

Adsorption of Nitrates Using Quaternized Chitosan Resin

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Abstract

Preparation of a terpolymer of melamine-glutaraldehyde cross linked chitosan was attempted. The resin was quaternized with Tetramethyl ammonium chloride (TMAC) to form Quaternized Melamine-Glutaraldehyde- Chitosan Resin (QMGR), which was used for the selective adsorption of nitrate from contaminated water. Prepared resin was characterized using FTIR and optimization adsorption conditions were done by batch method. Adsorption of nitrate to the resin was confirmed by FTIR analysis of the adsorbed resin and UV-Vis analysis of the left solution. Resin showed an adsorption capacity of 117.6 mg/g from 1000 mg/mL solution of nitrate. Adsorption capacity was also tested with water samples collected from four nearby rivers and the resins adsorption capacity was not much affected. Resin was regenerated and tested adsorption capacity up to 5 cycle. The Cl^- ions of quaternized resin was replaced by nitrate ions through selective adsorption and exchange mechanism

Keywords: QMGR; TMAC; Nitrate; Adsorption; Regeneration

Introduction

Not just for mankind but for the sustenance of all living beings water is the basic necessity. Good quality water falls into the category fundamental needs. However, this has become increasingly difficult due to the large scale pollution caused by agricultural and domestic and industrial activities, which generate wastewater which containing both organic and inorganic pollutants.

The main sources of nitrate pollution are the over usage of nitrogen fertilizers and poor pollution control measures from industrial sites. Due to the mining, industrial and agricultural activities, nitrate and phosphate are largely released to aquatic systems [1]. Nitrate could chronically exist in surface and ground water due to its high solubility and poor adsorption property, which is the reason behind difficulty in nitrate removal [2]. The accumulation of nutrients leads to fast growth of aquatic plants and algae, leading to depletion of dissolved oxygen, resulting in eutrophication [3]. Nitrate is also hazardous to human health; it can cause infant methemoglobinemia, the "blue baby" syndrome as well as generating nitrosamines and nitrosamides that are known to be carcinogenic [4]. Symptoms of nitrate poisoning in livestock include cyanosis in and about the non pigmented areas (mouth and eyes), shortening of breath, rapid heartbeat, staggered gait, frequent urination and collapse. In severe cases, coma and death may result within a few hours [5]. Because of the link between health problems and excessive concentration of nitrate in drinking water, the World Health Organisation (WHO) and regulatory agencies in various countries have stipulated nitrate concentration limits. The nitrate concentration limit recommended by WHO and the European Union is 50 mg NO_3^- per Litre. To protect the environment, it is sensible to have them removed from waters.

For the removal of nitrates and detoxication of wast water several physicochemical and biochemical processes have been investigated so far, namely, ion exchange [6], biological denitrification [7], reverse osmosis [8], electrochemical reduction [9], catalytic reduction [10] and adsorption [11,12]. But each the method had its own disadvantages. Ion exchange method though it works perfectly renewal of costly ions and disposal of waste brine made it less demanding. Biological method was in need of addition of carbon source and disposal of large amounts of biomass waste. Electrochemical reduction was also not without flaws as the electrodes were easily inactivated. High operational

cost was the problem with reverse osmosis, especially for commercial application. Nitrite and ammonia are hazardous by-products ruling out the possibility of catalytic reduction as a greener technology. Hence adsorption was found to be superior to other techniques in terms of its low cost, ease of operation and simplicity of design [13]. There is lesser amount of sludge and hence fewer disposal problem. It's essential to fabricate high capacity efficient adsorbents that are easy to operate and cheap. Materials such as clay adsorbents, hydrotalcite-like compounds, chitosan hydrogel beads, fly ash, and layered double hydroxides have been used as adsorbents.

Recently, efforts have been taken to remove nitrate from waste water using different kinds of adsorbents like carbon-based adsorbent [14], mineral-based adsorbent [15] and agricultural waste [16] were employed to remove nitrate from aqueous solution. However, these materials had some inherent limitation including small particle size or low desorption efficiency, which might hinder their practical application. Techniques like surface protonation [17], metal ions immersion [18] and surfactant modified mineral were also applied to enhance their adsorption of nitrate. But these modifiers had potential adverse effect on environment. As a consequence, developing an easily reusable, technically feasible and environmentally friendly adsorbent was of prime importance for the nitrate removal.

