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Removal of Nitrate and Nitrite Anions from Wastewater Using Activated Carbon Derived from Rice Straw

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Abstract

Rice straw (RS) has been activated using Na_2CO_3. Activated carbon samples (ARSC) were characterized using N_2-adsorption, elemental analysis, surface fractional dimension and pore volume to support the adsorption of nitrate and nitrite ions. The effects of various parameters such as solution pH, adsorbent concentration, contact time, temperature and initial nitrate and nitrite concentrations were examined. Various kinetics models including the Pseudo-first-order, Pseudo-second-order and intra particle diffusion models have been applied to the experimental data to predict the adsorption mechanism. The thermodynamics constants of the adsorption process, *viz.* ΔH^o, ΔG^o and ΔS^o were evaluated. The results showed that the adsorption of nitrate and nitrite ions onto activated carbon was exothermic and non-spontaneous. The adsorption data followed second-order kinetics supporting that chemisorption process was involved. The obtained results show that ARSC can be used as an effective and natural low-cost adsorbent for the removal of nitrate and nitrite anions from wastewater.
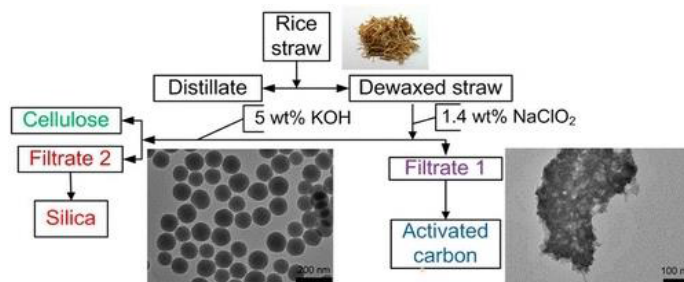
Schematic diagram for preparation of activated carbon produces from rice straw.

Keywords: Activated carbon; Rice straw; Adsorption; Nitrate; Nitrite; Wastewater

Introduction

Nitrogen (N) is an essential element for all living matter. Nitrogen exists in different oxidation states such as NO_3^- (+5), NO_2^- (+3) and ammonium NH_4^+ (-3). Among these, NO_3^-, NO_2^- and NH_4^+ (-3) are of more concern because they are soluble in water causing toxicity to human health [1]. Contamination of groundwater and surface water by nitrate coming from non-point sources such as agricultural fertilization has become a growing environmental problem so it becoming a common concern of both industrial and developing countries [2]. Nitrate contaminations increasingly occurs due to the widespread use of fertilizers containing nitrate and owing to poorly treated or untreated human and animal wastes. Nitrate is a by-product of many industrial processes, including paper and explosives manufacturing and the production of nitro-organic and pharmaceutical compounds [3]. The increasing nitrate concentration in the groundwater causes a serious health risk, responsible for the blue baby syndrome and a precursor to carcinogenic nitrosamines [4]. For these reasons, the European Community limits nitrate and nitrite concentrations in drinking water [5].

Nitrite and nitrate are also a form of non-radioactive waste present in more radioactive waste; nitric acid is employed in processing extremely toxic radioactive elements such as uranium, plutonium and americium during the production of nuclear weapons and nuclear fuel. However, if nitrate is also present in high concentrations, it may interfere with the formation of stable cement matrix, making it difficult to use this process for the long-term disposal of various metal processing wastes [6]. Therefore, removal of nitrate and nitrite is of significant importance from the health and environmental point of view.

Conventional methods for removing nitrate and nitrite anions from wastewater include reverse osmosis, ion exchange, combined membrane bioreactor/powdered activated carbon adsorption, the biofilm-electrode reactor (BER) and the BER/adsorption process [7]. Most of these methods suffer from some drawback, such as the high capital or high operational cost or the disposal of the resulting sludge [7,8].

Recently, numerous low-cost alternative adsorbents have been examined for the removal of nitrate and nitrite anions from wastewater [9-13].

