Modification of Activated Carbon for the Adsorption of Humic Acid

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ABSTRACT: Commercial activated carbon treated with sulphuric and phosphoric acids was used to remove humic acids (HAs) from water. To achieve this goal, the iodine indices of treated and untreated materials were characterized by X-ray diffraction and nitrogen physisorption. Adsorption assays for HAs evaluated the quantities adsorbed after a fixed time. Temporal evolution of HA adsorption was determined from the adsorption kinetics. Experimental results indicated that the sulphuric acid treatment was more efficient and had a higher HA adsorption at each time point evaluated. Evaluating the specific area helped to verify this fact, reflecting the number of mesopores in the used material.

1. INTRODUCTION

Excess organic matter in aquatic environments has always been a problem for engineers, chemists and other environmental professionals. Researchers are mainly interested in the following issues: increased oxygen demand during degradation, the agglutination and formation of complexes between heavy metals and these substances, and interactions between oxidant-forming carcinogenic by-products. Between 50% and 80% of all natural organic matter in water, soils and sediments are humic substances (HSs; Abate and Masini 2003). According to Thurman and Malcolm (1981), these substances make up a third to half of the dissolved organic matter in water.

Structurally, HSs have high molecular weights, are complex and are composed of oxygen, hydrogen, carbon and small amounts of nitrogen, phosphorus and sulphur (Jones and Bryan 1998). HSs are animal and plant organic matter in different stages of oxidative degradation and subsequent polymerization (Rauen *et al*. 2002). More specific observations indicate that HSs are mixtures of amorphous polyfunctional and polydisperse materials with heterogeneous polyelectrolyte characteristics whose conformations are influenced by environmental conditions (Kavurmaci and Bekbolet 2013).

HSs are further classified into the following three types based on their solubilities: fulvic acids, which are soluble in acid and basic media; humic acids (HAs), which are soluble in bases but not in acids (pH < 2); and humin, which rarely dissolves in either acids or bases (Yamashita *et al*. 2013). Various techniques have been developed to remove HAs efficiently from water. However, doing so is difficult because these compounds possess high molar masses and specific characteristics that resemble polyelectrolytes. Therefore, determining the properties of these substances is essential to identifying an adequate removal process for application in aquatic environments and for evaluating water-treatment system performances.

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Some materials have been tested for the removal of HAs from aquatic environments. Among them are vermiculite clays (Abate and Masini 2003), montmorillonite and bentonite (Anirudhan and Ramachandran 2007; Kavurmaci and Bekbolet 2013; Leodopoulos *et al*. 2012; Peng *et al*. 2005; Salman *et al*. 2007), palygorskites (Alekseeva and Zolotareva 2013; Wang *et al*. 2012), natural zeolites (Capassoa *et al*. 2005), natural materials modified with surfactants (Li *et al*. 2011; Zhan *et al*. 2010), chitosan and zeolite composites (Lin and Zhan 2012), and double hydroxides layered with iron (Ahmed and Gasser 2012; Gassera *et al*. 2008; Seida and Nakano 2000) and aluminium (Santosa *et al*. 2008; Vreysen and Maes 2008).

However, activated carbon is the most porous material historically used to remove HAs in water-treatment plants. This material is used as an adsorbent and as a support for heterogeneous catalysts owing to its high superficial area, porosity and relatively low reactivity (Gil *et al*. 1997). Importantly, the adsorption capacity of activated carbon depends on not only its specific area but also its internal pore structure, characteristics and the functional groups at the pore surface (Cuerda-Correa *et al*. 2006). Various chemical and/or thermal treatments can be applied to provide activated carbon with the specific properties required for adsorption. Among them, sulphurization reportedly improves the adsorption performance (Rivera-Utrilla *et al*. 2011) for organic compounds.

This study aims to evaluate the influence of H_2SO_4 and H_3PO_4 acid chemical treatments on a commercial activated carbon with respect to the efficiency and kinetic conditions for adsorption of HA from water.

