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To cite this article: M Vásquez-Osorio *et al* 2019 *IOP Conf. Ser.: Mater. Sci. Eng.* **519** 012036

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Zinc adsorption capacity with humic acids extracted from bituminous coal

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Abstract. The contamination of bodies of water by heavy metals represents not only a danger for the environment, but also for human health; because they do not have the capacity to biodegrade, accumulate in the environment and in the tissues of the living organisms that inhabit it. In order to minimize these impacts, Zinc adsorption (Zn) was studied in aqueous solutions using humic acids extracted from bituminous coal from the Cerrejón mine (Guajira). This investigation was divided into two phases: The extraction of Humic Acids and the adsorption study. In the first phase, an aqueous oxidation of coal samples with different particle sizes (125mm, 250mm, and 425mm) was performed, with hydrogen peroxide as the oxidizing agent, at a concentration of 30%. In the second phase Zn²⁺ removal using Humic Acids extracted from bituminous coals was studied in aqueous media as a function of pH, highest percentage of adsorption obtained was of 66.8% at a pH of 5.

1. Introduction

Contamination of bodies of water by heavy metals, which can reach dangerous levels for humans and ecosystems. It is due to the activity of different industrial sectors such as mining, the cement industry, dyes, tannery, electroplating, steel production, photographic material, corrosive paints, energy production, textile manufacturing, wood preservation, among others [1]. But one of the main sources of contamination, is the extraction of oil, because it generates a high environmental impact, reflected in the amount of water used as fracture water, as it is discharged, reaching groundwater, streams, aquifers or streams. About 632 million barrels of water can be consumed to produce 441 million barrels of oil. The resulting wastewater contains demulsifiers, defoamers, antioxidants, among others, providing a considerable amount of heavy metals such as Arsenic, Cadmium, Cobalt, Chromium, Mercury, Molybdenum, Nickel and Lead [2].

In order to remove these heavy metals from liquid waste, various methods have been used such as chemical precipitation, oxidation, reduction, electrochemical treatment, recovery by evaporation, filtration, ion exchange and membrane technologies [3]. But all these methods are very expensive and of low efficiency, when the concentration of metals in solution is very low, being a great disadvantage for these processes [1,3]. This has led to research aimed at obtaining new technologies that allow the reduction of heavy metals in the treatment of wastewater at environmentally acceptable concentrations



and at a low cost. Adsorption has been postulated as a promising technology in this respect, it has the potential to remove the dangerous metal efficiently, faster and at a lower cost compared to the other methods [4]. Humic acids have been studied and used as adsorbents for the removal of mercury, lead and other heavy metals in wastewater. On the other hand, coal in its natural structure has some capacity for ion exchange, however, this can increase drastically, when humic substances are extracted from them, as they have a greater capacity for adsorption [5].

The removal of heavy metals cadmium (Cd), lead (Pb) and mercury (Hg) was evaluated, using fulvic acids (humic substance) extracted from lignite coal as a chelating substance. For the removal of the metals, they prepared different solutions from previously lyophilized fulvic acids, with concentrations of 0.8% and 2% each. As a result, they determined that the chelating activity of fulvic acids, allowed a satisfactory removal of heavy metals, since the cadmium was between 80% and 100% removal, for Lead 23% and 99%, for Arsenic 44% and 97% of removal and finally for Mercury, 13% and 89%. With the statistical analysis they concluded that the removal of heavy metals does not present a normal distribution (which explains the difference in the percentages), since it depends on the metal and the acidification process, therefore it was analyzed non-parametrically [2].

Similarly, the adsorption of heavy metals cadmium (Cd), copper (Cu), nickel (Ni), lead (Pb) and zinc (Zn) with humic acids (AH) extracted from leonardite carbon samples has been studied. The results of adsorption of the metals were adjusted to the Freundlich model showed a different behavior of the adsorbents in relation to the metals studied, being the maximum adsorption capacity (K) and the retention force (n) of the different metals ($P < 0.05$). According to these parameters, the metal adsorption selectivity sequences presented the following order of preference, for K in humic acids: $Cd > Pb > Cu > Ni > Zn$ [6].

