



Adsorption studies for the removal of nitrate using chitosan/PEG and chitosan/PVA polymer composites



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ABSTRACT

This paper presents a study of the removal of nitrate ions using polyethylene glycol/chitosan and polyvinyl alcohol/chitosan composites were investigated. A series of batch experiments were conducted to examine the effects of contact time, adsorbent dosage and pH of the solution. Composite materials successfully adsorb nitrate from aqueous solutions at pH 3. Adsorption isotherm studies indicated that polymer composites satisfy Langmuir and Freundlich models. The rate of reaction follows pseudo-second-order kinetics. The adsorption capacities of PEG/chitosan & PVA/chitosan were found to be 50.68 and 35.03 mg g⁻¹ respectively. The prepared adsorbents were characterized by Scanning electron microscopy (SEM), Energy dispersive analysis of X-rays (EDAX), Fourier Transform Infra-Red (FTIR), BET surface area and X-ray Diffraction (XRD). The results of the study indicated that polyethylene glycol/chitosan and polyvinyl alcohol/chitosan composites are useful materials for the removal of nitrate from aqueous solution.

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1. Introduction

Water resources are heavily polluted by several nitrogen containing compounds, such as nitrate, nitrite, and ammonium, which may cause severe environmental problems including eutrophication. Nitrate, in particular, causes outbreaks of infectious diseases such as cancer of the alimentary canal and cyanosis among children [1]. Excess nitrate in drinking water may cause blue-baby syndrome, which results from the conversion of hemoglobin into methaemoglobin, which cannot carry oxygen [2].

Therefore, numerous techniques for the removal of nitrate from water samples have been reported. These include biological processes (denitrification, nitrification), chemical processes like breakpoint chlorination, reverse osmosis, electro dialysis, ion exchange, electrochemical technologies and catalytic reduction are well known process and these processes are used for water treatment in recent days [3–7]. Adsorption is one such a process. Adsorption in general, is a process of collecting soluble substances that are in solution on a suitable interface. In the past, adsorption process was not used extensively in wastewater purification but demands for a better quality of treated wastewater or effluent have led to an intensive examination and use of the process of adsorp-

tion on activated carbon. As an activated carbon is a very expensive adsorbent for the removal of pollutant other adsorbents must be investigated [8].

Recently, different types of adsorbents have been used such as resins, nanomaterials [9–16] including some industrial and agricultural wastes such as activated waste sepiolite [17] and modified wheat residue [18] have been used to remove nitrate from water. The biopolymer chitosan has gained importance in environmental biotechnology due to its very high adsorption capacity of dyes and metal ions [19]. Moreover, chitosan can be obtained on an industrial scale by chemical deacetylation of crustacean chitin. Chitosan has become a very effective biosorbent for the removal of heavy metals in the field of industrial wastewater treatment [20].

Recently, graphene and multi walled carbon nanotubes are used for adsorption of nitrate [21]. Polymer blending has become a method for providing polymeric materials with desirable properties for practical applications. In particular, chitosan blended with poly (vinyl alcohol) (PVA) has been reported to have good mechanical and chemical properties and, as a topic of great interest, has been extensively studied in the biomedical field. The enhanced property has been attributed to the interactions between PVA and chitosan in the blend through hydrophobic side chain aggregation and intermolecular and intramolecular hydrogen bonds. The adsorption properties and mechanisms of the PVA and chitosan blend for metal removal are however seldom been studied [22]. Polyethylene glycol (PEG) has been widely used because of their

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biocompatibility and minimal toxicity. PEG and chitosan hydrogel can swell extensively due to the positive charges on the network and in response to changes in the pH of the medium. It is reported already that it is possible to improve adsorption properties of chitosan through the formation of blends with PEG [23].

In the present study chitosan composites were prepared with polyvinyl alcohol and polyethylene glycol, studied the morphology, and the suitability of the prepared composites for the removal of nitrate from aqueous solutions was evaluated under different experimental conditions. The kinetics of nitrate removal was also observed. The capacity of the adsorbent to be reused was also tested. Perusal of literature did not show that a study had been carried out for the removal of nitrate from water using PEG/chitosan and PVA/chitosan composites.

2. Materials and methods

2.1. Materials required

Chitosan with a degree of deacetylation of 90% (80 meshes) was purchased from Pelican biotech and chemicals lab oratory, Kerala. Polyethylene glycol (PEG), Poly vinyl alcohol (PVA) (with a degree of polymerization of 1750), CaCO₃, HCl and potassium nitrate were purchased from Sigma–Aldrich, Mumbai, India. Stock solution of nitrate from potassium nitrate was prepared by dissolving an appropriate amount of substance in Millipore water.

