

Bentonite surface modification and characterization for high selective phosphate adsorption from aqueous media and its application for wastewater treatments

S. Yaghoobi-Rahni, B. Rezaei and N. Mirghaffari

ABSTRACT

Raw and modified bentonite has been used to develop effective sorbents to remove phosphate from aqueous solution. Acid thermoactivation, Rewoquate, Irasoft, calcium, Fe and Al were employed to treat the bentonite. Results show that samples adsorption capacity for phosphate is in the order of, unmodified bentonite = acid thermoactivation < Rewoquate < calcium \cong Irasoft < Fe < Al \cong Fe-Al. The phosphate adsorption with Fe-Al-bentonite (FAB) modification was more than 99% and the phosphate removal reached the peak value in the initial 30 min. The phosphate adsorption of FAB was pH independent in the range of 2–10. The common coexisting ions in wastewater have no effect on the phosphate adsorption. The phosphate adsorption results were very well fitted in the Freundlich and Langmuir isotherm model and the maximum adsorption capacity was 8.33 mg P/g at pH 6.5 for 1 hour, which was better than similar modified bentonite with low time and Fe-Al consumption. FAB was characterized by scanning electron microscopy, X-ray diffraction, X-ray fluorescence and Fourier transform infrared. Therefore, the results confirm that FAB is a selective phosphate sorbent and environmentally friendly for its potential application for phosphate removal from wastewater.

Key words | adsorption, bentonite, organoclay, phosphate, pillared clay

S. Yaghoobi-Rahni
Department of Environment,
Velayat University,
Iranshahr,
Iran

B. Rezaei (corresponding author)
Department of Chemistry,
Isfahan University of Technology,
Isfahan,
Iran
E-mail: rezaei@cc.iut.ac.ir

N. Mirghaffari
Department of Natural Resources,
Isfahan University of Technology,
Isfahan 8415683111,
Iran

INTRODUCTION

Removal and recovery of phosphorus compounds from wastewater has an important role in managing environmental and economic concerns, such as eutrophication of surface waters and depletion of phosphorus resources. Also, in most countries, stringent legal standards are followed for the phosphorus discharge range in water and wastewater. Several techniques have been widely investigated for phosphorus removal from wastewater including chemical precipitation, and physical and biological processes (Clark *et al.* 1997; de-Bashan & Bashan 2004; Mulkerrens *et al.* 2004).

Among these methods, phosphate removal from aqueous solutions by adsorption has recently been given more

attention, due to severe effluent standards, the high efficiency of this method and also the phosphate-loaded adsorbents that can be used in agriculture as fertilizer or soil conditioner (Zhang *et al.* 2009). Adsorption is an environmentally friendly, simple, feasible and economical method for phosphate removal from wastewater, leading to practical recycling and reuse of phosphorus.

Different materials have been used for phosphate adsorption that can be divided into two kinds: non-clay (such as natural, synthesis and waste materials) and clay adsorbent. The key problem in the phosphorus adsorption method is finding an efficient, available and low-cost sorbent. Clays are low-cost and easily available minerals that, due to their individual properties, are used as general sorbents in water and wastewater treatments (Atia 2008; Chen *et al.* 2008; Alkaram *et al.* 2009; Guo *et al.* 2009; Haghseresh

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et al. 2009; Koswojo *et al.* 2010; Gu *et al.* 2011; Wang *et al.* 2013; Siti *et al.* 2014). Clays are used as a natural scavenger for cationic and anionic pollutants through ion exchange or adsorption or both (Moharami & Jalali 2013). Various natural and modified clays have been used for phosphate adsorption, e.g. vesuvianite and lanthanum-doped vesuvianite (Li *et al.* 2009), natural bentonite, kaolinite and zeolite (Moharami & Jalali 2013), bentonite-hematite (Dimirkou *et al.* 2002), lanthanum-modified bentonite (Phoslock) (Haghsereht *et al.* 2009), bentonite modified with Fe polycations and cetyltrimethylammonium bromide (Ma & Zhu 2006), and hydroxy-aluminum, hydroxy-iron and hydroxy-iron-aluminum pillared bentonites (Yan *et al.* 2010). Notably, some of the adsorbents are vulnerable under a broad range of pH values (Dimirkou *et al.* 2002; Haghsereht *et al.* 2009; Yan *et al.* 2010) and this may be problematic for their application in wastewater treatment which may also need a long contact time (Li *et al.* 2009; Yan *et al.* 2010). Also natural bentonite has low adsorption capacity and needs a long contact time for phosphate adsorption (Moharami & Jalali 2013).

In this study, organic and inorganic bentonite was used for phosphate removal from aqueous solutions in a batch test. Several studies used bentonite as a phosphate sorbent from water and wastewater, but this study investigated different methods for bentonite modification and also optimized preparation. Four inorganic pillared bentonites, namely Ca-, Al-, Fe- and Fe-Al-bentonite (FAB), two organic bentonites, modified by Irasoft-T18 and Rewoquate-WE18 surfactants, and an acidthermoactivation bentonite were prepared and have been used in experiments. Ultimately, after selection of best modification process and parameters, their structures and mineralogy were thoroughly characterized.

