# Adsorption of Phosphate from Aqueous Solution Using Filter Cake for Urban Wastewater Treatment

Girmaye Abebe\* and Brook Lemma\*\*

\*Department of Landscape and Environmental Planning, EiABC (Ethiopian Institute of Architecture, Building Construction and City Development), Addis Ababa University, P. O. Box 1176, Addis Ababa, Ethiopia (E-mail: *girmayeabebe@gmail.com*)

\*\*Department of Landscape and Environmental Planning, EiABC (Ethiopian Institute of Architecture, Building Construction and City Development), Addis Ababa University, P. O. Box 1176, Addis Ababa, Ethiopia

(E-mail: <u>brooklemma@gmail.com</u>)

#### Abstract

Adsorption of phosphorus (P as  $PO_4^{3-}$ ) in filter cake was studied to assess the media's capability in removing phosphorous from wastewaters. The factors studied include the effect of pH of the solution. The percentage of  $PO_4^{3-}$  removal remains nearly constant within the pH range of 3-8. The adsorption data at ambient pH were well fitted to the Langmuir Isotherm and Dubinin–Radushkevick (D–R) isotherm model with a capacity of 25.84 and 157.55 mg/g of the adsorbent respectively. The adsorption kinetic was found to follow a pseudo-second-order rate equation with an average rate constant of 3.76 g.min<sup>-1</sup>.mg<sup>-1</sup>. The presence of bicarbonate or carbonate at higher concentrations (10–1000 mg/L) decreased the  $PO_4^{3-}$  removal efficiency slightly while other anions (Cl<sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, and NO<sub>3</sub><sup>-</sup>) have no significant effect within the concentration range tested. The overall result shows that the filter cake is an efficient  $PO_4^{3-}$  removing adsorbent against many parameters.

#### Keywords:

Wastewater, Filter Cake; Adsorption Capacity, Phosphate  $(PO_4^{3-})$ 

Corresponding Author: Girmaye Abebe, EiABC, Addis Ababa University, P. O. Box 1176, Ethiopia, girmayeabebe@gmail.com, Mobile: +251-911-002790

#### **1. INTRODUCTION**

Phosphorous (P) is predominately found in natural waters and wastewaters as phosphate ( $PO_4^{3-}$ ) [1] which is also the form so critical to living systems and irreplaceable element for human health and all living organisms as the critical nutrient of both aquatic and terrestrial species of plants and animals [2]. It has been reported that at a concentration (mg/L) of  $PO_4^{3-}$  higher than 0.01 [6], 0.02 [7], 0.05 [5, 6] and 1.0 [7] may contribute to increased eutrophication in water bodies [8]. These critical values can be set up as the criterion for the evaluation of water eutrophication. This process depletes dissolved oxygen levels by causing algae blooms and intensive decomposition which leads to the prevalence of weeds and deterioration of the quality of water [9]. Phosphorous removal is necessary for controlling eutrophication in natural waters and phosphorous recovery. Adsorption has been regarded as one of the most effective and economical methods for the removal of phosphorous. The key to the success of the method depends on the selection of adsorbent with high adsorption capacities and retention capabilities where phosphorous removal is the prime function [12, 13]. The standard discharge limit of treated domestic wastewater (5-15 mg/L) varies among countries and institutions. Ethiopia and USA will be required to have tertiary treatment, to reduce wastewater effluent concentrations of phosphorous to levels as low as 5.0 mg/L [14] and 1.0 mg/L [15] respectively.

In this study, the main objective is to investigate the ability of filter cake as adsorbent to remove  $PO_4^{3-}$  ion from aqueous solution leading to a better design of future sub-surface constructed wetlands. The filter cake was used as  $PO_4^{3-}$  removing media. The filter cake is highly acidic (pH of about 3) and hence it is considered as hazardous. At present, economically feasible methods for its disposal or reuse are not known. Therefore, it is necessary to find a solution for the application of filter cake for socially valuable function as adsorption of  $PO_4^{3-}$  from wastewater economically and environmentally sound.

