CHAPTER 1

INTRODUCTION

1.1 INTRODUCTION TO SOLID WASTE

Industrial sector becomes an important role in the growth of world economy. This sector provides services and products that change the way of life and improve the quality of people lifestyle. However, the rapid industrialization generates huge amount which greatly affect the environment. The current waste management systems especially in developing countries such as Malaysia are focusing more to end-pipe approach and promote the disposal treatment method rather finding the alternative method to utilize the waste for other application. The increasing amount of industrial waste parallel with the growth of industrialization requires larger space of landfill and expensive treatment of disposal. Some of the industries take irresponsible actions to reduce the cost of disposal by illegally dump the waste into the environment. This scenario will cause the detrimental pollution effect to the soil, water and air (Abdul Nasir, 2007).

Recent alternative method to overcome this problem is by utilization of the industrial waste to other valuable application. This alternative method allows the industrial sector to reduce the cost of disposal and at the same time reduce the cost of manufacturing process, enhance the efficiency of resources utilization and most importantly it reduce negative impacts on the environment and human health. Utilization of waste material for other valuable application will balance the increasing demands of limited natural resources by providing alternative resources and reduce the dependency on natural resources (Abdul Nasir, 2007).

One of the progressive industries that generate quite large amount of industrial waste is the pulp and paper production. Pulp and paper are manufactured from natural material containing cellulose fibre generally wood. Fortunately, nowadays, the pulp and paper are also produced from recycle material containing cellulose and fibre such as recycle paper and agriculture residue. However, this industry still produces larger amount of sludge as a result from their wastewater treatment plant.

According to O’Brien et al. (2003), the primary method of disposal for paper mill sludge is mainly through land application and land filling. However with the cost of the disposal, alternative methods to handle this problem are being investigated. Land filling cost in the European Union (EU) are rising because of stringent regulation, taxes, and declining capacity. With landfill space becoming scarce and expensive, some sludges are being burned or incinerated to reduce their volume and to recover part of the energy they contain (Navaee-Ardeh et al., 2006). In Malaysia, reutilization of paper mill sludge is limited to energy production by the respective mills. Big capacity mill such as Genting Sanyen Industrial paper Sdn Bhd has invested on a Waste-To-Energy plant as the alternative method to reduce the solid waste. However, such installation requires high capital cost, which is beyond the capability of small capacity mill and even then, the excess amount of sludge is still large and has to be incinerated or disposed as landfill (Wanet al., 2004). Expensive treatment of land disposal necessitates other means of treatment which is more economical and other alternatives used of these waste for beneficial application.

Previous alternative treatment of this solid waste are by utilizing the paper mill sludge in building material such as cements (Naik et al.,2004), bricks (Andreola et al.,2005), ceramics (Wiegand and Unwin, 1994), concrete (Naik et al.,2004) and landfill cover material (Gellman, 1990).Besides, the paper sludge also had been utilized in agriculture, land reclamation and forestry (Pichtel et al., 1994; Bellamy et al., 1995; Rodella et al., 1995; Lo et al., 1996; Beyer et al., 1997). Paper mill sludge were mainly composed of organic matter (mainly cellulose fiber from wood or recycled paper) in whichorganic compounds wereadded to the paper or pulp whereas inorganic compounds (mainly calcium carbonate, kaolinite and talc) were used as fillers and coating (Hojamberdiev et al., 2008).

Some studies had been done on using material containing calcium such as fly ash and calcite to remove phosphate from waste water (Karageorgiou et al., 2007). In view of the fact that the calcium content in the paper mill sludge is high, hence we investigate the efficiency of paper mill sludge as adsorbent for removal of phosphate from aqueous solution.

Phosphates are very important materials in many industrial applications include production of fertilizers, detergents preparation, water softening, water treatment, flame retardants, corrosion inhibitors, paints, food and beverages, pharmaceuticals and many others. The increasing of phosphates application creates a serious environmental problem because it produces large amount of phosphate bearing waste. All of these wastes usually discharge into the river or municipal and industrial effluent stream and cause detrimental effect to environment and human health. Phosphorus is often present at low concentrations in wastewater almost solely as phosphates, including organicphosphate, inorganic phosphate and polyphosphate. The principal phosphorus compounds in wastewater are generally orthophosphates. Municipal wastewater may contain from 4 to 15 mg/L phosphorus as PO_4^{3-}. However, industrial wastewaters such as detergent manufacturing and metal coating processes may contain phosphate levels in excess of 10 mg/L (Mezenner et al., 2009*)*.

Scientist estimates that human activities have increased the natural rate of phosphorus release into the environment about 3.7 fold (Miller, 2004). Large quantities of phosphate rock were mine for use in commercial organic and inorganic fertilizers and detergent. Excess of phosphate to aquatic ecosystem in run off animal wastes from livestock feeding, run off of commercial phosphate fertilizers from cropland and discharge of municipal sewage caused explosive growth of cyanobacteria which, in turn, has a harmful effect on fish and other aquatic life, microorganism and insects (Miller, 2004).

The excess of phosphorus will cause eutrophication which will cause an imbalance in the "production versus consumption" of living material in an ecosystem. The system then reacts by producing more phytoplankton and vegetation than can be consumed by ecosystem. This overproduction can lead to a variety of problems ranging from anoxic waters (through decomposition) to toxic algal blooms and decrease in diversity, food supply and habitat destruction (Miller, 2004). In order to avoid above environmental consequence, the excess of phosphate need to be treated before discharge into the environment. Recently, phosphate is treated using chemical, biological and physical treatment processes which have their own advantages and disadvantages. However, these treatments incorporate with expensive cost of treatment. In addition, employing environmental friendly methods for treatment is emphasized much more these days. The utilization of paper mill sludge as adsorbent for phosphate removal could help in this regard, in addition to reuse of these waste materials, can be an advantage.

Considering the environmental problem from both solid waste of paper mill sludge and phosphates contamination, the removal of phosphate using paper mill sludge may be one of a good solution for both problems. The objectives of this study are as follow:

1. To characterize the paper mill sludge using inductively coupled plasma-mass spectrometry) ICP-MS, fourier transform infrared spectrometry (FTIR), and X-ray diffraction (XRD).
2. To study the sorption of phosphate from aqueous solution by using paper mill sludge as an adsorbent. The effects of pH, initial concentration of phosphate, amount of paper mill sludge and contact time were examined.
3. To study the adsorption kinetics and adsorption isotherm of phosphate by paper mill sludge.
4. To examine the efficiency of paper mill sludge for removal of phosphate from fresh water samples.

CHAPTER 2

LITERATURE REVIEW

2.1 SOLID WASTE IN MALAYSIA

Solid wastes are defined as wastes resulted from human and animals activities that are normally unwanted and solid. Solid waste can be classified with a variety of scheme such as physical (solid, liquid, or gasses), original use (packing waste), materials (glass, paper, or plastics), physical properties (combustible, compostable) origin (domestic, commercial, industrial, agricultural) and safety parameters (hazardous, radioactive) (Agamuthu, 2001).

The generation of excessive solid waste has become one of the most serious problems due to rapid urbanization and substantial economic development in recent decades. In Malaysia, the amount of solid waste generated increased from 16,200 tonnes per day in 2001 to 19,100 tonnes in 2005 or an average of 0.8 kilogram per capita per day (Economic Planning Unit, 2006). Industrial sector in Malaysia contributed 30% of solid wastes and that wastes generation increased at about 4% annually (Nasir et al., 1998).

In future, the generation of solid waste will be more burdens and this problem needs to be addressed urgently for the sake of environmental protection. Nowadays, the most widely method worldwide for the disposal of solid waste is through land filling. However, the continuous growth in solid waste generation suggests that particularly countries will run out of landfill space far earlier than expected. In addition, the recovery rate of the disposed solid waste in the world's urban cities is still less than 30% out of the total solid waste generated annually on average (Babel and Kurniawan, 2003).

2.1.1 Solid Waste Management

Many governments had taken various strategies include introducing the concept of integrated solid waste management (ISWM) for effective way to manage and minimize the impact of solid waste generation. An effective ISWM system considers how to prevent, recycle, and manage solid waste in such ways that most effectively protect human health and the environment. ISWM involves evaluating local needs and conditions, and then selecting and combining the most appropriate waste management activities for those conditions. Waste prevention comes as a prior plan within the concepts of ISWM. Waste prevention strategies include using less packaging, designing products to last longer, and reusing products and materials. Waste prevention will helpto reduce handling, treatment, and disposal costs and ultimately reduces the generation of methane. The second plan of ISWM is recycling. Recycling is a process that involves collecting, reprocessing, and recovering certain waste materials such as glass, metal, plastics and paper to make new materials or products. Recycling generates many environmental and economic benefits such as jobs opportunity, supply valuable raw materials to industry, and reduce greenhouse gas emissions and the number of landfills and combustion facilities(Agamuthu, 2001).

As a part of integrated solid waste management (ISWM) plan above, the disposed solid waste, representing unused resources which cannot be reduced, reused and recycled in the production anymore such as industrial by-product that can be used for alternative beneficial application. Previously, these wastes usually end up with ultimate disposal such as land filling or combustion. However, coming of 21st century, the researchers keep on finding alternatives to utilize these wastes for sustainable waste management. For examples, recent study had been done on using these wastes as concrete additive, sub-base of roads constructions, soil stabilization, and geotechnical fill material in constructionprojects, daily cover at landfills, energy recovery, and aggregateproduction (Bureau of waste management, 2002).

Another alternative solid waste management is the utilization of waste product as low cost materials to treat contaminated wastewater with heavy metals, refractory compounds, and/or emerging contaminants (Babel and Kurniawan, 2003). Some of these materials can be used as adsorbents with little processing. Conversion of these materials into activated carbon, which can be used as an adsorbent for water purification, would improve economicvalue, helping industries reduce the cost of waste disposal in landfills (Kurniawan et al., 2006a; 2006b; 2006c).

2.2 ADSORPTION

2.2.1 Introduction

Adsorption refers to an accumulation of a substance at an interface between two phases such as solid and liquid or solid and gas. A substance that accumulates at the interface is called ‘adsorbate’ and the solid on which adsorption occurs is ‘adsorbent’. At the surface of the solids, there are unbalanced forces of attraction which are responsible for adsorption. In cases where the adsorption is due to Van der Waals forces, it is called physical adsorption which is the weak attraction force. On the other hand, there may be a strong force result from chemical bonding between adsorbent and adsorbate molecule and such type of adsorption is referred as chemisorption (Dabrowski, 2001).

Among various available water treatment technologies, adsorption process is considered better because of convenience, ease of operation and simplicity of design (Faust and Aly, 1987). The adsorption treatment is the one of the easiest, safest and most cost-effective method because it is widely used in effluent treatment process (Balkose and Baltacioglu, 1992). In the last few years, adsorption has been shown to be an economically feasible alternative method for removing trace metals from wastewater and water supplies (Allen and Brown, 1995; Gabaldon, et al.,1996; Mahvi, 2008). Adsorption also is an effective purification and separation technique used in industry, especially in water and wastewater treatments (Al-Asheh et al.,2000).

