RESEARCH ARTICLE

• Arch Hyg Sci 2017;6(4): 377-384
• Journal Homepage: http://jhygiene.muq.ac.ir

Nitrate Removal from Aqueous Solutions Using Almond Charcoal Activated with Zinc Chloride

Mohsen Arbabi[a], Akbar Rostami[a*], Mohammad Hassan Mahmoodian[b], Morteza Sedehi[c], Abbas Khodabakhshi[a]

[a]Department of Environmental Health Engineering, School of Health, Shahrekord University of Medical Sciences, Shahrekord, Iran.
[b]Research Center for Environmental Pollutants, Qom University of Medical Sciences, Qom, Iran.
[c]Department of Epidemiology and Statistical, School of Health, Shahrekord University of Medical Sciences, Shahrekord, Iran.

***Correspondence** should be addressed to Mr. Akbar Rostami, **Email:** rostami_akbar53@yahoo.com

A-R-T-I-C-L-EI-N-F-O

Article Notes:
Received: Feb 20, 2017
Received in revised form: Aug 29, 2017
Accepted: Sep 21, 2017
Available Online: Sep 30, 2017

Keywords:
Nitrate
Almond Charcoal
Zinc Chloride
Absorption
Isotherm
Activated Carbon
Iran.

A-B-S-T-R-A-C-T

Background & Aims of the Study: Nitrate is one of the most important contaminants in aquatic environments that can leached to water resources from various sources such as sewage, fertilizers and decomposition of organic waste. Reduction of nitrate to nitrite in infant's blood stream can cause "blue baby" disease in infants. The aim of this study was to evaluate the nitrate removal from aqueous solutions using modified almond charcoal with zinc chloride.

Materials &Methods: This study is an experimental survey. At the first charcoal almond skins were prepared in 5500C and then modified with $ZnCl_2$. Morphologies and characterization of almond shell charcoal were evaluated by using FTIR, EDX, BET and FESEM. Adsorption experiments were conducted with 500 ml sample in Becker. The nitrate concentration removal, contact time, pH and charcoal dosage were investigated. The central composite design method was used to optimizing the nitrate removal process. The results analyzed with ANOVA test.

Results: The best condition founded in 48 min, 1250 ppm, 125 mg/l and 3 for retention time, primary nitrate concentration, charcoal dosage and pH respectively. The results showed that the nitrate removal decreases with increasing pH. Modification of skin charcoal is show increasing of nitrate removal from aquatic solution.

Conclusion: In this study, the maximum nitrate removal efficiency for raw charcoal and modified charcoal was determined 15.47% and 62.78%, respectively. The results showed that this method can be used as an effective method for removing nitrate from aqueous solutions.

Please cite this article as: Arbabi M, Rostami A, Mahmoodian MH, Sedehi M, Khodabakhshi A. Nitrate Removal from Aqueous Solutions Using Almond Charcoal Activated with Zinc Chloride. Arch Hyg Sci 2017;6(4):377-384.

Background

Groundwater serves as the main source of drinking water in rural and urban communities. Toxic pollutants such as organic and inorganic chemical have increased public concern related groundwater quality (1). Increasing usage of fertilizers and low efficiency treatment of wastewaters from agricultural and industrial activities has led to increase in the concentration of nitrate in surface and groundwater in many land areas. A high concentration of nitrate in drinking water can increase outbreaks of cancer and the risks of diseases such as methemoglobinemia in newborn infant's population (2). The World Health Organization (WHO) has set the maximum concentration of nitrate at 50 mg/l for drinking water (3). Also according to the Iranian standard, maximum nitrate concentration in drinking water is 50 mg/l (4). Nitrate, due to its high water solubility can pass through soil layers and contaminate the groundwater (5). Removal of nitrate by ion exchange, electro-dialysis, reverse osmosis (1), immobilized enzymes, metals and microbial denitrification has been studied (6). Among the all water purification methods, the adsorption process is a cheap, universal and fast method. Development of inexpensive adsorbents has led to the rapid growth of research interests in the charcoal modification (7). Currently the low-cost adsorbents such as organic waste, agricultural and industrial products have been used to remove the nitrate from water and wastewater (8). Modification of charcoal with some chemical solutions such as acids, bases, microwave heating, has been studied (9-13). Langmuir and Freundlich are the most important isotherms that used to verify the adsorption process. Due to the necessity of reuse of agricultural wastes and the production of considerable amounts of almonds in Iran and the high concentration of nitrates in some water resources this adsorbent was selected. We used $ZnCl_2$ as chemical agent for modification of almond shell charcoal in nitrate removal from aquatic solutions.

