

Adsorption of Mercury (II) from Liquid Solutions Using Modified Activated Carbons

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Mercury is one of the most toxic metals present in the environment. Adsorption has been proposed among the technologies for mercury abatement. Activated carbons are universal adsorbents which have been found to be a very effective alternative for mercury removal from water. The effectiveness with which a contaminant is adsorbed by the solid surface depends, among other factors, on the charge of the chemical species in which the contaminant is in solution and on the net charge of the adsorbent surface which depend on the pH of the adsorption system. In this work, activated carbon from carbonized eucalyptus wood was used as adsorbent. Two sulphurization treatments by impregnation with sulphuric acid and with carbon disulphide, have been carried out to improve the adsorption capacity for mercury entrapment. Batch adsorption tests at different temperatures and pH of the solution were carried out. The influence of the textural properties, surface chemistry and operation conditions on the adsorption capacity, is discussed.

Keywords: mercury, aqueous solution, adsorption, activated carbon

1. Introduction

Mercury is an important and useful industrial material. Mercury and mercury compounds have been used from a long time as pigments in inks (cinnabar, red sulphide), as aids to early metallurgy (gilding copper) and instrumentation (thermometers, barometers) and in many industries (recovery of gold from its ores, manufacture of chlorine and sodium hydroxide by electrolysis of brine, etc.), or are present in their wastewaters.

Mercury is one of the most toxic metals present in the environment. Once mercury enters the food chain, large concentrations of this element accumulate in humans and animals, causing numerous adverse effects on their health. In order to prevent the problems due to the toxicity of mercury, several technologies have been proposed to remove this metal from aqueous media, which include ion exchange, adsorption, sulphide precipitation, electrodeposition, solvent extraction and membrane processes¹. Among the available technological alternatives for the removal of trace metals from water, adsorption has been considered an economically feasible one²⁻⁸.

Activated carbons are universal adsorbents that can be obtained from a wide variety of raw materials including wastes of industrial activities⁹⁻¹³. Activated carbons have been found to be a very effective alternative for mercury removal from water¹⁴⁻²¹.

Adsorption in liquid phase is a complex phenomenon because both, solute and solvent, compete for the solid surface. Briefly, the adsorption of a solute depends on its molecular size and chemical properties, on the textural properties of the adsorbent and on its surface chemistry²²⁻²³.

Most of the mercury in solution exists as complexed species, which can be either positive, negative or neutral, depending on the composition and pH of the solution. The situation is further complicated because the type of species preferentially adsorbed and

the extent of adsorption may depend on the state of ionization of the surface which, in turn, is dependent on the solution pH²⁴.

If the pH of an effluent cannot be modified (for example, when great volumes of liquid have to be decontaminated or when this modification produces an environmental problem), the capture of a contaminant can be enhanced by surface modification of the adsorbent by means of suitable treatments²⁵⁻²⁹. In other cases it is possible to change the pH of the solution in order to improve the adsorption.

In the past few years, considerable attention has been devoted to develop surface-modified adsorbents in order to enhance the adsorption capacity of solids to eliminate mercury from aqueous media. Sulphur has been reported as an element which favours the adsorption of mercury³⁰⁻³⁵, therefore, the surface treatment which incorporates sulphur should improve the entrapment of species that contain mercury.

This contribution presents a comparative study of three activated carbons obtained from eucalyptus wood, as adsorbents of mercury in liquid phase. The first adsorbent was obtained by physical activation of carbonized eucalyptus wood with water vapour, following the protocol detailed in previous works³⁶⁻³⁷. Two samples of this activated carbon were separated and treated with sulphuric acid and with carbon disulphide, respectively, in order to introduce sulphur as a heteroatom onto the adsorbent surface.

Batch adsorption assays to entrap mercury were performed for all the activated carbons and the adsorption isotherms were used to compare their performance.

The structural and textural parameters of the adsorbents, as well as the operation variables (temperature and pH) were analyzed and their influence on the adsorption capacity of the solids was discussed.

