ELECTROCHEMICAL AND CHEMICAL SORPTION OF LITHIUM IONS ONTO ACTIVATED CARBONS FROM AQUEOUS SOLUTION

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INTRODUCTION

Depollution of water and air purification are nowadays subjects of great interest. To solve such problems, activated carbons are mainly used. Those materials characterized by extended surface area, microporous structure and high degree of surface reactivity can adsorb big amounts of organic and inorganic pollutants [1, 2, 3, 4]. Particularly, they can adsorb metal ions present as trace amounts in water. Some authors have shown that such phenomena could be greatly enhanced by applying electrical forces on activated carbon during the adsorption process [5, 6].

This paper is concerned with operational parameters and preliminary treatment of activated carbon for optimum removal of lithium from water. Comparison is made between chemical and electrochemical sorption of lithium ions, but also between the activity of chemically and physically activated carbons. Various treatments were performed on the chars to modify their sorption activity. We also demonstrate the reversibility of the process using anodic current.

EXPERIMENTAL

Various activated carbons, provided by PICA Company, were used. Chemically activated carbons (powder) were prepared from wood by H_3PO_4 activation, whereas physically activated carbons were obtained from coconut shells (powder) or polymeric precursor (tissue) by steam activation. Chemically activated carbons were generally washed during 6 days in a Kumagawa extractor with distilled water. Some of them were treated by an ammonia solution (1.6 mol/l) until pH=9 or electrochemically desorbed with anodic current to remove excess H_3PO_4 present in the pores. The lithium (10ppm or 100ppm) and boron (1000ppm) aqueous solutions were made using a lithium chloride standard solution and boric acid powder (from Aldrich Company). Initial and equilibrium (after sorption) concentrations of lithium cations in the solution were determined by Atomic Absorption Spectrometry (Perkin Elmer 3300) using standards in the range 0 to 3ppm.

Surface areas of all the carbons were measured by the BET method [7] (N_2 adsorption at 77K) with a Sorptomatic 1900 from Carlo Erba Instruments, after heating the samples at 240°C under vacuum. Horvath-Kawazoe formula [8] permitted to calculate, from cumulative surface area, the surfaces of microporosity and mesoporosity.

Electrochemical experiments in galvanostatic mode were performed on a PRT 10-0,5 Tacussel potentiostat. During experiments the lithium-boron solution was stirred at room temperature. The carbons were kept under constant electric current between 0 and 4 mA at various durations (from 25 to 200 hours).

RESULTS AND DISCUSSION

Great differences were observed in the values of surface areas of the selected carbons (Table 1).

Sample	S_{BET} (m^2/g)	S_{micro} (m^2/g)	S_{meso} (m^2/g)
CAC0	1840	1630	420
CAC1	2250	2055	520
CAC2	2171	1972	496
CAC3	2220	2030	500
PACT	1320	1850	110
PACP	1360	1710	120

Table 1 : Specific surface areas, microporous and mesoporous surface areas of the activated carbons.

The chemically activated carbon without any additional treatment (CAC0) has a higher BET surface (1840 m^2/g) than the physically activated carbons prepared either from coconut (PACP : 1360m^2/g) or from polymer (PACT : 1320m^2/g). Contrarily to mesoporosity, microporosity is higher for both PAC than for CAC0. Some treatments performed on CAC0, such as washing (CAC1), neutralization by ammonia up to pH=9 (CAC2) and anodic electrochemical desorption (CAC3) significantly increased the BET surface area. This is due to the removal of phosphoric acid present in the pores.

