

Adsorption Kinetics of Nitrate by Activated Carbon from Wastewater

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Abstract: Nitrate is naturally occurring ions that are part of the nitrogen cycle. It is mainly used in inorganic fertilizers, explosive production and glass making. Excessive nitrate level in drinking water or food can cause many health problems like methemoglobinemia or blue baby syndrome potentially causing brain damage and death. In this study KMnO_4 oxidized rice straw activated carbon has been used for nitrate removal from aqueous solution. Both unoxidized and oxidized carbon samples are characterized using N_2 -adsorption, elemental analysis, Boehm's titration and surface fractal dimension. Results show that oxidation treatment enhanced surface area and pore volume. The modified carbon good nitrate adsorption compared to unoxidized one. The equilibrium was attained after shaking for about 10 h, beyond which there is no further increase in the adsorption. The kinetic data of the anions can be described well by the pseudo second order rate equation. This indicate that chemical sorption is predominant in the case.

Key words: Adsorption, rice straw, nitrate, active carbon, surface modification

INTRODUCTION

Nitrate poisoning has been recorded in several studies (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 (Boukerche *et al.*, 2006) reported that an increase in levels of glucose, cholesterol, creatinine, lactate dehydrogenase, AST and ALT in rats as result of nitrate poisoning. For these reasons, the European Community limits nitrate concentrations in drinking water are 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 Turkman, 2004).

The objective of the present research is to assess the ability of oxidized and unoxidized activated carbons derived from steam pyrolysis of rice straw for the removal of nitrate from water at contact times.

MATERIALS AND METHODS

Stock solution for the experiments was prepared by adding appropriate amount of sodium potassium nitrate (KNO_3) in the deionized water. Various standard solutions were obtained by diluting stock solution with the addition of distilled deionized water as required.

Preparation of activated carbons: The 0.5 kg dried rice straw is feeded into fluidized bed reactor, described elsewhere (Daifullah, 2003) at heating rate 50°C/10 min in the presence of N₂ flow (300 mL min⁻¹). The steam entered the reactor at a rate of 5 mL min⁻¹ when the furnace reached 350°C and the heating continued up to final temperature of 650°C. The hold time was 1 h and the furnace is switched off. The carbon was left to coal down and taken the abbreviation RS (unox.). The modified active carbon, RS (ox.) was obtained by mixing each 1 g of parent carbon with 50 mL 0.1 N KMnO₄ solution for 48 h at 50°C. The treated carbon was thoroughly washed with distilled water, dried at 120°C and stored in stoppered bottles.

Characterization of the carbons: The surface area and pore characteristics of the prepared carbons were determined by nitrogen adsorption at 77 K using (Quantachrome Instruments, Model Nova1000e series, USA). The samples were outgased at 250°C under N₂ flow for 16 h. The pH of a particular adsorbent is measured with pH meter (Acton, MA) as mentioned elsewhere. The simple mass titration method was used to estimate the pH_{pzc} of carbons as reported (Leon *et al.*, 1992). The Boehm Titration Method (Bandosz *et al.*, 1992) was used to estimate the acidic and basic properties of carbons. The 1 g of carbon sample (after washing) was placed in 50 mL vial of the following 0.05 N solutions: sodium hydroxide (NaOH), sodium carbonate (Na₂CO₃), sodium bicarbonate, (NaHCO₃) and hydrochloric acid HCL.

The vials were sealed and agitated using an orbital shaker for 24 h, 5 mL of each filtrate was pipetted and the excess of base and acid was titrated with HCl and NaOH, respectively. The number of acidic sites of various types was calculated under the assumption that NaOH neutralize carboxyl, phenolic and lactonic groups, Na₂CO₃ carboxyl and lactonic and NaHCO₃ only carboxyl groups. The number of surface basic sites was calculated from the amount of hydrochloric acid which react with the carbon.

Kinetic tests were conducted to study the effect of various parameters on adsorption efficiency of anions (NO₃⁻) onto oxidized carbon sample, RS (ox.). In this concern, 50 mg of adsorbent was shaken with 20 mL of the solution of initial concentration of 50, 5 mg L⁻¹ of nitrate for different intervals of time. The 50 are the concentration level of nitrate, found in many aquaculture and industrial wastewaters (Lin and Wu, 1997). After the required time intervals, the suspension was filtered through a Whatman No. 42 filter paper and analyzed for residual anion concentration.

pH effect: The pH of the solutions were adjusted from 2-11 by dilute NaOH or HCl solutions. The 20 mL of pH adjusted solution and 30 mg adsorbent were used in batch experiments conducted at the determined equilibrium time. The pH value providing the maximum anion removal was determined.

