Exploring Phosphate Sorption on Thermally Modified Kaolinite

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Abstract

The aim of this study is to investigate the capability and mechanism of phosphorus adsorption present in water through thermally treated kaolin. For this purpose, batch experiments are conducted to treat synthetic water samples with phosphate content using kaolin sourced from the northern region of Albania. The kinetics and mechanism of adsorption are examined. Experimental results indicated that a contact time of 3 hours achieves adsorption equilibrium, with the pseudo second-order model providing the best fit. Both Langmuir and Freundlich models describe the adsorption process, suggesting a combination of monolayer and multilayer adsorption. Furthermore, kaolin pre-treatment temperatures up to 500°C have minimal effect on adsorption capacity, apparently attributed to dehydration of bound water and densification of the clay structure.

Keywords: *Phosphate, adsorption, kaolin, kinetic models, adsorption isotherm.*

INTRODUCTION

Phosphorus is an important nutrient for ecosystems, playing a crucial role in biological processes. However, excessive phosphorus in aquatic environments poses significant ecological threats, leading to eutrophication, harmful algal blooms, and water quality degradation [1]. The primary sources of phosphate pollution include agricultural runoff, industrial discharges, and domestic wastewater effluents [2, 3]. Dealing with the phosphate contamination requires effective treatment methods to eliminate its negative impacts on the environment.

Several techniques have been investigated for the removal of phosphate from aqueous solutions using numerous treatment methods, including precipitation, biological procedures, and adsorption [4]. Adsorption is considered one of the best options because it is a simple, cost-effective, and flexible process [5]. Different adsorbent materials have been tested, including activated carbon, zeolites, and clay minerals [6].

Kaolin is one of the main clays tested in this field due to its natural abundance, low cost and removal characteristics, attributed to its structure and surface chemistry. In fact, it is widely studied for adsorption purposes of heavy metals, organic matter etc. [7-9]. It is a member of phyllosilicates group which contains water molecules between its silicon-oxygen tetrahedra (SiO_4) and aluminium-oxygen octahedra (AlO_6) layers with general formula $Al_2Si_2O_5(OH)_4$ ($Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$) [9]. The surface area, charge, porosity, chemical composition, as well as pH, are among factors that affect its adsorption capacity [10]. Having a porous nature with layers on it gives kaolin adsorptive sites while the negative surface charges (attributed also to the environment pH) attract positively charged ions and molecules through electrostatic interaction. Its chemical composition, including impurities and surface functional groups, also contributes to its adsorption ability [11, 12].

However, compared to other types of clays, kaolin ranks behind in terms of adsorptive efficiency [10, 13]. This occurs due to its layered structure. The hydrogen bonds between the layers are so strong that, under natural conditions, they do not allow the formation of

interlayer spaces, which in other clays are responsible for adsorption. To enhance its adsorptive nature, Kaolin undergoes mechanical, thermal, or chemical activation [14]. Mechanical treatment involves its abrasion, mechanical fracturing of the structure under the action of mechanical forces. As a result, adsorptive sites are exposed on the surface. Thermal treatment involves treatment at high temperatures. As a result, Kaolin undergoes structural changes that occur in several phases. In the first phase, usually up to 100°C, free water is removed. In the second phase, up to 600°C, dehydration occurs (bound water removal). In the third phase, at temperatures of 600-800°C, dihydroxylation enables the formation of metakaolin. While in the fourth phase, above 850°C, interlayer sintering of metakaolinite and the recrystallization of amorphous components [15].

In the efforts to clarify the dynamics of the adsorption process and to understand the detailed mechanism and kinetics (the rate-controlling step of the adsorption process), numerous mathematical models have been developed, such as pseudo first order model, pseudo second order model, Elovich, Intraparticle diffusion model, Bangham model, etc. [16]. Each of them takes into account specific aspects of the process. For example, the pseudo first order model explains processes that occur in systems with high concentrations of adsorbate. It suggests that the process is characterized by a rate that is proportional to the number of unoccupied sites on the adsorbent surface and thus depending on both the solution concentration and the number of available adsorption sites [17, 18]. The pseudo second-order model explains systems with low initial concentrations of adsorbate and the adsorbent material is abundant with active sites [19]. It assumes that the rate-limiting step is chemical sorption or chemisorption, and it offers predictions across the entire adsorption range. Under these circumstances, the adsorption rate relies on the adsorption capacity rather than the concentration of the adsorbate [16]. The Elovich kinetic model assumes that the adsorber surface is energetically heterogeneous [16]. The intraparticle diffusion model assume that the limiting step of the adsorption process is the diffusion of adsorbate within the adsorbent [19]. There are several intraparticle diffusion models, but the simplest one is Weber and Morris model. The Bangham model is developed to evaluate the dominance of pore diffusion in the adsorption process [18]. It describes the adsorption of solutes onto microporous adsorbents.

