Full Length Research Paper

Adsorption studies of phosphate ions on alginate-calcium carbonate composite beads

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Alginate-calcium carbonate composite beads was prepared by the sol-gel method and characterized by Fourier transform infra-red spectroscopy (FT-IR) and scanning electron microscope (SEM) instruments. Adsorption potential of phosphate ions have been studied on laboratory scale. The effects of contact time, adsorbent dosage, initial analyte concentration, pH and agitation speed were optimized at 298.15 K (25°C) in a single ion system. The adsorption process was in accordance with Freundlich model and pseudo second order kinetics. Thermodynamic parameters like $\Delta G°$, $\Delta H°$ and $\Delta S°$ have also been determined. Negative values of ΔG establish the favorability of the process. Values of ΔH and ΔS indicate that the process was endothermic and during the adsorption of phosphate ions (PO_4^{-3}), less randomness takes place at the adsorbent-adsorbate interface.

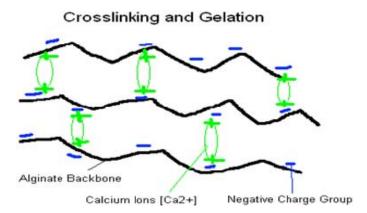**Key words:** Alginate-calcium carbonate, composite beads, phosphate ion adsorption.
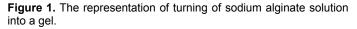
INTRODUCTION

It is an established fact that waste from industrial and agriculture sectors are the leading sources of contamination in water bodies. It introduces various chemical contaminants into the surface and ground water (Azizullah et al., 2011). Fertilizer industry, laundries and household washings produce waste water enriched in phosphate ions. Although phosphorous is beneficial to human being and agricultural lands, its excessive amount causes the phenomenon of eutrophication in the water bodies. The studies have indicated that effluents from major cities of Pakistan have higher concentrations of pollutants than the permissible limits, that is, National Envrionment Quality Standards (Khan et al., 2007). The

removal and rapid refinement of metallic and non-metallic pollutant have become vital for the environmental remediation. Many processes such as chemical precipitation, coagulation, solvent extraction, membrane separation, micro and ultra filtration, forward and reverse osmosis, electro dialysis, phytoremediation and phyto-extraction, ion-exchange and adsorption have been used to cleanse wastewaters (Farooq et al., 2010). Adsorption is the process in which atoms, ions or molecules from an effluent adhere to or accumulate on a suitable interface.

A number of adsorbent variety such as activated carbon, clays, fly ash, agri wastes, biomaterials, polymers and composites have been used as adsorbents (Gotoha

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Crosslinking and Gelation

Figure 1. The representation of turning of sodium alginate solution into a gel.
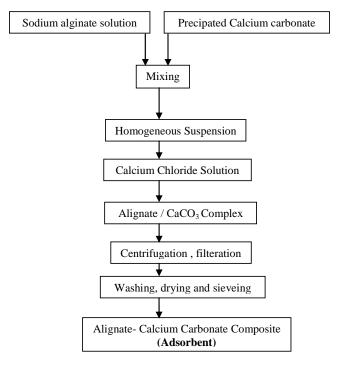

Figure 2a. Flow sheet for adsorbent synthesis.

et al., 2004). The adsorbents used should have some specific properties, such as a high ability to reduce the concentration of pollutant below the acceptable limits, high adsorption capacity, fit to purpose, durable, environmentally friendly and cost effective (Abu Al-Rub et al., 2002). Alginates have been used as low cost adsorbents for waste water purification. These are naturally occurring polysaccharides having D-mannuronic acid and L-guluronic acids. During adsorption process alginates makes a gel and appear to exchange with divalent and trivalent ions (Jorda and Mijangos, 2003).

Mechanical properties of alginates have been improved

by combining it with other materials. Sodium alginate has been combined with polyethylene oxide to remove phosphorous from waste water (Lin, 2009-02). Alginate gel beads have also been used effectively for phosphorous removal (Lin et al., 2007-08). Immobilized alginate beads suspended in an aerated activated sludge were used to remove phosphates from the activated sludge (Osee, 1995). Alum sludge combined with alginates has also been used for phosphate removal (Wadood and Sarmad, 2012). A significant increase in the removal of ammonium and soluble phosphorus ions was observed by the co-immobilization of the freshwater micro alga *Chlorella vulgaris* onto alginate beads (de-Bashan, 2002). It has been noted that volatile fatty acid (VFA) content, phosphorus load, pH, COD content, cation concentration and food to microorganism ratio (f/m) influence the biological removal of phosphate ions from wastewaters (Mulkerrinsa et al., 2004). More than 90% phosphate and >50% ammonium ions have been successfully removed during tertiary wastewater treatment using 10% (w/v) modified ca-alginate beads (Cruz et al., 2013).

