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JIMMA INSTITUTE OF TECHNOLOGY

SCHOOL OF CIVIL AND ENVIRONMNTAL ENGINNERING

ENVIRONMENTAL ENGINEERING CHAIR

DESIGN PHOSPHATE REMOVAL TECHNOLOGY USING VOLCANIC ROCKS: KINETICS AND EQUILIBRIUM STUDIES

BY: YOHANNIS FETENE

A THESIS SUBMITTED TO THE SCHOOL OF CIVIL AND ENVIRONMNTAL ENGINNERING, ENVIRONMENTAL ENGINEERING CHAIR, JIMMA INSTITUTE OF TECHNOLOGY, JIMMA UNIVERSITY FOR PARTIAL FULFILMENT OF THE REQUIREMENTS OF THE MASTER OF SCIENCE IN ENVIRONMENTAL ENGINEERING.

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October, 2015

Jimma, Ethiopia

Declaration

I, the undersigned, declare that this research paper is my original work and has not been presented for a degree in any other university and that all sources of materials used for the research proposal has been duly acknowledged.

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Abstract

Phosphorous discharged into the water bodies stimulates the growth of aquatic micro and macro organisms in nuisance quantities, which in excess can cause eutrophication in stagnant water bodies. Phosphorous removal from water and wastewater has been achieved by methods such as coagulation, chemical precipitation, biological treatment, ion exchange and adsorption. Adsorption by volcanic rocks is investigated as a possible alternative to conventional method of pollutant removal from aqueous solutions. In this work adsorption of P(V) on to Scoria (VSco) and Pumice (VPum) has been studied by using a batch method at room temperature. The effect of various design parameters, i.e. contact time, initial pH, adsorbent dose, agitation speed, adsorbent particle size, and initial P(V) ion concentration using the VPum and VSco, has been studied. The sorption process was relatively fast and equilibrium has been reached at 60 min contact time and the maximum adsorption yield, 92.50% for VSco and 94.70% for VPum , was obtained at an adsorbent loading weight of 15 g/L for VSco and 10 g/L for VPum. Kinetic data of P(V) adsorption followed well the pseudo-second order equation (R^2>0.99) suggested the chemisorptions mechanism of P(V) adsorption on VPum and VSco. The overall uptake for the VPum and VSco were maximum at pH 6 and 7 respectively. The sorption data were better represented by the Freundlich isotherm (R^2 = 99, 98: SSE ≈ 0.0034, 0.0084) than by the Langmuir, giving a coefficient of adsorption 0.50 and 0.34 L/g respectively. The coexistence of other anions in solutions has a significant effect on P(V) adsorption; a decrease in adsorption capacity followed the order of anions: Mixture > SO_4^{2-} > HCO_3^- > NO_3^- > Cl^- > CO_3^-. In addition, the adsorbed P(V) could be desorbed by 0.1 and 0.2 M NaOH solutions. The optimized method was applied for P(V) removal from real wastewater. The achieved P(V) removal efficiency was 91.48% and 95.23% using VSco and VPum respectively. Results indicate that the freely abundant, locally available, low-cost adsorbent, VSco and VPum can be treated as economically viable for the removal of P(V) from wastewater.

Key Words: Volcanic rocks, Phosphorus, Batch experiment, Isotherms

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'HOW CAN I REPAY THE LORD FOR ALL HIS ACTS OF KINDNESS TO ME' psalms 116:12

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Acronyms

A(%)   adsorbed amount give as percentage

C_e the phosphorus concentration in liquid phase at equilibrium (mg/L)

C_o initial concentration of P(V) in aqueous phase (mg/L)

C_t mass concentration of P(V) in aqueous phase at time t (mg/L),

EC   European Commission

K_D the distribution coefficient

K_f the pseudo-first order rate constant of adsorption (1/min)

K_F the total adsorption capacity (L/g)

K_s the pseudo-second order sorption rate constant (mg/min),

M   dry mass of the adsorbent (kg),

MBR   Membrane Bioreactor

PAO   Polyphosphate Accumulating Organisms

pH_{ZPC} pH Zeta point of Charge

PRC   Phosphorus Removal Capacity

rpm   revolution per minute

R^2 Coefficient Of Determination

q_t the amount of P(V) adsorbed per unit mass of the adsorbent (mg/kg),

Q_o the monolayer adsorption capacity (mg/g)

SSE   Sum of Square Error

UNEP   United Nation Environmental Protection

V   initial volume of the aqueous phase (L)

VPum   Virgin Pumice

VSco   Virgin Scoria

WWTP   Wastewater Treatment Plant

CHAPTER ONE: INTRODUCTION

1.1. Background

Water - one of the most precious natural resource - is very extensively used by mankind. It is an important and essential component of this universe and plays a vital role in the proper functioning of the Earth's ecosystems (Alemayehu & Lennartz, 2009). On the other hand, with rapid industrialization, modern methods of agriculture and domestic activities, the demand for water has increased tremendously, and this has resulted in the generation of large amounts of polluted water containing a number of pollutants e.g. phosphorous (P), that are dangerous because of adverse impacts due to nutrient overloading in sensitive ecosystems (Ali & Aboul-Enein, 2006).

Phosphorus pollution originates from either point source pollution (i.e., municipal or industrial wastewater discharge) or from non-point sources (i.e., agricultural runoff or atmospheric deposition) (Cheung, *et al*., 1994; Boesch, *et al*., 2001; Kyzas & Kostoglou, 2014; Marquez-Pacheco, *et al*., 2013). The presence of high phosphate levels along with a high level of nitrate in rivers and lakes is responsible for the Eutrophication phenomenon. Lakes and rivers are usually considered eutrophic for P level between 0.035 and 0.1 mg/ L and hypereutrophic for levels higher than 0.1 mg/L. Environments with $P(V)$ levels between 0.010 mg/L and 0.035 mg/L are considered mesotrophic towards this element (McMurray, *et al*., 2002); that is, its concentration level is optimal for the development of a balanced ecosystem. Nevertheless, because of an increase in the human activity, the level of $P(V)$ in water bodies has increased considerably in the past decades. For example, according to Tayor, *et al*., 2006, the concentration of $P(V)$ as high as 0.675 mg/L was noticed in Northern Ireland in Lough Egish (Glocheux, *et al*., 2014)

In the USA, regulations are establishing $P(V)$ reduction in wastewater treatment plant effluent to 10 µg/L by 2027 (Hansen, 2006). However, it is recognized that conventional biological and precipitation sorption nutrient removal processes of wastewater treatment plants (WWTPs) are unable to reduce $P(V)$ concentrations below 100 µg/L (Jenkins, *et al*., 1971; Jenkins & Hermanowicz, 1991; Kuba, *et al*., 1993) thus it is expected that advanced systems will be integrated to reduce nutrient concentrations (You, *et al*., 2015).

Phosphorous removal from water and wastewater has been achieved by methods such as coagulation, chemical precipitation, biological treatment, and ion exchange (Ragheb, 2013). Most of these methods involve high capital cost with recurring expenses, which are not suitable for many developing countries. The problems of water and wastewater treatments were seem more difficult in Ethiopia, conventional water treatment plants in Ethiopia are scarce and the existing plants are vulnerable to frequent interruption and technical malfunction. Expanding treatment plants in rural areas is difficult due to logistics and scarcity of chemicals, energy, and lack of know-how (Meierhofer, *et al*., 2002; Dessie, *et al*., 2014).

Recent researches have demonstrated that adsorption methods have received an attractive attention for the removal of pollutants from aqueous solutions. It has long been recognized that, if adsorbent is chosen carefully and the conditions are adjusted appropriately, adsorption based processes are capable of removing contaminants over a wide pH range and too much lower levels that conventional treatment methods (Alemayehu & Lennartz, 2010). Among the most promising types of low-cost adsorbents studied are volcanic rocks. In previous studies (Kwon *et al*., 2005; Alemayehu and Lennartz, 2009; 2010; Alemayehu *et al*., 2011), it was found that indigenous volcanic rocks of different chemical and mineralogical composition can be used as an adsorbent materials for removal of potentially harmful pollutants. The most abundant volcanic rocks include pumice, a finely rock frothy with air bubbles; and scoria, a rough rock that looks like furnace slag. Pumice and scoria deposits originate in areas with young volcanic fields. These rocks are abundant in Europe (Italy, Turkey, Greece, and Spain), Central America, Southeast Asia and East Africa (Eritrea, Djibouti, Kenya and Ethiopia). The Ethiopia Rift Valley, which covers around 30 percent of the area of the country, has several of these cinder cone and lava fields (Alemayehu & Lennartz, 2009). Volcanic rocks have received considerable interest for pollutant removal like heavy metal mainly due to their valuable properties: high surface area, low cost and local availability in large quantities.

1.2. Statements of the Problems

Phosphorus, while an essential nutrient for life, is a pollutant to aquatic systems when present in concentrations above a water body's natural background level (Babatunde & Zhao, 2010; Lewis, *et al*., 2011). Phosphorous is often a limiting nutrient in aquatic ecosystems and can lead to rapid degradation of water quality when the concentration increases beyond the natural threshold

(Cheung, *et al*., 1994; Boesch, *et al*., 2001; Kyzas & Kostoglou, 2014). Water quality degradation can occur from a variety of changes brought on by the presence of phosphorus including algal growth, eutrophication-driven hypoxia, increased turbidity, and decreases in submerged vegetative mass (Marquez-Pacheco, *et al*., 2013; Kyzas & Kostoglou, 2014). According to Duranceau, *et al*. (2014) excessive phosphorous is the most common cause of Eutrophication in freshwater lakes, reservoirs, streams, and headwaters of estuarine systems.

According to UNEP (1994) cited in Panasiuk (2010) more than half of all lakes in Europe (53%) and Asia (54%) are eutrophic, about the half (48%) in North America, 41% in South America and 28% in Africa. In the USA the water bodies that cannot be used for drinking, fishing, recreation, and irrigation or industry purposes are impaired in the 60% of cases because of Eutrophication (Carpenter, *et al*., 1998). This shows the scale of the problem and its importance. Moreover, a study carried out in Ethiopia to assess factors enhancing Eutrophication were phosphorus and nitrogen. The critical concentration of phosphate to trigger algal growth could reach a minimum of 0.005 mg/L (Mitiku, 1999). The U.S. discharge limit of phosphate is 0.5-1.0 mg/L. The Indian discharge limits for phosphate is 5 mg/L (Groterud & Smoczynski, 1986). Water treatment plants which draw water from such contaminated resources are thus facing growing problems in delivering desired quality. Phosphate removal techniques fall into three main categories: physical, chemical, and biological. Physical methods have proven to be either too expensive, as in the case of electrodialysis and reverse osmosis, or inefficient, removing only 10% of the total phosphate (Yeoman, *et al*., 1998). Chemical treatment is widely used for phosphate removal. The common chemicals used for treatments are aluminum sulfate and ferric chloride. At present, chemical treatments are not used due to disadvantages like high costs of maintenance, problems of sludge handling and its disposal, and neutralization of the effluent (Neufeld & Thodos, 1969; Boisvert, *et al*., 1997). In a biological treatment plant, it is necessary to transfer phosphate from the liquid to the sludge phase, and the removal efficiency usually does not exceed 30% (Stensel, 1991), which means that remaining phosphate should be removed by another technique. Therefore, it has become necessary to develop an innovative remediation technique to improve water quality.

Therefore, the need exists for a purification strategy that is simple, effective and low-cost. In this way, adsorption appears as a highly promising alternative to treat polluted waters. To take the

advantage of adsorption while overcoming some of conventional treatment drawbacks, a means has been designed for the development of a variety of economical materials for use in the removal of phosphorous from water/wastewater. Several adsorbents have been investigated for the removal of phosphorous from aqueous solution such as Iron oxide (Berner, 1973), Zeolite (Sakadevan & Bavor, 1998), hybrid impregnated polymeric sorbent containing hydrated ferric oxide (You, *et al.*, 2015), Schwertmannite (which is ferric oxyhydroxide sulfate) (Eskandarpour, *et al.*, 2006), clay soil (Mallikarjun & Mise, 2013), slag and fly ash (Ragheb, 2013), industrial acidified laterite by-product (Glocheux, *et al.*, 2014). Furthermore, various sorbents such as mixture of sand and dolomite (Prochaska & Zouboulis, 2006), goethite (Geelhoed, *et al.*, 1971) have been recommended as effective sorbents. However, the available methods have several disadvantages, which make them not effective and not suitable for non-developed areas around the globe (Gupta, *et al.*, 2009; Alemayehu & Lennartz, 2010).

As a result, looking for an appropriate water/wastewater treatment technology and strategy using locally available indigenous materials that may be used in poorly developed areas such as Ethiopia remains an issue that has to be dealt with. Among the natural adsorbents having better features to be used as low-cost adsorbents of pollutants are volcanic rocks (VPum and VSco). The potential of volcanic rocks to remove both cationic and ionic ions has been reported. For example, in previous studies (Kwon, *et al.*, 2010; Alemayehu & Lennartz, 2009; Alemayehu & Lennartz, 2010; Alemyahu, *et al.*, 2011), it was found that indigenous volcanic rocks of different chemical and mineralogical composition can be used as an adsorbent materials for removal of potentially harmful pollutants like heavy metals.

However, little or no information is available about the adsorptive interactions between phosphorus and the volcanic rocks (VPum and VSco) in the aqueous system. Thus, an attempt was made to study their feasibility as an adsorbent for removal of phosphorus from aqueous solution.

1.3.   Significance of the Study

There are concerns at all levels that fresh water resources particularly in the developing world could keep on getting polluted from the excessive domestics, agricultural and industrial discharges they receive and lead to serious health and ecological problems. Water treatment

plants which draw water from such water bodies are facing growing problems in delivering desired water quality. In developing countries such as in sub-Sahara African countries (e.g. Ethiopia) this problem is compounded by their financial resources. The lack of knowledge of the mechanisms of Phosphorus and other nutrient removal and the relatively high cost and complexity of providing the necessary treatment has led to either inadequate or no treatment. Thus, in many cases, the polluted water is often used for the domestic as well as irrigation purpose (Barca, et al., 2012).

Therefore, this study may give some information about adsorption technology to stakeholders for developing low cost adsorption water treatment technology. And the data will also be used as a baseline to apply the finding for pilot- and full-scale treatment plant systems.