In order to assess the adsorbent characteristics of materials, as well as to determine the parameters of the adsorption process necessary to predict its behaviour under certain conditions, a series of adsorption isotherms such as Langmuir, Freundlich, etc., have been developed. In principle, they are functions of the amount of adsorbed substance relative to their concentration in the solution under equilibrium conditions. Each of them assumes specific scenarios of adsorption, so the Langmuir model assumes monolayer adsorption whereas the Freundlich model to multilayer adsorption, with non-uniform distribution of adsorption sites over the heterogeneous surface [20, 21].

Published literature suggests that the kinetics and isotherms governing the adsorption of phosphates depend on the form of the phosphates, the type of adsorbent, and the conditions under which the adsorption occurs. Even though the pseudo second order kinetic model is the most used to describe the phosphate adsorption [4, 22-27] have also proven useful in predicting the process. Moreover, in some occasions multiple models have been used [28]. The same situation applies to the models explaining the mechanism of adsorption. Literature reports that both, the Freundlich [22, 25, 29] and Langmuir isotherms [4, 28, 30], have been proven to be suitable.

Given that the kaolin adsorptive capacities significantly depend on its geological origin, experimentally studies are necessary, both to examine their native sorption characteristics and to discover treatment methods to enhance these characteristics. Therefore, this study

aims to investigate the Albanian kaolin regarding its ability to adsorb aquatic phosphates and to assess the influence of the treatment temperature on this ability.

MATERIALS AND METHODS

Clay sampling, treatment and characterisation: The clay selected for this investigation originates from the kaoline deposits located in the Puka region of Albania, procured from the construction sector. Its chemical composition is determined by XRD using Bruker S8 TIGER series 2 apparatus.

After mechanical abrasion and fractionation into particle size smaller than 100μm, the kaolin was thermally treated at temperatures 100°C, 400°C, and 500°C for 4 hours. From this on, they are labelled as Kaoline100, Kaoline400 and Kaoline500.

Investigation of phosphate adsorption capacity of clay: Batch experiments are carried out according to a standardized protocol. In a sequence of chemical flasks, 50ml of phosphate solutions (synthetic wastewater) with specific concentrations are treated with 1g of clay under mechanical stirring. After a specified contact duration, the samples are filtered, and their phosphate content was subsequently analysed.

Determination of phosphate concentration in aqueous solutions: Molybdate blue-spectrophotometric method (APHA method) is used. It involves treatment of 20ml sample with 1mL of a combined reactive solution. This solution consists of 45mL of ammonium molybdate solution added to 200mL of sulphuric acid, along with 5mL of potassium antimonial tartrate solution. Subsequently, 0.5ml of ascorbic acid is added, and the absorbance is measured at a wavelength of 880nm using a UV1200 spectrophotometer following filtration.

Data analysis: Analysis of data for the evaluation of adsorption kinetic models involves the consideration of four models: pseudo first-order model (equation 1 and 2), pseudo second-order model (equation 2 and 3), Elovich (equation 4), intraparticle diffusion model (equation 5), and Bangham model (equation 6). Nonlinear regression is employed for all of them and assessments are conducted based on the regression coefficient (R^2).

$$\text{Pseudo-first order model: } q_t = q_e(1 - e^{K_1 t}) \tag{1}$$

Where: q_t and q_e are the amount of phosphate adsorbed at time t and equilibrium time (expressed as mg P/g clay); t is the time of adsorption (hour); K_1 is the pseudo first-order model constant (min^{-1}).