MATERIALS AND METHODS

Adsorbent preparation

Precipitated calcium carbonate was impregnated on sodium alginate gel to prepare adsorbent in the form of beads in aqueous calcium chloride solution. 5 g of commercial grade sodium alginate was dissolved in 200 mL of distilled water with vigorous stirring and heated at 40°C to get a gel like material (Figure 1). The fine calcium carbonate powder (20 g) was mixed thoroughly under constant mechanical stirring to get the homogeneous mixture. The suspension was injected dropwise into a 1 M solution of calcium chloride with the help of 25 mL syringe. Fine complex beads of alginate-calcium carbonate were obtained. The beads were separated from the solution through centrifuge process followed by filtration and drying for overnight at (70 ± 2°C). The dried mass of beads was sieved and used as an adsorbent. The flow sheet of the process is demonstrated in Figure 2a.

Adsorbent characterization

The characterization of adsorbent material was made by Fourier transform infra-red spectroscopy (FT-IR) and scanning electron microscope (SEM) techniques.

FT-IR spectra of alginate-calcium carbonate composite shown in Figure 2b was recorded in the range of 4,000-400 cm^{-1}. The spectra exhibits several peaks with variable intensities merged to form a broad band in the functional group region between 3,200-3,600 cm^{-1} associated with stretching vibrations of free or bonded -OH groups along with presence of inter and intra-molecular hydrogen bonding between these hydroxyl groups (Bojić et al., 2013). The distorted peaks of medium intensity corresponds to the asymmetric stretching vibrations of alkyl chains. The relatively distorted small bands at 1,634, 1,465, 1,109 and 874 cm^{-1} are assigned to the stretching vibrations of the functional groups like C=O, -COOH and -OH (Kirova et al., 2012). It can be inferred from the FT-IR results that a strong bonding has occurred between functional groups of alginate and host material, that is, calcium
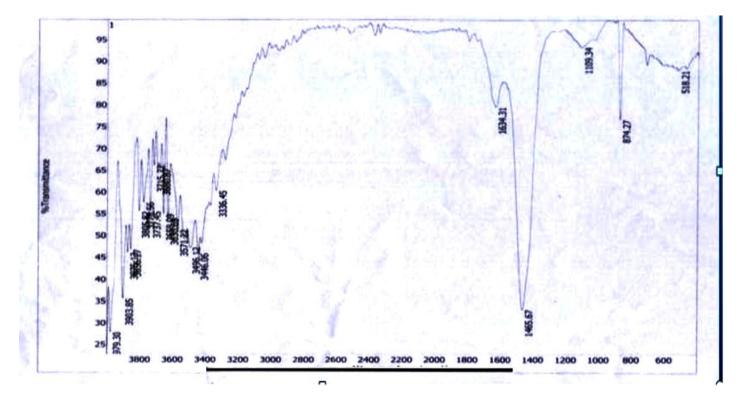
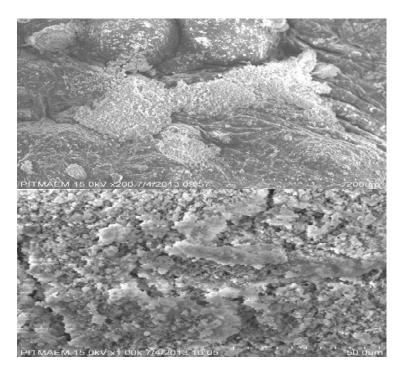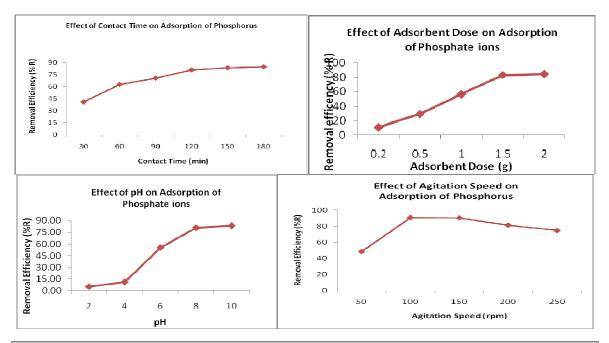**Figure 2b.** FT-IR spectra of alginate-$CaCO_3$.

Figure 2c. SEM image of alginate-$CaCO_3$.

carbonate.