Also, the adsorption of metal ions in humic acids extracted from lignite coal has been investigated, demonstrating that the strong bonding capacities of metals with humic acids from different origins are similar under the same loading conditions. The results obtained showed that humic acids have higher affinity for the lead ions (Pb), silver (Ag), mercury (Hg), copper (Cu), barium (Ba) and cadmium (Cd), of the 17 metals studied and that the union is carried out mainly through carboxylic and phenolic groups. In addition, they were able to demonstrate that Pb, Ag, Hg and Cu ions can interact with phenolic groups, even at low pH [7].

Taking into account the environmental problems generated by heavy metal pollution, it is proposed to use adsorption as a more economical and efficient treatment [4], using the humic acids extracted from bituminous coal as adsorbents, thanks to its ion exchange capacity. In this research, it evaluates the adsorption capacity of zinc heavy metal (Zn) in aqueous solutions, using humic acids (AH) extracted from samples of bituminous coals, from a mine in the Cerrejón region in the department of La Guajira (Colombia).

2. Experimental

2.1. Extraction of Humic Acids (AH): Aqueous oxidation

The bituminous coal sample with favorable thermal characteristics, with low ash level and low nitrogen oxides emissions, from the Del cerrejón mine (Guajira-Colombia). It was crushed in a ball mill, to reduce particle size; it was sifted to select the different sizes. No.40 mesh (420mm), No.60 mesh (250mm), and No.120 mesh (125mm) were used, as noted in figure 1. Subsequently, 100 g of the sample were immersed for 1 h at room temperature with hydrochloric acid (HCL) 0.5 N, to be demineralized. To remove the bitumen, an ethanol-benzene mixture was used in a ratio of 1: 1 v / v under reflux for 24 hours. The solvent was removed by distillation and vacuum filtration with distilled water. The excess moisture was removed by heating at 80 ° C for 12 hours [8].

Then, 5 grams of carbon were taken at the different sizes, and oxidized with 15mL of a hydrogen peroxide solution (H₂O₂) at a concentration of 30%. The resulting mixture was heated to a temperature of 60 ° C and under continuous stirring for 6 hours. To extract the humic acids from the mixture, to 5 g of the oxidized samples, 100 mL of 0.1 M Sodium Hydroxide (NaOH) was added [8], maintaining this

system at 60 °C for 1 hour in continuous agitation. The resulting solution was filtered under vacuum, and 100 mL of HCl (0.1 M) was added to the filtrate for the precipitation of the humic acids. This system was allowed to stand for 24 h, then it was centrifuged at 3600 rpm for 10 minutes. The colloid obtained was then washed with ethanol (reactive quality) and finally heated at 100 °C for 1 hour [8].