Evaluation of q_t and q_e is done according to equations:

$$q_t = \frac{(C_0 - C)V}{M}; q_e = \frac{(C_0 - C_e)V}{M} \tag{2}$$

$$\text{Pseudo second order model [19]: } q_t = \frac{q_e^2 * K_2 * t}{1 + K_2 * q_t * t} \tag{3}$$

Where K_2 is the pseudo second-order model constant (min^{-1}).

$$\text{Elovich model: } q_t = \frac{1}{\alpha}\ln(\alpha\beta) + \frac{1}{\alpha}ln(t) \tag{4}$$

Where α and β are the Elovich constants.

$$\text{Intraparticle diffusion model: } q_t = K_{W\&M}t^{1/2} + C \tag{5}$$

Where $K_{W\&M}$ is the Weber and Morris constant.

$$\text{Bangham model: } loglog\left(\frac{C_0}{C_0 - mq_t}\right) = \log\left(\frac{k_0 K_B}{2.303V}\right) + \alpha logt \tag{6}$$

Where C_0 is the initial concentration of phosphate in solution (mg/L); V is the volume of solution (mL); q_t is the amount of phosphate adsorbed (mg P/g clay) at time t; m is the weight of the adsorbent used (g/L); and k_0 & α [mL/(g/L)] are constants [4].

The adsorption mechanism is studied based on the Freundlich and Langmuir models. Linear regression has been considered for both of them, see equation 7 and 8.

$$\text{Linear Langmuir isotherm: } \frac{C_e}{\frac{X}{M}} = \frac{1}{ab} + \frac{1}{a}C_e \tag{7}$$

$$\text{Linear Freundlich isotherm: } ln\frac{X}{M} = lnK_F + \frac{1}{n}lnC_e \tag{8}$$

Where: X/M is the phosphate adsorbed per unit mass of clay (mg P/g clay); C_e is the concentration of phosphate in solution at adsorption equilibrium time (mg P/L); a and b are the Langmuir constants; K_f and n are the Freundlich constants.

EXPERIMENTAL RESULTS

Chemical composition of Kaolin

The chemical composition of the studied kaolin is presented in Table 1. It is noted that, in addition to its main constituents, SiO_2 and Al_2O_3, it also contains a significant amount of Fe oxides (3.09%). This Fe either may be present in free form or incorporated into the structure and is expected to enhance the Kaolin adsorptive capacity as it makes a strong contribution to the surface area [11].

Table 1. The chemical composition of the natural kaolin of the Puka region of Albania.

ID	Concentration, mg/l	ID	Concentration, mg/l
L.O.I	18.08	K_2O	0.11
SiO_2	44.16	Na_2O	0.47
Al_2O_3	24.09	TiO_2	0.1
Fe_2O_3	3.09	P_2O_5	0.01
CaO	3.95	MnO	0.057
MgO	4.8	Cr_2O_3	0.043
SO_3	0.01		

Adsorption kinetics study

To evaluate the adsorption rate and mechanism of aqueous phosphate in kaoline, a series of 50ml of synthetic phosphate samples, with initial concentration of 15mgP/L are treated with 1g of Kaoline100 for contact times ranging from 0.17 to 6 hours. Five kinetic models have been taken in consideration: pseudo first order model, pseudo second order model, Elovich, intraparticle diffusion model and Bangham model. The experimental and modelled results are presented in figure 1.

It is observed that the contact time needed to reach adsorption equilibrium and, thus, for the adsorbate to exhibit maximum adsorption ability is 3 hours. Consequently, this is the contact time used for all subsequent experiments.

