original article

Removal of nitrate from aqueous solution using nanocrystalline cellulose

Parisa Azadbakht[1,2], *Hamidreza Pourzamani*[1,3], *Seyed Rahman Jafari Petroudy*[4], *Bijan Bina*[1,3]

[1]Department of Environmental Health Engineering, School of Health, Isfahan University of Medical Sciences, Isfahan, Iran, [2]Student Research Committee, Isfahan University of Medical Sciences, Isfahan, Iran, [3]Environment Research Center, Research Institute for Primordial Prevention of Non-communicable disease, Isfahan University of Medical Sciences, Isfahan, Iran, [4]Department of Cellulose and Paper Technology, Faculty of Energy and New Technologies Engineering, Zirab Scientific and Research Campus, Shahid Beheshti University, Tehran, Iran

Address for correspondence:
Prof. Bijan Bina,
Department of Environment Health Engineering,
School of Health, Isfahan University of Medical
Sciences, Hezar Jerib Avenue, Isfahan, Iran.
E-mail: bbina123@yahoo.com

ABSTRACT

Aims: In this study, the removal of nitrate was investigated using nanocrystalline cellulose (NCC) extracted from sugarcane bagasse.

Materials and Methods: NCC was extracted by acid hydrolysis of bagasse at 40°C for 45 min and then used as an absorbent for the removal of nitrate. The properties of absorbent were evaluated by atomic force microscopy and dynamic light scattering. The effect of various parameters including pH, initial concentration of nitrate, adsorbent dose, and exposure time was investigated on the removal of nitrate.

Results: NCC was obtained in a diameter and length of <14.7 and 500 nm, respectively. Optimal conditions for removal of nitrate were determined in the initial nitrate concentration, adsorbent dose, pH, and exposure time of 100 mg/L, 6, 3 g/L, and 100 min, respectively. In optimal conditions, the maximum adsorption of nitrate was 8.33 mg/g.

Conclusion: The highest efficiency of nitrate removal at pH, 6 was obtained as 25%. The results showed that the NCC, extracted from bagasse, could be used as a very effective adsorbent to remove nitrate from water and wastewater resources.

Key words: Adsorbent, cellulose nanocrystal, NCC, nitrate, sugarcane bagasse

INTRODUCTION

The use of nitrogen fertilizers and improper treatment of industrial wastewater cause many environmental problems including increase of nitrogen-rich compounds in surface water and groundwater.[1] One of the most common forms of nitrogen-rich compounds is nitrate ion (NO_3^-).[2] Concentration of nitrate higher than the permissible exposure limit has potential risk to the environment and public health.[3] United States Environmental Protection Agency has announced that the maximum permissible levels of nitrate in drinking water is 10 mg/L $NO_3^- - N$.[4] In Iran, according to standard number 1053 of Industrial Research Institute of Standard, the maximum permissible concentration of nitrate in drinking water is 50 mg/L $NO_3^- - NO_3^-$.[5] High concentration of nitrate (over permissible exposure limit) in drinking water leads to methemoglobinemia, and disorders such as hypertension, increased infant mortality, gastric cancer, thyroid disorders, cytogenetic defects, meningitis, and Parkinson's disease.[6-8] The commonly used treatment methods

Access this article online
Quick Response Code:
Website: www.ijehe.org
DOI: 10.4103/2277-9183.190643

This article may be cited as: Azadbakht P, Pourzamani H, Petroudy SR, Bina B. Removal of nitrate from aqueous solution using nanocrystalline cellulose. Int J Env Health Eng 2016;5:17.