#### 2. MATERIALS AND METHODS

### 2.1. Phosphate Removal Adsorbent

The filter cake is generated as waste residue during the manufacture of alum using kaolin and sulfuric acid. Fresh samples were taken from more than 40 batches of alum production residues and then mixed to maintain homogeneity. The filter cake was sun-dried for 1 day and grinded to fine powder using mortar and considered as untreated adsorbent. To prepare the neutralized media, a portion of the untreated media was added in distilled water (pH about 6.0) and the resulting lower pH (about 3.5) was adjusted to pH of 7.30 using 0.1 M NaOH; then filtered after 1 day and dried at room temperature at an open air before use.

## 2.2 Reagent and Standard Solutions

 $PO_4^{3-}$  stock solution was prepared by dissolving 0.2195 g of anhydrous potassium dihydrogen phosphate (KH<sub>2</sub>PO<sub>4</sub>) and dried for 1 h at 105 °C in 1000 mL distilled water in volumetric flask. Standards and  $PO_4^{3-}$  spiked samples at a required concentration range were prepared by appropriate dilution of the stock solution with distilled water.

# 2.3. Instrumentation

UV-VIS Spectrophotometer (Agilent Technologies) was employed for the measurement of the initial and final  $PO_4^{3-}$  concentrations remaining in solutions using APHA [1] (Vanadomolybdophosphoric Acid Colorimetric Method). The UV-VIS Spectrophotometer was calibrated for all factors in order to determine the slope and intercept for valuing different variables. Samples were filtered, and then taken for absorbance measurements at wave length 470 nm. The measured absorbance was then converted to the residual concentration using a calibration curve.

The pH was measured with pH/ion meter using unfilled pH glass electrode (HANNA Instrument, pH 210 Microprocessor pH Meter) and equipped with temperature electrode. The meter was calibrated whenever the measurements were made by using pH calibration buffers.

### 2.4. Batch Adsorption Studies

Adsorption experiments were conducted in 500 mL Erlenmeyer flask containing 500 mL of phosphate-spiked distilled water at room temperature  $(22\pm2 \ ^{0}C)$ . The residual PO<sub>4</sub><sup>3-</sup> concentration was calculated from the measurement of absorbance of 10 mL prepared solution. The prepared solution was set as 50 mL by mixing 35 mL sample solution, 10 mL reagent and distilled water as filler. All the experiments were performed in triplicate and the mean values were reported. The adsorption capacity values A (mg/g) were calculated as

$$A = \frac{(CO - Ceq) * V * 1000}{m}$$
(1)

Where Co and Ceq are the concentrations of the adsorbate (mg/L) in initial and equilibrium solutions, respectively, V is the volume of the solution (mL) and m is the mass of the sorbent (g).

The effect of raw water pH on the adsorption of  $PO_4^{3-}$  on to the adsorbent was studied by varying the solution pH (2 to 10), which was prepared by adjusting the pH to the desired level either with 0.1 M NaOH or 0.1 M HCl.

Isotherm experiments were conducted by varying the adsorbent dose (1.0 to 20.0 g/L) by keeping the initial  $PO_4^{3-}$  concentration and pH at 50 mg/L and 7.0, respectively. The equilibrium time was 24 h under mixing condition. The samples were allowed to settle and residual  $PO_4^{3-}$  ion concentrations were calculated. The kinetic analysis of the adsorption data is based on reaction kinetics of pseudo-second-order mechanisms. Adsorption kinetics was determined using constant surface loading of 12, 6 and 3 g/L corresponding to the initial  $PO_4^{3-}$  concentration of 40, 20 and 10 mg/L, respectively, for the untreated adsorbent. The effect of co-existing anions ( $CI^-$ ,  $SO_4^{2-}$ ,  $HCO_3^-$ , and  $NO_3^-$ ) on  $PO_4^{3-}$  adsorption efficiency of the adsorbent was also studied at constant  $PO_4^{3-}$  concentration of 10 mg/L and adsorbent dose of 10 g/L by varying anion concentration (10 to 1000 mg/L). The selections of the anions concentrations are based on their availability in wastewaters.

