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Preparation and Application of a Novel Functionalized Coconut Coir Pith as a Recyclable Adsorbent for Phosphate Removal

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Abstract: This study was to develop a new adsorbent, Iron(III) complex of an amino-functionalized polyacrylamide-grafted coconut coir pith (CP), a lignocellulosic residue, for the removal of phosphate from water and wastewater. The kinetics of adsorption follows a pseudo-second-order model. The equilibrium sorption capacity of 96.31 mg/g was determined at 30°C from the Langmuir isotherm equation. Complete removal of 16.4 mg/L phosphate in 1 L of fertilizer industry wastewater was achieved by 1.5 g/L AM-Fe-PGCP at pH 6.0. The acid treatment (0.1 M HCl) and re-introduction of Fe^{3+} lead to a reactivation of the spent adsorbent and can be reused through many cycles of water treatment and regeneration without any loss in the adsorption capacity.

Keywords: Adsorption isotherm, coir pith, graft copolymerization, phosphate, wastewater

INTRODUCTION

The main cause for eutrophication in water bodies such as lakes, ponds, and inland seas is an accumulation of phosphate along with nitrates and ammonia. Phosphate is released into aqueous systems mainly from domestic and municipal wastes and industrial effluents, particularly fertilizer industries. The permissible discharge level of phosphate for effluent

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discharge ranges from 0.5 to 1.0 mg/L. (1). Removal of phosphate from effluents is therefore necessary to meet the discharge limit to control eutrophication. There are many methods for purifying wastewaters containing phosphate from aqueous systems, including chemical precipitation (2), coagulation-flocculation (3), crystallization (4), biological processes (5), ion exchange (6), and adsorption (7). Among these methods, adsorption has been found to be an efficient and economic process, and an effective and widely employed method of water and wastewater treatments (8). Commercial ion exchange resins have outstanding adsorption properties, but treatment with this material is very expensive. Cost-effective adsorbent materials such as slag, aluminium oxide, half burnt dolomite, bentonite, activated red mud, tamarind nut shell carbon, stem bark carbon, and gas concrete have been used by various investigators and have been reported by Oguz et al. (8). The novel ion exchangers based on individual and mixed metal hydrous oxides have been obtained by sol-gel method from easily available cheap raw materials and employed for the removal of phosphate (9). Selective adsorption of phosphate from seawater and wastewater with amorphous zirconium hydroxide has also been studied in detail (10).

The application of lignocellulosic biomass wastes in water treatment has been widely investigated during recent years. Several methods have been used to modify raw materials by either physical or chemical modifications. These modifications were proposed in order to improve the adsorption capacity, mechanical strength, chemical stability, hydrophilicity, biocompatibility, and to prevent the leaching of organic substances. A new adsorbent containing dimethylaminohydroxypropyl weak base groups has been prepared by the reaction of banana stem, a lignocellulosic residue, with epichlorohydrin and dimethylamine followed by treatment of HCl and successfully tested in removal of phosphate from fertilizer industry wastewater (11). Recent research has focused on the preparation of iron(III)-loaded chelating ion exchange resins since they were expected to exhibit a specific binding ability toward phosphate ions (12). Phosphate adsorption on iron(III)-loaded solid adsorbents is not only the result of ion exchange but also the result of the nucleophilic S_N2-i-replacement of OH (ligand) groups of the Fe(III) atoms by phosphate with the formation of intermediate complexes (9).

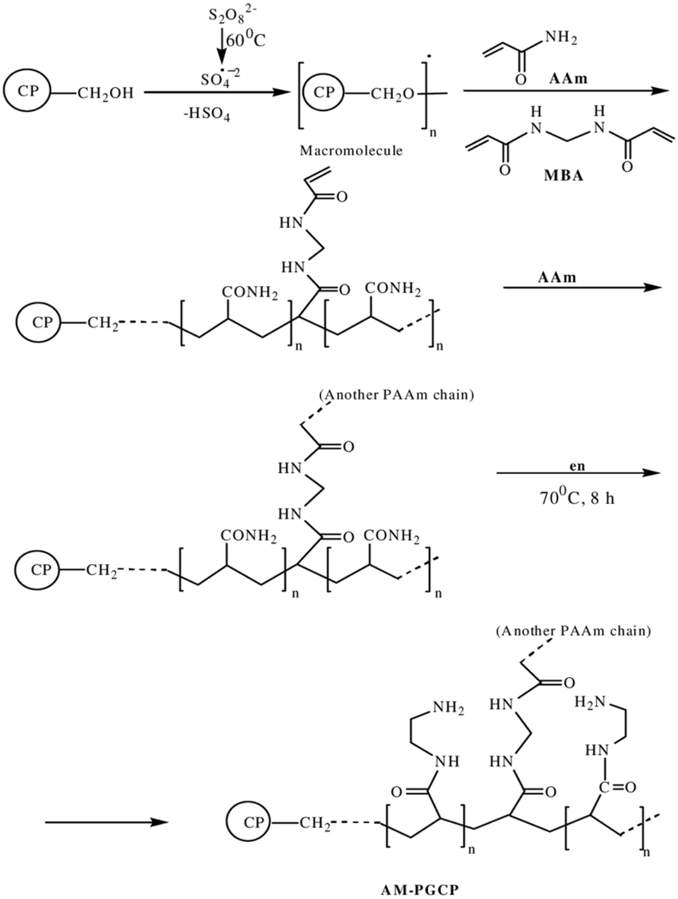
The coir process industry generates coir pith (CP), a lignocellulosic solid waste that presents a significant disposal problem. Any attempt to reutilize the CP will be worthwhile. CP is used in agriculture as a carrier for soil conditioning chemicals. Parab et al. (13) reported that CP could be used for uranium(VI) removal from aqueous solutions. The applicability of the unmodified CP has been found to be limited due to leaching of organic substances such as lignin, tannin, and pectin into the solution. In order to prevent its dissolution in acidic and basic media or to improve adsorption properties, chemical-mediated structural modifications such as cross-linking or insertion of new functional groups or grafting of vinyl monomers on CP have been performed (14,15). The results of these earlier studies showed that the products obtained from modified CP exhibit outstanding adsorption capacity for heavy metals. In this work, we have prepared a novel adsorbent amine-modified polyacrylamide grafted CP (AM-PGCP) by means of simple graft copolymerization reaction followed by loading with Fe(III) in the presence of HCl to utilize it for the effective removal of phosphate ions from various aqueous media.