for nitrate removal include ion exchange,[9] electrochemical reduction,[10] reverse osmosis,[11] catalytic,[12] biological denitrification,[13] and adsorption.[14] These methods are often expensive and ineffective, and produce by-product.[14] Among the method of removing contaminants, biosorption is the best compared to other methods in terms of initial cost, simplicity, and low cost.[15] Hence, cellulose is considered as the most abundant biopolymer because of the cheap, renewable, and biodegradability properties.[16] Cellulose is converted to the nanoscale particles through the special mechanical, chemical, physical, and biological processes.[17] The prepared nanocellulose is classified into three subcategories according to the methods and conditions of production, which are microfibrillated cellulose, nanocrystalline cellulose (NCC), and the bacterial nanocellulose.[18] The structure of cellulose contains amorphous and crystalline parts; during the reaction with sulfuric acid, amorphous (disordered) parts were hydrolyzed, and the crystalline parts (regular) remained, which the obtained nanocellulose is called as NCC.[19] NCC has been formed from rod-shaped particles with a width of 5–70 nm, and a length of 100 nm to a few micrometers.[20] NCC contains unique properties such as nontoxic, low density, high surface area, biodegradability, and surface properties which can be modified.[21] NCC is applicable for a wide range of purposes including electronics,[22] pharmaceuticals,[23] cosmetic, paper, and cardboard industries, food industry, medicine, and nanocomposites;[19] nevertheless, its consumption as adsorbent of pollutants, colors, etc., has not been studied extensively.[24]

In 2015, Samiey and Tehrani studied the removal of methylene blue (MB) and Janus green B dyes using NCC extracted from cotton linters.[25] In 2013, He *et al.* investigated the removal of MB dye using monolith, and NCC produced from MCC.[24]

Further researches showed that the extracted NCC through acidic hydrolysis of bagasse has not been used to remove nitrate ions. Therefore, herein, we studied the nitrate removal using NCC extracted from bagasse. In this study, NCC was obtained through acidic hydrolysis of sugarcane pulp (bagasse), and then, it was used as adsorbents for the removal of nitrate from aqueous solution. Subsequently, the effect of contact time, pH, initial concentration of nitrate, and adsorbent dosage were studied on the adsorption efficiency of NCC. The number of test for the interaction of these variables at different values was attained via Design of Experiments Software (DOE 6) [State University of New York at Buffalo Department of Civil].

MATERIALS AND METHODS

Materials

To extract NCC, bagasse was purchased from Shahid Beheshti University, Faculty of Energy, and New Technologies Engineering. Other chemicals were prepared from Sigma-Aldrich Company, which include KNO_3 (≥98%), KOH (≥85%), NaOH (≥98%), Acetic acid (≥99.7%), HCl (37%), and H_2SO_4 (≥95%).

Preparation of nanocrystalline cellulose

Initially, the alkali treatment of bagasse was accomplished according to the method of Gong *et al.*,[26] using a solution of potassium hydroxide (6%) and acetic acid, and then acidic hydrolysis was performed in the presence of sulfuric acid 64% (the ratio of acid: Pulp was 13:1) at 40°C for 45 min. Then, the hydrolysis was stopped by adding 10-fold distilled water in suspension. In the next step, the mixture was washed with distilled water using a centrifuge (model Remi, India) with 10000 rpm for 15 min to separate acid residues, and consequently, acidity of suspension reached to neutral pH. Afterward, the suspension was treated with ultrasonic homogenizer (BANDELIN Electronic, UW 3200, Germany) for 10 min with the power of 150 W.

The process of nitrate removal

The stock solution of nitrate was prepared by dissolving an appropriate amount of KNO_3 in distilled water. Then, the concentrations of 30, 50, 100, and 150 mg/L were prepared from the stock solution. The nitrate removal process using NCC was scanned in doses of 1, 3, 5, and 10 g/L; reaction time of 50, 100, 150, and 200 min; and pH: 5, 6, 7, and 8. the pH of samples was adjusted with HCl and NaOH (0.1 M) and was determined using a pH meter (Cyberscan pH 1500, The Netherlands). Samples were centrifuged) CLEMENTS 20000) for 15 min at a speed of 3500 rpm, and then filtered (0.22 CA). Finally, adsorption amount of nitrate ions was determined for all samples by a spectrophotometer (DR5000, HACH-LANGE, USA) at 220 and 275 nm. The amount of adsorbed nitrate on adsorbent (q_e) and removals (%R) were evaluated through equations (1) and (2):

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

$$\%R = \frac{(C_0 - C_e)}{C_0}.100 \tag{2}$$

Where, C_0, and C_e are the initial, and the equilibrium concentrations of nitrate (mg/L), while *m* and V are the weight of the adsorbent (g), and the volume of the solution (L).