The present work was directed at improving the capability of ARSC for removing nitrate and nitrite ions from wastewater. To achieve this goal, the following studies were undertaken: (a) preparation and characterization of ARSC, (b) establishment of the conditions under which the maximum adsorption of nitrate and nitrite ions onto ARSC occur using column technique, and (c) evaluation of the kinetic and thermodynamic parameters for nitrate and nitrite ions adsorption onto ARSC.

Experimental

Materials and methods

Materials: Rice straw (RS) is a distinguished type of precursor in comparison to other agricultural by-products. It obtained from agricultural regions in Sharqia-Egypt.

Preparation of activated carbons: Half a kilogram of dried rice straw is fed into the fluidity bed reactor, described elsewhere [8], at a heating rate 50°C per 15 min in the presence of N_2 flow (200 mL min^{-1}). Assess of the reactor was 5 mL min^{-1} when the furnace reached 350°C and the heating continued up to a final temperature of 650°C. The hold time was 1 h and the furnace was stopped. Carbon given the abbreviation. 1.0 g of carbon samples were mixed with 25 mL of 0.1 mol L^{-1} Na_2CO_3 solution for 72 h at 50°C, washed with water and stored in stopper bottle.

Samples characterization: Samples were characterized by using nitrogen adsorption at [77 K] using (Quantachrome Instruments, Model Nova1000e series, USA). The samples were outgased at 250°C under N_2 flow for 16 h. The pH of the samples was adjusted [9].

Adsorption studies: Sample Selection: A fixed amount of both non-oxidized and oxidized dry adsorbent (0.1 g) and 25 mL aliquots of the stock solution of initial concentration Co=25 mgL^{-1}, for each solute were shaken for 24 h. Each mixture was filtered and the residual, nitrate and nitrite content in the solution was determined for knowing the effect of equilibrium time.

The pH of the solutions was adapted from 2 to 11 by diluting NaOH or HCl solutions. We used 20 mL of the pH adjusted solution and 30 mg adsorbent in batch experiments conducted at the determined equilibrium time. The pH value provides the maximum anion removal was determined.

Experiments were carried out by taking 20 ml of a nitrate-ions-spiked aqueous solution of an initial concentration of 50 mg L^{-1} NO_3^- and carbon dose of 200 mg in the presence of different quantities of $Ca(HCO_3)_2$ in the range of 0-400 mg L^{-1}. Effect of shaking time was done at 24 h at 25°C, 45, and 55°C.

Methods

Metrohm 690 ion chromatography with column: 6.1006.000 anion column super-sep, elluent: 2.5 mmolL^{-1} phathalic acid, 7% acetonitrile, pH=4 with conductivity detector were used to determine anion concentrations.

Kinetic studies

Kinetic tests were conducted to study the effect of various parameters on the adsorption efficiency of the anions (NO_2^- and NO_3^- onto the oxidized carbon sample, RS (ox.). In this respect, 50 mg of adsorbent was shaken with 20 mL of the solution of an initial concentration of nitrate 50 mg L^{-1} and 5 mg L^{-1} of nitrite for different intervals of time. These are the concentration levels of nitrate and nitrite found in

various aquaculture and industrial wastewaters [12]. After the required time intervals, the suspension was filtered through a Whatman No. 42 filter paper and analysed for residual anion concentration.

Results and Discussion

Activated carbon characterization

The usual way of reporting oxygen content values from elemental analysis is based on the difference between the percentage content of all elements analysed with the residual ascribed to oxygen [13]. RS (ox.) sample, which show a considerable increase in oxygen content (from 0.92 to 5.7%) (Table 1).

DFT pore size distributions of the adsorbents were studied in Figure 1. The results of surface area and pore volume are given in Table 2. The microporous nature of carbons is demonstrated in Figure 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 of 1 nm and mesopores in the range 2-4 nm. The data also show that there was a widening of the pores after the oxidation treatment. There are some enhancement in the microregion and a slight reduction in the mesoporous range (2-4 nm). This may be due to a transition from pore width accommodating one adsorbed layer to two, and two layers to three respectively [14].

