Investigation of Phosphate Adsorption in Aqueous Solution Using Steel Slag and HCl Treated Steel Slag

By

Muhammad Fikri bin Ismail

(10827)

Dissertation submitted in partial fulfillment
Of the requirements for the
Bachelor of Engineering (Hons)
(Chemical Engineering)

MAY 2012

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CERTIFICATION OF APPROVAL

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Approved by,

(Prof Khairun Azizi Bt. M. Azizli)

UNIVERSITI TEKNOLOGI PETRONAS

TRONOH, PERAK

MAY 2012

CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

(MUHAMMAD FIKRI BIN ISMAIL)

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ABSTRACT

The excess of phosphate (PO_4^{-3}) concentration released in water bodies could cause problem to the environment in the form of eutrophication. One of the methods of phosphate removal is adsorption. The aim of this project was to study the adsorption of phosphate using HCl treated and untreated steel slag.

HCl acid was used to treat the steel slag by bathing the slag with HCl acid for 24 hours. The treated and untreated steel slag were then used for batch adsorption studies which included the effect of agitation rate (30-150 rpm), temperature (25-90°C), initial phosphate concentration (100-300ppm) and contact time (30-120 min) on the phosphate uptake by the steel slag.

FESEM result showed a more porous surface and a reduction in Ca^{2+} ions after HCl treatment. The average particle size of the steel slag was 20 µm. HCl treated steel slag gave lower adsorption performance than the untreated steel slag. The highest phosphate uptake was achieved by untreated steel slag experiments were 65% (150rpm) and 87.13% (90°C). HCl treated steel slag gave only 34.77% and 74.55% phosphate uptake for the previous conditions mentioned.

Langmuir and Freundlich isotherms were found to be favorable for the adsorption process as the results displayed correlation coefficient of 0.998 for untreated slag with q_m value of 125 mg/g and n value of 0.875. Correlation coefficient value of the HCl treated steel slag was 0.999 with $q_{m\ value}$ of 37 mg/g and n value of 0.752. Both steel slags followed the pseudo second order kinetics with highest correlation coefficient achieved at 0.999 and 0.998 for untreated and treated slags respectively.

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CHAPTER 1: INTRODUCTION

1.1 Background Study

Phosphate is a type of macronutrient that is essential to the growth of aquatic plants in water bodies such as lakes, rivers and seas. However, water pollution by phosphate due to discharge of wastewaters to these natural water bodies can promote eutrophication, a condition that cause the excessive amount of algae blooming that lead to the depletion of dissolve oxygen thus suffocating other living organism that inhabit the water. Therefore, it is a necessity to treat the excessive phosphate by applying different treatment methods.

Adsorption is a physical treatment that has been widely used which is proven to have high adsorption efficiency and can be considered as economical (Fu *et al*, 2011) since most of the adsorbent can be obtain or modified from waste materials such as red mud (Huang *et al*, 2008), sludge (Smith *et al*, 2009), fly ash (Mishra *et al*, 2009) and steel slag (Liu *et al*, 2010).Steel slag is chosen to be the adsorbent material for phosphate adsorption in this project due its known high adsorption capabilities for heavy metal removal in wastewater (M. Ahmaruzzaman, 2011) and that the steel slag can be found in this country due to steel making industry in Malaysia. Table 1.1 show research works done using steel slag as absorbent for phosphate.

Researcher	Steel slag used	Parameter Tested
Yongjie Xue *et al* (2009)	Basic Oxygen Furnace slag treated by milling and acid	-Selective ion adsorption -pH
Guozhuo Gong *et al* (2009)	Blast furnace slag treated with hydrated lime	- Temperature - Water to Solid Ratio
Ensar Oguz (2004)	Blast furnace slag	-pH -Temperature -Agitation rate
Jibing Xiong *et a*l (2008)	Steel slag (Magnetic separation)	-Adsorbent dose -Temperature -Phosphate concentration

Table 1.1: Research works on adsorption of phosphate using steel slag

After consideration, the author finds that only Xue *et al* (2009) and Gong *et al* (2009) utilize the usage of treated steel slag as adsorbent material for phosphate removal. Due to the lack of extensive research work done for different parameters on treated steel slag , this research project will focus on the usage of HCl treated steel slag adsorption on phosphate by taking stirring rate, initial phosphate concentration, contact time and temperature on the effect of phosphate removal.

1.2 Problem Statement

Phosphorus is often present in water in the form of phosphate, orthophosphate and polyphosphate. It is naturally formed for the benefit of the water natural inhabitant; plants for growth fertilizing and helps to oxidize the glucose in animal body. An excess of phosphate presence in water is due to detergent from household area, wastewater from fertilizer plant and water containing fertilizer from agricultural area can cause a catastrophic condition called eutrophication. The sources of phosphate as mentioned before can cause a high concentration of phosphate in lake, river or even seas which will lead to overgrowth of aquatic plants that will decrease the total dissolved oxygen. This will disturb the balance in the ecosystem and pose as a threat to the fish and animals that inhabit the water as referred in Figure 1.1.

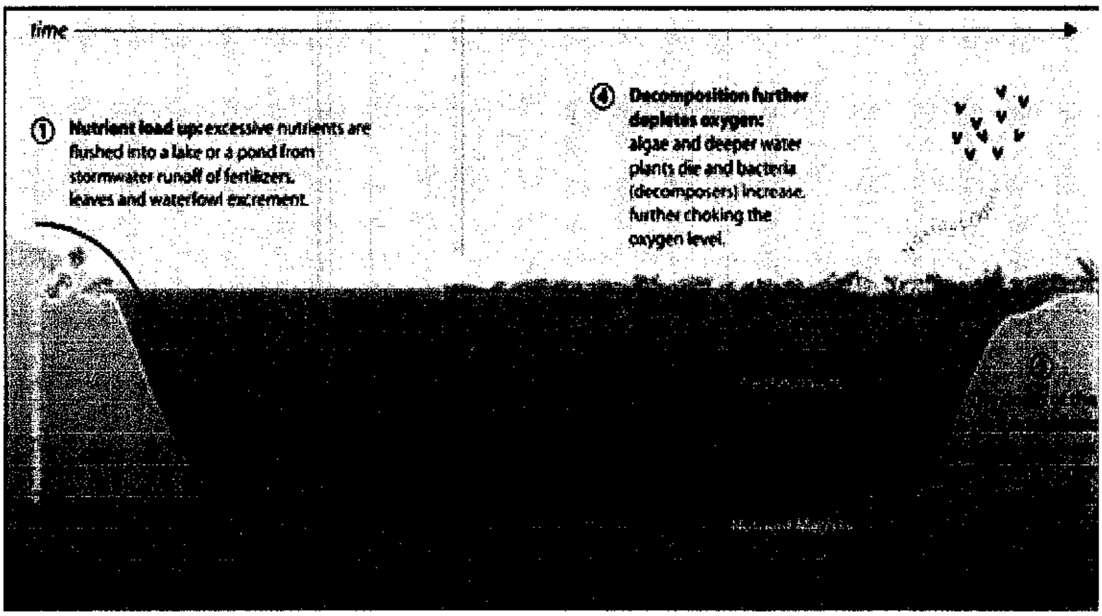


Figure 1.1: The eutrophication chronology and effects (Labarge, 2011)

In some cases the climax stage of algal blooming can release toxic chemical such as domoic acid to the aquatic environment (Cloern *et al* , 2010), that can cause death to fish, animal and even human. Phosphate concentration higher than 0.025 mg $^{1-}$ may stimulate the eutrophication (Mohammad, 2006). The current status of eutrophication of Lakes in Malaysia indicate that more than 60% of 90 lakes reviewed in the country is experiencing eutrophication (NAHRIM 2005, Zati *et al* 2007) Different lakes shows different symptom of eutrophication and non has yet shown the effect of algae bloom (NAHRIM, Zati *et al* 2008). However, eutrophication must be prevented at all cost as Malaysia is a developing country and surely the amount of phosphate channeled into the country water bodies will increase from time to time.

There are many methods of wastewater treatment to remove phosphate which are biological, physical and chemical (Oguz, 2004). One of the chemical treatments that have been studied is phosphate adsorption by acid treated steel slag. Although phosphate adsorption by untreated steel slag have been proven to be effective base on previous researches, it is interesting to study the effect of acid on enhancing the phosphate adsorption capacity and efficiency of steel slag. HCl treated steel slag is believed to have higher adsorption capacity than untreated steel slag due to the change of surface structure and chemical composition of the material (Yongjie Xue *et al* 2009). This means more phosphate can be adsorbed by acid treated steel slag compare to the same amount of untreated one. Nonetheless, there are many different parameters that need to be tested before this method of treatment can be commercialized.

Deeper understanding of parameter that affects the adsorption must be done in order to prove the effectiveness of acid treated steel slag. The project will be focusing on the effect of temperature and stirring rate since there is yet research done on HCl treated steel slag for both parameter as well as the effect of initial phosphate concentration. The use of material such as hydrated lime can be used to treat the steel slag (Guozhuo Gong *et al* 2009) to a certain extent but for this project hydrochloric (HCl) acid is selected for the treatment of the steel slag due to its laboratory availability and the pH can easily be change by dilution if required.

1.3 Objectives

The objectives for this project are:

i. To study the adsorption of phosphate on both untreated and HCl treated steel slag.
ii. To determine the characteristic of steel slag and the HCl treated steel slag before and after adsorption of phosphate.
iii. To study the parameters that can affect the efficiency of phosphate adsorption such as temperature, stirring rate and phosphate concentration.
iv. To study the adsorption kinetics and adsorption equilibrium of HCl steel slag adsorbent.

1.4 Scope of Study

The project scope of study focus on utilizing HCl treated steel slag as adsorbent material for adsorption of phosphate from aqueous solution. The adsorption capacity and the performance of the steel slag will be observed by analyzing the characteristic, equilibrium and kinetic aspect of the adsorption process. The project will gather and analyze information for both the adsorbent and the adsorbate material which steel slag and phosphate respectively. Previous work done is studied to come up with methodology for the HCl acid treatment of the steel slag, the adsorption studies and suitable characterization techniques. The methodology will then be used to carry the experiment and test for phosphate adsorption. The result of the experiment will then be analyzed to monitor the performance of the HCl treated steel slag on the adsorption of phosphate.

CHAPTER 2: LITERATURE REVIEW

2.1 Phosphate

2.1.1 Introduction

Phosphorus is an essential element that is needed by almost every living organism including human, animal and plant. It is an essential nutrient Phosphorus was discovered on 1669 in German by an alchemist named Henning Brand. Due to the highly reactive nature of the phosphorus, it is often found in the form of phosphate ions with molecular weight of 94.97 g/mol. One phosphorus atom that is bounded in tetrahedral form by four other oxygen atoms will form phosphate ion, a hypervalent molecules that carries three negative charges hence the formula (PO_4^{-3}). (FIPR, 2010)

Phosphates plays vital part in living organism as their ions can react with the atoms that can be found inside the organism to form various compounds that could perform different functions. In human, phosphates become the backbone for the structure of every DNA (deoxyribonucleic acid) and giving it the helix structural shape. Adenosine triphosphates (ATP) in human body stores energy absorbed from food and release the energy when the need arises. (FIPR, 2010)

Phosphate is a dietary requirement for human body. Daily recommended dosage is about 800mg/day although through balance diet, the amount of phosphate intake can increase from 1000mg/day to 2000mg/day but this depends on the type of food taken. Excessive phosphate intake however can cause health problem such as kidney damage and in some cases osteoporosis which is prone to happen as phosphate is one of the material that helps the strengthening of teeth and bone. (Lenntech, 2011)

Not all types of phosphates are water soluble in the normal atmospheric condition and room temperature but some of them are soluble such as cesium, sodium, potassium, ammonium and rubidium phosphate. The source of phosphate came from phosphate minerals in nature which needs to mine from phosphate ore mine and is an unrenewable source. The minerals will then be refined and purified to suit its purpose in many applications. (PFA, 2010)

Depending on the number of phosphorus atoms, phosphate can be characterized into different functional groups with various uses and application. The uses of phosphate are further expanded when it reacts with other common elements such as aluminum, calcium, sodium and potassium. These compounds sometimes can provide more than one uses to daily human lives as can be seen in Table 2.1:

Number of P Atoms	Formula	Names	Uses
1	PO_4^{-3}	Orthophosphates	Detergents, baking
2	$P_2O_7^{-4}$	Pyrophosphates	Water treatment, metal cleaning
3	$P_3O_{10}^{-5}$	Tripolyphosphates	Meat processing, dish detergent
>3	$P_nO_{(3n+1)}^{-(n+2)}$	Polyphosphates	Kaolin production, processed cheese

Table 2.1 : The different types of phosphates and its application (PFA, 2012)

2.2 Adsorption Theory

Adsorption is the process through which substance is accumulated at interface between two phases be it solid and liquid or solid and gas. It is a separation process where some materials (adsorbate) are concentrated from a bulk vapor or liquid phase onto a porous solid surface (adsorbent) which can be referred in the Figure 2.1.

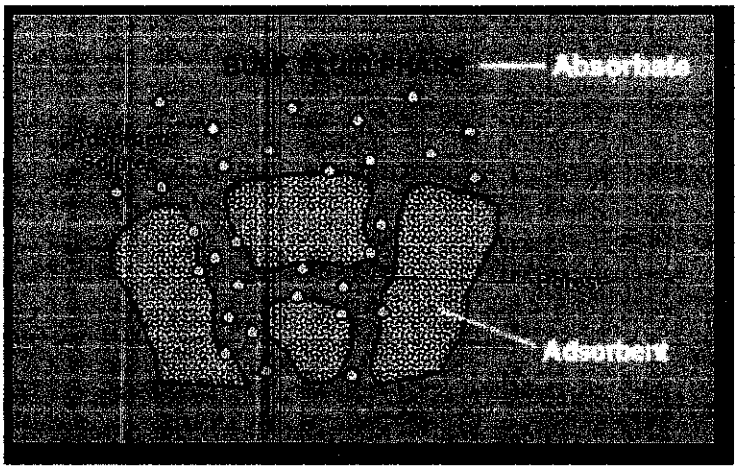


Figure 2.1: Adsorption Process Diagram

It is a different process from absorption as the adsorbate only diffuse on the surface of the adsorbent whereas adsorption will cause the substance to diffuse into the liquid or solid, forming a solution. (Kopecky F *et al*, 2007)

There are two types of adsorption namely physical adsorption and chemical adsorption. Physisorption or physical adsorption is where the adsorbate bonded with the surface of the adsorbent through Van der Waals force which is a weak intermolecular bond. Chemical adsorption which is also called chemisorptions will happen if the adsorbate forms a chemical bond with the adsorbent which is stronger bond than the physisorption. (Adamson, 1990)

2.3 Equilibrium Studies

Adsorption isotherms are vital in order to understand the interaction of adsorbate with the sorbent surface. Therefore, the Langmuir model and the Freundlich model will be used to understanding of the adsorption data that will be obtained. (Guozhuo Gong *et al*, 2009). The equation of Langmuir and Freundlich model can be referred in Equation 2.1 and Equation 2.2 respectively.

$$\frac{1}{Q_e} = \frac{1}{Q_{max} K_a C_e} + \frac{1}{Q_m}$$

Equation 2.1: Langmuir Model equation in linear form

$$log\, Q_e = \frac{1}{n} \lg C_e + \log K_f$$

Equation 2.2: Freundlich Model equation in linear form

where,

Q_e (mg g^{-1}) = the amount of solute adsorbed per gram of sorbent at equilibrium

C_e (mg L^{-1}) = the equilibrium concentration of solute in bulk of the solution

K_a (L mg^{-1}) = Langmuir equilibrium constant

Q_{max} (mg g^{-1}) = maximum uptake capacity

K_f (mg g^{-1}) & n (g L^{-1}) = Freundlich isotherm constant

2.4 Kinetic Studies

The pseudo-first-order model and pseudo-second-order model is used to describe the sorption kinetics of the project due to availability of its application in many cases (M. Ozacar *et al*, 2003). The equation pseudo-first-order model and pseudo-second-order model can be referred in Equation 2.3 and Equation 2.4 respectively.

$$\log(Q_e - Q_t) = log\, Q_e + k_1 t \qquad\qquad \frac{t}{Q_t} = \frac{1}{k_2 {Q_e}^2} + \frac{t}{Q_e}$$

Equation 2.3 : Pseudo-first-order in linear form

Equation 2.4:Pseudo-second-order in linear form

where,

Q_t (mg g^{-1}) = the amount ion adsorbed at time t (min^{-1})

Q_e (mg g^{1}) = the amount ion adsorbed at equilibrium

K_1 (min^{-1}) = Equilibrium rate constant (pseudo-first-order and pseudo- second-order respectively)
K_2 g(mg min^{-1})

2.5 Adsorption Parameters

According to the literature research papers, there are several operating parameters that will affect the adsorption process such as agitation rate, temperature, initial concentration of adsorbate and also particle size.

