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The effect of acid treatment of carbon cloth on the adsorption of nitrite and nitrate ions

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Abstract

The effects of functional groups on the adsorption efficiency of nitrate and nitrite from water by carbon cloth were investigated. The carbon cloth was treated by sulfuric acid and used for the adsorption of nitrate and nitrite from water samples at nearly neutral solutions. The concentrations of ions in the solution were monitored using in situ UV spectroscopy. Acid treatment caused a significant increase in the adsorption rate of ions and the adsorption capacity of the adsorbent.
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1. Introduction

Different technologies have been developed to remove ions species from waters: precipitation, ion exchange, membrane separation, but adsorption has been shown to be an economical alternative for removing trace ions from water [1–4]. Adsorption in general, is the process of collecting soluble substances that are in solution on a suitable interface. In adsorption, adsorbent surface area must be large.

Activated carbons can adsorb small but significant quantities of metal species from aqueous solutions. High-area carbon cloth (C-cloth), which has the advantage of having a very large specific surface area, e.g., $2500 \, \mathrm{m^2 \, g^{-1}}$, has been used for the successful adsorptive removal of various chemical species [5–13].

The surface chemistry of activated carbon is characterized by heteroatoms that compose the surface such as oxygen, nitrogen, hydrogen, sulfur, and phosphorous [14]. Those heteroatoms are in the form of functional groups such as ketones, carboxyls, phenols, ethers, lactones, or nitro groups and they have a significant effect on the chemical character, acidity, and degree of hydrophobicity of the carbon surface [15,16]. It was well known that the ion-adsorption efficiency of the carbon adsorbents can be strongly dependent on the pore microstructure and chemical functional groups.

Oxides of nitrogen, such as nitrate and nitrite are common pollutants in closed surface water systems and ground water contaminated with nitrogenous compounds. High concentrations of N-containing compounds in drinking water cause health problems such as cyanosis among children and cancer of the alimentary canal. Therefore, removal of nitrate and nitrite from water samples is of significant importance from the health and environmental point of view.

Different methods have been applied to the removal of nitrite and nitrate. These include adsorption [6,17] biological denitrification [18–20], ultrafiltration [21] and electrodialysis [22].

In the present work the effects of functional groups on the adsorption efficiency of nitrate and nitrite by C-cloth was investigated. For the modification of surface functional groups and porous structures, the carbon cloths were chemically etched in H_2SO_4 solution.

2. Experimental

2.1. Reagents

The C-cloth used in this work was obtained from Spectra Corp., coded as Spectracarb 2225 having a specific area of

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$2500\,m^2\,g^{-1}$. $NaNO_3$, $NaNO_2$ and sulfuric acid were reagent grade materials. Triply distilled deionized water was used for making up the test solutions from which adsorption at the C-cloth was measured.

2.2. Absorption measurements

Simultaneously *in situ* concentration measurements were made by means of UV absorption spectrophotometry. A V-shaped cell was used for conducting the adsorption studies [5,6]. A Perkin-Elmer Lambda 45 UV–vis spectrometer spectrophotometer, interfaced to a computer, was used for the absorbance measurements which could be conducted *in situ* during study of the adsorption process by the procedure described previously [6].

2.3. Treatment of C-cloth

It is well known [5,6,11–13] that Spectra Corp. C-cloth initially contained some traces of elutable ions as indicated by conductometric measurements. Hence, a deionization cleaning procedure was applied to avoid desorption of ions during adsorption studies [5]. A $\sim 2\,g$ C-cloth sample was first placed in a flow-through washing cup and eluted with a total of $5\,L$ of warm ($60\,^{\circ}C$) conductivity water in a kind of batch operation over 2 days. Nitrogen gas was bubbled continuously through the washing cup to avoid possible adsorption of CO_2 that might have been dissolved in the water. The outflow water from each batch was tested conductometrically for completeness of the washing procedure. The washed C-cloth modules were then dried under vacuum at $120\,^{\circ}C$ and kept in a desiccator for further uses. For the modification of surface functional groups and porous structures, the C-cloths were submersed in a $4.0\,mol\,L^{-1}$ solution of H_2SO_4 solution. The C-cloth was then washed with triply distilled deionized water and used.

