

Design Phosphate Removal Technology using Volcanic Rocks: Kinetics and Equilibrium Studies

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Abstract – 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 VSco and VPum were maximum at pH 6 and 7 respectively. The sorption data were better represented by the Freundlich isotherm ($R^2 = 99, 98$; $SSE \approx 0.0034, 0.0084$) 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^{2-} . 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.

Keywords: Volcanic rocks, Phosphate, Batch experiment, Isotherms

I. INTRODUCTION

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 [1, 2]. 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 [3]. According to [4] excessive phosphorous is the most common cause of

Eutrophication in freshwater lakes, reservoirs, streams, and headwaters of estuarine systems [5].

Phosphorous removal from water and wastewater has been achieved by methods such as coagulation, chemical precipitation, biological treatment, and ion exchange [6]. 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. Due to logistics and scarcity of chemicals, energy, and lack of know-how is difficult in expanding treatment plants in rural areas [7].

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 [8]. 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 hybrid impregnated polymeric sorbent containing hydrated ferric oxide [9], industrial acidified laterite by-product [10], clay soil [11], slag and fly ash [6], activated red mud [12], steel slags [13], biogenetic calcium carbonate minerals [14], Silicate hybride materials [15], Schwertmannite (which is ferric oxyhydroxide sulphate) [16], mixture of sand and dolomite [17], ZnCl₂ coir pith carbon [18]. However, the available methods have several disadvantages, which make them not effective and not suitable for non-developed areas around the globe [8, 19].

As a result, looking for an appropriate 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 [19, 20, 21, 22], 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 phosphate and the volcanic rocks (VPum and VScO) in the aqueous system. Therefore, the objectives of this study were: (1) to examine the P(V) sorption capacity of VScO and VPum under batch adsorption setup, (2) to optimize major design parameters (contact time, solution pH, adsorbent dose, particle size, initial P(V) concentration, and concentration of competing anions, pH of solution, initial concentration, contact time, adsorbent dose, particle size, and agitation speed) on P(V) adsorption onto VPum and VScO, and (3) to predict the adsorption process by using kinetics and isotherms models

II. MATERIALS AND METHODS

A batch adsorption experiments were performed using the following main components:

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

A. Adsorbent media preparation

All the VPum and VScO samples [23] used were representative samples, obtained from Jimma University, Jimma Institute of Technology (Dr. Ing Esayas Alemayehu Laboratory). 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 [23, 24]. 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 [25]. Finally, the sieved samples were kept in airtight plastic container at room temperature until commencement of the adsorption experiments.

B. 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 dihydrogen phosphate KH_2PO_4 .

C. Adsorption Experiment

Sets of batch adsorption experiments were conducted to understand the phosphate 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 $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ for 12 hours before the actual experiment [23]. 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) at a wavelength of 880 nm. The percentage of P(V) removed, A%, and the amount of P(V) adsorbed per unit mass of the adsorbent, q_t (mg/g), at any time t (min) are computed respectively using (1) and (2).

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

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

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/g), M = dry mass of the adsorbent (g), 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 [26].

The distribution coefficient (K_D) value for P(V) adsorption on the adsorbents (VScO and VPum) was calculated using (3) [23, 27]:

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

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.

D. Kinetics and Equilibrium Isotherm Models

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 [28] and Intra-particle diffusion models using (4), (5) and (6), respectively.

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

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

phosphorous adsorbed at time t and at equilibrium, respectively. Straight line plots of $\log(q_e - q_t)$ versus t at different times were plotted to calculate the rate constants and the determination coefficients (R^2).

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

Where K_s is the pseudo-second order sorption rate constant (mg/min), and q_e (mg/g). If the pseudo second-order kinetics is applicable, the plot of t/q_t versus t will give a linear relationship [29].

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

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 [29].

