1. Introduction

Heavy metals like Cd, Ni and Pb are widely used in modern chemical industries such as metal plating, battery manufacturing, fertilizer, paper, pesticides, electronics, and production of different plastics such as polyvinyl chloride [1]. Large amounts of wastewater are produced from these industries, and since heavy metals can easily accumulate in the living organisms’ bodies and because they possess high toxicities, the release of them in water is a permanent threat to health and to the environment. Therefore, an efficient treatment of industrial wastewater is crucial. For this purpose, the use of adsorbents is an economic and efficient option, and in recent years there has been a lot of interest on the development of novel materials, such as functionalized carbon materials.

Between the different available treatments for the modification of carbonaceous materials, oxidation is mostly used due to the simplicity of the method, and because the insertion of acidic functional groups can greatly enhance the materials heavy metals adsorption capacity. Moreover, these groups are the starting point for further functionalization of the carbon surface, thus the materials can be used for removal of other different pollutants in water. Among the different carbon materials, recently, activated carbon fibers (ACFs) have gained interest due to their fast adsorption and desorption rates, big volume and surface area, and easiness of handling. In our previous study [2], we evaluated different oxidation conditions for ACFs and obtained for the first time an oxidized activated carbon fiber (Ox-ACF) with exceptionally high adsorption capacities for aqueous Pb(II) (2.7 mmol g⁻¹), but at the same time, the porous structure of the fiber was highly decreased (385 m² g⁻¹). In the present study, we present recent results that showed that using higher concentrations of oxidant at shorter times could give similar high adsorption capacities, with the difference that the big specific surface area of the fibers remained almost unchanged (ca. 1500 m² g⁻¹). Moreover, the oxidized activated carbon fibers were characterized by their amount of soluble compounds in NaOH (oxidation debris), and it was determined to be less for samples produced at shorter oxidation times. Additionally, column adsorption-desorption experiments were done for a single metal solution of Pb(II) and for a mixture solution of Pb(II), Cd(II) and Ni(II), where Pb(II) ion was found to be preferably adsorbed by the oxidized activated carbon fiber.

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findings on the study of the oxidation conditions, and we could obtain Ox-ACFs with similar high adsorption capacities for aqueous Pb(II), which preserved the porous structure almost unchanged. Additionally, we measured the Ox-ACFs amount of soluble compounds in NaOH solution, a characterization that has lately been described for the oxidation of graphene and carbon nanotubes materials [3–6], but to our knowledge has not been described yet for activated carbon materials. These soluble compounds are referred as oxidation debris and correspond to carboxylated compounds with high aromaticity, and that are comparable to fulvic acids [7]. Their possible release in water represents a potential negative impact on the quality use of the adsorbents and wastewater treatment [8], thus it is an important characterization that should be considered for carbon adsorbent materials. Moreover, we evaluated the use of the produced Ox-ACFs in column adsorption-desorption experiments for aqueous Pb(II) solutions, and for a metal mixture solution of Pb(II), Ni(II) and Cd(II).

2. Materials and methods

Commercial activated carbon fiber KF 1500 LDA (KF) was purchased from Toyobo Co. Ltd., Japan. It is described by the manufacturer as a microporous material made from Rayon, and that has a fiber diameter around 0.5–10 nm. All reagents were purchased from Kanto Chemical Co., Inc. (Japan), used as received and their diluted solutions were prepared using distilled water.

2.1 Oxidation and characterization of the fibers

The activated carbon fiber KF was oxidized with ammonium persulfate solutions (APS) (\((\text{NH}_4)_2\text{S}_2\text{O}_8\) in 1 mol L\(^{-1}\) \(\text{H}_2\text{SO}_4\)), as described in our previous study [2]. The Ox-ACFs were denoted as \(a\)APS\(-b\)-\(c\), where \(a\), \(b\) and \(c\) indicate the oxidant solution concentration in mol L\(^{-1}\), the oxidation temperature in °C and the oxidation time in hours, respectively. For example, the sample 1.4 APS-30-72 was done under the following oxidation conditions: 1.4 mol L\(^{-1}\) APS, at 30 °C for 72 h.

