

Nitrite Equilibrium Studies onto Activated Carbon as Hazardous Anion in Animal System

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Received: 15th July, 2014

Accepted: 19th July, 2014

Published: 23rd July, 2014

Abstract: Nitrite toxicity has been shown to be approximately 10-fold higher than that of nitrate. Activated carbon from rice straw has been used for nitrite removal. Data show that increasing nitrite concentration increases the adsorption capacity and decrease the adsorption efficiency. At low anion concentrations, there is larger fraction of higher energy sites becoming unoccupied. At high anion concentration dose, the surface gets saturated faster as all types of sites are totally exposed for adsorption. Langmuir-freundlich adsorption isotherm model gave good fitting to the experimental due to it has three fitting parameters which not restricted to monolayer of molecules. This suggests that straw based activated carbon is efficient nitrite adsorbents and that they possess good potential for nitrite removal in waste water treatment.

Key words: Equilibrium isotherm, nitrite, active carbon, adsorption, energy

INTRODUCTION

Nitrogen (N) is an essential element for all living matter. Nitrogen chemistry in natural waters is complex because N exists in different oxidation states such as nitrate NO_3^- , nitrite NO_2^- and ammonium NH_4^+ . Nitrite is formed naturally by the nitrogen cycle during the process of nitrogen fixation and it is an intermediate product in bacterial nitrification and denitrification processes in the nitrogen cycle. Nitrite is subsequently converted to nitrate, a major plant nutrient (Aslan, 2004). In vertebrates, nitrite is converted to nitrite and other metabolites (nitric oxide and N-nitroso compounds) either in the saliva of most monogastric animals or in the stomach of ruminants due to microbiological action. Exposure to nitrite has been associated with potential adverse health implications, acutely methaemoglobin formation and chronically gastric neoplasia in mice for which in the case of the latter clear evidence in man is not confirmed. Nitrite is absorbed into red blood cells and combines with hemoglobin (oxygen-carrying molecule) to form methemoglobin. Methemoglobin cannot transport oxygen as efficiently as hemoglobin so, the animal's heart rate and respiration increase, the blood and tissues of the animal take on a blue to chocolate brown tinge, muscle tremors can develop, staggering occurs and the animal eventually

suffocates. Nitrite feed contamination and pigs and ruminants are particularly susceptible to its toxicity, based on their respective physiology. Overall, the acute toxicity of nitrite has been shown to be approximately 10-fold higher than that of nitrate and because of its natural presence in plants, silages, forages, water and feed, the Directive 2002/32/EC limits its content in commercial feed used for livestock, fish and pets, excluding birds and aquarium fish.

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 (Pitter, 1999). The increasing nitrate concentration in the ground water causes a serious health risk. The toxicity of nitrates for human beings is due to the body's reduction of nitrate to nitrite, responsible for the blue baby syndrome and a precursor to carcinogenic nitrosamines (Canter, 1996). For these reasons, the European Community limits nitrite concentrations in drinking water are 0.1 mg L^{-1} (Deganello *et al.*, 2000). The objective of the present work is to assess the adsorption equilibrium isotherm for nitrite removal from water using straw based activated carbons.

MATERIALS AND METHODS

Experimental: Stock solution for the experiments was prepared by adding appropriate amount of sodium nitrite (NaNO_2) or in the deionized water. Various standard solutions were obtained by diluting stock solution with the addition of distilled deionized water as required. Nitrite anion concentrations were determined using a Metrohm 690 ion chromatography with column: 6.1009.000 anion column super sep, Elluent: 2.5 mmol L^{-1} phthalic acid, 5% acetonitrile, $\text{pH} = 4.2$ with conductivity detector. Average analyte retention time was 9.5 min for nitrite.

Activated carbon from rice straw was prepared according previous study (Daifullah, 2003). Equilibrium Isotherm was determined by shaking 20 mL^{-1} of initial concentration 50 mg L^{-1} of NO_2 with various amounts of adsorbent. The flasks containing each anion solution and carbon were agitated for 24 h at room temperature. The equilibrium concentrations were analyzed. The pH value providing the maximum anion removal was determined by adjusting pH from 2-11 by dilute NaOH or HCl solutions.

RESULTS AND DISCUSSION

The effect of nitrite concentration on RS(ox.) was studied by using varying initial concentrations from 5-50 ppm. The results are shown in Fig. 1. It is clear that as the initial concentration increased the equilibrium uptake q_e increased till saturation. This indicates that the adsorption process appears to proceed rapidly when the number of available sites is much larger than the number of anion species that can be adsorbed and more favorable sites became involved first (Majid, 1996). As the anion

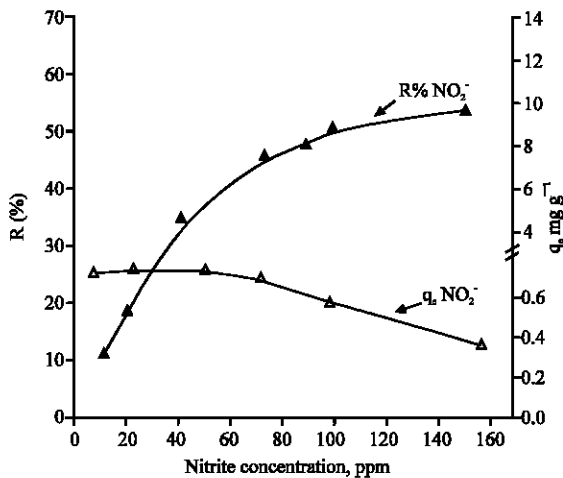


Fig. 1: The amount absorbed on the solid phase comparison

concentration increases, the high-affinity sites begin to reach saturation and energetically less favorable ones (low affinity surface sites) become involved in the adsorption process causing reduction of removal efficiency (Seco, 1999). It is evident from Fig. 1 that the amount adsorbed on the solid phase at a lower initial concentration of adsorbate was smaller than the corresponding amount when higher initial concentration were used.