The fractial 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=2.1. This indicates that the surface is very rough or irregular. Upon surface modification using Na_2CO_3, the fractal dimension decreases (D=2.2).

Sorbent	Ash (%)	O (%)	Elements (wt%)			Bulk density (gmL^{-1})	Moisture Content (%)
			C	H	N		
RS (unox.)	54.0	0.92	26.0	0.94	-	0.22	18.0
RS (ox.)	72.8	6.57	8.97	0.46	-	0.35	12.1

RS (unox.): Unoxidized activated carbon sample; RS (ox.): Oxidized activated carbon sample

Table 1: Physico-chemical characteristics of oxidized and non-oxidized activated carbons.
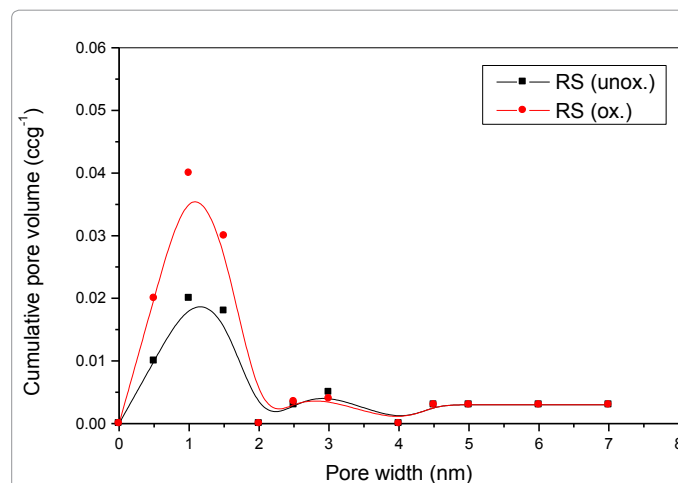
Figure 1: DFT pore size distribution of unoxidized and oxidized rice straw activated carbons.

Sorbent	DFT Surface area (m²g⁻¹)	DFT pore volume (cm³g⁻¹)	BET surface area (m²g⁻¹)
RS (unox.)	65.3	0.064	76.2
RS (ox.)	114.1	0.099	122.9

RS (unox.): Unoxidized activated carbon sample; RS (ox.): Oxidized activated carbon sample; DFT: Distribution pore size; BET: Surface area characterization of microporous materials

Table 2: Surface area and pore volume of adsorbent materials.

This suggests 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 greater than that of the crystallite carbon towards such type of reagent; therefore, the carbon in cross-link was mainly consumed. 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 [15,16].

Kinetic studies of anions adsorption

Effect of agitation time: The time-profile of adsorption of NO_3^- and NO_2^-, onto RS (ox.) carbon is presented in Figure 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, equilibrium was attained after shaking for about 10 h in both cases, beyond which there is no further increase in the adsorption.

Nitrate adsorbed greater than nitrite. This is caused by nitrate have high oxidizing strength. i.e., it is effectively able to extract enough charge from RS (ox.) surface to form sorbed nitrate than in case of nitrite [17].

The kinetic curve of nitrate and nitrite adsorption in Figure 2 indicates that not only the surface of RS (ox.) can adsorb these ions, but also, the inner surface is 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 are simulated by the pseudo first-order and pseudo second-order rate equation [18].

$$Log(q_e-q)=log\ q_e-(K1/2.303)t \qquad 1^{st}\ order \qquad (1)$$

$$\frac{t}{q_t} = \frac{1}{k_2q_e^2} + \frac{t}{q_e} \qquad ....2nd\ order \qquad (2)$$

where q_t and q_e are the amount adsorbed (mgg⁻¹) at time t and at equilibrium time respectively and K_1 and K_2 are first and second-rate constants of adsorption.

