Synthesis of Activated Carbon Mesoporous from Coffee Waste and Its Application in Adsorption Zinc and Mercury Ions from Aqueous Solution

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Abstract: We obtain activated carbons with high portion of meso pores using coffee residues as precursor for the application of adsorption of large adsorbates. Because of its natural properties, the coffee residue exhibited a large pore size. In this work, the coffee residue were impregnated with ZnCl₂ and KOH, and then carbonized under the nitrogen conditions and activated with CO₂ respectively. Obtained activated carbons are used in the adsorption of ions Hg(II) and Zn(II). These adsorbents are efficacious to remove these ions from aqueous solution, with monocomponent equilibrium adsorption capacities ranging from from 0.002 to 0.380 mmol·g⁻¹ for Hg on ACK3 and from 0.002 to 0.330 mmol·g⁻¹ for ACZ3. For Zn(II) on ACK2 from 0.002 to 0.300 mmol·g⁻¹, and from 0.001 to 0.274 mmol·g⁻¹ for ACZ2.

Keywords: Adsorption, isotherms, coffee residues, heavy metals, immersion calorimetry.

Introduction

Adsorption is now widely accepted in environmental treatment applications throughout the world, liquid–solid adsorption systems are based on the ability of certain solids to preferentially concentrate specific substances from solution onto their surfaces; this principle can be used for the removal of pollutants such as metal ions and organic compounds, from wastewaters. Extensive research has been carried out during the last ten years to find low-cost, high capacity adsorbents for the removal of metal ions. A wide range of adsorbents
have been developed and tested, including several activated carbons [1-5]. Several low-cost agricultural wastes and sludges [6-8] and other wastes, such as tire rubber [9, 10] and fly ash [11] have been used for a range of metal ions. Colombia is one of the largest producers of coffee, with 2007/2008 harvest estimated at 600,000 Tons per year [12]. During the process of industrialization of the coffee beans the amount of waste generated is equal to the amount of green coffee produced, or to obtain 1 kg of processed grains, you need 2 kg of coffee beans. Thus, only the processing of coffee will generate about 30 Tons per year of waste. These waste (lignocellulose), if improperly disposed, may cause pollution of soils and waters. An alternative to prevent the disposal of these wastes would be its use in the preparation or production of material of higher value, transforming the waste into raw material. The scroll, known as "cone" for being a film that involves the anatomical grain, is part of the waste generated by processing of the coffee is obtained when the pulp is made by wet. This material is characterized chemically by its high content of crude fiber (cellulose, lignin, and hemicellulose) and low levels extractives and ash [13]. In recent years, several studies have reported the production of activated carbons (AC) from waste such as fruit seeds, crushed sugar cane, leather scraps, tires, etc [14-16]. Activated carbon (CA) is a porous carbonaceous material prepared by carbonization and activation of organic substances, mainly from vegetal [17,18] are used widely for the adsorption of pollutants in gaseous and liquid phases, such as support for catalysts, purification of several compounds in wastewater treatment, etc. Production of activated carbons involves two steps: the carbonization of raw carbonaceous materials in an inert atmosphere and the activation of carbonized carbon. The carbonization consists of a thermal decomposition of the carbonaceous material, eliminating non-carbon species and producing a fixed carbon mass with a rudimentary pore structure. Activation can be carried out by physical (hydrothermal) or chemical means. In physical activation process, generally the precursors are activated with high temperature steam (H2O) or CO2 in range of 800-1100 °C [13-14] while chemical activation processes, the precursors are fixed with basic reagent (KOH, NaOH etc.)[15] or acidic reagent (ZnCl2, H3PO4, HCl, H2SO4 etc.) [16] and activated in the temperature ranging from 300-700 °C. However, the carbonization and activation steps are accomplished in a single step by carrying out thermal decomposition of raw material impregnated with chemical agents. In the literature [18] carbonized coconut shell impregnated with ZnCl2 at nitrogen atmosphere and activated with CO2 respectively. They found that CO2 enlarged fine pore and meso pore content of activated carbon from coconut and palm seed were 71% and 94% respectively. Conventional activated carbons with micro pores are used for the adsorption of gases and vapors, while the existence of mesopores enhances the adsorption capacity of large adsorbates. The ability adsorption of CA depends on the nature of the precursor, the size particles (granules or powder) and the production process chosen. The quality of CAs is evaluated in terms of their properties physical adsorption and area superficial [19]. This study aims to use types of benefit coffee waste for the preparation of activated carbons, with high portion of meso pores using as impregnating agents KOH and ZnCl2. Obtained activated carbons are used in the adsorption of Zn and Hg ions from aqueous solutions.