2.5.1 Agitation Rate

Agitation rate can be an important factor in adsorption process as it response to rate of external diffusion (Liu *et al*, 2009). Based on Liu (2009) work, the removal efficiency of lead ion onto steel slag adsorbent increase as the agitation rate increased from 30 to 150 rpm and kept constant at 96% removal rate at 150 rpm.

This is because as shaking rate increased, the diffusion coefficient of lead ion in the bulk liquid is also increased lead to the increase in mass transfer flux (Sheng, 2009). Another paperwork related is Ensar (2004) where the adsorption of phosphate using steel slag is done under the effect of agitation rate also shows that the same result and at agitation rate of 235 rpm, the removal efficiency even reach up to 99%.

2.5.2 Temperature

Another tested parameter as mentioned by Ensar (2004) is temperature which shows that phosphate adsorption increased with increasing temperature. This is because as the solution temperature increased the solution values of $FePO_4$, $AlPO_4$ and Ca $(PO4)_2$, it was suggested that metallic salts such as Al^{3+}, Fe^{3+} and Ca^{2+} precipitation will be less effective due to the electrostatic attraction between adsorbate and adsorbent which affected the phosphate removal from the aqueous solution (Xiong et al,2007). The result shows that removal of phosphate is mainly based on physical interaction and is not because of the mentioned metallic salt precipitation.

2.5.3 Initial Adsorbate Concentration

The initial concentration of adsorbate will also affect the overall adsorption process. For removal of lead ion through steel slag adsorption, as the concentration is increased from 10 mg L^{-1} to 150 mg L^{-1} and the result shows that at the highest lead concentration, the removal efficiency is 99% (Liu *et al*, 2009). This condition occurred because the higher the concentration, the higher the concentration curve that will lead to faster transfer of adsorbate from the liquid onto the surface of the solid adsorbent. Similar pattern of the results also gained by the work done by Ensar (2004) where the phosphate concentration was varied from 150 to 500 ppm at 60 g l^{-1}. The equilibrium concentration of phosphate will increase as the phosphate concentration increase with constant steel slag concentration.

2.5.4 Particle Size

Intra particle diffusion can be related with the particle size of the adsorbent. As the size of steel slag particle decrease from 25-18mm to 0.125-0.09mm, the removal efficiency of phosphate is increased from 46.5% to 96% (Liu et al, 2009). This is the indication that smaller particle sizes have more surface area for adsorption thus increasing the adsorption rate. The intra particle diffusion is the control step for adsorption rate which depends on the particle size of the adsorbent.

2.6 Steel slag as adsorbent material

Steel slag is the byproduct of steelmaking and steel refining processes. There are commonly three types of steel slag which are basic oxygen furnace (BOF) slag, electric arc furnace (EAF) slag and also ladle slag. Malaysia steel production is about 7.2 Million MT per annum (iCapital, 2005) and 10% of that amount is the steel slag waste produced in Malaysia (Teoh, 2008). Composition of steel slag produced varies due to different source of material, different stage of steel making process and efficiency of the furnace. Table 2.2 given is the approximate chemical composition of steel slag:

Chemical Composition	**Percentage (%)**
SiO_2	39.56
Al_2O_3	10.82
Fe_2O_3	0.33
MgO	6.79
CaO	37.68
SO_3	0.33
Others	4.49

Table 2.2: Chemical Composition of Steel Slag (Oguz, 2005)

In order to utilize the use of HCl treated steel slag as adsorbent, review on the previous works is done for better understanding of the treated steel slag adsorption capabilities in Table 2.3:

Researcher & Title	Description	Result
Yongjie Xue *et al* (2009) Characteristics and mechanisms of phosphate adsorption onto basic oxygen furnace slag	• Focus on the usage of untreated BOF steel slag and two different types of modified steel slag which are BTM (BOF slag treated by milling) and BTA (BOF slag treated by acid) • Comparing the result of the three different types of steel slag with different parameters such as initial phosphate concentration, pH • Selective ion adsorption and desorption study was also done.	• The phosphate adsorption on all three adsorbents tends to decrease with the increase of pH.value • The maximum adsorption capacities gained is highest for BTM followed by BTA and untreated steel slag by increasing initial phosphate concentration. • Phosphate ions selectivity was that 44-450 times to that of different anions and the desorbability is about 0.24-1.25% shows that it is difficult to be desorbed.
Guozhuo Gong *et al* (2009) Preparation of new sorbent with hydrated lime and blast furnace slag for phosphorus removal for aqueous solution	• Focus on the removal of dissolvable inorganic phosphate by using hydrated lime (HL) treated blast furnace slag BFS. • Hydration time of BFS, the weight ratio of BFS/HL, temperature of the slurry and ratio of water to solid are the parameters used to prepare the sorbent.	• Treatment of HL on BFS can increase its porosity and thus increasing the P adsorption capacity. • The weight ratio of BFS/HL is the most important variable to be considered during the preparation of HL treated BFS.
Mahamudur Islam *et al* (2011) Thermal activation of basic oxygen furnace slag and evaluation of its fluoride removal efficiency	• Focus on adsorption characteristic of fluoride adsorption onto the thermally activated basic oxygen furnace steel slag. • Parameters tested are contact time, temperature and competitive ion to be adsorb by the thermal activated BOF slag	• Thermal activated slags are more porous and have bigger surface area than thermally untreated one. • Fluoride removal is higher at higher reaction temperature, longer contact time. • At higher concentration, other anions such as phosphate, carbonate and chloride can impede the adsorption of fluoride

Table 2. 3: Research Work On Treated Steel Slag

Besides treated steel slag, there are many other research works that utilize different kinds of steel slag to remove different materials such as heavy metals, arsenic, and fluoride. It is also vital to review their works as additional information for comprehension of the adsorption mechanism of steel slag and the details are mentioned in Table 2.4:

Researcher & Title	Description	Result
Chamteut *et al* (2012) Removal characteristics of As(III) and As(II) by steel making slag	• Focus on promote the use of steel making slag as low cost adsorbent for arsenic (As) removal • Possibility of secondary contamination due arsenic leaching after adsorption • Parameters tested are initial concentration of As and the initial pH of the aqueous solution	• The removal efficiency of 95% to 100% can be achieve at initial pH of 2 • Small amount of As leaching only occur at pH value of 0.8 and 13.8. Low possibility of secondary contamination • Steel slag is appropriate adsorbent for As removal.
Sheng-Yu Liu *et al* (2009) Adsorption intrinsic kinetics and isotherms of lead ions on steel slag	• Focus on the adsorption of lead ions by steel slag. • Intra-particle diffusion and external diffusion was observed by altering various experimental parameters such size of the steel slag, and shaking rate.	• The removal efficiency increase with decreasing steel slag particle size from 25 -18 mm to 0.125-0.09 mm, and increasing shaking rate from 30 rpm to 240 rpm. • Intra-particle diffusion of lead ions was the controlling step when the size of steel slag was larger than 120 mesh. • External diffusion was promoted when initial concentration of lead ion was less than 150 mg/L and shaking rate lower than 150 rpm.

Table 2. 4: Research Work on Steel Slag on Various Material

CHAPTER 3: METHODOLOGY

3.1 Introduction

In this chapter, the methods and steps involved in utilizing both untreated steel slag and HCl for phosphate adsorption. Figure 3.1 showed the overall process taken to achieve the objectives of this project.

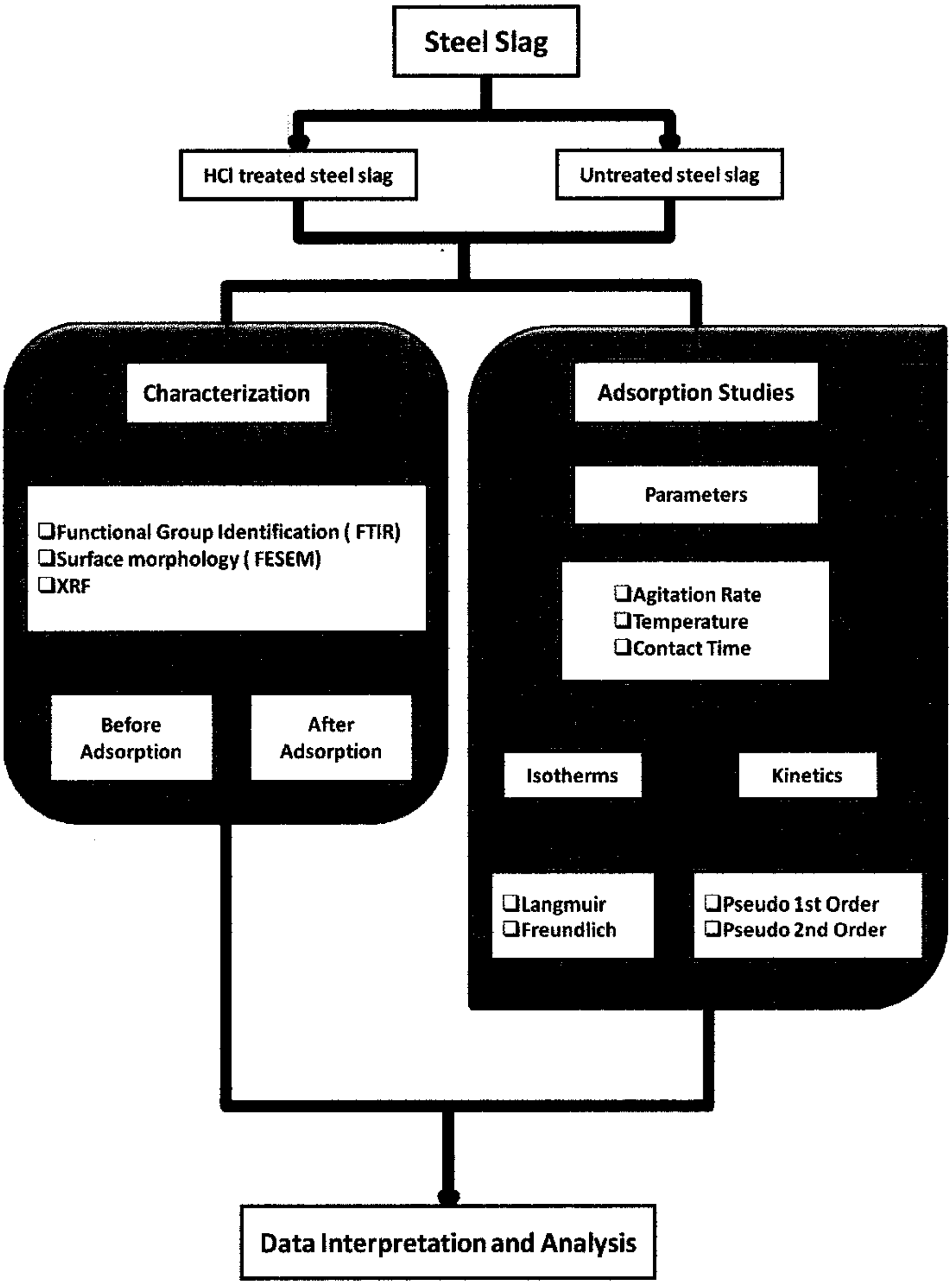


Figure 3.1: Project Work Diagram

3.2 Material Preparation

3.2.1 Material preparation: Phosphate solution

The potassium dihydrogen phosphate (KH_2PO_4) was dissolved to the desired concentration needed for the adsorption studies experiments at 100 ppm, 200 ppm and 300 ppm, each using volumetric flask and deionized water. The volumetric flasks were kept airtight to avoid exposure to air.

3.2.2 Treatment of Steel Slag with HCl

100 g of steel slag was weighted using the digital weighing scale and placed in a 500ml beaker. The beaker was then filled with 0.1 HCl acid and stirred using glass rod to ensure all portion of the slag to be contacted with the acid. The beaker was sealed using aluminum foiled and kept for 24 hours in a fume hood to avoid the odor from the reaction to spread in the laboratory. After the 24 hours period, the HCl drenched steel slag was washed with deionized water for 5 times to remove any residual acid and was filtered for drying in oven for 24 hours. 100g of steel slag was used because during the washing and the filtration after the acid treatment, some portion of the steel slag was removed due to small size of the particle. The dried HCl treated steel slag will then be taken and placed in a airtight container before being used in the experiments.

3.3 Characterization

3.3.1 Surface morphology (FESEM/ EDX)

FESEM stands for Field Emission Scanning Electron Microscopy and EDX stands for Energy-Dispersive X-Ray Spectrometry. The FESEM/EDX helped the project characterization of the steel slag by providing the particle morphology of the slags with high resolution image of nano-sized particles as well as elemental analysis for particles. The model used for this purpose is the Carl-Zeiss Supra 55 VP (Figure 3.2) which enables the examination of non-conducting specimens without time consuming preparation (Zeiss, 2012).

3.3.2 Fourier Transform Infrared (FTIR)

Fourier Transform Infra Red (FTIR) is a method used to determine the functional groups of a compound. The FTIR can also determine the chemical structure of both inorganic and organic compound in any solid, liquid and gas form. For this project, the FTIR was used to identify the steel slag functional groups for two different samples which are untreated steel slag and HCl treated steel slag, before and after the adsorption of phosphate takes place. The equipment used for this characterization studies was the Perkin Elmer (1600 series) spectrometer as shown in Figure 3.3.

3.3.3 X-Ray Fluorescence (XRF)

The XRF method is a method used to identify the elemental composition of a compound. This method is widely used due to stability, ease of use, the non-destructive nature of the process to the sample tested and the result can be obtained in a short time. For this project, the steel slag sample was sent for XRF analysis in USM due to the unavailability of the equipment during the period of the project.

3.4 Adsorption Studies

The adsorption studies were performed to see the performance of both untreated an HCl treated steel slag in phosphate adsorption. Different parameters were tested and set to see its effect of manipulating these parameters on phosphate adsorption using steel slag. There were a total of four experiments that were done for the adsorption studies purpose with HCl treated steel slag and then all four experiments were repeated with untreated steel slag.

3.4.1 Effect of temperature on phosphate adsorption:

A 1g sample of HCl treated steel slag was added to a 500 ml beaker which contain 150 ml of KH_2PO_4 solution ($P0_4^{-3}$ = 200mg L^{-1}). Five of the sample solution was prepared for different temperature test. Each sample was then heated using water bath shaker to 45°C, 60°C, 75°C and 90°C for 60 minutes at 60 rpm. One of the samples was kept at room temperature 25°C for control variable. Each samples were filtered after adsorption was done with filter paper and adsorption of phosphate was analyzed from the collected adsorbate after the adsorption process took place by using Hach Method 8190 utilizing Hach DR 5000 UV-Vis Spectrophotometer and DR 200 (see APPENDIX section).

3.4.2 Effect of stirring rate on phosphate adsorption:

A 1g sample of HCl treated steel slag was added to a 500 ml beaker which contain 150 ml of KH_2PO_4 solution ($P0_4^{-3}$=100mg L^{-1}). Five of the sample solution was prepared for different agitation rate test. The beaker sample was then put on the mechanical stirrer of jar test equipment and the stirring rate was set to 30, 60, 90, 120 & 150 rpm, with one stirring rate setting for one sample. Each sample was filtered after adsorption was done with filter paper to collect the reacted adsorbate and adsorbent. Hach Method 8190 mentioned in experiments 3.4.1 was then followed to get the value of phosphate concentration after adsorption took place.