2.2.2 Adsorbent from Solid Waste

A number of commercial adsorbent had been used for water pollution control. Some of them are activated carbon, zeolites, silica gel, and activated alumina. Among them, activated carbon is the most popular and widely used adsorbent in wastewater treatment. Activated carbon is produced by a process consisting of raw material dehydration and carbonization followed by activation. The activated carbon can remove different types of pollutants such as metal ions, anions, dyes, phenols, detergents, pesticides, humic substances, chlorinated hydrocarbons and many other chemicals and organisms (Bhatnagara and Sillanpaab, 2010).However, the application of activated carbon is restricted due to higher cost of production. In order to reduce the cost, the researchers are now interested in looking for a low cost adsorbent for water pollution control. Large quantities of agricultural waste or industrial by-products can be utilized as low-cost adsorbents. The use of these wastes will help the industries to reduce the cost of waste disposal in landfills, and most importantly, provide a potential alternative to costly activated carbon (Kurniawan et al., 2006a; 2006b; 2006c). A review about the adsorption capacities of various type of low cost adsorbent for different types of adsorbate are summarized and shown in the Tables 1.1, 1.2 and 1.3.

Table 1.1: Adsorption capacities of different agro-industrial wastes as adsorbents in removal of various pollutants from water.

No	Type of adsorbent	Adsorbate	Adsorption capacity (mg/g)	Reference
1	Rice husk	Cd(II)	8.58	Kumar and Bandyopadhya, 2006
		p-Chlorophenol, p-Nitrophenol	14.36, 15.31	Ahmaruzzaman and Sharma, 2005
2	Wheat bran	Pb(II)	69.0 – 87.0	Bulut and Baysal, 2006
3	Tea waste	Cu(II) and Pb(II)	48–65	Ahluwalia and Goyal, 2005
		Zn(II)	8.9	Wasewar et al., 2009
4	Coconut bunch waste	Methylene blue	70.92	Hameed et al., 2008
5	Coconut copra meal	Cd(II)	4.99	Ho and Ofomaja, 2006
6	Peanut hull	Cu(II)	21.25	Zhu et al.,2009
7	Orange peel	Ni(II)	158	Ajmal et al, 2000
8	Banana peel	Cd(II)	35.52	Memon et al., 2008
		Phenolic compounds	689	Achak et al., 2008
9	Chestnut shell	Cu(II)	12.56	Yao et al., 2009
10	Hazelnut shell	Pb(II)	28.18	Pehlivan et al., 2009
11	Sunflower stalks	Copper, cadmium, zinc, and chromium	29.3, 30.73 42.18 , 25.07	Sun and Shi, 1998
12	Sugarcane bagasse	Cd(II), Zn(II)	38.03, 31.11	Mohan and Singh, 2002

Table 1.2: Adsorption capacities of different industrial wastes as adsorbents in removal of various pollutants from water.

No	Adsorbent	Adsorbate	Adsorption capacity (mg/g)	References
1	Fly ash	Cu(II)	1.39	Panday et al., 1985
		Hg(II)	2.82	Sen and Arnab, 1987
		As(V)	19.46	Li et al., 2009
		Phenol, 4-Chlorophenol, 2,4-Dichlorophenol	5.58 – 6.48, 8.62 – 10.0, 8.16 – 8.72	Haribabu et al., 1993
2	Blast furnace slag	As(III)	1.40	Kanel et al., 2006
		Pb(II) and Cr(VI)	40, 7.5	Srivastava et al., 1997
3	Blast furnace sludge	Pb(II), Cu(II), Cr(III), Cd(II) and Zn(II)	64.17 – 79.87, 16.07 – 23.66, 9.55 – 16.05, 6.74 – 10.15, 4.25 – 9.65	Lopez- Delgado et al., 1998
4	Red mud	Cu^{2+}, Zn^{2+}, Ni^{2+}, Cd^{2+}	19.72, 12.59, 10.95, 10.57	Lopez et al., 1998
		Pb(II) and Cr(VI)	64.79, 35.66	Gupta et al., 2001
		Phosphate	0.58	Huang et al., 2008
5	Solid waste from leather industry	As(V) and Cr(VI)	26, 133	Oliveira et al., 2008
6	Waste Fe(III)/Cr(III) hydroxide	Phosphate	6.5	Namasivayam and Prathap, 2005

Table 1.3: Adsorption capacities of different types of sludge as adsorbents in removal of various pollutants from water.

No	Adsorbent	Adsorbate	Adsorption capacity (mg/g)	References
1	Metal hydroxide sludge	Red ink	34.48	Netpradit et al., 2004
		Remazol Brilliant Blue	91.0	Santos et al., 2008
2	Sewage sludge	Direct Dark Brown M, Acid Mordant Brown RH	502, 329.7	Chen et al., 2005
		Cu(II), Cr(III),	77 – 83	Rio et al., 2005
		Phenol	41 – 53	
3	Dried activated sludge	Phenol, o-chlorophenol and p-chlorophenol	86.1, 102.4, 116.3	Aksu and, Yerner, 1998
4	Distillery sludge	Cr(VI)	5.7	Selvaraj et al., 2003
5	Biological sludge	Phenol	50	Rio et al., 2006

2.2.3 Paper Mill Sludge as Adsorbent

The pulp and paper industry generates a considerable amount of wastewater from various processes in the production of pulp and paper manufacturing. Before discharge into the receiving waters, mill wastewater usually undergoes sedimentation and biological treatment, which results in the production of considerable quantities of sludge. This condition becomes a major solid waste problem for the pulp and paper industry. Expensive treatment of land disposal necessitates other means of treatment which is more economical and other alternatives used of these waste for beneficial application. Recently, some alternatives used of paper mill sludge in order to reduce the solid waste problem are such as the use in application on landfill cover material (Gellman, 1998),land reclamation and forestry (Pichtel et al., 1994; Bellamy et al., 1995; Rodella et al., 1995; Lo et al., 1996; Beyer et al., 1997), in building material such as ceramics (Wiegand and Unwin, 1994), cements (Naik et al., 2004), concrete (Naik et al., 2004), and bricks (Andreola et al., 2005).

Paper mill sludge also can be used as low cost adsorbent for removal of harmful compound from water. Paper mill sludge is a cheap raw adsorbent with high capacity to retain heavy metal(Battaglia et al., 2003), ammonium ions (Okada et al., 2007) and also phenol compound (Calce et al., 2002). This sludge appears to be extremely suitable for reducing environmental pollution due to the presence of toxic chemicals in water. Srivastava et al. (1997) had investigated the adsorption of Pb^{2+} and Zn^{2+} using black liquor which was a waste product originated from paper industry. High adsorption capacity was reported as 1865 mg/g for Pb^{2+} and 95 mg/g for Zn^{2+}at 40ºC. Shimada and co-workers (1999)used waste newspaper as raw material for the production of activated carbon. The developed adsorbent showed a good adsorption capacity of iodine and that of methylene blue which is 1310mg/g and 326mg/g respectively.

The adsorption of phenols on paper mill sludge was studied by Calce et al. (2002). The retention capacity of paper mill sludge was found in the following order: 2-nitrophenol, 4-nitrophenol < 2-chlorophenol < phenol < 4-chlorophenol ≤ 3–chlorophenol <2,4 dichlorophenol < 3,4-dichlorophenol, 2,4,5-trichlorophenol < 3,5-dichlorophenol. They also studied the removal of metal ion from water by sorption on paper mill sludge. The breakthrough curves showed that cadmium, copper, lead and silver could be removed from acid solution with the affinity series as follow: Pb(II) > Cu(II) > Ag(I) > Cd(II).

The adsorption of cadmium and lead by paper mill sludge-soil mixture was investigated by Battaglia et al. (2003). Their results showed that the addition of paper mill sludge in the mixture enable to increase the capability of retention of heavy metal. The increase isdue to the interactions between the paper mill sludge and the soil with modification of sorbing sites that reach equilibrium condition.Paper mill sludge also had been investigated for removal of Orange G dye which is an ionic dye from solution (Bhatnagar et al., 2007). The adsorptioncapacity of paper mill sludge adsorbent for orange G dye was foundto be 62.3 mg/g at 25 ºC.

In addition, Mendez et al. (2009) studied the removal of copper ionfrom water using adsorbents prepared from paperindustrial waste (de-inking paper sludge and sludge from virginpulp mill). Experimental results showed that de-inking paper sludge lead to mesoporous materials whereas the sludge from virgin pulp mill produced high microporous adsorbents. During water treatment, heavy metals lixiviation from adsorbent materials was not produced. However, calcium and magnesium leaching were observed.In general, the highest copper ion removal was obtained using adsorbent materials from de-inking paper sludge. This result could be due to their higher content in oxygenated surface groups, high average pore diameter, elevated superficial charge density, high $CaCO_3$ amount and high calcium and magnesium exchange content.

2.3.0 PHOSPHATE REMOVAL

2.3.1 Introduction

Phosphorous is one of the major nutrients which contribute to anincrease in eutrophication of lakes and natural waters. Phosphate in industrial wastewater can be removed by physicochemical and biological methods. The main commercial processes for removing phosphorus from wastewater effluents are chemical precipitation. Chemicals such as lime, alum, and ferric chloride are the common precipitants used for phosphate removal but their cost and sludge production make chemical treatment an unattractive option for wastewater treatments (Ugurlu and Salman, 1998).

Biological treatment also had been used to remove phosphate. However, this treatment can hardly reduce the concentration of phosphate to lower concentration due to the fact that phosphate is one of the necessary elements for metabolism of microorganisms, and some microorganisms cannot live in the absence of phosphate (Zhao and Sengupta, 1998). Enhanced biological treatment can remove up to 97% of total phosphorus, but this process can be highly variable due to operational difficulties.

Among these available approaches, chemical precipitation and biological removal are generally unable to meet the stringent effluent standards while reverse osmosis is a high capital cost. However, the adsorption methods proved to be more promising due to their low cost, effective treatment in dilute solutions, and high uptake capacity (Gaosheng et al., 2009). Adsorption is comparatively more useful and economical approach for the removal of phosphate from industrial wastewater, particularly for the treatment of low concentration of phosphate.

2.3.2 Phosphate Adsorption Using Industrial Waste

Some industrial by-products have been used as adsorbents for the removal of phosphate from wastewater. The advantage of using these by-products as adsorbents is cost effectiveness in addition to the alleviation of environmental pressure caused by industrial by-products (Namasivayam et al., 2005). It would be one of the useful ways if materials with good uptake ability can be prepared from waste material to overcome both the water pollution and waste problems at the same time.

In 2004, Zeng et al. investigated the effectiveness of iron oxide tailing from mineral processing industry for removal of phosphate from wastewater. The adsorption capacity of iron oxide tailing was 8.21 mg/g. The result indicates that the phosphate adsorption on the tailings tended to decrease with an increase of pH. Desorpability of phosphate was low, approximately 13–14% and this was resulted from a strong bonding between the adsorbed $PO_4^{3-}$and iron oxides in the tailings.

Phosphate removal also had being studied by Namasiyavam et al. (2004) usingzinc chloride ($ZnCl_2$) activated coir pith carbon.Coir pith is a light fluffy material, which is generated in the process of separation of the fiber from coconut husk. Langmuir adsorption capacity was found to be 5.1 mg/g. Adsorption followed second-order kinetics. The maximum removal of phosphate was in the pH range between 3 and 10. pH effect and desorption studies showed that adsorption occurred by both ion exchange and chemisorptions mechanisms. Adsorption was found to be spontaneous and endothermic.

