The Application of Iron-Coated Activated Carbon in Humic Acid Removal From Water

Hatam Godini*, Ghodratalah Shams Khorramabady, Seyed Hamed Mirhosseini
Environmental Health Department, Faculty of Public health, Lorestan University of Medical Sciences, Khorramabad, Iran

Corresponding author:
* Hatam Godini
Email: godini_h@ yahoo.com

Abstract—Humic acid come to water sources from the leaching of soils, sediments, aquatic animal and vegetal life and effluents. The high humic acid concentration in drinking water has the potential for some serious diseases, because it produces disinfection by-products such as trihalomethanes. So removal of humic from water supply is very important. The tests of humic acid adsorption onto iron-coated activated carbon (AC-Fe) samples were conducted in batch mode. The humic acid content values were measure and analysed under different operating conditions. The effect of various factors, e.g., pH, initial concentration, and carbon type on the adsorption capacity, was quantitatively determined. From the batch experiment results, the humic acid could be removed by the iron-coated activated carbon. These studies show that humic acid adsorption on AC-0 (activated carbon without carbon as blank) and AC-Fe was 48.56 mg/g and 60.72 mg/g respectively with 30 mg/l initial concentration, pH 5, and 28 oC temperatures. The maximum adsorption conducted at AC-Fe was 80.13 mg/g with 80 mg/l initial concentration. The efficiency of iron-coated activated carbon for the removal of humic acid adsorption will decrease with increasing pH. Iron-coated activated carbon is effective adsorbents for removal of humic acid from water.

Keywords: Humic acid, Activated carbon, Water treatment, Iron-coated activated carbon

I. INTRODUCTION

Humic acid (HA) is a significant portion (40–90%) of the dissolved organic matter found in nearly all water supplies. The chemical and physical characteristics of humic acid are strongly dependent on the source they originate [1-3]. The major characteristics of Humic acid are their amorphous, hydrophilic, acidic, high molecular weight, both aliphatic and aromatic character, contain functional groups such as carboxyl and phenolic groups. These generate some complicated chemical and physical properties [4,5]. The existence of carboxylic and phenolic groups results in predominantly carrying negative charges in aqueous solutions [1]. Soluble humic substances such as humic acid come from the leaching of soils, sediments, aquatic animal and vegetal life, as well as from the effluents of sewage treatment works [6,7].

Humic acid is an important natural organic compound present in surface and ground water [4,5,8]. Humic matter concentrations generally encountered in natural waters are in the range of 0.1 to 10 mg/L [9–10].

According to previous studies, the high humic acid concentration in drinking water has the potential for some serious diseases, such as stomach cancer [4,9,10]. Studies [5,8,11,12] have shown that humic substances form trihalomethanes (THMs) and other halogenated organic compounds during chlorination of water supplies. In addition, the capability of HA complication with heavy metals can increase the migration of heavy metal ions in water, which is also an important issue in water treatment [13,5]. It was reported than an intake of a huge amount of humic acid might be one of the etiological factors for the Blackfoot disease [1,2]. Therefore, the mineralization of the presence of humic acid in drinking and other process water is of significant importance and interest.

The conventional drinking water treatment processes of coagulation, settling, and sand filtration remove between 20 and 50% dissolved humic substances [5]. Various treatment techniques available for organics are reduction, ion exchange, evaporation, reverse osmosis and chemical precipitation. Most of these methods suffer from drawbacks like high capital and operational cost and there are problems in disposal of the residual sludge [14-15].

Traditional drinking water treatment processes may not be able to remove organic matters completely. Therefore, it is of importance to develop an innovative technique to enhance drinking water quality from organic matters contamination [16].

Previous research has suggested that activated carbon [1-4,13] can be reasonably used in order to remove humic acid from water. Activated carbon has been widely used in water treatment systems to remove disinfection by-products and compounds related to odor, taste, and color problems in drinking water [14, 17]. Activated carbons have specific properties depending on the material source and the mode of activation [5]. Therefore, there is a great interest in new adsorbents for effective removal of humic substances from water.

Iron oxides have relatively high surface area and surface charge, and they often regulate free metal and organic matter concentrations in water through adsorption reactions [16]. Recently, some researchers have developed techniques for coating iron oxide onto sand surface in order to overcome the difficulties of using iron oxide powders in the water treatment process [16].

