Efficacy of nanochitosan impregnated polyurethane foam in removing phosphate from aqueous solutions

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Abstract. A novel potential adsorbent was developed by impregnating chitosan nanoparticles on polyurethane foam (PFC) for the reduction of phosphate in aqueous solutions. The emergence of nanoparticles was first confirmed by the ultraviolet-visible (UV-Vis) spectroscopy. The mean size of chitosan nanoparticles between 56 nm and 112 nm was provided by the field emission scanning electron microscopy (FESEM). The presence of specific elements (C, O, P) in PFC before and after treatment was determined by energy dispersive X-ray (EDX) spectroscopy. The interplay between amino groups in PFC and phosphate ions during adsorption was identified by the Fourier transform infrared (FTIR) spectroscopy. X-ray diffraction (XRD) analysis of PFC showed nearly the same pattern before and after treatment, indicating the stability of sorbent. The point of zero charge experiment described the positive surface charge of PFC below pH 7.4. The experimental studies showed that phosphate removal efficiency by PFC increases from 35.04% to 69.78% with the decrease of influent phosphate concentration from 150 mg/L to 3 mg/L at contact time 6 h and pH 6.5. Hence PFC can be considered as an effective sorbent for removing phosphate at lower concentrations.

Keywords: Polyurethane foam, Chitosan nanoparticles, Impregnation, Phosphate, Adsorption

1. Introduction

Eutrophication has become a big danger to water bodies over the past few years. The main reason behind the same is the heavy phosphate load from industrial, agricultural and household activities [1,2]. The excess amount of phosphate also creates human health issues like kidney and liver damage, and osteoporosis. It also creates problems in water treatment plants [3]. Among various techniques used to remove phosphate, adsorption is considered to be the most effective due to simplicity, fastness, less production of sludge and high removal efficiency even at low phosphate concentration [4,5]. Some adsorbents used to remove phosphate are laterite [6], Moringa oleifera and saw dust [7], activated carbon [8], iron oxides [9], etc. The attempts to explore new adsorbents or modifying existing adsorbent to increase removal efficiency have never been stopping. Among non-conventional sorbents, chitosan has gained more attraction due to its reliability, non-toxicity and biocompatibility [10]. Chitosan can be easily modified to nanoscale by cross linking with sodium tripolyphosphate. The reactive amino and hydroxyl group of chitosan nanoparticles provide significantly improved adsorption capacity [11]. The major drawback of nanoparticles is their instability due to agglomeration. Impregnating nanoparticles on a suitable polymer will help to reduce agglomeration.
Polyurethane foam is one such polymer and has desirable properties like high flexibility, porosity and presence of carbonate group (-N(H)COO-) which binds with nanoparticles [12,13]. The present study investigated the effectiveness of a novel sorbent produced by impregnating nanochitosan on polyurethane foam (PFC) for phosphate elimination from the aqueous system. The prepared sorbent was characterized using field emission scanning electron microscopy (FESEM), energy dispersive X-ray (EDX) spectroscopy, Fourier transform infrared (FTIR) spectroscopy and X-ray diffraction (XRD). Effects of various operational parameters like contact time, pH, dosage of sorbent and influent phosphate concentration on phosphate adsorption were also found. The use of PFC in water/wastewater treatment has not been explored so far.

2. Materials and Methods

2.1 Materials
All chemicals of analytical grade were used throughout the study. Chitosan (medium MW) extra pure was purchased from Sisco Research Laboratories Pvt. Ltd. Sodium tripolyphosphate (Na5P3O10), acetic acid (CH3COOH), potassium chloride (KCl), potassium dihydrogen phosphate (KH2PO4), hydrochloric acid (HCl) and sodium hydroxide (NaOH) were supplied by Merck Millipore.

2.2 Sorbent preparation
Chitosan nanoparticles (CSNPs) were synthesised as per the methods specified by several researchers [14,15]. Sodium tripolyphosphate (TPP) of 0.1% concentration was added drop wise under magnetic stirring to the chitosan (CS) solution until the formation of opalescent nature of CSNPs solution. The impregnation of nanoparticles on polyurethane foam (PUF) was done by the method described in several studies [12,13,16]. The PUFs of size 50 mm x 50 mm x 6 mm were washed with distilled water, dried and soaked for 24 h in CSNPs solution. The excess solution was cleared and kept for solvent evaporation. The obtained PFC specimens were repeatedly washed with distilled water and stored for future use after drying.

2.3 Instrumental methods of analysis
The FESEM (HITACHI SU 6600) images were captured to get the shape and size of nanoparticles. The EDX patterns were recorded by Jeol 6390LA/OXFORD XMX N for the elemental analysis of sorbents. The nanoparticles formation was verified by the ultraviolet-visible (UV-Vis)spectrum by scanning the solution between 200 nm and 600 nm using UV-Vis spectrophotometer (Systronics 2202). The characteristic functional groups for the formation of nanoparticles and their role in impregnation on PUFs were analyzed by the FTIR spectra recorded with attenuated total reflectance method on spectroscope (Thermo Nicolet Avtar 370) at a resolution of 4 cm⁻¹. The XRD patterns were obtained by recording the relative intensities between 10° and 80° using Rigaku Ultima IV diffractometer, using Cu Ka radiation (wavelength 1.5406Å) at 25 °C. The surface charge of sorbent was evaluated by performing point of zero charge which is obtained by plotting a graph between final pH and initial pH. The pH of 0.1 M KCl solution was varied from 2 to 12. The initial pH was noted after adding PFC to each KCl solution. The final pH reading was taken after a period of 24 h. [17].

