Asian Journal of Green Chemistry 3 (2019) 1-12

Contents lists available at Avicenna Publishing Corporation (APC)

Asian Journal of Green Chemistry

Journal homepage: www.ajgreenchem.com

Original Research Article

Modification of activated carbon by $ZnCl_2$, $CaCl_2$, $MgCl_2$ and their applications in removal of nitrate ion from drinking water

Homa Shafiekhani[a,*], Roghiyeh Barjoizadeh[b]

[a] *Department of Chemistry, Payame Noor University, PO BOX 19395-4697 Tehran, Iran*

[b] *Department of Chemistry, Lamerd Branch, Islamic Azad University, Lamerd 74311, Iran*

ARTICLE INFORMATION

Received: 15 April 2018
Received in revised: 2 May 2018
Accepted: 5 May 2018
Available online: 29 June 2018

DOI: 10.22034/ajgc.2018.65164

KEYWORDS

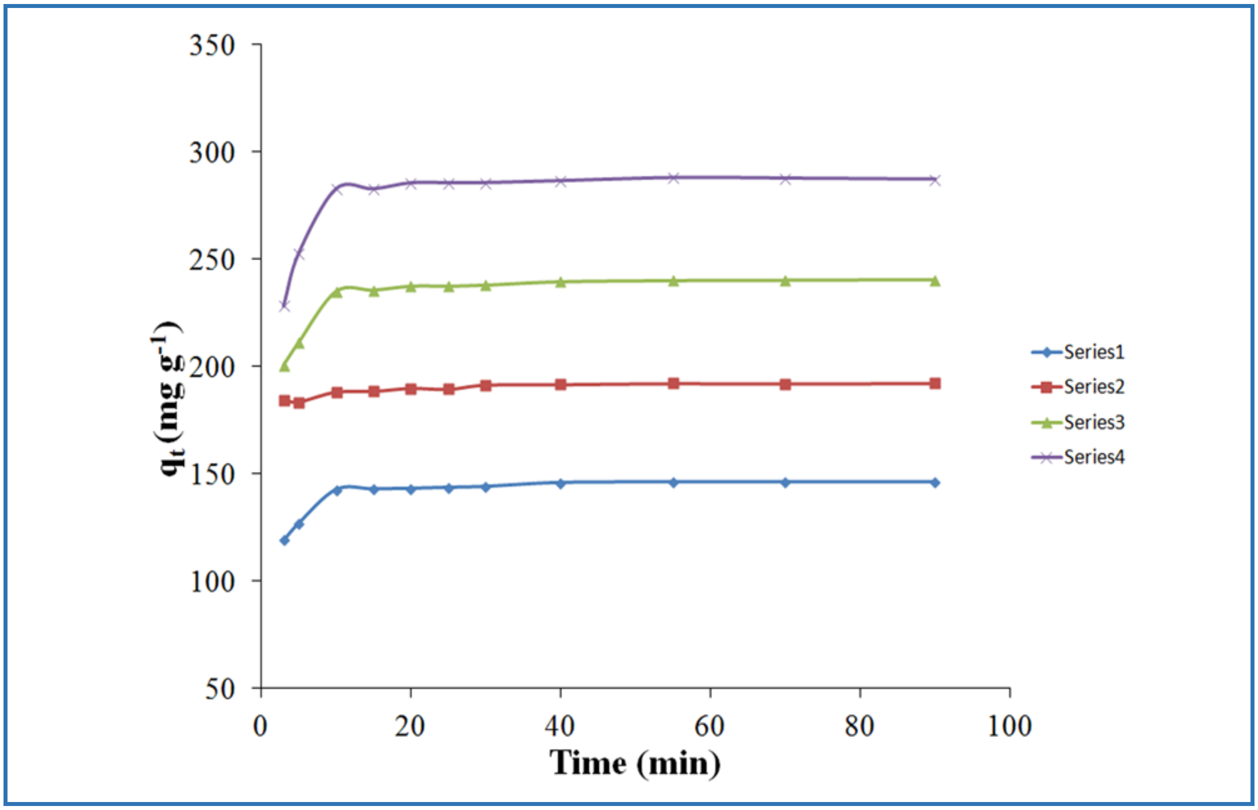
Nitrate removal
Adsorption isotherm
Activated carbon
Kinetic

