

Equilibrium modeling for adsorption of NO_3^- from aqueous solution on activated carbon produced from pomegranate peel

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Abstract. Nitrate removal from aqueous solution was investigated using ZnCl_2 and phosphoric acid activated carbon developed from pomegranate peel with particle size 0.4 mm. Potassium nitrate solution was used in batch adsorption experiments for nitrate removal from water. The effects of activated carbon dosage, time of contact, and pH were studied. The equilibrium time was found to be 45 min. Two theoretical adsorption isotherms namely Langmuir and Freundlich were used to describe the experimental results. The Langmuir fit the isotherm with the theoretical adsorption capacity (q_t) was found 78.125 mg g⁻¹. Adsorption kinetics data were modeled using the pseudo-first, pseudo-second order, and intraparticle diffusion models. The results indicate that the second-order model best describes adsorption kinetic data. Results show activated carbon produced from pomegranate is effective for removal of nitrate from aqueous solution.

Keywords: adsorption; kinetics; equilibrium; isotherm; activated carbon; pomegranate peel

1. Introduction

Several nitrogenous compounds, including ammonia, nitrite, and nitrate have been frequently present in drinking water and various types of agricultural, domestic, and industrial wastewater (Peavy and Rowe 1985, Lin and Wu 1996). Nitrate can cause several environmental problems. Nitrates and phosphates can stimulate eutrophication where pollution is caused in waterways by heavy algal growth, as they are both rate-limiting nutrients for the process. Nitrate, in particular, causes outbreaks of infectious diseases such as cancer of the alimentary canal and cyanosis among children (Baber and Stuckey 2000). Excess nitrate in drinking water may cause blue-baby syndrome, which results from the conversion of haemoglobin into methaemoglobin, which cannot carry oxygen (Golden and Weinstein 1998). The maximum contaminant level for nitrate set by the world health organization (WHO) and the US environmental protection agency (USEPA) for drinking water are 50 and 45 mg/l of NO_3^- respectively (WHO 2004, USEPA 2000).

Therefore, numerous techniques for the removal of nitrate from water samples have been reported. These include biological de-nitrification, chemical reduction, reverse osmosis, electrodialysis, and

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ion exchange (Bhatnagara and Sillanpääb 2011). The biological denitrification process is slow, particularly for industrial wastewater containing high concentrations of nitrate and for low temperatures. A chemical reduction process requires the addition of chemicals and may release toxic compounds such nitrite into the environment, especially when H_2 is used as a reductant (Henz 1995). Nitrite in the human body may cause methenoglobinaemia in new-born infants, and in stomach can formed N-nitrosamines a postulated cause of cancer (Horold *et al.* 1993). Reverse osmosis is too expensive to treat a large amount of wastewater. Compared with these methods, ion exchange is a simple and effective method. But the main problem is that the ion exchange resin is still quite expensive and retains some sulphate and hydrogen carbonate, which induce significant changes in the water composition. It also causes an increase in the chloride concentration of water because the ion exchange resin replaces nitrate with chloride (Bae *et al.* 2002).

For removal nitrate from wastewater, adsorption has become one of the most economic and effective method. The process is superior to many other methods of water reuse by virtue of its low initial cost, low energy requirements, simplicity of design and possibility of reusing the spent carbon via regeneration (Namasivayama and Kadirvelu 2001). Treatment of nitrate containing wastewater by high-area carbon cloth (Afkhmi 2003), coconut coir pith (Namasivayama and Sangeetha 2005), wheat residue (Wang *et al.* 2007), bamboo powder charcoal (Muzita *et al.* 2004) have been reported.

Pomegranate peel, a by-product of the pomegranate juice industry is therefore an inexpensive. It's a material composed of several constituents, including polyphenols, ellagic tannic and gallic and ellagic acids (Ben-Naser *et al.* 1996). In the present work the sorption of nitrate ions from aqueous solution by using activated carbon produced from pomegranate peel was investigated. The adsorption capacity of adsorbent was investigated using batch experiments. The influence of pH, contact time, and adsorbent concentrations were investigated and the experimental data obtained were evaluated and fitted using adsorbent equilibrium isotherms, and kinetic models.

