

The Adsorptive Properties of Fired Clay Pellets for the Removal of Phosphate in Wastewater Treatment

[Uduakobong A. Edet, Mark J. Bateman, Augustine O. Ifelebuegu, Adrian Wood]

Abstract— Removal of phosphate in wastewater treatment is crucial to reducing nutrient enrichment and eutrophication of aquatic bodies. This study explored the potential of fired clay pellets for use in phosphate removal during wastewater treatment. The mechanism of removal was evaluated in a batch adsorption study under different experimental conditions. Fired clay pellets were found to be effective in the adsorptive removal of phosphate from aqueous solution with a maximum adsorption capacity of 144mg/g. The experimental data showed a good fit to the pseudo-first-order kinetic model indicating a physical nature of the sorption process and also followed Dubinin-Radushkevich Isotherm model. Adsorption of phosphate favoured acidic pH with optimum removal at pH 3-4. The values of Gibbs free energy (-16.5 kJ/mol), enthalpy (-8.87 kJ/mol) indicated adsorption was spontaneous and exothermic. The mechanism was found to be predominantly physisorption supported by some diffusion.

Keywords—adsorption, kinetics, phosphate, clay, isotherm

I. Introduction

Excessive or elevated nutrients in the water system may enhance the increase in plant based organic matter hence causing eutrophication and algal blooms [1,2,3,4,5]. Phosphate has been cited as a vital and limiting nutrient in freshwater system and has been suggested that a decrease in phosphate can effectively control eutrophication in coastal and fresh water systems [2,6,7]. Phosphates in wastewater may originate from industrial use of phosphate as a raw material, domestic use of phosphate-containing detergents and runoff from application of phosphate fertilizers to agricultural lands [8]. As eutrophication is a major issue, the effective and efficient removal of phosphate during wastewater treatment is crucial. The Urban Waste Water Treatment Directive mandates an 80% reduction in phosphorus level or an effluent P concentration of 2mg/L P for 10,000- 100,000 p.e and 1mg/L for population estimate greater than 100,000. This directive has led to a decreasing low level of P in wastewater effluent during treatment through increased government regulatory pressure [1]. Several methods of phosphate removal have been employed in wastewater treatment. These include chemical precipitation involving the addition of calcium, iron and aluminium salts. This is the commonly used and the most effective method of phosphate removal in wastewater treatment plant (WWTP),

and often resulting in high phosphate removal levels [9,10]. The major drawbacks of the method are the high volume of sludge produced [11] and the cost of chemicals required for dosing [12]. Biological phosphate removal has also been used in wastewater treatment [13,14,15] and it depends on a combination of factors such as pH and temperature for effective performance [16,17]. Consequently, it has a variable and inconsistent removal rate which may require a complimentary treatment to produce low phosphate effluent levels [18,19].

Adsorption of phosphate to suitable materials is becoming a frequently used method of removing phosphate in wastewater treatment. This could be attributed to its advantages over chemical precipitation and biological P removal. These advantages include low cost, capacity to produce re-usable solid, the simplicity make this method a favourable option in wastewater treatment [16,20]. Fe, Al and Ca are the elements that are often credited with phosphate sorption and it is assumed that if these elements are present in any medium in a substantial amount, then that medium can be used for phosphate removal [21].

Several studies have been conducted using various low cost adsorbents such as: alunite [22,23], fly ash [24,25], opoka [26,27,28], Polonite [29], sand [30,31], Lightweight aggregate (LWA)/Light Expanded Clay aggregate (LECA) [32,33,34], ochre [35], red mud [36], and clay [8,37] for the removal of phosphate from wastewater. The studies have been carried out in a laboratory, small scale constructed wetland or a full scale constructed wetland with the adsorbents used as filter media [30].

Clay has been studied as a low cost adsorbent in the removal of phosphate from wastewater and different phosphate removal rates has been recorded. In a phosphate removal studies done with raw and acid treated clay from Malawi, a high brick dosage of 60g/L was required for a removal rate of 80% using the acid treated clay while the raw clay only achieved a maximum removal rate of 60% and was believed that different phosphate removal mechanisms were responsible for phosphate removal at different pH [8]. At a low pH, it was believed that the removal was through phosphate adsorption to iron oxide, while the phosphates were precipitated out by calcium ions at a higher pH [8].

