Adsorption of Nitrates Using Quaternized Chitosan Resin

Aneesh P and Jishna M
Department of Chemistry, St. Joseph’s College, Devagiri, Calicut, Kerala, India

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-Gluteraldehyde- Chitosan Resin (QMGCR), 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: QMGCR; 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 gout, 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 NO3− 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 have 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].

*Corresponding author: Jishna M, Department of Chemistry, St. Joseph’s College, Devagiri, Calicut, Kerala, India, Tel: 04952355901; E-mail: j munnie96@gmail.com

Received August 28, 2017; Accepted November 25, 2017; Published December 05, 2017

Citation: Aneesh P, Jishna M (2017) Adsorption of Nitrates Using Quaternized Chitosan Resin. J Chem Eng Process Technol 8: 360. doi: 10.4172/2157-7048.1000360

Copyright: © 2017 Aneesh P, et al. This is an open-access article distributed under the terms of the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original author and source are credited.
Chitosan-Melamine-Glutaraldehyde Resin (QMGCR): The chitosan
Analytical grade HNO3 was used as source for producing nitrate anions
Tetramethylammonium chloride were purchased from High Media.
KOH was purchased from Sigma-Aldrich. Gluteraldehyde, Melamine and
Acetic acid were also used. Glacial acetic acid, Na2HPO4 and NaH2PO4
were used as source for producing phosphate anions. Glacial acetic acid
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.

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
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
washed 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 qe is the
amount of anion adsorbed (mg/g), C0 is the initial concentration of anion (mg/L),
C 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.

\[ q_e = \frac{(C_0-C_e)V}{m} \]  

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

Table 1: Variation of adsorption capacity.
Absorptions in the range 3690-3100 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 to 1000 cm\(^{-1}\) are attributed to the C-O stretching vibration in C-OH. The broad band at 720-590 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\(_2\) 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\(_2\) 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: QMGCR before and after adsorption.
Figure 5: Synthesized QMGCR and regenerated resin.

Figure 6: UV Spectra before and after adsorption.
NaCl solution which replenished the Clˉ at the quaternary ammonium site. The regenerated resin retained the adsorption capacity at least for 5 cycles. In regenerated QMGR (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 groups in Heterocyclic ring (1552, 1443 and 814 cm⁻¹) of melamine are present.

### 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 optimised 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.