In 2004, Ensar investigated the removal of phosphate by blast furnace slag which was a residue from steel–iron factory processes. The kinetics of adsorption of PO_3^{4-} by blast furnace slag were found to be fast, reaching equilibrium in 20 minutes and following a pseudo second-order rate equation. The enthalpy (ΔH) and Gibbs free energy (ΔG) values of PO_3^{4-} adsorption on the blast furnace slag showed endothermic heat of adsorption. The negative free energy value, indicating that the process of PO_3^{4-} adsorption was favored at high temperatures.

Moreover, Kumar et al. (2007)used metal-loaded orange waste to remove phosphate contaminant from wastewater. The percentage of phosphate removal using La(III) and Ce(III)-loaded orange waste gel increased with increasing pH within the range of 5to 7 but decreased when the pH increased beyond this range. The equilibrium sorption was observed to be in accordance with Langmuir type adsorption and the maximum adsorption capacity was evaluated as 13.94 mg/g of dry gel for all the three types of gels. Kinetic studies revealed that 15 hours was enough to reach equilibrium in batch experiments.

Other work on phosphate adsorption was carried out by Xue et al. (2009). They conducted a research using basic oxygen furnace slag which was the waste from basic oxygen furnace steel making process. The adsorption capacity of basic oxygen furnace slag was found to be from 4.97 to 3.71 mg/g slag when the solution pH was increased from 2.0 to 13.0 indicating that adsorption capacity was largely dependent upon the pH of the system. Other low cost adsorbent used to adsorb phosphate from waste water was iron hydroxide-eggshell waste. This study was carried out by Mezzennerand Bensmaili (2009). Adsorption capacity of iron hydroxide eggshell was 14.49 mg/g. The kinetics of phosphate sorption by the waste material was fast, reaching 73% of the total adsorption capacity in 30 minutes.

2.3.3 Adsorption of Phosphate Using Paper Mill Sludge

Many studies were carried out using paper mill sludge to adsorb phosphate from water solution. However, all the studies underwent various pre-treatment to the sludge before use in phosphate adsorption. Khalili et al. (2002) successfully converted paper mill sludge into activated carbon by chemical activation using $ZnCl_2$. Moreover, Wajima et al.(2006) synthesized Zeolite Na-P1 from paper mill sludge using low temperature hydrothermal treatment at 90ºC which exhibited a high cation exchanged to sorb phosphate by precipitation of calcium phosphate without addition of extra calcium.

In 2006, Vinay et al. studied the amorphous $CaO-Al_2O_3-SiO_2$ prepared from solid state reaction of kaolinite and $CaCO_3$ by calcining paper sludge at 500-1000ºC. The result showed excellent sorption properties for various heavy metals, and eutrophication related phosphate and ammonium ions. In addition, Okada et al.,(2007), studied the hydrothermal treatment of mixtures of paper sludge with various silica and calcium sources to synthesized Al containing $CaO-SiO_2-H_2O$ for simultaneous uptake of eutrophication related to ammonium and phosphate ions.

Taking into account all the results cited above, most researchers studied the removal of phosphate by modification of paper mill sludge before using for phosphate removal. Nevertheless, in this study, raw paper mill sludge was used for phosphate adsorbent without any modification.

CHAPTER 3

METHODOLOGY

3.1 SAMPLING OF PAPER MILL SLUDGE

Paper mill sludge sample was collected from Union Paper Industries Sdn. Bhd. in Bentong, Pahang. The factory involved in paper and printing business and its main products was tissue products such as toilet tissues, facial tissues, and serviette and kitchen towels. The paper mill sludge was collected randomly and packed in plastic bag before kept in the freezer prior to further experimental steps.

3.2 PREPARATION OF ADSORBENT MATERIAL

Paper mill sludge was first crushed mechanically with a jaw crusher before shaken for 24 hours with distilled water to remove soluble impurities. The paper mill sludge then was dried in an oven at 110°C for 24 hours, and then crushed mechanically once again to provide smaller particles in order to increase the surface area of the paper mill sludge. Samples were sieved after mechanical crushing to obtain a particle size smaller than 2 mm and store in the desiccators.

3.3 ORTHOPHOSPHATE STOCK SOLUTION

Artificial orthophosphate standard solutions were used throughout the adsorption test. A stock solution of 1000 mg/L in orthophosphate was prepared by dissolving a certain amount of chemically pure sodium dihydrogen orthophosphate in ultrapure water. An aliquot of stock solution then further dilute with ultrapure water to prepare the desire experimental concentration. All standards are daily prepared to avoid possible precipitation of phosphate species.

3.4 PREPARATION OF ELUENT FOR PHOSPHATE ANALYSIS USING ION CHROMATOGRAPHY (IC)

IC eluent was prepared using sodium bicarbonate and sodium carbonate in the ratio of 8:1 in a 500mL of volumetric flask. The eluent was daily prepared to maintain eluent quality andcondition for phosphate quantification.

3.5 ADSORBENT CHARACTERIZATION

Adsorbent materials were characterized as follow:

a. Functional groups of adsorbent were investigated using Fourier transform infrared spectrometry (FTIR).The spectra were recorded on Perkin Elmer FTIR RX1Spectrophotometer at ambient temperature using a KBr disk method. The disk was prepared from finely ground 0.0010 g of the paper mill sludge sample with 0.3000 g of fine grade KBr and then was scanned at 16 scans at wavelength range of 400-4000 cm^{-1}.

b. Qualitative analysis of calcite using XRD

   X-ray diffraction was carried out by using XRD Siemens D5000 diffraction with Cu-K α radiation ($\lambda = 0.15406$nm). The diffractograms were scanned in the theta range of $2\theta = 5°$ to $80°$.

c. Determination of heavy metals in paper mill sludge using ICP-MS

   The samples were subjected to Agilent 7500CE ICP-MS to determine the concentration of metal ions in the paper mill sludge. Before ICP-MS analysis, the paper mill sludge needs to undergo acid digestion pretreatment.About 1 gram of the dried paper mill sludge sample was weighed accurately and placed in the beaker. After that, 10 mL of 1:1 HNO_3 were added to the beaker and covered with a watch glass. The beaker was then heated below the boiling point for 15 minutes and cooled at room temperature. After that, 5 mL concentrated HNO_3 were added to the beaker.The beaker was covered again with a watch glass and continued heating for 30 minutes. Additional HNO_3 was added dropwise until no brown fume was given off.The volume was then reduced to less than 5 mL and then the paper mill sludge was cooled again. 2 mL of distilled water and 3 mL of 30% H_2O_2 was added and continued the heating until effervescence ceased. The process was continued for approximately 2 hours and the volume was reduced to less than 5 mL. After that, 10mL of concentrated HCl was added and the paper mill sludge was heated again below the boiling point for 15 minutes.Finally, the paper mill sludge was filtered and transferred to a 100 mL volumetric flask and diluted to the mark with dionized water 100 times before analyzing using ICP-MS for heavy metal analysis.

3.6 BATCH ADSORPTION STUDY

The batch experiment was carried out with a defined amount of adsorbent sample in a 100mL bottle sample. A defined volume of the phosphate concentration was prepared from a stock solution by adding ultra pure water. The pH of the phosphate solution was then adjusted to the desired value and added to the bottle container. The mixture was stirred at 200 rpm for a defined period. After a certain period of stirring, filtering process was applied to separate solid from liquid. The supernatant then subjected to ion chromatography for analysis. The percentage of phosphate removal and the adsorption capacity were calculated as below:

$$\text{Percentage removal (\%)} = \frac{\text{(Initial concentration – Final concentration)}}{\text{Initial Concentration}} \times 100$$

$$\text{Adsorption Capacity (mg/g)} = \frac{\text{(Initial Conc. – Final Conc.) x Volume of solution (L)}}{\text{Weight of adsorbent (g)}}$$

a. Effect of pH

The effect of pH on the removal of orthophosphate species, through adsorption onto paper mill sludge was examined in the pH region between 7 and 12. The tests were carried out at constant experimental conditions with an initial solution concentration of 80 mg/L orthophosphate in 0.5 g of adsorbent. All the tests were carried out at room temperature and the shaking time was fixed at 30 minutes.

b. Effect of the amount of adsorbent

Batch tests were carried out with various weight of adsorbent from 0.2 g to 1.0 g at optimum pH condition. In all the cases, the phosphate concentration was maintained constant at 80 mg/L while the solid mass of the adsorbent increased. The shaking time was fixed at 30 minutes.

c. Kinetics and thermodynamic adsorption

The study of kinetic and thermodynamic adsorption was carried out with various shaking time starting from 15 minutes until 24 hours at 30°C, 45°C and 70°C. The initial concentration of phosphate is 100 mg/L and the pH was maintained at 12.

d. Effect of initial concentration and Adsorption isotherm

The study of effect of initial concentration and adsorption isotherm was carried out at different initial condition starting from 50 mg/L to 300 mg/L using 0.5 g of adsorbent. The pH of the solution was maintained at 12 and the shaking time was fixed at 24 hours respectively.

3.7 APPLICATION TO FRESH WATER SAMPLES

Fresh water samples from Tasik Taman Jaya and Sungai Batu were then subjected to the treatment at an optimization method to study the effectiveness of paper mill sludge for removal of phosphate in natural water samples. The entire samples were spiked with 20 and 90 mg/L phosphate solution before shaking for 24hours at optimum pH 12.

CHAPTER 4

RESULTS AND DISCUSSIONS

4.1 CHARACTERIZATION OF PAPER MILL SLUDGE

4.1.1 Fourier Transform Infrared (FTIR) analysis

FTIR analysis is important to determine the functional group present in paper mill sludge. Figure 4.1show the various band of functional group in the paper mill sludge which are summarized in Table 4.1. The appearance of bands between 3000 to 3500 $cm^{-1}$and the band around 2800-2900cm^{-1}could be attributed to O-H group of cellulose and the CH_2 groups respectively. The absorption band at 1630 cm^{-1}contribute to the deformation vibration of O-H group (Mendez et al., 2009)

The presence of $CaCO_3$ leads to a broad band at 1416cm^{-1} indicates the abundant of calcite in the paper mill sludge. Meanwhile an absorption band at 1161$cm^{-1}$and 1107cm^{-1} could be attributed to the C-O-C bond while the band 1031cm^{-1} is the vibration of glucose unit ring involving stretching of C-O and O-H. Finally, the absorption band at 872 cm^{-1} corresponds to the C-O-C bond (Mendez et al., 2009).

