Zirconium-Treated Fine Red Mud Impregnated in Zn-Alginate Beads as Adsorbent in Removal of Phosphate from Water

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Zirconium-treated fine red mud impregnated in Zn-alginate beads (ZRMAB) are investigated for their adsorption nature towards phosphate from water by varying various physico-chemical parameters such as pH, time of equilibration, sorbent dosage, initial concentration of phosphate, presence of co-anions and temperature. The extraction conditions are optimized for the maximum removal of phosphate and the sorption ability is found to be 13.64 mg/g of the adsorbent. Substantial amounts of phosphate are removed even after ten times of regeneration of the adsorbent. Repetitive use of the same adsorbent completely removes phosphate from water. Surface morphological studies using XRD, FTIR, FESEM and EDX confirm the phosphate is onto the surface of the adsorbent. Adsorption isotherms and kinetic of sorption are analyzed and thermodynamic studies are made. The procedure developed is successfully applied to the removal of phosphate from polluted ground water samples

Keywords: Zirconium treated red mud, Zinc-alginate beads, Phosphate.

INTRODUCTION

The un-conventional methods in treating the polluted waters are proving to be effective, simple and economical. Our research group successfully developed methods for the removal of various pollutants such as Cr(VI) [1-4], Zn(II) [5], Al(III) [6-9], F⁻ [10-15], NO₂⁻ [16,17], NH₃ [18-20], PO₄³⁻ [21,22] and dyes [23-25] based on the adsorbents derived from various plants.

In continuation of our efforts in these lines of research, we herewith report an adsorbent developed with treated red mud and its absorptivity towards phosphate ions from waste waters.

The literature survey indicates that the red mud, a waste product from aluminium industries, is explored for its sorption nature for the removal of various pollutants [26-34]. In our primary investigations, red mud obtained from aluminium industries is activated with various reagents such as different acids, bases, oxidizing agents (H₂O₂), reducing agents (hydrazine sulphate) and by treating with various salts (zirconium oxy chloride). It is observed that zirconium oxychloride treated red mud shows strong affinity towards phosphate ions. The treated red mud is immobilized in the zinc-alginate beads prepared by using zinc sulphate for cross linking. Thus obtained zirconium treated red mud entrapped in zinc-alginate beads (ZRMAB) is studied for its adsorption nature towards phosphate

ions from waste waters. The present work is a detailed account of optimizing the sorption nature of the adsorbent towards the maximum removal of phosphate from water and applications.

EXPERIMENTAL

All the chemicals used in this work are analytical grade and are purchased from Merck & Co. and SD Fine Chemicals Pvt Ltd. The red mud was obtained from Vedanta Aluminium Ltd, Utkal Alumina, Lanjigarh refinery, Rayagada, India and analyzed by standard procedures. The obtained chemical composition is presented in Table-1.

Treatment: The collected raw red mud sample was repeatedly washed with distilled water till the washings were neutral to

TABLE-1
CHEMICAL PROPERTIES OF RED MUD

Parameter	Result (%)
Alumina as Al ₂ O ₃	15.47
Iron as Fe ₂ O ₃	58.78
Silica as SiO ₂	6.58
Titanium as TiO ₂	4.39
Soda as Na ₂ O	3.63
Calcium as CaO	1.49
Phosphorus as P ₂ O ₅	0.159
Vanadium as V ₂ O ₅	0.110
Loss on ignition (LOI) (105-1000 °C)	7.22

pH and then the red mud was dried for 2 h at 105 °C in an oven. Then the red mud was grinded to fine powder and sieved to 75 μ . Then 1 % zirconium oxychloride solution was added to the fine red mud sample in the ratio of 1:2 (w/w) and the resulting solution was boiled for 2 h at 110 °C. The sample was filtered, washed with distilled water repeatedly and dried at 105 °C for 2 h and then stored in air-tight coloured bottle for further work.

