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Isotherm Studies on Removal of Phosphate from Aqueous Solution Using Magnetic Clay

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Abstract: *Magnetic-kaolinite composite (mkc) was prepared by loading* Fe_3O_4 *onto the clay surface through co-precipitation method. The adsorbent was characterized using Fourier transform infrared spectroscopy (FTIR) and Scanning electron microscopy (SEM) methods of chemical analyses. The mkc prepared was used as adsorbent for removal of phosphate from aqueous solution by batch equilibrium experiments. Four isotherm models were fitted to evaluate the adsorption efficiency and adsorption mechanism of mkc prepared. The results revealed that, quantity of phosphate removed from aqueous solution increases as initial concentration of the aqueous solution increases. The adsorption isotherm was best fitted with Langmuir model (60.610 mg/g) indicating monolayer adsorption pattern and confirming electrostatic attraction of adsorbing molecules unto the adsorbent.*

Keywords: Adsorption, Efficiency, Isotherm, Langmuir, Phosphate

I. Introduction

Despite the nutritional advantage of phosphate alongside other nutritional elements (e.g. nitrogen), popularly referred to as nutritional elements, its menace, if, discharged into the environment in excess has become quite worrisome. Hence, the management of this contaminant and valuable resource is very important [China Bureau of Environmental Protection, 1997]. Phosphate discharge into the surface water stimulates the growth of aquatic micro and macro organisms in nuisance quantities [Xu, *et.al.*, 2011, Liao, et.al., 2006; Zhang, *et.al.*, 2011]. Reduction of phosphate concentration in discharged wastewater and surface water to an appropriate and admissible low level is an important subject in aquatic environmental study [Akbar, *et.al.*, 2006]. Phosphate even at a very low concentration, can cause undesirable effects such as eutrophication [De-Bashan and Bashan, 2004; Noureddine and Ezzsddine, 2012], aesthetic and navigational problems in water [Oladoja, *et.al.*, 2017], severe fouling problem [Raphael, 2011] among others.

In the web of this formidable challenge of phosphate in the environment, several effort have been made to maintain a permissible level of phosphate in various wastewater and surface water. A number of techniques such as chemical coagulation, precipitation [Meenakshi and Maheshwar, 2006], reverse osmosis, ion exchange [Viswanathan and Meenakshi, 2009], electrodialysis, electrolysis, electro-coagulation [Ghos, *et.al.*, 2008], membrane separation [Shen, 2008] and adsorption [Goswani and Purkait, 2011; Goswani and Purkait, 2012] have been used. Among these, reverse osmosis, ion exchange, electrolysis and electrodialysis are quite expensive techniques, which largely prevent their uses [Seida and Nakano, 2002; Karachalios, 2012]. Chemical precipitation and conventional coagulation techniques leave behind secondary pollutants which result in post-treatment(s) that increase the overall cost of water treatment [Ho and Mckay, 1999]. Compared to other methods, adsorption is relatively useful and cost effective for phosphate removal due to its simplicity and flexibility of design, cost effectiveness, greater selectivity, faster regeneration kinetics, ease of operation [Mustafa, *et.al.*, 2006; Wan, *et.al.*, 2011] and, most importantly, it ability to adapt to unlimited number of adsorbents.

A number of adsorbents have been developed, and many of such employed in the removal of phosphate: these adsorbents are not most preferable due to unsatisfactory and low phosphate adsorption, very poor separation and regenerative capacity. However, it is necessary to find a way for separating and recycling adsorbents used in adsorption process effectively (Ning, *et.al.*, 2008). Recent environmental remediation studies have considered composite materials, most importantly; magnetic composite (*mc*) is at the center stage of such studies. These materials have been prepared primarily to aid separation and recovery in adsorption study, using an external magnetic field [Goswani and Purkait, 2014]. In addition, magnetic composite has dealt with one major problem associated with naked magnetic nanoparticles (*mnp*): aggregation [Liang, *et.al.*, 2006]. This problem is virtually unavoidable due to high surface energy, van-der-Waal force and dipole-dipole magnetic attraction among magnetic nanoparticles [Lu, *et.al.*, 2007; Wang and Astruc, 2014]. Other factors as well, have been quite responsible for aggregation of magnetite (Fe_3O_4) in aqueous medium [Duran, *et.al.*, 2008; Pershina, *et.al.*, 2014]. To solve this seemingly big challenge of aggregation, a typical method is to use matrix materials to isolate, stabilize and accommodate individual or naked magnetic nanoparticles [Liu, *et.al*., 2011; Wang and Astruc, 2014]. Among tested and applied matrix materials include grapheme [Herrman, *et.al*., 2009; Zieng, *et.al*., 2012], active carbon [Rudge, *et.al*., 2001], carbon nanotube [Jang, 2006], silica [Yi, e.al., 2006; Hu, et.al., 2008], clay mineral [Bartonkova, *et.al*., 2007; Son, *et.al*., 2010], polymer [Derfus, *et.al*., 2007; Baig and Varma, 2013], ionic liquid [Jung, *et.al*., 2009; Zhang, *et.al*., 2012a], starch [Lubbe, 2001] and collagen gel [DePaoli, *et.al*., 2006].

