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Short Communication

Biocomposite application for the phosphate ions removal in aqueous medium

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ABSTRACT

Mango stone biocomposite efficiency for the removal of phosphate ions (PO_4^{3-}) from aqueous solution was investigated as a function of pH (2–8), biocomposite dose (0.05–0.40 g/100 mL solution), contact time (5–120 min), initial PO_4^{3-} ions concentration (20–800 mg/L) and temperature (33–61 °C). Maximum PO_4^{3-} ions removal was achieved at pH 2, biocomposite dose 0.3 g, contact time 90 min and initial PO_4^{3-} ions concentration 200 mg/L. At optimized conditions, up to 95 mg/g PO_4^{3-} adsorption was achieved. Biocomposite pre-treatment with surfactants (SDS, Tween-80, C-TAB, VIM and Surf excel) were also investigated and it was observed that surfactants pre-treatments decreased the adsorption capacity of the biocomposite. Thermodynamic study (ΔG^0, ΔH^0 and ΔS^0) revealed that PO_4^{3-} adsorption process onto biocomposite was spontaneous and endothermic in nature. Adsorption data fitted well to the Freundlich isotherm and pseudo-second-order kinetic model. Adsorbed PO_4^{3-} was successfully desorbed using 1.0 M NaOH solution. Results revealed that biocomposite adsorbed PO_4^{3-}, which could possibly be used for the adsorption of PO_4^{3-} efficiently from wastewater.

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1. Introduction

The waste discharged from agricultural, industrial and domestic domains contain significant amount of PO_4^{3-} ions which pollute the aquatic environment [1]. The PO_4^{3-} ions > 2 μM in water is harmful and is enough to disturb the natural food chain by stimulating the growth of algae (eutrophication) and also decrease dissolved oxygen (DO), which not only is lethal to aquatic organisms, but also change the quality of water reservoirs [2–4]. Hence, there is a need to develop efficient wastewater treatment technologies that eliminate the micro-pollutants from wastewater and PO_4^{3-} ions are not easy to remove through the conventional techniques. Different physical, chemical and biological methods have been developed for the treatment of wastewater containing PO_4^{3-} ions. The biological treatments is difficult to operation because aerobic and anaerobic conditions have to main for efficient treatment of wastewater and osmosis and electro dialysis have been developed for PO_4^{3-} ions removal which are efficient, but these methods are costly [5]. Also, these methods also generate sludge, which cause secondary pollution. Under the

current scenario of pollution [6–20], there is a need to develop green and eco-friendly methods for the remediation of pollutants. Biosorption is regarded as efficient remediation tool and is equally efficient for the removal of organic and inorganic pollutants [3,4,6,13,21–31]. More recently, researchers developed adsorbents, which are cheap, easily available and do not need special maintenance during operational conditions [32]. In this regard, biocomposite based on agro-industrial by-products such as peanut hulls, rice husk, orange peel and cotton sticks are proved to be highly efficient, recyclable and cost effective. Number of studies have been conducted and biocomposites have shown high potential for elimination of metal ions, inorganic ions, dye and other organic compounds from wastewater [33–38].

In view of efficiency of biocomposite for the removal of micro-pollutants, mango stone biocomposite was prepared and used for the removal of PO_4^{3-} ions. The pH, biocomposite dose, contact time, initial PO_4^{3-} ions concentration and temperature were optimized for maximum ions removal. Moreover, effect of surfactant pre-treatment of biocomposite on adsorption capacity was also explored. Adsorption data was modeled using different kinetic and isotherms models. Thermodynamic was also computed in order to evaluate the PO_4^{3-} ions adsorption nature using biocomposite.

2. Material and methods

2.1. Chemical and reagents

The reagents and chemical used were of analytical grade, i.e., potassium dihydrogen orthophosphate (KH_2PO_4), ferric chloride ($FeCl_3$), potassium borohydride (KBH_4), ethanol, sodium hydroxide (NaOH) and hydrochloric acid (HCl) were purchased from Sigma–Aldrich. Ultra-pure water with a resistivity of $18.2 \, M\Omega \, cm$ from Milli-Q system (Millipore) was used for the preparation of solution throughout the study.

