INSIGHT OF THE REMOVAL OF NICKEL AND COPPER IONS IN FIXED BED THROUGH ACID ACTIVATION AND TREATMENT WITH SODIUM OF CLAY

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Abstract - The bentonitic clays show good adsorptive characteristics, being used as alternative material for removing metals. This study evaluates several treatments (calcination, acid activation and treatment with sodium) of bentonite type Bofe in the removal of nickel and copper. Analyses were performed for physicochemical characterization of clay using the techniques: X-ray fluorescence (XRF), thermal analysis (TG and DTA), X-ray Diffraction (XRD), the ethylene glycol monoethyl ether (EGME) method, N2 adsorption (BET) and Scanning Electron Microscopy (SEM). Among the changes induced by acid activation and sodium transformations, the treatment with sodium chloride in fixed bed showed the highest performance in the monocomponent removal of nickel and copper.

Keywords: Bentonite clay; Adsorption; Physicochemical characterization; Metals removal.

INTRODUCTION

Metals are highly reactive and bioaccumulative, and therefore the body is unable to eliminate them. The most common are Cu, Mn, Mo, Zn, Ni, V, Cd, Cr, Hg and Pb and some are physiologically essential for many plants and animals, in particular copper, which controls the enzyme that stimulates the formation of connective tissues and pigments that protect the skin, and thus contributes to human health. However, excessive levels of these elements can be extremely toxic (Saxena and Misra, 2010).

The application of various alternative materials for sorption or elimination of metals in wastewater has been investigated due to its numerous economic advantages (Vieira et al., 2014; Zola et al., 2012; Oueslati et al., 2011; Torab-Mostaedi et al., 2010; Attia et al., 2010; Yilmaz et al., 2010; Giraldo and Moreno-Piraján, 2008; Novakovic et al., 2008; Stathi et al., 2007; Ouhadi et al., 2006). The cost of clay is relatively low compared to other alternative adsorbents, including activated charcoal, natural and synthetic zeolites, and ion exchange resins. Clay minerals such as montmorillonite, vermiculite, illite and kaolinite are among the natural materials that have been investigated as adsorbents for metals (Turan et al., 2011; Otu-Owolabi and Unuabonah, 2011; Ghorbel-Abid et al., 2010; Mao et al., 2009; Bhattacharyya and Gupta, 2008; Sajidu et al., 2008). Another advantage of using clay as an adsorbent is due to its intrinsic
properties such as high specific surface area, excellent physical and chemical stability and other structural and surface properties (Chen et al., 2008).

Clays are widely used as barriers to prevent contamination of the subsoil and groundwater by the leaching of landfill containing metals. It is therefore important to study the adsorption of metals in these clays. These same adsorbents in the acid-activated and sodium acid-activated and sodium forms have been reported as adsorbents of metals (Oueslati et al., 2009; Özdemir and Yapur, 2009; Eren, 2008; Eren and Afsin, 2008; Bhattacharyya and Gupta, 2007).

Although the results involving the removal of metals with clays are significant and promising, there is still a need for a better understanding of these results considering the properties of adsorbents for optimizing the process conditions. Existing studies on the use of Brazilian bentonite type Bofe for removing metals have shown the need for research on the removal of metals by modified forms of that bentonite (Almeida Neto et al., 2014, 2012; Vieira et al., 2010a, b). Thus, this study has as its objective the evaluation of modified forms of Bofe clay in the removal of nickel and copper, individually, in a fixed bed system.

EXPERIMENTAL

Clay Adsorbent

Bofe type bentonite clay from the Northeastern region of Brazil (Boa Vista-PB) was used as adsorbent. Initially, a study was conducted with raw clay. However, this clay was not used as an adsorbent in a fixed bed due to its solubility. The clay was prepared by size classification and calcined at 500 °C for 24 hours in order to increase the mechanical resistance, dehydroxylation and to eliminate some impurities. In some cases, the adsorption capacity can also be enhanced on modified bentonitic clays. The temperature of calcination was determined by thermogravimetric analysis for a sample Bofe clay at a heating rate of 10 °C.min⁻¹ in air atmosphere; 24 hours of calcination was necessary for a decrease of the buffering pH of the clay.