**Experimental Section**

**Preparation of Sample**

The benefit coffee waste (parchment) was obtained by the processing of the coffee pulping wet of the coffee zone Caldas (Colombia). The material was dried and ground, resulting in
particle size between 250 to 420 micrometers. Characterization of parchment the contents of carbon, hydrogen and nitrogen were determined in a unit CHN Elemental Analyzer PE 2400. Zinc chloride of purity 95% Merk®. Nitrogen and carbon dioxide gases were industrial grade from Aga fano industrial Gas. To determination of ash content (mineral) was used to Norm ASTM D 3174. The other hand, analytical grade reagents were used for heavy metal solution (salts of Hg and Zn), ACS reagent grade concentrated nitric acid, NaOH and pH buffer solutions (E. Merck) were used to adjusted pH values of samples. In all experimental work, distilled demineralised water was used.

**Activation Process**

The mesoporous adsorbents were made by activation of coffee residues with zinc chloride and potassium hydroxide as a chemical agent in combination with carbon dioxide as a physical activating agent. The coffee residues were dried at 110°C, crushed and sieved to a uniform size of 1.0-2.0 mm. In general, the mixtures were dehydrated overnight at 110°C and pyrolized under a flow of nitrogen in a quartz tube held in horizontal furnace (carbolite). The temperature was ramped at 10°C/min up 700°C. Nitrogen was replaced by CO₂. When the temperature reached 700°C the carbon soaked at these conditions for 2-3 h the activated products were then cooled, washed successively with deionised water, hydrochloric acid (0.1 mol/L) and hot deionised water to remove the zinc, chloride, potassium and hydroxide compounds. Four types of activated carbons were prepared with different conditions as follows. Coffee residues were washed with water and dried at 110°C for 24 h. The dried coffee residues were divided into two portions. The first portion, KOH was dissolved in water and then impregnated into the coffee residues with ratios of chemical to coffee residues masses ranging from 2 : 1 to 3 : 1. These carbons were labeled as ACK1 and ACK3. The mixture was dehydrated in an oven at 110°C for 24 h. The other portion of coffee residues was in ZnCl₂ dissolved in water and then impregnated into the residues with ratios of chemical to coffee residues bagasse masses ranging from 2 : 1 to 3 : 1. These carbons were labeled as ACZ1 and ACZ3. The resulting homogeneous slurry was dried at 105°C. The activated carbons were washed with a 0.5 N HCl solution. Subsequently, the samples were repeatedly washed with hot distilled water until the pH of solution reached to [6–7].

**Textural Characterization of Activated Carbons.**

Textural properties of the synthesized activated carbons were analyzed using N₂ adsorption measurements at 77 K in a volumetric system (Quantachrome, Autosorb 3-B). Before the adsorption experiments, samples were submitted to an outgassing treatment at 523 K for 4h. The volume of micropores, V₀ (N₂), was obtained by application of the Dubinin-Radushkevich equation to the nitrogen adsorption data. The total pore volume, Vₚ, was obtained from the amount adsorbed at a relative pressure p/p₀ of 0.99 while the mesopore volume, Vₘeso, was obtained from the difference between the total pore volume and the micropore volume. Finally, the “apparent” surface area was obtained by application of the BET (Brunauer, Emmett and Teller) equation to the nitrogen adsorption data [20].

**Thermogravimetric Analysis (TGA)**

Thermogravimetric experiments were carried out by a thermogravimetric analyzer (Netzsch STA 409C) in order to determine the pyrolysis behavior of coffee residue and ZnCl₂-impregnated coffee residue. Three samples: coffee residue, ZnCl₂ and ZnCl₂-impregnated coffee residue were subjected to measure in the temperature range of 30–800°C at heating rate 10°C/min under flowing of nitrogen gas flow and held at 800°C for 10 min.