2.2. Biomass collection

Mango stone was collected from student market, University of Agriculture Faisalabad, Faisalabad, Pakistan. The mango stone extensively washed with water to remove particulate matter and dust and dried in open air followed by oven drying at $60 \, ^\circ C$ until constant weight. The dried mass was grinded (Moulinex, France), sieved (25 mm) and used for biocomposite preparation.

2.3. Biocomposite preparation

Mango stone powder (10 g) was mixed with 250 mL of $FeCl_3$, then, KBH_4 solution (~250 mL) was added drop wise with constant slow stirring. Here, KBH_4 acts as a reducing agent for the conversion of $FeCl_3$ to zero valent iron. After another 30 min stirring, the mixture was filtered; residue was extensively washed with ethanol (4 time, to remove un-reacted ions). Finally, the solid mass obtained was dried in oven at $60 \, ^\circ C$ for 24 h, grinded and passed through siever of $300 \, \mu$ (OCT-DIGITAL 4527-01).

2.4. Biocomposites pre-treatment

The biocomposite was treated with different surfactants i.e., SDS, Tween-80, C-TAB, VIM and Surf excel. All surfactants solution (5%) was prepared and agitated with biocomposite for 1 h at 120 rpm in orbital shaker at $30 \, ^\circ C$. After stipulated time period, the biocomposite was washed thoroughly with water and dried in an oven at $60 \, ^\circ C$ overnight [39] and used for adsorption process. Similar adsorption conditions were adopted both un-treated and surfactants pre-treated biocomposites.

2.5. Biosorption procedure

Stock solution of KH_2PO_4 (1000 mg/L) was prepared in distilled water and working concentrations were prepared by dilution. The pH of the solution was adjusted using 0.1 M NaOH and HCl solution. For batch biosorption experiments, pH 2–8, biocomposite dose 0.05–0.4 g/100 mL of solution, contact time 5–120 min, initial PO_4^{3-} ions concentration 20–800 mg/L and temperature 33–60 °C were investigated at fixed shaking speed of 120 rpm. Adsorption experiments were conducted in 250 mL flask taking 100 mL of PO_4^{3-} ions solution both for native biomass, surfactant pre-treated and un-treated biocomposites. After mixing of adsorbent with PO_4^{3-} ions solution and pH adjustment, flasks were covered with aluminum foil and set at 120 rpm in temperature controlled incubator shaker. After stipulated time period, the adsorbent was separated by filtration and residual PO_4^{3-} ions concentration was measured spectrophotometrically (CE Cecil 7200, UK) [40]. All experiments were carried out in triplicate, data was averaged and the adsorption capacity (mg/g) was estimated as shown in Eq. (1).

$$q_e = \frac{(C_0 - C_e)V}{W} \tag{1}$$

where C_0 is the initial PO_4^{3-} ions concentration (mg/L), C_e is the equilibrium PO_4^{3-} ions concentration (mg/L), V is the volume of the solution (L) and W is the mass of the biocomposite (g).

2.6. Desorption study

Desorption of PO_4^{3-} ions was carried out using 0.1–1.0 M NaOH solution. The loaded biocomposite was mixed with NaOH solution and stirred at 120 rpm for 2 h. The biocomposite was separated from solution and PO_4^{3-} ions concentration was measured and desorption percentage was estimated using relation shown in Eq. (2) [29]. Where, qd (%) is the percentage of PO_4^{3-} ions desorbed. D and R are representing the PO_4^{3-} ions adsorbed and desorbed, respectively.

$$qd(\%) = \frac{D}{R} \times 100 \tag{2}$$

2.7. Kinetics and isotherms molding

The kinetic models, pseudo-first-order [41] and pseudo-second-order [42] were applied to investigate the reaction rate, mass transport and rate controlling step for the adsorption of

$PO_4{}^{3-}$ ions on to biocomposite. The equilibrium experimental data was fitted using Langmuir [43] and Freundlich [44] and Harkins-Jurra [45] isotherms.