Textural characteristics of the fibers were evaluated by B.E.T. method using \(\text{N}_2\) adsorption and desorption isotherms at -196 °C, measured with surface area analyzers SA 3100 (Beckman Coulter, Inc., U.S.A.) and Belsorp mini II (MicrotracBEL Corp., Japan).

The fibers were treated with 0.1 mol L\(^{-1}\) NaOH to determine their soluble compounds. In a 50 mL Erlenmeyer flask, 0.5 g of the samples was added to 25 mL of 0.1 mol L\(^{-1}\) NaOH, heated and stirred at 70 °C for 2 h. The fibers were separated from the solution by filtration, and the filtrate was diluted to half with 0.08 mol L\(^{-1}\) HCl. UV-Visible Spectrometer UV-2550 (Shimadzu Corporation, Japan) was used for the measurement of the solutions absorption spectrums. Absorption values at 249.5 nm were normalized by dividing by the amount of sample used (g), to use them for comparison between the samples.

2.2 Batch and column adsorption experiments

Batch adsorption experiments for Pb(II) ion in aqueous solution were done as described in our previous study [2]. For column experiments, an arrangement as the one described in Fig.1 was used. A pyrex glass tube with an internal diameter of 7.6 mm and length of 40 cm was used as the column. Specified amount of the adsorbents was wet-packed in the column to prevent air gaps. About 1 cm of height of glass wool was placed on the top and bottom of the adsorbent bed to prevent loss of the adsorbent. A peristaltic pump was used to operate the experiment, for the initial runs in down-flow mode and for later runs in up-flow mode. The experiments were held at room temperature, around 22 °C. Distilled water was flowed overnight before the adsorption experiments to reduce the presence of air bubbles. The pH of the influent solutions was set to 5.0 by adding NaOH solutions. Effluent samples were collected at different interval times, and their pH values and element concentration were measured.

Columns experiments were done for 2.0 APS-30-3 (0.5 g, approximate bed height 4.5 cm), with an aqueous solution of 100 mg L\(^{-1}\) Pb(II). For the first experiment, the solution was flowed down the column at 5 mL min\(^{-1}\) (Fig. 1 (a)). After the adsorption experiment was finished, distilled water was flowed through the column for 2 h to remove any non-adsorbed metal ions. Later, the column was desorbed at the same flow rate using a solution of 0.5 mol L\(^{-1}\) HNO\(_3\). When desorption was finished, distilled water was passed through the column until the pH remained constant. Then, a second adsorption-desorption experiment was held, with the same conditions as described before. After the two first adsorption-desorption cycles, a third one was done but this time in an up-flow mode (Fig. 1 (b)), maintaining other conditions the same as before.
Up-flow column experiments were done for 2.0 APS-30-6 (0.3 g, approximate bed height 3.5 cm) with an equimolar mixture solution of Ni(II), Cd(II) and Pb (II) (0.15 mmol L\(^{-1}\)) at a flow-rate of 3 mL min\(^{-1}\). Other experiment conditions were kept the same as for the single solution experiments.

2.2.1 Analysis of the breakthrough curves

The breakthrough time (\(t_b\)) was determined to be the time when the effluent concentration was 1% or less than the influent concentration. The saturation time (\(t_s\)) is set as the time when the concentration of the effluent becomes constant and breakthrough curves become flat \[9\], in the present experiments it was established as the time when the effluent concentration was 90% or more than the influent concentration.