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2. Experimental

2.1. Preparation of adsorbents

The adsorbents were obtained from eucalyptus wood (EW). The start material was carbonized in a 5 L stainless steel retort, electrically heated, in absence of air from room temperature to 773 K and kept at the final temperature for 2 hours.

The carbonized material (CEW) was placed as a fixed bed in a 30 mm internal diameter stainless steel reactor, electrically heated, and activated with water vapour, following the protocol detailed in previous works³⁶⁻³⁷. Basically, the reactor was heated from room temperature to the activation temperature (1153 K) under nitrogen atmosphere. Then, the nitrogen stream was replaced by a water vapour flow (1.7 g of steam per g of carbonized material and per hour). An activation time of 105 minutes was adopted. When the activation process finished, the whole system was cooled from 1153 K to room temperature under nitrogen flow. The activation yield was 47,3%, measured as (mass of activated carbon/ mass of carbonized eucalyptus wood) × 100.

Two fractions of activated material (AC) were used to carry out the surface treatments of the adsorbent in order to incorporate sulphur as heteroatom onto the carbon surface. In one of the surface treatments, 50 g of AC were soaked in 250 mL of concentrated sulphuric acid, at room temperature, under stirring, for 24 hours. The liquid fraction was separated by filtration and the solid was washed free of acid with water and dried at 383 K for 3 hours. The solid was ground and sieved to -80 mesh particle size and labeled as AC-H₂SO₄.

The second sulphurization treatment was carried out using carbon disulphide as source of sulphur. 50 g of AC were soaked in 250 mL of carbon disulphide, at room temperature, and maintained under stirring for 24 hours. The sulphurized solid was filtered and dried in oven at 383 K for 3 hours, then was ground and sieved to -80 mesh particle size and labeled as AC-CS₂.

2.2. Characterization of adsorbents

2.2.1. Proximate and elemental analysis

The three adsorbents were characterized by proximate analysis, according to ASTM standards. All samples were previously dried in oven at 378 K until constant weight except for EW, that was analyzed as received. The elemental analysis was performed in a Carlo Erba EA 1108 CHNS-O equipment. The results are expressed on dry and ash free basis.

2.2.2. Textural properties

The specific surface and pore size distribution of AC, AC-H₂SO₄ and AC-CS₂ were determined from the nitrogen adsorption isotherms at 77 K, carried out in a Quantachrome Nova 2200 sorptometer. The

adsorption results were modelled by BET in order to determine specific surface, by DR to evaluate micropore volume and by BJH for pore size distribution.

2.2.3. Surface chemistry

2.2.3.1. Acid and basic groups

Surface acid groups were determined by contacting 0.2 g of the solid with 20 mL of 0.1 M NaOH solution. The excess of NaOH was measured by titration with 0.1 M HCl solution.

Surface basic groups were determined by contacting 0.2 g of the solid with 20 mL of 0.1 M HCl solution and the excess of HCl, by titration with 0.1 M NaOH solution.

2.2.3.2. Point of zero charge

The pH of the point of zero charge, i.e. the pH above which the total surface of the carbon particles is negatively charged, was measured by the so-called mass titration method proposed by Noh and Schwartz³⁸.

2.3. Batch adsorption studies

A solution of 40 mg.L⁻¹ of Hg (II) was prepared by dissolving 0.0541 g of HgCl₂ in 1L of distilled water. Batch adsorption tests, which consisted of mixing 50 ml of Hg (II) solution with different amounts of the adsorbent (10, 20, 30, 40, 50, 60, 80 and 100 mg) at an initial pH = 7, were carried out in 100 mL conical flasks under stirring until the equilibrium time is reached. The liquid phase was separated from the solid by centrifugation. The adsorption tests were performed at 298 and 318 K, in order to study the temperature influence and at pH = 3, pH = 7 and pH = 10 to study the pH influence. The concentration of mercury remnant in the solution was determined by spectrophotometry UV-VIS in a Hach 2010 model equipment. The liquid sample containing the non-adsorbed mercury was complexed with potassium iodine and rhodamine, according to the protocol detailed by Muralidhara³⁹ and Kardivelu¹⁷. The concentration of mercury in solution was determined measuring the absorbance at 575 nm.