Impregnating Zinc-alginate beads with the treated red mud: 3.0 g of sodium alginate powder was slowly added to a 100 mL of double distilled water taken into a 250 mL beaker by continuous stirring and maintaining 1000 rpm at 90 °C until the solution is clear and homogenous. Then to this solution, 1 g of zirconium treated red mud was slowly added by stirring at 90 °C and the resulting mixture was cooled to room temperature. This solution was then added in dropwise using burette to 100 mL of 2 % zinc sulphate solution which was kept at -2 °C. (Fig. 1). Uniform-sized red mud doped zinc alginate beads were formed. These beads were filtered, washed with double distilled water to remove the additional zinc sulphate on beads and dried at 70 °C and stored in coloured bottle.

Fig. 1. Zr-treated red mud Zn-alginate beads

Surface characterization: FESEM images of the adsorbent (ZRMAB) were taken at 500 to 15,000 X magnifications at accelerating voltage of 15000 V by using the instrument HITACHI S-3700N SEM, manufactured by HITACHI high-technologies Ltd., India. FTIR spectra of the adsorbent (ZRMAB) before and after adsorption of phosphate was recorded by using SHIMADZU (8400S) FTIR spectrophotometer in range 4000 to 500 cm^{-1} at room temperature. KBr pellet method was adopted at optical resolution of 4 cm^{-1} .

XRD spectra was recorded for the adsorbent (ZRMAB) before and after adsorption of phosphate by using SHIMADZU (XRD 7000) with continuous scan mode of range 10.000 to 80.000, scan speed 2.000 (deg/min), X-Ray Cu K α radiation

at 40 kV voltage and drive axis between θ -2 θ . By using HITACHI (S-3700N) EDX detector, EDX spectrum of the adsorbent before and after adsorption of phosphate was recorded.

The pH_{ZPC} of adsorbent (ZRMAB) was determined by using HANNA pH meter, model HI2211-02 by adopting the pH equilibrium method [35,36].

Method: Batch methods of adsorption experiments were adopted using as reported method [37-39]. 100 mL phosphate solutions of concentration 50 mg/L, were taken into 250 mL conical flasks and to them different quantities of adsorbent (0.5 to 5 g) were added. Then, the pHs were adjusted to 2 to 12 by using 0.1 M HCl and 0.1 M NaOH solutions and the conical flasks were shaken using the orbital shaker at 250 rpm for 180 min at room temperature ($30^\circ\text{C} \pm 1^\circ\text{C}$). After the completion of the required time intervals, the conical flasks were removed from the orbital shaker and filtered by using Whatman No.1 filter paper. The phosphate in the solution was analyzed spectrophotometrically by “Molybdenum Blue” method [40] using the instrument UV-159 model spectrophotometer (ELICO).

The adsorbed amount of phosphate and the percentage removal was calculated by using the following eqns. 1 and 2:

$$\text{Adsorbed amount } (q_e) = \frac{(C_i - C_e)}{m} V \quad (1)$$

$$\text{Removal } (\%) = \frac{(C_i - C_e)}{C_i} \times 100 \quad (2)$$

where C_i = initial concentration of the phosphate ion solution (mg/L), C_e = equilibrium concentration of the phosphate solution (mg/L), V = volume of the phosphate ion solution in litres and m = mass of the adsorbent in grams.

In finding the effect of various physico-chemical parameters such as adsorbent dosage, pH, initial concentration of phosphate ions, interference of co-ions and temperature on the % removal of phosphate by the zirconium treated red mud-zinc alginate beads as an adsorbent, the above experimental procedure was adopted.

RESULTS AND DISCUSSION

Characterization of ZRMAB

SEM: FESEM provides surface morphology of adsorbent (ZRMAB) before and after phosphate adsorption at micro-scale. The FESEM images at different magnifications were presented in Fig. 2. Before adsorption, the images show many cavities, micro and macro pores and corners. Moreover, some crystalline aggregates belongs to mineral phases such as hematite, goethite, gibbsite are also appeared. But the images show emphatic change after adsorption of the phosphate as seen from the decrease in pores and edges indicating that the phosphate is onto the surface of the adsorbent. The same is further confirmed from the electronic images (Fig. 3) taken before and after adsorption.

FTIR: The FTIR spectrum of before and after adsorption of the phosphate onto the adsorbent (ZRMAB) were presented in the Fig. 4.