2. Experimental

2.1 Biosorbent preparation

Pomegranate peel was as a waste obtained from juice-mill, Rouiba, Algeria. It was washed with distilled water, dried in an oven for two hours at 105°C , ground in a ball mill and sieved to particle size range 0.3-0.6 mm. The material after sieving is divided into two parts. The first part was placed in a purpose-made stainless steel tube in absence of air and positioned at the center of a muffle furnace for one hour at 500°C , and then the activated carbon produced is cooled in a desiccator (AC). The second part was soaked for twenty four hours in a solution prepared from phosphoric acid 1 M and zinc chloride 1 M in a ratio of 1:1 (V/V), then dried and carbonized as mentioned above. The activated carbon was then neutralized with solution 1% NaHCO_3 and, extensively washed with deionized water. After washing, the activated carbon was dried at 90°C in drying oven and stored in a desiccator (AC_1).

2.2 Analytical procedure

Batch adsorption studies were carried out by taking various dosage (0.25; 0.5; 1; 1.5; 2; 3 et 4 g AC_1 / 50 mL water shaking) of adsorbent, nitrate concentration (50; 100; 200; 250; 300 and 400 mg L-

1 NO_3^-) were prepared from analytical grade potassium nitrate (KNO_3), the initial pH values of nitrate solutions were varied from 3 to 12 by drop wise addition of 0.1 N HCl or NaOH solutions and, contact time variations (10; 20; 30; 60; 80; 100 and 120 min) with 50 ml of nitrate solution of known initial concentration in different conical glass flasks in a shaking thermostat with a constant speed of 150 rpm. The concentration of nitrate ions was determined using a UV/vis spectrophotometer (UV 1800 - SHIMADZU) with detecting wavelength at 410 nm (Rodier 2009). The FTIR spectrum of the adsorbent was recorded on a SHIMADZU (Model No 8400S) spectrophotometer using KBr disks (2 mg sample in 200 mg KBr). The scanning range was 400-4,000 cm^{-1} and the resolution was 2 cm^{-1} . SEM of the sample was obtained by Scanning electron microscope (JSM-7600 F, JEOL, Japan). The samples were mounted on metal grids and coated with platinum in vacuum evaporator before observation. The accumulation voltage and current were 3.0 kV and 10 μA , respectively.

Langmuir, and Freundlich isotherms were used to analyze the equilibrium adsorption data. The amount of nitrate adsorbed per mass unit of adsorbent at equilibrium (q_e) was calculated by the following expression

$$q_e = (C_0 - C_{eq}) \times V/W \quad (1)$$

where q_e is the adsorbent capacity (mg g^{-1}); C_0 is the initial concentration of nitrate in solution (mg L^{-1}); C_{eq} is the equilibrium concentration of nitrate in solution (mg L^{-1}); V is the volume of experimental solution (L) and W is the weight of adsorbent (g).

2.3 Results and discussion

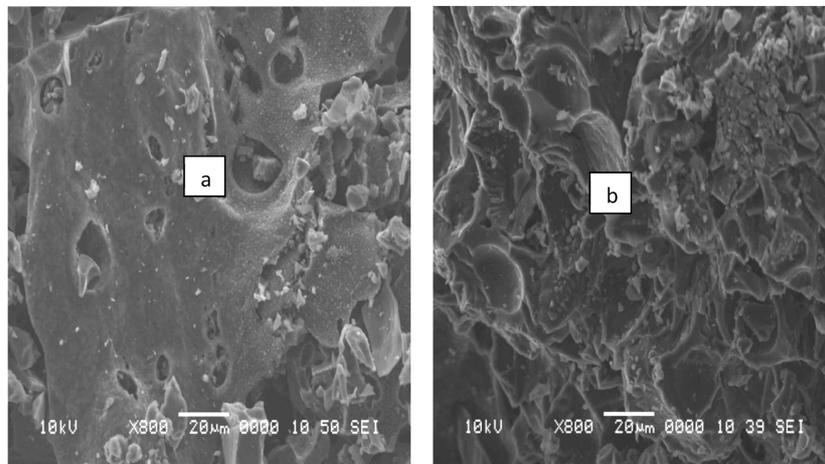
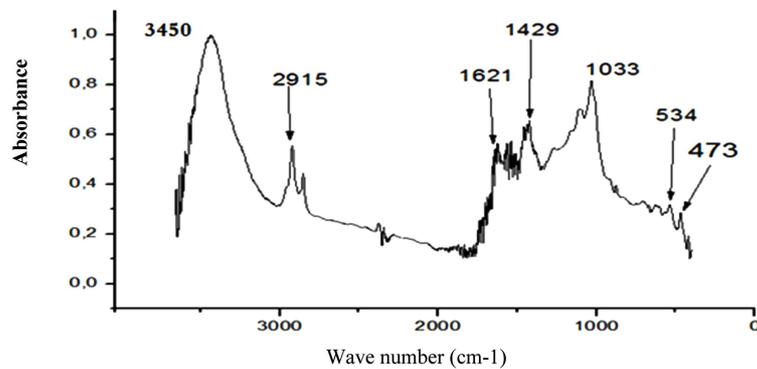
2.3.1 Characterization of the adsorbent