3. Results and Discussion

3.1. Proximate and elemental analysis

The results of the proximate and elemental analysis corresponding to samples EW, CEW, AC, AC-H₂SO₄ and AC-CS₂, are shown in Table 1.

Eucalyptus wood is characterized by a high volatile matter content (VM), low carbon (FC) and ash contents. After the pyrolysis and activation steps, CEW and AC solids present a lower content of

Table 1. Proximate and elemental analysis (expressed in a dry basis).

| Adsorbent | Proximate analysis (wt. (%)) | | | | Ultimate Analysis (wt. (%)) | | | | |
|--|------------------------------|-------|-------|------|-----------------------------|----------------|----------------|----------------|----------------|
| | Hum | VM | FC | Ash | C ^b | H ^b | N ^b | O ^b | S ^b |
| EW | 10.51 | 69.14 | 19.35 | 1.00 | 45.34 | 6.77 | 0.20 | 47.69 | 0.0 |
| CEW ^a | - | 27.60 | 69.30 | 3.10 | 80.44 | 7.54 | 0.10 | 11.92 | 0.0 |
| AC ^a | - | 7.55 | 89.40 | 3.05 | 88.90 | 1.62 | 0.05 | 9.43 | 0.0 |
| AC-H ₂ SO ₄ ^a | - | 8.08 | 88.70 | 3.22 | 82.31 | 1.85 | 0.10 | 12.84 | 2.9 |
| AC-CS ₂ ^a | - | 7.77 | 89.05 | 3.18 | 88.20 | 1.70 | 0.05 | 5.95 | 4.1 |

^aDry basis; ^bDry and ash free basis.

Table 2. Textural parameters of the adsorbents.

| Adsorbent | Specific area (m ² .g ⁻¹) | Pore volume (cm ³ .g ⁻¹) | Micropore volume (cm ³ .g ⁻¹) | Mesopore volume (cm ³ .g ⁻¹) |
|------------------------------------|--|---|--|---|
| AC | 701 | 0.51 | 0.26 | 0.25 |
| AC- H ₂ SO ₄ | 979 | 0.72 | 0.35 | 0.37 |
| AC-CS ₂ | 582 | 0.42 | 0.21 | 0.21 |

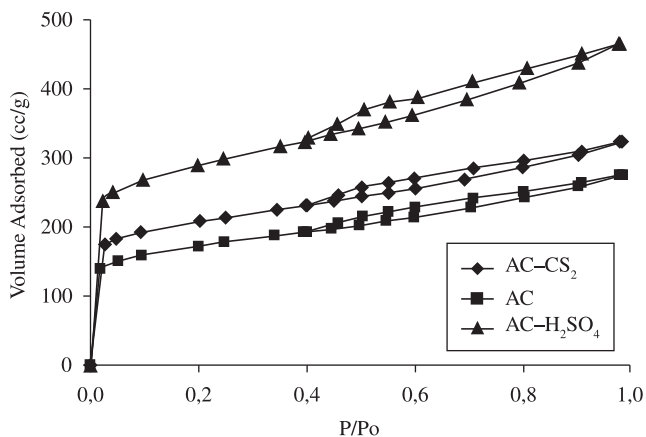


Figure 1. Adsorption-desorption isotherms for nitrogen at 77 K.

