.

Chapter 5 presents the results and discussion for phosphorus removal by EBPR induced with crystallization for its recovery and the effect of pH.

Chapter 6 outlines conclusions and the future scope of work.

CHAPTER 2

LITERATURE REVIEW

2.1 General

Due to the ever-increasing stringent regulations imposed on wastewater management around the world, researchers are actively working on new technology and improvements to meet the requirements. Biological treatment is the most efficient and cost-effective choice among the numerous wastewater treatment solutions. This chapter aimed to provide a review of current research in the field of study to highlight any flaws or gaps.

In this chapter, investigations carried out on the development of the sludge dewatering process and a review of the existing dewatering process variants are presented. A brief literature review of the biological process and crystallization for the removal and recovery of phosphorus is also reported.

2.2 Introduction

Due to the rapid growth of industrialization and population, the amount of sludge produced is increased. As every year, the sludge quantity is increasing, sludge handling and transportation costs are also increased, which often make up fifty percent of the treatment costs when compared to the entire wastewater treatment. The sludge quantity varies according to the population and sewerage expansions etc., the sludge content generation is increasing every year which leads to the increase in transportation and handling cost and also, the impacts on the environment (Sanin et al., 2011).

Various types of sludge are available like primary sludge, biological sludge, mixed sludge, digested sludge, mineral sludge, and physical-chemical sludge. Also, there are different forms of water in the sludge, shown in Figure 2.1 and 2.2, which are as follows,

1. Free water: - Water that can be easily isolated by gravitational settling. Free water is not chemically or mechanically bound to the sludge. Around 75% of the water in the sludge is free water.

2. Interstitial water: - The water which is surrounded by the sludge particle as a floc and which can be removed by mechanical dewatering means. About 20% of the water in the sludge is of interstitial water

3. Vicinal water: - It is also very difficult to extract the water that is physically attached to the sludge particles. Around 2% of the water in the sludge is vicinal water.

4. Water of hydration: - Water that is chemically bound to the particles of sludge. About 2.5% of the water in the sludge is the water of hydration.

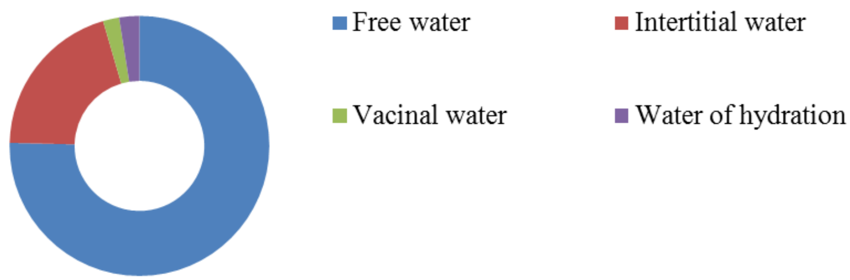


Figure 2.1 Variation of water content in the sludge (Mowla et al., 2013)

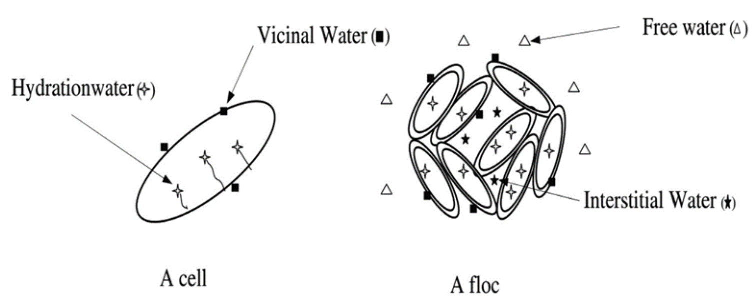


Figure 2.2 Different water forms in the sludge (Mowla et al., 2013)

The sewage sludge characteristics and the quantities are based on its sludge type and also the level of treatment. Sludges are classified into different forms

1. Primary sludge: - The sludge collected from the settling chamber.
2. Biological sludge: - Sludge obtained during the biological treatment
3. Digested sludge: - This is the sludge produced from the biological stabilization.
4. Mixed sludge: - It is a mixture of primary and biological sludge.
5. Physico-chemical sludge: - It is generated by the Physico-chemical treatment of wastewater.
6. Mineral sludge: - it is produced from the mineral industries, quarry, etc.,
7. Tertiary sludge: - it is generated from tertiary treatment of wastewater.

2.3 Characteristics of the sludge

Sludge has a very high convoluted nature due to which there is a vast change in its characteristics like physical, chemical, and biological. Understanding the behavior of sludge and its characteristics is the most difficult issue in the treatment of sludge. However, it is important to study its properties and understand the concept and also its effect on the treatment system.

In the earlier study it was shown that, as the sludge quantity increases, the phosphorous content decreases. So it was stated that, sludge characteristic changes with respect to the source (Xie et al. (2005). Table 2.1 shows the physical, chemical, and biological characteristics of the sludge).

After sludge conditioning, thickening, and digestion, sludge is dewatered before processing for incineration, landfilling, and composting, which leads to a reduction in sludge content and sludge transportation cost (Feng et al.,2009). Figure 2.3 shows the main stages involved in sludge treatment processes.

Sludge dewaterability is also sometimes referred to as sludge filterability. The main goal of dewatering is reducing the solid content volume. There are different ways to improve the dewaterability of bio sludge. Scholz et al., (2005) reported that the filterability of sludge is used to check initially the output of dewatering. Also, analysed and concluded that sludge treatment, transportation of sludge, and disposal of sludge requires 50 to 60% cost of wastewater treatment in the treatment plant.

Table 2.1 Physical, chemical, and biological characteristics of sludge

Sl No	Physical Characteristics	Chemical Characteristics	Biological Characteristics
1	Odor	pH	Microbial community
2	Colour	Alkalinity	Surface polymers
3	Drainability	Solid concentration	Sludge stability
4	Specific gravity	Surface charge	
5	Settleability	Fertilizer and nutrient value	
6	Particle size and shape	Heavy metal and toxic organics	
7	Water distribution	Digestibility	
8	Dewaterability	Fat content	
9	Filterability		
10	Rheology		
11	Floc porosity		
12	Floc structure		
13	Floc density		
14	Thermal conductivity		
15	thermal content		
16	Compressibility		

Sources: Xie et al., (2005)

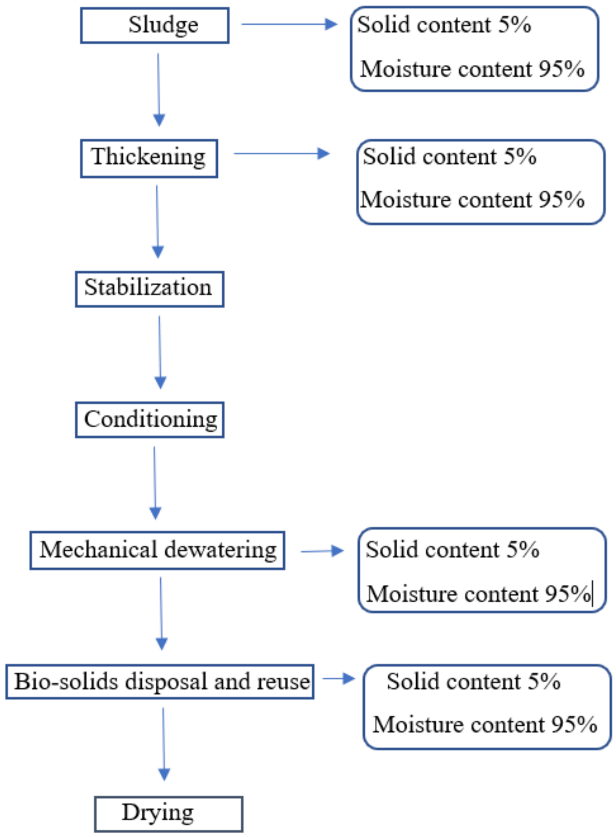


Figure 2.3 Main stages involved in sludge treatment processes (Feng et al.,2009)

2.4 Sludge conditioning

Solid-liquid separation is necessary and can be achieved by mechanical thickening and sludge dewatering by conditioning. Physical processes, biological and chemical processes are the methods used for sludge conditioning and these methods change the characteristics of the sludge by gaining the dewatering performance by enhancing the settleability, filterability, and also by releasing the trapped water.

2.4.1 Chemical conditioning

For the treatment of sludge in wastewater treatment plants, chemical conditioning is carried out using organic or inorganic additives. Chemical conditioning is done in small-scale researchers when compared to large-scale treatment. The main intention of sludge conditioning is to create a rigid lattice structure so that the liquid content easily flows between the sludge particles without resistance (Wang et al., 2019).

The efficiency of Chemical conditioning is affected by various factors, like properties of the sludge, type of sludge, type of conditioners used, pH, mixing rate, dewatering method, etc., The conditioners for the sludge conditioning are selected based on the sludge type to be dewatered. The two main mechanisms which take place in chemical conditioning are neutralization and particle bridging, for the formation of floc structure. Usually, the wastewater sludge possesses an anion charge hence for the neutralization process a cation charge additive is used so that individual particles are flocculated. Following are the various chemical conditioning methods.

- Organic additives: Organic polymers in the form of polyelectrolyte are used for many years to enhance the efficiency of mechanical dewaterability during the conditioning of sludge. Two different mechanisms may clarify sludge conditioning by polyelectrolytes: charging neutralization and interparticle bridging (Thapa et al., 2009b).
- Inorganic additives: Non-organic polymer approach of sludge conditioning to cut down, the possible unfamiliar hazards associated with the extended handling of polymers in wastewater treatment. Fenton's advanced oxidation process (AOP) of sludge is specified and its associated reagents, as possible alternatives for alum sludge conditioners as sludge ozonation for this reason (Lu et al., 2003).

2.4.2Physical conditioning

From an economic and environmental point of view, physical conditioning techniques are usually more beneficial among the methods used to increase the dewatering capacity of bio sludge. Various physical conditioners used for physical conditioning are shown in Table 2.2. Physical conditioners, including minerals and carbonaceous materials, have been used to help in the mechanical dewatering of sludge.

Table 2.2 Various physical conditioners

Form of filter aid	Skeleton materials
Inorganic	Alum sludge
	Fly ash
	Gypsum
	Lime
	Cement Kiln dust
Carbonaceous	Coal fines
	Wood chips
	Wheat dregs
	Bagasse
	Rice shells
	Sawdust
	Char

Non-chemical additives are also called physical conditioners. Physical conditioners are highly porous inert materials that minimize high compressibility, enhance solid permeability, and enhance sludge mechanical power. Carbonaceous materials have a high advantage in the process of dewatering sludge when compared to mineral materials since it contains a high heating value, high porosity, and low ash content. Measuring the difference in cake properties, such as resistance to variable filtration, the output of net sludge, permeability, and porosity of the cake, helps to identify the beneficial role of physical conditioners in increasing sludge dewaterability (Luo et al., 2013). Following are the various physical conditioning methods.

- Non-Chemical Additives: Due to their function in reducing sludge compressibility and improving the mechanical strength and permeability of sludge solids during compression, the most well-known classical form of physical conditioning is the application of some highly porous inert minerals that serve as skeleton builders or filter aids (Gungoren et al., 2018).

- Cavitation pre-treatment: Cavitation is a mechanism by which the local pressure in the aqueous phase is reduced below the equilibrium vapour pressure and some micro cavities or micro bubbles are created after reaching an unstable diameter, gradually rising and violently collapsing. This method generates a shock wave that locally causes high temperatures (500-15,000 K) and high pressure (10-500 MPa) in the media (Cai et al., 2018).
- Thermal pre-treatment: Water sludge is treated at 60-180℃ temperatures. Although sludge lipids and carbohydrates are easily degradable, the proteins are shielded from enzymatic hydrolysis by the cell wall. In this range, thermal pre-treatment will split the cell wall and release the biologically degrading protein (Gokce et al., 2019).
- Freeze/Thaw treatment: Freeze/thaw conditioning is one more physically effective way to alter the arrangement of the floc and to decrease the content of bound water in the sludge. Meanwhile, in the process, the temperature will be below the freezing point of water, the sludge is first frozen, about 15^{0}C, and kept at this state for some time, and then thawed at room temperature. Water and solid particles separate during the formation of ice crystals (Reed et al., 1986).

2.4.3Biological conditioning

By disrupting the gel structure of flocs by hydrolysis of EPS contained in the sludge, the biological or enzyme pre-treatment of sludge increases the dewaterability of sludge. Since enzymes are proteins and are therefore considered environmentally friendly, this technique can be very appealing, especially if it replaces synthetic polymers based on neurotoxic acrylamide (To et al., 2014).

The influence, individually or in combination, of industrial microbial cellulase, protease, and lipase enzymes on the decrease in solid disposal content of anaerobically digested wastewater sludge. A mixture of these enzymes has been found to decrease total suspended solids by 30-50 percentages in equal proportion by weight and increase solid settlement. To extract EPS from sewage sludge, enzymes and enzymes combined with sodium tripolyphosphate (STPP) were introduced. They concluded that enzymes released higher amounts of total EPS in combination with STTP relative to enzymes on their own (Phuong et al., 2018).

2.5 Sludge dewatering

Dewatering will be taken up before incineration or thermal drying because it reduces the fuel consumption and also a reduction in the leachate as the sludge disposal to landfill is less. Sludge dewatering helps to remove as much water from the sludge as possible, resulting in a decrease in the number of bio solids and subsequently, the transport costs. Dewatering methods widely used include mechanical methods and thermal processes. Sludge often needs a conditioning procedure before mechanical dewatering to improve the efficiency of water content removal (Xiao et al., 2019).Figure 2.4 shows the flow chart of various dewatering methods.

Based on the volume as well as characteristics of the sludge, different processes are identified. Mechanical dewatering processes are compared to thermal ones when considering the economy. There are two key criteria used as dewatering output representatives, which are the concentration of solid cake and the consistency of supernatant. The vital role of the dewatering process is to maximize the solid sludge content to reduce the volume of sludge; dry solid content should be specified as a parameter that represents the process's efficacy. Although supernatant quality represents the efficiency of solid capture during the process of conditioning and dewatering, in particular when the centrifugeis used as a dewatering process. It is necessary to extract as many solids as possible during conditioning and dewatering for the efficient operation of the sewage treatment (Gao et al., 2019). When the supernatant is returned to the head – of – works, it reduces solids disposal to the plant inlet. Meanwhile, the aim of dewatering sludge in all wastewater treatment plants is to produce a clean supernatant thus obtaining a cake with high solids content.

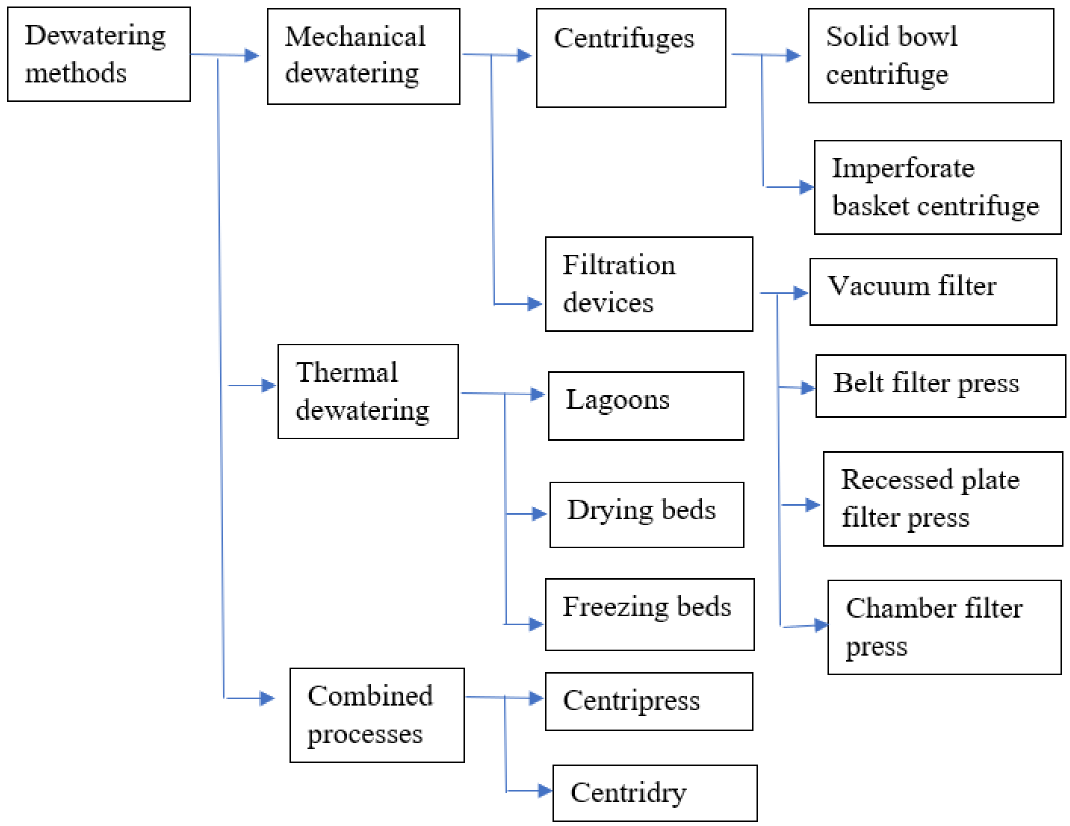


Figure 2.4 Flow chart of dewatering methods(r)(Xiao et al., 2019)

2.6 Assessment of sludge dewaterability

Several tests used to measure the efficiency of various conditioners often provide useful information that can be used to determine sludge dewaterability. Assessment of sludge dewaterability is important for any sludge treatment system and also the goal is to optimize the dewatering process. Nonetheless, due to the volatile and mysterious nature of the sludge forms along with differences in dewatering methods, this work is fairly challenging. Since the very first dewatering indices were established, numerous indicators for the dewatering process have been developed and applied over the years in combination with dewatering technology.

Despite these advances, however, there is no structured dewatering index yet that can fully represent the ability to dewater sludge. An accurate dewatering index is believed to not only approximate the actual water separation but also to estimate the overall achievable solid content of the sludge cake. One or both of these tend to lack traditional dewatering indices, and therefore they hardly convey the efficiency of dewatering properly. Following are the various indices for the assessment of sludge dewaterability.

i. SRF: Specific resistance is numerically equal to the pressure needed to generate a unit flow rate through a cake with a unit weight of dried solids per unit area if the liquid's viscosity is variable. SRF method has many significant benefits, as independent of the concentration of solids. It can be used particularly to estimate the concentration of the final cake after dewatering. Most of the techniques developed to determine the dewatering efficiency of filtration devices such as vacuum filters, belt presses, and filter presses. These tests were time-consuming and the procedures are very complicated and involve a high degree of skill (Vesilind et al., 2000).
ii. CST: The CST check is achieved by inserting a sludge sample in an upright metallic tube resting on a grade paper with chromatography. Paper's capillary suction extracts liquid from the sludge, dampens up the surface. The filtrate time needed to flow 1 cm is reported as CST. It is simpler and uncomplicated to test, and requires less expertise than measuring, making it more common recently. CST was originally designed to calculate the dewatering rate as a replacement for freshwater. Given that, in reality, CST is still not considered to be a fundamental method of measuring the dewaterability of sludge. Unlike SRF, CST is influenced by the solid concentration and cannot detect the final cake solids that can be achieved by dewatering devices (Chen et al., 2010).
iii. Time to filter (TTF): The TTF test consists of placing a sludge sample with a vacuum application in a Buchner funnel filled with a filter paper, and measuring the time needed for the collection in the graduated cylinder of a fixed volume of supernatant (usually 50 percentage of the sample volume). The amount of time it

takes to obtain the specified filtrate volume is the TTF. The minimum TTF value is set to imply optimum sludge conditioning. The Time-to-Filter (TTF) test is an attempt to simplify the complicated procedures involved in the more basic SRF testing. The TTF test involves measuring the time needed for filtration of sludge or a conditioned sludge sample, rather than the actual resistances, using the same laboratory technique as the SRF test (Rashmi et al., 2019).

iv. Zeta potential: Zeta potential (ZP) is the electrical potential that occurs over a solid particle at the shear plane. The shear plane is the interface that behaves as the barrier layer of water, that stays further from the particle that travels in alliance to the particle, with the solid and water. Due to its quantification of the electrical potential that induces interparticle repulsion, ZP measurements have been used to test particle stability and successful flocculation. A near-zero ZP indicates minimal electrical repulsion, allowing attractive van der Waals forces to affect the agglomeration of particles.

v. Rheology: In the management of sewage sludge, rheological parameters are very important, not only as of the design of parameters in transport, storage, landfilling, and spreading operations but also as the control of parameters in many treatments, such as stabilization and dewatering. While early research on the rheological behavior of sewage sludge has been carried out since the 1930s. Until recently, more studies have attempted to examine the rheology of sludge dewaterability with the goal of forecasting, monitoring, and optimizing conditioning and sludge dewatering. (Lidia et al., 2008).

Current dewatering indices are likely to lack and also dewatering efficiency was intended rarely. SRF is unmanageable in connection with the instrument and it is time-consuming, however, after filtration, it only estimates the sludge content. Although CST is commonly used and has gained popularity because it is simple to quantify sludge dewaterability, the only downside is that the concentration of solids cannot be predicted. CST and SRF are associated with free water, nearly 20% of the total water content will be taken part (Peng et al. 2017).

Qi et al., (2011) stated that the inclusion of filter aids increases in structural strength, permeability, and porosity of the cake while reducing compressibility. To find out what's influencing these advantages, having identified the particle size of the filter aid (fly ash) and *Moringa orifiers*, and discovered that fly ash with higher carbon content and a particle size of 10-30m works best. This indicates that the relationship between the particle size of the sludge and the filter aid is important in determining, how effective a particular filter aid will be.

Chen et al., (2010) conducted an in-depth study to elicit further understanding into the mechanisms by which filter aid action is occurring. They found, using a modified coal fly ash filter aid, that specific filtration resistance decreased, and proposed that the mechanisms causing this include charge neutralization, adsorption bridging leading to improved floc formation; as well as skeleton building. Adsorption and charge neutralization as processes generally involve electrostatic forces and/or chemical bonding/interaction of functional groups. Thus, the chemical characteristics of the material will likely influence its ability to adsorb or neutralize the charge. As Chen et al., (2010) demonstrate chemical modification of coal fly ash, was able to improve its effectiveness as a filter aid.

Meyer et al., (2017) investigated that dewatering of bio sludge is more difficult compared to primary sludge. Where the study on dewatering of bio sludge adding pulp and paper industry, primary sludge has enhanced the dewaterability of bio sludge in terms of dewatered sludge. It has been investigated that dewatering of bio sludge using various ratios of pulp and paper industry primary sludge. The addition of primary sludge up to 40% has led to an increase in the efficiency of dewatering whereas further addition has led to a very small increase in dewatering efficiency. Even the total suspended solids in the sludge sample were reduced. The monovalent and divalent ratio was higher in the primary sludge as the concentration of sodium is higher. Particle size distribution studies are carried and the colloidal particles of 1 – 100micro meter Equi diameter particles were seen largely in bio sludge when compared to primary sludge.

Gungoren et al., (2018) studied the characterization of flocs in the dewatering of coal plant tailings. For the flocculation of the samples, SNF-923 was used with varying dosages to determine the turbidity and particle size. During the study the settling behaviour of the coal tailings was examined, where the size of the particles was increasing with the increase of dosages, 150g/t was found to be the optimum dosage. The authors also stated that the efficiency of flocculation is determined in terms of size and strength of floc. During the process of dewatering coal plant tailings, SNF-923 was considered an important and simple tool for the characterization of floc.

Phoung et al., (2018) determined a novel method for sludge dewatering using a suitable polymer. Zetag 8165 and Zetag 8180 was used by dissolving in de-ionized water. Various characteristics of the sludge was studied and conditioned with the polymers. The Y-intercept and Higgins modified centrifugal technique are used in this analysis to determine the optimal dose. Results of Y-interpret technique, show that the amount of polymer required is high as the neutralization process takes place in anaerobic activated sludge, during the conditioning. For accomplishing anaerobically digested sludge, dewatering a polymer of high charge density or cross-linked polymers can be used. The Higgins approach optimized polymer use there by addressing the relationship between dewatering, digestion, and conditioning.

Gao et al., (2019) studied sludge dewatering by a new method combining hydrothermal carbonization and mechanical compression. Various conditions like mechanical pressure temperature and residence time with operating mode was determined. The results indicated that the mechanical compression has an efficient outcome compared to other modes when the investigation was done on the site. During the hydrothermal pre-treatment, within 60min, moisture content was reduced effectively at the temperature of 160^0-$240^0$and also the decrease in the solid content was less than 60%. Whereas the effect of the mechanical pressure was not significant hence it is suggested to use pneumatic filtration in the future study despite mechanical pressure for the filtration process.

Xiao et al., (2019) studied the effect of biological treatment with electrochemical pre-treatment for the sludge dewatering treatment. To determine the sludge dewaterability, CST was used as the main test. The authors stated that the effective dewatering was done at 5min of electrochemical pre-treatment and 12 hrs of biological treatment. The decrease in negative charge decreased viscosity, and protein content removal from the sludge, also indicated efficient sludge dewatering. Various bacteria's like *Nitrospera, Rodnobacter, Acidocella, and Alicylobacillus*supported sludge dewatering, overall, the new process was found to be efficient in the dewatering of sludge.

Liang et al., (2019) studied the removal of EPS and bound water to enhance dewaterability of the sludge using Skeleton materials like calcium hypochlorite oxidation, ferric coagulant re-flocculation, and walnut shell. In the sludge, if EPS and bound water content are high, it directly impacts sludge dewaterability. Here the authors stated that the above-mentioned conditioning process helps in the removal of EPS and bound water. Various tests have been conducted and saw the change inbound water, morphological structure, rheological behaviour, EPS distribution, and floc morphology. The sludge cake moisture content was reduced to half using the new technique of pressure filtration and conditioning with calcium hypochlorite oxidation and ferric coagulant. The three-step mechanism was found in this process,

- Protein and polysaccharides in the EPS and bound water were degraded.
- Charge neutralization.
- A rigid lattice structure was formed using walnut thereby reducing the viscosity and increasing the filterability.

The authors stated that this process has a lower impact on the environment as well as advantageous compare to other treatments.

Wang et al., (2019) studied on dewaterability of sludge using inorganic coagulants and cationic polyacrylamide. Either flocculants or coagulants are used in dewatering of the sludge but in this work, both coagulants and flocculants are used for sludge dewatering. An investigation was carried out using inorganic coagulants and cationic polyacrylamide for the dewatering of sludge. Based on the CST, results indicated that the effect on dewaterability using combined flocculants or coagulants is the same as using either flocculants or coagulants alone. But, combine flocculants or coagulants usage has led to minimizing the moisture content of the sludge. Based on the rheological and physicochemical properties of the sludge, it is stated that there is a decrease in viscosity and bound water and disintegration of a microbial cell which indicates that there is a synergetic effect on the sludge. It is proposed that usage of inorganic coagulants and cationic polyacrylamide mixture has improved in sludge dewaterability using either flocculants or coagulants alone. Table 2.3 shows the different dewatering properties using different sludge types and physical/ chemical conditioners.

Table 2.3 Dewatering properties

Sludge	**pH**	**Solid concentration (mg/L)**	**Conditioner (Physical /Chemical)**	**Sample (ml)**	**Rapid mixing time**	**Slow mixing time**	**SRF reduction**	**CST Reduction**	**Reference**
Alum sludge	6	2850	Fe^{2+}/H_2O_2	250	30Sec	1 Min	-	48	Tony et al., 2008
Alum sludge	6.6-7.3	6400-6800	Gypsum	200	30Sec	1 Min	51	-	Zaho 2002
textile dyeing sludge	6.7-6.9	1900-2000	Sawdust/cationic polyacrylamide (CPAM)	200	20Sec	40Sec	64	-	Luo et al., 2013
Anaerobic sludge	6	15000	Chitosan/ poly (acrylamide-co-diallyldimethylammonium chloride (PAM)	250	300/ 60sec	50/30sec	-	78	Lau et al., 2017
sewage sludge	6.7	6400	Modified, corn core powder	100	500/30 min	100/ 5 min	55	-	Guo et al., 2019
sewage sludge	6.9	8400	Ethanol and Fe(III)-rice husk	500	300/45 min	200/10 min	-	78.5	Chen et al., 2020

2.7 Optimization

In the statistical design of experiments, RSM plays a significant role in designing. RSM is a set of statistical and mathematical techniques that are beneficial for process growth, enhancement, and optimization (Myers et al., 2004). It has major applications in the design, manufacturing, and formulation of novel products, as well as the enhancement of existing product designs.

In this study BBD was used for the experimental model design with 3 factorial. In the sludge dewatering study, where optimization demanded 17 experimental runs, a 3-level BBD was employed. The independent variables for optimizing the responses of interest, including dosage, pH, and contact time. Sludge dewatering depends on various parameters (pH, dosage, speed, time, turbidity, ZP, sonication). To identify the better dewatering efficiency optimization procedure is applied. Optimization can be done by various methods, of which Box-Behnken is well applicable and efficient.

In order to describe the causes for changes in the output response, Montgomery (1997) describes an experiment as a series of tests, called runs, in which changes are made in the input variables. RSM is an experimental design technique that helps researchers construct models, determine the effects of multiple variables, and achieve the optimal conditions for favorable responses. Furthermore, it reduces the number of experiments in a sample(Shahin et. al., 2009).

Edmondson (1991) offers a fascinating approach of RSM to greenhouse research and in comparison, to an industrial setting, provides certain useful insights towards the use of RSM in an agricultural context. In a conventional farming environment, designs drawn from the RSM model can also be used to a better advantage.

Atapour&Kariminia (2013) concluded that in order to optimize the design parameters, RSM was an effective tool. The fuel properties of BaO biodiesel produced was similar to those of other research and verified in accordance with EN 14214 and ASTM 6751 specifications under ideal operating conditions.

The working circumstances needed for optimal potato tuber yield production in Kenya were examined by Muriithi (2015). The method of potato production was optimized by the combination of various three-level design and RSM factors. RSM has been used to examine and optimize the cumulative effects of water, nitrogen, and phosphorous mineral nutrients. 70.04% irrigation water, 124.75 Kg/Ha nitrogen supplied as urea, and 191.04 Kg/Ha phosphorus supplied as triple superphosphate were identified to be the optimum production situation for the potato tuber yield. In summary, improved potato productivity will boost the well-being of Kenya's smallholder potato farmers and also save farmers additional input costs.

Guan et al., (2017) explored the possibility of using a magnetic field for the disintegration of sludge. After different magnetic field treatment, roughly 41.01% disintegration degree (DD) was achieved after 30 min at 180 mT magnetic field pressure. Protein and polysaccharide content has increased significantly. This experiment was optimized using a BBD with RSM to suit the DD multiple equations. The overall DD was 43.75% and the amount of protein and polysaccharides raised to 56.71 and 119.44 mg/L, respectively, while the magnetic field strength was 119.69 mT, the response time in the optimization study was 30.49 min, and the pH was 9.8. Using BBD with RSM, the integrated experiment was also optimized to suit the various DD equation. This work has shown that waste-activated sludge can be efficiently disintegrated by a magnetic field and could be coupled with other physical methods for better performance, like ultrasound.

Panahi et al., (2019) studied the removal of cephalexin antibiotics from synthetic wastewater, mesoporous silica such as MCM-41 has been used as an adsorbent. The effects of the initial pH, adsorbent dosage, initial adsorbate concentration, contact time, and process efficiency temperature were evaluated using Box-Behnken statistical experiment design (RSM). pH, adsorbent dosage, initial antibiotic concentration, temperature, and quadratic pH were all found to be significant and likely to be less than 0.05. The optimal removal state, according to variance analysis and the quadratic model, was an initial pH of adsorbate solution of 3.00, an adsorbent dose of 800 mg L^{-1}, an initial concentration of adsorbate solution of 3.00, and 50.0 mg L^{-1} antibiotic at a temperature of 40.0 ° C and 30.0 min at the time of adsorption. Under these conditions, the cephalexin antibiotic elimination percentage was 90.3%. The mesoporous silica can therefore be used for the adsorption of cephalexin antibiotics under ideal conditions built by RSM.

Almahbashi et al (2020) developed activated carbon as raw material using sewage sludge. The enabled carbon-based sewage sludge processing process was optimized by implementing BBD to the RSM. The optimization method examined the effect on the surface area of activated carbon of the relation among chemical activation ratio, contact time, and activation temperature. A sequence of activated carbons in the tube furnace was chemically activated utilizing potassium hydroxide (KOH) and physically activated through pyrolysis. With a chemical activation ratio of 1, an activation contact time of 3 hours, and an activation temperature of 500 °C, a maximum surface area of 377,7 m^2/g was obtained. The most important parameter, according to statistical analysis, was contact time, preceded by the chemical activation ratio and temperature. Table 2.4 shows the optimization of different variables using the various optimization process.

Table 2.4 Optimization properties

Analytes	Samples	Analytical techniques	Objective of study	Optimization process	Reference
Metal removal	Anaerobically digested sludge	Ultrasonic Fenton system	Evaluate the dewaterability and metal removal	BBM	Rumky et al., 2018
Pigment content	Beetroot	Spectrophotometer	Extracting natural pigment from the beetroot	BBM	Swamy et al., 2014
COD, Turbidity, Color and TSS removal	Leachate sample	Coagulation and flocculation	Comparative suitability of PAC and alum as coagulant.	CCD	Ghafari et al., 2009
Pb II removal	Antep-Pistachio shell	Elemental analyser	Adsorption studies	BBM	Yetilmezsoy et al., 2009
Dewatering	Coal fine tailings	Settling rate	To achieve the desired settling performance	BBM	Hansdah et al., 2018
hexavalent chromium (Cr(VI))	cassava sludge-based activated carbon (CSAC)	adsorption	to optimize various factors influencing the removal of Cr(VI)	BBM	Guo et al., 2021

2.8 Necessity of phosphorous in the present scenario

Phosphorous is the second-largest nutrient in the human body. In our daily activities, phosphorous is provided by the effect of adenosine triphosphate (ATP) and deoxyribonucleic acid (DNA) as major constituents. Phosphorous is a required component in many items including toothpaste, detergents, corrosion inhibitors, and stabilizers in plastics (Cisse and Mrabet, 2004). Figure 2.6 shows the phosphorous cycle with human interruption.

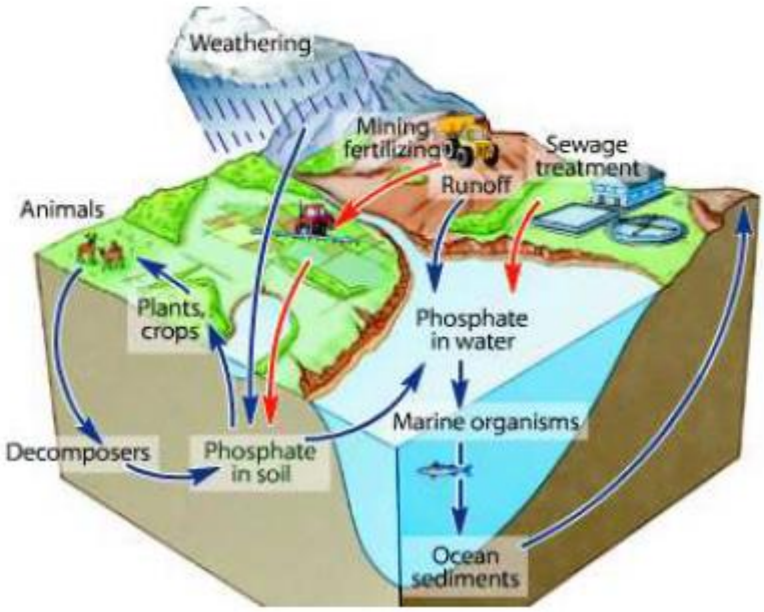


Figure 2.6 Phosphorous cycle with human interruption (Cain et al., 2006)

Demand for the production of chemical fertilizers increases around 1.8% each year protecting the food supply for the increasing world population. It is projected that global fertilizer demand would experience modest annual growth to hit 199.4 million tons over 2018 (Heffer et al., 2014). Improvements in the average annual growth rate of all three main nutrients are expected at 1.5, 2, and 2.9 percent respectively, for nitrogen, phosphorus, and potassium. Industrial chemical fertilizer output relies strongly on the usage of non-renewable fuels (e.g. natural gas) and small mineral reserves (e.g. phosphate rock).

Over 90% of phosphate rock deposits were found in just five nations, such as Morocco, Iraq, China, Algeria, and Syria. Western Europe and India depend entirely on imports to meet the domestic phosphorous fertilizer market. In several countries, nutrient supply is associated with modern agriculture and food stability. This situation calls for an immediate need to implement better nutrient management activities as well as to recognize alternate sources of phosphorous (Mohan et al., 2011). Understanding the presence of phosphorus in an aqueous solution requires effective control methods to be chosen.

Phosphorus can occur in different ways in natural bodies of water (Figure.2.7). However, algae development can only be stimulated by orthophosphate, causing eutrophication (Bhojappa, 2009). The orthophosphate can occur in specific organisms depending on the pH values of the aquatic medium. PO_4^{3-} is the predominant component in highly alkaline environments whereas HPO_4^{2-} is prevalent in weakly alkaline environments. H_2PO^{4-} prevails under weakly acidic conditions, while H_3PO_4 is most popular under highly acidic conditions. The ratio of various types of phosphorous may vary from one case to another. However, the researchers decided that orthophosphate was nearly 50% of the available phosphorous (Parsons and Smith, 2008).

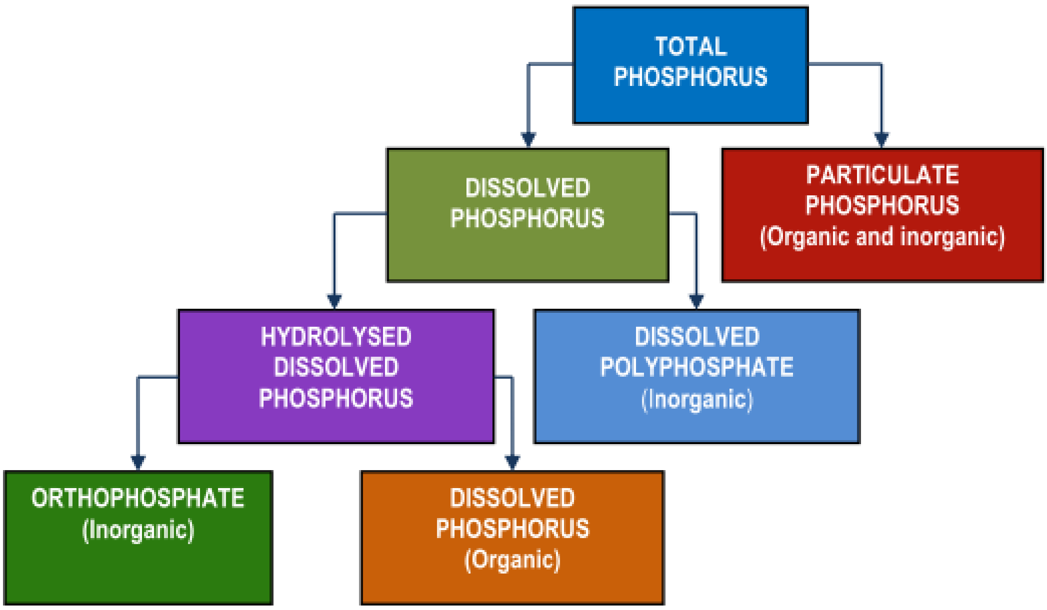


Figure 2.7 Different forms of phosphate in municipal wastewater (Modified from Bhojappa 2009)

Phosphorous is derived from phosphate rocks, a non-renewable form of existence that originates from igneous and sedimentary formations, and its supply is often in smaller amounts. Duley et al. (2001) stated that the phosphorous content is declining every year and also predicted that the phosphorous content will be fully exhausted in the next 100 years, so it is imperative to consider alternate methods for phosphorus supply to satisfy the needs.

