

Preparation of Fe/activated carbon directly from Orange Peel and its application in removal of nitrate from aqueous solutions

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Abstract

In this study activated carbon was synthesized from orange peel by ZnCl₂ solution at 60 °C for 12 h and then carbonized in a furnace at 475 °C for 90 min. The treated sample was impregnated with iron (III) chloride solution in the presence of NaBH₄ solution under a nitrogen atmosphere. The samples were characterized by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR), and scanning electron microscopy (SEM). The effects of various parameters such as pH, contact time, initial nitrate concentration, and adsorbent dosage were investigated for efficient removal of nitrate. The results showed impregnation activated carbon with Fe improved the adsorption ability by nearly two times more compared to the pure one. Kinetics data indicate that the adsorption of nitrate follows pseudo-second order kinetics model. The adsorption data are found to fit well with Langmuir isotherm and the maximum adsorption capacities for activated carbon and Fe/ activated carbon were obtained 16.23 and 41.32 mg/g, respectively.

Keywords: Nitrate, Activated carbon, Orange peel, Adsorption.

1. Introduction

Nitrate is possibly the most widespread water contaminant frequently present in drinking water and various types of agricultural, domestic, and industrial wastewaters [1-3]. Therefore, treatment of the wastewaters containing high nitrate concentrations is a serious challenge. Biological and chemical treatment methods have been developed as a nitrate removal technology [4].

Biological denitrification is an eco-friendly and cost effective method by which facultative anaerobic denitrifying bacteria reduce nitrate or nitrite into

harmless nitrogen gas in the absence of oxygen. The biological denitrification process is slow for particularly industrial wastewater containing high concentrations of nitrate [5].

The most conventional physico-chemical processes for nitrate removal are ion exchange [6], reverse osmosis [7, 8], electrodialysis, and adsorption [9]. Among the different methods the adsorption process is preferred because of low cost [10-13]. The adsorption efficiency depends on the nature of activated carbon (AC). In recent years, there has been considerable research concerning the preparation of

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low-cost activated carbon from agricultural wastes such as coconut shell, corn cob, hazelnut bagasse, palm shell, rice husk, cherry stone, and apricot stones [14]. Orange peel is one of organic matter is enriched in carbon particles so providing favorable conditions for preparation of activated carbon [15]. The preparation of activated carbon from the agricultural residue not only reduces environmental pollution but also reduces the cost of its production. Functionalized activated carbons (FACs) were promising catalysts and sorbents for various industrial applications [16, 17]. For example, iron containing catalysts had high catalytic activity for removal the nitrate ions from wastewaters [16]. Depending on the reaction conditions, iron may reduce nitrate to nitrogen, nitrite, or ammonium. In fact, Fe^0 may act as an electron donor for reducing different contaminants including nitrate, due to its strong reduction capacity [18, 19].

In this study, we developed an iron-modified activated carbon using orange peel (OP) as precursor, and the ability of the prepared adsorbent for nitrate ions removal from aqueous solutions was evaluated.

2. Experimental

2.1 Materials and Methods

$\text{ZnCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, NaOH , and HCl were purchased from Merck. All chemicals were of analytical grade and used without further purification. Orange peel was supplied from an orange juice factory.

2.2 Synthesis of Activated Carbon

Orange peel was washed with distilled water and dried at 60°C inside an oven for 24 h. The dried samples were milled and the particles with diameter 0.60 mm were selected. 10 g of OP was dispersed in 300 mL zinc chloride solution (0.4 mol L^{-1}) and then stirred for 12 h at 60°C . In second step, samples were placed in a stainless steel boat and carbonized in a furnace at 475°C for 90 min. The resultant activated carbon was washed with 0.5 N of HCl solution and then was washed sequentially several times by hot distilled water until the solution pH was reached neutral

2.3 Synthesis of Fe /Activated Carbon

2 g of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ was mixed with 6 g of AC by adding 50 mL DI water, the mixture was agitated for 2 h. NaBH_4 solution (1 g in 50 mL DI water) was added slowly to above solution under a nitrogen atmosphere and stirred for 90 min. Then the sample was filtered and washed with DI water and ethanol for several times, and dried in an oven at 60°C for 6 h.