2. EXPERIMENTAL ANALYSIS

2.1. Carbon Treatments

The activated carbon used in this study was obtained from Chemical Dynamics. Acid solutions of 1 mol/L were used for the treatments. Initially, the carbon was dried at 130 °C for 3 hours. After cooling, 3-g aliquots were added to 150 mL of each solution under agitation (150 rpm) for 1 hour. These mixtures were subsequently separated by filtration and washed with distilled water to achieve a pH of 5. Finally, the carbons were dried in an oven for 5 hours at 60 °C.

2.2. Characterization

The treated and untreated starting carbon were characterized using complementary techniques.

2.2.1. Iodine Number

The iodine numbers for untreated (WT) and treated carbon were determined in accordance with the Brazilian MB-3410-ABNTNBR12073 standard.

2.2.2. X-Ray Diffraction

For the X-ray diffraction characterization, we used a Bruker D2 PHASER with Cu-K_α radiation ($\lambda = 1.54$ Å), Ni filter, 0.02° step size, 10 mA current, 30 kV voltage and a LYNXEYE detector.

2.2.3. Nitrogen Physisorption

Nitrogen adsorption analyses were performed to determine the specific surface areas of the materials used. The samples were pre-treated at 300 °C for 12 hours.

2.3. Humic Acid Adsorption Tests

The HA adsorption was tested by evaluating the adsorption capacity of the carbon and by conducting a kinetics study.

2.3.1. Evaluating the Adsorptive Capacity

The tests involved a batch system with 25 mg of adsorbent and a 40 mL HA solution (Sigma-Aldrich) with a 20 ppm concentration (i.e. within the range found in natural aquatic environments). Experiments were conducted in triplicate with 200 rpm shaking for 11 hours (time determined based on untreated carbon) at room temperature. After the adsorption, the samples were filtered (2.0 μm), and the HA concentrations in the effluents were measured using a UV–VIS spectrophotometer (HACH DM 5000 model) at a wavelength of 254 nm. Furthermore, the ratio between the wavelengths of 465 and 665 nm (E4/E6) indicated the relative concentration of the aromatic groups (the reduction ratio related to increasing molecular weight and aromatic carbon condensation; Saab and Martin-Neto 2007).

2.3.2. Kinetic Adsorption Study

For this step, a fixed initial concentration (20 ppm) was adopted, and the adsorption kinetics of the activated carbon were evaluated. The measurement times ranged from 30 minutes to 24 hours.

3. RESULTS AND DISCUSSION

3.1. Iodine Number

Table 1 presents the data obtained for iodine number. The result for the untreated carbon (i.e. 813.139 mgI_2/g) indicates that only the sulphuric acid treatment significantly increased the iodine number. This shows that a structural change provided greater accessibility to I_2 molecules.

3.2. X-Ray Diffraction Analysis

Figure 1 shows X-ray diffractograms of the material before and after the acid treatments. The carbon had a reflection characteristic of quartz at a 2θ equal to 26.59 (Rivera-Utrilla *et al*. 2011).