The kinetic experimental data of nitrate and nitrite ions on RS (ox.) are presented in Figure 3 and Table 3.

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 is consistent with the experimental (Table 3).

Remarkably, the kinetic data of the anions can be described well by the pseudo-second-order rate equation (Table 3), the rate-limiting step may be chemical sorption involving valency forces through sharing or exchange of electrons between anions and adsorbent [19].

Table 4 discuss the comparison between adsorption capacities of nitrate and nitrite anions onto various adsorbents and showed that prepared has higher monolayer adsorption capacity than the other ones.

Intra-particle diffusion: The intra-particular diffusion rates (kp) were determined from the plots of q_e versus $t^{0.5}$ as shown in Figure 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 a 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, and 0.3 mg g⁻¹ h⁰·⁵ for nitrate, and nitrite respectively. However, the linear portion of the curves not goes the origin (Figure 4) i.e., the pore diffusion is gets another rate controlling step [20].

Effect of pH

Figure 5 shows that the effect of pH on the adsorption of nitrite and nitrate is rather small in case of NO_2 anions but amount adsorbed increase gradually at pH 8 in case of nitrate anions. The broad pH range (3-9) using RS (ox.) carbon makes it a promising adsorbent material to remove nitrate and nitrite from water. Analogous results have
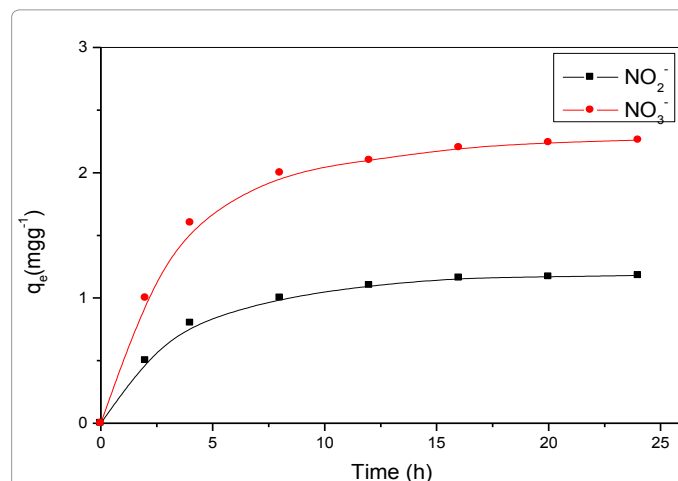

Figure 2: Influence of agitation time on adsorption of NO_3^- and NO_2^- by RS (ox.).
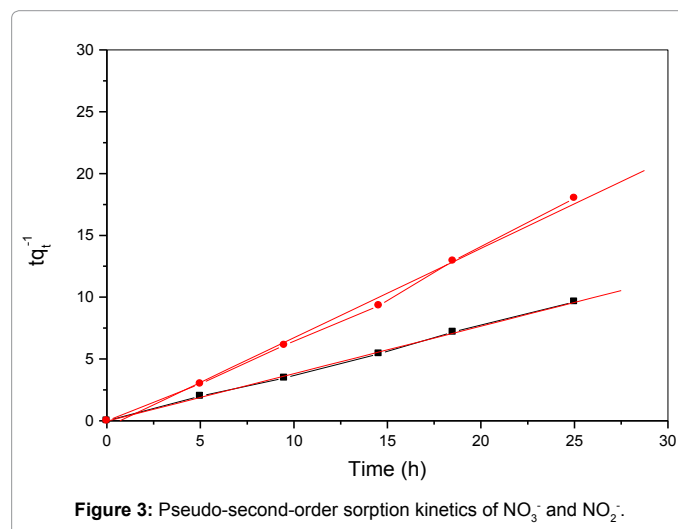