2.4. Adsorption experiments

Adsorption of nitrate ions onto the synthesized samples was studied by batch experiments. A stock NaNO_3 solution (500 mg L^{-1}) was used in adsorption process. The concentration of nitrate ions was determined by an UV spectrophotometer at 220 nm.

Removal percentages were calculated as follows:

$$\text{Removal}[\%] = \frac{C_0 - C}{C} \times 100 \quad (1)$$

where C_0 and C are the concentration of the nitrate before and after adsorption, respectively. The effects of different adsorption variables including pH, initial concentration of nitrate, adsorption time, and the adsorbent dosage for nitrate removal under AC and Fe/AC was investigated. The experimental data of the adsorption properties were obtained using a batch type process. The pH_{pzc} was determined at different values of pH (1.0 to 12.0). Based on the obtained results of determination pH_{pzc} the effect of pH on nitrate removal was studied over a pH range of 1.0–6.0.

The optimization experiment for pH was performed by using a solution with concentration 100 mg L^{-1} and 0.2 g of sorbents, then the samples were agitated at room temperature for 3 h. The effect of adsorption time studies were performed at optimum pH by using of solution with above condition within a range of 30–240 min. The effect of initial solution concentration was studied at the optimum time and pH within a range of 25–250 mg L^{-1} of nitrate. Also the effect of the

adsorbents dosage on removal of nitrate was investigated using different amounts of 0.1-1.4 g of AC and Fe/AC under optimal conditions.

2.5 Kinetic studies

The rate of adsorption of nitrate was studied at different time intervals (30-240 min). In kinetic studies, 100 mL of NaNO₃ solution (100 mg L⁻¹) and 0.2 g of sorbents were agitated on a shaker (140 rpm) at room temperature then samples were filtered and nitrate concentration was measured.

2.6 Adsorption isotherms studies

Equilibrium studies that give the capacity of the adsorbent and the equilibrium relationships between adsorbent and adsorbate are described by adsorption isotherms. In order to determine the adsorption isotherms of nitrate ions, the solutions with initial concentrations (25, 50, 75, 100, 150, 200, 250 mg L⁻¹) and with a fixed amount of sorbents (0.2 g) at the optimum pH were prepared and the samples were shaken at 140 rpm for 180 min. Finally solutions were filtered and the concentrations of remaining unadsorbed nitrate were determined.

3. Results and discussion

3.1 XRD Analysis

The XRD patterns of the Activated Carbon and Fe/Activated Carbon are shown in (Figure 1a-b). Figure 1a shows two amorphous halos ($2\theta=20-30^\circ$ and $40-50^\circ$) characteristic of activated carbon which can be attributed to carbon. As can be seen in Figure 1b in addition to Fe⁰ particles, some iron oxide (Fe₂O₃) also appears which shows the oxidation of Fe⁰ particles during process.

3.2 FT-IR Analysis

Figures 2a-b shows the infrared spectra of AC and Fe/AC. A broad absorption band centered at 3450 cm⁻¹ can be observed in the spectra of the both samples,

which is related to the stretching vibration of hydroxyl groups and it is typical of phenol, alcohols, and carboxylic acids groups. The band at 1702 cm⁻¹ is related to the stretching vibration of C=O bonds of carboxylic acids and ketones.

It should be also noted, the bands at 1100-1200 and 2320-2370 cm⁻¹, can be associated to the stretching vibrations of C-C bonds in AC. The strong absorption peak observed at 600 cm⁻¹ in Figure 2b, attributed to Fe-O band which confirms the presence of Fe in structure.

3.3 SEM Analysis

The SEM image of the Fe/AC composite is shown in Figure 3. As expected, particles with different sizes and irregular shapes were formed on the surface and the pores of activated carbon.