2.4. Determination of adsorption isotherms

The adsorption isotherms of the investigated anions on the carbon cloth were determined on the basis of batch analysis. Carbon cloth pieces of varying masses were allowed to equilibrate with solutions of anions with known initial concentrations. The concentrations after the equilibration period were measured spectrophotometrically. The amount of each anion adsorbed per unit mass of adsorbent, N_f, was calculated by the following equation:

$$N_f = \frac{V(C_0 - C_s)}{m} \tag{1}$$

where V is the volume of the solution of anions in L, C_0 and C_s are the initial and equilibrium concentrations, respectively, in $mmol\,L^{-1}$ and m is the mass of carbon cloth in g. Then Eq. (1) gives N_f in mmol adsorbate adsorbed per g carbon cloth.

Table 1
Spectral and calibration data for nitrate and nitrite

| Species	Wavelength (nm)	Absorptivity ($L\,mmol^{-1}\,cm^{-1}$)	Correlation coefficient
NO_3^-	201	9.597	0.9998
NO_2^-	201	9.745	0.9995

3. Results and discussion

The molar absorptivities of the investigated ions were measured, in order to monitor their adsorption by UV spectroscopy. After selection of an appropriate wavelength (λ_{max} for the absorption spectra of nitrate and nitrite), the absorbances of a series of standard solutions were measured and the molar absorptivities were obtained from Beer's law. The regression coefficients were very close to a value of one, which meant that Beer's law applied quantitatively over the concentration range (0.01–0.2 mM) employed in the experiments. The results are given in Table 1.

Adsorption of nitrate and nitrite on C-cloth was investigated separately. Nearly neutral (pH ~ 7) solutions of $115\,mg\,L^{-1}$ of nitrate and nitrite were allowed to reach adsorption equilibria with the C-cloth. The decrease in the absorbance of nitrate and nitrite solutions with time at 201 nm was monitored. The decrease in the absorbance of the solutions is due to the adsorption of these ions at C-cloth.

Fig. 1 shows the decrease in the concentration of the nitrate and nitrite solutions by adsorption at C-cloth treated with distilled water and with sulfuric acid. As the figure shows the concentration of nitrate and nitrite solutions decreased only by 8.7% and 3.7% of their initial concentrations, respectively, by adsorption at distilled water treated C-cloth after 60 min. But their concentration decreased by 29.5% for nitrate and 12.9% for nitrite by adsorption at acid treated C-Cloth after 60 min.

Adsorption of the anions on distilled water treated C-cloth involves displacement of previously adsorbed H_2O molecules according to the equation:

$$C–H_2O + X^- \rightarrow C–X^- + H_2O \tag{2}$$
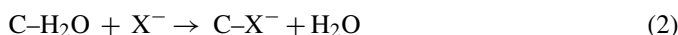
Treatment of C-cloth with acid tends to produce positive sites on the C-cloth, by protonation of surface –OH groups [5,23,24] that
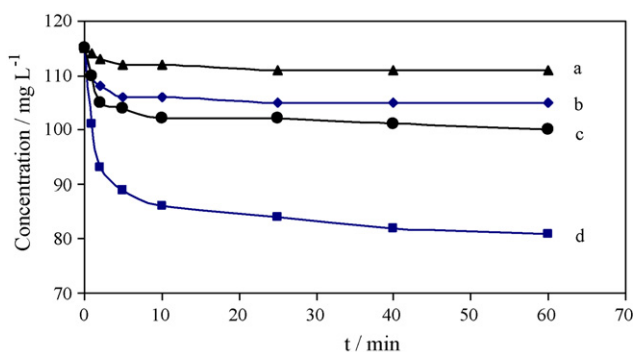

Fig. 1. Adsorption behavior of nitrite (a) and nitrate (b) on distilled water treated C-cloth and nitrite (c) and nitrate (d) on acid treated C-cloth.

would cause an increase in electrostatic adsorption of anions.

$$\equiv S-OH + H^+ \leftrightarrow \equiv S-OH_2^+ \qquad (3)$$

$$\equiv S-OH_2^+ + X^- \leftrightarrow \equiv S-OH_2X \qquad (4)$$

Therefore the dramatic increase in the adsorption of the investigated anions by treatment of C-cloth with acid is due to the strong electrostatic interaction between the negative charge of anions and positive charge of the surface. The acid-base interaction between base nitrite and acid of surface may also be effective.