Aims of the study:

The aim of this study is efficiency determination of zinc chloride-modified almond charcoal to remove nitrate from aquatic solution.

Materials & Methods

The present study is an experimental study on a laboratory scale. In this study, after modified almond charcoal, the experiments were performed according to the RSM design.

Chemical and materials

Sulfuric acid (H_2SO_4) 97%, sodium hydroxide (NaOH) 99.5%, potassium nitrate (KNO_3) 99%, hydrogen chloride (HCl) 99%, zinc chloride ($ZnCl_2$) 98%, phosphoric acid (H_3PO_4) 85% were obtained from Merck (Germany) company. All reagents were analytical grade and applied without further purification. All solutions were prepared with deionized water. Characterizations of almond shell charcoal were evaluated by using FTIR, EDX, FESEM (Table.1, Fig.3, Fig.4 respectively) and BET.

Preparation and modification of charcoal

The almond shell was prepared from an area located in the Chaharmahal and Bakhtiari Province. Firstly the almond shell was broken into small pieces, rinsed with distilled water and then was dried at 105 °C for 24 hours. Dried almond shell was placed an hour at a temperature of 550 °C (14). To reduce the alkalinity and remove the impurities, coal was submerged in phosphoric acid for 2hr at room temperature and washed with distilled water and then dried at 100 °C for 24 hours. 10 gr of prepared charcoal with 20 gr of zinc chloride brought to a volume of 100 ml, and then poured for an hour at a temperature of 80 °C and using a hot plate is well mixed, then put for 24 hours at 110 °C. After that coal was mixed with zinc chloride solution for one hour at 500 °C, and after cooling, rinsed with hydrochloric acid and deionized water several times. For classification of obtained coal, mesh sieve of 100 and 30 were used (15). According to mesh used, gradated particle sizes were between 0.15 and 0.6 mm.

Sample size and experiments

In order to determine the sample size, the experimental procedure based on Response Surface Method (RSM) and using Central Composite Design (CCD) was done. For data analyzing the ANOVA test was used and the effects of four parameters including pH, contact time, adsorbent and initial nitrate concentrations were evaluated. All experiments were performed using a beaker with a volume of 500 ml as batch reactor. Four variables were investigated and each variable have been five levels, including pH, reaction time, absorbent dose almond charcoal and NO_3^- concentration: 2-6, 15-60 min, 500-1500 mg, and 50-150 mg/l respectively. The experiments were carried out with RSM and using central composite design (CCD) test in Design Expert software. The effect of four parameters of pH, contact time, adsorption concentration and initial concentration of nitrate on the removal efficiency were analyzed. For mixing and creating good contact between the absorbent and nitrate, magnetic stirrer with 100 rpm was used. After separation of absorbent by filtration method, remaining nitrate concentrations were measured using a spectrophotometer DR5000 at 220 nm. Nitrate calibration curve, using concentrations of 25, 50, 75, 100, 125, 150, 175 and 200 mg per liter was drawn (Fig. 1). A stock solution of nitrate prepared using potassium nitrate according to guide line of standard methods for the examination of water and wastewater. Based on the number of variables and with using the design expert software, 30 runs of sample size were determined. Then the results were analyzed by cooperative means and ANOVA test.

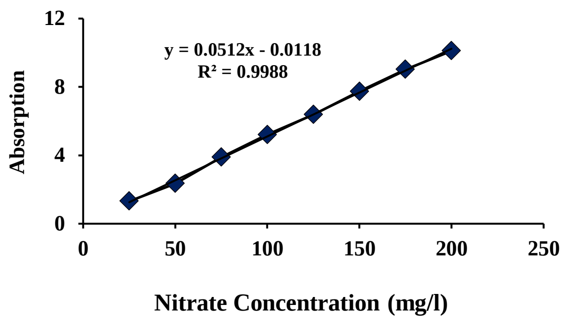


Figure 1) Nitrate calibration curve

In order to comparison of efficiency between before and after charcoal modification, the different concentration of $ZnCl_2$ as modification agent has been used.

a. Charcoal characterization:

Figure 2 has shown the FTIR spectrum of modified charcoal. Absorbent of some functional groups such as O-H, C=C, C-N, C-O and C-Cl are presented. The wide band is visible to ν (O–H) vibrations in hydroxyl groups. The band at 1559 cm^{-1} is caused by alkene group. After modification, the functional group C-CL has been added to the structure of charcoal that which showed an improvement in the absorption process will be promoted. Other functional groups are shown in Fig 2. The chemical characterization of the activated carbons can be seen in Table1.

