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# Removal of Nitrite from Aqueous Solution by Active Carbon: Adsorption Kinetics Modeling

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**Abstract:** Nitrite is formed naturally by the nitrogen cycle during the process of nitrogen fixation in vertebrates, nitrate is converted to nitrite and other metabolites (nitric oxide and N-nitroso compounds). Overall, the acute toxicity of nitrite has been shown to be ~10 fold higher than that of nitrate. In this study, $KMnO_4$ oxidized Rice straw activated carbon has been used for nitrite 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 nitrite 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 pseudo first and second order kinetic models were applied assuming that the external mass transfer can be neglected and the process is chemisorption controlled.

**Key words:** Adsorption, Rice straw, nitrite, active carbon, treatment

## 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. 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 ~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. 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. For these reasons, the European community limits nitrite concentrations in drinking water are 0.1 mg $L^{-1}$.

The objective of the present work is to assess the ability of oxidized and unoxidized activated carbons

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**Corresponding Author:** Sobhy M. Yakout, Department of Biochemistry, College of Science, King Saud University, P.O. Box 2455, 11451 Riyadh, Kingdom of Saudi Arabia derived from steam pyrolysis of Rice straw for the removal of nitrite from water at different concentrations, contact times and pH.

## 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.

**Preparation of activated carbons:** Activated carbon from Rice straw were prepared according previous study (Daifullah, 2003). Carbon were characterized by nitrogen adsorption at 77 K using (Quantachrome Instruments, Model Nova1000e series, USA). The pH of a particular adsorbent is measured with pH meter (Acton, MA) as mentioned elsewhere (Mckay, 1996). The simple Mass Titration Method was used to estimate the $pH_{pzc}$ of carbons as reported (Leon y Leon *et al*., 1992). The Boehm Titration Method (Bandosz *et al*., 1992) was used to estimate the acidic and basic properties of carbons.

Kinetic tests were conducted to study the effect of various parameters on adsorption efficiency of anions ($NO_2^-$) 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 nitrite for different intervals of time. The 50 and 5 mg $L^{-1}$ are the concentration level of nitrite, respectively found in many aquaculture and industrial waste waters (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.

In all experimental runs the anion concentrations were determined using a Metrohm 690 ion chromatography with column: 6.1009.000 anion column super-sep, Elluent: 2.5 mmol $L^{-1}$ phathalic acid, 5% acetonitrile, pH = 4.2 with conductivity detector. Average analyte retention time were 6.9 min for nitrite.

## RESULTS AND DISCUSSION

### Characterization of adsorbents

**Elemental composition:** 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 $KMnO_4$ treatment is evident from the elemental composition of the starting and RS (ox.) sample which show a considerable increase in oxygen content (from 3.4-10.5%). 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 (41.0 and 62.0%, 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 $KMnO_4$ 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 $KMnO_4$ treatment.

**Surface area and pore size distribution:** 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 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

Table 1: Concentration of surface functional groups of unoxidized and oxidized Rice straw activated carbons

| Sorbents | Carboxylic groups (meq $g^{-1}$) | Lactones groups (meq $g^{-1}$) | Phenolic groups (meq $g^{-1}$) | Total[a] (non-carbonyl) (meq $g^{-1}$) | Basic groups (meq $g^{-1}$) |
|---|---|---|---|---|---|
| RS (unox.) (%)[a] | 0.05 (2.5) | 1.89 (94.5) | 0.06 (3.00) | 2.0 | 8.13 |
| RS (ox.) (%)[a] | 0.50 (0.1) | 1.44 (28.8) | 3.06 (61.2) | 5.0 | 5.77 |

[a] Percentage of total noncarbonyl capacity

Table 2: Surface area and pore volume results

| Sorbent | DFT Surface area ($m^2/g$) | DFT pore volume ($cm^3/g$) | BET surface area ($m^2/g$) |
|---|---|---|---|
| RS (unox.) | 65.3 | 0.064 | 76.2 |
| RS (ox.) | 114.1 | 0.099 | 122.9 |

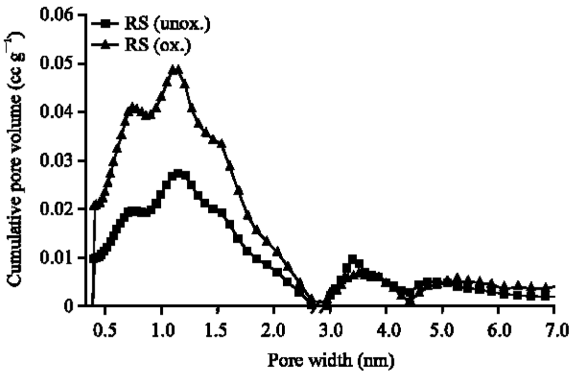

Fig. 1: DFT pore size distribution of unoxidized and oxidized Rice straw activated carbons

due to transition from pore wide accommodating one adsorbed layer to two and two layers to three, respectively (Villar-Rodil *et al*., 2002).