# 3. RESULTS AND DISCUSSIONS

# **3.1. Effect of Water pH**

Fig. 1 shows the influence of initial solution pH on the  $PO_4^{3-}$  removal efficiency and capacity of the adsorbent. It is apparent that the percentage of  $PO_4^{3-}$  removal remains nearly constant within

the pH range of 3 and 8. pH of the solution beyond this range between 3 and 8 decrease the removal efficiency. The declining trend of  $PO_4^{3-}$  treatment becomes significant at pH values >10. The PO<sub>4</sub><sup>3-</sup> uptake capacity of this media is not affected in the pH range between 3 and 8, possibly due to the presence of positively charged and neutral sites at the surface of the adsorbent [17, 22]. Lower pH is favoring the protonation of media surface and increased protonation is thought to increase the positively charged sites, enlarge the attraction force existing between the oxide surface and  $PO_4^{3-}$  ions and therefore increase the amount of adsorption in the lower pH region. The progressive decrease of  $PO_4^{3-}$  uptake at pH > 8 is possibly due to the electrostatic repulsion of  $PO_4^{3-}$  ion to the negatively charged surface and the competition for active sites by excessive amount of hydroxyl ions thus repulsing the negatively charged  $PO_4^{3-}$  in the solution [18, 23].

This result is in agreement with Gromadskaya et al. [24], Xiong et al. [17], Yang et al. [25], and Ioannou and Dimirkou [20] who also found a broad pH range for the adsorption of  $PO_4^{3-}$  on Hematite, Slag, Kaolinite, Kaolinite–Hematite and Dewatered Alum Sludge respectively. The chemical composition of the solid component of the adsorbent showed that it composed of silica (SiO<sub>2</sub>) as main component and oxides of aluminum and iron (Table 1). The surface hydroxyl groups in this composite oxide system are responsible for the retention of  $PO_4^{3-}$  to various extents depending of pH and surface modification [26]. Considering the experimental observation of pH variation, performance of thermally treated and neutralized media; the adsorption of  $PO_4^{3-}$  may be best represented by the following two-step protonation or ligand exchange (surface complexation reactions) mechanism [20]:

SOH (s) +  $H^+$  = SOH<sub>2</sub><sup>+</sup> (2)

 $SOH_2^+ + H_3PO_4 = SO^- + H^+$ (3)

 $SOH + H_3PO_4 = SH_2PO_4 + H_2O_4$ (4)

 $SOH + H_3PO_4 = SHPO_4^- + H_2O + H^+$ (5)

 $SOH + H_3PO_4 = SPO_4^{2-} + H_2O + 2H^{+}$ (6)

Where S represents silicon, aluminum, and iron solid surfaces and SOH in this study represents the surface functional group of filter cake.

Mechanical stability, great specific surface area and high reaction ability of silanol (=Si-O-H) groups allowing for surface modification are usually put forward as advantages of this support [27]. The surface hydroxyl groups on the adsorbent are the phosphate-reactive ( $PO_4^{3-}$ ) functional groups. PO<sub>4</sub><sup>3-</sup> adsorption occurs via a complex formation mechanism with these hydroxyl ions [28].



Figure 1. Effect of Raw Water pH on PO<sub>4</sub><sup>3-</sup> Removal Efficiency and Capacity of Untreated Adsorbent (Initial Conc. = 10 mg/L, Adsorbent Dose = 10 g/L, and Reaction Time = 60 min) **3.2. Adsorption Isotherm** 

The experimental data was fitted to Langmuir, Fruendlich, Dubinin and Radushkevich (D-R), and Temkin isotherm models. The Langmuir isotherm could be linearized as four different types, while the Freundlich isotherm had two different types. The simple linear regression would result in different parameter estimates [29-31]. The more-popular linear forms of two Langmuir forms and one Freundlich form are used.

The Freundlich adsorption isotherm equation is represented in Eq. (7):  $q_e = k_{f^*} C e^{1/n}$ 

The linearized Freundlich adsorption isotherm is of the form

$$\log q_{\rm e} = \log k_{\rm f} + \frac{1}{n} \log Ce \tag{8}$$

Where  $q_e$  is the adsorbed  $PO_4^{3-}$  at equilibrium per unit mass of adsorbents (mg/g),  $K_f$  the minimum sorption capacity (mg/g) and 1/n is the adsorption intensity. Ce is the equilibrium concentration of  $PO_4^{3-}$  (mg/L).