Activated carbons are a widely used adsorbent due to its high adsorption capacity, high surface area, microporous structure, and high degree of surface respectively. The wide usefulness of carbon is a result of their specific surface area, high chemical and mechanical stability. The chemical nature and pore structure usually determines the sorption activity. The physicochemical properties are listed in Table 1. The results were obtained from the mean of triplicate samples for every variable.

The scanning electron micrographs enable the direct observation of the surface microstructures of a material. Fig. 1a shows that some components interfere with the surface of activated carbon and reduce the development of pores. The components probably come from the untreated raw material. Thus they react with the surface of the raw material during carbonization and affect the pore distribution of activated carbon. Hence, it produces a smooth surface with lack development of pores. On the other hand, Fig. 1b clearly shows the roughly surfaces with many pores were developed. The development of pores was due to effect of H_3PO_4 and ZnCl_2 which minimizes the formation of tacks and other liquid, which could clog up the pores and inhibit the development of pores structure. Also, Zn presented at carbon surface as ZnO and increased positive charge of AC. This phenomenon increased ion adsorption such as nitrate (Socrates 1994, Rezee *et al.* 2008). The FTIR spectra of adsorbent (AC_1) is demonstrated by Fig. 2. The broad absorption band at 3450 cm^{-1} and medium band 2915 cm^{-1} indicated the presence of both free and hydrogen bonded $-\text{OH}$ groups on the surface. The spectra also showed the definite bands at 1621 cm^{-1} , which may be assigned to $\text{C}=\text{O}$ stretching vibrations of aldehydes, ketones, lactones or carboxyl groups (Socrates 1994). The bands at 1429 cm^{-1} may reflect the aromatic CH and carboxyl-carbonate structures and the peaks at 1033 cm^{-1} may correspond to $\text{C}-\text{OH}$ stretching and $-\text{OH}$ deformation values. The presence of

Table 1 Characteristics of activated carbon produced from pomegranate peel

Properties	Quantity
Particle size (mm)	0.4
Density (g cm ⁻³)	0.601
Moisture content (%)	6.6
pH of aqueous solution	6.8
pH _{zpc}	6.1
Iodine index (mg g ⁻¹)	1162
Iodine number (mg g ⁻¹)	180
Hash (%)	1.07

Fig. 1 SEM micrographs of: a-AC; b-AC₁Fig. 2 FT-IR spectra of activated carbon produced from pomegranate peel (AC₁)

several functional groups on carbon surface implies the presence of many types of pollutant-carbon interactions, also superficial hydroxyl groups, which are able to form a bond with the nitrate at low pH rang (Wu *et al.* 2005).

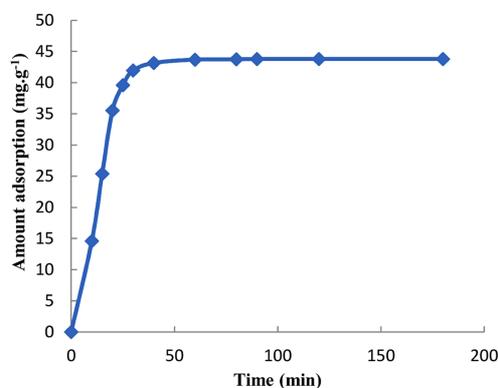


Fig. 3 Effect of contact time on the removal of nitrate by activated carbon produced from pomegranate peel

2.3.2 Effect of contact time

Effect of contact time on amount adsorption of nitrate by AC_1 is shown in Fig. 3. Basically, the adsorption kinetic of adsorbate is rapid during first 20 min of the adsorbate–adsorbent contact, but it gradually increases with time until it reaches equilibrium in 45 min. The adsorption was faster in the beginning due to a larger surface area of the adsorbent being available for the adsorption of the ions nitrate. The two stage sorption mechanism with the first rapid and quantitatively predominant and the second slower and quantitatively insignificant, has been extensively reported in literature (Saeed *et al.* 2005).