In this paper, we report an investigation of humic acid adsorption on iron-coated activated carbon as a new
adsorbent. We investigated the effect of various factors, e.g., contact time, activated carbon type, carbon dosage, pH, and initial concentration of humic acid on the adsorption capacity. The main aim of this study is to predict how much the humic acid will be removed by activated carbon without carbon as blank (AC-0) and iron-coated activated carbon (AC-Fe).

II. MATERIAL AND METHODS

A. Adsorbent and adsorbate

The activated carbon was selected from <1 mm in diameter. It was pretreated in HCl acid solution (pH=1.0) for 24 h, rinsed with de-ionized water, and dried at 103±2°C. To coat the activated carbon used to stock solution of 1 M FeCl₃·6H₂O. The solution of iron and 100 g activated carbon was poured in a 1 l Pyrex glass beaker. The mixture was placed in shaker (200 rpm) for 6h then filtering and drying oven at 50°C for 96 h. After that, the iron-coated activated carbon was washed with de-ionized water until run-off was clear, then it was redried at 50°C for 96 h. The produced iron-coated activated carbon was stored in polystyrene bottles for further uses [16].

HA used was obtained from Fluka, Switzerland. A 1 g/L concentration solution was prepared by dissolving 1 g of HA in 62.5 mL of NaOH solution (0.1 M) and completing at 1 L with deionized water. The solution was stirred for 1 h and stored [1]. Then the sample solutions for all adsorption tests were prepared by diluting the stock solution with distilled water to achieve the desired concentrations.

B. Batch adsorption experiments

The tests of HA adsorption onto the AC-0 and AC-Fe were conducted in batch experiments. For each run 100 ml of HA solution with varying initial concentrations (20-80 mg/l) was mixed with the adsorbents at a fixed loading of 50 mg in 250 ml bottles. The tests were conducted in an orbital-shaker at 100 rpm and shaken for varying time at 28°C to reach equilibrium. After an appropriate time, some of solution samples were taken out, separated by paper filter (45 μm) and examined to obtain the concentration of HA.

Several factors affecting the adsorption process, such as pH (3-9), initial concentration (20-80 mg/l), and carbon type (AC-0 and AC-Fe) were studied. In most of experiments, three samples were prepared and tested and the average values are reported.

C. physical and chemical tests

All the chemicals used were of analytical grade products and obtained from Merk. The concentration of humic acid was analyzed by using an ultraviolet spectrophotometer (UV−2100, Unico Inc.) at 254 nm and Matched 10mm quartz absorption cells were used [18]. pH was measured using pH meter (pH meter 120, Corning). The apparent density was calculated from the volume of the graduated cylinder closely packed with the powdered sample and from the sample weight. Ash content (wt. %) was determined from gravimetric measurement [5,19].

SEM photographs were taken at different magnifications. Surface morphology of Activated carbons was studied by scanning microscopy (XL30 Philips model). Specific surface area and porous properties were determined using mercury porosimeter (Pascal 440). The metals on Activated carbons were demonstrated by SEM equipped by edx (Energy dispersive x-ray microanalysis) and analysis system of ZAF software.

III. RESULTS AND DISCUSSION

A. Characteristics of AC-0 and AC-Fe

The images taken at 500X magnification showed evident changes on the AC surface examined (Fig. 1). The surface morphology of the AC-Fe has changed significantly after impregnation and a more homogeneous morphology became apparent.

The EDX spectrum shows that iron was present on the surface of AC-Fe, indicating that the complex iron ion indeed adsorbed onto the activated carbon surfaces [Fig. 2]. In addition, iron peaks can be observed in the spectrum.

The properties of the two adsorbents are given in Table 1. Surface areas of the AC-0 and AC-Fe are 760 and 596 m²/g, respectively. AC-0 has much high microporous volume while AC-Fe has higher mesoporous volume. From Table 1, it is shown that pH of the two solids is different. AC-Fe presents acidic around 5.2 while AC-0 is basic close to 7.9, which suggests that the surface charge of AC-Fe is positive but the AC-0 is negatively charged.