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 analysed by applying adsorption isotherm models. Langmuir and Freundlich models are the most frequently employed for describing the adsorption isotherms from experimental data [26]. 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.

$$q_e = \frac{bQ_o C_e}{1 + bC_e} \quad (7)$$

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 [30].

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:

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

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: for favorable adsorption $0 < R_L < 1$, for unfavorable adsorption $R_L > 1$, for linear adsorption $R_L = 1$ and for irreversible adsorption $R_L = 0$ [26].

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

Where K_F (L/g) is related with the total adsorption capacity while $1/n$ dimensionless number is related with the intensity of adsorption [30].

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 [26]. The mathematical statement of the Sum square error statistic is given by (10):

$$SSE = \sum (q_{e,cal} - q_{e,exp})^2 \quad (10)$$

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.

III. RESULT AND DISCUSSION

A. 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 P(V) in different volumetric flasks. The flasks were shaken for different time intervals in a shaker at room temperature. Fig. 1 shows the effect of contact time on adsorption of P(V) using both sorbents. The results show that 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 contact time. The 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 [19, 21, 22], 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 results indicate that P(V) has a higher affinity toward the adsorbents than heavy metals. This is probably due to the difference in physico-chemical properties of metals and non-metals.

B. Effect of pH

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 [31]. As shown in Fig. 2, it is obvious that P(V) adsorption onto VScO and VPum strongly pH dependent. There are two prominent points in the measured adsorption at pH 3 and 7. The adsorption of P(V) remains at a maximum level within this pH range, and decreases 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 [15] and ZnCl₂ activated coir pith carbon [18]. The observed trend is also

related to phosphate proton dissociation equilibria [31]. 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) [22]. 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 [31]. So it is evident that in the pH range of natural waters, P(V) remains in the anionic state which is highly favourable 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. 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 P(V) species and hydroxide groups on more negatively charged adsorbent surface sites to causes the lower adsorption of phosphate at higher pH [29].

C. 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 [6]. It was 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. 3). 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 [6, 12, 22].

E. Effect of particle size of the adsorbent

Effect of particle size of the adsorbent on P(V) adsorption was investigated at initial P(V) 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.4 indicated that the coefficient of distribution, K_D , increased with a decrease in particle size of the adsorbent from 4.75 to 0.425 mm (Fig. 4). However, the smallest particle size (<0.075 mm, 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. 4). This is in agreement with the findings from various studies done by [19, 22].

E. 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 (result not shown). This observation can be attributed to the increase of the availability of free adsorption sites. Furthermore, a distribution coefficient K_D reflects the binding ability of the surface for an element, which is mainly depends on pH of 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 using (3). It was seen that the K_D value increase with an increase in adsorbent concentration, indicating the heterogeneous surface of the adsorbent [27]. But, reference [23] said that If the surface was homogeneous, the K_D values at a given pH should not change with adsorbent concentration.

F. Effect of initial P(V) concentration

The effect of initial concentration of P(V) was assessed by varying the concentration from 0.5 to 20 mg/L at pH ~ 6 using 15 g/L VScO and pH ~ 7 using 10 g/L VPum. 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 mass 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. This is in agreement with the findings from various researchers that suggest the more concentrated solution is the better adsorption [10, 12, 13, 18].

On the contrary, the removal percentage of P(V) decreased with increasing initial P(V) concentration (result not shown). 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 [13].

G. Desorption experiment

Any adsorbent is economically viable for pollutant removal from aqueous environment if the adsorbent can be regenerated and reused [29]. The pH effect on the efficiency of P(V) adsorption on VScO and VPum showed (Fig. 2) 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 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 (data not shown). 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 P(V) removal.