CHAPTER TWO: LITRATURE REVIEW

2.1. Occurrence and Nature of Phosphorous

Unlike the nitrogen and carbon cycles that are global, the phosphorus cycle is local. This is because the main abiotic reservoirs of phosphates are rocks. Erosion from the rocks transforms phosphorus compounds into soluble phosphates (Smil, 2007). Phosphorus cycle in the nature could be described with the following scheme (Spellman, 2008) (Figure 1).
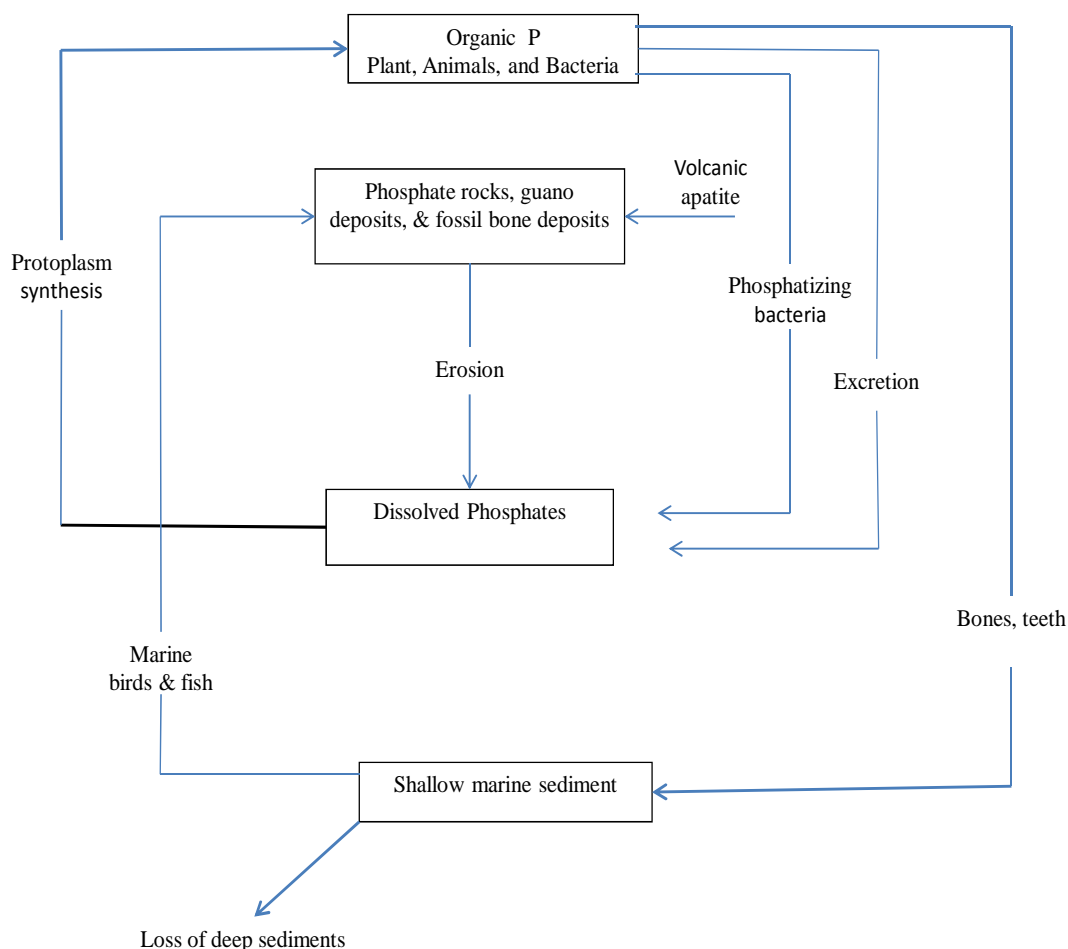
Figure 1: Phosphorus Cycle (adopted from Spellman, 2008)

In natural waters and in wastewaters phosphorus occurs almost solely as phosphates. These are classified as orthophosphates, condensed phosphates (pyro-, meta-, and other polyphosphates), and organically bound phosphates which occur in solution, in particles or detritus, or in the

bodies of aquatic organisms (Mahmut & Ayhan, 2003). These forms of phosphate arise from a variety of sources. For example, small amounts of orthophosphate or certain condensed phosphates are added to some water supplies during treatment. Larger quantities of the same compounds may be added when the water is used for laundering or other cleaning, because these materials are major constituents of many commercial cleaning preparations. Phosphates are used extensively in the treatment of boiler waters. Orthophosphates applied to agricultural or residential cultivated land as fertilizers are carried into surface waters with storm runoff and to a lesser extent with melting snow. Organic phosphates are formed primarily by biological processes. They are contributed to sewage by body wastes and food residues, and also may be formed from orthophosphates in biological treatment processes or by receiving water biota. Phosphorus is essential to the growth of organisms and can be the nutrient that limits the primary productivity of a body of water. In instances where phosphate is a growth-limiting nutrient, the discharge of raw or treated wastewater, agricultural drainage, or certain industrial wastes to that water may stimulate the growth of photosynthetic aquatic micro- and macro-organisms in nuisance quantities (Barca, *et al*., 2012).

The primary material that is used for phosphorus production is apatite [$Ca_5 (PO_4) 3OH$] (Smil, 2000). The process of phosphorus production is highly energy-consuming and causes a lot of environmental problems connected mainly to the stage of raw material extraction (Jenkins, *et al*., 1971).

2.2. Source and Pollution Effects of Phosphorus

Phosphorus (P) is a vital element for every plant and animal. Lack of phosphorus in ground can result in limited crop production. Phosphorus is mainly used in agriculture as a fertilizer or as food additive in the animal feed. The other applications of phosphorus include ingredients for human food, pharmaceuticals, detergents and some especial chemicals (Panasiuk, 2010).

The phosphorus content in natural waters is usually regulated by microorganisms, so there is a balance in the available phosphorus and ecosystem requirements. However, an excessive intake of P into water bodies such as rivers, lakes or lagoons stimulates the growth of aquatic micro and macro organisms in nuisance quantities, causes an abnormal growth of algae and aquatic plants, resulting in the degradation of the water quality. These aquatic species covering the surfaces of

water limit the transfer of oxygen from air to water by diffusion (Shukla, *et al*., 2008). When algae and aquatic plants die, they sink to the bottom of the water body and decay by microbial decomposition, thus reducing the concentration of dissolved oxygen and forming P-rich sediments. Over time, these sediments release P that is available for biomass growth, thus resulting in a trophic cycle and algal blooms (Recknagel, *et al*., 1995; Smil, 2000). This phenomenon of water quality degradation due to excessive trophic cycle is commonly referred to as "eutrophication" (Crouzet, *et al*., 1999).

Eutrophication has several negative impacts that result one from another and are interconnected: the proliferation of bloom-forming species that could be toxic or inedible; decreasing of water quality (e.g. color, transparency, odor, taste and water treatment problems); water plants die causing propagation of bacterial decomposers; bacteria consume more oxygen causing its shortage in water body, and thus, kills fish; loss of biodiversity; decrease of esthetic and recreational value of the water body (Panasiuk, 2010).

Municipal and industrial drainages and agricultural runoffs are the major sources of P loads into water bodies, and their P contents derived primarily from human and animal products, food waste, P-based detergents and P-based fertilizers. During the period of 1950 to 1995, approximately 600 million tones of phosphorus were used as a fertilizer globally. In the same period, about 250 million tons of P were collected in form of different crops. Fifty million tons of P came back to the croplands with the manure form the livestock eating part of harvested crops. It appears from this that 400 million tones of phosphorus were added to the soil during that period. Taking into account that 3 to 20% of that amount was washed to the water bodies it results in 12 to 80 million tones of phosphorus discharged in the surface water (Carpenter *et al*., 1999). In this case the P removal from wastewater is extremely important as it both saves enormous amount of non-renewable phosphorus and also prevent water eutrophication and contamination.

Therefore, legislation on P reduction into the surrounding environment is becoming stricter worldwide, especially in areas that present a high risk of eutrophication. Excess of P stimulates algae growth in water bodies, which in its turn decreases oxygen concentration and leads to eutrophication of the surface water bodies. Increased phosphorus concentration also results in higher water treatment costs, decreased recreational value, and livestock losses. There is also a

high probability of the sub-lethal effect because of toxins from algae in the drinking water (Panasiuk, 2010). The probability and effect of these problems are as higher as smaller the water body is. The EU Directive 2000/60/EC, 2000 requires controlling of P discharge to maintain or improve the water ecology (EC, 2000; Panasiuk, 2010; Amery, 2014).

2.3. Forms of Phosphorus in Aqueous Solution

Phosphorus in aqueous solution (water and wastewater) exists in three main forms, orthophosphates, polyphosphates and organic phosphorus (Almeelbi & Bezbaruah, 2012). Each of these P forms presents a different reactivity and affinity for processes of chemical precipitation, adsorption and biological removal. Therefore, the efficiency of the conventional P removal technique depends considerably on the form of P that predominantly occurs in the water/wastewater. The phosphates are referred to as the salts of the phosphoric acid (H_3PO_4). Phosphoric acid dissociates in solution producing the phosphate forms $H_2PO_4^-$, HPO_4^{2-} and PO_4^{3-} (PO_4-P). The chemical equilibra between the different PO_4-P forms depend on the pH of the solution as shown in Figure 2. $H_2PO_4^-$ is the primary form when pH ranges from 2 to 7, HPO_4^{2-} is the primary form when the pH ranges from 7 to 12, and PO_4^{3-} is the primary form when the pH is higher than 12 (Sperlich, 2010). Phosphate (P(V)) is a form of P that is readily available for chemical precipitation, adsorption, and biological removal. Therefore, the ratio of phosphate to total phosphorus of the water/wastewater is a parameter of great importance when evaluating the efficiency of conventional techniques for P removal.

The polyphosphates are the salts or ester of polyphosphoric acid. They consist of chains of phosphates bound to each other through one atom of oxygen. Polyphosphates in water/wastewater derive primarily from household detergents. Over the last 20 years, the phosphorus content in detergents has been considerably lowered in many countries in Europe (Crouzet, *et al.*, 1999). Therefore, the polyphosphate content in wastewater has been markedly reduced.
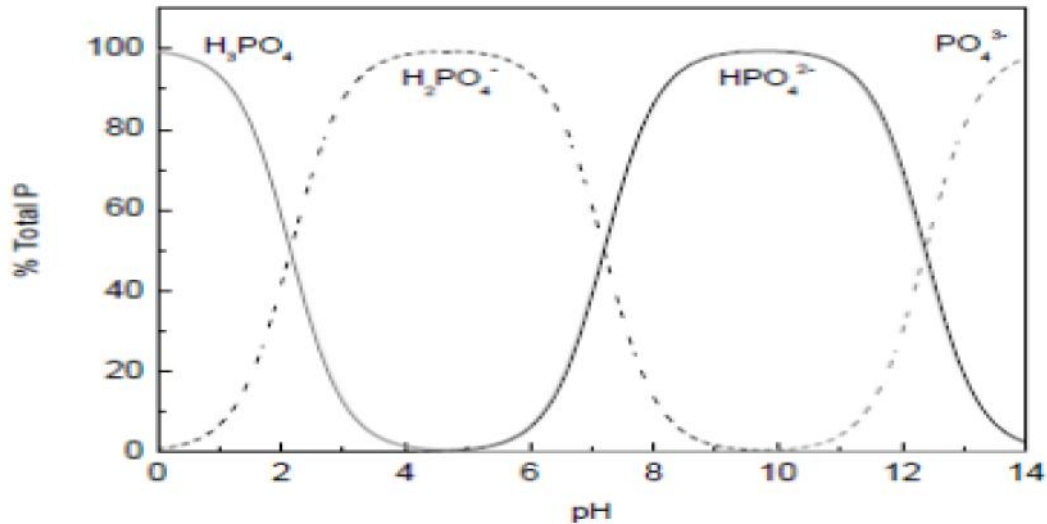
Figure 2: Chemical equilibra of phosphate as function of pH (adopted from Sperlich, 2010)

2.4. Technological Options to Remove Phosphorous

The need to develop new technologies for P removal and recovery from water/wastewater has become necessary due to an increasing demand for sustainable mineral resources, more stringent discharge limits to prevent eutrophication of natural water resources, and tightening sludge disposal restrictions. Phosphorus recovery for reuse by the phosphate industry and in agriculture is technically feasible and there are a number of technologies for recovering P from wastewater originating from various sources (municipal, industrial, run-off) (Panasiuk, 2010; Barca, *et al*., 2012).

Several processes, including physical methods, chemical and biological precipitation, crystallisation, and biosorption have been developed for removal and subsequent recovery of phosphorus from wastewater (Brett, *et al*., 1997). These processes need complex and strict control of the operating conditions, and some of them produce excess sludge that requires disposal. Furthermore it is difficult to recover, as opposed to remove, P by these processes.

Physical methods include membrane technologies, which have become recently of great interest for wastewater treatment. Later their application for P removal has been studied. It has been shown that membrane methods are able to remove not only P in total suspended solids but also the dissolved P. According to report (Reardon, 2006) methods involving membrane technology showed good results in full-scale plants: less than 1 mg/L of total P in their effluent. These

methods include membrane bioreactors (MBRs), reverse osmosis and tertiary membrane filtration. In the same report current reliable limits were suggested: 0.04 mg/L for tertiary membrane filtration and MBRs, and 0.008 mg/L for reverse osmosis.

Chemical precipitation is one of the most common ways of P removal used for a long time. It is a method that causes dissolved P to settle out of solution. In order to get precipitation to take place, the agent called coagulant need to be added. It causes small suspended matter to group into bigger aggregates. Compounds of iron, aluminum and calcium are chemicals primarily used in P precipitation: ferric chloride, ferrous sulfate, aluminum sulfate (alum), and lime. If lime is used, special conditions should be fulfilled to ensure the reaction between excess calcium ions and phosphate. This could be done if pH of the solution is not less than 10, so it is important to add sufficient amount of lime. (Tchobanoglous, *et al.*, 2002). In spite of the fact that lime is an effective agent for P removal, the application of this reagent is slightly diminished because of high volume of produced sludge. In case of iron or aluminum salts are used in P removal, insoluble metal phosphates are produced. The formation of these compounds is pH-dependent: pH level strongly affects the degree of insolubility of metal phosphates. Another issue that should be taken into account is different completing reactions that occur in the system in addition to the main one. As a result the amount of metal salts should be determined practically during the experiments for each case and cannot be calculated simply based on the chemical reaction with phosphorus (Tchobanoglous & Burto, 1991).

Study on precipitation (Song, *et al.*, 2002) based on thermodynamics showed that the theoretical removal rate of P depends on such factors as P concentration, temperature, pH, and ionic strength. Prediction of the best performance of P chemical precipitation also varies in different studies from 0.005 to 0.05 mg/L (Neethling, *et al.*, 2005)

Biological P removal in an activated sludge system is performed mainly by a group of microorganisms known as the polyphosphate accumulating organisms (PAO). These organisms can consume and store P in form of intracellular polyphosphate, and orthophosphate leaves the system in the excess sludge or can be stripped from the biomass and regained using any of the P recovery technologies. This fact leads to the decreasing P content in the liquid phase and a

concentration of P in the activated sludge (Henze, *et al*., 1997; Mino, *et al*., 1998; Tchobanoglous, *et al*., 2002).

SOURCE

Anthropogenic Source

Natural Source

Industrial, agricultural & domestic activities

POLLUTANT

Solid pollutants, by-products

Liquid pollutants, by-products

Dissolved & non-dissolved Chemicals

Heat

Biological agents

One of the utilization methods

T R E A T M E N T   M E T H O D S

Advanced processes

Biological processes

Physicochemical processes

- Coagulation
- Filtration
- Ion exchange
- Membrane technology
- Constructed wetland
- Activated Sludge system etc

Adsorption

Low-cost natural materials

- Activated carbon
- Zeolites & ion exchange
- Alumina & bauxite
- Silica gel

Volcanic rocks

Clay; coal; wood; peat; diatomite; etc

Figure 3: Schematic diagram of pollutant generation and their treatment methodology (adopted from Alemayehu, 2010)

2.5. Adsorption

Adsorption is a phenomenon in which atoms, ions or molecules (adsorbate) are removed from a gas or a liquid stream by adhering to the surface of a solid (adsorbent). The adsorption of different types of pollutants on the surface of an adsorbent may depend on a variety of mechanisms, which may be considered independently from each other (Delle Site, 2001).

Present treatment methods have some advantages but also a lot of disadvantages. In fact, the technique of chemical precipitation with the addition of Al, Fe, and Ca usually requires the strict control of the chemical parameters, such as pH and alkalinity, which enable P(V) precipitation. Moreover, an additional cost is given by removal, disposal and treatment of the precipitate-sludge. Situation is becoming worse if lime is used for the primary treatment (Tchobanoglous, *et al.*, 2002). In this case the volume of sludge can increase up to 50%. Application of alum instead of iron salts and, especially, lime results in much smaller amount of sludge but doesn't solve the problem completely (Strom, 2006). The biological removal process requires the employment of qualified workers and high energy costs due to the strict control of the anaerobic-aerobic phases. As a result the need exists for a purification strategy that is simple, effective and low-cost. In this way, adsorption appears as a highly promising alternative to treat such polluted waters.

2.5.1. Capacity of adsorption

The equilibrium capacity of adsorption q_t (mg/g) defines the amount of adsorbate (mg) that may be removed by adsorption on the surface of the adsorbent (g) until equilibrium in residual pollution concentration is reached. The value of q_t depends on the nature of the adsorbent and the adsorbate, on the initial concentration, on the temperature. The q_t represents a parameter of great importance to evaluate the ability of an adsorbent to remove a pollutant (Desjardins, 1997). The value of q_t for the adsorption of a pollutant on an adsorbent is determined empirically, via batch experiments.

2.5.2. Adsorption of Phosphorus

In most of the studies presented in the literature, the major mechanisms of P(V) adsorption were the adsorption on the surface of metal hydroxides (Das *et al.*, 2006) and the P(V) anion exchange (Blaney *et al.*, 2007).