2.9 Role of phosphorous in eutrophication

Eutrophication as described by the European wastewater treatment legislation (Council of the European Union, 1991); is the excessive growth of algae or floating plate mats and higher forms of plant life, which disturbs the development of organisms present in water and also includes water quality due to nutrient enrichment (nitrogen and phosphorous).

Floating dense algae mat during the algal bloom, blocks the light from entering the plants below the soil. When algal species die, they sink to the floor, where bacteria that reside in the sediments eat them. This process contributes to the blooming of bacteria in combination with an algal bloom, thereby increasing oxygen intake in improperly balanced bottom water contributing to anoxia. Over time, sediments release phosphorous, which enhances eutrophication (Kornberg et al., 1999).

Li et al. (2008) investigated and observed that river eutrophication is often present in rural areas and contributes to very severe danger due to the point source. Therefore, wastewater treatment plant effluent policies are required to reduce the discharge of phosphorus into the channel, lakes, and other nearby ecosystems.

2.10 Wastewater treatment technologies

The disparity between availability and water demand has resulted in the cost of additionally supplied water, increasing slightly. Developing innovative delivery methods has opened the way for the financial resolution of the demand-supply divide.

The type of treatment scheme or equipment to be used primarily depends on the characteristics of the wastewater.

Until recent years, every wastewater treatment scheme involves traditional physical (screening, filtering, sedimentation, floating, filtration, etc.), chemical (precipitation, adsorption, chemical oxidation, etc.), and biological processes. Compared to biological, some of the benefits of physical/chemical treatment are simple regulation, tolerance for a broad spectrum of flows, loading speeds, and several uses. The latter mentioned traditional solutions to any or more chronic chemical and biological toxins are either inefficient or unsuccessful. Chemical treatment reduces the chemical charge (solid waste) of the treated effluent, even though physical treatment often results in minimal effluent reclamation. Biological effluent management also follows the overall aim of environmental management with respect to improvements in physicochemical materials, which offers an avenue for healthy effluent disposal. Therefore, biological treatment is the most commonly known wastewater treatment system worldwide.

A concise overview of the benefits and demerits of the treatment methods utilized when handling wastewater for the removal of phosphorus is explained below. Building and running any of these technologies is comparatively easy, efficient, and economical. However, for the structures that need continuous servicing and frequent checks for their smooth runs, some of these simple and affordable treatment approaches might be unknown.

i. Chemical precipitation: Added salt precipitates phosphorous in the wastewater and the resulting residual solids are either removed by gravity settlement or filtration. Although the resulting precipitates can be rich in phosphorous, it can be hard to isolate chemically bonded phosphorous, rendering successful phosphorus-recovery and impossible for another use. This is a drawback for biological phosphorous removal systems because it restricts the potential advantages of the phosphorus-rich sludge's downstream applications. Even though a study has been carried to provide much more regulated precipitation and there are many practical approaches, there has been variable performance in such approaches. Furthermore, the rate of phosphorus extraction is normally proportional to the mass of chemicals added, affecting the number of extra solids created. As a result, the amount of salt used and the solid separation process used are intrinsically cost-effective (Karabegovic et al., 2013).

ii. Ion exchange: Technologies for the exchange of ions are well developed used in many contexts, like desalination and water deionization. The ion exchange theory can also be extended to the removal of phosphorous from wastewater and some believe that the method could be especially appropriate for use at decentralized locations. While not as much as the highly selective nature of some exchange media, widely studied or implemented as other Physico-chemical phosphorus removal methods, implies that their evaluation is permitted (Seo et al., 2013).

   In wastewater effluent, the prevalent type of phosphorous is anionic. Phosphate ions are exchanged reversibly between the liquid ions and the solid ion exchanger, concurrently offering removal and retrieval. The polymer exchange base, also known as a polymeric ligand exchanger, is usually formed from a metal cation, this generally proves to be difficult because of the comparatively complicated low phosphate ion amount in wastewater effluents, relative to competing species.

iii. Adsorption: The adsorption process can be used for the removal of toxic, persistent organic, and inorganic contaminants from wastewater. Adsorption is the process of adhering atoms and ions from a gas, liquid, or dissolved solids onto a surface of the adsorbent. The most commonly used adsorbents are powdered activated carbon and granular activated carbon. Some of the waste materials that can be used as an adsorbent are sawdust, steel slag, rice husk, fly ash, limestone, polonite, and many more. Adsorption processes are flexible and simple to design, low initial cost, easy to operate, insensitive to toxic pollutants. The limitations of the adsorption process are high maintenance costs, this process just transfers pollutants from one phase to another instead of eliminating them from the environment (Herrmann et al.,2014).

iv. Membrane technology: Inclusion in membrane bioreactors (MBR), granular sludge reactors, and sequencing of batch biofilm reactors are the latest EBPR developments (SBRs). The inclusion of EBPR in MBRs has been effective in achieving high levels of phosphorous removal from municipal wastewater, whether SBRs or continuous-flow. MBRs have a variety of benefits, including the preservation of solids within the reactor, resulting in high concentrations of suspended solids without the need for a wide device footprint.

    The benefits of better effluent consistency and limited physical presence make the need for an MBR desirable for any scale of treatment facility, such as minor works. Membrane fouling, though, remains a concern and as such, demands a greater degree of maintenance Furthermore, the initial cost of MBR systems may be one of the reasons why the technology's adoption has been limited to date, even on shorter timescales, and while the price may come down as the technology's popularity grows, it may currently be a barrier to decentralized applications (Simon et al., 2010).

v. Moving bed biofilm reactor (MBBR): Moving bed biofilm reactor is a type of aerobic hybrid system, where suspended attached biomass is responsible for the removal of nutrients such as nitrogen and phosphorus. Small cylindrical or circular polyethylene carrier media is incorporated into the reactor to support the biofilm. A fine bubble diffuser is used to circulate biofilm carriers inside the reactor. This treatment process is effective in the removal of COD, biochemical oxygen demand (BOD), and nutrients such as nitrogen and phosphorus. This system is reliable, easily operated, easy to retrofit for the existing treatment plant, No return activated sludge, utilized whole tank volume for biomass, No media clogging, less sludge production and better settling, small footprints. Whereas there are some limitations such as skilled laborers are required and bacterial activity have to be monitored regularly. Some complained that the fixed film media tends to wash out of the systems over time, even after installing the various strainer systems (Rusten et al., 1997).

vi. Biological phosphorous removal: The main objective of biological treatment is to transform or oxidize dissolved and particulate biodegradable constituents, suspended and non-settleable colloidal solids, nutrients such as nitrogen, phosphorus, and specific trace organic constituents into simple products. Biological treatment refers to the stabilization of wastewater solids by decomposing them into harmless inorganic compounds either by aerobic or anaerobic processes with the help of microorganisms. Carbon dioxide and biomass are the end products of decomposition in aerobic conditions, while carbon dioxide and methane are formed in anaerobic conditions.

There is great interest in biological methods that obtain the highest removal of phosphorous, as they assist to enhance the biological potential of activated sludge. The conventional biological purification process only eliminates 20-40% of phosphorous. By increasing the amount of sludge used, phosphorous removal can be maximized to 50%, but this is not sufficient because to achieve the MPC level, up to 95 percent of phosphates must be removed.

vii. EBPR: As the method of biological removal, EBPR has evolved from an incidental statement to a well-structured application through years of intensive study and full-scale work. EBPR is often prone to interference due to the location at the start of the treatment and specific influencing characteristics. Much information on the EBPR process has been produced; however, the techniques used for estimating the inhibition of the mechanism vary greatly. There is no easily applicable and accurate method available for rapid determination of inhibition of the EBPR mechanism. EBPR is highly reliant on the microbiological and organizational fields, as a biological system of changing anaerobic, aerobic, and anoxic phases. In addition to optimization of operation, design, and configuration, knowing the microbial identification basics especially for PAOs and GAO's provides potentially high phosphorous removal, phosphorous recovery, and sustainability (Oehman et al., 2007).

2.11 Removal of phosphorous by EBPR

Enhanced reduction of biological phosphorous (EBPR) is the method where the phosphorous is eliminated through biological treatment that relies on the capacity PAOs to consume excessive phosphorus. This method decreases the expense of applying additional chemicals and therefore decreases the amount of sludge generated as opposite to chemical processes. Phoredox(A/O) is one such EBPR approach where the micro-organisms are exposed in the traditional stream to aerobic and anaerobic environments. Figure 2.8 shows the schematic diagrams of the anaerobic and aerobic PAO metabolism

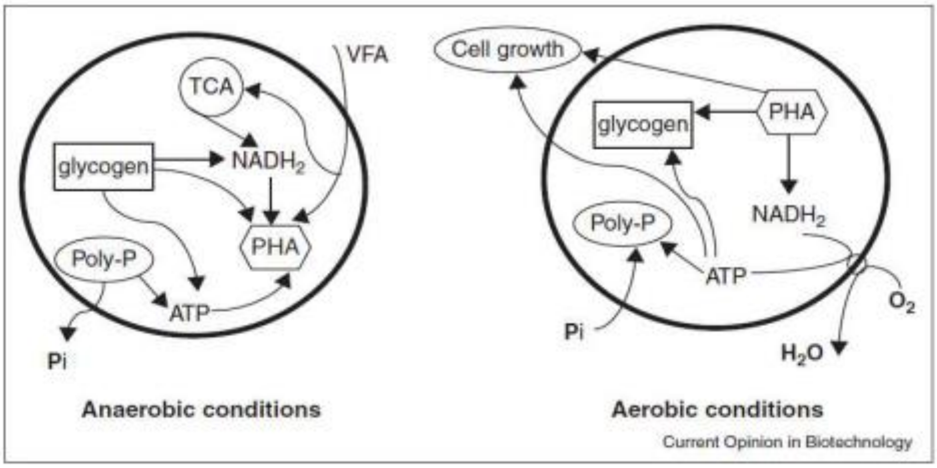


Figure 2.8 Schematic diagrams of the anaerobic and aerobic PAO metabolism. (Yuan et al 2012)

The hindrance of eutrophication can be effectively done by phosphorous removal in the wastewater using a closed water system. If the content of phosphorus is high, it leads to different water quality problems like recreation values will be low, the possibility of algal effects, loss in live-stock and treatment cost will be increased (Yeoman et al., 1988). Generally, the removal of phosphate from the wastewater is attained by chemical precipitation. Chemical precipitation is costly and also results in an increase in sludge production but the main advantage of this method is its relatively mere process. During this process the sludge increase was up to 30% of volume and also the sludge was contaminated with a high range of heavy metals. Hence it is necessary for an alternative of chemical precipitation for the removal of phosphorous.

Biological phosphate removal is one method that has distinct benefits when compared to chemical phosphorus removal. The sludge which comes out from the biological phosphorus removal processes has a high agricultural value because phosphate availability is high in the sludge and also a shortfall of other objectionable chemicals (Nieminen et al., 2010).

The primary advantages of EBPR are the eradication of chemicals and also a reduction in the sludge during the processes. Under anaerobic conditions, the Poly-P stored in the microorganisms is slightly released after EBPR in turn maximizing the phosphate production in the sludge system (Desmidt et al., 2015). If the phosphorus content removed using chemical precipitation using aluminum salts or iron salts, the phosphates usually remain in the metals by binding to it after anaerobic treatment(Parsons et al., 2008).

The EBPR sludge contains nearly 5-7% of enriched phosphorus whereas the normal activated sludge contains only 1-2%. After dewatering the rejection liquor or the phosphorus enriched sludge is used to recover the phosphorus by various means like precipitation, crystallization, etc., using various salts like calcium or magnesium and seed crystal to recover phosphorus as magnesium ammonium phosphate or calcium phosphate(Cornel et al., 2009). Various microorganisms like *Pseudomonas, Moraxella, Mycobacterium, E.coli, Corynebacterium, Acinetobacter, Aerobacter,* etc., digest phosphorus, which comes into the composition of many macromolecules in the cell. Phosphorus is stored as a polyphosphate in granules by various organisms which are capable of convertingstored phosphorus as polyphosphates. The linear polymer of residues like polyphosphate is linked by high-energy phosphoanhydride bonds and this may produce cellular dry weight up to 10 – 20% (Kornberg et al., 1999). For the growth of micro-organism, various cations are required like magnesium, calcium iron, and potassium which have to be above the limiting concentration in a culture media.

Mota-Filho et al., (2003) found concentrations of orthophosphate at a full-scale EBPR plant as large as 125 mg / L in filtrate filter presses. To mitigate the leakage of orthophosphate into the liquid form, the dewatering of undigested BNR sludge will take place as early as possible. Sludge is sometimes processed, depending on the ability of the downstream treatment facilities, before further processing. The sludge that is deposited under anaerobic conditions may facilitate secondary phosphorus release, the degree to which depends on the storage period and orthophosphate releases of 153 and 277 mg / L during sludge handling, which suggests that the high release of phosphorus was caused by the primary sludge's high soluble organic matter content.

Zheng et al., (2018) studied traditional biological removal of nitrogen and phosphorus due to lack of biodegradable carbon source is typically reduced, hence advanced techniques are necessary. A new choice is suggested, involving an advanced elimination of biological phosphorus (EBPR), supplemented by limited nitrification-anammox (PN/A), is suggested to increase the absorption of nutrients from urban wastewater. An experiment was taken up in a network of 2 batch sequencing reactors (SBRs) integrated on a laboratory scale.

In SBR1, phosphorus reduction was carried out in an SBR1 alternating anaerobic-aerobic environment where ammonium concentration remained the same as nitrifiers were wiped off from the reactor during a brief sludge retention period of 2-3 days. The residual ammonium was again treated in SBR2 where inoculation caused PN/A. It eventually reached a cumulative nitrogen removal rate of 0.12 kg N-m^3-day. During the stable phase, total phosphorus and total nitrogen concentrations of the effluent were 0.25 and 10.8 mgL^{-1}, respectively. This research indicates that the EBPR-PN/A method is feasible to facilitate the elimination of low inflow important carbon source nutrients from urban wastewater.

Tarayre et al., (2018) evaluated on Phosphate rock has been used for the manufacture of chemicals dependent on phosphorus for several years. However, despite the degradation of the reservoirs and the decrease of phosphate rock consistency, a possible demand is now developing for the recovery of phosphate from waste and its usage for different applications. Notably, a circular economy solution may involve the removal of phosphate from wastewater. This study reflects on the usage of microbial systems for phosphorus accumulation and recovery by taking into account the specific variety of analytical techniques available for tracking phosphorus accumulating bacteria, as well as the specific biochemical and metabolic engineering toolbox available for bioprocess optimization. Knowledge gathered from a method, device, and synthetic biology may theoretically contribute to creative process design in this context.

Bekiaris et al., (2018) studied the use of Fourier transform infrared photoacoustic spectroscopy (FTIR-PAS) to examine phosphorus species in biochar and to assess the influence of the temperature of pyrolysis on phosphorus species. The photoacoustic detector has several influences as opposed to more conventional FTIR reflectance or transmission detectors for the very dark biochar samples. The spectrum proved to be more informative in regions with phosphorus vibrations for biochar produced at temperatures more than 400°C, where most of the residual organic compounds were aromatic and therefore did not interfere with phosphorus vibrations.

An escalation in pyrolysis temperature contributed to the development of a huge variety of phosphorus species for biochar generated from the solid portion of digestate from biogas processing. Hydroxylapatite and tricalcium phosphate are the prevalent phosphorus species in the moderate to high-temperature range (600–900°C), whereas iron phosphates, variscite, and calcium phosphates were reported at 1050°C apatite. However, the variations in phosphorus speciation were smaller in biochar derived from a bone meal at various temperatures than in digested biochar. In the biochar formed at all temperatures, hydroxylapatite and calcium phosphates were found, while some evidence of struvite formation was present.

Bond et al., (1999) studied the existence of anaerobic phosphate release and also its PHA-shaped metabolic relation. In an anaerobic environment, the iodoacetate prevents the production of PHA and phosphate. It was also noticed that pH is the key parameter where the phosphate relies on the intercellular pH, the necessary phosphate is released in EBPR when there is an increase in pH and it is due to volatile fatty acid absorption. Also studied on the effect of initial pH in the anaerobic state on EBPR from wastewater comprising a propionic acid and acetic acids. The optimal pH for a greater release of orthophosphate was between 6.4 and 7.2.

Zhang et al., (2012) recorded improving EBPR's stability and efficiency, while few investigations reported the negative impact on the mechanism. Heterotrophs are the microorganisms in municipal WWTPs that mainly contain biomass, although a limited amount of PAOs is used. A molecular identification technique was conducted using in-situ fluorescence hybridization (FISH), it was found that the important community of microbes in EBPR are *acinetobacter* and *proteobacteriasubclass β-2*. An analysis of FISH and microautoradiography on EBPR sludge has shown higher concentrations of Rhodocyclus-related bacteria(*β-proteobacteria*).4% of the cultured bacteria have been identified. Except those of Dechlorimonasspp, denaturing gradient gel electrophoresis (DGGE) suggested *Rhodocyclus spp*. Analysis of whole-cell fatty acids of bacterial populations revealed that they displayed more than twenty general EBPR capacities, the most famous being *Staphylococcu*, *Acidovorax and Micrococcus*.

Oehman et al., (2007) demonstrated that the interaction between biological and chemical process dosing is not understood well as it is very much complex. In this study, it has been reported that aluminium is the one that inhibits the biological phosphorus release and uptake, and also iron salts if it is in range it has a weak effect on EBPR process. The author has examined the chemical dosing effect but not the effect of microbial communities in the biological processes.

Haiming Zou et al.,(2016) studied phosphorus removal and recovery from domestic wastewater in a novel process of EBPR coupled with crystallization. In this study, two reactors are anaerobic/anoxic tank (AAT)6L and phosphorus recovery tank

(PRT) 4L. SBR technology was used for AAT design. Endogenous respiration of biomass took place which reduces the sludge production. The operating temperature was 16^0C to 21^0C, MLSS was maintained at 4200mg/L, SRT was 20 days. Synthetic water was prepared seed, sludge was used took 80days to attain steady state. SEM & FISH characterization was done to study the microbial diversity which showed that bacillus was predominant in denitrifying phosphorus accumulating organism (DPAO) sludge. Crystallization was done for phosphorus recovery adding aeration because it fluidizes the seed crystals. Based on the results microorganism may be playing an important role in phosphorus removal in the EBPR-PR system. COD, N &P was removed effectively 82.6%, 87.5% and 91.6%. The phosphorus recovery was 59.3% by crystallization.

Yang et al.,(2017) stated that scarcity of carbon source in conventional biological removal, a new method of EBPR followed by partially nitrification-anommox(PN/A) was adopted to increase the efficiency of nutrient removal in the municipal wastewater. Two SBR was set up, one for phosphorus removal under anaerobic-aerobic conditions (120 liters) and another for nitrate removal by inoculation. Air compressor, mechanical stirrer, nitrogen gas producer are attached to SBR2. Temperature, Oxygen, and temperature probe were used.

Wang et al., (2020) studied using two sequencing batch reactors, with acetate (SBR-1) and propionate (SBR-2) as carbon sources, evaluated the effects of two carbon sources on the efficiency and population structure of granular EBPR systems at long-term low temperatures. Results revealed that extremely effective EBPR was successfully achieved, and SBR-1 and SBR-2's average PO_4^{3-}P and COD removal performance was 94.2 %, 87.1%, and 98%, 87% respectively. Also, to generate ATP for VFA absorption rather than glycogen, the acetate system chose to use intracellular Mg/K-polyP. High-throughput sequencing analysis showed that 31.7% (SBR-1) and 71.75 (SBR-2) of Rhodocyclaceae abundance and 60.5% of the Dechloromonas genus is enriched with propionate, certainly higher than acetate (1.2%). In addition, Dechloromonas might use nitrate as electron acceptors for phosphate uptake in addition to oxygen

The municipal wastewater sample's main characteristics were studied.SBR1 was inoculated with activated sludge were in initial concentration was 4000mg/L and 3500 mg/L. 6L of wastewater was feed to SBR1, one operation cycle consists of 30 min anaerobic and 90min aerobic. Dissolved oxygen (DO) was over 3mg/L. SBR was divided into 2 phases. Phase1 is operated for 1-100 days continuously aerated with DO 0.1 to 0.2mg/L. Phase 2 was operated on for 101 to 151 days aeration followed by anoxic reaction for 1 hr. DO was 0.3 to 0.4mg/L. Chemical analysis was done according to the standards.

The Phosphorus removal was 95% in SBR1 as nitrification was negligible. Nitrogen removal was 9% and soluble chemical oxygen demand (SCOD) removal was 62% as denitrification is avoided the removal of phosphorus was high in SBR2 phase1 as the temperature decreases the ammonia started to increase in the effluent hence PN/A is very much sensitive to temperature variation. Ammonium oxidizing bacteria present in the sludge were mainly responsible for the reduction of sludge. In Phase2 aeration was carried out and then followed by an anoxic period for 1 hr, the performance of PN/A was improved during the anoxic phase with the nitrogen removal efficiency of 81%.

2.12 Factors influencing EBPR

2.12.1 Carbon source

Carbon availability is one of the important factors, carbon in the mode of biodegradable COD/VFAs shows the advance of activated sludge plants for EBPR. The utilization source and price of carbon source are important hence the selection of carbon or substrate source is demanding (Puig et al., 2008). Currently, there is an increased study on EBPR performance impact by propionate and various substrates. Studies explained that the downturn of phosphorus removal is due to the microbial competition between the GAOs with PAOs, whereas the use of carbon source as acetate in EBPR system is stated to be a stable phosphorus removal and yield robust performance (Oehmen et al., 2007). Investigations have proved that the use of propionate than acetate is much more advantageous for the successful performance of

EBPR (Wang et al., 2010). PAOs and/or GAOs could take up VFAs other than propionate and acetate (Levantesi et al., 2002). It is been unclear that the above-mentioned substrate affects the PAO–GAO. The most broadly referred carbon substrate is glucose apart from VFAs (Jeon et al., 2000).

The carbon source such as acetate, ethanol, and others could produce the fastest growth of PAO (Johansson et al., 1994) The carbon source uptake has to be very quick from the microorganism as there is a limited time in the anaerobic phase (Christensson, 1997). To achieve high removal efficiency of nutrients in an SBR process along with carbohydrates such as glucose, acetate should be present in the media of nutrients. To nourish the bacteria in the sludge there are various ways like external addition of industrial wastewater and external addition of acetic acid (Henze et al., 1996). Increased detention time due to internal addition VFA in the anaerobic tank by increased hydrolysis/fermentation. The kind and amount of carbon source available for the microorganism act as an important factor in the EBPR process. The acetic acid in the form of VFA is lesser in an amount in the sludge which is used by microorganisms hence, the amount has to be increased by fermentation or hydrolysis. For the induced high EBPR activity, ethanol is also a carbon source. In the anaerobic zone, a prolonged detention time is tedious when using ethanol as it is divided into VFA before the microorganism could take up.

2.12.2 Sulphate

The sulphate concentration increases as the phosphate removal increased also at strong alkaline conditions free calcium decreases phosphate removal increases as a high concentration of sulphate in the solution can promote the discharge of calcium from calcite to likely form hydroxyapatite (Yun Liu et al., 2012).

2.12.3 Calcium

Calcium could be an important factor for the stabilisation but it is stated during a cycle the calcium concentration did not vary (Christensson et al., 1997). However, Miya et al., (1987) discovered that with the addition of a great amount of carbon source calcium content decreases during aeration hence it leads to a higher pH. It results in slower uptake and release of phosphates.

2.12.4 Nitrate

Nitrate can act as an electron acceptor during the absence of oxygen. Hence it is significant that the water which enters into the anaerobic phase should not contain any nitrate. The condition leads to the same as aerobiosis, that is electron acceptor is served by nitrate and poly-hydroxybutyric acids(PHB) behalf of stored metabolism of intracellularly instead of a collection of new carbon source (Christensson et al., 1997).

2.12.5 Potassium and Magnesium

The presence of potassium and magnesium ions affects the biological phosphorus uptake. Potassium and magnesium polyphosphates are very fast released and are unstable under anaerobic conditions. Magnesium and potassium act as counter ions during the release and uptake of phosphorus in the EBPR sludge(Machnicka et al.,1999). the release of phosphates is certifying that the possibility of simultaneous formation of intercellular and external polymers and also polyphosphates available in various forms with the comparison of a variable in time rate of potassium and magnesium release. Change of rate of potassium and magnesium release in time has proved that there is a formation of different forms polyphosphates.

2.12.6 COD/P ratio

For the proper operation and design of the phosphorus removal systems, the influent COD or BOD to the phosphorus ratio is vital. There is a stoichiometric need for COD for the removal of phosphorus in each unit. The quantity of excess phosphorus from the solution can be removed and the extent to which PAOs can function is determined from the system limited by COD (or BOD) or phosphorus. Oehmen et al (2007) observed that at COD:P ratios of 10-20 mg-COD/mg-P PAOs influence to dominate whereas at COD:P ratios less than 50 mg-COD/mg-P GAOs tend to dominate. hence, maintenance of good control over the operational condition and optimum COD:P ratio, the rivalry between PAOs and GAOs for substrates, which gives a positive outcome, needs to be used.

2.12.7 Temperature

In most biological reactions, the lower rate of biochemical transformations is due to the lower temperature in EBPR systems (Brdjanovic et al., 1998). Whereas in the lab-scale study, low temperatures are beneficial in improving EBPR performance (Panswad et al., 2003). The change in the process is due to the replacement of GAOs to PAOs by the microbial group. Whang and Park (2002) found at 20^{o}C SBR EBPR, performance was satisfactory whereas in another SBR with higher anaerobic acetate uptake at 30^{0}C there was a lower release and uptake level of phosphorus. Due to the increasing impact of GAOs high temperatures lead to a decrease in the performance of phosphorus removal. Compared to PAOs, GAOs can predominate at higher temperatures as GAOs increase the ability to uptake acetate at those temperatures. During summer months and warm climates, the competition between GAOs with PAOs in EBPR plants is highly complicated. 28-30^{0}C is an optimum temperature for the better operation of the EBPR process. Christensson, (1997) stated that phosphorus removal is also achieved at 6^{0}C. Johansson (1994) observed that the temperature was raised from 10^{0}C to 20^{0}C and from 15^{0}C to 25^{0}C, respectively, two times of phosphate release was observed in the sludge. Studies also say that with the increase of temperature from 24^{0}C to 29^{0}C phosphorus release increases to 75% (Johansson, 1994).

2.12.8 pH

Selection of PAOs over GAOs can be done by increasing the pH, hence pH is important and highly influences the competition between PAO–GAO. The critical point of pH in anaerobic processes is that the GAOs take up VFA anaerobically higher than those PAOs at the pH below 7.25 whereas the PAOs take up acetate in a higher range only when pH is more than 7.25. The phosphorus removal efficiency is higher when the aerobic or/and anaerobic level of pH is raised from 7 to 8.5(Schuler et al., 2002) It is also assumed that the reason for the improvement in the performance is due to the change in the microbial competition from GAOs to PAOs. Zhang et al., (2005) stated that when there was a decrease in the pH from 7.0 to 6.5 a reduction of phosphate-removing organisms and change in the microbial community was observed. It has been noticed that at pH more than 8.0 there is a reduction in the phosphorus release, VFA uptake, and phosphorus uptake (Oehmenet al., 2005). EBPR process strongly depends on the pH of the liquor. With the increase in pH, the phosphorus release rate also increases (Kuba et al., 1997). Bond et al., (1998) investigated that during anaerobic phosphorus release, it is not only built upon the pH of the mixed liquor but also on the intracellular pH.

2.12.9 Effect of pH on the Phosphorus/Acetate (P/Ac) ratio

At pH 5.0 to 6.5 acetate uptake rate and the phosphorus release rate raised linearly at pH 6.5 to 8.0 whereas the acetate uptake rate remained constant while phosphate release rate continued to increase. Therefore about 1.0 (pH 5.0-6.5) to 1.75 (pH 6.5-8.0) was the increase of P/Ac ratio (molar). Within the pH range 5.5-8.5 there was an increase in P/Ac ratio from 0.6 to 1.9 Smolders et al., (1994). The anaerobic phosphorus release decreases when the pH reaches 8.0 and more(Liu et al., 1996a). Due to the chemical precipitation, there was a decrease of the P/Ac ratio at increased pH values (>7.5) Kuba et al. (1997) The increase of the P/Ac ratio is described by the assumption that greater pH values give higher electrical potential difference beyond the membranes of the cell, i.e. to take up the negatively charged acetate ion more energy is needed for the cell. To adopt the same quantity of acetate at higher pH values than lower pH values there should be higher phosphate release by the bacteria. To mask the energy demand at low pH, the need for less phosphorus at lower pH, during the anaerobic phase the total uptake of substrate might increase, appearing in a higher fraction of PAO in the process (Smolders et al., 1994).

2.12.10 Effect of intracellular pH

The intracellular pH of EBPR sludge was lifted in the existence of a weak base along with the substantial anaerobic phosphorus release, without any VFA uptake (Bond et al. (1998). The prohibition of anaerobic phosphate release was resulted still when VFA was present even though the acidification is caused by the acetic acid of the sludge. These results may describe when, why supernatant pH is allowed to raise, the anaerobic phosphorus release increases even in sludges with phosphorus removing capabilities are extremely poor. Sludge characteristics are that almost no phosphorus transformation occurs even though at neutral pH values, acetate is taken up to a normal extent.

2.12.11 Cations

In maintaining the stability and binding of the mechanism of phosphorus in the EBPR process and activated sludge, composition as well as the concentration of cations in the influent plays a significant role. Phosphate molecules will not pass through the cell membrane by itself as it contains three negative charges, hence the phosphate molecules should bond with the positively charged ions like potassium and magnesium. As these two opposites charged molecules bonds each other, it develops into a neutral phase thereby phosphate molecules are easily passed through the cell membrane. It has also been observed that magnesium and potassium are not only required for neutralization but it is also one of the required cations in biological phosphorous removal. The important step in the anaerobic stage of the biological phosphorous removal system is the release of phosphate from PAO cells. In the sewage treatment plants designed for EBPR process timely there will be a change in the influent short or long-term shortage of potassium whereas higher potassium content greatly influences the activated sludge properties and results in less efficient effluent quality and dewatering property Schönborn et al., 2001).

2.12.12 Dissolved oxygen

The heterotrophic aerobic organisms utilize the oxygen present in the anaerobic zone as an electron acceptor and they compete with PAOs for VFAs which eventually gives minimum storage of VFA, finally reduces the biological phosphorus removal. The biological phosphorus removal (BPR) process is affected negatively by excess aeration as the cessation of P-uptake occurs due to the reduction of poly-hydroxy-butyrate (PHB) in a high-aerated process (Brdjanovic et al., 1998) It is also assumed that the competition between PAOs and GAO's is due to the concentration of DO, henceforth affecting the EBPR attainment. EBPR performance will be affected when the high concentration of 5mg/L DO is recirculating from aerobic to the anaerobic zone neglecting PAO and GAO completion. Enabling uptake of poly-phosphates, dissolved oxygen (DO) is consumed in the aerobic phase. At DO concentrations of 2 mg/L, a satisfactory phosphate uptake could take place when the sludge is aerated for a required amount of time (Christenssonet al., 1997). Tonkovic et al., (1998) stated that although a high DO level, aerobic respiration might be finite. This can occur if the amount and kind of carbon source added to sludge affects the performance of the microorganisms in an objectionable manner.

2.12.13 Solid retention time (SRT)

SRT has been identified as a factor that can affect EBPR performance and competition between PAOs and GAOs. Normally, the EBPR process is unaffected by the SRT, and it has been demonstrated in practice that good phosphorus removal can be achieved with SRTs varying from 3 to 68 days. It was shown that increase SRT reduces biomass yield thereby reducing the amount of phosphorus removed through excess sludge discharge (Brdjanovic et al., 1998). (Barnard et al., 1993) stated that SRT plays a smaller role in phosphorus removal than one would expect in the context of EBPR. PHA and glycogen polymerization reactions are affected by the SRT in EBPR system and it was investigated while examining the underlying biochemical methods. At a long SRT, GAOs were able to compete successfully with PAOs, resulting in a decrease phosphorus removal efficiency in the EBPR system (Seviour et al., 2003).Rodrigo et al., (1999) observed that EBPR biomass activity decreased as the SRT was extended, shorter SRT is advantageous for PAO, implying that GAO may tend to dominate at longer SRT.

2.12.14 Dynamic stress state

For the choice of POAs and other operational and/or environmental conditions imposition of anaerobic stress is necessary and sufficient condition to elect the organisms that accumulate poly-P, because the organism may deficit the energy to battle for the substrate under anaerobic conditions (Gebremariam et al., (2011).

2.12.15 Feed composition

It was investigated that the blend of glucose and acetate in a reactor, a complete anaerobic carbon uptake with no phosphorus release was noticed in which the group of G-bacteria was dominated in the reactor sludge. Impede EBPR and GAO proliferation were enhanced by glucose. Whereas 50/50% of a mixture of glucose/acetate was found efficient in the removal of phosphorous when compare to acetate dose in a sequencing batch reactor (SBR). At 75/25% glucose/acetate mixture feed, there was a deterioration in phosphorus removal (Gebremariam et al. (2012). The anaerobic-anoxic/nitrifying (A2N) process was unstable when the COD/P dose ratio was less.

2.13 Effects of idle time on biological phosphorus removal process

The idle time of SBRs impacts the biological phosphorus removal increasingly with rising phosphorus concentration in the influent. The systems that had a long idle time ted slow bacterial growth, which was insufficient to remove the high concentrations of phosphorus. The hydrolysis of polyphosphates due to the secondary phosphorus release contributed to the deterioration of the phosphorus removal capacity of the systems. Based on the PCR-DGGE analysis, the presence of GAOs in systems and the change of the PAO population were important reasons for the decrease in their phosphorus removal efficiency.

Zhu at al., 2003 studied on the impact of idle time on SBR, When wastewater is generated again and delivered to the treatment plant, the microorganisms in the activated sludge plant may have lost activity, and the activated sludge flocs may have disintegrated. From previous observation, it is assumed that granular activated sludge is more resistant against long-term storage than activated sludge flocs. Experiments using a laboratory scale SBR were conducted to study the impacts of a 7-weeks anaerobic idle time on structural integrity and metabolic activity of granular activated sludge, and the time required to regain the former operational status of the plant. Oxygen consumption rate (OCR) was used as an indicator to evaluate the metabolic activity of the sludge. The results revealed that the size, color and sedimentation characteristics of the granular sludge
did hardly change during the storage period. Sludge activity, however, dropped to values as low as 0.17mg min_1 L_1. After restarting the reactor, the OCR increased within 1 day to a level of 0.57mg min_1L_1, kept rising at a linear rate in the following days, and reached after 1 week, a value of 5.74mg min_1L_1 typical for the

former activity status. These results imply that granular activated sludge can be stored for a considerably long period of time, and brought into service again relatively quickly. After an idle period of 7 weeks, it took less than a week to regain full capacity of the SBR.

2.14 Benefits of phosphorus recovery

Phosphorus pathways may be split into many groups stemming from WWTP and future applications. The most popular technique used for the recovery of phosphorus is EBPR where phosphorus sludge is processed through anaerobic digestion to enable the release of phosphorus from the biomass into a fluid stream. Pelletized phosphorus is then precipitated as struvite ($NH_4MgPO_4{\cdot}6H_2O$) or hydroxyapatite ($Ca_5(PO_4)_3(OH)$) from this side- flow in an up-flow fluidized bed reactor. Effluent may then be recovered from this process or added to the plant head. Approximately 80% of phosphorus from the centrate can be extracted during this crystallization phase. The phosphorus-enriched materials can then be reused for other industries as slow-release fertilizers (struvite) or feedstock (hydroxyapatite) (Latimer et al., 2012).

The available literature indicates large-scale phosphorus recovery at a wastewater treatment facility. Specific factors for the suggestion of implementation of the phosphorus recovery in the wastewater treatment plants minimizing effluent phosphorus levels by decreasing the phosphorus load returned to the head of the work and minimizing the quantity of chemical coagulants required, thereby decreasing the amount of material produced which are rich in phosphorus that can be utilized in the fertilizer industry.

The true results of phosphorus recovery should be analyzed and recorded to improve the absorption of phosphorus recovery in WWTPs. Without evidence of the operating advantages gained by phosphorus water recovery firms would possibly not be able to implement new technology. Work focused on the potential direct effects of recovery from phosphorus, could further benefits/limitations of phosphorus recovery to involve indirect and explicitly realized expenses, savings, impacts on WWTP systems, etc.

The decrease in phosphorus and NH_4 concentration leads to an increase in the potential to extract phosphorus and minimize the need for readily biodegradable chemical oxygen (rbCOD) for phosphate-accumulating organisms (PAO), enabling high rbCOD as a usable for denitrification. It is anticipated that the decreased NH_4 load would increase the nitrification potential and that the overall N effluent but no evidence of such effects has been published.

2.15 Phosphorus recovery methods and challenges to MAP recovery

There are various approaches required for phosphorus recovery from pollution from the treatment system for wastewater. Wastewater, dewatered sludge, untreated sludge, sludge ash are different forms of waste materials from wastewater treatment plants. There are various techniques required for the recovery of phosphorus. Precipitation, crystallization, wet chemical process, and thermo chemical system are the techniques used for recovery of phosphorus. Figure 2.9 shows the avenues of recovering phosphorus from wastewater and the potential use of the product.

