

Adsorption characteristic of phosphate ion on functional magnetic natural kaolin

T.G. ABAYOMI¹, A. A. ADEYI², J.M. JABAR³, A.G OLAREMU⁴, O.E, OYENEYIN⁵

^{1,4,5}Department of Chemical Sciences, Adegunle Ajasin University Akungba Akoko, Ondo State, Nigeria

²Chemistry Department, University of Ibadan, Oyo State, Nigeria

³Department of Chemistry, Federal University of Technology, Akure, Ondo State, Nigeria

*Corresponding author E-mail address: toluwalope.abayomi.aaua.edu.ng, toluwalopeabayomi1201@gmail.com

Abstract

Keywords:

Magnetic-kaolin,
co-precipitation, phosphate,
Langmuir...

Magnetic-supported kaolin composite was synthesized by co-precipitation method to augment the available pool of adsorbents (natural or synthetic) to remove phosphate from water bodies. The magnetic-kaolin composite (MKC) was characterized by XRD, FESEM-EDS and BET analyses. Characterization results showed the successful preparation of MKC with good magnetic property. The effect of adsorbent dosage process variable was investigated and was used for batch experiment study of phosphate adsorption by MKC. The adsorption experiment of phosphate onto MKC showed that the adsorption process followed the Langmuir isotherm model and the maximum capacity $q_e = 52.91$ mg/g. The dimensionless separation factor (R_L) indicated that the adsorbent had affinity for the phosphate ion. This result is comparable with what has been reported for some magnetic material used as adsorbents in batch phosphate adsorption processes.

Accepted: 27 June 2019

© Science Research Annals. All rights reserved.

INTRODUCTION

One big challenge that faces our age is inadequate water supply especially, for consumption. Industrialization has contributed in a large way to this problem. In recent times, water meant for human consumption has been competitively used in many industrial processes leaving humans with much water inadequacy. In addition, a large part of raw materials input in production has ended up as waste and often times as effluents by which toxic materials are released into the environment (Anastas and Kirchhoff, 2002). Other humans' activities as agricultural practice have contributed to wastewater which impaired severely on human health and living conditions within the ecosystem. Waste discharge from agricultural practices do present phosphorus (P) as part of their major constituent which to a large extent affect available water from different sources; surface and ground waters. Phosphorus in water bodies increases the

task of available clean, drinking water for rapid growing population. Phosphate from agricultural runoffs, erosion of phosphate rich materials, and, through mine waste water creates significant problem in aqueous environments. This acts as a fertilizer for the rapid growth of algae and microorganism, thus results in the depletion of dissolved oxygen content which deteriorates water quality (Conley *et al.*, 2009).

This significant challenge caused by phosphate has therefore opened up an avenue of research aimed at removing it from the environment. Removing phosphate from water bodies has become a critical environmental issue worldwide (Liu *et al.*, 2014). Considerable attention has therefore been paid to water treatment in recent years especially, phosphate-ridden water (Verma *et al.*, 2012; Mezohgyi *et al.*, 2012). However, due to its high chemical, biological instability and cost by operational personnel, most conventional water treatment techniques, except for adsorption

treatment have low phosphate removal efficiency. As low-cost and convenient method, adsorption is a promising method for the removal of pollutants from wastewater, and it is widely used in water treatment (Oliveira *et al.*, 2016; Shang *et al.*, 2012; Wan *et al.*, 2011).

Adsorption capacities of many adsorbents depend on a number of factors where surface area is highly favored (Wang *et al.*, 2015). The availability of high surface area with many ion exchange sites have been found to enhance the adsorption capacity of many adsorbents (Asuha *et al.*, 2015). In addition, the ease of separation of contaminants-laden adsorbents from treated water is another factor recently considered in water treatment system (Okupnik *et al.*, 2015). Based on this considerations, the synthesis of magnetic-kaolin composite (MKC) with high surface area would undoubtedly be a welcome development in water remediation process.

In this study, we reported, (i) synthesis of magnetic-kaolin composite by chemical co-precipitation technique (ii) investigate the characteristics of MKC with various instrumental analysis (iii) evaluate the adsorption capacity of phosphate onto MKC.