EXPERIMENTAL

Adsorbent Preparation

The CP collected from a local coir industry was washed several times with distilled water to remove the surface impurities and oven dried at 80°C for 24 h. The dried CP was ground and particles of 80–230 mesh size were used for the preparation of adsorbent. The CP basically contains α-cellulose; hemicellulose and lignin which were determined using the standard methods described by Ott (16) and were found to be 46.1, 18.7, and 27.3%, respectively. Scheme 1 represents the general procedure adopted for the preparation of AM-PGCP. About 20 g CP was immersed in 200 mL distilled water in 1 L reaction flask. About 5 g of N,N′-methylenebisacrylamide (MBA) as cross linking agent and 2 g of potassium peroxydisulphate ($K_2S_2O_8$) were added to the above suspension with constant stirring. Purified N_2 was passed through the vessel for 10 min. The polymerization was started by adding 25 g of acrylamide (AAM) monomer. The sensitive component for polymer grafting might be the methyl hydroxyl groups of the cellulose unit, present in CP (CP-CH_2OH). The mixture was stirred regularly at 70°C in a water bath until a solid mass was obtained. The polymerized product was extracted with water in a Soxhlet for 6 h in order to remove the homopolymer, (PAAM) formed during the grafting reaction. The polyacrylamide grafted CP (PGCP) obtained was collected. Grafting yield was determined and was found to be 78.8%. The dried mass was refluxed with 10 mL ethylenediamine (en) continuously for 8 h. The product AM-PGCP was separated and washed with toluene and dried.

Iron(III)-loaded AM-PGCP (AM-Fe-PGCP) was prepared using the batch adsorption technique. In order to determine the optimum pH value



Scheme 1. Proposed mechanistic pathway for synthesis of AM-PGCP.

for the incorporation of iron(III) into the AM-PGCP from aqueous solutions, preliminary batch adsorption experiments were performed over the pH range 1.0–4.5. The optimum pH for the maximum loading of iron(III) was found to be 3.0. To design operational conditions for maximum loading of iron(III) onto AM-PGCP, adsorption isotherm experiments were also performed at pH 3.0. The adsorption isotherm of iron(III) was obtained at 30°C by dispersing 0.1 g of AM-PGCP in 50 mL of metal solution in the concentration ranging from 10 to 300 mg/L. The pH of the solutions was adjusted to 3.0. After shaking for 6 h in a water bath shaker, the solutions and solid phase were separated by centrifugation at 6000 rpm for 10 min. The iron(III) concentrations in the liquid phase were measured with a GBC atomic absorption spectrophotometer (Avanta-A 5450). The loading capacity of iron(III) was calculated using the relation $qe = V\Delta C/w$, where V was the volume of the liquid phase, w was the mass of the solid, and ΔC was the difference between the initial and final concentration of iron(III) at solutions. Isotherm data were analyzed using the Langmuir isotherm model and the maximum loading capacity was calculated. Based on these experiments, it was possible to design operational conditions for loading the maximum amount of iron(III) onto AM-PGCP. In the present study 20 g of AM-Fe-PGCP was prepared using batch technique. For this, 20 g of AM-PGCP was dispersed in 1 L of 3000 mg/L iron(III) solution. The pH of the solution was initially adjusted to 3.0. The suspension was shaken for 6.0 h at 30°C and the adsorbent (AM-Fe-PGCP) was separated using a centrifugation step (6000 rpm) over 10 min. Iron(III) concentration in supernatant was analyzed. The adsorbent was washed with water and then dried at 60°C for 24 h. Several studies of adsorption onto various adsorbents have been carried out by other workers using different particle size ranging between 0.08 and 0.30 mm. Adsorbents with small particle diameter have been reported for the high potentials of adsorption, principally due to large external surface areas and greater accessibility of the adsorption sites (17). The adsorbent with small particle size may also contribute intraparticle diffusion resistance onto kinetic limitations and thus adsorption follows a surface controlled rather than intraparticle diffusion controlled process. In the present work, the adsorbent with an average particle size of 0.096 mm was used for adsorption experiments. To investigate the role of amino functionalization and iron(III) coordination on phosphate adsorption, batch experiments were performed using the original CP, AM-PGCP, Fe-CP, i.e., CP contain 29.97 mg/g Fe^{3+} and AM-Fe-PGCP.

Equipments and Method of Characterization

The FTIR spectra of CP and AM-Fe-PGCP were obtained using the pressed disk technique on a Schimadzu FTIR model 1801. The XRD patterns of the adsorbent samples were obtained with a Siemens D 5005 X-ray unit using Ni-filtered Cu K_α radiation. The specific surface area of CP and AM-Fe-PGCP was measured by BET N_2 adsorption using a Quantasorb surface analyzer (QS/7). A potentiometric titration method was used to determine the pH of point of zero charge, pH_{pzc} (18). Phosphate absorbance was recorded using a UV-visible spectrophotometer (Jasco model V 530). The apparent density of the adsorbents was determined using specific gravity bottles. A systronic microprocessor pH meter (model 362, India) was used to measure the potential and the pH of the suspension. For kinetic and isotherm studies a Labline temperature controlled water bath shaker with a temperature variation of ±1.0°C was used. The concentration of iron(III) in solution was determined using AAS (GBC-A5450). The amine content of the AM-PGCP was estimated by the following procedure. About 0.1 g AM-Fe-PGCP was equilibrated with 25 mL 0.1 M HCl. The contents of the reaction flask were shaken for 24 h. The adsorbent material was collected by filtration, washed with distilled water to remove unreacted HCl, and the filtrate was titrated against 0.1 M NaOH using a phenolphthalein indicator.