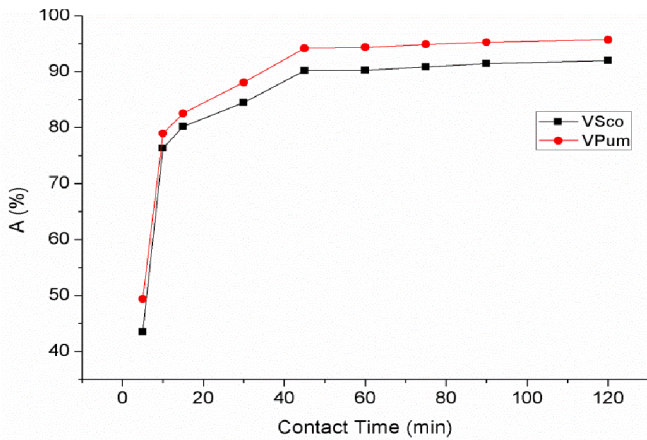


Fig. 1 Effect of contact time on P(V) adsorption by VSco and VPum

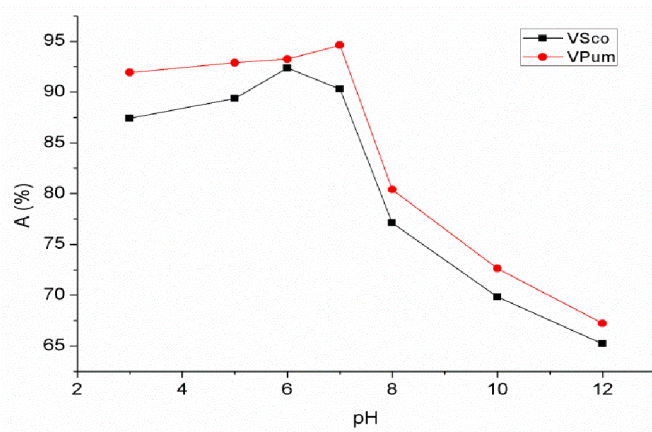


Fig. 2 Effect of pH on P(V) adsorption by VSco and VPum

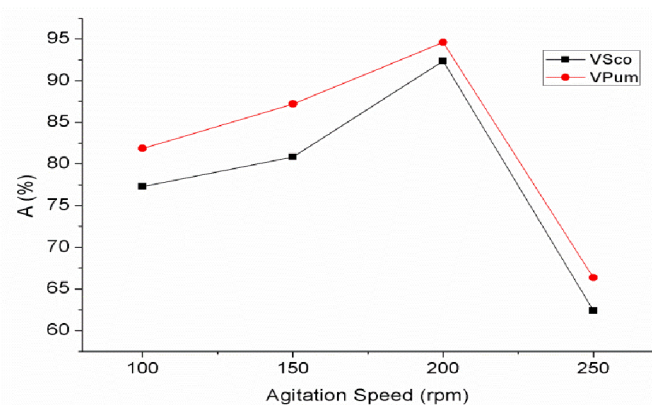


Fig. 3 Effect of agitation speed on P(V) adsorption by VSco and VPum

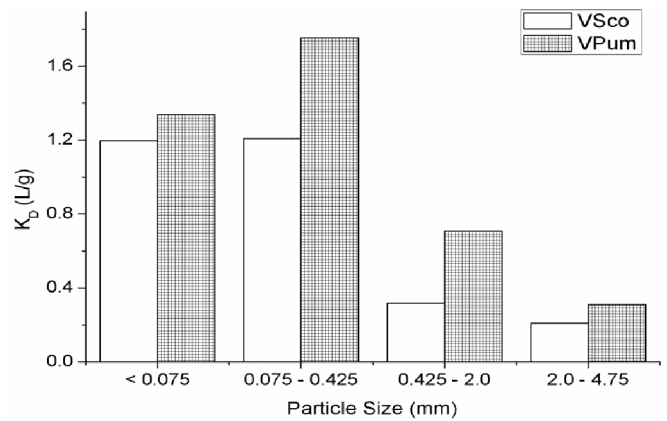


Fig. 4 Effect of particle size on P(V) adsorption by VSco and VPum

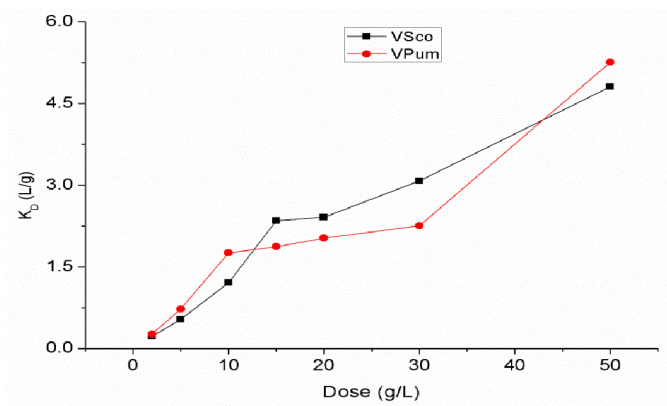


Fig. 5 Effect of adsorbents dose on P(V) adsorption

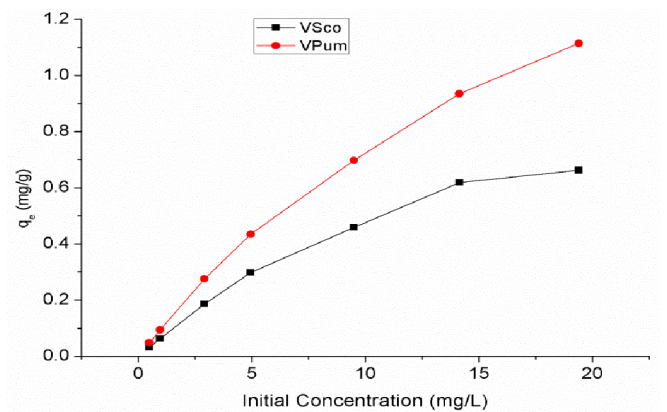


Fig. 6 Effect of initial concentration on the removal of P(V) by VSco and VPum

H. Effects of Co-existence Ions

The phosphate contaminated surface water is always associated with other co-ions like nitrate, sulphate, chloride, carbonate and bicarbonate, which can compete with phosphate ions during adsorption process for active sites on VSco and VPum. Thus, the effects of these competitive ions on uptake of P(V) were separately investigated by adding 10, 100 and 300 mg/L of competing anions: HCO_3^- , CO_3^{2-} , Cl^- , NO_3^- , and SO_4^{2-} adopted from [27, 29] individually and in mixture to a container of 100 mL solution at constant initial P(V)