The Langmuir adsorption isotherm equation is represented in Eq. (9):

$$q_e = q_m \frac{BCe}{1 + BCe} \tag{9}$$

And there are four linearized forms that can be represented as Eq. (10-13):

$$\frac{Ce}{qe} = \left(\frac{1}{qm}\right) Ce + \frac{1}{Bqm}$$
(10)  

$$\frac{1}{qe} = \frac{1}{qm} + \frac{1}{Bqm} \left(\frac{1}{Ce}\right)$$
(11)  

$$q_e = q_m - \frac{1}{B} \left(\frac{qe}{Ce}\right)$$
(12)  

$$\frac{qe}{Ce} = B.q_m - Bq_e$$
(13)

Where,  $q_e$  is the amount of solute adsorbed per unit mass of adsorbent (mg/g),  $q_m$  is the maximum adsorption capacity (mg/g), B is the Langmuir constant (L/mg) related to adsorption capacity and energy of adsorption, and Ce is the equilibrium solute concentration (mg/L). The essential characteristic of the Langmuir isotherm can be expressed by the dimensionless constant called equilibrium parameter,  $R_L$ , defined by:

$$R_{L} = \frac{1}{1 + BCo} \tag{14}$$

Where  $C_o$  is the initial adsorbate concentration (mg/L),  $R_L$  values indicate the type of isotherm to be irreversible ( $R_L = 0$ ), favorable ( $0 < R_L < 1$ ), linear ( $R_L = 1$ ) or unfavorable ( $R_L > 1$ ) [35-37]. The  $R_L$  value for the adsorption of  $PO_4^{3-}$  by filter cake is shown in Table 2. Another equation used in the analysis of adsorption isotherm was the D-R model [32, 38, 39]:

$$q_e = q_s \exp(-\beta \epsilon^2) \tag{15}$$

The sorption data was modeled by D-R isotherm to determinate the adsorption type (physical or chemical). The linear form of this model is expressed by:

lnq<sub>e</sub> = lnq<sub>S</sub> – βε<sup>2</sup> (16) Where q<sub>s</sub> is the D-R constant (mg/g) /monolayer sorption capacity (mol/g)/, q<sub>e</sub> is the amount of PO<sub>4</sub><sup>3-</sup> adsorbed per unit dosage of the adsorbent (mol/g), and β is the activity coefficient related to mean sorption energy (mol<sup>2</sup>/kJ<sup>2</sup>). ε is the Polanyi potential (J/mol) described as:

$$\varepsilon = \operatorname{RT} \ln \left( 1 + \frac{1}{c_{\varepsilon}} \right) \tag{17}$$

The mean sorption energy, E (kJ/mol), can be calculated by Eq. (19) [32, 38, 39]:

$$E = \frac{1}{\sqrt{-2\beta}}$$
(18)

The Temkin Isotherm [40] is given as:

$$q_e = \frac{RT}{b} \ln (ACe)$$
(19)

which can be linearized as:

$$q_e = B_1 lnA + B_1 lnCe \tag{20}$$

Where  $B_1 = RT/b$ ,  $B_1$  is related to the heat of adsorption, b is the Temkin constant related to heat of sorption (J/mol), R is the gas constant (8.314 J/mol.K), T is the absolute temperature (K),  $q_e$  is the amount of  $PO_4^{3-}$  adsorbed onto per unit dosage of the adsorbent (mol/g), Ce the equilibrium  $PO_4^{3-}$  concentration (mol/L), and A is the Temkin isotherm constant (L/g).