Adsorption Experiments

A stock solution of phosphate (1000 mg/L) was prepared by dissolving an appropriate amount of KH_2PO_4 (E. Merck, India) in distilled water. It was diluted with distilled water to desired concentrations. Batch adsorption experiments were performed using a 100 mg adsorbent with 50 mL of phosphate solutions in 100 mL Erlenmeyer flasks. The pH of the solution was adjusted using 0.1 M HCl and/or 0.1 M NaOH. The contents in the flask were shaken in a temperature-controlled water bath shaker operated at 30°C and 200 rpm. Samples were taken from the flask at appropriate time intervals as necessary, and the residual concentrations of phosphate were analyzed spectrophotometrically (19). The amount of phosphate adsorbed into the adsorbent was calculated from the difference between the initial and the final concentration of aqueous solutions. Duplicate adsorption experiments were performed, and the averaged results were reported. The experimental parameters studied are: the amount of adsorbent (0.4–10.0 g/L), pH (2.0–10.0), contact time (1–180 min), initial phosphate concentration (25.0–600.0 mg/L), and temperature (30–60°C).

Desorption and Recyclability Experiments

To investigate the possibility of repeated use of the adsorbent, desorption and recyclability experiments were also conducted. The phosphate-loaded adsorbent (0.1 g), obtained in the adsorption experiment ($C_0 = 25$ mg/L; pH = 6.0), was gently washed with distilled water to remove any unadsorbed phosphate ions. The spent adsorbent was added to 50 mL of 0.1 M desorption medium (NaOH, Na_2SO_4, NaCl, $NaNO_3$, HCl, and HNO_3) and the content was shaken for 2 h. The phosphate ions desorbed into solution was estimated as before. For the reuse of AM-Fe-PGCP, following the desorption, the spent adsorbent was washed with distilled water before being subjected to the second phosphate adsorption process. The adsorption and desorption processes were repeated for 4 cycles using 0.1 M HCl as desorbing agent.

RESULTS AND DISCUSSION

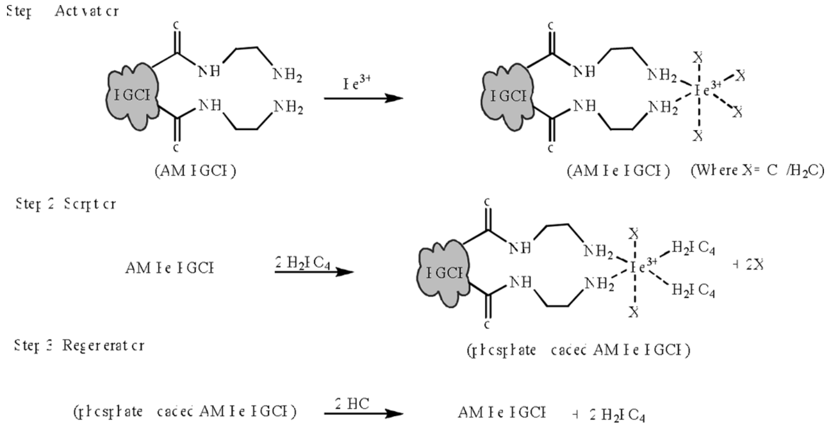
Iron(III) Adsorption onto AM-PGCP

In order to determine the optimum pH value for the incorporation of Fe(III) into the AM-PGCP from aqueous solution, adsorption of iron(III) has been studied over the pH range 1.0–4.5 using two different initial iron(III) concentrations of 10 and 25 mg/L. When the pH value of the solutions increased from 1.0 to 3.0, the equilibrium adsorption capacity increased from 3.52 to 11.63 mg/g and 7.65 to 22.13 mg/g for an initial iron(III) concentration of 10 and 25 mg/L, respectively. However, when the solution $pH > 3.0$, the adsorption decreases to a minimum value up to pH 4.5. This is due to the hydrolysis of iron(III) at the pH range 3.0–4.5. The optimum pH for the incorporation of iron(III) into AM-PGCP is considered to be approximately 3.0.

To quantify the adsorption capacity of the AM-Fe-PGCP for iron(III) loading, the Langmuir linear adsorption isotherm equation was applied on experimental isotherm data. The Langmuir isotherm plot $\left(\frac{C_e}{q_e}\text{ vs. }C_e\text{ plot}\right)$ was found to be linear (figure not shown) over the entire concentration range studied with a good correlation coefficient ($R^2 = 0.98$), showing that the Langmuir model fitted the experimental data very well for the adsorption of Fe(III) ions onto AM-PGCP. The maximum adsorption capacity corresponds to saturation of AM-PGCP with iron(III) was calculated as high as 57.80 mg/g. After knowing the maximum loading capacity of the AM-PGCP, the adsorbents were loaded with iron(III) at their optimum concentration and pH range in order to further investigate their adsorption characteristics for phosphate ions. To determine whether there is any dissolution of iron(III) from the adsorbent during the phosphate adsorption process, the supernatant solution was analyzed for both iron(II) and iron(III). It was observed that iron(III) is strongly bound to the adsorbent, so that it is not easily released from the adsorbent even in the pH range of 3.0–10.0.

Adsorbent Characterization

The amine content of the AM-PGCP determined by back titration was found to be 2.38 meq/g. The molar ratio of amine to iron(III) in iron(III) loaded AM-PGCP was calculated and found to be approximately 2.0



Scheme 2. Activation and regeration cycle of AM-Fe-PGCP.

indicating that two ethylenediamine groups are involved to bind one Fe(III) ion (Scheme 2). The coordination number of iron(III) (d^5) complexes is usually 6, Hence it is believed that Cl^- and/or H_2O molecules are coordinated to iron(III). It is likely that the positive charge of Fe(III) is neutralized by Cl^- (Scheme 2).

Figure 1 shows the FTIR spectrum for CP, AM-PGCP, AM-Fe-PGCP, and the phosphate- adsorbed AM-Fe-PGCP. An asymmetric absorption band was observed at around 3280 cm^{-1} in the spectrum of CP and this is assigned to the hydrogen bonded O–H stretching vibration from the cellulose structure of CP. The bands observed at 1682 and 538 cm^{-1} are attributed to the C=O stretching of hemicellulose and β-glycosidic linkages in CP. In addition, absorption bands appeared at 2922 and 1028 cm^{-1} are due to the aliphatic C–H stretching and bending modes, respectively. The shift of stretching frequency corresponding to the presence of –OH groups at 3280 cm^{-1} in CP to 3740 cm^{-1} in AM-PGCP indicates the involvement of –OH groups in the grafting of acrylamide on CP. The bands at 3315 and 1665 cm^{-1} are assigned to the N–H stretching and C=O stretching vibrations of amide groups. The prominent bands at 1620 and 1060 cm^{-1} are characteristic to N–H bending and C–N stretching, respectively due to the ethylenediamine bonded to the PGCP through transimidation reaction (20). These results clearly indicate the formation of a chain (backbone) and the presence of amine functionality in AM-PGCP.