Phosphate sorption was highly correlated with Fe-oxide and clay content of the soil. In this study, kaolinite clay has been chosen and modified for phosphate removal from aqueous medium. Although, kaolinite clay minerals are not very efficient in removing micro-pollutants from water when compared with other minerals in its class, due in part to lower surface area [Unuabonah and Taubet, 2014]. This inadequacy has made kaolinite clay modification a matter of scientific interest with achievable good results. A unique feature of magnetic composite, and its surface modified with organic/inorganic moieties are associated its high surface area to volume ratio, least toxic, biodegradable, biocompatible and ease to synthesize [Hyeon, *et.al*., 2001; Gupta and Gupta, 2005; Afkhami, *et.al*., 2010; Boyer, et.al., 2010; Huang, et.al., 2003]. To overcome the inadequacies of both bare magnetic particles and kaolinite clay as separately used, magnetic-kaolinite nanocomposite was developed. This material has gained immense attention in recent past. Blending magnetite (Fe_3O_4) and inorganic clay mineral has resulted in a class of material which are microcomposite and nanocomposite in nature (depending on the modification procedure). Compared to the individual components, magnetic-kaolinite composite exhibits dramatic improvement in several important properties, including mechanical strength, heat resistance and adsorption capacity. Magnetic-kaolinite composite therefore shows exceptional promise of not only being cheap as a result of wide spread of kaolin on the earth surface, but also being effective in removing micro-pollutants. The aim of this study among other things is to evaluate the adsorption capacity of phosphate from aqueous solution of magnetic-kaolinite composite using several adsorption isotherms in this evaluation. However, this adsorbent shall be placed side by side with existing adsorbents for efficient removal of phosphate from bodies of water.

II. Experimental

2.1 Materials

The synthetic kaolinite used in this study was obtained from Merck, India and used without further purification. All the reagents used are AR or GR-grade and were obtained from the same source.

2.2 Methodology

2.2.1 Synthesis of magnetic-kaolinite composite (*mkc*)

At constant room temperature of 25^0C, 100 mL each of solution of Fe^{2+}(1.9 g) and Fe^{3+}(3.9 g) were discreetly prepared in a deionized water that had been previously degassed under the protection of N_2-gas, with a molar ratio of $Fe^{2+}/Fe^{3+} = \frac{1}{2}$. 5.85 g of kaolinite clay was dispersed into the Fe^{3+} solution and mixed thoroughly. Then the mixture-solution was transferred into a 500 mL three-neck flask which was placed in a thermostat water bath. Thereafter, Fe^{2+} solution was added into the flask and the entire mixture was stirred (200 rpm) at 70^0C to keep it as sufficient suspension. This overall mixture gave a kaolinite/iron-oxide ratio of 1:1. After 30 min, the stirring speed was increased (400 rpm) followed by drop wise addition of NaOH solution (5 M). At about 35 min after the drop wise addition of NaOH solution, the initial brown color of the solution began to change and became black afterward, indicating the formation of the magnetic-kaolinite composite. However, in the entire course of the reaction, N_2-gas was flown through the reaction flask at flow rate of 10 mL/min, to prevent spontaneous oxidation. Subsequently, the precipitate was isolated by using an external magnetic field placed right at bottom of the reaction vessel and the supernatant was decanted. The obtained solid part was quickly washed four times with deionized and deoxygenated water and then dried at 110^0C for 5 h under air oven. The process of synthesis of water based colloidal particle was co-precipitation [Voit, *et.al*., 2001]. The chemical reaction during the co-precipitation of ferrous and ferric salts occurs as follows:

$$Fe^{2+}+2Fe^{3+}+8OH^{-} \longrightarrow Fe_3O_4+4H_2O$$

2.2.2 Characterization Technique

Fourier transform infrared spectroscopy (FTIR, Perkin Elmer, USA, model LR 64912C) was used to analyze the functional groups of the adsorbent. The morphology study was performed using a Field emission scanning electron microscopy (FESEM), (Zeiss LSM 510 Meta).