MATERIALS AND METHODS

Materials

The bentonite used for this study was purchased from the Semnan-Iran bentonite mine and NH_3 , $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$, CaCl_2 and KH_2PO_4 , were all of analytical grade, obtained from Reidel-de Haenand Merck Company from Germany. Irasoft-T18 and Rewoquate-WE18 surfactant were purchased from NiliPadideh Chemistry, Iran and

Gold-Schmidt, Germany, respectively. Sorbents for all stages were ground to 35 meshes (0.5 mm).

Synthesis of modified bentonites

Preparation of pillared bentonites by Fe/Al and Ca

A total of 25 mL of pillaring solutions (Fe and/or Al) were added to 10 g of bentonite, stirred for 10 min and then remained for different times (1, 2, 4, 8, 16, 24 h) to check its adsorption capability at room temperature (25 °C). The results showed that after 2 h the adsorption ability remained constant, so 4 h was used for further experiments. Then the mixture was filtered, and 50 mL ammonia solution 20 mM was added and remained for 30 min at room temperature. The mixture was filtered again and washed with 100 mL dilute ammonia solution 2 mM and deionized water, and dried at 70–75 °C. The dried product was ground to 35 meshes, and kept for adsorption experiments.

For Ca modification, 500 mL CaCl_2 (0.5 M) with 50 g bentonite was shaken for 1 h and centrifuged (this stage was repeated three times). Then the product was washed with 500 mL distilled water (twice) and finally with 200 mL ethanol, stirred for 1 h and centrifuged. The final product was dried at 70–75 °C in an oven.

Preparation of organic and acidthermoactivation bentonites

Two grams of Irasoft or Rewoquate surfactant was dissolved in 50 mL ethanol and acetone solution (50% V/V). Fifty grams of bentonite was added to the prepared solution and shaken for 30 min, then dried at 50–55 °C. The dried product was ground to 35 meshes and used for adsorption experiments.

Also for preparation of acidthermoactivation bentonites, 250 mL, HCl (1 mol/L) was added to 30 g bentonite and shaken on a hotplate at 80 °C for 4 h, the centrifuged product was washed with distilled water and dried at 70–75 °C.

Characterization methods

The cation exchange capacity (CEC) values were determined by the ammonium acetate method (Bashour &

Sayegh 2007). X-ray powder diffraction patterns were obtained using an X-ray diffractometer D8 advance of Bruker (Germany) with an X-ray tube anode Cu of wavelength 1.5406 (Cu K α). The X-ray diffraction (XRD) patterns were obtained from 3 to 60°. Major elements were determined using an X-ray fluorescence (XRF) spectrometry analyzer model S4 Pioneer (Bruker, Germany).

Fourier transform infrared (FTIR) spectra were obtained in the transmission mode on a Jasco 680 Plus Fourier transform IR spectrometer. Samples were mixed with KBr in an agate mortar with ratio W/W 1:30, then powdered to prepare the KBr pellets. The adsorption bands in the range of 400–4,000 cm⁻¹ were recorded. The bentonite samples were coated with Au under vacuum in an argon atmosphere for scanning electron microscopy (SEM) by Philips series XL30 Scanning Electron Microscope (The Netherlands).

General phosphate adsorption procedure

Adsorption experiments were carried out using the batch equilibration technique. One gram of the desired sorbent was mixed with 50 mL phosphate solution containing 25 mg P/L in a 100 mL Erlenmeyer flask and capped by aluminum sheets. The mixture was shaken at 125 rpm for 1 h at 25 °C. After centrifugation, the phosphate concentration in supernatant was analyzed with the ascorbic acid method (Clesceri et al. 1999). For better comparison, all experiments were performed for both sample and control solutions (phosphorus solution without adsorbent) as a blank, and the phosphate adsorption percentages were calculated according to Equation (1):

$$\% \text{Adsorption} = \frac{C_i - C_f}{C_i} \times 100 \quad (1)$$

where C_i and C_f are the blank and final concentrations of phosphate in the sample solution (mg/L) after adsorption, respectively.

Selectivity of phosphate adsorption

The effect of common coexisting ions in wastewater such as chloride, sulfate, nitrate and bicarbonate on the adsorption of phosphate was investigated by adding solutions containing

sodium chloride, sodium sulfate, sodium nitrate and sodium carbonate at two concentration levels. The pH of solutions was adjusted close to 6.5 by HCl and 2 g of FAB was added to the 100 mL mixed solutions. Then they were agitated at 125 rpm for 1 h at 25 °C and the residual concentration of phosphate was analyzed after centrifugation.

Phosphate adsorption from wastewater

The efficiency of modified bentonite for phosphate removal from urban wastewater was tested using a batch experiment (2 g adsorbent, 100 mL wastewater, 125 rpm, 1 h).

RESULTS AND DISCUSSION

Important parameters such as the cost of material, the adsorbate selectivity and stability of the sorbent in the environmental conditions (pH range and temperature) must be considered in selection of adsorbent material.