The N–H bending and stretching frequencies of the iron(III) complex are lower than those of the free amines. Upon coordination, the N–H bond is weakened, and consequently the N–H vibrational frequencies are lowered. The N–H bending frequency observed at 1620 cm^{-1} in the

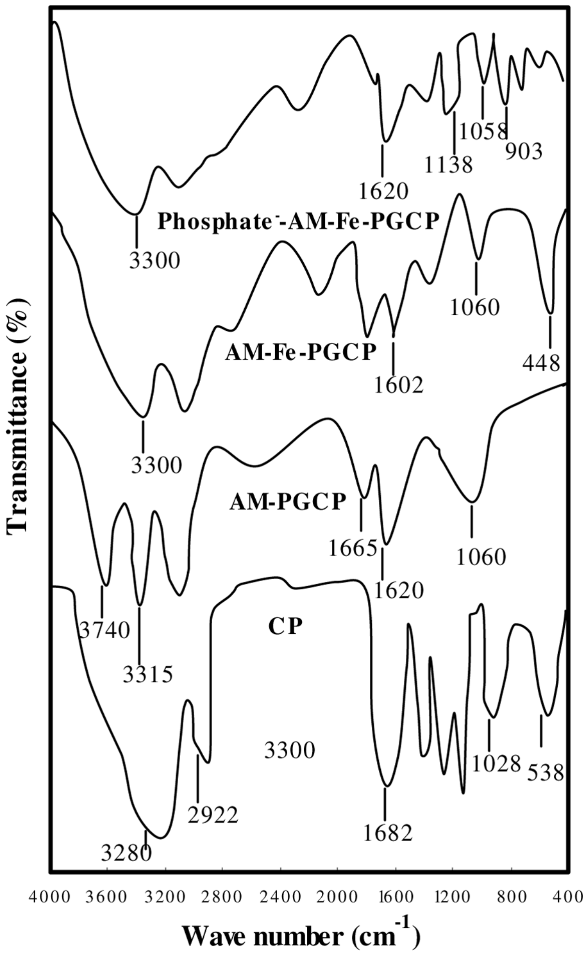


Figure 1. FTIR spectra of CP, AM-PGCP, AM-Fe-PGCP and phosphate-adsorbed AM-Fe-PGCP.

spectrum of AM-PGCP is shifted to 1602 cm^{-1} with a different magnitudes for AM-Fe-PGCP. This clearly indicates the incorporation of amine groups for coordination with iron(III). A new band appeared at 448 cm^{-1} corresponds to Fe–N stretching vibrations. Three bands at 1138 cm^{-1} (P=O stretching), 1058 cm^{-1} (P-OH stretching), and 903 cm^{-1} (Fe-H_2PO_4 structure) observed in the spectrum of the phosphate adsorbed AM-Fe-PGCP correspond to the characteristic frequencies from the adsorbed phosphate (21). Furthermore, as shown in Fig. 1, the IR spectrum measured after phosphate adsorption on

AM-Fe-PGCP still exhibited two absorption bands at 1620 and 1060 cm^{-1} which are assigned to the N–H bending and C–N stretching of the amine group in the framework. These results suggest that amine functionality is not involved in phosphate adsorption process.

The XRD patterns of the CP, AM-PGCP and AM-Fe-PGCP are shown in Fig. 2. The XRD pattern of the original CP shows distinct peaks at $2\theta = 12.3$, 19.4, and 21.8° assigned to the corresponding diffraction planes of (110), (110), and (200) in the crystalline domain of cellulose structure. The crystallinity of the AM-PGCP is lower than that of CP, as evidenced from the decrease in intensity of the peak at $2\theta = 19.4°$ in AM-PGCP, suggesting that cellulose crystalline in CP is more easily destroyed because of the effects of interaction between CP and polyacrylamide in the presence of MBA cross-linking agent. The decrease in crystalline domain AM-PGCP results in the loss of tensile strength of the polymer chain and consequently enhances the mobility of the chain. It favors the protrusion of the amine functional groups into the aqueous medium and as a result, the adsorption ability of iron(III) on AM-PGCP (57.80 mg g) is higher than that of the original CP (29.97 mg g). The XRD pattern of the AM-Fe-PGCP shows distinct and complex peaks, indicating the deposition of iron(III). AM-Fe-PGCP shows new peaks centered at $2\theta = 26.1$ and 33.3° indicate the presence of iron(III). The peak at $2\theta = 21.4°$ observed in the spectrum of AM-PGCP is shifted to a slightly higher angle by Fe^{3+} complexation.

The values surface area obtained from the BET N_2 adsorption isotherm method were 84.2, 36.5, and 29.8 m^2/g for CP, AM-PGCP, and AM-Fe-PGCP respectively; the corresponding values of the pore volume were 0.42, 0.33, and 0.29 mL/g. The CP exhibits a higher surface area, possibly due to the adsorption of N_2 in the wider micropores and mesopores. After grafting with AAM in the presence of MBA, the surface area of CP was decreased due to the fact that most of the pores with large diameters are clogged with AAM units, presumably because the inner surface of the pores is not uniformly covered with functional groups. The pH of point of zero charge (pH_{pzc}) is defined as the pH at which surface charge density is zero. The values of σ_0 as a function of pH at 0.01 M $NaNO_3$ for CP, AM-PGCP and AM-Fe-PGCP were determined by potentiometric titration method (18). The point of intersection σ_0 with the pH curves gives the value of pH_{pzc}. The values of pH_{pzc} (Figure not shown) were found to be 6.0, 7.4, and 7.7 for CP, AM-PGCP, and AM-Fe-PGCP, respectively. The increase in pH_{pzc} after polymer grafting and iron(III) loading indicates that the surface becomes more positive and this facilitates the electrostatic interaction with anions. A variation in anion exchange capacity (0.32 meq/g for CP, 0.43 meq/g for AM-PGCP and 0.73 meq/g for AM-Fe-PGCP) was also observed.