Table 4.1: Summary of FTIR spectra

Band	Functional group
3000-3500 cm^{-1}	O-H group of cellulose
2800-2900cm^{-1}	CH_2 groups
1630 cm^{-1}	Deformation vibration of O-H group
1416cm^{-1}	Characteristics band of $CaCO_3$
1161$cm^{-1}$and 1107cm^{-1}	C-O-C bonds
1031cm^{-1}	Vibration of glucose unit ring involving stretching of C-O and O-H
872 cm^{-1}	C-O-C bonds

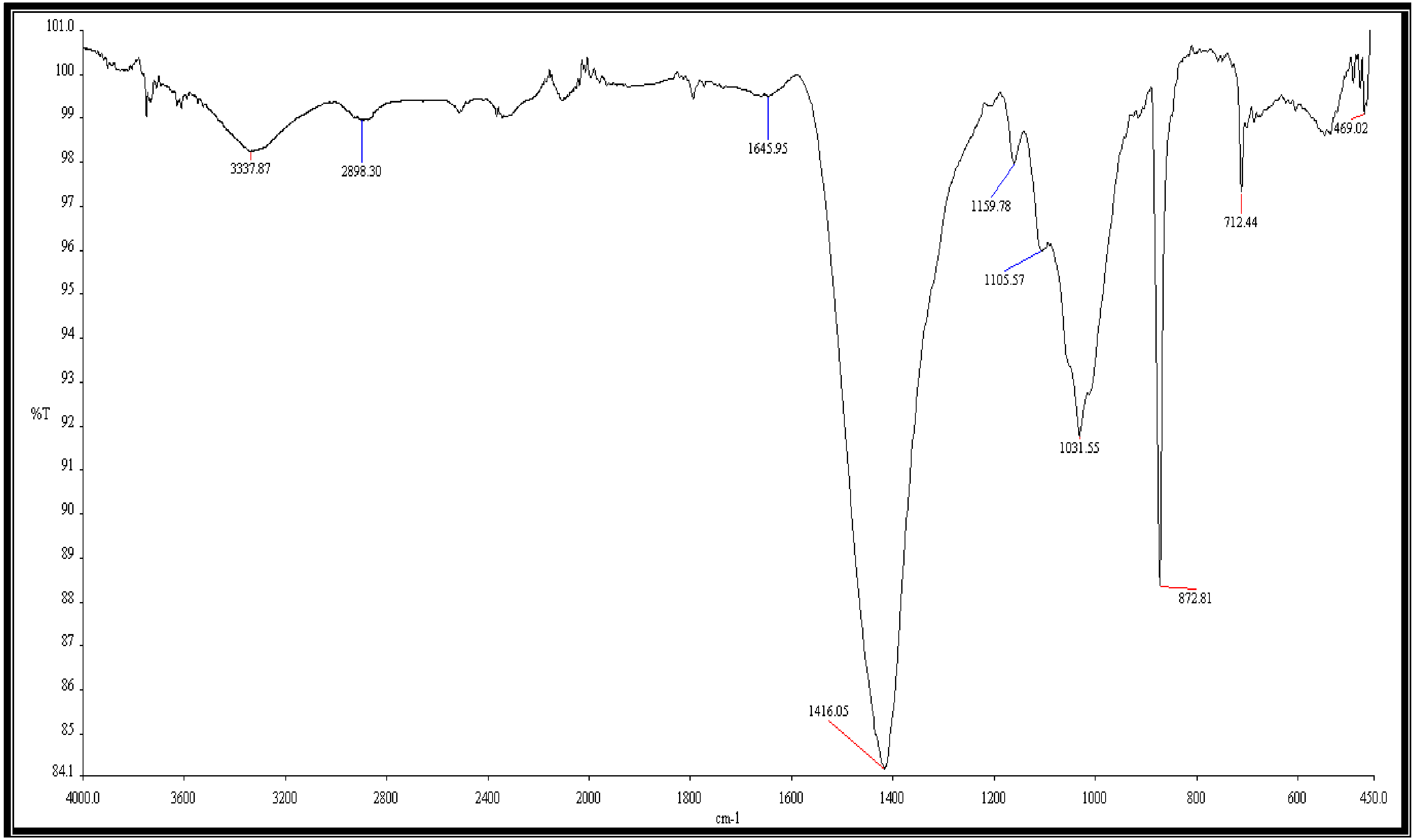

Figure 4.1: FTIR spectra of paper mill sludge

4.1.2 X-Ray diffraction (XRD) analysis

FTIR analysis had shown the broad band of $CaCO_3$ in the paper mill sludge. The presence of $CaCO_3$ was reassured by XRD analysis as shown in Figure 4.2. The most intense peak of calcite is at 2θ ≈ 30º. XRD result confirmed the abundance of $CaCO_3$ in the paper mill sludge. The abundance of calcite in paper mill sludge is important for phosphate adsorption from water solution since its presence will enhance the reaction of calcium phosphate precipitation (Karageorgiouet al., 2007).

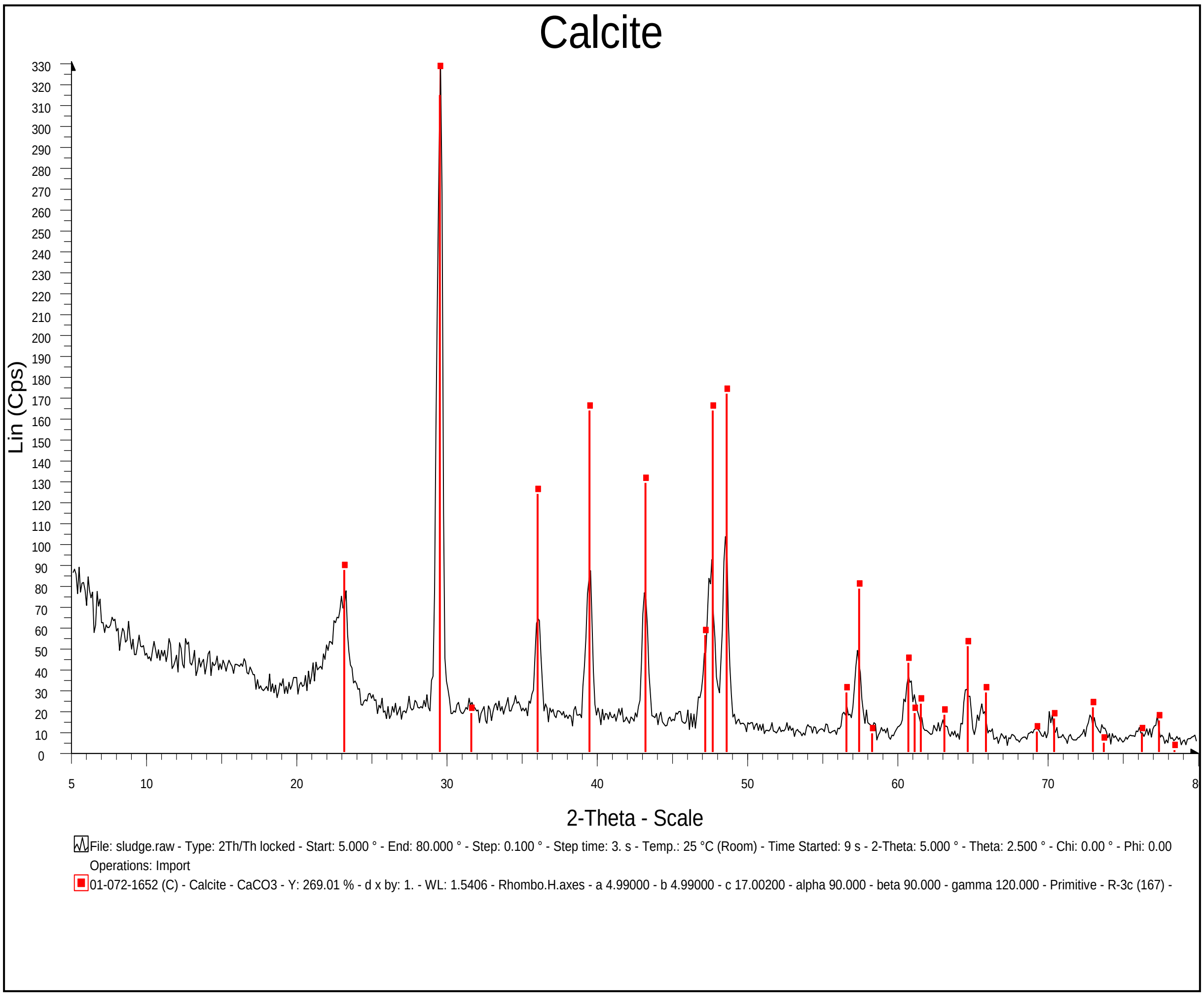

Figure 4.2: XRD plot of calcite in the paper mill sludge

4.1.3 Determination of heavy metals.

It is important to determine the concentration of heavy metal in the paper mill sludge before utilizing it as natural adsorbent. This is to prevent more contamination in the water as a result of contaminated sludge. In this study, determinations of heavy metals in paper mill sludge were carried out and the results obtained are shown in Table 4.2.

Table 4.2: Heavy metal concentration in the paper mill sludge

Elements	Concentration (mg/L)
Copper (Cu)	0.012
Zinc (Zn)	0.028
Lead (Pb)	0.016
Cadmium (Cd)	0.001
Chromium (Cr)	0.006

4.2 BATCH ADSORPTION STUDY

4.2.1 Effect of pH on phosphate removal by paper mill sludge

The pH of a system is an important parameter in adsorption of phosphate species using paper mill sludge as an adsorbent. In this work, the effect of pH was examined in the pH region between 7 and 12. The relationship between the initial pH of the solution with the adsorption capacity of phosphate and percentage of phosphate removal are shown in Figure 4.3. The adsorption capacity is increased from 0.56 mg/g to 2.21mg/g with increasing initial pH from 8 to 12.The orthophosphate uptake is comparatively lower in slightly basic pH region approximately 20% but it increased for higher pH value indicating that the percentage of phosphate removal was 55%.

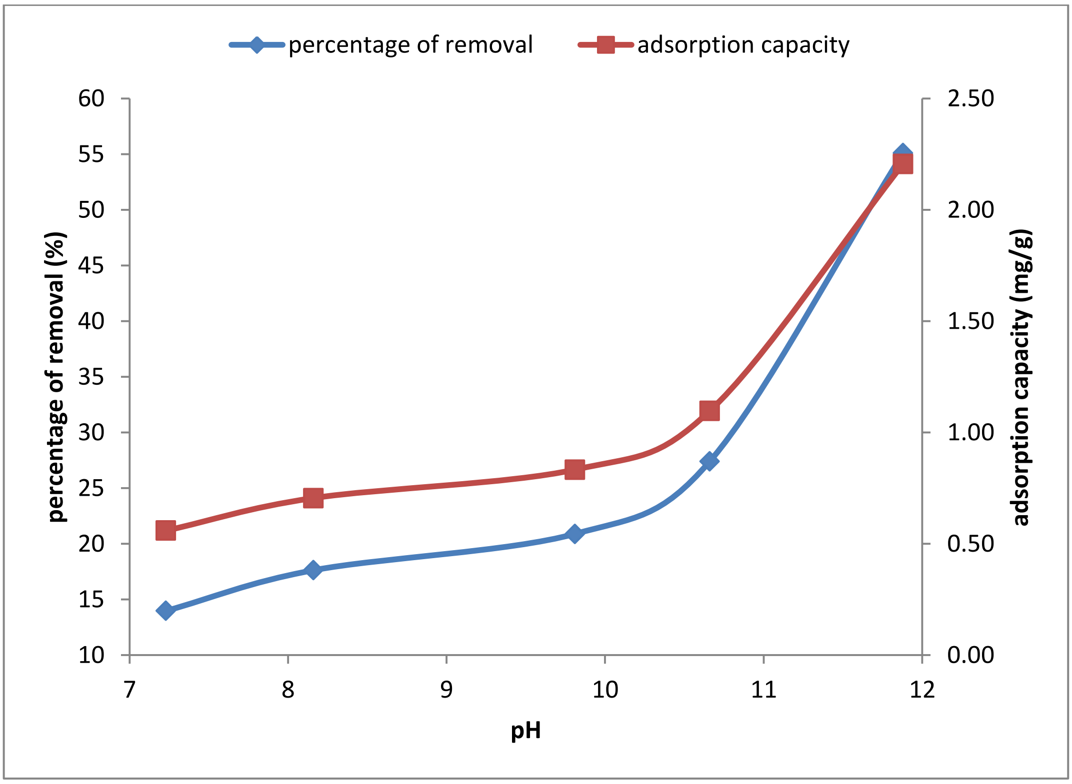

Figure 4.3: Adsorption capacity and percentage of phosphate removal by paper mill sludge at various pH conditions

The protonation reactions of phosphate are illustrated in the speciation diagram in Figure 4.4. It shows that the increasing of pH produced more negative charge to the phosphate species. $H_2PO_4^-$ and HPO_4^{2-} species are present in the pH region between 5-10.The concentration of $H_2PO_4^-$ species is higher for pH below 7 while HPO_4^{2-} species is higher in pH region 7-10. For pH between 10 and 12, HPO_4^{2-} predominates over PO_4^{3-}, but when the pH is higher than 12.5, the concentration of PO_4^{3-} becomes significant and exceeds HPO_4^{2-}.