TABLE 1. Iodine Number Indices Obtained for the Activated Carbon

Treatment	Iodine number
H_2SO_4	879.3 ± 10.9
H_3PO_4	828.5 ± 9.4
WT	813.1 ± 13.4

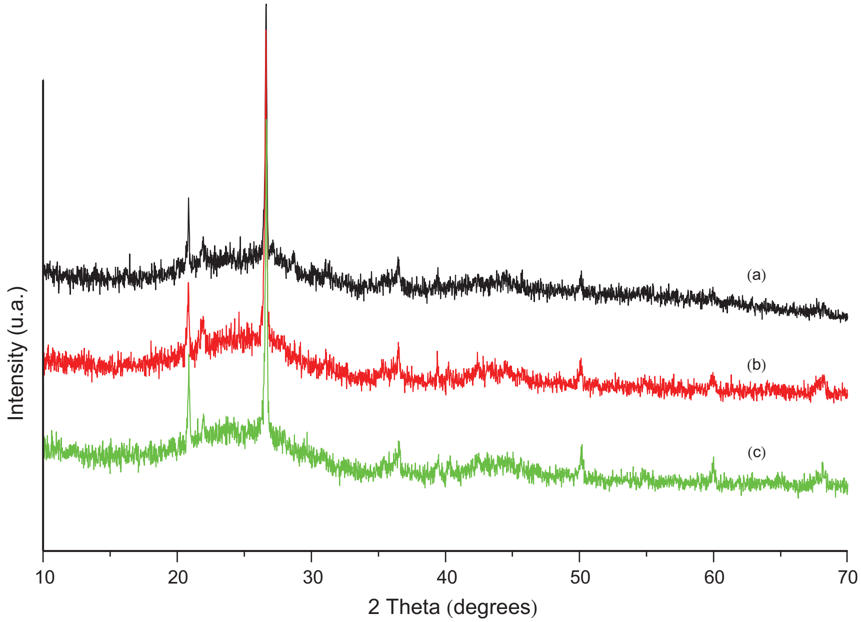

Figure 1. Diffractograms of carbon samples: (a) without treatment; (b) with H_3PO_4 treatment and (c) H_2SO_4 treatment.

TABLE 2. Nitrogen Physisorption Data

Parameter	Without treatment	H_3PO_4	H_2SO_4
Total BET area (m^2/g)	659	711	724
Microporous area/t plot (m^2/g)	377	411	413
External superficial area/t plot (m^2/g)	282	300	311

The X-ray diffraction pattern is typical of an amorphous material, such as the activated carbon. After the treatments, the materials remained amorphous, and the reflection maintained its intensity relative to the quartz, which indicates that the treatment did not remove this impurity.

3.3. Nitrogen Physisorption

The nitrogen physisorption data are presented in Table 2. The acid treatments increased the BET area. In addition, the H_2SO_4 treatment performed better, primarily because of the increase in mesopores (external area *t* plot). In a previous study, using biomass from agricultural waste material (rice husk), activated carbon samples were prepared by chemical activation using phosphoric acid (Daifullah *et al*. 2004). The intention was also to adsorb HAs in aqueous solution at the time the BET analysis showed the surface area of carbons to be between 376 and 352 (m^2/g). In 2008, Kalderis *et al*. used adsorbents from activated carbon-rich organic materials (rice husk and bagasse) for adsorption of arsenic acid, HA and phenol coals. The activated carbons obtained had BET surface area of 811 and 864 m^2/g, respectively, and were essentially microporous.

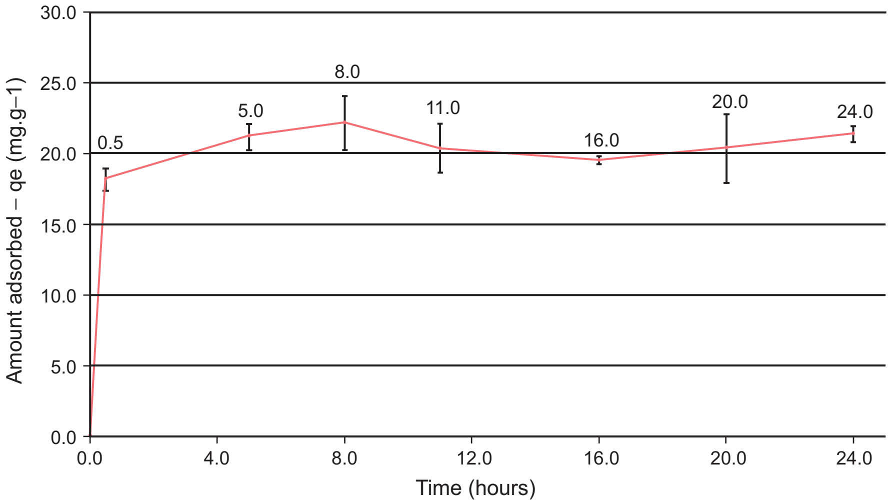

Figure 2. Adsorption kinetics for HAs on untreated activated carbon.

Terdkiatburana *et al*. (2008) used a commercial carbon (Calgon, USA) for adsorption of HAs. The performance of this adsorbent was compared with zeolites MCM-22 synthesized in the laboratory. Experimental results indicated that the activated carbons had BET surface area of 972 m^2/g. Recently, Rivera-Utrilla *et al*. (2011) listed and compared the advantages and disadvantages of various methods used to modify the surface of activated carbons for their application as adsorbents of organic and inorganic pollutants in aqueous phase. The oxidative and acidic treatments are responsible for the increase in specific area and performance of coals. It can be seen that although the specific area found in the analysis (724 m^2/g) is not remarkably high, it is an acceptable value for the adsorption of molecules of highly complex values, such as HAs.