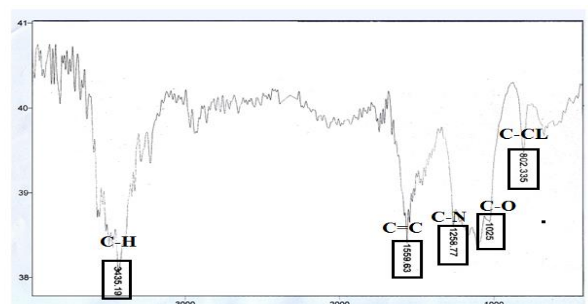


Figure 2) FTIR Spectrum of modified almond shell charcoal with $ZnCl_2$

.

Results

Table 1) Chemical characterization of before and after charcoal modification

sample	Charcoal element composition (wt%)						
	Au	Cl	Zn	Ca	K	O	C
Before modification	1.64	0	0	0.88	1.19	12.51	74.77
After modification	5.22	7.65	5.8	0.14	0.16	5.02	75.99

The EDX micrograph of almond shell before and after the modification is shown in Figure 3. The weight percent of Cl and Zn increased from zero to 7.6% and 5.8% respectively. Figure 4 shows the FESEM patterns of prepared charcoal samples before and after activation with zinc chloride. The FESEM images before and after the modification process of charcoal show significantly increased the number of pores in the adsorbent. The results of BET show that the surface area of almond shell charcoal before and after modification was 388 and 532 (m^2/g), respectively. The modification of almond shell increased around 37% of the surface area.

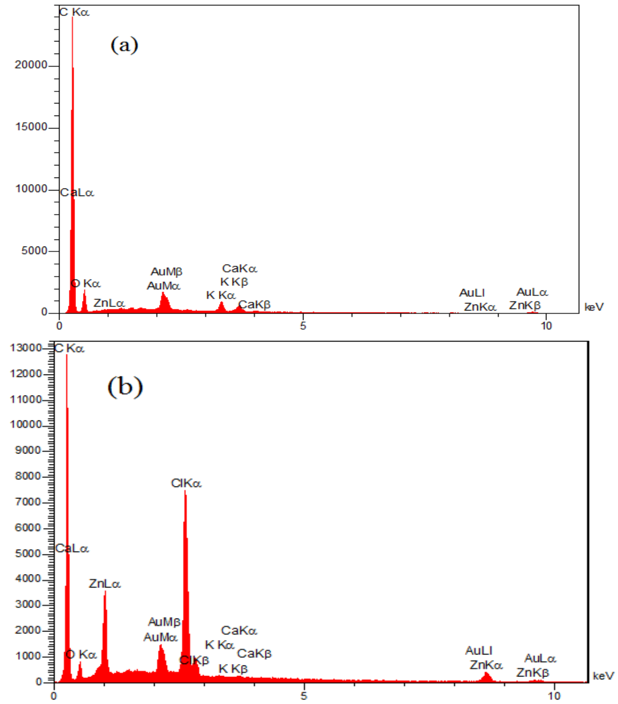


Figure 3) EDX analysis of charcoal almond shell a) before activation b) after modification with zinc chloride