Based on the R^2 values obtained from the mathematical modelling, it appears that the pseudo second-order model has the best fit to the experimental data, followed closely by the Elovich model and the Bangham model. These results suggest that the adsorption process may involve both chemisorption and diffusion-controlled mechanisms, and the pseudo second-order model might provide the most comprehensive description of the kinetics of adsorption in this system.
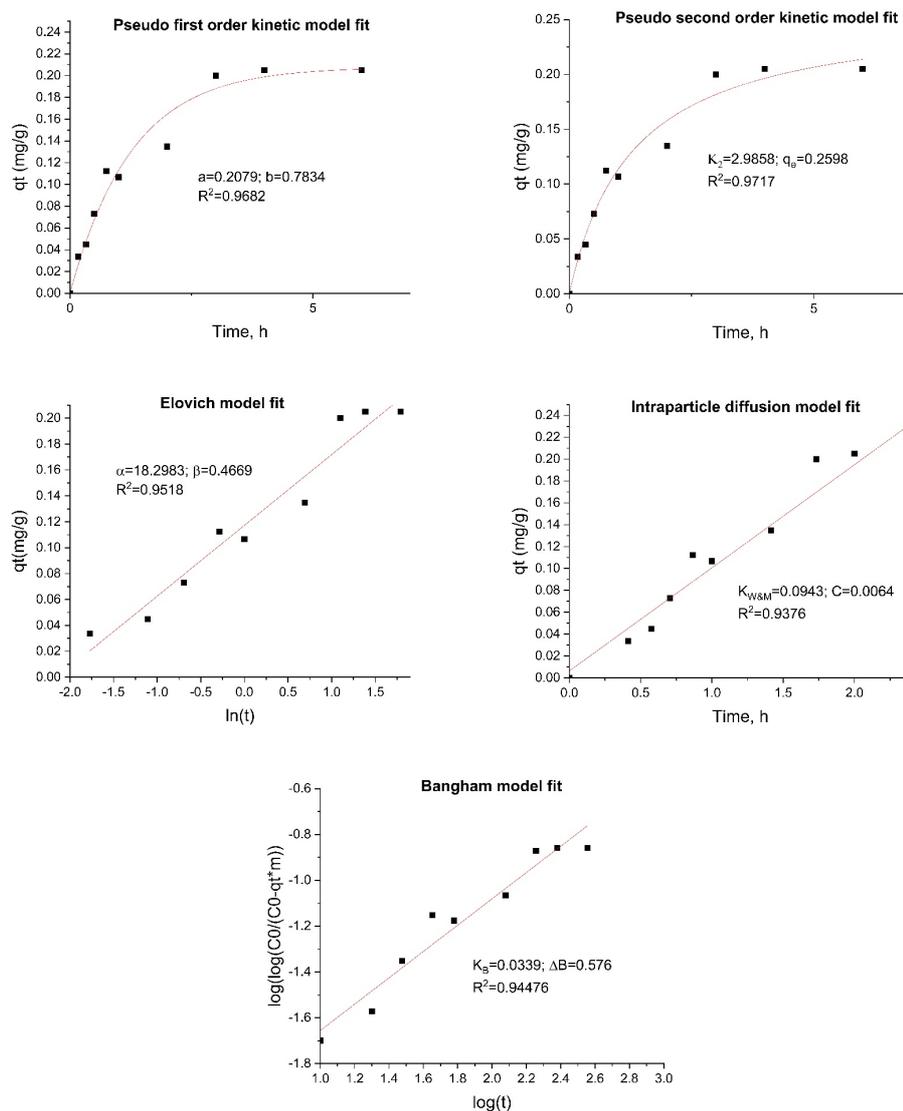
Figure 1. The kinetic models for the adsorption of phosphate in Natural Kaolin and thermally treated Kaolin in temperature 100°C.

Adsorption model investigation

Firstly, the influence of the initial concentration of the aqueous phosphate solution on the kaoline adsorption capacity is studied. The initial concentration range considered is 15-50mgP/L. The experimental results for all the clay samples (Natural Kaoline, Kaoline100, Kaoline400 and Kaoline500) are presented in figure 2. The amount adsorbed is expressed in mg P/L and %.

It is observed that, for all cases, with the increase in the initial concentration of the solution, the amount of adsorbed phosphates, in mg P/L, increases. The opposite occurs with the removal efficiency, expressed in %, which decreases with the increase in the initial concentration, thus indicating an increase in competition among ions to occupy adsorption sites on the surface of the adsorbent.
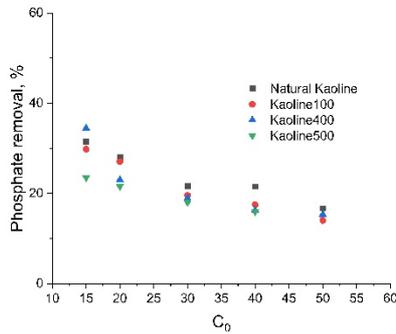
Figure 2. Experimental results of phosphate adsorption efficiency of natural and thermally treated Kaolin vs initial concentration.
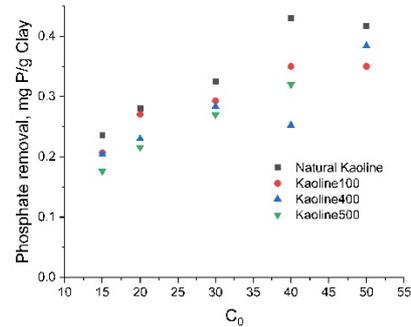
Figure 3. Experimental results of phosphate adsorption capacity of natural and thermally treated Kaolin, in mg P/g clay vs initial solution concentration, in mg/L.