Natural polymers, in particular polysaccharides such as chitin and its derivate chitosan have gained much attention as an efficient adsorbent for many ions in the waste water. Chitosan has a high content of amino and hydroxyl functional groups which are essential for the adsorption and removal of aquatic pollutants [19]. The choice of chitosan as the adsorbent was due to its remarkable physico-chemical characteristics, chemical stability, high reactivity, excellent chelation behaviour and high selectivity toward many aquatic pollutants [20-24].

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Even then chitosan has the shortcomings, namely, poor chemical stability and mechanical strength [25]. For example, being completely soluble below pH=5, chitosan could not be utilized as adsorbent in wastewater that is acidic [26]. These drawbacks demands for the development of composite materials due to their tunable properties and synergistic natures. Chitosan appropriately modified by incorporated into a composite; it's ideated to enhance the properties of chitosan. Several Physical and Chemical methods have been investigated so far for the selective adsorption of various aquatic pollutants.

Nitrates get very easily adsorbed in the quaternary ammonium groups [27]. The amino groups of chitosan has been utilised for introduction of carboxylic group, protons, various metal ions and quaternary ammonium groups for the application of water treatment. Introduction of more amino groups in chitosan through grafting with monomers which are rich in amino groups and its modifications also have gathered attention in this field. Studies focused on the adsorptive removal of nitrate and using chitosan based materials are very few. Melamine having three primary amino groups in its structure is able to cross-link strongly with aldehydes. This work has been carried out with the intention of grafting melamine into chitosan skeleton with glutaraldehyde as the cross-linker to produce a novel chitosan derived hybrid material with enhanced efficiency. A terpolymer of chitosan-melamine-glutaraldehyde has been successfully prepared and it was quaternized with TMAC to make it suitable for the adsorption of nitrate. The adsorption behaviour of the QMGCR towards nitrate was studied in batch mode. The efficiency of QMGCR was analysed with 5 regeneration cycles (Table 1).

Materials and Methods

Materials

Ninety Five Percent deacetylated Chitosan powder was purchased from Sigma-Aldrich. Gluteraldehyde, Melamine and Tetramethylammonium chloride were purchased from High Media. Analytical grade HNO₃ was used as source for producing nitrate anions for the optimization of resin. Glacial acetic acid, Na₂HPO₄ and NaH₂PO₄ used as phosphate buffer for Gluteraldehyde, NaCl were also analytical grade. Water contents were analysed using standard Water Testing Kits (Figure 1).

Methods

Preparation of Quaternary Ammonium Chloride Functionalised Chitosan-Melamine-Glutaraldehyde Resin (QMGCR): The chitosan powder was dissolved in 2% acetic acid solution by stirring for 48



Figure 1: Prepared Chitosan Beads.

hrs. The dissolved chitosan was uniformly transformed to melamine-glutaraldehyde dispersion (2 g of melamine was dispersed in 2.5 wt.% glutaraldehyde solution) using a dropper adjusted at 10 cm above the beaker. The solution was continuously stirred for 48 hrs. The resultant chitosan-melamine-glutaraldehyde beads were filtered and washed with double distilled water to remove unreacted melamine and glutaraldehyde. The wet chitosan-melamine-glutaraldehyde beads were treated with 20% Tetramethyl ammonium Chloride (TMAC) at 60°C for 24 hrs. The quaternized terpolymer beads were washed well with double distilled water to remove excess of TMAC and dried at room temperature to get QMGCR. The preparation route is shown in Figure 2.

Analytical instrumental techniques: FTIR spectra were collected on Thermo Nicolet, Avatar 370 model. The analysis of nitrate was carried out using UV/VIS Spectrophotometer (Spectrophotometer JASCO V-730).