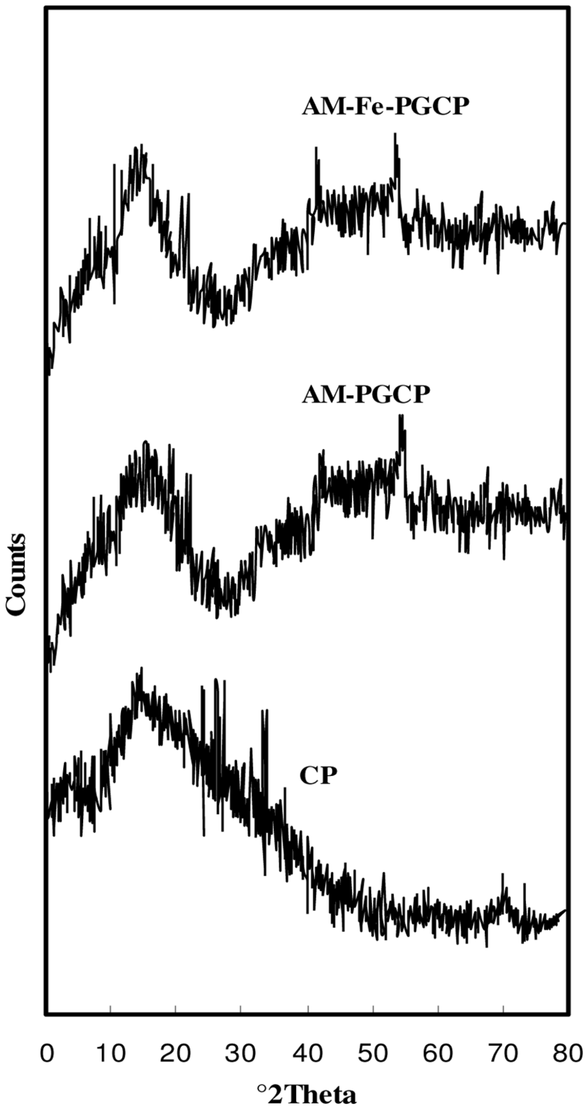


Figure 2. X-ray diffraction patterns of CP, AM-PGCP and AM-Fe-PGCP.

Effect of Surface Modification on Phosphate Adsorption

The effect of the adsorbent dose on the removal of phosphate by CP, Fe-CP, AM-PGCP, and AM-Fe-PGCP is shown in Fig. 3. It is evident from Fig. 3 that for lower adsorbent doses, AM-Fe-PGCP is adsorbent

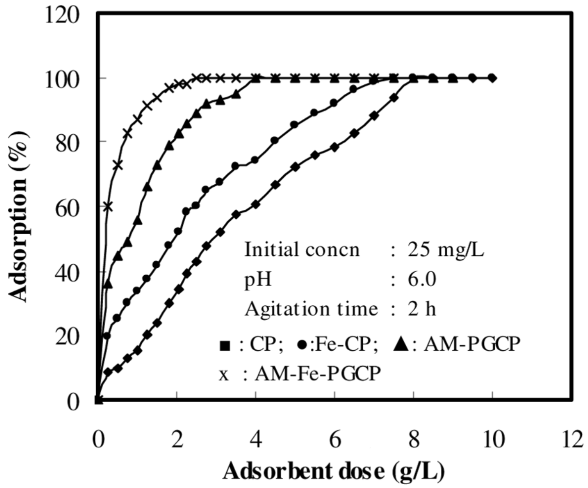


Figure 3. Effect of surface modification on phosphate adsorption.

of choice which achieved a complete removal of phosphate at 2 g/L. The efficiency of the CP, Fe-CP, and AM-PGCP was lower and could achieve a complete removal at a higher dose of 8.0, 7.0, and 4.0 g/L, respectively. The adsorption capacity of phosphate on the AM-Fe-PGCP is approximately 4.0, 3.5, and 2.0 times higher than that observed in CP, Fe-CP, and AM-PGCP, respectively. The CP-Fe showed much lower adsorption capacity than AM-Fe-PGCP, indicating that the amino functional groups on the surface of the CP strongly enhance the activity of Fe^{3+} for phosphate adsorption. As such subsequent adsorption experiments with phosphate were performed on AM-Fe-PGCP.

Effect of pH on Phosphate Removal

An important parameter which controls the adsorption process is the pH of the solution. The effect of solution pH on the removal of phosphate by AM-Fe-PGCP is shown in Fig. 4. The maximum percentage removal of phosphate by AM-Fe-PGCP was obtained in the pH range 4.0–7.0. Below and above this pH range, the removal was found to be considerably low. Thermodynamic calculations reveal that phosphate exists in solution in the forms of H_3PO_4, $H_2PO_4^-$, HPO_4^{2-}, and PO_4^{3-}, at different ratios depend on pH of the solution. The perusal of the speciation diagram (22) clearly indicates that in the range (4.0–7.0) of the highest sorption efficiency, the dominant species are $H_2PO_4^-$. The adsorption can be considered to be ligand exchange reaction between coordinated

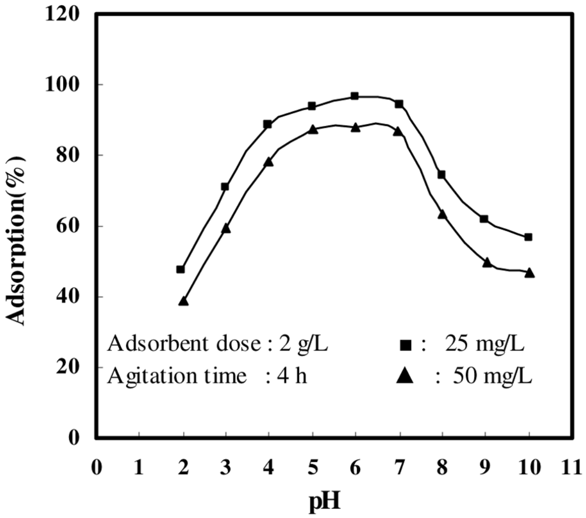
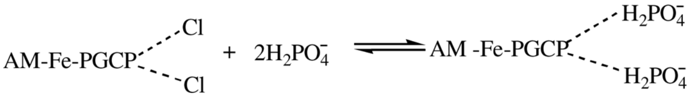


Figure 4. Effect of pH on the adsorption of phosphate on AM-Fe-PGCP.