Comparison of different methods for modification

Figure 1 illustrates the efficiency of phosphate adsorption by prepared modified bentonites. Results show that the phosphate adsorption of different modified bentonites is in the order of: raw sorbent = acidthermoactivation < Rewoquate < calcium \cong Irasoft < Fe < Al \cong Fe-Al. Clay minerals have a mostly negative charge in their structure that can be balanced by exchangeable cations. This gives important cation adsorption and exchange capacity to clays, which have been widely used to remove cationic pollutants from water and wastewater. This could be due to two reasons: first, the negative

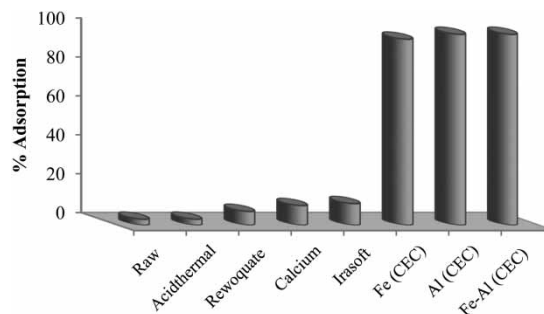


Figure 1 | Effect of different modifications on adsorption of phosphate by bentonite.

structural charge impedes the electrostatic attraction between clay particles and anions as phosphate. Also, the stable siloxane groups located on the surfaces of clays have no considerable affinity for reaction with phosphate anions (Fontes & Weed 1996; Borgnino *et al.* 2009; Borgnino *et al.* 2010). Hence in studies, different methods are used for surface modification of bentonite to resolve this drawback. The bentonite modification with surfactants showed that they could not greatly improve the phosphate adsorption ability by bentonite, however, the surface modification by surfactant is suitable for organic pollutants adsorption (Zhu & Zhu 2007; Zhu *et al.* 2007; Zhu *et al.* 2009b).

It was believed that a structural change in the clay surface, to improve a specific surface area and also decrease negative charges of the adsorbent surface after treatment with acid, had an important role in increasing adsorption capacities of modified clay for adsorption of different anions, such as phosphate, from solution (Ye *et al.* 2006). Ye *et al.* (2006) reported phosphate adsorption on acid-thermal treated > acid treated > unmodified palygorskites (Ye *et al.* 2006). However in this study it was found that acid-thermoactivation of modified bentonite is not generally effective for phosphate adsorption due to decreasing of Al and Fe ions and also surface area in a concentration of 1 M HCl (Ajemba & Onukwuli 2012; Bendou & Amrani 2014).

Al and Fe-bearing minerals are the most effective minerals for P sorption and the sorption is credited to the presence of Al-OH and Fe-OH functional groups on the mineral surface (Kasama *et al.* 2004).

Clay modification with hydroxyl Fe or Al species readily increased the phosphate adsorption capacity of clays (Borgnino *et al.* 2010). Modifying surface clay minerals with Al/Fe can form the Fe/Al-OH and/or Fe/Al-H₂O groups (which are active sorption sites for phosphates in solution) which could enhance phosphate adsorption capacity of clays by ligand exchange with OH groups (Zhu *et al.* 2007; Zhu *et al.* 2009a).

Phosphate may partly be adsorbed by forming binuclear complexes or by an electrostatic force mechanism. Also, it can form P-bearing materials, which is accompanied by dissolution of Fe/Al-bearing minerals which is important in the P sorption at low pH media or high P concentration (Kasama *et al.* 2004; Zhu *et al.* 2009a).

Phosphate adsorption by clays can be readily increased by their modification with Fe or Al hydroxylated species

(Borgnino *et al.* 2010). Therefore, Fe-Al treatment was selected for bentonite modification, in which the increased absorption capacity could be attributed to decreasing crystallinity of Al and Fe oxides in the FAB during aging and drying, causing higher sorption capacities due to higher reactivity of surface functional groups (Zhu *et al.* 2009a). This result is compatible with studies that displayed the modification on montmorillonite phosphate adsorption (Zhu *et al.* 2009a). However, another study about modification of bentonite showed a reverse order: Al- > Fe- > Fe-Al-Bentonite (Yan *et al.* 2010) which could be due to a different modification method on the surface of sorbent. Therefore in this study, modification by Al-Fe was selected for bentonite modification and different modification parameters were studied.

Optimization parameter in preparation of FAB

Effect of Fe/Al concentration

The effect of Fe and Al concentration for modification of sorbent on the phosphate adsorption was investigated (Figure 2). Increasing Fe and Al concentration, raises the adsorption capacity of modified bentonite for phosphate.

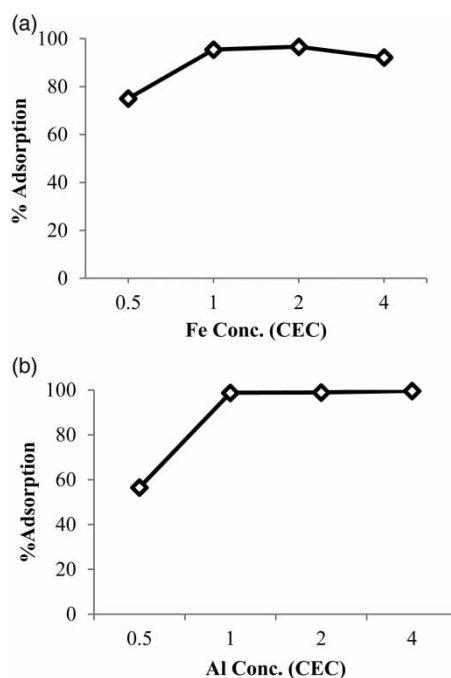


Figure 2 | Effect of Fe (a) and Al (b) on adsorption of phosphate.

Porous materials and clay mineral surfaces loaded with Al/Fe can form the Fe/Al-OH and/or Fe/Al-H₂O groups, which are active sites for phosphate sorption in a solution. Firstly, the phosphate adsorption capacity of bentonite can be readily increased with increasing Fe and Al concentrations until the equivalent CEC concentration is reached, but it mainly remains constant after this concentration.