Batch experiments

Batch adsorption studies have been carried out in stopper bottles containing 50 mL of nitrate and phosphate solutions (100 mg/L) and 0.1 g of adsorbent at solution pH. Then reaction mixture was agitated in mechanical shaker (120 rpm) at room temperature for desired time followed by filtration. The left out concentration in the supernatant solution after adsorption process was analysed spectrophotometrically. The adsorption capacity was calculated from Eq. (1) where q_e is the anion adsorbed (mg/g), C_0 is the initial concentration of anion (mg/L), C_e is the concentration of anion in solution at equilibrium time (mg/L), V is the solution volume (L), and m is the adsorbent dosage (g) [27]. Experiment was repeated by changing adsorbent dosage. Regeneration of QMGCR after the adsorption studies of both nitrate and phosphate were carried out using 0.025 M NaCl at various contact times. The efficiency of the regenerated samples was checked.

$$q_e = (C_0 - C_e)V/m \quad (1)$$

Results and Discussion

FTIR analysis

In order to fully characterize the starting materials, a spectrum of pure chitosan (Figure 3) was recorded. The main bands appearing in that spectrum were due to stretching vibrations of O-H groups in the range from 3800 cm⁻¹ to 3100 cm⁻¹, which are overlapped to the stretching vibration of N-H; and C-H bond in -CH₂ (2920 cm⁻¹). Bending vibrations of methylene group was also visible at 1380 cm⁻¹. Absorption 1650 cm⁻¹ was due to the stretching vibrations of carbonyl bonds (C=O) of the secondary amide group CONHR. Absorption in the range from 1300 to 1000 cm⁻¹ has been attributed to vibrations of C-O group. The band located at 1080 cm⁻¹ is related to asymmetric vibrations of C-O in the oxygen bridge resulting from deacetylation of chitosan. The small peak at ~910 cm⁻¹ corresponds to wagging of the saccharide structure of chitosan. The peak around 2320 cm⁻¹ is due to interference atmospheric carbon dioxide which was not eliminated during background collection [28].

Initial Concentration	Adsorbent Dosage (g)	Adsorption Capacity (mg/g)
100 mg/L	0.1	29.9
	0.2	30.8
	0.3	32.8
	0.4	33.6
	0.5	37.4
1000 mg/L	0.1	117.6
2000 mg/L	0.1	143.1

Table 1: Variation of adsorption capacity.

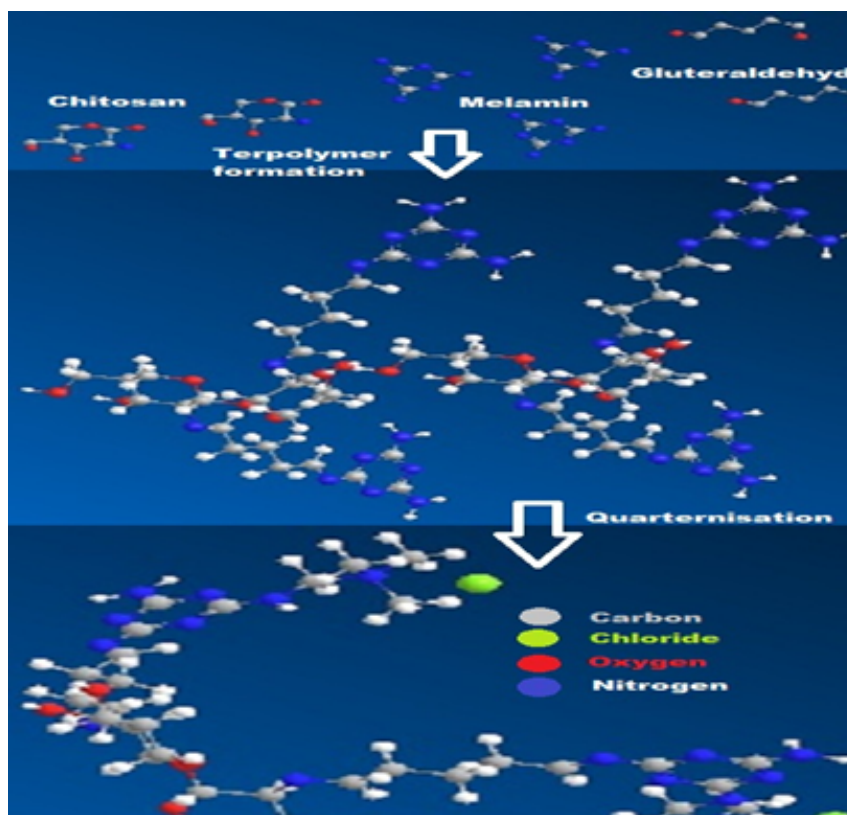


Figure 2: Scheme of Quarterisation.