Analysis of data

To determine the relation between the factors and optimized condition, Design of Experiments software (DOE 6) was used. The Taguchi orthogonal array plan was applied by four factors at four levels [Table 1], and accordingly, 16 runs were carried out for 3 times, and consequently, a total number of 48 samples were analyzed.

Characterization of nanocrystalline cellulose

To characterize the morphology of the adsorbent particles, atomic force microscopy (AFM) image was obtained by AFM (JPK Instruments, Berlin, Germany).

The size distribution and zeta potential of prepared nanocrystals were determined through dynamic light scattering (DLS) method under the following conditions: Refractive index of 1.50, temperature of 25°C, viscosity of 0.8872 cP, the absorption coefficient 0.3, and the refractive index of water 1.33 using a DLS (DLS, version 5.00, Malvern) instrument.

RESULTS

Characterization of adsorbent

AFM image of the extracted NCC is shown in Figure 1. DLS diagram and zeta potential of NCC are shown in Figures 2 and 3, respectively.

Determination of optimum conditions of nitrate removal

The effect of factors and the interaction among them are summarized in Table 2. One-way ANOVA displayed a significant correlation between the different variables, and the nitrate removal ($P < 0.05$). According to the Figure 4, with the change of pH from 5 to 6, the nitrate removal efficiency was increased, and when the pH was changed from 6 to 7, removal efficiency decreased. To investigate the effects of initial concentration of nitrate on its adsorption by the absorbent, the experiment was accomplished in a nitrate concentration range of 30–150 mg/L. Figure 5 shows the effect of the initial concentration of nitrate on its adsorption using NCC. The results on the effect of contact time and adsorbent dosage on nitrate removal are shown in Figures 6 and 7, respectively.

DISCUSSION

The AFM image and DLS graph NCC are shown in Figures 1-3, respectively. Based on AFM image, the extracted NCC are rod-shaped materials with a length, and diameter <500, and 14.7 nm, respectively, which is in accordance with the results of Jin *et al.*,[27] DLS diagram and zeta potential of NCC are shown in Figures 2 and 3, respectively. The results of DLS showed that all the particles (100%) have a diameter < 14.7 nm. Nanocrystals of sugarcane bagasse in the study of Mandal and Chakrabarty,[28] which was produced by acidic hydrolysis had a diameter in the range of 40 nm. In a study conducted by Farasati *et al.*, nanoparticles of *Phragmites australis* with a diameter of <327.5 nm were obtained using a ball mill.[29] Average zeta potential of adsorbent at pH 5, 6, 7, and 8 was −45.4, −14.8, −61.9, and −45.8 mV, respectively.

Table 1: Controlling factors and their levels

Factors	Level 1	Level 2	Level 3	Level 4
Nitrate concentration (mg/L)	30	50	100	150
NCC dose (g/L)	1	3	5	10
pH	5	6	7	8
Contact time (min)	50	100	150	200