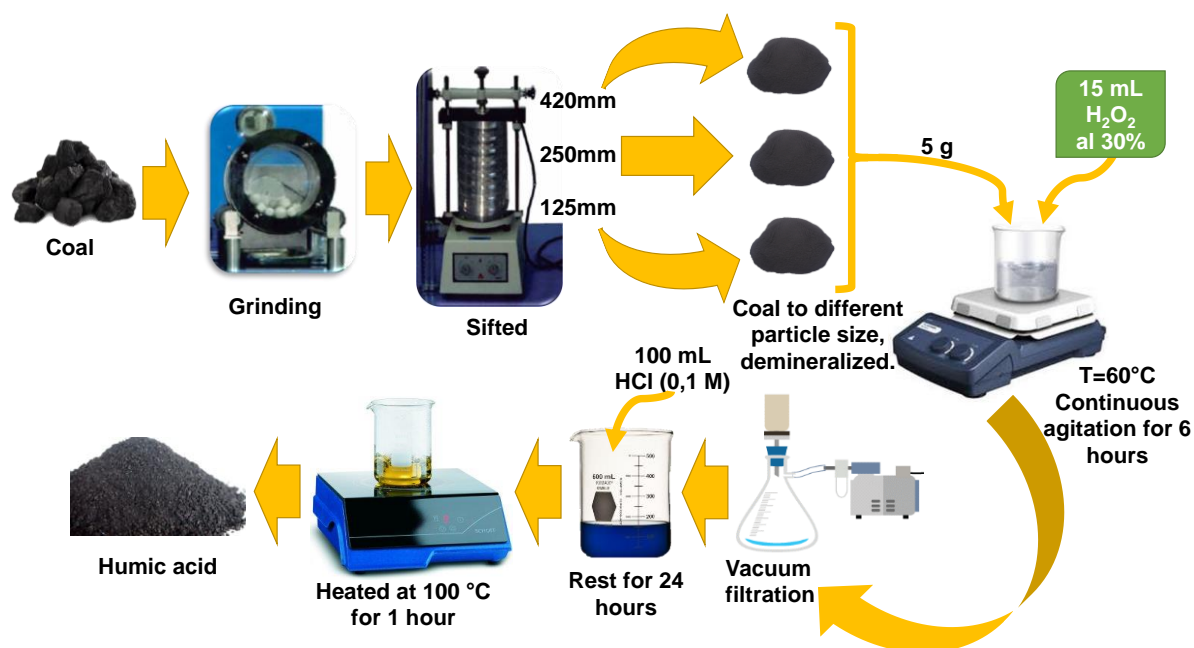


Figure 1. Aqueous oxidation of carbon.

The percentage of AH extracted was calculated taking into account the relationship between the mass extracted with the initial weight of the sample, according to equation 1 [8].

$$\frac{\text{Humic acid mass}}{\text{Coal mass}} * 100 \quad (1)$$

The samples of carbon and humic acid were characterized by infrared spectrometry (FTIR) using a Perkin Elmer model 1600.

2.2. Adsorption Study

To determine the cation exchange capacity, the effect of pH on Zn^{2+} adsorption was first studied, from samples of 50mg of HA with 10mL of 100 ppm solution of the metal under study, in a 250 mL Erlenmeyer, at 25°C and in constant agitation for 2 h. The analysis was carried out at different pH values, which varied between 3 and 6, adjusting by adding 0.1M HNO_3 solution and 0.1M NaOH. Then, 100 mL of a 0.1 M HCl solution was added, to precipitate the AH and to filter the solution 0.4 mL of HNO_3 was added, to preserve the medium. The above, allowed to find an optimal pH value, where the highest percentage of adsorption of the metal is obtained [9].

Later, the adsorption capacity using AH extracted from carbon samples of different sizes was studied. 50mg of AH was mixed with 10mL of 100 ppm solution of the metal under study, in a 250 mL Erlenmeyer, at 25 °C and in constant agitation for 2 h at an optimum pH value (previously determined) [9]. The amount of metal adsorbed was determined using equation 2:

$$\% \text{ adsorción} = \frac{(C_o - C_e)}{C_o} * 100 \quad (2)$$

Where: C_0 , is the initial concentration Zinc of in mgL^{-1} ; C_e , the concentration in equilibrium of Zinc in mgL^{-1} .

The concentration was analyzed by atomic absorption spectrophotometry.

3. Results and Discussion

3.1 Extraction of Humic Acids (AH)

Humic acids were extracted from carbon samples at different particle sizes, the percentages of extraction are recorded in Table 1. The highest amount of AH extracted ($60 \pm 0.1\%$) was from the sample with particle size 125 mm, oxidized with H_2O_2 , at a concentration of 30%, and an extraction time of six (6) hours. These treatment conditions lead to the decomposition of oxygenated functional groups of coal, which are favored by the presence of structures similar to humic acids, such as fulvic acids, among others [8].

Table 1. Percentages of extraction of humic acids with different particle sizes.