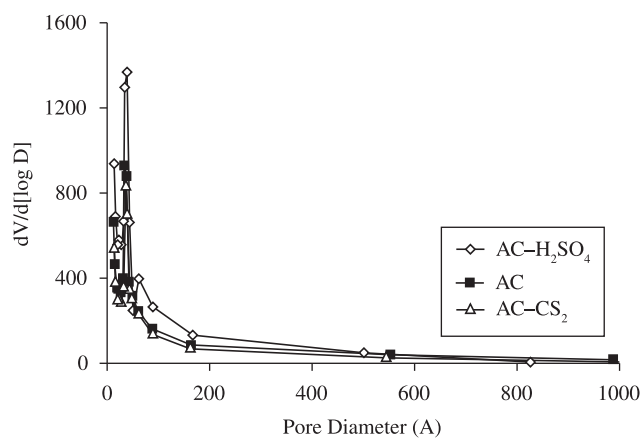


Figure 2. Pore size distribution of the adsorbents.

volatile matter and a higher carbon and ash content, compared with that of EW.

The higher content of volatile matter and sulphur of the AC-H₂SO₄ and AC-CS₂ adsorbents compared with that of the AC solid indicates the effective incorporation of sulphur onto the adsorbent surface.

By comparing the sulphur content of samples AC-CS₂ and AC-H₂SO₄, it can be concluded that the impregnation treatment with CS₂ was more efficient than that with H₂SO₄.

3.2. Textural characterization of the adsorbents

Figures 1 and 2 show the adsorption isotherms and the pore size distributions corresponding to the three studied adsorbents. Table 2 summarizes the main textural parameters of the adsorbents.

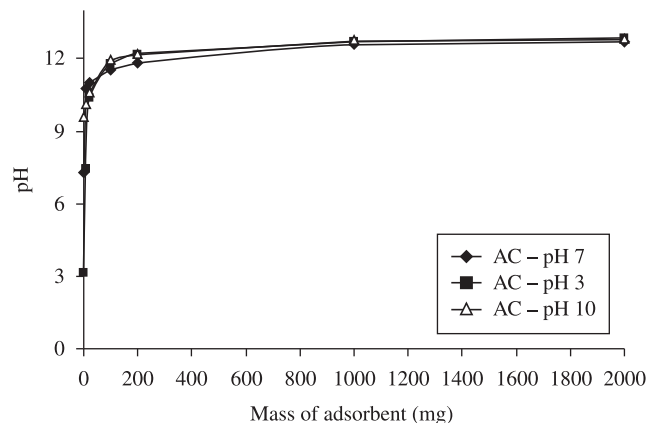


Figure 3. Point of zero charge of AC adsorbent by mass titration.

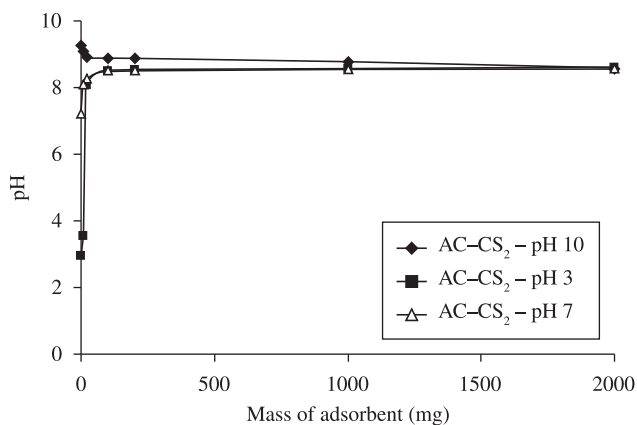


Figure 4. Point of zero charge of AC-CS₂ adsorbent by mass titration.

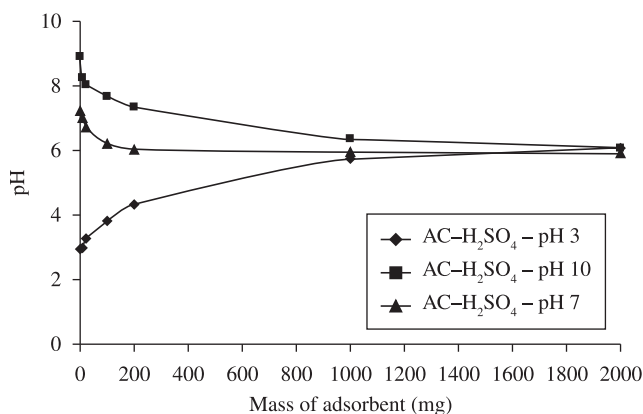


Figure 5. Point of zero charge of AC-H₂SO₄ adsorbent by mass titration.