**Proximate Analysis**
The proximate analysis was conducted according to ASTM D 3172-3175 standards [21] and the results were expressed in terms of moisture, volatile matter, ash and fixed carbon contents. One gram of sample was loaded in a crucible with cover and heated from room temperature to 110°C in an oven until complete dehydration was accomplished. Then, the sample was decomposed in tube furnace at 950°C for 6 min to determine the quantity of volatile matters. The covered crucible was removed from the tube furnace and cooled to room temperature in a desiccator. To determine the ash content, approximately 1 g of sample was placed in covered crucible and heated with the flame for 10 min followed with heating in the muffle furnace from room temperature to 750°C for 3 h. Then, the crucible was placed in a desiccator and allowed to cool at room temperature. The fixed carbon content was obtained by subtracting moisture, volatile matter and ash content from 100%.

**Adsorption of Zinc, Cadmium and Mercury from Aqueous Solution**

Perkin Elmer 4110 atomic adsorption spectrometer (AAS) operating with an air acetylene flame was used to analyze the concentration of heavy metals. The minimum detection limit was equal to or less than EPA requirement. Three standard solutions with concentrations of heavy metal ions in the linear range of the instrument were used to construct each calibration curve. During analysis of the samples for heavy metals concentration, those samples in which the concentration of heavy metals is observed beyond the linear range of the references were diluted to appropriate concentrations. All measurements were repeated three times and those results in which the standard deviations were found greater than 0.1 mg/L were not accepted.

The pH measurements were performed with a controlled pH analyzer (Benchop Meters 2100 meter, USA). The pH meter was standardized using buffer solutions of pH values: 4, 7, 9, and 12.

**Adsorbate Solution**

Synthetic stock solution of heavy metals was prepared by dissolving required quantity of Analytical grade salts (Merck®) in the distilled demineralised water. The salts used are cadmium chloride, zinc chloride, manganese chloride, mercury chloride, nickel nitrate, copper nitrate, lead nitrate for Zn(II), and Hg(II), respectively, for the preparation of stock solution. The stock solution was further diluted with distilled demineralised water to desired concentration for obtaining the test solutions.

**Immersion Enthalpy**

Immersion enthalpies of activated carbons were determined in solutions of Zn$^{2+}$ and Hg$^{2+}$ with concentrations ranging from 20 to 100 mg∙L$^{-1}$ for the maximum adsorption pH of 5.1. Immersion enthalpies were also determined for 100 mg∙L$^{-1}$ solutions at all pH values studied. This determination was performed in a heat conduction microcalorimeter with a stainless steel calorimetric cell (Fig. 1) [22]. 30 mL of the solution to be used were pre-heated at 298 K; then placed in the cell. A sample of approximately 0.500 g activated carbons was weighed and placed inside the calorimetric cell in a glass ampoule. Microcalorimeter was then assembled. When the equipment reached the temperature of 298 K, potential readings were registered after a period of approximately 15 minutes, with readings every 20 seconds, glass ampoule was broken and generated thermal effect registered. Electric potential readings continue for approximately 15 minutes more and at the end of the experience, the equipment was electrically calibrated.
Results and Discussion

$N_2$ Adsorption–Desorption Isotherms

Figure 2 shows the nitrogen adsorption–desorption isotherms of ZnCl$_2$-activated and KOH-activated carbons obtained (ACZ2, ACZ3, ACK2, and ACK3). Identification of the activated carbons according to the chemical agent and temperature of activation were given in Table 1. From the shape of the isotherms, it may be stated that all activated carbons exhibit Type I isotherms with an almost horizontal plateau at higher relative pressures, indicating highly microporous materials with a narrow pore size distribution. Some of the isotherms show an increasing slope for values $P/P_0 > 0.85$. This characteristic indicates the development of wider pores. The desorption branches of the isotherms show hysteresis loops which reveal a development of meso and
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macroporosity\[9\]. This figure shows additionally H\(_3\) hysteresis loop; these hysteresis are usually found on solids consisting of aggregates or agglomerates of particles forming slit shaped pores (plates or edged particles like cubes), with nonuniform (type H\(_3\)) size and/or shape. Hysteresis is usually due to a different behavior in adsorption and desorption. For example in pore formed by parallel plates the meniscus is at (radius=\(\infty\)) during adsorption (condensation does not take place at any relative pressure) and cylindrical (radius .half the distance between plates) during desorption. Typical examples of this class are active carbons and zeolites [2, 3, 14, 15].

Physical properties of the activated carbon prepared at different impregnation ratios are shown in Table 1. The surface areas and total pore volumes of the ZnCl\(_2\)-activated and KOH-activated carbons increase from ACZ2 to ACZ3 at 700˚C and ACK2 to ACK3 at the same temperature.