MATERIALS AND METHODS

Chemicals

Chemical reagents used involve potassium dihydrogen phosphate (KH_2PO_4), ferrous-chloride tetra-hydrate ($\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$), ferric-chloride-hexa-hydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$), sodium hydroxide (NaOH), hydrochloric acid (HCl), hydrogen peroxide (H_2O_2), sulfuric acid (H_2SO_4), ascorbic acid ($\text{C}_6\text{H}_7\text{O}_8$), ammonium-molybdate [$(\text{NH}_4)_6\text{MoO}_{24} \cdot 4\text{H}_2\text{O}$] and potassium antimony tetratate [$\text{K}(\text{SbO})\text{C}_4\text{H}_4\text{O}_7 \cdot 1/2\text{H}_2\text{O}$] were purchased from AB & Co India. All reagents used were analytical grade and were used as purchased without further purification.

Sample Collection and Preparation

The kaolin material used in this study was collected from Ado, Ekiti State Southern state of Nigeria. This location has a long history of large deposit of kaolin (Oluseyi *et al.*, 2016). Preliminary procedures such as crushing, washing, sedimentation and drying were employed to remove solid impurities from the clay mineral (Adebowale *et al.*, 2005). Natural kaolin requires some degree of preparations owing to particularly, sources of the material. This preparation in essence would ensure the removal of some solid impurities from the clay mineral. However, it would subsequently improve the clay-mineral adsorption capacity. The collected kaolin sample was firstly sun-dried to remove moisture. Finally, the sample was crushed and sieve to 180-mesh size and again,

oven dried at 105°C overnight to obtain the natural kaolin (NK) used in the present study.

Synthesis of magnetic-kaolin composite adsorbent

The synthesis of magnetic-kaolin composite was carried out in a 3-neck volumetric flask (500mL). Each of the neck of the flask was as designed designated for various reagents and nitrogen-gas (N_2) used in the entire process. The composite was prepared by chemical co-precipitation method (Abayomi, 2018). The method involves the following steps: the salts of ferrous-chloride tetra-hydrate and ferric-chloride hexa-hydrate with molar ratio of $\text{Fe}^{2+}/\text{Fe}^{3+} = 0.5$ were dissolved in doubly-distilled water that has been previously de-oxygenated by bubbling N_2 -gas over it for 30min. The amount of the total iron salt powder was 3g in 200mL de-ionized/oxygenated water. The entire solution vessel was kept under N_2 -protection to prevent instantaneous oxidation and was vigorously stirred for 5 min in a water-bath at 70°C . Then, solution of NaOH (5M) was added drop wise into the entire solution-mixture until a black precipitate was formed at pH 9.0. The mixture was aged for 60 min at 70°C in a water-bath. The black precipitate was isolated by using external magnetic field and the supernatant was decanted. The obtained solid part was quickly washed four times with deionized and later deoxygenated water and later dried at 50°C under oven (air-oven). The prepared magnetic-kaolin composite (MKC) was stored in plastic bottle kept in a vacuum desiccator and for adsorption experiment.

Characterization

X-ray diffraction (XRD) or crystal phase of the sample used was determined by a Bruker D8-Advance X-ray diffractometer. The diffractograms were obtained by using $\text{CuK}\alpha$ radiation ($d=1.5405$ scanning speed of $1 (2\theta) \text{ min}^{-1}$ from 10 to 90°) at 40KV and 30mA. Surface morphology along with its chemical composition were also examined. The surface morphology was obtained by Zeiss LSM 510 meta-Field emission scanning electron microscope coupled with energy-disperse-x-ray analyser (FESEM-EDX). The surface area (S_{BET}) was measured at 80K by the BET method with a Quantachrome Autosorb-1 instrument using N_2 -gas. The cation exchange capacity (CEC) of the MKC and its precursor – natural kaolin-NK was determined using ammonium acetate method (Van Reeuneijk, 1992).