The Cation Exchange Capacity (CEC) was determined in triplicate for raw and calcined samples of Bofe clay, using for the ionic exchange 2.5 g of solid for 100 mL of exchange solution. The concentration of Na⁺ ions displaced by NH₄⁺ from a 3 mol.L⁻¹ ammonium acetate solutions (Gupta and Bhattacharyya, 2008), brought into contact under stirring for 12 hours, was measured by Atomic Absorption and expressed in meq.(100g⁻¹) of solid according to Eq. (1):

\[
\text{CEC} = \frac{C_{Na^+} \cdot V_{NH_4^+}}{10 \cdot m \cdot f}
\]  

(1)

The surface area and meso- and micropore volumes were obtained by a nitrogen adsorption test at 77 K by using a Micromeritics Gemini device employing the BET method.

The ethylene glycol monoethyl ether (EGME) method was performed according to Cerato and Lutenegger (2002) in order to determine the specific surface area with a liquid. A total of 1 g of sample (75 μm sieved, oven-dried at 80 °C and cooled in a sealed desiccator) was spread into the bottom of a Petri dish with a diameter 90 mm and a height of 30 mm. The mass of the clay was determined using an analytical balance with an accuracy of 0.0001 g. All Petri dishes had plexiglass lids on top to prevent the clays from being pulled out of the dish during the evacuation process. Approximately 3 mL of laboratory-grade EGME was added to the clays and mixed together to create a uniform slurry. Afterward, the dishes were placed into glass-sealed vacuum desiccators and allowed to equilibrate for 20 min. As drying agent, a mix of 100 g of 40-mesh anhydrous calcium chloride and 20 mL of EGME desiccant was placed in a glass dish at the bottom of the desiccators. The desiccators were evacuated using a vacuum of approximately 0.2 mmHg. After being evacuated, the dishes were weighed every 48 – 65 h using an analytical balance. If the mass difference between the two measurements was more than 0.001 g, then the samples were placed in the desiccators again for additional vacuum. This process was continued until the sample weight did not change more than 0.001 g.

The quantity of EGME required to cover 1 m² of clay surface with a monomolecular layer is 2.86 × 10⁻⁴ g. The specific surface can be calculated from Eq. (2)

\[
SSA = \frac{W_a}{0.000286 \cdot W_s}
\]  

(2)

The XRD analysis was performed using copper Kα radiation, voltage 40 kV, 40 mA current, step size of 0.02°, step time of 1s and 2θ range of 30-50°. The sample was packed in powder form (< 0.075 mm), pressed on a pedestal.

The micrographs for morphological analysis of the clays were obtained in a scanning electron microscope LEO, coupled to an Energy-dispersive X-ray
spectrum by EDX. The samples were initially vacuum dried for approximately 12 hours. Then, they were coated with gold using a voltage of 1 V and current of 3 Na for 180 seconds under argon atmosphere.

The chemical compositions of clays were determined with an X-rays fluorescence spectrometer, using samples in a fused borate matrix.

**Acid Activation and Treatment with Sodium Ion**

The acid activation of Bofe clay was performed to improve its adsorptive properties, as described in the literature (Vengris et al., 2001; Bailey et al., 1999; Altin et al., 1998). The authors report that some of the modified adsorbents show good adsorption capacities for metals due to the increased number of active binding sites formed by modification, optimizing the properties of ion exchange and the formation of new functional groups that promote the absorption of the metal.

The acid activation of the adsorbent carried out in this work is described in Bhattacharyya and Gupta (2007) and consisted of a treatment with sulfuric acid. A quantity of 20 g of clay was refluxed with 200 mL of 0.25M H2SO4 for 3 hours. The resulting clay was vacuum filtered and washed with deionized water several times until it was free of SO42- and dried at 383 K to constant weight (24 hours). The material was finally calcined at 773 K for 24 hours and used as adsorbent, which is the first modified form of clay used in this work.

Treatment with sodium ions was the second modification of Bofe clay evaluated in this work. Calcined clay was treated with 1% NaCl solution (pH 3) in order to assess the influence of the treatment with sodium ions (sodium form) in the adsorption of nickel and copper in aqueous medium. The clay treatment with sodium ions was carried out in a fixed bed and consisted of letting a solution of 1% NaCl dissolved in water and pH adjusted to 3 with 1M HCl pass through the bed during 4 hours, so that Na+ cations were incorporated into the clay. The clay was washed with distilled water to be used as adsorbent.