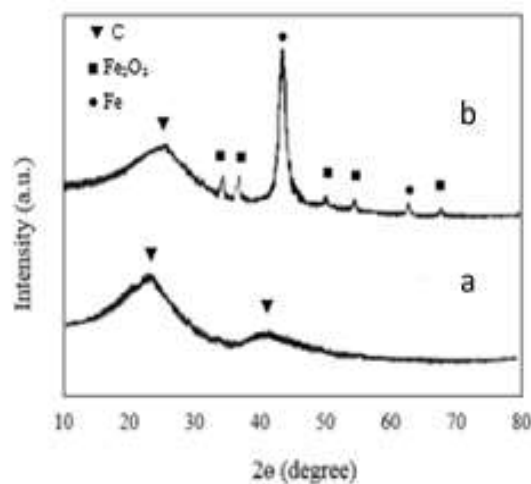


Fig. 1 XRD pattern of AC and Fe/AC

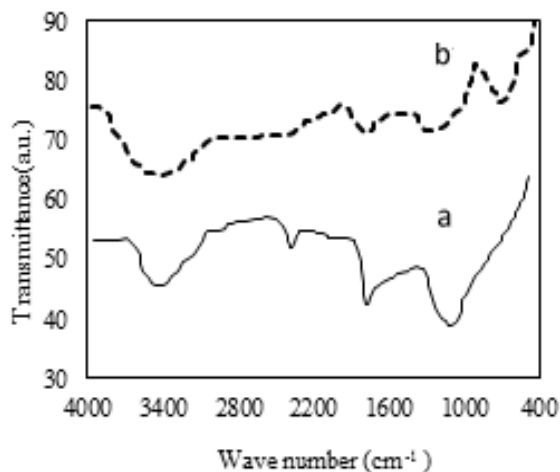


Fig. 2 FT-IR spectra of AC (solid line) and Fe/ AC (dashed line)



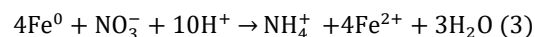
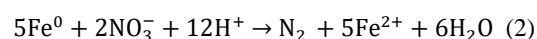
Fig. 3 SEM image of the activated carbon supported iron particles

3.4 Determination of pH of point of zero charge

The pH of point of zero charge (pH_{pzc}) is an important characteristic which provides information about the nature of the carbon surface. When the pH of the solution is lower than pH_{pzc} , the number of positively charged sites increase which favors for the adsorption of the anions due to electrostatic attraction. While At higher pH values than pH_{pzc} , the surface charge of the sorbent is positive and anions adsorption is not favorable [20]. In this work determination pH_{pzc} (Figure 4) was carried out according to a method previously reported by Carrott et al. [21], and the pH_{pzc} value was determined to be 6.1.

3.5 Effect of pH

The pH of the solution is considered to be the most important controlling parameter in the adsorption process. Figure 5 shows the effect of initial solution pH on the removal of nitrate at a fixed initial concentration of 100 mg L^{-1} and sorbent dose of 0.2 g. It is clear that the adsorption of nitrate ions by Fe/AC is higher than pure AC. The maximum removal efficiency (61%) occurred at pH 2.0–3.0. The removal percentage was decreased dramatically from 60 to 38% as the initial solution pH increased from 3.0 to 6.0. The high removal efficiency at low pH can be attributed to the fact that the surface of the adsorbent becomes highly protonated and positively charged below the pH_{pzc} (6.1), which favors the uptake of nitrate anions through electrostatic attraction. Also as can be seen in equations 2 and 3, the reaction between the Fe^0 and nitrate is a redox reaction and the hydrogen ions for the reaction, are necessary [15].



3.6 Effect of reaction time

Figure 6 shows the relation between nitrate uptake and contact time. As can be seen in Figure 6 the adsorption of nitrate increased with increasing contact time from 30 to 150 min and became almost constant after 150 min for both adsorbents.

3.7 Effect of initial nitrate concentration

As can be seen in Figure 7, the nitrate removal efficiency decreased by increasing the initial concentration of nitrate, because the absorption sites are occupied by molecules of nitrate with increasing of the nitrate concentration.

3.8 Effect of adsorbent content

The sorbent/solution ratio is an important factor for determination the capacity of a sorbent [22]. The effect

of AC and Fe/AC dosage on the adsorption of nitrate ions from aqueous solutions was investigated using various adsorbent amounts (0.1–1.4 g) at a constant nitrate concentration of 100 mg L⁻¹. AC compared to Fe/AC exhibited much lower removal efficiency. As shown in Figure 8, the removal efficiency of NO₃⁻ by Fe/AC increased sharply as the sorbent dosage increased from 0.1 to 0.4 g, then reached to an almost constant value.