The adsorbed amount of the metal was calculated as:

\[
Q = \frac{R}{Wm} \int_0^t (C_0 - C) dt
\]

where \(R\) corresponds to the solution flow rate (mL min\(^{-1}\)), \(W\) corresponds to the molar mass of the element (g mol\(^{-1}\)), \(m\) is the adsorbent weight (mg), \(C_0\) is the influent solution concentration (mg L\(^{-1}\)), \(C\) is the effluent solution concentration (mg L\(^{-1}\)) at any time \(t\) (min).

The volume of effluent treated, \(V\) (mL), was calculated using

\[
V = Rt
\]

3. Results and discussion

3.1 Properties of the oxidized activated carbon fibers (Ox-ACFs)

Activated carbon fiber KF was oxidized under different oxidant concentration and oxidation time conditions; the properties of the obtained Ox-ACFs are listed in Table 1. As described in our previous study, the specific surface area \(S_{BET}\) of the microporous fibers was reduced with increasing time because the porous structure gradually got destructed and the pores of the fiber started progressively to get blocked by the increasing amount of acidic functional groups, inhibiting the N\(_2\) gas adsorption. The adsorption of the lead ions was mainly influenced by the strong interaction of them with the acidic functional groups that act as the adsorption sites, rather than the porous structure of the fiber.

For the present results, oxidized samples with high adsorption capacities for Pb(II) and that maintained high specific surface area values were obtained at very short oxidation times (2.0 mol L\(^{-1}\) APS, 1–12 h). Moreover, the amount of soluble compounds in NaOH solution was higher for samples oxidized at longer times. These compounds concentrations are reflected in the solution coloration, as shown in Fig. 2. For the samples prepared at the longest periods of time, there was a brownish color, in relation to the increasing absorption values in the UV-Vis spectrum, as shown in Fig. 3. The highest peak of absorption was around 250 nm, in agreement with the

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**Fig. 1** Arrangements used for column adsorption-desorption experiments, (a) down-flow mode, (b) up-flow mode. The arrow indicates the flow direction.
results for oxidation debris of graphene oxide [6] and close to the wavelength used to determine organic matter in water solutions [10, 11].

For graphene oxide, these substances have been classified as fulvic-like or humic-like structures, where the first ones possess higher molecular weights and are insoluble in water under pH 2 [12]. For the filtrate solutions of the Ox-ACFs, there was no visible precipitation when decreasing the pH to 1.9, as an indication of the small size of the compounds. Several studies for oxidized carbon materials have proposed that these soluble compounds structures have weights around 200‒900 Da [7, 8, 13]. The decomposition of these compounds reflects aggressive oxidation conditions and their solubilization in alkaline solutions will represent a threat to the quality of water, as it is an organic matter [8]. However, for the adsorption of heavy metals presented in this study, it does not represent a problem since all the heavy metals solutions had low pH values (<6).

A scheme of the behavior of the soluble fragments is shown in Fig. 4. Analogous to the oxidation debris of graphene oxide [4], in acidic solution the carboxy groups of the alkaline soluble compounds are protonated, thus, they adhere to the surface of the ACF, due to the strong van der Waals forces, π-π interactions and hydrogen bond. However, in basic solutions, the carboxy and phenol compounds