The surface of activated carbon also becomes increasingly negatively charged as the pH is increased. Thus, less HA adsorption is observed [18]. Results are consistent with Terdkiatburana who reported same results [13].
B. HA adsorptions

Fig. 3 presents adsorption of HA onto AC-0 and AC-Fe in the initial HA concentration of 30 mg/L. As shown, the adsorption of HA will reach equilibrium after 18 h. The two carbons are favorable for the adsorption of HA but AC-Fe has higher removal efficiency.

![Figure 3](image)

It was generally found that the HA removal increased with increase in contact time. Almost quantitative removal of HA obtained by using AC-0 and AC-Fe, for an adsorbate concentration of 30 mg/L and 28 °C.

It is found that the AC-Fe (60.72 mg/g) has adsorption ability more than to AC-0 (40.56 mg/g). This indicates the promise of AC-Fe for adsorption applications. The initial uptake rate for HA was high as a large number of adsorption sites were available for adsorption at the onset of the process. Adsorption slowed down in later stages because after some time the remaining vacant surface sites may be difficult to occupy due to the repulsive forces between HA molecules on the solid and liquid phase [1, 20-22].

The effect of initial concentration of humic acid on the amount of humic acid adsorbed onto AC-0 and AC-Fe in the range of initial HA concentration of 20–80 mg/L was also investigated (Fig. 4).

![Figure 4](image)

The rate of HA sorption onto AC-0 and AC-Fe was studied using initial HA concentrations ranging from 20 to 80 mg/L. On increasing solute concentration from 20 to 80 mg/L, HA uptake per unit weight of adsorbent increased from 50.73 to 80.13 mg/g. This is due to the increase in the mass driving force which allows more HA molecules to pass from the solution to the adsorbent surface [1].

Fig. 5 illustrates the effect of solution pH on HA adsorption on AC. HA adsorption will decrease as pH is increased. For HA adsorption, many investigation have shown the similar observation as found in this work [5, 9, 18].

It was observed that the maximum removal of HA was achieved at pH 3 and initial HA solution concentration of 80 mg/L, a decrease in the solution pH from 9 to 3 substantially increased HA removal from 41.18 to 75.36 mg/g for AC-Fe. It has been reported that HA adsorption onto other adsorbents, such as activated carbon also follow similar trends [1, 18, 23].

The effect of pH on the adsorption can be explained considering that HA’s diffusion properties vary due to size difference at different values of solution pH. At low pH humic acid diffuses faster and the difference is more remarkable at low ionic strength [1].
Humic acid adsorption can be enhanced by the presence of iron oxide, due to the formation of metal-legend complexes on iron-coated activated carbon surface. HA adsorption to iron-coated activated carbons was found to increase in the presence of iron. **CONCLUSION**

Huminic acid could be removed efficiently from water by the iron-coated activated carbon. Adsorption behavior of humic acid on iron-coated activated carbons may include pores diffusion and chemical reaction. Iron-coated activated carbon is potentially suitable for applying to the adsorption of humic acid from water. This study demonstrates that iron oxides offer favorable attachment sites for HA on the surfaces of Fe-AC and further improves the knowledge of HA removal in Fe-AC.

**ACKNOWLEDGMENTS**

Authors are grateful to Eng. Rezaee, Department of Technical Faculty, Tarbiat Modares University, Tehran, Iran for the analysis of porous properties and SEM photographs of the carbons.

**REFERENCES**


Figure 1. SEM Photographs of AC-0(a) and AC-Fe(b).

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>S (m²/g)</th>
<th>V_{total} (cm³/g)</th>
<th>V_{micro} (cm³/g)</th>
<th>V_{meso} (cm³/g)</th>
<th>pH</th>
<th>Apparent Density</th>
<th>Ash content</th>
</tr>
</thead>
<tbody>
<tr>
<td>AC-0</td>
<td>760</td>
<td>0.425</td>
<td>0.367</td>
<td>0.0324</td>
<td>7.9</td>
<td>0.340</td>
<td>43.34</td>
</tr>
<tr>
<td>AC-Fe</td>
<td>596</td>
<td>0.379</td>
<td>0.0196</td>
<td>0.214</td>
<td>5.2</td>
<td>0.375</td>
<td>44.25</td>
</tr>
</tbody>
</table>