The use of fired clay for removal of pollutants in wastewater treatment has been reported [38,39,40,41]. This work explored the feasibility of employing fired clay pellets for the removal of phosphate from wastewater. The phosphate adsorptive properties (calcination temperature of the pellets, pH, sorption kinetics, isotherm and thermodynamics) were investigated in batch experiments.

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II. Materials and Method

A. Preparation of Clay Pellets

The clay used in this study was obtained from a clay pit in Marks Tey-Essex, United Kingdom. Deionised water was added to the clay to improve its handling. The clay was spread on to a metal grid measuring 1 cm x 1 cm x 1.5 mm which served as a mould for the pellets and left to air dry for two days. The pellets were fired in a Lenton Thermal Design General purpose chamber furnace ECF/12/22 at temperature from 540 °C to 1050 °C

B. Batch Adsorption Studies

Anhydrous potassium dihydrogen phosphate (KH_2PO_4) was used as the source of phosphate in this study. All reagents used were analytical grade and were obtained from Fisher Scientific of Sigma Aldrich UK.

100 mg/l stock phosphate solution was prepared by dissolving 0.4393 g of KH_2PO_4 in 1000 ml of deionised water. Phosphate solution used in the adsorption experiment was obtained by diluting appropriate volume of stock phosphate solution in deionised water.

Adsorption of phosphate was carried out by typically adding 3 g of calcined clay tiles to 150 ml of 50 mg/l phosphate solution in a stoppered Erlenmeyer flask and stirring in an orbital shaker at 170 rpm for 120 minutes. Aliquots were drawn at regular intervals, filtered before analysis using FOSS FIAstar 5000 analyzer. Adsorbed phosphate was calculated as the difference in the concentration of phosphate added and the phosphate concentration remaining in the equilibrating solution. All experiments were carried in triplicates. The rate of phosphate adsorption was calculated as:

$$\text{Phosphate removal (\%)} = \frac{C_0 - C_t}{C_0} \times 100 \quad (1)$$

Where C_0 is initial phosphate concentration and C_t is phosphate concentration at time t

The equilibrium adsorption capacity (q_e) was calculated using the equation:

$$q_e = \frac{(C_0 - C_e) \times V}{m} \quad (2)$$

Where C_0 and C_e is the initial and equilibrium phosphate concentration respectively (mg/l), V is the volume of phosphate solution (l) and m is the mass of clay pellets.

The point of zero charge (pH_{zpc}) of the sample was determined using a procedure previously described. [42,43].

To investigate the effect of pH on the adsorption of phosphate, 3 g of calcined clay pellets was added to 150 ml of 50 mg/L phosphate of different initial pH ranging from 2.0 to 12.0 adjusted by adding 0.10 M HCl or NaOH. Similar mass of clay pellets and concentration of phosphate solution was used to study the effect of phosphate at different temperature. The effect of initial concentration was investigated by adding 5 g of calcined clay pellets to 200 ml of phosphate solution containing varying initial concentration.

The experimental data obtained from the study were analysed using various kinetic models: Lagergren pseudo-first order, pseudo second order, Intraparticle, Elovich and Bangham's kinetic models. Thermodynamic parameters including Gibbs free energy, entropy and enthalpy were also investigated. The adsorption isotherm was also investigated using Langmuir, Freundlich, Tempkin and Dubinin-Radushkevich isotherm models.

III. Results and Discussion

A. Effect of Firing Temperature

The effect of firing temperature of clay pellets on the adsorption of phosphate was studied using 3 g clay pellets fired at temperature from 540 °C to 1050 °C and 150 ml of 50 mg/l phosphate solution. The results are illustrated in Fig 1.

It can be observed from Fig. 2 phosphate adsorption was enhanced with increase in firing temperature as the temperature increased from 540 °C to 960 °C before declining. Phosphate adsorption reached a maximum when the clay pellets were fired at 850 °C. Phosphate sorption declined slightly when the firing temperature was between 900 °C and 1000 °C. There has been limited research on the effect of firing temperature of clay for use as an adsorbent in water and wastewater treatment. A pivotal study in this area was the study on defluoridation of drinking water which showed fluoride adsorption decreased with increasing firing temperature [38]. Fluoride adsorption using clay fired at 600°C was found to be most effective, while those fired above 700°C and above showed a decreased fluoride adsorption [38,39,40]. Another study on the removal of Cr(VI) using fired brick clay showed a decrease in the removal of Cr(VI) when firing temperature increased from 200°C to 600°C [41]. These findings are contrary to results obtained in this study.