Temkin isotherm contains a factor that explicitly takes into the account of adsorbing species and adsorbent interactions. The heat of adsorption of all the molecules in the layer would decrease linearly with coverage due to adsorbate / adsorbate interactions [32]. This isotherm assumes that (i) the heat of adsorption of all the solute in the layer decreases linearly with coverage due to adsorbent and adsorbate interactions, and that (ii) the adsorption is characterized by a uniform distribution of binding energies, up to some maximum binding energy [33]. A is the equilibrium binding constant (L/mol) corresponding to the maximum binding energy and constant B<sub>1</sub> is related to the heat of adsorption. The constants A and B<sub>1</sub> are calculated from the intercept and slope of the plot and are listed in Table 2.

**Table 2.** Isotherm Parameters for the Removal of  $PO_4^{3-}$  by Untreated Adsorbent (Initial  $PO_4^{3-}$  Concentration = 50 mg/L, Reaction Time = 24 h, pH = 7.0±0.1, and Temperature = 24  $^{0}C$ )

Freundlich constants	$K_{\rm f} ({\rm mg}/{\rm g}) = 0.230$	1/n = 1.5811	$R^2 = 0.9718$
Langmuir constants	qm (mg/g) = 25.84	B (L/mg) =0.093; R <sub>L</sub>	$R^2 = 0.9919$
		= 0.18	
D-R constants	qs (mg/g) = 157.55	E (kJ/mol) = 9.71	$R^2 = 0.9823$
Temkin constants	A (L/mg) = 162,754.79	B1 = 0.00005	$R^2 = 0.9801$
	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	1.00 1.20 1.40	

**Figure 2.** Linearized Freundlich Isotherm (Initial  $PO_4^{3-}$  Conc. = 50 mg/L, Equilibrium Contact Time = 24 h, pH = 7.0±0.1, and Temperature = 22  $^{0}$ C)

As Fig. 2 found that the related correlation coefficient  $R^2$  value for the Freundlich model is 0.97 from a plot. Freundlich isotherm has minimum adsorption capacity of 0.230 mg/g of the adsorbent. The experimental data fit well to the Fruendlich isotherm model. The condition for the validity of a Freundlich type adsorption model is adsorption on heterogeneous surfaces [34]. All four forms of Langmuir sorption model are well fitted sorption. For instance, in Fig. 3 plot of

1/qe versus 1/Ce yield a straight line that shows Langmuir sorption are well fitted sorption data. The values of  $q_m$  (mg/g) (25.84) and the langmuir constants B (0.18) for Langmuir sorption isotherm. The value of RL is 0.18 in Table 2 that indicate favourable sorption of PO<sub>4</sub><sup>3-</sup> on to the adsorbent. The results are summarized in Table 2.



Figure 3. Langmuir Isotherm (Initial  $PO_4^{3^-}$  Conc. = 50 mg/L, Equilibrium Contact Time = 24 h, pH = 7.0±0.1, and Temperature = 22 <sup>0</sup>C)

Fig. 4 shows the D-R plot for the adsorption of  $PO_4^{3-}$  and the corresponding constants are presented in Table 2. The correlation coefficients for the D-R isotherm are almost the best fit isotherm and in comparison to the values obtained for the Langmuir, Temkin and Freundlich isotherms. The monolayer sorption capacity ( $q_s$ ) was evaluated as  $1.66*10^{-3}$  mol/g. The mean sorption energy (E) was found to be 7.91 kJ/mol for the adsorption of  $PO_4^{3-}$  on the adsorbent. The E value ranges from 1.0 to 8.0 kJ/mol for physical adsorption and from 9.0 to 16.0 kJ/mol for chemical adsorption [38, 39]. The value of E, which is nearly 8.0 kJ/mol, may suggest that, the mechanism for the adsorption of  $PO_4^{3-}$  on the adsorbent is a combination of chemical and physical in nature. Chemisorption dominates at lower concentrations whereas as the concentration increases physical adsorption becomes more important [41]. In general, it is well known that  $PO_4^{3-}$  adsorption reaction belongs to chemical reaction for most adsorbents [10, 16, 18].



**Figure 4.** D-R Isotherm (Initial  $PO_4^{3-}$  Conc. = 50 mg/L, Equilibrium Contact Time= 24h, pH = 7.0±0.1, and Temperature = 22 <sup>0</sup>C)

Fig. 5 shows the Temkin isotherm plot for the adsorption of  $PO_4^{3-}$  and the corresponding constants are presented in Table 2. A linear relationship between qe and lnCe indicates the applicability of this model to understand the adsorption mechanism. The corresponding constants are given in Table 2.