As Fig. 1 shows the rate of the adsorption of nitrate on both C-cloths is greater than that for nitrite.

The C-cloth was also treated with HCl and applied to the adsorption of nitrite and nitrate from water. The results were nearly the same as those obtained by C-cloth treated with sulfuric acid.

The adsorption on C-cloth shows kinetic characteristics of kinetically first-order process. The first-order kinetic behavior was confirmed by applying directly a classical test plot of $\log[C(t)/C_0]$ *versus* time which was linear. Note that the observed kinetic behavior is probably to be regarded as pseudo first-order; a result arising from the large real area of the C-cloth electrodes used being initially substantially covered by solvent water. The first-order rate constants were evaluated as $(4.28 \pm 0.15) \times 10^{-4}$ and $(2.93 \pm 0.08) \times 10^{-4} \, \text{min}^{-1} \, \text{m}^2$ ($n = 5$) for the adsorption of nitrate and nitrite on C-cloth treated with distilled water, respectively, and as $(5.95 \pm 0.25) \times 10^{-4}$ and $(3.52 \pm 0.17) \times 10^{-4} \, \text{min}^{-1} \, \text{m}^2$ ($n = 5$) for their adsorption on C-cloth treated with acid.

3.1. Adsorption isotherm

The adsorption isotherms for nitrate and nitrite from water on both C-cloths are shown in Fig. 2. The number of mmols adsorbed per gram of adsorbent (N_f) *versus* the equilibrium concentration of cations are illustrated. For the series of isotherms the data reveal that the adsorption processes conform to the Langmuir model. Such isotherms are generally associated with monolayer adsorption. The initial slope in Fig. 2 for adsorp-

tion of nitrate on acid treated C-cloth lies very close to the *y*-axis, which shows that the affinity of nitrate for this adsorbent is strong. The Langmuir isotherm shows that the amount of anions adsorbed increases as the concentration increases, up to a saturation point. As long as there are available sites, adsorption will increase with increasing anion concentrations, but as soon as all of the sites are occupied, a further increase in concentrations of anions will not increase the amount of anions on adsorbents.

The Langmuir equation was used to calculate the maximum retention capacity (N_s) and standard Gibbs free energy of adsorption (ΔG_{ads}) [25–27]. The general form of Langmuir isotherm is

$$Y = \frac{KC_s}{(1 + KC_s)} \qquad (5)$$

where Y is the fraction of adsorbent surface covered by adsorbed species, K a constant and C_s the equilibrium concentration of the anion solution. In our case, $Y = N_f/N_s$, where N_f represents the number of mmols of anion adsorbed per gram of adsorbent (mmol g^{-1}) at equilibrium concentration, C_s, and N_s is the maximum amount of solute adsorbed per gram of surface (mmol g^{-1}) which depends on the number of adsorption sites. After linearization of the Langmuir isotherm, Eq. (5), we obtain:

$$\frac{C_s}{N_f} = \left(\frac{C_s}{N_s}\right) + \left(\frac{1}{KN_s}\right) \qquad (6)$$

All these adsorption studies were based on the linearization form of the Langmuir isotherm derived from C_s/N_f as a function of C_s. These plots for nitrate and nitrite anions on acid treated C-cloth and distilled water treated C-cloth are shown in Figs. 3 and 4. For all adsorption isotherms of nitrate and nitrite on both C-cloths (Fig. 2) the plot of C_s/N_f *versus* C_s gives a straight line with slope equal to $1/N_s$, and intercept equal to $1/KN_s$. Therefore the Langmuir isotherm is an adequate description of the adsorption of nitrate and nitrite on both C-cloths. The maximum retention capacity (N_s) was determined for each anion–surface interaction
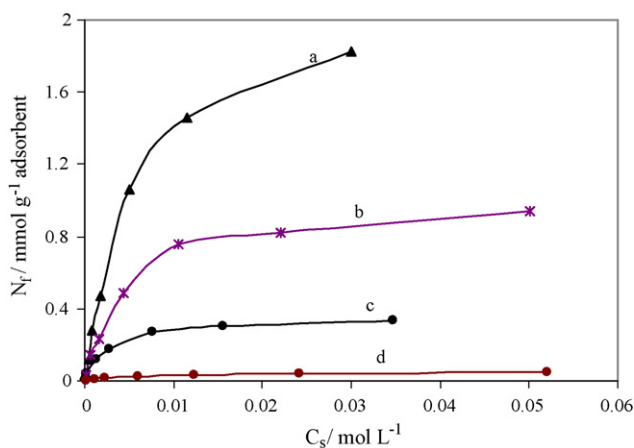