3.4.3 Effect of phosphate concentration on phosphate adsorption:

150 ml of KH_2PO_4 solution at different concentration, each containing 100 mg L^{-1}, 200mg L^{-1} and 300 mg L^{-1} of phosphate ion ($P0_4^{-3}$) was prepared before the experiment. 1g of sample of HCl treated steel slag was added to each sample and the mechanical stirrer of jar test equipment was used to stir the samples for 60 minutes at 60 rpm. Each sample was filtered after adsorption was done with filter paper to collect the reacted adsorbate and adsorbent. Each sample was filtered after adsorption was done with filter paper to collect the reacted adsorbate and adsorbent. Hach Method 8190 mentioned in experiments 3.4.1 was then followed to get the value of phosphate concentration after adsorption took place.

3.4.4 Effect of contact time on phosphate adsorption:

150 ml of KH_2PO_4 solution at 200 mg $L^{-1}$of phosphate ion ($P0_4^{-3}$) was prepared in 5 different 500ml beakers. 1g of sample of HCl treated steel slag was added to each sample and the mechanical stirrer of the jar test equipment was used to stir each 5 samples in the beaker for 30, 60, 90 and 120 minutes at 60 rpm. The experiment was repeated with different concentration of 100 mg L^{-1} and 300 mg L^{-1}. Each sample was filtered after adsorption was done with filter paper to collect the reacted adsorbate and adsorbent. Hach Method 8190 mentioned in experiments 3.4.1 was then followed to get the value of phosphate concentration after adsorption took place.

CHAPTER 4: RESULT AND DISCUSSION

In this chapter, the result of the project work will be presented and discussed accordingly. The result includes the characterization studies of the steel slag (see Figure 4.1) and the HCl treated steel slag adsorbent and the batch adsorption studies which include different parameters can affect the phosphate adsorption. The explanation on the equilibrium and the kinetic studies will also be revealed in this chapter. From the results, the difference in performance of the untreated and the HCl treated steel slag can be observed for further understanding and as a reference for any future project that will utilize the materials as adsorbent materials.

Figure 4.1: Ground Granulated Blast Furnace Slag (GGBS)

4.1 Characterization Results

4.1.2 FESEM Results

Four samples of steel slag were sent for 3D imaging using the FESEM in order to see the difference between untreated and HCl treated steel slag:

4.1.1.1 Untreated Steel Slag

Figure 4.2 and Figure 4.3 had shown the original form of the steel slag without any treatment. By applying 5000 times magnification (Figure 4.2), the result showed the coarse surface area of the steel slag and the 500 times magnification (Figure 4.3) showed the steel slag in the form of small particles in group.

4.1.1.2 HCl Treated Steel Slag

After the acid treatment with HCl, there were several changes that can be observed from the steel slag surface porosity. Comparing the Figure 4.2 and Figure 4.4 which were both magnified 5000 times, it showed that Figure 4.4 which was the HCl treated steel slag exhibit increased in porosity. Same goes to the 500 times magnification image (Figure 4.3 and Figure 4.5) showed that increase of porosity on the particles of the HCl treated steel slag. This condition was expected and the increase in porosity was necessary for increasing the phosphate adsorption capability of the steel slag (Gong et al and Xue et al, 2009).

Figure 4.2: 5000X Magnification

Figure 4.3: 500X Magnification

Figure 4.4: 5000X Magnification

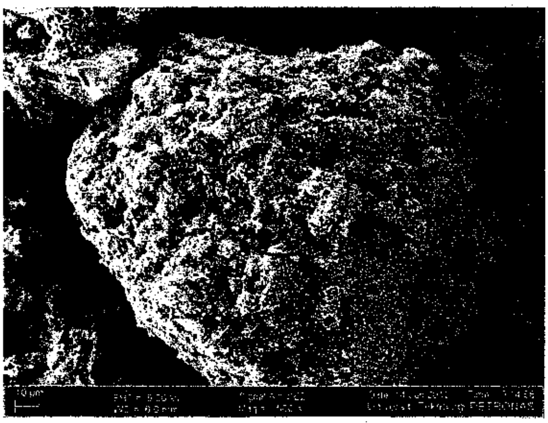


Figure Figure 4.5: 500X Magnification

4.1.1.3 Untreated Steel Slag and HCl treated Steel Slag after experiments

Figure 4.6, 4.7, 4.8 and 4.9 showed that the effect of phosphate adsorption onto steel slag both treated and untreated cannot be seen by the FESEM. However, the adsorption effect can be seen by using the EDX which identified the components in the adsorbents for untreated steel slag and HCl treated steel slag before and after the experiments had been done.

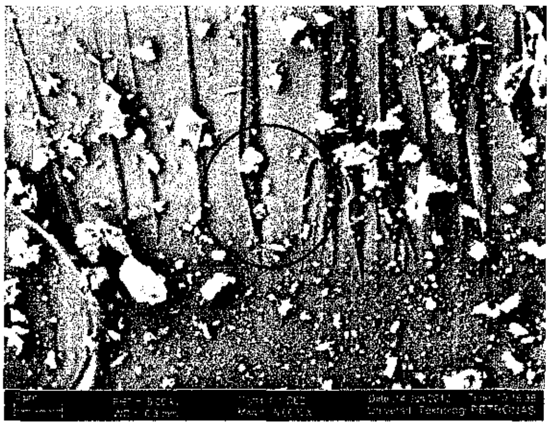


Figure 4.6: 5000X Magnification (Steel Slag)


Figure 4.7: 500X Magnification (Steel Slag)

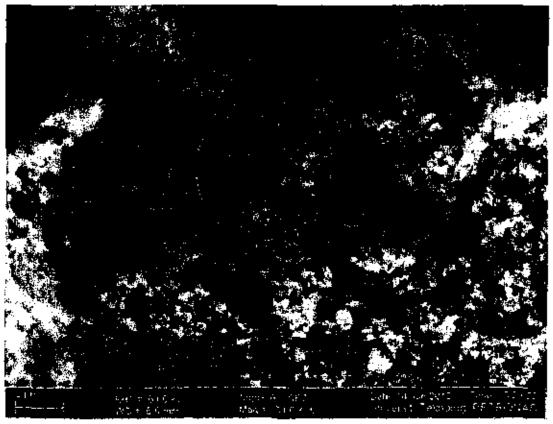


Figure 4.8 5000X Magnification (HCl Treated Steel Slag)

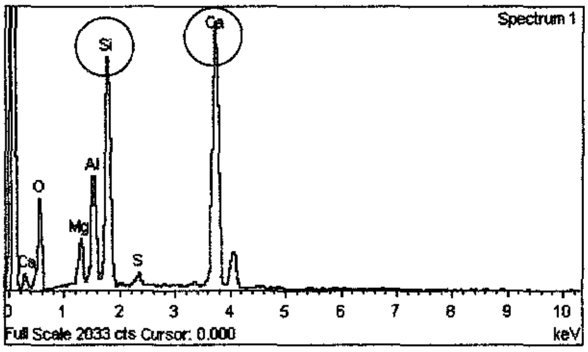

Figure 4.9: 500X Magnification (HCl Treated Steel Slag)

4.1.2EDX Results

The four samples sent for FESEM also undergone EDX analysis for the determination of key components within the adsorbent materials. Note that this method only identifies the major elements of the adsorbent materials.

4.1.2.1 Untreated Steel Slag

From Table 4.1 and Figure 4.10, the highest concentration of element in the steel slag is calcium (Ca) in the form of Wollastonite ($CaSiO_3$) followed by silicon (Si) in the form of silicon dioxide (SiO_2), aluminum (Al) in the form of aluminum oxide (Al_2O_3), magnesium (Mg) in the form of magnesium oxide (MgO) and the least concentration is sulfur (S) in the form of iron disulfide (FeS_2).



Elements Detected	Existing Form	Weight %
Mg	MgO	5.93
Al	Al_2O_3	12.62
Si	SiO2	27.84
S	FeS2	1.78
Ca	Wollastonite	51.83
	TOTAL	100

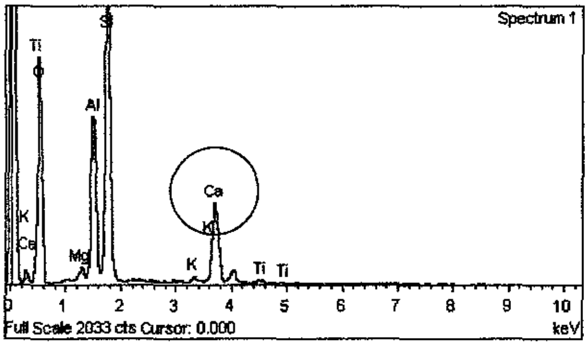
Figure 4.10 & Table 4.1 : EDX spectrum & composition table of untreated steel slag

4.1.3.2 HCl Treated Steel Slag

Based on table 4.2 and Figure 4.11, it showed that after the treatment with HCl acid, the percentage amount of Ca was reduced significantly. This is because of the following chemical reaction,

$$CaCO_3(s) + 2\ HCl\ (aq) \longrightarrow CaCl_2\ (aq) + CO_2\ (g) + H_2O(l)$$

where the $CaCl_2$, a soluble salt which was removed with remaining water after the acid pretreatment. Presents of titanium and absence of sulfur was due to the fact that the steel slag contains different kinds of elements in different part of the sample.

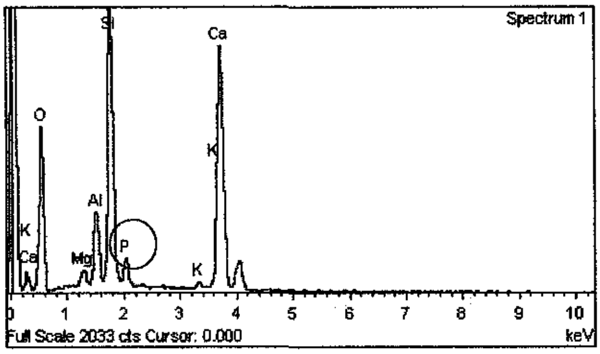


Elements Detected	Existing Form	Weight %
C	$CaCO_3$	30.6
Mg	MgO	0.94
Si	SiO2	38.26
Ca	Wollastonite	11.74
Ti	Ti	1.25
Al	Al_2O_3	17.21
	TOTAL	100

Figure 4.11 & Table 4.2: EDX spectrum & composition table of HCl treated steel slag

4.1.2.3 Untreated Steel Slag (after adsorption experiment)

The result after the adsorption experiment in Table 4.3 and Figure 4.12 showed that there was indeed an adsorption of phosphate onto the steel slag even though only with small percentage. This was assumed to be cause by the contact time of adsorption process. For the actual experiment, the contact time was increased from 30 to 60 minutes so that more phosphorus/phosphate can be adsorbed.



Elements Detected	Existing Form	Weight %
P	GaP	4.59
Mg	MgO	2.32
Si	SiO2	34.57
Ca	Wollastonite	48.55
K	MAD-10 Feldspar	0.93
Al	Al_2O_3	9.04
	TOTAL	100

Figure 4.12 & Table 4.3: EDX spectrum & composition table of untreated steel slag after experiment

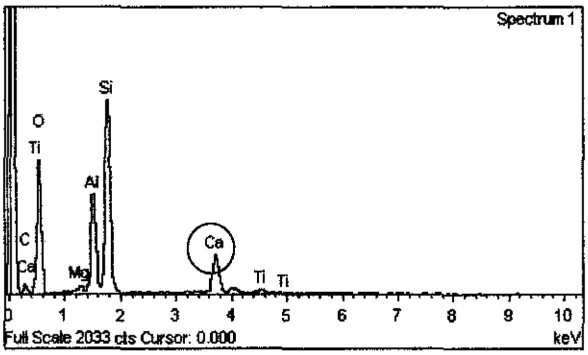
4.1.2.4 HCl treated Steel Slag (after adsorption experiment)

The EDX test for HCl treated Steel Slag in Figure 4.13 and table 4.4 was expected to have higher concentration of phosphorus/phosphate. No traces of phosphorus /phosphates were found however. This lead to assumption that:

- The treated steel slag sample was contaminated or spoilt due to potential human error such as mishandling of the material.

- The treated steel slag with its reduced calcium concentration have less potential as an adsorbent material such as mentioned by Lu et al (2007). However, this matter can be compared by other research articles in the Table 2.2 of Chapter 2 of this report which suggest that the acid treatment on steel slag able to enhance the adsorption of phosphate.

Other than that, the trace of potassium in the form MAD-10 Feldspar was also found because of the different part of the steel slag contained different materials. Steel slag was a type of waste from steelmaking plant which the elemental property and composition was not determined and content many kinds of elements.



Elements Detected	Existing Form	Weight %
P	GaP	4.59
Mg	MgO	2.32
Si	SiO2	34.57
Ca	Wollastonite	48.55
K	MAD-10 Feldspar	0.93
Al	Al_2O_3	9.04
	TOTAL	100

Figure 4.13 & Table 4.4 : EDX spectrum & composition table of HCl treated steel slag after experiment

4.1.3 Particle Size Analysis

The Malvern Mastersizer 2000 was used to determine the particle size of the steel slag. Particle size can affect the performance of an adsorbent material as smaller the particle size the higher the removal efficiency of the adsorbate which mentioned by Liu et *al* (2009). From Figure 4.14, it showed that the particle size of the steel slag used in the experiment range from 20 μm to 22 μm where the volume percent was highest with the average of 5.76 %.

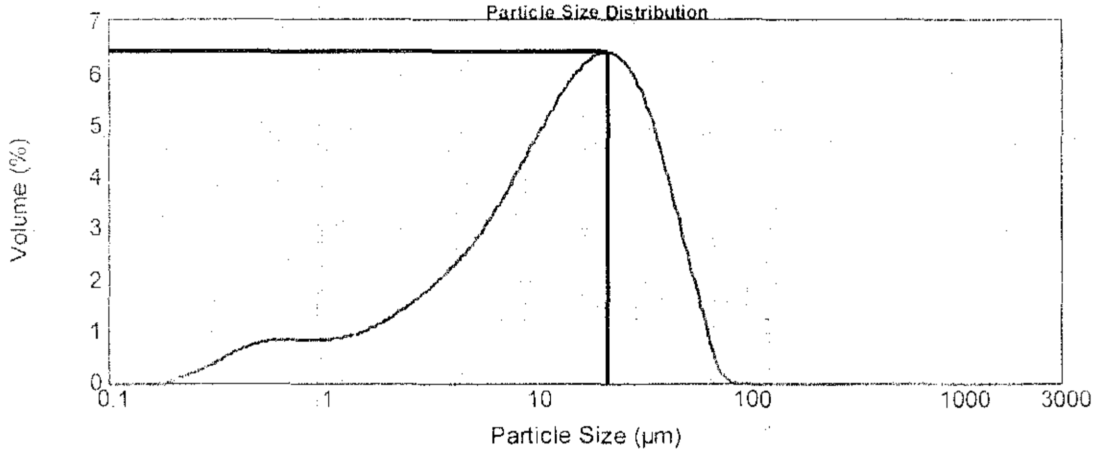


Figure 4.14: Particle Size Distribution

4.1.4 FTIR Results

Fourier Transform Infra Red (FTIR) is a method used to determine the functional groups of a compound. For this project, the FTIR was used to identify the steel slag functional groups for two different samples which are untreated steel slag and HCl treated steel slag, before (Figure 4.15 & 4.16) and after (Figure 4.17 & 4.18) the adsorption of phosphate takes place.

4.1.4.1 Before Adsorption

Comparison was made between the functional groups of both untreated (Figure 4.15 & Table 4.5) and (Figure 4.16 & Table 4.6) HCl treated steel slag before the adsorption took place showed that the amount of O-H bond (3200-3600 cm-1) was increased after the treatment with HCl acid. This was possibly due to the reaction of $CaCO_3$ with HCl as mentioned previously which promotes the formation of O-H bonds from formation of H_2O.

Since the HCl treated steel slag was only dried at only room temperature for 24 hours, there were chances that the residual water moisture from the pretreatment process to be attached to the slag particles, causing the detection of O-H bonds in the FTIR spectra. Besides that, there was a possibility that the O-H bonds were detected due to formation of hydrated crystal for any of the inorganic materials on the steel slag.