2.2.3 Preparation and Standardization of Phosphate Stock Solution

Stock solution of 1000 mg/L phosphate ion concentration was prepared by dissolving 4.39 g of KH_2PO_4 in 1 L deionized water. Experimental solutions of desired concentrations (2.5, 5.0, 10.0, 20.0 and 30.0 mg/L) were prepared by serial dilution from the stock solution. The phosphate stock solution was colored using the molybdate blue method and actual phosphate concentrations were determined using UV-spectrophotometer (shc-3000model) at maximum wavelength 880 nm.

2.2.4 Adsorption Study

Batch adsorption experiments were performed using 50 mL phosphate solution in 100 mL conical flask at ambient temperature (25^0C). The initial concentration effect on the phosphate adsorption using *mkc* was observed by agitating different concentrations of phosphate solution with 0.1 g of adsorbent, separately at room temperature (25^0C). Samples were collected at the end of 6 h agitating time and centrifuged. After 6 h, the solution attains equilibrium and the amount of phosphate adsorbed (mg/g) on the surface of the adsorbent was determined by difference of the two concentrations (i.e. initial and final). The experiments were carried out in triplicate for all the operating variables studied and only the average values were taken into consideration.
The amount of phosphate adsorbed per unit weight of *mkc* at time t, q_t (mg/g) was calculated as:

$$q_t = \frac{C_o - C_t}{M} x V$$

$$R = \frac{C_o - C_t}{C_o} x 100$$

Where C_o is the initial phosphate concentration (mg/L), C_t is the concentration of phosphate at any time t, V is the volume of solution (L) and M is the mass of adsorbent (g).

III. Results and Discussion

3.1. Characterization of magnetic-kaolinite composite (*mkc*)

The functional groups in *mck* composite used as adsorbent before and after adsorption are shown in Fig. 1. The strong band at 910 cm^{-1} is attributed to Si–O stretch vibration, while adsorption of Fe–O was observed at 598 cm^{-1} in Fig. 1a. Fig. 1b shows appearance of a new intense adsorption band at 1034 cm^{-1}indicating P–O functional group.

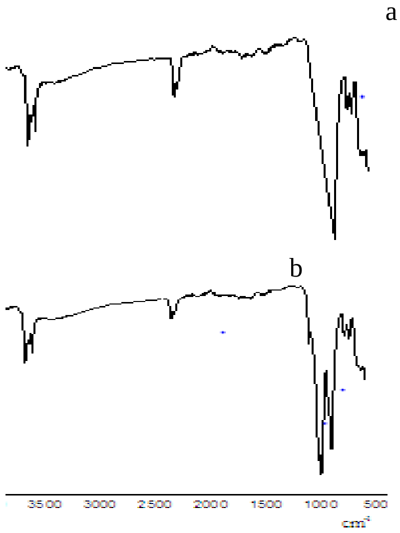

Figure 1: Infrared spectra of *mkc* adsorbent before (a) and after (b) adsorption process

One can say that PO_4^{3-} was removed from aqueous solution by adsorbent through electrostatic attraction. This observation agreed with the finding of Jiang [Jaing. *et.al.*, 2017] in removal and recovery of phosphate from water by a magnetic Fe_3O_4@ASC adsorbent. The sharp peak of Si–O occurred at 916 cm^{-1} just like in MK before adsorption process. It equally showing adsorption band at 603 cm^{-1} indicating Fe–O functional groups in adsorbent after adsorption.
Fig. 2 shows the results of scanning electron microscope (SEM). It can be seen that morphology of the MK composite has a rough surface that may promote mechanical adhesion of the PO_4^{3-} to adsorbent besides the electrostatic attraction seen in the spectrum of MK composite after adsorption. This observation was in line with that of Chen [Chem, *et.al.*, 2016], in efficient removal of phosphate by facile prepared magnetic diatomite and illite clay from aqueous solution.