Without applying current, when 100ml of lithium/boron solution (10ppm/1000ppm) were stirred with 1g of CAC2, the lithium concentration slowly decreased in 20 hours until 0.45 mg Li/g

CAC2 were trapped (Fig 1). On the contrary, due to their positive surface charges, PAC in such conditions did not reduce lithium concentration.
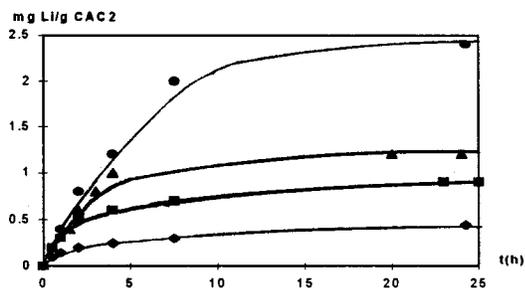

Figure 1 : Effect of the ratio mass CAC2/volume of 10ppm lithium solution on the lithium sorption. Chemical adsorption : ♦ 1g of CAC/100ml lithium solution. Electrosorption : ■ 1g of CAC/100ml lithium solution, 1g of CAC/200ml lithium solution, ● 1g of CAC/400ml of lithium solution.

Electric cathodic current strongly enhanced the sorption of lithium ions on both PAC and CAC. With PACT the concentration of lithium solution could be strongly decreased from 10 to 2ppm applying a 4 mA cathodic current during twenty hours (Fig 2). All the lithium cations of this solution were trapped after 43 hours leading to 1mg of lithium per gram of PACT. In the case of PACP, no more than 0.5mg Li/g of PACP were electrochemically adsorbed. This difference between the two PACs might be due to the respective morphologies. The fibrous PACT has a great number of edge sites with a high reactivity.
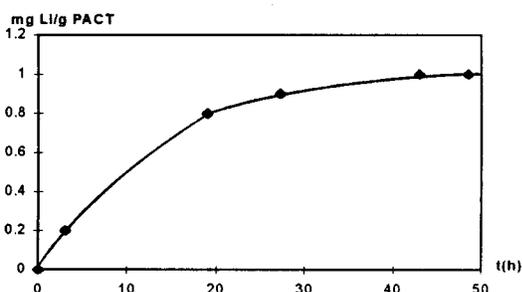

Figure 2 : Electrosorption of lithium ions in PACT
(I = 4mA, M_{PACT} = 1g, V_{SOL} = 100ml)

Using CAC2, the amount of adsorbed lithium was depending on the ratio mass CAC2/volume of lithium solution (Fig 1). When 100 ml of lithium solution at 10ppm were treated by 1g of CAC2, the plateau was obtained at the value of 0.9mg Li/g CAC. Increasing the volume of solution to 200ml or 400ml, the maximum adsorption level was respectively close to 1.2mg Li/g of CAC2 and 2.4mg Li/g of CAC2. It is likely that the amount of lithium ions adsorbed is strongly influenced by the concentration of the residual solution which is in equilibrium with the active carbon. For instance, using a 100ppm lithium solution, the activated carbon was saturated with 4.5mg of lithium per

gram of carbon, showing that the electrosorption is mainly limited by the diffusion rate of Li^+ towards the active sites.
In all cases, lithium sorption could be totaly reversed, using anodic current, and even cationic impurities could be desorbed.

CONCLUSION

Sorption of lithium cations, from aqueous solution, on activated carbon was strongly enhanced by using cathodic current. Depending on the activation process (physical or chemical) the carbons behaviour in chemical adsorption is different. Indeed, contrarily to CAC, due to their positive surface charge both PAC did not adsorb any lithium ions without applying current. The electrosorption capacity for lithium is strongly influenced by the concentration of the solution in equilibrium with the active carbon at the end of the process, showing that diffusion is the main parameter controlling the sorption.
A more complex mechanism must be imagined because after diffusion of Li^+ to the active sites, exchange of the hydrogen from surface groups with Li^+ takes place, afterwards the diffusion of protons to the bulk of solution proceeds. Additionally to diffusion, the interaction of Li^+ with surface groups may play an important role. It depends on the origin of carbon, i.e. the kind of surface groups, the pH of the solution, the potential of zero charge, the porosity (accessibility for water molecules). These parameters should be carefully controlled in further experiments.

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