Fig. 2. Adsorption isotherms at 25 °C for adsorption of nitrate (a) and nitrite (b) on acid treated C-cloth and nitrate (c) and nitrite (d) on distilled water treated C-cloth.
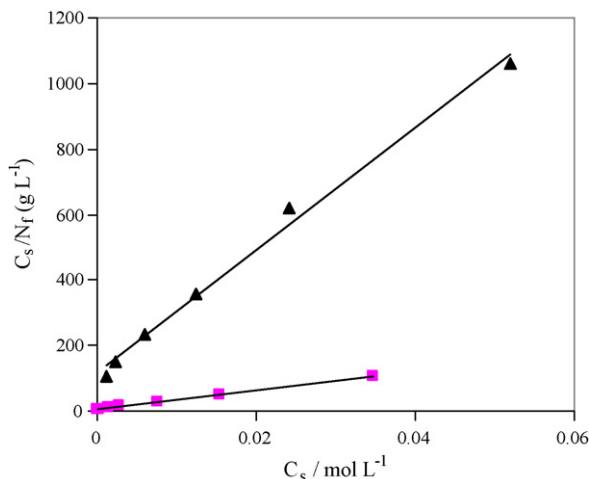

Fig. 3. Linearization of adsorption isotherms for nitrite (▲) and nitrate (■) on distilled water treated C-cloth.
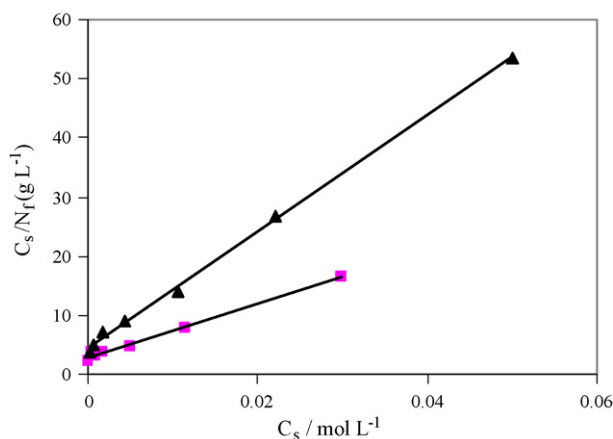
Fig. 4. Linearization of adsorption isotherms for nitrite (▲) and nitrate (■) on acid treated C-cloth.

from the slope, and the value of K from the intercept of the curves.

The N_s values obtained from Figs. 3 and 4 are listed in Table 2. As Table 2 shows the absorption capacity of both C-cloths for nitrate is higher than that for nitrite. The adsorption capacity of acid treated C-cloth for nitrate and nitrite is 2.03 and 1.01 mmol g^{-1}, respectively. These values are much higher than those obtained for distilled water treated C-cloth (0.38 and 0.05 mmol g^{-1} for nitrate and nitrite, respectively).

Since Na$^+$ constitutes the cation of both salts studied, the variations in the extent of adsorption reflect mainly the specificity of adsorption of anions. The adsorption behavior is expected to be closely related to the state of hydration of the ions. Size, shape and charge effects play an important role in determining the hydration behavior of ions. The results for these ions are not surprising when the hierarchy of shifts of potential of zero charge of Hg by adsorption of various ions given by Conway [28] is examined. According to Conway's list [28], nitrate exhibits greater adsorption than nitrite. The constant K is related to the equilibrium constant, $K°$, by $K° = KC°$, where $C°$ is the standard concentration (1 mol L^{-1}) [25–27] while the standard Gibbs free energy of adsorption ($\Delta G°_{ads}$) is given by:

$$\Delta G°_{ads} = -RT \ln K° \tag{7}$$

The $\Delta G°_{ads}$ values, obtained from Eq. (7) are listed in Table 2. This values show that the standard Gibbs free energy of NO$_3^-$ adsorption is larger than that for NO$_2^-$ for both surfaces, which indicate the greater affinity both surfaces for NO$_3^-$ adsorption.