<table>
<thead>
<tr>
<th>Sample</th>
<th>(N_2) a 77 K</th>
<th>(S_{BET}) m(^2)/g</th>
<th>(V_0) cm(^3)/g</th>
<th>(V_{meso}) cm(^3)/g</th>
<th>(V_t) cm(^3)/g</th>
<th>(V_o/V_t)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ACZ2</td>
<td>745</td>
<td>0.61</td>
<td>0.17</td>
<td>0.80</td>
<td>0.76</td>
<td></td>
</tr>
<tr>
<td>ACZ3</td>
<td>823</td>
<td>0.68</td>
<td>0.22</td>
<td>0.92</td>
<td>0.74</td>
<td></td>
</tr>
<tr>
<td>ACK2</td>
<td>934</td>
<td>0.78</td>
<td>0.28</td>
<td>1.02</td>
<td>0.77</td>
<td></td>
</tr>
<tr>
<td>ACK3</td>
<td>1058</td>
<td>0.85</td>
<td>0.34</td>
<td>1.23</td>
<td>0.69</td>
<td></td>
</tr>
</tbody>
</table>

The maximum surface areas were obtained at 700˚C for IRs (impregnation ratio) 1:3. We synthesized the activated carbons prepared by ZnCl\(_2\) at 700˚C as optimum temperature were also used by other researchers [10,11]. The increase in porosity with IR can be attributed to the release of tars from the cross-linked framework generated by treatment of the chemical reagents. In the KOH-activated carbons, synthesized at 700˚C causes an increase on the BET surface areas and total pore volumes. Maximum porosity occurred again at a IR’s 1:3. The maximum surface area and total pore volume were obtained as 1058 m\(^2\)/g and 1.23 cm\(^3\)/g, respectively for activated carbon ACK3. The minor obtained was surface area and total pore volume for the sample ACZ2 with 745 m\(^2\)/g and 0.80 cm\(^3\)/g, respectively for activated carbon. The presence of metallic potassium will intercalate to the carbon matrix. This phenomenon results in widening of the spaces between carbon atomic layers and increase in the total pore volume and surface area.

The impregnation ratio (IR) has a strong effect on the development of the porosity. With increasing chemical ratio from 2 to 3, the surface areas and total pore volumes of the activated carbon increase. In ZnCl\(_2\) series, the surface area and total pore volume of the activated carbon increased from 745 to 843 m\(^2\)/g and from 0.80 to 0.92 cm\(^3\)/g, respectively, as the chemical ratio increased from 1 to 3 (ACZ2 and ACZ3). However, the micropore volume of the activated carbon only slightly increase from 0.61 to 0.68 cm\(^3\)/g as the chemical ratio increased from 2 to 3. The experimental results suggested that ZnCl\(_2\) not only developed new pores but also enlarged existing pores by choosing an appropriate ZnCl\(_2\)/bagasse ratio. In KOH series, surface area, \(V_{total}\) and \(V_{micro}\) increase with increasing IR. Maximum values of \(S_{BET}\), \(V_{total}\) and \(V_{micro}\) were obtained as 1058 m\(^2\)/g, 085 cm\(^3\)/g and 1.23 cm\(^3\)/g, respectively. This indicates that both surface pyrolysis and interior etching process occur simultaneously during the preparation of activated carbons. Similar results were obtained by other researchers.
The composition of the waste of coffee is shown in Table 2. Low ash content (1.97%) in the waste coffee is a positive factor for production of activated carbons, since the mineral matter, due to the character hydrophilic, promoting the adsorption of water, competing with other compounds of interest. We can observe the increase in content carbon (between waste coffee and the activated carbons synthesized), due to the elimination of hydrogen and oxygen in the process of pirolysis [14].

Table 2. Composition elemental of waste coffee.