3.4. Evaluating the Adsorption Capacity

Initially, the adsorption kinetics were determined for untreated carbon (Figure 2). The determined parameter was then applied for all the following tests to standardize the adsorption time. The presented data show that the adsorption process reached equilibrium after 11 hours, where the amount of adsorption (q) plateaued. Therefore, an adsorption time of 11 hours was adopted for further studies comparing the HA adsorptive capacity of the treated and untreated carbons.

Despite this verification, we still observed variations in the data between 11 and 24 hours (although not significant), which generated a curved line. This variation may result from heterogeneity in the HA molecules and carbon pore sizes. Higher molecular weight fractions of the HA require more time to mobilize and can also be adsorbed in larger pores. Figure 3 shows the evaluated HA adsorption capacities for each carbon after 11 hours. The carbon treated with H_2SO_4 exhibited the highest adsorption capacity [i.e. greater adsorbed amount (q)]. This result agrees with those for the iodine number and BET specific area, where the H_2SO_4 treatment exhibited the highest values. The H_3PO_4 treatment approximated the untreated carbon results. The association between adsorption capacity and surface area values is well-known in the literature. Starek *et al*. (1994) studied the adsorption of HAs on viscose rayon-based activated carbons and

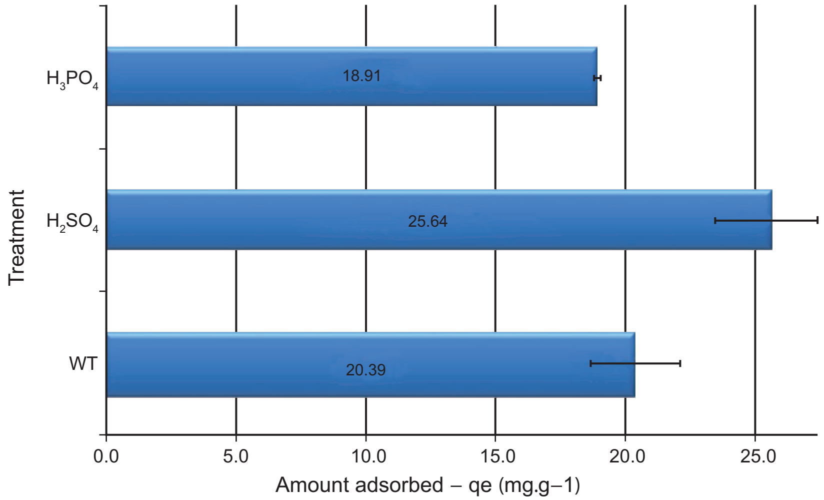

Figure 3. Quantities of HAs adsorbed on carbon samples without treatment (WT) and with acid treatment (H_2SO_4 or H_3PO_4).

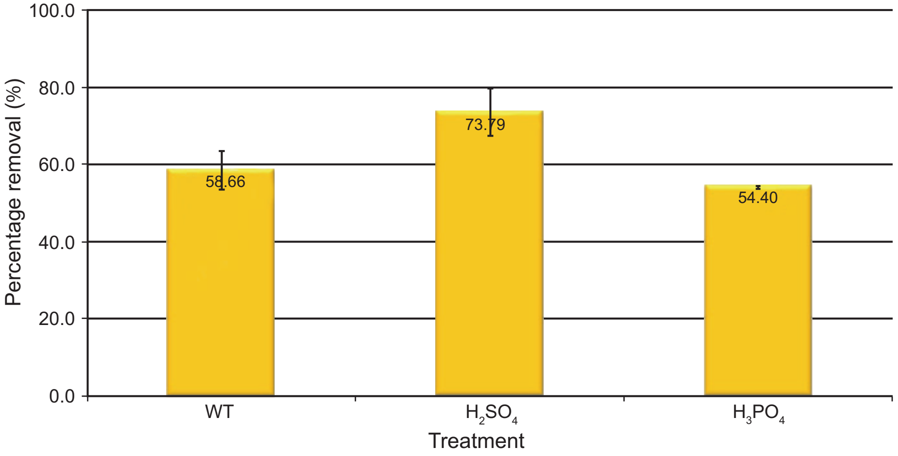

Figure 4. HAs removal efficiencies for carbon samples without treatment (WT) and with acid treatment (H_2SO_4 or H_3PO_4).

on granulated coal particles (SLZ JZN Hnusta Co). In their study also, the adsorption capacity values followed the same trend as that of the specific surface areas.