Firing of clay generally reduces water trapped between the silicate sheets of the clay producing hard granules that, even when fully saturated with water, do not disintegrate easily [46]. During fluid bed drying, which is the first stage of firing, occurring between 120°C and 174°C, moisture content is reduced to 6% - 9% from 40% - 45% and further moisture reduction is achieved up to 0% in some cases, when the temperature is between 460°C and 800°C. Sorption properties of clay are enhanced during firing as a result of the aggregation of clay particles creating a stable porous internal structure [46]. Although firing may reduce the exchange capacity of the clay, internal pores and surface binding can ensure the retention of the sorption properties. Heat treatment has been shown to cause the collapse of the interlayer in 2:1 Ca-montmorillonite

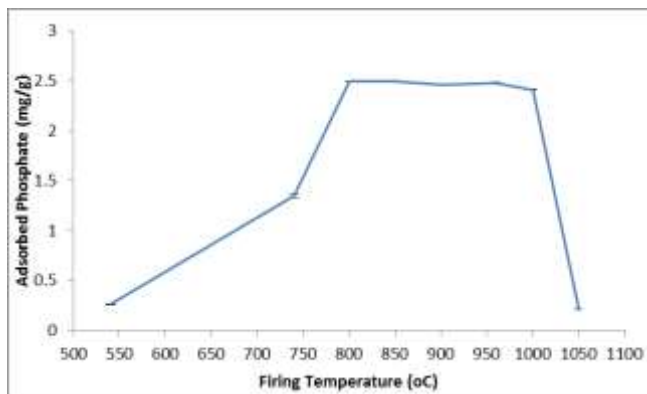


Figure 1. Effect of calcination temperature on adsorption of phosphate by calcined clay pellets (n=3)

through the incorporation of cations into the tetrahedral or unoccupied octahedral sheets when the calcination temperature was between 200°C and 400°C [47]. The physicochemical properties such as micropore volume, specific area and total surface acidity generally decrease with increasing temperature when the temperature exceeds 450°C. Acidic binding has been shown to increase with increasing temperature particularly at the regions of dehydration and dehydroxylation 100°C to 500°C and 550°C to 700°C respectively [48].

Decomposition of the silicate layer in the clay sheets and the collapse of the mesopore and micropore due to inter- and intraparticle sintering occurs when the temperature is increased causing a rapid decline in the specific surface area and specific micropore volume [48]. This is believed to cause the sudden decline in the adsorption of phosphate using clay tiles fired at 1050°C seen in this study.

B. Effect of Mass of Adsorbent

The effect of the mass of clay pellets was investigated for phosphate adsorption with other experimental condition left constant (150 ml of 50 mg/l phosphate; temperature 20 °C ± 2 °C; pH 7). The adsorption of phosphate was shown to increase with an increase in mass of clay pellets (Fig 2), however, there was no change in the adsorption of phosphates between 3g and 5g pellets. This could be attributed to the overlapping of active reaction sites as the mass of tile increased [49]. The increase in phosphate adsorption is due to a greater surface area and consequently increased available binding sites when the adsorbent dose increases [50,51].