<table>
<thead>
<tr>
<th>Material</th>
<th>C  (%)</th>
<th>H  (%)</th>
<th>N  (%)</th>
<th>O1 (%)</th>
<th>Ash (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Waste Coffee</td>
<td>41.00</td>
<td>6.43</td>
<td>1.23</td>
<td>49.36</td>
<td>1.98</td>
</tr>
<tr>
<td>ACZ2</td>
<td>62.00</td>
<td>4.21</td>
<td>1.03</td>
<td>31.31</td>
<td>1.45</td>
</tr>
<tr>
<td>ACZ3</td>
<td>66.43</td>
<td>3.98</td>
<td>1.15</td>
<td>26.98</td>
<td>1.46</td>
</tr>
<tr>
<td>ACK2</td>
<td>68.23</td>
<td>3.76</td>
<td>1.76</td>
<td>24.14</td>
<td>2.11</td>
</tr>
<tr>
<td>ACK3</td>
<td>70.14</td>
<td>3.24</td>
<td>1.87</td>
<td>22.43</td>
<td>2.32</td>
</tr>
</tbody>
</table>

The carbon contends increased with the treatment chemical reaching a value 70.14% with ACZ3.

Monocomponent Adsorption of Metal Ions

Figure 3 and figure 4 show the isotherm curves of both metal ions onto the two activated carbons. Adsorption isotherms were modelled following Freundlich’s equation [23-25]:

\[ q_e = K_f c_e^{1/n} \]

where \(q_e\) is equilibrium adsorption capacity (mmol·g\(^{-1}\)); \(c_e\) is equilibrium concentration (mmol·L\(^{-1}\)); \(K_f\) is the Freundlich parameter (mmol\(^{1-1/n}\) L\(^{1/n}\) g\(^{-1}\)); \(1/n\) is the Freundlich parameter.
Figure 3. Monocomponent isotherm of Zn(II) onto ACK2 and ACZ2.

![Figure 3](image.png)

Figure 4. Monocomponent isotherm of Hg(II)) onto ACK3 and ACZ3.

The Freundlich parameters, $K_f$ and $1/n$, are presented in Table 3 where $r^2$ is the correlation coefficient of the linearized equation. Values of Freundlich’s parameter $1/n$ lower than 1 show a favorable adsorption of metal ions onto the activated carbon from residues coffee, equilibrium adsorption capacities $q$ are high, from 0.002 to 0.380 mmol·g$^{-1}$ for Hg on ACK3 and from 0.002 to 0.330 mmol·g$^{-1}$ for ACZ3. For Zn(II) on ACK2 from 0.002 to 0.300 mmol·g$^{-1}$, and from 0.001 to 0.274 mmol·g$^{-1}$ for ACZ2. These range show better adsorption capacities for the same ions with previous studies performed onto granular activated carbons [5]. Moreover, Hg(II) isotherm present a better adsorption capacity than that obtained on rayon-based activated carbon fibers reported in literature [31]: adsorption capacities are about 0.20 mmol·g$^{-1}$ for equilibrium concentrations ranging from 0 to 0.3 mmol·L$^{-1}$.

Table 3. Results of adsorption isotherms for Cu(II) and Pb(II) in monocomponent an binary system.

<table>
<thead>
<tr>
<th>Metal ion</th>
<th>CBC</th>
<th>Freundlich parameters</th>
<th>$r^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$K_f$</td>
<td>$1/n$</td>
</tr>
<tr>
<td>Monocomponent adsorption</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hg(II)</td>
<td>ACK3</td>
<td>0.345</td>
<td>0.145</td>
</tr>
<tr>
<td></td>
<td>ACK2</td>
<td>0.296</td>
<td>0.265</td>
</tr>
<tr>
<td>Zn(II)</td>
<td>ACZ3</td>
<td>0.283</td>
<td>0.335</td>
</tr>
<tr>
<td></td>
<td>ACZ2</td>
<td>0.249</td>
<td>0.121</td>
</tr>
<tr>
<td>Multicomponent adsorption</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hg(II)</td>
<td>ACK3</td>
<td>0.256</td>
<td>0.476</td>
</tr>
<tr>
<td></td>
<td>ACZ3</td>
<td>0.186</td>
<td>0.557</td>
</tr>
</tbody>
</table>
For the activated carbons synthesized, the following order of both metal ions, the following order is observed for metal ions adsorption: Hg(II) > Zn(II). We can imagine that the high ionic radius of Zn(II) (1.34 Å) compared to that of Hg(II) (1.16 Å) induces a quick saturation of adsorption sites, because of a steric over-crowding. The adsorption surface available for Hg(II) ions is then larger than that available for Zn(II) ions. It results in lower maximum adsorption capacities for Hg(II) than for Zn(II). Previous research has reported that the preference of hydrous solids for metals has been related to the metal electronegativity [26-31]. The reported effect is a stronger attraction for the higher electronegativity, which seems to be also observed in the case of adsorption onto activated carbons. Moreover, for both metal ions the adsorption capacity \( K_f \) decreases following the order: ACK > ACZ showing a better adsorption onto ACK3 than onto of ACZ3 and ACZ2. In the present case, for pH of 5.1, metal ions Hg(II) and Zn(II) are mainly under the ionic form \( \text{Hg}^{2+} \) and \( \text{Zn}^{2+} \). Thus the development pore volume, specially mesopores, of the ACK and ACZ allows a larger adsorption than that of some granular activated carbon.