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| Sample    | $S_{BET}$ (m$^2$ g$^{-1}$) | $Q_e$ (mmol g$^{-1}$) | Soluble compounds in 0.1 mol L$^{-1}$ NaOH | Relative absorbance at 249.5 nm (g$^{-1}$) |
|-----------|---------------------------|-----------------------|------------------------------------------|------------------------------------------|
| KF        | 1560                      | 0.21                  | 0.3                                      |                                          |
| 2.0 APS-30-1 | 1447                  | 0.93                  | 2.5                                      |                                          |
| 2.0 APS-30-2 | 1513                  | 1.2                   | 1.0                                      |                                          |
| 2.0 APS-30-3 | 1510                  | 1.8                   | 4.3                                      |                                          |
| 2.0 APS-30-6 | 1227                  | 2.4                   | 3.4                                      |                                          |
| 2.0 APS-30-12 | 1134                 | 2.4                   | 5.6                                      |                                          |
| 2.0 APS-30-16 | 713                   | 2.3                   | 11                                       |                                          |
| 2.0 APS-30-24 | 681                   | 2.5                   | 24                                       |                                          |
| 2.0 APS-30-72 | 7                     | 2.8                   | 51                                       |                                          |
| 1.4 APS-30-3 | 1200                    | 1.3                   | 7.3                                      |                                          |
| 1.4 APS-30-6 | 1175                    | 1.8                   | 5.5                                      |                                          |
| 1.4 APS-30-12 | 1286                  | 1.7                   | 6.1                                      |                                          |
| 1.4 APS-30-24 | 735                    | 2.4                   | 23                                       |                                          |
| 1.4 APS-30-48 | 385                   | 2.6                   | 50                                       |                                          |
| 1.4 APS-30-72 | 346                    | 2.8                   | 47                                       |                                          |
| 0.8 APS-30-72 | 485                    | 2.5                   | 36                                       |                                          |
| 0.4 APS-30-72 | 1381                   | 1.7                   | 36                                       |                                          |
are negatively charged, so repulsion dominates and these compounds are desorbed into the solution. This was verified by adding HCl solutions to a flask that contained one of the solutions that presented coloration and the NaOH treated Ox-ACF, and it was observed that after some time, the color disappeared caused by the readsorption of the soluble compounds on the ACF surface. These results are in agreement with those presented by Wang et al. for oxidized multi-walled carbon nanotubes [7].

3.2 Column Experiments

Pb(II) adsorption experiments were done in a column for 2.0 APS-30-3. Fig. 5 presents an adsorption and a desorption curve, and Table 2 lists the obtained data for these curves.

Figure 5(a) shows the adsorption data for the column in down-flow mode, at a rate of 5 mL min⁻¹. A very steep adsorption breakthrough curve can be seen, and with the same tendency, the pH of the effluent solution changed. The pH initially dropped with respect to the influent solution because of the liberation of protons from the Ox-ACF surface, due to their exchange with the heavy metal cations. As the active sites gradually started to be less available, there was less exchange of metal ions and protons, thus, the effluent solution pH and metal concentration increased. As listed in Table 2, breakthrough was reached after treating 550 mL of solution (Vₜ), corresponding to an adsorption of 0.53 mmol g⁻¹ of Pb (II) (Qₜ). The adsorption value at saturation point was 0.67 mmol g⁻¹(Qₛ), which is smaller than the batch adsorption experiments (1.8 mmol g⁻¹). This difference may be the result of the incomplete exhaustion of the column, and that a higher pH for the initial solution might be necessary to reduce the competition between protons and Pb(II) ions for the adsorption sites.

After the first adsorption, desorption was done for the column with 0.5 mol L⁻¹ HNO₃ at a flow rate of 5 mL min⁻¹, whose results are presented in Fig. 5(b). A sharp decrease in concentration can be seen, and after 30 min (150 mL treated), there was no more desorption of ions as the concentration remained close to zero. Similar results have been observed for other metal ions desorption curves for adsorbents [14]. Nevertheless, the desorption removal was 77%, indicating that some Pb(II) ions remained adsorbed by very strong sites in the column adsorbent. However, after desorption, a second adsorption experiment was done and the results were almost the same to the first cycle.

| Cycle            | Adsorption | Desorption |
|------------------|------------|------------|
|                  | t_b (min)  | V_b (mL)  | Q_b (mmol g⁻¹) | t_s (min) | V_s (mL) | Q_s (mmol g⁻¹) | Removal (%) |
| 1st down-flow    | 110        | 550       | 0.53           | 210        | 1050     | 0.67           | 77          |
| 2nd down-flow    | 120        | 600       | 0.56           | 200        | 1000     | 0.70           | 99          |
| 3rd up-flow      | 90         | 450       | 0.58           | 230        | 1150     | 0.81           | 95          |