Table 2
The properties of surfaces (N_s) and ion–surface interaction (K, $\Delta G°_{ads}$)

	Distilled water treated C-cloth		Acid treated C-cloth	
	NO$_3^-$	NO$_2^-$	NO$_3^-$	NO$_2^-$
N_s (mmol g^{-1})	0.38	0.05	2.03	1.01
K (L mol^{-1})	242.5	193.2	260.6	222.1
$\Delta G°_{ads}$ (kJ mol^{-1})	−13.49	−12.91	−13.65	−13.25

3.2. Effect of other ions

Effect of the ions NH$_4^+$, SO$_4^{2-}$, PO$_4^{3-}$, Cl$^-$, CO$_3^{2-}$ adsorption of nitrate and nitrite on both the adsorbents was investigated. The results showed that 50 mg L^{-1} of these ions had no considerable effect on the adsorbtion of the same concentration of nitrate on C-cloth treated with distilled water. Also it was found that 50 mg L^{-1} NH$_4^+$, SO$_4^{2-}$, Cl$^-$ did not interfere on the adsorption of nitrate on C-cloth treated with acid but 50 mg L^{-1} carbonate and phosphate ions interfered. Adsorption of 50 mg L^{-1} nitrite on both the adsorbents decreased in the presence of 50 mg L^{-1} in the presence of Cl$^-$, PO$_4^{3-}$ and CO$_3^{2-}$ ions but NH$_4^+$, SO$_4^{2-}$ had no considerable effects.

4. Conclusion

Acid treatment of high area C-cloth in a proprietary form designed "Spectracarb 2225" causes a dramatic increase in its absorption capacity for the adsorption of NO$_3^-$ and NO$_2^-$ ions. Acid treatment also increases the rate of the adsorption of both ions. The Langmuir isotherm is an adequate description of the adsorption of nitrate and nitrite on both C-cloths. The rate of the adsorption of NO$_3^-$ on both C-cloths was greater than that for NO$_2^-$. Also the adsorption capacity of both C-cloths for NO$_3^-$ was larger than that for NO$_2^-$.

References

[1] T.S. Singh, K.K. Pant, Experimental and modelling studies on fixed bed adsorption of As(III) ions from aqueous solutions, Sep. Purif. Technol. 48 (2006) 288–296.

[2] C.H. Lai, S.L. Lo, C.F. Lin, Evaluating an iron-coated sand for removing copper from water, Water Sci. Technol. 30 (1994) 175–182.

[3] N.L. Dias, D.R. do Carmo, A.H. Rosa, Selective sorption of mercury(II) from aqueous solution with an organically modified clay and its electroanalytical application, Sep. Sci. Technol. 41 (2006) 733–746.

[4] S.J. Allen, P.A. Brown, Isotherm analyses for single component and multicomponent metal sorption onto lignite, J. Chem. Technol. Biotechnol. 62 (1995) 17–24.

[5] A. Afkhami, B.E. Conway, Investigation of removal of Cr(VI), Mo(VI), W(VI), V(IV), and V(V) oxy-ions from industrial waste-waters by adsorption and electrosorption at high-area carbon cloth, J. Colloid Interface Sci. 251 (2002) 248–255.

[6] A. Afkhami, Adsorption and electrosorption of nitrate and nitrite on high-area carbon cloth: an approach to purification of water and waste-water samples, Carbon 41 (2003) 1309–1318.

[7] C. Faur-Brasquet, K. Kadirvelu, P. Le Cloirec, Removal of metal ions from aqueous solution by adsorption onto activated carbon cloths: adsorption competition with organic matter, Carbon 40 (2002) 2387–2392.

[8] B.M. Babic, S.K. Milonjic, M.J. Polovina, S. Cupic, B.V. Kaludjerovic, Adsorption of zinc, cadmium and mercury ions from aqueous solutions on an activated carbon cloth, Carbon 40 (2002) 1109–1115.