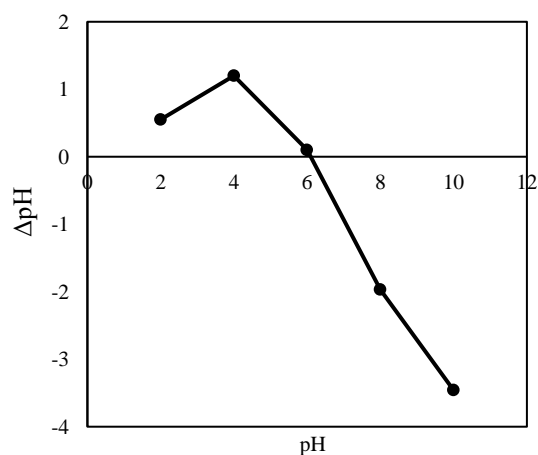


Fig. 4 pH_{pzc} determination of Activated Carbon

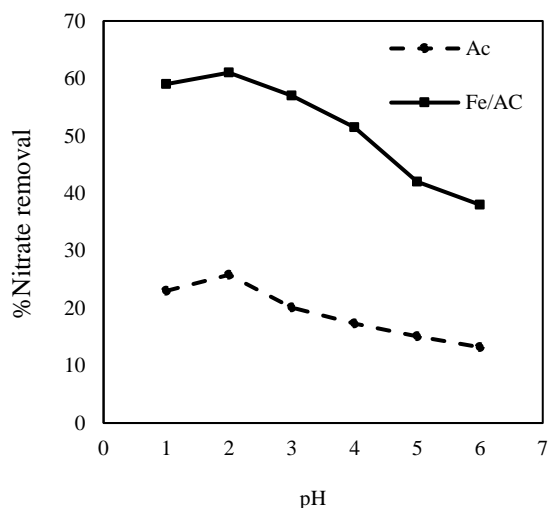


Fig. 5 The effect of pH on the removal of nitrate (sorbent dose = 0.2 g; initial nitrate concentration = 100 mg L⁻¹; contact time = 180 min)

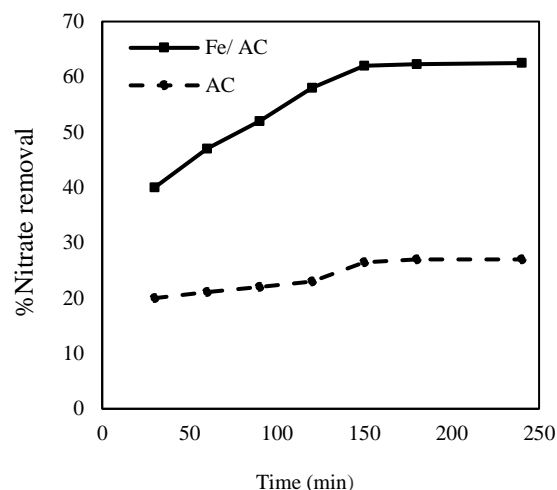


Fig. 6 The effect of contact time on the removal of nitrate (sorbent dose = 0.2 g; initial NO₃⁻ concentration = 100 mg L⁻¹; pH 2.0-3.0).

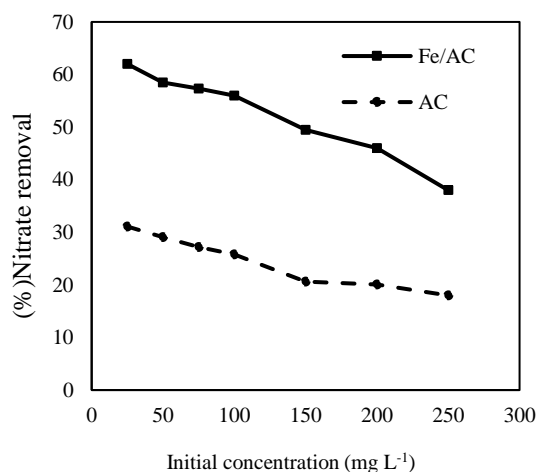


Fig. 7 The effect of initial nitrate concentration on its removal (sorbent dose = 0.2 g; contact time = 150 min; pH 2.0-3.0)