ABSTRACT

Nitrate is one of the most crucial pollutants in the urban and rural drinking water resources. Many techniques have been used to remove these contaminants. In this study, granular activated carbon (GAC), modified with a mixture of $ZnCl_2$, $CaCl_2$ and $MgCl_2$ was isutilized for the removal of nitrate from the water. Results of removing this adsorbent by batch method and changing the effective factors; including, contact time, adsorbent dose, nitrate concentration, pH, and temperature, were investigated. Two theoretical adsorption isotherms; namely Langmuir and Freundlich were used to describe the experimental results. The Langmuir isotherm model effectively explained the sorption process and showed the best coefficient of determination (0.9947). The nitrate sorption kinetic data were successfully fitted to pseudo-second order kinetic model. Adsorption was maximized between pH ranges from 4 to 8. The overall results demonstrated potential applications of modified GAC for nitrate removal from the aqueous solutions.

Corresponding author, email: shafieehoma@yahoo.com (H. Shafiee).
Tel: +98917 7106991.

Graphical Abstract



Introduction

Advancements in agricultural and industrial activities have caused the creation of anionic inorganic toxic pollutants such as nitrate. Nowadays, these pollutants in environment have caused public concern about the quality of underground water [1, 2].

Nitrate is created and entered into the water resources through industrial processes such as fertilizing, cellophane, pectin, and ammunition making [3]. Hence, the World Health Organization (WHO) and the United State Environmental Protection Agency (USEPA) have recommended maximum concentration of nitrate in drinking water; 50 mg/L in terms of nitrogen and 10 mg/L in terms of nitrate [4, 5]. Elevated nitrate concentrations in drinking water which are more than the maximum acceptable contaminant level are associated with problems problem such as methemoglobinemia in babies and stomach cancer in adults. For these reasons, removal of nitrate from water is essential. When the nitrate concentration of the drinking water surpasses the most extreme allowable concentration, the nitrate removal becomes a technical challenge. To remove different forms of nitrogen from aqueous solutions, various methods have been reported. These methods include ion exchange, adsorption, reverse osmosis, electrodialysis, denitrification, algal removal, ozonation, and activated carbon filter [6, 7]. Among these processes, the adsorption process of nitrate ions was the object of a very small number of research [8, 9]. During recent years, adsorption process has been considered for its ease of operation, design, economic considerations, as well as regeneration of low-cost adsorbents for pollutant removal.

In this study, the activated carbon was modified with a mixture of $ZnCl_2$, $CaCl_2$, and $MgCl_2$ and used to remove nitrate from the aqueous solution by sorption. Accordingly, the effects of the various parameters on the adsorption process such as pH, sorbent concentration (Cs), and time were investigated. Adsorption isotherms were performed at different nitrate concentrations.

Experimental

Materials and methods

All chemicals and reagents which were used in the modification and adsorption experiments were purchased from Merck. A Shimadzu 1601 (UV/Vis) spectrophotometer with a 1.0 cm quartz cell was used for absorbance measurement at a fixed wavelength. A Metrohm pH meter 827 was employed for pH measurements. Commercial granular activated carbon (GAC) as a solid sorbent with a particle size between 1 to 2 mm was used. The standard stock solution of nitrate (100 mg/L) was prepared by dissolving 0.0137 g of $NaNO_3$ in water in 100 mL volumetric flask. Calcium chloride, magnesium chloride and zinc chloride were used to chemically modify the activated carbon surface. A 500 mL solution of 500 mg/L^{-1} $CaCl_2$, $MgCl_2$, and $ZnCl_2$ was prepared in a 500 mL beaker. Then, 10 g of GAC was added, and the solution was stirred for 3 h. Following the filtration of the solution, the coal retained by the filter was dried for 24 h in an oven at 150 °C.

Batch experiments

For each batch adsorption test, 25 mL of the solution containing 100 mg/L^{-1} of nitrate with granular activated carbon modified with $CaCl_2$, $MgCl_2$, and $ZnCl_2$ was used. The tests were performed at room temperature (25±3 °C) for 45 min under the constant stirring in a shaker. Subsequently, the solution was filtered with filter paper and, then, the concentration of the residual nitrate determined by UV-vis spectrophotometer (λ=220 nm) as described in the standard methods [10]. The amount of nitrate was adsorbed to the GAC-modified material was calculated by the following equation.

$$q_{e}=\left(\frac{(C_i-C_e)}{M_s}\right)\times(V) \qquad (1)$$

q_e represents the amount of adsorbate adsorbed per unit mass of adsorbent at equilibrium (mg/g), C_i is the initial sorbate concentration (mg/L^{-1}), C_e is the equilibrium concentration (mg/L), V is the volume of the solution (L), and M_s is the mass of sorbent (g). The effect of pH on the sorption process was evaluated by varying the pH of the sorption solution. The pH values were established for each test and kept constant by regular monitoring.