Das *et al*. (2006) found that metal adsorption on metal hydroxides is spontaneous and exothermic process in nature, and it follows a first order kinetic. They studied also the effect of competing anions on P adsorption, and they found that divalent anions (CO_3^{2-}, SO_4^{2-}, SeO_3^{2-}) have higher interfering effect compared to monovalent anions (HCO_3^-, NO_3^-, Cl^-), most probably because divalent anions competed with divalent phosphates (HPO_4^{2-}) for the adsorption sites on metal hydroxides. Several international studies have demonstrated that the Al and Fe hydroxides formed during the chemical precipitation with Al and Fe salts are efficient supports for P(V) adsorption (Boisvert *et al*., 1997; Fytionos *et al*., 1998).

P anion exchange occurs when adsorbent materials presenting anion exchange groups are puts in contact with P in aqueous solutions (Blaney *et al*., 2007). However, anions such as chloride, nitrate, carbonate and sulfate, which commonly occur in wastewater may compete with phosphate in the process of anion exchange thus limiting the efficiency of P removal.

Several studies have demonstrated that filtration through materials with high affinities for P binding is an appropriate technology to improve P removal in small and extensive wastewater treatment plants. Since common filter substrates (such as sand and gravel) have limited P removal capacities (Arias *et al*., 2001), research on alternative materials has become a priority. In the last two decades, a large number of potential substrates has been tested. These substrates can be classified according to their source of origin into three main categories (Johansson-Westholm, 2006): natural materials, industrial by-products and man-made products.

A large number of natural materials have been tested in the literature, including mineral and rocks (bauxite, apatite, limestone, dolomite, zeolite), soils (opoka, peat) and sediments (shall sand, maerl). Most of these materials have a high content of Ca, Al, and/or Fe, which are elements with a strong affinity for P binding (Johansson-Westholm, 2006).

And also various industrial by-products, including iron and steel slags, ashes of thermal incineration plants (oil shale ashes, fly ashes), and waste of the alumina industry (red mud) have been tested for P removal with the aim of valorizing by-products of the industry in wastewater treatments (Gupta, *et al*., 2009).

2.5.3. Batch experiments

Batch experiments are usually performed to evaluate the P removal capacities (PRCs) of candidate materials. In fact, PRC is an important parameter when comparing and selecting candidate materials to be used as filter media (Drizo, *et al*., 2006). Main results from selected batch studies that tested P removal capacities of candidate substrates are reported in Table 1. The maximum P removal capacities varied by several orders of magnitude, from less than 0.5 to up than 100 mg P/g (Table 1). Among the materials tested, anion exchange fibres, BF and BOF slag presented the highest PRCs (> 44 g P/g).

Table 1: Natural materials & Industrial by-product: maximum experimental PRCs observed in selected batch experiments (adapted from Vohla *et al*., 2011).

Material tested	Particle size (mm)	Initial PO_4-P (mg P/L)	Agitation mode	Contact time (h)	PO_4-P removed (%)	Maximum PRC (mg P/g	Authors
Zeolite	N.A	40	60 rpm	24	25	0.25	Drizo *et al*., 1999
Bauxite	N.A	40	60 rpm	24	60	0.6	Drizo *et al*., 1999
Limestone	N.A	40	60 rpm	24	55	0.55	Drizo *et al*., 1999
Dolomite	N.A	1-100	N.A	24	N.A	0.30	Pant *et al*., 2001
Apatite	2.5-10	5-150	N.A	24	N.A	0.41	Bellier *et al*., 2006
Shell sand	3.0-7	480	N.A	24	67	9.60	Adam *et al*., 2007
Fly ash	N.A	40	60 rpm	24	70	0.70	Drizo *et al*., 1999
Schwertmannite	N.A	10	N.A	50	N.A	9.5	Eskanderpour., 2006
Fly ash	N.A	1000	200 rpm	24	42	8.50	Xu *et al*., 2006
Oil shale ash	N.A	40	60 rpm	24	42	0.42	Drizo *et al*., 1999
Red mud	N.A	1	70 rpm	6	20	0.29	Huang *et al*., 2008
BF slag	N.A	0-10000	100 rpm	48	N.A	44.20	Sakadevan and Bavor, 1998
BOF slag	< 0.02	320	N.A	24	49	78.90	Jha *et al*., 2008
BOF slag	< 6	500	150 rpm	24	18	89.90	Bowden *et al*., 2009

N.A = Non-applicable

2.6.3. Adsorption using Volcanic Rocks

As it was mentioned above, current methods of P removal have significant drawbacks. An alternative solution for P adsorption suggested in this work is utilization of volcanic rocks.

2.6.1. Volcanic Rocks

Rocks, naturally occurring solid aggregates of minerals and/or mineraloids, are classified by chemical and mineral composition, by the texture of the constituent particles and by the processes that formed them (Warner, 1990; Press & Siever, 1998). These indicators separate rocks into igneous, sedimentary and metamorphic (Alemayehu, 2010).

Igneous rocks are formed when molten magma cools and are divided into two main categories: plutonic and volcanic rock. Plutonic or intrusive rocks result when magma cools and crystallizes slowly within the earth's crust (e.g. granite), while volcanic or extrusive rocks result from magma reaching the surface either as fragmental ejecta or larva (Aadnoy & Looyeh, 1998).

According to Klein and Hurlbut, (1985) cited in Alemayehu (2010), volcanic rocks often have a vesicular texture, which is the result of voids left by volatiles escaping from molten lava. Accordingly, they can be classified into two texture: microvescular (pumice) and macrovescular (scoria), which are abundant in many part of the world (Alemayehu, 2010). The most abundant volcanic rocks include Basalt and Rhyolite. Basalt (e.g. scoria) is a very common volcanic rock with low silica content. Rhyolite (e.g. pumice) is a volcanic rock with high silica content (Warner, 1990).

Pumice (VPum) is a texture term for a volcanic rock that is solidified frothy lava typically created when super-heated, highly pressurized rock is violently ejected from a volcano. It can be formed when lava and water are mixed. This unusual formation is due to the simultaneous actions of rapid cooling and rapid depressurization. The depressurization creates bubbles by lowering the boiling point of the lava. Pumice is composed of highly microvescular pyroclastic with very thin, translucent bubble walls of extrusive igneous rock. It is commonly, but not exclusively of silicic or felsic to intermediate in composition (e.g. Rhyolite). Pumice is commonly pale in color, ranging from white, cream, blue or grey, to green-brown or black. It varies in density according to the thickness of the solid material between the bubbles; many samples float in water. However, when the vesicles are open and interconnected the pumice

becomes easily water logged and sinks in water (Miguel, 2015). In addition, according to (Alemayehu, 2010), pumice is characterized by a high water adsorption capacity (20 -30%) due to its high degree of porosity and a very low density. It has a skeleton structure that allows ions and molecules to reside and move within the overall framework. Pumice is amorphous with mainly quartz and feldspar (e.g. K-feldspar is known as Orthoclase) as crystalline phases, such mineral composition is typical for Rhyolite rocks (Kelm, *et al*., 2003; Khandaker & Hossain, 2004).

Similarly, scoria (VSco) is also a textural term for macrovescular volcanic rock. It is commonly, but not exclusively, basaltic or andesitic in composition. Scoria is light as a result of numerous macroscopic ellipsoidal vesicles, but most scoria has a specific gravity greater than 1 (Kwon, *et al*., 2010). Scoria differs from pumice in being denser, with larger vesicles and thicker vesicle walls; it sinks rapidly. The difference is the result of the lower viscosity of the magma that formed scoria. With regard to its mineral composition, scoria consists of most of the mafic minerals: Pyroxene, Olivine, Plagioclase, amphibole (hornblende) and hematite. Such mineral composition is typical for basaltic rocks (Miguel, 2015; Kwon, *et al*., 2010).

The formation of volcanic rocks, their geological characteristics, mineralogical compositions as well as their applicability as construction materials and as an abrasive have been well recognized (Khandaker & Hossain, 2004). In contrast, very little is known about their applicability as water and wastewater treatment agents (Akbal, 2005; Kwon, *et al*., 2010). The characterizations of the volcanic rock grains confirmed that VPum and VSco reasonably meet the criteria that have been established for water and wastewater treatment processes due to its high natural porosity, very low price, good mechanical resistance, and suitability for pollutant adsorption. The rough surface of the adsorbents and the presence of metal oxides (Fe, Al, Ca, Mg and Si oxide) are also beneficial in the removal of pollutants from solution (Alemayehu, 2010). Chemical analyses of the adsorbents reveal that, the major constituents are SiO_2, Al_2O_3 and Fe oxide (Table 2).

Hence, in this work, as an alternative to sand and/or natural adsorbents, VPum and VSco were used as treatment media to investigate their adsorptive phosphorus removal potential from simulated waters and real wastewater. The rock samples can be taken from the main rift valley of Ethiopia; approximately 100 km East of Addis Ababa. The rocks are indigenous volcanic rocks

of different chemical and mineralogical composition. In fact, the rocks are representative of the Ethiopian Rift valley, which covers around 1/3 of the area of the country (Assefa, 1985; Reimann, *et al*., 2003).

2.6.2. Volcanic Rocks in Water treatment and Characterization

Some studies have been done in order to investigate the possible volcanic rocks (VPum and VSco) application in water/wastewater treatment to remove different pollutants. VPum and VSco is often used for heavy metals removal. Paper written by Alemayehu and Lennartz (2009) describes the application of VPum and VSco for water treatment. The results show that VPum and VSco has advantages for and was found to be an improved, simple, and an inexpensive method for water treatment (Alemayehu & Lennartz, 2009).

In the study made by Alemayehu and Lennartz (2009; 2010) removing of some metals (mainly nickel and cadmium) from aqueous solution using VPum and VSco has been investigated. It was shown that such factors as dosage of VPum and VSco, its particle size, contact time with solution and pH of the solution have effect on the method efficiency. It was found that efficiency of the method increases dramatically at particle decrease to nanosize. In general, application of VPum and VSco was found to be promising for Ni and Cd removal from aqueous solutions.

Studies about utilization of VSco (a vesicular pyroclastic rock with basaltic composition) for removal of divalent heavy metals (Pb(II), Cu(II), Zn(II), Cd(II)) and trivalent arsenic (As(III)) from aqueous solutions also showed good results (Kwon, *et al*., 2010). The paper suggested that natural scoria studied is an efficient sorbent for concurrent removal of divalent heavy metals and arsenic.

VPum can be used for Cu^{2+} and Cr^{3+} removal from wastewater (Yavuz, *et al*., 2008). The study concludes that pumice powder has big potential for Cu^{2+} and Cr^{3+} removal and could be employed as a low-cost adsorbent for the removal of metal ions from aqueous solutions.

CHAPTER THREE: OBJECTIVE

3.1. General Objective

➢ The general objective of this study was to examine adsorptive removal of P(V) from aqueous solution using volcanic rock (VSco and VPum).

3.2. Specific Objectives

➢ To measure the P(V) adsorption capacities of VPum and VSco
➢ To optimize major design parameters (pH of solution, initial concentration, contact time, adsorbent dose, particle size, and agitation speed) on P(V) adsorption onto VPum and VSco
➢ To investigate the influence co-existing ions
➢ To predict the adsorption process by using kinetics and isotherms models

CHAPTER FOUR: METHODS AND MATERIALS

4.5.1. Materials

Batch adsorption experiments were performed using the following main components;

- ➢ Preparations of the adsorbents
- ➢ Simulated solution of P(V) ions and true wastewater.

Equipments

- ❖ Spectrophotometer (Thermo Fischer Scientific, JACO, V-630)
- ❖ pH meter (pHenomental, TM)
- ❖ Weight Balance (KERN PCB
- ❖ Shaker (Horizontal, SM30C, Edmund Bühler)
- ❖ Centrifuge (Centrifuge 5804, R-8000)
- ❖ Volumetric flask (25ml, 100 mL, 500 mL, 1000 mL)
- ❖ Erlenmeyer Flask (25ml, 100 mL, 250, 500 mL,)
- ❖ Cuvette 10mm
- ❖ Mortar
- ❖ Sieve (0.075, 0.425, 1.0, 2.0, 4.75 mm size)

4.5.2. Adsorbate (artificial solution)

Phosphorus solution has been prepared and used in the laboratory. Simulated stock solution of phosphorus (50 mg/l) was prepared by dissolving the required quantity of an annular grade of the respective salt in distilled water. The salt used is: anhydrous potassium di-hydrogen phosphate KH_2PO_4 (0.2195 g).

4.5.3. Adsorbent media and Preparation

Adsorbent media: All the VPum and VSco samples (Alemayehu, 2010) used were representative samples, obtained from Jimma University, Jimma Institute of Technology (Dr. Ing Esayas Alemayehu Laboratory)

Table 2: Chemical composition and physical properties of VPum and VSco (adopted from Alemayehu and Lennartz, 2010)

Components	VSco	VPum
SiO_2 (%wt)	47.4	68.6
Al_2O_3 (%wt)	21.6	8.9
Fe_2O_3 (%wt)	8.9	4.9
CaO (%wt)	12.4	1.8
K_2O (%wt)	0.5	5.5
Na_2O (%wt)	3.0	4.1
MgO (%wt)	3.3	0.2
TiO_2 (%wt)	1.7	0.3
Others (%wt)	1.2	5.7
pH	7.6	7.7
Density (g/cm^3)	2.98	2.46
Specific surface area (BET) (m^2/g)	2.49	3.50

Adsorbent Preparation: Batch experiment was conducted as follows. At the beginning, the collected VPum and VSco granules were washed with distilled water and dried in an oven at 105°C for 12 hours to remove moisture (Alemayehu, 2010; Moradi, *et al*., 2015). The dried samples were crushed by hand in a mortar, and separated into four sieve size fractions: silt (<0.075 mm), fine (0.075 – 0.425 mm), medium (0.425 – 2.0 mm), and coarse (2.0 – 4.75 mm) sand size in diameter using the American Society for Testing and Materials (ASTM D 422), soil textural classification system (Liu & Evett, 2003). Finally, the sieved samples were kept in airtight plastic container at room temperature until commencement of the adsorption experiments.

4.5.4. Chemicals

All the chemicals used were analytical grade reagents obtained from Jimma University Laboratories (Environmental biology, Inorganic & organic, Soil, Postharvest laboratories). A 50 mg/L phosphorus stock solution was prepared by dissolving 0.2195 g anhydrous potassium dihydrogen phosphate (KH_2PO_4) in 1 L of distilled water. Working solutions of phosphorus were

prepared by appropriately diluting the stock solution. Potassium salts of chloride, nitrate, and sulfate, and Sodium salt of bicarbonate, carbonate anions were used in the investigation of the effects of competing anions. The pH of solution was adjusted using 0.1 M NaOH and/or 0.1 M HCl.

Chemicals and Regents

- ❖ Anhydrous potassium dihydrogen phosphate
- ❖ Sodium carbonate (Na_2CO_3)
- ❖ Sodium bi-carbonate ($NaHCO_3$)
- ❖ Sodium hydroxide (NaOH)
- ❖ Hydrochloric acid (HCl)
- ❖ Potassium chloride (KCl)
- ❖ Potassium Nitrate (KNO_3)
- ❖ Potassium sulfate (K_2SO_4)
- ❖ Potassium antimony tartrate ($K(SbO)C_4H_4O_6 \cdot 1/2H_2O$)
- ❖ Sulfuric acid (H_2SO_4)
- ❖ Ammonium molybdate (($NH_4)_6 Mo_7O_{24} \cdot 4H_2O$)
- ❖ Ascorbic acid ($C_6H_8O_6$)

4.5.5. Adsorption Experiments

Sets of batch adsorption experiments were conducted to understand the phosphorus adsorption process of VSco and VPum under various experimental conditions. In all sets of the experiments, a known concentration of phosphorus and a desired amount of VSco and VPum independently were mixed in 100 mL of solution in 250 mL acid-washed Erlenmeyer flask. The adsorbent were equilibrated by shaking with 0.01 M $CaCl_2.2H_2O$ for 12 hours before the actual experiment (Alemayehu, 2010). The pH of all mixtures was set to 7.0 using 0.1 M HCl and NaOH. Then, it were shaken on a horizontal shaker (SM 30C, Edmund Buhler) at 200 rpm to homogenize and facilitate the reaction. Shaking was performed at 60 min contact times. After this process, 50 ml of prepared solution was centrifuged (Centrifuge 5804) at 3000 rpm for 15 min. Finally, P(V) concentration of solutions was determined using Spectrophotometer (Spectrophotometer, V-630 JASCO, Japan). The percentage of P(V) removed, A%, and the amount of P(V) adsorbed per

unit mass of the adsorbent, q_t (milligrams per gram), at any time t (minutes) are computed respectively using Eq. 1 and Eq.2.

$$q_t = (C_o - C_t)\frac{V}{M} \qquad (1)$$

$$A_{(\%)} = \frac{(C_o - C_t)}{C_o} * 100 \qquad (2)$$

Where: C_o = initial concentration of P(V) in aqueous phase (mg/L) C_t = mass concentration of P(V) in aqueous phase at time t (mg/L), q_t = The amount of P(V) adsorbed per unit mass of the adsorbent (mg/kg), M = dry mass of the adsorbent (kg), V = initial volume of the aqueous phase in contact with the adsorbents during the adsorption test (L), A(%) = adsorbed amount give as percentage at time t (Chantawong, 2004; Fruit *et al.*, 2014).