### References

1. Prakasa REVS, Puttanna K (2000) Nitrates, agriculture and environment. Curr Sci 79: 1163-116.
2. Camargo JA, Livaro A (2006) Ecological and toxicological effects of inorganic nitrogen pollution in aquatic ecosystems: A global assessment. Environ. Int 32: 831-849.
3. Levine SN, Schindler DW (1989) Phosphorus, Nitrogen, and Carbon Dynamics of Experimental Lake 303 during recovery from Eutrophication. J Fish Aquat Sci 46: 2-10.
4. Murphy AP (1991) Chemical removal of nitrate from water. Nature 350: 223-225.
5. Chatterjee S, Woo SH (2009) The removal of nitrate from aqueous solutions by chitosan hydrogel beads. J. Hazard. Mater 164: 1012-1018.
6. Bhatnagar A, Sillanpaa M (2011) A review of emerging adsorbents for nitrate removal from water. Chem Eng J 168: 493-504.
7. Loganathan P, Vigneswaran S, Kandasamy J (2013) Enhanced removal of nitrate from water using surface modification of adsorbents - A review. J Environ Manage 131: 363-374.
8. Hu Q, Chen N, Feng C, Hu W (2015) Nitrate adsorption from aqueous solution using granular chitosan-Fe₃O₄ complex. Appl Surf Sci 347: 1-9.
9. Sowmya A, Meenakshi S (2014) A novel quaternized chitosan-melamine-glutaraldehyde resin for the removal of nitrate and phosphate anions. Int J Biol Macromol 64: 224-232.
10. Wada K, Hirata T, Hosokawa S, Iwamoto S, Inoue M (2012) Effect of supports on Pt-Cu bimetallic catalysts for nitrate and nitrite reduction in water. Catal Today 185: 81-87.
11. Chatterjee S, Lee DS, Lee MW, Woo SH (2009) Nitrate removal from aqueous solutions by cross-linked chitosan beads conditioned with sodium bisulfite. J. Hazard. Mater 166: 508-513.
12. Shen CS, Shen Y, Wen YZ, Wang HY, Liu WP (2011) Fast and highly efficient remediation of dyes under alkaline conditions using magnetic chitosan-Fe₃O₄ hydrogel. Water Res 45: 5200-5210.
13. Bhatnagar A, Sillanpaa M (2009) Applications of chitin- and chitosan-derivatives for the detoxification of water and wastewater - A short review. Advances in Colloid and Interface Science 152: 26-38.
14. Alkhani A, Madrakian T, Karimi M (2007) The effect of acid treatment of carboncloth on the adsorption of nitrite and nitrate ions. J Hazard Mater 144: 427-431.
15. Bhardwaj D, Sharma M, Sharma P, Tomar R (2012) Surface and surfactant modification of clinoillite and mottmorillonite for the removal of nitrate and phosphate by slow release fertilizer. J. Hazard Mater 227-228.
16. Xing X, Gao BY, Zhong QQ, Yue QY, Li Q (2011) Sorption of nitrate onto amino-crosinkled wheat straw: Characteristics, column sorption and desorption properties. J Hazard Mater 66: 206-211.
17. Yin CY, Aroua MK, Daud WMWV (2007) Review of modifications of activated carbon for enhancing contaminant uptake from aqueous solutions. Sep Purif Technol 52: 403-415.
18. Cheng IF, Muftikian R, Fernando Q, Korte N (1997) Reduction of nitrate to ammonia by zero valent iron. Chemosphere 35: 2689-2695.
19. Bhatnagar A, Sillanpaa M (2009) Applications of chitin- and chitosan-derivatives for the detoxification of water and wastewater - A short review. Advances in Colloid and Interface Science 152: 26-38.
20. Ravi MNV (2000) Characterization and Biodegradation Studies for Interpenetrating Polymeric Network (IPN) of Chitosan-Amino Acid Beads. React Funct Polym 46: 1-27.
21. Guibal E (2004) Interactions of metal ions with chitosan-based sorbents: a review. Sep Purif Technol 38: 43-74.
22. Varma AJ, Deshpande SV, Kennedy JF (2004) Anodic Stripping Voltammetric Determination of Nitrite Using Carbon Paste Electrode Modified with Chitosan. Carbohydr Polym 65: 77.
23. Gerente C, Lee VKC, Cloieic PL, McKay G (2007) Application of Chitosan for the Removal of Metals From Wastewaters by Adsorption - Mechanisms and Models Review. Crit Rev Environ. Sci Technol 37: 41-127.
24. Crini G, Badol PM (2008) Application of Chitosan, a natural aminopolysaccharide, for dye removal from aqueous solution by adsorption processing batch studies: A Review of Recent Literature. Prog Polym Sci 33: 399.
25. Espejo N, Cantor KP, Malats N, Silverman DT, Tardón A, et al. (2015) Nitrate in drinking water and bladder cancer risk in spain. Environmental Research 137.
26. Sun X, Peng B, Ji Y, Chen J, Li D (2009) Chitosan (chitin)/cellulose composite...
biosorbents prepared using ionic liquid for heavy metal ions adsorption. AIChE Journal 55: 2062-2069.

27. Sowmya A, Meenakshi S (2014) A novel quaternized chitosan-melamine-glutaraldehyde resin for the removal of nitrate and phosphate anions. International Journal of Biological Macromolecules 64: 224-232.

28. Silva SML, Braga CRC, Fook MVL, Raposo CMO, Carvalho LH, et al. (2012) Application of Infrared Spectroscopy to Analysis of Chitosan/Clay Nanocomposites. Infrared Spectroscopy-Material Science, Engineering and Technology 43:62.

29. Berger J, Reist M, Mayer JM, Felt O, Peppas NA, et al. (2004) Structure and interactions in covalently and ionically crosslinked chitosan hydrogels for biomedical applications. European Journal of Pharmaceutics and Biopharmaceutics 57: 19-34.

30. Wang YL, Mebel AM, Wu CJ, Chen YT, Lin CE, et al. (1997) IR spectroscopy and theoretical vibrational calculation of the melamine molecule. Journal of the Chemical Society, Faraday Transactions 93: 3445-3451.

31. Data from NIST Standard Reference Database 69: NIST Chemistry Web Book.