

# Adsorption and Removal Kinetics of Phosphonate from Water Using Natural Adsorbents

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**ABSTRACT:** The removal of phosphonate from water was studied using some natural adsorbents. Potassium phosphonate is a fungicide used for the control of *Phytophthora capsici*, which is prevalent in black pepper (*Piper nigrum* L.). Batch adsorption kinetic experiments were conducted on the adsorption of phosphonate onto the adsorbents. The concentration of phosphonate was measured on a high-performance liquid chromatograph fitted with a conductivity detector. The percentage removal of phosphonate by powdered laterite stone (PLS) from water was 40.4%, within a residence time of 15 minutes. The mechanisms of the rate of adsorption were analyzed and compared using the pseudo-second-order, Elovich, and intraparticle diffusion models. The experimental data was found to correlate well with the pseudo-second-order kinetic model, indicating adsorption as a chemisorption process. A possible reaction in the phosphonate-PLS system also has been proposed. The PLS can be used as a low-cost natural adsorbent for phosphonate removal from water. *Water Environ. Res.*, 82, 62 (2010).

**KEYWORDS:** potassium phosphonate, adsorption kinetics, pseudo-second-order, powdered laterite stone.

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## Introduction

Adsorption is one of the important phenomena in water treatment. The large-scale increase in the use of pesticides over the past few decades has resulted in the pollution of aquatic systems. In the natural conditions of aquatic systems, suspended load and sediments have an important function of buffering higher pesticide concentrations in water, particularly by adsorption or precipitation. The pesticides in an aquatic system can be removed by using suitable adsorbents. The study of various adsorbents and their sorptive properties can provide valuable information relating to the tolerance of a system to increased loads of pesticides and

may determine their fate and transport in the aquatic environment (Jain, 2001).

Charcoals, wood sawdust, soils, clay, sediments, and so on are reported to have a good adsorptive capacity towards pesticide residues in water. Soil itself is a good adsorbent for many pesticides (Jeevan Rao, 1999). Naturally occurring agri-based materials play an effective role in the removal of cations and anions from water. Activated charcoal of a different origin (prepared from wood and vegetables) is reported by many workers for the removal of chromium(VI) and arsenic(III) from an aqueous solution (Demirbas et al., 2004; Mise and Rajamanya, 2003; Nagarnaik et al., 2003; Nomanbhay and Palanisamy, 2005). Different types of clays, such as hydroxyapatite, fluorspar, quartz, activated with ferric ions, calcite, and quartz, are useful for the removal of fluoride (Chidambaram et al., 2003; Fan et al., 2003). Tshabalala et al. (2004) reported cationized pine bark to be a good remover of orthophosphate from water.

Laterite soil, which is rich in iron and aluminum, interacts with orthophosphate ion by strong adsorption over the surface of oxides and hydroxides of aluminum and iron (Breeuwsma, 1973) and on the edges of clay minerals (De Hann, 1965). Natural materials also are potent adsorbents for organophosphonates, for example, wastewater sludge (Fischer, 1992; Horstmann and Grohmann, 1988), sediments (Fischer, 1992), and soils (Held, 1989). Calcium has a strong positive effect on organophosphonate adsorption (Nowack and Stone, 1999). Glyphosate, an organophosphonate, is adsorbed to the soil through the phosphonic acid moiety in its phosphonate anion form, as phosphate is in soil (Sprankle et al., 1975).

Activated carbon has an extraordinarily large surface area and pore volumes, which give it a unique adsorption capacity (Baker et al., 1992). The specific mode of action is extremely complex and has been the subject of much study and debate. Activated carbon has both chemical and physical effects on substances where it is used as a treatment agent. Activity can be separated into (1) adsorption, (2) mechanical filtration, (3) ion exchange, and (4) surface oxidation. Adsorption is the most studied of these properties in activated carbon. The process of adsorption can be physical or chemical in nature, and frequently involves both. Physical adsorption involves the attraction by electrical charge differences between the adsorbent and the adsorbate. Chemical adsorption is the product of a reaction between them.

*Ion exchange* is defined as a reversible chemical reaction between a solid and an aqueous solution, which allows the interchange of ions (Ockerman, 1991). The ion exchange process can be enhanced by chemical activation. Carbon surfaces have

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both negative (anionic) and positive (cationic) charges to attract free ions in solution or suspension, depending on how they are treated.