Municipal wastewater with low phosphorus rates is well-recognized but large amounts will have strong phosphorus mass loads for MAP recovery. There is also an increasing tendency to consider urban wastewater as a source of phosphorus rather than a problem for the ecosystem (Huchzermeier, 2011). It has been calculated that about 250,000 tons of phosphorus can be recovered from drainage annually in Western Europe, which is equal to the phosphate industry demand (Biswas et al., 2007).Urban wastewater of10 m^3 produces 1 kg of MAP. Around 330 $kmq1^3$ of municipal wastewater is created worldwide annually (Mateo-Sagasta et al., 2015). MAP's retail price is USD 1885/ton. This means that, if the phosphorus in urban wastewater is treated as MAP, more than 6 billion USD will be saved per year. Until this method is given enough attention, benefits are negligible. In comparison, small concentrations of heavy metals in urban runoff are likely to result in the recovered MAP becoming extremely clean. This can be regarded as a major benefit of urban wastewater for MAP recovery over certain raw materials (e.g. sludge, ash) (Lanning, 2008).

Municipal wastewater with low phosphorus rates is well-recognized but large amounts will have strong phosphorus mass loads for MAP recovery. There is also an increasing tendency to consider urban wastewater as a source of phosphorus rather than a problem for the ecosystem (Huchzermeier, 2011). It has been calculated that about 250,000 tons of phosphorus can be recovered from drainage annually in Western Europe, which is equal to the phosphate industry demand (Biswas et al., 2007).

Urban wastewater of10 m^3 produces 1 kg of MAP. Around 330 kmq1^3 of municipal wastewater is created worldwide annually (Mateo-Sagasta et al., 2015). MAP's retail price is USD 1885/ton. This means that, if the phosphorus in urban wastewater is treated as MAP, more than 6 billion USD will be saved per year. Until this method is given enough attention, benefits are negligible. In comparison, small concentrations of heavy metals in urban runoff are likely to result in the recovered MAP becoming extremely clean. This can be regarded as a major benefit of urban wastewater for MAP recovery over certain raw materials (e.g. sludge, ash) (Lanning, 2008).

The recovery of MAP from urban wastewater has not been a proven procedure until now (Nieminen, 2010). That could be attributed to the low phosphorus content in urban wastewater. For urban wastewater, the average phosphorus amount was 4-16 mg/L (Nieminen, 2010). Nevertheless, it was suggested to use the solution with a phosphorus concentration above 50 mg/L (Cornel and Schaum, 2009) to make the recovery of phosphorus as MAP an economically feasible method. Hence, it is necessary to establish a viable method that can pre-concentrate phosphorus to a sufficiently high level in municipal wastewater before recovery as MAP (Tyagi and Lo, 2013).

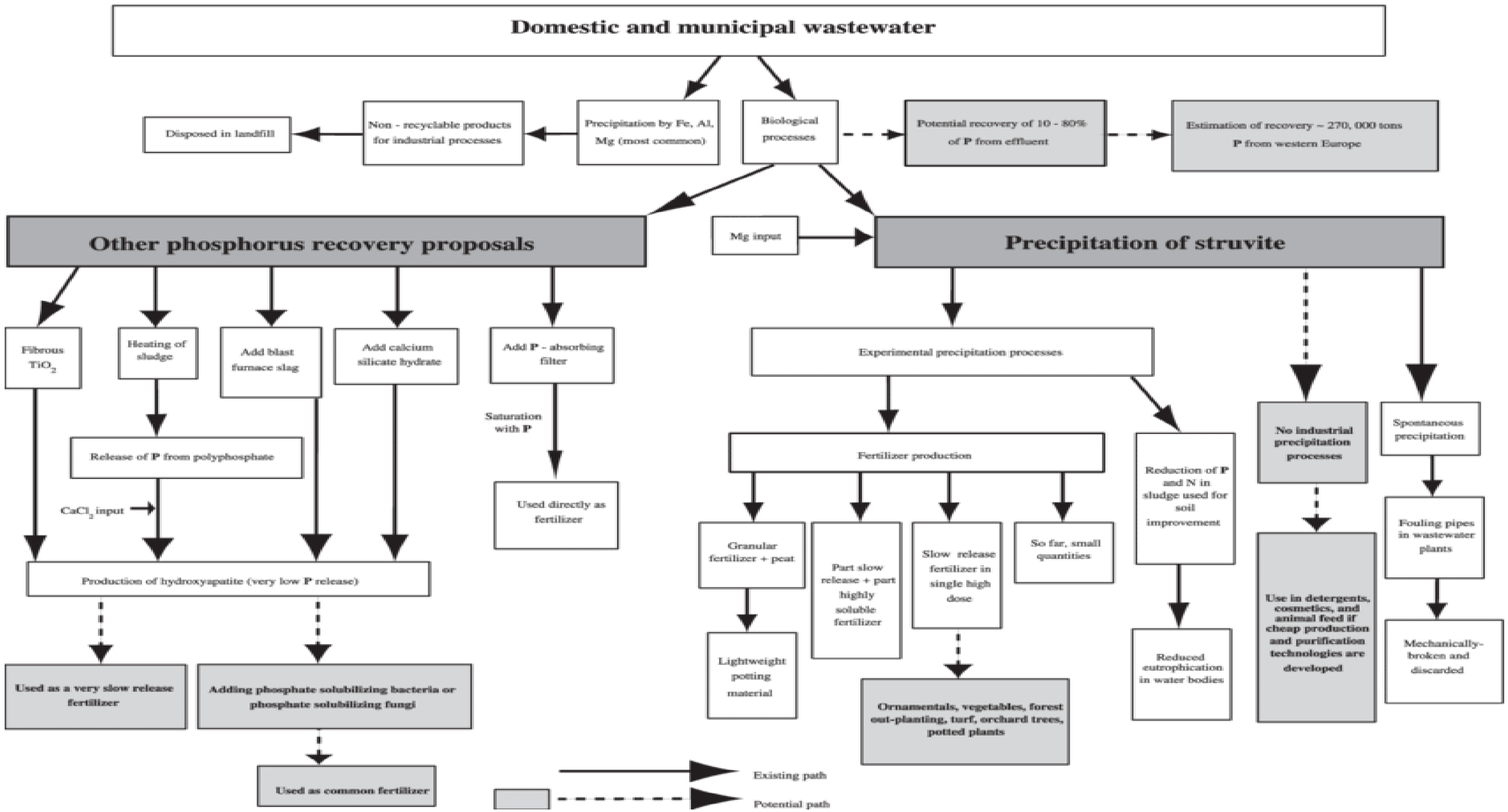


Figure 2.9 Avenues of recovering phosphorus from wastewater and the potential use of the product (De-Bashan et al., 2004)

In the meantime, it is well-documented that an adsorption is an effective tool for pollutant pre-concentration. Metal-chelating polymer increased its phosphate concentration 147.9 times. Similarly, Ohura et al., (2011) observed that phosphate pre-concentration with Zr^{4+} primed orange waste was accomplished by 55-fold.Li et al., (2012) also found that phosphorus in desorption solution has been enriched 530 times as opposed to XDA-7 resin feed solution. Therefore, the combination of adsorption and crystallization is used for the phosphorus recovery from municipal wastewater

2.16 Crystallisation

The recovery of phosphorus as MAP is desired by several methods. This is because the cycle requires all nitrogen and phosphorus to be removed from drainage at the same time (Ackerman, 2012). The usage of MAP as a slow-release fertilizer often mitigates the leaching of pollutants and hence prevents the surface water from eutrophication (Garcia-Belinchon et al., 2013).Until now, the full-scale implementations of wastewater MAP crystallization include Ostara Pearl in Canada, Phosnix in Japan, and AirPrex in Germany (Karabegovic et al., 2013).

Sludge used to be a standard raw material for the recuperation of MAP in the past. However, high costs arising from phosphorus leaching chemical use are a major factor restricting its large use (Nieminen, 2010).Also, the usage of sludge for MAP recovery is significantly limited due to the threats of heavy metals and/or pathogens from the sludge (Karabegovic et al., 2013). As a consequence, the usage of wastewater for MAP recovery is becoming rapidly popular.

Phosphorus recovery is usually achieved using crystallization approach accompanied by precipitation that is applied in processes such as Crystalactor, Airprex, and Ostara. Crystallisation and precipitation transform liquid-soluble phosphate into a stable state. (Nieminen et al., 2010). Precipitation of phosphorus may occur naturally and is usually suggested through the inclusion of metal ions such as Fe^{3+}, $Ca^{2+,}$ or Mg^{2+}. (Rittmann et al., 2011a). Agglomeration can often occur as a consequence of particle development or by utilizing the seed materials such as dirt, sand, etc. Once phosphorus is extracted by using Mg(Struvite, $MgNH_4Po_4.6(H_2O)$)

crystallization, which is obtained at pH more than 8. Here the creation of the struvite is in the crystal that is to be isolated from the oil. phosphorus can also be precipitated with calcium in the mode of hydroxyapatite (HAP) ($Ca_5(PO_4)_3OH$). The use of Fe and Al from wastewater treatment plants will precipitate bound phosphate from the wastewater.

Doyle et al., (2002) stated that nutrient removal may result in a greater concentration of phosphorus, nitrogen (N), and magnesium (Mg) in wastewater, waste sludge, and sludge dewatering liquors. Such ions contained in combination can result in the struvite deposits, especially in EBPR processes. Struvite is a white crystalline material consisting of equimolar amounts of magnesium, ammonium, and phosphate.

$$\boldsymbol{Mg^{2+}} + \boldsymbol{NH^{4+}} + \boldsymbol{PO_4{}^{3-}} + \boldsymbol{6.\,H_2O} \rightarrow \boldsymbol{MgNH_4PO_4.(H_2O)} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots(2.1)$$

Struvite deposits develop layer after layer decreasing the internal diameter of the pipe and increasing the energy needed to push the sludge into a pipe. It is a beneficial tool as it can be saved by establishing an income stream for the WWTP as a phosphorus-rich fertiliser.

Nitrogenous waste is damaged main sludge contains ammonia, and magnesium arises from organic content oxidation and poly-P hydrolysis. Molar ratios of magnesium to phosphate higher than 1.05:1 are usually needed to confirm phosphorous removal as struvite (Jaffer et al., 2012).

Fujimoto et al., (2016) researched the influence of pH on struvite precipitation and identified the optimum pH range for the formation of struvite at 8.5 to 9.Struvite solubility increases with pH, and the pH should be increased to at least 8 to efficiently form struvite, which can be achieved by incorporating sodium hydroxide, lime, or aeration.

Bianxia et al., (2013) studied the morphology and quality of induced struvite crystals derived from hydrolyzed urine using seawater and desalination brine as low-cost sources of magnesium. The findings revealed that both seawater and brine are successful sources of magnesium to recycle phosphorus from hydrolyzed urine. Crystals collected from synthetic and natural urine showed that feather and coffin form shape morphology. The structural characterisation of the precipitates indicated that the key element was crystallized struvite. However, as seawater was applied to synthetic and natural urine, co-precipitates of magnesium calcite and calcite were detected, respectively. It was noticed that the existence of calcium in sources of magnesium could threaten the purity of the struvite. Better struvite consistency may be achieved in magnesium sources with a better Mg/Ca ratio. Comparative research found that seawater and brine have comparable impacts on the strength of the crystallized struvite.

2.17 Factors affecting MAP formation

MAP crystallization is regulated by several factors. Considering important variables offers potential for operation optimization (Ackerman, 2012).

2.17.1 pH

One of the most significant factors affecting MAP crystallization is allegedly solution pH (Liu et al., 2013). The pH-solution results are as follows**.**

2.17.1.1 Influence of pH on the availability of MAP component ions

Lower pH for the supply of the MAP variable ions appears to be safer. Both NH_4^+ and Mg^{2+} can be removed from the solution at large pH levels, rendering them inaccessible for MAP crystallization (Ackerman, 2012). Substantial volatilization of NH_3 exists in an open environment at pH point 9.3 (Hao et al., 2008). As pH hits 10.7 (Ali and Schneider, 2008;), Mg^{2+} is extracted from solution in the form of $Mg(OH)_2$. At pH 9.0 (Huchzermeier, 2011), nearly 98% of orthophosphate is available as HPO_4^{2-}. MAP is least soluble at pH > 8.5 (Nieminen, 2010). Keeping all these things into account, the optimal pH level for MAP crystallization would be 8.5 < pH < 9.3. Lanning (2008) indicated that pH during MAP recovery would not be elevated too high, because the effluent has to be neutralized before discharging into the atmosphere. In particular, if wastewater has a strong buffer capacity, it is essential to absorb significant amounts of chemicals for pH modification, thus raising the cost of reclaimed Area. Very high pH tends to be a struggle to MAP crystallization for that purpose.

2.17.1.2 Influence of pH on MAP purity

The rise in pH has been shown to reduce the quality of MAPs in reclaimed goods. Hao et al., (2008) recorded a drop in the MAP percentage from 96.8 to 15.5%, with a pH rise from 7.0 to 10.5, respectively. Li et al., (2012) showed that the purity of MAP reduced from 81.3 to 3.9% with a pH rise from 9 to 11. Wang et al., (2005) findings showed that precipitation at pH > 8.7 yielded certain compounds other than MAP.As pH plays a crucial role in MAP crystallization, the specification of optimum pH values (Table 2.5) has been dealt with by several researchers on MAP crystallisation. This was achieved to improve the recovery cycle in terms of quality of phosphorus reduction and purity to MAP. It appears that synthetic wastewaters need optimal pH values lower than real wastewaters.

The optimal pH for synthetic wastewater MAP crystallization was within a range of 7-7.5 (Hao et al., 2008).On the other side, for MAP crystallization, the strongest pH values were 8.5-9.5 for milk manure (Huchzermeier, 2011), 9 for pig waste biogas digester effluent (Perera et al., 2007), 9.5 for cola beverage (Foletto et al., 2013), and 9.5-10.5 for swine wastewater (Song et al., 2007). That can be due to the result of ions coexisting in the natural wastewaters. Such findings can be used as guides when analyzing the impact of pH on urban wastewater recovery from a MAP. It's important to notice that crystallization with MAP may also influence the pH value of the solution. Lanning (2008) proposed that the development of MAP culminated in solution acidification, as HPO_4^{2-} ions were reduced to PO_4^{3-} ions and emitted H^+ ions.

Huchzermeier (2011) found that solution pH rapidly decreased within the first 5-10 minutes that could be correlated with MAP forming, and then slowly increased until equilibrium was reached. And pH may be used as a proxy for completion of the crystallization reaction. It includes constant pH analysis and corresponding modification during the process.

Table 2.5 various studies on phosphorus recovery

Process	Type of wastewater	P removal efficiency	Recovered Products	Reference
Lab scale, direct crystallization	Cola beverage: 415 mg PO 4 /L	97%	MAP	Foletto et al., (2013)
Lab-scale, direct precipitation	Sewage sludge ash		CaHPO 4 .2H 2 O	Gorazda et al., (2012)
Lab scale, direct crystallization	Synthetic wastewater	96.8%	MAP	Hao et al., (2008)
Jar test	Liquor of thermally pre-treated waste activated sludge: 650 mg P/L	80%	MAP and some calcium and magnesium phosphates	Karabegovic et al., (2013)
Lab scale, Anion exchange + crystallization	Eutrophic water: 1.3 mg PO 4 /L	75.8%	MAP	Li et al., (2012)
Lab scale, direct crystallization	Swine waste biogas digester effluent: 42 mg PO 4 /L	97%	MAP	Perera et al., (2007)
Lab-scale, direct crystallization	Swine wastewater	97%	MAP	Song et al., (2007)
crystallization	pig farm biogas slurry	98.47%	MAP	Zeng et al.,(2020)
crystallization	sludge supernatant	97.42	MAP	Chang et al., (2019)

2.17.2 Magnesium (Mg^{2+}) supplementation

Magnesium is one of the three base ions used for crystallizing MAP. The theoretical Mg: N: P molar crystallization ratio for MAP is 1:1:1. Most wastewater forms, however, have low rates of Mg^{2+} relative to NH_4^+ and PO_4^{3-}. Mg^{2+} must be applied to wastewater to ensure optimal MAP formulation (Huchzermeier, 2011). Mg's molar ratio: NH_4^+: PO_4^{3-}could be a crucial element affecting the crystallization of MAP (Liu et al., 2013). MAP crystallization has been studied in different sources of magnesium, such as $MgCl_2.6H_2O$ (Xu et al., 2012), $MgSO_4.7H_2O$ (Hao et al., 2008), and MgO (Karabegovic et al., 2013). Investigations are carried out to look for the right source of Mg^{2+} which can generate high MAP yield and has a suitable price. $MgCl_2.6H_2O$ and $MgSO_4.7H_2O$ are readily soluble in water, according to Nieminen (2010), and are also the most common precipitants in both lab-scale and full-scale applications. In comparison, MgO and $Mg(OH)_2$ are insoluble in water and take a longer disassociation period. Such compounds must be used with small particle size and intense agitation to become operational. MgO and $Mg(OH)_2$ are rarely used in industries. $MgCl_2.6H_2O$ and $MgSO_4.7H_2O$ are costlier than MgO and $Mg(OH)_2$.

To minimize the expense of crystallization, it is suggested that seawater be used as an alternate supply of Mg^{2+} such that WWTPs are adjacent to the coast (Liu et al., 2013). Also, $MgCl_2$ will improve solution acidity (Lanning, 2008). Table 2.6 describes experiments conducted with differing Mg: P molar ratios on MAP crystallisation from wastewater. It appears that an extra supply of Mg^{2+} is normally applied to ensure high phosphorus elimination, suggested by Mg: P molar ratio greater than 1. Liu et al. (2013) clarified that four forms of magnesium phosphate salts may be produced based on the solution pH, namely $MgNH_4PO_4.6H_2O$, $MgHPO_4.3H_2O$, $Mg_3(PO_4)_2.22H_2O$, $Mg_3\ (PO_4)_2.8H_2O$. The real volume of Mg^{2+} applied will also be greater than the potential estimate. Overuse of magnesium salts, however, may cause undesirable impacts, such as increased chemical prices, precipitation of $Mg(OH)_2$ in high alkaline environments, and excessive effluent residual Mg^{2+} and Cl ions (Huchzermeier, 2011). Consequently, unnecessary Mg^{2+} in the effluent will need to be eliminated before discharge into the atmosphere (Lanning, 2008).

2.17.3 Chemical addition sequence and rate

Studies have looked into various feeding cycles. Hao et al., (2008) proposed that optimum MAP crystallization from industrial wastewater could be accomplished by applying $NaH_2PO_4.2H_2O$ to the $MgSO_4.7H_2O$ and NH_4Cl combination, accompanied by pH modification. On the opposite, Xu et al. (2012) observed that introducing $MgCl_2.6H_2O$ to the phosphorus solution, accompanied by pH modification and corresponding NH_4Cl replacement, was the strongest feeding series for MAP precipitation from sewage sludge ash. Kim et al., (2007) tested eight chemical feeding sequences and observed that the introduction of magnesium and phosphate accompanied by a pH modifying chemical produced the best crystallization of MAP.

Table 2.6 optimum pH and molar ratio for MAP crystallization from wastewater

Sl No	Type of wastewater	Mg source	Mg: P molar ratio	Optimal pH	P recovery	Reference
1	Synthetic wastewater	$MgCl_2.6H_2O$	1:2	8.5	98%	Çelen et al., (2007)
2	Cola beverage	$MgCl_2.6H_2O$	1:1	9.5	97%	Foletto et al., (2013)
3	Anaerobic digester centrate	$MgCl_2.6H_2O$	2.5:1	7.3-8.3	60-81%	Garcia-Belinchón et al., (2013)
4	Synthetic wastewater	$MgSO_4.7H_2O$	1.2:1	7.0-7.5	80%	Hao et al., (2008)
5	Synthetic wastewater	$MgCl_2.6H_2O$	1.3:1.1	9.9-9.5	99.9%	Jia, (2014)
6	Digested swine manure centrate	$MgCl_2.6H_2O$	1.6:1	9.0	81%	Jordaan et al., (2010)
7	Liquor of waste activated sludge	MgO	1.2:1	9.2	80%	Karabegovic et al., (2013)
8	Eutrophic water	$MgCl_2.6H_2O$	1.2:1	<8.0	80%	Li et al., (2012)
9	Synthetic wastewater	$MgCl_2.6H_2O$	1.1:1	9.0	70.3%	Pastor et al., (2010)
10	Swine waste biogas digester effluent	$MgCl_2.6H_2O$	1:1	8.7	97%	Perera et al., (2007)
11	Swine wastewater	$MgCl_2.6H_2O$	1.4:1	9.5-10.5	97%	Song et al., (2007)
12	Sewage sludge ash extraction	$MgCl_2.6H_2O$	1.6:1	10	97.2%	Xu et al., (2012)
13	pig farm biogas slurry	MgO	1.5:1	10	98.47%	Zeng et al., (2020)
14	sludge supernatant	$MgCl_2.6H_2O$	1.8:1	9.5	97.42%	Chang et al., (2020)

The rise in pH before adding phosphate could lead to the formation of $Mg(OH)_2$, thus decreasing the availability of Mg for MAP crystallization. Similarly, calcium phosphate was produced instead of MAP, if the introduction of magnesium was in sequence step during the phosphate feeding. With respect to the effect of the chemical supplement pace, Jia (2014) found that the feeding pace had little influence on the recovery of phosphorus.

2.17.4 Presence of calcium (Ca^{2+})

Owing to the reaction of Ca^{2+} with orthophosphate to the creation of different compounds of calcium phosphate such as $CaHPO_4.2H_2O$ (brushite), $CaHPO_4$ (monetite), $Ca_8H_2(PO_4)_6.5H_2O$ (octa calcium phosphate), $Ca_3(PO_4)_2$ (tricalcium phosphate), $Ca_5(PO_4)_3OH$ (hydroxylapatite), $Ca_3(PO_4)_2nH_2O$ (amorphatite), $Ca_3(PO_4)$ It was found that the percentage of pure MAP decreased from 85 to 61 and 38% with elevating Ca: P molar ratio of 0.5:1 to 1:1 and 2:1, respectively (Wang et al., 2005).Such results agreed well with Ackerman's (2012) findings, which noted that the Ca: P molar ratio above 2 might reduce the precipitation value of MAP to zero. That is, calcium can block active sites and interact with orthophosphate magnesium (Huchzermeier, 2011). Likewise, Moerman et al. (2009) stated that in Europe, when Ca: P molar ratio in anaerobically digested potato wastewater was as large as 2.36. no MAP was developed in a full-scale MAP reactor.

Shen et al. (2011) used acidification accompanied by the introduction of EDTA and oxalate to reduce the impact of Ca^{2+} on MAP accumulation in liquid dairy manure. However, it was worth remembering rising prices and the side effects of chemicals. Ackerman (2012) proposed that precipitation be performed at low pH (pH 6.8) to avoid the production of calcium phosphate from hog manure. The author suggested that the amount of Ca^{2+} in urban sludge dewater liquor is generally low and can not present a concern for the creation of MAPs. Instead, animal wastewater frequently contained large Ca^{2+} concentrations and therefore needed careful treatment before MAP recovery.

2.17.5 Alkalinity

Huchzermeier (2011) stated that carbonate (CO_3^{2-}) may be complex with magnesium (Mg^{2+}) and ammonium (NH_4^+) to form magnesium carbonate ($MgCO_3$), magnesium bicarbonate ($MgHCO_3$), and ammonium bicarbonate (NH_4HCO_3) on the high alkalinity medium. Such processes are based on two MAP factor ions ($Mg^{2+}$and

NH_4^+) that would otherwise be required for precipitation of MAP. As a consequence, the forming of MAP is minimized, and the introduction of Mg^{2+} is therefore required.

2.17.6 Total suspended solids (TSS)

According to Lanning (2008), elevated amounts of organic matter in the form of TSS may also pose an obstacle to the development of MAP. The author clarified that the complexation of organics with MAP component ions would contribute to a decrease in MAP component ion abundance and an improvement in MAP solubility. Alternatively, high TSS content may find it difficult to distinguish MAP from organic matter. Huchzermeier (2011) claimed that TSS could impede the development of MAP by up to 1000 mg/L. Nieminen (2010) found that the impurities in the recovered phosphorus products were decreased by TSS at 150-200 mg/L. While Ostara Pearl technology could work at 3000-4000 mg/L of TSS level, TSS level is below 1000 mg/L is suggested. The long settling period could be a solution to the issue of high TSS (Ackerman, 2012).

2.18 Summary of literature

Sludge dewatering, phosphorus removal, and recovery from wastewater have all gained a lot of attention in recent years. Numerous conclusions were taken from this literature review:

To achieve optimum dewatering efficiency, a suitable porous and incompressible sludge cake structure has to be developed and managed. Enhancing the porosity and permeability of solid cake formation by using skeleton materials or filter aids such as slag or agricultural wastes. Carbon-based physical additives are usually more effective in sludge dewatering than inorganic materials due to their increased porosity. Due to its low price and eco-friendliness of used materials, this technique is encouraged. For sludge with strong compressibility, chemical conditioning itself will not always attain a sufficient improvement in dewatering quality. Physical conditioners that serve as skeleton constructors have been utilized to improve sludge dewaterability by providing more stable and incompressible structures to the sludge solids. For every sludge treatment system where enhancing the dewatering process is the goal, assessment of the dewaterability of sludge significantly necessary.

Phosphorus is needed for the growth of living organisms and the production of agricultural products. It is, however, a non-renewable resource that could be depleted in the near future. Alternatively, an abundance of phosphorus in the water medium is primarily responsible for eutrophication, which causes environmental degradation and threatens ecosystem biodiversity. the elevated level of phosphorus must be removed and recovered from wastewater to avoid eutrophication, save the phosphate rock reserve, protect engineered structures from MAP scale, and follow strict regulations.

Phosphorus can be recovered from a variety of WWTP products, including wastewater, sludge, and ash. As a result, phosphorus recovery technologies may be classified as crystallization/precipitation, wet-chemical, or thermochemical. Even though wet-chemical and thermo-chemical methods can achieve higher recovery rates than crystallization/precipitation, they are less common due to high chemical and energy costs, as well as the need for specialized equipment. Calcium phosphate and MAP are the most preferred precipitating materials.

2.19 Research findings

Several knowledge gaps can be identified from the sludge dewatering, EBPR, and recovery, especially in the development of technologies from waste to more useful products. The challenge in the sludge dewatering process is most of the research is for lab-scale experiments and difficult to implement on large scale and also cost cannot be easily determined.

Dewatering and phosphorus recovery are attracting topics that have piqued the interest of many researchers. Dewatered sludge and liquor can be used as many useful products. Hence there is a need to investigate low-cost technologies. The ultimate target should be that part of the amount invested in the treatment of the sludge, has to be financially helped by recovering struvite as a fertilizer thereby bearing its own cost.

Research into simple technologies conversion of the sludge into physical forms with fertilizer values can promote ease way of transportation as well as ease in application of struvite in the area of need. Studies on low-cost technologies of extracting non-renewable phosphorus are also still lacking.

Based on the fact-findings, sludge production and its management is a challenging task because it occupies a lot of space in landfilling and if it is addressed properly cost of wastewater treatment will come down. Hence, assessment of sludge dewaterability is required for any sludge treatment system because of the unpredictable and volatile behaviour of all types of sludge, especially bio–sludge as well as variations in solid-liquid separation methods. From the establishment of the indices of first dewatering, several indicators for the dewatering process are increased and advanced. Even though there is advancement yet there is no universal index for dewatering that showcases the ability for sludge dewatering. As sludge is a nutrient-rich product and is getting wasted. Hence it is attempted to address nutrient removal (phosphorus) from the dewatered sludge. Knowledge on interactions between biological nutrient removal and chemical nutrient removal must be broadened to improve the removal and recovery by biological processes.

MAP has been successfully recovered in several forms from wastewater rich in phosphorus, such as cola beverage of swine wastewater, eutrophic water, sludge liquor, membrane centrate. However, MAP recovery through crystallization has been rarely studied. Also, while some studies were available on MAP reclamation by adsorption/ion exchange and crystallization, few works were done for this purpose on the beneficial use of dewatered sludge.

CHAPTER 3

MATERIALS AND METHODOLOGY

3.1 General

This chapter deals with the materials used; methodology adopted to carry out the objectives. It is presented in three phases. Phase I deals with the sludge dewatering aspect with granulated blast furnace slag (GBFS) and coconut shell biochar (CSB). Phase II: deals with performance evaluation of SBR (Anaerobic-Aerobic) for the EBPR and Phase III: Investigation of phosphorus recovery potential. Each phase is explained in successive sections.

Phase I: Experimental investigation on sludge dewatering using GBFS and CSB

The objective of phase-I experiments was to study the efficiency of GBFS and CSB for sludge dewatering and also optimizing the various parameters using the BBM.

- Experimental investigation on sludge dewatering using GBFS

An experimental investigation was carried out to assess the initial characteristics of sludge and GBFS. The dosage of skeleton materials, pH, and contact time were optimized to achieve maximum sludge dewatering by BBM. Evaluation of sludge dewatering properties like CST, moisture content, turbidity, Zeta potential, protein, polysaccharides, and heavy metals. Characterization of dewatered sludge by Scanning Electron Microscope equipped with Energy Dispersive X-Ray analysis (SEM-EDAX), X-ray diffractometer (XRD), and Fourier Infrared Spectroscopy (FTIR)was carried out.

- Experimental investigation on sludge dewatering using CSB

An experimental investigation was carried out to assess the initial characteristics of the sludge. Since CSB is not a flocculant, it does not have the capability to flocculate the particles in the sludge. Hence a flocculant, ferric chloride was used with CSB, so that CSB acts as a skeleton material, giving a beneficial cake structure. Utilizing both CSB and ferric chloride has a synergic effect in the removal of maximum water content from the sludge and simultaneously removal of heavy metals and phosphate. Evaluation of sludge dewatering properties (CST, moisture content, settleability, Zeta potential, heavy metals, and phosphate). Characterization of dewatered sludge by SEM, XRD, and FTIR was carried out. Further experiments are conducted to determine the CST using significant input variables such as the modified coconut shell biochar with ferric chloride (MCSB-$FeCl_3$) dose, rapid mixing time (RMT), and slow mixing time (SMT) using BBM.

Phase II: Performance evaluation of SBR (Anaerobic-Aerobic) by EBPR

The objectives of the study were to examine phosphorus removal efficiency by enhancing the biological phosphorus removal process and to evaluate the performance of anaerobic and aerobic reactors connected in series for the effective removal of phosphorus under various operating conditions. Characterization of the samples was carried out by SEM equipped with EDAX, and FTIR. The samples were collected and kept for drying in a hot air oven at 105˚C for 24 hours.

Phase III: To investigate the recovery potential by crystallization and adsorption process

This study focuses on the recovery of phosphorus as a struvite through a crystallization process with varying pH and molar ratio from the digested sludge using magnesium chloride as a magnesium source. Morphological studies were carried out for struvite using SEM, the composition quality of struvite crystals was identified by XRD. FTIR was used to find and confirm the presence/absence of various functional groups present in the samples. Infrared spectra were recorded in the range of 400 cm^{-1} to 4000 cm^{-1} using the Thermo Nicolet Avatar. Further, the adsorption process was carried out using the GBFS. Initially, the slag was washed with distilled water and dried at 26^0C. The overall methodology adopted in the present study is depicted in the form of the flowchart (Figure 3.1).

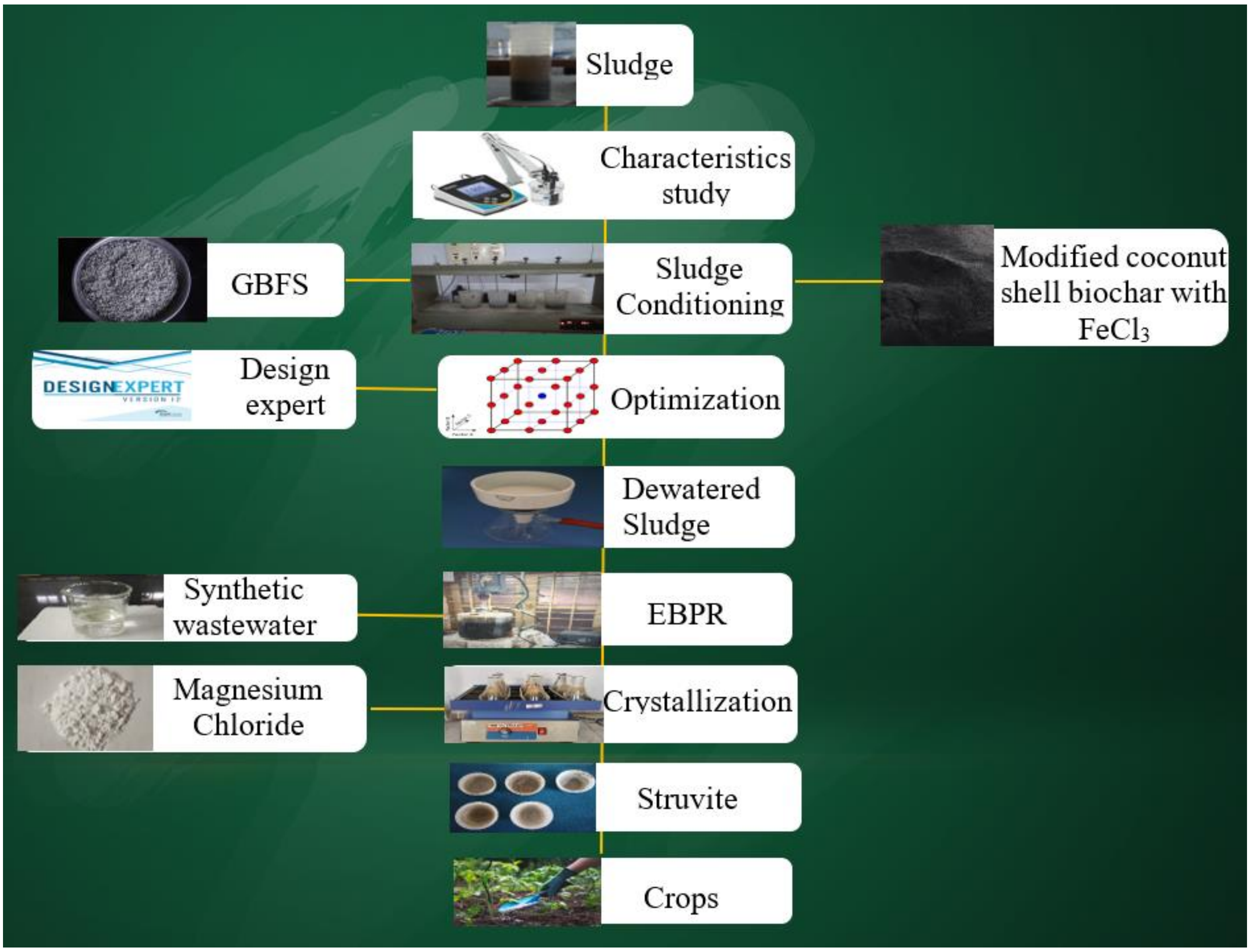


Figure 3.1 Flowchart of the overall methodology

3.2. Material and methodology

3.2.1 Phase I: Experimental investigation on sludge dewatering using GBFS and MCSB-$FeCl_3$ as skeleton material

3.2.1.1 Materials used

Sewage sludge was obtained from the treatment plant of the National Institute of Technology-Karnataka (NITK) Karnataka, India. The sludge samples were bought in an air-tight container, and it was preserved in a refrigerator at 4˚C to minimize microbiological decomposition. Before proceeding with the experiments, the sample was kept in a water bath at 20^0 to 30^0C.

3.2.1.2 Dewatering using GBFS as skeleton material

GBFS is industrial waste material and was used as a physical conditioner in the present study. GBFS influences sludge dewatering by reducing the maximum moisture content. The presence of oxides of calcium, magnesium, and aluminium is high in GBFS, and these oxides facilitate the action of GBFS as a conditioner in sludge dewatering. The chemical composition of GBFS is given in Table 3.1. Calcium oxide (Loba Chemicals) was used for pH control and conditioning.

Table 3.1Chemical composition of GBFS

Chemical composition	**Composition in percentage (%)**	
Calcium oxide (Cao)	41.2	
Silicon dioxide (SiO_2)	35.4	
Aluminium oxide (Al_2O_3)	13.6	
Magnesium oxide (MgO)	7.2	
Ferric oxide (Fe_2O_3)	0.16	
Loss of ignition (LOI)	0.82	

The sludge characteristics such as pH, moisture content, electrical conductivity (EC), temperature, total solids (TS), total dissolved solids (TDS), volatile solids (VS), turbidity, COD, and CST were found out experimentally. The pH value of the sludge obtained was 6.9 by using a digital pH meter (Henna). The moisture content of the raw sludge was 96.4%. The TS, TDS, VS, and COD were found as per IS: 3025 Bureau of Indian Standards (BIS) methods. The characteristics of raw sludge were determined and are presented in Table 3.2.

3.2.1.3 Dewatering Methodology

Skeleton material (GBFS) and CaO (Quick lime) were used to enhance the dewaterability of secondary sludge. A set of 500 ml conical flask was used to perform batch-mode experiments. To study the effect of pH on sludge dewatering, quick lime was added to the sludge sample to achieve target pH (8.0, 9.0, 10, and 11) for maximum dewatering. The mixture was then subjected to 5 min rapid mixing at 300 rpm and 5 min slow mixing at 60 rpm to make sure of dispersion with 200ml of secondary sludge.

Table 3.2 Raw sewage sludge characteristics

Denotations	**Values**
pH	6.9
Temperature(^{0}C)	31.2
Electrical conductivity (ms/cm)	3.23
Total solids, TS (mg/L)	19586
Specific gravity	1.023
Moisture content (%)	96.4
Zeta Potential(mV)	-7.8
Turbidity	24.6
Alkalinity(mg/L)	2200
Chemical oxygen demand, COD (mg/L)	18240
Capillary Suction Time, CST (sec)	92
Total Suspended solids	12754
Total volatile solids	7146

Later, the effect of skeleton material on sludge dewatering was studied by varying the dosage of slag (0.12,0.25,0.37, 0.50% DS) and mix for 2 min at 300 rpm and 3 min at 60 rpm. After agitation, the resulting sludge experimented for CST and moisture content. The other significant properties of raw and dewatered sludge such as zeta potential, turbidity, heavy metals, and biopolymers were carried out. The raw and dewatered sludge sample was dried and then analyzed by SEM equipped with EDS, XRD, and FT-IR. The detailed methodology is represented in Figure 3.2. RSM is used to determine the optimal performance parameters of a system by optimizing variables at different levels. The BBD was used to approximate a response function using Design Expertv11.1.2.0. For the current study, experiments are conducted to determine the filtrate volume using significant input variables like the effects of dosage, pH, and contact time was investigated. Every independent variable was serially coded at three-level slow (-1), medium (0), and high (1).

