

Equilibrium Isotherm Studies for Removal Nitrate from Aqueous Solution as Hazardous Anion in Animal System

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Abstract: Rice straw activated carbon has been used for nitrate removal from aqueous solution. Results showed that increasing adsorbent concentrations increase the adsorption efficiency and decrease the adsorption capacity. At low adsorbent dose, all types of sites are entirely exposed for adsorption and the surface gets saturated faster. At higher particle concentrations, there is larger fraction of higher energy sites becoming unoccupied. Langmuir-freundlich Adsorption Isotherm Model gave higher fitting to the experimental data compared to Freundlich and Langmuir isotherms. This due to Langmuir-Freundlich Model has three fitting parameters which not restricted to monolayer of molecules as it was in the Langmuir isotherm. A comparative study on the nitrate adsorption revealed that the prepared carbon had better nitrate adsorption capacity (82 mg g^{-1}) as compared to other adsorbents. This suggests that straw based activated carbon is efficient nitrate adsorbents and that they possess good potential for nitrate removal in wastewater treatment.

Key words: Equilibrium isotherm, nitrate, active carbon, adsorption, wastewater

INTRODUCTION

Nitrate poisoning has been noted in numerous investigations (Muslih, 1991) and it can occur in all animals. In human nitrate is reduced to nitrite before ingestion in saliva and in the gastrointestinal tract. Nitrate poisoning affects several biochemical parameters. A previous study indicates that nitrate poisoning cause decreased levels of glucose and alkaline phosphatase in sheep (Majid, 1996) and responsible for the blue baby syndrome and a precursor to carcinogenic nitrosamines. Also it was reported that an increase in levels of glucose, cholesterol, creatinine, lactate dehydrogenase, AST and ALT in rats as result of Nitrate poisoning (Boukerche *et al.*, 2007). For these reasons, the European Community limits nitrate concentrations in drinking water to 50 mg L^{-1} (Deganello *et al.*, 2000).

Water may be a source of toxic levels of nitrate for livestock. Water may become contaminated by fertilizer, animal wastes or decaying organic matter which has become a growing environmental problem so it becomes a common concern of industrial and developing countries (Hallberg, 1987). Nitrate contamination is increasingly due to widespread use of fertilizers containing nitrate and from poorly or untreated human and animal wastes. Nitrate is a by-product of many industrial processes, including paper and explosives manufacturing and production of nitro-organic and pharmaceutical compounds (Pinar *et al.*,

1997). Also, in regions where pesticide contamination is problem, nitrate concentrations are often high (Hallberg, 1987). Studies on the removal of nitrate by different methods have been reported in a number of publications. To remove nitrate in water, the activated carbon/ion exchange process, reverse osmosis, combined membrane bioreactor/powdered activated carbon adsorption, the Biofilm-electrode Reactor (BER) and the BER/adsorption process were developed (Aslan and Türkman, 2004).

The objective of the present work is to assess the adsorption equilibrium isotherm for nitrate removal from water using straw based activated carbons.

MATERIALS AND METHODS

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. Nitrate anion concentrations were determined using a Metrohm 690 ion chromatography with column: 6.1009.000 anion column super sep, Eluent: 2.5 mmol L^{-1} phthalic acid, 5% acetonitrile, pH = 4.2 with conductivity detector. Average analyte retention time was 9.5 min for nitrate.

Activated carbon from rice straw was prepared according previous study (Daifullah, 2003). Equilibrium Isotherm was determined by shaking 20 mL of initial

concentration 50 mg L⁻¹ of NO₃ with various amounts of adsorbent. The flasks containing each anion solution and carbon were agitated for 24h 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

Effect of adsorbent concentration: Figure 1 shows that increasing the carbon concentrations increase the percent removal (R%) but decrease the adsorption capacity (q_e). Increasing the adsorbent dosage increases the percent removal (R%) of anions and attained constant removal after a particular carbon concentration (optimum dosage, 80 mg) beyond which there is no significant increase in removal for the anions studied. The decreases of loading capacity with the increase in the adsorbent dose is consistent with the argument that surface sites of carbon are heterogeneous. According to the Surface Site Heterogeneity Model, the surface is composed of sites with a spectrum of binding energies. At low adsorbent dose, all types of sites are entirely exposed for adsorption and the surface gets saturated faster. But at higher particle concentrations, there is larger fraction of higher energy sites becoming unoccupied. So, the active adsorption sites are more at a fixed adsorbate concentration with no saturation (Das *et al.*, 2003).