The treatment of carbon with a base increases the capacity of carbon to exchange anions, and acidulation of the surface makes carbon a powerful cation exchanger (Jankowska et al., 1991). Surface oxidation involves the chemisorption reaction of the surface oxides that chemically react with other substances, which are oxidized.

Potassium phosphonate is a fungicide used for the control of *Phytophthora capsici* prevalent in black pepper, cardamom, turmeric, and ginger plantations. It is applied as a soil drench or foliar spray during the onset of the monsoon to the crops, which are susceptible to the foot rot disease (quick wilt) caused by the species. Thus, during the rainy season, there is a great chance for the surrounding water bodies to be contaminated by the chemical. Even though the mammalian toxicity of phosphonate is similar to that of phosphate and less than that of aspirin (Dunhill, 1990), it may affect human beings indirectly, as phosphate does, by the way of eutrophication of water bodies. Thus, information on the removal of the chemical from water by naturally occurring and low-cost adsorbents is desired.

#### Adsorption Kinetics and Linear Regression ( $R^2$ ) Analysis

The study of adsorption dynamics describes the solute uptake rate. This rate controls the residence time of adsorbate uptake at the solid-solution interface, and it is one of the important characteristics defining the efficiency of an adsorbent (Krishnan and Anirudhan, 2003). Adsorption kinetics can be controlled by several independent processes, which could act in series or in parallel, such as bulk diffusion, external mass transfer (film diffusion), chemical reaction (chemisorption), and intraparticle diffusion (Ho et al., 2000). Kinetic equations have been developed to explain the transport of metals onto various adsorbents.

To explain the mechanism of phosphonate sorption over different adsorbents, it is necessary that different kinetic models be tested to determine their fitness to the experimental sorption data. Linear regression ( $R^2$ ) was chosen as the error function for the kinetic model analysis, because it implicitly minimizes the sum of the squares of the errors to determine the equation parameters (Ho et al., 2002).

The kinetic equations tested were the pseudo-second-order (Ho and McKay, 1998), the Elovich equation (Chien and Clayton, 1980; Sparks, 1986), and the intraparticle diffusion model (Demirbas et al., 2004; Srivastava et al., 1989; Weber and Morris, 1963). These kinetic models are concerned only with the effect of the observable parameters on the overall rate of sorption (Ho, 2006).

The conformity between experimental data and the model-predicted values is expressed by linear regression ( $R^2$ ). A relatively high  $R^2$  value (close or equal to 1) indicates that the model successfully describes the kinetics of phosphonate adsorption.

The present study was carried out on the removal and adsorption kinetics of phosphonate of potassium phosphonate from water using natural adsorbents, such as coconut shell charcoal (CSC), both activated and non-activated; mussel shell (MS); and powdered laterite stone (PLS). To determine phosphonate removal capacity, the performances of the adsorbents were compared with Amberlite IRA-400 LR (A) (SD Fine Chemical

Limited, Mumbai, India), a polymeric anionic exchange resin. The mechanisms of the rate of adsorption were analyzed for  $R^2$  values and compared using the pseudo-second-order, Elovich, and intraparticle diffusion models.

#### Methodology

**Adsorbents.** The adsorbents used in this study are discussed in the following sections.

**Coconut Shell Charcoal.** Coconut shells were broken mechanically into small pieces and passed through a 4-mm sieve, charred on a low flame, and the material was heated to a temperature of 400 C in a muffle furnace for 6 hours. The charcoal was crushed and passed through a 1-mm sieve. The sample was washed with distilled water, until the washings became colorless and free of any suspended particles; filtered through Whatman No. 1 filter paper (International Biological Laboratories, Haryana, India), by suction; and dried in an air oven at 110 C for 6 hours.

**Activated Coconut Shell Charcoal.** Coconut shells were broken into small pieces using a hammer and passed through a 4-mm sieve. The chemically activated coconut shell charcoal (ACSC) was prepared according to the method of Demirbas et al. (2004). The coconut shell pieces were mixed with concentrated sulfuric acid in 1:1 weight-by-weight ratio and allowed to soak for 24 hours at room temperature (approximately 30 C). The sample was placed in an oven and heated to 200 C for approximately 12 hours, allowed to cool to room temperature, washed with distilled water, and soaked in 1% sodium bicarbonate ( $\text{NaHCO}_3$ ) solution to remove traces of the acid. The sample was then washed with distilled water to pH 6.0, filtered, dried at 110 C for 6 hours, and passed through a 1-mm sieve.