Particle size	% extraction of AH
420mm	35.7 ± 0.01
250mm	47 ± 0.03
125mm	60 ± 0.01

In Table 1, it is observed that an oxidation during 6 hours causes a decrease in the amount of humic acids in the structure of the coals, when the particle size of the carbon sample increases. In all cases statistically significant differences were found ($p < 0.05$).

The FTIR spectra of the humic acids obtained after oxidation with 30% hydrogen peroxide (see Figure 2), present between $3500\text{-}3200\text{ cm}^{-1}$ a broad and strong band of absorption of -O-H groups, distinctive of the carboxylic groups. Likewise, the increase of narrow bands between $3000\text{-}2800\text{ cm}^{-1}$ was observed, which are due to the C-H vibrations in aliphatic structures, which explains that during the oxidation process with H_2O_2 , there was a breakdown of macrostructures that caused the presence of groups aliphatics that can be as substituents in aromatic structures or as bridges between them [10].

Other bands were observed between $1800\text{-}1600\text{ cm}^{-1}$ generated by the stretching vibrations of $\text{C}=\text{O}$, in 1270 cm^{-1} by the presence of $\text{C}=\text{C}$ or Ar-OR , and between $1300\text{-}1000\text{ cm}^{-1}$ by the C-O-C bonds. These results correspond to the molecular structure of humic acids reported in the literature [11-13].

3.2 Adsorption capacity of humic acids

The union of Zn^{2+} cations to Humic Acids extracted from bituminous coals, was studied in aqueous media as a function of pH. In Figure 3, it is observed that this is a factor that affects the adsorption of the heavy metal. At low pH values, a low Zn^{2+} adsorption is observed, due to the electrostatic repulsion force of the H^+ on the surface of the AH with the metal ion, making it difficult for them to interact with the adsorbent [14]. But when increasing the pH, this repulsive force becomes weak, benefiting the diffusion of the Zn^{2+} ions towards the surface of the adsorbent, where the adsorption increases.

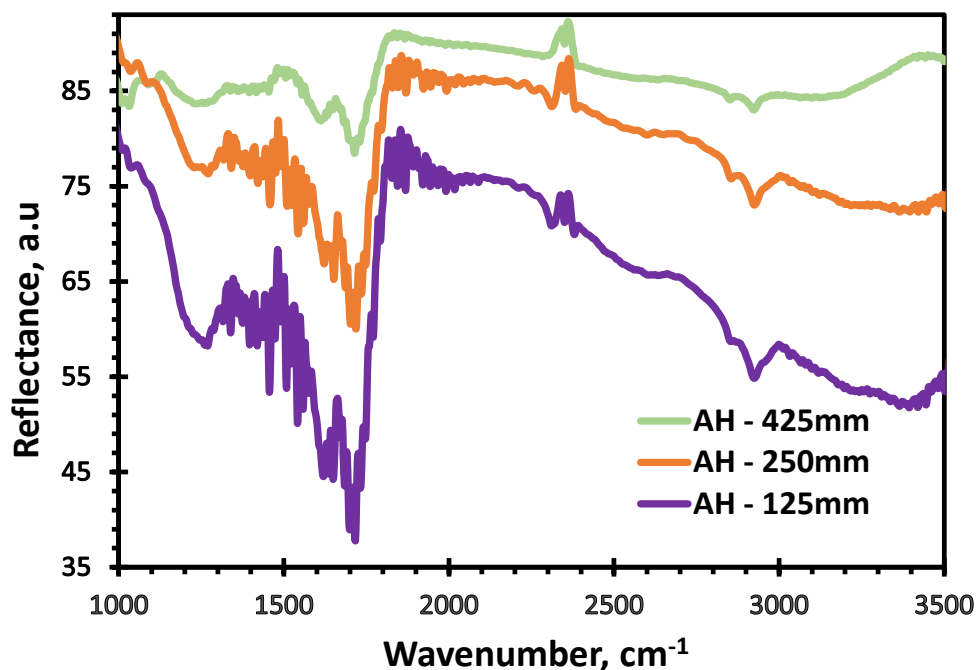


Figure 2. FTIR Spectra of Humic Acids at different particle sizes.