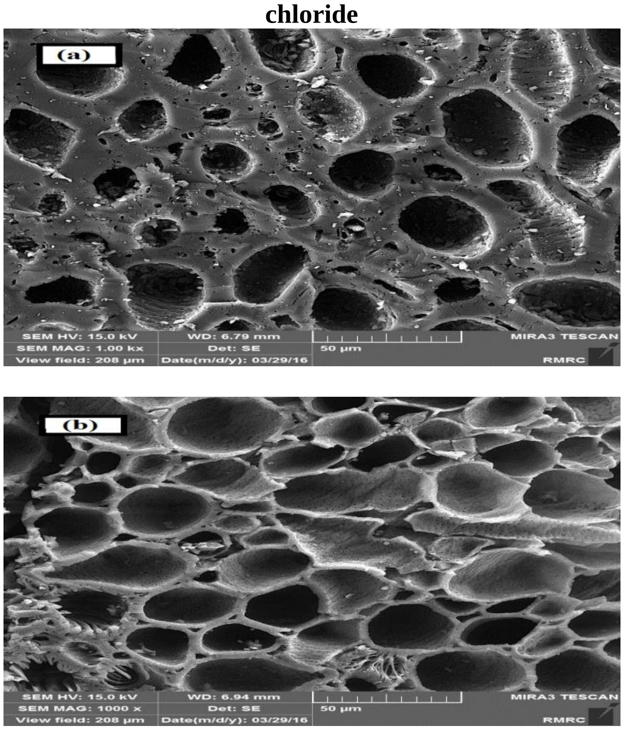


Figure 4) FESEM image of a) raw charcoal, b) modified charcoal with zinc chloride

After data analysis with CCD, the Equation 1 was determined. Based on this equation, calculation of various removals efficiency has been possible.

Equation 1:

Removal (%)=+74.58–(9.48×pH)+(0.03×T)+(6.47×10×A)+(0.03×C)

Where: T=Time, A=Almond charcoal dose, C= Initial nitrate concentration, pH=pH.

Effect of pH on absorption efficiency

Fig 5 to 7 shows the relationship between of pH, contact time, absorbent concentration and initial nitrate concentration with nitrate removal efficiency. The nitrate absorption efficiency increased with pH decrease and remained approximately constant in lower pH. Also the effect of pH and concentration on the removal adsorbent is presented in figure 8. According to figures 5-8 and the data analysis and ANOVA test, we find that the correlation between parameters such as absorbent concentration, initial nitrate concentration and contact time on nitrate removal efficiency is directly. But the effect of contact time was not meaningful ($\alpha>0.05$).

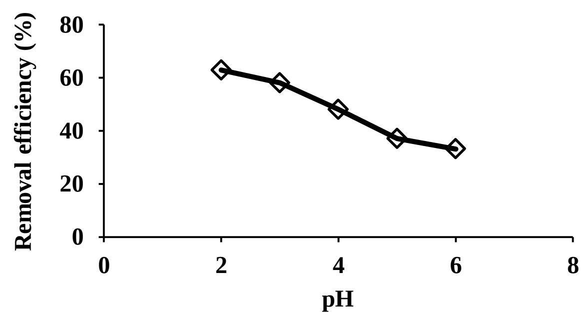


Figure 5) Effect of pH value on the average removal of nitrate in optimum contact time and absorbent dose

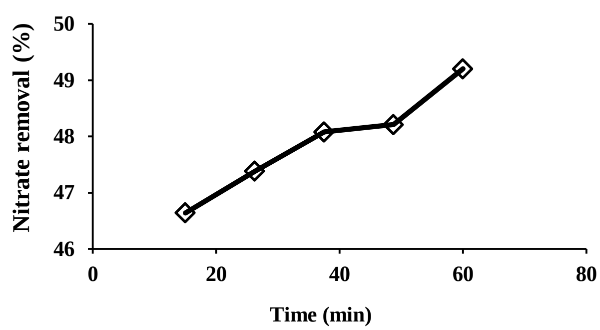


Figure 6) Effect of contact time on the average removal of nitrate in optimum pH and absorbent dose

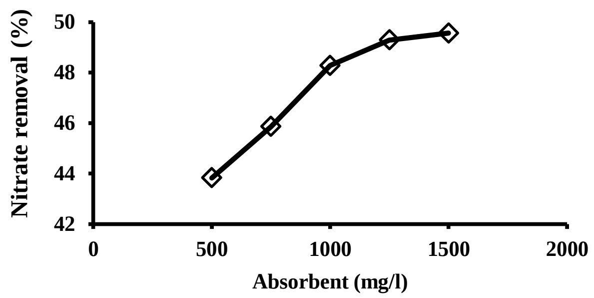


Figure 7) Effect of adsorbent concentration on the average removal of nitrate in optimum pH and contact time