The adsorption isotherms corresponding to AC-H₂SO₄ and AC-CS₂ show important variations compared with that of AC, mainly in the position of the knee of the isotherm, which basically indicates that the microporous structure has been substantially modified by the sulphurization treatments. The increase of the micropore volume in the AC-H₂SO₄ adsorbent could be the result of a chemical activation caused by the sulphuric acid which generates more cavities.

The decrease of the micropore volume observed for the AC-CS₂ sample could be associated to a pore blocking effect due to the surface sulphurized groups. Increment in the mesoporous volume corresponding to the AC-H₂SO₄ adsorbent is also produced. However, from the hysteresis loop shape, the mean connectivity of the porous net does not vary after the sulphurization treatments⁴⁰⁻⁴².

From the textural properties, the adsorption capacity of a solid depends on the specific surface area, the pore size distribution and the mean connectivity of the porous net. Because of its higher specific surface and pore volume AC-H₂SO₄ should be better adsorbent than AC and AC-CS₂. Furthermore, from the surface chemistry point of view, AC-H₂SO₄ is better adsorbent than AC because the surface sulphurized groups are specially favourable for mercury adsorption³⁰⁻³⁵.

A lower mercury adsorption capacity should be observed for the AC-CS₂ adsorbent due to the important decreasing of specific surface and pore volume compared to the AC adsorbent. However the adsorption capacity of AC-CS₂ adsorbent is higher than that of AC, because its unfavourable textural properties are balanced by the surface chemistry which improves the mercury adsorption.

3.3. Surface chemistry

Figures 3, 4 and 5 show the results of the mass titration carried out in order to obtain the pH corresponding to the point of zero charge

Table 3. Acid and basic surface groups and pH_{PZC} experimental results.

| Adsorbent | Acid groups (mEq.g ⁻¹) | Basic groups (mEq.g ⁻¹) | Acid/Basic ratio | pH _{PZC} |
|-----------------------------------|------------------------------------|-------------------------------------|------------------|-------------------|
| AC | 1.08 | 4.52 | 0.24 | 13.1 |
| AC-H ₂ SO ₄ | 1.46 | 4.94 | 0.30 | 6.1 |
| AC-CS ₂ | 1.06 | 2.31 | 0.46 | 8.5 |

Table 4. Parameters of the Freundlich equation.

| Adsorbent | log k | 1/n | R ² |
|-----------------------------------|-------|------|----------------|
| AC | 0.92 | 1.09 | 0.976 |
| AC-H ₂ SO ₄ | 1.65 | 0.88 | 0.981 |
| AC-CS ₂ | 0.55 | 1.57 | 0.980 |

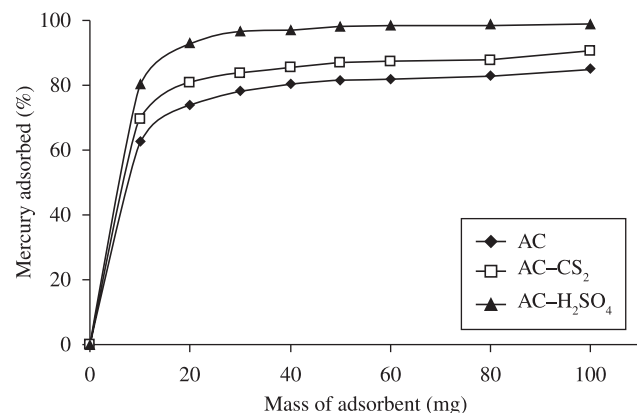


Figure 6. Adsorption isotherms of mercury.

for the studied adsorbents. Table 3 summarizes the results of the acid and basic surface groups and pH_{PZC} of the studied adsorbents.