The distribution coefficient (K_D) value for P(V) adsorption on the adsorbents (VSco and VPum) was calculated using Eq. (3) (Alemayehu, 2010; Kebede, *et al.*, 2014):

$$K_D = \frac{q_t}{C_t} \qquad (3)$$

Where: q_t is the concentration of P(V) in the solid particles (mg/g) and C_t is the concentration of P(V) in water (mg/L).

To check the repeatability of the experimental data, each experiment was conducted at least twice and data represent the mean value. Furthermore, control (only the test substance without adsorbent) and blank (only the adsorbent without the test substance) experiments had been conducted for each set of experiments in order to obtain accurate and precise analytical data. The errors in the data were typically less than 5%, which were calculated using the statistical functions included with Microsoft Excel, office 2007 software. Optimum design parameters were determined using the following batch adsorption experiments:

4.5.5.1.   Contact Time

The effect of contact time was investigated using 3 mg/L P(V) concentration (Ragheb, 2013) and 10 g/L VSco and VPum dose (Alemyahu, *et al.*, 2011) separately with particle of size categorized as fine (0.075 - 0.425 mm) (Alemyahu, *et al.*, 2011) at neutral pH 7. The solution

samples were agitated at a rate of 200 rpm (Alemayehu, 2010) and the supernatant solution samples were collected at different contact times from 5 to 120 min adopted from (Moradi, *et al*., 2015) and determine optimum contact time (in minute).

4.5.5.2.   pH of Solution

The influence of solution pH was investigated to determine the optimum pH for maximum adsorption of P(V) over the initial pH range from 3 to 12 adopted from (Zhang, *et al*., 2011) by allowing 10 g/L VSco and VPum to adsorb 3 mg/L P(V) in the aqueous solution. Variable amounts of 0.1 M HCL or 0.1 M NaOH were added to the prepared solutions, in order to adjust the initial pH and then, the solutions were permitted to attain to equilibrium without further pH control. After shaking the samples, the suspension was allowed to settle for 1 minute, 50 mL of the supernatant were sampled. The remaining solids were separated by filtration (0.2 μm, membrane filters, Whatman) and the final pH was measured following the procedure (Alemayehu, 2010).

4.5.5.3.   Agitation Speed

Adsorption studies were carried out with a horizontal shaker at an initial concentration of P(V) of 3 mg/l; VSco and VPum dosage was 10 g/L with contact time 60 min and pH 6 for VSco and 7 for VPum. The agitation speed varied from 100 to 250 rpm.

4.5.5.4.   Effect of adsorbent particle size

The influence of adsorbent particle size was evaluated on the removal of P(V) ions over the particle size ranged from silt to coarse sand size (subsection 4.5.3) by keeping other parameters constant (Alemayehu, 2010)

4.5.5.5.   Adsorbent Dose

To determine the optimum dose required for the design of adsorption technology, adsorbent dose was studied by varying the amount of the adsorbent from 5 to 50 g/L (Alemayehu, 2010). VSco and VPum were separately added into a 3 mg/L P(V) aqueous solution of pH 6 (VSco) and 7 (VPum) shaken at 200 rpm for 60 min.

4.5.5.6. Effect of initial concentration

The effect of initial concentration P(V) was examined varying the concentration from 0.5 to 20 mg/L adopted from (Chen, *et al.*, 2013) while maintaining the solution at optimum pH (6 for VSco and 7 for VPum), dose (15 for VSco and 10 for VPum), shaking speed (200 rpm) and contact time (60 min).

4.6. Co-existing Ions

The effect of co-existing anions (HCO_3^{2-}, CO_3^{3-}, Cl^-, NO_3^- and SO_4^{2-}) at different concentration levels were prepared by dissolving appropriate amount of their potassium and sodium salts. Adsorption experiments are performed by adding 10, 100 and 300 mg/L of nitrate, sulfate, chloride, bicarbonate and carbonate ions adopted from (Fufa, *et al.*, 2014; Kebede, *et al.*, 2014)) individually and in mixture to a container of 100 mL solution at constant initial phosphorus concentration of 3 mg/L. Then 10 g/L VPum and 15 g/L VSco is added to each flask above stated separately and adsorption study is performed under experimental conditions; initial pH: 6 (VSco) and 7 (VPum), contact time: 60 min, agitation speed: 200 rpm at room temperature.

4.7. Real wastewater Sample

A sample of wastewater was collected from Jimma town, Oromia Regional State, Western Ethiopia. Then the physicochemical characteristics of the sample were analyzed following standard methods water and wastewater (APHA, 1999): Temperature (Multi-parameter), pH (Multi-parameter), EC (Multi-parameter), carbonate, bicarbonate, chloride (Argentometric)), nitrate (Phenoldisulfonic acid), sulfate (Gravimetric), phosphate (Ascorbic acid), COD (Open Reflex), DO (Multi-parameter), and BOD. The water sample was spiked with 3 mg/L P(V) and treated afterwards with 15 g/L VSco and 10 g/L VPum to evaluate the P(V) adsorption efficiency of the adsorbent under natural surface water conditions.

4.8. Desorption Experiment

For phosphorus desorption experiments, phosphorus loaded adsorbents were prepared by agitating 15 g/L and 10 g/L of the VSco and VPum adsorbents respectively with 3 mg/L P(V) concentration at 200 rpm for 60 min at pH 6 (VSco) and 7 (VPum). After adsorption, the solids were separated from the supernatant solution by filtration (0.45 µm whatman filter paper). The

solids on the filter paper were washed with distilled water. The phosphorus loaded VSco and VPum were dried at 105 °C for 24 h in an oven. Desorption experiments were carried out by shaking the oven dried spent VSco and VPum at 200 rpm for 60 min in 0.1 and 0.2 M NaOH solution separately following (Fufa, *et al*., 2014; Kebede, *et al*., 2014). The amount of phosphorus desorbed was determined via the analysis of phosphorus in the supernatant solution.

4.9. Analysis

The concentration of phosphorus was analyzed using the ammonium phosphomolybdate blue (Ascorbic Acid) method (APHA, 1999), with the absorbance was measured with a spectrophotometer (JASCO, V-630). The measurements were made at the wavelength   = 880 nm, which corresponds to maximum absorbance. Phosphorus concentration was calculated using a linear regression equation derived from the measurements of the standard solutions at acceptable R^2 (0.998).

4.10. Kinetics and Equilibrium Isotherm Models

4.10.1. Adsorption Kinetics

The knowledge of the pollutant adsorption kinetics of materials is of a great importance when dimensioning filters for pollutant removal. The adsorption kinetics is usually determined by batch experiments, monitoring the pollutant concentrations over time until equilibrium in pollutant adsorption is reached.

The Pseudo first-order and second-order kinetic models are the most popular models used to study the sorption kinetics of pollutants and to quantify the extent of uptake in sorption kinetics. In order to evaluate the kinetics of phosphorous adsorption and potential rate controlling steps, the pseudo first and pseudo second order models were checked.

To determine kinetic adsorption parameters, the obtained kinetic adsorption data were evaluated by using simple Langergren pseudo-first order equation, pseudo-second order equation (Ho and McKay, 1999) and Intra-particle diffusion models using Eq. 4, Eq. 5 and Eq. 6, respectively.

Pseudo first order kinetics
The pseudo first-order rate expression is:

$$log(q_e - q_t) = \log q_e - \frac{K_f t}{2.303} \qquad (4)$$

Where K_f is the pseudo-first order rate constant of adsorption (1/min), q_t and q_e (both in mg/g adsorbent) is the amount of phosphrous adsorbed at time t and at equilibrium, respectively. Straight line plots of $log(q_e - q_t)$ versus at different times were plotted to calculate the rate constants and the determination coefficients (R^2).

Pseudo Second Order Kinetics

The pseudo second-order rate expression is:

$$\frac{t}{q_t} = \frac{1}{K_s q_e^2} + \frac{t}{q_e} \qquad (5)$$

Where K_s is the pseudo-second order sorption rate constant (mg/min), and qe (mg/g). f the pseudo second-order kinetics is applicable, the plot of t/q_t versus t was give a linear relationship (Deng *et al.*, 2013).

The pseudo-first order kinetics employed to describe the pseudo-first order reaction, where as the pseudo-second order kinetics to describe the pseudo-second order reaction (Ho & McKay, 1998). If pseudo-first order kinetics is applicable, thus suggests a reaction whose rate of reaction is determined by the concentration of one chemical species. Whereas, if pseudo-second order kinetics is applicable, this suggests a reaction is determine by the concentration of two chemical species.

Intra particle Diffusion Model

Due to rapid stirring in the batch reactor, ions are transported from aqueous phase to the surface of the adsorbent and subsequently they may diffuse into the interior of the particles if they are porous. The intra-particle diffusion can be expressed by the equation (Weber and Morris, 1963) cited in (Alemayehu & Lennartz, 2010; Fufa, *et al.*, 2014; Kebede, *et al.*, 2014):

$$q_t = K_p t^{0.5} + C \qquad (6)$$

Where q_t is the amount of P(V) adsorbed (mg/g) at a given time t (min); k_p $[mg/(g.min^{0.5})]$ is the intra-particle diffusion rate constant; and C (mg/g) is the intercept of the intra-particle diffusion model. The plots of q_t versus $t^{0.5}$ yield straight lines passing through the origin and the slope gives the diffusion rate constant, k_p.

4.10.2. Adsorption isotherms

To evaluate the phosphorus sorption capacity of VSco and VPum, the relationship between the amount of P(V) adsorbed at equilibrium per unit mass of the adsorbent and the concentration of P(V) in the aqueous phase at equilibrium was analyzed by applying adsorption isotherm models. Langmuir and Freundlich models are the most frequently employed for describing the adsorption isotherms from experimental data (Foo & Hameed, 2010). These models can be used to design and optimize an operating procedure. Furthermore, they provide information to predict removal efficiency of solute and an estimation of adsorbent amounts needed to remove solute ions from aqueous solution. In this work, those non-linear isotherm models were used to compare the P(V) adsorption mechanisms of VPum and VSco.

Langmuir Isotherm

Langmuir isotherm is based on the assumption that the point of valance exists on the surface of the adsorbent and that each of these site is capable of adsorbing one molecule. It is assumed that the adsorption sites have equal affinities for molecules of adsorbate and that the presence of adsorbed molecules at one site will not affect the adsorption of molecules at an adjacent site (Srinivas & Kushtagi, 2013).

The general equation:

$$q_e = \frac{bQ_oC_e}{1+bC_e} \qquad (7)$$

Where q_e (mg/g) is the specific amount of phosphorous adsorbed, and C_e (mg/L) is the phosphorus concentration in liquid phase at equilibrium. The Langmuir constants Q_o (mg/g) represent the monolayer adsorption capacity and b (L/mg) relates the heat of adsorption (Gandhi *et al*., 2014).

In order to evaluate the feasibility of the process, the Langmuir isotherm can be described in terms of the dimensionless constant; separation factor or equilibrium parameter;

$$R_L = \frac{1}{1 + bC_o} \qquad (8)$$

C_o (mg/L) is the initial concentration of phosphorus. The shapes of the isotherm are expressed by R_L. There are four probabilities for the R_L value (Foo & Hameed, 2010):

> ➢ For favorable adsorption $0 < R_L < 1$
> ➢ For unfavorable adsorption $R_L > 1$
> ➢ For linear adsorption $R_L = 1$ and
> ➢ For irreversible adsorption $R_L = 0$

Freundlich Isotherm

Freundlich isotherm provides the detailed idea about the effectiveness of the adsorbent and the maximum amount of adsorbate was get adsorbed by the adsorbent. The Freundlich equation is basically empirical but it is often useful as a means for data description. It describes the heterogeneous surface energies by multilayer adsorption (Srinivas & Kushtagi, 2013).

The general equation:

$$q_e = K_F C_e^{1/n} \qquad (9)$$

Where K_F (L/g) is related with the total adsorption capacity while 1/n dimensionless number is related with the intensity of adsorption (Attar, 2010).

To identify a suitable these isotherm models for the sorption of P(V) on VSco and VPum, the sum of the squares of the errors (SSE) analysis was carried out (Foo & Hameed, 2010). The mathematical statement of the Sum square error statistic is given by Eq. 10:

$$SSE = \sum (qe, cal - qe, exp)^2 \qquad (10)$$

Where $q_{e,calc}$ (milligrams per gram) is the equilibrium capacity obtained by calculation from the model, and $q_{e,exp}$ (milligrams per gram) is the experimental data on the equilibrium capacity. If

data from the model are similar to the experimental data, SSE will be a small number; while if they differ, SSE will be a bigger number (Foo & Hameed, 2010). Therefore, it is necessary to analyze the data set using the non-linear sum of the squares of the errors test to confirm the isotherm that best describes the sorption system.

4.8. Quality control

Duplicate experiments were carried out to avoid any discrepancy in results with the reproducibility and the relative deviation of the orders. Control (only the test substance without adsorbent) and Blank (only the adsorbent without the test substance) experiments were carried out for each set of experiments and average data were reported.

4.9. Ethical Consideration

The study was conducted after getting permission from ethical committee of Jimma University, Institute of Technology.

4.10. Dissemination Plan

The final result of this study was presented to school of Civil and Environmental Engineering, Jimma Institute of Technology (Jimma University) and will be disseminated to concerning ministers and non-governmental organizations which are concerned with the study findings. Publication in national and international journal is considered.

CHAPTER FIVE: RESULT

5. Batch Study

Batch adsorption experiments were conducted for the removal of Phosphorus from water by VSco and VPum separately. Evaluation of various parameters, contact time, initial pH, adsorbent dose, agitation speed, particle size and initial concentration, is of vital importance in the design of any adsorption technology system for the removal of P(V). The effect of these parameters on the adsorption of P(V) onto VSco and VPum are presented.