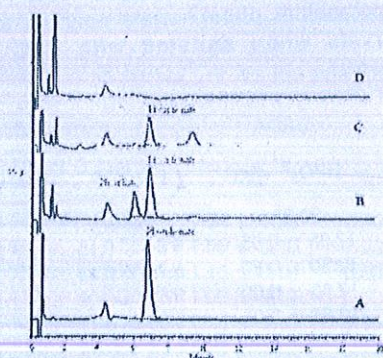
**Mussel Shell.** Mussel shells were washed with phosphate-free detergent solution to remove dirt adhered to the surface and crushed mechanically into small pieces. The material was passed through a 1-mm sieve, washed three times with distilled water to remove suspended particles, filtered, and dried in an air oven at 110 C for 6 hours.

**Powdered Laterite Stone.** Locally found laterite stones were crushed mechanically into small pieces. The material was then passed through a 1-mm sieve, washed three times with distilled water to remove suspended materials, filtered, and air-dried.

**Synthetic Polymer, Amberlite.** Approximately 30 g of Amberlite IRA 400 LR (SD Fine Chemical Limited), which is an anion-exchange resin made up of polystyrene-divinyl benzene copolymer containing tertiary amine groups, was treated with 50 mL of 1 M sodium hydroxide (NaOH) solution to replace chloride ions with hydroxyl ions and was kept for 1 day for the reaction to take place. The material was washed with distilled water to pH 7, and was free of chloride ion (Vogel, 1978). The sample was filtered and air-dried. All the adsorbents were preserved in a desiccator.

**Phosphonate Stock Solution ( $1000 \text{ mg HPO}_3^{2-} \cdot \text{P/L}^{-1}$ ).** Approximately 2.7156 g of phosphorous acid (SD Fine Chemical Limited, purity = 97.5%) was dissolved in 100 mL of water and further diluted to approximately 500 mL. To this solution, 0.5 N potassium hydroxide (KOH) was added dropwise, to adjust the pH of the solution to 6.2. The solution was cooled and transferred quantitatively into a 1-L standard flask and was made up to the mark with water. This represents  $1000 \text{ mg HPO}_3^{2-} \cdot \text{P/L}^{-1}$  present in an equilibrium mixture of phosphite and phosphonate of potassium.





**Figure 1—Chromatogram: (a) for phosphonate standard, (b) showing peaks for phosphate and phosphonate (CSC treatment), (c) showing peak for phosphonate (PLS treatment), and (d) showing the absence of phosphonate peak (Amberlite treatment).**

**20 mg  $\text{HPO}_4^{2-}$ -P/L $^{-1}$  Phosphonate Solution.** Approximately 20 mL of phosphonate stock solution (1000 mg  $\text{HPO}_4^{2-}$ -P/L $^{-1}$ ) was diluted to 1000 mL with water.

The reagents used were of analytical-reagent grade. The experiments were conducted at room temperature. For the studies, 7.5 g of adsorbent and 150 mL of 20 mg  $\text{HPO}_4^{2-}$ -P/L $^{-1}$  solution (potassium phosphonate solution-adsorbate) were agitated continuously for 6 hours at 180 rpm in stoppered glass bottles. Approximately 2 mL of aliquots were withdrawn for the quantitative analyses.

**Analysis of the Adsorbate.** The  $\text{HPO}_4^{2-}$ -P concentrations of the adsorbate were measured on a high-performance liquid chromatograph (HPLC) (Shimadzu, Kyoto, Japan) fitted with a conductivity detector (Shimadzu CDD-10Avp) and an anion-exchange column (Hamilton 10 $\mu$  PRP-X 100 OA; Hamilton, Bonaduz, GR, Switzerland) of 150 mm  $\times$  2.1 mm with 10- $\mu$ m particle size. The mobile phase consisted of 4 mM *p*-hydroxy benzoic acid solution. The flowrate was set at 1 mL/min. The column temperature was maintained at 40 C. The standards and samples were delivered through a 20- $\mu$ L injection loop using a 25- $\mu$ L-capacity Hamilton microliter syringe. A run time of 20 minutes was set for each analysis. Shimadzu Class-VP software (chromatography data system) on a personal computer was used for integration and computation of signals. The HPLC was stabilized for 30 minutes before introducing the analytes. The phosphonate standards (5, 10, and 20 mg  $\text{HPO}_4^{2-}$ -P/L $^{-1}$ ) and sample solutions were filtered using a 0.2- $\mu$ m nylon filter (Nylon Acrodise Syringe Filter, Pall Corporation, Pall India Pvt. Ltd., Mumbai, India) and collected in 5-mL glass vials. Approximately 20  $\mu$ L of standards and samples were injected manually. The instrument was calibrated with standards, and the phosphonate peak of each sample was analyzed using the software (Figure 1).