The morphology of the adsorbent beads was observed by scanning electron microscope. SEM images from different areas of adsorbent material were taken at 15.0 kv with varying resolutions (Figure 2c). The SEM images indicate the formation of a composite material along with sites responsible for adsorp-
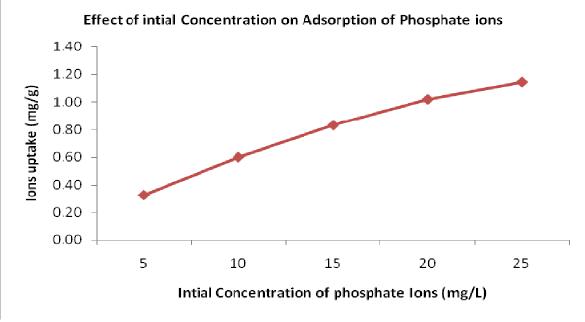
Figure 3. Optimization of parameters: **(a)** Effect of contact time, **(b)** effect of adsorbent dose, **(c)** effect of pH, (d) effect of agitation speed, **(e)** effect of initial metal ion concentration.

tion at the absorbent interface.

Batch experiments

Batch experiments were conducted to remove phosphate ions from the synthetic wastewater. The parameters like adsorbent dose, pH, contact time, shaking speed and initial concentration were optimized at 298.15 K (25°C). The residual concentration of phosphate ions were measured by colorimetric method on spectronic 20 at

460 nm.

RESULTS AND DISCUSSION

Process optimization

Factors affecting adsorption of phosphate ions on alginate-calcium carbonate complex beads were optimized by batch experiments. Figure 3a shows the graphical

Table 1. Optimized parameters for phosphate ions adsorption.

Parameter	Contact time (min)	Adsorbent dose (g)	pH	Agitation speed (rpm)	Initial concentration (mg/L)	Temperature (K)
Cadmium	150	1.5	10	100	10	298.15

Table 2. Langmuir constants calculated from Langmuir isotherm.

Adsorbate	Slope	Intercept	q_{max} (mg/g)	b	R^2
PO_4^{-3}	8.423	-3.245	0.12	-2.60	0.86

Table 3. Freundlich constants calculated from Freundlich isotherm.

Adsorbate	Intercept Log K_f	Slope (1/n)	K_f	n	R^2
PO_4^{-3}	-0.219	0.300	0.60	3.33	0.95

representation of contact time studies taken during batch experiments. The equilibrium was established after 150 min with 83.2% removal efficiency.

The effect of adsorbent dose on the adsorption of phosphates was determined by keeping other parameters constant. It has been observed that adsorption increased with increase in adsorbent dose up to certain point and then it remains constant. The increase in solid-to-liquid ratio develops some additional number of sites thus making adsorption process more efficient. Figure 3b indicate that 1.5 g adsorbent dose was sufficient to remove maximum adsorbed ions.

The effects of pH change on adsorption of phosphate ions was investigated and presented in Figure 3c with maximum removal efficiency noted at pH 10. It has been concluded from the study that the adsorbent behaviour is better under alkaline conditions, that is, at higher pH values. The effect of shaking speed is plotted in Figure 3d, at 100 rpm shaken speed maximum removal was noted. Figure 3e indicates the effect of initial concentration on adsorption capacity of phosphate ions. It was noted that adsorption was higher at lower concentrations. Optimized conditions extracted from batch experiments have been summarized in Table 1.

Adsorption models

Adsorption models provide fundamental physicochemical data for evaluating the applicability of the adsorption process as a unit operation (Vadivelan and Kumar, 2005). For modeling of the phosphate ions from wastewater commonly used, Langmuir and Freundlich models were applied. The Langmuir isotherm (Graph 4a) was obtained by the plotting the data between functions C_f (mg/L) and q (mg/g). The values of Langmuir constants "q_{max}" and "b" were calculated from slope and intercept of the isotherm (Table 2). The Langmuir constant "b" is the parameter which gives affinity of a species towards adsorption (Atkins, 1994). The value of q_{max} (0.12 mg/g) calculated from this model does not agreed with the experimentally determined value (0.62 mg/g). Furthermore, the value of R^2 is far away from unity. It is therefore concluded from observations that Langmuir model does not describe the adsorption of phosphate ions (Malakootian et al., 2009; Lin et al., 2009-02).

Freundlich isotherm (Figure 4b) was constructed by plotting log q vs. log C_f. The value of Freundlich constant, $K_f^{"}$ and Freundlich exponent, n" (Table 3) were calculated from slope and intercept of the corresponding isotherm. It is an established fact that,1<n< 10 is an indication of the favorability of the adsorption process (Harikumar and Litty, 2012).

