ACTIVATED CARBON SURFACE GROUPS INFLUENCE ON THE ANCHORAGE OF IRON NANO PARTICLES AND THEIR CONTRIBUTION TO THEIR ARSENIC ADSORPTION FROM WATER

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Introduction

The activated carbon surface modification is an increasingly attractive route to develop novel materials that can be applied in areas such as catalysis, sensors and as adsorbents for both gas-phase and liquid phase. These modifications improve the operational conditions of the activated carbon and/or impart properties that the carbon does not exhibit previously. In this context, some foreign elements have been anchored onto the activated carbon surface, increasing the adsorption capacity of pollutants not commonly removed by activated carbon such as cyanide, fluoride and arsenic [1-3]. For the last, the modifications have been focused mainly on anchoring iron oxides, due to the high affinity of the oxoanions of arsenic for iron hydroxides, getting a binary material able to remove arsenic efficiently from water [3, 4].

Forced hydrolysis has been employed recently to synthesize iron oxide particles without the addition of voluminous chemicals that have a poor diffusion into the activated carbon pores. It consists on increasing the temperature of a solution that contains the metal cation to be precipitated [5]. This methodology implies the self-aggregation of iron aqueous - hydroxilated complexes by means of a nucleophilic addition [6]. When the forced hydrolysis is carried out in the presence of activated carbon, it is expected that the oxygenated surface groups present in the activated carbon influence this process. Hence the aim of this research is to study the influence of the surface chemistry activated carbon on the shape, type and quantity of iron hydroxides loaded on the carbon surface, and its contribution to the arsenic adsorption.

Experimental

The anchorage procedure was based on the forced hydrolysis methodology, previously reported to synthesize iron nanoparticles [7] and to modify activated carbon [4]. To study the effect of activated carbon surface groups, three different carbons were tested: Filtrasorb-400, commercial activated carbon from Calgon, which is made from bituminous coal under physical activation (F400); agave bagasse based activated carbon produced by chemical activation with ZnCl2 (AC-Z) and H3PO4 (AC-P). 17 samples for each activated carbon were developed, according to a central composite experimental design. The studied variables were the iron concentration (0.3 to 3.67 mol/L), the hydrolysis time (4 to 14 hours) and the hydrolysis temperature (70 to 120 ºC). The general procedure followed the next steps: (1) 200 mg of activated carbon of grain sizes of U.S. mesh no. 100 × 140 (148–105 µm) were contacted with 10 mL of FeCl3 solution; (2) this mixture was shaken for 24 hours at 25 ºC to allow the diffusion of iron into the pores; (3) forced hydrolysis was carried out in a preheated air furnace for a determined hydrolysis time; (4) after that the samples were rinsed with deionized water until no detection of iron by the phenantroline test (detection limit 10 µg/L) and then dried at 100 ºC for 24 hours. The iron content and the arsenic adsorption capacity were determined for all the samples. The data were analyzed with the software STATISTICA 7.0 according with the surface response methodology.

Results and Discussion

Table 1 shows the iron content and the arsenic adsorption capacity presented by the modified activated carbons. This table also includes the arsenic adsorption properties of a commercial ion exchange resin (FerrIX from Purolite). As it can be observed, the modified activated carbons can reach higher arsenic adsorption capacities (q) than the commercial available material. About the iron content, the impregnated F-400 activated carbon exhibited a minor impregnation degree compared with the agave bagasse based activated carbons.

<table>
<thead>
<tr>
<th>Activated carbon</th>
<th>Surface area (m²/g)</th>
<th>% O</th>
<th>% Fe</th>
<th>q* (mg/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>F-400</td>
<td>950</td>
<td>5</td>
<td>0.1 - 0.7</td>
<td>2.7 – 3.7</td>
</tr>
<tr>
<td>AC-Z</td>
<td>837</td>
<td>21</td>
<td>0.9 – 4.6</td>
<td>0.5 – 2.6</td>
</tr>
<tr>
<td>AC-P</td>
<td>846</td>
<td>25</td>
<td>4.3 – 7.3</td>
<td>0.6 – 3.2</td>
</tr>
<tr>
<td>IER:FerrIX</td>
<td>32</td>
<td>-</td>
<td>7.09</td>
<td>3.2</td>
</tr>
</tbody>
</table>

*Arsenic adsorption capacity at an initial concentration of 8 mg/L of As.

This effect can be explained as follows: the steps that follow the precipitation of iron oxide/hydroxides by the forced hydrolysis involve nucleophilic reactions which promote the agglomeration of hexa aquo iron complexes. In the early stages of the solid formation, the negative charge of the oxygen of the OH group in some hydroxylated iron complexes eliminate water, beginning in this way the nucleation of the iron particle. When the forced hydrolysis is carried out in the presence of activated carbon, the oxygenated surface groups present in the activated carbon can act as initiator of this dehydration mechanism, generating a covalent bond between the carbon surface and the iron particle (Fig. 1). This effect is evident when comparing the iron loaded on the carbons studied, since the oxygen and the iron loaded followed the same tendency: ACP > ACZ > F-400.

Figure 2 shows representative scanning electron micrographs of the materials that exhibit higher arsenic adsorption capacities. F-400 modified activated carbon showed a wide dispersion of spherical particles (Figure 2A), with media particle size of 23 nm. ACZ samples showed two
different ranges of particles size macroscopic particles with particle diameter ranging from 450 to 850 nm, with a media particle size of 675nm; and nanometric scale particles with particle diameter ranging from 8 to 63 nm. Finally some of the ACP synthetized at specific production conditions displayed the anchorage of acicular shape iron oxide particles, covering most of the activated carbon surface.

![Fig. 1. Proposed mechanism of the iron hydrolysis. The oxygenated surface groups promote the water elimination and later agglomeration of iron clusters.](image)

Generally, the incorporation of particles on the surface of activated carbon considerably reduces the surface area of activated carbon. Analyzing the surface area of the modified samples, it was found that surface area of ACZ samples decrease to 246 m$^2$/g. In contrast, the surface area of F-400 modified samples did not exhibit a considerable change (951m$^2$/g)

![Fig. 2. Scanning electron micrographs of selected samples: F400 commercial activated carbon (A); Agave bagasse based activated carbon activated with ZnCl$_2$ (B) and H$_3$PO$_4$ (C).](image)

Finally the surface area of ACP samples increased from 837 m$^2$/g to 1280 m$^2$/g, mainly by the particular morphology of the iron oxide loaded.

As can be observed in Table 3, F400-Fe activated carbon samples did not diminish their surface area, mainly by the low impregnation degree and also by the small particle size anchored. In contrast, ACZ sample presented a large decrease in surface area, this because most of the iron particles anchored showed a particle diameter of about 650 nm, blocking most of the pores. However, this effect was not observed for the other two carbons tested. Something to remark is the considerable increase in surface area of ACP samples, mostly by the contribution of the iron oxide structures.

**Conclusions**

This study demonstrated that forced hydrolysis is an excellent method to anchor highly dispersed iron nanoparticles into granular activated carbon. According with our results we can conclude that the shape and the quantity of iron loaded on carbons depend on the surface chemistry of the activated carbon. Finally, the modified materials have similar arsenic adsorption capacities than commercial specialized materials to remove arsenic from aqueous solutions.

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**References**