Cl$^-$ ion and e>$H_2PO_4^-$ species (Scheme 2). The reaction can be schematically represented as:



$$\text{AM-Fe-PGCP}\begin{matrix}\cdot\cdot\text{Cl}\\ \cdot\cdot\text{Cl}\end{matrix} + 2H_2PO_4^- \rightleftharpoons \text{AM -Fe-PGCP}\begin{matrix}\cdot\cdot H_2PO_4^-\\ \cdot\cdot H_2PO_4^-\end{matrix} + 2\,Cl^- \qquad (1)$$

The value of pH_{pzc} of the AM- Fe- PGCP was 7.7. Above this pH the surface of the adsorbent is negatively charged. A decrease in the uptake of phosphate in the region of the pH greater than 7 may be due to the fact that the surface charge of the adsorbent becomes more negative at higher pH and causes higher electrostatic repulsion toward the more negatively charged phosphate anions such as $H_2PO_4^-$ and PO_4^{3-}. A decrease in the pH below 4.0 shows a decrease in adsorption even though the adsorbent surface is positively charged and the sorbate species are negatively charged. In this case, the phosphate ions more protonated are less adsorbable than the less protonated one. In view of electrostatic interaction between the sorbent-sorbate systems, it was decided to maintain the pH at 6.0 in further experiments.

Effect of Contact Time and Initial Concentration

The sorption of phosphate onto AM-Fe-PGCP was studied as a function of contact time for various concentrations and the results are shown in Fig. 5. Depending on the initial concentrations, about 70–80% removal of

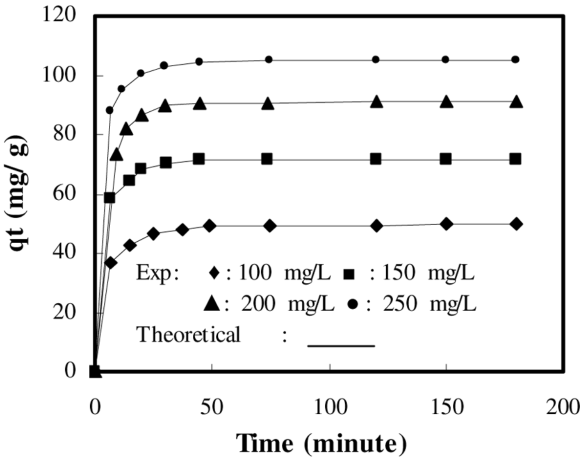


Figure 5. The effect of contact time and initial concentration on the adsorption of phosphate onto AM-Fe-PGCP and comparison of pseudo-second-order kinetic model with the experimental data.

phosphate was achieved during the first 30 min of the contact time, whereas only 15–20% of additional removal occurred in the following 2 h of contact time. The equilibrium time was found to be 2 h for all the concentrations studied. This kinetic behavior is different to that observed previously with surfactant–modified akaganeite (4 h), zirconium hydrous oxide (24 h), iron(III)– crosslinked chitosan (1 h), and the lanthanum-treated lignocellulosic adsorbents (30 h) (7,9,23,24). However, Anirudhan et al. (11) reported that equilibrium was achieved in 2 h in their phosphate adsorption kinetic studies, in which they used a chemically modified banana stem. The initial concentration did not have a significant effect on the time to reach equilibrium. The removal of phosphate after equilibrium was 49.71 mg/g (99.6%), 72.03 mg/g (95.4%), 90.40 mg/g (90.4%), and 106.57 mg/g (85.3%), respectively, at initial concentrations of 100, 150, 200, and 250 mg/L. The results show that an increase in the initial phosphate concentration leads to an increase in the phosphate uptake. The increase in the adsorption capacity of the sorbent in response to a higher initial phosphate concentration is due to the high driving force for mass transfer. So the better adsorption is achieved at higher phosphate concentration (25).

Adsorption Kinetics

The kinetic data were analyzed using pseudo-first-order and pseudo-second-order kinetic models (26). The following equations represent two kinetic models:

$$\text{Pseudo-first-order equation: } q_t = q_e[1 - e^{(-k_1 t)}] \tag{2}$$

$$\text{Pseudo-second-order equation: } q_t = \frac{k_2 q_e^2 t}{1 + k_2 q_e t} \tag{3}$$

Where k_1 is the first-order rate constant of adsorption and k_2 is the pseudo-second-order rate constant of adsorption and q_e and q_t are the amounts of phosphate ion sorbed at equilibrium and at time t, respectively. The values of rate constants were determined by a nonlinear regression analysis using ORIGIN Program (version 7.5). The values of correlation coefficient (R^2) and chi square (χ^2) are shown in Table 1. Based on R^2 and χ^2 values it is found that the adsorption of phosphate onto AM-Fe-PGCP can be best described by the pseudo-second-order kinetic model. Also, the calculated q_e values agree very well with the experimental data. The qt vs. t plots showed good agreement of experimental data with the pseudo-second-order kinetic model for different concentrations (Fig. 5). All these observations indicate that the adsorption of phosphate on AM-Fe-PGCP follows the pseudo-second-order kinetic model. This behavior implies that the dependence of the reaction rate on the external properties of the adsorbent. The pseudo-second-order phosphate removal kinetics were also postulated for the adsorption of phosphate on various adsorbents like activated coir pith carbon (27), metal hydrous oxide ion exchanger (4), functionalized–polyacrylonitrile ion exchange fibers (6), lanthanum–loaded lignocellulosic adsorbents (24), and metal–ions–loaded collagen fiber (28). As expected, increasing the initial phosphate concentration involves an increase in the amount of adsorption and a decrease in the k_2 values. A similar trend is observed in the case of phosphate adsorption by metal hydrous oxides ion exchangers (9).