Other significant change was that the HCl treated steel slag contains higher amount of -C=C- bonds (1680-1640) than the untreated ones. Steel slag contains many different elements due to the nature of the steel slag production which came from the waste of steel making industry at different levels of a steel making process. Therefore, it is possible to say that the amount -C=C- bonds increased due to unforeseen chemical reaction between the carbons in the adsorbent material during the HCl acid treatment.

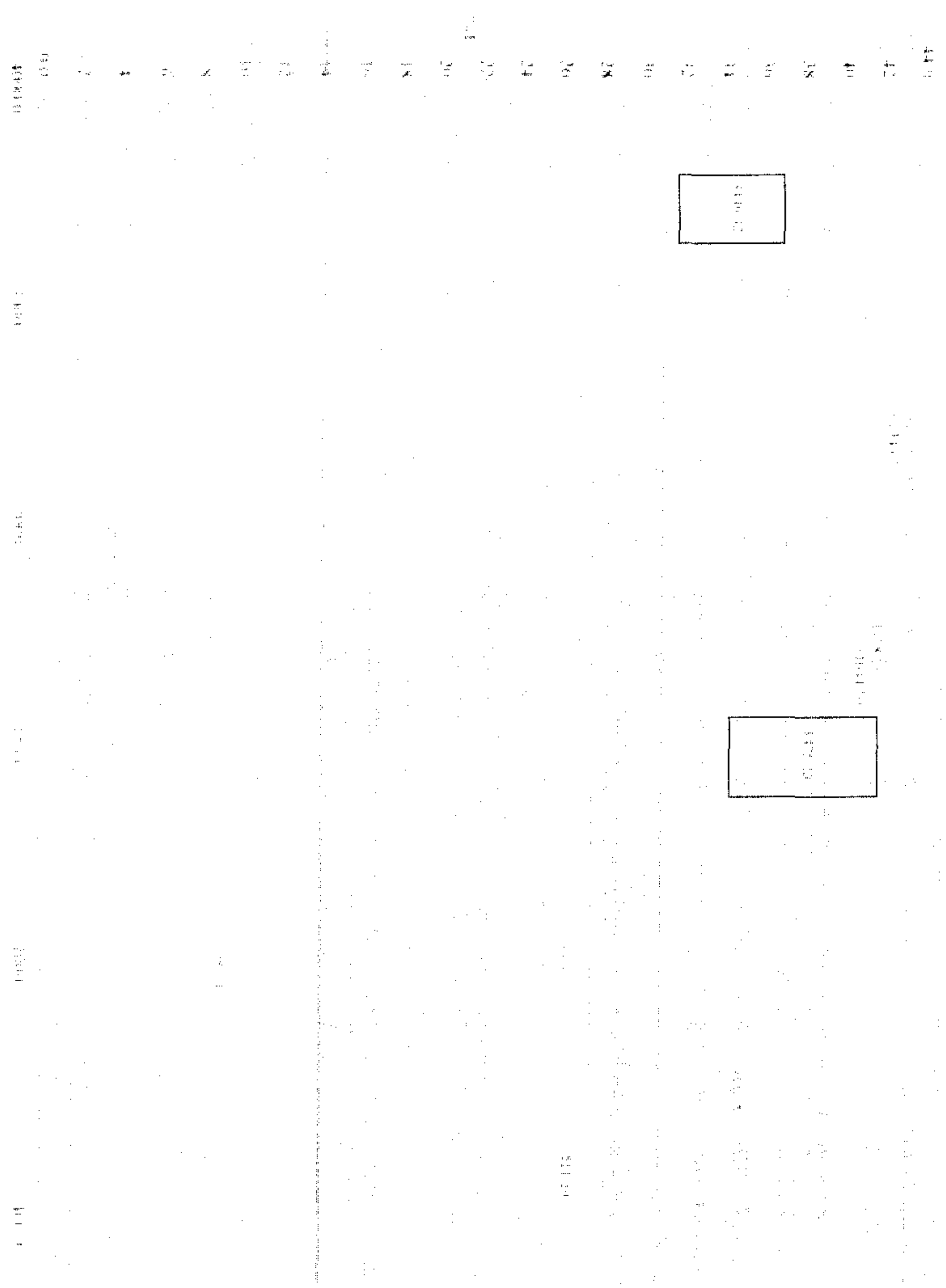


Figure 4.15: Untreated Steel Slag Spectra Before Adsorption

Functional Groups	CharacteristicAbsorptions (cm-1)
Alcohol (O-H)	3200-3600
Unsaturated esters (C=O)	1730-1715
Alkenes (-C=C-)	1680-1640
Aromatics (C-C)	1500-4100
Alkenes (=C-H)	1000-650
Alkyl Halides (C-Br)	750-500

Table 4.5: Functional groups of Untreated Steel Slag Before Adsorption

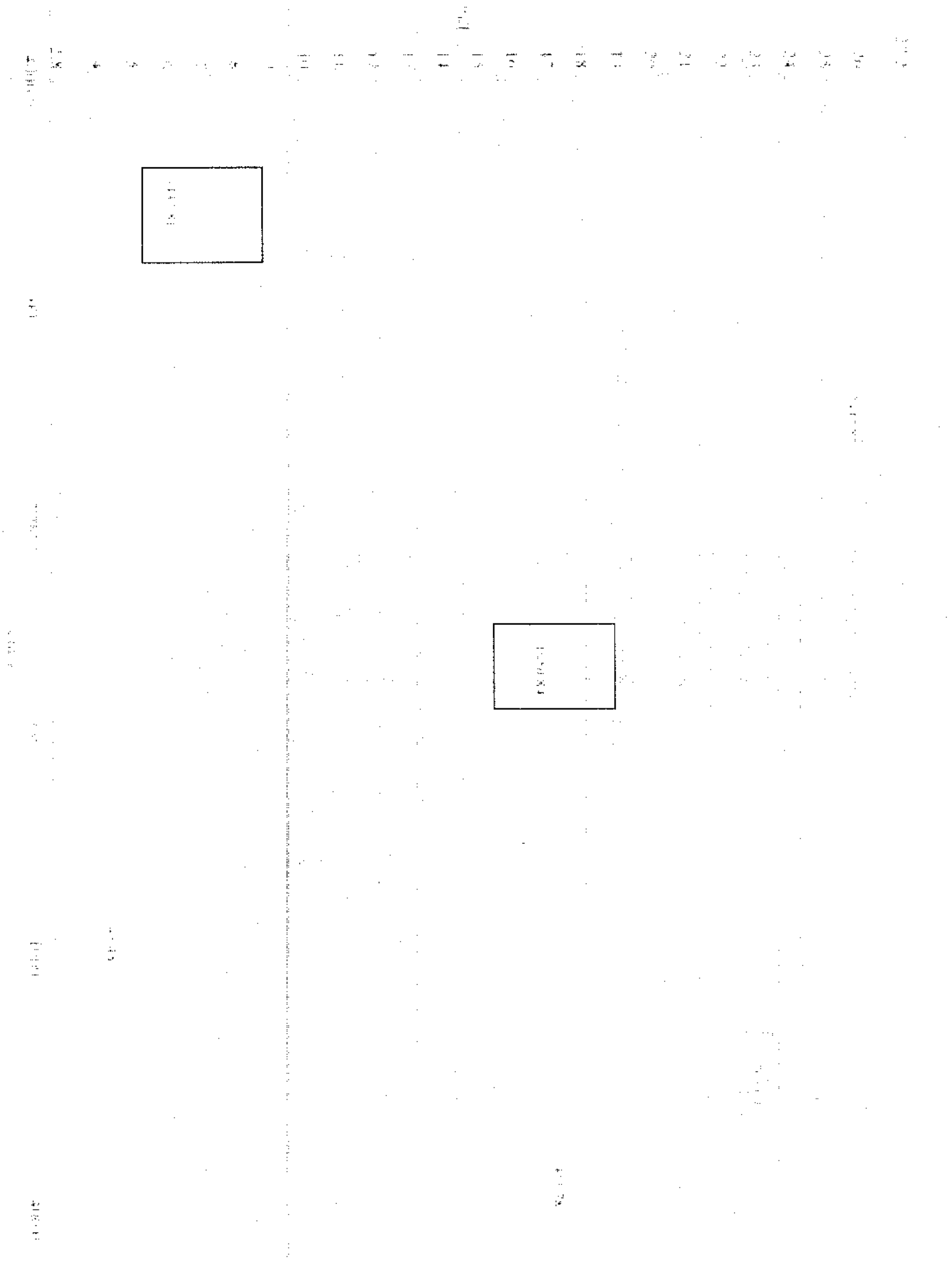


Figure 4.16: HCl Treated Steel Slag Spectra Before Adsorption

Functional Groups	CharacteristicAbsorptions (cm-1)
Alcohol (O-H)	3200-3600
Alkenes (-C=C-)	1680-1640
Aliphatic Amines (C-N)	1250-1020
Amines (N-H)	910-665
Alkyl Halides (C-I)	~500

Table 4.6 : Functional groups of HCl treated Steel Slag Before Adsorption

4.1.4.2 After Adsorption Experiment

Based on the results gathered (Figure 4.17, Table 4.7, Figure 4.18 and Table 4.8), the FTIR analysis did not show any significant change for other compounds within both of the adsorbent materials after adsorption experiment. However, the peak range from 1000 to 900 cm-1 showed an increment after the adsorption experiment and the spectra showed the value was seen closing to the range of the phosphines bond (P-H) 1090-810 cm-1.This could be caused by the adsorption of phosphate onto the both treated and untreated steel slag although the effect on the functional groups is harder to see due to some of the functional groups share the same adsorption characteristic. Further studies should be done on the formation of these phosphines bond and how it connected to the reaction of phosphate ion and elements within the steel slags.

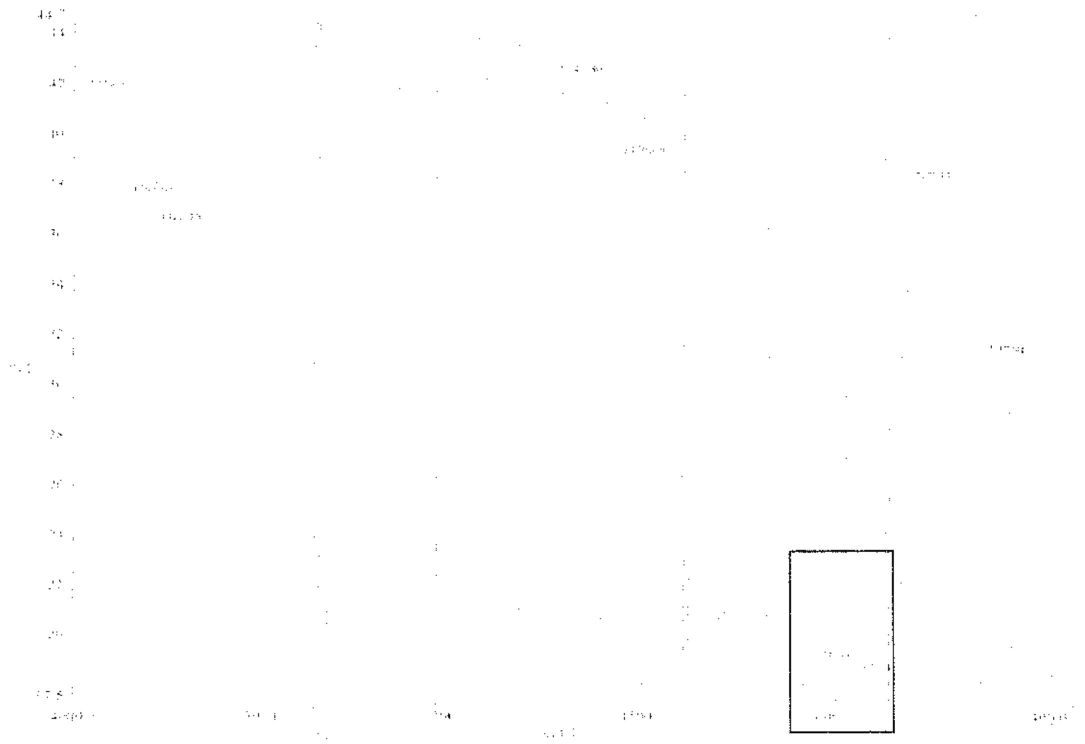


Figure 4.17: Untreated Steel Slag Spectra After Adsorption

Functional Groups	Characteristic Absorptions (cm-1)
Alcohol (O-H)	3200-3600
Alkenes (-C=C-)	1680-1640
Amines (N-H)	910-665
Alkynes	700-610
Phosphines (P-H bend)	1090-810

Table 4.7 : Functional groups of Untreated Steel Slag After Adsorption

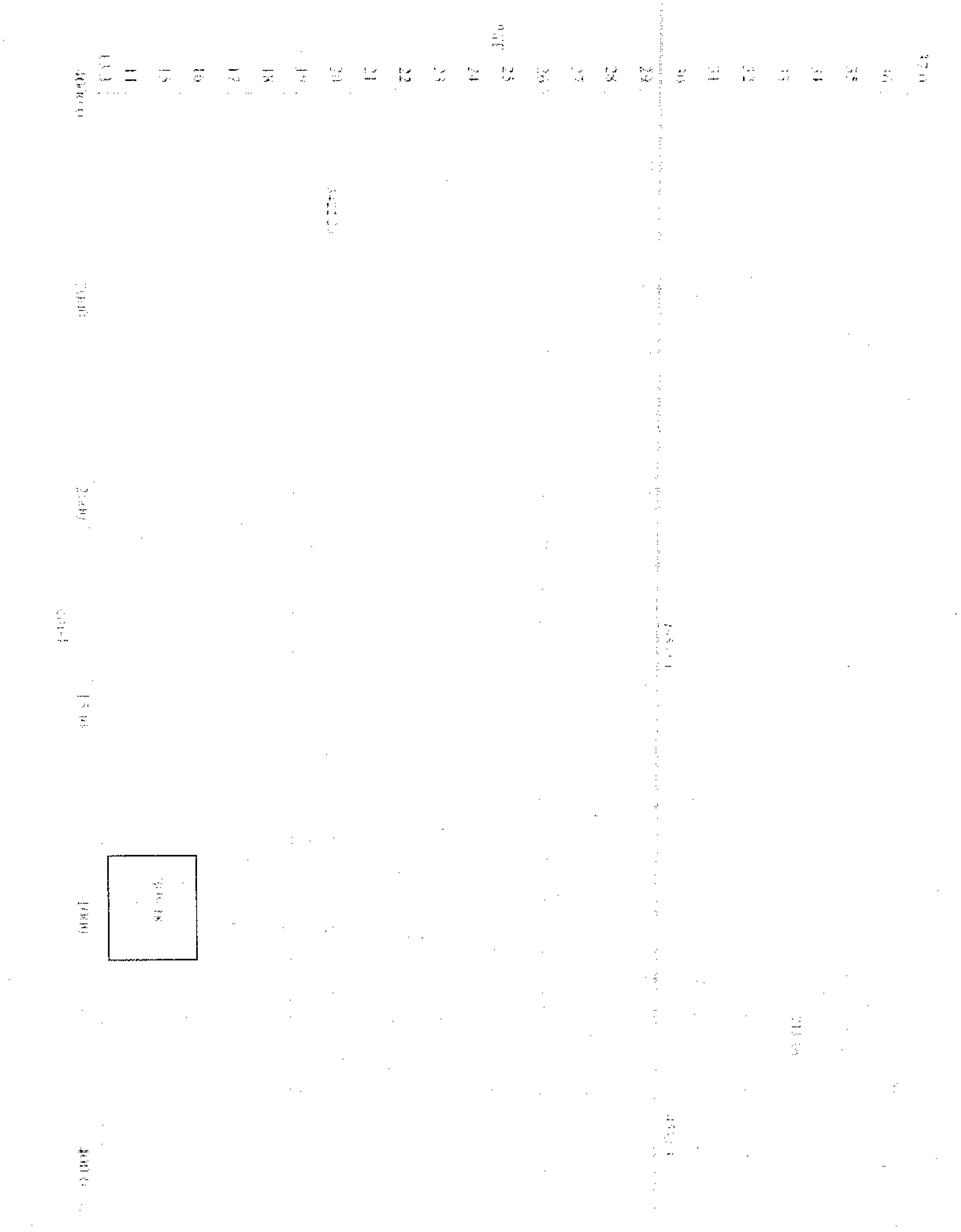


Figure 4.18: HCl Treated Steel Slag Spectra After Adsorption

Functional Groups	Characteristic Absorptions (cm-1)
Alcohol (O-H)	3200-3600
Alkenes (-C=C-)	1680-1640
Amines (N-H)	910-665
Alkynes	700-610
Phosphines (P-H bend)	1090-810
Alkyl Halides (C-I)	~500

Table 4.8: Functional groups of Untreated Steel Slag After Adsorption

4.1.5 XRF Results

In order to identify the composition of the untreated steel slag, the XRF analysis was done. The XRF analysis results can be seen in Table 4.18 along with results from other research work for comparison purposes.