**Figure 5.** Temkin Isotherm (Initial  $PO_4^{3-}$  Conc. = 50 mg/L, Equilibrium Contact Time= 24 h, pH = 7.0±0.1, and Temperature = 22 <sup>0</sup>C)

#### 3.4. Adsorption Kinetics of Phosphate

The adsorption kinetics was studied with initial  $PO_4^{3-}$  concentrations of 40.0, 20.0, and 10 mg/L and corresponding adsorbent dose of 16.0, 8.0, 4.0 g/L, respectively, to maintain constant surface load of 2.5 mg  $PO_4^{3-}$ /g of adsorbent. The kinetic analysis of the adsorption data is based on reaction kinetics of pseudo-first-order (Lagergren's first-order rate equation) [19], well described by pseudo-second-order mechanisms that developed by Ho and McKay [52] [19, 42, 43].

The uptake of  $PO_4^{3-}$  on untreated adsorbent occurred rapidly, and reached equilibrium within 60 min. The kinetics of adsorption was analyzed by using the Lagergren equation (21) as shown below [44]:

$$\frac{dqt}{dt} = k2 \left(q_e - q_t\right)^2 \tag{21}$$

For the boundary conditions t=0 to t = t and  $q_t = 0$  to  $q_t = q_t$ , the integrated form of Eq. (22) becomes:

$$\frac{1}{(qs-qt)} = \frac{1}{qs} + k_2 t \tag{22}$$

which is the integrated rate law for a pseudo-second-order reaction.

Eq. (22) can be rearranged to obtain Eq. (23), which has a linear form:

$$\frac{t}{qt} = 1/k_2 q_e^2 + \frac{1}{qt}$$
 (t) (23)

where  $k_2$  (g.mg<sup>-1</sup>.min<sup>-1</sup>) is the equilibrium rate constant of second-order sorption.

 $k_2$  can be determined by plotting t/q<sub>t</sub> against t of Eq. (23). The larger the  $k_2$  value, the slower the adsorption rate [21]. The untreated adsorbent can be described very well by the pseudo second-order rate equation as shown in Fig. 6. The correlation coefficients were found as near to unity for the different initial PO<sub>4</sub><sup>3-</sup> concentrations. The three rate constants of the adsorbent were averaged to obtain a single rate constant of 3.76 g min<sup>-1</sup> mg<sup>-1</sup> as shown in Fig. 7.



**Figure 6.** Pseudo-Second-Order Plot of  $PO_4^{3^-}$  Adsorption Kinetics on Untreated Adsorbent with Initial  $PO_4^{3^-}$  Concentrations to Adsorbent Dose of 40.0, 20.0, and 10.0 mg/L, and 12.0, 6.0, 3.0 g/L, respectively (pH 7.0±0.1)



**Figure 7.** Average pseudo-second-order plot of  $PO_4^{3-}$  adsorption kinetics on untreated adsorbent with an initial load of 3.33 mg/g (pH = 7.0±0.1)

Generally, the process of the adsorbate adsorbed by adsorbent can be divided into four steps [12]: adsorbate molecules transferred to the nearby adsorbent, adsorbate molecules diffusion through the liquid film up to the surface of absorbent particles, this step usually was called external diffusion or mass transfer, adsorbate molecules diffused through the absorbent particles and reached the inner side; this step is usually called intraparticle diffusion or diffusion, adsorbate molecules were attracted at the active sites in the interior of the particles sequentially. Step one and four were not the rate-controlling steps due to their happening so fast. The kinetics of the adsorption or sorption rate is controlled by either film diffusion or intraparticle diffusion mechanism. Hence, in this study, one model was investigated to find out the rate-controlling step of the adsorption process.

