# REMOVAL OF NITRATE (NO<sub>3</sub><sup>-</sup>) FROM AQUEOUS SOLUTION USING ADSORBENT FROM AGRICULTURAL RESIDUES: EQUILIBRIUM AND KINETIC STUDIES

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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 fond 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<sub>1</sub>) was fond 78.125 mg/g. Adsorption kinetics data were modeled using the pseudo-first and 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.

Key words: 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 [1],[2]. 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 [3]. Excess nitrate in drinking water may cause blue-baby syndrome, which results from the conversion of haemoglobin into methaemoglobin, which cannot carry oxygen [4]. 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<sub>3</sub><sup>-</sup> respectively [5],[6].

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 ion exchange [7]. 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 into the environment, especially when  $H_2$  is used as a reductant [7],[8]. 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 [9].

Adsorption in general, is the process of collecting soluble substances that are in solution on a suitable interface. Activated carbon adsorption is one of the recommended technologies for nitrate removal from aqueous solution [10]. Activated carbon is a very expensive adsorbent for removal of pollutant so other adsorbents must be investigated [11]. Recently, agricultural residues or plant materials have been studied extensively as low cost adsorbents to remove nitrate from water [12].

Pomegranate peel, a by-product of the pomegranate juice industry is therefore an inexpensive. Pomegranate peel is a material composed of several constituents, including polyphenols, ellagic tannic and gallic and ellagic acids [13]. 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 procedure**

### 2.1. Biosorbent preparation

Pomegranate peel was washed with distilled water, dried in an oven for two hours at  $105^{\circ}$ 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 1M in a ratio of 1:1 by volume, then dried and carbonized as mentioned above. The activated carbon was then neutralized with solution 1% NaHCO<sub>3</sub> 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<sub>1</sub>).

## 2.2. Preparation of nitrate solution and analytical measurements

A stock solution (1 g L–1) of nitrate was prepared by dissolving potassium nitrate (KNO<sub>3</sub>) in deionized water, and experimental solutions of desired nitrate concentrations were obtained by successive dilutions. The concentration of nitrate ions in the experimental solution was determined using a UV/vis spectrophotometer (UV 1800 - SHIMADZU) with detecting wavelength at 410 nm .

## 2.3. Adsorption studies

Batch adsorption studies were carried out by taking various dosage (0.25; 0.5; 1; 1.5; 2; 3 et 4 AC/50mL water shaking 100mL) of adsorbent, nitrate concentration  $(50; 100; 200; 250; 300 \text{ and } 400 \text{ mg/L NO}_3^-)$ , 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, constant temperature (288, 298, .....308 K) 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. Langmuir, Freundlich isotherms were used to analyze the equilibrium adsorption data. The amount of nitrate adsorbed (mg g-1) was calculated based on a mass balance equation as given below:

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

where: q is the adsorbent capacity (mg g-1);  $C_0$  is the initial concentration of nitrate in solution (mg L-1);  $C_{eq}$  is the final or 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).

# 3. Results and discussion3.1. Characterization of the adsorbent

Activated carbons are a widely used adsorbent due to its high adsorption capacity, high surface area, micro porous 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 physic chemical 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<sub>3</sub>PO<sub>4</sub> and ZnCl<sub>2</sub> which minimizes the formation of tacks and other liquid, which could clog up the pores and inhibit the development of pores structure. Surface coverage in the form of flakes is evident which shows the presence of Zn. Also, Zinc presented at carbon surface increased positive charge of AC which increased ions nitrate adsorption [14]. 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 –OH groups on the surface. The spectra also showed the definite bands at 1621 cm-1, which

may be assigned to C=O stretching vibrations of aldehydes, ketones, lactones or carboxyl groups [15],[16]. 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 C–OH stretching and –OH deformation values.

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
pHzpc	6.1
Iodine index (mg g-1)	1162
Iodine number (mg g-1)	180
Hash (%)	1.07



Figure 1. SEM micrographs of: a- AC; b-AC1



#### 3.2 Effect of contact time

Effect of contact time on amount adsorption of nitrate by  $AC_1$  is shown in Fig. 1. Basically, the amount adsorption of adsorbat is rapid during first 20 min of the adsorbat-sadorbent 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 [17].



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

# 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 adsorbat. 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 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 Low et al. [18], lower removal at pH 2 is due to the competition of Cl<sup>-</sup> 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.



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

## 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, Ce (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:

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

where  $C_e$  is the equilibrium concentration of adsobate (mg L-1), and  $q_e$  is the amount of nitrate ions adsorbed pergram 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,  $R_L$  [19] which is defined as given below:

$$R_{\rm L} = 1/(1 + bC_0) \tag{3}$$

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 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,  $R_L = 0$ . 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:

$$\log q_e = \log K_f + 1/n \log C_e \tag{4}$$

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 [20]. 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 bat the Langmuir model would be applicable.

Isotherm model	Parameters		
Freundlich	<b>R</b> <sup>2</sup>	0.7898	
	$K_F (mg g-1)$	2.756	
	n(L mg-1)	1.422	
Langmuir	$\mathbb{R}^2$	0.9938	
	b(L mg-1)	0.092	
	$Q_0(mg g-1)$	78.125	

Table 2.	Langmuir a	and Freundlich	model's regre	ession consta	ants for activ	ated carbon	produced	from
pomegrana	te peel							



Figure 5. Isotherm plots for the adsorption of nitrate onto activated carbon produced from pomegranate peel, T = 20 °C; pH = 7.2

## 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 [21]

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

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

where  $k_2$  g min-1 mg-1 is the rate constant of second-order adsorption [21]. 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 [22] :

$$q_{\rm t} = {\rm K}_{\rm d} {\rm t}^{0.5}$$
 (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).

Kinetic model	Equations	Parameters		
Pseudo 1 <sup>st</sup>	t	$\mathbb{R}^2$	0.9658	
Order	$Log(q_e - q_t) = Log(q_t) - K_1 \frac{t}{2.202}$	$K_1$ (min-1)	0.0944	
Lagergren	2,303	$q_t (mg.g-1)$	26.51	
Pseudo 2 <sup>nd</sup> Order	+ 1 +	$\mathbb{R}^2$	0.9748	
	$\frac{t}{q_t} = \frac{1}{q_e^2 K_2} + \frac{t}{q_e}$	K <sub>2</sub> (min-1)	2.69 10-3	
		q <sub>e</sub> (mg.g-1)	48.309	
Intraparticle diffusion	$a = V_{-} 40.5$	$\mathbb{R}^2$	0.6263	
	$q_t - \mathbf{x}_d t^{-\alpha}$	K <sub>d</sub> (mg g-1min-0.5)	3.049	

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

**4. Conclusion:** 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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