Also, the results of an investigation into the effect of the ratio of Fe and Al on phosphate adsorption are shown in Table 1. The results showed that a negligible difference exists between the concentration ratios of one and two times the CEC. In this study, due to probable precipitation of Al and Fe on the surface of bentonite, and/or formation of hydroxyl Al and hydroxyl Fe cations in the interlayer spaces of clays, and also their adsorption on the external planar surfaces and/or at the edges (Zhu et al. 2009a), confidently a total concentration of two times the CEC (1.5 Al and 0.5 Fe with adsorption percent greater than 99%) was selected for modification.

Effect of contact time and ammonia concentration

Contact time between a solution containing Al-Fe as the modifiers and bentonite is one of the physical parameters that may affect the adsorption of phosphate, but the results show that this parameter had negligible effect on phosphate adsorption.

Al and Fe hydroxide can be formed in alkaline solutions. Therefore, the effect of ammonia concentration for modification of bentonite was investigated. The results show that ammonia concentration has no effect on phosphate adsorption. This has shown that pH of bentonite is significant for formation Al and/or Fe hydroxides.

Effect of chemical and physical parameters on phosphate adsorption

Ultimately an adsorbent was prepared under these conditions: contact time of 4 h for pillaring solution, Fe/Al up

to 2×CEC (1.5 Al + 0.5 Fe) and without adjustment of pH, and then the effective chemical and physical parameters in phosphate adsorption were investigated.

Effect of time on phosphate adsorption

An investigation into the effect of contact time on the phosphate removal shows that more than 96% removal is achieved in the initial minutes and removal reaches a maximum value of 99.9% after 30 min. Electrostatic sorption on the outer surfaces and at pore entrances of the adsorbent and the direct ion exchange process can elucidate this rapid sorption. Also, phosphate can be adsorbed on the inner surfaces of deep pores by diffusion into the sorbent matrix through meso- and micropores (Zhu et al. 2009a). For confidence of complete phosphate adsorption, a contact time of 1 hour was selected for future tests.

Effect of pH on phosphate adsorption

Adsorption is affected by the surface charge of adsorbent and the surface charge is influenced by the pH of the solution (Jeon & Yeom 2009). To investigate the influence of pH on the phosphate adsorption, experiments were carried out by adding 1 g of the adsorbent sample into a 100 mL Erlenmeyer flask, containing 50 mL of 25 mg P/L phosphate solution at constant pH. Experiments were performed in binary repeat and together with control solution. The pH was adjusted by adding drops of 0.1 mol/L HCl or NaOH.

The results demonstrate the phosphate removal was evidently independent of pH with the greatest adsorption occurring under a wide pH range (3–10). Only slight decreases can be seen at a pH = 2 which is probably due to formation of weak adsorbent H₃PO₄ as a predominant species in phosphate solution (Namasivayam & Sangeetha 2004). The ligand-exchange mechanism is much less dependent on pH than the electrostatic mechanism; therefore ligand exchange is the dominant mechanism for phosphate sorption in this study

Table 1 | Effect of Fe and Al ratio on phosphate adsorption by modified bentonite (25 mg P/L, 1 h, 125 rpm)

Modification	0.25Al + 0.25Fe ^a	0.5Al + 0.5Fe	1Al + 1Fe	0.5Al + 1.5Fe	1.5Al + 0.5Fe
%Adsorption	81.95	97.64	97.26	96.72	99.08

^aNumbers show ratio of Al and Fe equivalent CEC.

(Zhu *et al.* 2009a). pH is an important factor for some synthetic and nano adsorbents (Liu *et al.* 2011; Long *et al.* 2011; Hamdi & Srasra 2012; Su *et al.* 2015) but the important property of the developed sorbent is its capability to be used for wastewater treatment in various pH conditions. Efficient phosphate adsorption on La-modified tourmaline was achieved at a wide pH range (Li *et al.* 2015).

Effect of adsorbent dose on phosphate adsorption

The effect of adsorbent dosages in the range of 10–40 g/L on the phosphate adsorption at pH near 6.5, initial phosphate concentration 500 mg P/L and 25 °C, at a constant stirring speed of 125 rpm for 60 min, was studied (Figure 3). The results show that the removal percent increased with increasing adsorbent dose due to the increase in the total available surface area of the adsorbent particles (Xiong *et al.* 2011).

It was observed that the final pH value of the solution increased with increasing phosphate adsorption. It can be expressed by ligand exchange with the -OH groups on the hydroxylated surface which indicated that hydroxyl ions were released into the solution after uptake of phosphate onto the surface of the adsorbent (Zhu *et al.* 2007; Ning *et al.* 2008; Long *et al.* 2011).