From figure 3, it can be deduced that the highest percentage of adsorption is obtained at a pH of 5, with a value of 66.8%. These results agree with that reported by Pehlivan & Arslan [14], comparing the adsorption capacity of Zn^{2+} and Cd^{2+} cations using relatively young brown coals YBC (lignite), humic acids, and commercial humic acid; Observing that effective metal removal was demonstrated at pH values between 5-5.7 [14].

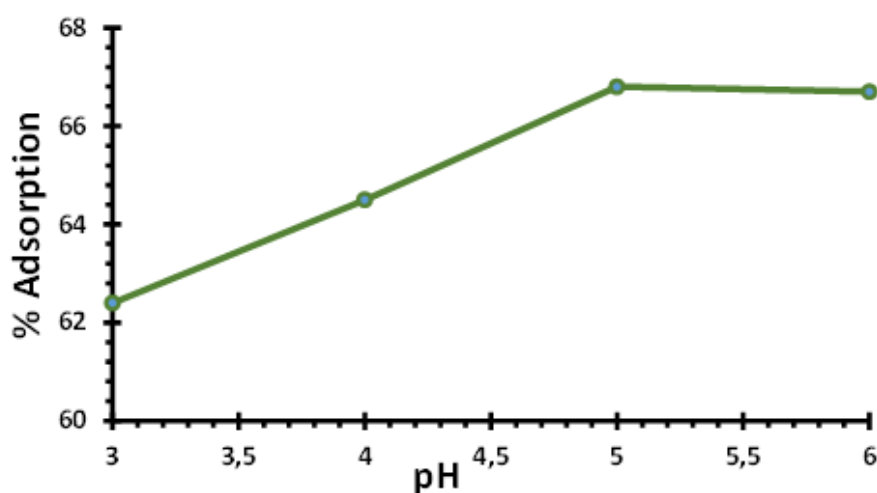


Figure 3. Effect of pH on the adsorption of Zn^{2+} with AH.

Similarly, the adsorption capacity of humic acids extracted from carbon samples at different particle sizes was studied. The percentages of adsorption in relation to the size of the coal samples are shown in Table 2.

Table 2. Percentages of Zn^{2+} Adsorción with AH extracted from carbon samples of different sizes.

Sample	Particle size (mm)	Adsorption (%)	Average Adsorption (%)
M1	425	62,716	63,002
M2	425	62,698	
M3	425	63,591	
M1	250	63,084	63,293
M2	250	63,135	
M3	250	63,66	
M1	125	66,999	67,245
M2	125	67,361	
M3	125	67,376	

Where it is observed that the highest percentage of Zinc adsorption, was achieved with the AH extracted from carbon sample with particle size of 125mm. However, in all cases the adsorption percentages were efficient, due to the low concentrations of the contaminant in the water used. Where generally the common methods are economically unfavorable or technically complicated [14, 15].

4. Conclusion

The highest percentage of humic acid extraction was obtained with the 125mm carbon sample, oxidized with hydrogen peroxide at a concentration of 30% and for 6 hours of extraction. The FTIR spectra of the humic acids, obtained by treating the carbon with the oxidizing agent corroborate that the material extracted in the oxidations are humic acids, according to the macromolecular structure defined for this type of substance. In addition, it was possible to identify that the particle size of the coal influences in the amount of humic acids that can be extracted from the coal sample. Also, the bituminous coal from the Cerrejón mine in the department of La Guajira (Colombia) can be a potential raw material to obtain humic acids, useful as heavy metal absorbers. The results show that the pH has an important role in the determination of the Zinc adsorption capacity when AH is used. The high Zinc-adsorption values make the method useful for wastewater treatment.

Conflict of Interest.

The authors report there are no conflicts of interest.

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