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. The result showed that a decrease in P(V) removal was observed when the concentration of competitive ions were increased from 10 to 300 mg/L. Results also reveal that, bicarbonate and sulphate have great significant interfering effect on the adsorption of P(V) by VScO and VPum. The order of interference for P(V) 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 phosphate removal [15]. Thus, the decrease in the adsorption capacity may be explained on the basis of ion exchange mechanism where SO_4^{2-} and HCO_3^- possess the highest affinity for the adsorbent material and competes most effectively against P(V) adsorption.

I. Removal of P(V) from Wastewater

Based on the promising results of P(V) removal from aqueous solutions, the optimized method (except pH) that were determined by synthetic aqueous solution, tests were applied for the removal of P(V) onto VScO and VPum using real wastewater sample of pH 5.4 (Table I). The wastewater used was taken from Jimma town, South-western Ethiopia. The removal efficiency achieved were 91.48% (VScO), and 95.23% (VPum) in the real wastewater sample. The effect of VScO and VPum on the removal of COD, BOD, Nitrate, Chloride and Sulphate are also depicted in Table I. The present study thus reveals that, the VScO and VPum are an excellent adsorbents for P(V) removal from aqueous solution. The investigations are quite useful in developing an appropriate technology for designing a water/wastewater treatment plant.