5.1. Effect of contact time

The effect of contact time on the adsorption of P(V) ions by VSco and VPum were investigated by taking 10 g/L sorbent with 3 mg/L phosphorus in different volumetric flasks. The flasks were shaken for different time intervals in a shaker at room temperature. Fig. 4 shows the effect of contact time on adsorption of phosphorus using both sorbents. The results show that the percentage of phosphorus adsorption by both sorbents increased with increasing time. The uptake is rapid in the first 45 min of contact period. Beyond the 60 min contact time, the amount of P(V) adsorbed on the VSco and VPum remains constant as shown in Fig. 4 These data indicate that, the equilibrium is attained at 60 min.
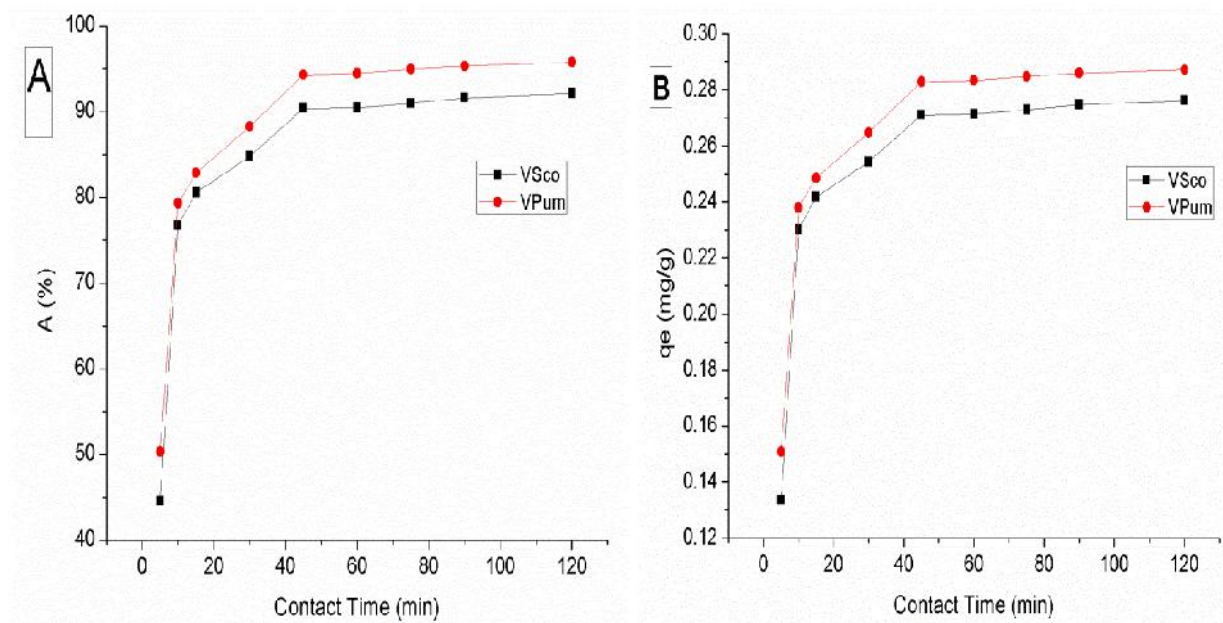
Figure 4: Effect of contact time on P(V) adsorption by VSco and VPum

5.2. Effect of pH

To characterize the influence of pH on P(V) sorption on to VPum and VSco separate set of batch equilibrium experiments were conducted by modifying the pH between 3 and 12. The results showed that, the percentage of P(V) adsorbed and P(V) adsorption capacity progressively increased as the pH of the solution increased from 3 to 6 for VSco and to 7 for VPum, respectively (Fig. 5).
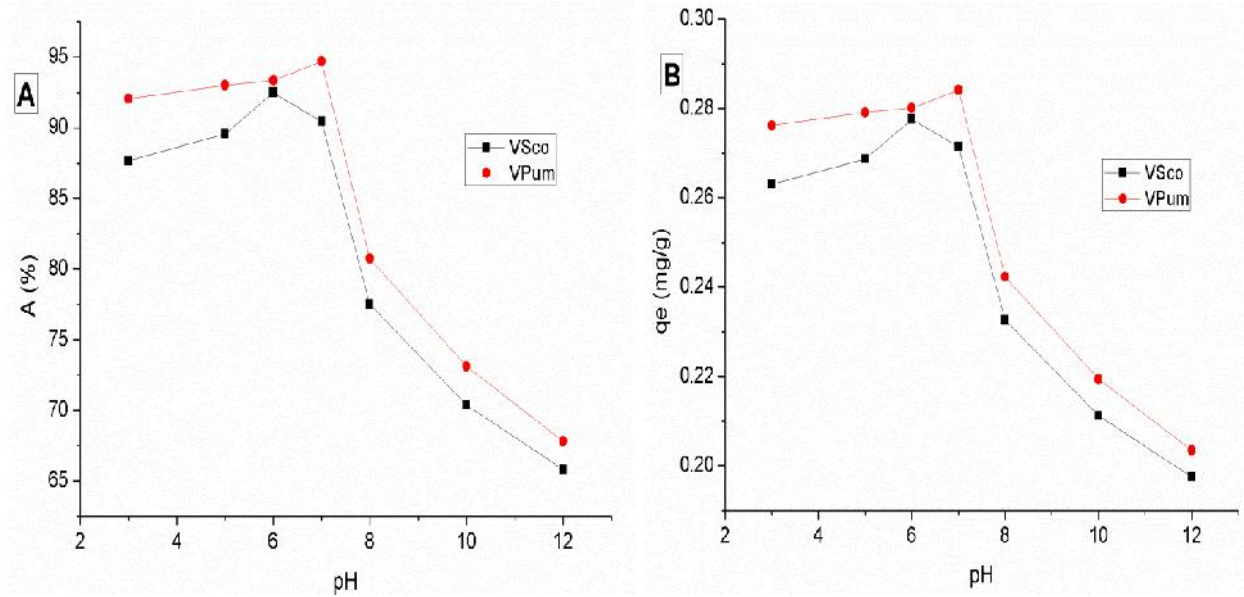
Figure 5: Effect of pH on P(V) adsorption by VSco and VPum

5.3. Effect of mixing speed

Adsorption studies were carried out with a horizontal shaker at an initial concentration of P(V) of 3 mg/l; VSco (15 g/L) and VPum (10 g/L) dosage with contact time 60 min and pH 6 for VSco and 7 for VPum. The agitation speed varied from 100 to 250 rpm adopted from (Ragheb, 2013). It was observed that through increasing agitation speed, the removal efficiency of P(V) in predetermined optimum contact time, pH and dose of adsorbents increased significantly from 77.29 to 92.36% in the case of VSco and 81.87 to 94.61% in the case of VPum (Fig. 6).
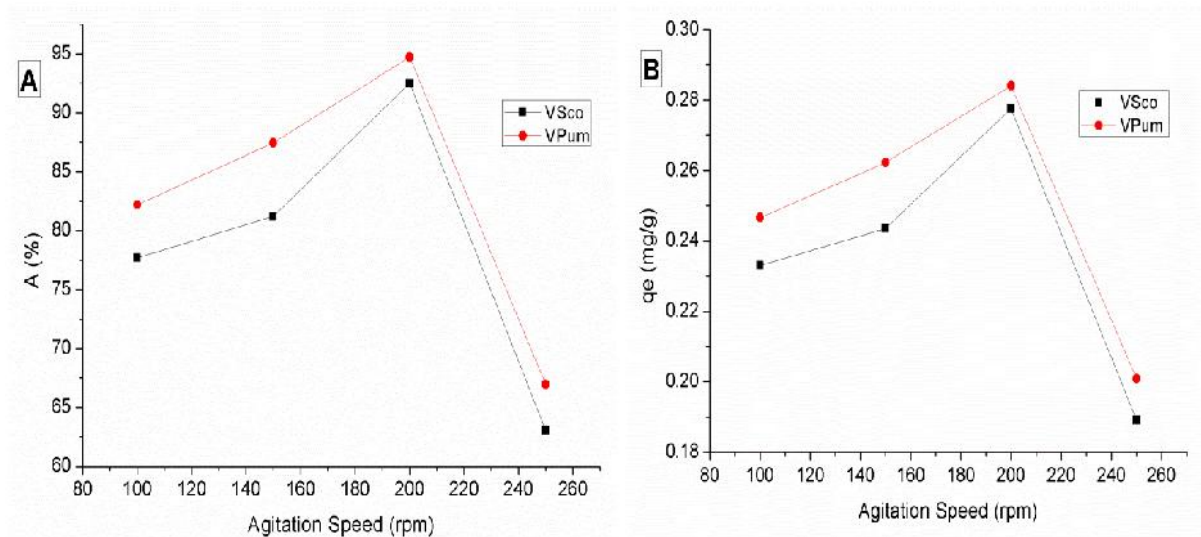
Figure 6: Effect of agitation speed on P(V) adsorption by VSco and VPum

5.4. Effect of particle size of the adsorbent

Effect of particle size of the adsorbent on P(V) adsorption was investigated at initial phosphorus concentration of 3 mg/L, dose of adsorbent = 10 g/L (VPum) and 15 g/L (VSco), agitation rate = 200 rpm, contact time = 60 min and pH = 6 (VSco) and 7 (VPum). The results are presented in Fig.7 indicated that the percentage of P(V) adsorbed increased with a decrease in particle size of the adsorbent from 4.75 to 0.075 mm (Fig. 7).
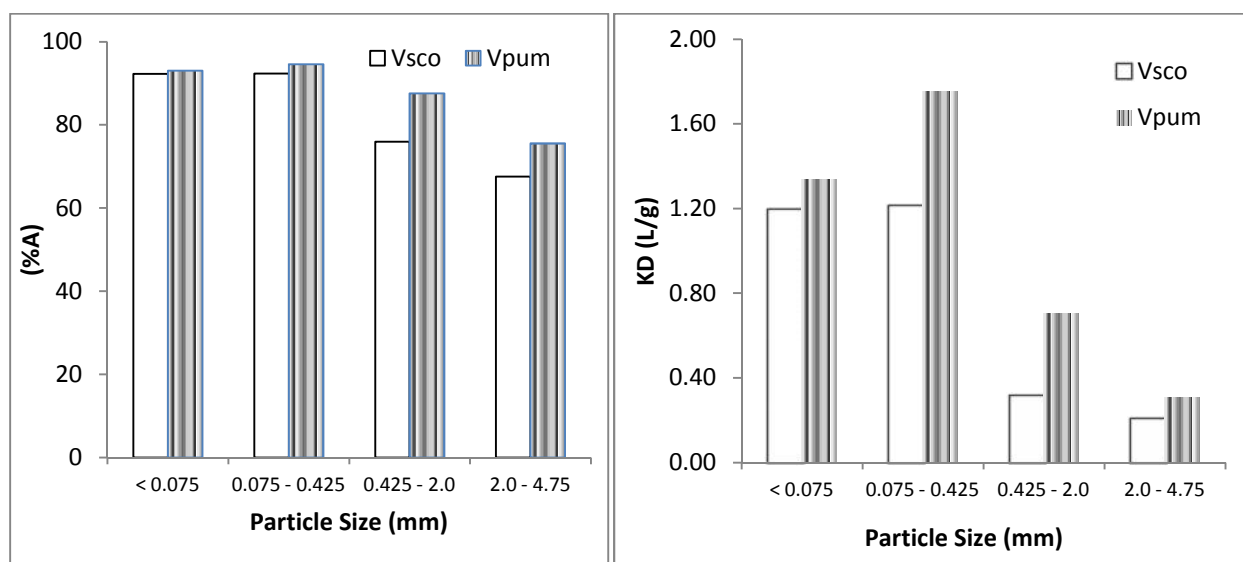
Figure 7: Effect of particle size on P(V) adsorption by VSco and VPum

5.5. Effect of VSco and VPum dosage on adsorption

To determine the optimum dose of adsorbent, VPum and VSco powder dosage ranges (2 - 50 g/L) were considered as variable and other parameters as constant. The experiments for both adsorbents revealed that the removal efficiency of P(V) in a fixed contact time of 1 hour increases significantly from 69.04 to 98.13% in the case of VSco and 72.61 to 98.13% in the case of VPum (Fig. 8).
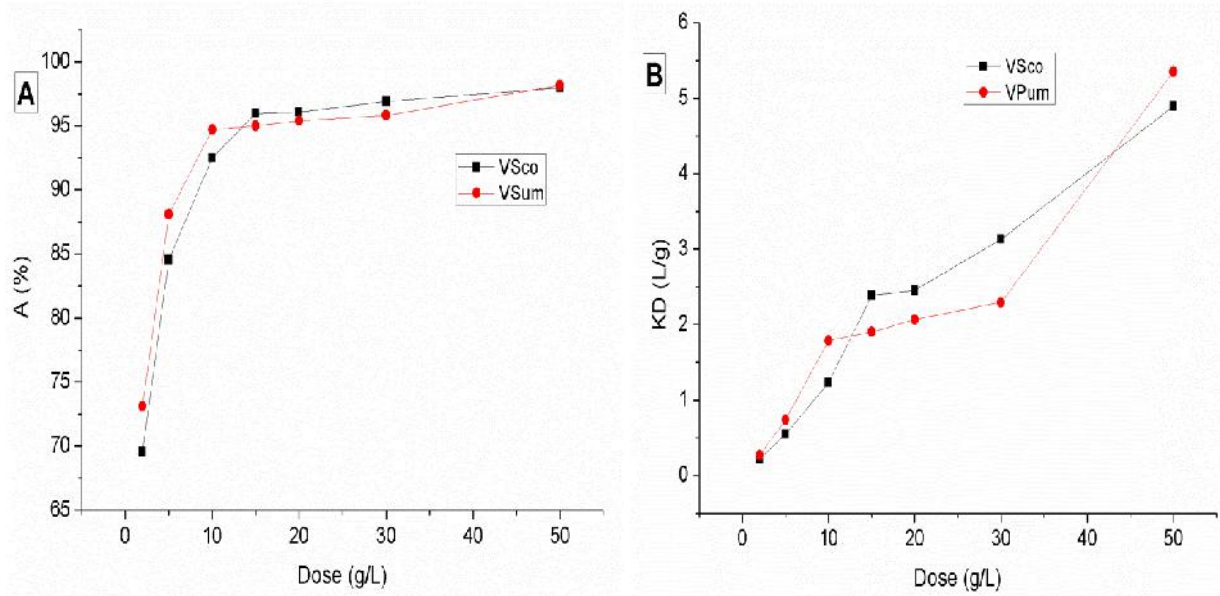
Figure 8: Effect of adsorbents dose on P(V) adsorption

5.6. Effect of initial P(V) concentration

The effect of initial concentration of phosphorus was assessed by varying the concentration from 0.5 to 50 mg/L at pH ~ 6 using 15 g/L VSco and pH ~ 7 using 10 g/L VPum. The percentage of P(V) adsorbed and P(V) adsorption capacity at various initial concentrations of P(V) are presented in Fig. 9. As can be seen from Fig. 9, the increment of the uptake with the increase of initial P(V) concentration from 0.5 to 5 mg/L was smaller than that with the increase from 10 to 50 mg/L, the uptake increased from 0.0486 to 1.1149 mg P(V)/g of VPum and from 0.0321 to 0.662 mg of P(V)/g of VSco, respectively.
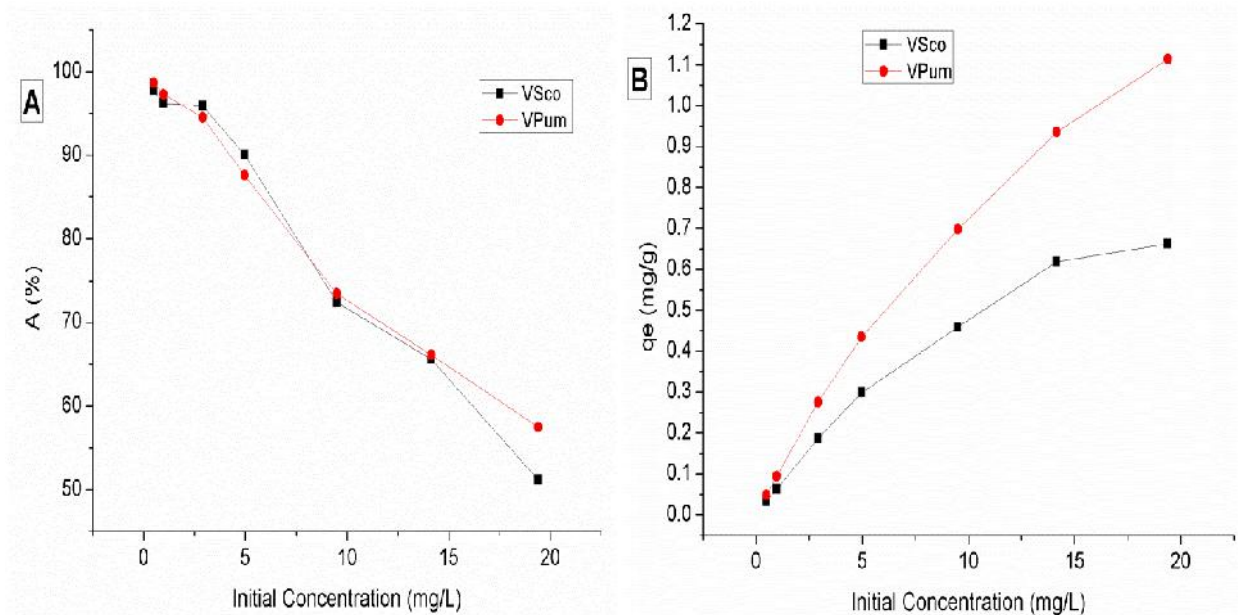
Figure 9: Effect of initial concentration on the removal of P(V) by VSco and VPum

5.7. Desorption experiment

The reusability of an adsorbents mainly depends on the ease with which adsorbate is released from the spent adsorbent. 3 mg/L P(V) was allowed to adsorb onto 15 g/L VSco and 10 g/L VPum for 60 min contact time at shaking speed of 200 rpm. The solids loaded with P(V) were separated from the solution from the supernatant solution by filtration and dried. Desorption study was then carried out using the P(V) loaded VSco and VPum to investigate the regenerability of the exhausted adsorbents. The regenerative properties of the P(V) loaded VSco and VPum were investigated using NaOH solution of different concentrations. The batch desorption of P(V) from the P(V) loaded VSco and VPum were conducted using 100 mL solution of 0.1 and 0.2 M NaOH separately under optimum batch adsorption conditions (dose 15, 10 g/L, particle size < 0.075 mm of VSco and 0.075-0.425 mm of VPum, agitation rate = 200 rpm and contact time = 60 min). It was found that the percentages of P(V) desorbed by 0.1 and 0.2 M NaOH solution were 71.23 and 97.3% in the case of VSco and 82.92 and 98.01% in the case of VPum, respectively in the first cycle (Table 3).