2.8. Statistical analysis

The adsorption experiments were performed in triplicate and data was reported as mean ± SD. The regression coefficients (R^2) values of isotherms and kinetics models were calculated using statistical functions of Microsoft Excel (version Office XP, Microsoft Corporation, USA).

3. Results and discussion

3.1. Optimization of process variables

The screening study was done between native and biocomposite biosorbent for $PO_4{}^{3-}$ ions removal from aqueous solution and results are shown in Fig. 1. Result indicated that biocomposite had possessed high potential for elimination of $PO_4{}^{3-}$ ions from wastewater as compared to native biomass. The optimization of process variables for the adsorption of $PO_4{}^{3-}$ ions was done for biocomposite due to its higher efficiency. Initial pH plays an important role in biosorption of ions by affecting the charge on the surface of biosorbent, degree of ionization of functional groups and solution chemistry [46]. Removal of $PO_4{}^{3-}$ ions using biocomposite was studied at a range of pH 2.0–8.0. The pH profile for $PO_4{}^{3-}$ ions removal was studied using dosage of 0.1 g, initial $PO_4{}^{3-}$ ions concentration of 50 mg/L at 33 °C for the contact time of 90 min and results are shown in Fig. 2A. From results, it was observed that the maximum biosorption capacity (60.1 mg/g) was achieved at pH 2 and after increasing pH, reduction in biosorption capacity was observed. The optimum pH was found to be 2. The higher removal of $PO_4{}^{3-}$ at lower pH might be due to production of more positive active sites on biosorbent surface, which favors the biosorption because of creating electrostatic interaction among $PO_4{}^{3-}$ and biosorbent surface [47]. Kose and Kivanc [48] found the same trend in $PO_4{}^{3-}$ ions adsorption process using calcined waste egg shell. Previous studies also showed at the adsorption of $PO_4{}^{3-}$ ions on to activated rice husk, fruit juice
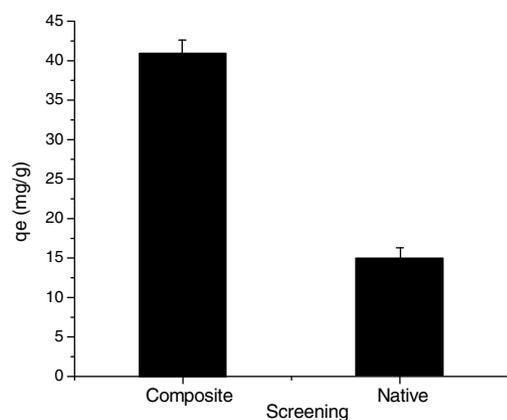