Fig. 4 Scheme of the behavior of the soluble compounds in NaOH solution. The black portion represents the Ox-ACFs and the chemical structure represents the soluble compounds.
adsorption curve, and the second desorption was reached almost completely. These results show the possibility of reusing the Ox-ACF after its regeneration. After the second cycle, adsorption was done again but in an up-flow system, to prevent channeling and evaluate if this had some effect on the adsorption results. As shown in Table 2, the adsorbed amount of Pb(II) was higher, indicating a more effective performance of the column. The third desorption cycle was also very effective to remove the previously adsorbed metal ions (95%). These results suggest that indeed there was a better contact of the solution with the adsorption bed in the up-flow mode, this is the reason why other experiments were continued using that arrangement.

Industrial effluent solutions present more than one heavy metal ion, thus column adsorption experiments were done for 2.0 APS-30-6, with a mixture of Pb(II), Cd(II) and Ni(II), as shown in Fig. 6. The breakthrough curve has a similar shape to that of the single metal adsorption of Pb(II), though breakthrough can be seen at different adsorption volumes. As listed in Table 3, breakthrough for Cd(II) and Ni(II) occurred after 192 mL of treated volume and presented a very similar behavior. The obtained adsorption capacities at the breakthrough time \( Q_b \) and at saturation time \( Q_s \), were only slightly higher for Ni(II) than for Cd(II). For Pb(II), breakthrough was reached at much higher volumes, and consequently higher adsorption capacity values were obtained. The pH values of the effluent solution changed similarly to the single metal solution experiment, where the first change reflected the breakthrough of Cd(II) and Ni(II), and the second change the breakthrough of Pb(II).

In general, for all experiments, the breakthrough times followed the increasing order: Cd = Ni < Pb. This selectivity order is the same for the weakly acid cation exchange resin Amberlite IRC 86 (carboxylic acid) [15], and it can be explained by the capacity of the cations to neutralize the COOH groups [16], namely, the facility to form a stable complex between the proton donors and the metal cation (Fig. 7). According to the complexation theory [17], the RCO\(_2\)\(^-\) group acts as a ligand, that because of its high charge density and because it is not very polarizable, can be described as a hard base. As for the metal cations, Cd(II) is classified as a soft acid and Pb(II) and Ni(II) as intermediate acids. These can explain why Cd(II) has
less affinity for the adsorption sites since hard bases tend to form more stable complexes with hard acids. Moreover, Pauling electronegativity values for the metals follow the order: Pb(II) > Ni(II) > Cd(II) (Table 4). A higher electronegativity means that they hold more strongly their electrons, so they are less polarizable, and thus can form a more stable complex with the carboxylate anion. Moreover, the bigger ionic radius of Pb(II) (Table 4), could favor the possibility of it binding with distant acidic functional groups [18] since the distribution of them in the surface is probably not homogeneous.

![Structure of the possible complex formed by the divalent metal cations and the carboxy groups.](image)

**Table 4** Properties of the heavy metal ions used in the mixture adsorption experiments.

| Metal  | Hydrated radius (Å) | Electronegativity |
|--------|---------------------|-------------------|
| Cd(II) | 0.96                | 1.69              |
| Ni(II) | 0.72                | 1.91              |
| Pb(II) | 1.2                 | 2.31              |

### 4. Conclusions

High adsorption capacities for aqueous Pb(II) in batch system were obtained for oxidized activated carbon fibers (Ox-ACFs) prepared at high concentrations of oxidant and short periods of time (1-12 h) since longer periods of oxidation time tend to destruct the original fiber structure in a higher degree, with the detachment of carboxylate fragments in alkaline solutions. The obtained Ox-ACFs could be used for column experiments of a single metal solution of Pb(II), and a mixture of Pb(II), Cd(II) and Ni(II), demonstrating the preferable adsorbability of Pb(II) by the modified ACFs.

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