Adsorption isotherms

Adsorption isotherm model of Langmuir and Freundlich isotherms was utilized to describe the experimental adsorption data. The Langmuir isotherm has been broadly utilized by many researchers in order to describe the adsorption of heavy metals, dyes and organic pollutants onto materials for example, activated carbon, clay and food industry wastes [11–13]. The Langmuir isotherm model estimates the maximum adsorption capacity resulted from the complete monolayer coverage on the adsorbent surface [14]. The non-linear Langmuir isotherm model can be expressed by the following equation:

$$\frac{C_e}{q_m} \quad \frac{1}{q_m K_L} = \frac{C_e}{q_e} \tag{2}$$

Where q_m represents the maximum capacity of sorption (mg/g), C_e is the equilibrium concentration (mg/L), and K_L is the constant of surface energy (L/mg).

While Freundlich isotherm presumes that the adsorption process happens on heterogeneous surfaces with non-uniform distribution of adsorption heat [15], it can also describe the Freundlich equation as an empirical relationship, in light of the fact that the sorption capacity is unlimited when the solution concentration increases. For strongly favorable isotherms, the Freundlich equation generally fits the empirical data, especially for solid-liquid sorption. Equation 3 represents the Freundlich model.

$$q_e = K_f {C_e}^{1/n} \tag{3}$$

Where C_e is the equilibrium concentration (mg/L), K_f and n are Freundlich constants with n giving an indication of how favorable the adsorption process is (mg/g) $(L/mg)^{1/n}$ is related to the adsorption capacity of the adsorbent.

In this study, Langmuir and Freundlich isotherm models were used to describe the relationship between the amounts of adsorbed nitrate and its equilibrium concentration in a solution at 28 °C using adsorbate (1 g), nitrate solutions (60, 80, 100, 120 mg/L) pH (7) and contact time (45 mi). The results are shown in Figure 1.

Results and discussion

Optimization of pH of solution

The pH is one of the most important parameters controlling the removal of pollutants from waste water [16]. Adsorption of nitrate by a modified and activated carbon was investigated in the pH range of 4–8. The pH was varied by adding different volumes of NaOH and HCl solutions. After the desired pH was fixed for nitrate solution, 1 g of adsorbent was mixed with it. The mixture was then shaken at 28 °C for 45 min and nitrate analysis was performed. The result showed that when the pH increased from 4–7, the adsorption efficiency increased, whereas it decreased from 7 to 9 (Figure 2) and the highest removal efficiency of nitrate (72.2 %) occurred at pH = 7. As a result, in subsequent studies, the optimum pH of 7 was selected. Also, the effect of buffer volume on nitrate removal by activated carbon was shown in Figure 3.

Effect of contact time

Contact time is an important parameter to determine the equilibrium time of adsorption process [17]. To determine the equilibrium time, 1 g of the adsorbent was mixed with nitrate solutions (25 mL, 100 mgL) with pH 7. Experimental determination of nitrate ion was conducted after the mixture was shaken at 30 °C and for the desired time. The experiment was done for different contact times of 10, 25, 35, 45, 55 and 65 min. The results are illustrated in Figure 4. As seen in Figure 4, the nitrate adsorption onto the activated carbon increases when increasing the treatment time starting from 0 to 45 min. This trend could be attributed to the fact that between 0–45 minutes, there exists a number of vacant sites on the adsorbent. But, after 45 min , these sites became filled with the adsorbate molecules in which, at a point between 55 and 65 min, the repulsive force between solute molecules and bulk phase became significant and the vacant sites remained constant with time.