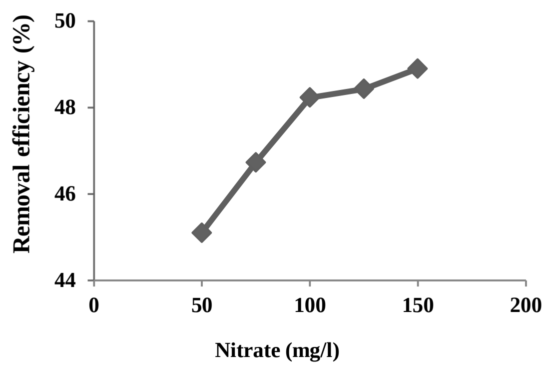
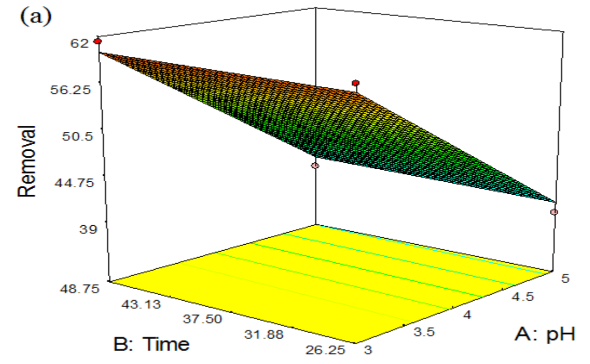


Figure 8) Effect of initial nitrate concentration on the average removal of nitrate in optimum pH and contact time



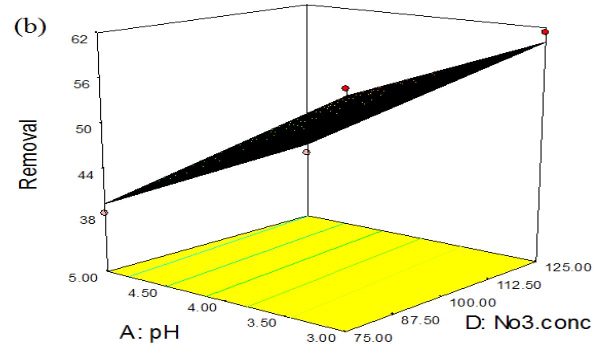


Figure 9) Effect of pH with regard to (a) time and (b) initial nitrate concentration on the removal efficiency

Study of adsorption isotherms

In order to describe the balance between nitrate concentration and modified charcoal, Langmuir and Freundlich isotherm models were used. To introduce these isotherms experiments, pH=3, contact time of 48 min and charcoal modification concentration of 0.25 to 1.75 gr/l and initial nitrate concentration of 125 mg/l has been considered (table 2).

Table 2) Constants and correlation coefficients of Langmuir and Freundlich isotherms

Isotherm	Isotherm equation	Constants and correlation coefficients		
Langmuir	$\frac{1}{q_e} = \frac{1}{q_m k_L C_e} + \frac{1}{q_m}$	q_m (mg/g)	K_L	R^2
		250	0.004	0.92
Freundlich	Log q_m = Log K_f + $\frac{1}{n}$Log C_e	K_f	$\frac{1}{n}$	R^2
		0.33	0.99	0.914

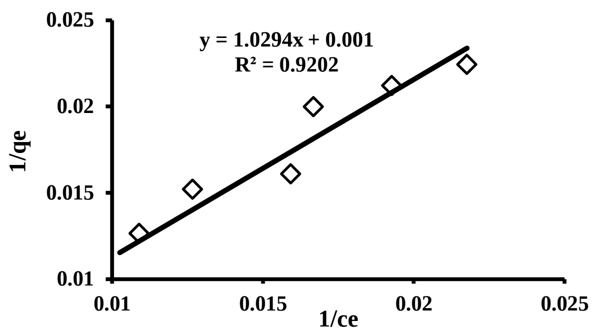


Figure 10) Langmuir isotherm plot for adsorption of nitrate removal in optimum condition

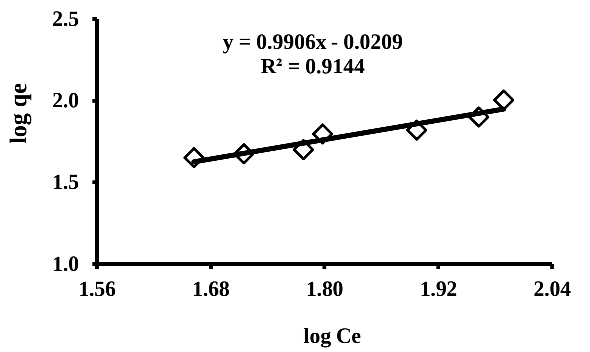


Figure 11) Freundlich isotherm plot for adsorption of nitrate removal in optimum condition

