Desalination and Water Treatment
www.deswater.com
doi:10.5004/dwt.2017.20705

76 (2017) 265–275
May

Removal of nitrate from aqueous solution using activated carbon modified with Fenton reagents

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Received 7 February 2016; Accepted 12 March 2017

ABSTRACT

In this study, we modified a commercial granular activated carbon (GAC) with Fenton reagents (Fe^{2+} and H_2O_2) using a chemical activation approach. The modified granular activated carbon (MGAC) was characterized using SEM, BET, and EDX techniques and used as an adsorbent for removal of nitrate (NO_3) from aqueous solution in batch experiments. Various factors affecting the uptake behavior including ratio of Fe^{2+} to H_2O_2, pH, contact time, adsorbent dose, initial nitrate concentration, and desorption behavior were investigated. The maximum adsorption capacity was found to be 43.1 mg/g at equilibrium time of 60 min. Experimental data were fully described by pseudo-second-order kinetic and Freundlich isotherm models with high correlation coefficient. Under obtained optimum conditions, the MGAC shows higher removal efficiency compared to a GAC adsorbent. Ultimately, MGAC can be applied as an efficient and promising agent for nitrate adsorption in aqueous solution.

Keywords: Chemical activation; Activated carbon; Adsorption modeling; Nitrate

1. Introduction

In recent years, there has been growing concern worldwide regarding nitrate (NO_3^-) contamination in groundwater and associated health problems. Most of conducted research have shown that the presence of large nitrate concentrations in potable water resources can potentially lead to the serious troubles, including eutrophication phenomenon and infectious diseases, such as cyanosis and cancer of the alimentary canal [1] and blue-baby syndrome among infants [2]. The World Health Organization (WHO) and US EPA have established the maximum contaminant level (MCL) of 10 mg/L for NO_3–N in drinking water. Therefore, the removal of large nitrate concentrations from solution before their discharge into the drinking water resources is so crucial.

To date, lots of environmental remediation techniques such as ion exchange, electrodialysis, reverse osmosis, catalytic denitrification and biological denitrification, chemical reductions using zero-valent iron (ZVI), and adsorption [3,4] were developed to remove nitrate from water. However, their financial restrictions and operational difficulties, excessive biomass production, and secondary wastes generation and requirement to regeneration made researchers hesitant to employ them in large scale [5]. Biological de-nitrification is not effective at temperatures below 7°C and therefore, may not be useful for treating groundwater. Reverse

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osmosis is a very expensive approach for treating large quantities of wastewater [6]. Among the above mentioned techniques, the adsorption known as one of the most desirable processes from the point of cost-effectiveness, wastewater reuse, simplicity and flexibility in design, easy operation, high efficiency, being environmentally friendly, and lack of sensitivity to the contaminants and toxic substances, has widely been preferred [7,8]. In recent years, several research have been performed on removal of various contaminants from water by different adsorbents such as clay, powder and granular activated carbon [9–11], carbon nanotubes (CNTs) [12], zeolite [13] and bamboo powder charcoal [14].

Activated carbon with unique physical and chemical features including high porosity and adsorption capacity, cost-effectiveness, and effective regeneration for removal of a wide spectrum of contaminants has been more emphasized than the other adsorbents by environmentalists [15–17]. It is well known as a good adsorbent to effectively adsorb pollutants from contaminated water and industrial wastewaters [18].

Recently, modification and impregnation techniques have been performed to improve removal efficiency and surface adsorption thereby adding selectivity to carbon. AC can be modified through physical, chemical, and biological processes. Moreover, oxidative and non-oxidative methods of surface treatments of AC have been reported in the literature [19]. In comparison with physical methods, modification of carbon surfaces by using chemical treatment is mostly preferred, due to the low temperature needed in the process, and shorter treatment time [18]. Moreover, to improve AC adsorption capacity using this process, some researchers have impregnated it with iron [20], aluminum [21]and Cl^- [22] for removing various pollutants.

Fenton oxidation,consisting of catalyst (Fe^{2+}/Fe^{3+}) and hydrogen peroxide (H_2O_2), has been considered as an efficient approach to remove and mineralize organic pollutants in wastewater. Fenton process can be performed by reaction between H_2O_2 as an oxidant and Fe^{2+}/Fe^{3+} ions as a catalyst [23]. Although several studies have been conducted on the application of Fenton process, none aimed at modifying adsorbent using Fenton reagents. Additionally, the removal of nitrate using modified activated carbon by Fenton process has not been studied well in the literature. Therefore, the present study focused on modification of a granular activated carbon (GAC) by Fenton reagents (H_2O_2 and Fe^{2+}) and its application as a new adsorbent for nitrate removal from aqueous solution. It seems that the Fenton process follows a complex mechanism and subsequently, increases the nitrate adsorption efficiency by GAC. In this work, firstly, the modified GAC (MGAC) was synthesized and then, characterized by using various techniques. The influence of different input variables on the process performance was examined in a batch system. The in vitro capabilities have been optimized and the studies regarding isotherms and kinetics of the adsorption processes were carried out in detail.

2. Materials and methods

2.1. Reagents

All the reagents were of analytical grade and used without further purification. Hydrogen peroxide solution (35% v/v), hydrochloric acid (HCl), sodium hydroxide (NaOH), ferrous sulfate ($FeSo_4{\cdot}7H_2O$), and potassium nitrate (KNO_3) were purchased from Merck (Germany). A commercial activated carbon in the form of granular was obtained from Sigma-Aldrich, USA. The granules were crushed and sieved to make a particle size of 1–2 mm. Deionized water (DI-water) was applied to prepare the solution in all experiments.

