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Kinetic, isotherm and thermodynamic investigations of nitrite (NO_2^-) removal from water by anion exchange resins

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Abstract

This study presents the evaluation of a strong base (Purolite A200) and weak base (Purolite PFA847) polymeric anion exchange resins for nitrite removal. The different parameters on the removal of NO_2^- were investigated in batch sorption mode. Common isotherm models; Langmuir and Freundlich, were used in order to present a description of the equilibrium data. Experimental results showed that the equilibrium data tend to follow Freundlich isotherm model for weak base resin and Langmuir model for strong base resin. The sorption of NO_2^- on anion exchange resins was found to follow the pseudo-second order kinetic model. The values of thermodynamic parameters proved that ion exchange reaction of NO_2^- onto such resins are endothermic ($\Delta H > 0$).

Keywords: ion exchange, nitrite, strong base resin, weak base resin.

1. Introduction

Nitrite ion is one of the most hazardous chemicals which may be present in water. Its acid form nitrous acid is very reactive towards many organic compounds such as amines, phenols, alcohols, etc. Much of reactions involving nitrous acid (HNO_2) proceed via radical mechanisms and these reactions are rapid (Biçak and Senkal, 1998). The presence of nitrite ions and ammonia in drinking water is an indication of the presence of bacterial activity and organic pollution. Moreover, traces of nitrite ion in environmental samples give an excellent indication of the extent of eutrophication (Diriba *et al.*, 2014). The concentration of nitrite in natural water is typically low in the µM range. Elevated concentrations of nitrite can be found in water receiving nitrogenous effluents, in various hypoxic environments or in effluents from industries producing metals, dyes and celluloid (Kroupova *et al.*, 2005).

Determination and speciation of NO_2^- and NO_3^- in waters and foodstuffs have received increasing attention in recent years because of their potential harmful impact on human health. NO_2^- is highly toxic to certain species of fish. NO_2^- enters the bloodstream through the gill by a mechanism that normally transports chloride. After entering the bloodstream NO_2^- oxidizes iron in the hemoglobin molecule from ferrous state (Fe^{2+}) to the ferric state (Fe^{3+}). The resultant product, called methemoglobin, is incapable of reversibly binding with oxygen, so exposure to NO_2^- causes respiratory distress because of the loss in oxygen-carrying capacity of blood. It has been also reported that NO_2^- can react in vivo with secondary or tertiary amines to form N-nitroso compounds, some of which are known to be carcinogenic, teratogenic, and mutagenic (Yılmaz *et al.* 2006).

The daily NO_2^- intake ranges from 0.3 to 2.6 mg/day, primarily from cured meat. Nitrite present in cured meat has been reported to account for up to 70% of total dietary intake of this substance, depending on the intake of such meat and the origin and type of cured meat consumed. Mean dietary NO_2^- intake from all food sources has been reported to range from <0.1 to 8.7 mg of NO_2^- per person per day for European diets. The guideline for NO_2^- of 3 mg/l as NO_2^- is based on human data showing that doses of NO_2^- that cause methaemoglobinaemia in infants range from 0.4 to more than 200 mg/kg of body weight. By applying the lowest level of the range (0.4 mg/kg of body weight), a body weight of 5 kg for an infant and a drinking-water consumption of 0.75 liter, a guideline value of 3 mg/l can be derived (WHO, 2007)

Traditional methods for nitrogen removal from wastewater are denitrification, nitrification, chemical coagulation, adsorption, selective ion exchange, ammonia stripping, electrodialysis, filtration, reverse osmosis (Öztürk and Köse, 2008).

In this work; strong base and weak base anion exchange resins were used for NO_2^- removal from water. The objective of this study is to investigate the efficacy of these resins for NO_2^- removal under different experimental conditions such as, resin dosage, temperature and pH.

2. Experimental

2.1. Materials

The ion exchange resins were kindly provided by Purolite Company. Physical properties and specifications of the resins as reported by the supplier are shown in Table 1.

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Table 1. Physical properties of anion exchange resins

Resin	***Purolite A200***	***Purolite PFA 847***
Type	Strong Base Anion Exchange Resin	Weak Base Anion Exchange Resin
Polymer Structure	Gel polystyrene cross-linked with divinylbenzene	Gel Polyacrylic cross-linked with Divinylbenzene
Functional group	Type II Quaternary Ammonium	Tertiary amine
Total Capacity (min.) eq/L	1.3	1.6 (free base)

The pretreatment of the resins was carried out as follows. The resins were immersed in 2 M HCl solution for 24 hours and then washed with pure water till the excess acid was completely removed (checked with pH meter) from resin. The resins were then immersed in 2 M NaOH for 24 hours and washed for to remove excess NaOH. In final stage resins were converted to Cl^- form by immersing in 2M HCl for another 24 hours. Resins were then washed with pure water to remove excess HCl. After that, resins were dried in an oven at 40˚C and then resins were used in the experiments.