Daifullah *et al*. (2004) highlighted another important factor necessary to be considered while increasing the efficiency of adsorption on coals. The incorporation of acid into the mixture of activated carbon increases the acidity in the final product. This acidity promotes adsorption, because the HA contains functional groups that generate an affinity for the surface of the activated carbon.

Therefore, the improvement in performance of coals treated with H_2SO_4 can also be related to the presence of acidity in the coal samples. The removal efficiency (i.e. adsorbed quantities) of the carbon samples (untreated and H_3PO_4 treated) was between 54% and 59% (Figure 4). The HA

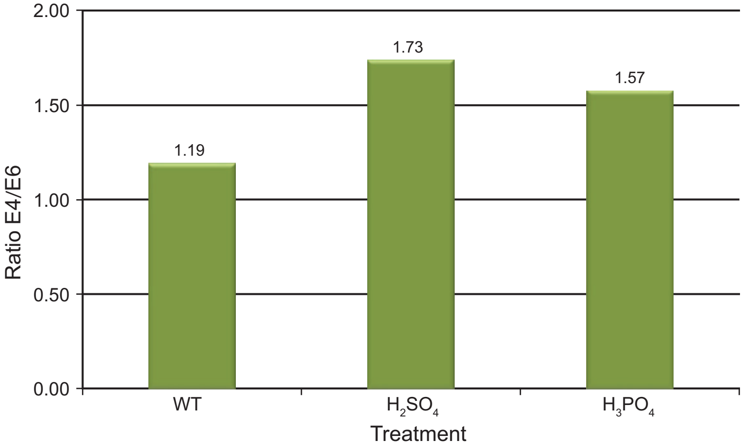

Figure 5. E4/E6 ratios for the effluents before treatment with carbon samples without treatment (WT) and with acid treatment (H_2SO_4 or H_3PO_4).

removal using H_2SO_4-treated carbon showed an average increase of 15.13% relative to the untreated carbon. The E4/E6 ratios (Figure 5) indicate that the effluent for carbon treated with H_2SO_4 had a lower relative concentration of aromatic groups compared with the untreated carbon.

These results indicate that the high efficiency and adsorption were not only related to the removal of lower molecular weight fractions but also to the removal of bulky groups on the HA molecules. This result was explained by the increased mesoporosity indicated in the nitrogen adsorption analysis. Recently, Wang *et al*. (2014) used the E4/E6 ratio to evaluate the structure of HA before and after UV radiation, and identified the degree of condensation of aromatic carbon. The results showed that with the increase in radiation time, there is a significant decrease in the E4/E6 ratio, indicating an increase in the degree of condensation of aromatic carbon chains. Thus, the acid treatment of activated carbons is a critically important step because the process increases the mesoporosity of coal, and consequently the adsorption of HAs from the effluent becomes more harmless due to the reduction in the degree of aromaticity.

3.5. Kinetic Evaluation of Adsorption

The kinetic adsorption curves of the treated carbons were determined to evaluate their temporal evolution of HA adsorption. Figure 6 compares the results between the treated and untreated materials. However, significant differences between the treatments were observed. Similar to the 11-hour evaluation, the H_2SO_4-treated activated carbon yielded the best results at all times. This observation corroborates the assertion that carbon treated in this way exhibits improved adsorption (Rivera-Utrilla *et al*. 2011) of organic compounds.

Another notable factor is the changes in the slope of the curve between 11 and 24 hours for the treated carbons. As previously mentioned, the treated carbons possess larger pores, which may enhance the adsorption–desorption competition between smaller fractions and the aromatic rings present in the HA. To gather more information on the adsorption characteristics, kinetic models were used to differentiate untreated activated carbon from the H_2SO_4-treated carbon, which showed the best performance.