2.2. Sorbent preparation and properties

The GAC rinsed sequentially with distilled water and dried in an oven at 105ºC overnight. Then, it was soaked in Fenton solution containing Fe^{2+} and $H_2O_2$with different ratios (Fe^{2+}/H_2O_2: 0.01, 0.04 and 0.06 w/w) for 24 h and shaken in a jar using a stirrer with speed of 200 rpm and neutral pH at a constant temperature of 25 ± 1ºC. Afterwards, the Fenton solution was filtered and the solid GAC particles were washed several times with distilled water. Finally, the obtained solid product, called modified granular activated carbon (MGAC) was dried at 80–85ºC and kept at vacuum desiccator until future use.

The surface morphology of the MGAC was analyzed using a scanning electron microscope (SEM, MIRA3, Tescan, Czech Republic), at 15 keV. The specific surface area, pores volume, and size of adsorbent were measured by Brunaeur, Emmett, and Teller (BET, Quantachrome, NOVA 2000) method using N_2 adsorption-desorption isotherms at 77.3ºK. Additionally, the elemental analysis of GAC and MGAC composites was determined using scanning electron microscope equipped with EDX (PHILIPS, XL-30). Fourier transform infrared spectrophotometer (FT-IR) spectra of the GAC and MGAC were obtained before and after the adsorption using Tensor 27, Bruker model (Germany) to confirm the functional groups present in them.

2.3. Adsorption studies

Batch experiments were performed in a laboratory to examine the performance of the MGAC on nitrate removal from aqueous solution. For optimization of several variables such as pH of solution (2–10), contact time (0–120 min), adsorbent dosage (0.5–2.5 g/L), and initial nitrate concentration (10–50 mg/L), the adsorption efficiency of nitrate on the MGAC was investigated at room temperature (25 ± 1ºC). In this regards, the experiments were performed in several 100 mL plastic bottles, each including 50 mL of nitrate solution. The solution pH was adjusted via addition of 0.1 M HCl and NaOH. To ensure the ideal mixing of the adsorbent and the adsorbate, the samples were put on a shaker at 200 rpm for 120 min. After completing the experiments, the adsorbents were extracted from the solution using a 0.45-m filter (Whatman, USA) and the residual concentration of nitrate was determined according to the standard method using a UV-Visible spectrophotometer (HACH DR5000) [24]. Nitrate concentration was determined at 220 nm and corrected by subtracting the second absorbance at 275 nm. Afterward, the optimum contact time was obtained at a pre-evaluated pH and subsequently, kinetic modeling was developed by sampling at different time intervals during 120 min. The effect of initial nitrate concentrations, the adsorbent dosages at the optimal pH, and contact time was evaluated in order to determine the equilibrium isotherms parameters of the adsorption. All the experiments were carried out in triplicate and the mean value was reported as final results. The efficiency of nitrate removal and the adsorption capacity, q (mg/g), were determined as:

$$\text{Re}\ (\%) = \left(1 - \frac{C_e}{C_o}\right) \times 100 \tag{1}$$

$$q_e(\text{mg/g}) = \left(\frac{C_o - C_e}{W}\right) V \tag{2}$$

where C_0 and C (mg/L) are the initial and residual adsorbate concentrations, respectively, V (L) is the volume of solution, and W (g) is the weight of adsorbent.

2.4. Adsorption kinetics

The adsorption kinetic is one the most important issues for understanding both the mechanisms of adsorption and assessment of influential factors on the reaction rate. Kinetics describe solute uptake rates and also defines the residence time of the adsorbate at the solid–liquid interface. The kinetics of nitrate adsorption on the MGAC were analyzed using pseudo-first-order [25], pseudo-second-order [26], and intraparticle diffusion [27] models. More details of these models are presented in Supplementary data.

2.5. Adsorption equilibrium isotherms

The adsorption equilibrium has always been explained by the isotherm equations such that their parameters indicate the surface characteristics and affinity of the adsorbent toward the adsorbate. In order to evaluate the adsorption capacity of the MGAC for nitrate, the adsorption equilibrium of nitrate was studied as a function of nitrate concentration. In this study, three widely–used adsorption isotherm models (Langmuir [10], Freundlich [28], Temkin [29]) were employed to describe the adsorption equilibrium of nitrate onto the MGAC. Further information of these models are shown in Supplementary data.

The basic features of the Langmuir isotherm can be explained in terms of dimensionless separation factor R_L; ($R_L = 1/(1 + K_L C_0)$). The type of isotherm is indicated by R_L values. Adsorption is undesirable when $R_L > 1$, desirable when $0 < R_L > 1$, irreversible when $R_L = 0$, and liner when $R_L = 1$ [30].

3. Results and discussion

3.1. Characteristics of the adsorbent

The SEM images of the GAC and MGAC before and after adsorption of nitrate are presented in Fig. 1. As observed, GAC has various irregularities and pores on its surfaces which created a highly porous structure that is favorable for the adsorption of adsorbates (Fig. 1a).

As can be seen in Fig. 1a, pores on the activated carbonare non-uniformly distributed on the GAC surface. However, compared to GAC, the MGAC morphology before the adsorption shows an asymmetric porous structure and irregular and heterogeneous surface with micro cavities capable of absorbing nitrate ions (Fig. 1b). As seen in Fig. 1c, the surfaces of the MGAC after nitrate adsorption