The broad spectral bands with peak at 3441 cm^{-1} (before adsorption) and 3450 cm^{-1} (after adsorption) pertain to O-H stretching vibrations of coordinate water molecules. The peak

Fig. 2. SEM images of adsorbent (ZRMAB)

Fig. 3. Electronic images of adsorbent (ZRMAB) before and after phosphate adsorption

Fig. 4. FTIR spectra of adsorbent (ZRMAB)

at 1626 cm^{-1} in both before and after adsorption spectrum is assigned to hydroxyl (OH) bending vibrations. The drastic contrast between before and after adsorption peaks is found in the appearance of a strong peak at 2356 cm^{-1} pertains to OH stretchings in O=P-OH functional group in the spectrum taken after adsorption of phosphate [41]. This is clear evidence that the phosphate is on to the surface of the adsorbent.

XRD: The crystalline phases of adsorbent (ZRMAB) before and after adsorption of phosphate were studied by XRD spectrum. The observed spectral phases are presented in the Fig. 5. As per the data in JCPDS, the spectrum clearly show the existence of the phases such as, hematite ($\alpha\text{-Fe}_2\text{O}_3$), goethite ($\alpha\text{-FeO(OH)}$), calcite (CaCO_3), gibbsite ($\gamma\text{-Al(OH)}_3$), rutile/anatase (TiO_2) and quartz (SiO_2) and further more zirconium oxide peaks also appeared at 33.51 and 38.66 as the adsorbent is treated with zirconium salts. The increase in intensity of hematite ($\alpha\text{-Fe}_2\text{O}_3$), goethite ($\alpha\text{-FeO(OH)}$) and gibbsite ($\gamma\text{-Al(OH)}_3$) and zirconium oxide peaks in the after adsorption spectrum indicate that phosphate was onto the surface of adsorbent (ZRMAB).

Fig. 5. XRD spectra of adsorbent (ZRMAB) before and after adsorption of phosphate

EDX spectrum: EDX spectrum of adsorbent (ZRMAB) before and after adsorption of phosphate were shown in Fig. 6. A clear peak of phosphorus was noticed in the after adsorption spectrum when compared with the before adsorption spectrum. This is the best evidence that phosphate is successfully adsorbed onto the adsorbent surface (ZRMAB). Moreover, the existence of spectral peaks pertain to zirconium at 2.3 in both the spectrums reflect that the zirconium is well doped in the adsorbent beads.

Fig. 6. EDX spectra of adsorbent (ZRMAB) before and after adsorption of phosphate

Impact of different physico-chemical factors on phosphate removal: Under various physico-chemical parameters such as pH, contact time, sorbent dosage, initial concentration of phosphate solution, temperature and interfering anions, the percentage removal of phosphate was studied using ZRMAB as an adsorbent. The obtained results were presented hereunder comprehensively.

pH: It is known that pH plays an important role in whole adsorption process in view of the fact that the pH influences the dissociation, or association of the functional groups present on the adsorbent at solution-adsorbent interface. Hence, the optimum pH for the successful removal of phosphate has been investigated by varying the pH conditions from 2 to 12 while keeping the other conditions of extraction at optimum levels namely agitation time: 120 min, rpm: 250, sorbent dosage: 1 g/100 mL, initial concentration: 50 mg/L and temperature 30 ± 1 °C, the observations are presented in Fig. 7(b).

It is inferred that the maximum 90.0 % of phosphate is removed at pH: 8. Below and above of this optimum pH, the percentage removal of phosphate is decreased. To understand the nature of adsorption, pH_{zpc}, has been investigated and a graph is drawn between initial pH and final pH as depicted in Fig. 7(a). The curves cross at 8.1 and it is called as pH_{zpc}. Its significance is that below this value, the adsorbent surface

Fig. 7(a). pHZPC of adsorbent (ZRMAB)

Fig. 7(b). Effect of pH on the adsorption of Phosphate

acquires positive charge due to the protonation of surface functional groups and above this value, the surface is endowed with negative charge due to the dissociation of the functional groups. As the species of phosphate are negatively charged at pH: 8, their affinity towards the negatively charged surface at higher pH value is low and hence low % of removal. However, with the decrease of pH, the dissociation of surface functional groups is not favoured and it results in the increase of phosphate removal. However at very low pH values, the predominant phosphate species is neutral and hence % removal decreases. For good adsorption, the phosphate species must possess negative charge and the adsorbent surface must have positive charge. These conditions seem to be acquired at pH: 8.