The adsorbate also was analyzed for initial and final sodium, potassium, and calcium concentrations. The sodium, potassium, and calcium concentrations were estimated by a flame photometer (flame photometer 128 model, Systronics, Ahmedabad, India) after calibration and proper dilution of the adsorbate.

**Adsorption Kinetic Equations.** The amount of phosphonate adsorbed,  $q_t$  (in mg/kg), at time  $t$  was computed using the following equation:

$$q_t = \frac{(C_0 - C_t) V}{m_s} \quad (1)$$

Where

$C_0$  and  $C_t$  = phosphonate concentrations (mg/L) initially and at a given time  $t$ , respectively;  
 $V$  = volume of the phosphonate solutions (mL); and  
 $m_s$  = weight of the adsorbent (kg).

The percentage of removed phosphonate ions ( $R$ ) in solution was calculated using eq 2.

$$R = \frac{(C_0 - C_t) 100}{C_0} \quad (2)$$

**Pseudo Second-Order Equation.** The pseudo second-order adsorption kinetic rate equation (Ho et al., 2000) is expressed as follows:

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \quad (3)$$

Where

$k_2$  = rate constant of pseudo-second-order adsorption (kg/mg $\cdot$ min), and  
 $q_e$  = sorption capacity value.

For the boundary conditions:  $t = 0$  to  $t = t$  and  $q_t = 0$  to  $q_t = q_t$ , the integrated form of eq 3 becomes the following:

$$\frac{t}{(q_e - q_t)} = \frac{1}{q_e} + k_2 t \quad (4)$$

Which is the integrated rate law for a pseudo-second-order reaction. Equation 4 can be rearranged to obtain eq 5, which has a linear form, as follows:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} (t) \quad (5)$$

If the initial adsorption rate,  $h$  (mg/kg $\cdot$ min) is the following:

$$h = k_2 q_e^2 \quad (6)$$

Then eq 5 becomes the following:

$$\frac{t}{q_t} = \frac{1}{h} + \frac{1}{q_e} (t) \quad (7)$$

The plot of  $(t/q_t)$  and  $t$  of eq 7 should give a linear relationship, from which  $q_e$  and  $k_2$  can be determined from the slope and intercept of the plot, respectively.

**Elovich Equation.** The Elovich model equation (Chien and Clayton, 1980; Sparks, 1986) generally is expressed as follows:

$$\frac{dq_t}{dt} = \alpha \exp(-\beta q_t) \quad (8)$$

Where

$\alpha$  = initial adsorption rate (mg/kg $\cdot$ min), and  
 $\beta$  = desorption constant (kg/mg) during any one experiment.

To simplify the Elovich equation, Chien and Clayton (1980) assumed  $\alpha/\beta t \gg 1$ , and, by applying the boundary conditions  $q_t = 0$



Table 1—Elemental composition of the adsorbents.

Element	CSC (%)	ACSC (%)	MS (%)	PLS (%)	A (%)
Na	0.005	0.011	0.502	0.051	0.001
K	0.001	<0.001	0.021	0.101	<0.001
Ca	0.001	<0.001	40.012	0.730	<0.001
Fe	<0.001	<0.001	<0.001	0.310	<0.001

at  $t = 0$  and  $q_t = q_i$  at  $t = t$ , eq 8 becomes the following:

$$q_t = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} \ln(t) \quad (9)$$

If phosphonate adsorption fits the Elovich model, a plot of  $q_t$  versus  $\ln(t)$  should yield a linear relationship with a slope of  $(1/\beta)$  and an intercept of  $(1/\beta) \ln(\alpha\beta)$ .

**Intraparticle Diffusion Model.** The intraparticle diffusion model (Srivastava et al., 1989; Weber and Morris, 1963) is expressed as follows:

$$R = k_{id}(t)^a \quad (10)$$

A linearized form of the equation is as follows:

$$\log R = \log k_{id} + a \log(t) \quad (11)$$

Where

$R$  = percent phosphonate adsorbed;

$t$  = contact time (minutes);

$a$  = gradient of linear plots, which depicts the adsorption mechanism;

$k_{id}$  = intraparticle diffusion rate constant ( $\text{minute}^{-1}$ ), which also may be taken as a rate factor (i.e., percent phosphonate adsorbed per unit time).