Table 1. Kinetic parameters for the adsorption of phosphate onto AM-Fe-PGCP

	Pseudo-first-order					Pseudo-second-order			
Concentration (mg/L)	q_e exp (mg/g)	$k_1 \times 10^{-2}$ (min^{-1})	q_e cal (mg/g)	R^2	χ^2	$k_2 \times 10^{-2}$ (g/mg/min)	q_e cal (mg/g)	R^2	χ^2
100	49.85	1.75	43.51	0.87	1.3	2.33	49.6	0.98	0.99
150	71.83	1.77	68.36	0.99	2.31	1.88	71.4	0.99	0.79
200	90.97	2.14	83.16	0.98	2.11	1.35	90.06	0.99	0.71
250	109.01	2.51	101.17	0.99	1.91	0.85	108.04	0.99	1.01

Adsorption Isotherm

The adsorption isotherm studies are of fundamental importance in determining the adsorption capacity of phosphate onto AM-Fe-PGCP and to diagnose the nature of adsorption. Experimental isotherms determined at 30, 40, 50, and 60°C are presented in Fig. 6. It is evident from the figure that the adsorption capacity increased with the equilibrium concentration of the phosphate ions in the solution progressively reaching saturation of the adsorbent. According to Giles' classification (29) the adsorption isotherm for all temperatures belongs to the L-type, Subgroup 2, which explains the high reactivity of the AM-Fe-PGCP towards phosphate adsorption. This shape forced the modeling of the isotherm by the following Langmuir equation:

$$q_e = \frac{Q_0 b C_e}{1 + b C_e} \tag{4}$$

where q_e and C_e are the amount adsorbed (mg/g) and sorbate concentration in solution (mg/L), both at equilibrium. Q_o is the monolayer capacity of the adsorbent (mg/g) and b is the energy of adsorption (L/mg). The Langmuir isotherm constants were determined

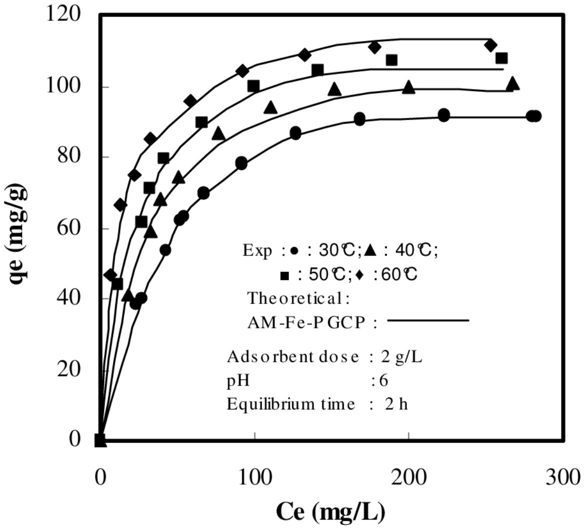


Figure 6. Comparison of the experimental and model fits of the Langmuir isotherm (lines) for the adsorption of phosphate onto AM-Fe-PGCP at different temperatures.

by a nonlinear regression analysis. The values of the Rup>2 and χ^2 obtained were found to be 0.99 and 1.3 for 30°C, 0.99 and 0.90 for 40°C, 0.99 and 1.8 for 50°C, and 0.99 and 0.76 for 60°C, respectively. The theoretical q_e values were very close to the experimental q_e values (Fig. 6). The values of Q° and b were found to be 90.01 mg/g and 0.021 L/ mg for 30°C, 104.16 mg/g and 0.038 L/mg for 40°C, 108.69 mg/g and 0.056 L/mg for 50°C, and 111.11 mg/g and 0.094 L/mg mg for 60°C, respectively. The increase in adsorption with temperature may be attributed either to an increase in the number of active surface sites available for adsorption. On the absorbent or the dissolution of the adsorbing species and to decrease in the thickness of the boundary layer surrounding the absorbent with temperature, so that the mass transfer resistances of the adsorbate in the boundary layer decreases. The Q° values for the adsorption of phosphate onto activated carbon (30), red mud (31), hydrous metal oxide ion exchanger (9), lanthanum-treated–lignocellulosic sorbent (24), and dimethylamine hydroxypropyl lignocellulosic residue (6) were reported to be 1.79, 74.90, 14.28, 33.35, and 72.46 mg/g, respectively. These results show that the AM-Fe-PGCP could be effectively used as an adsorbent for the removal of phosphate from wastewaters.

Thermodynamic Study

The variation in the extent of adsorption with respect to temperature explained on the basis of thermodynamic parameters such as changes in standard free energy (ΔG°), enthalpy (ΔH°), and entropy (ΔS°). These parameters were calculated using the following equations.

$$\Delta G^\circ = -RT \ln b \tag{5}$$

$$\ln b = \left(\frac{\Delta H^\circ}{RT} - \frac{\Delta S^\circ}{R} \right) \tag{6}$$

where R is the gas constant, T is the temperature on the absolute scale, and b is the Langmuir constant. From the slope and intercept values of the linear plot of ln b vs. 1/T, ΔH° and ΔS° values can be obtained. The values of the thermodynamic parameters are shown in Table 2. The negative and small values of ΔG° indicate the spontaneous nature of adsorption process. The positive value of ΔH° indicates the endothermic nature of the adsorption process. The enthalpy or the heat of adsorption is a measure of interaction between the adsorbate and adsorbent. The higher the heat of adsorption the stronger is the interaction between

Table 2. Thermodynamic parameters for the sorption of phosphate onto AM-Fe-PGCP

Temperature (°C)	ΔG (kJ/mol)	ΔH (kJ/mol)	ΔS (J/K/mol)
30	−17.83	38.73	186.6
40	−19.42		
50	−20.26		
60	−21.6		

the adsorbate and the adsorbent. The lower value obtained in the present study suggests that the adsorption takes place primarily through weak physical bonding between the adsorbate and the adsorbent. The ideal adsorbent for the separation of phosphate would have a high adsorption capacity and low heat of adsorption. The value of ΔS° was found to be positive due to the exchange of the phosphate ions with more mobile ions present on the adsorbent, which would cause an increase in entropy. The results also show that $[\Delta H^\circ] < [T\Delta S^\circ]$ at all temperatures. This indicates that the adsorption process is dominated by entropic rather than enthalpic changes.