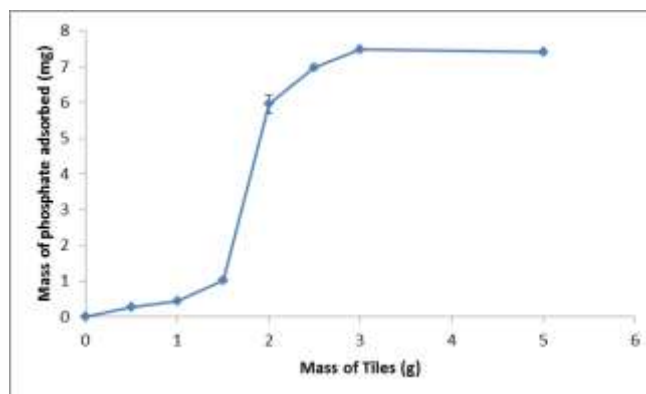


Figure 2: Effect of mass of adsorbent on the adsorption of phosphate

C. Effect of pH

The effect of pH on phosphate adsorption was studied at pH between 2 and 12. It was observed that phosphate adsorption increased sharply when pH increased from 2 to 3, followed by a slight decline as pH increased to 12 (Fig. 3). The highest level of phosphate adsorption was achieved at pH 4. The results obtained were consistent with other studies on the mechanism for the adsorption of phosphate onto solid waste [52]. Phosphate adsorption with other water-adsorbent interfaces is strongly dependent on pH [53]. The general trend reported for the effect of pH on phosphate adsorption follows the pattern described in Fig. 3, however, it is suggested that phosphate adsorption can occur within two pH ranges [8] although phosphate adsorption across three pH ranges have also been known to occur [54,55]. Phosphate adsorption using red mud was reported to decrease with increase in pH, due to the alkaline properties of red mud at low pH resulting in greater adsorption of acidic ions [36]. This contradicts the results of this study as 91% removal was obtained at pH 12.

Clay predominantly contains oxides of metals such as Ca, Fe and Al; and nonmetals such as Si. These oxides play a role in phosphate adsorption as they are hydroxylated when in contact with water and positive or negative charged developed on the interface depending on the pH [56]. The positive charged interface serves as bonding sites for phosphates adsorption. Surface charges on the pellets are produced as a result of the hydrolysis of the Si-OH or Al-OH bonds along the clay lattice [57]. These charges could be positively and negatively charged, depending on the pH and structure of the silica. The zero point charge (pH_{zpc}) of the clay pellets was 8.13 and is within the range reported for smectite which is the predominant mineral found in the clay [58,59]. When the pH is less than pH_{zpc} the clay surface has a net positive charge and the propensity to attract anions increases. When pH is greater than pH_{zpc} the clay surface is negatively charged and the attraction of anions decreases. Phosphate adsorption in this study was found to be higher at pH lower than pH_{zpc} . This result is consistent with reports of other studies [8,43].

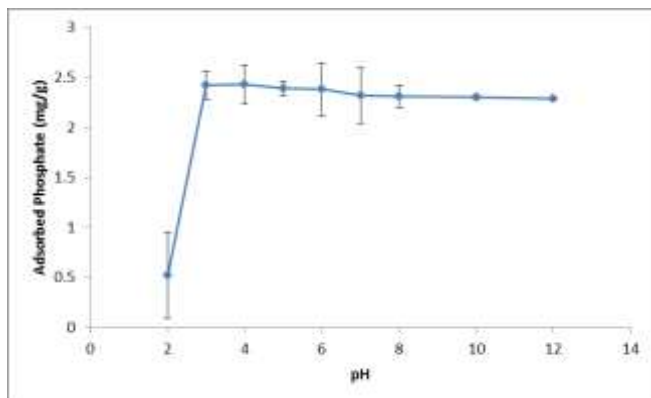


Figure 4: Phosphate adsorption at different pH

D. Adsorption Kinetics

Adsorption kinetics is one of the most crucial factors in the design of adsorption. During the design and optimization of full scale applications, adsorption kinetics is essential in choosing optimum operating conditions and examining potential rate controlling mechanism [60,61]. Adsorption mechanism of phosphate from aqueous solution was investigated using various kinetic models; pseudo first order, pseudo second order, Elovich, and Bangham's kinetic models were used in this study.

Pseudo first order kinetics model explains the relationship between the occupation of adsorption sites and the number of occupied sites on the adsorbent. It is defined using Lagergren equation [62,63]

$$\ln(C_t/C_o) = -kt \quad (3)$$

where C_o and C_t is the initial concentration of the adsorbate and C_o is adsorbate concentration at time t (mg/l) respectively, k_1 is the equilibrium rate constant (min^{-1}). A plot of $\ln(C_t/C_o)$ against t should yield a linear relationship and k_1 determined from the slope.

Pseudo second order kinetic is used to describe the dependency of the adsorption capacity of the adsorbent on time. It is calculated using equilibrium adsorption capacity as is expressed as

$$1/[C_t] - 1/[C_o] = kt \quad (4)$$

where $k_2q_e^2$ is the initial adsorption rate when $t \rightarrow 0$ and k_2 is the pseudo second order rate constant (g/mg/min). A plot of the $1/C_t - 1/C_o$ against time is used to determine k_2 .