Higher values of  $k_{id}$  illustrate an enhancement in the rate of adsorption and better adsorption mechanism related to an improved bonding between phosphonate and the adsorbent surface.

## Results and Discussion

The elemental compositions of CSC, ACSC, mussel shell, PLS, and Amberlite, with respect to sodium, potassium, calcium, and iron, are presented in Table 1.

The variations in the elements sodium, potassium, and calcium in the adsorbate at the initial and final stages, when kept in contact with the adsorbents, are given in Table 2. The high level of sodium in the adsorbate, when kept in contact with ACSC, is the result of the use of sodium bicarbonate for neutralizing excess sulfuric acid present in the charcoal, as a result of acid treatment.

Table 2—Elemental composition (in mg/L) of phosphonate solution after the study.

Element	*PS	CSC	ACSC	MS	PLS	A
Na	0.5	5.5	26.0	6.0	2.5	1.0
K	33.0	54.0	9.2	36.0	19.5	34.0
Ca	7.0	13.0	5.8	17.0	5.0	7.5

\* Phosphonate solution before the study.

Table 3—Concentrations of  $\text{HPO}_3^{2-}$ -P and  $\text{PO}_4^{3-}$ -P (in mg/L) in potassium phosphonate solution at different time intervals when agitated with CSC (mean  $\pm$  standard error).

Contact time (minutes)	$\text{HPO}_3^{2-}$ -P	$\text{PO}_4^{3-}$ -P	Effective mg $\text{HPO}_3^{2-}$ -P removed/L
0	20.00	0.00	0.00
15	12.35 $\pm$ 0.05	5.64 $\pm$ 0.15	2.01
30	12.50 $\pm$ 0.20	5.79 $\pm$ 0.14	1.71
60	12.50 $\pm$ 0.00	5.52 $\pm$ 0.06	1.98
90	12.65 $\pm$ 0.05	5.69 $\pm$ 0.11	1.66
120	12.50 $\pm$ 0.20	5.63 $\pm$ 0.05	1.87
180	12.65 $\pm$ 0.05	5.82 $\pm$ 0.03	1.53
240	12.40 $\pm$ 0.20	5.80 $\pm$ 0.19	1.80
300	12.60 $\pm$ 0.10	5.67 $\pm$ 0.06	1.73
360	12.55 $\pm$ 0.05	5.67 $\pm$ 0.03	1.78

The high level of calcium in the adsorbate, when kept in contact with mussel shell, is the result of calcium carbonate, which is the major constituent of the material.

Sodium and calcium present in the original solution of potassium phosphonate (Table 2) are the result of the presence of impurities in potassium hydroxide, which is used to neutralize phosphorous acid to obtain potassium phosphonate. The presence of these elements in the final extract after adsorption with CSC, ACSC, mussel shell, PLS, and Amberlite also can be attributed to this: an exception is mussel shell for calcium.

The amount of  $\text{HPO}_3^{2-}$ -P present in the adsorbate after reaching equilibrium is considered for assessing the effectiveness of the material used for the removal of the fungicide from water.

When phosphonate solution was treated with CSC, phosphate ( $\text{PO}_4^{3-}$ ) also was detected in the solution (Table 3), as shown in the chromatogram (Figure 1b) having a retention time ( $R_t$ ) of 6 minutes for phosphate and 7 minutes for phosphonate. The formation of phosphate in the solution is the result of the oxidation of phosphonate to phosphate. This oxidation can be the result of the presence of alkali and alkaline earth metal oxides in CSC, which are released into the solution (Table 2).

Though ACSC was found to be a better adsorbent for the removal of potassium, it was not found to be as effective in phosphonate removal (Table 4). There was no change in the level of adsorption during the entire period of the study, and the maximum adsorption was found to be only approximately 1.5 mg  $\text{HPO}_3^{2-}$ -P/L<sup>-1</sup>.

The mussel shell also was found to be a poor adsorbent for potassium phosphonate (Table 4). The amount of phosphonate adsorbed was less than 1 mg  $\text{HPO}_3^{2-}$ -P/L<sup>-1</sup>. Though calcium influences the removal of phosphonate as insoluble calcium phosphonate (Kumar et al., 2005), the use of mussel shell was not found to be effective for phosphonate removal. This could be the result of the presence of calcium as carbonate, which forms the mussel shell matrix of low calcium activity.