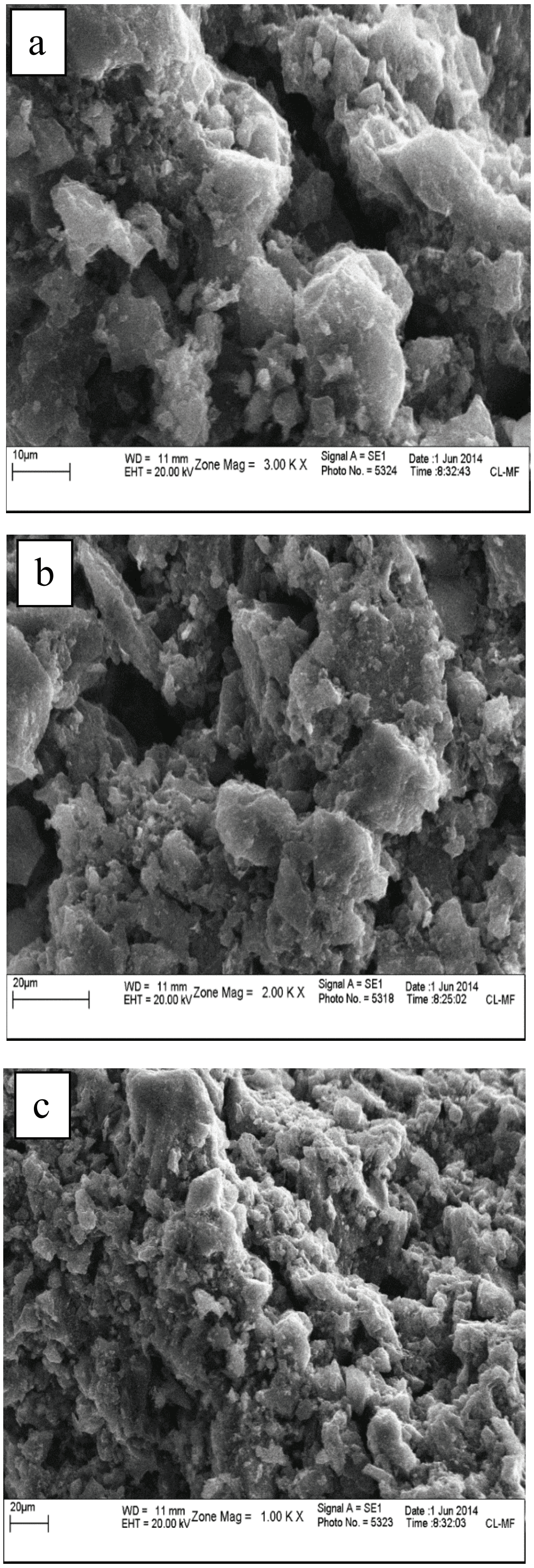


Fig. 1. SEM images of GAC (a), MGAC before (b) and after (c) the adsorption of nitrate.

were relatively smoother than that of the GAC asthe cavities were filled by nitrate ions.

Results of EDX analysis confirmed that several elements such as carbon, oxygen, iron, calcium, aluminum, and silicate are present in the structure of the GAC and MGAC adsorbents. It was noticeable that the amount of iron in MGAC structure increased after the modification of the GAC with Fenton reagents. The GAC contained only 0.3% of iron, while it was 0.54% in the MGAC and therefore, after the Fenton reaction, not only Fe^{2+} but also the other cationic iron species may be adsorbed on the MGAC surface, i.e., Fe^{3+} and the hydroxylated ions $Fe(OH)^+$, $Fe(OH)^{2+}$, and $Fe(OH)_2^+$. The physical properties (e.g., specific surface area, pore volume, and mean size of pores) of the GAC and MGAC adsorbents were measured using BET analysis and accuracy of BET given in Table 1. The values of specific surface area of GAC and MGAC were found to be 973.6589 and 895.1600 m²/g, respectively.

The high surface area of both the adsorbents indicates the more probability of surface characteristics in the potential adsorption mechanism of nitrate. This analysis suggested that the surface area of the MGAC was decreased, compared to that of the GAC. This decrease can be explained by the adsorption of iron species from Fenton modification process on MGAC surface, which leads to the blockage of some pores and active sites of GAC. According to Table 1, the average pore sizes of 1.9 and 2.1 nm were obtained for the GAC and MGAC, respectively. Based on the IUPAC classification (micropores ($d < 2$ nm), mesopores ($2 < d < 50$ nm), and macropores ($d > 50$ nm)), it was concluded that both the adsorbents can be classified into mesopores groups [31].

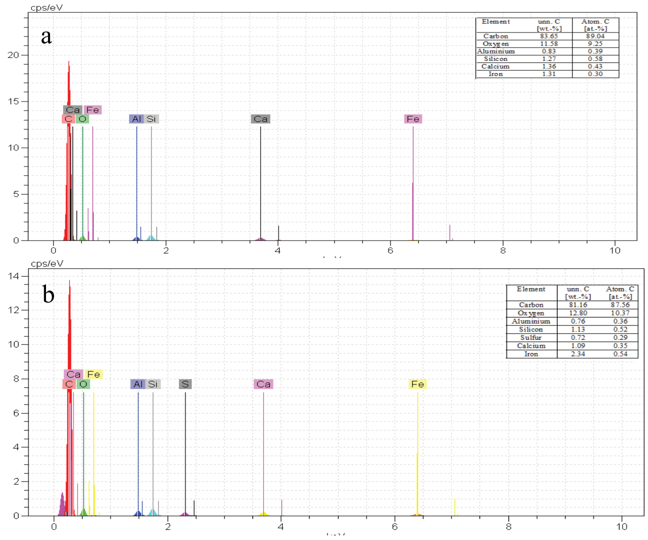
The functional groups can have an important effect on the adsorption efficiency as adsorption reactions mainly occur on the adsorbent surfaces. In this work, FTIR spectra were applied in order to identify the surface nature of GAC and MGAC, before and after adsorption (Fig. 3). Pellets were prepared by thoroughly mixing activated carbon and KBr at the 1:50 carbon/KBr weight ratio in a small size agate mortar. The resulting mixture was pressed under 8 tons of pressure for 2 min. The bands around 3372 cm⁻¹ in the GAC spectrum indicated that the presence of –OH and –NH is stretching vibrations [32,33]. This peak was disappeared after the modification with Fenton reagents, suggesting that the removal of –OH and –NH is the stretching vibrations.