Absorptions in the range $3690\text{--}3100\text{ cm}^{-1}$ are due to the O-H and N-H stretching in cross-linked chitosan (Figure 4). A peak at 1630 cm^{-1} was observed due to the N-H bend. The band 1375 cm^{-1} was attributed to C-H symmetric bend. Peaks from $1250\text{ to }1000\text{ cm}^{-1}$ are attributed to the C-O stretching vibration in C-OH. The broad band at $720\text{--}590\text{ cm}^{-1}$ was contributed by O H out-of-plane bend [29].

The IR bands in the spectrum of melamine (Figure 4) in the region of 1552 and 1443 cm^{-1} were attributed to the heterocyclic ring stretching and the band at 814 cm^{-1} corresponds to the bending vibration of the same. The bands corresponding to NH_2 groups are 3467 , 3417 , 2684 (asymmetric stretch), 3334 (symmetric stretch), 1641 (bending) and 617 cm^{-1} (waging) [30].

The IR bands in TMAC (Figure 4) observed near 550 cm^{-1} is assigned to C-N-C skeletal vibration and the band observed at 820 cm^{-1} is assigned to C-N stretching mode of vibration. The rocking of CH_3 is assigned to the bands observed at 1270 cm^{-1} . The band at 1490 cm^{-1} is assigned to the in-plane bending mode of CH_3 and the out of plane bending is assigned to the band at 1520 cm^{-1} . Symmetric and asymmetric stretching of CH_3 is observed at 3020 cm^{-1} and 3030 cm^{-1} respectively. The characteristic bending absorption of CH_3 is obtained at 1392 cm^{-1} . The band observed around 1650 and 3470 cm^{-1} assigned to the O-H bending and stretching vibration respectively [31].

In QMGCR (Figure 5) the corresponding peaks of cross linked Chitosan and heterocyclic ring (1552 , 1443 and 814 cm^{-1}) of melamine are present. The intense peak at 3390 cm^{-1} was due to the N-H and O-H groups in quaternized resin. N-H bend contributes at 1633 cm^{-1} . Sharp peak at 1380 cm^{-1} in the nitrate adsorbed QMGCR (Figure 5) was contributed by N-O stretching [27].

UV-Vis analysis

The left out concentration in the supernatant solution after adsorption process was analysed spectrophotometrically in which the absorbance was measured at wavelength at 300 nm (Figure 6). A decrease in absorbance was observed. When adsorbent dosage was increased there was a corresponding reduction in absorbance (Figure 7).

Effect of various parameters

The variation in adsorption capacity of resin was studied using 100 mg/L nitrate solutions. Five samples of same initial concentration were analysed using UV after treatment with different doses of adsorbent varying from 0.1 g to 0.5 g . As the adsorbent dosage was increased there occurred an exponential increase in adsorption capacity of the resin. There was significant increase in adsorption capacity with increase in initial concentration as well as increase in adsorbent dosage. Significant removal of nitrate was observed within 5 minutes and contact time was optimised to 30 minutes. When the adsorption was carried out from a solution containing both phosphate and nitrate ions there was preferential adsorption on nitrate than phosphate. But presence of phosphate accelerated fungal growth on water sample when kept open for few days. Adsorption was also studied using water samples from near by rivers namely; chaliyar, kallayi river, korappuzha and kadalundi river the resin retained adsorption capacity even in presence of other ions like fluoride, sulphate and chloride, though there a slight decrease in adsorption capacity.