Out of all the natural materials tried, the PLS had a better adsorption capacity for phosphonate (Table 4). In this study, the decrease in the phosphonate concentration was rapid initially and became gradual thereafter. However, the increased adsorption shown by the PLS could be the result of the inherent chemical property of the material rather than the adsorption capacity.



Table 4—Removal of  $\text{HPO}_3^{2-}$ -P by the adsorbents at different time intervals (mean  $\pm$  standard error).

Contact period (minutes)	CSC		ACSC		MS		PLS		A	
	*mg	%	*mg	%	*mg	%	*mg	%	*mg	%
15	2.01	10.05	1.30 $\pm$ 0.20	6.50	0.80 $\pm$ 0.20	4.00	8.08 $\pm$ 0.10	40.40	20.00	100.00
30	1.71	8.55	1.50 $\pm$ 0.10	7.50	0.25 $\pm$ 0.15	1.25	8.70 $\pm$ 0.70	43.50	20.00	100.00
60	1.98	9.90	1.10 $\pm$ 0.10	5.50	0.25 $\pm$ 0.05	1.25	9.70 $\pm$ 0.20	48.50	20.00	100.00
90	1.66	8.30	1.00 $\pm$ 0.10	5.00	0.20 $\pm$ 0.20	1.00	9.95 $\pm$ 0.15	49.75	20.00	100.00
120	1.87	9.35	1.10 $\pm$ 0.10	5.50	0.40 $\pm$ 0.30	2.00	10.00 $\pm$ 0.20	50.00	20.00	100.00
180	1.53	7.65	1.10 $\pm$ 0.20	5.50	0.20 $\pm$ 0.20	1.00	10.45 $\pm$ 0.25	52.25	20.00	100.00
240	1.80	9.00	1.50 $\pm$ 0.10	7.50	0.35 $\pm$ 0.15	1.75	11.05 $\pm$ 0.15	55.25	20.00	100.00
300	1.73	8.65	1.45 $\pm$ 0.05	7.25	0.45 $\pm$ 0.15	2.25	10.85 $\pm$ 0.05	54.25	20.00	100.00
360	1.78	8.90	1.45 $\pm$ 0.05	7.25	0.20 $\pm$ 0.00	1.00	11.45 $\pm$ 0.27	57.25	20.00	100.00

\* mg of  $\text{HPO}_3^{2-}$ -P removed by the adsorbent from 20 mg/L  $\text{HPO}_3^{2-}$ -P solution.

Because laterite has a high level of iron and aluminum oxides/hydroxides, which are phosphorus scavengers, the removal of phosphonate from the solution could be attributed to precipitation of the phosphonate as iron and aluminum phosphonates and its strong binding (Kumar et al., 2005).

With the synthetic adsorbent, Amberlite, the decrease in phosphonate concentration was rapid and was not detected (Figure 1d) throughout the study.

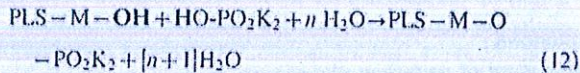
Because, in the case of PLS, significant phosphonate removal took place, the kinetic rate equations were applied to it only. In other cases, the percentage removal of phosphonate was relatively low (Table 4).

Figures 2, 3, and 4 provide a graphical representation of the intraparticle diffusion, pseudo-second-order, and Elovich kinetic models, respectively, for phosphonate removal. Linear regression ( $R^2$ ) was used to determine the best fitting kinetic model for phosphonate removal. Tables 5, 6, and 7 present the values of various parameters and  $R^2$  calculated from the linearized form of the intraparticle diffusion, pseudo-second-order, and Elovich kinetic model equations.

Examination of Tables 5, 6, and 7 shows that the pseudo-second-order kinetic equation had the highest  $R^2$  values. Thus, this kinetic

model was taken as the best-fit equation for the description of the mechanism of sorption of phosphonate. Examination of the sorption capacity values ( $q_e$ ) of the pseudo-second-order model shows that the values are in the same range as the experimental sorption capacity values,  $q_e$ , at 360 minutes (Tables 7 and 8). Therefore, the sorption of phosphonate from aqueous solution onto PLS was found to follow the pseudo-second-order kinetic equation, which is based on the assumption that sorption follows a second-order mechanism, with chemisorption as a probable adsorption process.