Fig. 1 – Phosphate ions adsorption comparison of native and biocomposite adsorbents (values are mean ± SD of triplicate adsorption experiments).
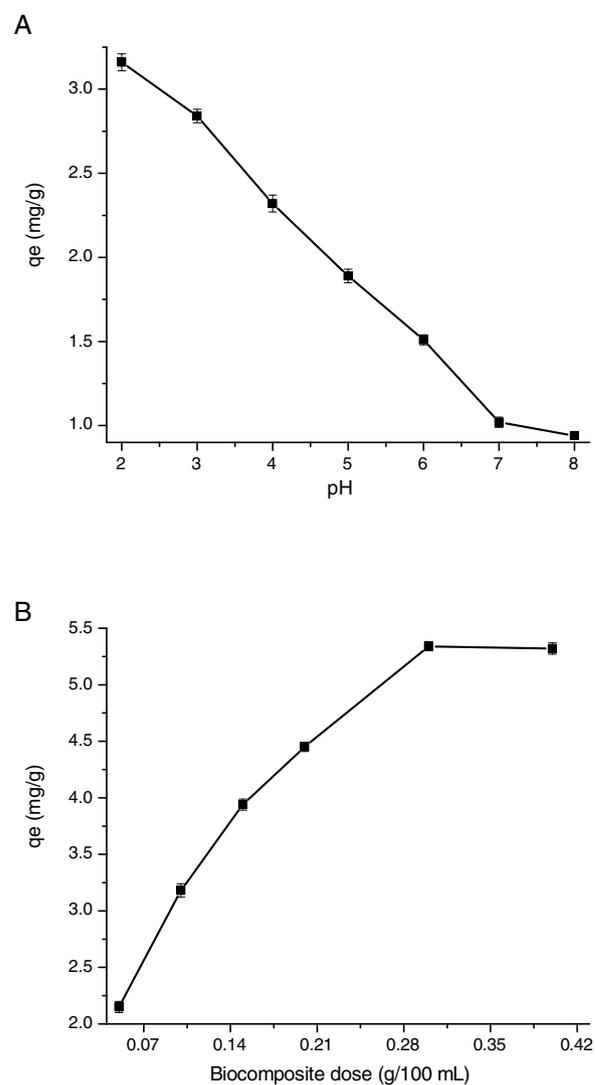

Fig. 2 – (A) Effect of pH (2–8) on the adsorption of phosphate ions on to biocomposite, (B) effect of adsorbent dose (0.05–0.40 g/L) on the adsorption of phosphate ions on to biocomposite (values are mean ± SD of triplicate adsorption experiments).

residue rice husk and fruit juice residue was highly pH dependent and adsorptions of $PO_4{}^{3-}$ ions were maximum at pH 6 and by further increasing the pH beyond this values the adsorption capacities of $PO_4{}^{3-}$ ions decreased and author correlated this behavior of $PO_4{}^{3-}$ ions adsorption with pH_{PZC} [49]. Similarly, La-modified clinoptilolite showed maximum adsorption in the pH range of 5.0–8.0 [50] and authors correlated this behavior with the formation of hydroxides. So far, under alkaline condition (pH > 8), the increased hydroxide ions would compete with $PO_4{}^{3-}$ ions for the adsorption and resultantly, complexation of $PO_4{}^{3-}$ ions suppressed and adsorbent capacity reduced.

The effect of biocomposite dose (0.05–0.4 g) on biosorption of $PO_4{}^{3-}$ was studied at optimum pH 2, 50 mg/L of initial $PO_4{}^{3-}$ ions concentration and temperature 33 °C. The results are shown in Fig. 2B. Results indicated that the adsorption capacity increased from 40.77 to 78.99 mg/g by increasing dose from 0.05 to 0.3 g/100 mL of solution and beyond this dose,

the adsorption did not increase and maximum removal was achieved at 0.3 g/100 mL of solution. The enhanced adsorption with biocomposite dose revealed the availability of active binding sites for PO_4^{3-} ions and the reduction beyond certain dose was due to overlapping of biocomposite particles, which reduced the contact between PO_4^{3-} ions and functional groups [51]. Similar results have been reported previously for the biosorption of PO_4^{3-} on to mine wastes [52].

Equilibrium time is an important parameter for designing of an economical system for the treatment of wastewater. The effect of contact time on adsorption was studied in the range of 5–120 min. The equilibrium was achieved with in 90 min at pH 2.0, biocomposite dosage 0.3 g, initial PO_4^{3-} ions concentration 50 mg/L and 33 °C (Fig. 3A). The PO_4^{3-} ions adsorption was very fast initially which was due to accessibility of high number of vacant active binding sites. Later, the removal capacity of biosorbent was slowed down due to coverage of active sites