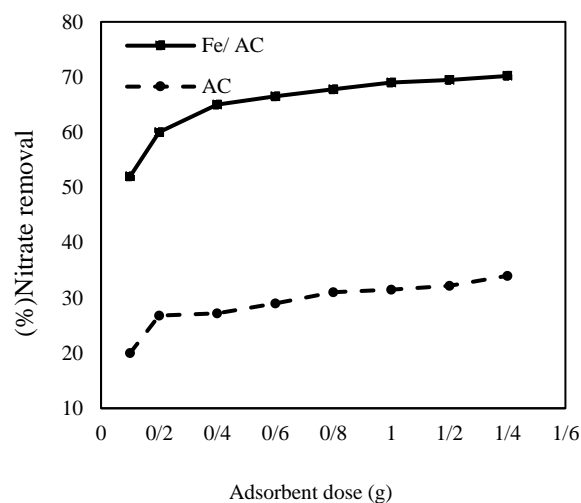


Fig. 8 The effect of adsorbent dosage on the adsorption of nitrate (initial NO₃⁻ concentration = 100 mg L⁻¹; reaction time = 150 min; pH 2.0-3.0)

3.9 Adsorption kinetics

Adsorption kinetics data were analyzed by three models including the pseudo-first-order, pseudo-second order, and the intra-particle diffusion model [23]. The linear form of the pseudo-first-order equation can be expressed as:

$$\text{Log}(q_e - q_t) = \text{Log}q_e - K_1 t / 2.303 \quad (4)$$

Where q_e and q_t (mg g⁻¹) are the amounts of nitrate adsorbed at equilibrium and at time t (min), respectively and k_1 (1/min) is the rate constant of the pseudo-first-order model. The values of q_e and k_1 can be obtained from the intercept and slope of a plot of $\text{Log}(q_e - q_t)$ versus t .

The linear form of the pseudo-second-order equation is given as follows:

$$t/q_t = 1/K_2 q_e^2 + t/q_e \quad (5)$$

Where, k_2 is the pseudo-second-order rate constant.

The parameters q_e and k_2 can be estimated from the slope and the intercept of the plot (t/q_t) versus t .

The intra-particle diffusion model is given by equation (6):

$$q_t = K_p t^{0.5} \quad (6)$$

Where K_p is the rate constant of intra-particle diffusion and will be determine by slope of the plot q_t versus $t^{0.5}$.

The comparison of different kinetic models for the adsorption of nitrate onto AC and Fe/AC at different initial concentrations is plotted in Figure 9. All kinetic parameters and correlation coefficients are listed in Table 1. As seen in Figure 9, the pseudo-first-order model did not show a good agreement to the experimental

kinetic data, this can also be concluded from the low R² value. However, the pseudo-second-order model fit the experimental data quite well with all correlation coefficients R² higher than 0.98, and good agreements between q_{cal} and q_{exp} , so it is an ideal model to describe the adsorption of nitrate ions by AC and Fe/AC.