RESULTS AND DISCUSSION

Characterization of adsorbents: A usual way of reporting oxygen content values from elemental analysis is based on the difference between the percentage content of all elements analyzed with the residual ascribed to oxygen (Salame and Bandosz, 2001). The number and type of functional groups quantified by Boehm's titration was used to calculate the amount of structural oxygen atoms attributed to each type of group (e.g., carboxyl contains two oxygen atoms). RS (ox.) sample contains a greater amount of oxygen than the unoxidized carbon (Table 1). The formation of considerable quantities of oxygen surface groups during the KMnO₄ treatment is evident from the elemental composition of the starting and RS (ox.) sample which show a considerable increase in oxygen content (from 1.42-7.53%). This is in accord with the data presented by Salame and Bandosz (2001) who reported an increase in oxygen content for oxidized carbonaceous adsorbents. Both unoxidized and oxidized carbons contain relatively large amounts of mineral admixtures (44.0 and 65.8%, respectively). An increase amount of ash in the oxidized sample may be due to increase the inorganic constituent such as manganese compounds. Also, the moisture content of the adsorbents is relatively high due to rice straw ash consists mainly of silica which has high affinity for water. However, it can be seen that the moisture content of RS (ox.) is lower than the parent carbon RS (unox.). This is logic considering the excess of inorganic residues after oxidation. Also, the oxidation using KMnO₄ was certainly effective in increasing the bulk density of RS (ox.) larger than of RS (unox.). This indicative of the deposition and retention of mixed oxide structure within the pores of the carbon as a result of KMnO₄ treatment. Figure 1 presents the DFT pore size distributions of the adsorbents studied. The results of surface area and pore volume are shown in Table 2. The microporous nature of carbons is demonstrated in Fig. 1. Oxidation enhances pore volume and surface area of the adsorbents without significant changes in the pore size distribution. The surface area and pore volume of oxidized carbon RS (ox.) increased by about 43 and 35%, respectively compared to those of the unoxidized carbon sample. Oxidized and unoxidized

Table 1: Elemental analysis of the adsorbents

Sorbents	Ash (%)	O (%)	Elements (wt. %)			Bulk density (g mL ⁻¹)	Moisture content (%)
			C	H	N		
RS (unox.)	44.0	1.42	31.00	1.21	-	0.32	23.0
RS (ox.)	65.8	7.57	10.97	0.56	-	0.45	15.1

Table 2: Surface area and pore volume results

Sorbents	DFT surface area (m ² g ⁻¹)	DFT pore volume (Cm ³ g ⁻¹)	BET surface area (m ² g ⁻¹)
RS (unox.)	65.3	0.064	76.2
RS (ox.)	114.1	0.099	122.9

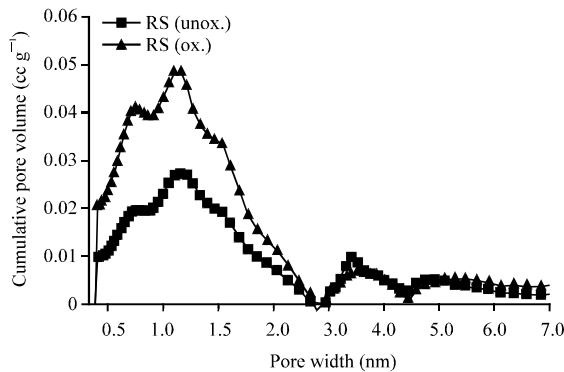


Fig. 1: DFT pore size distribution of unoxidized and oxidized rice straw activated carbons

carbon samples possess a significant amount of micropores with a maximum at 1 nm and mesopores in the range 3-5 nm. The data also show that there was a widening of the pores after the oxidation treatment. There is some enhancement in the microregion and a slight reduction in the mesoporous range (3-5 nm). This may be due to transition from pore wide accommodating one adsorbed layer to two and two layers to three, respectively (Villar-Rodil *et al.*, 2002). The distribution of surface functional groups at the surface of the adsorbent materials are presented in Table 3. The Boehm's titration results show that the carbonaceous adsorbents possess acidic and basic surface functionalities. The increase in the individual types of acidic functional groups after oxidation does not occur in equal proportions. In contrast, to the modified carbon, RS (unox.) possess a greater number of basic functional groups. However, oxidation of carbon using KMnO₄ increases the concentration of phenolic groups (Table 3).