Effect of adsorbent dosage

Different amounts (0.3–2.0 g) of adsorbent was placed into conical flasks, and, then, nitrate solutions (25 mL, 100 mg/L) with pH 7 were also added to it. The mixture was then shaken for 45 min at 30 °C. As indicated in Figure 5, removal of nitrate increased with increase in adsorbent mass. With the increasing dosage of adsorbent from 0.3 to 1 g, the removal efficiency of nitrate increased from 72.7 to 77%. The increase in the dosage of adsorbent can provide a larger specific surface area and more adsorption sites for nitrate removal. However, as the adsorbent dosage increased from 1 g/100 mL to 2 g/100 mL, the removal efficiency of nitrate decreased slightly and became stable. This may be due to the aggregation of adsorbent particles with the increase in the adsorbent dosage, leading the surface adsorption sites to fail to be fully utilized. Therefore, 1 g adsorbent was used in the subsequent studies as the optimum amount.

Figure 1. Langmuir plot for adsorption of nitrate solution (100 mg/L)

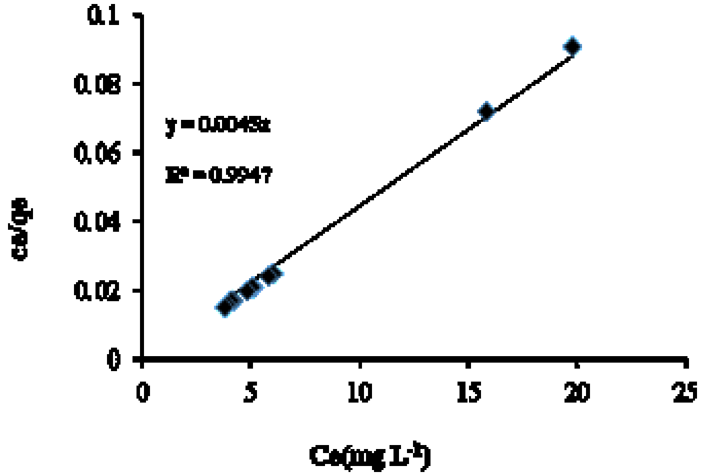


Figure 2. Effect of pH on nitrate removal by activated carbon

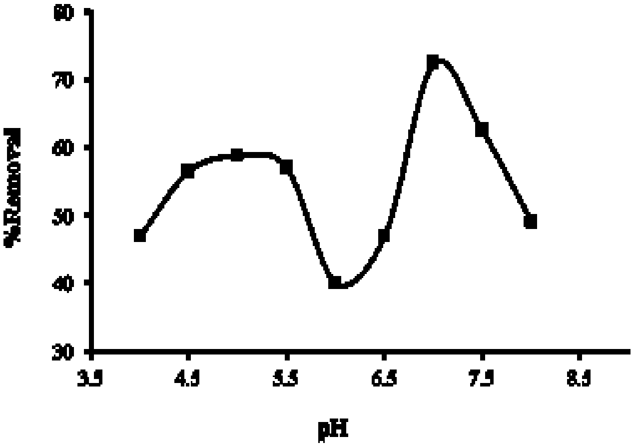
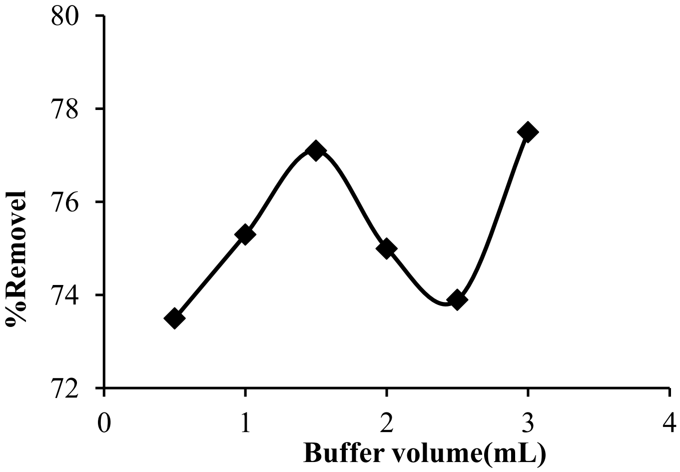