Effect of contact time: The % removal of phosphate at different time intervals while keeping other conditions of extraction constant at optimum levels has been studied and the results are present in Fig. 7(c). As the agitation time is increased from 0 to 150 min, the removal of phosphate is increased from 55.0 to 90.0 %. Initially the adsorption is more and infact 55.0 % removal is found even within 15 min of agitation but the removal is slowed down with time and the maximum of 90.0 % is attained only at 120 min of agitation and it remains almost constant with further increase agitation

Fig. 7(c). Effect of time on the adsorption of phosphate

of time up to 150 min. This indicates the reaching of equilibrium state between the adsorbent and adsorbate (phosphate) after 120 min of agitation. The rapid adsorption initially is due to the more availability of vacant sites on the adsorbent for causing the adsorption of phosphate ions but with time, the vacant sites are used up and their availability less for phosphate ions and hence the adsorption is slow down.

Effect of adsorbent dosage: The optimum dosage of adsorbent concentration is assessed by investigating the % removal by varying the dosage from 0.25 g to 1.5 g of beads/100 mL while maintaining other conditions of extraction at optimum levels. The obtained results are presented in Fig. 7(d).

Fig. 7(d). Effect of sorbent dosage on the adsorption

With increase in the adsorbent dosage, the percentage removal of phosphate also increases: 60.0 % with 0.25 g; 75.0 % with 0.50 g, 82.0 % with 0.75 g, 90.0 % with 1.0 g, 92.0 % with 1.25 g and 93.0 % with 1.5 g. As is noted that % removal almost remains constant even when the adsorbent dosage is increased from 1.0 to 1.5 g/100 mL indicating the reaching of equilibrium. The optimum dosage is 1.0 g/100 mL (in terms of beads).

Initial concentration: The effect of initial concentration of phosphate in the simulated solution on the % removal is studied by varying the initial concentration from 20 to 90 mg/L while maintaining other conditions of extraction at optimum levels. The results obtained are presented in the Fig. 7(e). It can be noted that as the concentration of phosphate ions increases from 20 mg/L to 90 mg/L, % removal decreases from 95.0 to 67.0 %.

Fig. 7(e). Effect of initial concentration on the adsorption

At lower concentrations of phosphate ions, the availability of binding sites of the adsorbent (ZRMAB) are more and hence extraction of phosphate ions is more. With the fixed amount of adsorbent, only a definite amount of adsorption sites are available and hence as the initial concentration of phosphate ion increases, there is a multiple competition to secure the sorption sites and this results in the decrease in the % removal.

Effect of co-ions: The effect of commonly found co-ions in natural waters on the % removal of phosphate has been studied by keeping the concentration of the foreign ions by 5 fold excess. The ions studied are SO_4^{2-} , NO_3^- , Cl^- , F^- and HCO_3^- . The results are presented in Fig. 7(f). It can be inferred that bicarbonate and fluoride has no effect while chloride and nitrate

Fig. 7(f). Effect of interfering anions on the adsorption

has marginal effect. Sulphate is found to interfere to some extent and % of removal has come down from 90 to 82 %.

Thermodynamic studies: With increasing the temperature from 303 to 333 K, adsorption of phosphate ions onto the adsorbent (ZRMAB) also increases from 90 to 97 % while maintaining the other conditions of extraction at optimum level namely: pH: 8, contact time: 120 min, initial concentration of phosphate: 50 mg/L, rpm: 250, adsorbent dosage: 1 g/100 mL. This indicates that adsorption of phosphate onto the ZRMAB is favoured at high temperatures and the findings are shown in Fig. 8(a-b).