The analysis of the acid and basic surface groups indicates that the sulphurization treatment with H₂SO₄ has increased the number of both types of sites, compared with that of the AC adsorbent, due to the changes in the textural properties of the modified solid and the changes in the surface chemistry. The (acid groups: basic groups) ratio shows variations in the surface chemistry due to this sulphurization treatment.

More important changes in the number and type of surface groups have been observed in the AC-CS₂ adsorbent, compared to those corresponding to the AC adsorbent, due not only to the structural changes in the sulphurized adsorbent but also to the surface chemical changes, basically measured by the number of acid and basic groups per gram of the adsorbent and by the (acid groups: basic groups) ratio, substantially different to that of the untreated adsorbent.

The pH_{PZO} values corresponding to the sulphurized adsorbents are considerably different to that of the untreated solid which predicts different behaviour of the three solids with the pH of the solution.

3.4. Batch adsorption studies

Figure 6 shows the percentage of mercury adsorbed with respect to the original content in the solution, after the batch adsorption test at 298 K and pH = 7. The highest adsorption of mercury corresponds to the AC-H₂SO₄ adsorbent and the lowest one to the AC solid. The experimental datapoints were modelled by the Freundlich equation and the results of the linear regression are summarized in Table 4.

The analysis of the Freundlich model parameters for the adsorption data at a fixed pH and temperature shows that the highest adsorption capacity corresponds to the AC-H₂SO₄ adsorbent (highest value of the k Freundlich parameter), which is due mainly to the variations in the textural properties of the solid provoked by the sulphuric acid. This sulphurization treatment produced slight changes in the surface chemistry in comparison with the AC adsorbent (similar values of the 1/n Freundlich parameter).

More important changes in the surface chemistry were produced when carbon disulphide was used as sulphurizing agent (different 1/n Freundlich parameter compared to those corresponding to AC and AC-H₂SO₄ adsorbents). This modification balanced the unfavorable change in the textural properties so the observed mercury adsorption capacity of the modified solid was higher than that of the untreated adsorbent. These results are in agreement with those corresponding to the surface acid and basic groups.

3.4.1. Temperature influence

The temperature of the adsorption tests does not influence the adsorption capacity of the studied adsorbents. As an example, Figure 7 corresponding to the AC-H₂SO₄ adsorbent, is included. Similar behavior is observed for the other tested adsorbents. This is because, although the adsorption process is exothermic in nature, the condensation of a solute onto the adsorbent surface only occurs by the displacement of a solvent molecule previously adsorbed (endothermic process). If the heat of adsorption of a solute molecule is similar to that of the desorption of the solvent molecule, the whole process will not be influenced by the temperature.

3.4.2. pH influence

The effectiveness with which a solute is entrapped by an adsorbent is influenced by the pH of the solution. The speciation also depends on the pH of the solution²⁴. The adsorption of mercury by the studied adsorbents could be enhanced when the net surface charge and the

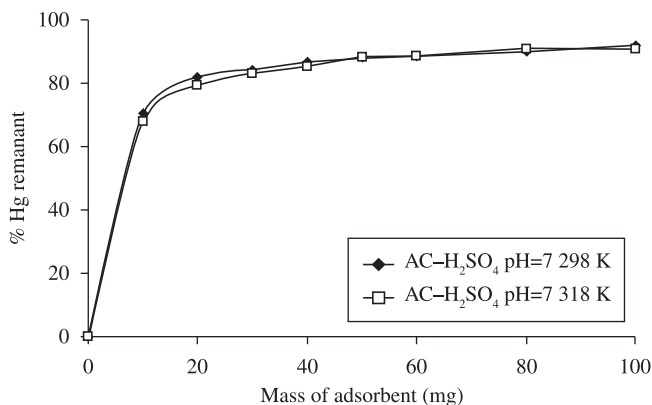


Figure 7. Effect of temperature on removal of Hg(II) for AC-H₂SO₄.