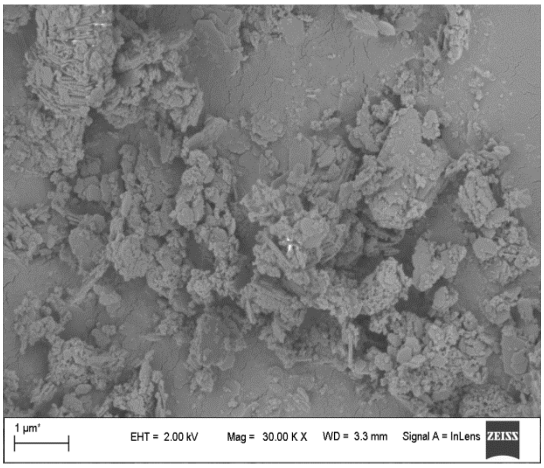

Figure 2: Scanning electron microscopic image of *mkc* adsorbent

3.2 Effect of initial phosphate concentration

The quantity of phosphate removed from the stock solution at varying phosphate concentration from 2.5 – 30.00 mg/L is shown in Fig. 3.

It can be seen that as concentration of phosphate in the solution increases the phosphate uptake equally increases (Fig. 3). Similar result was observed by Gongden*etet.al*., (2016) in equilibrium, kinetic and thermodynamic assessment of the adsorption of cadmium using water lily leaf biomass.

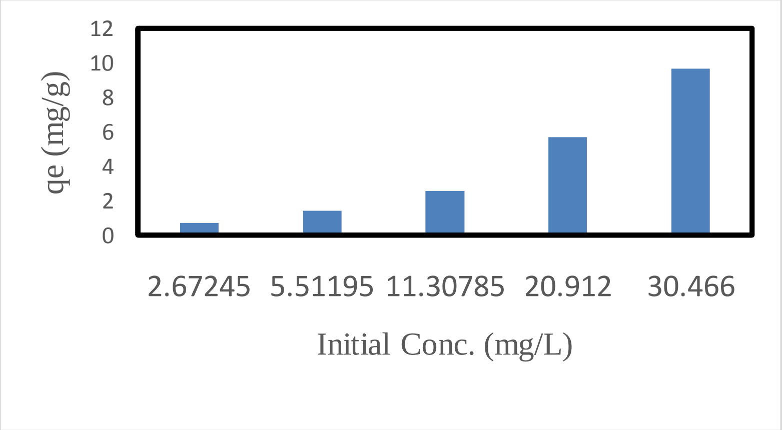

Figure 3: Phosphate uptake at varying initial concentration

3.3 Adsorption Isotherm

Four isotherm models were used to investigate the effect initial concentration on phosphate removal from its aqueous solution. These isotherm studies show relationship between quantity of adsorbate removed from aqueous solution and unit mass of adsorbent (Gongden*e*t*et.al*., 2016). The linearized form of the four isotherm models were used to compare them.

Langmuir isotherm: $\frac{1}{q_e} = \frac{1}{q_e K_l C_e} + \frac{1}{q_{max}}$ (1)

Determination of adsorption property of Langmuir makes use of dimensionless separation factor r, which is given as: $r = \frac{1}{1+K_l C_o}$ (2)

The value of r indicates nature of the adsorption in Langmuir isotherm. When r = 0 (adsorption is irreversible), 0 < r < 1 (favourable), r = 1 (unity) and r > 1 (unfavourable).

Freundlich isotherm: $ln q_e = ln K_f + \frac{1}{n} ln C_e$ (3)

The Freundlich isotherm is applicable to heterogeneous surfaces and use to estimate the adsorption intensity of the adsorbent.

Temkin isotherm: $q_e = BlnA + BlnC_e$ (4)

Temkin isotherm takes into account the interactions between adsorbents and metal ions to be adsorbed and is based on the assumption that the free energy of sorption is a function of the surface coverage.

Harkin – Jura Isotherm: $\frac{1}{q^2{}_e} = \frac{A}{B} - \left(\frac{1}{A}\right) log C_e$ (5)

This model assumes possibility of multilayer adsorption on the surface of the adsorbents having heterogeneous pore distribution.

Where: q_e= Uptake at equilibrium (mg/g)
K_l= Langmuir equilibrium constant (L/mg)
C_e = Concentration of phosphate in solution
q_{max} = Maximum uptake (mg/g)
r = Dimensionless separation
C_o = Initial concentration of phosphate
K_f = Freundlich constant (maximum adsorption capacity)
n = Freundlich constant (adsorption intensity)
B = Temkinheat of adsorption
A = Temkin maximum binding energy

Figs. 4 – 7 show the graphs of Langmuir, Freundlich, Temkin and Hakin–Jura isotherm respectively. The data obtained from these graphs are listed in Table 1.