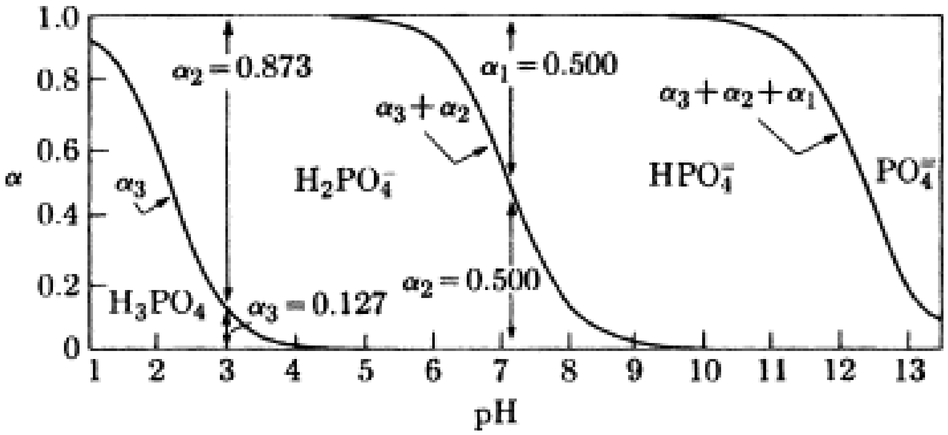

Figure 4.4: Distribution diagram for phosphate present as different protonated species as a function of pH (Karageorgiouet al., 2007)

In the paper mill sludge, hydrolysis reaction of calcite produces cationic species which prevail for pH less than 8 rendering the mineral surface positively charged. For pH more than 8, the negative species is produced but the concentration of the positive species is still considerable (Karageorgiouet al., 2007).

The adsorption process could be possibly described by following reaction:

$Ca^{2+} + H_2PO_4^{-} \longrightarrow CaH_2PO_4^{+}$

$Ca^{2+} + HPO_4^{2-} \longrightarrow CaHPO_4$

$Ca^{2+} + PO_4^{3-} \longrightarrow CaPO_4^{-}$

With the increase of the pH, the deprotonation reaction of phosphate obtained more negative charges which enhance the electrostatic interaction between phosphate species and calcite in the paper mill sludge. Therefore, pH 12 was selected as the optimum pH for phosphate removal from solution.

4.2.2Effect of adsorbent dosageof paper mill sludge on phosphate removal

In this study, the effect of adsorbent dosage was determined at optimum pH 12 by varying mass of adsorbent at shaking time of 30 minutes at room temperature and 100 mg/L of initial phosphate. While increasing the adsorbent mass from 0.2g to 1.0g, the percentage of phosphate removal increases rapidly from 46% to 85%.However, the adsorption capacity decreases from 4.27 to 1.62 mg/g respectively (Figure 4.5).

The increase of phosphate removal with the increase of paper mill sludge amount is due to the increase in surface area and adsorption site available for adsorption. The decline in adsorption capacity is basically due to the site remaining unsaturated during the adsorption process (Suresh and Babu., 2009). For 0.5g of adsorbent dosage, the optimum value of phosphate removal and adsorption capacity are found to be 71% and 2.1mg/g respectively. The amount of paper mill sludge for further adsorption experiment was selected as 0.5g.

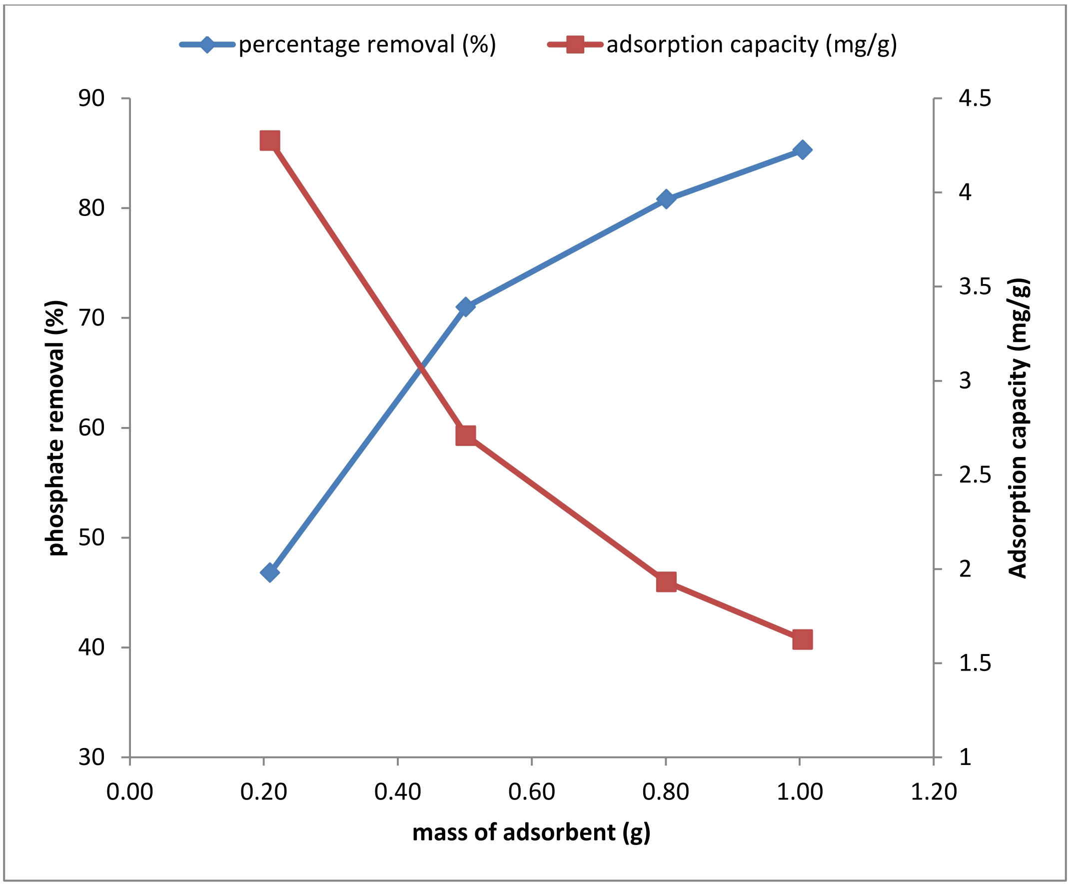

Figure 4.5: Effect of adsorbent dosage of paper mill sludge on the adsorption capacity andpercentage removal of phosphate (pH 12, 30 minutes of shaking time at room temperature, 0.5 g of adsorbent, initial phosphate concentration of 100 mg/L)

4.2.3 Kinetics and thermodynamic adsorption of phosphate by paper mill sludge

The rate of phosphate adsorption by paper mill sludge was measured as a function of time shaking at three different temperatures (30°C, 45°C and 70°C). The adsorption process of phosphate was rapid at the initial stage and rather slowed when approaching equilibrium (Figure 4.6). The equilibrium time for phosphate adsorption can be considered at 24 hours. The kinetics results indicated that the sorption process is increased with increased the solution at temperature 30 to 70°C

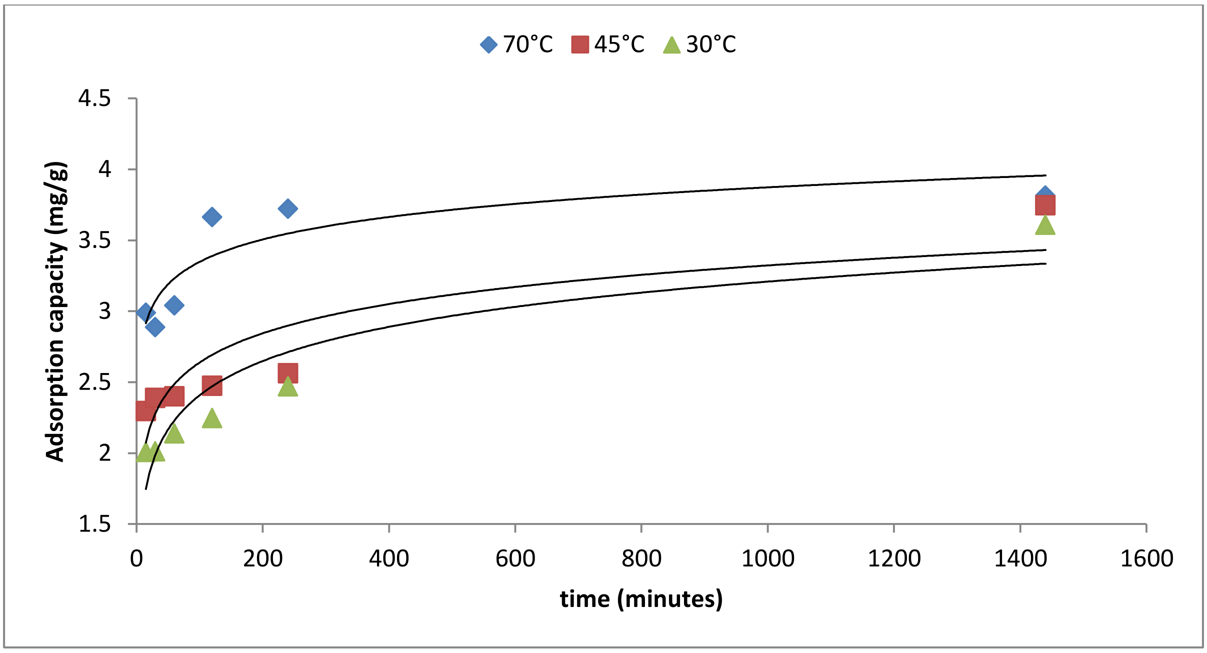

Figure 4.6: Adsorption rate of phosphate by paper mill sludge

The kinetics of removal of phosphate is explicitly explained in the literature using pseudo first order and second order kinetics models (Ho et al., 1998; Ho et al., 1999)

Pseudo-first order kinetics

Non linear form of pseudo first order is given by equation:

$$\frac{Dq_t}{d_t} = K_1(q_e - q_t) \qquad (1)$$

Where K_1 (min^{-1}) is the rate constant of pseudo-first order sorption, $q_t$and $q_e$denotes the amount of phosphates adsorption (mg/g) and the amount of phosphate adsorption (mg/g) at equilibrium and at time (t) in minutes respectively.