2.2. Chemicals

The extra pure Sodium nitrite ($NaNO_2$ 69,00 g/mole), analytical grade NaOH, HCl and H_3PO_4 were provided by Merck, Germany. Sulfanilamide (98%) and N-(1-Naphthyl) ethylenediamine dihydrochloride (96%) obtained by Alfa Aesar. Stock solutions of reagents were prepared using pure water.

2.3. Analysis of Nitrite

The analysis of NO_2^- was carried out as explained in Standard methods for the examination of water and wastewater (Clescerl *et al.*, 1999). Principle of the method is based on the spectrophotometric measurements of NO_2^- through formation of a reddish purple azo dye produced at pH 2.0 to 2.5 by coupling diazotized sulfanilamide with N-(1-naphthyl)-ethylenediamine dihydrochloride (NED dihydrochloride). The applicable range of the method for is 10 to 1000 µg NO_2^- -N/L.

3. Results and discussions

3.1. Effect of resin dosage on NO_2^- removal

The experiments were carried out in 50 mL plastic bottles containing 25 mL of NO_2^- solution (25 mg NO_2^-/L). The various amounts of resins were added in to NO_2^- solution and then solutions were stirred for 24 hours using a shaker.

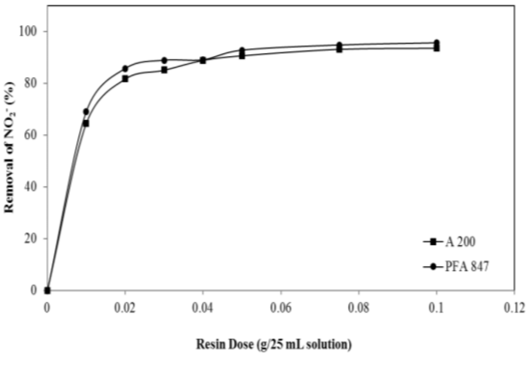

Figure 1. Effect of resin dosage on NO_2^- removal

After a period of time, resins were separated from the solutions by decantation and final concentrations of NO_2^- were determined. The obtained results are depicted in Fig.1.

As can be seen from Figure 1, when the resin dosage was increased the removal of NO_2^- increased. This is because for a fixed initial NO_2^- concentration, increasing resin amount provides greater ion exchange sites (Tofan *et al.*, 2017). The optimum resin dose was found to be 0.075 g/25 mL of solution for such resin.

3.2. Effect of solution pH on NO_2^- removal

In this set of experiment, the optimum resin amount (0.075 g) was contacted with 25 mL solution with different pH. Solution pH varied from 2 to 8. The nitrite concentration in the solution was 25 mg NO_2^-/L. The effect of solution pH on NO_2^- removal is shown in Fig.2.

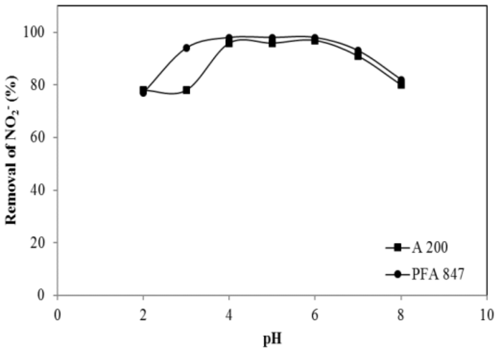

Figure 2. Effect of solution pH on NO_2^- removal

HNO_2 is a weak acid with a dissociation constant of 7.1×10^{-4} at 25 °C (pKa 3,15) (Harris, 1998). When pH of solution<3; molecular form of HNO_2 is dominant thus removal rate is low. Increasing the solution pH (pH > 3) leads to NO_2^- species dominant thus enhances the NO_2^- removal. However, after pH 7 removal of NO_2^- decreased again. Both of resins are in Cl^- form; when the pH of solution was increased the OH^- concentration increased and OH^- ion may have negative effect on nitrite removal. The ideal pH range is 4-7 for NO_2^- removal.

3.3. Kinetic performance of resins

Kinetic tests were performed by contacting 3.0 g resin with 1.0 L of NO_2^- solution (25 mgNO_2^-/L.) at 25 °C. Solution was stirred with overhead mixer. Nitrite concentrations were monitored by taking the samples at prescribed times intervals, and these samples were analyzed. The amount of NO_2^- sorbed on to ion exchange resins versus time is shown in Fig. 3, showing that, sorbed amount of NO_2^- increased at the initial stage and then reached to plateau. In 45 minutes, more than 97% of nitrite removed from solution.