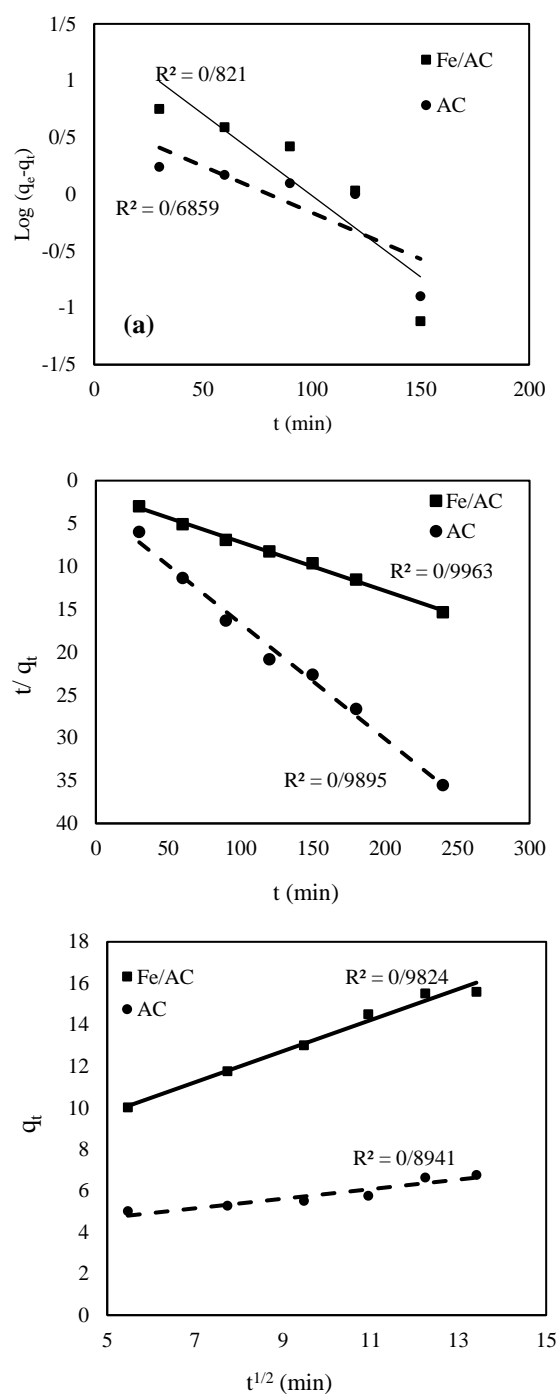


Fig. 9 Kinetic models of pseudo-first-order (a); pseudo-second-order (b); intra-particle diffusion (c) for nitrate solution onto AC and Fe/AC (volume of nitrate solution: 100 mL, sorbent dose: 0.2 g, pH: 2.0, shaking time: 30-240 min and agitation: 140 rpm)

Table 1. Pseudo-first-order, pseudo-second-order and Intra-particle diffusion kinetic parameters for the adsorption of nitrate

Absorbents	First-order kinetic model $\text{Log}(q_e - q_t) = \text{Log} q_e - K_1 t / 2.303$			Second-order kinetic model $t/q_t = 1/K_2 q_e^2 + t/q_e$			Intra-particle diffusion model $q_e = K_p t^{1/2}$		q_{exp}
	K_1 (1/min)	q_e (mg/g)	R^2	k_2 (g/mg min)	q_e (mg/g)	R^2	K_p (mg/g min ^{1/2})	R^2	
AC	0.019	4.520	0.680	0.006	7.40	0.989	0.231	0.894	6.57
Fe/AC	0.030	26.470	0.820	0.002	17.57	0.996	0.749	0.982	15.57

3.10. Adsorption isotherms

In order to study the mechanism of sorbent distribution between the solution and adsorbent, three models including Langmuir, Freundlich, and Temkin were used to determine adsorption of nitrate on to adsorbent [24].

In the Langmuir theory, the main assumption is that the sorption takes place at homogeneous sites on the surface of adsorbent, while Freundlich model was developed to explain adsorption takes place on heterogeneous surfaces. In addition to these two models the heat of the adsorption and the adsorbent-adsorbate interaction were investigated by Temkin model. The Langmuir, Freundlich, and

Temkin forms are given by equations (7), (8), and (9) respectively as follow:

$$\frac{C_e}{q} = \frac{1}{K_1 q_{\text{max}}} + \frac{C_e}{q_{\text{max}}} \quad (7)$$

$$\text{Log} q_e = \text{Log} K_f + \text{Log} \frac{C_e}{n} \quad (8)$$

$$q_e = B \text{Ln} A_T + B \text{Ln} C_e \quad (9)$$

9 for the Langmuir isotherm is significantly higher than the Freundlich and Temkin isotherms. So the Langmuir isotherm was found to fit the data for nitrate adsorption. As can be seen in Table .3 maximum nitrate adsorption capacities obtained in the present work, as evaluated according to the Langmuir model, were higher than most of those recently reported by other researchers for different ACs