Equilibrium adsorption Isotherm: As shown in Fig. 2, the isotherms were classified as L-type (Giles *et al.*, 1960). 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 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 molecules already covering the surface sites. 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):

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

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

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

Where:

- n = The heterogeneity of site energies of the adsorbent surface
- 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., (bC_e)^{1/n} << 1.0, it reduces to the Freundlich equation (Dohrowolski *et al.*, 1986). The isotherm parameters are given in Table 1. The applicability

Table 1: Freundlich, Langmuir and Langmuir–Freundlich parameters for adsorption of nitrate

Isotherm	Parameters	Values
Freundlich	K (mg g ⁻¹)	1.600
	n	0.950
	R ²	0.780
Langmuir	q ⁰ (mg g ⁻¹)	32.200
	b (L mg ⁻¹)	0.010
	R ²	0.790
Langmuir-Freundlich	q ⁰ (mg g ⁻¹)	82.000
	b (L mg ⁻¹)	0.040
	n	0.113
	R ²	0.990

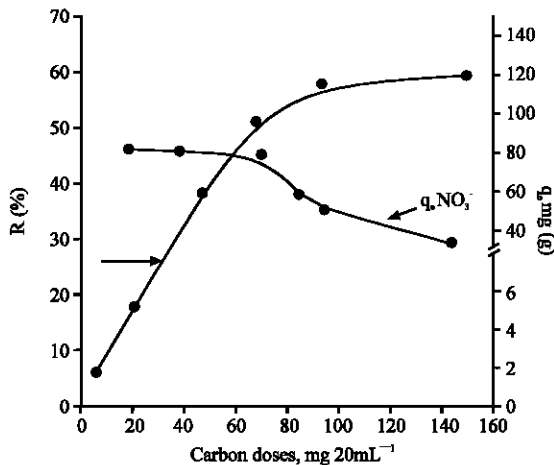


Fig. 1: Effect of adsorbent dosage on nitrate adsorption

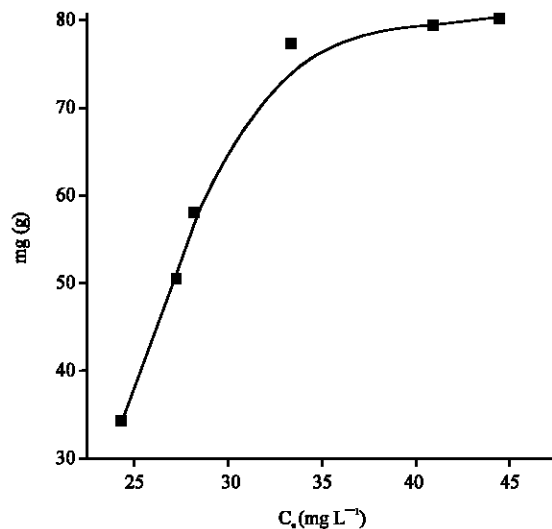


Fig. 2: Equilibrium adsorption isotherms of nitrate

Table 2: Comparison of the maximum monolayer adsorption capacities of nitrate anion on various adsorbents

Adsorbent	q ⁰ (mg g ⁻¹)	References
RS ₂ /KMnO ₄	82.00	This research
Bamboo powder charcoal	1.25	Mizuta <i>et al.</i> , (2004)
Commercial activated carbon	1.09	Mizuta <i>et al.</i> (2004)
<i>M. oleifera</i> hull (anion exchanger)	11.78	Orlando <i>et al.</i> (2003)
Lauan sawdust (anion exchanger)	8.68	Orlando <i>et al.</i> (2003)
Coconut husk	7.44	Orlando <i>et al.</i> 2003
Persimmon tealeaf (anion exchanger)	5.58	Orlando <i>et al.</i> (2003)
Pine bark (anion exchanger)	4.34	Orlando <i>et al.</i> (2003)
Rice hull (anion exchanger)	6.20	Orlando <i>et al.</i> (2003)
Sugarcane bagasse (anion exchanger)	3.72	Orlando <i>et al.</i> (2003)
Chinese tealeaf (anion exchanger)	2.48	Orlando <i>et al.</i> (2003)
Surfactant-modified zeolite (100% HDTMA loading)	3.97	Li (2003)
Surfactant-modified zeolite (150% HDTMA loading)	6.63	Li (2003)
Surfactant-modified zeolite (200% HDTMA loading)	5.64	Li (2003)

of the isotherm equation is compared by judging the non-linear correlation coefficients R². LF-isotherm gives good fit (R²>0.97). This result may be due to LF isotherm has three fitting parameters. Langmuir-Freundlich q⁰ values represents the maximum adsorption per unit weight of adsorbent, not restricted to monolayer of molecules as it was in the Langmuir isotherm.

Comparison with other adsorbents: The comparisons in nitrate equilibrium adsorption capacity of various adsorbents and activated carbon conducted in this study or reported in the literature are given in Table 2. These results indicate that straw based activated carbon is much better or even superior than many of these sorbents. This is probably related to the sorption mechanism which including both ion exchange and complexation.

CONCLUSION

Straw based activated carbon showed good adsorption ability for nitrate ions from aqueous solutions. Adsorbent dosage and equilibrium isotherm was studied. Was gave the optimum adsorption capacity at studied condition. The three parameters Langmuir-Freundlich isotherm describe the experimental data better than two parameter Langmuir and Freundlich adsorption isotherm. The studied carbon showed superior adsorption performance for nitrate as compared to many types of other adsorbents conducted reported in the literature. Overall, straw based activated carbon may be used as a low-cost, natural and abundant source for the removal of nitrate from water and wastewater.

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