Elovich kinetic model was initially used to describe chemisorption of gases onto heterogeneous surface and is now used to study removal of pollutants from aqueous solution. It describes second order kinetics with the assumption that the solid surface has heterogeneous energy [64]. The Elovich model is represented as

$$\frac{dq}{dt} = a_e^{-\alpha q} \quad (5)$$

Where q is the amount of adsorbate adsorbed at time t ; a_e is the adsorption constant and α is the initial rate of adsorption (g/g/min). Integrating Equation (5) assuming the boundary conditions of $q=0$ at $t=0$ and $q=q$ at $t=t$ yields

$$q = \alpha \ln(\alpha a_e) + \alpha \ln t \quad (6)$$

The linear form is expressed as

$$qt = \frac{\ln \alpha b}{b} + \frac{1}{b} \ln t \quad (7)$$

where b is related to the extent of surface coverage and activation energy for chemisorption. A plot of q_t against $\ln t$ yields a straight line and α and b determined from the slope and intercept respectively.

Bangham's kinetic model is used to evaluate the dominance of pore diffusion in the adsorption process [65]. It is expressed as:

$$\text{Log Log } [C_o/(C_o - qtM)] = \text{Log } [k_o/2.303V] + \alpha \text{Log } t \quad (8)$$

Where C_o is the initial concentration of adsorbate (mg/l), V is the volume of the solution (ml), M is the mass of adsorbent (g/l) qt is the amount of adsorbate adsorbed at time t and k_o and α are constant. The plot of $\text{Log Log } [C_o/(C_o - qtM)]$ against $\text{Log } t$ is used to determine k_o and α from the slope and intercept. Table 1 shows the results obtained for pseudo first order, pseudo second order, Elovich and Bangham's kinetic model for phosphate.

Table 1 presents kinetic parameters of the sorption of phosphate onto clay pellets. The kinetic plot showed good fit of sorption equilibrium data for pseudo first order model suggesting physisorption was the rate controlling

E. Intra-particle Diffusion Kinetics

The adsorption mechanism of solute onto adsorbent can be described using the intra particle diffusion kinetic model expressed as [61]:

$$q_t = K_{di} \sqrt{t} + C_i \quad (9)$$

where K_{dif} is the intra particle rate constant ($\text{mg g}^{-1} \text{min}^{0.5}$). A plot of q_t against the square root of time should be linear and the line passing through the origin if intra particle diffusion is the rate controlling step. The plot showed a poor fit ($R^2 = 0.78$) and a multi-linear profile that do not pass through the origin (Fig. 5). The profile shows a multi-step process, where the initial section may be considered as an area of fast uptake as a result of the boundary layer diffusion on the surface of the pellet and the middle section is the stage limited by intra particle diffusion [66].

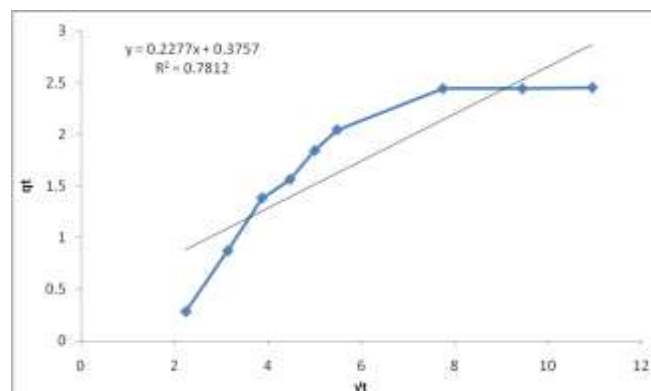


Figure 5: Intra particle kinetic model plot for phosphate.

The last stage is shows a decreasing adsorption due to low residual phosphate concentration in the solution [61,66].

F. Adsorption Isotherms

Adsorption isotherms help to model design parameters and to understand the distribution of adsorbate between the aqueous and solid phase [61]. The equilibrium data was analyzed using Langmuir, Freundlich, Tempkin, and Dubinin- Radushkevich isotherm models. The Langmuir, Freundlich, Tempkin, and Dubinin- Radushkevich (D-R) isotherm models are represented by Equations (10) to (13) respectively []:

$$q_e = Q_m K_L C_e / (1 + K_L C_e) \quad (10)$$

$$Q_e = K_f C_e^{1/n} \quad (11)$$

$$q_e = B \ln A_T + B \ln C_e \quad (12)$$

$$\ln q_e = \ln q_s - \beta \varepsilon^2 \quad (13)$$

$$\text{where } \varepsilon = RT \ln (1 + 1/C_e) \quad (14)$$

where Q_m is the maximum monolayer adsorption capacity (mg/g), K_L is Langmuir adsorption constant (L/mg), n is adsorption intensity, K_f is the Freundlich isotherm constant, A_T is Tempkin isotherm equilibrium binding constant (L/g), B is constant related to heat of sorption (J/mol) and R is universal gas constant (8.314 J/mol/K). Table 2 represents adsorption isotherms coefficients for single solute adsorption isotherms and their correlation coefficients after analyzing linear plots of Equations (9) to (12). The data obtained showed a better fit for the D-R isotherm model, the E value was 2.87 kJ/mol indicating the adsorption was a physical process as E value < 8 kJ/mol is classified as physical adsorption. Q_m value of 144.93 mg/g implies a significant potential for phosphate removal from wastewater at an industrial scale using fired clay pellets and is similar to result obtained in previous study [42].

Table 1. Kinetic models adsorption parameters for calcined clay pellets

Kinetic Model	Parameter	
Pseudo first order	K_1 (/min)	0.03
	R^2	0.9932
Pseudo second order	K_2 (g/mg/min)	0.02
	h (mg/g/min)	8.8
	R^2	0.6506
Elovich	a (mg/g/min)	0.32
	b (g/mg)	1.10
	R^2	0.9872
Bangham's	K_0 (ml/g/l)	0.41
	α	0.11
	R^2	0.9755

Table 2. Adsorption Isotherm constants for adsorption of phosphate onto fired clay pellets

Adsorption Isotherm Model	Parameter	
Langmuir	Q_m	144.93
	K_L	0.09
	R_L	0.02
	R^2	0.9096
Freundlich	K_f	6.50
	$1/n$	0.26
	n	3.84
	R^2	.5688
Tempkin	A_T	1.08
	b	68.50
	B	35.58
	R^2	0.7989
D-R	K_{ad}	0.06
	E	2.87
	R^2	0.9537

G. Effect of Temperature

The effect of temperature on the adsorption of phosphate was investigated at temperatures of 20°C, 25 °C, 30 °C and 35 °C, while other conditions were kept constant. Phosphate adsorption was found to decrease with an increase in temperature. Thermodynamic parameters such as changes in Gibbs free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) are used to determine the spontaneous nature of the adsorption process and evaluate the applicability of the adsorbent [68]. The parameters were determined using Equations (15) to (17):

$$\Delta G^\circ = -RT \ln K_d \quad (15)$$

$$\Delta G^\circ = (\Delta H^\circ) - T(\Delta S^\circ) \quad (16)$$

$$- RT \ln K_d = (\Delta H^\circ) - T(\Delta S^\circ) \quad (17)$$

Where R is the universal gas constant, T is temperature in Kelvin (K) and $K_d = (q_e - C_e)$ is the quantity of adsorbate adsorbed onto the adsorbent (1/g). The plot of $\ln K_d$ against $1/T$ yielded a straight line graph with ΔH° and ΔS° determined from the slope and intercept respectively. The thermodynamic parameters obtained from the graph are shown in Table 3. The Gibbs free energy obtained was -16.5 kJ/mol, the negative value indicates the spontaneous nature of the sorption process and the process was thermodynamically favourable. The value of ΔG° suggests a physisorption process as values of ΔG° between -20 kJ/mol and 0 kJ/mol are classified as physisorption. The negative value of of the enthalpy (-8.87 kJ/mol) confirms the exothermic nature of the process and the positive entropy

Table 3. Thermodynamic parameters for phosphate

Parameter	Phosphate
Gibbs free Energy (kJ/mol)	-16.5
Enthalpy (kJ/mol)	-8.87
Entropy (kJ/mol)	0.026

value (0.026 kJ/mol) indicates an increased randomness at the solid-solution interface and a good affinity of phosphate ions towards the clay pellets [68]

H. Conclusion

The adsorptive properties of fired clay for the removal of phosphate in wastewater treatment were investigated. The removal of phosphate was favoured at acidic pH with optimum removal at pH 3- 4. The adsorption of phosphate showed a good fit with pseudo first order kinetic model, which indicated the physical nature of the sorption process, and Dubinin-Radushkevich Isotherm model. The Gibbs free energy was -16.5 kJ/mol, indicating the adsorption process was spontaneous. The enthalpy value for phosphate (-8.87 kJ/mol) confirmed the exothermic nature of the process. The thermodynamic and isotherm data obtained all supported the mechanism of adsorption of phosphate to be physisorption supported by some diffusion.

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