Adsorption Experiment

A stock solution (1000mg/L) of phosphate was prepared using KH_2PO_4 . A working phosphate solution of 30mg/L was prepared from initial-stock phosphate solution. 0.1g of MKC was added to 50 mL of phosphate solution (30mg/L). The mixture

(adsorbent-adsorbate) was shaken on a constant temperature oscillator at 200rpm for 16 h, based on the previous study (Abayomi *et al.*, 2018). The solution (adsorbate) was separated from the solid (adsorbent) by the use of external magnet. The residual concentration of phosphate was determined by molybdate blue spectrophotometric method (Yan *et al.*, 2010). The phosphate adsorption capacity q_e (mg/g) or removal ratio $R(\%)$ were obtained from Eq. 1 and Eq. 2 respectively.

$$q_e = (c_0 - c_e) \frac{v}{m} \tag{1}$$

$$R = \frac{(c_0 - c_e)}{c_0} \times 100\% \tag{2}$$

Where C_0 and C_e are the initial and equilibrium concentration of phosphate in solution (mg/L). m is the adsorbent dry weight (g) and v is the suspension volume (L).

RESULTS AND DISCUSSION

Characterization of MKC

XRD pattern for MKC is shown in Fig. 1. In the XRD pattern, there were characteristic diffractions at angle $2\theta = 18.60, 31.59, 35.32, 43.08$ and 63.39 which correspond to the crystal surface of Fe_3O_4 . Thus, these patterns confirmed the existence of the Fe_3O_4 pure phase (Hu *et al.*, 2015). Other diffractions noticeable in this pattern indicated the existence of kaolinite phases. The kaolinite phase could be altered only by thermal and acid treatment as reported in the works by (Dickson and Wachira, 2015; Ewelina *et al.*, 2013). The field emission-scanning electron microscope (FESEM) micrograph of MKC is shown in Fig. 2. The micrograph alongside EDX pattern showed the results of elemental composition by the material.

The micrograph showed a rough surface with oval ridges and micro pores which confirmed the presence of Fe_3O_4 . The image of natural kaolin (NK) as presented in the study by (Oladoja *et al.*, 2012) showed that natural kaolin has smooth surface with linear ridges. So, the MKC image presented in this study confirmed that iron-oxide (Fe_3O_4) was successfully loaded onto the surface of naturally sourced kaolin. The specific surface area $S_{(BET)}$ and cation exchange capacity (CEC) values of MKC and natural kaolin (NK) were presented in Table 1. After, modification by Fe_3O_4 , both CEC and $S_{(BET)}$ values of MKC increased when compared with the values of natural kaolin. The iron-oxide modification contributed to the increase which eventually enhanced the adsorption capacity of MKC.

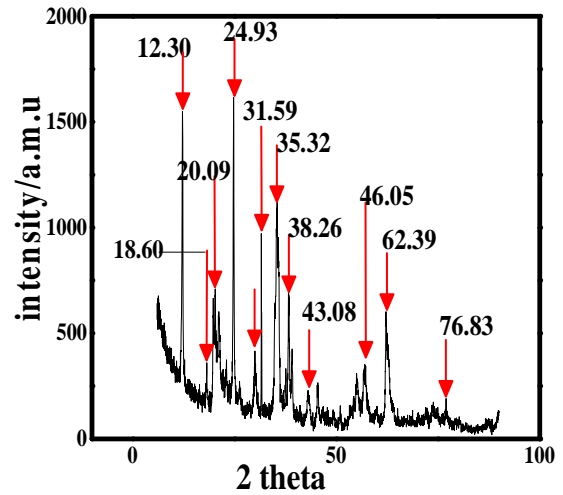


Figure1: XRD-spectra of magnetically-modified synthetic kaolin (MKC)