Adsorption isotherm

Freundlich and Langmuir adsorption isotherm models were applied to study the adsorption capacity of FAB for the phosphate removal, at the optimum conditions, from water. The most important multi-site sorption isotherm for

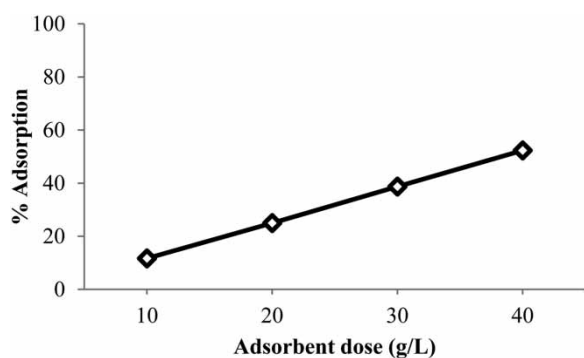


Figure 3 | Effect of adsorbent dose on phosphate adsorption (500 mg P/L, 125 rpm, 1 h).

heterogeneous surfaces is the Freundlich isotherm (Equation (2)) (Triantafyllidis *et al.* 2010).

$$\log\left(\frac{x}{m}\right) = \log K_f + \frac{1}{n} \log C_e \quad (2)$$

where x/m (mg/g) is the adsorbed amount of adsorbate in unit weight of the adsorbent, k_f is the Freundlich constant related to adsorption capacity, and n is a constant related to energy or intensity of adsorption. This isotherm does not predict any surface saturation of the adsorbent, thus indicating physisorption on the surface (Namasivayam & Sangeetha 2004). k_f and n are determined from the linear plot of $\log(x/m)$ vs $\log C_e$ (Zheng *et al.* 2009) (Figure 4(a)).

The Langmuir isotherm is expressed by Equation (3)

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

where C_e is the concentration of phosphate in a solution (mg/L) at equilibrium, q_{max} is the Langmuir constant related to adsorption capacity (mg/g), and K_L is a constant related to phosphate binding energy on an adsorbent (L/mg) (Namasivayam & Sangeetha 2004; Xiong & Mahmood

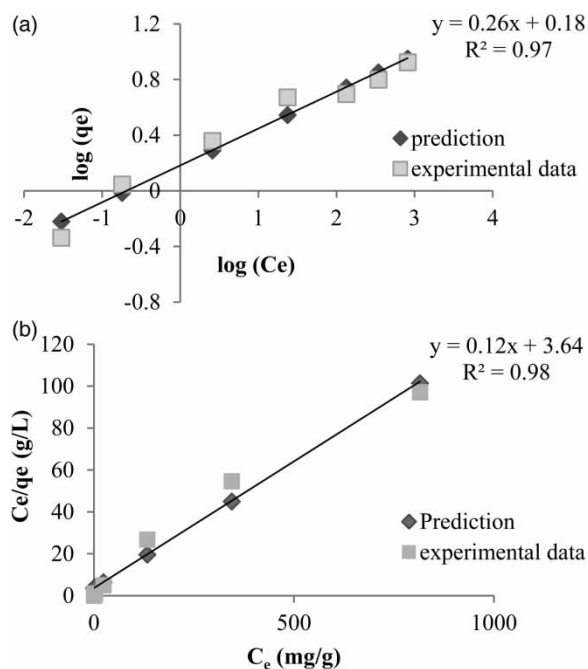


Figure 4 | Freundlich plots (a) and Langmuir plots (b) for adsorption of phosphate by FAB.

2010). The linear relationship between C_e/q_e vs C_e shows the adsorption mechanism is obeyed from the Langmuir isotherm (Figure 4(b)). Isotherm constants for phosphate adsorption are reported in Table 2.

The high correlation coefficient (R^2) of the Langmuir and Freundlich model indicate that the experimental data are fitted by both models. The Freundlich constant n , not only indicates the deviation from linearity of the adsorption (heterogeneity factor), but also indicates the intensity of the adsorption ($n < 1$ means poor adsorption, from 1 to 2 means moderately difficult adsorption, and $n > 2$ means good adsorption) (Ma et al. 2012). The obtained n value of the adsorbent was 3.85 indicating a good adsorption between FAB and phosphate.

The Langmuir model behavior in this system establishes the strong electrostatic sorbent-adsorbate attraction forces, and also indicates the monolayer coverage for adsorption of

phosphate onto the FAB surface (Ma et al. 2012). The affinity of the adsorbent towards the adsorbate can be estimated by measuring K_L in the Langmuir model (a higher value of K_L means a higher adsorption level at a low concentration) (Xiong & Mahmood 2010). The maximum adsorption capacity of phosphate by the Langmuir isotherm was 8.33 mg P/g.

The characteristics of the Langmuir isotherm can be expressed by a dimensionless constant, called the equilibrium parameter or separation factor (R_L), that is given by the following equation (Namasivayam & Sangeetha 2004; Putra et al. 2009; Zheng et al. 2009):

$$R_L = \frac{1}{1 + bC_0} \quad (4)$$

where b is the Langmuir constant and C_0 is the initial phosphate concentration (mg/L). The value of R_L indicates the type of isotherm to be unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$), or irreversible ($R_L = 0$) (Ma et al. 2012).

Values of R_L are found to be between 0.33 and 0.78 for phosphate concentrations in the range of 9–982 mg P/L onto the FAB which indicates that adsorption is favorable.