Besides the adsorption at the outer surface of the adsorbent, the adsorbate molecules may also diffuse in to the interior of the porous adsorbent [28]. Intra-particle diffusion is a transport process involving movement of species from the bulk of the solution to the solid phase. In a well stirred batch adsorption system, the intra-particle diffusion model has been used to describe the adsorption process occurring on a porous adsorbent. A plot of the amount of sorbate adsorbed,  $q_t$  (mg/g) and the square root of the time, gives the rate constant (slope of the plot). Intra-particle diffusion model is based on the theory proposed by Weber and Morris equation [49] tested to identify the diffusion mechanism [45, 46]. According to this theory:

 $q_t = k_p t^{1/2} + Ci$  (24)

Where  $q_t$  is the amount adsorbed (mg/g) at a given time t (min);  $k_p$  (mg/g.min<sup>1/2</sup>) is the intraparticle diffusion rate constant (measure of diffusion coefficient). Ci = intra-particle diffusion constant i.e. intercept of the line (mg/g). It is directly proportional to the boundary layer thickness. It was used to identify the diffusion mechanism.

As can be seen in Fig. 8, a linear increase was not observed between the amount of  $PO_4^{3-}$  adsorbed and square root of time ( $q_t$  vs  $t^{1/2}$ ), which indicates the control of surface adsorption [28, 45]. If there is intraparticle diffusion, a linear relation willnot be observed. Hence, this result supports the fast equilibrium time. In addition, the plot of  $q_t$  against  $t^{1/2}$  the plots ( $q_t$  vs  $t^{1/2}$ ) are not totally linear and intercept Ci for all plots less than zero (around 0.9), show the mode of transport is affected by more than one process and present a multi-linearity, which indicates that two or more steps occur in the adsorption processes that limit the reaction [45, 47].



**Figure 8.** Intra-particle Diffusion Model of  $PO_4^{3-}$  Adsorption Kinetics on Untreated Adsorbent with Initial  $PO_4^{3-}$  Concentrations to Adsorbent Dose of 40.0, 20.0, and 10.0 mg/L, and 12.0, 6.0, 3.0 g/L, respectively (pH  $7.0\pm0.1$ )

It is clear that pseudo-second-order equation is better than intra-particle diffusion model in describing the adsorption kinetics of  $PO_4^{3-}$  by samples of filter cake.

Langmuir and Freundlich isotherms were applied to describe the relationship between the amount of  $PO_4^{3-}$  absorbed on absorbent and its equilibrium concentration in aqueous solution. These two equations were listed in Table 3, where B (L/mg) is Langmuir constants related to adsorption capacity and energy of adsorption and kf (mg/g) and n are the constants of the Freundlich isotherm that measure the adsorption capacity and intensity of adsorption, respectively. In Freundlich equation, 1/n values between 0 and 1 indicated a good adsorption.

Materials	$q_m (mg/g)$	B (L/mg)	<i>kf</i> (mg/g)	1/n	References
Red mud	0.58	146.39	0.632	4.281	[10]
Wheat straw	2.81	0.008	0.044	1.087	[49]
Zeolite	6.45	0.139	0.91	0.437	[50]
Peat	8.91	0.033	0.713	2.042	[51]
Nano Fe loaded Biomass Char	35.43	0.091	6.045	0.388	[24]
Filter cake	25.84	0.093	0.23	1.58	This study

#### **Table 2.** Phosphate Adsorption Parameters of Different Waste Materials

#### **4. CONCLUSIONS**

The results reveal that low cost locally available industrial waste material generated from alum manufacturing process is promising material to remove excess  $PO_4^{3-}$  from wastewater. Based on the results obtained it can be concluded that about 90% of  $PO_4^{3-}$  was removed within the first 5 min at an optimum adsorbent dose of 10 g/L in pH range of 2 to 10 for initial  $PO_4^{3-}$ concentration of 10 mg/L. The adsorption followed second-order rate kinetics, and data fit in to linear form of Langmuir and D-R isotherm model with a capacity of 25.84 and 157.55 mg/g of the adsorbent.

Since most of the urban populations in Ethiopia cannot easily pay for wastewater treatment in their day to day activities, this efficient, easily and locally available material has to be considered to set up sustainable onsite treatment method to the  $PO_4^{3-}$  trouble.

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