Table 3: Desorption of P(V) from VSco and VPum by NaOH Solution

Cycle	Adsorption (%)		Desorption (%)			
	VSco	VPum	VSco		VPum	
			0.1 M NaOH	0.2 M NaOH	0.1 M NaOH	0.2 M NaOH
1	91.91	95.19	71.23	97.31	82.92	98.01
2	86.40	89.86	77.04	96.52	77.57	94.59
3	80.34	77.10	78.84	98.12	70.89	92.53
4	72.26	75.01				

5.8. Effects of Co-existence Ions

The phosphorus-contaminated surface water is always associated with other co-ions like nitrate, sulfate, chloride, carbonate and bicarbonate, which can compete with phosphorus ions during adsorption process for active sites on VSco and VPum. Thus, the effects of these competitive ions on uptake of phosphorus were separately investigated in the presence of following competing anions: HCO_3^-, CO_3^{2-}, Cl^-, NO_3^-, and SO_4^{2-}. As shown in Fig. 10, a decrease in P(V) removal was observed when the concentration of competitive ions was increased from 10 to 300 mg/L. Results reveal that, bicarbonate and sulfate have only significant interfering effect on the adsorption of P(V) by VSco and VPum.
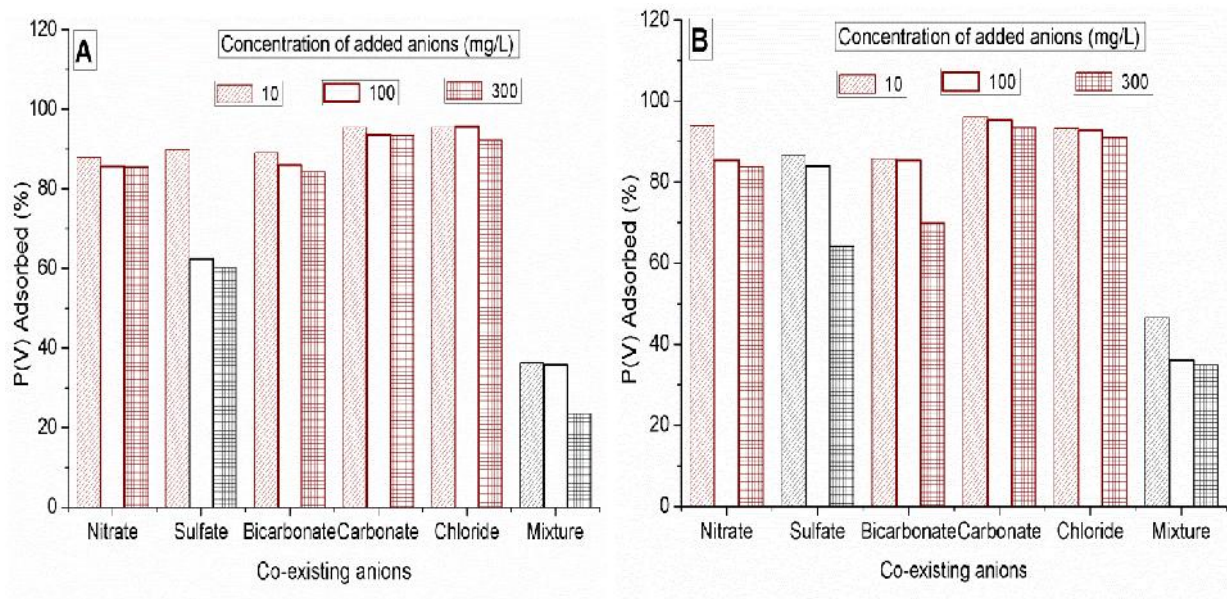
Figure 10: Effect of co-existing anions on the removal of P(V) by (A) VSco and (B) VPum

5.9. Removal of Phosphorus from Wastewater

Based on the promising results of phosphate removal from aqueous solutions, tests were conducted to evaluate these results using real wastewater. The wastewater used was taken from Jimma town. The effect of VSco and VPum on the removal of COD, BOD, Nitrate, Chloride and Sulfate is depicted in Table 4.

Table 4: Physco-chemical analysis of wastewater before and after treatment with VSco and VPum

Parameters	Influent	Wastewater After Adsorption			
		VSco	%	VPum	%
Temperature (^{o}c)	24	24.31	-	24.42	-
pH	5.4	6.23	-	6.19	-
EC	342	356	-	386	-
COD (mg/L)	480	343.2	28.5	291.84	39.2
BOD (mg/L)	384	235.58	38.65	292.61	23.8
DO (mg/L)	3.5	3.41	1.14	3.28	6.29
Nitrate (mg/L)	271	154.2	43.1	174.54	35.6
Chloride (mg/L)	54.90	38.35	30.15	35.52	35.30
Sulfate (mg/L)	2.71	2.14	21.03	1.86	31.37
Bicarbonate (mg/L)	91.50	46.26	49.44	38.87	56.43
Reactive Phosphate mg/L	6.91 (3.0)	0.256	91.48	0.143	95.23

5.10.   Kinetics and Equilibrium Isotherm Models
5.10.1. Adsorption Kinetics

The kinetics of P(V) adsorption on VSco and VPum was investigated using 10 g/L and 15 g/L dose respectively, and 3 mg/L P(V) concentration, agitated for 60 min at pH ~ 6 (VSco) and pH ~7 (VPum). The linear plots of the pseudo-first -order, pseudo-second-order and intra-particle diffusion sorption kinetics are given in Fig. 11, 12 and 13 respectively, and the values of K_f, K_s, K_p, $q_{e, cal}$ (calculated), and $q_{e,exp}$ (experimental) are reported in Table 4. The analysis of the kinetics data showed that the values of the coefficient of determination $R^2 > 0.99$ for pseudo second-order plot.

Table 5: The kinetics parameters for adsorption of P(V) onto VSco and VPum

Model	Parameter	VSco	VPum
		Value	
Pseudo-First-Order	$q_{e, exp}$ (mg/g)	0.2659	0.2779
	$q_{e, calc}$ (mg/g)	0.2707	0.2402
	K_f [g/(mg.min)]	0.1384	0.1232
	R^2	0.8800	0.8962
Pseudo-Second-Order	$q_{e, exp}$ (mg/g)	0.2659	0.2779
	$q_{e, calc}$ (mg/g)	0.2800	0.2910
	K_s [g/(mg.min)]	1.0121	1.0464
	Vo [mg/(g.min)]	0.0784	0.0886
	R^2	0.9993	0.9996
Intra-particle Diffusion	K_p [mg/(g.min$^{0.5}$)]	0.0205	0.0211
	C (mg/g)	0.0979	0.1045
	R^2	0.6697	0.6708
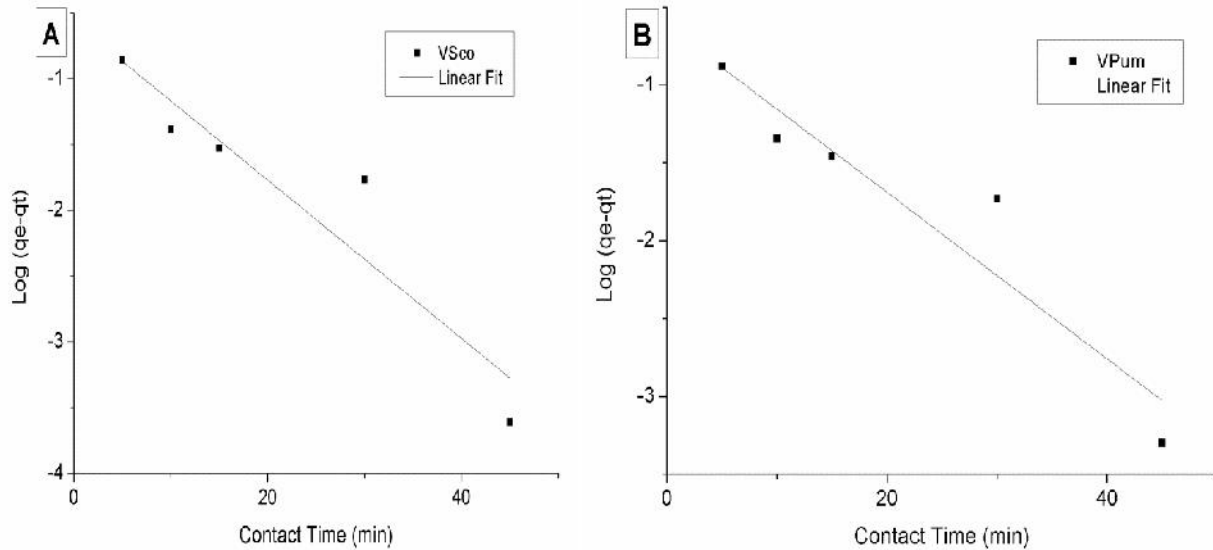
Figure 11: Plot of pseudo-first-order model for P(V) adsorption on to (A) VSco and (B) VPum
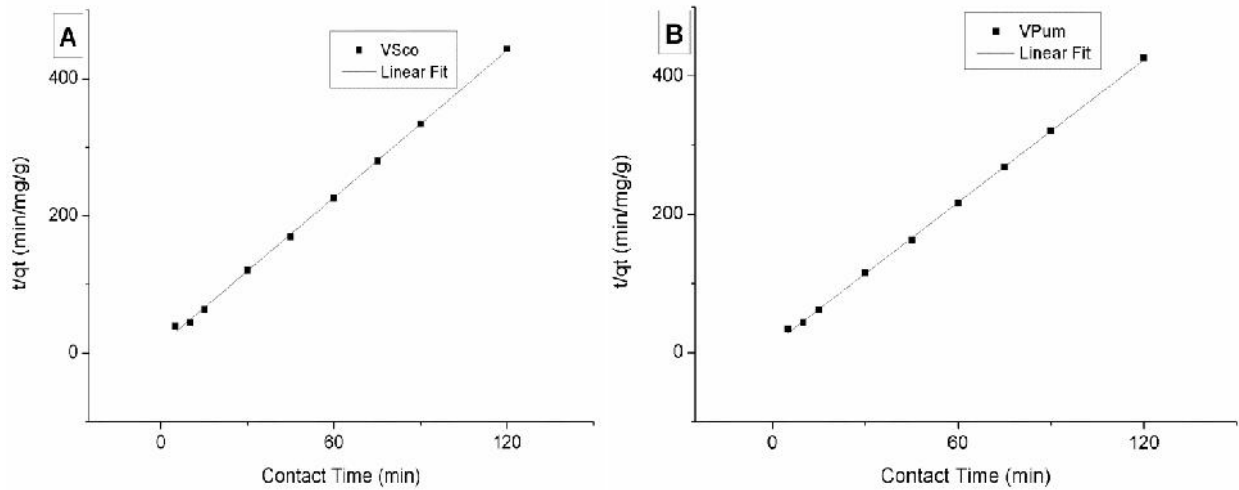
Figure 12: Plot of pseudo-second-order model for P(V) adsorption on to (A) VSco and (B) VPum
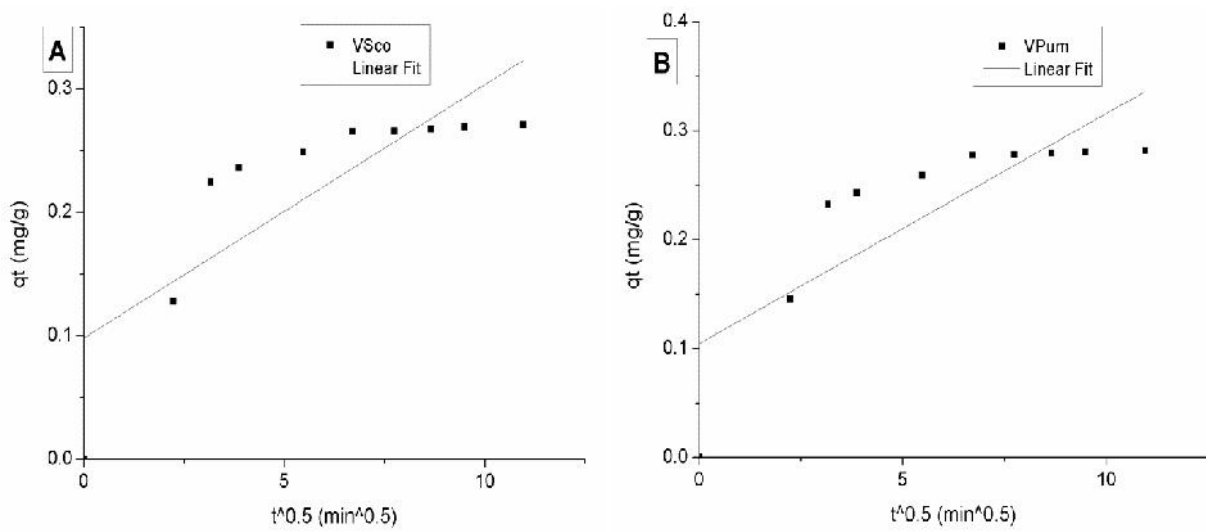
Figure 13: Plot of intra-particle diffusion model for P(V) adsorption onto (A) VSco and (B) VPum

5.10.2. Isotherm Models

The isotherm plots of the equilibrium adsorption of P(V) are graphically presented in Fig. 14, and the values of the equilibrium constants computed from the isotherm models are given in Table 6.
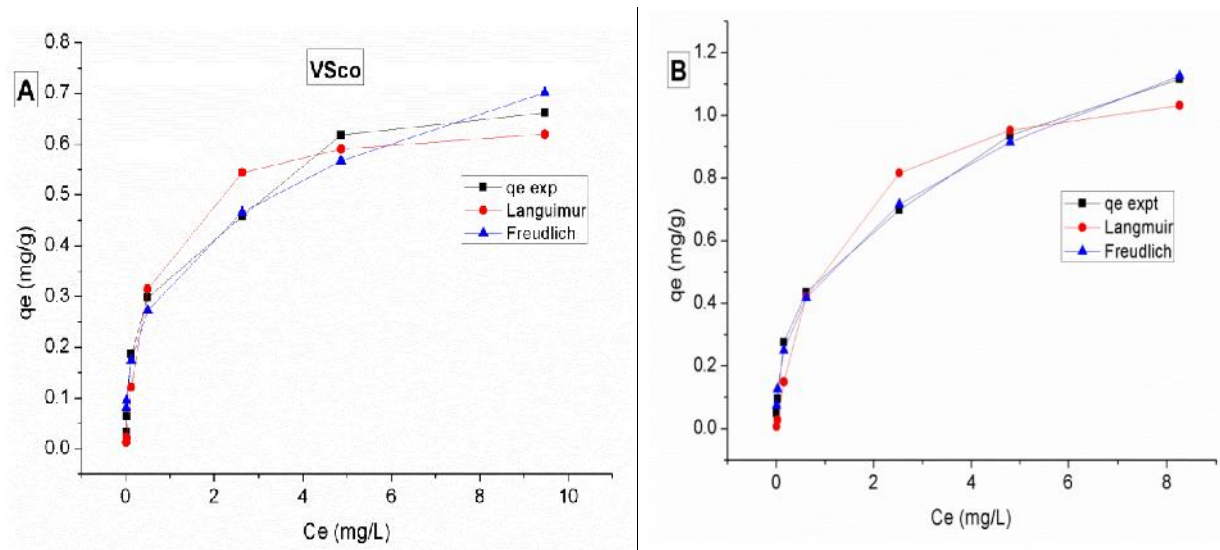
Figure 14: Isotherms of equilibrium adsorption of P(V) on (A) VSco and (B) VPum

Table 6: Freundlich and Langmuir constants of VSco and VPum

Adsorbent	Freundlich Constants				Langmuir Constants			
	K_F (L/g)	1/n	R^2		Q_o (mg/g)	b (L/g)	R^2	R_L
VSco	0.34	0.32	0.98		0.65	1.88	0.97	0.187 ± 0.19
VPum	0.50	0.38	0.99		1.17	0.92	0.97	0.271 ± 0.25

CHAPTER SIX: DISCUSSION

Findings of the present study indicated that the highest removal rate of P(V) for both adsorbents (VPum and VSco), occurs at the initial 60 minutes. However, in the previous studies (Alemayehu and Lennartz, 2009; 2010; 2011), using similar adsorbents for the removal of heavy metals from water by adsorption, it was found that the equilibrium time needed for it was longer (>2 h) than is shown by the current study. These result indicate that P(V) has a higher affinity toward the adsorbents than heavy metals. This is probably due to the difference in physco-chemical properties of metals and non-metals. It was also found that the removal efficiency rate was increased further due to increasing the adsorbent dose (Fig. 8) rather than increasing the contact time (Fig. 4). The adsorption rate with increasing initial contact time in a given mass of sorbent is raised and then gradually reaches equilibrium because the adsorbing surfaces of a given particular mass of adsorbent involve particular sites to adsorb P(V) concentration. So, those sites would be occupied by adsorbate ions within short period of time due to increasing adsorbents dose and contact time.