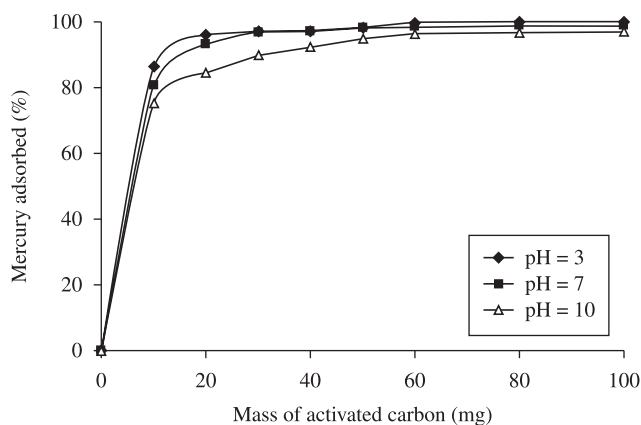


Figure 8. Effect of pH on removal of Hg(II) for AC-H₂SO₄.

charge that of the specie which contains the metal in the solution are different. Simultaneous studies of speciation and point of zero charge will allow to determine the pH of the solution for a maximum adsorption.

Figure 8 shows that the AC-H₂SO₄ adsorbent presents higher adsorption capacity at pH = 3 compared to pH = 7 and pH = 10. This behavior can be explained through the analysis of the net surface charge of the adsorbent and the charge of the species in which mercury is in solution. For example, $pH_{PZC} = 6$ for the AC-H₂SO₄ adsorbent. When the adsorption test is carried out at pH = 3, the net charge of the solid surface is positive. At $pCl = 3.8$ and pH = 3 the dominant species in solution are (HgCl₂) (HgCl₃)⁻. Then the electrostatic attraction forces between the solid surface and the negative charged species will enhance the adsorption. When the adsorption test is carried out at pH = 7 (closed to the pH_{PZC} of the adsorbent) the net charge of the surface is closed to zero. In this case, no matter the speciation, there is not an important electrostatic effect compared to that at pH = 3 and the adsorbent capacity of the solid diminishes compared to that at pH = 3. For the adsorption test at pH = 10, the net charge of the solid surface is negative and the main species in solution are (HgCl₂) (HgCl₃)⁻. In this case there is a repulsion electrostatic effect between the solid surface and the negative charged species. Then, the adsorption of the mercury species is more difficult compared to that observed at pH = 3 and pH = 7. A similar analysis of the AC and AC-CS₂ adsorbents can explain the adsorption capacities observed at different solution pH.

4. Conclusions

The activated carbon from carbonized eucalyptus wood is an adequate adsorbent for mercury entrapment from aqueous solutions and its adsorbent efficiency can be enhanced by the modification of its surface chemistry. The improvement in the adsorbent capacity depends not only on the surface modifications, but also on the charge of the solute in the solution. Both factors depend on the pH of the solution.

The surface sulphurization treatments produce important variations in the zero charge point, in the textural properties of the solid (basically specific surface and pore size distribution) and in the number of acid and basic surface groups.

From the analysis of the above mentioned factors, the dependency of the adsorption capacity of a solid with the pH of the solution can be explained. The temperature does not influence significantly the adsorption properties of the solid studied. A slight increment of the adsorption capacity with temperature is observed. This behavior is due to the energetic changes which occur when a solute molecule replaces a solvent molecule onto the solid surface.

From the adsorption data, modelled by the Freundlich equation, it can be concluded that the surface treatment with sulphuric acid produces important changes on the porous structure of the adsorbent and on the surface chemistry which explains its highest adsorption capacity. The sulphurization treatment with carbon disulphide also produces important changes in both, textural properties and surface chemistry of the solid. In this case, the decrease in the surface area and pore volume is balanced by a favourable surface chemistry for mercury adsorption which makes this adsorbent better than the untreated solid (AC).

This information will be useful in order to predict the behaviour of the adsorbents in dynamic adsorption studies which in turn will allow to determine, after the scale up, the size of the industrial adsorption units.

Acknowledgements

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