

Pseudo-First and Second-Order Models for P Adsorption onto Termite Mound Soil (TMS)

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Abstract: based on the present study, TMS which is abundantly available and an effective low-cost adsorbent for the removal of P from wastewater. Adsorption kinetic studies were investigated using batch adsorption experiments. Since adsorbent undergoes different molecular stages, kinetic studies are important to understanding the mechanism of the adsorption process. The linear regression correlation coefficient (for 3 mg/L of P concentration) value of $R_1^2=0.917$ and $R_1^2=0.945$ for 10 mg/L P concentration shows that the pseudo-first-order model cannot predict the adsorption kinetics. The linear regression correlation coefficient for Pseudo-second-order model (3 mg/L P concentration) was $R_2^2=0.999$ and $R_2^2=0.997$ for 10 mg/L P concentration which confirms that the TMS adsorption data well represented by the pseudo-second-order kinetic model for P adsorption. Soils containing higher percentage of clay, CEC, and organic matter adsorbs more P. The scanning electron microscope results showed that TMS is the porous surface, which plays a significant role in P adsorption process.

Keywords: Adsorption, Models, Phosphorous, Termite mound soil

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I. Introduction

Wastewater which contains pollutants beyond its permissible limit generated from both point and non-point sources released into the environment without treatment is a fret of our world today [1]. Wastewater containing high concentration of P discharge from sewage and industries are the major component of water pollution, contributing to oxygen demand and nutrient loading of the water bodies, promoting toxic algal blooms and leading to a destabilized aquatic ecosystem [2]. Recent reports show that worldwide more than half of the population of less developed countries do not have access to sanitation and over 80% of the wastewater generated is directly discharged into surface and groundwater bodies [3]. Different national and international institutions try to develop permissible limit for all hazardous chemical and elements released in waste water and inter into the river, stream and stagnant water bodies [4]. P is one of those elements which limit the growth and if in access cause the loss of aquatic life and death of water bodies. The general purpose of P removal is to eliminate the excess P content from wastewater discharged to receiving waters and then to use this excluded P load in the way which is the most proper for the natural phosphorus cycle in nature [5]. This method should prevent surface waters against Eutrophication-related problems[6].

P is a naturally occurring element that can be found in different parts of earth's crust, water bodies, and in all living organisms [7]. P is one of 16 elements essential for plant growth and it is found in a natural environment in the form of condensed phosphate (polyphosphate), organic phosphates and orthophosphates [8]. The excess content of P in receiving waters leads to extensive algal growth which is called The phenomenon of Eutrophication usually decreases the water quality and as a result it may increase significantly the cost of water treatment at treatment plants for surface water [9]. The load of phosphorus discharged to receiving waters comes from various groups of sources of a point source and non-point sources of which the main sources are agricultural use of fertilizers, domestic and industrial wastewater, and atmospheric deposition[10].

Termites are social insects that influence the physical, chemical and biological properties of tropical and sub-tropical soils [11]. The feeding habit, the food processing and mound construction operations introduce significant modifications to the soils organic and mineralogical content on which the mound is built[12]. Termites perform several activities that qualify them as soil engineers. They collect organic material as the food source and for nest construction, transport it to their nest, and alter it during digestion. For the transportation, they build galleries into the soil and also on the soils surface[13]. The physico-chemical characteristics of soils largely influence the parameters of adsorption process and this eventually governs the

availability of nutrient ions to the growing plants [14]. The aim of this paper was to investigate the adsorption kinetic model of P onto TMS.

II. Material and method

2.1. Adsorbent preparation

Samples of mound soil were collected from two TMs surrounding of Adama, Oromia Regional state, Ethiopia. A sample was taken from a single mound hill and control soil (non- termite) was taken away from TMS. Particle size analysis of the soil sample was performed according to (ASTM D 422) and soil textural classification system used was (ASTM). Then soil sample was air dried for two days at room temperature and crushed by hand in a mortar, and sieved to different particle size > 4.75 , $1- 0.425$, $0.425-0.075$ and < 0.075 mm particle size. The moisture content was determined by heating in an oven at $105\text{ }^{\circ}\text{C}$ for 24 h. The pH of the adsorbent was measured using a Microprocessor pH meter (pH 196, WTW, Germany) at a 1:2.5 TM/water ratio according to the standard method [15].