NCC: Nanocrystalline cellulose

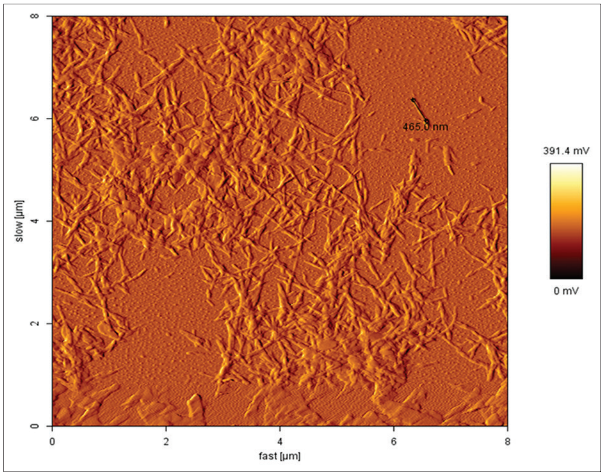

Figure 1: Atomic force microscopic image of nanocrystals cellulose (hydrolyzed in 40°C, 45 min)

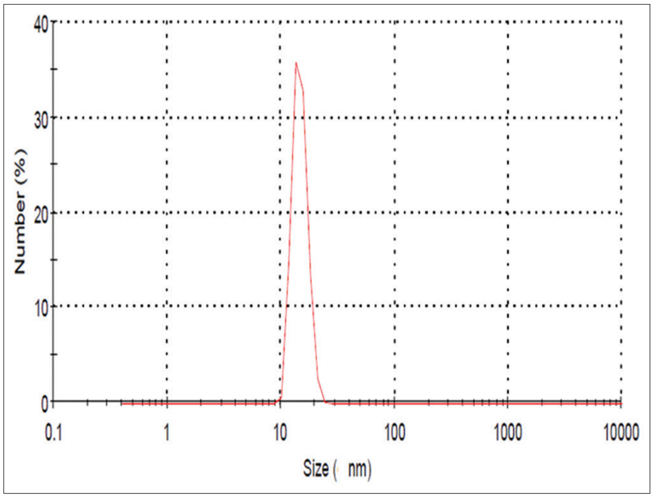

Figure 2: Distribution of average diameter of nanocrystal cellulose

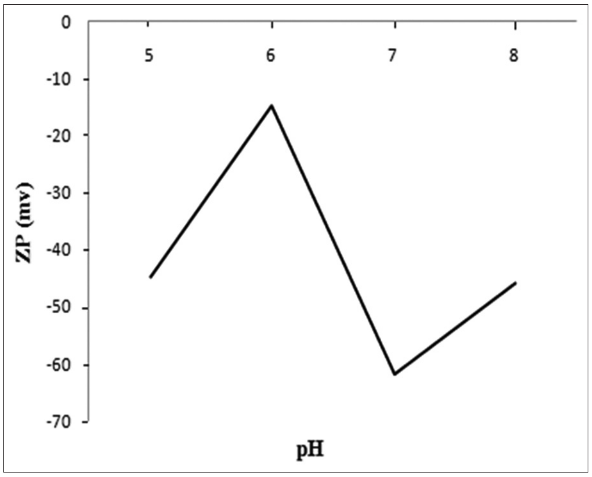

Figure 3: Zeta potential of nanocrystalline cellulose at varied pH

Table 2: Effects of the factors and interactions obtained by fractional factorial design

Factor/interaction	Degree of freedom	Sum of squares	Mean squares	$P>F$	Contribution (%)
Nitrate concentration (mg/L)	3	1437.14	479.05	<0.0001	50.76
NCC dose (g/L)	3	157.16	52.54	<0.0001	5.56
Contact time (min)	3	656.49	218.83	<0.0001	23.18
pH	3	248.88	82.96	<0.0001	8.79
AB interaction	3	331.15	110.38	<0.0001	11.69
Lack of fit	3	331.15	110.38		
Residuals	35	11.69	9.56		
Pure error	32	0.000			0.000