The reaction between PLS and phosphonate is suggested to be as follows:



Where potassium phosphonate is in its phosphite form (one of its isomeric forms), PLS-M-OH representing hydroxide/oxide of iron/aluminum (shown as M) present in PLS and PLS-M-O- $\text{PO}_2\text{K}_2$  is the phosphonate-soil complex formed after the reaction. The overall rate can be explained by the concentrations of PLS-M-OH, HO- $\text{PO}_2\text{K}_2$ , and  $\text{H}_2\text{O}$ . Because water is present in the reaction

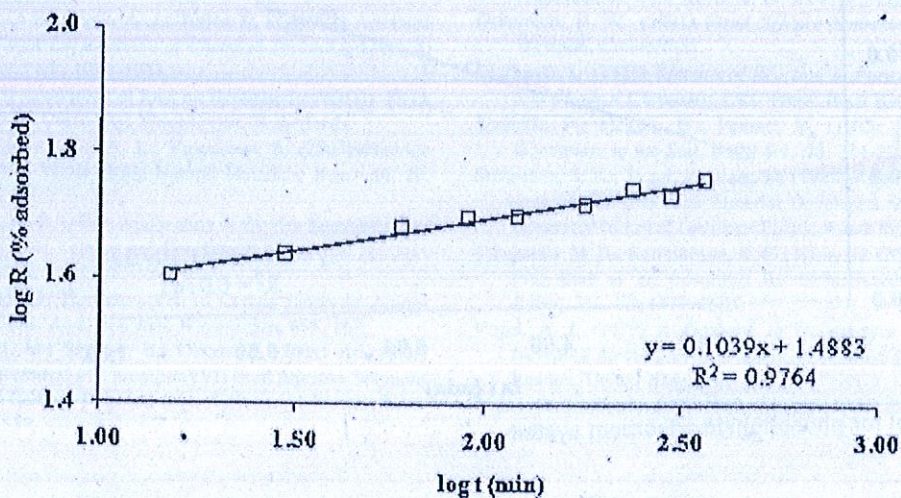


Figure 2—Intraparticle diffusion model for phosphonate-adsorbent system.



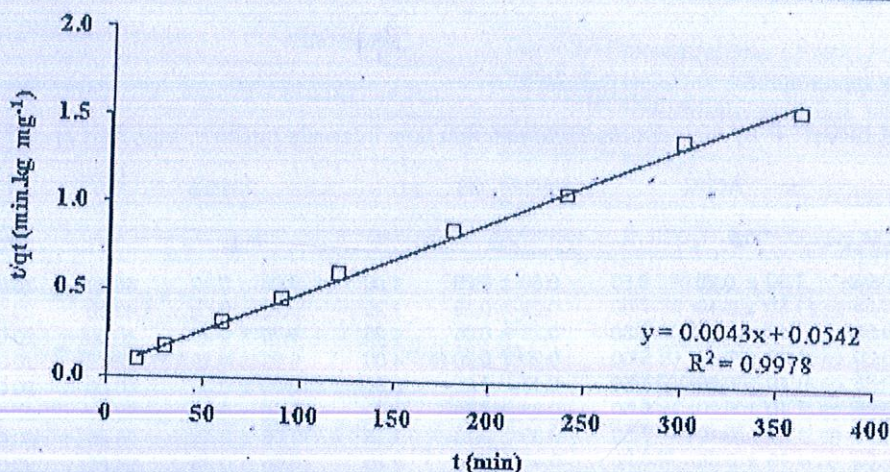
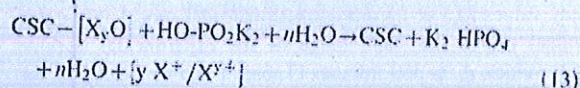


Figure 3—Pseudo-second-order model for phosphonate-adsorbent system.

medium in infinite quantity, the overall rate can be explained by the concentrations of PLS-M-OH and HO-PO<sub>2</sub>K<sub>2</sub>. Hence, the kinetic of the reaction is pseudo-second-order.

The reaction between CSC and phosphonate is suggested to be as follows:



Where potassium phosphonate is in its phosphite form. The CSC - [X<sub>y</sub>O] represents alkali/alkaline earth metal oxide present over the surface of CSC. The X<sup>+</sup> is alkali metal ion, X<sup>y+</sup> is alkaline earth metal ion, and y is an integer (1 or 2). The oxidation of phosphonate to phosphate releases alkali and alkaline earth metal ions to the solution.

### Conclusions

The removal of potassium phosphonate in water by low-cost naturally occurring adsorbing materials, such as CSC, ACSC, mussel shell, and PLS, was studied and compared with Amberlite.