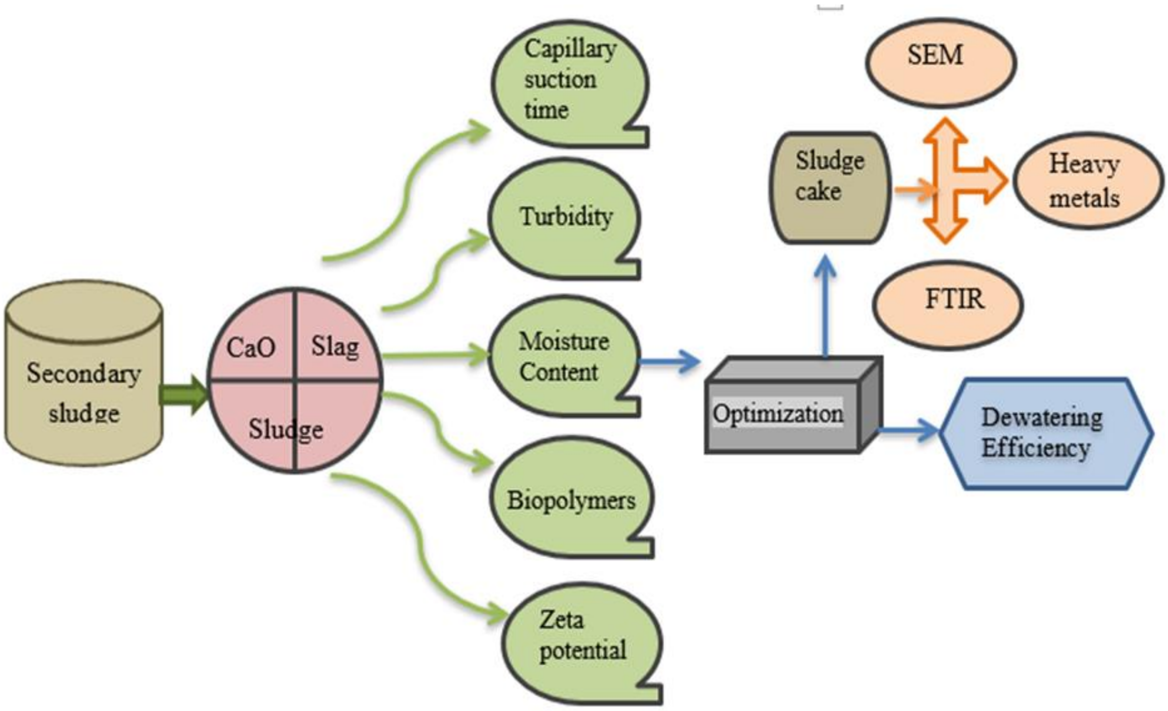


Figure 3.2 The schematic representation of the study

3.2.1.4 Dewatering using MCSB-$FeCl_3$ as skeleton material

Coconut shell is a bio waste and its availability is high as to waste in the Coastal region of Karnataka, India. The raw coconut shell was brought to the laboratory and was crushed using a mixer and coconut shell powder was prepared. The chemical composition of the coconut shell is shown in Table 3.3. Later it was sieved and the particle size of 210-micron meter was collected and burnt in the muffle furnace (Rotex) at 600^0C and for 1 hr.

For coconut shell powder modification $FeCl_3$ of various concentrations was used. 10g of CSB was immersed in 1000 ml of HCl (2 mol/L) for about 24 hrs. Obtained biochar was filtered, cleaned, and dried in the oven (Sakova) at 105^0C. 1:15 ratio of CSB was soaked in $FeCl_3$ for 2 hrs and sonicated (Skytron) at 35^0C and later it was filtered, dried, and used for further analysis. Figure 3.3 shows the flow chart of sludge dewatering using MCSB-$FeCl_3$.

Table 3.3 Chemical composition of the coconut shell

Chemical composition	Composition in percentage (%)
Silicon dioxide (SiO2)	45.08
Aluminium oxide (Al_2O_3)	15.4
Ferric oxide (Fe_2O_3)	12.6
Calcium oxide (Cao)	0.56
Magnesium oxide (MgO)	16.1

The sewage sludge initial characteristics were experimented in the laboratory according to standard methods and obtained results are tabulated in Table 3.4.

Table 3.4 Overview of raw sludge

Sl No	Parameter	Unit	Value
1	pH	-	7.24
2	Electrical Conductivity	Microsimens/cm	318
3	Temperature	Degree	27
4	Moisture content	%	96.5
5	Total solids (TS)	mg/L	17659
6	Total dissolved solids	mg/L	6710
7	Total suspended solids (TSS)	mg/L	10224
8	Alkalinity	mg/L	2169
9	Zeta potential	Mv	-7.96
10	CST	Sec	138

The initial characteristics of secondary sludge are pH, Moisture content, TS, VS, Alkalinity, etc., were experimented with. The results show the presence of organic matter, and also it consists of water and solids that can be divided into mineral and organic (volatile) solids. pH is in the neutral range. Sludge conditioning was taken up in jar test apparatus. 200 ml of sludge is filled in all 6 beakers and 1st beaker will be the controller. Later add MCSB-$FeCl_3$in the rest of all 5 beakers. The dose of coconut shell biochar is like 10, 20, 30, 40, and 50 % DS and measures the CST and moisture content with respect to optimum rapid mixing which is done at 200 rpm for 10 min followed by 30 rpm for 15 min slow mixing.

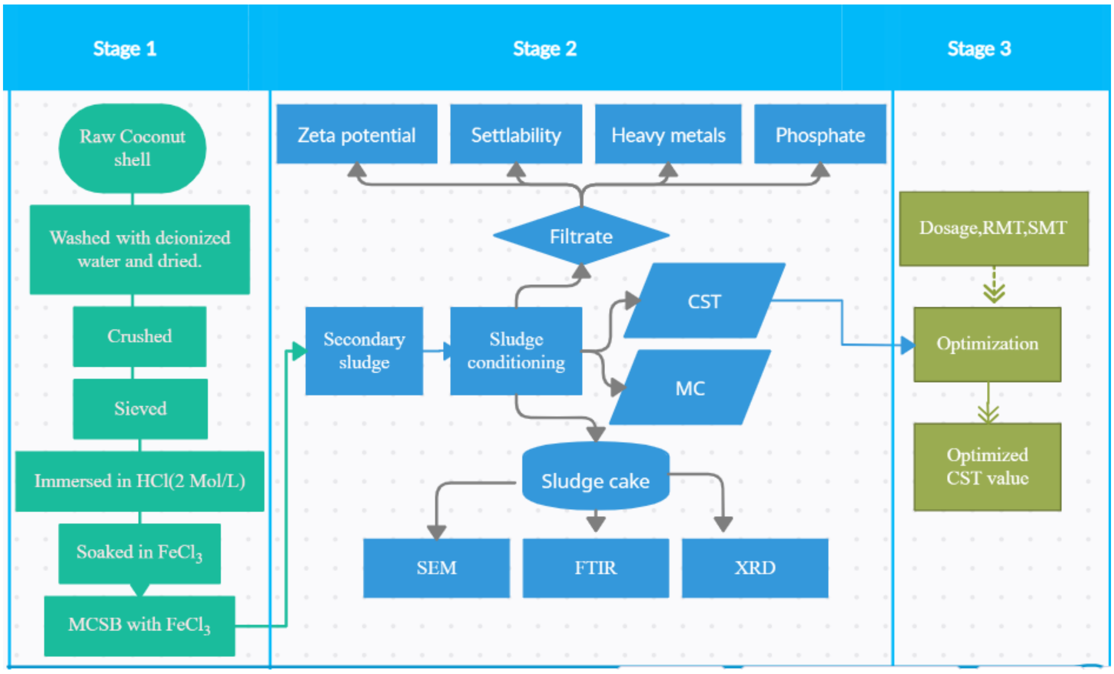


Figure 3.3 Flow chart of sludge dewatering using MCSB-FeCl3

Optimization was carried out using BBD method, wherein CST was measured as a response for BBD. The conditioned sludge is filtered through vacuum filtration and the sludge cake is dried and The raw and dewatered sludge sample was dried and then analyzed by SEM equipped with EDS, XRD, and FT-IR. Every experiment was performed three times, and the mean value is taken to test the efficiency of the sludge dewatering. The other significant properties of raw and dewatered sludge such as moisture content, zeta potential, settleability, heavy metals, and phosphate were carried out.

3.2.1.5 Analytical methods

i. CST: - CST test was carried using a whatman paper #17. Draw two circles of dia 1.5 and 3 cm from the center and place a glass tube in the center of the circles, a height of 5 cm is marked on the tube which is open at both ends. The stirred sludge is transferred to the test tube and note down the timings when the moisture reaches from 1.5cm dia to 3.0cm. CST test was carried out in accordance with Lee and Liu (2000) as shown in Figure 3.3.

ii. Moisture content: - The moisture content and filter volume were determined using a vacuum filter. Fifty milliliters of sludge was poured onto a vacuum filter, and a pressure of 50 kPa was applied. Then, the liquid was collected in the bottom chamber. The sludge remaining in the top chamber was collected, and the moisture content was determined as per a standard method (APHA 2012).

iii. Zeta potential:- Zeta potential of secondary sludge is measured using HORIBA Scientific, SZ-100. The sludge was mixed with quick lime and skeleton material in a jar test apparatus. The mixed sludge was then centrifuged (REMI R-23) at 4000 RPM for 15 min and the sludge supernatant was used to measure the zeta potential using HORIBA Scientific, SZ-100, and turbidity using Digital Nephlo-turbidity meter132. The zeta potential was measured for raw and conditioned sludge with a varying dosage of skeleton material (Ma et al. 2017). Every sample was measured at least 3 times and the average is presented.

iv. The polysaccharides and protein content in raw and treated sludge was determined by Anthrone and Lowry method (Felz et al. 2019).To determine the protein content of EPS, the Lowry method was used. As a benchmark, BSA was used. Reagents: 270 mM Na_2CO_3 and 1:143 mM NaOH. 2:57 mM $CuSO_4$ reagent 124 mM Na-tatrate (Reagent 3). Reagent 4 was rendered by combining reagents 1 through 3 in a 100:1:1 ratio. Folin reagent diluted 5:6 with distilled water (Reagent 5). Procedure: A 0.5 ml sample was mixed with 0.7 ml reagent 4 in a whirlpool. Reagent 5 (0.1 ml) was applied and the solution was whirled together. The absorbance at 750 nm was measured after 45 minutes at room temperature.

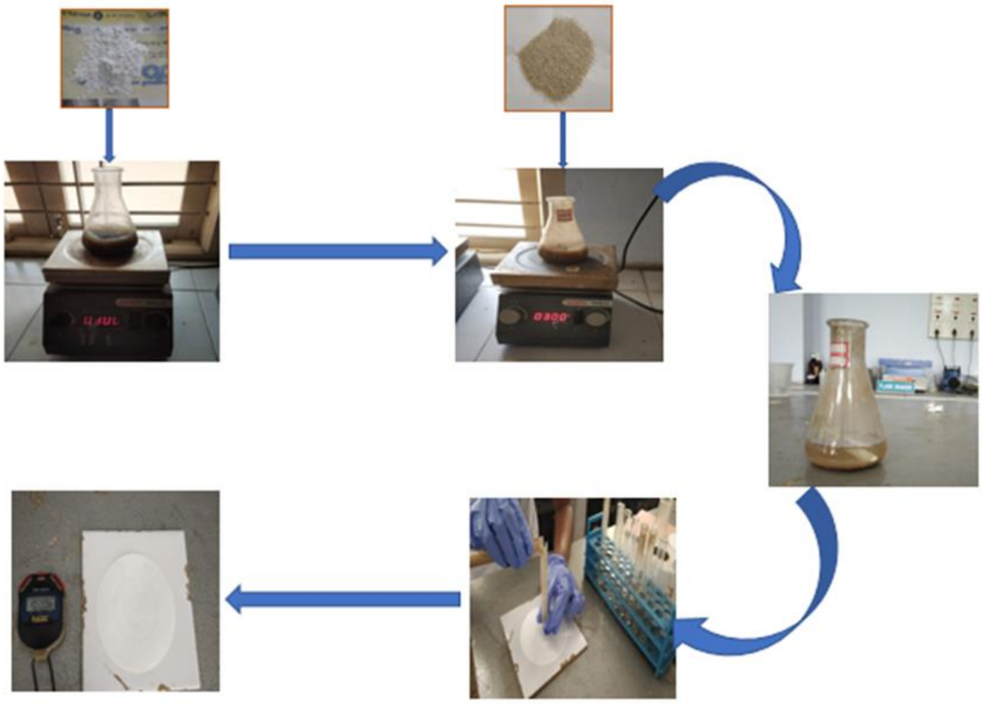


Figure 3.4 Steps involved in the sludge dewatering by CST

v. The heavy metal concentrations detection in the solutions were determined using atomic absorption spectrophotometer (TIFAC, GBC 932 plus) for the filtrate. Standard solutions of 0.4, 0.8, 1.2, 1.6, and 2 ppm of Cd, Cr, Pb, and Ni were prepared from a 1000 ppm standard solution of Cd, Cr, Pb, and Ni with two times dilutions performed to obtain the calibration curve. At a wavelength of 324.74 nm and a phase size of 2.7 and 0.8 nm, the standards and samples were read, respectively. The percentage of adsorption for each of the solutions in contact with GBFS was calculated using the data obtained.

vi. The collected mixture was mixed before being moved to a 1 L graduated glass cylinder to study the settling behavior of the conditioned sludge. The sludge volume index (SVI) is a critical criterion for determining settling activity. Settleability is described as the volume (mL) covered by one gram of conditioned sludge after 30 minutes of settling.

vii. Phosphate: - The ammonium molybdate spectrophotometric method was used to evaluate the remaining phosphate. If the pH of the sample is more than 8.20, then treat the sample as follows. To 100 mL sample containing not more than 200 mg P and free from color and turbidity, add 1 drop of phenolphthalein indicator. If the sample turns pink, a strong acid solution discharges the color. Prepare a series of standards of concentrations ranging from 0.0 to 2.0 mg/L by diluting 0, 1, 2, 3, 4 mL of phosphate standards to 100 mL to get a series concentration of 0, 0.5, 1.0, 1.5 and 2.0 mg/L. Add, with thorough mixing after each addition, 4.0 mL molybdate reagent and 0.5 mL stannous chloride reagent. After 10 min., but before 12 min., measure the color calorimetrically at 690 nm for standards and sample.

viii. The raw and dewatered sludge were collected and kept for drying in a hot air oven at 105˚C for 24 hours. Morphology of raw and dewatered samples was performed using SEM, JEOL along Energy Dispersive X-Ray analysis (EDAX).

ix. XRD study was carried out to determine the crystal phase of dewatered sludge. It was operated at 2θ range from 10^0 to 60^0 using Cu- Kα̇ radiation.

x. The chemical modifications by FTIR (Thermo Nicolet) in the sludge can be verified by the presence/absence of functional groups present in it. For 30 seconds, a given amount of sample is preground with 25 mg of KBr. After that, 275 mg of KBr is applied, and the mixture is ground for another 30 seconds before being pressed.

3.2.1.6 Optimization studies

The RSM is used in this analysis to extract the model and assess the maximum effect. This approach creates the experiment matrix by taking into account the number of variables as well as the maximum and minimum limits set for each variable. This approach is used to assess the number of tests and the levels of each variable in each test. The experimental design is significant. As a result, this approach simplifies the analysis process while also reducing the time and costs involved. The tests were created with the help of Design-Expert software, and statistical analysis was run on them.

The Design Expert is a comprehensive software for statistically simulating several processes. It allows statistical simulation of the desired processes. Also develops 3D graphs to define and evaluate different processes. Further, experiments are conducted to determine the CST using significant input variables such as the MCSB-$FeCl_3$ dose, RMT, and SMT using BBM. Experimental studies were performed at least three times to validate the model results obtained in the laboratory and were reported as average CST values. 17group tests were performed. The BBD is introduced, development and experimental data are analysed using Design Expert v 12.

3.2.2. Phase II: Performance evaluation of SBR(Anaerobic-Aerobic) for the EBPR

3.2.2.1 Anaerobic-Aerobic experimental setup

A laboratory-scale SBR of Anaerobic-Aerobic process was operated using 4 litres reactor made up of acrylic sheet with brass valve, working volume is of 3 litres operated for more than four months as shown in Figure 3.4. A cycle of experiments was conducted for around 180 days including stabilization period.

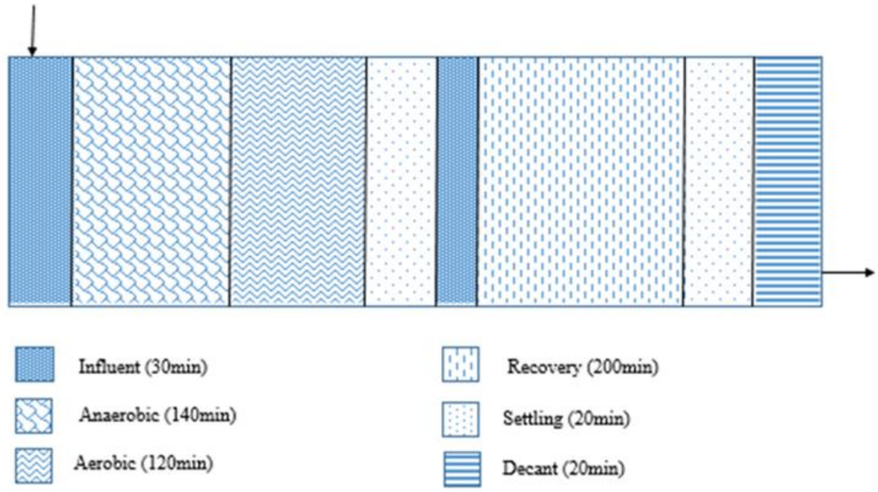
Figure 3.5 Lab-scale sequential batch reactor

The setup consists of an inlet tank of 3 litres. A peristaltic pump was provided for the flow from the inlet tank to the anaerobic reactor. The anaerobic reactor was continuously mixed with a mechanical mixer with a rectangle peddle so that the particles are mixed continuously and also to avoid clogging of biomass. During the aerobic process, the reactor was aerated by a fine bubble diffuser. The operation cycle consists of 8 phases which are shown in Table 3.5. The reaction time for each operation was controlled. pH was continuously monitored using a pH probe. The entire operation was carried out at a room temperature of 24^0-26^0C. The solid retention time was set at 16 days. Batch studies were conducted to investigate the PAOs in detail. After achieving steady-state in the SBR, a batch study was performed using a 500 ml sludge sample collected in a 1000 ml conical flask.

To investigate the anaerobic phosphorus release as well as aerobic phosphorus uptake capacities, the sample was washed with the trace elements solution and filled into the 1-liter conical flask. Before the anaerobic phase, 500 ml of dewatered liquor was added into the conical flask and noted down the initial phosphorus concentration. After this, 2 hrs of aerobic conditions were provided. Finally, at the end of the anaerobic and aerobic phase samples were analysed for phosphorus release and uptake. The difference in microbial diversities was investigated by using SEM. The operational cycle of the experiment is shown in Table 3.5

Table 3.5. Operational cycle of the experiment

Reactor	**Procedure**	**Time(min)**
Anaerobic (ANR)	Influent	30
	Anaerobic	140
Aeration (AE)	Aerobic	120
	Settling	30
Crystallization (PR)	Influent	20
	Recovery column	200
	Settling	30
	Decanting	20



3.2.2.2 Wastewater and Seed sludge

The mixture of primary and secondary sludge was dewatered. In SBR dewatered granular sludge was used for design and operation for the removal of phosphorus with minimum sludge production. The reactor was seeded with activated sludge collected from the kavoor treatment plant, Mangalore. The inoculum was stored in an incubator for 4 days before adding to the digestor. Alternative anaerobic-aerobic conditions were maintained in the novel SBR. Mixtures of glucose and acetate were used as a carbon source during the removal process. Aeration was provided in the aeration column so that the pH of the wastewater is increased by removing CO_2. The composition of the synthetic wastewater (per liter) used as an influent for 1 liter are Solution I (0.5L)contains 6.6 g of$CH_3COONA.3H_20$, 6.8 g of $C_6H_{12}O_6$, 3.8 g of NH_4Cl, yeast extract of 0.06, 3.6 g of $MgSO_4 \cdot 6H_2O$, and 0.47 g of $CaCl_2 \cdot 2H_2O$.Solution II (0.95L) contains 56 g of K_2HPO_4, 40 g of KH_2PO_4, 1.35 g of $FeCl_3$, 0.37 g of H_3BO_3, 0.04 g of $CuSO_4 \cdot 5H_2O$, 0.27g of KI, 0.18 g of $MnCl_2 \cdot 4H_2O$, 0.5 g of $Na_2MoO_4 \cdot 2H_2O$, 0.18 g of $ZnSO_4 \cdot 7H_2O$, 0.02 g of $CoCl_2 \cdot 6H_2O$ and 15 g of Ethylenediamine tetraacetic acid.

3.2.2.3 Analytical methods

The concentration of Alkalinity, COD, PO_4^{3-}P, NH_4^{3-} -N, MLVSS, and MLSS were measured according to the standard methods (APHA 2005). The pH of the samples was measured using a digital pH meter (Henna). UV spectrophotometer was used to measure the phosphate, and it was analysed by the molybdovanadate method. The samples collected from the reactor are centrifuged at 10000 rpm for 15 min and the supernatant was filtered through 0.45-micron meter cellulose microfiber filters before analysing the samples. Instrumental Analysis such as SEM, EDX, and FTIR was done for samples and struvite.

The samples were collected and kept for drying in a hot air oven at 105˚C for 24 hours. Thereby obtained results can be compared. Good quality surface imaging was done for samples using JEOL SEM. EDAX which is analysed together with the SEM gives the chemical analysis and percentage weight of heavy metal concentration samples. The chemical modifications in the sludge can be verified using the functional groups present in it. (FTIR is used to find and confirm the functional groups present in the samples. Infrared spectra were recorded in the range of 400 cm^{-1} to 4000 cm^{-1} using Thermo Nicolet Avatar. Approximately 2 mg of biological material sample was prepared and compressed with 200 mg of KBr.

3.2.3 Phase III: To investigate the recovery potential by the crystallization process

3.2.3.2 Methodology

The process was taken up for different mg/ P molar ratio of 0.5:1, 1:1, 1.5:1 and 2:1. Magnesium sources as magnesium chloride, the pH need to be increased for 7, 8, 9, 10, and 11. The aeration also causes a good mixing in the reactor. The mixing was done for 20 min so that, to ensure uniform and complete mixing so that precipitation takes place. Later the supernatant is collected and checked for purity. In all the experiments, the mixture was then centrifuged at 5000 rpm for 10 min to separate the precipitates. The precipitates were dried overnight at 90^0C for various characterization analyses. The supernatants were filtered through 0.45 μm pore size membrane filter before the analysis of the remaining phosphate. All batch experiments were carried out at room temperature (25 ± 1^0C). Figure 3.5 shows the batch study conducted for different mg/ P molar ratios.

Figure 3.6 Batch study

3.2.3.3 Analytical methods

Instrumental Analysis such as SEM, EDX, and FTIR was done for samples and struvite. The samples were collected and kept for drying in a hot air oven at 105˚C for 24 hours. Thereby obtained results can be compared. Good quality surface imaging was done for samples using JEOL SEM. EDAX which is analyzed together with the SEM gives the chemical analysis and percentage weight of heavy metal concentration samples. The chemical modifications in the sludge can be verified using the functional groups present in it. FTIR is used to find and confirm the functional groups present in the samples. Infrared spectra were recorded in the range of 400 cm^{-1} to 4000 cm^{-1} using Thermo Nicolet Avatar. Approximately 2 mg of biological material sample was prepared and compressed with 200 mg of KBr.

CHAPTER 4

SLUDGE DEWATERING USING SKELETON MATERIALS

4.1 General

The growing trend to use industrial waste and agricultural waste-based skeleton materials for sludge dewatering. It has been shown that in most cases, waste-based skeleton materials in the natural form can hardly dewater the sludge. Thus, modification plays a significant role in sludge dewatering. Laboratory studies were conducted using two skeleton materials for sludge dewatering. Characterization studies was carried out for raw and treated sludge. Based on dewaterability criteria, the determination of optimum dosages of conditioning and evaluation of their capacity were reported in this chapter.

4.2. Batch test results

The GBFS and CaO were added to sludge to examine the effect of their doses on sludge dewaterability. At the initial pH of the raw sludge (6.9), the dewatering efficiency was measured in terms of CST and was found to be low. Hence, the addition of CaO was performed. The maximum dewatering efficiency was confirmed at pH 10, as shown in Figure 4.1(a). When the pH was further increased, the absorption of water was high because the efficiency of dewatering was reduced. For better dewaterability, the CST should be low.

It was observed that the dose of 0.37 g/g DS of slag was sufficient for obtaining satisfactory dewatering. At the above-mentioned dose, the CST obtained was 38 sec. It can be noted that the addition of CaO and slag is able to achieve a CST of 38 sec, as shown in Figure 4.1(b). Thus, the addition of GBFS and CaO helped to improve the dewatering capability.

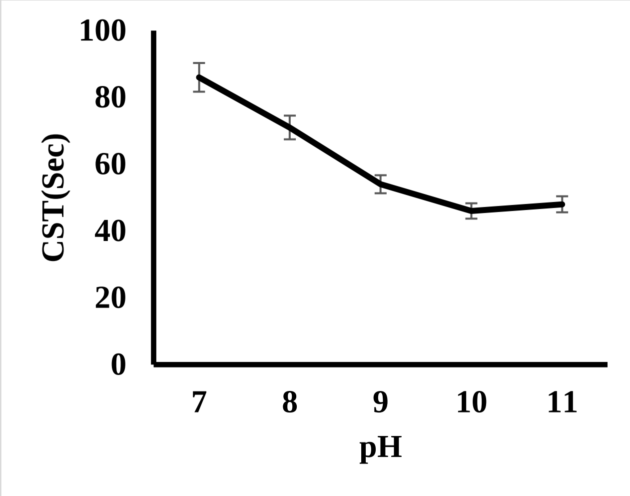


Figure 4.1(a) Effect of pH on sludge dewaterability, CST Vs pH

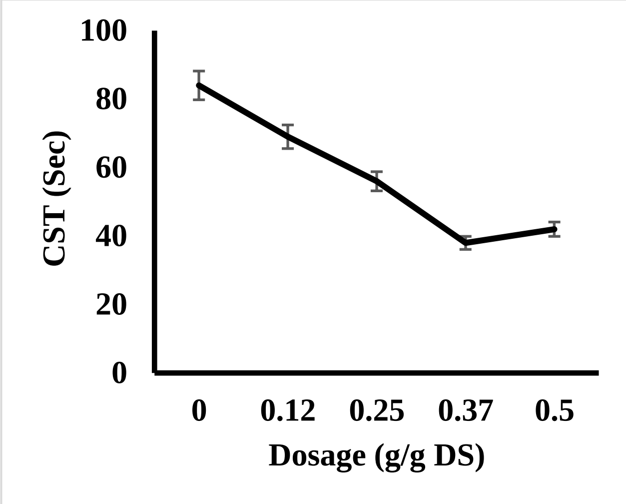


Figure 4.1(b) Effect of pH and Dosage on sludge dewaterability, CST Vs Slag dosage

Figure 4.1 Effect of pH and Dosage on sludge dewaterability.

4.3. Effect of conditioners on sludge dewatering properties using GBFS as skeleton material

4.3.1 Moisture content and turbidity

The distribution of moisture content with varying slag dose is shown in Figure 4.2 (a). The moisture content decreased to 78% at pH 10 due to the reactivity of CaO. At pH 10, the addition of slag lowered the moisture content to 68% at a 0.37 g/g DS dose and resulted in a rigid lattice structure with more voids than in the raw sludge structure. The addition of slag resulted in a bridging effect of the sludge particles for the passage of water and reduced the compressibility of the sludge cake.

After the addition of slag to the sludge, more voids and pores were produced (Dincer et al. 2007), which enhanced the reduction in moisture content. The addition of a large quantity of slag also produced a higher solids content in the sludge during filtration, the deformation of fine particles, and a decrease in the porosity of the sludge cake, resulting in a reduction of permeability. Hence, the sludge dewatering decreased with increasing fine particle deformation. In the present study, the moisture content did not decrease much with the increasing slag concentration beyond 0.37 g/g DS due to the presence of fine particles. Hence, it was inferred that a dose of 0.37 g/g

DS was sufficient for a significant reduction of the moisture content. Our results are in agreement with those found for sludge dewatering using wood chips and gypsum as skeletal materials (Zhao et al., 2002).

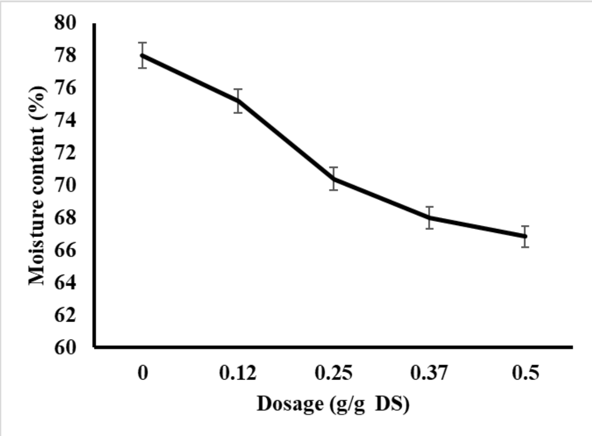


Figure 4.2(a) Distribution of moisture content with a varying slag dosage

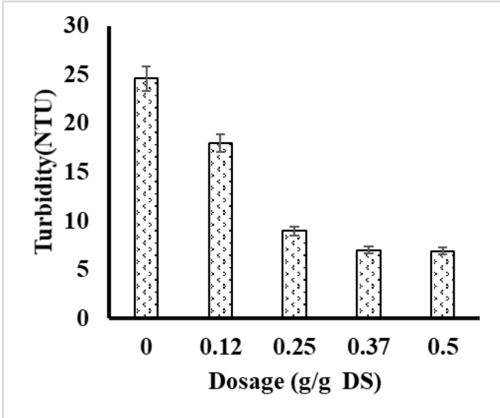


Figure 4.2(b) Responses of turbidity with respect to the varying slag dosage

Figure 4.2 Distribution of moisture content and responses of turbidity with respect to varying slag dosage

The initial turbidity (24.6 NTU) was measured in the supernatant of the centrifuged sludge. Later, various doses of slag were added to the sludge, the centrifuged supernatant was measured, and the results are portrayed in Figure 4.2 (b). Reduction in the turbidity happened with respect to the increasing slag dose, and turbidity of 8 NTU was obtained at the slag dose of 0.37 g/g DS. A further increase in the slag dose resulted in an increase in turbidity.

4.3.2. Zeta Potential

The zeta potential is a key factor in understanding the surface properties of sludge flocs with respect to flocculation and dewatering. Typically, the zeta potential of sludge obtained from wastewater treatment plants is negative (To et al., 2018). It was observed that decrease in zeta potential through charge neutralization using quicklime (Ca^{2+}) and slag was efficient (Figure 4.3). The zeta values changed from -7.8 mV for the raw sludge to -1.7 mV for the dewatered sludge at a dose of 1.5 g. The addition of quicklime increased the pH value of sludge. pH and electrical conductivity are related to the structure of the sludge floc.

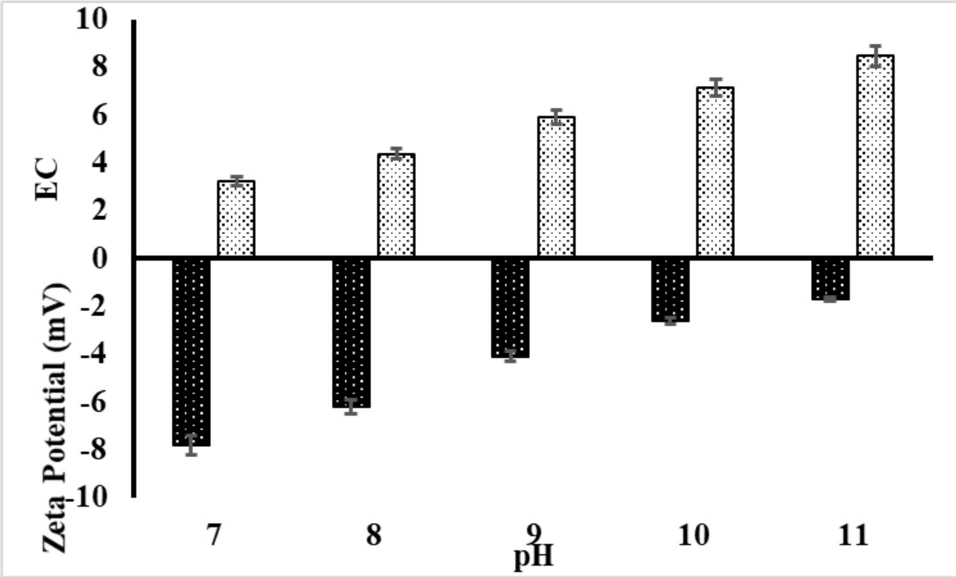


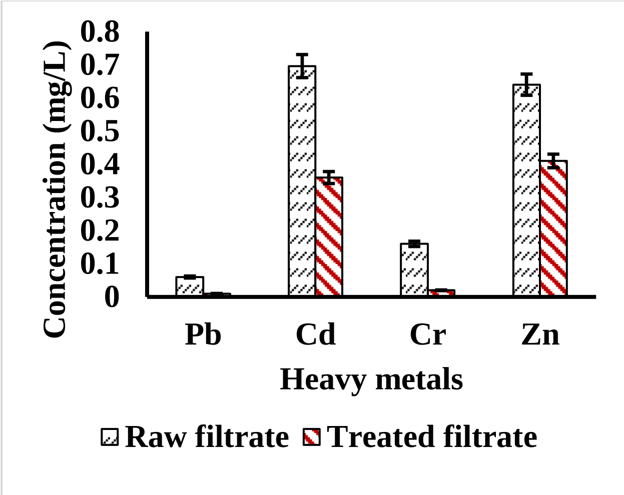
Figure 4.3 Response of zeta potential and electrical conductivity with respect to varying conditioner

The formation of an alkaline environment in the sludge could increase the dissolved EPSs and destroy the matrix structure of the EPSs. Thus, the obtained sludge dewatering performance was satisfactory and occurred by releasing bound water and small particles from the sludge floc.

4.3.3. Heavy metal content

The concentrations of heavy metals in the raw sludge and treated sludge filtrate are shown in Figure 4.4 (a).The slag mainly consists of calcium oxide and aluminum oxide. These oxides adsorb heavy metals, thereby reducing the concentration of heavy metals in the filtrate (Thuy et al., 2018). The reduction of Pb, Cd, Cr, and Zn was 76%, 42%, 41%, and 70%, respectively.

The soluble fraction of heavy metals observed in the raw and treated sludge cakes by EDAX is shown in Figure 4.4 (b). A major reduction in the concentration of elements, such as lead (Pb), cadmium (Cd), chromium (Cr), and zinc (Zn), was observed in the solid phase after conditioning with GBFS.



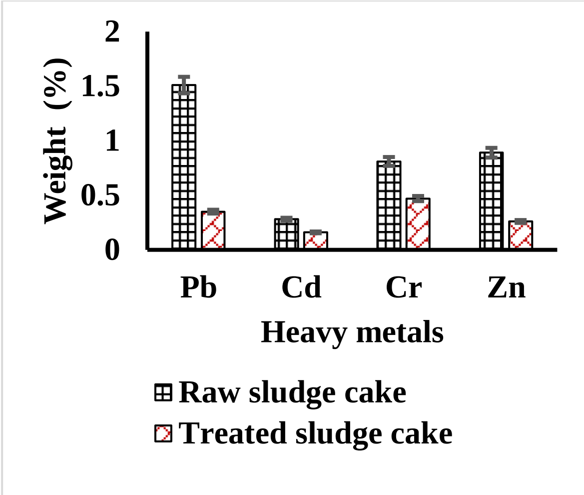


Figure 4.4 (a) Concentration of heavy metals in the raw sludge filtrate and treated sludge filtrate

Figure 4.4 (b) Soluble fraction of heavy metals in the raw sludge cake and treated sludge cake

The findings showed that there was a significant reduction in the heavy metal content compared to that in the raw filtrate. The heavy metal concentration in the filtrate after reduction with the addition of GBFS was within the permissible limit for effluent discharge into inland surface water (CPCB, 2000).

4.3.4 Protein and polysaccharide determination

The major factors considered in the sludge dewatering process are EPSs, proteins, and polysaccharides (Xiao et al., 2019). The presence of EPSs was measured for both the raw and treated samples and is presented in Figure 4.5. The results show that the presence of polysaccharides was greater than the protein component in the sludge.

The initial concentrations of protein and polysaccharides in the raw sludge were 108 g/L and 1249 g/L, respectively, which significantly increased to twice the concentrations in treated sludge (826 g/L and 2316 g/L). Hence, the results indicate that the destruction of EPSs occurred and that biopolymers were released into the dewatered liquor, whereas protein and polysaccharides remained in the sludge filtrate. This may be due to the rough surface of slag resulting in the stripping of sludge EPSs and the breakage of cells.

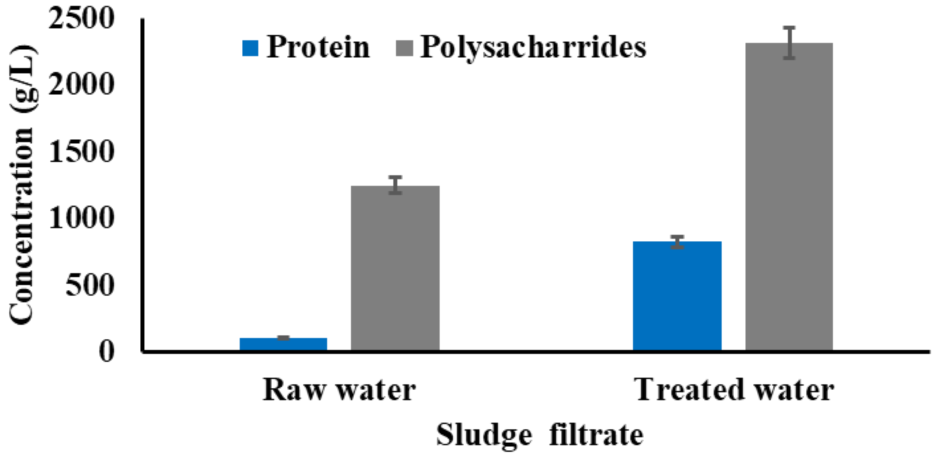


Figure 4.5 The concentration of Protein and polysaccharide in raw sludge and treated sludge

4.4 Characterization study

4.4.1 Surface morphology

The SEM images of the raw and dewatered sludge are depicted in Figures 4.6 (a) and 4.6 (b). The morphological analysis of the raw sludge indicated its nonporosity and that it has a dense structure. However, in the case of the treated sludge, the morphology had a higher porosity than that of the raw sludge, and the destruction of the particles and the surface tend to be convoluted. This may be due to reactions that occurred when CaO was added. The slag helped to increase the number of water pore channels, which leads to an increase in the dewaterability of the conditioned sludge. The sludge cake obtained after dewatering had unconnected surfaces with voids; therefore, during mechanical dewatering, the formation of impermeable thin layers in the upper layer of the filter medium can be prevented (Ning et al., 2013).