Figure 3. Effect of buffer volume on nitrate removal by activated carbon



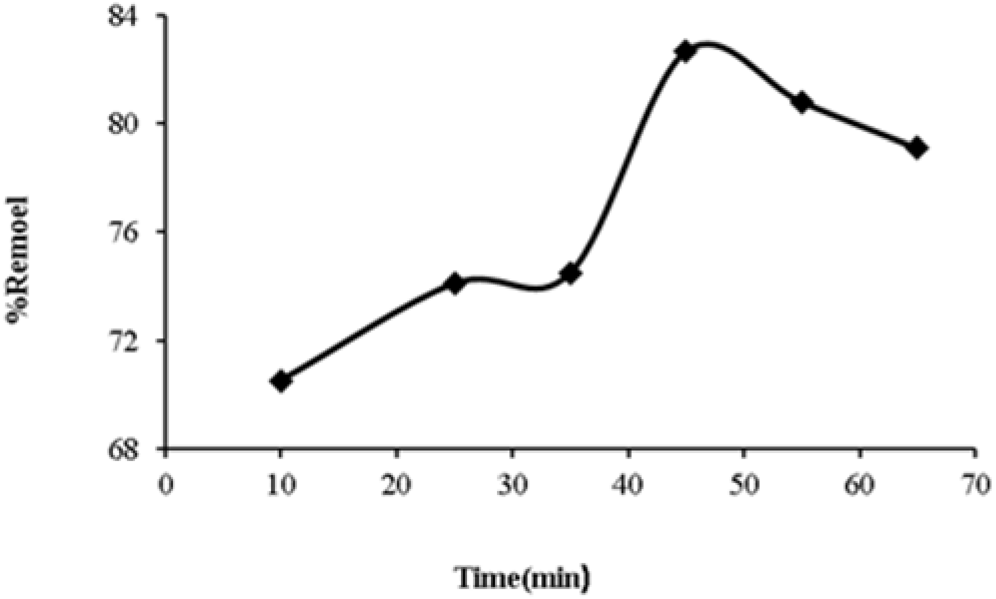


Figure 4. Effect of contact time on nitrate removal by activated carbon

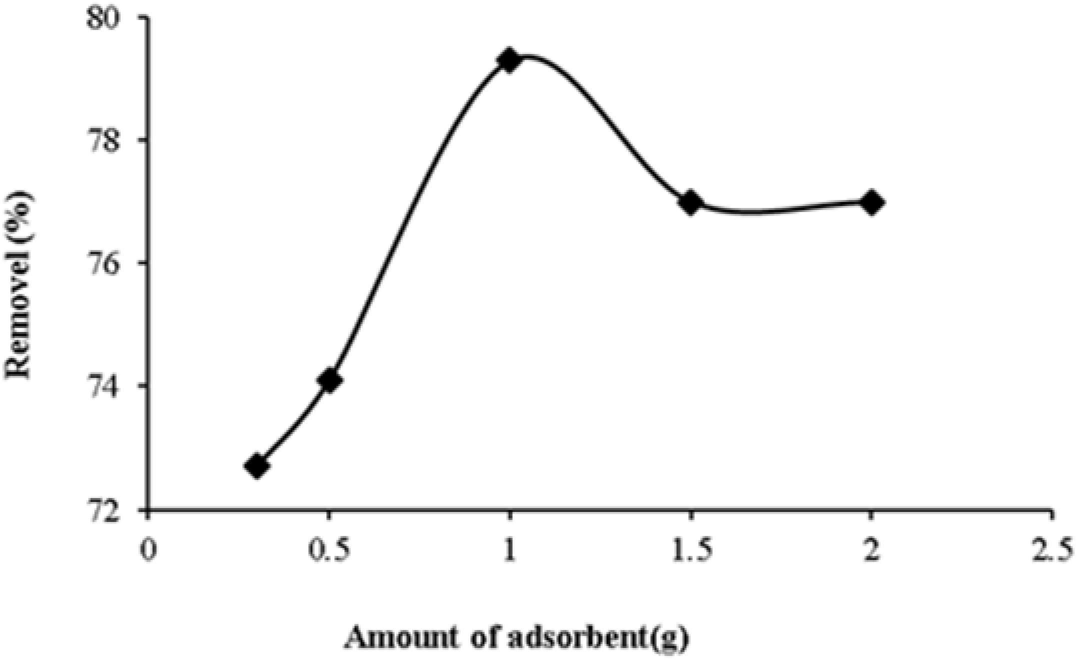


Figure 5. Effect of mass of adsorbent on nitrate removal by activated carbon

Effect of temperature

Temperature affects the adsorption rate by altering the molecular interactions and the solubility of the adsorbent [18] and thus affects adsorption. To find an optimum temperature, the adsorption was done at temperatures of 5, 15, 20, 25, 30, 40, 50, and 60 °C. The result showed that the percentage of nitrate adsorption increased when the temperature increased to 25 °C. Therefore, temperature 25 °C was used in subsequent studies as the optimum temperature (Figure 6).