NCC: Nanocrystalline cellulose

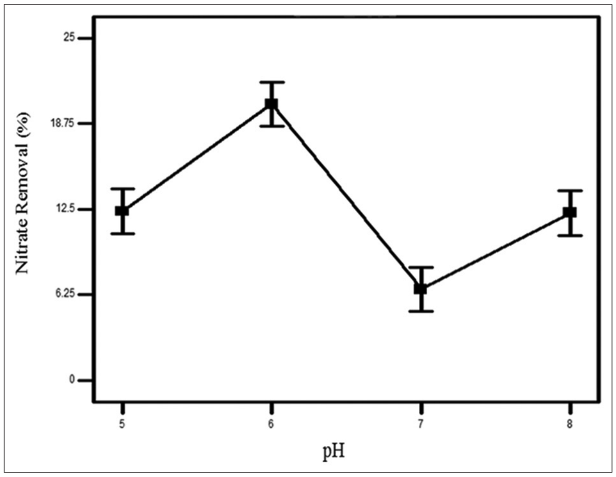

Figure 4: The effect pH on nitrate removal

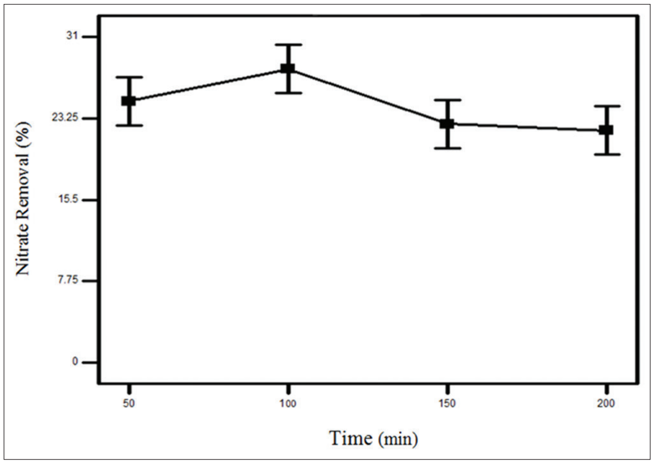

Figure 6: The effect of contact time on nitrate removal

Based on the statistical analysis shown in Table 2, the F_{value} test exhibited that the initial concentration of nitrate had the maximum effect over absorption performance (50.76%). In addition, the contact time and concentrations of NCC have the minimum effect on the absorption performance due to their F_{value} (8.79, and 5.56, respectively). Priority of factors affecting nitrate removal is as follows:

Initial nitrate concentration > pH > interaction AB > contact time > concentration of NCC.