Chemical Composition	Percentage (%) (XRF)	Percentage (%) (Oguz, 2005)	Percentage (%) (Lu et al, 2008)	Percentage (%) (Xue et al, 2009)
MgO	6.38	6.79	3.14	7.3
Al_2O_3	14.50	10.82	8.46	6.8
SiO_2	36.19	39.56	36.11	13.7
CaO	39.21	37.68	36.23	45.4
Fe_2O_3	0.27	0.33	0.63	17.8
Others	3.45	4.82	15.43	9

Table 4.8 XRF Results

Based on the results, the two main components of steel slag were silicone oxide (SiO_2) and calcium oxide (CaO) as both of the materials were highest in content even when compared to other research papers results. The magnesium oxide (MgO) and aluminum oxide (Al_2O_3) percentages also showed consistency with other results gathered. Iron (III) Oxide (Fe_2O_3) showed only in small percentage throughout the comparison but was higher in Xue results. The other elements were not shown as individual data due to variety of different elements with different of percentage amount.

The elements listed in Table 4.8 showed that although steel slag composition may vary due to different sources and stage of steelmaking process, the amount main composition was still the almost the same. This condition allowed the result gathered done in this project to be more comparable to other project works done although it was also depended on the parameters tested and the methodology done throughout the project.

Unfortunately, due to certain constraints, the HCl treated steel slag composition could not be obtained and the effect of HCl acid treatment on the steel slag could not be seen or compared to the untreated steel slag. However, the EDX in chapter 4.13 results did show some changes in composition before and after the acid treatment so the observation of the change in composition of the slag was able to be done.

4.2 Adsorption Studies

4.2.1 Effect of Agitation Rate

The effect of agitation rate on phosphate adsorption was studied on both steel slag and HCl treated steel slag with five different agitation rates which are 30, 60, 90, 120 and 150 rpm. The increasing agitation rates were used from the lowest to the highest point of which the mechanical stirrer can handle. The experiments were done at a constant 25°C with 150 mL of 200 ppm phosphate solution for 60 minutes using the mechanical stirrer from the jar test equipment.

The pH was set to 7 for neutral adsorption process environment and the amount of adsorbent used was 1g. These values were set to constant so that they will not affect the adsorption rate in any manner and the adsorption of phosphate will only be affected by the increasing agitation rate. Figure 4.19 shows the graph of phosphate removal versus agitation rate.

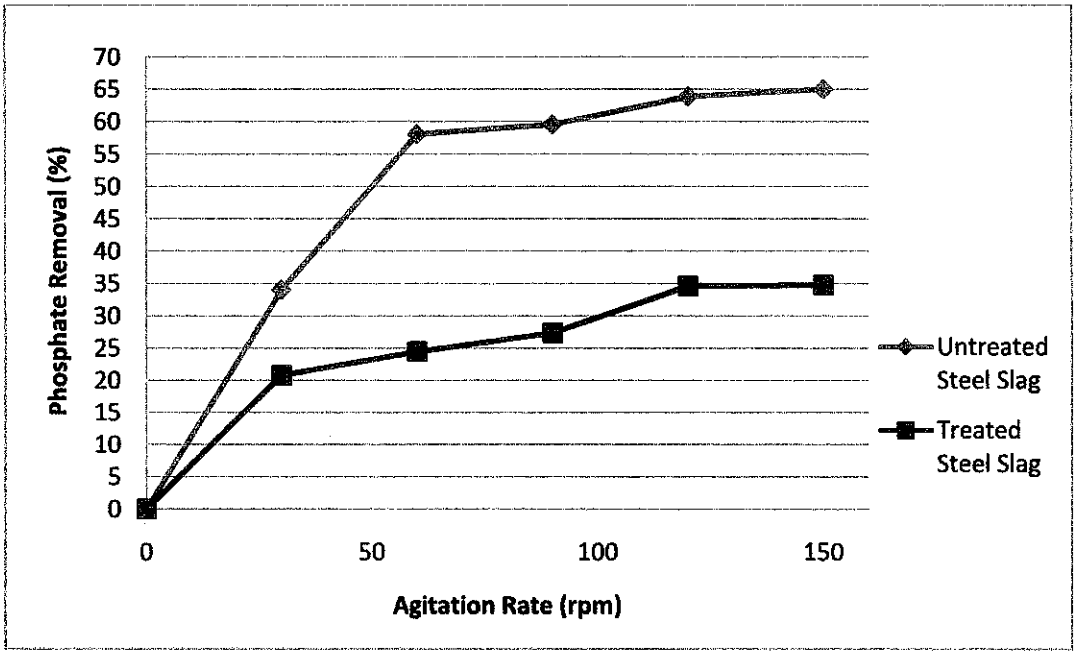


Figure 4.19: Effect of Agitation Rate On Phosphate Adsorption

The results gathered were as expected and consistent with earlier research works such as Oguz E. (2004) and Liu et al (2010). From the graph, the increased of agitation rate will increased the phosphate removal from the phosphate solution. As the agitation rate increase, the phosphate ions were diffused from the phosphate solution into the pores on the surface of the adsorbents.

The agitation rates positively increase the interaction between the adsorbate and the adsorbent thus increasing the amount of phosphate adsorbed with increasing agitation rates (Oguz E. 2004). The highest amount of phosphate removed is at 150 rpm but for optimum and for energy saving purposes, the agitation rate recommended to be used was 60 rpm as after that, the increment of rpm showed only small increase in phosphate removal.

4.2.1.1 The Performance of Untreated versus HCl Treated Steel Slag

Another observation that can be done based on the graph was the performance of both treated and untreated steel slag. It showed that although the adsorptions on both treated and untreated steel slag were increased by the agitation rates, the treated steel slag gave lower yield in terms of phosphate removal. This was anticipated and that this trend where the untreated steel slag will have higher phosphate removal than the HCl treated steel slag will also be expected to continue for other experiments with different parameters.

The main cause of this was the reductions of Ca^+ ions in steel slag during the HCl treatment which greatly reduced the phosphate adsorption ability of the HCl treated steel slag. There were research works results shown that the acid pretreatment can increase the surface porosity of the steel slag which will gives higher phosphate adsorption capabilities (Gong et al and Xue et al, 2009).

However, Lu et (2008) explained that the Ca^+ ions in the $CaCO_3$ and $Ca(OH)_2$ play significant role in phosphate adsorption due to precipitation of Ca phosphates via surface adsorption. Based on the EDX results (Figure 4.13) gathered before, the Ca concentration on the steel slag did decrease after HCl pretreatment and this contributed to lower performance of HCl treated steel slag. This will also reduce the active sites in the pores of the adsorbent material which in turn will reduce the adsorption of phosphate onto the steel slag.

4.2.2 Effect of Temperature

For this parameter testing, the time taken for the adsorption, the pH, the adsorbent and the phosphate solution was also set at the previously mentioned values while the shaking rate used was 60 rpm due to 30 rpm was too slow to help promote the adsorption process. The experiment was done using a water bath shaker unit because of its ability to maintain shaking rate and set temperature for both adsorption studies on untreated and treated steel slag simultaneously.

As other parameters were set, the experiments were done at different temperatures ; 25°C, 45°C, 60°C, 75°C and 90°C. The results of the effect of temperature on phosphate adsorption can be seen in Figure 4.20. The phosphate removal as observed will increase with the increase of contact time between the adsorbent materials and the phosphate solution. The increasing temperature will increase the kinetic energy of the phosphate ions the solution. This condition will promote the collision between the ions and the adsorbent which lead to more ions being adsorbed electrostatically onto the adsorbent surface.

As discussed previously, the temperature effect also showed that the untreated steel slag performed better at phosphate removal than the HCl treated steel slag. The highest phosphate removal percentage acquired is at 87% at 90°C using the untreated steel slag.

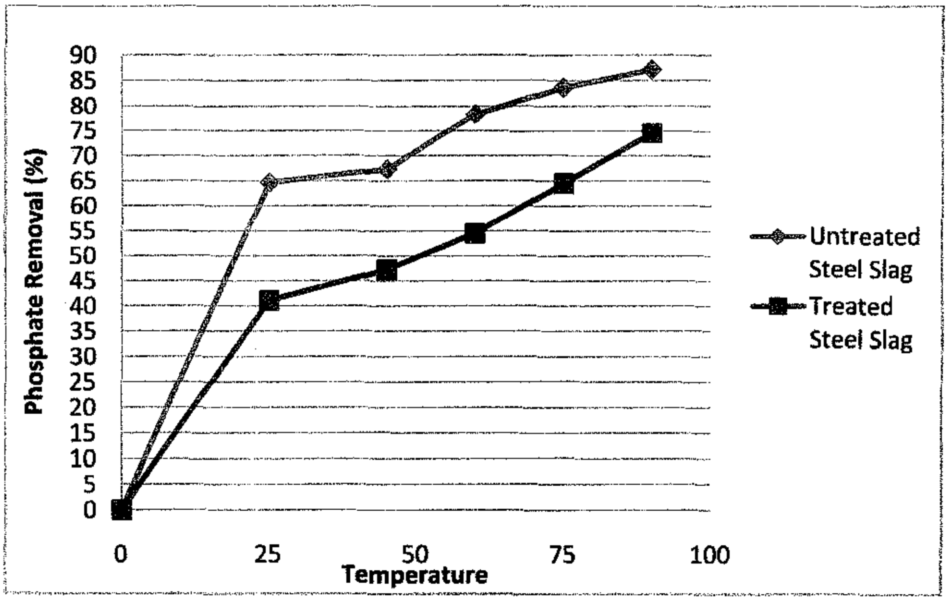


Figure 4.20: Effect of Temperature On Phosphate Adsorption

4.2.3 Effect of Contact Time and Initial Phosphate Concentration

The adsorption of phosphate on untreated steel slag and HCl treated steel slag was tested based on the contact time with variation of different concentration. The contact time was set to 30, 60, 90 and 120 minutes and the concentration used in this adsorption studies was set to 100ppm, 200ppm and 300ppm. The temperature was set to 25°C with the agitation rate was set to 60 rpm, utilizing once again the magnetic stirrer from the jar test equipment. Other parameters were set that of both previously mentioned experiments. The results of the experiment were illustrated in Figure 4.21 and Figure 4.22.

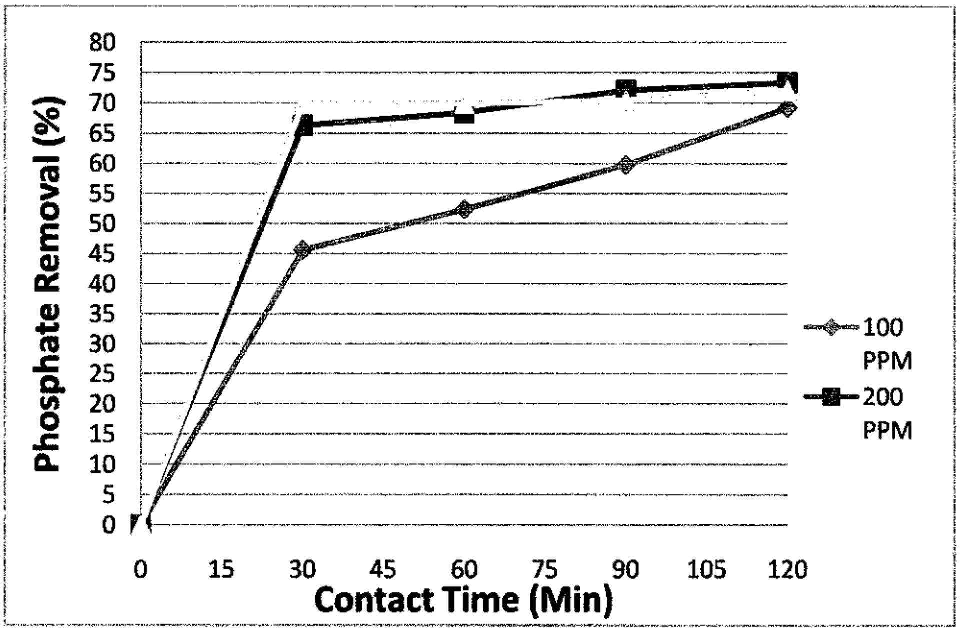


Figure 4.21: Effect Of Contact Time (Untreated Slag) On Phosphate Adsorption

The graphs showed that for each concentration, the phosphate removal was increased with increasing contact time for each of the concentration. This was due to the increasing chance of phosphate ions to be adsorbed onto the adsorbent materials as the contact time between them was longer. The first 30 minutes for each concentration of steel slag and HCl treated steel slag have shown a rapid increase of phosphate adsorption onto the adsorbent materials.

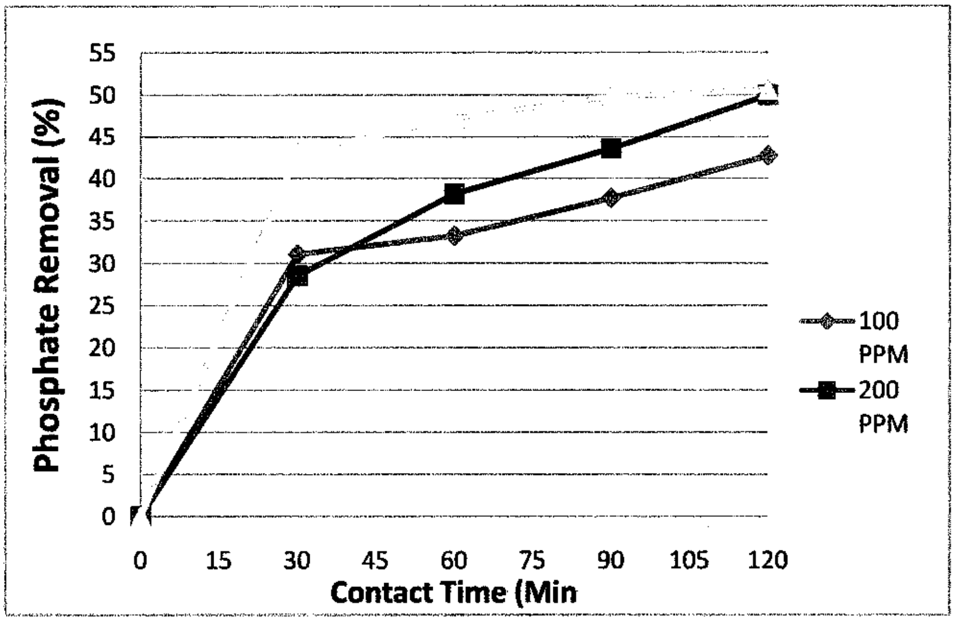


Figure 4.22 : Effect Of Contact Time (HCl Treated Slag) On Phosphate Adsorption

The active sites on the adsorbent at the start of the experiment were vacant and when the adsorption process starts, the phosphate ions rapidly occupy the empty space in on the surface, causing the rapid increase at the early stage of the adsorption process. As time goes by, the surface of the adsorbent materials began to be filled by the phosphate ions and the vacancy of active sites of the surface was reduced.

Longer period of adsorption had cause the adsorbent to be saturated with phosphate and finally reach an equilibrium concentration. The equilibrium concentration was reached at 120 minutes for both types of steel slag. The exact value of the equilibrium concentration after that time cannot be detected due to the constraint caused by limited reagent for phosphate concentration analysis. As a result, longer contact time experiment cannot be done.