Interference studies

Various ions were added to the solution containing 100 mg/L of nitrate and the general batch procedure was applied. The tolerance limit was set as the concentration required to cause ± 5% error in determination of the nitrate. The obtained results are given in Table 1. Among the studied anions and cations, many of them did not interfere even when it was more than 10 times of concentration of nitrate. So, the proposed method can be applied for the determination of nitrate in water samples containing the studied ions in the reported concentrations.

Effect of agitation time and initial nitrate concentration

The amount of adsorbed nitrate (mg/g) increased with increase in nitrate concentration and, then, remained nearly constant after equilibrium time (Figure 7). The equilibrium time was found to be 45 min for all the studied concentrations. The equilibrium (q_e) increased the amount of the adsorbed nitrate from 119 to 287 mg/g as the concentration was increased from 60-120 mg/L. The plots are smooth and continuous leading to saturation, suggesting the possible monolayer coverage of nitrate on the surface of the adsorbent.

Adsorption kinetics

The adsorption kinetic data of nitrate are analyzed using the Lagergren first order rate equation (Lagergren, 1898):

$$\log(q_{e-}q) = \log q_{e-}\, {}^{k_t}/_{2.303} \tag{4}$$

Where q_e and q are the amount of the adsorbed nitrate (mg/g) at equilibrium and at time (min) respectively, and K_1 is the Lagergren rate constant of pseudo first order adsorption ($1\ min^{-1}$). Values of K_1 are calculated from the slope of the plot of (q_e−q) versus t. It was found that the calculated values don't agree with the experimental values. This suggests that the adsorption of nitrate does not follow pseudo first order kinetics [20]. The second order kinetics can be represented as:

$$\frac{t}{q_t} = \frac{1}{k_2 {q_e}^2} + \frac{t}{q_e} \tag{5}$$

Figure 6. Effect of temperature on nitrate removal by activated carbon

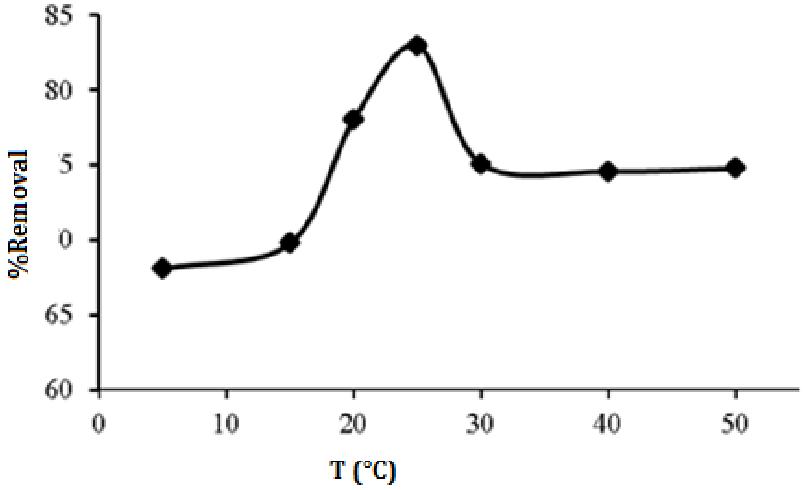


Figure 7. Effect of agitation time and concentration of nitrate on removal

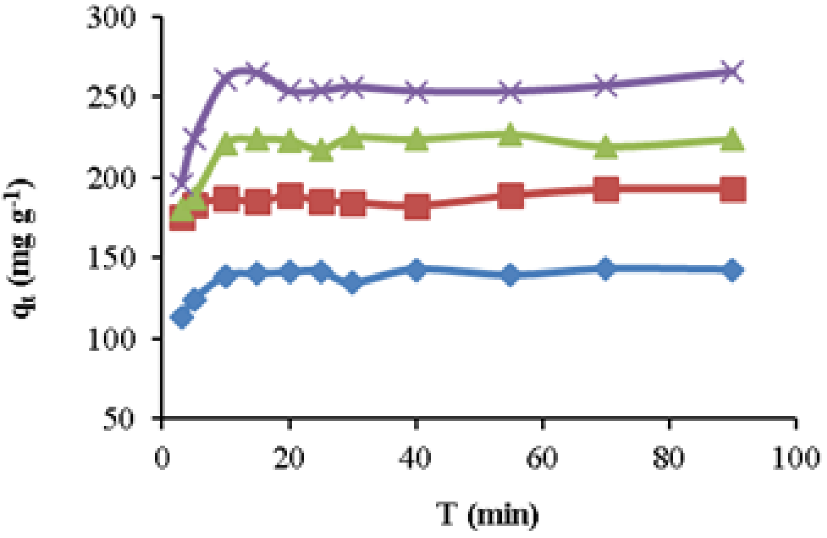


Table 1. Tolerance limit of the method for interference studied. The NO_3^- concentration in samples was 100 mg/L^{-1}

Interference ion	Tolerance limit Ratio (mg/L^{-1})
NH_4^+ ،cu$^+$ ،Ni^{2+} ،I^- ،K^+ ،Ca^{2+} ،Na^+ ،SO_3^{2-} ،Urea ،Sn^{2+} ،Ag^+ Fe^{3+} ، Zn^{2+} ،Co^{2+}، Fe^{2+}، Tartrate	1000
PO_4^{3-} ،$C_2O_4^{2-}$ ،Cu^{2+}	500
HCO_3^- ،CO_3^{2-}	200
Al^{3+} ،Mg^{2+}	100
Mn^{2+}	5

Where k_2 is the equilibrium rate constant of pseudo second order adsorption (g/mg/min). Values of k_2 andq_e were calculated from the plot of the $\frac{t}{q}$ versus t (Figure 8). The calculated q_e values agreed with experimental q_e values and also the correlation coefficients for the second order kinetic plots at all the studied concentrations were above 0.99 (Table 2). These results indicate that the studied adsorption system belongs to the second order kinetic model. Similar phenomenon has been observed in the adsorption of Cr (VI) by using tires and saw dust [21].

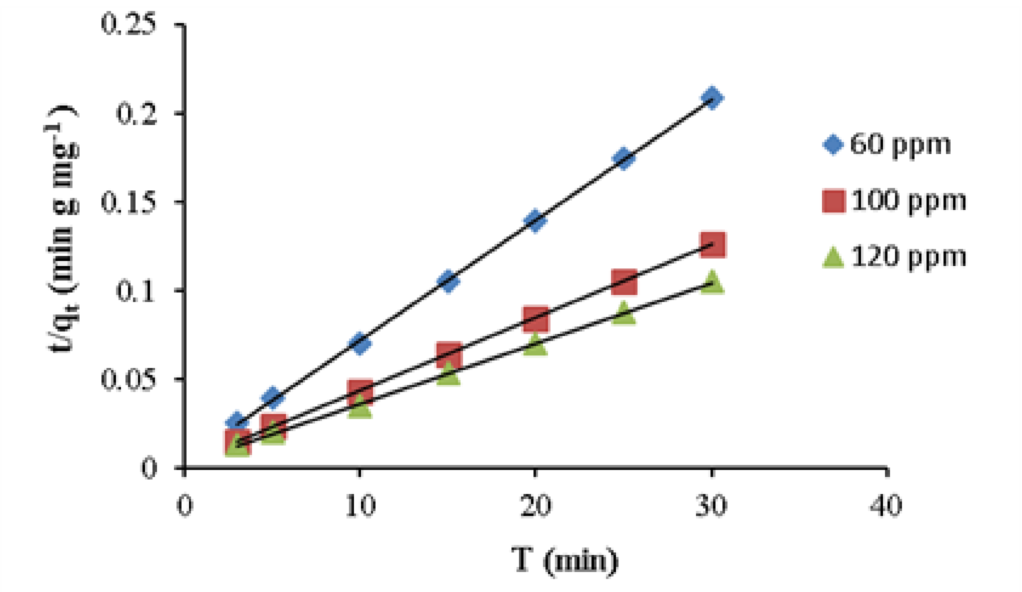


Figure 8. Plot of the pseudo second–order model at different initial nitrate concentratio

Table 2. Parameters of second order adsorption experimental values for different initial nitrate concentrations

Initial nitrate conc.(µg/mL^{-1})	Parameter	R^2
60	$\frac{t}{q} = 0.0068\,t + 0.004$	0.9998
100	$\frac{t}{q} = 0.0041\,t + 0.0024$	0.9998
120	$\frac{t}{q} = 0.0034\,t + 0.0023$	0.9997