and then equilibrium was reached with 90 min of contact time and at the time of 80.5 mg/g adsorption was observed. After achieving equilibrium, the effect of contact time was insignificant and this trend was in line with already reported studies [53]. Das et al. [54] also found the same trend in PO_4^{3-} ions removal from aqueous solution using double layered hydroxides. The initial PO_4^{3-} ions concentration gives information about driving force to reduce the diffusion mass transport resistance between adsorbate and biocomposite [29]. Adsorption capacity of biocomposite for the removal of PO_4^{3-} ions was studied in the initial concentration range of 20, 40, 60, 80, 100, 150, 200, 300 (mg/L) and results thus obtained are shown in Fig. 3B. Results showed the direct relation between biosorption capacity and initial PO_4^{3-} ions concentration, the PO_4^{3-} ions adsorption increased by increasing the concentration of PO_4^{3-} ions. The maximum removal of PO_4^{3-} ions was observed at 200 mg/L initial concentration. The highest amount of PO_4^{3-} ions taken up by biocomposite was 95 mg/g. The higher PO_4^{3-} ions uptake might be because of more probability of collision between PO_4^{3-} ions and biosorbent at higher initial PO_4^{3-} ions concentration. After coverage of all active binding sites, there was no increment in biosorption capacity was observed by increasing more initial PO_4^{3-} ions concentration [55]. Similar behavior was observed in a comparative adsorption study of PO_4^{3-} ions using different agricultural wastes [56].

Temperature is critical parameter that describes the feasibility and nature of biosorption process. Fig. 4 shows the removal of PO_4^{3-} ions from aqueous solution as a function of temperature (33–61 °C) using 0.3 g of biocomposite, pH 2, initial PO_4^{3-} ions concentration 50 mg/L and shaking speed 120 rpm. The optimum temperature was found to be 54 °C. Results demonstrated that the biosorption process was endothermic in nature because significant increment in PO_4^{3-} ions removal was observed as the temperature was increased from 33 to 61 °C. The reason behind such increment might be due to more interaction between PO_4^{3-} ions and biosorbent functional binding active sites because of high kinetic energy at high temperature [57]. Namasivayam and Prathap [58] investigated that the biosorption of PO_4^{3-} ions by Fe(III)/Cr(III) hydroxide and adsorption was endothermic of PO_4^{3-} ions.
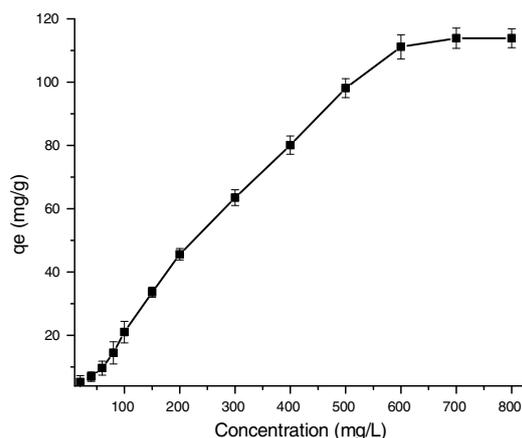
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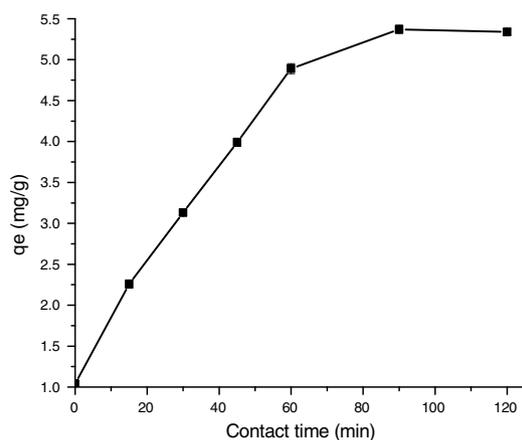
B

Fig. 3 – (A) Effect of contact time (20–120 min) on the adsorption of phosphate ions on to biocomposite, and (B) effect of phosphate ions initial concentration (20–120 min) on the adsorption of phosphate ions on to biocomposite (values are mean ± SD of triplicate adsorption experiments).