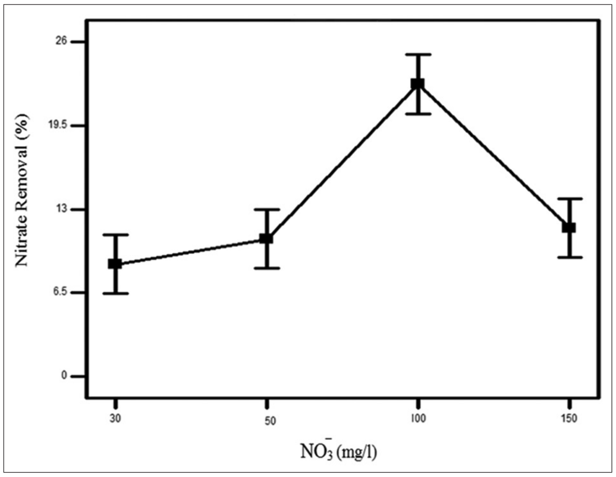

Figure 5: The effect of initial nitrate concentration on its removal

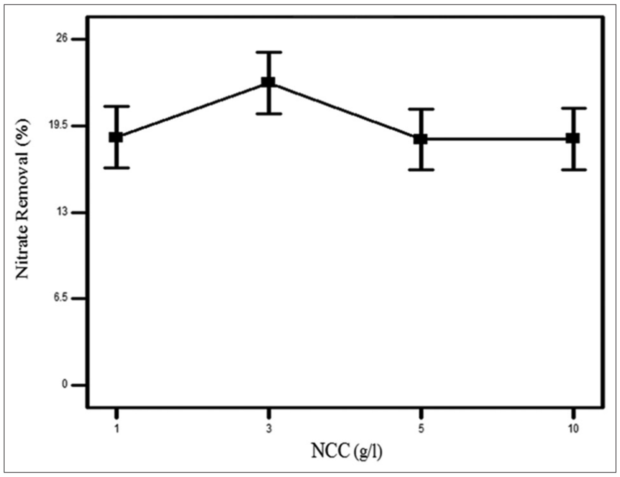

Figure 7: The effect of adsorbent dosage on nitrate removal

The nitrate removal by the NCC could be represented as equation 3:

$$\text{Nitrate removal (\%)} = 6.64 + (1.89 \times \text{nitrate concentration}) + (1.08 \times \text{NCC dose}) - (1.42 \times \text{pH}) + (2.31 \times \text{contact time}) + (9.3\,(\text{nitrate concentration} \times \text{NCC dose})). \quad (3)$$

Considering the results of zeta potential of the adsorbent [Figure 3], it is obvious that at pH = 6, the negative charge of surface is less than that at other pHs, and thus, the efficiency of the nitrate removal at pH = 6 was increased. The highest efficiency of nitrate removal at pH, 6 was obtained as 25%. In a study conducted by Farasati *et al*. On nitrate removal using the modified nanoparticles of cane, the highest nitrate removal was achieved at pH = 6.[5] Due to the negative charge of the surface at pH = 7 which leads to electrostatic repulsion between adsorbent and absorbing nitrate, removal rate was decreased. At higher pH values, removal of nitrate is reduced because of the competition of OH^- ions with nitrate ions for the active sites.[30]

The most efficiency of nitrate removal was obtained in a concentration of 100 mg/L of nitrate ions [Figure 5]. With an increase of initial nitrate concentration, the efficiency of nitrate removal is decreased which is in accordance with the results of Malakootian *et al*. studies.[31] It is probably because of the saturation of adsorption sites by the nitrate ions in high concentrations. Increasing the initial concentration of nitrate leads to increase of the electrostatic interactions which consequently causes to formation of sites with lower affinity to interact with nitrate ions.[32] As shown in Table 2, among different parameters, initial concentration of nitrate ion has the maximum effect on the efficiency of nitrate removal.

As shown in Figure 6, the maximum amount of nitrate removal is occurred at 100 min after beginning of the reaction, and nitrate removal rate decreases with increasing the contact time. This is probably because of the saturation of the adsorption sites over the time.[33] To investigate the effect of adsorbent dosage on the nitrate removal, the experiment was accomplished in different dosage values of adsorbent including 1, 3, 5, and 10 g/L. The effect of adsorbent dosage on the removal of nitrate is shown in Figure 7. Increasing the absorption dosage from 1 to 3 g/L cause to increase of the nitrate removal which is because of the large surface area, and more availability of adsorption sites.[15,34] With an increase of the adsorbent dosage from 3 to 10 g/L, the efficiency of removal is decreased which is in accordance with the results of Hsu *et al*.'s study. It is possibly due to the enhancement of the adsorbent dosage and contact time between the joined particles and particles of adsorbent, and subsequently, removal efficiency is increased.[34,35]

CONCLUSIONS

In this study, NCC was extracted from sugarcane bagasse by acidic hydrolysis. AFM image analysis and DLS results showed that the dimensions of the extracted cellulose crystals are in nanoscale range. Initial nitrate concentration has the greatest effect among the examined factors, and contact time has the least impact on nitrate adsorption by the nanocrystals. However, due to the total negative charge of nanocrystalline and negative charge of nitrate, there was not a very high adsorption, but because the negative charge of nanocrystals at pH = 6 is less than the others, the maximum adsorption was obtained. The effect of the interaction of initial nitrate concentration with adsorbent dosage could also be an effective factor on nitrate removal. Based on the obtained results, NCC prepared from bagasse by acid hydrolysis, can be relatively an effective adsorbent in nitrate removal from contaminated water and wastewater.