Conclusion

In sum, on the basis of the obtained results, it maybe concluded that the activated carbon modified with a mixture of $CaCl_2$, $MgCl_2$ and $ZnCl_2$ can be regarded as an effective sorbent for the removal of nitrate from aqueous solutions. The increase in sorbent dosage augmented the percent removal of nitrate due to an increase in sorbent surface and dosage. Maximum removal was observed between pH 4 to 8. In this range, 72.2% of the nitrate was removed, indicating that the sorption of nitrate with the mixture of $CaCl_2$, $MgCl_2$, and $ZnCl_2$ -modified activated carbon can be accomplished over a wide range of pH. Langmuir isotherm curves were found to be significant as compared to Freundlich isotherm. Finally, it was found that sorption kinetics obeyed a second-order kinetic model.

Acknowledgment

We would like to show our gratitude to the Lamerd Azad University for their assist and encouragements.

Disclosure statement

No potential conflict of interest was reported by the authors.

References

[1]. Arora M., Eddy N.K., Mumford K.A., Baba Y., Perera J.M*., Stevens* G.W*. Cold. Reg. Sci. Technol*., 2010, **62**:92

[2]. Ptil I.D., Husain M., Rahane V.R. *Int. J. modern. Eng. Research.*, 2013, **1**:346

[3]. Ghafari Sh., Hasan M., Aroua M.K. *Bioresour. Technol.*, 2008, **99**:3965

[4]. Kamaraj R., Pandiarajan A., Jayakiruba S., Naushad M., Vasudevan S. *J. Mol. Liq.*, 2016, **215**:204

[5]. Salam M.A., Fageeh O., Al-Thabaiti S.A., Obaid A.Y. *J. Mol. Liq.*, 2015, **212**:708

[6]. Loganathan P., Vigneswaran S., Kandasamy J. *J. Environ. Mange.,* 2013, **131**:363

[7]. Ota K., Amano Y., Aikawa M., Machida M. *Appl. Surf. Sci.*, 2013, **276**:838

[8]. Hanafi H.A., Azeema S.M.A. *J. Environ. Anal. Toxicol.,* 2016, **6**:346

[9]. Kalantary R.P., Dehghanifard E., Mohseni-Bandpi A., Rezaei L., Esrafili A., Kakavandi A., Azari A. *Desal. Water treat.,* 2016, **57**:16445

[10]. Apha A. *WPCF Standard methods for the examination of water and wastewater*; American Public Health Association: Washington DC, 1995; p 24

[11]. Bahrami H., Safdari J., Moosavian M.A., Torab-Mostaedi M. *Chem. Ind. Chem. Eng. Q.*, 2012, **18**:497

[12]. Shrestha S., Son G., Lee S.H., Lee T.G. *Chemosphere,* 2013, **92**:1053

[13]. Torab-Mostaedi M. *Chem. Ind. Chem. Eng. Q.*, 2013, **19**:79

[14]. Langmuir, I. *J. Am. Chem. Soc.,* 1918, **40:**1361

[15]. Suzuki M. *Adsorption engineering;* Elsevier: New York , 1990

[16]. Nuhoglu Y., Oguz E. *Process Biochem.,* 2003, **38**:1627

[17]. Kilic M., Apaydin-Varol E., Pütün A.E. *J. Hazard. Mater.,* 2011, **189**:397

[18]. Singh D., Srivastava B., Bharadwaj R. *Pollut. Research,* 2001, **20**:173

[19]. Lagergren S.K. *Sven. Vetenskapsakad. Handingarl*, 1898, **24**:1

[20]. Aksu Z., Tezer S. *Process Biochem.,* 2000, **36**:431

[21]. Carvalho A., Pires J., Veloso P., Machado M., de Carvalho M.B., Rocha J. *Micropore mesopore mater.,* 2003, **58**:163

How to cite this manuscript: Homa Shafiekhani*, Roghiyeh Barjoizadeh. Modification of activated carbon by $ZnCl_2$, $CaCl_2$ $MgCl_2$ and their applications in removal of nitrate ion from drinking water. *Asian Journal of Green Chemistry*, 3 (1) 2019, 1-12. DOI: 10.22034/ajgc.2018.65164