In the MGAC spectrum, before and after the nitrate adsorption, the peaks appearing at 2357 and 2363 cm⁻¹ belonged to the amino protonation of $–NH_2$ and $–NHCOCH_3$ groups, respectively. Moreover, the bands around 1650 and 1561 cm⁻¹ were corresponding to the C=O stretching vibration of acetyl groups and the amine group stretching vibration, respectively [34]. The peak observed at 1522 cm⁻¹ in the FTIR spectrum of the MGAC after the adsorption was referring to the secondary amine group. The symmetric bending of CH_3 was observed in the wavenumber range from ~ 1444 to 1462 cm⁻¹ [35]. The peaks at 1388, 1043, and 1127 cm⁻¹ may be defined as C–O–C stretches vibration and C–H symmetric bending vibration, separately [34]. The characteristic peak assigned to nitrate was observed at around 1386 cm⁻¹, as previously reported in the literature [34,36]. Hence, the FTIR analysis clearly verified the adsorption nitrate on the MGAC surface.

Table 1
Physicochemical characteristics of applied materials in this study

Physical parameters	GAC	MGAC
Specific surface area (m²/g)	973.6	895.1
Langmuir surface area (m²/g)	1192	1177
Micropore volume (cm³/g)	0.483	0.472
Average pore diameter (A°)	19	21

The peaks at 895 cm⁻¹ and 670 cm⁻¹ can be respectively attributed to C–H out-of-plane bending vibration and N–H wagging vibration [34]. Compared with the FTIR spectrum of the GAC, slight changes were observed in the FTIR spectrum after nitrate adsorption. These changes were corresponding to the –OH and –NH stretching vibrations, C=O stretching, vibration and symmetric bending of CH_3, illustrating that the adsorption process may be occurringphysic-chemically. However, two peaks at 2418 (sharp and strong) and 671 cm⁻¹ observed in the FTIR spectra after nitrate adsorption could be attributed to H–O stretch and O–Fe–O, respectively [37].



Element	unn. C [wt.-%]	Atom. C [at.-%]
Carbon	83.65	89.04
Oxygen	11.58	9.25
Aluminium	0.83	0.39
Silicon	1.27	0.58
Calcium	1.36	0.43
Iron	1.31	0.30

Element	unn. C [wt.-%]	Atom. C [at.-%]
Carbon	81.16	87.56
Oxygen	12.80	10.37
Aluminium	0.76	0.36
Silicon	1.13	0.52
Sulfur	0.72	0.29
Calcium	1.09	0.35
Iron	2.34	0.54

Fig. 2. EDS analysis for GAC (a) and MGAC (b).

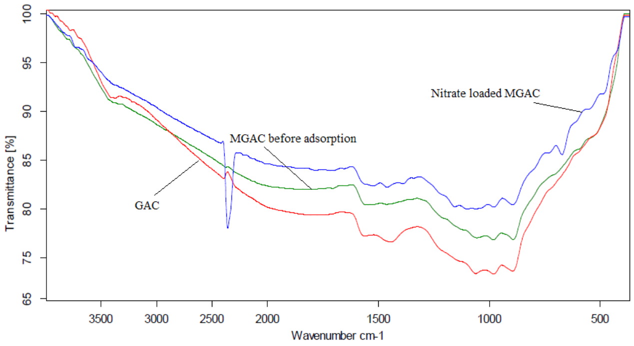


Fig. 3. FTIR spectra for GAC and MGAC before and after the adsorption of nitrate.

3.2. Determination of optimal concentrations of Fenton reagents

In this work, the effect of different ratios of [Fe^{2+}] to [H_2O_2] on the efficiency of nitrate removal using a modified GAC was evaluated. In this regards, a specific amount of GAC was added to the solutions containing various ratios of [Fe^{2+}] to [H_2O_2] (0.01–0.06 w/w). The samples were placed on a shaker and then severely agitated with a speed of 250 rpm for 2 h. After completing the reaction, the solids were separated from the aqueous solution and dried at 100ºC in an oven for 2 h. Three modified GAC were then applied as adsorbents for removal of nitrate under the following experimental conditions: 50 mg/L nitrate, 1 g/L adsorbent, 7.0 pH, and 120 min contact time. Fig. 4 shows the removal percentage of nitrate by five types of the modified GAC adsorbents obtained from different concentrations of Fenton reagents.

An increase in the ratios of [Fe^{2+}] to [H_2O_2] from 0.01 to 0.06 led to the enhancingnitrite adsorptive removal from 23 to 36.5%. Hence, the [Fe^{2+}] to [H_2O_2] ratio of 0.06 was selected as an optimum ratio for future experiments.

3.3. Effect of initial pH of solution

pH of solution plays a key role in the adsorption processes which influences on the interactions between adsorbent and adsorbate, due to its impact on the ionization of target contaminants, surface charges of functional groups of the adsorbent, and the degree of solubility of ions in aqueous media [38]. Therefore, in this study, the effect of pH variations on nitrate adsorptive removal using MGAC was examined during 120 min. The results showed that increasing solution pH from 2 to 10 caused declining the removal efficiency of nitrate from 41 to 30%.

The maximum nitrate removal was obtained at pH 4, while the minimum adsorption capacity was observed at alkaline conditions (Fig. 5). At lower pH values, the MGAC surface was positively charged which followed by a gradual decrease in the extent of positive charging and became negative when the pH values increased. This observation can be ascribed to the attraction between the nitrate anions and the positively charged MGAC surface [33]. At higher pH values, however, a competition emerges between hydroxide and nitrate ions for adsorption sites and an increase is observed in diffusion resistance of nitrate caused by abundant hydroxide ions [34].

3.4. Effect of MGAC dosage

The influence of various dosage of MGAC (0.5–2.5 g/L) on the removal efficiency (Fig. 6a) and adsorption capacity of nitrate (Fig. 6b) was evaluated under the above optimum conditions.