The magnitude of the Freundlich constant K_f less than unity signs shows that the adsorption process under study was viable (Schwarzenbach et al., 2003). The trend of straight line (R^2 = 0.95) also set the applicability of Freundlich model to the experimental data.

Adsorption kinetics

Pseudo first order kinetic equaiton is stated as:

$$\ln (q_e-q_t) = \ln q_e-K_1t \tag{1}$$

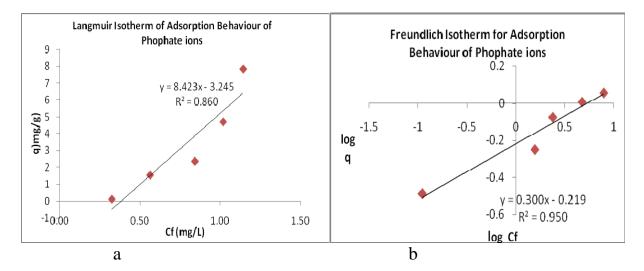Pseudo Second Order Rate Kinetics equation is demonstrated as:

Figure 4. Langmuir isotherm (a) Isotehrm adsorption behaviour of phosphate ions. (4b) Freundlich Isotherm adsorption behaviour of phosphorus.
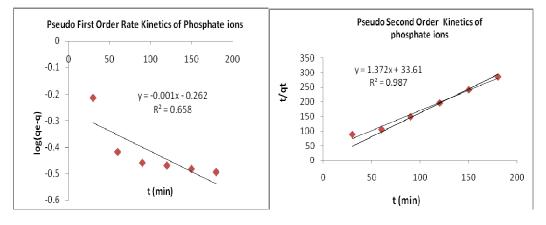

Figure 5. Kineteic isotherms.

Table 4. Rate constants calculated from pseudo first order kinetics isotherm.

Adsorbate	Intercept	Slope	$q_{e\ A.log}$ (Intercept)	$K1_{2.303}$ (Slope)	R^2
PO_4^{-3}	-0.262	-0.001	0.547	-0.0023	0.658

Table 5. Rate constants calculated from pseudo second order kinetics isotherm.

Adsorbate	Intercept	Slope	$q_e^{1/(Slope)}$	$K2^{1/(intercept)(qe)2}$	R^2
PO_4^{-3}	33.61	1.372	0.72	0.0298	0.987

$$t/qt = 1/k2qe^2 + t/qe \qquad (2)$$

From the results of Figure 5, it is clear that pseudo second order kinetic model (Ho model) is in good compatibility (R^2 = 0.987) to the process as copmared to the pseudo first order kinetic model (R^2 = 0.658) (Table 4). Furthermore, the theoretically calculated value of q_e (0.72 mg/g) from pseudo second order reaction (Table 5)

Figure 6. Graph of lnk versus 1/T for phosphate ions adsorption.

Table 6. Thermodynamic constants for phosphates adsorption at various temperatures.

Temperature (k)	ΔG (kJ/mol)	Slope (-ΔH/R)	Intercept (ΔS/R)	ΔS^0 (KJ/mol k)	ΔH^0 (KJ/mol)
293	-2.463				
298	-3.518				
303	-4.573	-7141.26	25.34	0.211	59.36
308	-5.628				
313	-6.683				
318	-7.738				

corresponds to the experimentally determined value of q_e (0.62 mg/g). These facts suggest that adsorption of phosphate ions follow the pseudo second order reaction, which was the result of chemisorption, that is, chemical adsorption (Bernard et al., 2013).

Thermodynamic parameters

Thermodynamic parameters, the standard enthalpy change ($\Delta H°$), standard entropy change ($\Delta S°$), and standard Gibbs energy (ΔG^o) of adsorption were determined. Figure 6 was plotted between lnk and 1/T. ΔG confirmed that the process was spontaneous and feasible (Ho and McKay, 2009). The values of ΔS and ΔH were calculated from the slope and intercept of the

graph (Table 6). The value of ΔH indicates that the process is endothermic, lower value of ΔS for phosphate ion adsorption indicates a very less randomness in the sorption process at the adsorbent-adsorbate interface.

Conclusions

The developed absorbent material can effectively be used for the removal of phosphate ions from waste-water. The recovery of phosphorous is a significant factor regarding the tertiary treatment of waste-water. It is inferred from this research work that alginates modified with calcium carbonate could be an effective alternative material to recover phosphate ions from contaminated water. This investigation may be extended for the confis-

cation of organic pollutants and hazardous metals from wastewater.

Conflict of interest

The authors did not declare any conflict of interest.

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