Acknowledgments

This article is part of a Master's thesis with the code of 393506. The financial support from the Deputy of Research, and Technology, Isfahan University of Medical Sciences, the cooperation of Cellulose, and Paper Technology Department, Faculty of Engineering, and New Technologies, Shahid Beheshti University in Tehran, and other colleagues involved in this research would be appreciated.

Financial support and sponsorship

Isfahan University of Medical Sciences, Isfahan, Iran.

Conflicts of interest

There are no conflicts of interest.

REFERENCES

1. Mizuta K, Matsumoto T, Hatate Y, Nishihara K, Nakanishi T. Removal of nitrate-nitrogen from drinking water using bamboo powder charcoal. Bioresour Technol 2004;95:255-7.
2. Shrimali M, Singh KP. New methods of nitrate removal from water. Environ Pollut 2001;112:351-9.
3. Bhatnagar A, Sillanpää M. A review of emerging adsorbents for nitrate removal from water. Chem Eng J 2011;168:493-504.
4. Ren HT, Jia SY, Zou JJ, Wu SH, Han X. A facile preparation of Ag_2O/P25 photocatalyst for selective reduction of nitrate. Appl Catal B 2015;176:53-61.
5. Farasati M, Nasab SB, Moazed H, Haghighifard NJ, Koupai JA, Seyedian M. nitrate removal from contaminated waters by using anion exchanger *Phragmites australis* nanoparticles. J Water Wastewate. 2013; 85:34-43.
6. Ayyasamy PM, Shanthi K, Lakshmanaperumalsamy P, Lee SJ, Choi NC, Kim DJ. Two-stage removal of nitrate from groundwater using biological and chemical treatments. J Biosci Bioeng 2007;104:129-34.
7. Gaurav K, Devi P, Bansod BK. Study of effect of interferent in the determination of nitrate in water. Aquat Procedia 2015;4:1094-8.
8. Moazeni M, Ebrahimi A, Atefi M, Mahaki B, Rastegari HA. Determination of nitrate and nitrite exposure and their health risk assessment in 21 brands of bottled waters in Isfahan's market in 2013. Int J Environ Health Eng 2014;3:28.
9. Alikhani M, Moghbeli MR. Ion-exchange polyhipe type membrane for removing nitrate ions: Preparation, characterization, kinetics and adsorption studies. Chem Eng J 2014;239:93-104.
10. Öznülüer T, Özdurak B, Doğan HÖ. Electrochemical reduction of nitrate on graphene modified copper electrodes in alkaline media. J Electroanal Chem 2013;699:1-5.
11. Richards LA, Vuachère M, Schäfer AI. Impact of pH on the removal of fluoride, nitrate and boron by nanofiltration/reverse osmosis. Desalination 2010;261:331-7.
12. Wada K, Hirata T, Hosokawa S, Iwamoto S, Inoue M. Effect of supports on Pd–Cu bimetallic catalysts for nitrate and nitrite reduction in water. Catal Today 2012;185:81-7.