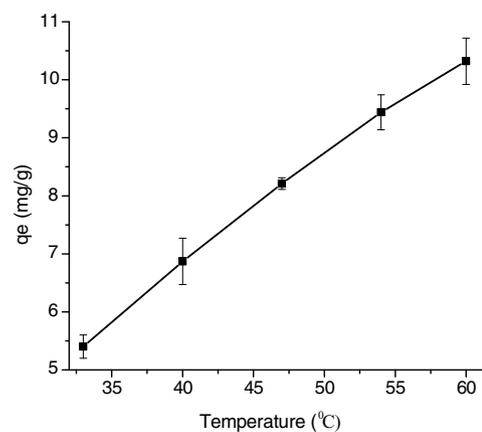Fig. 4 – Effect of temperature (33–60 °C) on the adsorption of phosphate ions on to biocomposite (values are mean ± SD of triplicate adsorption experiments).
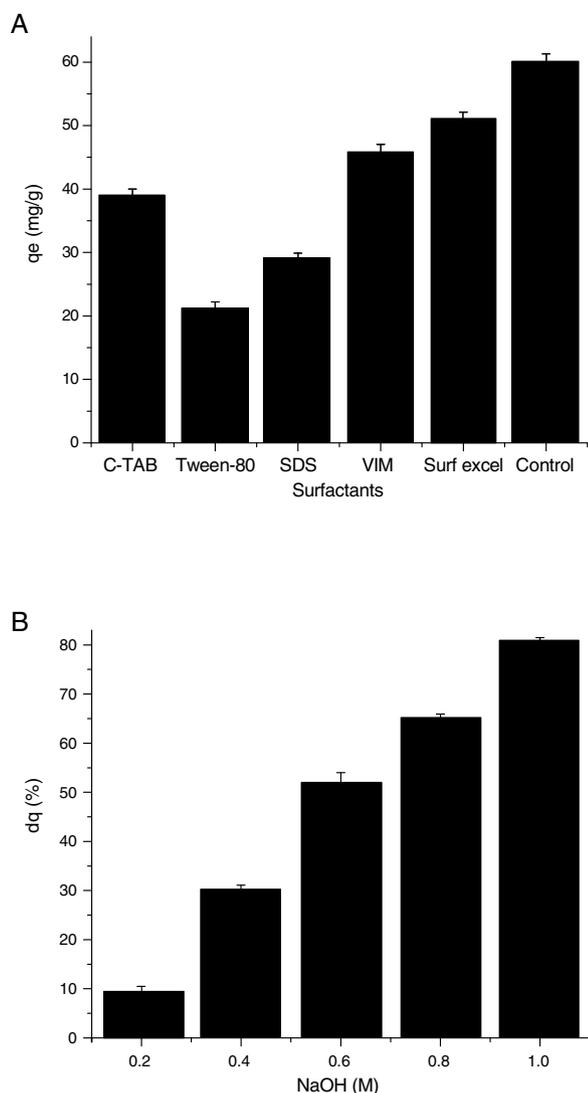
A

B

Fig. 5 – (A) Effect of surfactants pre-treatments on the adsorption of phosphate ions on to biocomposite and (B) desorption of phosphate ions using NaOH (0.2–1.0 M) as desorbing agent (values are mean ± SD of triplicate adsorption experiments).

3.2. Effect of surfactants

The effect of surfactants on biosorption capacity of biocomposite for PO_4^{3-} ions was also investigated, which showed the adsorption capacity decreased with addition of surfactants (CTAB, Tween-80, SDS and two commercial scale detergents vim and Surf Excel). Nonionic surfactant Tween-80 effect decreased the sorption capacity significantly. The results are shown in Fig. 5A. It might be due to the masking of binding sites by interaction with surfactants [59].

3.3. Kinetic modeling

The rate of removal of PO_4^{3-} ions using biocomposite was studied by applying two kinetic models i.e., pseudo-first-order [41] and pseudo-second-order [42]. The linear forms of pseudo-

Table 1 – Comparison of rate constants and coefficient of correlation for pseudo-first-order and pseudo-second-order kinetic model.