The results of fitting the experimental data to the pseudo-first order, pseudo-second order kinetic equations (represented in Eq. 4 and 5, respectively) and intra-particle diffusion (Eq. 6) models are presented in Table 5. The values of the pseudo-first-order adsorption rate constant k_f (Table 5) are determined using Eq. (4) by plotting $\log(q_e - q_t)$ against t for P(V) adsorption onto the adsorbent (VSco and VPum) with initial P(V) = 3 mg/L at room temperature for the first 45 minutes only. Experimental results did not follow first-order kinetics given by as there was difference in log qe and the intercept of the plot of log ($q_e - q_t$) against t and the coefficient of determination (R^2) for the pseudo-first-order kinetic model (Fig. 11A) was found to be lower value (0.88, 0.90). The pseudo-second order rate constant (K_s), calculated equilibrium capacity ($q_{e, calc}$) and adsorption affinity ($V_0 = K_s q_e^2$) were computed from linear plot of t/q_t versus t (Fig. 12). Numerical values of parameters of the pseudo-second order equation are given in Table 5. The plots of t/q_t versus t were straight lines with the coefficients of determination, $R^2 > 0.99$ for both adsorbents (VSco and VPum). In addition, the values of the modeled equilibrium capacities, $q_{e,calc}$ (0.2800, 0.2910), were comparable to the experimental equilibrium capacities, $q_{e,exp}$ (0.2659, 0.2779). Thus, the kinetic of P(V) adsorption on both VSco and VPum well described by the pseudo-second order equation, implying that the rate-limiting step could be chemical

adsorption involving valence forces through the sharing or exchange of electrons between adsorbent and adsorbate (Fufa, *et al*., 2014). Similar results are obtained in the removal of P(V) from water using Schwertmannite (Ferric Oxyhydroxide Sulfate) (Eskandarpour, *et al*., 2006).

Besides adsorption at the outer surface of the adsorbent, the P(V) may also diffuse into the interior of the adsorbent (Kemer *et al*. 2009). The intra-particle diffusion model (Eq. 6) based on the theory proposed by Weber and Morris (1963) was tested to determine if the particles' diffusion is the rate-limiting step for the P(V) adsorption onto VSco and VPum. The intra-particle diffusion rate constant (K_p) value estimated from the slope of plot of q_t versus square root of time ($t^{0.5}$) was found to be 0.0205 mg/(g. min$^{0.5}$) (VSco) and 0.0211 mg/(g. min$^{0.5}$) (VPum) for the initial phosphorus concentration of 3 mg/L (Table 5). According to Weber and Morris, if intra-particle diffusion is a rate-controlling step, then the plots should be linear and pass through the origin (Weber and Morris 1963 cited in (Kebede, *et al*., 2014; Fufa, *et al*., 2014)). As shown in Fig. 13, though the plot is not passing through the origin in both adsorbent conditions. These indicates that the phosphorus adsorption onto both VSco and VPum is a complex process and this is indicative of some degree of boundary layer control (Yakout & Elsherif, 2010), and this further show that the intra-particle diffusion was not the sole rate controlling step, but other kinetic models may control the rate of adsorption.

The adsorption of P(V) onto VSco and VPum are believed to be dominated by complexation between surface groups and the adsorbing molecules. Depending on pH, the VSco and VPum surface sites react as acid or base, resulting in a pH dependent surface charge causing electrostatic interactions with the surrounding aqueous phase (Sperlich, 2010). As shown in Fig. 5, it is obvious that phosphorus adsorption onto VSco and VPum strongly pH dependent. There are two prominent points in the measured adsorption at pH 3.0 and 6.0. The adsorption of phosphate remains at a maximum level within this pH range, and deceases dramatically beyond this pH range. A similar result was also observed by other researchers investigating phosphate adsorption on Fe-coordinated amino-functionalized 3D mesoporous silicates hybrid materials (Zhang, *et al*., 2011) and ZnCl$_2$ activated coir pith carbon (Namasivayam & Sangeetha, 2004). The observed trend is related to phosphate proton dissociation equilibra. At pH values less than the pH$_{ZPC}$ of the adsorbent, the net charge is positive, facilitating the adsorption of anions. The pH$_{ZPC}$ of the adsorbents has been found to be 7.5 (VSco) and 9.3 (VPum) (Alemyahu, *et al*.,

2011). At pH range between 3 and 6, P(V) occurs mainly in the monovalent form of $H_2PO_4^-$, while at higher pH values (>7.1) a divalent anion HPO_4^{2-} dominates (pK_{a1} = 2.15; pK_{a2} = 7.1; pK_{a3}= 11.5); in the intermediate region of pH 6 - 8, both species co-exist (Fig. 1) (Sperlich, 2010). So it is evident that in the pH range of natural waters, P(V) remains in the anionic state which is highly favorable for adsorption as the adsorbent surface remains positively charged at that pH range owing to its higher pH_{ZPC}. Also, the surface charge of VSco and VPum become more negative with increasing pH, resulting in more neutral and negatively charged groups on the surface. This explains the sharper decrease in adsorption capacity from pH 7 to 12 compared to the less pronounced decrease from pH 6 to 7 in the case of VSco. The higher pH not only causes the adsorbent surface to carry more negative charges, but also leads to a high concentration of hydroxide groups. Therefore, there may also be increased competition between negatively charged phosphate species and hydroxide groups on more negatively charged adsorbent surface sites to causes the lower adsorption of phosphate at higher pH (Fufa, *et al*., 2014).

Moreover, in order to characterize the influence of adsorbents on the solution pH, a separate set of batch equilibrium experiments at a fixed initial pH in the blank system were conducted at equilibrium. As expected, for both adsorbents significant pH changes occurred during the equilibrium time in the blank system, which stemmed from an acid neutralization effect and proton adsorption of hydroxylated rock surface. The pH variation during the experiments was between 1.0 - 3.0 units in average. The observations obtained may be suggesting that the adsorption of P(V) were influenced by the adsorbents and not solely by the solution pH. The rough surface of the adsorbents and the presence of P(V) from oxides (Fe, Al, Mg, and Si) are beneficial in the removal of P(V) from solution. In conclusion, the P(V) adsorption is due to electrostatic phenomenon as well as surface complexation that work individually or in combinations for the adsorption of P(V) ions on the adsorbents.

It was also observed that the adsorption percentage of P(V) onto the adsorbents increased with increasing agitation speed reaching a maximum of 92.36% for VSco and 94.61% for VPum at 200 rpm then decreased with the increasing of agitation speed reaching 62.36% and 66.34% at 250 rpm, respectively (Fig. 6). It found that the removal of P(V) increased with increases in rpm to some extent. This is due to dispersal of the adsorbent particles in the aqueous solution which

leads to reduced boundary mass transfer and even then it may increase the velocity of particles, so that it increases the percent removal of P(V) ions (Alemyahu, *et al*., 2011; Baraka, *et al*., 2012; Ragheb, 2013).

The effect of both adsorbents on the sorption of P(V) was studied at pH of 6 for VSco and 7 for VPum. Results showed that VPum was more efficient than VSco, producing maximum removal of P(V) ions at the levels of adsorbent dosage assayed (VPum: 94.61% and VSco: 92.36% at 10 g/L). Further increment of adsorbent dosage did not caused significant change on the removal efficiency in the case of the VPum system (Fig. 8), implying enough attachment sites for P(V) ions. However, the removal of P(V) ions increased with an increase in the amount of VSco. On changing the VSco dose from 10 to 15 g/L, removal of P(V) ions significantly increased from 92.36 to 95.91% (Fig. 8A). Optimum removal was exhibited at 15 g/L of the VSco (Fig. 8). This observation can be attributed to the increase of the availability of free adsorption sites. A distribution coefficient K_D reflects the binding ability of the surface for an element. The K_D values of a system mainly depends on pH any type of surface. The distribution coefficient K_D values for P(V) at pH of 6 and 7 for VSco and VPum, respectively were calculated Eq. 3. It is seen that the distribution coefficient K_D increase with an increase in adsorbent concentration, indicating the heterogeneous surface of the adsorbent. It is observed in Fig. 8(B) that K_D increases with an increase in adsorbent concentration at constant pH. If the surface is homogeneous, the K_D values at a given pH should not change with adsorbent concentration (Alemayehu, 2010).

Furthermore, the effects of the adsorbent particle size for a constant dose on the removal of P(V) was studied. The removal and the K_D value of P(V) increased systematically with decreasing particle size. On changing the particle size from 4.75 to 0.075 mm, the amount adsorbed from 0.208 to 1.196 mg/g and from 0.309 to 1.338 mg/g of VSco and VPum (Fig .7), respectively. However, the smallest particle size (< 0.075mm, powder) did not exhibited an enhanced removal that which was attributed to a loss of porosity, and thus of diffusion controlled sorption of P(V) (Fig.7). This further confirms that both surface complexation and electrostatic attraction as well as diffusion in to micro-pores of the adsorbent are responsible for the immobilization of P(V) in the presence of volcanic material. This is in agreement with the findings from various studies done by (Alemayehu & Lennartz, 2009; Alemayehu & Lennartz, 2010; Alemyahu, *et al*., 2011).

Attempt made by researchers revealed that the presence of oxides in aqueous solutions considerably affect the adsorption process since it forms groups of agent factor on the surface area (Moradi, *et al*., 2015). The study done by (Alemayehu & Lennartz, 2010) showed that the VSco and VPum characteristics contain 47.4% SiO_2, 21.6% Al_2O_3, and 68.6% SiO_2, 8.9% Al_2O_3, respectively. In addition, Yenisoy-Karakas *et al*., (2004) cited in (Moradi, *et al*., 2015) indicated that the chemical characteristic of adsorbent surface plays a significant role in removing ions rather than adsorbent pore size and Dubinin (1967) cited in (Alemayehu & Lennartz, 2010) proposed that pore size distribution plays a more important role than surface area, in adsorption processes. He suggested that the pore structure of adsorbent particles consists of macrospores, transitional pores and microspores. Moreover for any porous materials, especially in an agitated system, the main resistance to mass transfer occurs during the movement or diffusion of solute within the pores of the particles (Alemayehu, 2010).

The equilibrium uptake of P(V) ions on to both VPum and VSco increased when increasing initial concentration (Fig. 9). With changing the concentration from 0.5 to 20 mg/L, the absolute amount of P(V) ions per unit of adsorbent increased from 0.0321 to 0.662 mg P(V) per gram of VSco and from 0.0486 to 1.1143 mg of P(V) per gram of VPum, in 100 mL solution, respectively. This is in agreement with the findings from various researchers that suggest the more concentrated solution is the better adsorption (Xu *et al*., 2006; Huang *et al*., 2008; Bowden *et al*., 2009) who found the same behavior by studying the adsorption capacity of 8.5, 0.29, 89.9 mg/g respectively for the removal of P(V) from aqueous solutions (Table 1).

On the contrary, the removal percentage of P(V) decreased with increasing initial P(V) concentration (Fig. 9A). On changing the initial concentration from 0.5 to 20 mg/L, the removal percentage of P(V) significantly decreased from 97.81 to 51.18% in the case of VSco system and from 98.70 to 57.44% in the case of VPum system. This is one of the principles of adsorption isotherms that is, the sites with greater affinity by adsorbate are occupied first followed by other sites with less affinity by adsorbate, until the saturation of the adsorbent. This is a common finding and has been largely reported in the literature (Almeelbi & Bezbaruah, 2012; Barca, *et al*., 2012; Babatunde & Zhao, 2010).

The adsorption equilibrium is usually described by an isotherm equation whose parameter express the surface properties and affinity of the adsorbent. The data from these models provide

information to predict removal of P(V) to the adsorbents, and an estimation of the adsorbent amounts needed to remove P(V) ions from an aqueous solution. Analysis of the relationship between the adsorption capacity of the materials (VPum and VSco) and different P(V) initial concentrations at equilibrium was performed using the equations of Langmuir (Eq.7) and Freundlich adsorption isotherm (Eq. 9), as seen in subsection 4.10.2, chapter four.

The adsorption of P(V) on VPum as well as VSco follow both Freundlich and Langmuir type adsorption isotherms (Fig 14). The Langmuir isotherm constants for P(V) determined by non-linear regression using Sum of square error function are presented in Tables 6. The results demonstrate that the values of the constants b and Q_o obtained by non-linear regression have similarity with the linear transform values. The coefficients of determination (R^2) values presented in Table 6 support this fact, with P(V) isotherms giving seemingly better fits of the experimental data with the model. The result confirms that the Freundlich adsorption capacity, K_f, of VPum (0.50 L/g) was larger as compared to that of VSco (0.34 L/g). Moreover, Freundlich constant, $1/n$, can also be measure of adsorption intensity or surface heterogeneity (also considered a measure of deviation from linearity of adsorption,). In fact, if $1/n = 1$ the adsorption is linear, indicating that the adsorption sites are homogeneous in energy and no interaction occurs between the adsorbed species (Foo & Hameed, 2010). Our result revealed that the $1/n$ values for both adsorbents (0.32, VSco and 0.38, VPum) were less than unity, which indicates that an increased adsorption can modify the adsorbent and that a chemical rather than a physical adsorption was dominant (Foo & Hameed, 2010). Moreover, the Langmuir monolayer capacity, Q_o, was appreciably larger for VPum (1.17 mg/g) compared to that of VSco (0.65 mg/g). The larger value of Q_o as obtained for P(V)-VPum indicate the strong interactions between P(V) and VPum. Beside, the essential characteristics of the Langmuir isotherm may be expressed in terms of R_L value (Subsection 4.10.2, chapter four). In all cases, the R_L values for the experimental data fell between 0 and 1 (Table 6), which is indicative of the favorable adsorption of P(V) on the adsorbents (Ncibi, 2008). Hence, according to Table 6, is seems that the Freundlich model is the most suitable model to satisfactorily describe the studied sorption phenomenon for both VSco and VPum. Indeed, the highest R^2 value and the lowest SSE value was found when modeling the equilibrium data using the Freundlich, for both linear and non-linear regression analysis (Table 6).

Any adsorbent is economically viable for pollutant removal from aqueous environment if the adsorbent can be regenerated and reused (Fufa, *et al*., 2014). The pH effect on the efficiency of P(V) adsorption on VSco and VPum showed (Fig. 5) that P(V) adsorption capacity was very low at pH > 7, suggesting the possibility of desorbing adsorbed P(V) from the saturated VSco and VPum using alkaline solution. Based on this, batch desorption of > 92 % P(V) adsorbed was carried out under identical experimental conditions of the batch sorption studies using 100 mL of 0.1 and 0.2 M NaOH solution separately. The percentages of P(V) desorbed at pH > 12 using 0.1 and 0.2 M NaOH solutions were 71.23% and 97.30% in the case of VSco system and 82.92 % and 98.01 % in the case of VPum system, respectively (Table 3). Consequently, P(V) loaded VSco and VPum could be successfully regenerated using NaOH solution. To test the adsorption potential of regenerated adsorbents, two more cycles of adsorption–desorption studies were carried out by maintaining the initial conditions of the same. In third cycle, the adsorbent capacity has shown 80.34% for VSco and 77.10% for VPum. From the observations these adsorbents have reuse potential for phosphorus removal.