The integrated rate law after application of the initial condition of $q_t = 0$ and $t = 0$ becomes linear equation as given by equation below:

$$\ln(q_e - q_t) = \ln(q_e - K_1 t) \qquad (2)$$

Plot of ln $(q_e - q_t)$ versus t gives a straight line for the first order adsorption kinetics, which allow the computation of the adsorption rate constant, K_1

Pseudo-second order kinetics

A pseudo second order equation based on adsorption equilibrium capacity may be expressed as follows:

$$\frac{Dqt}{dt} = K_2(q_e - q_t)^2 \qquad (3)$$

Where K_2 is the rate constant of pseudo second order adsorption.

Integrating equation 3 and applying initial condition gives:

$$\frac{t}{q} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \qquad (4)$$

The plot t/q versus t should give a straight line if second order kinetic is applicable and the value of q_e and K_2 can be calculated from the slope and the intercept of the plot respectively.

For the pseudo first-order, the results obtained from the plots of ln $(q_e – q)$ versus t at different temperature were shown in Figure 4.7. The data do not fall on the straight line and have a low correlation coefficient, indicating that the first-order kinetic model is less appropriate. In addition, the q_e estimated by this model differs substantially from those measured experimentally as shown in Table 4.3.

On the other hand, the second order kinetics fitted very well with the obtained result. The plot of t/q against t in Figure 4.8 gave high correlation coefficient. In addition the data in Table 4.3 showed that the q_e value calculated were similar with the experimental values indicating that the sorption system follows to second-order kinetic model. The second-order sorption rate increased with increase the solution temperature. It may be concluded that the adsorption of phosphate onto paper mill sludge follows physisorption mechanism (Ozcan et al., 2006)

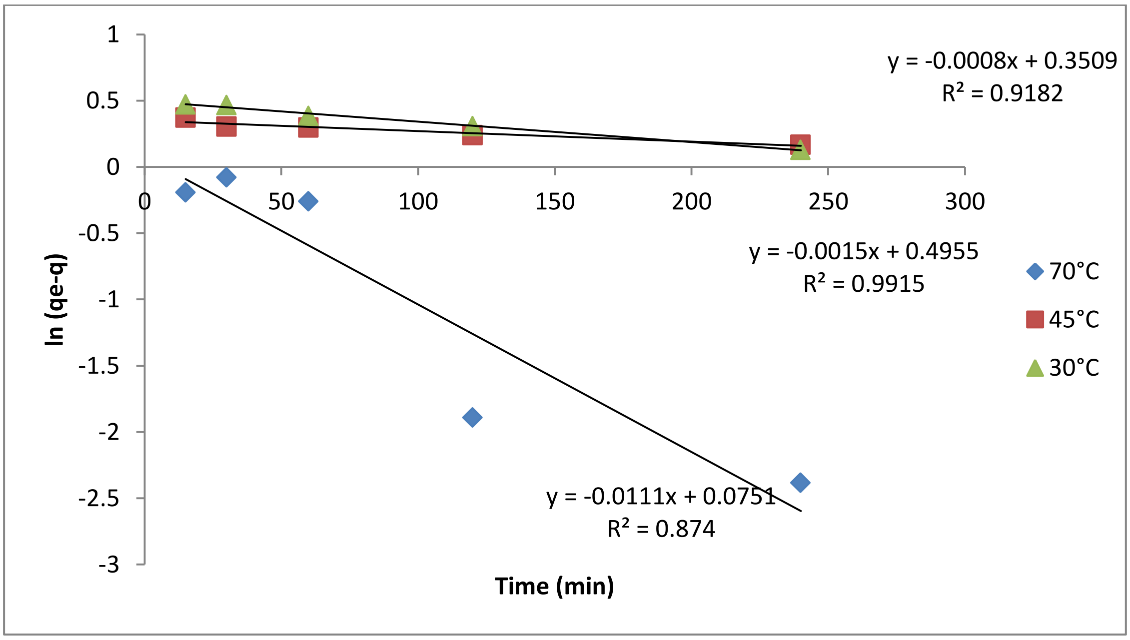

Figure 4.7: First-order kinetic plot for sorption of phosphate by paper mill sludge

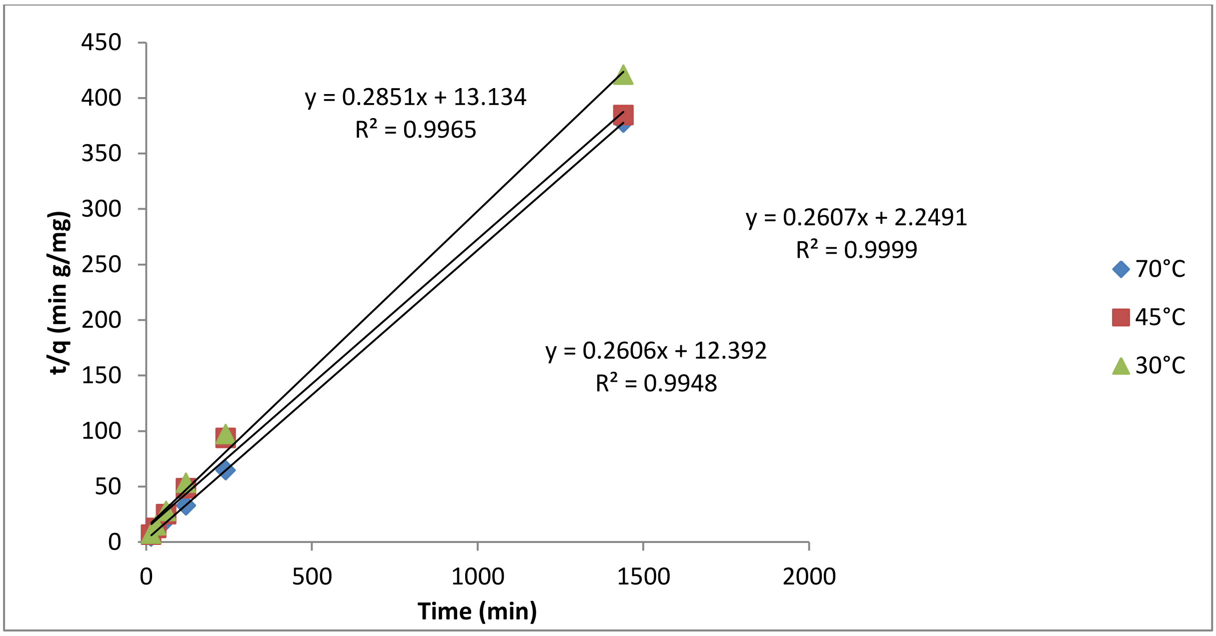

Figure 4.8: Second-order kinetic plot for sorption of phosphate by paper mill sludge

Table 4.3: Kinetic parameter for adsorption of phosphate onto paper mill sludge of various temperature

Temp	pH	q_e (Exp)	First order (minutes^{-1})			Second order (minutes^{-1})		
°C		mg/g	K_1 X 10^{-3}	q_e (mg/g)	R^2	K_2 X 10^{-3}	q_e (mg/g)	R^2
70	12	3.81	11	1.08	0.874	30.22	3.85	0.999
45	12	3.74	2.0	1.40	0.969	8.17	3.77	0.998
30	12	3.61	1.0	1.64	0.991	6.18	3.51	0.996

Table 4.3 shows the adsorption capacity, q_e increased with the increase of temperature from 30°C to 70°C. This indicates that the adsorption process is endothermic. It can be explained by availability of more active sites of adsorbent at higher temperature. The endothermic nature of the process can be confirmed using the enthalpy value (ΔH) as can be calculated using Van Hoff equation given below:

$$\ln K_d = \Delta\frac{S}{R} - \Delta\frac{H}{RT} \qquad (5)$$

K_d is the distribution coefficient which is defined as q_e (the sorption capacity at equilibrium, mg/g divide by Ce (concentration of phosphate at the equilibrium mg/L), R is the gas constant (8.314 J/Kmol) and T is temperature in Kelvin.

The value of enthalpy (ΔH) and entropy (ΔS) can be obtained from the slope and the intercept after the plot, log K_d versus 1/T as shown in Figure 4.9. The enthalpy and entropy value were 57.73 J/mol and 185.9 J/Kmol, respectively.

Meanwhile, Gibbs free energy can be calculated based on an equation as shown below:

$$\Delta G = \Delta H - T\Delta S \qquad (6)$$

Positive value of enthalpy (ΔH) indicates the energy barrier in the adsorption and endothermic process. The positive value of entropy change (ΔS) reflects the good affinity of phosphate ion towards the adsorbent and the increasing randomness at the solid solution interface during the adsorption process. The negative value of Gibbs free energy (ΔG) reflects the adsorption of phosphate onto paper mill sludge which is feasible and spontaneous. The ΔG value decreased from (-56.27 kJ/mol) to (- 63.71 kJ/mol) when temperature increased from 30°C to 70°C, suggesting the more absorbable of phosphate species with increasing temperature (Table 4.4).

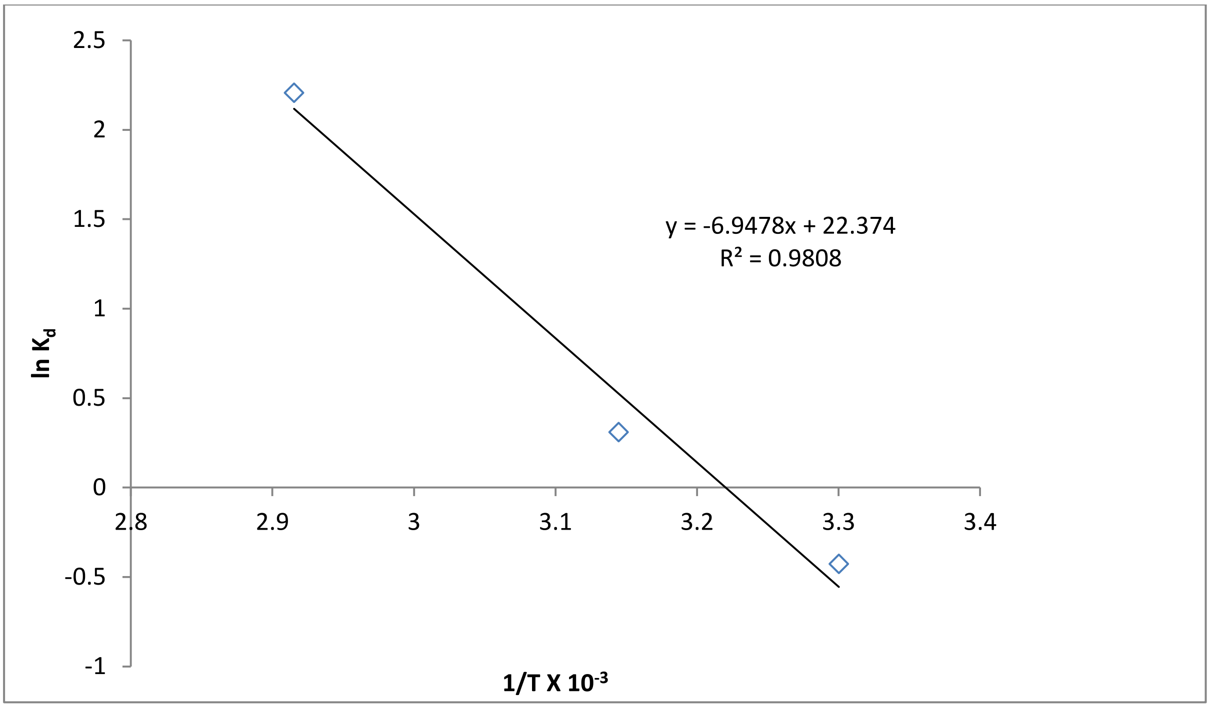

Figure 4.9: Van Hoff plot for sorption of phosphate by paper mill sludge

Table 4.4: The value of Enthalpy, Entropy, and Gibbs free energy

Temperature	Enthalpy, ΔH J/mol	Entropy, ΔS J/Kmol	Gibbs energy, ΔG kJ/mol
70°C	57.757	185.984	-56.295
45°C	57.757	185.984	-59.085
30°C	57.757	185.984	-63.735

The rate constantnormally depends strongly on temperature, typically increasing rapidly with increasing T. The rapid increasing in k as temperature increase is due mainly to the increase in the number of collision whose energy exceeds the activated energy.In Arrhenius, it is noted that the k (T) data for many reactions fit the equation below;

$$\ln K = \ln A - \frac{E_a}{RT} \qquad (7)$$

Where A and E_a are constant characteristics of the reaction and R is the gas constant (8.314 J/Kmol) and T is temperature in Kelvin. E_a is the Arrhenius activation energy and A is the pre –exponential factor or the Arrhenius factor. A plot of ln k versus 1/T is a straight line with slope –Ea/R and intercepts ln A (Figure 4.10). The magnitude of activation energy gives an idea about the type of adsorption which is mainly physical or chemical(Nollet et al., 2003).The value of E_a obtained from the slope is 37.01 J/mol. According to Arrhenius equation, low activation energy reflects a fast reaction while the high activation energy means a slow reaction.