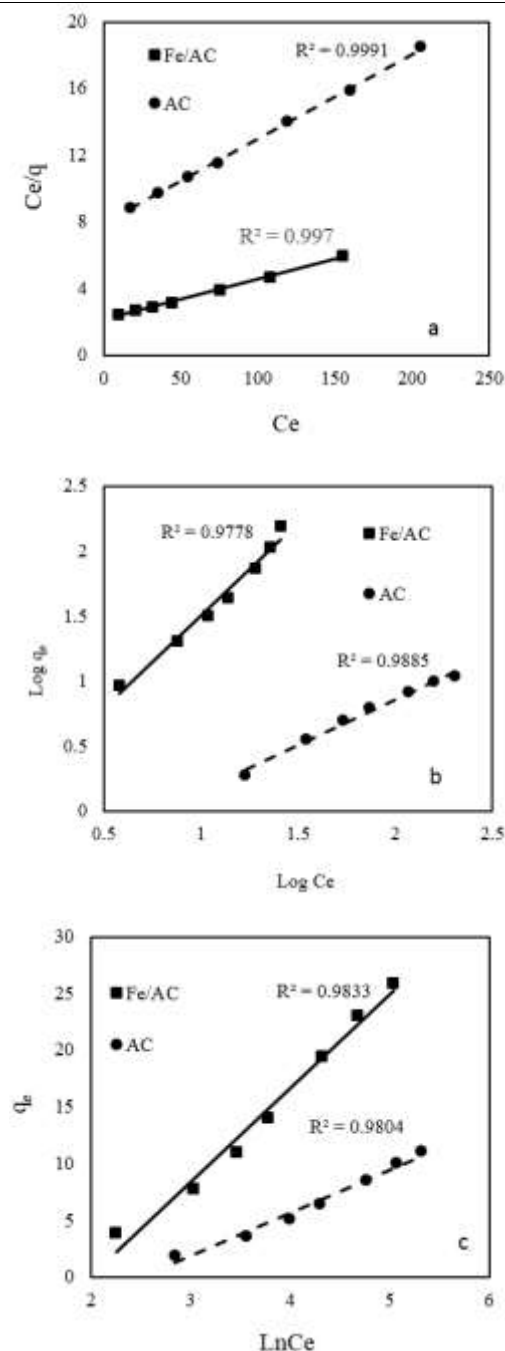


Fig. 10 Adsorption isotherms for nitrate solution at room temperature: Langmuir (a); Freundlich (b); and Temkin (c) (volume of nitrate solution: 50 mL, initial NO_3^- concentration 25-250 mg L⁻¹; sorbent dose 0.2 g; pH: 2.0, shaking time: 150 min and agitation: 140 rpm).

Table 2. Langmuir, Temkin, and Freundlich isotherm parameters for the adsorption of NO_3^- by AC and Fe/AC

Isotherm	AC	Fe /AC
Langmuir		
q_m (mg g^{-1})	19.640	41.320
b (L mg^{-1})	0.006	0.011
R^2	0.999	0.997
Freundlich		
K_f	0.280	1.017
$(\text{mg/g})(\text{L/mg})^{1/n}$	1.410	0.700
n	0.988	0.977
R^2		
Temkin		
B (J mol^{-1})	3.820	8.271
A (L g^{-1})	0.081	0.130
R^2	0.980	0.983

Table 3. Comparison of nitrate maximum adsorption capacities (q) obtained in this work with other previously reported

Sample	q (mmol/g)	Reference
AC derived from orange peel with ZnCl_2	0.31	Present work
AC/Fe derived from orange peel	0.66	present work
AC derived from sugar beet bagasse	0.15	[1]
AC derived from coconut shell	0.03	[25]
AC postreated with ZnCl_2	0.16	[25]
AC derived from Pinus canariensis cones (PC-P)	0.16	[26]
AC derived from sugar beet bagasse with ZnCl_2	0.44	[1]
Granular activated carbon made from lignite (Jarcarbon, Korea)	0.23	[27]

4. Conclusion

In this study, modified activated carbon prepared from orange peel, proved to be an effective adsorbent for nitrate removal from wastewaters. The adsorption of nitrate by AC and Fe/AC was most favorable under acidic conditions. The adsorption system followed pseudo-second-order Kinetics. Experimental equilibrium data were in good agreement with the Langmuir model. The maximum adsorption capacity was 19.640 and 41.320 mg g^{-1} for AC and Fe/AC, respectively.

Acknowledgments

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