2.4 Efficacy of PFC in phosphate removal
The sorbent performance was assessed by conducting experiments in batch mode under equilibrium conditions. The pH measurement was taken using water analyzer (Systronics 371). The synthetic phosphate solution using KH2PO4 in distilled water was prepared. The phosphate adsorption efficacies of PFC with varying contact time (1 h to 7 h (at an interval of 1 h) and 24 h), pH (4, 5, 6, 6.5, 7, 9 and 11), adsorbent dosage (0.5 g/L to 4 g/L) and influent phosphate concentration (150 mg/L to 3 mg/L) were investigated at room temperature (27°C).

Phosphate removal efficiency (%) is given by,

\[ E = \left[ \frac{C_e - C}{C_0} \right] \times 100 \]  (1)
Adsorption capacity (mg/g) is calculated by,

\[ q_t = \left( C_0 - C_t \right) \times \frac{V}{m} \]  

(2)

Where \( C_0 \) is the phosphate ions concentration in the influent solution in mg/L, \( C_t \) is the phosphate ions concentration in the effluent solution in mg/L, \( V \) is the quantity of solution in L and \( m \) (g) is the amount of sorbent.

3. Results and discussion

3.1 Characterisation of sorbents

The formation of nanoparticles was verified by UV-Vis spectroscopy. The absorption spectrum of CSNPs was recorded in the range 200 to 600 nm. The highest absorption was obtained around 280 nm. The FESEM image of CSNPs (Figure 1 a) depicted the spherical shape of CSNPs with size in the range between 56 nm and 112 nm. The agglomeration tendency of CSNPs was prevented by impregnating them on PUF (Figure 1b).

The presence of phosphorus in PFC was given by EDX analysis. The appearance of peak corresponding to the phosphorus in EDX pattern (Figure 2) confirmed the presence of CSNPs formed by ionic gelation with TPP.

The major IR frequencies of CS, CSNPs, PUF and PFC are shown in Table 1. The FTIR spectrum of PFC (Figure 3) displayed characteristic bands of PUF in addition to stretching peaks of P=O and P-O of CSNPs. The peak at 1093.49 cm\(^{-1}\), represents the frequencies of C-O of PUF and/or P-O of CSNPs. The slight shifting of the peak representing N-H stretching (3274.43 cm\(^{-1}\)) and N-H bending (1618.82 cm\(^{-1}\)) vibrations of PUF after impregnating with CSNPs, established the interaction of N-H group of PUF and CSNPs in the formation of PFC. The presence of N-H stretching and bending vibration in the IR spectrum of PFC, showed the availability of free amino groups favourable for phosphate sorption.

| Possible assignments | CS       | CSNPs    | PUF      | PFC*    |
|----------------------|----------|----------|----------|---------|
| OH/N-H (stretch)     | 3444.51  | 3299.16  | 3274.43  | 3284.68 |
| C-H(stretch)         | 3109.17  | 2909.53  | 2847.55  | 2869.12 |
| C=O(stretch)         | 1658.62  | 1638.72  | 1703.86  | 1713.51 |
| N-H(bend)            | 1573.58  | 1543.43  | 1618.82  | 1628.47 |
| C-N(stretch)         | 1403.50  | 1333.53  | 1533.7   | 1533.78 |
| C-O(stretch)         | 1023.52  | -        | 1093.49  | 1093.49 |
| P=O(stretch)         | -        | 1203.26  | -        | 1228.59 |
| P-O(stretch)         | -        | 1093.49  | -        | 1093.49 |
| N-C-O(stretch)       | -        | -        | 2273.82  | 2273.82 |

* before treatment

XRD pattern of PFC (Figure 4) showed that both PUF and CSNPs retained the amorphous nature after impregnation. The CS lost its crystalline nature due to cross linking with TPP to form CSNPs. The amorphous nature of CSNPs enhances the sorption ability [18,19].

The point of zero charge of PFC is shown in Figure 5. The curves intersect at pH 7.4 which is the point of zero charge of PFC. The sorbent surface bears positive charge below pH 7.4 and negative charge above pH 7.4. The positive surface charge of sorbent is preferable for anionic adsorption and negative surface charge is preferable for cationic adsorption [17].
3.2 Batch studies on the effect of operational parameters

3.2.1 Effect of contact time. The study was conducted at room temperature by keeping the pH (6), adsorbent dose (3 g/L) and phosphate concentration (150 mg/L) as constant. The effect of contact time on removing phosphate by PFC is shown in Figure 6. The percentage adsorption of phosphate
increased with time and reached equilibrium at 6 h. The phosphate sorption was high at initial stage from 1 h to 3 h due to the accessibility of surplus unengaged sites in the adsorbent surface. After 3 h, the rate of phosphate sorption was found to slow down due to intraparticle diffusion and reached the equilibrium phase at 6 h.[20,21]. The maximum phosphate removal efficiency obtained was 34.65%. The equilibrium time was taken as 6 h for further experiments.