The obtained results were analyzed using pseudo-first-order (eq.1) and pseudo-second-order (eq. 2) kinetic models, additionally the initial sorption rate (h) was calculated by using eq.3 (Ho, 2006, Ho and McKay, 1998) and the results were summarized in Table 3.

$$\log(q_e - q_t) = \log(q_e) - \frac{k_1 t}{2.303} \tag{1}$$

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

$$h = k_2 q_e^2 \tag{3}$$

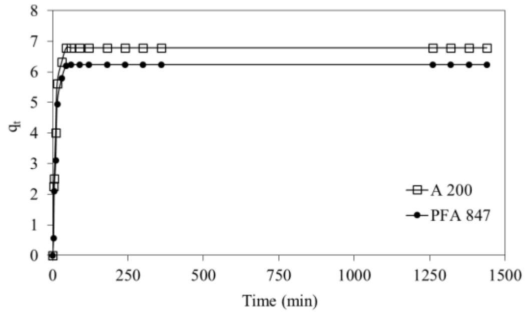

Figure 3. Plot of concentration of NO_2^- sorbed on to ion exchange resins versus time

The values of the determination coefficient (R^2) indicate the applicability of the pseudo second-order model for describing the experimental results to a higher degree of accuracy ($R^2 > 0.99$) for such resins. The maximum sorption capacities q_e calculated from the pseudo second order model are in accordance with the experimental values (q_{exp}=6.78 mg NO_2^-/g resin). This implies that the adsorption obeys a pseudo second order model. The initial sorption rate can evaluate the sorption rate of solute (NO_2^- in our case) onto sorbent at the beginning status of sorption (Ho, 2006). The h value for A200 resin is higher than PFA 847, which indicate that, at the beginning, removal of NO_2^- by A200 resin was faster than removal by PFA 847 resin. This finding is in a good agreement with obtained results. For example, at 3rd minute removal of NO_2^- was 9% for PFA 847 and it was 32% for A200 and at 15th minutes such values were 77% for PFA 847 and 80% for A200 and at 45th minutes removal rates were 96% for PFA 847 and 97 % for A200 resin.

Table 2. The calculated parameters of pseudo first and pseudo second order kinetic model

Kinetic model	*Parameter*	*PFA 847*	*A 200*
Pseudo First order	k_1 (min^{-1})	0.10	0.11
	q_e (mg/g)	7.07	6.97
	R^2	0.94	0.96
Pseudo Second order	k_2 (g/mg min)	0.02	0.04
	q_e (mg/g)	6.45	6.89
	h (mg/gmin)	0.77	1.77
	R^2	**0.99**	**0.99**

3.4 Adsorption thermodynamics

The effect of temperature on the removal of NO_2^- was studied. The optimum resin amount (0.075 g) was contacted with 25 mL solution at different temperatures (20,30, 40 and 50 °C). In order to understand the sorption process from the aspect of energy change, three basic thermodynamic constants: standard free energy change ($\Delta G°$, kJ/mol), standard enthalpy change ($\Delta H°$, kJ/mol) and standard entropy change ($\Delta S°$, J/mol K) were calculated by the following equations (Genç, 2015).

$$\Delta G^0 = -RT\ln K_d \tag{4}$$

$$K_d = \frac{q_e}{C_e} \tag{5}$$

$$\ln K_d = \frac{\Delta S^{\circ}}{R} - \frac{\Delta H^{\circ}}{RT} \tag{6}$$

$$\Delta G° = \Delta H° - T\Delta S° \tag{7}$$

where K_d is the distribution coefficient, R is universal gas constant (8.314 J/mol K), and T is the temperature in Kelvin (K). The qe versus Ce is shown in Fig.4, on the other hand $\Delta H°$ and $\Delta S°$ obtained from the slope and intercept plot of $\ln K_d$ versus $1/T$, which is shown in Fig. 5. Calculated thermodynamic parameters at different temperature are listed in Table 3.