**Adsorption Competition between Both Metal Ions**

Figure 5 presents isotherm curves obtained for co-adsorption of Hg(II) and Zn(II) onto ACK and ACZ. For both metal ions and the two activated carbons, co-adsorption induces a decrease of adsorption capacity but percent of decrease depends on both metal ion and adsorbent as presented in Table 2 where Freundlich parameters are given for binary isotherms. For a same initial concentration (0.30 mmol·L\(^{-1}\)) the ratio of initial adsorption rates of Hg(II) and Zn(II) \( \gamma_{\text{Hg(II)}}/\gamma_{\text{Zn(II)}} \) were, respectively, equal to 0.85 on ACK and 0.73 on ACZ. The faster adsorption on ACK of the higher molecular weight and ionic radius ion, Hg(II) and Zn(II), was indeed related to the meso or macroporous character of these activated carbons as noted in other studies [28-31]. The comparison of initial adsorption rates for the two adsorbents could explain the co-adsorption behavior of metal ions. On one hand, the slower adsorption kinetic of Zn(II) on ACK2 may explain its larger removal decrease (30 %) when mercury is present in solution and decrease a 35 % for Hg(II) onto ACK3 in presence of Zn(II). On the other hand, show identical results for the decrease of the Zn(II) in presence of Hg(II) onto ACZ2 and ACZ3.
Figure 5. Adsorption competition of both metals ions, Zn(II) and Hg(II) onto activated carbon synthesized.

Immersion Enthalpies

Figure 6 show of results show that immersion enthalpies is increased a low concentrations initial concentrations onto ACZ and ACK. Initial concentrations above 0.2 mmol·L\(^{-1}\) exhibits a steady enthalpic increment up to 30 J·mol\(^{-1}\). The highest value of enthalpy was obtained for the immersion of ACK3 in the mercury ions solutions, with the while the lower value of immersion enthalpy was obtained for the immersion of zinc) with onto ACZ2. Enthalpy values were between \(-31.0 \text{ J·g}^{-1}\) (Hg(II)-ACK3 with Zn(II)) and \(-28.0 \text{ J·g}^{-1}\) (Zn(II)–ACZ2), as shown in Figure 6. This behavior agrees with textural characteristics of AC’s and the sizes of the ions under study. It should be noted that the behavior of immersion enthalpies in the solid prepared in this work, is very similar to that of an isotherm. These results show that of Calorimetry is a tool also allows the monitoring of ion adsorption on activated carbon and their results are consistent with those obtained by conventional techniques.

![Figure 6. Immersion enthalpies of the Monocomponent and binary for Hg(II) and Zn(II) system onto BCN.](image)

Conclusions

This work has investigated metal ions adsorption onto economical adsorbents, activated carbon from waste of coffee. These adsorbents seem to be efficacious to remove metal pollution from water, with monocomponent equilibrium adsorption capacities ranging from from 0.002 to 0.380 mmol·g\(^{-1}\) for Hg on ACK3 and from 0.002 to 0.330 mmol·g\(^{-1}\) for ACZ3. For Zn(II) on ACK2 from 0.002 to 0.300 mmol·g\(^{-1}\), and from 0.001 to 0.274 mmol·g\(^{-1}\) for ACZ2. These values are larger than those obtained with other granular activated carbon, and are dependent on both activated carbon properties (specific surface area, micropore volume between other properties) and metal ions characteristics (ionic radius, electronegativity). The ACK3 present a major adsorption capacity that ACZ2 related with the area properties. The adsorption competition between both metal ions was related to monocomponent kinetic rates, a faster adsorption velocity involving a quicker saturation of
adsorption sites. The calorimetric results shows that allow monitoring thses type the system obtain results agree with conventional techniques.

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