The study indicated that PLS is most efficient for the removal of phosphonate from water. The removal is the result of the presence of

oxides of aluminum and iron in the system. The CSC also was found to be a good phosphonate reducer from water, but phosphate was produced during the course of adsorption. As the chemical activation of coconut shell was done by sulfuric acid, ACSC became a good cation exchanger rather than an anion exchanger, as evident from the low concentrations of potassium and calcium ions in the solution after the study. Mussel shell was thought to be a good phosphonate remover, but the percentage of phosphonate removal was low, possibly as a result of the presence of calcium carbonate of low calcium activity, which forms the mussel shell matrix.

The pseudo-second-order kinetic model was found to be in good agreement with the experimental data ( $R^2 > 0.997$ ), showing chemisorption as the predominant reaction for the removal of phosphonate from water by PLS. The PLS can be used as a low-cost natural adsorbent for phosphonate removal from water, because laterite stone, which is the raw material for preparing PLS, is easily available and a cheap natural source.

### Credits

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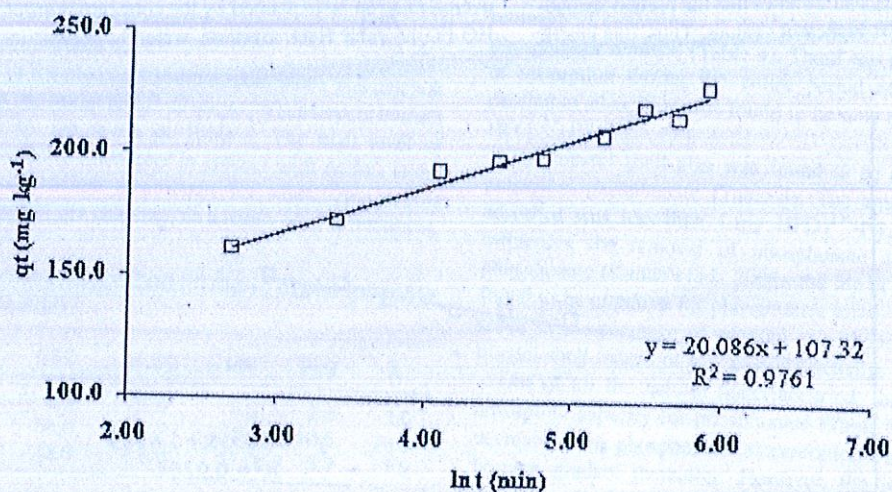


Figure 4—Elovich model for phosphonate-adsorbent system.



**Table 5—Intraparticle diffusion model constants for phosphonate-PLS system.**

log $k_{id}$	$k_{id}$ ( $\text{min}^{-1}$ )	$a$	$R^2$
1.4883	30.7822	0.1039	0.9764

**Table 6—Pseudo-second-order model constants for phosphonate-PLS system.**

$1/q_e$	$q_e$ ( $\text{mg kg}^{-1}$ )	$1/h$	$k_2$ ( $\text{kg mg}^{-1} \text{min}^{-1}$ )	$R^2$
0.0043	232.5581	0.0542	0.0003	0.9978

**Table 7—Elovich model constants for phosphonate-PLS system.**

$1/\beta$	$\beta$ ( $\text{kg mg}^{-1}$ )	$\ln(\alpha/\beta)$	$u$ ( $\text{mg kg}^{-1} \text{min}^{-1}$ )	$R^2$
20.086	0.050	5.3430	$4.2009 \times 10^3$	0.9761

**Table 8—Parameters for kinetic equations for the removal of  $\text{HPO}_3^{2-}$ -P by powdered laterite stone at different time intervals.**

Time (minutes)	$q_t$ ( $\text{mg kg}^{-1}$ )	% Removed	log R	$1/q_t$	log t	ln (t)
15	161.5	40.4	1.61	0.1	1.18	2.708
30	174.0	43.5	1.64	0.2	1.48	3.401
60	194.0	48.5	1.69	0.3	1.78	4.094
90	199.0	49.8	1.70	0.5	1.95	4.500
120	200.0	50.0	1.70	0.6	2.08	4.787
180	209.0	52.3	1.72	0.9	2.26	5.193
240	221.0	55.3	1.74	1.1	2.38	5.481
300	217.0	54.3	1.73	1.4	2.48	5.704
360	229.0	57.3	1.76	1.6	2.56	5.886

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