**Boehm's titration:** 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 $KMnO_4$ 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 $KMnO_4$, the fractal dimension 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).

Table 3: Elemental analysis of the adsorbents

| Sorbents | Ash (%) | O (%) | Elements (wt.%) C | H | N | Bulk density (g mL$^{-1}$) | Moisture content (%) |
|---|---|---|---|---|---|---|---|
| RS (unox.) | 41.07 | 3.40 | 31.00 | 1.21 | - | 0.32 | 23.0 |
| RS (ox.) | 62.40 | 10.50 | 10.97 | 0.56 | - | 0.45 | 15.1 |

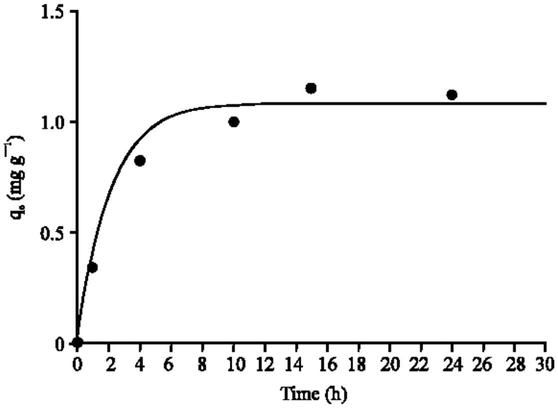

Fig. 2: Influence of agitation time on adsorption of $NO_2^-$ by RS (ox.)

**Kinetic studies of anions adsorption**

**Effect of agitation time:** The time-profile of adsorption of $NO_2^-$, 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 an 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 nitrite 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 pseudo second order rate equation (Ho and McKay, 2000):

Pseudo first order rate equation:

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

Pseudo second order rate equation:

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

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 nitrite 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 model developed by Weber and Morris (1963) was applied and can be defined as follows:

$$q_t = k_p t^{0.5}$$

The intra-particular 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 0.3 mg $g^{-1}$ $h^{0.5}$ for nitrite. However, the linear portion of the curves does not pass the origin (Fig. 4). The pore diffusion is not the only rate controlling step (Cox *et al*., 2005).

Table 4: Comparison of the pseudo first second order adsorption rate constants and the calculated/experimental $q_e$ values for and $NO_2^-$

| Models | Parameters | $NO_2^-$ |
|---|---|---|
| First order | $q_{e,\ exp}$ (mg $g^{-1}$) | 1.200 |
| | $K_1$ ($h^{-1}$) | 0.080 |
| | $q_{e,\ cal}$ (mg $g^{-1}$) | 0.600 |
| | $R^2$ | 0.720 |
| Second order | $K_2$ (g mg $h^{-1}$) | 0.400 |
| | h (mg g $h^{-1}$) | 0.600 |
| | $q_{e,\ cal}$ (mg $g^{-1}$) | 1.220 |
| | $R^2$ | 0.998 |

**Effect of adsorbent concentration:** Figure 5 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 from 20 mL solution containing