The effects of coexisting anions such as HCO_3^-, CO_3^{2-}, Cl^-, NO_3^-, and SO_4^{2-} on P(V) adsorption by the VSco and VPum adsorbents were examined and the results are given in Fig. 4. Chloride and nitrate did not perceptibly interfere with P(V) removal even at a concentration of 300 mg/L, while bicarbonate began to show some adverse effects when the HCO_3^- concentration increases. However, SO_4^{2-} showed great competitive adsorption with phosphorus. The P(V) adsorption amount decreased quickly from 89.75 to 60.19% with the increase of SO_4^{2-} concentration 10 - 300 mg/L. This may be attributed to the competition of SO_4^{2-} with the phosphorus ions at the active site, on the surface of the sorbents. The selective nature of the phosphorus by the sorbent depends on size, charge, polarizability, electro-negativity difference, etc. The order of interference for phosphorus removal observed as in the following order: Mixture > SO_4^{2-} > HCO_3^- > NO_3^- > Cl^- > CO_3^{2-} for the adsorbent VSco and VPum. Similar trend was reported while studying Fe-coordinated amino-functionalized 3D mesoporous silicates hybrid materials as a sorbent for phosphorus removal (Zhang, *et al*., 2011). Thus, the decrease in the adsorption capacity may be explained on the basis of ion exchange mechanism where sulfate possesses the highest affinity for the adsorbent material and competes most effectively against P(V) adsorption. The order of the effect of the other anions on the phosphate adsorption may also be related to affinity of the anions toward the adsorbent.

In order to widen the applicability of the removal technique, the optimized method (except pH) that were determined by synthetic aqueous solution, was applied for the removal of P(V) onto VSco and VPum using wastewater sample of pH 5.4 (Table 4). The removal efficiency achieved were 91.48% (VSco), and 95.23% (VPum) in the real wastewater sample. As shown in table 4 VSco and VPum also achieved some removal of COD, BOD and Nitrite. The present study thus reveals that, the VSco and VPum are an excellent adsorbents for phosphorus removal from aqueous solution. The investigations are quite useful in developing an appropriate technology for designing a water/wastewater treatment plant. The process is economically feasible and easy to carry out (Alemayehu, 2010).

CHAPTER SEVEN: CONCLUSION AND RECOMMENDATION

This study provides valuable information about the design of phosphorous removal technology from aqueous solution using VPum and VSco. Both VPum and VSco were capable of removing P(V) ions from water. Although the study parameters such as the contact times, particle sizes, presence of other anions and initial P(V) concentrations of solution significantly affected the removal efficiency of P(V).

The adsorption of P(V) by VSco and VPum increased with the increase in contact time, and equilibrium was attained within 60 min within which ~90 % adsorption efficiency was achieved. A high percentage (~87 %) of P(V) removal was obtained within a pH range of 3 - 7, which is of great importance in practical application. For VSco it was found that the amount of P(V) adsorbed at pH 6 was the greatest. VPum, reached maximum P(V) adsorption at neutral pH value 7.

The fitting of the kinetic data of P(V) adsorption to the pseudo-second order with the coefficient of determination, $R^2 > 0.99$ was suggestive of the dominant chemisorptions mechanism of P(V) adsorption on the adsorbent VPum.

The equilibrium data satisfied both the Langmuir and Freundlich isotherm models, and the related parameters satisfied both the Langmuir and Freundlich isotherm models, and the related parameters indicated that VPum was able to adsorb P(V) ions to a large extent compared to VSco, and the removal percentage was higher at the lowest P(V) concentration. The adsorption process most satisfactorily described by the Freundlich isotherm model ($R^2 = 0.98$, 0.99 and SSE = 0.0084, 0.0034) indicating the heterogeneous distribution of active sites on the surface of VSco and VPum. The adsorption coefficients agreed well with the conditions supporting favorable adsorption.

P(V) adsorption was significantly reduced in the presence of sulfate, bicarbonate, and a mixture of co-existing anions, whereas slightly increased in the presence of chloride, and carbonate ions. The overall influence of competing anions on the efficiency of P(V) removal by VSco and VPum followed the order: Mixture $> SO_4^{2-} > HCO_3^- > NO_3^- > Cl^- > CO_3^-$. The results of the adsorption–desorption–adsorption cycle showed that the P(V) loaded VSco and VPum can be regenerated using 0.1 M and 0.2 M NaOH solution for reuse. In treatment with VSco and VPum, the removal

of P(V) from real wastewater sample is high whereby the percentage of removal is more than 91% (VSco) and 95% (VPum) of the initial concentration. Since VSco and VPum are freely abundant, locally available, low-cost adsorbents and has a considerable high adsorption capacity, it may be treated as economically viable for removal of P(V) from real wastewater.

Therefore, VSco and VPum could be useful for tackling the impacts of high concentrations of P(V) in water/wastewater. For large-scale application, further column experiments needs to be conducted to determine the real adsorption capacity and regeneration rate.

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Annexes

Annex 1. Batch Experiment Procedure (Ali & Gupta, 2007)

Conversion of reactive materials into adsorbents

1. Collect selected material and sieve to remove other particles such as stone, soil, paper etc.
2. Wash with ddH$_2$O and dry in an oven at 100°C for about 2 h.
3. Carbonize organic precursors by heating to 400–800°C for 5 –24 h.
4. Treat with hydrogen peroxide at 60°C for 24 h to remove adhered organic matter.
5. Wash with ddH$_2$O three times to remove hydrogen peroxide and dry in an oven at 100°C for ≈ 2 h.
6. Heat to 500°C in a furnace for 6 –12 h to activate the adsorbent.
7. Determine density, porosity and ignition loss by the usual methods.
8. Establish the stability of the adsorbent by suspending in ddH$_2$O, HCl and NaOH (0.1 to 1.0 M) for about 1–2 h.
9. Establish mineral and crystal structure by X-ray diffractometry and Scanning electron microscope (SEM), using published methods.
10. Carry out elemental analysis by chemical methods, as described.
11. Collect adsorbent of different particle sizes by sieving and keep in a vacuum desiccators. At this stage, the adsorbent is ready for water purification.

Batch experiments

12. Use a 50-ml Erlenmeyer flask to carry out batch experiments in a thermostatic shaking water bath. Take a known amount of pollutant in 10–25 ml H$_2$O and add a dose of adsorbent. The dose of adsorbent depends on the type of adsorbent and adsorbate.
13. Agitate flask mechanically in a water bath at desired temperature. Normally temperature is fixed between 25 and 35°C for 1–3 h.
14. Repeat Steps 12–13 to optimize concentration of pollutant, pH, adsorbent dose, temperature and contact time after varying their values.
15. Centrifuge or filter the mixture and determine the concentration of pollutant in the aqueous phase.
16. Calculate the amount of pollutant adsorbed from the aqueous solution by determining the equilibrium concentration in solution.

Kinetic studies

17. Set up 50-ml Erlenmeyer flasks containing various amounts of standard solutions of pollutant and shake in a thermostatic shaking water bath.

18. Add a known amount of adsorbent to each flask.

19. Allow flasks to agitate mechanically in the water bath at a constant temperature. Contact time, temperature and other conditions should be selected based on preliminary experiments.

20. Centrifuge the mixture at pre-decided time intervals and analyze the concentration of pollutant in the supernatant.

21. Determine the equilibrium concentration (C_e) and time to reach equilibrium.

22. Calculate thermodynamic parameters as detailed and run adsorption models.

Annex 2: Effects of Contact Time

Contact Time	Co	VSco				VPum			
(min)	(mg/L)	C_e(mg/L)	%A	q_t(mg/g)	K_D(L/g)	C_e(mg/L)	%A	q_t (mg/g)	K_D(L/g)
5	2.945	1.6641	43.50	0.1281	0.0770	1.4908	49.38	0.1454	0.0975
10	2.945	0.6972	76.32	0.2248	0.3224	0.6195	78.96	0.2325	0.3754
15	2.945	0.5825	80.22	0.2362	0.4055	0.5141	82.54	0.2431	0.4729
30	2.945	0.4568	84.49	0.2488	0.5447	0.3515	88.06	0.2593	0.7377
45	2.945	0.2887	90.20	0.2656	0.9200	0.1712	94.19	0.2774	1.6207
60	2.945	0.2863	90.28	0.2659	0.9288	0.1661	94.36	0.2779	1.6725
75	2.945	0.2697	90.84	0.2675	0.9921	0.1511	94.87	0.2794	1.8488
90	2.945	0.2529	91.41	0.2692	1.0644	0.1398	95.25	0.2805	2.0068
120	2.945	0.2370	91.95	0.2708	1.1428	0.1265	95.70	0.2818	2.2279

Annex 3 : Effects of pH of solution

pH_{in}	Co	VSco				VPum			
	(mg/L)	C_e(mg/L)	%A	q_e(mg/g)	pH_f	C_e(mg/L)	%A	q_e(mg/g)	pH_f
3.02	2.945	0.3701	87.43	0.2575	4.04	0.2379	91.92	0.2707	5.61
4.97	2.945	0.3131	89.37	0.2632	5.74	0.2093	92.89	0.2736	6.07
6.00	2.945	0.2250	92.36	0.2720	5.98	0.1992	93.24	0.2746	6.90
6.98	2.945	0.2863	90.28	0.2659	6.82	0.1587	94.61	0.2786	6.45
7.93	2.945	0.6744	77.10	0.2271	6.70	0.5771	80.40	0.2368	7.20
10.01	2.945	0.8884	69.83	0.2057	7.80	0.8061	72.63	0.2139	6.80
11.93	2.945	1.0252	65.19	0.1920	10.24	0.9652	67.22	0.1980	10.80

Annex 4 : Effects of Agitation Speed

Ag. Speed (rpm)	Co (mg/L)	VSco				VPum			
		C_e(mg/L)	%A	q_e(mg/g)	K_D(L/g)	C_e(mg/L)	%A	q_e(mg/g)	K_D(L/g)
100	2.945	0.6687	77.29	0.2276	0.3404	0.5339	81.87	0.2411	0.4516
150	2.945	0.5645	80.83	0.2380	0.4217	0.3768	87.21	0.2568	0.6816
200	2.945	0.2250	92.36	0.2720	1.2087	0.1587	94.61	0.2786	1.7554
250	2.945	1.1084	62.36	0.1837	0.1657	0.9913	66.34	0.1954	0.1971

Annex 5 : Effects of Particle Size

Par. Size (mm)	Co (mg/L)	VSco				VPum			
		C_e(mg/L)	%A	q_e(mg/g)	K_D(L/g)	C_e(mg/L)	%A	q_e(mg/g)	K_D(L/g)
< 0.075	2.945	0.2273	92.28	0.2718	1.1959	0.2048	93.05	0.2740	1.3382
0.075 - 0.425	2.945	0.2250	92.36	0.2720	1.2087	0.1587	94.61	0.2786	1.7554
0.425 - 2.0	2.945	0.7071	75.99	0.2238	0.3165	0.3651	87.60	0.2580	0.7065
2.0 - 4.75	2.945	0.9551	67.57	0.1990	0.2083	0.7199	75.55	0.2225	0.3091

Annex 6: Effects of Dose of Adsorbent

Dose g/L	Co (mg/L)	VSco				VPum			
		C_e(mg/L)	%A	q_e(mg/g)	K_D(L/g)	C_e(mg/L)	%A	q_e(mg/g)	K_D(L/g)
2	2.945	0.9119	69.04	0.2033	0.2230	0.8066	72.61	0.2138	0.2651
5	2.945	0.4641	84.24	0.2481	0.5345	0.3573	87.87	0.2588	0.7242
10	2.945	0.2250	92.36	0.2720	1.2087	0.1587	94.61	0.2786	1.7554
15	2.945	0.1205	95.91	0.2824	2.3436	0.1496	94.92	0.2795	1.8690
20	2.945	0.1175	96.01	0.2828	2.4068	0.1383	95.31	0.2807	2.0302
30	2.945	0.0927	96.85	0.2852	3.0757	0.1252	95.75	0.2820	2.2530
50	2.945	0.0600	97.96	0.2885	4.8068	0.0550	98.13	0.2890	5.2534

Annex 7: Effects of Initial Concentration

Co (mg/L)	VSco				VPum			
	C_e(mg/L)	%A	q_e(mg/g)	K_D(L/g)	C_e(mg/L)	%A	q_e(mg/g)	K_D(L/g)
0.492	0.0108	97.81	0.0321	2.9719	0.0064	98.70	0.0486	7.6112
0.968	0.0184	96.27	0.0633	3.4479	0.0262	97.29	0.0942	3.5962
2.910	0.1205	95.86	0.1860	1.5430	0.1587	94.55	0.2751	1.7333
4.960	0.4923	90.07	0.2978	0.6050	0.6141	87.62	0.4346	0.7076
9.500	2.6250	72.37	0.4583	0.1746	2.5226	73.45	0.6977	0.2766
14.145	4.8682	65.58	0.6185	0.1270	4.7949	66.10	0.9350	0.1950
19.400	9.4705	51.18	0.6620	0.0699	8.2570	57.44	1.1143	0.1350

Annex 8: Isotherm Model for VSco

Co (mg/L)			$q_{e\ exp}$ (mg/g)	Langmuir			Freundlich	
A	B	Avg.		$q_{e\ calc}$ (mg/g)	SSE	R_L	$q_{e\ calc}$ (mg/g)	SSE
0.0047	0.0169	0.0108	0.0321	0.0130	0.0004	0.5200	0.0802	0.0023
0.0077	0.0290	0.0184	0.0633	0.0218	0.0017	0.3551	0.0951	0.0010
0.1482	0.0928	0.1205	0.1860	0.1207	0.0043	0.1548	0.1736	0.0002
0.5522	0.4325	0.4923	0.2978	0.3144	0.0003	0.0970	0.2724	0.0006
2.7060	2.5440	2.6250	0.4583	0.5442	0.0074	0.0531	0.4654	0.0001
4.8022	4.9343	4.8682	0.6185	0.5901	0.0008	0.0363	0.5672	0.0026
9.4879	9.4531	9.4705	0.6620	0.6198	0.0018	0.0267	0.7018	0.0016
					0.0166			0.0084

Annex 9: Isotherm Model for VPum

Co (mg/L)			$q_{e\ exp}$ (mg/g)	Langmuir			Freundlich	
A	B	Avg.		$q_{e\ calc}$ (mg/g)	SSE	R_L	$q_{e\ calc}$ (mg/g)	SSE
0.0010	0.0118	0.0064	0.0486	0.0068	0.0017	0.6879	0.0736	0.0006
0.0401	0.0122	0.0262	0.0942	0.0275	0.0044	0.5284	0.1260	0.0010
0.1813	0.1361	0.1587	0.2751	0.1490	0.0159	0.2715	0.2501	0.0006
0.6802	0.5480	0.6141	0.4346	0.4218	0.0002	0.1794	0.4185	0.0003
2.4912	2.5540	2.5226	0.6977	0.8159	0.0140	0.1025	0.7165	0.0004
4.9392	4.6506	4.7949	0.9350	0.9514	0.0003	0.0712	0.9149	0.0004
8.2670	8.2470	8.2570	1.1143	1.0312	0.0069	0.0529	1.1251	0.0001
					0.0434			0.0034

Annex 10: Effects of Co-existing anion at different concentration

Co-existing anion	Concentration of P (mg/L)					
	VSco			VPum		
	10	100	300	10	100	300
NO_3^-	0.3520	0.4181	0.4239	0.1765	0.4259	0.4715
SO_4^{2-}	0.2983	1.0948	1.1585	0.3928	0.4648	1.0437
HCO_3^-	0.3167	0.4105	0.4552	0.4180	0.4286	0.8777
CO_3^{2-}	0.1325	0.1818	0.1920	0.1133	0.1367	0.1890
Cl^-	0.1331	0.1273	0.2259	0.1926	0.2122	0.2639
Mixture	1.8554	1.8712	2.2267	1.5553	1.8660	1.8938