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ADSORPTION KINETICS OF NITRATE IONS ON ACTIVATED CARBONS

Henriette MOUSSOUNDA BOUNDZANGA[1], Benoît CAGNON[1], Christine VAUTRIN-UL[1], Sylvie BONNAMY[1]

[1] *CNRS, Orléans University, ICMN UMR 7374, F-45071 Orléans, France*
*sylvie.bonnamy@cnrs-orleans.fr

Introduction

The development of effective processes and specific materials that can reduce nitrate ions in water medium has attracted much attention recently [1]. Nitrate pollution is a major problem, on one hand, to the environment, because it can lead to water eutrophication and, on the other hand, for the public health due since it can cause diseases such as cancer, infant methemoglobinemia, and damage to nervous tissue and cognitive functions [2]. The development of specific activated carbons (AC) produced from biomass residues for the removal of pollutants, specifically nitrate ions in water, has been recognized as the cheapest and most effective material and furthermore it is easy maintenance [3]. However, in the nitrate removal processes for industrial applications, the characteristics and properties of specific adsorbents have to be improved. Recent studies showed that the adsorption capacity of activated carbons in nitrate ions can be promoted by acidic and/or basic functional groups or/and by textural characteristics of materials [4].

In order to better understand the mechanisms of nitrate ion adsorption we focused our study on commercial activated carbons having either acidic or basic functional groups and different types of pores (micro-and/or mesopores). Then, we studied the influence of various experimental parameters, such as pH and temperature of the nitrate solution, the nitrate initial concentration and also the effect of competing anions such as phosphates, carbonates, sulfates and chlorides on the adsorption kinetic and adsorption capacity of nitrate ions on activated carbons.

In order to model the nitrate ion adsorption, Ho and Mc Kay kinetic model and Langmuir model were used.

Materials and Methods

Different commercial AC provided by Jacobi Carbon® (Vierzon, France) were analysed. Three of them (X17, L27 and S21) having different textural and chemical were selected. The porous texture of the materials was analyzed using the nitrogen adsorption isotherms at 77 K (Micromeritics ASAP 2020). pK_A distribution of surface chemical functionalities and pH_{PZC} (pH value corresponding to an AC net charge of zero) were carried out by potentiometric titration with NaOH 0.1 mol/L using a very low incremental volume (0.01 mL) in a wide range of pH (2-12).

Concerning the adsorption kinetics of nitrate ions, experiments were carried out in a closed reactor under stirring. A fixed amount of adsorbent was added to a solution of potassium nitrate and the mixture was maintained at 25°C at a fixed pH value. At regular intervals, the mixture was filtered using a 0.45µm membrane filter. Nitrate concentrations were determined by chemiluminescence (TOC-L CPH, SHIMADZU)

Results and Discussion

Concerning the porous texture of AC, the materials possess high total surface areas (Table 1). Their micropore size distributions, determined by DFT method (Micromeritics software), are reported in Figure 1. L27 material presents the broadest distribution with high mesoporous and microporous volumes (Table 1). S21 material is essentially microporous and X17 material has a microporous volume poorly developed (Table1).

Concerning the surface chemistry of the AC samples, the potentiometric titration method was used to quantify the oxygenated groups. Data reported in Figure 2 are focused on L27 material and they show that this material has acidic surface groups and its pH_{PZC} value is equal to 3.2. X17 material has basic functional groups and its pH_{PZC} value is equal to 8.2. S21 material has low amounts of acidic and basic oxygenated groups, hence has a neutral character (pH_{PZC} equal to 7.4).

Table 1. Textural characteristics of the activated carbons (AC).

AC	W_0 (cm^3/g)	L_0 (Angstrom)	S_{total} (cm^2/g)	S_{micro} (cm^2/g)	S_{meso} (cm^2/g)
L27	0.57	18.5	1060	616	444
X17	0.29	15.1	514	384	130
S21	0.47	9.7	987	969	18

***W_0 : specific microporous volume, cm^3/g**
**** L_0: mean pore size, Å**

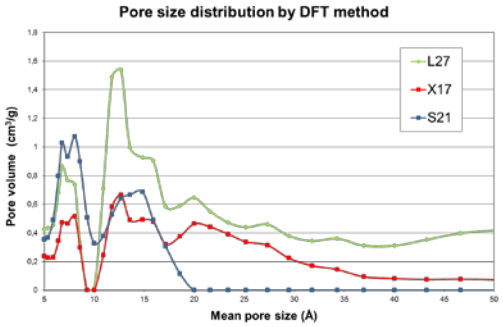

Figure 1: Pore size distributions of the activated carbons studied (nitrogen adsorption at 77 K).

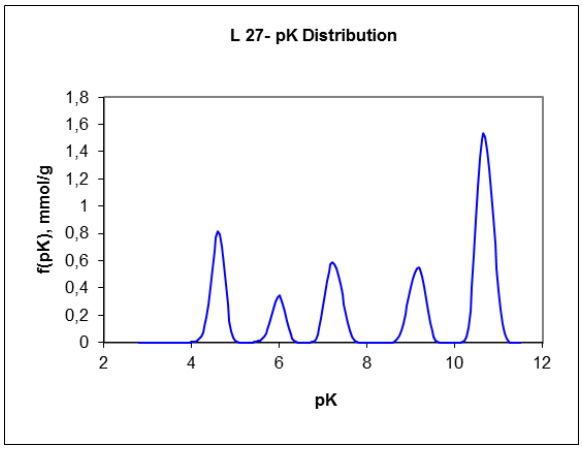

Figure 2: pK_A distribution of surface functionalities by potentiometric titration for L27 material.

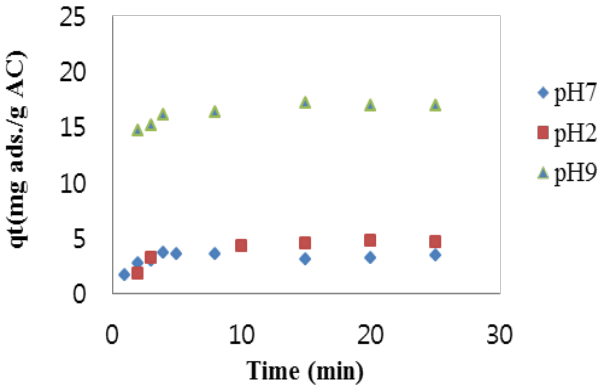

Figure 3: The effect of initial pH on nitrate adsorption for L27 material.

The effect of initial pH on the nitrate removal on AC L27 is shown in Figure 3. When the pH is acidic, the amount of nitrates adsorbed on L27 material is similar to that adsorbed at pH 7. The low adsorption of nitrates at acidic pH =2 is related to the competition of Cl^- ions with nitrate ions (Cl^- coming from HCl, added to adjust the pH). The surface charge is positive ($pH < pH_{PZC}$), Cl^- ions being smaller are adsorbed at first. The highest nitrate adsorption occurs at pH 9, even with a material having a negative surface charge ($pH > pH_{PZC}$). In this case, the repulsion of the smaller Cl^- ions allows a better NO_3^- adsorption. Furthermore, a surface protonation occurs at basic pH.

Acknowledgments

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