2.2. Reagent

All the chemicals and reagents used in this study were of analytical grade. All glassware and sample bottles were soaked in diluted $0.01\text{ M H}_2\text{SO}_4$ solution for 24 hrs, washed and then rinsed three times with distilled water and dried in an oven at $105\text{ }^{\circ}\text{C}$ for 2 hrs and after conducting one parameter the bottles were washed well and filled with distilled water over night for next parameter to minimize contamination according to

2.3. Batch adsorption

Series of batch adsorption experiments were carried out using 1000 ml solution of PO_4^{2-} with initial concentrations of 3 mg/L and 10 mg/L . The adsorbent (TMS) with a concentration of 10 g/L TM was added in the bottle and agitated on an orbital shaker (Type SM 30 C, Germany) agitated at a rate of 200 rpm and the supernatant solution samples were waiting for ten minutes to allow sedimentation of adsorbent in solution followed with centrifugation at speed of 5000 rpm by using (Eppendorf AG 22331 Hamburg, Germany) for fifteen minutes. After that it is filtered by using Whatman filter paper ($0.45\mu\text{m}$) and then all important reagents prepared was added. Then it is read by using double bin spectrophotometer (V-630, Japan) with in thirty minutes after adding reagents.

2.4. Adsorption kinetics

2.4.1. Pseudo-first-order model

Langergren's pseudo-first order equation is the earliest known that describing the adsorption rate based on the adsorption capacity. the linear form of langergren's and nonlinear equations of pseudo first order model is expressed as eq. 1. nonlinear and eq.2. linear [16].

$$q_t = q_e [1 - \exp(-k_1 t)] \quad (1)$$

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad (2)$$

Where q_t (mg/g) is the amount of P adsorbed per unit mass of the adsorbent at any time t (minutes), q_e (mg/g) is the calculated equilibrium capacity, and k_1 (min^{-1}) is the equilibrium rate constant based on the pseudo-first-order equation.

2.4.2. Pseudo-second-order model

The adsorption kinetics of the system explained by pseudo-second-order equation (Eqs. 4 and 5) when the removal of an adsorbate from aqueous solution increases during the initial agitation time, and followed by a slow increase until the equilibrium time was reached[17].

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

Where q_t (mg/g) is the amount of P adsorbed per unit mass of the adsorbent at any time t (min), q_e (mg/g) is the calculated equilibrium capacity, and K_2 ($\text{g} \cdot \text{mg}^{-1} \cdot \text{min}^{-1}$) is the equilibrium rate constant based on the pseudo-second-order equation. Integrating Eq. (4) for the boundary conditions $q_t = 0$ to $q_t = q_t$ at $t = 0$ to $t = t$ is simplified and linearized to obtain Eq. (4).

$$\frac{t}{q_e} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (4)$$

III. Result and discussions

3.1. Physicochemical properties

Clays are not the only indicators of CEC but also play a great role for P availability in soil through its high adsorptions capacity [18]. The clay content of a soil has impact on P adsorption. Soils containing higher

percentage of clay adsorbs more P than those with less clay content. As presented in clay soils are very silty in size it has more surface area that exposed with a given adsorbent, so it has the greater tendency to retain P which is similar with other study [19]. The SEM results showed that TMS is irregular in shape Fig. 1, which indicates high surface areas for adsorption. It has been known that the crystal structure and space play a significant role in adsorption process.

3.2. Effect of agitation time

The effect of agitation time on the adsorption of P ions by TMs was studied and the result is presented on Table 1. From the Table initially adsorption was increased sharply up to 60 min and get almost constant after 60 min. For 3mg/L initial concentration of P the result obtained was 72.30 and 95.36% for 5 and 60 min, respectively. For 10 mg/L initial concentration of P also shows that 68.26 and 90.01 for 5 and 60 min, respectively. The result shows that agitation time of 60 min was sufficient to achieve equilibrium and adsorption did not change significantly with further increases in the contact time [20]. Therefore, the uptake and unadsorbed P concentrations at the end of 60 min are given as the equilibrium values.

3.3. Adsorption kinetic models

3.3.1. Pseudo-first-order model

Adsorbent undergoes different molecular stages, kinetic studies are important to understanding the mechanism of the adsorption process. For pseudo-first-order model The adsorption rate constant k_1 and q_{e-cal} can be determined from the intercept and slope of $\log(q_e - q_t)$ versus t , respectively as shown in Fig. 2(a and b) for 3 mg/L and 10 mg/L P initial concentration. The linear regression correlation coefficient (for 3 mg/L of P concentration) value found to be $R_1^2 = 0.917$ and for 10 mg/L of P concentration was $R_1^2 = 0.945$. The calculated rate constant (K_1) and adsorption capacity q_{e-cal} was 0.032 (min)^{-1} and 0.336 mg/g for 3 mg/L P concentration which is not nearer to the equilibrium adsorption capacity from experiment (q_{e-exp}) value 0.280 mg/g as shown in Table 2. As presented in table 3 for 10 mg/L P concentration value the calculated rate constant (K_1) and adsorption capacity (q_{e-cal}) was 0.039 (min)^{-1} and 0.537 mg/g which is also not nearer to the equilibrium capacity adsorption for experimental value 0.880 mg/g . These shows that the model cannot predict the adsorption kinetics for this process which is similar with previous study [21].