Pseudo first order kinetic Model			Experimental Value	Pseudo second order kinetic Model		
q_e (mg/g)	K_1 (1/min)	R^2	q_e (mg/g)	q_e (mg/g)	K_2 (1/min)	R^2
5.186	0.0357	0.803	80.5	78.56	0.17	0.98

first-order and pseudo-second order kinetic models are given in Eqs. (3) and (4).

$$\log(q_e - q_t) = \log q_e - K_1 \cdot \frac{t}{2.303} \tag{3}$$

The q_e and q_t represent the value of biosorption capacity at equilibrium and at time t, respectively. The rate constant of pseudo-first-order is represented by k_1 (min^{-1}). It was calculated from slope by plotting the log $(q_e - q_t)$ against t.

$$\left(\frac{t}{q_t}\right) = \frac{1}{K_2 q e^2} + \frac{t}{qe} \tag{4}$$

where q_e (mg/g) is the biosorption capacity at equilibrium, while q_t (mg/g) is the biosorption capacity at time t. The k_2 (g/mg min) is the pseudo-second-order rate constant. k_2 was be calculated from the intercept by plotting t/q_t against t. The values of kinetic parameters are given in Table 1. The pseudo-second-order kinetic model was found to be well fitted to the PO_4^{3-} ions adsorption data. The R^2, experimental and calculated biosorption capacity values were more reliable in case of pseudo-second order kinetic model as compared to pseudo-first order kinetic model. So far, the PO_4^{3-} ions followed second-order kinetic model since the q_e value determined experimentally was in agreement with the calculated value. Moreover, the R^2 value was also higher in case of second-order kinetic model.

3.4. Equilibrium modeling

The equilibrium experimental data was fitted into linear forms of three isotherms namely Langmuir, Freundlich and Harkins-Jurra. The mathematical form of Langmuir isotherm [43] is shown in Eq. (5):

$$\frac{C_e}{q_e} = \frac{1}{q_m b} + \frac{c_e}{q_m} \tag{5}$$

where C_e (mol/L) is the PO_4^{3-} ions concentration at equilibrium, while q_e (mg/g) is the biosorption capacity. b is the biosorption binding energy and q_{max} (mg/g) is monolayer biosorption capacity.

The Freundlich isotherm relation is shown in Eq. (6) [44].

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \tag{6}$$

where K_F (mg/g) and $1/n$ are the Freundlich constants and these represented the biosorption capacity and biosorption intensity, respectively, which were calculated from intercept and slope by plotting the graph between log q_e and log C_e. q_e

Table 2 – Langmuir, Freundlich and Harkins-Jura isotherm parameters for phosphate uptake by biocomposite.									
Langmuir			Exp. value	Freundlich			Harkins-Jura		
$q_{(max)}$ mg/g	B	R^2	$q_{(max)}$ mg/g	n	K	R^2	A	B	R^2
28.901	0.08258	0.955	95	0.51	91	0.987	25.90	401.65	0.761

(mg/g) is the amount of PO_4^{3-} ions biosorbed per unit biocomposite.

The Harkins-Jurra isotherm linear form is shown in Eq. (7) [45].

$$\frac{1}{qe^2} = \left(\frac{B}{A}\right) - \left(\frac{1}{A}\right) \log C_e \tag{7}$$

where A and B are the Harkins-Jurra isotherm constants. The calculated values of PO_4^{3-} ions adsorption on to biocomposite for different isotherms are given in Table 2. Among three isotherms, Freundlich showed the best fitness which explained the formation of multilayer of PO_4^{3-} ions on the surface of biocomposite. The R^2 values in case of Freundlich isotherm was considerably higher versus other two isotherms. The q_e value determined experimentally was also in agreement with calculated q_e value in case of Freundlich isotherm. So far, the Freundlich isotherm showed best fitness for the adsorption of PO_4^{3-} ions on to the biocomposite. The Freundlich isotherm describes the sorption of PO_4^{3-} ions was occurred on heterogeneous surfaces and multilayer adsorption was favorable. It assumes that the uptake of adsorbate ion occurs on a heterogeneous adsorbent surface. The Freundlich isotherm also describes an empirical relation that the stronger binding sites were occupied first and binding strength decreased by increasing the degree of binding sites occupation [31].