The effect of contact time and initial phosphate concentration on phosphate adsorption contained vital information which are the equilibrium concentration and that helped in acquiring the equilibrium and the kinetics results which will be discussed in the next sub chapter. All the result gathered from the adsorption studies can be seen in the APPENDIX section.

4.3 Equilibrium Studies

4.3.1 Langmuir Isotherm

The distribution of adsorbate molecules between two phases of the adsorption process, namely solid and liquid can be represented by the adsorption isotherms. The two widely used isotherms are the Langmuir and the Freundlich isotherm. Based on the Langmuir model, the adsorption occurs uniformly and homogenous on the active sites of the adsorbent and when the sites are occupied by the adsorbate, there will be no more adsorption occurred. The Langmuir model can be described in the equation 2.4.1:

$$\frac{1}{Q_e} = \frac{1}{Q_{max} K_a} \frac{1}{C_e} + \frac{1}{Q_{max}}$$

Equation 4.1: Langmuir Isotherm (Linear)

Where Q_{max} is the saturated monolayer adsorption capacity and K_a can be defined the adsorption equilibrium constant with Qe and Ce are both equilibrium uptake and equilibrium concentration respectively. The Langmuir isotherm can be plotted in linear form in 1/Qe Vs 1/Ce graph using the data gathered in the previous experiment for equilibrium concentration value. The equation from the graphs can be used to get the value of the mentioned constants.

Figure 4.23 and 4.24 represented the linear plot of Langmuir adsorption isotherms for untreated steel slag and HCl treated steel slag respectively. Both figure showed promising estimated value of correlation coefficient, R^2 as the value were closed to 1 and the adsorption of phosphate onto the steel slag was assumed to be favorable and followed the assumptions of the Langmuir isotherm where the adsorption process occurred on the monolayer of the surface of the slags.

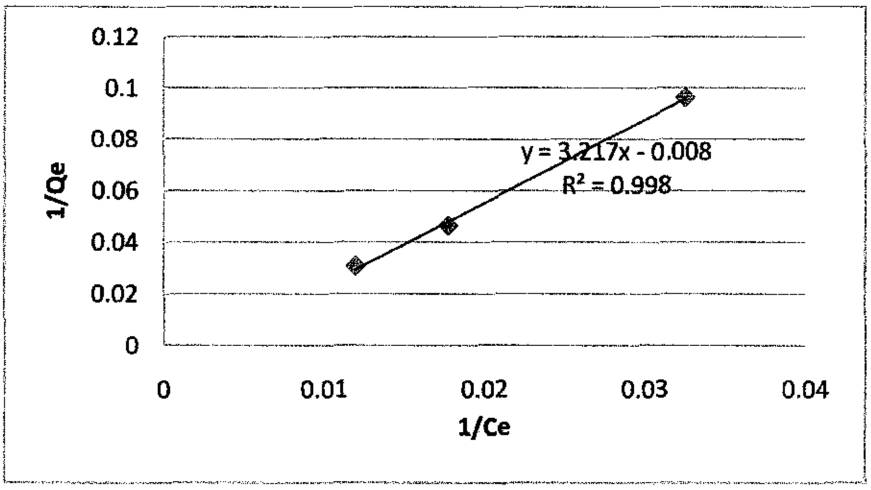


Figure 4.23: Langmuir Adsorption Isotherm (Untreated Slag)

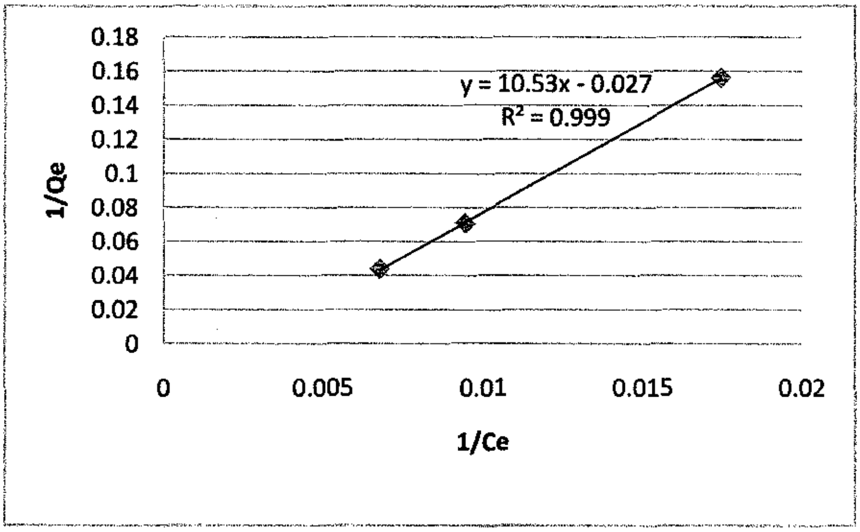


Figure 4.24: Langmuir Adsorption Isotherm (HCl treated Slag)

4.3.2 Freundlich Isotherm

The Freundlich isotherm was developed empirically and in some cases depicts the adsorption equilibrium more accurately than the latter model. Unlike the Langmuir model, the Freundlich isotherm focuses on the adsorption on heterogeneous surfaces in a sense that the adsorption energy is distributed throughout the active sites. The adsorption energy described before can be defined as the interaction energy of the phosphate adsorbate and the steel slag adsorbent. Equation 4.2 shown was linear form of the Freundlich model formula.

$$\mathit{log}\, Q_e = \frac{1}{n} \lg C_e + \log K_f$$

Equation 4.2: Freundlich Isotherm (Linear)

K_f and *n* represents Freundlich constant in which the K_f represent adsorption capacity and sorption intensity respectively. The Freundlich isotherm can be fitted in linear form by drawing the graph of Log Q_e Vs Log C_e where the graph plotted can be used to get the value both constants.

Figure 4.25 and 4.26 represents the linear plot of Freundlich isotherm from the data gathered from the experiments. Freundlich isotherm was developed empirically which means it was based on data gathered from experiments and ideally more suitable to describe any adsorption process such as done in this project. This can be seen from the correlation coefficient R^2 which approaching the value of 1.

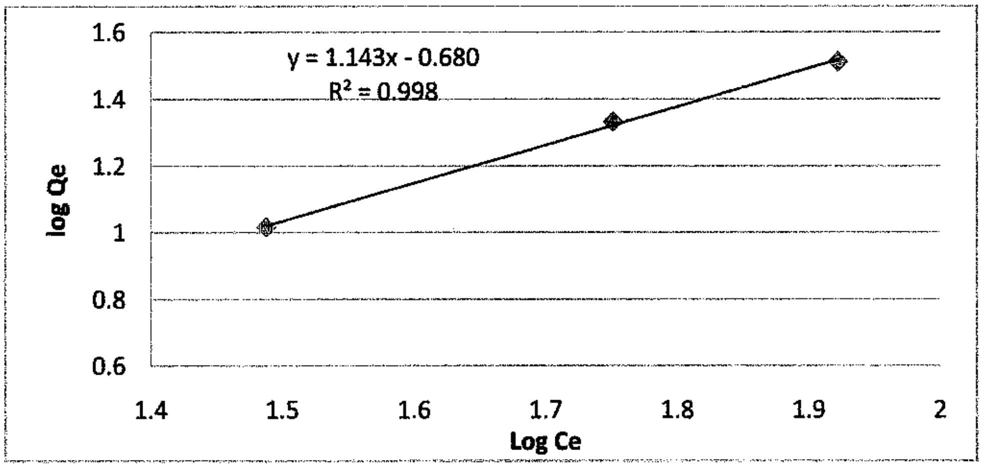


Figure 4.25 : Freundlich Adsorption Isotherm (Untreated Slag)

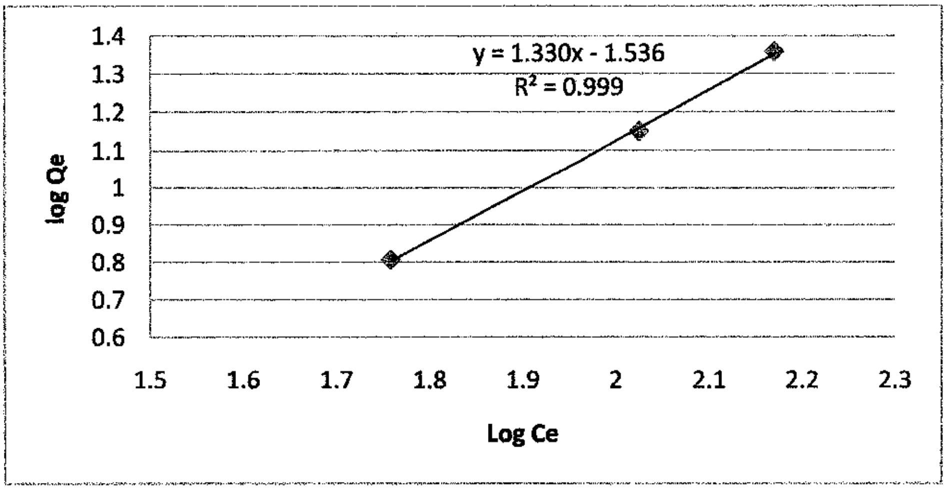


Figure 4.26: Freundlich Adsorption Isotherm (HCl treated Slag)

4.3.3 Results of Equilibrium studies

Table 4.9 shown the detail results of Langmuir and Freundlich isotherm for both untreated and HCl treated steel slag:

Type of adsorbent	**Freundlich Isotherm**			**Langmuir Isotherm**		
Constants	K_f	n	R^2	K_L	q_m(mg/g)	R^2
Untreated Steel Slag	4.786	0.875	0.998	0.026	125	0.998
HCl treated Steel Slag	34.557	0.752	0.999	0.284	37	0.999

Table 4.9: Result For Freundlich and Langmuir Isotherm

Based on the results, the maximum amount of uptake q_m or Q_{max} for untreated and HCl treated steel slag can be obtained as 125 mg/g and 37 mg/g respectively. Both models seemed to be suitable in describing the adsorption of phosphate onto steel slags due to the value of the R^2. The calculated result can be seen in the APPENDIX section.

The adsorption process was following both Langmuir and Freundlich isotherms due to the mechanism of the adsorption did not follow the ideal monolayer adsorption and was possibly a hybrid adsorption process that can be described better using the Redlich-Peterson isotherm (J.Cejka et al, 2005).The Redlich-Peterson model operated on both elements from Langmuir and Freundlich isotherms and suggested that some heterogeneity in the on the surface or in the pores of the both treated and HCl treated steel slag which gives the adsorbent material the ability to fit into both aforementioned model. Due to the complexity of the model and time constraint of the project, the result for the Redlich-Peterson isotherm was not available (J.Cejka et al, 2005).. However this can be rectified in future research by studying on the adsorption of phosphate on steel slag more extensively.

4.4 Kinetic Studies

The pseudo first order and the pseudo second order equations were use to investigate the dynamics of the ion exchange, the mass transfer and chemical reaction in the process of phosphate adsorption using steel slags. The equation for the pseudo first order is given in equation 4.3:

$$\text{Pseudo first order} \rightarrow \log(Q_e - Q_t) = \log Q_e + (\frac{k_{ads}}{2.303})$$

Equation 4.3:Pseudo First Order Kinetic

where Qe and Q_t are the uptake at equilibrium and at time t respectively while k_{ads} is the rate constant for pseudo first order adsorption process. To get the value of k_{ads} and correlation coefficients R^2, the straight line plot is necessary for $\log(Q_e - Q_t)$ against t. Calculation can be made from the plot to get the said values. The pseudo first order plot can be seen in figure 4.27and 4.28.

$$\text{Pseudo Second order} \rightarrow \frac{t}{Q_t} = \frac{1}{h} + \frac{t}{Q_e}$$

Equation 4.4:Pseudo Second Order Kinetic

where Q_e and Q_t are the uptake at equilibrium and at time t respectively while the h value is equal to $k_2 {Q_e}^2$ where k_2 is the rate constant for pseudo second order adsorption process. To get the theoretical value of Q_e and the value k_2, the plot of t/ Q_t against time needs to be plotted. The pseudo second order plot can be seen in Figure 4.29 and Figure 4.30.

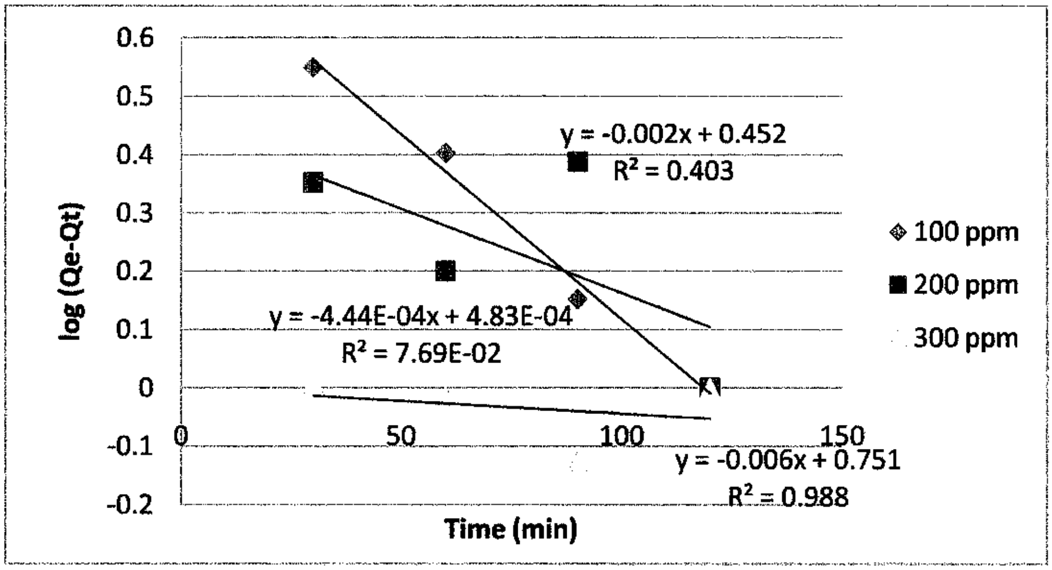


Figure 4.27: Pseudo First Order (Untreated Steel Slag)

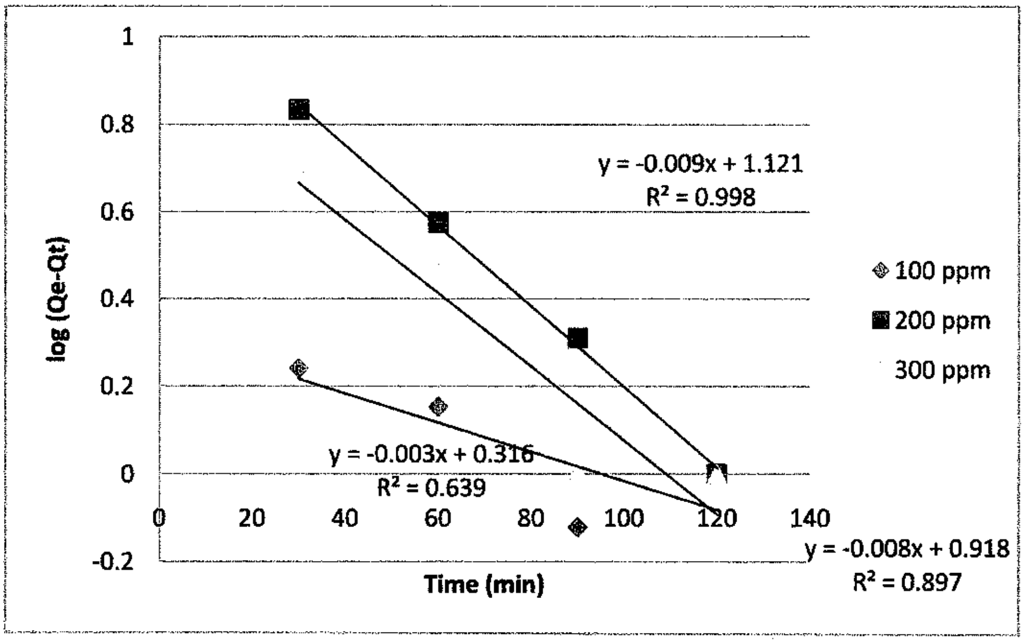


Figure 4.28: Pseudo First Order (HCl treated Steel Slag)