The results showed a direct relationship between the adsorbent dosage and the adsorption efficiency of nitrate. It was observed that the nitrate removal efficiency increased from 45.3 to 68.5% by increasing the MGAC dosage from 0.5 to 2.5 g/L. Increasing nitrate adsorption as a result of increasing the adsorbent dosage may be attributable to the enhancement of available active sites and a higher surface area available at higher adsorbent dosages for a constant initial nitrate concentration [34]. As can be seen from Fig. 6b, the adsorption capacity witnessed a dramatic decrease

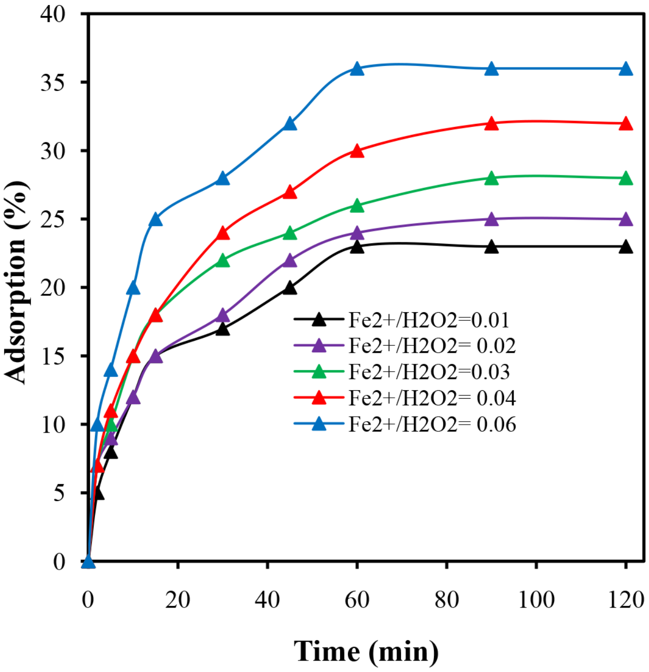


Fig. 4. The effect of different ratios of Fenton's reagents (Fe^{2+} and H_2O_2) on the adsorption efficiency of nitrate using GAC (temperature = 25°C, time= 120 min, adsorbent dose = 1 g/L and nitrate Conc. = 50 mg/L).

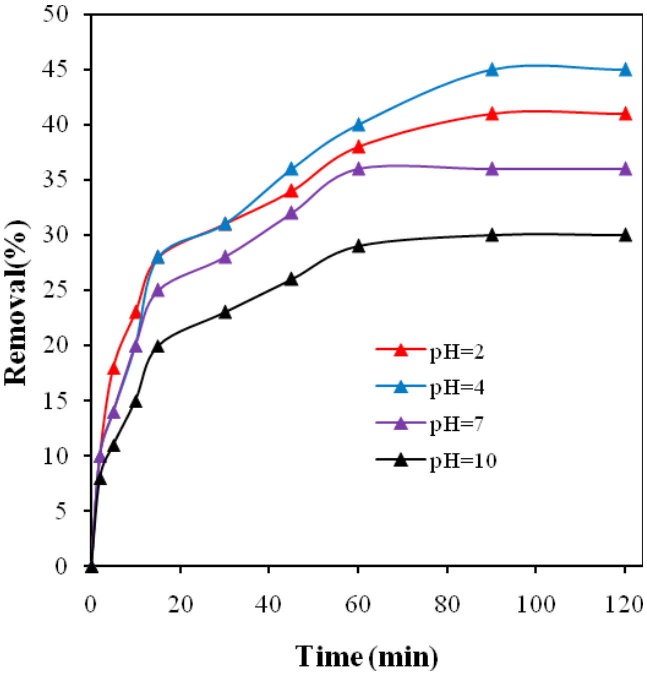


Fig. 5. Effect of initial pH of nitrate solution on the nitrate adsorption efficiency (temperature = 25°C, adsorbent dose = 1 g/L, Fe:H_2O_2 ratio = 0.06, rpm = 200 ± 10, nitrate Conc. = 50 mg/L, time = 120 min).

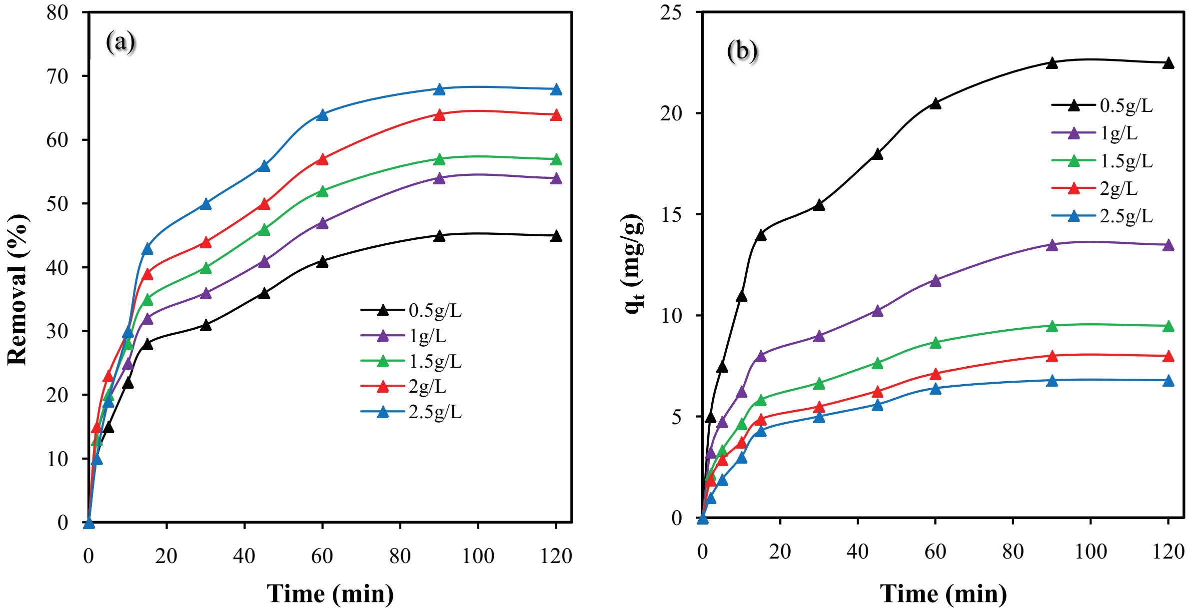


Fig. 6. Effect of various dosages of MGAC on adsorption efficiency (a) and adsorption capacity (b) (temperature = 25°C, pH= 4, Fe:H_2O_2 ratio = 0.06, rpm = 200 ± 10, nitrate Conc. = 50 mg/L, time = 120 min).

with increasing adsorbent dosage which was followed by a decreasing trend from 22.5 mg/g to 6.8 mg/g when the adsorbent dosage increased from 0.5 to 2.5 g/L. The split in the flux or the concentration gradient between the ion concentration both in the solution and at the surfaces of the adsorbent can decrease adsorption capacity [39]. Moreover, by increasing the adsorbent dose, the content of nitrate adsorbed onto unit weight of adsorbent decreases, causing a decrease in q_e value [40,41].