XRD was used to identify the mineralogical compounds and crystalline phases present in the samples. Figure 4.6 shows the XRD of treated sludge. The major peaks obtained were identified as quartz, calcium hydroxide, and calcite.

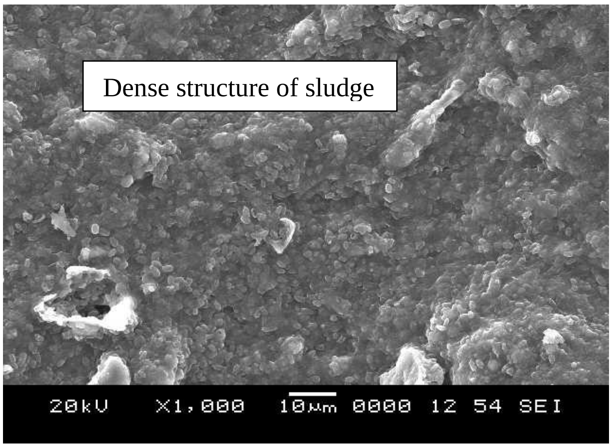


Figure 4.6(a) Morphology of raw sludge

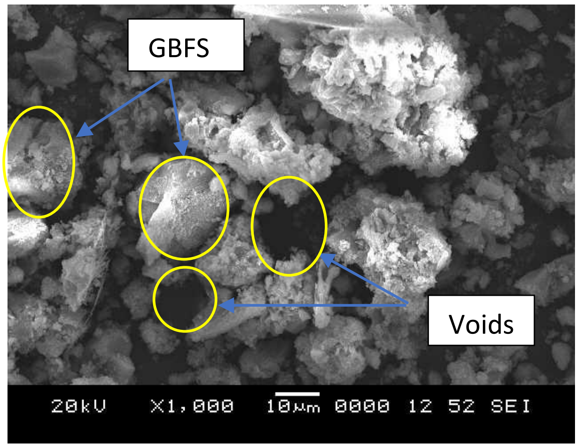


Figure 4.6(b) Morphology of treated sludge

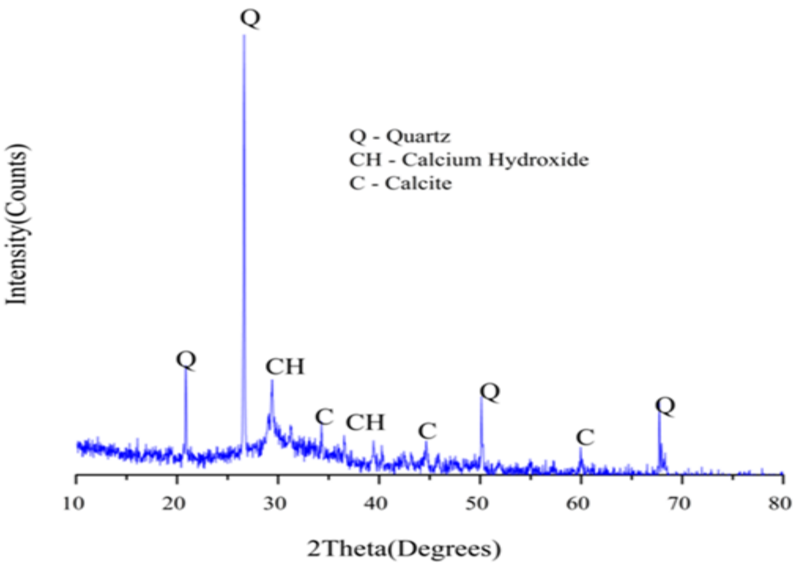


Figure 4.6(c) XRD of treated sludge

4.4.2 Surface analysis

The information regarding the functional groups presents in the raw and treated sludge was obtained from FTIR spectra in the range of 500 cm^{-1} to 4000 cm^{-1}. The FTIR spectra of the raw and treated sludge are shown in Figure 4.7(a) and 4.7(b), respectively. FTIR analysis allows for the monitoring of atoms experiencing stretching vibrations in which the distance between the atoms increases or decreases. The broad peak obtained in the range of 3800 cm^{-1} to 3600 cm^{-1} was attributed to the

O-H and N-H vibrational stretching overlap. The peaks observed in the region below 700 cm^{-1} were present due to halogenated stretching (Betatache et al., 2014).

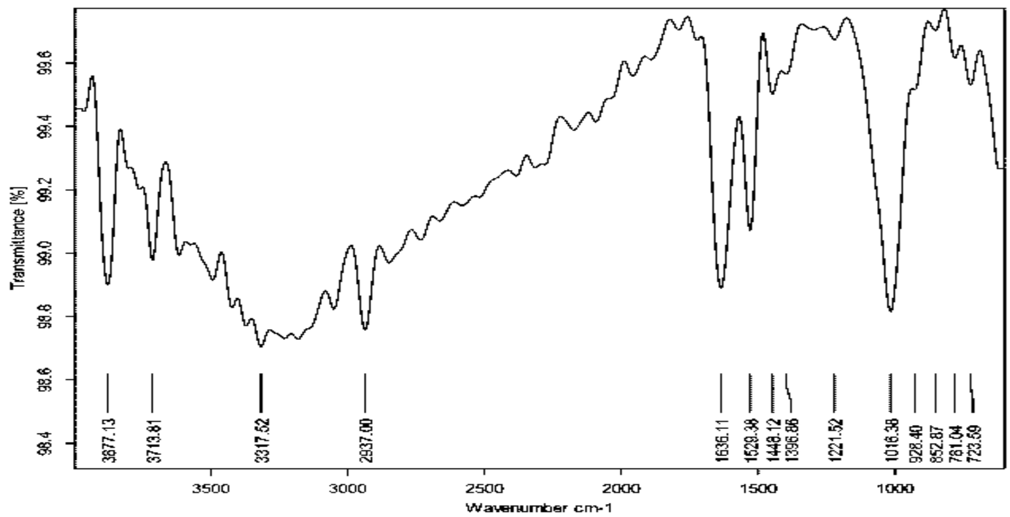


Figure 4.7(a) FTIR spectra of raw sludge

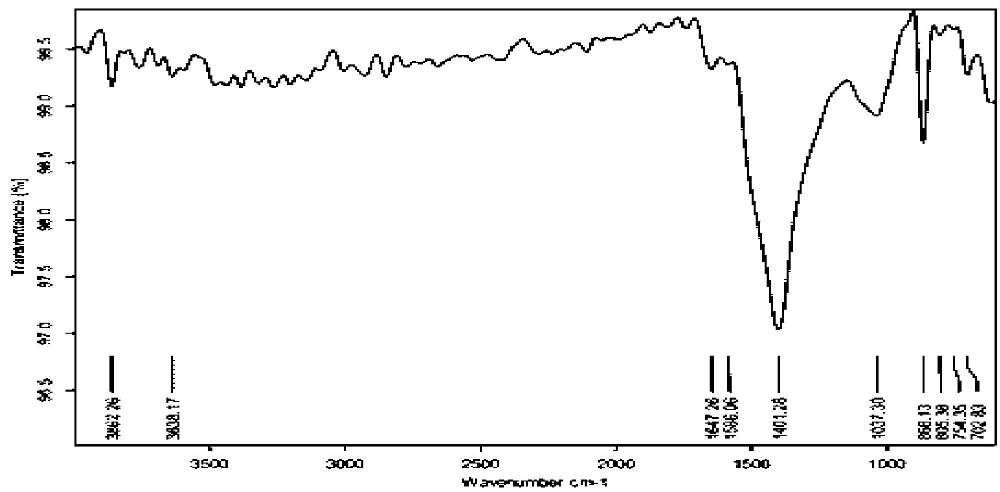


Figure 4.7(b) FTIR spectra of treated sludge

Figure 4.7 FTIR spectra of raw sludge and treated sludge

The band located at 1647.26 cm^{-1} was related to the stretching and deformational vibration of the peptic bonds of proteins, such as C=O, C-N, and N-H. The peak at 1037.30 cm^{-1} and a shoulder at 1067 cm^{-1} were attributed to CO_3^{2+} splitting due to the presence of hydrated monocalcium aluminate. The bands observed in the range between 780 cm^{-1} and 560 cm^{-1} indicated the generation of CO_2 and H_2O due to the reaction of organic acids and saccharides.

FTIR analysis of the treated sludge showed a broad peak at 3638.17 cm^{-1}, attributed to the O-H stretching and N-H stretching in alcohols, acids, and alkyl structures. The S=O stretching vibration was assigned to the peak at 866.13 cm^{-1}. The peaks ranging from 1300 cm^{-1} to 850 cm^{-1} were attributed to the O-H stretching due to the decomposition of minerals present in the treated sludge. When the raw sludge and treated sludge spectra were compared, a peak at 1401.28 cm^{-1} was observed, confirming the presence of C=C double bonds and therefore aromatic rings in the treated sludge. Overall, there was a decrease in the number of peaks in the treated sludge spectra when compared to that in the raw spectra.

4.5 Optimization

Response surface methodology is used to determine the optimal performance parameters of a system by optimizing variables at different levels. The Box-Behnken design was used to approximate a response function using Design Expert v11.1.2.0. For the current study, the effects of slag dose, pH, and contact time were investigated. Every independent variable was serially coded at three levels: low (-1), medium (0), and high (1). Table 4.1 shows the independent variables that were selected, which all interacted with the sludge and had a significant impact on the system. The Box–Behnken design is more efficient when utilized as a spherical design and when factors are run at three levels. Experimental studies were performed in the laboratory to confirm the model-obtained results; the experiments were conducted at least three times and are reported as the average values of filtrate. A quadratic model was fitted to the experimental data, as the F-value was higher and the p-value was lower than those of the 2FI, cubic and linear models from the sequential model sum of squares. Normally, “The lack of fit” is an inadmissible factor for the design; hence, it has to be insignificant, i.e., when the given data properly fit the filtrate volume.

The dewatering efficiency was illustrated by a second-order polynomial equation in coded form using the shown responses and by implementing multiple regression analysis in the design matrix:

$$\text{Filtrate (ml)} = 80.48+3.54A-0.7375B+0.5250C-0.8500AB-0.6750AC-0.000BC-4.32A^2-4.02B^2-1.19C^2$$

Table 4.1 Experimental responses of the liquid separation

Experimental Run order	pH	Dosage(g)	Contact time (min)	Actual filtrate value	Predicted filtrate Value
1	10	1.5	15	80	80.48
2	10	2	20	74.9	75.04
3	9	1	15	68.4	68.50
4	9	2	15	69.1	68.73
5	10	1.5	15	80.8	80.48
6	10	1	20	76.9	76.56
7	11	2	15	74.2	74.10
8	10	1.5	15	81	80.48
9	11	1.5	10	78.9	78.66
10	10	1	10	75.6	75.46
11	9	1.5	10	70.2	70.24
12	9	1.5	20	72.4	72.64
13	11	1	15	76.9	77.28
14	10	1.5	15	80.6	80.48
15	10	2	10	73.7	74.04
16	11	1.5	20	78.4	78.36
17	10	1.5	15	80	80.48

where the dewatering efficiency is expressed in terms of filtrate. A, B, and C are the coded terms for the three independent test variables dose, pH, and contact time, respectively. From the above equation, the optimum values of the selected variables were obtained. ANOVA was carried out to determine the significance of the second-order polynomial equation. Table 4.2 shows the ANOVA analysis of the model.

The determination coefficient (R^2) is one way to determine the model's goodness of fit. The obtained determination coefficient (R^2 = 0.9945) expresses that more than 95% of the experimental responses were well fitted to our model. To analyze the model fitness and adequacy, prediction of the adjusted R^2 was necessary.

Table 4.2 Statistical and ANOVA analysis of the model

Source	Sum of Square	DF	Mean Square	F-Value	P-Value	
Model	277.33	9	30.81	140.93	<0.0001	Significant
A	100.11	1	100.11	457.88	<0.0001	
B	4.35	1	4.35	19.90	0.0029	
C	2.20	1	2.20	10.08	0.0156	
AB	2.89	1	2.89	13.22	0.0083	
AC	1.82	1	1.82	8.34	0.0234	
BC	0.025	1	0.025	0.0114	0.9178	
A^2	78.40	1	78.40	358.56	<0.0001	
B^2	67.87	1	67.87	310.44	<0.0001	
C^2	5.96	1	5.96	27.27	0.012	
Residual	1.53	7	0.2186			
Lack of fit	0.6825	3	0.2275	1.07	0.4547	Not significant
Pure error	0.8480	4	0.2120			
Cor total	278.86	16				

The model showed high significance, as the value of the adjusted determination coefficient was R^2adj= 0.9875. In our model, the R^2adj value was very close to the predicted R^2 value, and the difference between the adjusted R^2 (0.9875) and predicted R^2 (0.9561) was less than 0.2. Hence, our experimental results and the predicted values show a significant correlation coefficient (R). The coefficient of variation was low (0.615), which implies that the experiments were carried with a high degree of precision.

The “Adeq precision” value was determined by the signal-to-noise ratio. In our model, the Adeq precision value was 33.40, indicating that the model can be used effectively (Wang and Guo 2019; Behera et al., 2018). The variation inflation factor (VIF) describes that the model variance in the design is magnified by the absence of originality. For all the independent and dependent factors in the current work, the VIF was found to be 1, which denoted that all the factors in the model and the desired factor were orthogonal. The results indicate that the model utilized for the liquid separation process was capable of identifying the optimal operational conditions for the separation of liquid from the sludge.

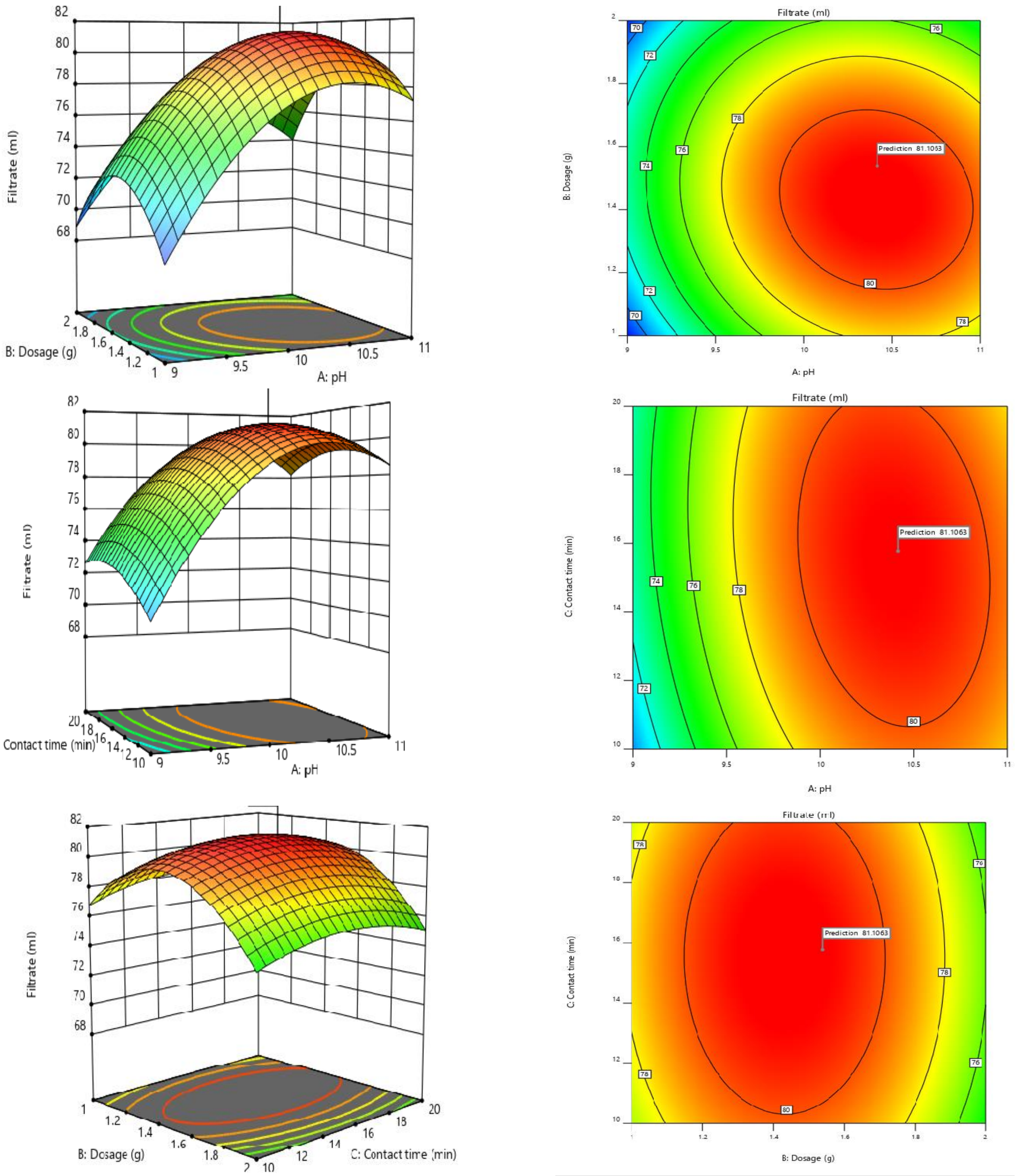


Figure 4.8 3D surface graphs and contour plots of liquid separation with two variables

Figure 4.8 shows the 3D response surface contour plots, illustrating the effects of dose, pH, and contact time on the liquid separation from the sludge. In all 3D surface plots, the effect of two variables was shown while keeping the other variables constant. The 3D response surfaces were generated with respect to the equation formed in the model. The interaction effects between pH and dose and pH and contact time showed positive effects. The interaction effect of every independent variable, such as that of pH and dose, is shown in the response surface plots, which exhibits a strong positive quadratic effect on the liquid separation of the sludge. The curvature formed in the 3D response surface for all variables indicates that the removal of water from the sludge was high.

Derringer's desirability function was used for every independent variable in the optimization process. The desirability function ranged between zero and one, where the former specifies an undesirable response and the latter specifies a fully desirable response (Awotwe-Otoo et al., 2012; Ferreira et al., 2007). For individual desirability, a weight factor of one was preferred in the current work. Figure 4.9 shows the ramp desirability for liquid separation.

The optimized process variables were achieved by implementing the desirability function. This indicated that liquid separation at pH=10.2, dose=0.34 g/g DS, and contact time= 14 min would yield 81.1 ml of collected filtrate from sludge with an overall desirability value of 1.

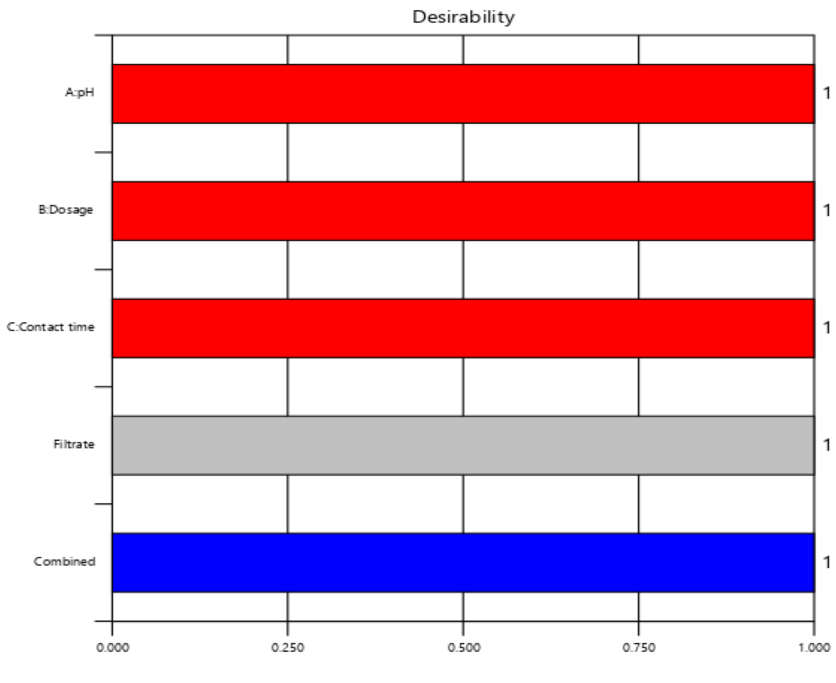


Figure 4.9 Ramp desirability for liquid separation

The addition of quicklime was carried out carefully; otherwise, it would have caused a large increase in pH even with aminor variation in dose. If the quantity of quicklime was low or high, it led to a reduction in sludge dewatering efficiency. The relatively high-water absorption capacity at a high pH is one of the properties of quicklime, which, in turn, affects sludge dewatering. Hence, the amount of quicklime was limited to that resulting in a pH of 10, so that the effect of the skeletal material could be established. Quicklime addition alone would not contribute to any void formation; hence, the addition of GBFS was introduced to reduce the compressibility of the sludge when a high pressure was applied. Using quicklime, the pH of the sludge was increased to more than 12.

GBFS influences sludge dewatering by reducing the maximum moisture content. The presence of oxides of calcium, magnesium, and aluminium is high in GBFS, and these oxides facilitate the action of GBFS as a conditioner in sludge dewatering. A high solid content was produced during conditioning with the skeletal material, which was beneficial for developing a more stringent lattice structure. Surface morphology analysis indicated that the slag, as a skeletal material, exhibited a rigid structure with more voids than those in the raw sludge when pressure was applied to the sludge.

Further reduction in the compressibility of the sludge led to the development of channels for the removal of excess water from the sludge. Hence, the adopted combination of the conditioners may also serve as skeletal additives in landfill cover materials and construction materials and for mining site reclamation (Li et al. 2014). Furthermore, GBFS is not flocculent, as it does not have the ability to flocculate sludge particles. Hence, it is worth noting that even GBFS alone does not yield better results of dewatering. To achieve flocculation, CaO was, used as a flocculent, thereby establishing GBFS as a promising skeletal material in terms of economy and scalability. The slag acted as skeletal material by achieving good dewatering efficiency with the reduction of environmental risk and treatment cost.

4.6 Effect of conditioners on sludge dewatering properties using MCSB-$FeCl_3$ as skeleton material

4.6.1 Test to determine the effect of MCSB-$FeCl_3$ on moisture content and CST

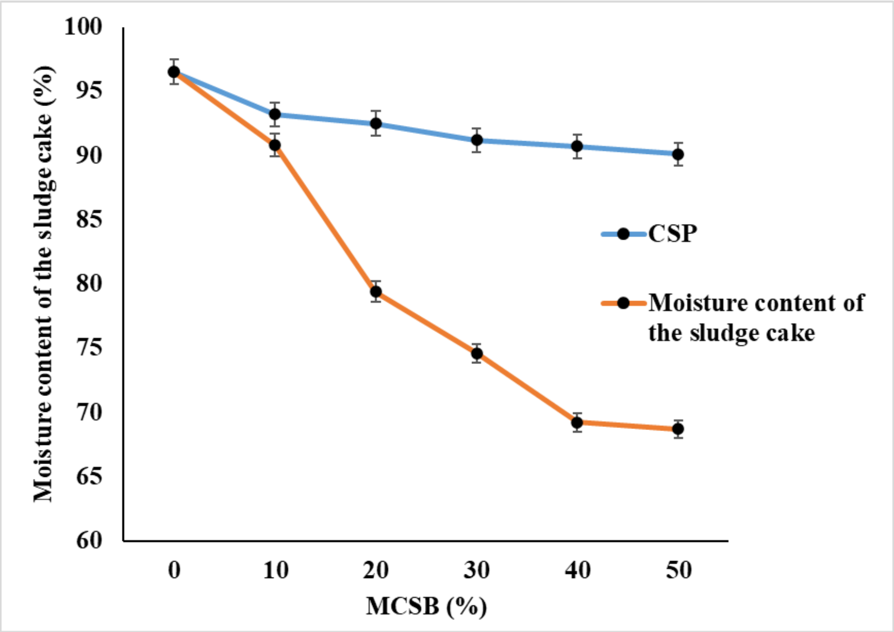


Figure 4.10 a) Influence of MCSB-$FeCl_3$on moisture content

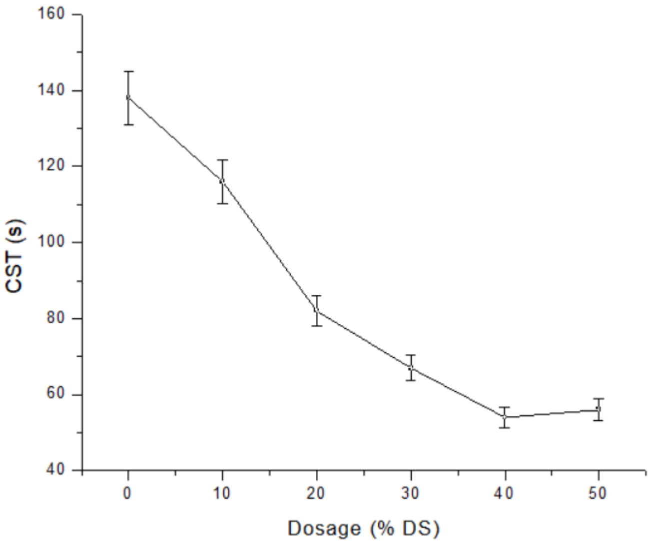


Figure 4.10 b) Influence of MCSB-$FeCl_3$ on CST

Figure 4.10 a) shows the Influence of MCSB-$FeCl_3$ on moisture content. Results indicated that MCSB-$FeCl_3$ can enhance the water release rate by reducing the moisture content. MCSB-$FeCl_3$ acts as dual conditioning both chemical and physical conditioners on sludge dewatering. The moisture content of the conditioned sludge cake with MCSB-$FeCl_3$ decreased significantly when compared to the raw sludge with CSB. This is due to the cationic interaction of $FeCl_3$ with the anionic sludge particles in the sludge, during which the particles lose their stability thereby transforming bound water into free water (He et al., 2017). The reduction of moisture content was 69.2% at the dosage of 40% DS. Further addition of MCSB-$FeCl_3$ dint shows a much significant decrease in moisture content because as conditioner increases, it increases the sludge viscosity and the collision effect will be reduced (Pinotti et al., 2001).

Figure 4.10 b) shows the Influence of MCSB-$FeCl_3$ on CST. The dewaterability of the sludge can be determined by CST. The lower the value of CST, the higher is the dewatering efficiency. MCSB-$FeCl_3$ was applied to the sludge for assessing the effect of dosing. The controller sample was analysed by adding sludge without any conditioner. The obtained value for a controller was 138 sec. Meanwhile, the dosage of MCSB-$FeCl_3$ was varied and the lower value obtained was at 40% DS. An increase in the addition of MCSB-$FeCl_3$ causes an increase in CST value.

4.6.2 Settleability of the sludge

Figure 4.11 demonstrates the sludge's settling owing to the varying dose of MCSB- $FeCl_3$. Moreover, the settleability of sludge particles was also studied with the addition of CSB. The settleability of the controller sludge particles was very low when compared to the conditioned sludge due to the reduction of interstitial water in the sludge. The settlement amount shall be higher when the sludge volume percentage is low. The volume of sludge decreased with the increasing dosage of MCSB- $FeCl_3$, while the introduction of CSB did not significantly affect the reduction of the volume of sludge. Efficient sludge settling as the efficiency of mechanical dewatering increased.

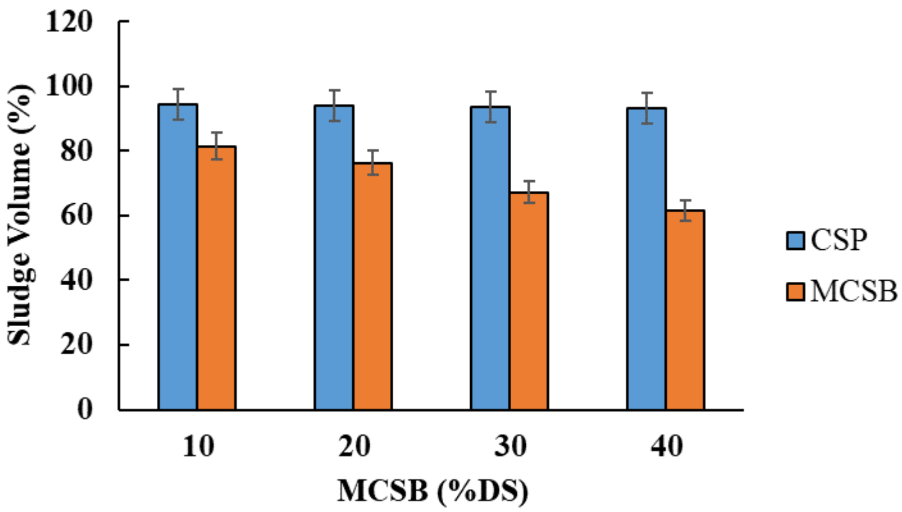


Figure 4.11 Influence of settleability of the sludge with respect to the varying MCSB-$FeCl_3$

4.6.3 Zeta Potential

The zeta potential is a vital factor in influencing the dewaterability of the sludge. Surface charge (zeta-potential) plays an important role in both their physiological and aqueous colloidal stability and functionality. Considering the electrostatic interaction, a high positive or negative zeta potential value suggests higher colloidal sludge stability.

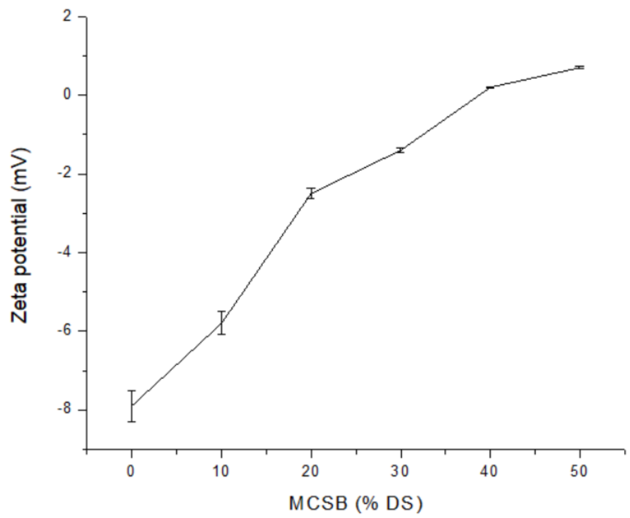


Figure 4.12 Influence of MCSB-$FeCl_3$ on zeta potential

The zeta potential of the sludge from the wastewater treatment plants is generally negative (Junyuan et al., 2019). Zeta potential of the dewatered sludge liquor using MCSB-$FeCl_3$ is illustrated in Figure 4.12. When the dosage of MCSB-$FeCl_3$was increased, Zeta potential was also increased leading to disintegration of EPS in the sludge (Zhang et al., 2016) due to the interaction of ions, and even the adsorption by electrostatic attraction of anions. The Zeta potential reached near to 1, which indicates the excellent dewatering ability by MCSB-$FeCl_3$. The efficiency of sludge dewatering was enhanced due to the exchange of anion and cation (Charge neutralization) and also particles of the sludge were gathered to form a cluster, which is why dewatering of the sludge with MCSB- $FeCl_3$ is superior when compared to CSB.

4.6.4 Removal of phosphate and heavy metal by MCSB-$FeCl_3$

Figure 4.13 a) shows the concentration of heavy metal using MCSB-$FeCl_3$. The removal of cadmium, chromium, lead, and nickel by MCSB-$FeCl_3$ is high and efficient due to the ion exchange between sludge and biochar or due to the adsorption process. Biochar is a highly carbonated porous material. The affinity of heavy metals to biochar is very high, due to the porous structure and the presence of various functional groups. The MCSB-$FeCl_3$has increased the capacity for adsorption because the process of adsorption is influenced by porosity.

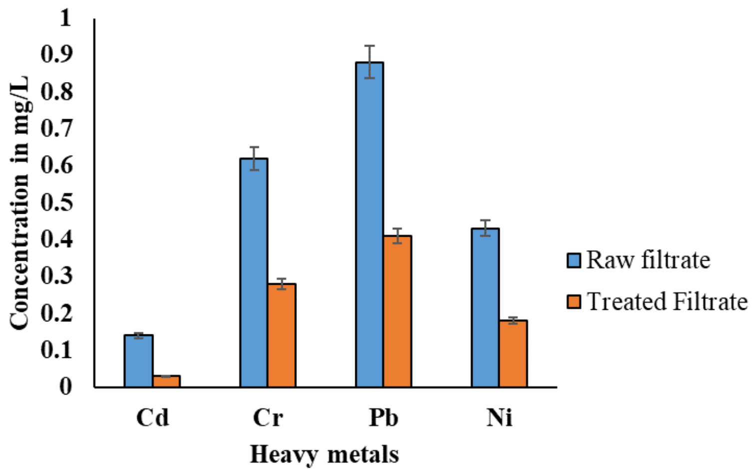


Figure 4.13a) Distribution of heavy metals in the untreated and treated sludge filtrate

Porosity is one of the physical properties which is important. Because of the high content of lignin in the biomass, the pore scale of the biochar is macro-pores (Hongbo et al., 2017). Figure 4.13 b) Reflects the impact of MCSB-$FeCl_3$ on phosphate removal. A feasible investigation was done for the removal of phosphate using low-cost and readily available conditioners. The initial concentration of phosphate was 148 mg/L. As the dosage of MCSB-$FeCl_3$ was increased, the concentration of phosphate was also reduced.

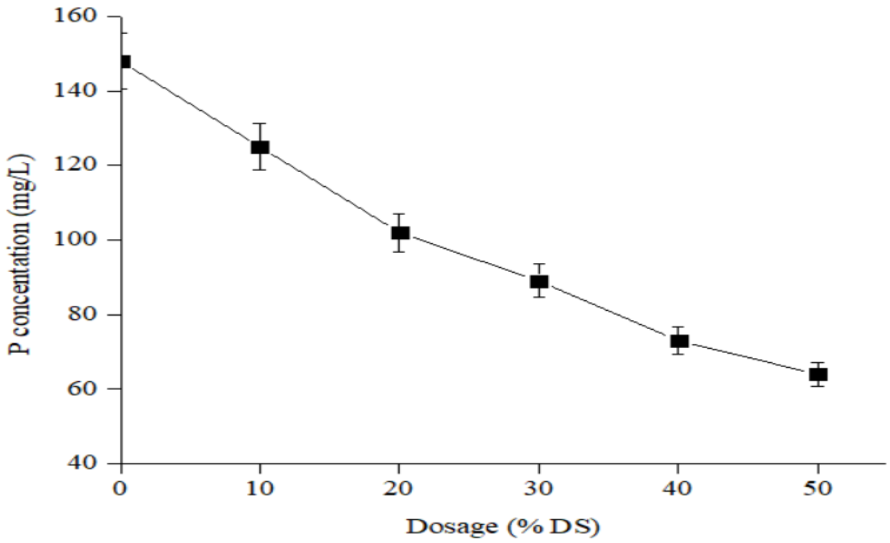


Figure 4.13b) Reflects the effect of MCSB-$FeCl_3$ on the removal of phosphate

The removal efficiency of phosphate from the sludge during the sludge dewatering process was 50.62%. The adsorption capacity of phosphate from the biochar was satisfactory due to the highly porous structure and surface area. Removal of phosphorus was more efficient when a combination of CSB and $FeCl_3$ are used rather than CSB alone (Qi et al.,2017). Hence MCSB-$FeCl_3$ has a strong influence on phosphorus removal and is worthy of further investigation.

4.7 Characterization study

4.7.1 Microscopic structure

Figure 4.14 shows the SEM analysis carried out for raw sludge, coconut shell powder, MCSB-$FeCl_3$, and dewatered sludge. The image of raw sludge clearly shows the dense structure without any voids whereas the dewatered sludge images show the agglomeration of the sludge particles with more voids while raw coconut shell powder shows the heterogeneous solid in nature with different particles sizes. The modified CSB with ferric chloride image shows more agglomeration with macropores.

The formation of macropores is due to the presence of lignin and the release of volatile. The MCSB-$FeCl_3$ helps to increase the water pore channel which contributes to an increase in the conditioned sludge's dewaterability. The sludge cake obtained after dewatering can be prevented from forming impermeable thin layers by connecting surfaces with voids at the upper layer of the filter medium (Ning et al. 2013).

Based on the EDX results of CSB, the dominating elemental composition is carbon and oxygen. Wherein the carbon and oxygen content in the raw coconut shell is 48.84% and 48.62%. But Carbon and oxygen content changed drastically to 76.14% and 22.43% to the removal of water and volatile matter.

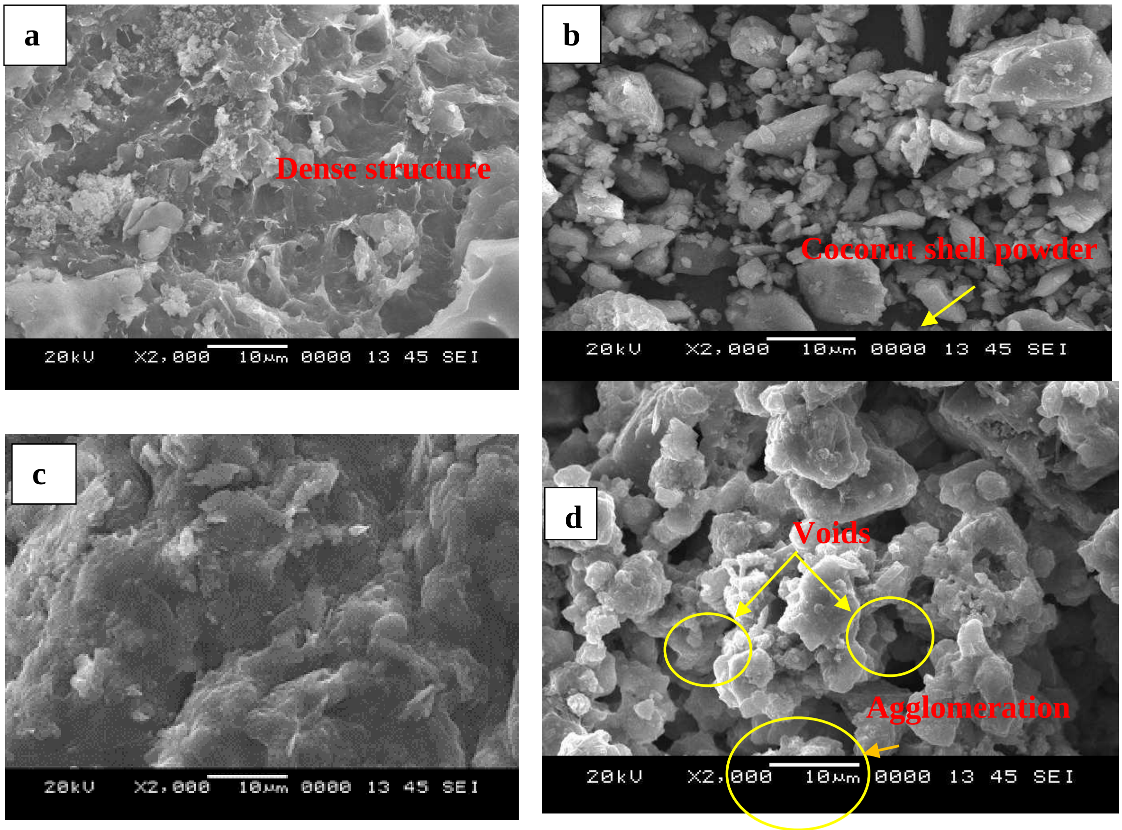


Figure 4.14 Surface morphology of a) raw sludge b) raw coconut shell powder c) modified biochar and d) dewatered sludge

4.7.2 FTIR

FTIR spectrum of MCSB-$FeCl_3$is presented in the Figure 4.15 a). Aromatic, hydroxyl functional group plays an important role in sludge dewatering and in metal adsorption. FTIR spectra were commonly used to classify functional groups on the surface of the Biochar. The large peak at 3000-4000 cm^{-1} obtained from the sample reflects the stretching hydroxyl group (-OH) and the strong hydrogen bond. The peak at 1625 cm^{-1} shows the presence of C = C stretching of aromatic groups present in lignin. 989-500 cm^{-1} shows carbon group presence. The interaction between quarts and the glassy phase of the ash is at the region 1441.86 and 1263.73 (Madakson et al., 2012).