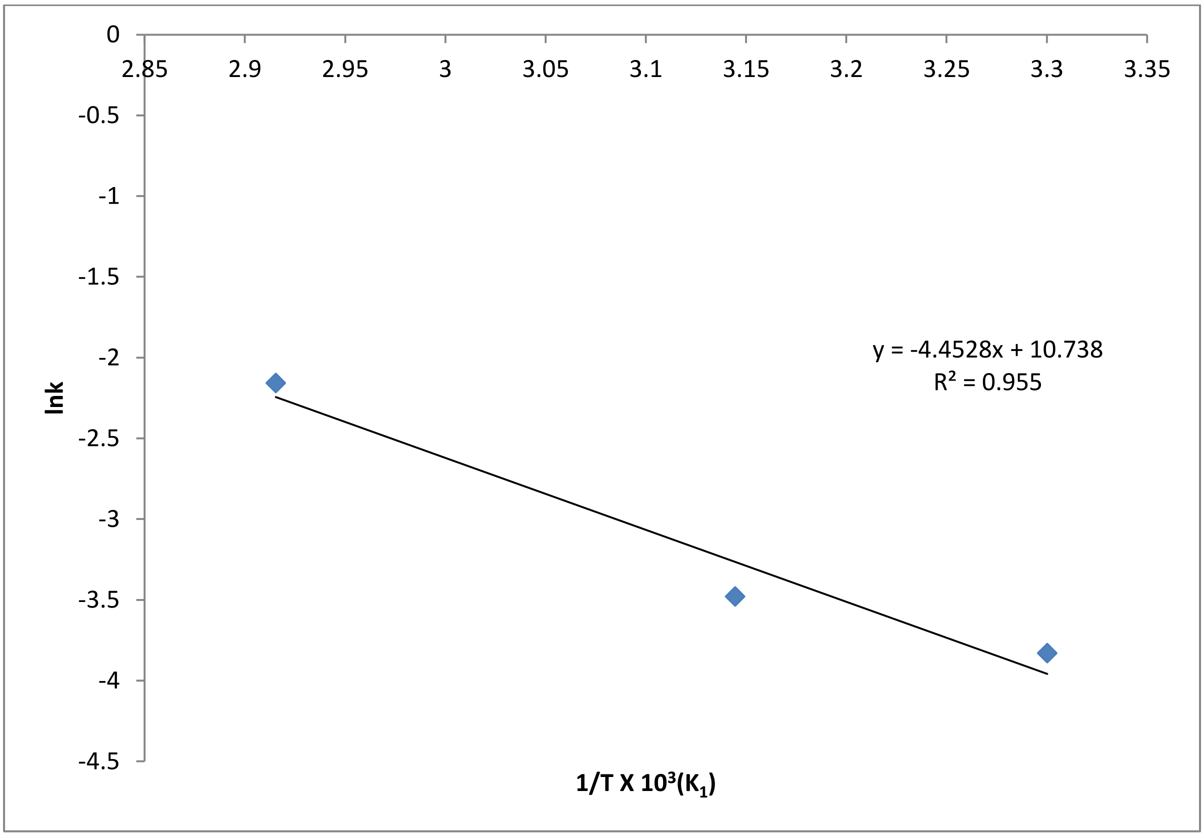

Figure 4.10: Arrhenius plot for adsorption of phosphate by paper mill sludge

4.2.4 Effect of initial concentration of phosphate on adsorption

The adsorption experiments were performed to study the effect of initial phosphate concentration by varying it from 50 to 300 mg/L while maintaining the amount of paper mill sludge amount (0.5 g) and obtained results are presented on Figure 4.11. The results indicate that with the increase in phosphate concentration, the percentage of removal decreases from 95% to 83% and adsorption capacity increases from 2.07 to 9.97mg/g.

The decrease in percentage removal can be explained by the fact that the adsorbent had a limited number of active sites which would become saturated above a certain concentration. The increasing phosphate concentration at constant calcium concentration in the paper mill sludge therefore influences supersaturating and decreases the efficiency of the precipitating system (Song et al., 2002). The increase in adsorption capacity with the increase in phosphate concentration may be due to the utilization of more active sites available in the paper mill sludge for the adsorption at higher concentration (Kamiyango et al., 2009)

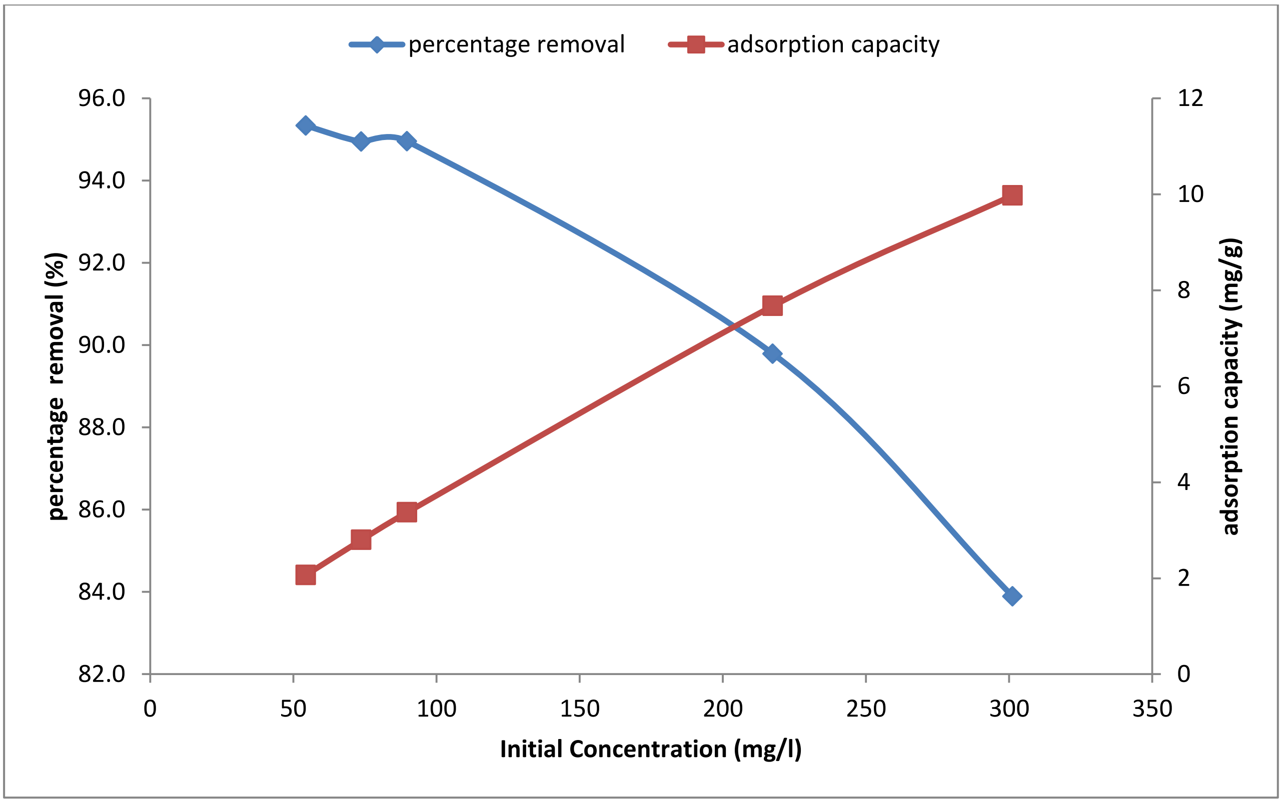

Figure 4.11: Effect of Initial concentration of phosphate on the adsorption capacity and percentage removal of phosphate (Condition: pH 12, room temperature, 24 hours shaking time, 0.5 g adsorbent)

4.2.5 Adsorption isotherm of phosphate by paper mill sludge

The amount of material adsorbed is determined as a function of concentration at constant temperature and could be explained in sorption isotherms. The sorption isotherm of phosphate by paper mill sludge was measured by shaking it for 24 hours at different initial concentration at pH12 at room temperature.

In this study, the isotherm data were analyzed using Langmuir and Freundlich equilibrium models were analyzed to investigate the suitable adsorption isotherm. These two models are commonly used to describe the adsorption equilibrium from aqueous solution.

The adsorption isotherm of phosphate is explicitly explained in the literature using Langmuir (Langmuir, 1918) and Freundlich models (Freundlich, 1906)

I. Langmuir Isotherm

The Langmuir isotherm is used to obtain maximum adsorption capacity produced from complete monolayer coverage of adsorbent surface.

Non linear expression of Langmuir isotherms is

$$\frac{q_e}{Q_m} = \frac{bC_e}{1+bC_e} \qquad (9)$$

where *b* is adsorption equilibrium constant related to the apparent energy of adsorption and Q_m is the quantity of adsorbent required to form a single monolayer on unit mass of adsorbent, and q_e is the amount adsorbed on unit mass of the adsorbent at the equilibrium concentration,$C_{e.}$

The linearized form of this expression is:

$$\frac{C_e}{q_e} = \frac{1}{bQ_m} + \frac{C_e}{Q_m} \qquad (10)$$

The slope and intercept of the plot of C_e/q_e and C_e then gives the value of Q_m and *b*.

The essential feature of the Langmuir isotherm can be expressed in term of dimensionless constant called separation factor,$R_L$which is defined by the following equation:

$$R_L = \frac{1}{(1+bC_e)} \qquad (11)$$

The value of R_L lies between 0 and 1 for a favorable adsorption while R_L more than 1 represents an unfavorable adsorption. R_L = 1 represent the linear adsorption and R_L = 0 is irreversible operation.