Discussion

Various types of adsorbent have been used for the removal of inorganics, including fluoride; nitrate, bromide and perchlorate. The effect of pH on the nitrate removal in analyzing of the results with CCD and assumption constant of other parameters, can be found out with a pH reduction of nitrate removal will increase. Comparison of the results show that by increasing the pH nitrate removal has decreased. The reason for this is that at in low pH, more protons will be available for charging hydroxide groups. Increasing the charge can increase the absorption efficacy by increasing the electrostatic bonds between nitrate (negative ion) and functional group. This functional group always has positive charge (16). In a study in order to remove nitrite and nitrate ions from aqueous solution by olive cores was carried out that the maximum amount of nitrate removal efficiency in pH=2, 75% was observed (17). In another study carbon from coconut shells and bamboo charcoal were reported the maximum nitrate removal in pH=3-4 (18). The effect of contact time on nitrate removal according to the data analysis the removal efficiency increased with increasing contact time. However, the effect of contact time is lesser effect than pH. As shown in Figure 6 is the highest nitrate removal efficiency of 60 minutes while based on design experiment software the optimum time is sated at 47 minutes. In a study, optimal retention time of nitrate removal by modifying coal with granular activated carbon has been 60 min (19). In another study reported 120 minutes is the best time for the nitrate removal 120 min has been reported (20). Effect of adsorbent concentration on nitrate removal Based on figure 7 by increasing the amount of nitrate removal adsorbent has been increased. In optimal conditions, the optimum adsorbent dose was 1250 mg/l. Nitrate removal using activated carbon modified with zinc and zinc sulfate was analyzed in the study. The optimum adsorbent dose of 1600 mg/l has been reported in this case (21). Removal of nitrite and nitrate ions from aqueous solution was done by Mr. Hiba Nassar. The optimal concentration of absorbent of 0.7 gr/l mentioned (22). The impact of the initial nitrate concentration on the nitrate removal efficiency by increasing the initial nitrate concentration, the removal of nitrate increases slowly (Fig 8). The highest nitrate removal efficiency was 49% that observed at an initial nitrate concentration of 150 mg/l therefore with increasing of the nitrate concentration, the chance of adsorption and removal efficiency were increases. In a survey, initial nitrate concentration was investigated. The removal efficiency in the concentration (of 50 mg/l and less) increased and then in more concentration was decreased. (23) Langmuir and Freundlich isotherms to determine Langmuir isotherm parameters we used the dimensionless RL and according to available data, its value calculated 0.66. This is demonstrator of suitability of Langmuir isotherm. To determine Freundlich isotherm parameters, is used 1/n that the value of this was found 0.99. According to these values it can be concluded that experimental results are consistent with Langmuir and Freundlich models1. Conclusion analytical results of the Design Expert Software show that the optimum conditions for the pH, initial nitrate concentration, absorbent dosage and contact time as follows: 3, 125 mg/l, 1250 mg/l and 48 min, respectively. But in the experiments test, the optimum condition was found at 2, 100mg/l, 1000 mg/land 37.5 min, respectively. Average efficiency of nitrate removal with raw almond skin charcoal and modified almond skin charcoal determined as 11.7% and 47.8% respectively. The results showed that the reducing of the pH has the greatest impact on nitrate removal efficiency.

Conclusion

According to the results of the analysis, the results of the data were determined by Design Expert software. The optimum removal conditions were determined at PH=3, nitrate concentration 125 mg/l, modified almond charcoal concentration 1250 mg/l, and contact time 48 min. The average absorption of nitrate by inactive charcoal of almonds was about 11.7% and for modified charcoal 47.8%, which shows an average of 36% increase in adsorption in modified charcoal compared to inactive charcoal. The results show that the pH has the greatest effect on increasing nitrate removal efficiency compared to other parameters. The study of adsorption isotherms shows that Langmuir isotherm has a better fit to Freundlich isotherm.

Footnotes

Acknowledgement:
The authors are grateful to Deputy of Research and Technology of Shahrekord University of Medical Sciences (SKUMS) for financial support (No.2369) and laboratory assistance of Department of Environmental Health Engineering, School of Health, SKUMS.

Conflict of Interest:

The authors declared no conflict of interest.