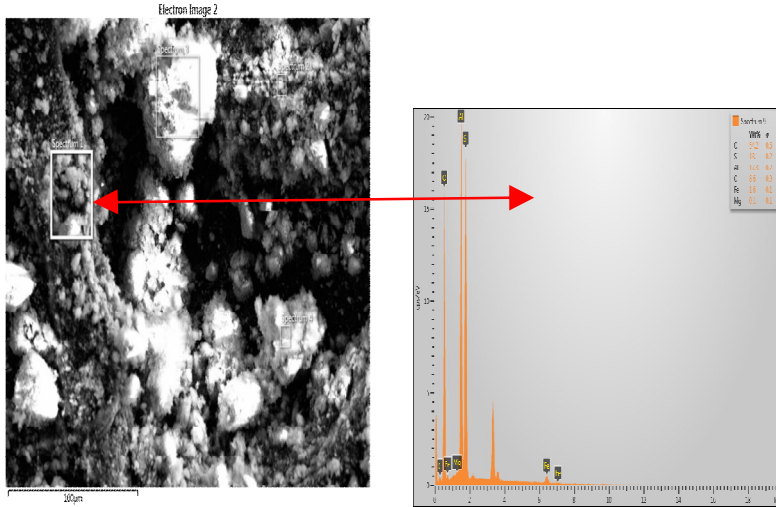


Figure2:FESEM-micrograph of magnetically-modified kaolin coupled with the EDX-spectrum indicating Fe-element presence.

Table 1. Summary result of surface area and CEC of natural and magnetic modified kaolin

Sample	S _(BET) (m ² /g)	CEC (meg/100g)
MKC	68.7	24
NK	33.3	16

Effect of adsorbent dosage

The effect of adsorbent dosage on phosphate adsorption is illustrated in Fig. 3. It was observed that the phosphate adsorption capacity increased steadily with the augment in adsorbent dosage from 0.1 g to 0.5 g. The phosphate removal efficiency increased from 35% to 64% for the material. This result corresponds with the work of previous author (Xu *et al.*, 2009). This trend can be explained by the progressive increase in dosage. The increase however reached a plateau at the adsorbent dosage of 0.4g. Above this level, with further increase of MKC dosage, the removal ratio of phosphate increased steadily and subsequently assumed a reduced trend.

Adsorption isotherm

Phosphate adsorption mechanism on MKC was studied based on the optimum conditions. A series of phosphate solution with different concentrations (2.5 – 30mg/L) were used with fixed mass of MKC at 0.4g and room temperature of 298K. The experimental data were applied to fit both Langmuir and Freundlich isotherm models. The linearized models are represented as follows.

$$\frac{1}{q_e} = \frac{1}{(K_L C_e)} + \frac{1}{q_{max}} \tag{3}$$

$$\text{Log}_{10} = (\text{Log}_{10}) + \frac{1}{n}(\text{Log}_{10}) \tag{4}$$

Where q_{max} (mg.g⁻¹) and K_L (L.mg⁻¹) are the Langmuir monolayer maximum

sorption capacity and Langmuir constant respectively. K_f and $1/n$ represent the Freundlich capacity factor and the Freundlich intensity parameter respectively. These adsorption isotherms (Langmuir, 1916) are the most widely used isotherms for adsorption in solid-liquid system. Table 3 gives the Langmuir and Freundlich isotherm parameters for phosphate adsorption on MKC. The Langmuir model gives more satisfactory fitting to the adsorption isotherm on MKC and the maximum capacity $q_e = 52.91$ mg/g. This adsorption capacity was far greater compared with the adsorption of virgin natural kaolin as reported by the work of (Oladoja *et al.*, 2012). This result may suggest that a monolayer adsorption process occurs on the surface of the MKC, with the adsorption taken place at specific homogenous site within the adsorbent and a uniform distribution of energetic adsorption site. As a consequence, once the adsorbent molecule/ion occupies a site, no more adsorption can take place on this site. The adsorption energy is constant and does not depend on the degree of occupation of an adsorbent active centers and there are no interactions among molecules adsorbed in neighboring sites.

Subsequently, another Langmuir parameter, the dimensionless separation factor R_L , defined by (Hall *et al.*, 1966) was used to predict the affinity between the adsorbate and the adsorbent or, to

check the feasibility of the Langmuir isotherm (Hall *et al.*, 1966). The dimensionless separation factor R_L is presented as follow in (Eq. (3)):

$$R_L = \frac{1}{1 + K_L C_0} \tag{5}$$

The relationship between the separation factor R_L , and the characteristic of adsorption isotherm is given in Table 2. The favorability of the Langmuir isotherm model must be indicated by the values of R_L being less than 1 of the condition of the adsorption process especially; different adsorbent dosage. The result in Table 3 shows that the adsorption of PO_4^{3-} onto magnetic kaolin is favorable.