3.5. Effect of contact time and initial nitrate concentration

The influence of contact time on nitrate removal using MGAC was studied at an initial nitrate concentration of 10–50 mg/L, adsorbent dosage of 2.5 g/L, pH of 4.0, and temperature of 20°C during 120 min.

As seen in Fig. 7, the initial adsorption rate of nitrate onto the MGAC is rapid which then reached to equilibrium at 60 min. The adsorption rate reached maximum within the first 60 min of contact time and then, became constant without any significant changes. This phenomenon may be attributed to a sufficient number of unsaturated active sites on the GMAC surface at the initial times. It is observed from Fig. 7 that the adsorption efficiency of nitrate was almost constant after 60 min at all the studied concentrations. This means that the adsorption process reached the equilibrium state at 60 min. Therefore, it was chosen as an equilibrium time of nitrate adsorption onto the MGAC surfaces. Fig. 7 also reveals that the percentage of nitrate adsorption decreased from 85.4 to 68.1% when the initial nitrate concentration increased from 10 to 50 mg/L. This behavior can be explained by the increase in the driving force of the concentration gradient resulted from the increase in the initial nitrate concentration. These results are in good agreement with those of the previous studies for the nitrate adsorption on different adsorbents [3,42].

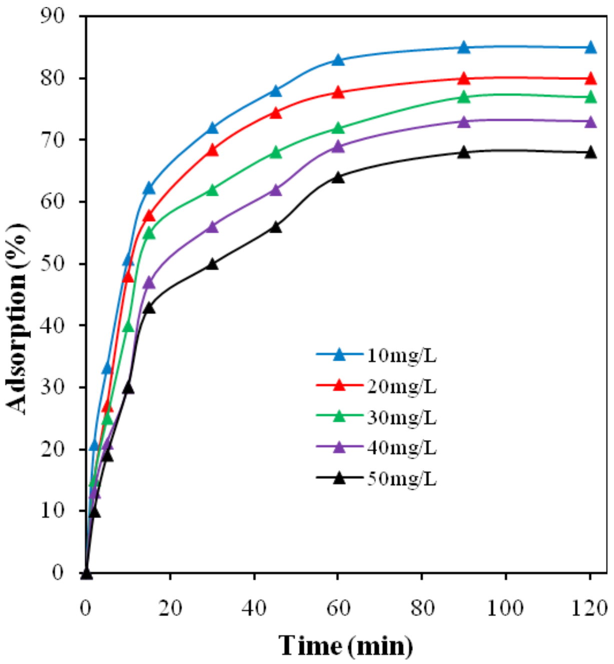


Fig. 7. Effect of contact time and initial nitrate concentration on the adsorption efficiency of nitrate using MGAC (pH = 4.0, temperature = 25°C, adsorbent dose = 2.5 g/L, Fe:H_2O_2 ratio = 0.06).

3.6. Adsorption kinetic studies

Herein, the kinetic study of nitrate adsorption was performed by fitting the experimental data onto three conventional kinetic models for finding the adsorption rate constant. Table 2 reveals that the values of the rate constant of pseudo-second-order, k_2, decreased with increasing initial nitrate concentration. The rate constant values decreased

Table 2
The parameters regarding the adsorption kinetic models of nitrate on MGAC at various concentrations (mg/LNO_3^-)

Kinetic models	Initial nitrate concentration of (mg/L)				
	10	20	30	40	50
Pseudo-first-order					
$q_{e,\,Cal}$(mg/g)	27.4	40.7	38.86	70.52	93.7
k_1(min^{-1})	0.05	0.062	0.037	0.076	0.074
R^2	0.9401	0.951	0.6923	0.9821	0.9583
Pseudo-second-order					
$q_{e,Cal}$(mg/g)	35.7	52.63	71.43	90.1	100
k_2(g/mg)(min^{-1})	0.005	0.002	0.0023	0.003	0.0018
R^2	0.9993	0.9981	0.9999	0.9999	0.9999
Intraparticle diffusion					
k_i	0.8	1.16	1.33	1.65	2.12
C_i	23.6	34	47.1	63.6	63.24
R^2	0.643	0.605	0.741	0.593	0.597
Experimental q_e (mg/g)	34.31	48.25	64.62	83.24	90.5

from 0.005 to 0.0018 mg/g min when initial nitrate concentration increased from 10 to 50 mg/L. This phenomenon can be attributed to high competition of adsorbate molecules for occupying the surface reactive sites at high concentration which causes enhancing adsorption [43,44].

Similar observation has been reported in studying adsorption of contaminants in the literature [45]. Based on the higher values of the correlation coefficient ($R^2 > 0.99$), it is obvious that the kinetic model of pseudo-second-order was the most appropriate to represent the nitrate adsorption onto the MGAC. In addition, pseudo-second-order kinetic model, compared to other models, resulted in the values of $q_{e,\,cal}$, to be much closer to the experimental value for all the studied concentrations, verifying the validity of this model for the adsorption of nitrate onto MGAC. The confirmation of this model suggests that the concentrations of both the adsorbent and adsorbate are associated with the rate determining step of nitrate adsorption onto the MGAC. This model also indicates that the adsorption process is controlled by chemisorption. The chemisorption is either sharing or exchanging electrons between the nitrate anions and the binding sites of MGAC. Earlier researchers also proposed pseudo-second-order kinetic equation for describing the adsorption of nitrate on activated carbon [3,46].