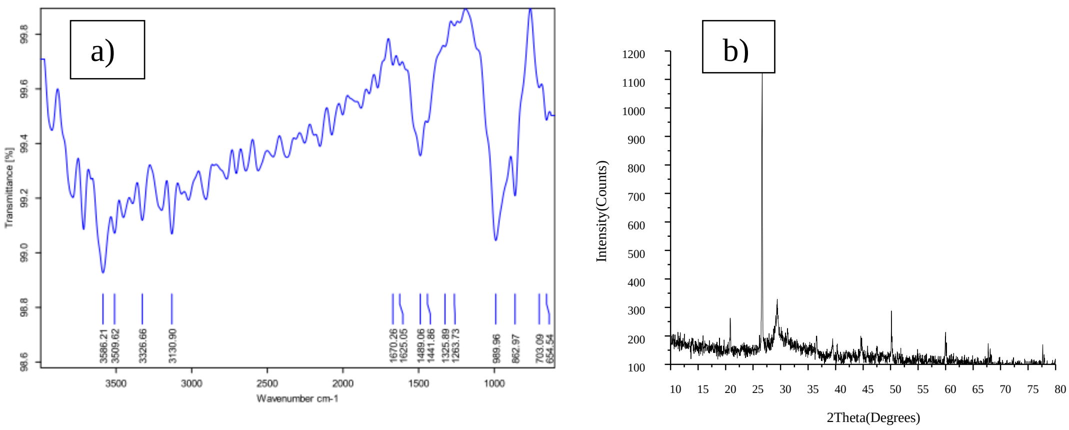


Figure 4.15 a) FTIR spectrum of MCSB-$FeCl_3$ b) XRD pattern of MCSB-$FeCl_3$

The X-Ray diffraction (XRD) pattern of MCSB-$FeCl_3$ is shown in Figure 4.15 b). XRD analysis is used for the detection of mineralogical compounds and crystalline phases in the sample. The diffraction pattern consists of 1 high peak at 26 degrees (Mohan et al., 2011) when the sample was heated at 600^0C and modified with ferric chloride and it is indexed as an amorphous phase of carbon. The peaks at 30^0 and 50^0 were indicating the presence of $FeCl_3$ (Han et al., 2016). The major peak obtained is identified as quartz and the remaining peaks as calcite, moissanite.

4.8 Optimization

The Box-Behnken Experimental Design and RSM were selected for the evaluation of the combined effects of three independent variables on three stages. MCSB-$FeCl_3$ dosage, rapid mixing time (RMT) and slow mixing time (SMT) was the dominant factor based on preliminary tests; CST was taken as output. The examined experimental variables was selected according to single factor measures. Table 4.3 describes certain ranges and levels of factors used for optimization. In this study, 17 group tests were performed. The Box – Behnken is introduced, development and experimental data were analysed using Design Expert v 12. Table 4.4 gives the BBD matric for actual and predicted responses of CST values

Table 4.3 Ranges and levels of factors used for optimization

Study type: Response surface	Runs: 17		
Design: BBD	Design model: Quadratic		
Blocks: No blocks			
Variables	Range and levels		
	+1	0	-1
MCSB-$FeCl_3$ dosage (%DS)	30	40	50
RMT(Min)	5	10	15
SMT(Min)	10	15	20

The effects of MCSB-$FeCl_3$ dosage, rapid mixing time, and slow mixing time were investigated in the present study. Independent variables were chosen because their interaction with the sludge has a substantial impact on the system as a whole.

Box – Behnken architecture is highly effective, three-level spherical structures and factors are used. Experimental studies have been conducted to validate the model results obtained in the laboratory at least thrice and were recorded as average CST values. For the dewatering experimental results, the various statistical models such as linear, 2FI, quadratic, and cubic were set. In general, the above models can be tested based on the scores from the number of squares in the sequential model. In this analysis, the quadratic model was found to have a high score based on the assessment. Table 4.5 shows the Sequential model sum of squares. The higher value of F (309.30) and lower value of p (<0.0001) indicate that the quadratic model is significant.

Table 4.4 BBD matric for actual and predicted responses of CST values

Run order	MCSB-$FeCl_3$ dosage	Rapid mixing time (RMT))	slow mixing time (SMT)	Actual CST value	Predicted CST Value
1	30	15	15	61.20	61.39
2	40	15	10	58.84	59.72
3	40	5	20	59.82	59.94
4	40	10	15	57.50	58.80
5	30	5	15	60.20	61.04
6	40	5	10	57.00	59.24
7	40	15	20	60.10	59.86
8	40	10	15	58.60	58.80
9	30	10	20	61.40	61.25
10	40	10	15	57.80	58.80
11	50	15	15	60.10	60.46
12	50	10	20	60.20	61.27
13	50	5	15	60.60	60.41
14	30	10	10	59.70	61.63
15	40	10	15	58.02	58.80
16	50	10	10	60.10	60.05
17	40	10	15	58.60	58.80

Table 4.5 Sequential model sum of squares

Source	Sum of squares	df	Mean square	F-Value	P-Value	
Mean vs Total	58784.71	1	58784.71			
Linear vs Mean	17.58	3	5.86	0.8729	0.4801	
2FI vs Linear	5.83	3	1.94	0.2386	0.8674	
Quadratic vs 2FI	**80.82**	**3**	**26.94**	**309.30**	**< 0.0001**	**Suggested**
Cubic vs Quadratic	0.0584	3	0.0195	0.1413	0.9301	Aliased
Residual	0.5513	4	0.1378			
Total	58889.55	17	3464.09			

The results obtained by BBD were evaluated by standard analysis of variance (ANOVA) shown in Table 4.6. The Model F-value of 132.96 indicated that the model was important. There was only a 0.01 percent probability that this broad Model F-value could be due to noise. Values of P less than 0.05 mean that the terms of the model are important. In the present case A, B, C, D, AB, AC, A^2, B^2 are notable model terms. Fisher statistical test (F Test) was investigated For the value of each independent variable. Fisher's value for CST is more than 0.05, which correlates to the fact that the model is persuasive. Treatment combinations are very important, as they have been largely supported by the Fisher variance ratio. The model is statistically effective if the P-value is less than 0.05. From now on, in our model for all responses except AC and C^2, P values are less than 0.05. The Lack of Fit value of 0.14 indicated that the model was significant.

Table 4.6 ANOVA analysis for the quadratic model of CST

Source	Sum of Square	DF	Mean Square	F-Value	P-Value	
Model	104.23	9	11.58	132.96	< 0.0001	Significant
A	12.88	1	12.88	147.85	< 0.0001	
B	1.20	1	1.20	13.79	0.0075	
C	3.50	1	3.50	40.16	0.0004	
AB	5.09	1	5.09	58.38	0.0001	
AC	0.3025	1	0.3025	3.47	0.1047	
BC	0.4422	1	0.4422	5.08	0.0589	
A^2	72.13	1	72.13	828.14	< 0.0001	
B^2	5.49	1	5.49	62.99	< 0.0001	
C^2	0.1132	1	0.1132	1.30	0.2917	
Residual	0.6097	7	0.0871			
Lack of fit	0.0584	3	0.0195	0.1413	0.9301	Not significant
Pure error	0.5513	4	0.1378			
Cor total	104.84	16				

The CST was shown by the second-order polynomial equation developed using three factors in coded form and also by implementing multiple regression analysis in the design matrix.

$$\mathbf{CST = 56.24 - 1.27A - 0.387B - 0.66C - 1.13AB + 0.33BC + 4.14A^2 + 1.14B^2}$$

Where A, B, and C are the coded independent variables of MCSB-$FeCl_3$ dosage, rapid mixing time, and slow mixing time respectively. Optimum values of the selected variables are extracted from the above equation.

Coefficient (R^2) is one way to assess the fitness of the model. The coefficient of determination (R^2 = 0.99) shows that more than 95% of the experimental responses are well correlated with the results of our model. For the study of the fitness and adequacy of the model, it is important to predict the adjusted R^2. The model shows a good significance because the modified determination coefficient value is (R^2adj=0.98). In our model R^2adj is very similar to R^2 pre and the gap between the adjusted R^2(0.986) and the predicted R^2(0.982) is less than 0.2. Therefore, it can be acknowledged that our experimental results and the expected values indicate a high coefficient of correlation (R). The coefficient of variance is small (0.5), ensuring experiments are conducted with a high degree of precision.

'Adeq Accuracy' measures the ratio of signals to noises. A value over 4 is desirable. A ratio of 32.2 corresponds to an adequate Model signal and also be used to navigate the design space with this model indicating that the model can be used efficiently (Han et al. 2016). The inflation factor of variation (VIF) tests whether the model variance is inflated by the lack of orthogonality in the design. For all the individual and interactive variables, VIF was found to be unity in this experimental design. These values imply that every desired factor in the model is orthogonal to all other factors.

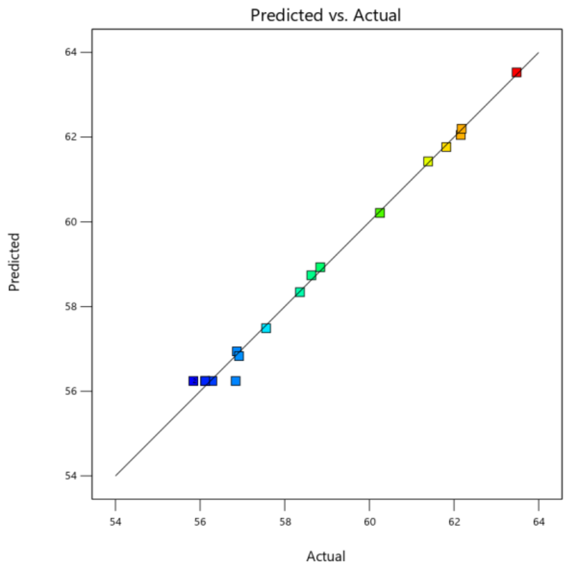
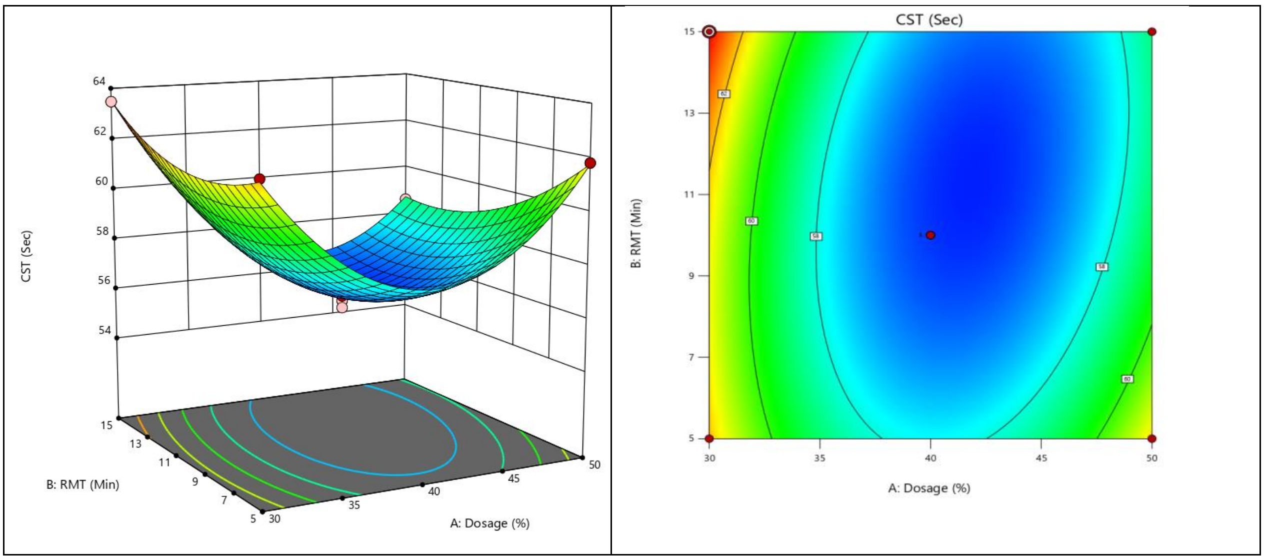


Fig. 4.16 predicted vs. Actual CST values

Figure 4.16 shows predicted vs. Actual CST values where the experimental CST ranged from 63.48 Sec to 56.12Sec, and the predicted CST ranged between 63.53Sec to 56.24 Sec. This indicates a fairly strong correlation between the real value and the estimated value of the model. The coefficient of correlation between the actual and the predicted value of the CST was considered to be 0.99. The leverage is the capacity of the design point to influence the model's coefficients within the design area. Leverage values can't be equal to 1. For both runs, the amount of leverage (0.2 to 0.75) was less than 1 in experimental form. Internally studentized residual is the standard deviation in number that separates the real and expected responses. The actual and predicted efficiency (percent) of the CST reduction is displayed in Figure 4.16. Actual values are the details of the assessed response for a particular run, and the predicted values are from the model and generated with approximate function.

Figure 4.17 shows the CST reduction showing the effect of two variables by surface and contour graph. For other variables, the effect of the two variables remained constant in all 3D surface plots. The surfaces of the 3D response are formed with respect to the equation formed in the model. The relationship between the MCSB-$FeCl_3$ dosage & rapid mixing time was positively affected. The surface response map shows the interaction effect of each independent variable, such as the MCSB-$FeCl_3$ dose, rapid mixing time, and slow mixing time, which has a strong positive quadratic effect on CST. For all variables, the curvature developed in the 3D response surface implies that the CST reduction is high.



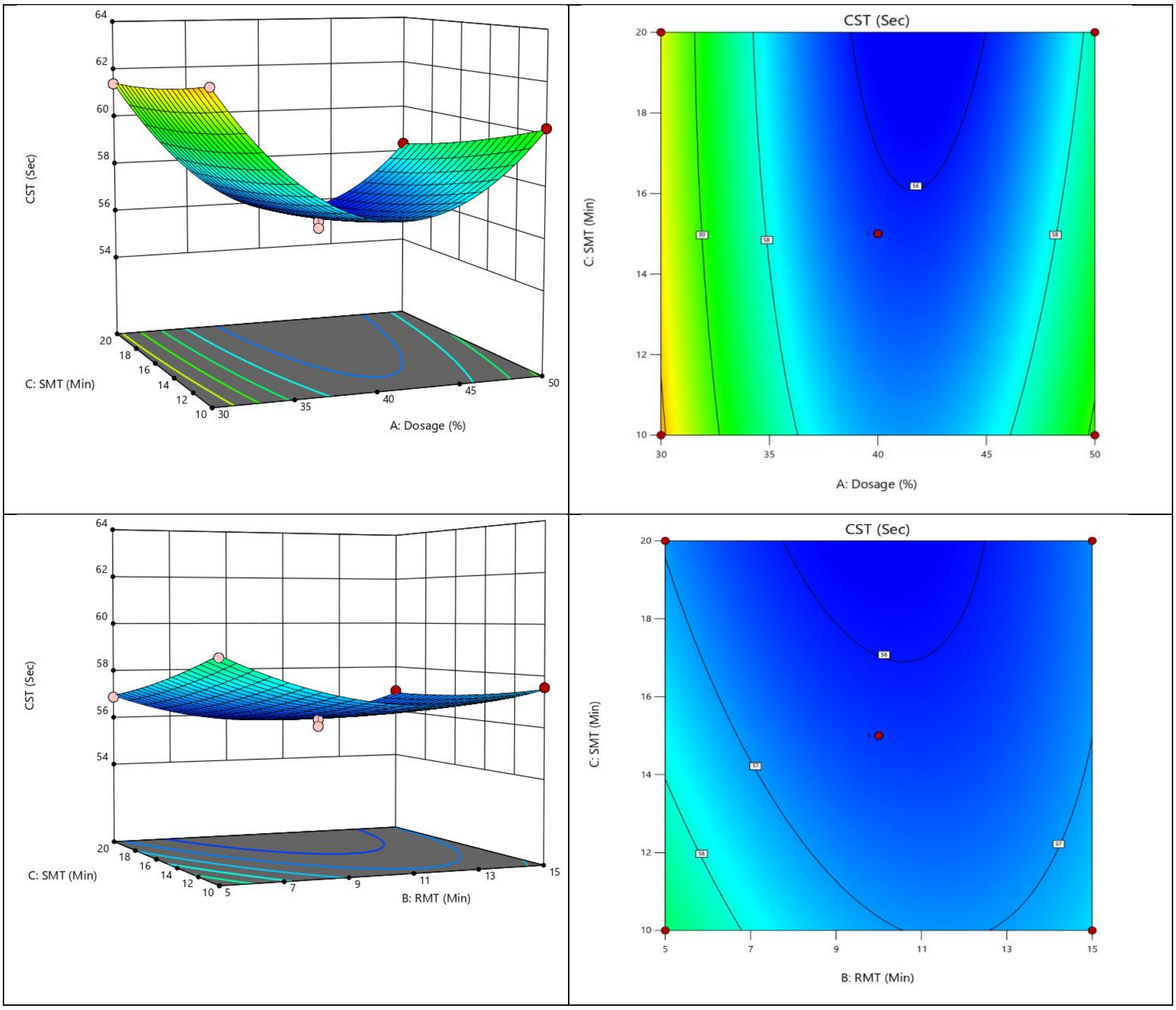


Figure 4.17 CST reduction showing the effect of two variables by surface and contour graph

Derringer's desirability function is used in the optimization procedure for any independent variable. The desirability function is in between ZERO and ONE. Where 'ZERO' specifies the undesired response and 'ONE' specifies the perfectly acceptable response (Rashmi et al., 2019). For all input variables such as MCSB-$FeCl_3$ dose, quick mixing time, and slow mixing time for extracting water from the sludge, numerical optimisation was conducted. It is carried out to identify a point for the desirability function that results in a higher value. The goal was changed to achieve those desirable points by adjusting lower and upper limits. Figure 4.18 a), histogram plot presents individual desirability and the combination of all the factors.

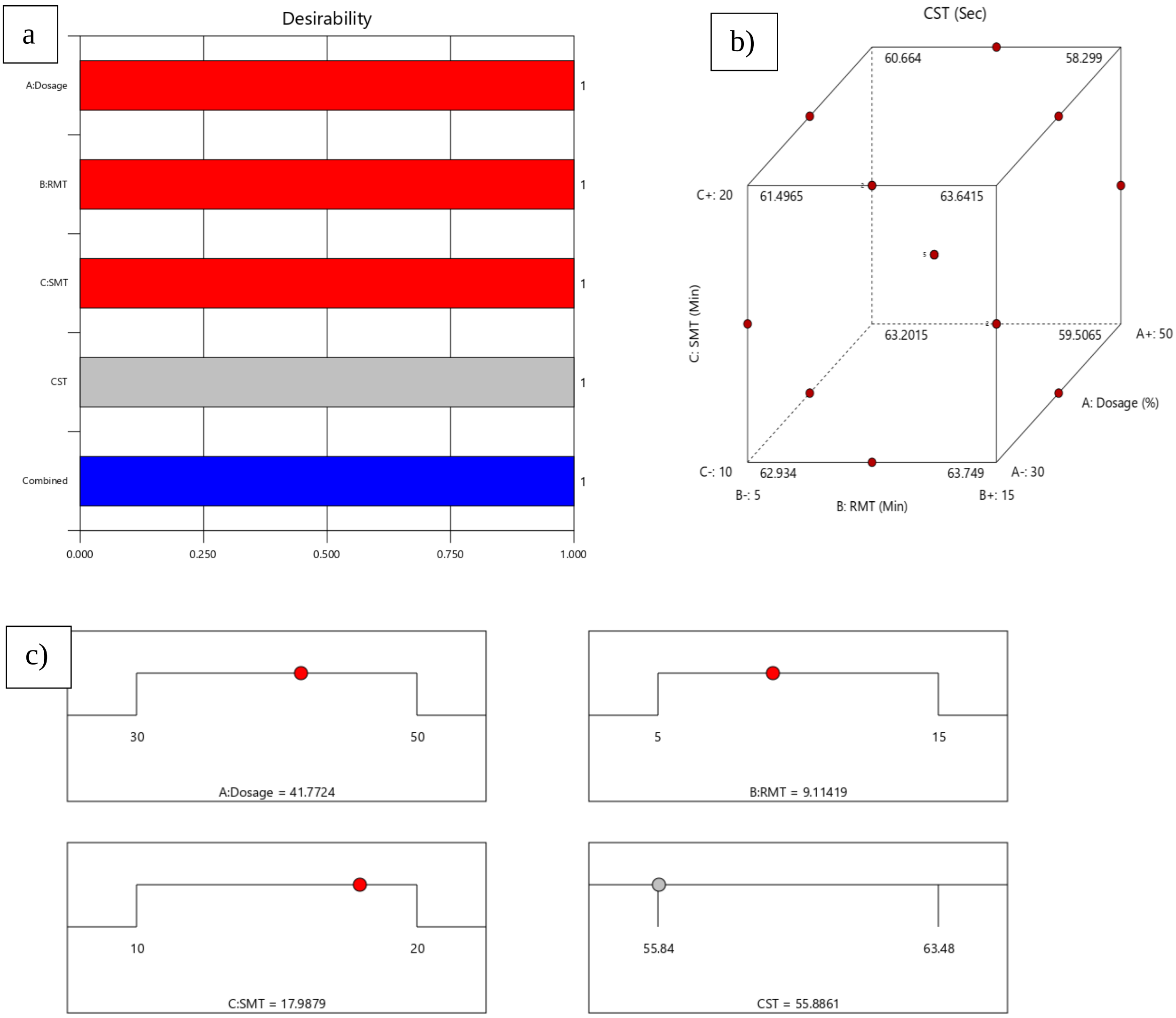


Figure 4.18 Ramp desirability for liquid separation

The value was found to be 1 for individuals and for the combination of all variables such as MCSB-$FeCl_3$ dose, quick mixing time, and slow mixing time.

In the current study, a weight factor of "ONE" was recommended for individual desirability. Figure 4.18 b) indicates the maximum desirability of the Ramp for CST. The cubic diagram shows changes in CST values against changes in all three variables at the same time. It shows simultaneous effects on CST values of the parameters MCSB-$FeCl_3$ dose, quick mixing time, and slow mixing time. According to this diagram, the maximum CST value (63.74Sec) was achieved at MCSB-$FeCl_3$

dosage of 50 % DS, RMT of 15, and SMT of 20, while the minimum CST value (62.93) is obtained for MCSB-$FeCl_3$ dosage of 30 % DS, RMT of 5, and SMT of 10. The optimized process variable was achieved by implementing the desired function. It was reported that the CST at MCSB-$FeCl_3$dosage = 42 % DS, RMT=9.11 min, and SMT = 17.98, the CST obtained is 55.88 sec with an overall desirability value of 1to obtain significant sludge dewatering.

Approximate cost analysis was carried out for the sludge dewatering using MCSB-$FeCl_3$. And the result was compared with fentons reagent method and with polymer condition. The dewatering efficiency with respect to the moisture content of treated sludge cake of MCSB-$FeCl_3$ was 69.2% and 46.2Rs whereas 46.5% and 70.25Rs (Zang et al., 2014) & 62.2% and 62.54Rs(Liu et al., 2012) was observed in fentons reagent method and with polymer, conditions treated sludge cake. Hence when compared to fenton process and polymer conditioning, MCSB-$FeCl_3$ achieved better dewaterability.

Fentons reagent method cost was higher, which may be due to the dual reagent conditioning. But Polymer conditioning usage has a limitation, where it perceives long-term risk associated with polymer residue in the environment. Fenton process works in an acidic condition whereas MCSB-$FeCl_3$ works in neutral condition with better dewaterability thereby reducing further extra cost.

The present study focused on utilizing both physical and chemical conditioner to enhance the sludge dewaterability. the argument of increase dewaterability was achieved while using both the conditioners was satisfied as suggested by Yan et al., (2016).

MCSB-$FeCl_3$ is a combination of both physical and chemical conditioners used in the present study. When coconut shell is burnt in an oxygen-free container, biochar is obtained which has a macro-pore with a larger surface area than other agricultural waste and $FeCl_3$ is a commercial product available at low cost. Ferric chloride salt is used to increase biopolymers and help remove heavy metals and phosphates from the secondary sludge. Further experiments were performed to obtain better efficiency with respect to pH, dosage, temperature, and contact time. Since

CSB is not a flocculant, it does not have the capability to flocculate the particles in the sludge. Hence a flocculant, ferric chloride was used with CSB, so that CSB acts as a skeleton material, giving a beneficial cake structure. The main focus in sludge dewatering is to improve compressibility and also to modify the characteristics of the sludge particles (Yafei et al., 2015). From the characterization study, XRD showed the highest peak of quartz, FTIR indicated the presence of carbon phase and SEM images reflect the change in sludge particle structure.

Utilizing both CSB and ferric chloride has a synergic effect in the removal of maximum water content from the sludge and simultaneously removal of heavy metals and phosphate. The obtained sludge can be used to prepare concrete or as a fertilizer (Johnson et al., 2014; Shugeng et al, 2009). Hence MCSB-$FeCl_3$ was observed to produce good dewatering efficiency with reduced environmental risk and further cost involved in sludge handling.

4.9 Summary

This chapter investigated sludge dewaterability using skeleton materials. Jar tests, which are based on visual perception, may be used to screen the conditioning chemicals initially.

- Experimental investigation on sludge dewatering using GBFS

This investigation concerned the combined utilization of quicklime and GBFS to improve sludge dewatering. The experimental work included the initial characterization of the sludge and GBFS and evaluation of the dewatering ability of the treated sludge (CST, moisture content, turbidity, zeta potential, and heavy metal and biopolymer contents). Optimization using the Box-Behnken design was carried out with various operational parameters, and the best performance was found to be at a pH of 10, a dose of 0.34 g/g dry solids, and a contact time of 14 min. Characterization study was carried out by SEM in conjunction with EDXS, XRD, and FTIR to confirm the structural features (dense), elemental composition, and the presence of different functional groups.

- Experimental investigation on sludge dewatering using CSB

Feasibility of using simple CSB has been exposed in this study for sludge dewatering. The investigation was carried out using CSB but, CSB did not contribute to sludge dewatering hence modification was carried out using ferric chloride. The combination of CSB and ferric chloride proved to be a conditioner with better sludge dewaterability. The experimental work included the initial characterization of the sludge. evaluation of the dewatering ability of the treated sludge (CST, moisture content, settleability, zeta potential, and heavy metal and phosphate contents). Optimization using the Box-Behnken design was carried out independent variables like MCSB-$FeCl_3$ dosage, RMT, and SMT.CST was taken as output. The optimized process variable was achieved at MCSB-$FeCl_3$dosage = 42 % DS, RMT=9.11 min, and SMT = 17.98, the CST obtained is 55.88 sec. A characterization study was carried out by SEM in conjunction with EDXS, XRD, and FTIR to confirm the structural features (dense), elemental composition, and the presence of different functional groups.

CHAPTER 5

PHOSPHORUS REMOVAL BY SBR INDUCED WITH CRYSTALLIZATION FOR ITS RECOVERY

5.1 General

In this chapter, proposed lab scale setup was evaluated and the removal of phosphoruswas examined. The effect of release and uptake of phosphorus from endogenous digestion is also examined. Characterisation studies were conducted.

5.2. Phosphorus removal efficiency in anaerobic-aerobic process

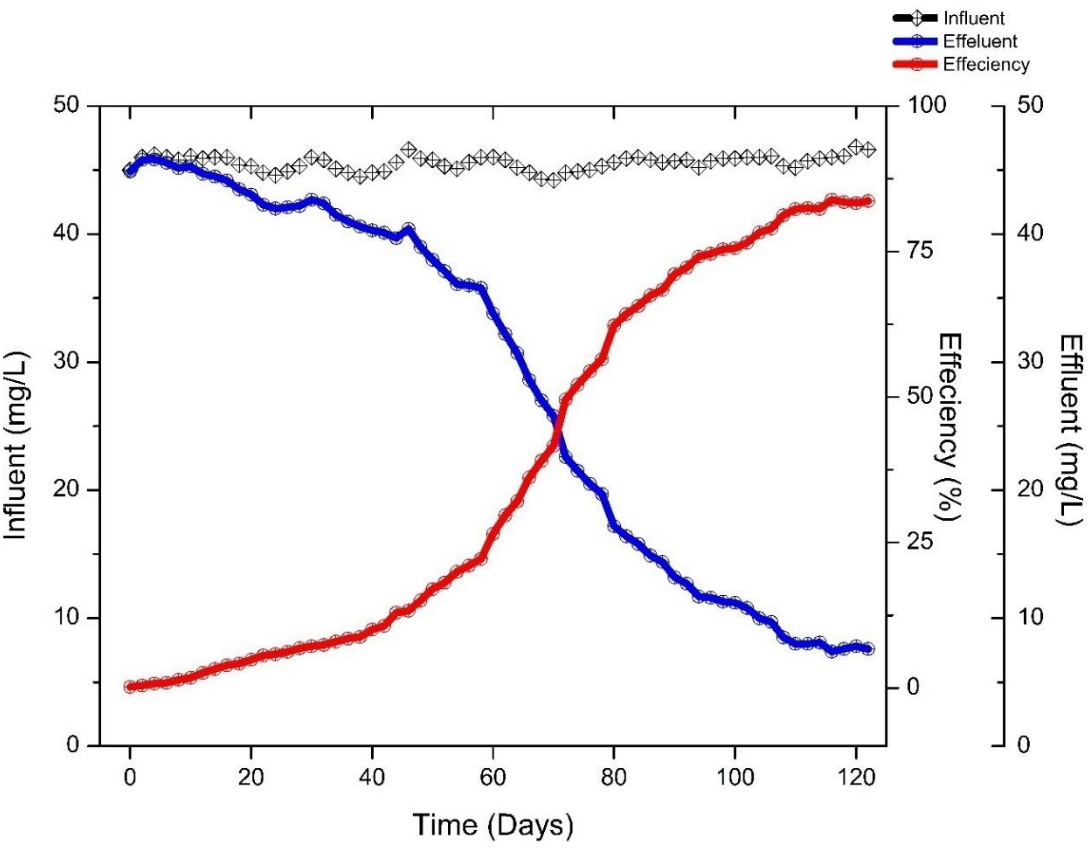


Figure 5. 1 PO_4^{3-}-P removal efficiency performance during 125 days

The SBR was operated under alternative anaerobic and aerobic conditions. Figure 3 presents a typical profile of the phosphorus concentration in the influent, effluent, and recovery efficiency. Stable phosphorus removal was achieved after 125 days of enrichment by alternative operation of the anaerobic-aerobic process. The colour of the PAOs sludge significantly changed compared with the seed sludge. Despite the variation of temperature(24^0-26^0C), DO(1.62 mg/L), pH, and influent phosphate of 42 – 45mg/L, the removal efficiency of biological phosphorus was achieved as84% with an effluent concentration of 7.06 mg/L indicating a good phosphorus removal. The removal of phosphorus is achieved by an alternative anaerobic and aerobic environment to provide PAOs with a selective advantage over other populations, thus facilitating the efficacy of PAOs enrichment and phosphorus removal. The main driving factor for the removal of phosphorus is PAOs as these organisms can store larger quantities of phosphorus as polyphosphates in their cells under aerobic conditions and accumulate organic material at the anaerobic level (Ruyi et al.,2016; Abhilash et al., 2020).

5.3 pH and phosphorus concentration change during one cycle of Anaerobic-Aerobic

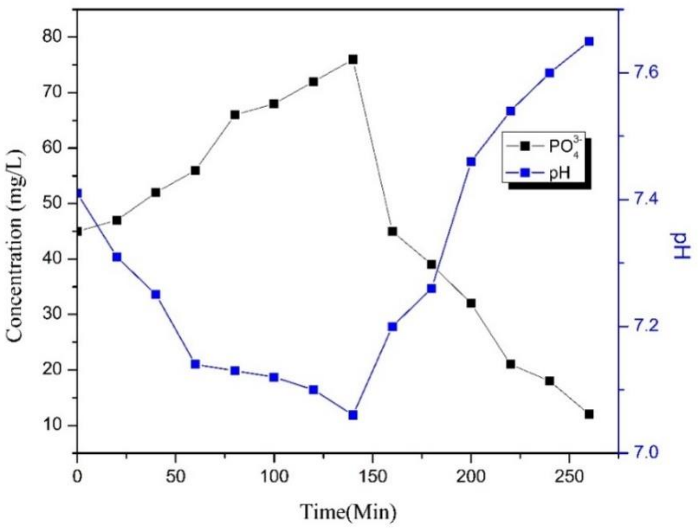
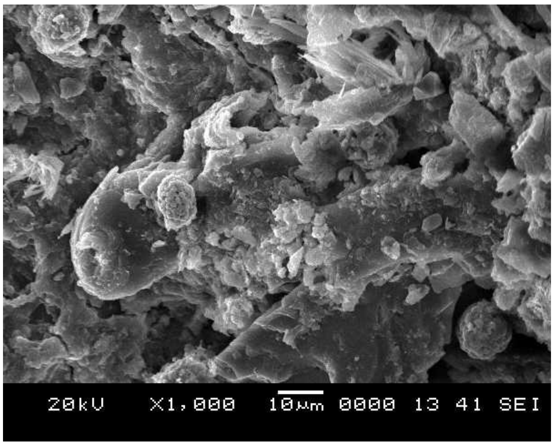


Figure 5.2 Variation of phosphate and pH during whole Anaerobic-Aerobic cycle

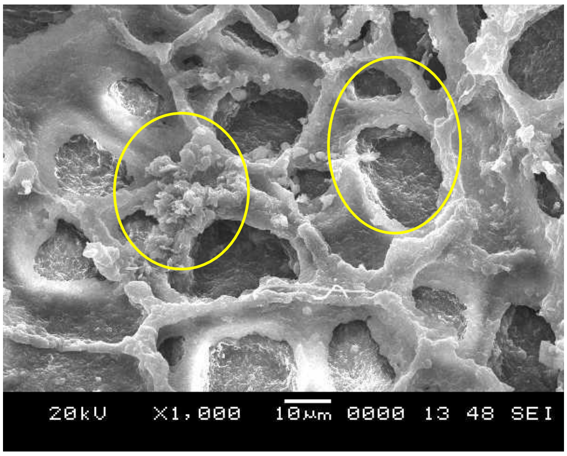
In the SBR, the biochemical reaction was found to be observed in one cycle with varying pH and phosphorus concentration profile. Figure 5.2 shows a typical transformation of the pH and phosphorus concentration change during one cycle of the anaerobic-aerobic. In the SBR process, the phosphorus uptake almost reached zero, and the removal efficiency reached 95% under aerobic conditions. This is because the PAOs have consumed the phosphorus under aerobic conditions.

During the entire SBR phase, variations in pH have been observed. The pH began to decrease during the anaerobic stage due to phosphate release. In aerobic conditions, a further rise in pH was observed due to phosphate uptake (Jinghua et al., 2015). At the end of phosphate uptake, the pH reaches relatively constant in the aerobic state. Therefore, the end of phosphate uptake can be concluded by monitoring the pH. Based on pH the retention time can be adjusted.

5.4. Microscopic morphology studies



a) Seed sludge



b) PAOs enriched sludge

Figure 5.3 Electron scanning photomicrographs (X1000) of seed sludge and PAOs enriched sludge

The SEM image indicates the presence of numerous morphological distinct bacteria in the inoculum like Coccoid, rod, and long filamentous cells. After continuous four months of SBR operation with acetate and glucose as a carbon source, the microbial communities were simplified. During the continuous operation at 125 days, the sample showed a homogeneous background layer with a honeycomb-like structure (Figure 5.3).