Table I Physico-chemical analysis of wastewater before and after treatment with VScO and VPum

| Parameters | Influent | Wastewater After Adsorption | | | |
|---------------------------|----------|-----------------------------|-------|-------|-------|
| | | VScO | % | VPum | % |
| Temp. (°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 | 291.8 | 39.2 |
| BOD (mg/L) | 384 | 235.6 | 38.7 | 292.6 | 23.8 |
| DO (mg/L) | 3.5 | 3.41 | 1.14 | 3.28 | 6.29 |
| NO_3^- (mg/L) | 271 | 154.2 | 43.1 | 174.5 | 35.6 |
| Cl^- (mg/L) | 54.9 | 38.35 | 30.2 | 35.52 | 35.30 |
| SO_4^{2-} (mg/L) | 2.71 | 2.14 | 21.0 | 1.86 | 31.37 |
| HCO_3^- (mg/L) | 91.5 | 46.26 | 49.44 | 38.87 | 56.43 |
| PO_4^{2-} (mg/L) | 6.91 | 0.256 | 91.48 | 0.143 | 95.23 |

J. Kinetics and Equilibrium Isotherm Models

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 constant values of K_f , K_s , K_p , $q_{e, \text{calc}}$ (calculated), and $q_{e, \text{exp}}$ (experimental) are reported in Table II. 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, $q_{e, \text{calc}}$ (0.2800, 0.2910), were comparable to the experimental equilibrium capacities, $q_{e, \text{exp}}$ (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 [29]. Similar results are obtained in the removal of P(V) from water using Schwertmannite (Ferric Oxyhydroxide Sulfate) [16].

Besides adsorption at the outer surface of the adsorbent, the P(V) may also diffuse into the interior of the adsorbent [27, 29]. 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 $\text{mg}/(\text{g} \cdot \text{min}^{0.5})$ (VScO) and 0.0211 $\text{mg}/(\text{g} \cdot \text{min}^{0.5})$ (VPum) for the initial P(V) concentration of 3 mg/L (Table II). 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 [27, 29]). The plot of q_t versus $t^{0.5}$ is not passing through the origin in both adsorbent conditions. These indicates that the P(V) adsorption onto both VScO and VPum is a complex process and this is indicative of some degree of boundary layer control [32], and this further show that the intra-particle diffusion was not the sole rate controlling step.

Table II The kinetics parameters for adsorption of P(V) onto VScO and VPum

| Model | Parameter | VScO | VPum |
|--------------------------|------------------------------------|--------|--------|
| | | Value | |
| Pseudo-First-Order | $q_{e, \text{exp}}$ (mg/g) | 0.2659 | 0.2779 |
| | $q_{e, \text{calc}}$ (mg/g) | 0.2707 | 0.2402 |
| | K_f [g/(mg.min)] | 0.1384 | 0.1232 |
| | R^2 | 0.8800 | 0.8962 |
| Pseudo-Second-Order | $q_{e, \text{exp}}$ (mg/g) | 0.2659 | 0.2779 |
| | $q_{e, \text{calc}}$ (mg/g) | 0.2800 | 0.2910 |
| | K_s [g/(mg.min)] | 1.0121 | 1.0464 |
| | V_o [mg/(g.min)] | 0.0784 | 0.0886 |
| Intra-particle Diffusion | R^2 | 0.9993 | 0.9996 |
| | K_p [mg/(g.min ^{0.5})] | 0.0205 | 0.0211 |
| | C (mg/g) | 0.0979 | 0.1045 |
| | R^2 | 0.6697 | 0.6708 |

2. *Isotherm Models*: The isotherm plots of the equilibrium adsorption of P(V) are graphically presented in Fig. 7 and 8, and the values of the equilibrium constants computed from the isotherm models using non-linear regression using Sum of

square error function are given in Table III. The coefficients of determination (R^2) values presented in Table III 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, is 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 [26]. 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 [26]. Moreover, the Langmuir monolayer capacity, Q_0 , was appreciably larger for VPum (1.17 mg/g) compared to that of VScO (0.65 mg/g). The larger value of Q_0 as obtained for P(V)-VPum indicate the strong interactions between P(V) and VPum (Fig. 8). Beside, the essential characteristics of the Langmuir isotherm may be expressed in terms of R_L value (Subsection D, chapter III). In all cases, the R_L values for the experimental data fell between 0 and 1 (Table III), which is indicative of the favourable adsorption of P(V) on the adsorbents [33].