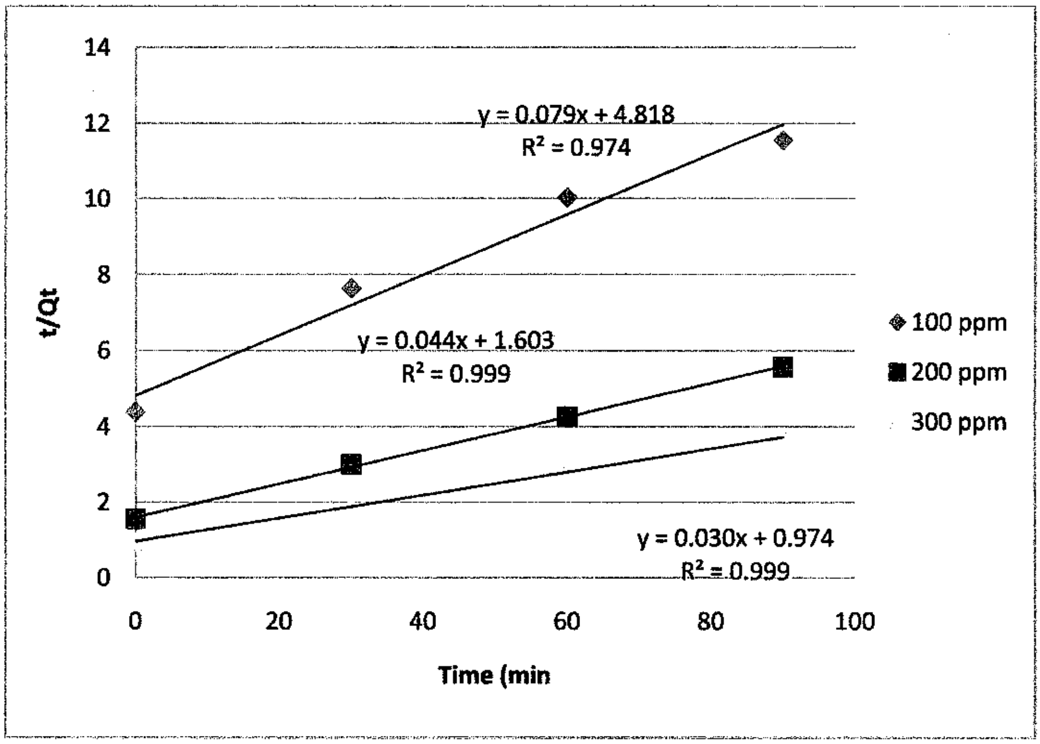


Figure 4.29: Pseudo Second Order (Untreated Steel Slag)

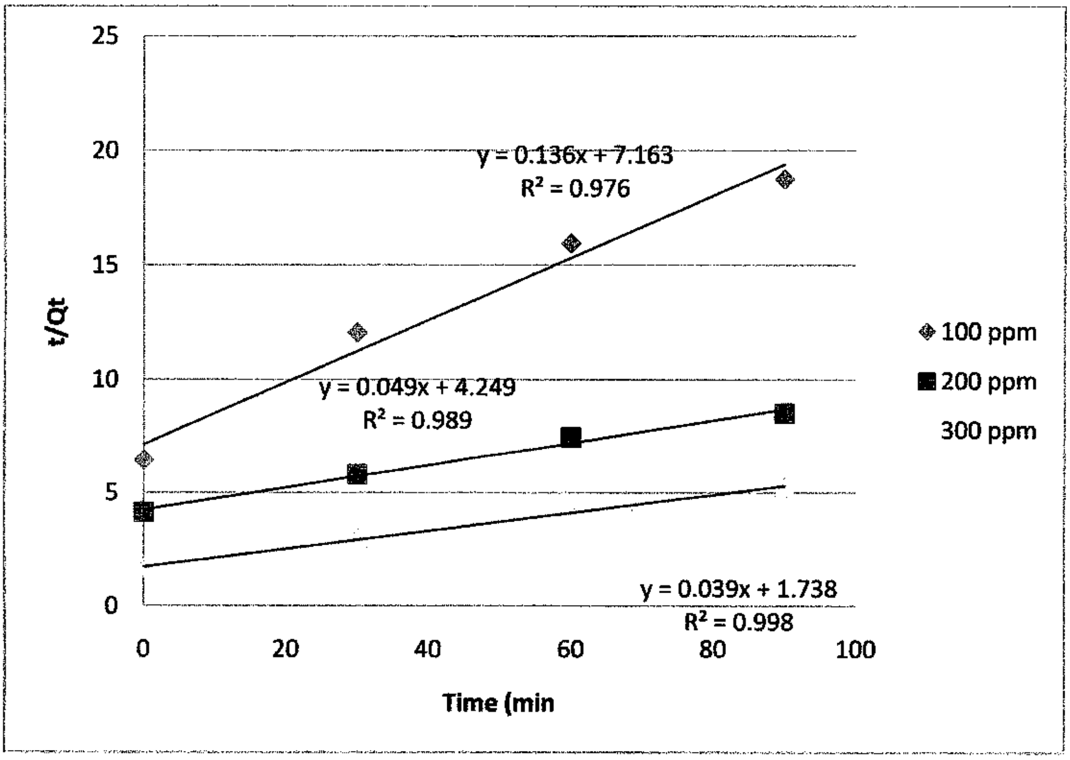


Figure 4.30: Pseudo Second Order (HCl treated GGBS)

4.4.1 Results of Kinetic Studies

For the kinetic models to be applicable to the adsorption process, the plots must yield a straight line. The results that can be calculated from the plot of the pseudo first order can be observed in the table 4.10. The pseudo second order kinetics results can also be seen in both table 4.11 and table 4.12.

Pseudo First Order	**Untreated GGBS**				**HCl treated GGBS**			
Initial PO_4^{-3} ion concentration (mg/L)	**k_{ads}** (min^{-1})	**Q_e** (mg/g)	**R^2**	**Qe (exp value)** (mg/g)	**k_{ads}** (min^{-1})	**Q_e** (mg/g)	**R^2**	**Qe (exp value)** (mg/g)
100	-0.005	2.831	0.403	10.389	-0.002	6.730	0.940	6.404
200	-0.006	1.004	0.077	21.537	-0.021	13.213	0.998	14.102
300	0.403	5.636	0.988	32.457	-0.018	8.279	0.897	22.788

Table 4.10: Result Of Pseudo First Order Kinectic

Based on the graphs and the results of the pseudo first order, the untreated steel slag was not following the pseudo first order kinetics as the value correlation coefficient R^2 displayed low value and that the Q_e reading was different from the experimental values. The HCl treated steel slag however showed different results altogether as the R^2 value closer to 1 than the untreated steel slag and the Q_e value gathered from the graph showed promising results when compared to the experimental value of Q_e. It is interesting to see whether the introduction of HCl treatment can change the adsorption kinetics of the steel slag in future research works.

Pseudo Second Order	**Untreated Steel Slag**				
Initial PO_4^{-3} ion concentration (mg/L)	**k_2** (min^{-1})	**Q_e** (mg/g)	**R^2**	**h** (mg/g min)	**Qe (exp value)** (mg/g)
100	$1.295\text{x}10^{-3}$	12.658	0.974	0.208	10.389
200	$1.208\ \text{x}10^{-3}$	22.727	0.999	0.624	21.537
300	$1.118\ \text{x}10^{-3}$	30.303	0.999	1.027	32.457

Table 4.11: Result Of Pseudo Second Order Kinectic (Untreated)

Pseudo Second Order	HCl treated Steel Slag				
Initial PO_4^{-3} ion concentration (mg/L)	k_2 (min^{-1})	Q_e (mg/g)	R^2	h (mg/g min)	Qe (exp value) (mg/g)
100	$2.736x10^{-5}$	7.353	0.126	0.062	6.404
200	$5.651x10^{-4}$	20.408	0.989	0.235	14.102
300	$8.751x10^{-4}$	25.641	0.998	0.575	22.788

Table 4.12: Result Of Pseudo Second Order Kinectic (Treated)

For both treated and untreated steel slag, pseudo second order kinetics exhibited better result than the first order as the adsorption studies done was not following the method of pseudo first order approximation. This method required one of the reactant concentration i.e steel slag mass or phosphate solution to be used in excess as to cause only small portion of it was consumed during the adsorption process and can be considered as constant. This was not the case for the adsorption studies of this project since the initial phosphate concentration was changed for kinetic studies and although the steel slag mass used was constant, it was not in excess as 1g was only a small amount to be used for the experiments.

The correlation coefficients were closed to value one and the theoretical Q_e values gave a close resemblance to those of the experimental values. Therefore, it can be said that the adsorption of phosphate onto steel slag followed the pseudo second order kinetics because of the fit value between the experimental and the theoretical data of Q_e and the correlation coefficient $R^2 = 0.999$ as supported by Oguz (2005).

Both pseudo first order and pseudo second order graphs also showed that as concentration of the PO_4^{-3} ions increased, the Q_e values reached closer to the experimental values and the R^2 value got closer to 1. This pattern in a sense proved that higher amount of phosphate can be adsorbed by the steel slag with increasing PO_4^{-3} ions. The calculated results for the kinetic studies can be seen in the APPENDIX section.

CHAPTER 5: CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

- FESEM/EDX results showed the more porous surface and a reduction of the Ca^+ ion in the HCl treated steel slag. Particle size of the steel slag was found to be in the range of 20-22μm. The FTIR result showed an increased of O-H bond and C=C- bonds after the HCl acid treatment while the formation of P-H bond was detected after the adsorption experiments.

- The increased in agitation rate, temperature, contact time, and initial phosphate concentration did increased the phosphate adsorption. The highest phosphate uptake for optimum agitation rate, temperature and contact time were 65%, 87.13%, and 73% respectively for untreated steel slag. HCl treated steel slag showed lower phosphate uptake of 34.77%, 74.55% and 50.64% for optimum agitation rate, temperature and contact time respectively.

- The adsorption process followed Langmuir and Freundlich equilibrium isotherms with the value of correlation coefficient, R^2 of 0.998 for untreated steel slag for both model and maximum uptake value, q_m of 125mg/g. HCl treated steel slag gave R^2 value of 0.999 with q_m value of 37 mg/g. Both steel slags followed the pseudo second order kinetics with highest correlation coefficient achieved at 0.999 and 0.998 for untreated and treated slags respectively.

- As a conclusion, steel slag has a potential as adsorbent materials for phosphate removal. HCl treated steel slag although visually shows a more porous surface to, however it did not perform as well as the untreated steel slag due to the reduction of Ca^+ ions content through the acid pretreatment.

5.2 Recommendations

- For future studies, it is recommended to use different kind of steel slag such as the electric arc furnace slag to see the difference in adsorption performance in comparison to that of the blast furnace slag.
- The pretreatment method can also be changed preferably using other material than acid as in this project; the acid treatment has reduced the adsorption capability of the steel slag.
- The characterization using FESEM is highly recommended but the magnification used can be increased further to see the effect of pretreatment on the adsorption materials with greater details. The usage other characterization methods such as BET surface porosity analyzer and XRD analysis can also be introduced to learn gather more details on the adsorbent material.
- Other parameters such as adsorbent particle size, pH manipulation and amount of adsorbent should also be studied further to determine the effects on the adsorption process.

REFERENCE

Ahmaruzzaman, M. (2011). Industrial wastes as low-cost potential adsorbents for the treatment of wastewater laden with heavy metals. *Advances in Colloid and Interface Science, Volume 166, Issues 1–2* , 36-59.

Capital Dynamics Sdn. Bhd. (2005). *http://www.icapitaleducation.biz/index.php?section=5&sub=3*. Retrieved from http://www.icapitaleducation.biz.

F., K. (1996). Laboratory manual for physical chemistry. Farmaceutical faculty of Comenius University, Bratislava.

Fenglian Fu, Q. W. (2011). Removal of heavy metal ions from wastewaters: A review. *Journal of Environmental Management, Volume 92, Issue 3* , 407-418.

FIPR. (2010). *http://www1.fipr.state.fl.us/PhosphatePrimer*. Retrieved from http://www1.fipr.state.fl.us.

Guozhuo Gong, S. Y. (2009). Preparation of a new sorbent with hydrated lime and blast furnace slag for phosphorus removal from aqueous solution . *Journal of Hazardous Materials, Volume 166, Issues 2–3* , 714-719.

James E. Cloern, T. K. (2010, November 17). *http://www.eoearth.org*. Retrieved 2012, from The Encyclopedia Of EARTH.

Jibing Xiong, Z. H. (2008). Phosphate removal from solution using steel slag through magnetic separation . *Journal of Hazardous Materials, Volume 152, Issue 1* , 211-215.

Jirí Cejka, N. Z. (2005). Molecular Sieves: From Basic Research to Industrial Applications. Oxford ; New York ; Amsterdam : Elsevier.

K.M. Smith, G. F. (2009). Sewage sludge-based adsorbents: A review of their production, properties and use in water treatment applications. *Water Research, Volume 43, Issue 10* , 2569-2594.

Labarge, T. (2011). *http://info.triplepointwater.com/blog/bid/52804/Eutrophication-Stop-it-Before-it-Starts*. Retrieved from http://info.triplepointwater.com.

Lenntech B.V. (2011). *http://www.lenntech.com/periodic/elements/p.htm*. Retrieved from http://www.lenntech.com.

Liskiewicz, T. W., Morina, A., & Neville, A. (2008). *Challenges in Lubricant Additives Tecnology* .

Oguz, E. (2004). Removal of phosphate from aqueous solution with blast furnace slag. *Journal of Hazardous Materials, Volume 114, Issues 1–3* , 131-137.

Oguz, E. (2005). Thermodynamic and Kinetic Investigations of Phosphate ion Adsorption On Blast Furnace Slag. *Journal of Colloid and Interface Science 281* , 62-67.

P. Koilraj, S. K. (2010). Phosphate uptake behavior of ZnAlZr ternary layered double hydroxides through surface precipitation. *Journal of Colloid and Interface Science, Volume 341, Issue 2* , 289-297.

P.C. Mishra, R. P. (2009). Removal of lead and zinc ions from water by low cost adsorbents. *Journal of Hazardous Materials, Volume 168, Issue 1* , 319-325.

PFA. (2010). *http://www.phosphatesfacts.org/what.asp*. Retrieved from http://www.phosphatesfacts.org.

Şahset İrdemez, Y. Ş. (2006). Optimization of phosphate removal from wastewater by electrocoagulation with aluminum plate electrodes . *Separation and Purification Technology, Volume 52, Issue 2* , 394-401.

Sheng-gao LU, S.-q. B.-d. (2008). Mechanism of phosphate removal from aqueous solution by blast furnace slag and steel furnace slag. *Journal of Zheijang University SCIENCE A* , 125-132.

Sheng-Yu Liu, J. G.-J.-C.-X. (2010). Adsorption intrinsic kinetics and isotherms of lead ions on steel slag. *Journal of Hazardous Materials, Volume 173, Issues 1–3* , 558-562.

W, A. A. (1990). *Physical Chemical of Surfaces 5th Edition.* New York: John Wiley & Sons.

Weiwei Huang, S. W. (2008). Phosphate removal from wastewater using red mud. *Journal of Hazardous Materials, Volume 158, Issue 1* , Pages 35-42.

Yi, T. C. (2008). Performance Evaluation Of Steel Slag As Natural Aggregates Replacement In Asphaltic Concrete. 183.

Yongjie Xue, H. H. (2009). dsorption removal of reactive dyes from aqueous solution by modified basic oxygen furnace slag: Isotherm and kinetic study. *Chemical Engineering Journal, Volume 147, Issues 2–3* , 272-279.

Zati Sharip, S. Z. (2008). Lakes and Reservoir in Malaysia: Management and Research Challenges. *Proceedings of Taal 2007: The 12th World Lake Conference* , 1349-1355.

APPENDIX

APPENDIX I

Hach Method 8190

DR/4000 PROCEDURE

PHOSPHORUS, Total

✔ Method 8190

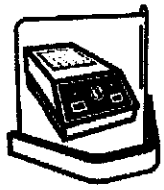
PhosVer 3 with Acid Persulfate Digestion

(0.00 to 3.50 mg/L PO_4^{3-})

Test 'N Tube™ Vials

(0.00 to 1.10 mg/L P)

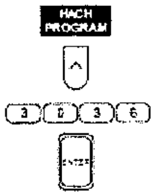
Scope and Application: *For water, wastewater and seawater. USEPA accepted for reporting wastewater analyses. The estimated detection limit for program number 3036 is 0.06 mg/L* PO_4^{3-}.