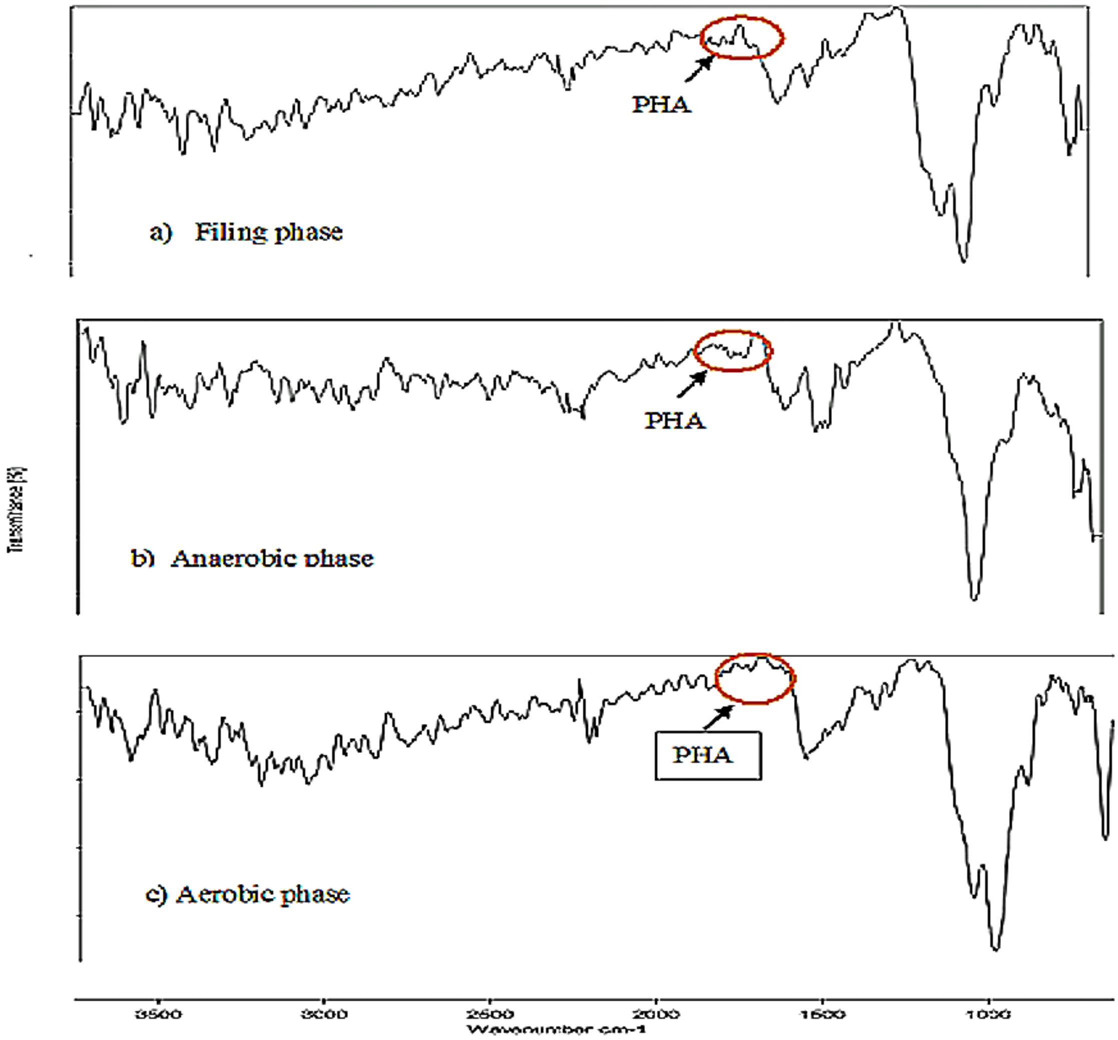


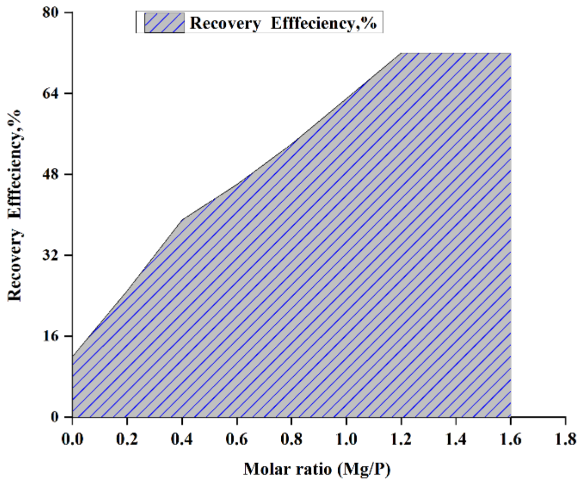
Figure 5.4 FTIR spectra of the sludge at – (a) filling, (b) anaerobic, and (c)aerobic phase

The FTIR spectra of the sludge at the anaerobic and aerobic phases are shown in Figure 5.4. The peak obtained at 1741cm^{-1} indicates the presence of PHA (Hong et al., 1999). The PHA presence in the sludge was weak during the start of the reactor. A significant increase in the peak of the PHAs was observed during the anaerobic phase of the SBR process. After the anaerobic phase, the aerobic phase was started wherein the PHA presence in the sludge decreased significantly. Based on the infrared absorption peak, the decrease, and increase in the PHA can be noticed due to the generated PHA in the anaerobic zone and PHA degradation in the aerobic zone.

5.5 Phosphorus recovery efficiency

The further recovery efficiency of phosphorus through crystallization was assessed. The influent of phosphorus on the crystallization process was7.3mg/L. MAP was used to recover the phosphorus. Batch studies were conducted with respect to pH and Mg/P molar ratio for maximum recovery of phosphorus at a reaction time of 20min.

a)



b)

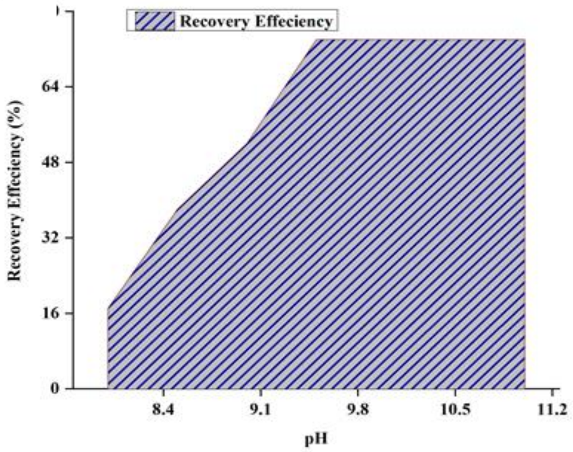
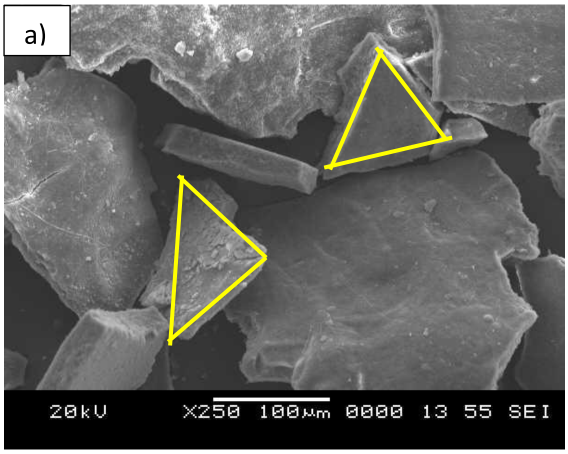


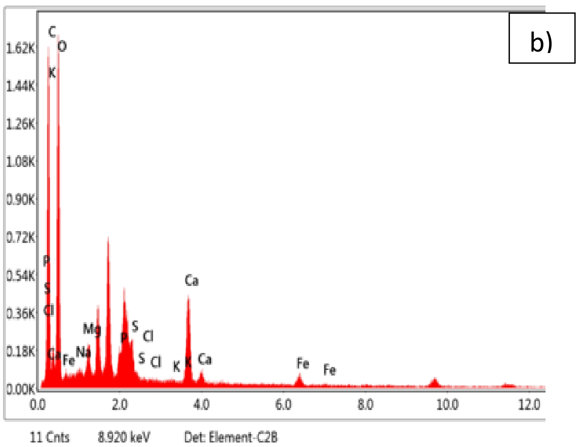
Figure 5.5 The efficiency of Mg/P molar ratio and pH on the recovery rates of phosphate

The obtained struvite from the crystallization process requires the presence of a 1:1:1molar ratio of Mg, P, and Initially, the concentration of PO_4^{3-} was determined in the effluent from the aerobic phase. The NH_4^+concentration in the effluent was relatively much higher than the PO_4^{3-} concentration. The Mg/P molar ratio may be the rate inhibitory factor in the MAP process. The recovery efficiency of phosphorus with respect to varying molar ratios is shown in Figure 7**.** It indicates that the recovery efficiency of PO_4^{3-} increased due to the increase in molar ratio. Whereas, when the molar ratio was 1.2, the recovery efficiency was constant.

The important parameter in the MAP reaction is the pH because the PO_4^{3-}ion concentration depends on the pH. Although ion equilibrium is not directly affected by H^+, the pH is very influential on the yield and purity of the struvite. In the present study, to determine optimum pH in the crystallization process, the pH was varied from 8 to 10. The PO_4^{3-} recovery efficiency with respect to pH is shown in Figure5. From the results, it can be observed that the recovery of phosphorus is attained at 9.5. Further increase in pH recovery efficiency stayed constant. When the pH increases, the phosphate recovery efficiency also increases, but a further increase of pH,i.e., more than 9.5 recovery remains unchanged. The possible reason could be that the solubility of the MAP reduced with the increase in pH (Doyle et al., 2002).

5.6 Morphology of struvite





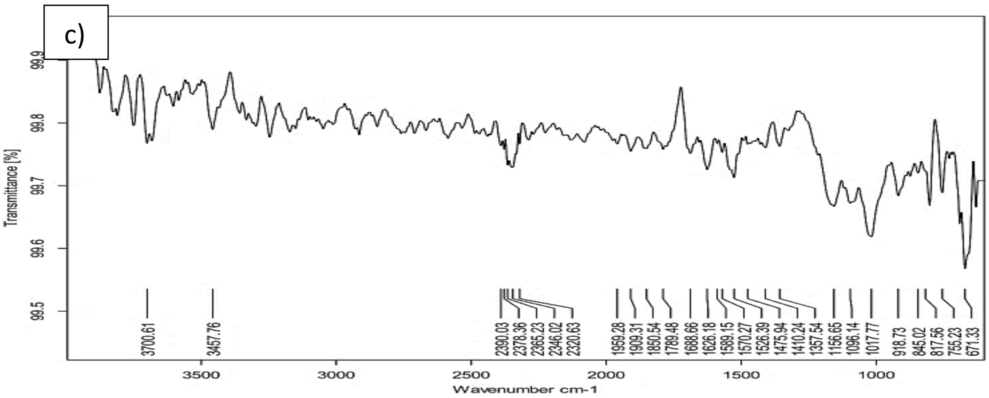


Figure 5.6: a) SEM analysis, b) EDAX, and c) FTIR spectra of struvite obtained by addition of $MgCl_2$

The struvite formed during the crystallization process at pH 9.5, 1.2:1 Mg/P molar ratio, and 20min of reaction time was analysed by SEM and EDAX (Figure 8a and b). It can be seen that the crystals are in a pyramid shape (Arvind et a., 2014). Struvite can be formed in different morphologies like prismatic type, pyramid type, coffin-shaped, feather-shaped, needle type, etc., based on the growth parameter (Yi et al.,2018). The composition of struvite is determined by EDAX, and the result indicates that the molar ratio of Mg and P is nearly 1:1.

The FTIR spectra of the precipitates produced from $MgCl_2$ are presented in Figure 8(c). The peaks between1680-1788cm^{-1} represent the N-H bending vibration in the ammonium group(Chauhan and Joshi 2013). The peaks between 1017cm^{-1}-1156cm^{-1} and 845 cm^{-1} represent the phosphate stretching vibration, whereas the peaks between 400-671 cm^{-1} are identified as metal-oxygen. Hence, based on the FTIR spectra, the precipitates obtained during the crystallization process are struvite crystals.

5.7 Phosphorus removal by adsorption

In the present study, a comparison was made with the adsorption process using the GBFS slag. The influent concentration of PO_4^{3-} was 42.1mg/L, was passed through the GBFS in column experimental setup. The concentration of PO_4^{3-} significantly reduced to 8.5 mg/L. This is due to the greater surface area of the adsorbent, and the GBFS consists of high levels of Ca, Al, and Fe oxides, which absorb the phosphorus. The removal of PO_4^{3-} was mainly due to physical interaction.

During the process, the temperature and pH of the influent were between 25-26^{0}C and 8-9. The result demonstrated that the slag adsorption capacity of phosphorus is comparable with removal efficiency obtained by the proposed anaerobic-aerobic SBR process.

Overall, in the present investigation, the integrated process of the SBR with crystallization presented a good phosphorus removal and recovery performance from dewatered sludge. Even though the concentration of phosphorus was very high in the dewatered sludge, most of the phosphorus was removed by the SBR.

Accumulation of phosphorus was achieved in SBR by alternative anaerobic-aerobic processes in which PAOs was enriched with the continuous operation (125 days) to obtain stable phosphorus removal. In the anaerobic phase, the degradation of Poly-P takes place with the release of phosphorus as orthophosphate, whereas in the aerobic phase, PAOs uptake orthophosphate from the liquid (Mino et al., 1998). PAOs utilize oxygen as an electron acceptor. To enhance phosphorus release, an external carbon source was provided. Hence, a mixture of glucose and acetate was utilized and was found to be an efficient carbon source by removing maximum phosphorus (84%), and the COD removal efficiency was 82%.

The remaining excess phosphorus in the effluent of SBR was recovered through crystallization. pH and molar ratio Mg/P are the required essential parameters to precipitate the phosphorus into struvite (Munch and Bar et al., 2001). Appropriate pH (9.5) and Mg/P molar ratio (1.2:1) was determined during experimental work. If crystallization was applied for the solid fraction, the process would have been inefficient because the separation of struvite crystals from the solid materials would be difficult. Hence, the liquid was collected from the mid-portion of the aerobic reactor, and settling was provided such that the solid particles could settle down and only the liquid part could be taken for the crystallization process.

The settled solid particles were recirculated into the anaerobic tank. About 72% of phosphorus was recovered through the struvite crystallization method. By this new access, the sludge production was less and 88% of the phosphorus was removed from the dewatered sludge. The removal efficiency of phosphorus was 86% by chemical means using GBFS via an adsorption process (Table 5.1). The obtained results are in agreement with the chemical process also. Further, in the proposed setup, as the sludge obtained from the aerobic tank was directly used for the recovery process sludge generation was minimum and achieved a viable and sustainable way for the removal and recovery of phosphorus. This method needs further continuity for continuous operation for the removal of phosphorus and other nutrients like nitrates, and microbial studies.

Table 5.1 Removal and recovery of phosphorus in the new process

Phase	Parameter	Removal/Recovery efficiency (%)
SBR	Influent	84
	Effluent	
Crystallization	Influent	72
	Effluent	
Adsorption	Influent	86

5.8 Summary

This chapter investigated phosphorus removal by EBPR and recovery of phosphorus from the effluent of the aerobic tank through crystallization in the batch mode experiments. The results demonstrated that it was feasible to eliminate phosphorus from aqueous solutions using conditioned sludge in aSBR. The effect of pH was examined. The phosphorus removal efficiency by the SBR is 84%. Because of the low concentration of phosphorus and a large amount of wastewater to be treated, researchers are still working on recovering phosphorus from wastewater. This study examines a novel technique for phosphorus recovery from the effluent of the aerobic tank by crystallization. The effects of pH and molar ratio on the recovery process were examined. Recovery efficiency was most favored in the pH range of 9.5 and molar ratio of Mg/P of 1.2. It is compared with the adsorption process using GBFS as an adsorbent for removal of phosphorus and achieved 86%. The result indicates that the proposed process achieves not only good phosphorus removal but also significant phosphorus recovery.

CHAPTER 6

CONCLUSIONS

This chapter deals with conclusion that are drawn based on the proposed objectives. The experimental investigations were carried out are in three stages. First stage includes the sludge dewatering using skeleton materials, secondly removal of phosphorus from synthetic wastewater by EBPR process using dewatered sludge. At last recovery of phosphorus through crystallization was carried out.

First stage includes the sludge dewatering using skeleton materials, GBFS was used as a skeleton material for sludge dewatering. Sludge characteristics and effect of GBFS on CST, moisture content, turbidity, zeta potential, and heavy metal and biopolymer contents was studied. To optimize the filtrate volume, optimization was carried out using design expert software. CSB was used for sludge dewatering due to the low efficiency of sludge dewatering, CSB was modified with ferric chloride so as to enhance the sludge dewatering. Further effect of MCSB-$FeCl_3$onCST, moisture content, settleability, zeta potential, and heavy metal and phosphate contents was investigated. To increase the efficiency of the sludge dewatering optimization was carried out for CST using design expert. For both the sludge dewatering process characterization studies were carried out using SEM-EDX, XRD and FTIR.

Secondly removal of phosphorus by EBPR from the synthetic wastewater was carried out for 125 days. A laboratory set up consists of 4-liter sequential batch reactor operated alternatively anaerobic-aerobic process. A continuous mix of sludge was carried out using mechanical stirrer and aerated in aerobic process. Effect of pH on EBPR was studies for one complete cycle in a batch mode. At last recovery of phosphorus through crystallization was carried out for different molar ratio of Mg/P and pH. And characterization studies were carried out for struvite by SEM-EDX, XRD and FTIR.

Based on the investigation, following conclusions were drawn

Phase I: Sludge dewatering using skeleton materials

GBFS and MCSB was used for sludge dewatering and were found to be a significant skeletal material for dewatering secondary sludge.

i) Specific findings of GBFS as skeleton material

The dewatering ability of the sludge was successfully evaluated by studying various properties of the dewatering process.

- The initial characteristics of sludge was studied and the CST of raw sludge was found to be 92sec and reduced to 38sec after dewatering using GBFS.The maximum dewatering efficiency was obtained at pH 10 with the slag dosage of 0.37 g/g DS. Reduction in the moisture content (68%), turbidity (8 NTU), protein (826 g/L), polysaccharides (2316 g/L) and heavy metal content was observed in treated filtrate when compared to that in the raw filtrate.
- The BBD was used to optimize the dewatering efficiency with various influencing parameters (pH, dosage and contact time). The optimum values obtained at pH of 10.2, a dose of 0.34 g/g DS, and a contact time of 14 min, resulting in a liquid separation efficiency from sludge that yielded 81.1 mL filtrate.
- Based on the characterization study, surface morphology analysis indicated that the slag, as a skeleton material, exhibited a rigid structure that could act as a channel for the removal of excess water from the sludge.

ii) Specific findings of MCSB-$FeCl_3$ as skeleton material

- The initial characteristics of sludge was study and the CST of raw sludge was 138 sec and reduced to 56 sec after dewatering using MCSB-$FeCl_3$.The dewatering efficiency was achieved at MCSB-$FeCl_3$ dosage of 40% DS. The effect of MCSB-$FeCl_3$ on moisture content (69.2%), settleability, heavy metal and phosphate (50.62%) was observed in sludge dewatering process.

- Optimum conditions for the best output in each cycle was achieved by BBD. The optimum CST result happens at an MCSB dosage=41%DS, RMT=10 min, and SMT=19Min. Based on ANOVA for surface response Quadratic pattern, P value was less than 0.05 showing that the model is significant at a confidence level of 0.98.
- SEM images confirm that CSB modified with ferric chloride has influenced in providing voids for easy flow of water. The X-Ray diffraction (XRD) pattern of MCSB-$FeCl_3$ showed the amorphous phase of carbon. FTIR spectra shows the presence aromatic groups present in lignin and carbon group presence.

Phase II: Phosphorus removal by EBPR

A lab-scale sequential batch reactor was established and operated under anaerobic-aerobic process in a closed system and smoothly operated for 125 days with synthetic wastewater for the removal of phosphorus in an EBPR process.

Some specific findings of this study are drawn as follows.

- The initial characteristics of the synthetic wastewater was studied. The parameters viz influent temperature(24^0-26^0C), DO(1.62 -4mg/L), pH (7.2), and phosphate is of 42 – 45mg/L.After the batch experiments, the removal efficiency of biological phosphorus was achieved as 84% with an effluent concentration of 7.1 mg/L indicating a good phosphorus removal.
- SEM analysis showed a homogeneous background layer with a honeycomb structure. Based on the infrared absorption peak, the decrease and increase in the PHA were noticed due to the generated PHA in the anaerobic zone and PHA degradation in the aerobic zone.

Phase III: Recovery of phosphorus by crystallization process

Recovery of phosphorus was experimented for the effluent obtained from the aerobic tank(EBPR).Magnesium chloride was used as a magnesium source to carry out the crystallization process with varying pH and molar ratio(Mg/P).

Some specific findings of this study are drawn as follows.

- The optimum value for the recovery of phosphorus through crystallization was obtained at pH 9.5 and molar ratio of Mg/P is 1.2. Recovery of phosphorus through crystallization as struvite was found to be 72%.
- SEM result shows that the struvite formed during the crystallization process is in a pyramid shape. Based on the FTIR spectra, the precipitates obtained during the crystallization process are struvite crystals as the peaks 1680-1788cm^{-1} and 1017cm^{-1}-1156cm^{-1} represent the ammonium and phosphate group.
- A comparison study was made with the adsorption process using the GBFS slag as an adsorbent. The adsorption efficiency of phosphorus removal by slag was 86%.

TOPICS WITH SCOPE FOR FUTURE STUDY

The present investigation can be extended to:

1. For future research, sludge dewatering can be carried out using various agricultural wastes.
2. A study on removal of nitrogen in a continuous process could be carried out.
3. Low-cost magnesium source can be applied to improve the performance of recovery.

REFERENCES

Ackerman, J.N., 2012. “Reclaiming phosphorus as struvite from hog manure.” (Doctoral thesis). University of Manitoba, Winnipeg, Canada.

Ali, M.I., & Schneider, P.A. (2008). “An approach of estimating struvite growth kinetic incorporating thermodynamic and solution chemistry, kinetic and process description.” Chem. Eng. Sci. 63, 3514-3525.

Almahbashi, N.M.Y., S.R.MKutty., Muhammad, A. you., NooraI., USalihi., AhmedAl-Ninia.H., Jagaba., B.N.S, Aldhawia.,A. and Ghaleb.,A.S. (2020). “Optimization of Preparation Conditions of Sewage sludge based Activated Carbo”, Ain Shams Engineering Journal .82,340-352.

Amokrane, A., Comel, C. and Veron J. (1997). “Landfill leachates pretreatment by coagulation-flocculation”. Water Res., 31:2775–2782.

APHA (2012) Standard methods for the examination of water and wastewater. 22nd edn, American Public Health Association, American Water Works Association, Water Environment Federation.

Arvind Sinha., Amit Singh., Sumit Kumar., Sunil Kumar Khare. and Arunachalam Ramanan. (2014). “Microbial mineralization of struvite: A promising process to overcome phosphate sequestering crisis.” water research .2014 54, 33-43.

Asakura H., Endo K. and Yamada M. (2009). “Improvement of permeability of waste sludge by mixing with slag or construction and demolition waste”. Waste Manage. 29 (6), 1877–1884.

Atapour, M, &Kariminia, H. (2013). “Optimization of Biodiesel Production from Iranian Bitter Almond Oil Using Statistical Approach.” Waste Biomass. Valor 4:467-474.

Awotwe-Otoo, C.A., Patrick, J.F., Muhammad, J.H., Lee, S,, Mansoor, A.K.and Rakhi, B.S. (2012). “Application of quality by design elements for the development and optimization of an analytical method for protamine sulfate.” J Pharm Biomed Anal. 62:61–67

Ayat Hossein Panahia., SeyedDavoudAshrafib., Hossein Kamanic., Maryam Khodadadia., Eder Claudio Limad., FerdosKordMostafapourc. and Amir Hossein Mahvie.(2019). “Removal of cephalexin from artificial wastewater by mesoporous silica materials using Box-Behnken response surface methodology.” Desalination and Water Treatment. 159,169–180.

Barnard, J.L.(1983). “Design consideration regarding phosphate removal in activated sludge plants.” Water Sci Technol. 15: 319-28.

Behera, S.K., Meena, H., Chakraborty, S and Meikap, B.C. (2018). “Application of response surface methodology (RSM) for optimization of leaching parameters for ash reduction from low-grade coal.” Int J Min Sci Technol. 28:621–629.

Bekiaris,G., Peltre, C., Jensen, L.S. and Bruun, S. (2016). “Using FTIR-photoacoustic spectroscopy for phosphorus speciation analysis of biochars.” Spectrochim Acta - Part A Mol BiomolSpectrosc. 168:29–36 https://10.1016/j.saa.2016.05.049

Benttez, J., Rodriguez, A., & Suarez, A. (1994). “Optimization technique for sewage sludge conditioning with polymer and skeleton builders”. Water Resource. 28(10), 2067–2073.

Betatache, H., Aouabed, A., Drouiche, N., &Lounici, H. (2014). “Conditioning of sewage sludge by prickly pear cactus (Opuntia ficus Indica) juice”. Ecol Eng. 70, 465–469.

Bianxial Liu., Apostolos Giannis., JiefengZhang,. Victor, W.C., Chang and Jing Yuan Wang .(2013). “Characterization of induced struvite formation from source separated urine using seawater and brine as magnesium source.”Chemosphere, 93, pages 2738-2745.

Bing Li., Irina Boiarkina., Wei Yu., Hai Ming Huang., Tajammal Munir., Guang Qian Wang. and Brent. R. Young. (2019). “Phosphorous recovery through struvite crystallization: Challenges for future design.” Science of the Total Environment. 648,1244–1256.

Biswas, B.K., Inoue, K., Ghiire, K.N., Ohta, S., Harada, H., Ohto, K.,&Kawakita,H., (2007). “The adsorption of phosphate from an aquatic environment using metalloaded orange waste.” J. Colloid Interf. Sci. 312, 241-223.

Box, G.E.P., W.G. Hunter & Hunter, J.S. (1987). “Statistics for Experimenters: An Introduction to Design, Data Analysis and Model Building.” John Wiley, New York

Brdjanovic, D., Logemann, S., Van Loosdrecht, MCM., Hooijmans, CM., Alaerts, GJ. and Heijnen J.J(1998). “Influence of temperature on biological phosphorus removal: process and molecular ecological studies.” Water Res.32(4): 1035–48.

Can Gungoren., Yasin Baktarhan., IlginKursun., Safak G. Ozkan., Orhan Ozdemir.(2018). “Characterization of Flocs in Dewatering of Coal Plant Tailing.”, Journal of Science and Engineering,5 (3) 215-218.

Carucci A., Lindrea K., Majone M. and Ramadori, R. (1993). “Different mechanisms for the anaerobic storage of organic substrates and their effect on enhanced biological phosphate removal (EBPR).” Water Sci. Technol. 39(6): 21–28.

Çelen, I., Buchanan, J.R., Burns, R.T., Robinson, R.B. and Raman, D.R. (2007). “Using a chemical equilibrium model to predict amendments required to precipitate phosphorus as struvite in liquid swine manure.” Water Res. 41, 1689-1696.

Changjin Guo., Lei Ding., Xia Openg Jing., Huiewn Zhang. and DeweiZhang.(2021). “Application of response surface methodology to optimize chromium (VI) removal from aqueous solution by cassava sludge-based activated carbon.” Journal of Environmental Chemical Engineering. Volume 9, Issue 1, 104785.

Chauhan, C. K, and Joshi, M. J. (2013). “In vitro crystallization, characterization and growth inhibition study of urinary type struvite crystals.” J. Cryst. Growth 362, 330–337.

Chen, G., Lin, W.& Lee, D. (2010), ‘Capillary suction time (CST) as a measure of sludge dewaterability’, Water Science and Technology, vol. 34, no. 3, pp. 443-448.

Chen, L. L., Xiong, Q., Haobo Hou, H. L., & Zhou, M., (2020). “Enhancement of the sewage sludge dewaterability by using ethanol and Fe(III)-rice husk.” Environmental Science and Pollution Research 27, 8696–8706.

Choi, J., Lee, S., Kim, J., Park, K., Kim, D., & Hong, S., (2012). “Comparison of surface modified adsorbents for phosphate removal in water”. Water Air Soil Pollution 223, 2881-2890.

Christensson, M. (1997) Enhanced Biological Phosphorus Removal – Carbon Sources, Nitrate as Electron Acceptor and Characterisation of the Sludge Community. Department of Biotechnology, Lund University, Sweden

Chunhong Shi., Wenquan Sun., Yongjun Sun., Lei Chen., Yanhua Xu. and Mengdan Tang. (2019). “Synthesis, Characterization, and Sludge Dewaterability Evaluation of the Chitosan-Based Flocculant CCPAD”. Polymers 11, 95.

Cisse, L.and Mrabet, T. (2004). “World Phosphate Production : Overview and Prospects.” Phosphorus Research Bulletin. 15, pp. 21–25.

Arun kumarthalla., Devatha, C.P, and Michel Torrijos.(2012). Experimental Evaluation of Activated Sludge-Biofilm Reactor: Influence of Composite Media. Journal of Hazardous, Toxic, and Radioactive Waste 16(2):134-141

Colin, F., Leschber, R. &Mininni, G. (1988), ‘Physical and chemical characterisation of sewage sludge’, Sewage Sludge Treatment and Use: New Developments, Technological Aspects and Environmental Effects.

Cornel, P. and Schaum, C., (2009). “Phosphorus recovery from wastewater: needs,technologies and costs.” Water Sci. Technol. 59, 1069–1076.Craggs, R., 2005.

CPCB (2000) Environmental standards for ambient air, automobiles, fuels, industries and noise. PCLS-4.

Daniel Puyol., Damien, J., Batstone., Tim Hulsen., SergiAstals., Miriam Peces. and Jens O.Kromer. (2017). “Resource Recovery from Wastewater by Biological Technologies: Opportunities, Challenges, and Prospects.” Frontiers in microbiology, https://doi.org/10.3389/fmicb.2016.02106.

De-Bashan, L. E. and Bashan, Y. (2004). Recent advances in removing phosphorus from wastewater and its future use as fertilizer (1997-2003). Water Res. 38, 4222-4246.

Desmidt, E., Ghyselbrecht, K., Zhang, Y., Pinoy, L., Van der Bruggen, B., Verstraete,W. and Meesschaert, B. (2015). “phosphorus scarcity and full-scale P-recoverytechniques-a review.” Crit. Rev. Environ. Sci. Technol. 45, 336–384.

Dinçer, A.R., Gunes, Y., Karakaya, N., &Gunes, E., (2007). “Comparison of activated carbon and bottom ash for removal of reactive dye from aqueous solution”. Bioresour Technol 98, 834–839.

Ding, A., Qu, F., Liang, H., Guo, S., Ren, Y., Xu, G. and Li, G. (2014). “Effect of adding wood chips on sewage sludge dewatering in a pilot-scale plate-and frame filter”. RSC Adv, 24762–24768.

Doyle, J.D., & Parsons, S.A. (2002). “Struvite formation, control and recovery”. Water Res. 36 , 3925–3940.

Duan, J., & Gregory, J. (2000). “Coagulation by hydrolysing metal salts”. Advanced Colloid Interface Science. 100–102, 475–502.

Ealias, A.M., Jose, J.V. &Saravanakumar, M.P. (2016). “Biosynthesised magnetic iron nanoparticles for sludge dewatering via Fenton process”. Environmental Science Pollution Resource. 23, 21416 – 21430.

Edmondson, R.N. (1991). “Agricultural response surface experiments based on four-level factorial designs.” Biometrics, 47, 1435–1448.

Eljamal, O., Okawauchi, J., Hiramatsu, K. & Harada, M. (2013). “Phosphorus sorption from aqueous solution using natural materials”. Environment Earth Science. 68, 859-863.

Enujeke, A., &Canakci, M. (2010). “Optimization of pretreatment reaction for methyl ester production from chicken fat”. Fuel .89, 4035-4039.

Erdal, U.G., Erdal, Z.K. and Randall, C.W. (2003). “The competition between PAOs (phosphorus accumulating organisms) and GAOs (glycogen accumulating organisms) in EBPR (enhanced biological phosphorus removal) systems at different temperatures and the effects on system performance.” Water Sci.Technol. 47(11): 1–8.

Erdal, U.G., Erdal, Z.K. and Randall, C.W. (2006). “The mechanism of enhanced biological phosphorus removal washout and temperature relationships.” Water Environ Res. 78(7): 710-15.

Felz, S., Vermeulen, P., Loosdrecht, M.C.M. & Lin, Y.M. (2019). “Chemical characterization methods for the analysis of structural extracellular polymeric substances (EPS)”. Water Res, 201–208.

Feng, X., Deng, J., Lei, H., Bai, T., Fan, Q. & Li, Z. (2009), ‘Dewaterability of waste activated sludge with ultrasound conditioning’, Bioresource Technology, vol.100, no. 3, pp. 1074-1081.

Ferreira, S.L.C., Bruns ,R.E., Ferreira,H.S., Matos, G.D., David,J.M., Brandao, G.C, da., Silva, E.G.P., Portugal, L.A., Dos Reis, P.S., Souza,A.S. and Dos Santos, W.L.N. (2007). “Box-Behnken design: an alternative for the optimization of analytical methods.” Anal Chim Acta. 597:179–186.

Filipe, C.D.M., Daigger, G.T., Grady, C.P.L. (2001). “pH as a key factor in the competition between glycogen-accumulating organisms and phosphorus-accumulating organisms.” Water Environ. Res. 73(2): 223–32.

Foletto, E.L., dos Santos, W.R.B., Mazutti, M.A., Jahn, S.L. and Gündel, A. (2013). "Production of struvite from beverage waste as phosphorus source." Mater. Res. 16,242-245.

Fujimoto N., Mizuochi T. and Togami Y. (2016). "Phosphorus exation in the sludge treatment system of a biological phosphorus removal process".Water Science and Technology,23,635±640.

Gao, N. (2019). 'Journal of Analytical and Applied Pyrolysis A new method combining hydrothermal carbonization and mechanical compression in-situ for sewage sludge dewatering : Bench-scale verification', Journal of Analytical and Applied Pyrolysis. 139, pp. 187–195. doi: 10.1016/j.jaap.2019.02.003.

Garcia-Belinchon, C., Rieck, T., Bouch, L., Gali, A., Rouge, P. & Fabregas, C. (2013). "Struvite recovery: pilot scale results and economic assessment of different scenarios". Water Practice Technol, 8, 119-130.

Gebremariam, S. Y., Beutel, M. W., Christian, D. and Hess, T. F. (2011). "Research Advances and Challenges in the Microbiology of Enhanced Biological Phosphorus removal-a critical review." Water environment research, 83(3) , 195-219.

GokceKor-Bicakci. and CigdemEskicioglua. (2019). "Recent developments on thermal municipal sludge pretreatment technologies for enhanced anaerobic digestion." Renewable and Sustainable Energy Reviews. 110, 423–443.

Gorazda, K., Kowalski, Z. and Wzorek, Z., (2012). "From sewage sludge ash to calcium phosphate fertilizers." Pol. J. Chem. Tech. 14, 54-58.

Guan, S., Deng, F., Huang, S., Liu, S., L., Ai, & She, P. (2017). "Optimization of magnetic field-assisted ultrasonication for the disintegration of waste activated sludge using Box–Behnken design with response surface methodology". Ultrasonics Sonochemistry. 38, 9-18.

Gungoren, C., Safak, Y.I., Ozkan G. &Ozdemir, O. (2018). "Characterization of Flocs in Dewatering of Coal Plant Tailings Hittite". Science and Engineering. 5, 215-218.

Guo, Z., Liping, M., Q, Dai., Yang, J., Ao, R. & Wang, L. (2019). "Dewatering performance of sewage sludge under pretreatment with modified corn-core powder", Science of the Total Environment. 684, 402–412.

Guo. C, L., Ding, X., Jin, H., & Zhang, D. (2021). "Application of response surface methodology to optimize chromium (VI) removal from aqueous solution by cassava sludge-based activated carbon". Environmental Chemical Engineering. 9.

Haiming Zou., & Yan Wang., (2016). "Phosphorus removal and recovery from domestic wastewater in a novel process of enhanced biological phosphorus removal coupled with crystallization". Bioresource Technology. 211, 87–92.

Hamidi, S.G., Hamidi, A.A., Aziz, A., Hasnain M., Hasnain, I.M., Zinatizadeh, I.A.A., &Zinatizadeh, A.A., (2008). "Application of Response Surface Methodology (RSM) to Optimize Coagulation–Flocculation Treatment of Leachate Using Poly-Aluminum Chloride (PAC) and Alum". Hazardous Materials 163.

Han, Y., Zhou, M., Wan, S., &Xue, F., (2016). "Optimization of sludge dewatering process by inorganic conditioners under mild thermal treatment. Desalination and Water Treatment."

Hansdah, P., & Kumar, S., (2017). "Performance optimization of dewatering of coal fine tailings using Box–Behnken design, Energy sources, part a: recovery, utilization, and environmental effects". 40(1), 75–80.

Hansdah, P., Kumar, S., &Mandre, N. R., (2018). "Performance optimization of dewatering of coal fine tailings using Box–Behnken design", Energy Sources, Part A: Recovery, Utilization and Environmental Effects, 40, 75–80.

Hao, X.D., Wang, C.C., Lan, L. and van Loosdrecht, M.C.M. (2008). "Struvite formation, analytical methods and effects of pH and $Ca2^{+}$." Water Sci. Technol. 58,1687-1692.

He, D.Q., Zhang, Y.J., He, C.S. & Yu, H.Q. (2017). "Changing profiles of bound water content and distribution in the activated sludge treatment by NaCl addition and pH modification". Chemosphere. 186, 702–708.

Heffer, P., & Prudhomme, M., (2014). Fertilizer outlook 2014–2018. In: 82nd IFA Annual Conference, Sydney.

Henze, M., Harremoës, P., la Cour Jansen, J. and Arvin, E. (1996). 'Wastewater treatment – Biological and chemical processes."

Herrmann, I., Nordqvist, K., Hedstrom, A., and Viklander, M. (2014). "Effect oftemperature on the performance of laboratory-scale phosphorus-removingfilter beds in on-site wastewater treatment." Chemosphere. 117, 360–366.doi: 10.1016/j.chemosphere.2014.07.069

Hong, K.S., Sun, W., Tian, G.Q., Chen,W.& Huang. (1999). “A rapid method for detecting bacterial polyhydroxyalkanoates in intact cells by Fourier transform infrared spectroscopy”. Appl Microbiol Biotechnol. 51: 523-526.

Hongbo, L., Dong, X., &Evandro, B. (2017). “Mechanisms of metal sorption by biochars: Biochar characteristics and modifications, Chemosphere. 178, 466-478.

Hua Wei, Boqiang Gao, Jie Ren, Aimin Li. and Hu Yang. (2018). “Coagulation/flocculation in dewatering of sludge: A review, Water Research Volume 143, Pages 608-63.https://doi.org/10.1016/j.watres.2018.07.029.

Huanlong Peng., Songxiong Zhong., Jiangxin Xiang., Qintie Lin., Chuang Yao., Jiahua Dong., Guangcai Yin., Kun Yao., Siyuan Zeng. and Jie Zhong. (2017). Characterization and secondary sludge dewatering performance of a novel combined aluminum-ferrous-starch flocculant (CAFS). Chemical Engineering Science. 173 (2017) 335–345.

Huchzermeier, M.P. (2011). “Overcoming challenges to struvite recovery from anaerobically digested dairy manure.” (Master of Science thesis). State University of New York, New York, USA.

Hyangyoun Chang., Nari Park., Yeoju Jang., Hyunman Lim. and Weonjae Kim (2020). “Application of the hydroxyapatite crystallization-filtration process to recover phosphorus from wastewater effluents.” Water science and technology. doi: 10.2166/wst.2020.292,

Jeon, C.O., & Park, J.M.(2000) “Enhanced biological phosphorus removal in a sequencing batch reactor supplied with glucose as a sole carbon source.” Water Res. 34(7): 2160–70.

Jia, G., (2014). “Nutrient removal and recovery by the precipitation of magnesium ammonium phosphate)(Master of Science thesis). The University of Adelaide, South Australia, Australia.

Jialin Liang., Jinjia Huang.,Siwei Zhang., XianYang., Shaosong Huang., LiZheng., MaoyouYe, and ShuiyuSun. (2019). “A highly efficient conditioning process to improve sludge dewaterability by combining calcium hypochlorite oxidation, ferric coagulant re-flocculation, and walnut shell skeleton construction.” Chemical Engineering Journal. Volume 361, Pages 1462-1478

Jinghua Lv. &Linjiang Yuan. (2015). “Effects of chemical phosphate precipitation in the sidestream process on biological phosphorus removal at the anaerobic stage in an anaerobic-aerobic sequencing batch reactor.” Desalination and Water Treatment 54 3011–3019.