References

1. Bhatnagar A, Sillanpää M. A review of emerging adsorbents for nitrate removal from water. Chem Eng J 2011;168(2):493-504.
2. Fan AM, Steinberg VE. Health implications of nitrate and nitrite in drinking water: an update on methemoglobinemia occurrence and reproductive and developmental toxicity. Regul Toxicol Pharmacol 1996;23(1):35-43.
3. Zhou Y, Lu P, Lu J. Application of natural biosorbent and modified peat for bisphenol a removal from aqueous solutions. Carbohydr Polym 2012;88(2):502-8.
4. ISIRI. Physical and chemical properties of drinking water standards. Institute of Standards and Industrial Research of Iran; 1997. (Presian)
5. McLay CD, Dragten R, Sparling G, Selvarajah N. Predicting groundwater nitrate concentrations in a region of mixed agricultural land use: a comparison of three approaches. Environ Pollut 2001;115(2):191-204.
6. Shrimali M, Singh KP. New methods of nitrate removal from water. Environ pollut 2001;112(3):351-9.
7. Ali I, Gupta VK. Advances in water treatment by adsorption technology. Nat Protoc 2006;1(6):2661-7.
8. Worch E. Adsorption technology in water treatment: fundamentals, processes, and modeling. Germany: Walter de Gruyter; 2012.
9. Chingombe P, Saha B, Wakeman RJ. Surface modification and characterisation of a coal-based activated carbon. Carbon 2005;43(15):3132-43.
10. Nabais JV, Carrott PJ, Carrott MR, Menéndez JA. Preparation and modification of activated carbon fibres by microwave heating. Carbon 2004;42(7):1315-20.
11. Vinke P, Van der Eijk M, Verbree M, Voskamp A, Van Bekkum H. Modification of the surfaces of a gasactivated carbon and a chemically activated carbon with nitric acid, hypochlorite, and ammonia. Carbon 1994;32(4):675-86.
12. Shim J-W, Park S-J, Ryu S-K. Effect of modification with HNO3 and NaOH on metal adsorption by pitch-based activated carbon fibers. Carbon 2001;39(11):1635-42.
13. Nakagawa Y, Molina-Sabio M, Rodríguez-Reinoso F. Modification of the porous structure along the preparation of activated carbon monoliths with H3PO4 and ZnCl2. Microporous Mesoporous Mater 2007;103(1):29-34.

14. Mohan D, Sarswat A, Singh VK, Alexandre-Franco M, Pittman CU. Development of magnetic activated carbon from almond shells for trinitrophenol removal from water. Chem Eng J 2011;172(2-3):1111-25.

15. Bhatnagar A, Ji M, Choi YH, Jung W, Lee SH, Kim SJ, et al. Removal of nitrate from water by adsorption onto zinc chloride treated activated carbon. Sep Sci Technol 2008;43(4):886-907.

16. 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(3):255-7.

17. Ghaneian MT, Momtaz M, Dehvari M. An investigation of the efficacy of Cuttlefish bone powder in the removal of Reactive Blue 19 dye from aqueous solutions: equilibrium and Isotherm studies. J Health Res 2012;1(2):68-78.

18. Ohe K, Nagae Y, Nakamura S, Baba Y. Removal of nitrate anion by carbonaceous materials prepared from bamboo and coconut shell. J Chem Eng Japan 2003;36(4):511-5.

19. Khan MA, Ahn YT, Kumar M, Lee W, Min B, Kim G, et al. Adsorption studies for the removal of nitrate using modified lignite granular activated carbon. Sep Sci Technol 2011;46(16):2575-84.

20. Rezaee A, Godini H, Dehestani S, Khavanin A. Application of impregnated almond shell activated carbon by zinc and zinc sulfate for nitrate removal from water. J Environ Health Sci Eng 2008;5(2):125-30.

21. Boudrahem F, Aissani-Benissad F, Ait-Amar H. Batch sorption dynamics and equilibrium for the removal of lead ions from aqueous phase using activated carbon developed from coffee residue activated with zinc chloride. J Environ Manag 2009;90(10):3031-9.

22. Nassar HNI. Nitrate and nitrite ion removal from aqueous solutions by activated carbon prepared from olive stones. [MSc Thesis]. Palestine: An-Najah National University; 2012.

23. Yari AR, Shirzad SM, Hashemi S, Alizadeh M. Removal of heavy metals from aqueous solutions by natural adsorbents (A review). Arch Hyg Sci. 2013;2(3).