Regeneration of resin

The resin was easily regenerated by soaking it for an hour in 0.25 M

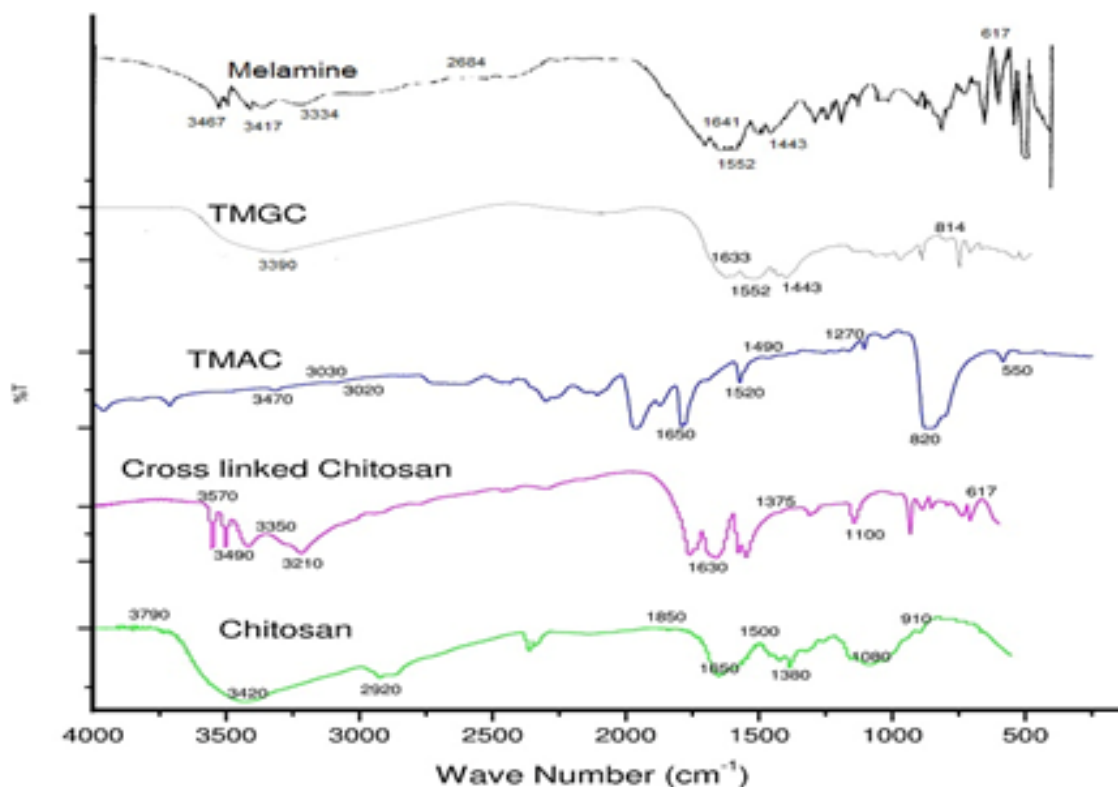


Figure 3: FTIR Analysis.

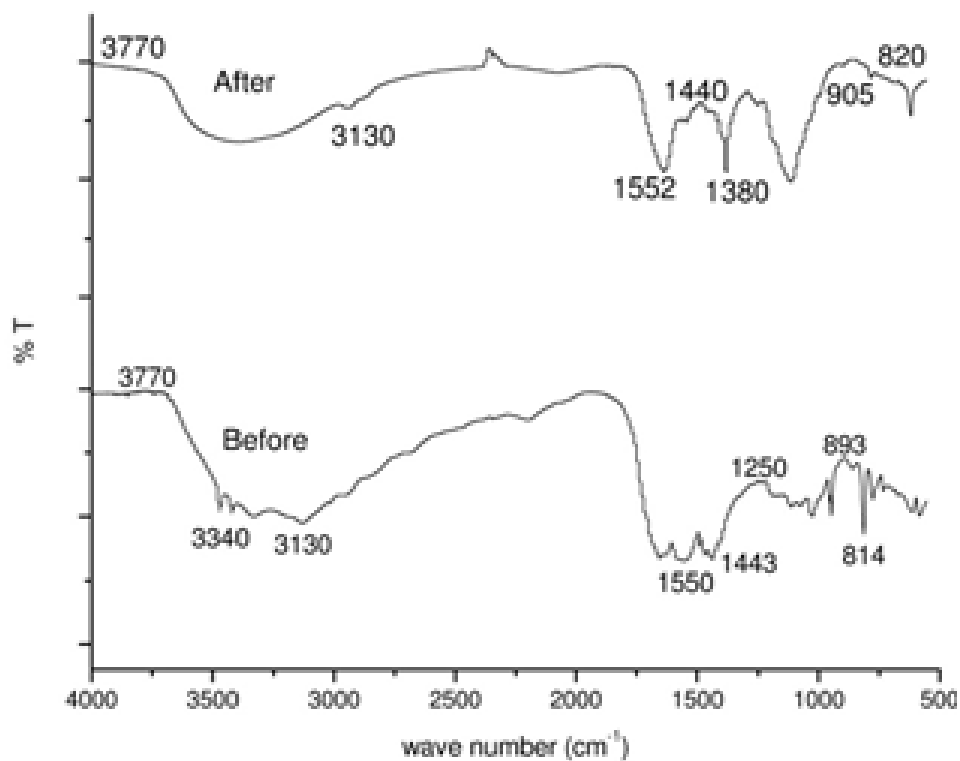


Figure 4: QMGR before and after adsorption.