The adsorption process mainly takes place through the following multi step mechanisms: i) external film diffusion, ii) intraparticle diffusion and iii) interaction between adsorbate and active site. The first step is excluded by shaking the solution, so the rate determining step of the process is one of the other two steps. Herein, to understand whether the intraparticle diffusion has been the main step controlling the adsorptive removal of nitrate onto the MGAC adsorbent, the results for the adsorption kinetic were fitted with the intra particle diffusion models. The results indicated the values of correlation coefficients (R^2) for the intraparticle diffusion model are lower than that of the pseudo-second-order kinetic model, illustrating this model's lack of applicability to describe nitrate adsorption on the MGAC. As observed in Table 2, the values of C_i were not equal to zero at all the studied concentrations, suggesting that intraparticle diffusion is not the only controlling step for the nitrate adsorption and the process is also controlled, to some extent, by boundary layer diffusion [47,48].

Table 3
The values of isotherms of nitrate adsorption on MGAC adsorbent

Equilibrium models	Parameters	Value
Langmuir:	q_0 (mg/g)	43.1
Eq: $C_e/q_e = C_e/q_0 + 1/K_L q_0$	k_L(L/mg)	0.057
plot: (C_e/q_e) *vs.* C_e	R^2	0.961
Freundlich:	k_F(mg/g(Lmg)$^{1/n}$)	1.51
Eq: $ln q_e = ln K_F + n^{-1} ln C_e$	n	2
plot: $ln\ q_e$ *vs.* $ln\ C_e$	R^2	0.998
Temkin:	K_T	1.84
Eq: $q_e = B_1 ln\ K_T + B_1\ ln C_e$	B_1	1.71
plot: q_e *vs.* $ln\ C_e$	R^2	0.951

3.7. Equilibrium isotherms studies

Equilibrium studies evaluated the best-fit isotherm models for explaining the adsorption of nitrate on the MGAC. Table 3 shows the obtained isotherm parameters of nitrate adsorption.

The obtained results indicated that the Freundlich model provided higher linear correlation coefficient (R^2) compared to other models. The correlation coefficients were found less than 0.96 and 0.95 for the Langmuir and Temkin isotherm models, respectively, whereas, they were calculated as >0.99 for the Freundlich equilibrium model. This observation illustrates that the experimental data of adsorption process are in good agreement with those obtained by the Freundlich isotherm model. This model suggests that nitrate adsorption onto MGAC follows a heterogeneous (multilayer) mechanism. It has also been reported in the literature that the Freunlich isotherm was the best model for the experimental data of nitrate adsorption on different adsorbents [1]. The desirability of the adsorption process was verified by the values of $0 < R_L < 1$ in the Langmuir model, depicting that nitrate has been desirably adsorbed on the MGAC adsorbent. This issue was also confirmed by the Freundlich exponent, n, since its value was $1 < n < 10$.

Upon the Langmuir equilibrium model, the maximum amount of nitrate uptake per unit mass of the MGAC was found to be 43.1 mg/g. The adsorption capacities of several adsorbents taken from the literature were compared with those of the present study and are shown in Table 4. From the results, it is possible to verify that the MGAC has a relatively good and satisfactory adsorption capacity in comparison with other sorbents. Therefore, it can be applied as a highly efficient remediating agent for nitrate adsorptive removal. Herein, higher adsorption capacity of the applied adsorbent may be attributed to the variations in its structure, surface area and functional groups characteristics with the other adsorbents.

Table 4
Maximum adsorption capacity of some adsorbents for nitrate removal from aqueous solution

Adsorbent	pH	Isotherm	Kinetic	q_m (mg/g)	Ref.
Nano-alumina	4.4	Langmuir	Pseudo-second-order	4.0	[4]
Activated carbon	3.0	Langmuir	Pseudo-second-order	27.55	[50]
MSWVOI	7.0	Freundlich	–	20.39	[53]
Raw wheat residue	6.8	Freundlich	Pseudo-second-order	1.24	[1]
$ZnCl_2$ treated coconut granular activated carbon	5.5	Langmuir	Pseudo-second-order	0.2	[14]
Modified wheat residue	6.8	Freundlich	Pseudo-second-order	128.9	[1]
Granular chitosan-Fe^{3+}complex	3.0–10.0	Langmuir Freundlich, D-R	Pseudo-second-order	5.0	[39]
Fe_3O_4/ZrO_2/chitosan	3.0	Langmuir	Pseudo-first-order	89.3	[37]
Chitosan hydrogel beads	3.0	Langmuir-Freundlich	Pseudo-second-order	92.1	[10]
Powdered activated carbon	>5.0	Freundlich	–	620	[17]
Granular activated carbon modified with Fenton reagents	4.0	Freundlich	Pseudo-second-order	43.1	This work

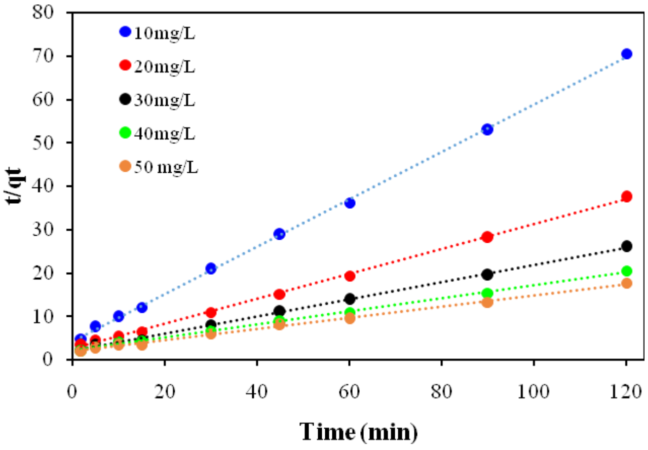


Fig. 8. Pseudo-second-order kinetic model of nitrate adsorption on MGAC (pH = 4.0, temperature = 25°C, adsorbent dose = 1.5 g/L, Fe:H_2O_2 ratios = 0.06).