According to Liu and Liu (2008) two models—pseudo-first-order and pseudo-second-order equations [equations (1) and (2), respectively]—are generally used to describe kinetic adsorption

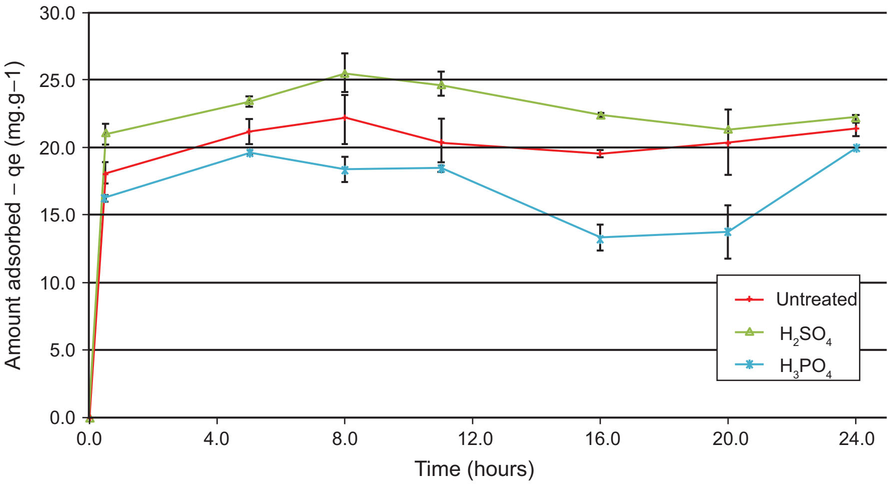

Figure 6. Kinetic curves for adsorption of HAs using carbon samples without treatment (untreated) and with acid treatment (H_2SO_4 or H_3PO_4).

data. In this study, the following equations were used for the kinetic modelling analysis (Sui *et al*. 2011):

$$\frac{t}{q_t} = \frac{1}{q_e^2 \times K_2} + \frac{1}{q_e} t \tag{1}$$

$$\ln \frac{q_e - q_t}{q_e} = -k_1 t \tag{2}$$

where q_e is the adsorption at equilibrium (mg/g), q_t is the adsorption at time t (mg/g), K_1 is the pseudo-second-order constant (l/minute) and K_2 is the pseudo-first-order constant (mg·minute/g).

The correlation coefficients (R^2) for equations (1) and (2) indicate that both carbons fit the pseudo-second-order model. This model provides two important variables, namely, the initial adsorption rate h [mg/(g min)] and the half-life ($t_{1/2}$), that is, the time to adsorb one half of the q_e. The following equations were used to calculate the aforementioned variables (Sui *et al*. 2011):

$$t_{1/2} = \frac{1}{K_2 \times q_e} \tag{3}$$

$$h = q_e^2 \times K_2 \tag{4}$$

Table 3 presents the adsorption variables for the kinetic model. A good correlation between the pseudo-second-order model was observed for both the carbons analyzed. The q_e value was higher for the activated carbon treated with H_2SO_4, which confirmed the good treatment performance. The $t_{1/2}$ of the untreated carbon was superior. In other words, the carbon treated with H_2SO_4

TABLE 3. Adsorption Variables for the Kinetic Model

Carbon	R^2	q_e (mg/g)	K_2 (l/minute)	$t_{1/2}$ (minute)	h [mg/(g·minute)]
Without treatment	0.9956	20.75	0.168	0.287	72.205
Treatment with H_2SO_4	0.9949	21.55	0.079	0.587	36.695

required more time to absorb. The data for these variables are consistent with the initial adsorption rate, h [mg/(g·minute)], which was lower for the treated carbon than the untreated carbon. This behaviour occurred due to the superficial areas. Because the HA molecules vary in sizes, the bulk molecules may have low initial velocities and low half-lives, $t_{1/2}$, for the carbon with the highest area (treated with H_2SO_4).

4. CONCLUSIONS

Based on the data obtained, we verified that the carbon treated with H_2SO_4 exhibited a significant efficiency for HA adsorption. Notably, this improved adsorption capacity was observed for all of the evaluated times. Treatment with H_3PO_4 did not significantly change the carbon and even lowered the efficiency relative to the untreated material in some instances (kinetic curve).

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