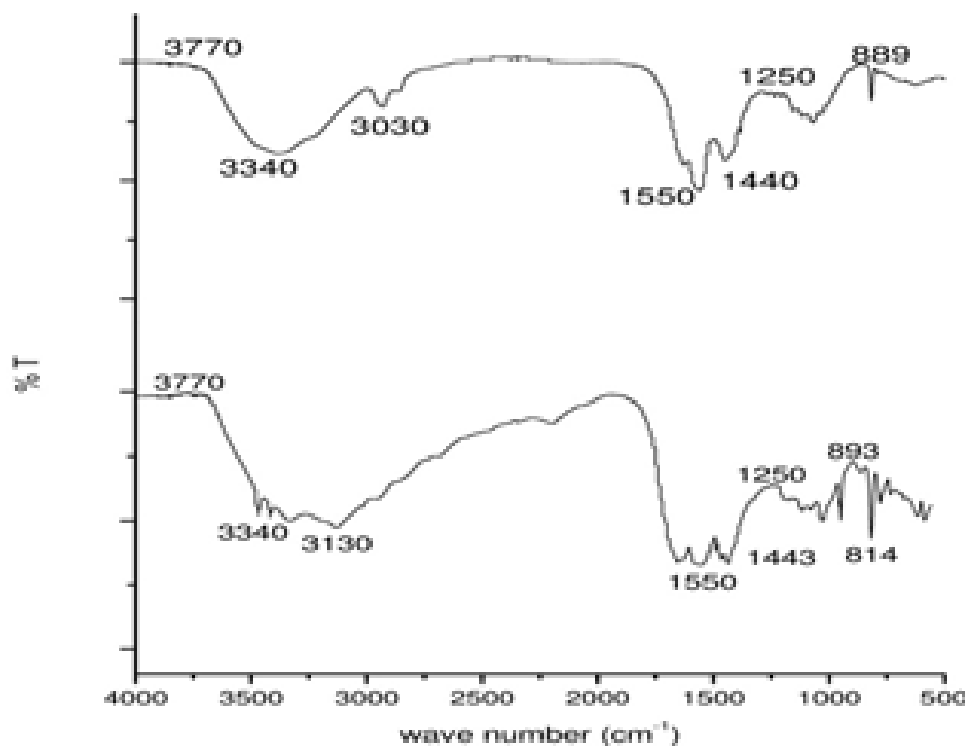


Figure 5: Synthesized QMGCR and regenerated resin.