Fig. 8(a). Effect of temperature on adsorption of phosphate

Fig. 8(b). Effect of temperature on adsorption of phosphate

In order to evaluate the adsorption process, energy, enthalpy and entropy considerations are to be taken into account to determine the nature of the adsorption. At different temperatures, free energy change (ΔG) (kJ/mol), enthalpy change (ΔH) (kJ/mol) and entropy change (ΔS) (kJ/mol) are determined by using the eqns. 3 to 5.

$$\Delta G = -RT \ln K_d \quad (3)$$

$$\ln K_d = \Delta S/R - \Delta H/RT \quad (4)$$

$$K_d = q_e/C_e; \Delta G = \Delta H - T\Delta S \quad (5)$$

where, q_e is the adsorbed amount of phosphate onto the adsorbent at equilibrium, K_d is the distribution coefficient, C_e

is the equilibrium concentration of phosphate ion solution, R is the gas constant and T is the absolute temperature in Kelvin and the values obtained are presented in the Table-2 [42,43].

TABLE-2 THERMODYNAMIC PARAMETERS OF ADSORPTION OF THE PHOSPHATE ON ADSORBENT						
ΔH (kJ/mol)	ΔS (J/mol)	ΔG (kJ/mol)				R^2
36.074	126.69	-2.313 (303K)	-3.579 (313K)	-4.846 (323K)	-6.113 (333K)	0.976

The negative ΔG values (calculated from the equation $\Delta G = \Delta H - T\Delta S$) indicates that the nature of the adsorption is spontaneous and the positive ΔH value (36.074) reflects that the adsorption process is endothermic and physisorption in nature. Further, the positive value of entropy change (ΔS) reveals the increase in randomness at the solid/solution interface during the adsorption process and good affinity of phosphate ions towards the adsorbent (ZRMAB).

Adsorption isotherms: The adsorption isotherms reveal how the adsorbed molecules spread between the solid phase and liquid phase when the sorption process attains an equilibrium stage. Four adsorption isotherm models namely Freundlich [44], Langmuir [45], Temkin [46] and Dubinin-Radushkevich [47], related to sorption equilibrium have been examined in the present investigation. The Freundlich adsorption isotherm model is satisfactory for a low concentrations of adsorbate and at heterogeniuos surface. It is described by eqn. 6 as follows:

$$\log (q_e) = \log k_f + \left(\frac{1}{n}\right) \log C_e \quad (6)$$

where C_e is the adsorption capacity (mg g^{-1}) and n is the empirical parameter. These parameters can be computed from the slope and intercept of the liner plot of $\log C_e$ vs. $\log q_e$. The linear form of Langmuir isotherm model presumes the homogeneous surface and mono layer adsorption. The equation for Langmuir isotherm model is:

$$(C_e/q_e) = (a_L/k_L)C_e + 1/k_L \quad (7)$$

$$R_L = 1/(1 + a_L C_i) \quad (8)$$

where q_e is the amount of adsorbed phosphate ions, k_L and a_L are the Langmuir constants. The formula (eqn. 8) gives the dimensionless separation factor (R_L) [48]. If $R_L = 1$, the adsorption is linear; $R_L > 1$, the adsorption process is unfavourable; $R_L = 0$, the adsorption is irreversible and $0 < R_L < 1$, the adsorption is favourable. The obtained results and plots while studying these two adsorption isotherms are presented in the Table-3 and Fig. 9(a-b).

For Freundlich model and Langmuir model, R^2 values found are: 0.9135 and 0.9987, respectively. This implies that Langmuir adsorption isotherm model is more acceptable indicating the homogenous nature of the adsorbent and the mono layer formation of phosphate onto the surface of the adsorbent. Furthermore, the R_L value: 0.0464 ($0 < R_L < 1$) indicates the favourable nature of the adsorption of phosphate onto the adsorbent (ZRMAB).