The Langmuir equation is plotted between C_e/q_e versusC_e as shown in Figure 4.12. The maximum capacity at equilibrium Q_m which measures the monolayer adsorption capacity of paper mill sludge is obtained as 12.65 mg/g at the optimum pH 12 (Table 4.5). The Langmuir constant b, which denotes adsorption energy, is found to be 0.77. The high value regression correlation coefficient (R^2=0.998) confirmed the monolayer adsorption of phosphate onto the paper mill sludge surface. The adsorption favorability is measured by dimensionless parameter R_L which is found in the range of 0.83 and 0.21.The value of R_L which falls between 0 and 1 ($0<R_L<1$) isshown in Table 4.6, indicating that the adsorption process for phosphate removal using paper mill sludge is favorable.

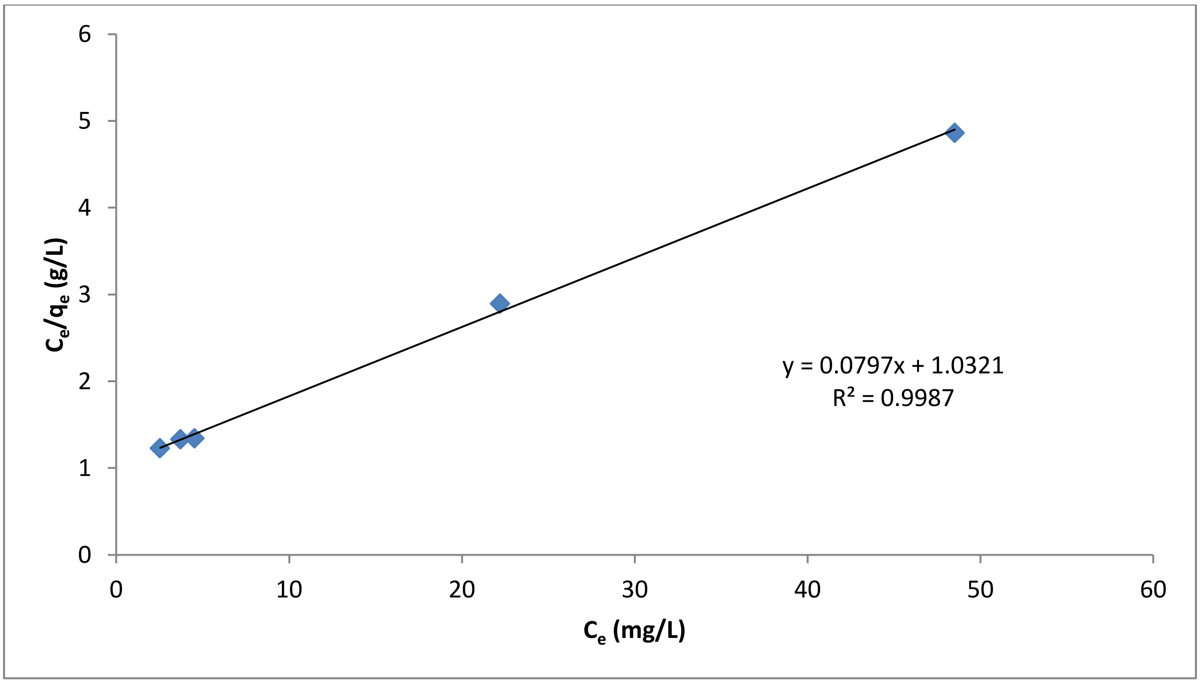

Figure 4.12: Langmuir plot for solution of phosphate by paper mill sludge at room temperature

II. Freundlinch Isotherm

Non linear Freundlinch equation is expressed as:

$$qe = K_f C_e^{nf} \quad (12)$$

where K_f is the Freundlinch constant, indicates the relatives adsorption capacity of the adsorbent related to bond energy and n_f is the heterogeneity factor representing the deviation from linearity of adsorption and is also known as Freundlinch coefficient. K_f and n_f can be determined by linearized equation below:

$$\text{Log } q_e = \log K_f + n_f \log C_e \quad (13)$$

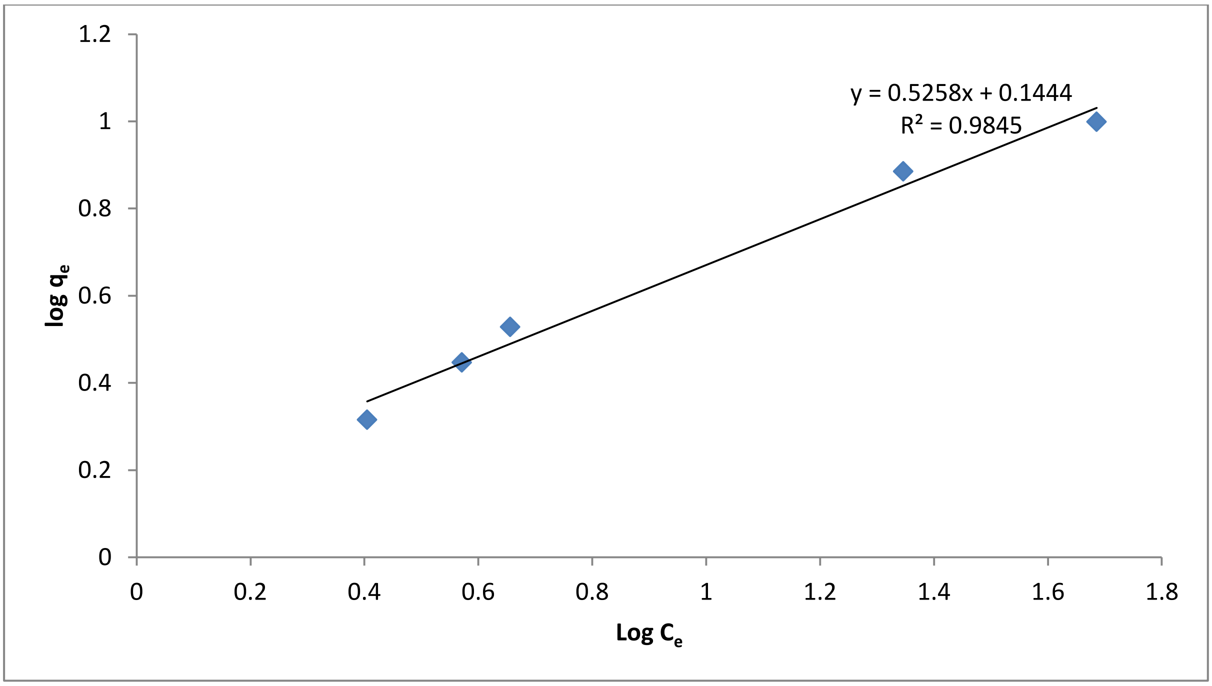

Figure 4.13: Freundlich plot for solution of phosphate by paper mill sludge at room temperature

The Freundlich isotherms were analyzed based on adsorption on the heterogeneous surface using the same equilibrium data of phosphate adsorption on paper mill sludge. Freundlich constant K_f and n were obtained by plotting the graph between log q_e versus log C_e as given in Figure 4.13. The value of K_f and n are 1.393 and 1.905, respectively. It was found that the regression correlation coefficient obtained from Freundlich isotherms model for paper mill sludge was 0.984 which was lower than Langmuir isotherm model. The obtained result indicates that the equilibrium data fit well with the Freundlich isotherms model.

Table 4.5: Isotherm constants and regression data for Langmuir and Freundlich isotherm model for adsorption of phosphate on paper mill sludge

No	isotherm model	isotherm constant		R^2
1	Langmuir	Q_m	12.65 mg/g	0.998
		b	0.077	
2	Freundlich	K_f	1.393 mg/g	0.984
		n	1.905	

Table 4.6: R_L value at different initial concentration of phosphate

No	Initial Phosphate concentration (mg/L)	R_L value
1	60	0.8364
2	80	0.7769
3	100	0.7414
4	200	0.3690
5	300	0.2111

III. Comparison of maximum adsorption capacity (Q_m) of phosphate for some low cost adsorbent

The comparison of maximum adsorption capacity for some low cost adsorbent as shown in table 4.7 clearly indicated that paper mill sludge is an effective adsorbent for phosphate removal from water.

Table 4.7: Reported adsorption capacities (Q_m) of phosphate for some low-cost adsorbent

No	Adsorbent	Q_m (mg/g)
1	Geothite	0.286 (Wang et al., 2008)
2	Natural Zeolite	6.42 (Borggaard et al., 2005)
3	Na-Natural Zeolite	2.15 (Sakadevan and Bavor., 1998)
4	Synthetic iron oxide coated sand	2.19 (Zeng et al., 2004)
5	Coated crushed brick	1.75 (Boujelben et al.,2008)
6	Naturally iron oxide coated sand	0.88 (Boujelben et al.,2008)
7	Iron-hydroxide eggshell	14.49 (Mezenner and Bensmaili., (2009)
8	Iron oxide tailing	8.21(Boujelben et al.,2008)
9	Paper mill sludge	**12.65** (**this study**)

4.3 REMOVAL OF PHOSPHATE FROM WASTEWATER SAMPLES BY PAPER MILL SLUDGE.

Two types of freshwater samples were collected from different area. Sample A was taken from Taman Jaya Lake and sample B was taken from Sg Batu inside University of Malaya. Initial analysis on these sampleshad shown that the phosphate concentration is very low around 0.3-0.5 mg/L. In order to check the efficiency of the phosphate removal by paper mill sludge, thesamples were spiked with 20 and 90mg/L phosphate solution before shaking with 0.5 g of the adsorbent for 24hours at optimum pH 12. The results were compared with the removal using ultrapure water in the previous experiment.

Table 4.8: Percentage removal of phosphate from freshwater sample

	Phosphate concentration		
Samples	Initial mg/L	Final mg/L	% removal
A:Taman Jaya Lake	21.92	5.43	75.23
	97.25	24.21	75.11
B:Sungai Batu	20.15	3.34	83.42
	94.25	15.32	83.75
Ultrapure	21.25	0.52	97.55
	91.2	5.53	93.94

The results tabulated in Table 4.8 show that there are slightly decrease in percentage of phosphate removal from real freshwater samples compared to ultrapure water. This may be due to the presence abundance of matrix interference which normally presentin the real samples that slightly reduce the effectiveness of the paper mill sludge for removal of phosphate.

CHAPTER 5

CONCLUSION AND RECOMMENDATIONS

In conclusion, paper mill sludge has the potential to be used as low cost adsorbent for phosphate removal from aqueous solution effectively. The paper mill sludge was found effective in removing phosphate at higher pH region approximately at pH 12. In kinetic study, it was found that the rate of phosphate adsorption increased rapidly at the initial stage and then reduced until it reached the equilibrium. The adsorption of phosphate reached the equilibrium at 24 hours. When compared to Lagergren pseudo first-order model, second-order kinetic equation is better fit for adsorption kinetic data. The capacity of phosphate increased with increasing initial concentration. The result showed the applicable of Langmuir model for the phosphate adsorption with maximum adsorption capacity of 12.65 mg/g. The adsorption capacity increased with increasing temperature showing the process is endothermic. The enthalpy value is 57.75 J/mol and the value of E_a is 37.01 $Jmol^{-1}$. Comparing adsorption capacitywith other low cost adsorbent in previous studies, it is found that the paper mill sludge shows better adsorption capacity and can be used as adsorbent for phosphate removal from aqueous solution.

Recommendations

1. The effect of phosphate removal using paper mill sludge with the presence of other anions species such as SO_4^{2-}, CO_3^{2-} and NO_3^-
2. Modification of paper mill sludge for better adsorption efficiency
3. To make use of the phosphate-paper mill sludge product for other application such as for acid soil treatment or land application.