Surface fractal dimension: The fractal Dimensions (D) of two adsorbents are calculated from Frenkel Halsey Hill (FHH) Models. The unoxidized carbon sample activated at 650°C has fraction dimension of D = 2.9. This indicates that the surface is very rough or irregular. Upon surface modification using KMnO₄, the fractal dimension

Table 3: Concentration of surface functional groups of unoxidized and oxidized Rice straw activated carbons

Sorbent	Measurement (meq g ⁻¹)				
	Carboxylic groupes	Lactones groupes	Phenolic groupes	Total ^a (non-carbonyl)	Basic groupes
RS (unox.)	0.05	1.89	0.06	2.0	8.13
(%) ^a	2.50	94.50	3.00		
RS (ox.)	0.50	1.44	3.06	5.0	5.77
(%) ^a	0.10	28.80	61.20		

^aPercentage of total noncarbonyl capacity

decreases (D = 2.5). This indicates that the structure of modified carbon became more ordered as the small crystallite and cross-linked structures were partially decomposed. The reactivity of disorganized carbon is higher than that of the crystallite carbon towards such type of reagent therefore, the carbon in cross-link was mainly consumed. It is presumed that the decomposition of the cross-link leads to the release of plugged pores which results in an increase of surface area and pore volume and a decrease of the fractal dimension compared to parent carbon (Pyun and Rhee, 2004; Hayashi *et al.*, 2002).

Kinetic studies of anions adsorption

Effect of agitation time: The time-profile of adsorption of NO₃⁻ onto RS (ox.) carbon is presented in Fig. 2. As agitation time increases, anion removal also increases initially but then gradually approaches a more or less constant value, denoting attainment of equilibrium. Obviously, the equilibrium was attained after shaking for about 10 h beyond which there is no further increase in the adsorption.

The kinetic curve of nitrate adsorption in Fig. 2 indicates that not only the surface of RS (ox.) can adsorb these ions but also the inner surface are accessible for ions to diffuse. The former rapid adsorption may be due to the ions adsorbed on the surface of RS (ox.) directly and the latter shows adsorption mainly attributes to long-range diffusion of anions in the inner surface of RS (ox.) where a marginal increase in adsorption is observed up to time after which it is essentially constant.

Kinetic rate parameters: The kinetic experimental data of anions on RS (ox.) sorbent is simulated by the pseudo first order and second order rate equation. Pseudo first order rate equation:

$$\text{Log} (q_e - q) = \text{log} q_e - (K_1/2.303)t$$

Pseudo second order rate equation:

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e}$$

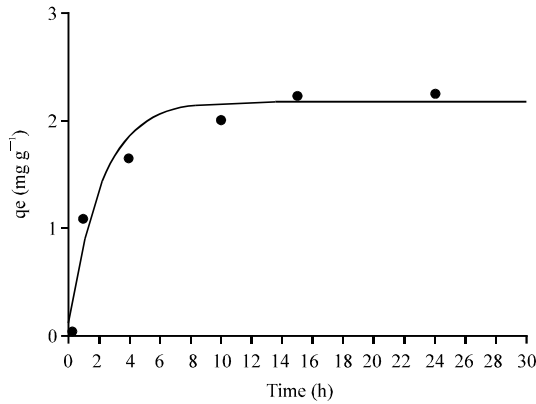


Fig. 2: Influence of agitation time on adsorption of NO_3^- by RS (ox.)