Furthermore, the type of adsorption isotherm that best describes the process is studied by plotting the dependence of phosphate amount adsorbed vs the equilibrium concentration. The isotherms considered are Freundlich and Langmuir. The results are presented in figure 4 and 5, while the values of the isotherms constants, together with the R^2, in table 2.
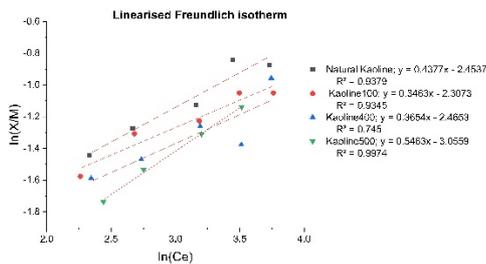
Figure 4. Linearized Freundlich isotherm for the adsorption of phosphate on natural and thermally treated kaoline clay.
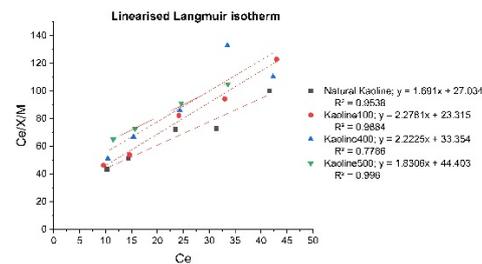
Figure 5. Linearized Langmuir isotherm for the adsorption of phosphate on natural and thermally treated kaoline clay.

It is noticed that, for all clay samples, both isotherms manage to describe the process, with a slight preference for the Langmuir isotherm. In both cases, the R^2 values are higher than 0.9 (except for Kaoline400 which has R^2 values of 0.7). These results suggest a combination of monolayer and multilayer adsorption process, in which, initially, adsorption might follow Langmuir behaviour until the surface is fully covered with a monolayer, after which additional adsorbate molecules start forming multilayer structures following Freundlich behaviour [20].

Influence of Kaolin Pre-treatment Temperature on the Adsorption Capacity

As for the influence of treatment temperature on the adsorption capacity of Kaolin, it is noted that treating the clay at temperatures ranging from 100 to 500°C does not significantly affect the adsorption capacities of kaolin. A very slight decline is observed between the natural kaolin and the thermally treated ones manifested in the reduction of the Langmuir constant, a, values. Based on the literature, kaolin treated at these temperatures undergoes the process

of dehydration of bounded water causing the interlayer spacing collapse, without undergoing significant structural changes or alteration in the bonding of SiO_2 and Al_2O_3, and thus deteriorating the adsorptive capacity [15]. In order to activate our clay, thermally treatment should be made for temperatures above 500ºC, where dehydroxylation and metakaolinite formation occurs [14, 15, 31].

Table 2. The Freundlich and Langmuir isotherm constants.

Clay sample	Freundlich isotherm			Langmuir isotherm		
	K_f	n	R^2	a	b	R^2
Natural Kaolin	0.0860	2.2847	0.938	0.5914	0.0626	0.954
Kaoline100	0.0995	2.8877	0.935	0.4390	0.0977	0.988
Kaoline400	0.0850	2.7367	0.745	0.4499	0.0666	0.779
Kaoline500	0.0471	1.8305	0.997	0.5463	0.0412	0.996

CONCLUSIONS

In conclusion, our experimental findings provide insight to the adsorption kinetics and mechanisms of aqueous phosphate on the kaolin of Puka region, Albania. We observed that a contact time of 3 hours was optimal for achieving adsorption equilibrium, with the pseudo second-order model providing the best fit to the data, suggesting a combination of chemisorption and diffusion-controlled mechanisms. Additionally, we investigated the influence of initial phosphate concentration, finding that higher concentrations led to increased adsorption but decreased removal efficiency due to intensified competition for adsorption sites. Isotherm analysis revealed that both Langmuir and Freundlich models sufficiently described the adsorption process, indicating a combination of monolayer and multilayer adsorption. Furthermore, our study explored the impact of kaolin pre-treatment temperature on adsorption capacity, noting a slight decline in adsorption efficiency with thermal treatment up to 500ºC, likely due to dehydration of bounded water and densification of the clay structure. However, treatment temperatures exceeding 600ºC are recommended for dehydroxylation and metakaolinite formation, which are likely to enhance adsorption abilities. These findings contribute to our understanding of kaolin's adsorption behaviour and offer insights for optimizing its applications in various industries.

CONFLICT OF INTERESTS

The authors would like to confirm that there is no conflict of interests associated with this publication and there is no financial fund for this work that can affect the research outcomes.

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