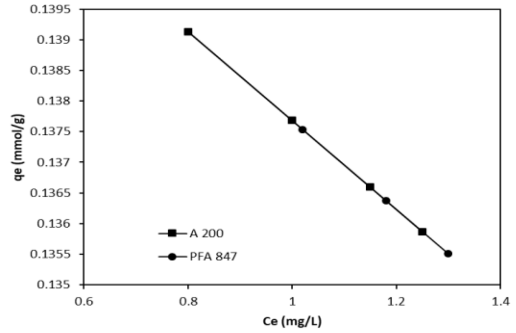

Figure 4. qe vs. Ce for the sorption of NO_2^- as a function of temperature

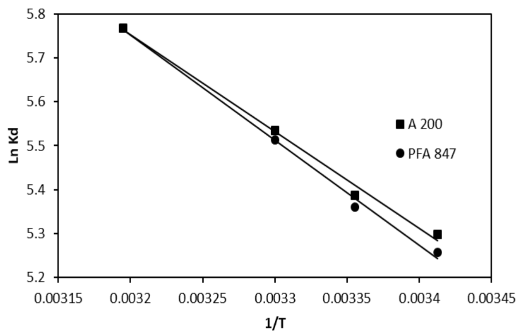

Figure 5. Plot of K_d vs. 1/T for estimation of thermodynamic parameters for the sorption of NO_2^- onto ion exchange resins.

Table 3. Thermodynamic parameters for NO_2^- removal by ion exchange resins.

Temperature (K)	***ΔG (kJ/mol)***		***ΔH (kJ/mol)***		***ΔS (J/mol.K)***	
	A200	PFA 847	A200	PFA 847	A200	PFA 847
293	-12.9	-12.8	18.3	19.9	106.4	111.4
298	-13.4	-13.3				
303	-13.9	-13.9				
313	-15.0	-15.0				

As shown in Table 3 the negative values of ΔG indicated the spontaneous nature of the adsorption process. Positive value of ΔS showed the increasing randomness at the resin–solution interface during the sorption process. The positive values of ΔH suggested the endothermic nature of the ion exchange interaction (Güngör *et al.*, 2017).

3.5. Sorption isotherms

In order to determine the sorption capacity of such resins for the removal NO_2^- get an insight into the sorption mechanism; Freundlich and Langmuir equations that are often used to describe the experimental isotherm data were applied to the experimental results (Alyüz and Veli, 2009; Özacar and Şengýl, 2004).

The Langmuir sorption isotherm is often used to describe sorption of a solute from a liquid solution as eq. (8)

$$\frac{C_e}{q_e}=\frac{1}{bq_0}+\frac{C_e}{q_0} \tag{8}$$

C_e is the equilibrium concentration (mg/L), q_e the amount adsorbed at equilibrium (mg/g) and Q_0 and b are Langmuir constants related to adsorption capacity and energy of adsorption, respectively.

To determine the nature of the absorption, Freundlich isotherms are also widely used as eq. (9)

$$\log q_e=\log K_F+\frac{1}{n}\log C_e \tag{9}$$

Where q_e (mg/g) is the adsorption capacity at equilibrium, C_e (mg/L) is the equilibrium concentration of sorbate in solution, and K_F and n are the physical constants incorporating the factors affecting the adsorption processes like adsorption capacity and intensity of adsorption. Langmuir isotherm fitted better for A200 resin. Therefore, it can be presumed that the uptake of all NO_2^- ions preferably follows the monolayer process.

Sorption of NO_2^- by weak base PFA847 resin fitted well with Freundlich isotherm fitted. The data obtained for both isotherm parameters with the correlation coefficients (R^2) were listed in Table 4.

Table 4. Isotherm constants for NO_2^- sorption on the ion exchange resin.

Resin	***Langmuir Isotherm Constants***			***Freundlich Isotherm Constants***		
	Q_0 (mg/g)	b (L/mg)	R^2	K_F (mg/g)	n	R^2
A200	97.09	0.05	0.99	3.05	2.06	0.96
PFA 847	92.59	0.04	0.98	10.09	2.50	0.99

The constant n refers to the interaction between exchange sites in the sorbent and NO_2^- ions. A high value for n > 1 indicates favorable sorption. The sorption capacity (K_F) was 10.09 mg/g. The maximum sorption capacity of strong base resin (A200) is 97.09 mg-NO_2^- /g-resin.

4. Conclusions

In this research, strong base and weak base anion exchange resins were evaluated to remove the NO_2^- from aqueous solutions. The resins showed an excellent performance for NO_2^- removal. The solution pH has significant effect on sorption efficiency. Nitrite can be removed from solution pH between 4-7. The thermodynamic results showed that the sorption of NO_2^- by such resins were spontaneous and endothermic process.

The ion exchange process was relatively fast and the removal of NO_2^- completed in 45 minutes. Applying the kinetic models to the experimental data showed that NO_2^- removal by such resins follow the pseudo-second-order rate kinetic.

The ion exchange process obeys the Freundlich adsorption isotherm for PFA 847 resin and Langmuir isotherm for A 200 resin. The maximum sorption capacity of resins are 97.09 mg-NO_2/g for strong base resin and 92.59 mg-NO_2/g for weak base resin.

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