3.5. Thermodynamic study

Temperature effect on removal of PO_4^{3-} ions using biocomposite was studied in the temperature range of 306–334 K and changes in standard enthalpy ($\Delta H°$), standard entropy ($\Delta S°$), and Gibbs free energy ($\Delta G°$) were calculated as shown in relations (8) and (9).

$$\ln(K_d) = \frac{\Delta S°}{R} - \frac{\Delta H°}{R} \times \frac{1}{T} \tag{8}$$

$$\Delta G° = -RT \ln K_d \tag{9}$$

where K_d is the coefficient of distribution and it was calculated using the expression $K_d = q_e/C_e$. "T" represents the temperature in Kelvin (K) and R is the universal gas constant. The value of $\Delta H°$ (kJ/mol) and $\Delta S°$ (kJ/mol K) were calculated from slope and intercept by plotting the ln K_d against 1/T. From thermodynamic study, it was observed that the process for the removal of PO_4^{3-} ions using biocomposite was endothermic in nature. The high value of entropy indicating the ordering of system as biosorption process was proceeded. The value of $\Delta G°$ (kJ/mol) represented the degree of non-spontaneity of biosorption process and it was reflected energetically favorable because its value was increased with rise of temperature (Table 3).

Table 3 – Thermodynamic parameters for the adsorption of phosphate ions onto biocomposite.			
Temperature (K)	$\Delta G°$ (kJ/mol)	$\Delta H°$ (kJ/mol)	$\Delta S°$ (kJ/mol K)
306	−3.7239	45.238	0.13627
313	−2.4480		
320	−1.4388		
327	−0.6681		
334	0.129		

3.6. Desorption study

The biomass used in biosorption should be reused to make the process attractive, efficient and economical. For desorption, selection of efficient eluent is important. Desorption depends on the biosorption process, biosorbate and biosorbent can be recovered and regenerated, respectively. Since the adsorption was efficient at low pH value, so the desorption was studied using basic solution. NaOH (0.2–1.0 M) was used for the desorption of PO_4^{3-} ions [60] from loaded biocomposite. It was noted that PO_4^{3-} ions was desorbed efficiently at higher concentration of NaOH (Fig. 5B). Desorption of PO_4^{3-} ions was achieved up to 82% using 1.0 M NaOH. Overall, the biocomposite showed promising efficiency for the adsorption and desorption of PO_4^{3-} ions and could possibly be used for the removal of PO_4^{3-} ions from industrial wastewater.

4. Conclusions

Biocomposite was prepared from mango stone and used for the removal of PO_4^{3-} ions from aqueous solution. The process variable such as pH (2–8), biocomposite dose (0.05–0.40 g/100 mL solution), contact time (5–120 min), initial PO_4^{3-} ions concentration (20–800 mg/L) and temperature (33–61 °C) were optimized for maximum PO_4^{3-} ions adsorption. The PO_4^{3-} ions adsorption was achieved up to 95 mg/g at pH 2, biocomposite dose 0.3 g, contact time 90 min and initial PO_4^{3-} ions concentration 200 mg/L. The biocomposite pre-treatments with surfactants (SDS, Tween-80, C-TAB, VIM and Surf excel) decreased the adsorption capacity of the biocomposite. Adsorption data fitted well to the Freundlich isotherm and pseudo-second-order kinetic model. The thermodynamic study revealed that the PO_4^{3-} ions adsorption process was spontaneous and endothermic in nature. Biocomposite showed promising adsorption efficiency, which could possibly be used for the adsorption of PO_4^{3-} ions from wastewater and this biocomposite is also extendable to other inorganic ions sequestration from wastewater.

Conflicts of interest

The authors declare no conflicts of interest.

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