**Figure 3:** Pseudo-second-order sorption kinetics of NO_3^- and NO_2^-.

Model	Parameter	NO3-	NO2-
	q_e, (mg g^{-1})	2.1	1.1
First-order model	K_1 (h-1)	0.12	0.06
	q_e, cal (mg g^{-1})	0.2	0.4
	R^2	0.945	0.62
Second-order model	K_2 (gmg^{-1} h^{-1})	0.17	0.3
	h (mg g^{-1}h)	1.34	0.4
	q_e, cal (mg g^{-1})	2.19	1.12
	R^2	0.94	0.92

NO3-: Nitrate anion; NO2-: Nitrite anion

Table 3: Comparison of the pseudo first/second-order adsorption rates constants and the calculated/experimental q_e values for NO_3^- and NO_2^-.

Adsorbent	qo (mg/g)	Ref.
RS2/Na$_2$CO$_3$	8.2	This work
Bamboo powder charcoal	1.25	[29]
Commercial activated carbon	1.09	[29]
M. oleifera hull (anion exchanger)	11.78	[30]
Lauan sawdust (anion exchanger)	8.68	[30]
Coconut husk	7.44	[30]
Persimmon tealeaf (anion exchanger)	5.58	[30]
Pine bark (anion exchanger)	4.34	[30]
Rice hull (anion exchanger)	6.2	[30]
Sugarcane bagasse (anion exchanger)	3.72	[30]
Chinese tealeaf (anion exchanger)	2.48	[30]
Surfactant-modified zeolite (100% HDTMA loading)	3.97	[30]
Surfactant-modified zeolite (150% HDTMA loading)	6.63	[30]
Surfactant-modified zeolite (200% HDTMA loading)	5.64	[30]

Table 4: Comparison of the maximum monolayer adsorption capacities of nitrate anion on various adsorbents.
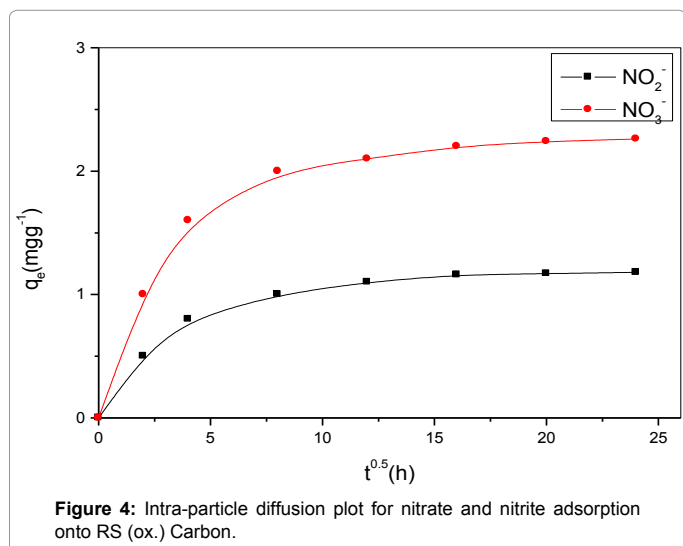
Figure 4: Intra-particle diffusion plot for nitrate and nitrite adsorption onto RS (ox.) Carbon.

been reported for the removal of nitrate on palladium-based catalysts supported on activated carbons [21,22], nitrate by sepiolite [23], nitrate by modified amine coconut coir [12], and nitrate and nitrite on ion exchangers [24].

Possible working mechanisms: The adsorption sites in active carbons can be divided into two major types; these are

(i) Hydrophobic surfaces comprising of the graphene layers; and (ii) oxygen functional groups which are primarily hydrophilic. This provides two main possibilities for nitrate and nitrite adsorption (a)

adsorption by interaction between the p orbitals of the graphene layers and anions; or (b) an ion exchange mechanism involving the functional groups [25].

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 nitrate and nitrite adsorbed in the present work remained nearly constant in the pH range of 2.0 -10.0 (Figure 6), and therefore, the adsorption of NO_3^- and 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).