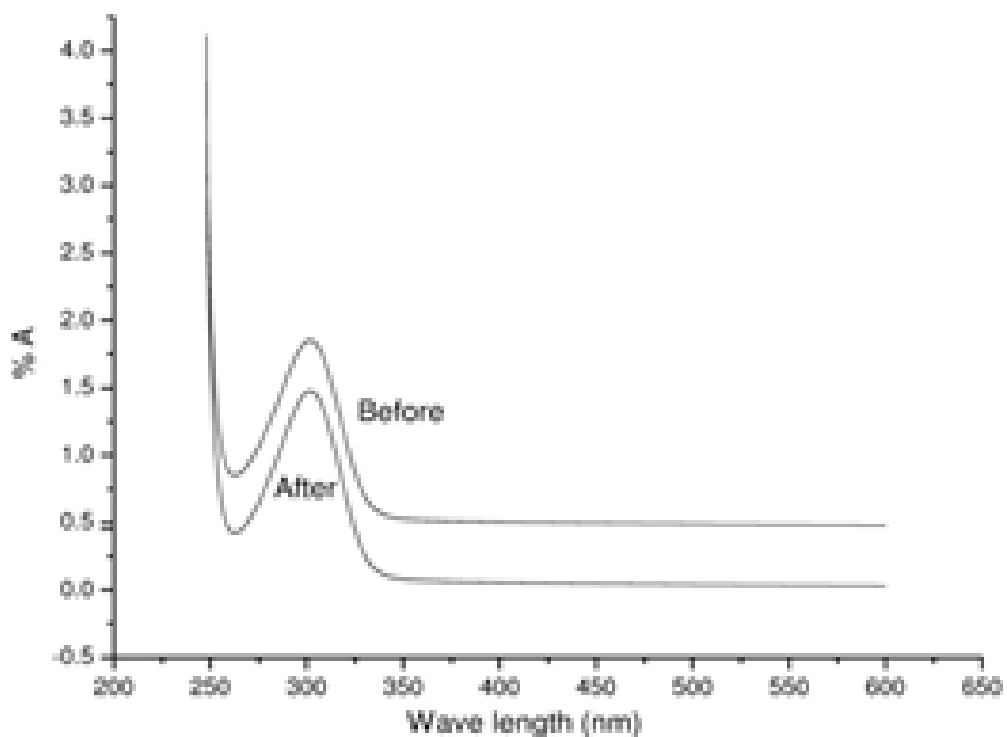


Figure 6: UV Spectra before and after adsorption.

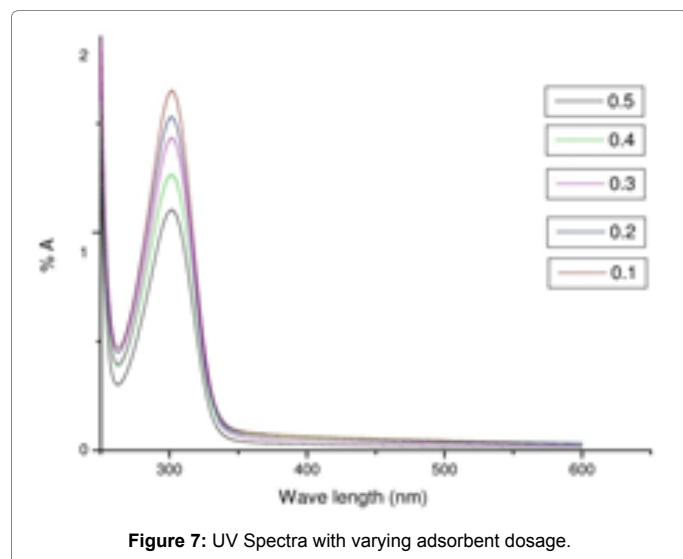


Figure 7: UV Spectra with varying adsorbent dosage.

NaCl solution which replenished the Cl^- at the quaternary ammonium site. The regenerated resin retained the adsorption capacity at least for 5 cycles. In regenerated QMGCR (Figure 4) was characterized once again using FTIR and the corresponding peaks of cross linked Chitosan and heterocyclic ring (1552 , 1443 and 814 cm^{-1}) of melamine are present. The intense peak at 3390 cm^{-1} was due to the N-H and O-H groups in quaternized resin. N-H bend contributes at 1633 cm^{-1} .

Conclusion

A quaternary ammonium chloride functionalized crosslinked chitosan-melamine-glutaraldehyde resin (QMGCR) for the selective removal of nitrate was synthesized and characterized using FTIR. The adsorption capacity of resin was observed to be due to the replacement of Cl^- at the quaternary ammonium group by nitrate ions through exchange mechanism. Resin showed an adsorption capacity 29.9 mg/g when 0.1 g of adsorbent was added to a solution containing 100 mg/L of nitrate ions. The adsorption capacity of the resin for the removal of nitrate was checked by varying adsorbent concentration from 0.1 to 0.5 g . A steady increase in adsorption capacity was observed as the adsorbent dosage increased. The increase in adsorption capacity of the resin is due to the availability of more active sites. The contact time was optimized to 30 minutes as further increase in time didn't influence the adsorption capacity. This may be due to the complete occupancy of active sites. There was a slight decrease in adsorption capacity when checked from water samples of near by rivers. This may be due to the fact that some of the Cl^- could be replaced by ions other than nitrate having similar size. Adsorption capacity of resin was good enough for practical use even at room temperature and the resin retained its capacity over a wide pH range of 3-10. The regeneration of resin required simply the treatment with NaCl solution and it retained the adsorption capacity for 5 cycles of regeneration process. As a conclusion this resin could be a cheaper, viable and efficient practical solution for the selective removal of nitrate ions from water resources.

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