2.3.3 Effect of pH

The pH of the solution has a significant impact on the uptake of nitrate ions, since it determines the surface charge of the adsorbent, the degree of ionization and speciation of the adsorbate. In order to establish the effect of pH on the biosorption of nitrate ions, the batch equilibrium studies at different pH values were carried out in the range of 2–11 (Fig. 4). Maximum removal (86%) of

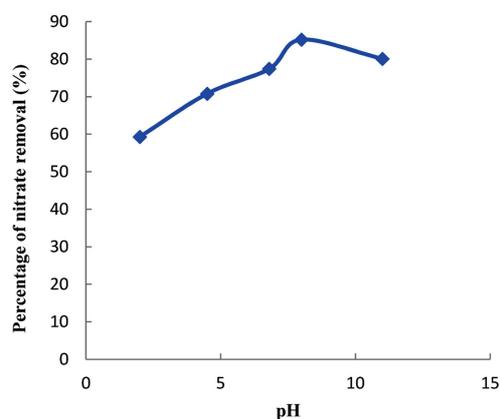


Fig. 4 Effect of pH on nitrate adsorption onto activated carbon produced from pomegranate peel, 100 mg L⁻¹ and at 25°C

nitrate ions occurs in the pH 7.5-8.5, and significantly decreased by reducing the pH values and slightly decreased at higher pH values. At pH 2 and 11 the removal was lower 58% and 77% respectively. According to Aggarwal *et al.* (1999), lower removal at pH 2 is due to the competition of Cl⁻ ions (from HCl added externally to adjust the pH) with nitrate ions to the adsorbent sites; at pH 11 the highly negatively charged adsorbent surface sites do not favor the adsorption of oxanion due to the electrostatic repulsion.

2.3.4 Adsorption isotherm

The Langmuir and Freundlich models have been employed as adsorption isotherm models. These isotherms relate the amount of solute adsorbed at equilibrium per unit weight of adsorbent, x/m (mg g⁻¹), to the adsorbate concentration at equilibrium, C_e (mg L⁻¹) (Fig. 5). The Langmuir model represents one of the first theoretical treatments of non-linear sorption and suggests that the uptake occurs on a homogenous surface by monolayer sorption without interaction between the adsorbed molecules. The linear form of the Langmuir adsorption isotherm is represented as

$$C_e/q_e = (1/Q_0b) + (1/Q_0) C_e \quad (2)$$

where C_e is the equilibrium concentration of adsorbate (mg L⁻¹), and q_e is the amount of nitrate ions adsorbed per gram at equilibrium (mg g⁻¹). Q_0 (mg g⁻¹) and b (L mg⁻¹) are Langmuir constants related to adsorption capacity and rate of adsorption, respectively. The values of Q_0 and b were calculated from the slope and intercept of the Langmuir plot of C_e vs. C_e/q_e and are given in Table 2. The essential characteristics of Langmuir isotherm can be expressed in terms of dimensionless constant separation factor for equilibrium parameter, R_L (Liu *et al.* 2010) which is defined as given below

$$R_L = 1/(1+bC_0) \quad (3)$$

where b is the Langmuir constant (L mg⁻¹) and C_0 (mg L⁻¹) is the initial concentration of nitrate ions. The R_L parameter is considered as a reliable indicator of the adsorption. There are four

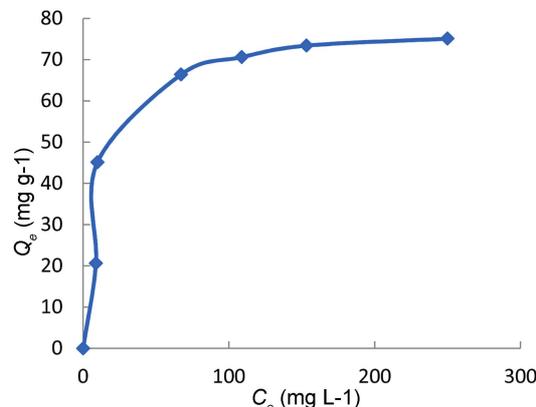


Fig. 5 Isotherm plots for the adsorption of nitrate onto activated carbon produced from pomegranate peel, $T = 20^\circ\text{C}$; $\text{pH} = 7.2$

Table 2 Langmuir and Freundlich model's regression constants for activated carbon produced from pomegranate peel

Isotherm model	Parameters	
Freundlich	R^2	0.7898
	K_F (mg g ⁻¹)	2.756
	n (L mg ⁻¹)	1.422
Langmuir	R^2	0.9938
	b (L mg ⁻¹)	0.092
	Q_0 (mg g ⁻¹)	78.125

probabilities for the value of R_L : 1- for favorable adsorption, $0 < R_L < 1$, 2- for unfavorable adsorption, $R_L > 1$, 3- for linear adsorption, $R_L = 1$, 4- for irreversible adsorption, $R_L = 0$ (Ho *et al.* 2005). The value of R_L for the studied system were found 0.0212 using $C_0 = 500$ mg L⁻¹ is well within the defined range and indicate the acceptability of the process.