3.3.2. Pseudo-second-order model

The K_2 and q_{e-cal} was determined from the linear plot intercept and slope of (t/q_e) versus (t) according to Fig. 3 (c and d) for 3 and 10 mg/L P concentration. The calculated rate constant (K_2) and adsorption capacity (q_{e-cal}) was $1.553 \text{ (g.mg}^{-1}.\text{min)}^{-1}$ and 0.276 mg/g for 3 mg/L P concentration shows (q_{e-cal}) is nearer to the equilibrium adsorption capacity from experiment (q_{e-exp}) value 0.280 mg/g as shown in Table 2, for 10 mg/L P concentration value the rate constant (K_2) and adsorption capacity (q_{e-cal}) was $0.563 \text{ (g.mg}^{-1}.\text{min)}^{-1}$ and 0.868 mg/g , respectively which shows that (q_{e-cal}) also nearer to the equilibrium adsorption capacity for experimental value 0.880 mg/g Table 3. The linear regression correlation coefficient for Pseudo-second-order model (3 mg/L P concentration) was $R_2^2 = 0.999$ and $R_2^2 = 0.997$ for 10 mg/L P concentration which confirms that the TMS adsorption data well represented by the pseudo-second-order kinetic model for P adsorption [22]

IV. Conclusion

Based on the present study, TMS which is abundantly available and an effective low-cost adsorbent for the removal of P from wastewater. Adsorption kinetic studies were investigated using batch adsorption experiments. Since adsorbent undergoes different molecular stages, kinetic studies are important to understanding the mechanism of the adsorption process. The linear regression correlation coefficient (for 3 mg/L of P concentration) value of $R_1^2 = 0.917$ and $R_1^2 = 0.945$ for 10 mg/L P concentration shows that the pseudo-first-order model cannot predict the adsorption kinetics. The linear regression correlation coefficient for Pseudo-second-order model (3 mg/L P concentration) was $R_2^2 = 0.999$ and $R_2^2 = 0.997$ for 10 mg/L P concentration which confirms that the TMS adsorption data well represented by the pseudo-second-order kinetic model for P adsorption. For 3 mg/L initial concentration of P the result obtained was 72.30 and 95.36% for 5 and 60 min, respectively. The result shows that agitation time of 60 min was sufficient to achieve equilibrium and adsorption did not change significantly with further increases in the contact time, which is considered as an equilibrium. Soils containing higher percentage of clay, CEC, and organic matter adsorb more P. The scanning electron microscope results showed that TMS is porous surface, which plays a significant role in P adsorption process.

Table caption

Table 1 The effect of agitation time on the adsorption of P onto TMS

Table 2 Pseudo-first and second order parameters for P adsorption using TMS

Figure caption

Figure 1 SEM photograph of termite mound soil

Figure 2 Pseudo-first-order plot for (a) 3 mg/L and (b) 10 mg/L of P concentration

Figure 3 Pseudo-second-order plot for (c) 3 mg/L and (d) mg/L of P concentration

Table 2: The effect of agitation time on the adsorption of P onto TMS

Time (min)	Co = 3 mg/L			Co = 10mg/L			pH	
	Ce (mg/L)	qe (mg/g)	A (%)	Ce (mg/L)	qe (mg/g)	A%	pH _i	pH _f
5	0.78	0.20	72.30	3.02	0.65	68.26	7.00	5.92
10	0.72	0.22	74.48	2.21	0.73	76.80	7.12	5.9
15	0.70	0.24	74.98	1.82	0.77	80.92	7.00	5.75
30	0.50	0.25	82.15	1.49	0.80	84.35	6.97	5.42
45	0.44	0.26	84.28	1.16	0.84	87.82	7.02	5.52
60	0.13	0.28	95.36	0.95	0.88	90.01	7.04	5.21
75	0.12	0.27	95.84	1.00	0.86	89.52	6.99	5.42
90	0.12	0.27	95.90	0.89	0.86	90.65	7.21	5.39
120	0.11	0.27	96.12	0.96	0.86	89.88	7.08	5.22

Table 2: Pseudo-first and second order parameters for P adsorption using TMS

Model	Parameters	P concentration	
		3 (mg/L)	10 (mg/L)
Pseudo-first-order	q _e .exp (mg/g)	0.280	0.880
	q _e .cal (mg/g)	0.336	0.537
	K ₁ (min) ⁻¹	0.032	0.039
	R ₁ ²	0.917	0.945
Pseudo-second- order	q _e .exp (mg/g)	0.280	0.880
	q _e .cal (mg/g)	0.276	0.868
	K ₂ [g/(mg.min)]	1.553	0.563
	R ₂ ²	0.999	0.997