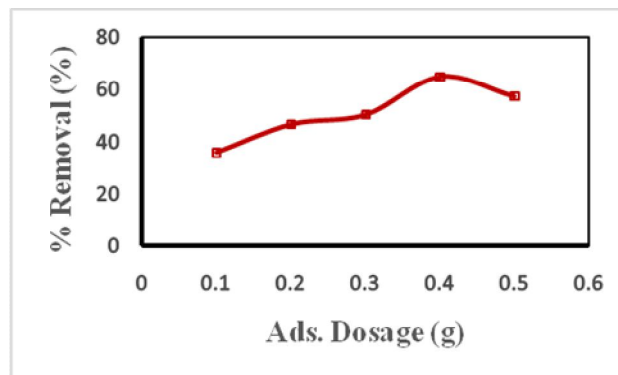


Fig. 3: Effect of Adsorbent dosage on the phosphate ion adsorption by MKC.

Table 2: Characteristic of adsorption Langmuir isotherm

Separation factor R_L	Characteristic of Adsorption Langmuir isotherm
$R_L > 1$	Unfavorable
$R_L = 1$	Linear
$0 < R_L < 1$	Favorable
$R_L = 0$	Irreversible

Table 3: Adsorption isotherm constants for phosphate ion adsorption

Adsorbent	Langmuir model				Freundlich Model		
	$K_L(\text{L}\cdot\text{mg}^{-1})$	R_L	$Q_m(\text{mg}/\text{g})$	R^2	K_f	$1/n$	R^2
MKC	0.11	0.509	52.91	0.9856	1.63	0.9107	0.9519

CONCLUSION

The study has provided some valuable information about the characteristic of the magnetic-kaolin composite and mechanism of phosphate by adsorption by this composite adsorbent. The major conclusions are as follows:

- The adsorbent, magnetic-kaolin composite (MKC) was successfully modified by magnetite (Fe_3O_4)
- The Langmuir isotherm model provides a better fitting to the experimental data than the Freundlich isotherm model.
- The adsorption capacity of MCK was quite significant and more than the adsorption of natural kaolin without modification in previous works.
- Magnetic modification has proven to be an advantage in phosphate adsorption as demonstrated by MKC.

REFERENCES

- Abayomi, T.G. (2018). Isotherm Studies on Removal of Phosphate from Aqueous Solution Using Magnetic Clay. *International Journal of Scientific and Technical Research in Engineering (IJSTRE) Volume 3 Issue 4 May 2018 Available at www.ijstre.com*
- Adebowale, K.O., Unuabonah, E.I. and Olowolabi, B.I. (2005). Adsorption of some heavy metals ions on sulfate- and phosphate-modified kaolin. *Applied clay science* – 29. 145-148.
- Anastas, P.T., Kirchhoff, M.M. 2002. Origin, current status and future challenges of green chemistry. *Acc. Chem. Res.* 35. 686- 694.
- Asuha, S., Gao, Z., Li, X., Wu, H., Zhao, S., Deligeer, W. (2015). Magnetic modification of acid-activated kaolin: synthesis, characterization and adsorptive properties. *Microporous and mesoporous materials.* 202. 1-7.
- Conley, D.J., Paeri, H.W., Howarth, R.W., Boesch, D.F., Seltzinger, S.P., Havens, K.E., Lancelot, C., Liken, G.E. (2009). Controlling eutrophication: nitrogen and phosphorus, *science* 323. 1014-1015.
- De Oliveira, F.M., Segatelli, M.G. and Tarley, C.R.T. (2016). Hybrid molecularly imprinted poly(methacrylic-acid-TRIM)-silica chemically modified with (3-glycidylxypropyl) trimethoxysilane for the extraction of folic acid in aqueous medium. *Materials Science & Engineering C-Materials for Biological Applications*, 59), 643-651.
- Dickson A and Wachira, M. (2015). Reversal of plasticity of acid leached kaolinite clays from mukurwe-Ini. *African Journal of Pure and Applied Chemistry. Vol. 9 (4), pp. 71-80.*
- Ewelina, K. W, Jan, M, Pawel, M (2013). Sintering behavior of kaolin with calcite. *Procedia Engineering* 57, 572-582.
- Hall, K.R., Eagleton, L.C., Aerivos, A. and Vermeulen, T. (1966). Pore and solid-diffusion kinetics in fixed-bed adsorption under constant-pattern condition. *I & EC Foundam.* 5, 212-223.
- Hu, P., Zhang, Y.H., Tong, K., Wei, F.F., An, Q., Wang, X.K., Chu, P.K. and Lv, F.Z. (2015), Removal of organic pollutants from red water by magnetic-activated coke. *Desalination and Water Treatment*, 54 (10), 2710-2722.
- Langmuir, I. (1916). The constitution and fundamental properties of solids and liquids. *J. Am. Chem. Soc.* 38, 2221-2295.
- Liu, H., Chen, W., Liu, C., Liu, V., Dong, C. (2014). Magnetic mesoporous clay adsorbent: preparation, characterization and adsorption capacity for atrazine. *Microporous and mesoporous materials* 194. 72-78. Doi: 10.1010/j.micromeso.2014.03.038 [1387-1811/@2014elsevier.inc.](https://doi.org/10.1010/j.micromeso.2014.03.038)
- Mezohegyi, G., van der Zee, F.P. Font, J., Fortuny, A. Fabregat, A. (2012). Towards advanced aqueous dye removal processes: A short