2.2. Preparation of PEG/chitosan and PVA/chitosan composites

PEG/CaCO₃ and PVA/CaCO₃ powder were added to 150 mL distilled water and blended by a mechanical stirrer in a boiling water bath for 2 h. Then chitosan was introduced to the above solution, shaken at 80 °C for 6 h. The obtained mixture was cooled to room temperature, HCl (5 M) was added to the solution and the mixture was stirred vigorously to dissolve CaCO₃ and to produce CO₂ gas bubbles, finally it was filtered, dried and the material obtained was used as adsorbent. The above mentioned procedure was followed for the preparation of PVA/chitosan composites. The mixed solution of PEG/CaCO₃/chitosan and PVA/CaCO₃/chitosan was prepared according to the following weight ratios: 10/5/2, 10/5/4, 10/5/6, 10/5/8 and 10/5/10. The ratio 10/5/10 was fixed taking into consideration of its good adsorption capacity [24].

2.3. Adsorbent characterization

The surface morphology and elemental composition of the adsorbent before and after adsorption was analyzed by scanning electron microscopy (SEM) and Energy dispersive analysis of X-rays (EDAX). The surface area and the pore structure of the synthesized catalyst were investigated by performing N₂ physical adsorption–desorption studies at 77.35 K. N₂ adsorption/desorption isotherm and pore size distributions using Barret–Joyner–Halenda (BJH) method. The IR spectra of the adsorbent before and after adsorption were recorded by a Fourier transform infrared spectrometer. The composites were characterized by X-ray diffraction studies (XRD) also.

2.4. Adsorption experiments

Adsorption experiments were carried out by batch study. About 0.1 g of the polymer composite adsorbent [polyethylene glycol/chitosan and polyvinyl alcohol/chitosan] was added to 50 mL of 10 mg L⁻¹ adsorbate solution. Mixture was shaken by a mechanical shaker at 200 rpm under room temperature. The adsorption efficiency of polymer composite for nitrate was studied with varying

parameters such as contact time (10–60 min), dosage (0.1–0.5 g), pH (3–11) etc.

The percentage removal of nitrate and equilibrium adsorption uptake in the solid phase, q_e (mg g⁻¹), was calculated using the following relationship.

Amount of adsorbed nitrate,

$$q_e = (C_o - C_e) \frac{V}{w} \quad (1)$$

where C_o is the initial concentration of nitrate solutions (mg L⁻¹), C_e is the equilibrium concentration of nitrate (mg L⁻¹), V is the volume of the solution (L), and w is the mass of the adsorbent PEG/chitosan and PVA/chitosan (g).

2.5. Desorption experiments

Desorption study would give a clear idea about the stability of the adsorbent for further use. The PEG/chitosan and PVA/chitosan composites were regenerated using 0.025 M NaCl solution. The optimum time and volume of regenerant were fixed and the process was continued upto five cycles.

3. Results and discussion

3.1. Characterization of PEG/Chitosan and PVA/Chitosan composites

SEM pictures taken before and after adsorption of nitrate onto PEG/chitosan and PVA/chitosan composites are shown in Fig. 1 respectively. Surface exhibits well-developed open pores which facilitate mass transfer of nitrate ions onto the adsorbent [25]. The change in micrographs of the PEG/chitosan and PVA/chitosan before and after nitrate treatment indicates a layer of adsorbate covered in the adsorbent while its internal structure stays the same. This is additionally supported by Energy dispersive analysis of X-rays (EDAX) method which provides a direct proof of the adsorption of nitrate ion onto PEG/chitosan and PVA/chitosan. The EDAX spectra of PEG/chitosan and PVA/chitosan after adsorption of nitrate confirm the presence of respective ion. Fig. 2 shows EDAX spectra of nitrate ions in the treated PEG/chitosan and PVA/chitosan adsorbents [26].

3.2. FTIR spectral analysis

FTIR analysis of (a) PEG/chitosan (b) phosphate adsorbed PEG/chitosan were carried out and are depicted in Fig. 3(A) PEG/chitosan composite displayed characteristic peak at 3424 cm⁻¹ is attributed to –NH₂ and –OH groups stretching vibration in the chitosan matrix [27]. The chitosan amide peaks slightly shifted to 1632 cm⁻¹ and 1525 cm⁻¹, respectively. The shifts were possibly due to hydrogen bonding between amide carbonyl with PEG hydroxyl [28]. Furthermore, the increased intensity of the peaks at around 2884 cm⁻¹ and 1100 cm⁻¹ indicated the CH₂ groups and C–O–C stretch of PEG. The disappearance of peaks at 953 and 839 cm⁻¹ is attributed to the formation of PEG/chitosan (well mixed) [29]. Sharp peak at 1382 cm⁻¹ in the nitrate adsorbed on PEG/chitosan was contributed by N–O stretching [30]. The other bands are characteristics of the sorbent PEG/chitosan.

Fig. 3(B) shows the FTIR spectra of (a) PVA/chitosan (b) nitrate adsorbed PVA/chitosan. Peak at 3428 cm⁻¹ is indicative of OH and NH stretching vibrations [31]. The bands at 1645 cm⁻¹ and 1377 cm⁻¹ are due to the presence of –NH₂ bending vibrations and –CH symmetric bending vibrations in –CHOH [32]. Band at 2917 cm⁻¹ indicated C–H stretching. The peak at 1727 cm⁻¹ is characteristic of C=O bands. After the sorption of nitrate broadening of band was adsorbed at 3433 cm⁻¹ in PVA/chitosan which

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