Thermodynamic Studies for NO_3 anions

Temperature effect: The isotherm constants for the sorption of NO_3^- ions onto RS (ox.) carbon by the three models: Freundlich (F), Langmuir (L), and Langmuir–Freundlich (LF) at different temperatures are presented in Table 5.

Based on the correlation coefficient values, R^2, generally, LF isotherm still found to be a good representative for the experimental data over the whole concentration range with high correlation coefficient values.
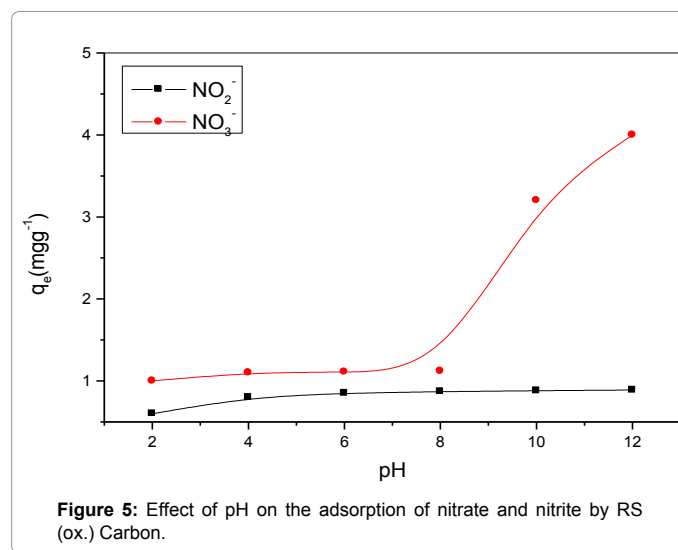
Figure 5: Effect of pH on the adsorption of nitrate and nitrite by RS (ox.) Carbon.
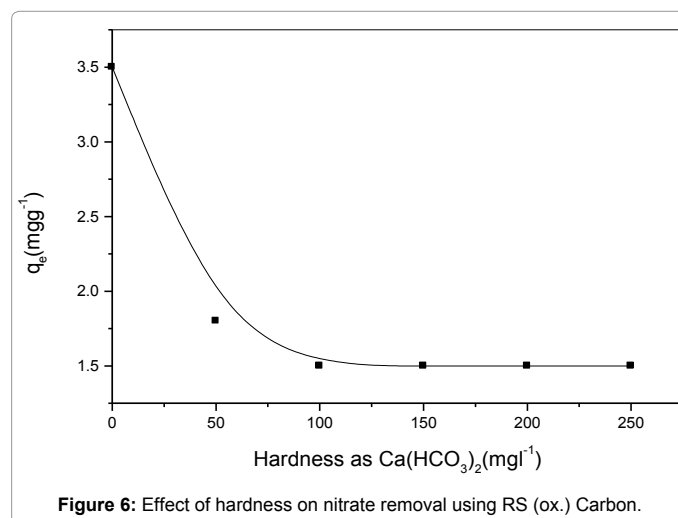
Figure 6: Effect of hardness on nitrate removal using RS (ox.) Carbon.

The q^o values calculated from LF model were found to decrease by increasing temperature. This is referred to the solubility of the adsorbate. The solubility of KNO_3 increases from 31.6 g per 100 g water at 20°C to 110 g per 100 g water at 60°C.

An alternative hypothesis would be due to an increase of temperature causes a shift of the point of zero charge (pzc) of carbon to low pH values and the surface charge density at a given pH becomes more negative. This creates unfavorable conditions for adsorption of anions [26].

Thermodynamic parameters: The value of enthalpy change (ΔH^o) and entropy change (ΔS^o) were obtained in Table 6.