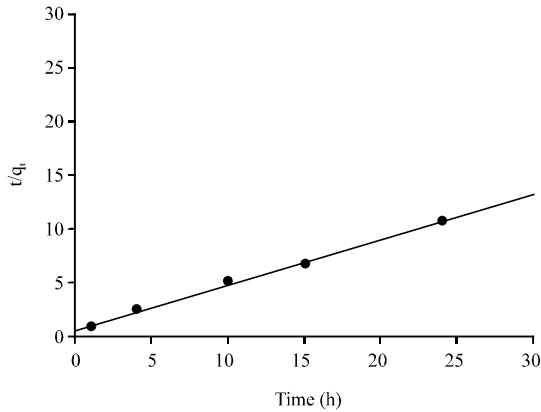


Fig. 3: Pseudo second order sorption kinetics of NO_3^-

Where:

q_t and q_e = The amount adsorbed (mg/g) at time t and at equilibrium time, respectively

K_1 and K_2 = First and second rate constants of adsorption

The kinetic experimental data of nitrate, ions on RS (ox.) are presented in Fig. 3 and Table 4. The correlation coefficient R^2 for the pseudo second order adsorption model has high value for the two anions and the calculated equilibrium adsorption capacities $q_{e, cal}$ is consistent with the experimental (Table 4). Remarkably, the kinetic data of the anions can be described well by the pseudo second order rate equation (Table 4). These results suggest that the rate-limiting step may be chemical sorption involving valency forces through sharing or exchange of electrons between anions and adsorbent (Gucek *et al.*, 2005).

Intra-particle diffusion: In order to show the existence of intra-particle diffusion in the adsorption process, the

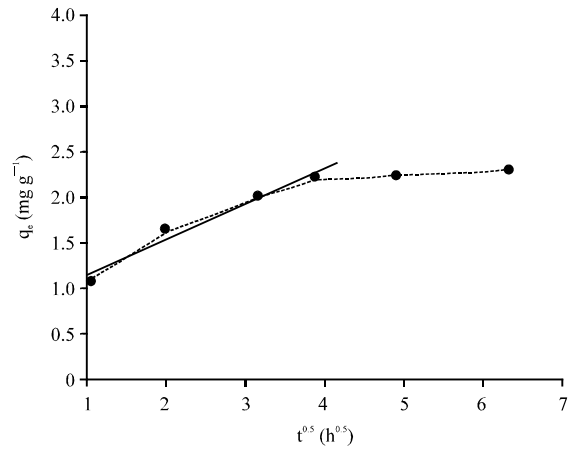


Fig. 4: Intra-particle diffusion plot for nitrate adsorption onto RS (ox.) carbon

Table 4: Comparison of the pseudo first second order adsorption rate constants and the calculated/experimental q_e values for NO_3^-

Models	Parameters	NO_3^-
First order model	$q_{e, exp}$ (mg g^{-1})	2.300
	K_1 (h^{-1})	0.136
	$q_{e, cal}$ (mg g^{-1})	1.400
	R^2	0.965
Second order model	K_2 (g $mg^{-1}h$)	0.270
	h (mg $g^{-1}h$)	1.540
	$q_{e, cal}$ (mg g^{-1})	2.390
	R^2	0.999

model developed by Weber and Morris (1963) was applied and can be defined as follows: $q_t = k_p t^{0.5}$. The intra-particle diffusion rates (k_p) were determined from the plots of q_t versus $t^{0.5}$ as shown in Fig. 4. It can be observed that the plots are not linear over the whole time range and reflect a dual nature with initial linear portion followed by plateau. This implies the anions are slowly transported via intra-particle diffusion into the particles and is finally retained in the pores. The rate constants of intraparticle diffusion were obtained from the slopes of the straight lines and were found to be $0.62 \text{ mg } g^{-1} h^{0.5}$. However, the linear portion of the curves does not pass the origin (Fig. 4), i.e., the pore diffusion is not the only rate controlling step (Cox *et al.*, 2005).

CONCLUSION

Rice straw as a by product could be used as readily available and inexpensive adsorbent for water treatment. Adsorbent produced from rice's straw could be used by industries for the treatment of wastewater to remove NO_3^- using of rice straw as starting materials for wastewater treatment will reduce a cost since it is a waste product. Furthermore, treatment processes using this material will reduce the population of plant parasites.

Reduction of plant parasite will increase agricultural yield. Indeed, one of the methods for decreasing the large volumes of waste and toxic effluents produced by a variety of chemical processes is the development of low-cost adsorbents. In this sense, the steam activated carbon derived from rice straw and modified by potassium per-manganate as solid phase showed the good adsorption ability for nitrate ions from aqueous solutions. In this concern, equilibrium was attained after shaking for about 10 h, beyond which there is no further increase in the adsorption. The kinetic data of the anions can be described well by the pseudo second order rate equation. This indicate that chemical sorption is predominant in the case.

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