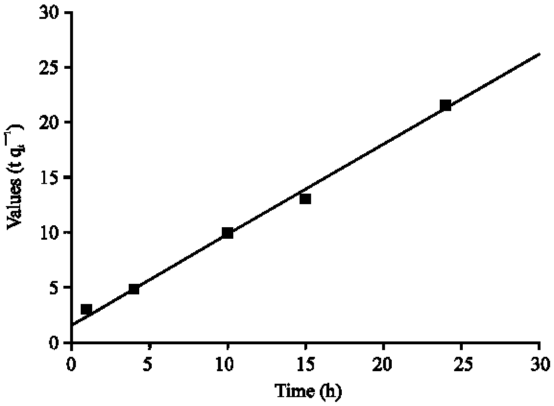

Fig. 3: Pseudo second order sorption kinetics of $NO_2^-$

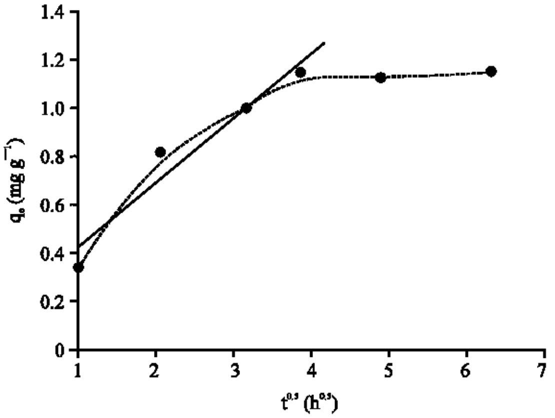

Fig. 4: Intra-particle diffusion plot for nitrite adsorption onto RS (ox.) carbon

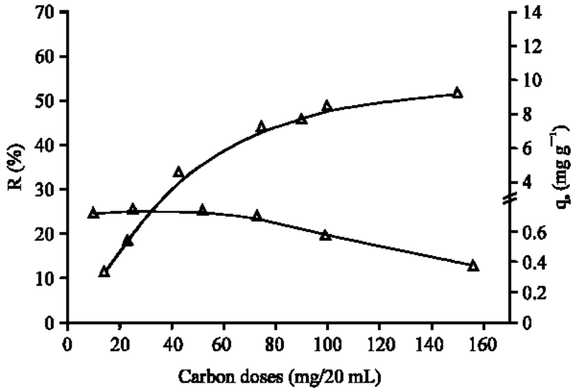

Fig. 5: Effect of carbon doses on adsorption capacities and percent removal of the nitrite

50 and 5 mg $L^{-1}$ of $NO_3^-$ and $NO_2^-$, respectively and attained constant removal after a particular carbon concentration (optimum dosage) beyond which there is no significant increase in removal for the anions studied. A minimum adsorbent dosage of 80, 90 mg was required for $NO_3^-$, $NO_2^-$, respectively. The decreases of loading capacity $q_e$ of RS (ox.) 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).

**Effect of pH:** Figure 6 shows that the effect of pH on the adsorption of nitrite is rather small. The broad pH range (3-9) using RS (ox.) carbon makes it a promising adsorbent material to remove nitrite from water. Similar results have been reported for the removal of nitrate on palladium-based catalysts supported on activated carbons (Lemaignen *et al*., 2002), nitrate by sepiolite (Ozturk and Bektas, 2004), nitrate by modified amine coconut coir (Baes *et al*., 1997) and nitrate and nitrite on ion exchangers (Lin and Wu, 1997).

**Possible working mechanisms:** The adsorption sites in active carbons can be divided into two major types these are: hydrophobic surfaces comprising of the graphene layers and oxygen functional groups which are primarily hydrophilic. This provides two main possibilities nitrite adsorption (Jia *et al*., 1998): adsorption by interaction between the p orbitals of the graphene layers and anions or an ion exchange mechanism involving the functional groups.

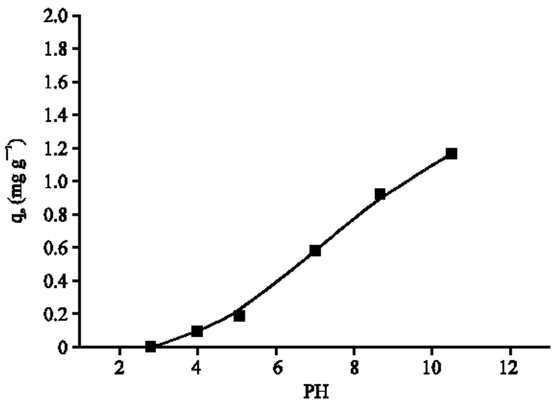

Fig. 6: Effect of pH on the adsorption of nitrite by RS (ox.) carbon

The pH of the medium would definitely influence the course of the 2nd mechanism but the 1st mechanism may operate over a large range of pH without being affected much. The amount of nitrite adsorbed in the present work remained nearly constant in the pH range of 2.0-10.0 (Fig. 6) and therefore, the adsorption of $NO_2^-$ on RS (ox.) is expected to occur between the delocalised π-electrons of the oxygen free Lewis basic sites and the free electrons of the anions (π-π argument).

## 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 waste water to remove nitrite. Using of Rice straw as starting materials for waste-water 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 efluents 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 nitrite 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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