On a relative basis, however, the percentage Removal (R%) was greater at lower initial concentration and smaller at higher initial concentrations (Fig. 1). In diluted solutions, the mobility of anions is high, probably for this reason; the interaction of these ions with the adsorbent was increased. By increasing uranium and thorium concentration, hydrolyzation among their ions can increase and these ions cannot reach the bounding sites of the adsorbent.

Adsorption data for wide range of adsorbate concentrations are most conveniently described by adsorption isotherm which relate adsorption density q_e (anion uptake per unit weight of adsorbent) to equilibrium adsorbate concentration in the bulk fluid phase, C_e . The adsorption isotherms of nitrite were obtained in an attempt to get a more thorough insight to the adsorption mechanism and maximum adsorption capacity of nitrite onto the activated carbons (Orlando *et al.*, 2003).

In this concern, the experimental results obtained for the adsorption of nitrite at room temperature ($25 \pm 1^\circ\text{C}$) were given in Fig. 2. Initially the isotherm rose rapidly over the initial stage of adsorption where low C_e and q_e values existed. This behavior indicates that there were plenty of readily accessible sites available on the

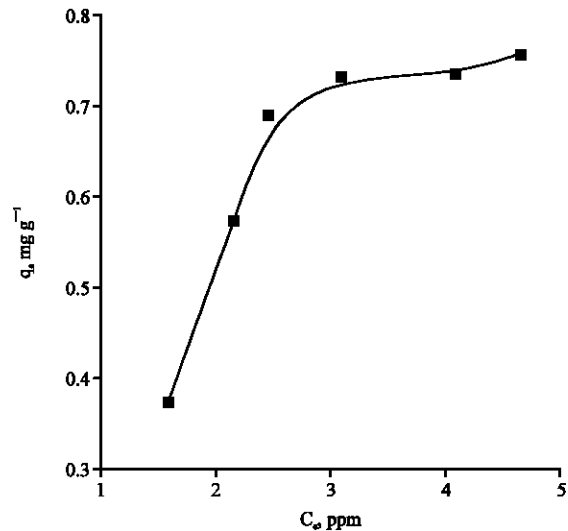


Fig. 2: Equilibrium adsorption isotherms of nitrite

adsorbents. Eventually a slow approach to equilibrium at high concentrations occurred. As more sites are filled, it becomes difficult for the solute molecules to find a site for adsorption and/or the difficulty of molecules in penetrating the layer of adsorbed anion already covering the surface sites. As result, the rate of adsorption decreases giving a plateau covers a wide range of solution concentrations i.e., considerably increasing the C_e values for a small increase in q_e (Giles *et al.*, 1960).

The experimental data of equilibrium isotherms were modeled using the most frequently used isotherms: Freundlich (F), Langmuir (L) and Langmuir-Freundlich (LF) (Roostaei and Tezel, 2004, Hallberg, 1987):

$$\text{Freundlich (F)} \quad q_e = K_f C_e^{1/n_f}$$

$$\text{Langmuir (L)} \quad q_e = \frac{q^0 b C_e}{1 + b C_e}$$

$$\text{Langmuir - Freundlich (LF)} \quad q_e = \frac{q^0 (b C_e)^{0.1/n}}{1 + (b C_e)^{1/n}}$$

In (LF) Eq. the letter n represents the heterogeneity of site energies of the adsorbent surface. The $1/n$, varying from zero to unity. For $1/n = 1$, it becomes the classical Langmuir isotherm characteristic for homogeneous adsorbents. At lower solute concentrations, i.e., $(b C_e)^{1/n} \ll 1.0$, it reduces to the Freundlich equation (Dohrowolski *et al.*, 1986). The isotherm parameters are given in Table 1. The applicability of the isotherm models is compared by judging the non-linear correlation coefficients R^2 . LF-isotherm gives good fit ($R^2 > 0.97$). This result may be due to LF isotherm has three fitting parameters. Langmuir-Freundlich q^0 values represents the maximum adsorption per unit weight of adsorbent, not restricted to monolayer of molecules as it was in the Langmuir isotherm.

Table 1: Freundlich, langmuir and Langmuir-Freundlich parameters for adsorption of nitrite

Isotherm	Parameters	Values
Freundlich	K (mg g ⁻¹)	0.39
	n	2.10
	R ²	0.74
	q ₀ (mg g ⁻¹)	1.24
Langmuir	b (1 mg ⁻¹)	0.40
	R ²	0.80
	q ₀ (mg g ⁻¹)	0.80
Langmuir-Freundlich	b (1 mg ⁻¹)	0.60
	n	0.22
	R ²	0.99

CONCLUSION

Activated carbon from straw and chemically modified showed good adsorption capacity for nitrite ions. Adsorption capacity increases with increasing anion concentration while adsorption efficiency decreases. The three parameters Langmuir-Freundlich isotherm describe the experimental data better than two parameter Langmuir and Freundlich adsorption isotherm. General, straw based activated carbon may be used as a low-cost, natural and abundant source for the removal of nitrite from water and wastewater.

ACKNOWLEDGEMENT

This project was supported by King Saud University, Deanship of Scientific Research, College of science Research Centre.

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