- review on the versatile role of activated carbon. *J. Environ. Manage.* 102. 148-164.
- Okupnik, A., Contardo-Jara, V. and Pflugmacher, S. (2015), Potential role of engineered nanoparticles as contaminant carriers in aquatic ecosystems: Estimating sorption processes of the cyanobacterial toxin microcystin-LR by TiO₂ nanoparticles. *Colloids and Surfaces A-Physicochemical and Engineering Aspects*, 481), 460-467.
- Oladoja, N.A., Aboluwoye, C.O., Ololade, I.A., Adebayo, O.L., Olaseni, S.E., Adelagun, R.O.A. (2012). Interrelation of gastropod shell derived calcium oxide in clay and application in phosphate removal from actual medium. doi.org/10.1021/ie301520v/*ind. Eng. Chem. Res.*
- Oluseyi, A.K., Olarenwaju, A., Pal, M., Das, K.S. (2016). Evaluation of Nigeria source of kaolin as a raw material of mullite synthesis. *Oriental Journal of Chemistry*. Vol. 32. No (3). 1571-1582.
- Shang, Y., Zhang, D., Guo, L. 2012. CuCl-intermediated construction of short-range-ordered Cu₂O mesoporous spheres with excellent adsorption performance *J. Matter. Chem.* 22. 856-861.
- Van R, L.P. (1992). Procedures for soil analysis, international soil reference and information Centre, Wageningen. pp 91.
- Verma, A.K., Dash, R.R., Bhunia, P. (2012).A review on chemical coagulation/flocculation technologies for removal of color from textile wastewaters. *J. Environ. Manage.* 93. 154-168.
- Wan-Nghah, W.S., Teonga, L.C., Hanafiah M.A.K.M. (2011). Adsorption of dyes and heavy metal ions by chitosan composites: A review. *Carbonhyd. Polym.* 83. 1446-1456.
- Wang, Y., Liu, D.F., Lu, J.B. and Huang, J. (2015). Enhanced adsorption of hexavalent chromium from aqueous solutions on facily synthesized mesoporous iron-zirconium bimetal oxide. *Colloids and Surfaces A-Physicochemical and Engineering Aspects*, 481), 133-142.
- Xu, X., Gao, B., Wang, W., Yue, Q., and Wang, Y and Ni, S. (2009). Adsorption of phosphate from aqueous solution unto modified wheat residue: characteristics, kinetic and column studies. *Colloid and Surfaces B. Biointerfaces.* 70(1). 46-52.
- Yan, L.G., Xu, Y.Y., Yu, H.Q., Xiu, X.D., Wei, Q., Du, B. (2010). Adsorption of phosphate from aqueous solution by hydroxy-aluminum, hydroxy-iron and hydroxy-iron-aluminum pillared bentonites. *J. Harzard Matter.* 179. 244-250.