Johansson, P. (1994). “SIPHOR – a kinetic model for simulation of biological phosphate removal.” PhD Thesis. Department of Water and Environmental Engineering, Lund Institute of Technology, University of Lund, Sweden.

Jordaan, E.M., Ackerman, J. and Cicek, N. (1997). “Phosphorus removal from anaerobically digested swine wastewater through struvite precipitation.” Water Sci.Technol. 61, 3228-3234.

Junyuan., Guo Shilin., Jiang. and Yujje Pang. (2019). “Rice straw biochar modified by aluminium chloride enhances the dewatering of the sludge from municipal sewage treatment plant.” Science of the total environment. Volume 654, pages 338-344.

KaanYetilmezsoy, SevgiDemire, & Robert Vanderbei. (2009). “Response Surface Modeling of Pb(II) Removal from Aqueous Solution by Pistacia vera L.: Box–Behnken Experimental Design.” Journal of Hazardous Materials 171(1-3):551-62.DOI: 10.1016/j.jhazmat.2009.06.035

Karabegovic, L., Uldal, M., Werker, A. & Morgan-Sagastume, F. (2013). “Phosphorus recovery potential from a waste stream with high organic and nutrient contents via struvite precipitation.” Environ. Technol. 34, 871-883.

Kornberg A., Rao N.N., Ault-Riche D (1999). “Inorganic polyphosphate: a molecule of many function.” Annu. Rev. Biochem. 68, 89-121.

Kuba, T., van Loosdrecht, M.C.M. and Heijnen, J.J. (1997). “Biological dephosphatation by activated sludge under denitrifying conditions: pH influence and occurrence of denitrifying dephosphatation in a full-scale waste water treatment plant.” Water Science and Technology, 36:75-82.

L Lei Chen., Qiao Xiong., He Li., Haobo Hou, & Min Zhou. (2020). “ Enhancement of the sewage sludge dewaterability by using ethanol and Fe(III)-rice husk.” Environmental Science and Pollution Research.27:8696–8706. https://doi.org/10.1007/s11356-019-06621-w.

Lanning, M.C.E.(2008). “Phosphate recovery from wastewaters comparing two different sources of magnesium oxide in the precipitation of struvite” (Master of Science thesis). The University of Guelph, Ontario, Canada.

Latimer, R., Rohrbacher, J., Nguyen, V., Khunjar, W.O. and Jeyanayagam, S., (2015). “Towardsa Renewable Future: Assessing Resource Recovery as a Viable TreatmentAlternative (NTRY1R12b)”. Water Environment Research Foundation.

Lau, S.W., Sen, T.K., Chua, H.B., & Ang, H.M. (2017). “Conditioning of Synthetic Sludge and Anaerobically Digested Sludge Using Chitosan, Organic Polyelectrolytes and Inorganic Metal Cations to Enhance Sludge Dewaterability.” Water Air Soil Pollution. 228, 35.

Lee, C.H.M., & Liu, J.C.M. (2000). “Enhanced sludge dewatering by dual polyelectrolytes conditioning”. Water Res .34, 4430–4436.

Levantesi, C., Serafim, L.S., Crocetti, G.R., Lemos, P.C., Rossetti, S., Blackall, L.L., Reis, M.A.M. and Tandoi, V. (2002) “Analysis of the microbial community structure and function of a laboratory scale enhanced biological phosphorus removal reactor.” Environ. Microbiol. 4(10): 559–69.

Li, H.J., Chen, Y.G. and Gu, G.W. (2008). “The effect of propionic to acetic acid ratio on anaerobic aerobic(low dissolved oxygen) biological phosphorus and nitrogen removal.” Bioresour. Technol. 99(10): 4400–4407.

Li, N., Wang, X., Ren, N., Zhang, K. and Kang, H. S. (2008). “Effects of Solid Retention Time (SRT) on Sludge Characteristics in Enhanced Biological Phosphorus Removal (EBPR) Reactor.” Chem. Biochem. Eng. Q 22(4): 453–58.

Li, B., Boiarkina, I., Yu, W., Huang, H.M., Munir, T., Wang, G.Q., Brent, R. & Young. (2019) “Phosphorous recovery through struvite crystallization: Challenges for future design”. Science of the Total Environment. 648, 1244–1256.

Li, H., Song, L., Han, B. and Song, H. (2019). “Highly efficient enhancement of municipal sludge dewaterability using persulfate activation with nZVI/HA”. Water Science & Technology. 79, 1309-1315.

Li, H., Ye, Z. and Wang, F. (2012). “Phosphorus recovery as struvite from eutrophic waters by XDA-7 resin.” Water Sci. Technol. 65, 2091-2097.

Li, S., Zhang, K. & Zhou, S. (2009). “Use of dewatered municipal sludge on Canna growth in pot experiments with a barren clay soil. Waste Management. 29, 1870-1876.

Li, Y.L., Liu, J.W., Chen, J.Y., Shi, Y.F., Mao, W., Liu, H., Li, Y., He, Y.S., & Yang, J.K. (2014). “Reuse of dewatered sewage sludge conditioned with skeleton builders as landfill cover material”. Environ Sci Technol, 11, 233–240.

Liang, J., Zhang, J.H.S., Yang, X., Huang, S., Zheng, L., Ye, M. & Sun, S. (2019). "A highly efficient conditioning process to improve sludge dewaterability by combining calcium hypochlorite oxidation, ferric coagulant re-flocculation, and walnut shell skeleton construction." Chemical Engineering, 361,1462-1478.

Lidia Wolny., Pawed Wolski. and Iwona Zawieja. (2002). "Rheological parameters of dewatered sewage sludge after conditioning." Desalination. 222 (2008) 382–387.

Liu, WT., Mino , T., Nakamura. K, & Matsuo, T., (1996). "Glycogen accumulating population and its anaerobic substrate uptake in anaerobic–aerobic activated sludge without biological phosphorus removal." Water Res, 30(1): 75–82.

Liu, C., Lai, L., & Yang, X. (2016). "Sewage sludge conditioning by Fe(II)-activated persulphate oxidation combined with skeleton builders for enhancing dewaterability". Water Environ J, 30, 96–101.

Liu, Y.H., Kumar, S., Kwag, J.H. & Ra, C.S., (2013). Magnesium ammonium phosphate formation, recovery and its application as valuable resources: a review.J. Chem. Technol. Biotechnol. 88, 181-189.

Lu, M.C., Lin, C.J., Liao, C.H., & Huang, R.Y. (2003). "Dewatering of activated sludge by Fenton's reagent". Advances in Environmental Research. 7, 667-670.

Luo H., Ning X an. & Liang X., (2013). "Effects of sawdust-CPAM on textile dyeing sludge dewaterability and filter cake properties". Bioresour Technol. 139:330–336.

Luoa, Y., Lia, H., Huanga, Y., Zhaoa, T.L., Yaob, Q.Z., Fuc, S.Q. &Zhoua, G.T., (2018). "Bacterial mineralization of struvite using MgO as magnesium source and its potential for nutrient recovery". Chemical Engineering. 351, 195–202.

Lv, J., Linjiang, & Yuan, (2015). "Effects of chemical phosphate precipitation in the sidestream process on biological phosphorus removal at the anaerobic stage in an anaerobic-aerobic sequencing batch reactor". Desalination and Water Treatment. 54, 3011–3019.

Ma, W., Zhao, L., Liu, H., Liu, Q., & Ma, J., (2017). "Improvement of sludge dewaterability with modified cinder via affecting EPS". Front Environ Sci Eng 11, 1–14.

Machnicka, J..Suschka and K. Grubel, (2008) "The importance of potassium and magnesium ions in biological phosphorus removal from wastewater". 43-309 Bielsko-Biała, Poland.

Madakson, P., Yawas, D., &Apasi, A. (2012). “Characterization of Coconut Shell Ash For Utilization In Metal Matrix Composites For Automotive Applications.” Engineering Science and Technology 4. 1190-1198.

Manu,D.S, and Arun Kumar Thalla,(2017). Artificial intelligence models for predicting the performance of biological wastewater treatment plant in the removal of Kjeldahl Nitrogen from wastewater. Appl Water Sci, DOI 10.1007/s13201-017-0526-4.

Mateo-Sagasta, J., Raschid-Sally, L. and Thebo, A. (2015). “Global wastewater and sludge production, treatment and use.” Springer, 15-24.

Mazaheri, R., Ghazani, M.T., &Alighardashi, A., (2018). “Effects of Moringa Peregrina and Ferric Chloride (FeClf) On Water Treatment Sludge Dewatering”. BiosciBiotechnol Res Asia 15, 975–980.

Mc Grath J.W., Cleary S., Mullan A. and Quinn J.P. (2003). “Acid-stimulated phosphate uptake by activated sludge microorganisms under aerobic laboratory conditions.” Wat. Res. 35, 4317-4322.

Meaghan, K., Gibbons., Md. Maruf Mortula. and Graham A. Gagnon. (2009). “Phosphorus adsorption on water treatment residual solids”. Water Supply 58 (1), 1-10.

MeiqiangCaia., Jianqiang Hu., Guanghu Lian., Ruiyang Xiao., Zhijun Song., MicongJin.,Chunying Dong., Quanyuan Wang., Dewen Luo., ZongsuWeia.(2018).”Synergetic pretreatment of waste activated sludge by hydrodynamic cavitation combined with Fenton reaction for enhanced dewatering.” Ultrasonics - Sonochemistry 42, 609–618,610.

Mino, T., van Loosdrecht, M.C.M. and Heijnen, J.J. (1998). “Microbiology and bio-chemistry of the enhanced biological phosphate removal process.”Water Res 32(11):3193 – 3207.

Miya, A., Kitagawa, M. and Tanaka, T. (1987) “The behavior of magnesium in biological phosphate removal In. Biological phosphate removal from wastewaters.” R. Ramadori, Pergamon Press, 135-146.

Moerman, W., Carballa, M., Vandekerckhove, A., Derycke, D., &Verstraete, W., (2009). Phosphate removal in agro-industry: Pilot and full scale operational considerations of struvite crystallization. Water Res. 43, 1887-1892.

Mohan, D., Sarswat, A., & Singh, V.K., (2011). “Development of magnetic activated carbon from almond shells for trinitrophenol removal from water. Chemical Engineering Journal 172, 1111-1125.

Montgomery, D.C., (1997). “Design and Analysis of Experiments”. 5th Edition, John Wiley and Sons, Inc New York.

Mota-Filho, C.R. and Batista, J.R., 2003. “The influence of sludge holding times on the leaching of P in enhanced biological phosphorus removal (EBPR) systems.” Proceedings of the Water Environment Federation, WEFTEC 2003: Session 71 through Session 83, pp.310-26(17).

Mowla, D., Tran, H.N., & Allen, D.G., (2013). “A review of the properties of biosludge and its relevance to enhanced dewatering processes”. Biomass Bioenergy 58, 365-378.

Munch E, and K. Barr, (2001). Controlled struvite crystallization for removing phosphorus from anaerobic digester sidestreams. Water Res. 35:151-159.

Muriithi, D. K., (2015). “Application of Response Surface Methodology for Optimization of Potato Tuber Yield”. Theoretical and Applied Statistics 4, 300-304.

Muster, T.H., Douglas, G.B., Sherman, N., Seeber, A., Wright, N., &Guzukara, Y., (2013). “Towards effective phosphorus recycling from wastewater: quantity and quality”. Chemosphere 91, 676-684.

Myers, R. H., Montgomery, D. C., Vining, G. G., Borror, C. M. & Kowalski, S. M. (2004). “Response Surface Methodology: A Retrospective and Literature Survey,” J. Qual. Technol., 36, 5377.

Nancharaiah Y.V., Venkata Mohan S. andLens, P.N.L. (2016). “Recent advances in nutrient removal and recovery in biological and bioelectrochemical systems.” 215:173-185.

Nguyen, T.C., Loganathan, P., Nguyen, T.V., Kandasamy, J., Naidu, R., & Vigneswaran, S., (2018), “Adsorptive removal of five heavy metals from water using blast furnace slag and fly ash”. Environ Sci Pollut Res 25, 20430–20438.

Nieminen, J. (2010). “Phosphorus recovery and recycling from municipal wastewater sludge (Master of Science thesis)”. Aalto University, Espoo, Finland.

Ning, X., Luo, H., Liang, X., Lin, M., & Liang, X., (2013). “Effects of tannery sludge incineration slag pre-treatment on sludge dewaterability”. Chem Eng 22.

Oehmen, A., P. C. Lemos, G. Carvalho, Z. Yuan, J. Keller, L. L. Blackall & M. A. Reis.,(2007). “Advances in enhanced biological phosphorus removal: from micro to macro scale”. Water research, 41(11), 2271-2300.

Panahia, A.H., Ashrafib, S.D., Kamanic, H., Khodadadia, M., Limad, E.C., Mostafapour, F. K., &Mahvie, A.H., (2019). “Removal of cephalexin from artificial wastewater by mesoporous silica materials using Box-Behnken response surface methodology”. Desalination and Water Treatment 159, 169–180.

Panswad, T., Doungchai, A. and Anotai, J.(2003). “Temperature effect on microbial community of enhanced biological phosphorus removal system.” Water Res. 37(2): 409–15.

Parsons, S.A., & Smith, J.A.,(2008).“Phosphorus removal and recovery from municipal Wastewaters”. Elements 4, 109–112.

Perera, P.W.A., Han, Z.Y., Chen, Y.X., and Wu, W.X. (2007). “Recovery of nitrogen and phosphorous as struvite from swine waste biogas digester effluent.” Biomed. Environ. Sci. 20, 343-350.

Phuong, V.H., Nguyen, T.T.V., Vigneswaran, S., Bustamante, H., Higgins, M., &Rys, D. (2018). “Novel methodologies for determining a suitable polymer for effective sludge dewatering.” Environmental Chemical Engineering 6, 4206-4214.

Pinotti, A., &Zaritzky, N., (2001). “Effect of aluminum sulfate and cationic polyelectrolytes on the destabilization of emulsified wastes”. Waste Management 21, 535-542.

Puig, S., Coma, M., Monclus, H., Van Loosdrecht, M.C.M., Colprim, J., Balaguer, M.D.(2008) “Selection between alcohols and volatile fatty acids as external carbon sources for EBPR.” Water res. 42(3): 557-66.

Puja Hansdah. and Shravan Kumar,(2017). “Performance optimization of dewatering of coal fine tailings using Box–Behnken design,” Energy sources, part a: recovery, utilization, and environmental effects, VOL. 40, NO. 1, 75–80.

Qi Lingling., Tang Xu., Wang Zhaofeng. and Peng Xinshan.(2017). “Pore characterization of different types of coal from coal and gas outburst disaster sites using low temperature nitrogen adsorption approach.” International journal of mining science and technology, Volume 27, issue 2, page no 371-377.

Qi, Y., Thapa, K.B., & Hoadley, A.F., (2011). “Benefit of lignite as a filter aid for dewatering of digested sewage sludge demonstrated in pilot scale trials”. Chemical Engineering166, 504-510.

Randall, C.W., Barnard, J.L., Stensel, H.D, (1992). Design and retrofit of wastewater treatment plants for biological nutrient removal. Lancaster: Technomic Publishing; p. 25–78.

Rashmi Hosurdoddi Ramachandra, &ChellaPurushothaman Devatha. (2020) “Experimental investigation on sludge dewatering using granulated blast furnace slag as skeleton material.” Environmental Science and Pollution Research, https://doi.org/10.1007/s11356-020-07614-w.

Rittmann, B. E., Mayer,. B, Westerhoff, P. and Edwards M (2011). “Capturing the lost phosphorus” *Chemosphere* **64** 846–53.

Rodrigo, M.A., Seco, A., Ferrer. J. and Penya-Roja, J.M. (1999). “The effect of the sludge age on the deterioration of the enhanced biological phosphorus removal process.” Environ Tech 20(10): 1055-1063.

Rumky, J. (2018) ‘Science of the Total Environment Optimization of integrated ultrasonic-Fenton system for metal removal and dewatering of anaerobically digested sludge by Box-Behnken design’, Science of the Total Environment. The Authors, 645, pp. 573–584. doi: 10.1016/j.scitotenv.2018.07.125.

Rusten, B, O. Kolkinn, and H. Odegaard, “Moving bed biofilm reactors and chemical precipitation for high efficiency treatment of wastewater from small communities,” Water Science and Technology, vol. 35, no. 6, pp. 71–79, 1997.

Ruyi Wang., Yongmei Li., Wenling Chen., Jinte Zou. and Yinguang Chen. (2016). “Phosphate release involving PAOs activity during anaerobic fermentation of EBPR sludge and the extension of ADM1.” Chemical Engineering Journal 287, 436–447.

Reed, S., Bouzoun, J., Meddi,M. (1986). “A rational method for sludge dewatering via freezing” Journal (Water Pollution Control Federation), Vol. 58, No. 9, Conference Issue,pp. 911-916.

Sarasanseena Mithra, Ramesh,S.T., Gandhimathi, R,Nidheesh,P.V.(2017).Studies on the removal of phosphate from water by electrocoagulation with aluminium plate electrodes. Env Eng Management Journal Science.16(10),1173-1181.

Sanin, F. D., Clarkson, W. W. &Vesilind, P. A. (2011), Sludge engineering: The treatment and disposal of wastewater sludges, DEStech Publications, Inc.

Scholz, M. (2005), 'Review of recent trends in capillary suction time (CST) dewaterability testing research', Industrial and engineering chemistry research, vol. 44, no. 22, pp. 8157-8163.

Schönborn, Ch., Bauer, H. D. and Roske, I. S. (2001). "Stability of Enhanced Biological Phosphorus Removal and Composition Polyphosphates Granules." Water Res., 35, 3190-319.

Schuler AJ, and Jenkins D (2002) Effects of pH on enhanced biological phosphorus removal metabolisms. Water Sci. Technol. 46(4–5): 171–78.

Seiichirou Ohura., Hiroyuki Harada., Biplob Kumar Biswas., Mitsunori Kondo., Susumu Ishikawa., Hidetaka Kawakita., Keisuke Ohto. And KatsutoshiInoue.(2011). "Phosphorus recovery from secondary effluent and side-stream liquid in a sewage treatment plant using zirconium-loaded saponified orange waste." J Mater Cycles Waste Manag.,13:293–297

Seo, Y. I., Hong, K. H., Kim, S. H., Chang, D., Lee, K. H., and Kim,Y., Do (2013). "Phosphorus removal from wastewater by ionic exchange using a surface-modified Al alloy filter." J. Ind. Eng. Chem. 19, 744–747.

Seung Hwan Lee, S. Vigneswaran, &HeeMoon.(1997). "Adsorption of phosphorus in saturated slag media columns." Separation and Purification Technology 12, 109-l 18.

Seviour R. J., T. Mino & M. Onuki., (2003). "The microbiology of biological phosphorus removal in activated sludge systems". FEMS Microbiology Reviews, 27(1), 99-127.

Shahin, G., Hamidi, A.A., Mohamed, H., & Ali, A.Z., (2009). "Application of response surface methodology (RSM) to optimize coagulation–flocculation treatment of leachate using poly-aluminum chloride (PAC) and alum". Hazardous Materials 163, 650–656.

Shaopo Wanga., Zhu Lia., Dong Wanga., Yajing Lia., Liping Sun. (2020) "Performance and population structure of two carbon sources granular enhanced biological phosphorus removal systems at low temperature." Bioresource Technology., 300, 122683.

Shen, Y., Ogejo, J.A. and Bowers, K.E., (2011). "Abating the effects of calcium on struvite precipitation in liquid dairy manure." T. Asabe, 54, 325-336.

Shi, C., Sun, W., Y., Sun, Chen, L., Xu, Y., & Tang, M., (2019). “Synthesis, Characterization, and Sludge Dewaterability Evaluation of the Chitosan-Based Flocculant CCPAD”. Polymers 11, 95.

Shi,Y., J.,Yang, W., & Yu, (2015). “Synergetic conditioning of sewage sludge via $Fe^{2+/}$persulfate and skeleton builder: Effect on sludge characteristics and dewaterability”. Chemical Engineering Journal 270, 572-581.

Shiew Wei Lau., Tushar Kanti Sen., Han Bing Chua & Ha Ming Ang.(2017) “Conditioning of Synthetic Sludge and Anaerobically Digested Sludge Using Chitosan, Organic Polyelectrolytes and Inorganic Metal Cations to Enhance Sludge Dewaterability.” Water Air Soil Pollution (2017) 228: 35, DOI 10.1007/s11270-017-3545-8.

Simon, J. The MBR book: Principles and Application of Membrane Biorector in Water and Wastewater Treatment, 2nd ed.; Elsevier: Amsterdam, The Netherlands, 2010.

Sinha, A., Singh, A., Kumar, S., Khare, S.K., & Ramanan, A.,(2016) “Microbial mineralization of struvite: A promising process to overcome phosphate sequestering crisis”. Water research 54, 33-43.

Smolders, G.J.F., van Loosdrecht, M.C.M. and Heijnen J.J. (1994). “pH: Keyfactor in the biological phosphorus removal process.” Water Science and Technology, 29:71-74

Smollen, M., &Kafaar, A., (1997). “Investigation into alternative sludge conditioning prior to”. Water Sci Technol 36, 115–119.

Su Guan., Feng Deng., Si Qi Huang., Shu yang Liu., Li Xian Ai. and Pu Yung She. (2017). **“**Optimization of magnetic field-assisted ultrasonication for the disintegration of waste activated sludge using Box–Behnken design with response surface methodology.” Ultrasonic Sonochemistry,Volume 38, page 9-18.

Sudiana. I.M, Mino, T, Satoh, H., Nakamura, K. and Matsuo. T. (1999) “Metabolism of enhanced biological phosphorus removal and non-enhanced biological phosphorus removal sludge with acetate and glucose as carbon source.” Water Sci. Technol. 39(6): 29–35.

Swamy, G. J., Sangamithra, A., & Chandrasekar, V., (2014). “Response surface modeling and process optimization of aqueous extraction of natural pigments from Beta vulgaris using Box-Behnken design of experiments”. Dyes and Pigments.

Tarayre, c., de clercq, l., charlier, r., michels, e., meers, e., camargo-valero, m. &delvigne, f. 2016. “New perspectives for the design of sustainable bioprocesses for phosphorus recovery from waste.” Bioresource Technology, 206, 264-274.

Thapa K, Qi Y and Hoadley A (2009b). “Interaction of polyelectrolyte with digested sewage sludge and lignite in sludge dewatering.” Colloid Surf. A-Physicochem. Eng. Asp **334 (1)**, 66–73.

To, V. H. P., Nguyen, T. V., Vigneswaran, S., Nghiem, L., Murthy, S., Bustamante, H.& Higgins, M. J. (2014), ‘Modified centrifugal index and sludge characteristics in assessing sludge dewatering’, IWA 7th International Young Water Professional Conference, Taipei, Taiwan.

To, V.H.P., Nguyen, T.V., Vigneswaran, S., Bustamante, H., Higgins, M., & Van, R.D., (2018). “Novel methodologies for determining a suitable polymer for effective sludge dewatering.” Environ Chem Eng., 6, 4206–4214.

Tonkovic, Z. (1998). “Energetics of enhanced biological phosphorus and nitrogen removal processes.” Water Science and Technology, 38:177-184.

Tony, M.A., Zhao, Y., Fu, J., & Tayeb, A.M. (2008). “Conditioning of aluminium-based water treatment sludge with Fenton’s reagent: Effectiveness and optimising study to improve dewaterability”. Chemosphere, 72(4), 673-677.

Torsten Meyer., Xu Chen., Honghi, N. Tran, D. Grant Allen, Elizabeth, A. Edwards ,(2017), “Natural Freezing-Thawing and Its Impact on Dewaterability and Anaerobic Digestibility of Biosludge.” Environmental Engineering Science. Vol. 34, No. 5.

Tsai., C.S, and Liu., W.T. (2002). “Phylogenetic and physiological diversity of tetrad-forming organisms in deteriorated biological phosphorus removal systems.” Water Sci. Technol46(1–2): 179–84.

Tu, Y., You, C., Chang, C., & Chen, M., (2015). “Application of magnetic nano-particles for phosphorus removal/recovery in aqueous solution". J. Taiwan Inst. Chem 46, 148–154.

Tyagi, V.K., & Lo, S., (2013). “Sludge: a waste or renewable source for energy and resources recovery.” Renew. Sust. Energ. Rev. 25, 708-728.

Cornel, P., Schaum, C., (2009). “Phosphorus recovery from wastewater: needs, technologies and costs.” Water Sci. Technol. 59, 1069-1076.

Vesilind, P.(2000). “A modified capillary suction time apparatus for measuring the filterability of super-flocculated sludges”, Water Science and Technology, vol.42, no. 9, pp. 135-139.

Vu Hien Phuong To., Tien Vinh Nguyena., Heriberto Bustamante., Saravanamuthu Vigneswaran. (2019). “Deleterious effects of soluble extracellular polymeric substances on polyacrylamide demand for conditioning of anaerobically digested sludge”. Journal of Environmental Chemical Engineering 7, 102941.

Vu Hien Phuong., Toa Tien Vinh Nguyen., Saravanamuthu Vigneswaran., Heriberto Bustamante., Matthew Higgins., and DerekvanRys. (2018). “Novel methodologies for determining a suitable polymer for effective sludge dewatering.” Journal of Environmental Chemical Engineering Volume 6, Issue 4, Pages 4206-4214.

Wang, J., Burken, J.G., Zhang, X.Q., &Surampalli, R. (2005). “Engineered struvite precipitation: Impacts of component ion molar ratios and pH.” J. Environ. Eng.-Asce 131, 1433-1440.

Wang, ND., Peng, J., & Hill, G. (2002) “Biochemical model of glucose induced enhanced biological phosphorus removal under anaerobic condition.” Water Res.36 (1): 49–58.

Wang, R., Li, Y., Chen W., Zou J., & Chen, Y., (2016). “Phosphate release involving PAOs activity during anaerobic fermentation of EBPR sludge and the extension of ADM1”. Chemical Engineering Journal 287, 436–447.

Wang, S., Yang, Y.K., & Chen, X.G., (2017). “Effects of bamboo powder and rice husk powder conditioners on sludge dewatering and filtrate quality”. Int BiodeteriorBiodegrad 124, 288–296.

Wang, Y., & Guo, L. (2019). “Optimization of operating conditions for the acidification metabolites production with waste sludge using response surface methodology (RSM)”. Environ Sci Pollut Res 26, 30303–30312.

Wang, Y., Jiang, F., Zhang, Z., Xing, M., Lu, Z., Wu, M,, Yang, J., & Peng Y.(2010). “The long-term effect of carbon source on the competition between polyphosphorus accumulating organisms and glycogen accumulating organisms in a continuous plg-flow anaerobic/aerobic (A/O) process.” Bioresour. Technol. 101: 98-104.

Wang., & Hou-feng. (2019). ‘Combined use of inorganic coagulants and cationic polyacrylamide for enhancing dewaterability of sewage sludge’, Journal of Cleaner Production. Elsevier Ltd, 211, pp. 387–395. doi: 10.1016/j.jclepro.2018.11.208.

Wei, H., Gao, B., Ren, J., Li, A., & Yang, H., (2018). “Coagulation/flocculation in dewatering of sludge: a review”. Water Research 143, 608-631.

Weishen Zeng., Dehan Wang., Zifeng Luo., Jie Yang., Z. &haoyun Wu. (2020). “Phosphorus recovery from pig farm biogas slurry by the catalytic ozonation process with MgO as the catalyst and magnesium source.” Journal of Cleaner Production Volume 269, 122133.

Whang., LM, & Park, JK. (2002) “Competition between polyphosphate- and glycogen-accumulating organisms in biological phosphorus removal systems—effect of temperature.” Water Sci. Technol.46(1-2): 191–94.

Wu, Y., Zhang, P., & Zhang, H., (2016). “Bioresource Technology Possibility of sludge conditioning and dewatering with rice husk biochar modified by ferric chloride”. BioresourceTechnology 205, 258–263.

Xiao, K., Deng, J., Zeng, L., Guo, T., Gong, Y., Yang, B., & Duan, H., (2019). “Enhancement of municipal sludge dewaterability by electrochemical pre-treatment”. Environ Sci 75, 98–104.

Xie, W., Wang, Q., Ma, H., Ohsumi, Y. & Ogawa, H. I. (2005). ‘Study on phosphorus removal using a coagulation system’, Process Biochemistry, vol. 40, no. 8, pp. 2623-2627.

Xu, H., He, P., Gu, W., Wang, G., & Shao, L. (2012). “Recovery of phosphorus as struvite from sewage sludge ash.” J. Environ. Sci. 24, 1533-1538.

Yadav, D., Anand, R.S., Pruthi, V. and Kumar, P. (2017). Enhanced biological phosphorus removal using dried powdered sludge in an aerobic baffled reactor. J. Environ. EngrgASCE,. DOI: 10.1061/(ASCE)EE.1943-7870.0001189, 04017006.

Yan Wu., Panyue Zhang., &Haibo Zhang. (2017). “Possibility of sludge conditioning and dewatering with rice husk biochar modified by ferric chloride”. Bioresource Technology, 205 (2016). 258-263.

Yandong Yang., Liang Zhang., Hedong Shao., Shujun Zhang., Pengchao Gu., Yongzhen Peng. (2018). “Enhanced nutrients removal from municipal wastewater through biological phosphorus removal followed by partial nitritation/anammox. Front.” Environ. Sci. Eng. 2017, 11(2): 8.

Yeoman S., Stephenson T., Lester J., Perry R. (1988). “The removal of phosphorus during wastewater treatment: a review.” Environ. Pollut, 49, 183-233.

Yetilmezsoy, K., Demirel, S., Robert, S.D., &Vanderbei, V.R., (2009). “Response Surface Modeling of Pb(II) Removal from Aqueous Solution by Pistacia vera L.: Box–Behnken Experimental Design. Hazardous Materials, 171, 551-562.

Yi Han., Min Zhou., Sha Wan., & Fei Xue. (2016). “Optimization of sludge dewatering process by inorganic conditioners under mild thermal treatment.” Desalination and Water Treatment. doi: 10.1080/19443994.2016.1193771.

Yi Luo., Han Lia., Ya-Rong Huang., Tian-Lei Zhao., Qi-Zhi Yao., Sheng-Quan Fu., & Gen-Tao Zhou. (2018). “Bacterial mineralization of struvite using MgO as magnesium source and its potential for nutrient recovery.” Chemical Engineering Journal, 351, 195–202.

Yun Liu., Xia Sheng., Yuanhua Dong. &Yijie Ma. (2012). “Removal of high-concentration phosphate by calcite: Effect of sulfate and pH.” Desalination, 289 66–71.

Zall, J., & Galil, N. (2015). “Skeleton oily sludge builders for conditioning”. Water Pollution Control Federation 59(7), 699-706.

Zhang, H.L., Fang, W. and Wang, Y.P. (2012) “Phosphorus removal in an enhanced biological phosphorus removal process: roles of extracellular polymeric substances.” Environ Sci Technol., 47(20):11482– 11489.

Zhang T., Liu Y., & Fang HHP. (2005). “Effect of pH change on the performance and microbial community of enhanced biological phosphate removal process.” Biotechnol. Bioeng. 12(2): 173–82.

Zhang, W., Cao, B., & Wang, D. (2016). “Influence of wastewater sludge treatment using combined peroxyacetic acid oxidation and inorganic coagulants reflocculation on characteristics of extracellular polymeric substances (EPS). Water Res, 88, 728-739.

Zhao, Y.Q., Zhao, X.H., & Babatunde, A.O., (2009). “Use of dewatered alum sludge as main substrate in treatment reed bed receiving agricultural wastewater: Long-term trial”. Bioresource Technology, 100, 644-648.

Zhao., Y.Q.(2002). “Enhancement of alum sludge dewatering capacity by using gypsum as skeleton builder. Colloids and Surfaces A: Physicochem”. Eng. Aspects 211, 205-212.

Zheng, X., Zhou, W., and Wan, R., (2018). “Increasing municipal wastewater BNR by using the preferred carbon source derived from kitchen wastewater to enhance phosphorus uptake and short-cut nitrification-denitrification.” Chem Eng., J 344:556–564.

Zhiying Guo., Liping Ma., Quxiu Dai., Jing Yang., Ran Ao., &Lichun Wang. (2019) “Dewatering performance of sewage sludge under pretreatment with modified corn-core powder”. Science of the Total Environment., 684, 402–412.

Zhou, Y., M., Pijuan, A., Oehmen Z., & Yuan. (2010). “The source of reducing power in the anaerobic metabolism of polyphosphate accumulating organisms (PAOs)—A mini-review”. Water Science and Technology., 61(7), 1653.

Zhu, C., Zhang, P., Wang, H., & Ye, J. (2018). “Conditioning of sewage sludge via combined ultrasonication-flocculation-skeleton building to improve sludge dewaterability”. Ultrasonics Sonochemistry, 40, 353–360.

Zou, H., & Wang, Y. (2016). “Phosphorus removal and recovery from domestic wastewater in a novel process of enhanced biological phosphorus removal coupled with crystallization”. Bioresource Technology., 211, 87–92.

APPENDIX-1

PUBLICATIONS

International journal

1. Rashmi Hosurdoddi Ramachandra and C P Devatha. "Experimental investigation on sludge dewatering using granulated blast furnace slag as skeleton material".***Environmental science and pollution research, springer, 2020,*** **Doi.org/10.1007/s11356-020-07614-w. (SCI)**
2. Rashmi Hosurdoddi Ramachandra and C P Devatha. "Dewatering performance of sludge using coconut shell biochar modified with ferric chloride."***International Journal of Environmental Science and Technology, Springer Journal.*** (**Under Review**)
3. Rashmi Hosurdoddi Ramachandra and C P Devatha.Phosphorus Removal by Sequential Batch Reactor Induced with Crystallization for its Recovery (AnrAr-C-Ad)". ***Environmental science and pollution research, springer*** (**Under Review**)

Conferences

1. H R Rashmi and C P Devatha "Experimental studies on dewatering of sewage sludge using skeleton material". ***– Third International Conference on Sustainable Energy and Environmental Challenges (3 rd. SEEC),*** IIT Roorkee, India, 18 –21 December, 2018.

2. H R Rashmi and C P Devatha. "Phosphorus recovery as induced struvite from deep dewatered liquors using magnesium chloride as a magnesium source"- **International Conference on *Material Science and Manufacturing Technology (ICMSMT),***Coimbatore, April 12-13, 2019.

3. H R Rashmi and C P Devatha, "Sludge dewatering using coconut shell biochar modified with ferric chloride"-***National Symposium on Environmental Pollution Prevention and Control: Future perspective (EPPC: FP.:2019),***NITK, Surathkal, 23-25 August 2019.

4. H R Rashmi and C P Devatha, "Phosphorus recovery from the dewatered liquor by struvite crystallization using sea water as magnesium source"- ***National conference on "New and effective Innovations, Technologies and Key Challenges 2020" (NCCE)*** **-** NITK, Surathkal, January 30th & 31st, 2020.

5. H R Rashmi and C P Devatha, "A Review on various parameters which affects the enhanced biological phosphorus removal process."-***National conference on "New and effective Innovations, Technologies and Key Challenges 2020" (NCCE)*** **-** NITK, Surathkal, January 30th & 31st, 2020.

APPENDIX-II

General Standards for Discharge Of Environmental Pollutants

Sl. No.	Parameter	Standards			
		Inland surface water	**Public sewers**	**Land of irrigation**	**Marine /coastal areas**
1	Colour and odour	---	---	---	---
2.	Suspended solids mg/l, max.	100.	600	200	*For process waste water 100 *For cooling water effluent 10 per cent above total suspended matter of influent
3	Particle size of suspended solids	Shall pass850 micron IS Sieve	--		*Floatable solids, solids max. 3mm. *Settable solids. Max 856 microns
4.	pH value	5.5 to 9.0	5.5 to 9.0	5.5 to 9.0	5.5 to 9.0
5	Temperature.	Shall not exceed $5^{o}C$ above the receiving water temperature.	--	--	Shall not exceed $5^{0}C$ above the receiving water temperature.
6	Oil and grease, Mg / l max.	10	20	10	20
7	Total residual chlorine, mg/l max	1.0	--	--	1.0
8	Ammonical nitrogen (as N),mg/l, max.	50	50	--	50
9	Total nitrogen (asN); mg/l, max	100	--	--	100
10	Free ammonia (as	5.0	--	--	5.0

	NH_3),mg/l,				
11	Biochemical Oxygen demand (3days at 27°C), mg/l, max.	30	350	100	100
12	Chemical oxygen demand, mg/l,max. .	250	--	--	250
13	Arsenic (as As) mg/l, max	0.2	0.2	0.2	0.2
14	Mercury (As Hg),mg/l, max.	0.01	0.01	--	0.01
15	Lead (as Pb) mg/l,max.	0.1	0.1	--	2.0
16	Cadmium (as Cd) mg/l, max.	2.0	1.0	--	2.0
17	Hexavalent chromium (as Cr +, mg/l, max.	0.1	0.2	--	1.0
18	Total chromium (as Cr) mg/l, max.	2.0	2.0	--	2.0
19	Copper (as Cu) mg/l, max.	3.0	3.0	--	30
20	Zinc (as Zn) mg/l, max.	5	15	--	15
21	Selenium (as Se) mg/l, max.	0.05	0.05	--	0.05
22	Nickel (as Ni) mg/l, max.	3.0	3.0	--	50
23	Cyanide (as CN) mg/l, max.	0.2	2.0	0.2	0.2
24	Fluoride (as F) mg/l, max.	2.0	15	--	15

25	Dissolved phosphates (as P), mg/l, max.	5.0	--	--	--
26	Sulphide (as S) mg/l, max.	2.0	--	--	5.0
27	Phenolic compounds (as C_6H_5OH) mg/l, max.	1.0	--	5.0	5.0
28	Manganese (as Mn)	2 mg/l	12 mg/l	mg/l	2 mg/l
29	Iron (as Fe)	3 mg/l	3 mg/l	3 mg/l	3 mg/l
30	Vanadium (as V)	0.2 mg/l	0.2 mg/l	--	0.2 mg/l
31	Nitrate Nitrogen	10 mg/l	--	--	20 mg/l

RESUME

Name :Mrs. Rashmi H. R

Permanent Address : No 1167, Jawaharlal Nehru road,

Opp to (Balakrishna Rangamandir), 3rd stage BEML layout, R R Nagar,

Bangalore,Karnataka, India- 560098

Contact Number : 9743266764

E-mail ID :rashusmile14@gmail.com

ACADEMIC QUALIFICATION:

Degree	Specialization	Institute	Duration
M.Tech	Environmental Engineering	PESCE, Mandya	2009-2011
B E	Civil Engineering	BCET, Bangalore	2004-2009