Hence, according to Table III, it 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 modelling the equilibrium data using the Freundlich, for non-linear regression analysis (Table III).

Table III Freundlich and Langmuir constants of VScO and VPum

| Parameters | Adsorbent | |
|-------------------|------------|------------|
| | VScO | VPum |
| Freundlich | Value | |
| K_f (L/g) | 0.34 | 0.5 |
| $1/n$ | 0.32 | 0.38 |
| R^2 | 0.98 | 0.99 |
| Langmuir | Value | |
| Q_0 (mg/g) | 0.65 | 1.17 |
| b (L/g) | 1.88 | 0.92 |
| R^2 | 0.97 | 0.97 |
| R_L | 0.187±0.19 | 0.271±0.25 |

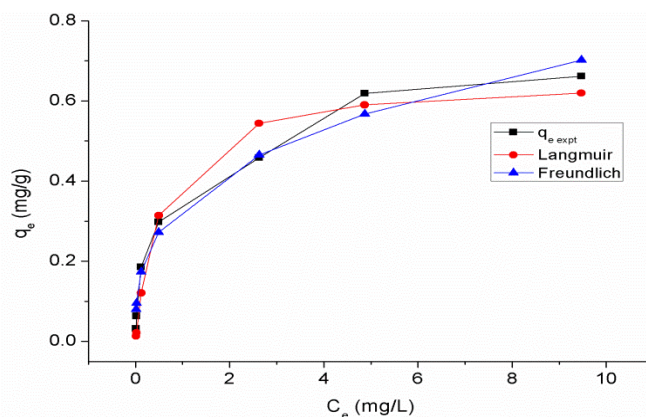


Fig. 7 Isotherms of equilibrium adsorption of P(V) on VScO

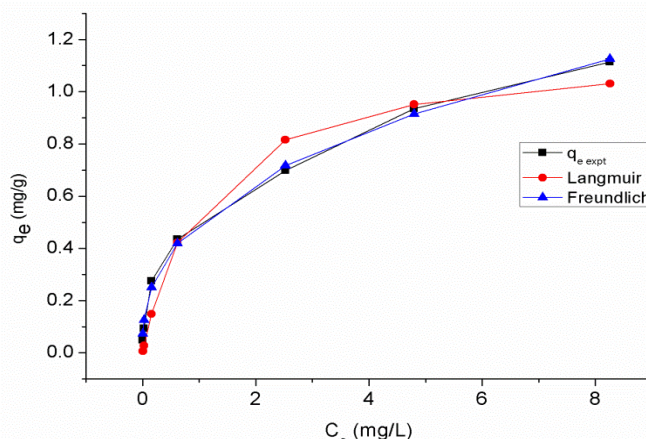


Fig. 8 Isotherms of equilibrium adsorption of P(V) on VPum

IV. CONCLUSION

This study provides valuable information about the design of P(V) removal technology from aqueous solution using VPum and VScO. 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. The fitting of the kinetic data of P(V) adsorption to the pseudo-second order with $R^2 > 0.99$ was suggestive of the dominant chemisorption mechanism of P(V) adsorption on the adsorbents. The equilibrium data 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. P(V) adsorption was significantly reduced in the presence of SO_4^{2-} , HCO_3^- , and a mixture of co-existing anions. 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. For large-scale application, further column experiments needs to be conducted to determine the real adsorption capacity and regeneration rate.

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