3.8. Comparison between the GAC and MGAC

The adsorptive removal efficiency of nitrate using the GAC and MGAC adsorbents was evaluated under the above mentioned optimum conditions. It is noticeable from Fig. 9 that MGAC has higher removal efficiency than GAC.

Under the optimum experimental conditions, the removal efficiencies of 83.4 and 67.2% were obtained for MGAC and GAC, respectively. This reveals that the modification of GAC with Fenton reagents is an effective method which increased its adsorption capacity. Herein, the high adsorption efficiency of nitrate using MGAC can be attributed to the positive surface charge of the MGAC.

4. Conclusion

Activated carbon as an effective adsorbent with high specific surface area has been widely utilized in the water treatment processes. In this work, a commercial granular activated carbon was modified with Fenton reagents (Fe^{2+} and H_2O_2) to prepare a new adsorbent for removing nitrate from solution. Textural, physic-chemical features were characterized using various techniques. The removal efficiency of nitrate was carried out at different effective experimental factors on the adsorption process, including pH, contact time, adsorbent dosage, temperature, and initial nitrate concentration. The pseudo-second-order and Freundlich models represented best correlation with the experimental data

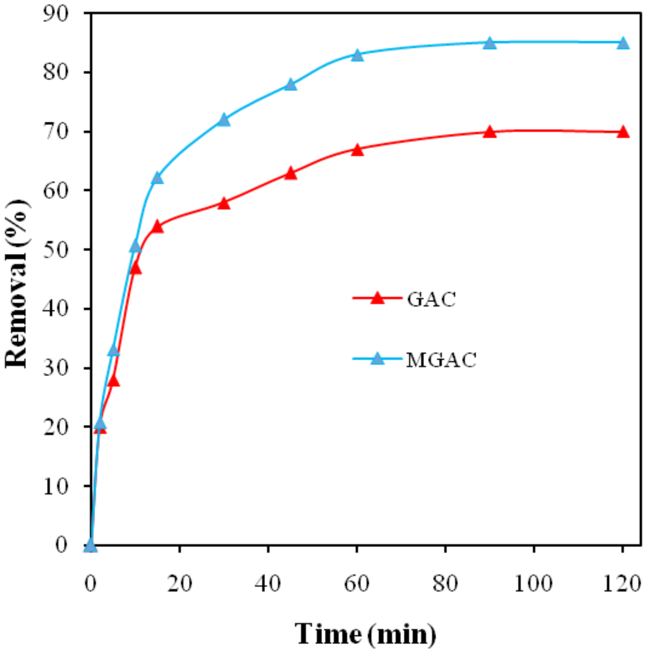


Fig. 9. The comparison between the performance of GAC and MGAC on the adsorption of nitrate (pH = 4.0, temperature = 25°C, adsorbent dose = 1.5 g/L, Fe:H_2O_2 ratios = 0.06 and nitrate Conc. = 10 mg/L).

of nitrate removal. Increasing adsorbent dosage and initial nitrate concentration was proved to respectively have direct and reverse effects on adsorption efficiency. Moreover, the adsorption process was observed to have better efficiency at acidic conditions and pH of 4.0 was selected as an optimum value. Results also showed that the adsorption efficiency of nitrate was significantly higher on the MGAC than on the virgin GAC. This reveals that the modification of the GAC with Fenton reagents was an effective method which provides a higher adsorption capacity for GAC. Further, the results of experiments suggest that the modification of the GAC with Fenton reagents can be an effective method for enhancement of nitrate adsorption efficiency. Our results showed that the MGAC can be used as a promising adsorbent for treating nitrate-contaminated water resources.

Acknowledgment

This work was financially supported by the Environmental Technologies Research Center, Ahvaz Jundishapur University of Medical Sciences (Grant No. ETRC-9010).

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Supplementary data

Kinetic models:

Pseudo-first order: $ln(q_e – q_t) = ln\ q_e - k_f t$

Pseudo-second-order: $t/q_t = t/q_e + 1/k_s\ q_e^2$

Intraparticle diffusion: $q_t = k_i\ t^{0.5}$

where, q_t (mg/g) is the amount of adsorption capacity at a given time t; and k_1, and k_2 are the rate constant of pseudo-first-order and pseudo-second-order sorption, respectively. h_0 (mg/g min) stands for the initial sorption rates ($h_0 = k_{1,2} \cdot q_e^n$); q_e is the adsorbed amount at equilibrium state and n is the order of the kinetic model.

The intraparticle diffusion model was also used to fathom the adsorption process mechanism. k_{id} (mg/g min$^{0.5}$) is the constant rate of the intraparticle diffusion; and, C_i (mg/g) is the constant which depicts the effects of boundary layer. If the value of C_i was equal to zero, it would indicate that the intra-particle diffusion model could be the controlling factor in determining the kinetics of the process.

Isotherm models

Langmuir: $C_e/q_e = C_e/q_0 + 1/k_L q_0$

Freundlich: $ln\ q_e = lnk_F + n^{-1}\ lnC_e$

Temkin: $q_e = Bln\ K_T + B\ lnC_e$

In the Langmuir model, K_L (L/mg) is an empirical constant which is related to either energy or enthalpy of the adsorption. The parameters K_F and n are constants of the Freundlich isotherm, which stand for the adsorption capacity and intensity, respectively.

For Temkin model, k_T is the equilibrium binding constant, corresponding to the maximum binding energy; and also, $B = RT/b_T$, b_T (J/mol) is Temkin constant relating to the heat of adsorption. R (8.314 J/mol K) and T (K) are the universal gas constant and solution temperature, respectively.