TABLE-3
ADSORPTION PARAMETERS

S. No.	Adsorption isotherms and kinetics		Slope	Intercept	R ²
1	Freundlich isotherm		0.3446	0.5296	0.9135
2	Langmuir isotherm	R _L = 0.0464	0.0997	0.243	0.9987
3	Temkin isotherm	B = 1.9981	1.9981	3.1489	0.9598
4	Dubinin-Radushkevich isotherm	E = 1.1180	-4E-07	2.0709	0.8574
5	Pseudo-first-order model		-0.0095	0.6043	0.9912
6	Pseudo-second-order model		0.1322	2.3339	0.9930
7	Elovich model		1.2978	0.4219	0.9692
8	Bangham's pore diffusion model		0.2522	-1.9179	0.9800

Fig. 9(a). Freundlich adsorption isotherm

Fig. 9(c). Temkin adsorption isotherm

Fig. 9(b). Langmuir adsorption isotherm

Fig. 9(d). Dubinin-Radushkevich adsorption isotherm

Further, Temkin and Dubinin-Radushkevich isotherms are also used in analyzing the sorption process and the results are presented in Fig. 9(c-d). Temkin linear equation used is:

$$q_e = B \ln C_e + B \ln A \quad (9)$$

where A and B are the Temkin isotherm constant (L/g) and heat of sorption (J/mol) respectively and B is calculated from the eqn. 10:

$$RT/b = B \quad (10)$$

where b is the Temkin isotherm constant linked to the energy parameter, R is the gas constant (J/mol/k) and T is the absolute temperature in kelvin. Linear form of Dubinin-Radushkevich equation used is

$$\ln q_e = -\beta \epsilon^2 + \ln q_m \quad (11)$$

where $\epsilon = RT \ln (1 + 1/C_e)$, β is a constant related to energy and q_m is the Dubinin-Radushkevich monolayer adsorption

capacity (mol/g). The linear plots of these isotherms are presented in Fig. 9(c-d) and the correlation coefficient and isothermal constants are presented in Table-3. By using the formula $E = 1/\sqrt{2}\beta$ and by slope of Temkin isotherm constants, the mean free energy (E) and heat of sorption (B) are calculated, respectively. As mean free energy (E) is less than 8 kJ/mol (*i.e.*, 1.118) and B is less than 20 kJ/mol (*i.e.*, 1.998), the mechanism of adsorption is “physisorption” in nature *i.e.* non-specific adsorption due to long range weak vander Waals forces between adsorbents and adsorbates.

Adsorption kinetics: The kinetics of adsorption are analyzed using four well known models namely pseudo-first order [49], pseudo-second order [50], Bangham’s pore diffusion [51] and Elovich model [52] using eqns. 12 to 15 as follows:

Pseudo-first order:

$$\log (q_e - q_t) = \log q_e - \frac{K_1}{2.303} t \quad (12)$$

Pseudo-second order:

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} t \quad (13)$$

Bangam’s pore diffusion model:

$$\log \left[\log \left(\frac{C_i}{C_i - q_t m} \right) \right] = \log \left(\frac{K_o}{2.303 V} \right) + \alpha \log (t) \quad (14)$$

Elovich equation:

$$q_t = \frac{1}{\beta} \ln (\infty \beta) + \frac{1}{\beta} \ln (t) \quad (15)$$

The results are presented in Fig. 10(a-d) and Table-3. The correlation coefficient value (R^2) are found in the order: pseudo-second-order (0.9930) > pseudo-first-order (0.9912) > Bangham’s pore diffusion model (0.9800) > Elovich model (0.9692). Hence, pseudo second-order model describe well the kinetics of adsorption.

Applications: The methodology developed in this work is applied to real polluted lake water samples collected in the Bapatla Mandalam of Guntur District of Andhra Pradesh (India)

Fig. 10(b). Pseudo-second order kinetics

Fig. 10(c). Elovich model

Fig. 10(a). Pseudo-first order kinetics

Fig. 10(d). Bangam pore diffusion model

where the phosphate contamination of lake waters is more due to excess utilization of fertilizers in the vast stretches of agricultural fields. The observations noted are presented in Table-4. It is seen from the Table-4 that the adsorbent and procedure developed in this work is successful in removing the phosphate not less than nearly 80 %.