The thermodynamic equilibrium constant K_o equal to q^{o*} b of LF isotherm. The thermodynamic parameters determined for the adsorption of NO_3^- onto RS(ox.) carbon is given in Table 6 using the following thermodynamic equations [27]:

$$\ln k_o = \frac{\Delta S^o}{R} - \frac{\Delta H^o}{RT}$$
$$\Delta G^o = -RT\ln k_o$$

where ΔG^o is the standard free energy, R=Universal gas constant (1.987 calmol^{-1} K^{-1} or 8.314 jmol^{-1} K^{-1}) and T=Absolute temperature in kelvin (K).

The exothermic nature of adsorption is indicated by the negative value of ΔH^o. The entropy (ΔS^o) value suggests no significant change occurs in the internal structure of RS (ox.) carbon during the adsorption [28]. The sorption process takes place with an increase in the order of the system. The positive value of ΔG^o indicates the formation of thermodynamically unstable adsorbed species. This positive value of ΔG^o indicates that better adsorption, is obtained at a lower temperature.

Effect of hardness on nitrate removal

The co-existing ions selected were calcium hydrogen carbonate that is typically found in ground water and cause temporary hardness. It is demonstrated in Figure 6. The nitrate removal is appreciably decreased in the presence of $Ca(HCO_3)_2$. The inhibiting effect of these species can be ascribed to the identical structures of NO_3^- and HCO_3^- ions. They are both planar, and the angles between the N–O and C–O bonds are identical and equal to 120°C. It can be thus reasonably believed that HCO_3^- anions competitively adsorb to the same active sites on the surface of the RS (ox.) carbon [29,30].

These results indicate that $KMnO_4$ modified activated carbon produced from rice straw is much better or even superior than any of these sorbents. This is probably related to the sorption mechanism which including both ion exchange and complexation.

Conclusion

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, which is one of the major goals of green chemistry. In this sense, the steam activated carbon derived from rice straw and modified by potassium permanganate showed good adsorption ability for nitrate and nitrite ins from aqueous solutions. In this concern, Factors affecting the removal of nitrate and nitrite ions in single-component systems were investigated: temperature, pH, adsorbent concentration and carbon dosages. In the binary system (NO_3 and HCO_3), the inhibitive effect of hardness on nitrate removal is referred to the identical structure of NO_3 and HCO_3 ions and in the system (NO_3 and NO_2), the nitrate sorption was suppressed due to the

Anion	Temp. °C	Frundlich			Langmuir			Langmuir–Freundlich			
		K	n	R²	qo	b	R²	qo	b	n	R²
NO3-	25	0.12	0.92	0.75	17.7	0.01	0.66	3.3	0.03	0.11	0.990
	45	0.08	0.82	0.66	15.6	0.01	0.4	2.5	0.04	0.06	0.993
	55	0.03	0.6	0.7	12.6	0.01	0.62	2.2	0.03	0.05	0.999

K: Freundlich constant; q^0: The amount of solute adsorbed at equilibrium per unit; n: Freundlich constant weight of adsorbent required for monolayer of the surface; R²: Correlation coefficient values b constant related to the heat of adsorption

Table 5: Characteristic parameters of the experimental data according to the Langmuir, Freundlich and Langmuir-Freundlich equations for the adsorption of NO3- onto RS (ox.).

Anion	ko (L g^{-1})			ΔHo (kJmol^{-1})	ΔSo (J mol^{-1} K^{-1})	ΔGo (KJmol^{-1})		
	298K	318K	328K			298K	318K	328K
NO3-	0.33	0.25	0.2	-12.8	-0.76	2.8	3.7	4.4

k_0: Thermodynamic equilibrium constant; ΔHo: Enthalpy change; ΔSo: Entropy change; ΔGo: The standard free energy

Table 6: Thermodynamic parameters of NO3- sorption on to RS (ox.) carbon.

competitive effect whereas the nitrite sorption was promoted due to the cooperative adsorption. In presence or absence of NOM, the adsorptive capacity was similar, indicating that the affinity of nitrate for the carbon surface is stronger than the attraction between nitrate and NOM.

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