3.2.2 Effect of pH. The phosphate in aqueous solution can occur in various forms depending upon pH; at pH <2 ($H_3PO_4$), 2-7 ($H_2PO_4^-$), 7-12.5 ($HPO_4^{2-}$) and >12.5 ($PO_4^{3-}$) [1,20,21]. The study was conducted by varying pH of the solution (4, 5, 6, 6.5, 7, 9, and 11). Other parameters viz. room temperature ($27^\circ C$), contact time (6 h), amount of adsorbent (3 g/L) and phosphate concentration (150 mg/L) were kept constant. The effect of pH in removing phosphate is shown in Figure 7. The phosphate removal efficiency increased with pH up to 6.5 and thereafter showed a declining nature. When the solution pH increases, the accumulation of hydroxyl ions on the sorbent surface increases resulting in decreased phosphate sorption. Besides, the solution pH below the zero point of charge (7.4) favours the adsorption of phosphate. The maximal phosphate sorption efficiency of 35.04% was obtained at pH 6.5.

![Figure 6. Effect of contact time on phosphate sorption](image1)

![Figure 7. Effect of pH on phosphate sorption](image2)

3.2.3 Effects of adsorbent dosage and influent phosphate concentration. The effects of adsorbent dosage (Figure 8) and influent phosphate concentration (Figure 9) on phosphate sorption were studied by varying the dosage from 0.5 g/L to 4 g/L and concentration from 3 mg/L to 150 mg/L. The increase in sorbent dosage increased the phosphate removal efficiency due to the obtainability of more sorption sites. However, the addition of PFC, beyond optimum value, did not provide any remarkable increase in adsorption. This is due to the overcrowding of adsorbent which results in insufficient exposure of the adsorbent surface to pollutants. This low utilization of the sorbent surface at higher dosage resulted in low phosphate adsorption capacity[18,21].

The phosphate removal efficiencies were found to increase from 35.04% to 69.78% with decreasing phosphate concentrations from 150 mg/L to 3 mg/L. This is because of the lesser availability of sorption sites at higher phosphate concentration. The availability of adsorption sites decreases with the increase of adsorbate concentrations [18]. The optimum dosage of sorbent was found to increase with the increasing phosphate concentration, due to the need for more adsorption sites at higher concentrations.

PFC was found to be more effective in removing phosphate for all influent concentrations (less than 60 mg/L) when compared to the previously reported adsorbents such as powdered activated carbon (51.62% of phosphate removal from 5 mg/L of phosphate solution) [22], granular activated carbon (40.29% of phosphate removal from 5 mg/L of phosphate solution) [22] and silver...
nanoparticles loaded activated carbon (54.62% of phosphate removal from 50 mg/L of phosphate solution) [2].

![Graph](image1.png)

**Figure 8.** Effect of adsorbent dosage on phosphate sorption

![Graph](image2.png)

**Figure 9.** Effect of influent phosphate concentration on phosphate sorption

### 3.3 Mechanism of phosphate adsorption by PFC

The mechanism of phosphate sorption by PFC was established by FTIR spectroscopy. The phosphate sorption by PFC is mainly due to the interaction between ammonium ions and phosphate ions. The same can be described by the emergence of a new band at 3051.87 cm\(^{-1}\) after phosphate sorption in the FTIR spectrum of PFC (Figure 10). The schematic representation of mechanism is given in Figure 11. The XRD pattern before and after the phosphate sorption process of PFC (Figure 12) showed almost similar pattern, indicating the stability of adsorbent [23]. The EDX patterns of PFC after treatment (Figure 13) showed an increase in weight % of phosphorus, confirming uptake of phosphate from solution.
4. Conclusion
The present study investigated the capacity of a novel sorbent PFC in removing phosphate ions from aqueous solutions. The FESEM images conveyed the presence of nano-sized particles and the EDX pattern confirmed the presence of CSNPs on PFC. The presence of suitable functional groups for phosphate sorption was identified by the FTIR spectrum of PFC. The XRD results verified the amorphous nature of PUF and CSNPs before and after impregnation. Batch studies at optimum operating conditions revealed the efficacy of PFC in phosphate sorption, especially at low influent phosphate concentrations. The effectiveness of PFC in removing phosphate is due to the presence of amino groups. The lesser availability of sorption sites at higher phosphate concentrations resulted in reduced removal efficiency. The incorporation of additional functional groups along with amino groups may enhance the phosphate removal efficiencies at higher influent concentrations. Thus, PFC can be considered as a promising sorbent for phosphates from natural water and wastewater with phosphate concentration below 60 mg/l.

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