[9] K. Kadirvelu, C. Faur-Brasquet, P. Le Cloirec, Removal of Cu(II), Pb(II), and Ni(II) by adsorption onto aactivated carbon cloths, Langmuir 16 (2000) 8404–8409.

[10] C. Moreno-Castilla, M.A.A. Álvarez-Merino, M.V. López-Ramón, J Rivera-Utrilla, Cadmium ion adsorption on different carbon adsorbents from aqueous solutions. Effect of surface chemistry, pore texture, ionic strength, and dissolved natural organic matter, Langmuir 20 (2004) 8142–8148.

[11] E. Ayranci, N. Hoda, Adsorption of bentazon and propanil from aqueous solutions at the high area activated carbon-cloth, Chemosphere 57 (2004) 755–762.

[12] E. Ayranci, N. Hoda, Adsorption kinetics and isotherms of pesticides onto activated carbon-cloth, Chemosphere 60 (2005) 1600–1607.

[13] E. Ayranci, O. Duman, Adsorption behaviors of some phenolic compounds onto high specific area activated carbon cloth, J. Hazard. Mater. 124 (2005) 125–132.

[14] K. Lászlo, E. Tombácz, P. Kerepesi, Surface chemistry of nanoporous carbon and the effect of pH on adsorption from aqueous phenol and 2,3,4-trichlorophenol solutions, Colloids Surf. A 230 (2004) 13–22.

[15] C.R. Fox, Industrial wastewater control and recovery of organic chemicals by adsorption, in: L. Slejko (Ed.), Adsorption Technology: A Step-by-Step Approach to Process Evaluation and Application, Dekker, New York, 1985, pp. 167–183.

[16] Y. El-Sayed, T.J. Bandosz, A study of acetaldehyde adsorption on activated carbons, J. Colloid Interface Sci. 242 (2001) 44–51.

[17] S. Dursun, Nitrite removal form the water using the wood sawdust, Cell. Chem. Technol. 38 (2004) 457–463.

[18] K. Abe, A. Imamaki, M. Hirano, Removal of nitrate, nitrite, ammonium and phosphate ions from water by the aerial microalga *Trentepohlia aurea*, J. Appl. Physiol. 14 (2002) 129–134.

[19] L.A. Schipper, M. Vojvodic-Vukovic, Five years of nitrate removal, denitrification and carbon dynamics in a denitrification wall, Water Res. 35 (2001) 3473–3477.

[20] D. Bougard, N. Bernet, P. Dabert, J.P. Delgenes, J.P. Steyer, Influence of closed loop control on microbial diversity in a nitrification process, Water Sci. Technol. 53 (2006) 85–93.

[21] X.S. Zhu, K.H. Choo, J.M. Park, Nitrate removal from contaminated water using polyelectrolyte-enhanced ultrafiltration, Desalination 193 (2006) 350–360.

[22] A. Elmidaoui, F. Elhannouni, M.A. Menkouchi Sahli, L. Chay, E. Elabbassi, M. Hafsi, D. Largeteau, Pollution of nitrate in Moroccan ground water: removal by electrodialysis, Desalination 136 (2001) 325–332.

[23] K. Kinoshita, Carbon: Electrochemical and Physicochemical Properties, Wiley, New York, 1988.

[24] B.E. Conway, Electrochemical Supercapacitors: Scientific Fundamentals and Technological Applications, Kluwer Academic, New York, 1999, 183-221.

[25] A.G.S. Prado, C. Airoldi, Adsorption, preconcentration and separation of cations on silica gel chemically modified with the herbicide 2,4-dichlorophenoxyacetic acid, Anal. Chim. Acta 432 (2001) 201–211.

[26] G. Attard, C. Barnes, Surfaces, Oxford University Press Inc., New York, 1998.

[27] C. Kaewprasit, E. Hequet, N. Abidi, J.P. Gourlot, Application of methylene blue adsorption to cotton fiber specific surface area measurement: part I. Methodology, Cotton Sci. 2 (1998) 164–173.

[28] B.E. Conway, The solvation factor in specificity of ion adsorption at electrodes, Electrochim. Acta 40 (1995) 1501–1512.