The Freundlich model can be applied for non-ideal sorption onto heterogeneous surfaces involving multi layer sorption. The linearized Freundlich isotherm was applied for the adsorption of nitrate ions and is expressed as

$$\log q_e = \log K_f + 1/n \log C_e \quad (4)$$

where K_f (mg g⁻¹) and n (L mg⁻¹) are Freundlich adsorption isotherm constants, affecting the adsorption capacity and intensity of adsorption. Values of K_f and n were calculated from the intercept and slope of the plots and are given in Table 2. The larger the K_f and n values, the higher the adsorption capacity. It is generally stated that values of n in the range 2-10 represent good, 1-2 moderately difficult and less than one poor adsorption characteristics (Treybal 1981). Results of Langmuir and Freundlich isotherm are summarized in Table 2. According to the coefficient of correlation, the Freundlich isotherm is inadequacy of the isotherm model to explain the adsorption process but the Langmuir model would be applicable.

2.3.5 Adsorption kinetic

In order to examine the controlling mechanisms of adsorption process such as mass transfer and chemical reaction, several kinetic models are used to test the experimental data. The rate constant of adsorption is determined from the following pseudo-first-order equation expression given by Lagergreen (Wu *et al.* 2001)

$$\log(q_e - q_t) = \log q_e - (k_1/2.303)t \quad (5)$$

where q_e and q_t are the amounts of nitrate adsorbed (mg g⁻¹) at equilibrium and at time t (min), respectively, and k_1 (min⁻¹) is the rate constant of pseudo- first-order equation. A pseudo-second-order equation based on adsorption equilibrium capacity may be expressed in the form

$$t/q_t = 1/k_2 q_e^2 + 1/q_e t \quad (6)$$

Table 3 Kinetic parameters for the removal of nitrate ions by activated carbon produced from pomegranate peel

Kinetic model	Equations	Parameters	
Pseudo 1st order lagergren	$\text{Log}(q_e - q_t) = \text{Log}(q_t) - K_1 \frac{t}{2,303}$	R^2	0.9658
		K_1 (min-1)	0.0944
		q_t (mg.g-1)	26.51
Pseudo 2nd order	$\frac{t}{q_t} = \frac{1}{q_e^2 K_2} + \frac{t}{q_e}$	R^2	0.9748
		K_2 (min-1)	2.69 10-3
		q_e (mg.g-1)	48.309
Intraparticle diffusion	$q_t = K_d t^{0.5}$	R^2	0.6263
		K_d (mg g-1min-0.5)	3.049

where k_2 ($\text{g min}^{-1} \text{mg}^{-1}$) is the rate constant of second-order adsorption (Wu *et al.* 2001). If the above two equations cannot give definite mechanisms, the intraparticle diffusion model is tested. The initial rates of intraparticle diffusion can be obtained by linearization of the curve expressed in the form (Annadurai *et al.* 2002)

$$q_t = K_d t^{0.5} \quad (7)$$

The fit of these models was checked by each linear plot of $\log(q_e - q_t)$ versus t , (t/q_t) versus t and q_t versus $t^{0.5}$ respectively and by comparing to the regression coefficients for each expression. The results show that first-order kinetic model and intraparticle diffusion model are not fully valid for the present adsorption system due to low correlation coefficients (Table 3). For the first order rate expression, the experimental q_e values do not agree with the calculated ones obtained from the linear plots (Table 3). A good agreement of the experimental data with the second-order kinetic model was observed for adsorbent. The correlation coefficients for the second-order kinetic models are greater than 0.97 and the calculated q_e values agree very well with the experimental data (Table 3).

3. Conclusions

Activated carbon produced from pomegranate peel has been found to be an effective biosorbent for the removal of nitrate from an aqueous solution. The adsorption process is dependent on pH, and the adsorption capacity optimal with rang of pH 7.5-9.5. The Langmuir adsorption isotherm fit well to the equilibrium adsorption data. The Langmuir isotherm is acceptable and the adsorption process is homogeneous. This adsorption process follows a pseudo-second-order- kinetics model. Intra-particle diffusion plays insignificant role at the initial stage of adsorption process.

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