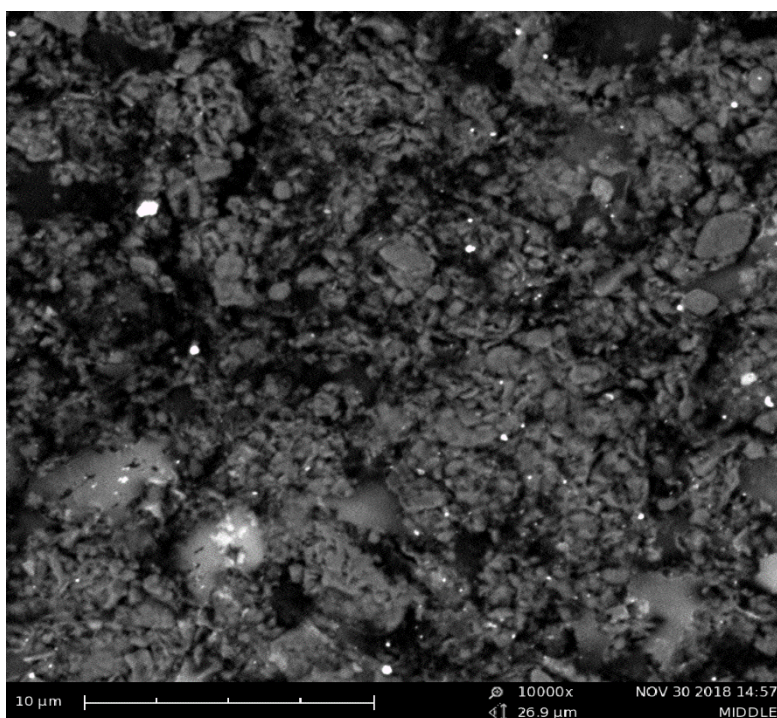


Figure 4: SEM photograph of termite mound soil

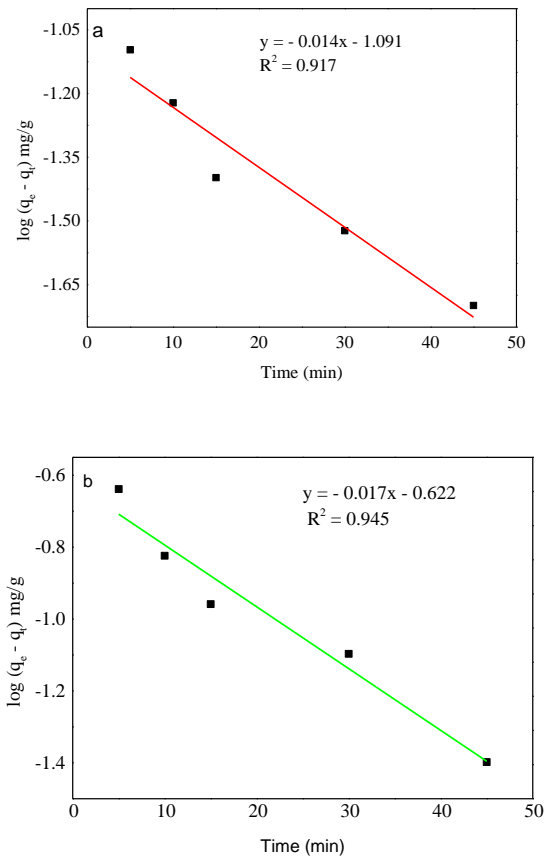


Figure 5: Pseudo-first-order plot for (a) 3 mg/L and (b) 10 mg/L of P concentration

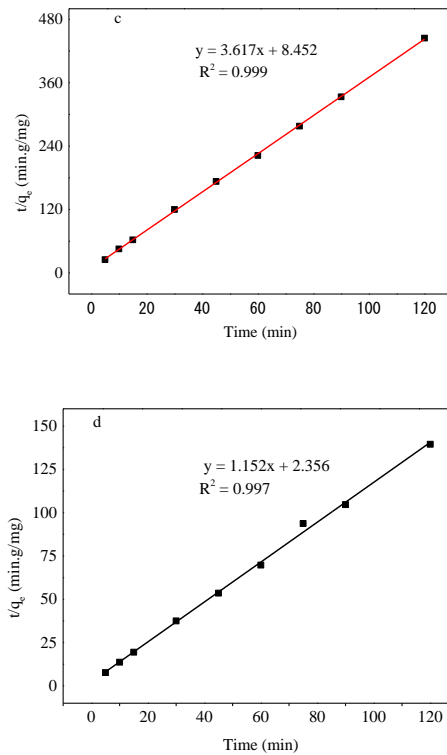


Figure 6: Pseudo-second-order plot for (c) 3 mg/L and (d) 10 mg/L of P concentration

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