Table 3 shows the comparison of obtained q_{max} for FAB and other reported modified bentonites. The results show

Table 2 | Parameters of the Freundlich and Langmuir models fitted to the experimental phosphate adsorption

Langmuir			Freundlich		
q_{max} (mg/g)	K_L (L/mg)	R^2	$1/n$	K_f (L/g)	R^2
8.33	0.03	0.98	0.26	0.18	0.97

Table 3 | Comparison of Langmuir q_{max} and ratio of Al/Fe in different modifications of bentonite in other studies

Adsorbent	Ratio ^a	q_{max} ^b	pH	Time (h)	$q_{max}/(Al/Fe)^c$	Reference
Al-Bent	10	–	–	4 or 10	–	Zhu et al. (2009b)
Fe-CTMAB-Bent	2.01	9.82–13.32	–	4	4.9–6.6	Ma & Zhu (2006)
Al-CTMAB-Bent	0.5	1.83	–	4	3.7	Zhu et al. (2007)
Al-CTMAB-Bent	1	3.20	–	4	3.2	Zhu et al. (2007)
Al-Bent	10	7.10	5.5	4	0.7	Zhu & Zhu (2007)
Al-CTMAB-Bent	1	5.81	5.5	4	5.8	Zhu & Zhu (2007)
Al-CTMAB-Bent	4	6.83	5.5	4	1.7	Zhu & Zhu (2007)
Al-CTMAB-Bent	10	7.63	5.5	4	0.8	Zhu & Zhu (2007)
Al-Bent	10	12.7	3	6	1.3	Yan et al. (2010)
Fe-Bent	10	11.2	3	6	1.1	Yan et al. (2010)
Fe-Al-Bent	10	10.5	3	6	1.1	Yan et al. (2010)
Fe-Al-Bent	0.79	8.33	6.5	1	10.5	This study

^aRatio Fe and/or Al used (mmol/g bentonite).

^bLangmuir q_{max} (mg P/g).

^cDeviation q_{max} to ratio Fe/Al (column 3/2).

that the proposed modified bentonite with lower Al/Fe and time consumption has better adsorption efficiency ($q_{max}/(Al/Fe)$ ratio = 10.5). As well, the main disadvantage of phosphate adsorbents is their pH dependency which changes the adsorption capacity, but in this study pH has a weak effect on phosphate adsorption. This shows the practicability and remarkability of the modification method for bentonite.

Characterization of raw and modified adsorbent

The CEC of bentonite was 118 meq/100 g. The chemical composition of the raw and modified bentonite was determined by XRF analysis (Table 4). The results show aluminum and iron silicates are the most prevalent compounds. So the Fe/Al poly-cation could intercalate bentonite through the cation-exchange reaction and form hydroxyl-Fe/Al-pillared bentonite that can increase the surface area and pore volume of bentonite (Chen & Zhu 2009; Gil et al. 2011).

XRD patterns of the raw and modified samples are illustrated in Figure 5. Maximum basal spacing was 1.9 nm for raw bentonite. Basal spacing can increase after pillaring (Li et al. 2010). Main compounds are cristobalite (40.8% W/W) and montmorillonite (33.1% W/W).

Table 4 | Elemental analysis (%W/W) of raw bentonite and pillared bentonite samples

Compound	SiO ₂	Al ₂ O ₃	CaO	Na ₂ O	Fe ₂ O ₃	MgO
Bentonite	65.85	12.20	2.85	2.27	1.76	1.53
FAB	66.05	13.80	0.752	0.240	4.30	1.29

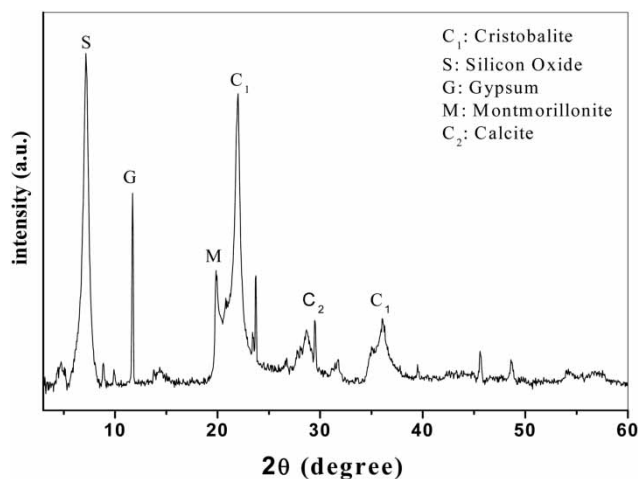


Figure 5 | XRD diffraction patterns of bentonite.

Figure 6 shows the IR spectra of raw and modified bentonite. Differences between the IR spectra of the raw and Al-Fe bentonite are indistinguishable. The IR absorption bands around 3,627 cm⁻¹ are attributed to Al(Mg)-OH vibration (Putra et al. 2009). The relatively weak IR absorption bands around 3,300–3,600 cm⁻¹ are ascribed to O-H stretching vibration (Darvishi & Morsali 2011) and at 1,637 cm⁻¹ are due to H-O-H bending (Putra et al. 2009). The intensive band around 1,041 cm⁻¹ can be assigned to Si-O stretching vibrations (Xin et al. 2011), the peak at 795 cm⁻¹ may correspond to the stretching vibration of Al-O-Si (Darvishi & Morsali 2011). Also the peak at 918 cm⁻¹ is from a stretching vibration of Al-O(OH)-Al (Zhao et al. 2008), and Si-O-Al and Si-O-Si bending vibrations appeared at 519 and 470 cm⁻¹, respectively (Gu et al. 2011; Xin et al. 2011). The peaks at 519 cm⁻¹, 846 cm⁻¹, 624 cm⁻¹ and 918 cm⁻¹ were assigned to Al-O-Si deformation, Al-Mg-OH deformation, coupled Al-O and Si-O, out of plane and Al-Al-OH deformation, respectively (Yuan et al. 2006). Chen & Zhu (2009) alluded that due to the characteristic stretching frequencies of bentonite, the peaks assigned to Fe-O and Fe-O-Fe asymmetric stretching of Fe-bentonite could not be clearly identified (Chen & Zhu 2009).