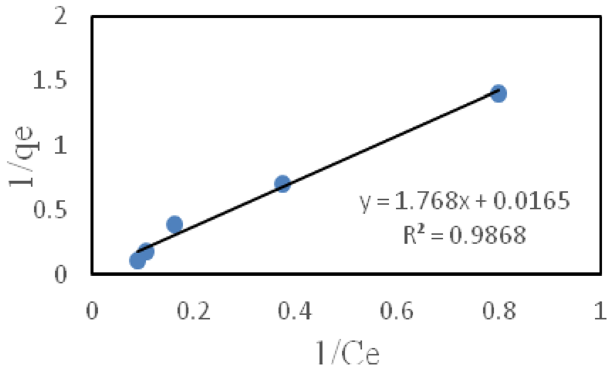

Figure 4: Langmuir isotherm graph

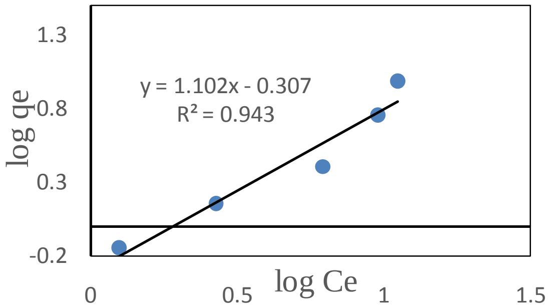

Figure 5: Freundlich isotherm graph

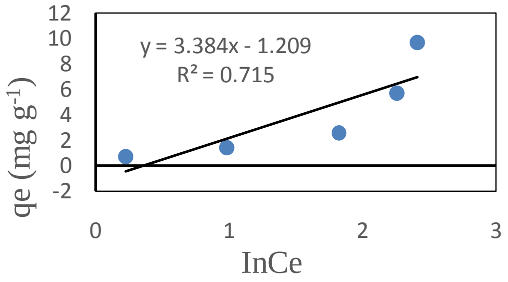

Figure 6: Temkin isotherm graph

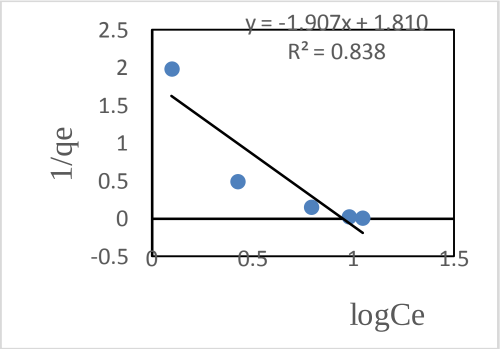

Figure 7: Harkin–Jura isotherm graph

Table 1: Adsorption isotherm constant

Langmuir isotherm	Freundlich isotherm	Temkin isotherm	Hakin-Jura isotherm
q_{max} = 60.610 mg/g	K_f = 1.3603 mg/g	A = 1.429	A = 0.5244
K_e = 0.009 Lmg-1	1/n = 1.1028	B = 3.3847	B = 0.2896
R^2 = 0.9868	n = 0.907	b_T =739.36 $kJmol^{-1}$	R^2 = 0.8383
r = 0.977	R^2 = 0.943	R^2 = 0.7153	

It can be seen from Table 2 that adsorption isotherm is best fit with Langmuir model, because of its highest value of R^2. This show that it is monolayer, and the interaction is electrostatic attraction between adsorbate molecules and adsorbent as confirmed in Fig. 1. Equally, Langmuir isotherm maximum adsorption capacity ($q_{max)}$ >> (A) < (K_f) < (A) in Tempkin, Freundlich and Hakin–Jura isotherm maximum adsorption capacity respectively. Dimensionless constant r < 1 indicates that Langmuir adsorption is favourable and that 1/n > 1 meaning that there is a cooperative adsorption in Freundlich. Very high heat of adsorption in Temkin adsorption indicates that adsorption process was not as fit as expected in the model.

CONCLUSION

Magnetic clay can be said to be moderately effective adsorbent for the removal of phosphate from aqueous solution. Langmuir isotherm fitted best in the adsorption process.

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