TABLE-4
PHOSPHATE CONCENTRATION (BEFORE AND AFTER)
OF POLLUTED WATER SAMPLES AT DIFFERENT
PLACES IN ANDHRA PRADESH, INDIA

Water samples	C _i (mg/L) (initial concentration of Phosphate ions)	C _f (mg/L) (final concentration of Phosphate ions)	Removal (%)
Sample 1	13.5	1.74	87.1
Sample 2	17.7	2.40	86.4
Sample 3	20.3	3.34	83.5
Sample 4	25.8	4.46	82.7
Sample 5	29.2	5.89	79.8

Comparison: The phosphate sorption ability of ZRMAB is compared with the various adsorbents reported hitherto in the literature and comparison is presented in Table-5. It may be inferred that the present developed adsorbent has good adsorption ability than many adsorbents developed so far and further, the immobilization of the zirconium activated red mud in zinc-alginate beads, renders the filtration easy.

Regeneration and reuse: The reusability of adsorbent (ZRMAB) is studied by treating the adsorbent with different solutions namely acids, base and salt solution. With 0.1 M NaOH, the bead structure is completely lost with formation of gel and with 0.1 M Na₂SO₄ solution, the beads are bulged more weakening the cross links of the beads and furthermore the trapped activated red mud in the beads is coming out. But 0.1 M HCl is found to be good eluent for regeneration studies.

The effect of number of regenerations on the % removal of phosphate is studied using 0.1 N HCl and the results are shown in Fig. 11. It is seen that even after 10 regenerations, % removal has not come down below 84.0 % indicating the successful achievement of the developed bead-based adsorbent (ZRMAB) in the removal of phosphates. Hence, by repetitive use of the same adsorbent, it is found to remove phosphate completely from the waters.

Conclusion

An adsorbent is prepared by impregnating zirconium oxychloride treated fine red mud into the zinc-alginate beads (ZRMAB). Thus developed adsorbent has been probed for its sorption nature towards phosphate ions from water by varying the various physico-chemical parameters such as pH, time of

Fig. 11. No. of regenerations vs. removal (%)

equilibration, sorbent dosage, initial concentration of phosphate, presence of co-anions and temperature and the conditions have been optimized for the maximum extraction of phosphate. It is found that 90 % removal of phosphate is observed at pH: 8, sorbent dosage: 0.33 g (of doped red mud in 1 g of ZRMAB beads)/100 mL, 120 min of time of equilibration, 250 rpm and at 30 ± 1 °C. The commonly found co-anions even in five fold excess have marginally interfered. By immobilizing the activated red mud in the beads, the filtration process is made easy.

The surface morphological studies are made using XRD, FTIR, FESEM and EDX revealed that the phosphate is onto the surface of adsorbent. Thermodynamic parameters have been evaluated and found that the adsorption is spontaneous and “physisorption” in nature. The nature of adsorption is analyzed using Freundlich, Langmuir, Temkin and Dubinin-Radushkevich models and found that the adsorption is well described by Langmuir indicating homogenous surface of the adsorbent and mono-layer formation of the adsorbate (phosphate) on the surface of the adsorbent. The kinetics of adsorption is analyzed using various models and found that the adsorption is well described by pseudo-second-order with $R^2 = 0.9930$.

0.1 M HCl is found to be good eluent for regeneration of the adsorbent and found that even after 10 cycles of regeneration and subsequent use, the adsorbent is effectively removing substantial amounts of phosphate (to an extent of 84 %). Hence, by repetitive use of the same adsorbent, it is possible to remove phosphate completely from the waters. The method developed using ZRMAB as adsorbent is found to be remarkably successful when applied to polluted lake waters.

TABLE-5
COMPARISON OF MAXIMUM ADSORPTION CAPACITY OF ADSORBENT WITH OTHER ADSORBENTS FROM LITERATURE

S. No.	Adsorbent	pH	q _e (mg/g)	Reference
1	HCl treated red mud	5.5	0.58	[53]
2	ZnCl ₂ activated carbon	4.0	4.2	[54]
3	Lanthanum hydroxide- doped activated carbon	7.0	15.3	[55]
4	Al pillared bentonite	3.0	5.05	[56]
5	Iron hydroxide-eggshell waste	6.7	14.4	[57]
6	Industrial solid waste, Fe(III)/Cr(III) hydroxide	4.0	6.5	[58]
7	ZRMAB	8.0	13.636	Present work

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