SEM images of the raw and modified bentonite were used to observe the pillared clay surface before and after modification and after phosphate adsorption (Figure 7). Significant differences were observed between the micrographs of the raw adsorbent surfaces taken before and after modification. Bentonite exhibited an aggregated morphology. The morphology of the bentonite after the pillaring process with Al becomes more porous and fluffy (Gu et al. 2011). Furthermore, the surface feature of FAB after phosphate adsorption was different with raw sorbent, suggesting that the metal-hydroxyl-phosphate ligand component and phosphate-metal chemical precipitation might bring about these morphological changes of FAB surface during phosphate adsorption (Yang et al. 2013). Similar findings have been reported by Yan et al. (2010) and Moharami & Jalali (2013).

Effect of coexisting anions

The effect of common coexisting ions in wastewater such as chloride, sulfate, nitrate and bicarbonate in two

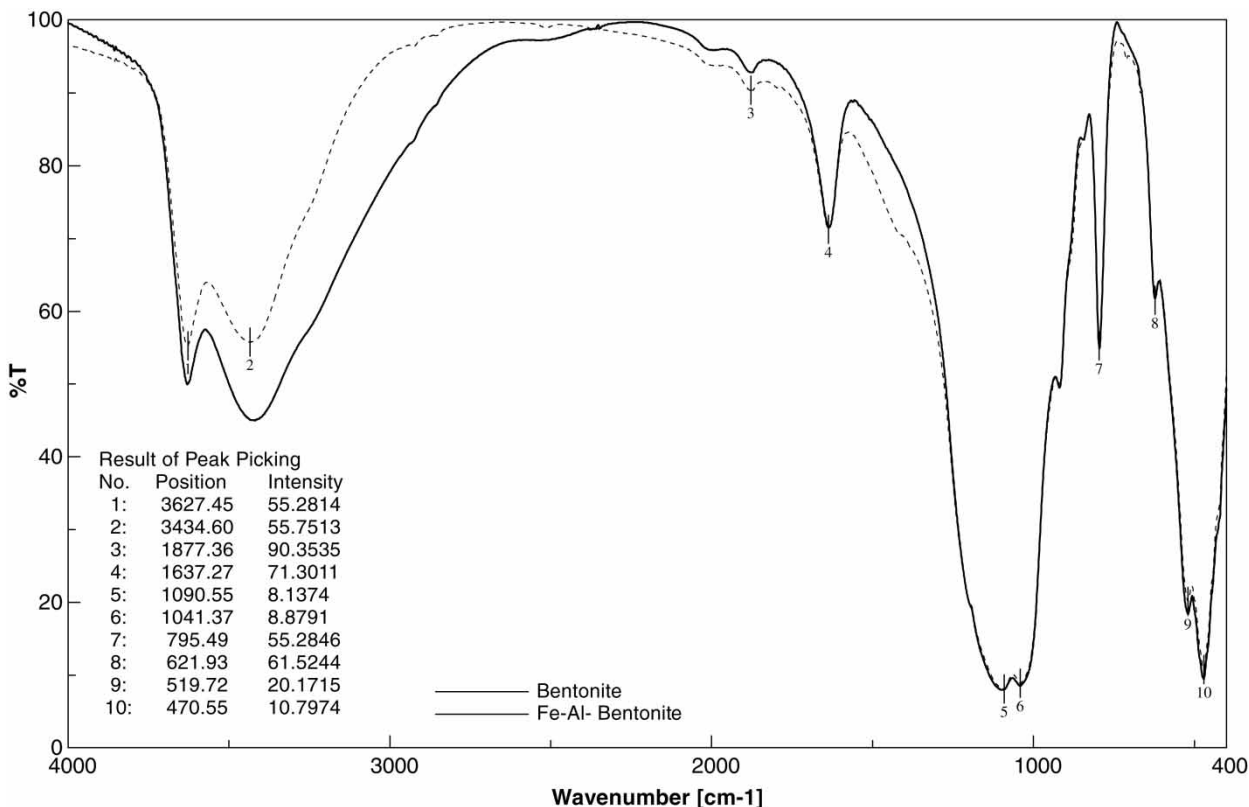


Figure 6 | FTIR spectra of bentonite and FAB.

concentration levels of 10 and 100 mg/L were studied on the adsorption of phosphate with FAB (Figure 8). The results show that these anions have no effect on phosphate adsorption and the efficiency of adsorption is more than 99%. But in some adsorbents such as aluminum and lanthanum/aluminum pillared montmorillonite (Tian *et al.* 2009), Lanthanum (III) doped mesoporous silicates (Zhang *et al.* 2010), chitosan hydrogel (Dai *et al.* 2011) and magnetic Fe-Zr binary oxide (Long *et al.* 2011) phosphate adsorption percentage decreases in the presence of some anions.

Phosphate adsorption from wastewater sample

Phosphate adsorption from urban wastewater by modified bentonite exhibited affinity of removal of more than 99% at the concentration of 4.15 mg P/L. Tian *et al.* (2009) ascribed the reduction in phosphate adsorption from

yellow phosphorus industry wastewater by lanthanum/aluminum pillared montmorillonite to the competitive effect of concomitant anions. Also, the phosphate adsorption onto the adsorbent strongly depends on the initial pH (Tian *et al.* 2009). All these results suggest that the FAB can be used as an adsorbent for phosphate removal from wastewater.