13. Chung J, Amin K, Kim S, Yoon S, Kwon K, Bae W. Autotrophic denitrification of nitrate and nitrite using thiosulfate as an electron donor. Water Res 2014;58:169-78.
14. Chatterjee S, Lee DS, Lee MW, Woo SH. Nitrate removal from aqueous solutions by cross-linked chitosan beads conditioned with sodium bisulfate. J Hazard Mater 2009;166:508-13.
15. Hu Q, Chen N, Feng C, Hu W. Nitrate adsorption from aqueous solution using granular chitosan-Fe^{3+} complex. Appl Surf Sci 2015;347:1-9.
16. Yousefi H, Nishino T, Faezipour M, Ebrahimi G, Shakeri A. Direct fabrication of all-cellulose nanocomposite from cellulose microfibers using ionic liquid-based nanowelding. Biomacromolecules 2011;12:4080-5.
17. Frone AN, Panaitescu DM, Donescu D. Some aspects concerning the isolation of cellulose micro-and nano-fibers. UPB Bul Stiint Ser B Chem Mater Sci 2011;73:133-52.
18. Klemm D, Kramer F, Moritz S, Lindström T, Ankerfors M, Gray D, *et al.* Nanocelluloses: A new family of nature-based materials. Angew Chem Int Ed 2011;50:5438-66.
19. Habibi Y, Lucia LA, Rojas OJ. Cellulose nanocrystals: Chemistry, self-assembly, and applications. Chem Rev 2010;110:3479-500.
20. Kaboorani A, Riedl B. Surface modification of cellulose nanocrystals (CNC) by a cationic surfactant. Ind Crops Prod 2015;65:45-55.
21. Rahimi M, Behrooz R. Effect of cellulose characteristic and hydrolyze conditions on morphology and size of nanocrystal cellulose extracted from wheat straw. Int J Polym Mater 2011;60:529-41.
22. Sadasivuni KK, Kafy A, Zhai L, Ko HU, Mun S, Kim J. Transparent and flexible cellulose nanocrystal/reduced graphene oxide film for proximity sensing. Small 2015;11:994-1002.
23. Jackson JK, Letchford K, Wasserman BZ, Ye L, Hamad WY, Burt HM. The use of nanocrystalline cellulose for the binding and controlled release of drugs. Int J Nanomedicine 2011;6:321-30.
24. He X, Male KB, Nesterenko PN, Brabazon D, Paull B, Luong JH. Adsorption and desorption of methylene blue on porous carbon monoliths and nanocrystalline cellulose. ACS Appl Mater Interfaces 2013;5:8796-804.
25. Samiey B, Tehrani AD. Study of adsorption of janus green B and methylene blue on nanocrystalline cellulose. J Chin Chem Soc 2015;62:149-62.
26. Gong G, Mathew AP, Oksman K. Strong aqueous gels of cellulose nanofibers and nanowhiskers isolated from softwood flour. TAPPI J 2011;10:7-14.
27. Jin L, Li W, Xu Q, Sun Q. Amino-functionalized nanocrystalline cellulose as an adsorbent for anionic dyes. Cellulose 2015;22:2443-56.
28. Mandal A, Chakrabarty D. Isolation of nanocellulose from waste sugarcane bagasse (SCB) and its characterization. Carbohydr Polym 2011;86:1291-9.
29. Farasati M, Jafarzadeh N, Boroomand S, Moazed H, Abedi kJ, Seyedian M. Use of agricultural nano adsorbents for nitrate removal from aqueous solutions. Iran Water Resour Res. 2013;8:28-38.
30. Bhatnagar A, Kumar E, Sillanpää M. Nitrate removal from water by nano-alumina: Characterization and sorption studies. Chem Eng J 2010;163:317-23.
31. Malakootian M, Yaghmaian K, Tahergorabi M. The efficiency of nitrate removal in drinking water using Iron nano-particle: Determination of optimum conditions. Toloo-E-Behdasht. 2011;10:35-44.
32. Baldrian P. Interactions of heavy metals with white-rot fungi. Enzyme Microb Technol 2003;32:78-91.
33. Nourmoradi H, Zabihollahi S, Pourzamani H. Removal of a common textile dye, navy blue (NB), from aqueous solutions by combined process of coagulation–flocculation followed by adsorption. Desalination Water Treat 2015;57:1-12. [ahead-of-print]
34. Rahmani A, Mousavi HZ, Fazli M. Effect of nanostructure alumina on adsorption of heavy metals. Desalination 2010;253:94-100.
35. Hsu JC, Liao CH, Wei YL. Nitrate removal by synthetic nanoscale zero-valent iron in aqueous recirculated reactor. Sustain Environ Res 2011;21:353-9.