The heat of adsorption determined at constant amounts of sorbate adsorbed is known as the isosteric heat of adsorption (ΔH_x) and is calculated using the Clausius–Clapeyron equation.

$$\frac{d(\ln Ce)}{dt} = \frac{-\Delta H_x}{RT^2} \tag{7}$$

The plots of ln Ce vs. 1/T for different amounts of phosphate adsorption (Figure not shown) were found to be linear and the values of ΔH_x were measured from the slopes of the plots. These values of ΔH_x were found to remain almost constant (≈34.4 kJ/mol) with an increase in surface loading from 20.00 to 70.00 mg/g. This indicates that the surface of AM-Fe-PGCP is energetically more or less homogeneous and the lateral interactions between the adsorbed phosphate ions do not exist. The lower values of ΔH_x (<40.0 kJ/mol) reflects that the adsorption of phosphate on AM-Fe-PGCP is predominantly physical with lower complexation stability.

Test with Fertilizer Industry Wastewater

A real industry wastewater sample collected from a local fertilizer industry situated in Cochi city, India, was treated with AM-Fe-PGCP to demonstrate the adsorption potential and utility in removing phosphate from wastewater in the presence of other ions. The wastewater sample was characterized using the standard methods (19) and the composition is: PO_4^{3-}, 16.4 mg/L; Cl^-, 163 mg/L; NO_3^-, 53.3 mg/L; NO_2^-, 3.1 mg/L; SO_4^{2-}, 3.8 mg/L; Total NH_3, 115.2 mg/L; F^-, 8.3 mg/L; Pb^{2+}, 3.9 mg/L; Cd^{2+}, 6.9 mg/L and pH 4.7. The effect of the adsorbent dose on phosphate removal from wastewater and pure water system was studied. The percentage adsorption of phosphate with the adsorbent dose of 0.25, 0.50, 0.75, 1.00, 1.25, and 1.50 g/L was found to be 50.4, 68.2, 84.1, 92.1, 97.6 and 99.8% respectively, from wastewater containing 16.4 mg/L phosphate; the corresponding percentage adsorption of phosphate from the pure water system containing only 16.4 mg/L. phosphate was found to be 53.8, 71.9, 85.1, 95.4, 98.3, and 99.9%. The adsorption of phosphate increased with an increase in the adsorbent dose. This may be attributed to increased adsorbent surface area and availability of more adsorption sites resulting from the increase in the adsorbent dose. From these results, it is evident that almost complete removal of phosphate (99.8%) is possible from 1 L wastewater with 1.5 g of AM-Fe-PGCP. The efficiency of the adsorbent for the adsorption of phosphate from wastewater is not significantly different from the results obtained on the pure water system containing phosphate only. Under these conditions the lowest phosphate concentration attained by this material was 0.03 mg/L, this is less than the permissible discharge limit (0.5–1.0 mg/L) of phosphate (1).

The possible release of any organics into the solution during phosphate adsorption by AM-Fe-PGCP is also investigated. For this, the amount of Chemical Oxygen Demand (COD) in the water sample before and after adsorption, was determined by means of the dichromate method (19). When the amount of AM-Fe-PGCP increased from 0.25 to 1.50 g/L, the amount of COD increased from 39.5 to 61.1 mg/L in the treated water sample and these values are lower than that of the initial amount present in wastewater sample (148.7 mg/L). From these results, AM-Fe-PGCP could be applied in real wastewater treatment, particularly the fertilizer industry wastewater.

Recovery and Recyclability Tests

The use of an adsorbent in the wastewater treatment depends not only on the adsorption capacity, but also on how well the spent adsorbent can be regenerated and used again. Among the various desorbing agents using (NaOH, Na_2SO_4, NaCl, $NaNO_3$, HCl, and HNO_3), 0.1 M HCl was found suitable to desorb phosphate from the spent adsorbent. Desorption (recovery) of phosphate from AM-Fe-PGCP was about 73.4, 82.5, 95.6 and 99.2% with 0.001, 0.01, 0.05, and 0.1 M HCl, respectively. From these results, it may be concluded that ion exchange is occurring in the adsorption process.

Even though almost complete recovery of phosphate in spent adsorbent was achieved we have observed that the HCl treatment simultaneously leads to the leaching of some iron(III) from the coordination sites due to acidic dissolution. After each desorption experiments we re-introduced Fe^{3+} to restore the adsorption sites, almost the same as the original values and subsequent adsorption experiments were conducted using re-introduced Fe^{3+} in AM-Fe-PGCP(AM-re-Fe-PGCP). The amount of Fe^{3+} restored in the regenerated adsorbent after removal of phosphate by HCl treatment was 8.6, 9.3, 9.7, and 8.1 mg/g in the first, second, third, and fourth cycle, respectively. After four cycles the adsorption capacity of AM-Fe-PGCP decreased from 24.90 mg/g (99.60%) to 24.40 mg/g (97.6%), while the recovery of phosphate decreased from 99.4% in the first cycle to 96.0% in the fourth cycle. The regenerated adsorbent showed an uptake efficiency comparable to that of the fresh ones over four cycles.

CONCLUSIONS

The ability of a newly developed adsorbent, iron(III) coordinated amino-functionalized polyacrylamide grafted coconut coir pith to adsorb phosphate ions from aqueous solutions were studied, taking into account the kinetic and the equilibrium aspects. The sorption of phosphate is pH-dependent and the best results are obtained at the pH range of 4.0–7.0. Removal of >99.0% has been achieved under optimum conditions. The kinetics of the sorption process is found to follow the pseudo–second–order rate law. The Langmuir isotherm model is used to fit the experimental data obtained at different temperatures. As the temperature increased from 30 to 60°C the maximum phosphate adsorption capacity of AM-Fe-PGCP calculated by the Langmuir model increased from 90.10 to 111.11 mg/g. The quantitative removal of 16.40 mg/L phosphate in 1.0 L of fertilizer industry wastewater is achieved by 1.5 g/L adsorbent at pH 6.0. The acid treatment (0.1 M HCl) and the re-introduction of Fe^{3+} lead to a reactivation of the used adsorbent, in which more than 97.0% of the original adsorption capacity is obtained. The spent adsorbent can be reused for several cycles consecutively without noticeable loss of capacity. The results of this study suggest that AM-Fe-PGCP exhibits significant potential as an adsorbent in the removal of phosphate from aqueous solution and industrial wastewater.

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