CONCLUSIONS

Results show that phosphate adsorption by raw sorbent = acidthermoactivation < Rewoquate < calcium \cong Irasoft < Fe < Al \cong Fe-Al treatment. The Al and Fe activation at the ratio 1.5 and 0.5 CEC, respectively, was more effective. Favorable phosphate removal by this bentonite occurs at pH values from 2 to 10. The phosphate adsorption results were very well fitted in the Freundlich and Langmuir

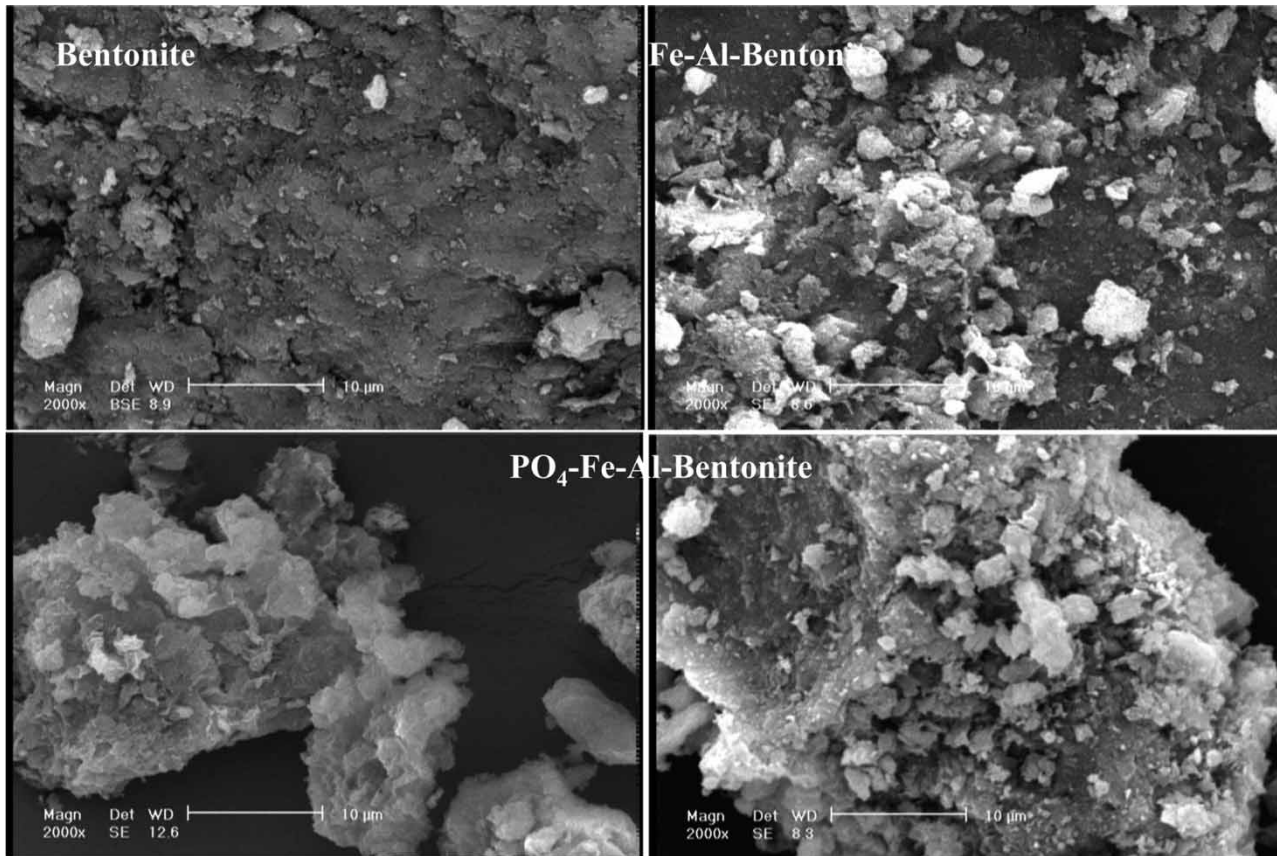


Figure 7 | SEM micrograph of the particles of bentonite before and after modification by Fe-Al and FAB after phosphate adsorption (1,000 mg P/L, pH 6.5; 1 h, 125 rpm).

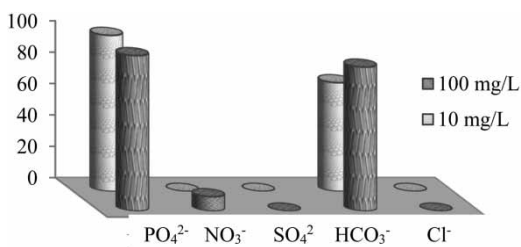


Figure 8 | Effect of coexisting anion in phosphate adsorption on FAB.

isotherm models and the maximum adsorption capacity (q_{max}) was 8.33 mg P/g for 1 hour, which was better than similar modified bentonite with low time and Fe-Al consumption. Besides, the modified bentonite is a selective phosphate adsorbent and environmentally friendly for its potential application to phosphate removal from wastewater. It may also be suitable for use as a fertilizer and soil conditioner.

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