1. Turn on the COD Reactor. Heat to 150 °C. Place the plastic shield in front of the reactor.

Note: *Ensure safety devices are in place to protect the analyst from splattering should leakage occur.*

Note: *See COD Reactor Manual for temperature adjustment instructions.*



2. Press the soft key under ***HACH PROGRAM***.

Select the stored program for Test 'N Tube total phosphorus by pressing **3036** with the numeric keys.

Press: **ENTER**

Note: *If samples cannot be analyzed immediately, see Sample Collection, Storage and Preservation following these steps.*

HACH PROGRAM: 3036
P Total As. TNT

3. The display will show:

HACH PROGRAM: 3036
P Total As. TNT

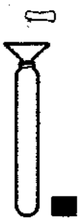
The wavelength (λ), **890 nm**, is automatically selected.

Note: *Determine a reagent blank for each new lot of each reagent as follows: Prepare a reagent blank by repeating Steps 4 through 15, using deionized water as the sample. Insert the reagent blank and the blank value will be displayed. Correct for the reagent blank by pressing the soft keys under* ***OPTIONS, (MORE)****, and then* ***BLANK: OFF****. Enter the reagent blank value and press* **ENTER**. *Repeat for each new lot of reagent.*

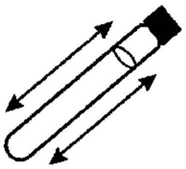
4. Use a TenSette Pipet to add 5.0 mL of sample to a Total and Acid Hydrolyzable Test Vial.

Note: *For proof of accuracy, use a 1.0 mg/L Phosphate (0.33 mg/L P) Standard Solution in place of the sample (see OPTIONAL REAGENTS AND STANDARDS).*

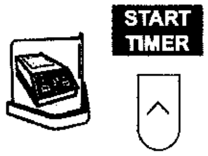
Note: *For non-preserved samples with extreme pH, see Interferences.*



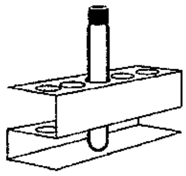
5. Using a funnel, add the contents of one Potassium Persulfate Powder Pillow for Phosphonate to the vial.



6. Cap tightly and shake to mix.



7. Place the vial in the COD Reactor, and start a 30-minute heating period by pressing the soft key under ***START TIMER***.

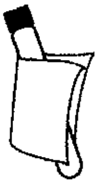


8. Carefully remove the vial from the reactor. Place it in a test tube rack and allow to cool to room temperature.

Note: *Tubes will be hot.*

9. Using a TenSette Pipet, add 2 mL of 1.54 N Sodium Hydroxide Standard Solution to the vial. Cap and mix.

10. Insert the Test Tube Adapter into the sample cell module by sliding it under the thumb screw and into the alignment grooves. Fasten with the thumb screw.



11. Clean the outside of the vial with a towel.

***Note:** Wiping with a damp towel, followed by a dry one, will remove fingerprints or other marks.*

12. Place the sample vial in the cell holder and close the light shield.

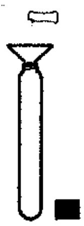
13. Press the soft key under ***ZERO***.

The display will show:

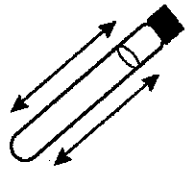
0.00 mg/L PO_4^{3-}

***Note:** If you are using a reagent blank correction, the display will show the correction.*

***Note:** For alternate concentration units, press the soft key under **OPTIONS**. Then press the soft key under **UNITS** to scroll through the available options. Press **ENTER** to return to the*

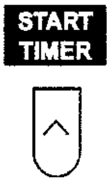


14. Using a funnel, add the contents of one PhosVer 3 Powder Pillow to the vial.



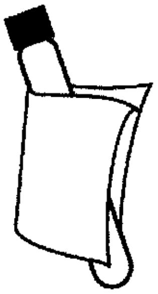
15. Cap tightly and shake to mix for 10-15 seconds.

***Note:** The powder will not dissolve completely.*



16. Press the soft key under ***START TIMER***.

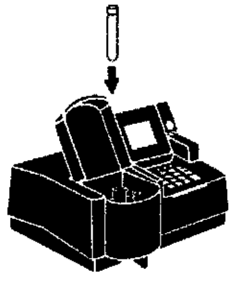
A 2-minute waiting period will begin.



17. After the timer beeps, clean the outside of the sample vial with a towel.

***Note:** Wiping with a damp towel, followed by a dry one, will remove fingerprints or other marks.*

***Note:** Read the sample 2-8 minutes after the addition of the PhosVer 3 reagent.*



18. Place the prepared sample vial into the cell holder and close the light shield. Results in mg/L PO_4^{3-} (or chosen units) will be displayed.

***Note:** Results may be expressed as phosphorus (P) or as phosphorus pentoxide (P_2O_5). Press the soft keys under **OPTIONS** and then **FORM**: to scroll through the available options.*

***Important Note:** The test range for total phosphate is limited to 0 to 3.5 mg/L PO_4^{3-}. Values greater than 3.5 mg/L may be used to estimate dilution ratios, but should NOT be used for reporting purposes. If the value is greater than 3.5 mg/L, dilute the sample and repeat the digestion and colorimetric test.*

Calculation Of Uptake (mg/g)

$$Q = \frac{V(C_o - C_t)}{m}$$

where

Q = amount of phosphate(PO_4-3) ion adsorbed on the steel slag (mg/g)

C_o = Initial phosphate concentration before adsorption (mg l^{-1})

C_t = Initial phosphate concentration after adsorption (mg l^{-1})

V = Volume of phosphate solution(L)

m = amount of steel slag use for the adsorption process (g)

Example

Phosphate uptake for adsorption of 200ppm uptake at 60 minutes

C_o = 200 ppm = 200 mg l^{-1}

C_t = 66.98 mg l^{-1} = 66.98 ppm

V = 150 ml = 0.15 l

m =1 g

So,

$$Q=\frac{150(200-66.98)}{1} = 19.95 \text{ mg/g}$$

Adsorption Efficiency / Phosphate Removal (%)

$$\eta = \frac{(C_o - C_t)}{C_o} x\ 100\%$$

where

C_o = Initial phosphate concentration before adsorption (mg l^{-1})

C_t = Initial phosphate concentration after adsorption (mg l^{-1})

Example:

Calculations of phosphate removal for 200 ppm at 60 minutes contact time given

C_t = 66.98 mg l^{-1}.

$\eta = \frac{(200-66.98)}{200} x\ 100\% = 66.51$ % of phosphate removal

Phosphate solution preparation

1. Stock solution preparation

MW KH_2PO_4 = 136.09 g/mol

MW PO_4 = 94.97 g/mol

1 gram of KH_2PO_4 contains 0.698 g PO_4

So, 1.433 g of KH_2PO_4 = 1g of PO_4

To make 1L of 1000ppm of PO_4 solution, weight KH_2PO_4 powder to 1.433g and put in 1L volumetric flask. The flask is then filled to the 1L level with deionized water .

2. Dilution for different concentration

To dilute the stock solution to the desired concentration and volume, the volume of stock solution needed have to be calculated using the given formula:

Dilution Formula: **C1V1 = C2V2**

C1 = Stock solution concentration

V1 = Stock solution volume

C2 = Desired solution concentration

V2= Desired solution volume

Example

Dilute the stock solution to200 ppm for volume of 500ml.

C1 = 1000 ppm C2 = 200 ppm

V1 = ? V2= 500 ml

C1 = (200x500)/1000 = 100 mL of stock solution

3. Project Work Material Usage Table

This table is establishing to keep track of the material usage throughout the experiments. Material usages can be optimized throughout the project without any excessive usage that could waste the precious material for the experiment.

Experiment / Analysis	Possible n of repetiti	Material (Steel Slag)	
		Amount	Total Amount
Effect of temperature on phosphate adsorption	3	1g per reading 5 reading 3 times	15 g of steel slag
Effect of stirring rate on phosphate adsorption	3	1g per reading 5 reading 3 times	15g of steel slag
Effect of initial phosphate concentration c phosphate adsorption	3	1g per reading 3 reading 3 times	9 g of steel slag
Effect of contact time concentration on phosphate adsorption	3	3 concentration 4 reading 1g per reading 3 times	36g of steel slag
Total amount of steel slag for adsorption studies (HCl treated slag)		75 g	
Total amount of steel slag for adsorption studies (untreated slag)		75 g	
Approximate material usage for characterization purposes (50 % the amount used in experiment)		37.5 g	
Reserved material in case of error (20%) per experime		15g X 4 = 60 g	
Approximate overall amount of Steel Slag consumptio		75+75+37.5+60 = **247.5 g of steel slag**	

APPENDIX II

Adsorption Spreadsheet

Effect of Agitation Rate On Phosphate Adsorption

Constant Parameter: 25 °C, 60 minutes & pH 7

Untreated Steel Slag			
Agitation (rpm)	**Initial phosphate Concentration (Mg/l)**	**Residual phosphate Concentration (Mg/l)**	**Phosphate Removal Efficiency,η (%)**
30	200	132.05	33.975
60	200	83.83	58.085
90	200	80.91	59.545
120	200	72.29	63.855
150	200	69.96	65.02

HCl Treated Steel Slag			
Agitation (rpm)	**Initial phosphate Concentration (Mg/l)**	**Residual phosphate Concentration (Mg/l)**	**Phosphate Removal Efficiency,η (%)**
30	200	158.41	20.795
60	200	151.04	24.48
90	200	145.3	27.35
120	200	130.76	34.62
150	200	130.46	34.77

Effect of Temperature On Phosphate Adsorption

Constant Parameter: 60 rpm, 60 minutes & pH 7

Untreated Steel Slag			
Temperature (°C)	**Initial phosphate Concentration (Mg/l)**	**Residual phosphate Concentration (Mg/l)**	**Phosphate Removal Efficiency,Ƞ (%)**
25	200	70.61	64.695
45	200	65.32	67.34
60	200	43.21	78.395
75	200	32.7	83.65
90	200	25.75	87.125

HCl Treated Steel Slag			
Temperature (°C)	**Initial phosphate Concentration (Mg/l)**	**Residual phosphate Concentration (Mg/l)**	**Phosphate Removal Efficiency,Ƞ (%)**
25	200	117.84	41.08
45	200	105.53	47.235
60	200	90.91	54.545
75	200	70.94	64.53
90	200	50.91	74.545

Effect of Initial Phosphate Concentration and Contact Time On Phosphate Adsorption

Constant Parameter: 60 rpm, 60 minutes & pH 7

Untreated Steel Slag			
Contact Time (Min)	**Initial phosphate Concentration (Mg/l)**	**Residual phosphate Concentration (Mg/l)**	**Phosphate Removal Efficiency,Ƞ (%)**
0	100	54.4	45.6
30	100	47.62	52.38
60	100	40.2	59.8
90	100	30.74	69.26
120	100	54.4	45.6

Untreated Steel Slag			
Contact Time (Min)	**Initial phosphate Concentration (Mg/l)**	**Residual phosphate Concentration (Mg/l)**	**Phosphate Removal Efficiency,η (%)**
0	200	71.42	66.31
30	200	66.98	68.40
60	200	59.15	72.10
90	200	56.42	73.38
120	200	71.42	66.31

Untreated Steel Slag			
Contact Time (Min)	**Initial phosphate Concentration (Mg/l)**	**Residual phosphate Concentration (Mg/l)**	**Phosphate Removal Efficiency,η (%)**
0	300	90.4	69.87
30	300	90.08	69.97
60	300	88.62	70.46
90	300	83.69	72.10
120	300	90.4	69.87

Constant Parameter: 60 rpm, 60 minutes & pH 7

HCl Treated Steel Slag			
Contact Time (Min)	**Initial phosphate Concentration (Mg/l)**	**Residual phosphate Concentration (Mg/l)**	**Phosphate Removal Efficiency,η (%)**
0	100	68.9	31.1
30	100	66.78	33.22
60	100	62.35	37.65
90	100	57.31	42.69
120	100	68.9	31.1

HCl Treated Steel Slag			
Contact Time (Min)	**Initial phosphate Concentration (Mg/l)**	**Residual phosphate Concentration (Mg/l)**	**Phosphate Removal Efficiency,η (%)**
0	200	151.48	28.54
30	200	131.04	38.18
60	200	119.6	43.58
90	200	105.99	50.00
120	200	151.48	28.54

HCl Treated Steel Slag			
Contact Time (Min)	**Initial phosphate Concentration (Mg/l)**	**Residual phosphate Concentration (Mg/l)**	**Phosphate Removal Efficiency,η (%)**
0	300	170.67	43.11
30	300	158.24	47.25
60	300	150.76	49.75
90	300	148.08	50.64
120	300	170.67	43.11

Langmuir and Freundlich Isotherm Spreadsheet

Constant Parameter: 60 rpm, 60 minute, pH 7,

Adsorbate volume 0.15 L & Adsorbate Mass 1g

Untreated Steel Slag						
Concentration (ppm)	**Ce (Mg/l)**	**1/Ce**	**Log Ce**	**Qe (mg/g)**	**1/Qe**	**Log Qe**
100.00	30.74	0.03	1.49	10.39	0.10	1.02
200.00	56.42	0.02	1.75	21.54	0.05	1.33
300.00	83.62	0.01	1.92	32.46	0.03	1.51
HCl treated Steel Slag						
Concentration (ppm)	**Ce (Mg/l)**	**1/Ce**	**Log Ce**	**Qe (mg/g)**	**1/Qe**	**Log Qe**
100.00	57.31	0.02	1.76	6.40	0.16	0.81
200.00	105.99	0.01	2.03	14.10	0.07	1.15
300.00	148.08	0.01	2.17	22.79	0.04	1.36

Pseudo First Order And Pseudo Second Order Kinetics

Constant Parameter: 60 rpm, 60 minute, pH 7,

Adsorbate volume 0.15 L & Adsorbate Mass 1g

Contact Time (Min)	**Ct (mg/l)**	**Co (mg/l)**	Qt (mg/g)	t/Qt	Qe	Qe-Qt
100 ppm	**Untreated Steel Slag**					
30	54.4	100	6.84	4.39	10.39	3.55
60	47.62	100	7.86	7.64	10.39	2.53
90	40.2	100	8.97	10.03	10.39	1.42
120	30.74	100	10.39	11.55	10.39	0.00

200 ppm	**Untreated Steel Slag**					
30	71.42	200	19.29	1.56	21.54	2.25
60	66.98	200	19.95	3.01	21.54	1.58
90	59.15	200	21.13	4.26	21.54	0.41
120	56.42	200	21.54	5.57	21.54	0.00
300 ppm	**Untreated Steel Slag**					
30	90.4	300	31.44	0.95	32.46	1.02
60	90.08	300	31.49	1.91	32.46	0.97
90	88.62	300	31.71	2.84	32.46	0.75
120	83.62	300	32.46	3.70	32.46	0.00
Contact Time (Min)	Ct (mg/l)	Co (mg/l)	Qt (mg/g)	t/Qt	Qe	Qe-Qt
100 ppm	**HCl treated Steel Slag**					
30	68.90	100	4.67	6.43	6.40	1.74
60	66.78	100	4.98	12.04	6.40	1.42
90	62.35	100	5.65	15.94	6.40	0.76
120	57.31	100	6.40	18.74	6.40	0.00
200 ppm	**HCl treated Steel Slag**					
30	151.48	200	7.28	4.12	14.10	6.82
60	131.04	200	10.34	5.80	14.10	3.76
90	119.60	200	12.06	7.46	14.10	2.04
120	105.99	200	14.10	8.51	14.10	0.00
300 ppm	**HCl treated Steel Slag**					
30	180.67	300	17.90	1.68	22.79	4.89
60	167.24	300	19.91	3.01	22.79	2.87
90	154.76	300	21.79	4.13	22.79	1.00
120	148.08	300	22.79	5.27	22.79	0.00