In order to investigate changes in the capacity of removal of nickel and copper by treatment with sodium ions, another study of transformation of natural clay in its sodium form was also performed. This transformation was conducted with 1%NaCl (pH 3), room temperature, and 500 rpm agitation for 3 hours. The clay was then filtrated, dried at 60 °C for 48 hours, broken and calcined at 500 °C for 24 hours.

**Metal Adsorbate**

The adsorption experiments were conducted using aqueous solutions with Ni2+ and Cu2+ separately. A stock solution of 1000 ppm of metal ion was prepared by dissolving Ni(NO3)2·6H2O or Cu(NO3)2·3H2O in deionized water and used to prepare the adsorbate solutions in the desired concentrations.

The Ni (II) and Cu (II) solutions pH was maintained at a level below minimal precipitation in order to assure the occurrence of the adsorption process and not the chemical precipitation of nickel and copper ions in the hydroxide forms (Ni(OH)2 or Cu(OH)2). The pH range values adopted in this study were determined by metal speciation. Thus, nitric acid or ammonium hydroxide were used to adjust the natural pH of each solution of metal in contact with the solid adsorbent. The pH of the solutions was measured with a pH meter with automatic temperature compensation.

The concentration of the metal existing in the aqueous phase of the solutions submitted to nickel and copper adsorption assays was determined in the Atomic Absorption Spectrophotometer. The samples were collected using a continuous system (Automated Fraction Collector).

**Metal Speciation**

Speciation diagrams of copper and nickel as a function of pH were simulated using the programs Hydra and Medusa (Puigdomenech, 2004) in order to identify the different species in aqueous medium. These diagrams were plotted for removal at concentrations that correspond to the maximum concentrations of chemical species in ionic solution. The speciation was determined by considering the stoichiometric ratios of metal salts used.

**Dynamic Tests**

Dynamic adsorption experiments were performed in a porous bed system, consisting of an acrylic column 14 cm long and 1.4cm of internal diameter. The assays were performed using a mono-compound nickel and copper solutions with different concentrations employing Bofe calcined clay at 500 °C as adsorbent. The conditions for these assays were defined based on the study conducted in batch and preliminary fixed-bed tests.

The concentrations of copper and nickel ions used to feed the column, defined by metal speciation, were 1.57 and 1.70 mmol.L−1, respectively. The initial pH of the feed solution prepared by dissolving...
salts of copper and nickel was measured. When the pH of the solution differed from 5.0, it was adjusted by adding nitric acid solution or ammonium hydroxide solution, both 1 mol.L\(^{-1}\), until the desired pH value. The amount of clay used in the column experiments was 17 grams.

In order to determine the mass transfer zone (MTZ), the amounts of useful and total removal were calculated, which correspond to the capacity of metal removal until the breakthrough point \(q_u\) and saturation point \(q_s\), respectively. Eqs. (3) and (4) were obtained through mass balance in the column using its saturation data based on its breakthrough curves, where the area below the curve \((1−C/C_0)\) until the breakthrough point is proportional to \(q_u\), and until the bed exhaustion is proportional to \(q_s\):

\[
q_u = \frac{C_0V}{1000m} \int_{0}^{L} (1 - \frac{C}{C_0})dt
\]

(3)

\[
q_s = \frac{C_0V}{1000m} \int_{0}^{L} (1 - \frac{C}{C_0})dt
\]

(4)

The mass transfer zone (MTZ) can then be calculated based on the \(q_u/q_s\) ratio according to Eq. (5) (Geankoplis, 1993):

\[
MTZ = \left[1 - \frac{q_u}{q_s}\right]H_t
\]

(5)

MTZ has a maximum value which corresponds to the bed height \(H_t\) and, as the efficacy of mass transfer increases, this value decreases until reaching the ideal condition where MTZ is zero and the breakthrough curve is a step function.

The percentage of total removal (%RT) during adsorption was obtained considering the metal fraction in solution retained in the solid adsorbent, from total effluent used in the adsorption process until bed saturation. The amount of adsorbed metal is calculated by considering the curve area \((1−C/C_0)\) versus \(t\). The integral of metal adsorption curves was determined through Origin version 6.0 software.

**RESULTS AND DISCUSSION**

**Clay Characterization**

The chemical composition obtained by X-ray Fluorescence of raw and calcined clays is presented in Table 1. All elements present in the average composition show values similar to those of this clay class.

The results of the thermal analyses of the raw sample are shown in Fig. 1. The DSC curves show an endothermic loss of moisture and interlamellar water from ambient temperature to approximately 200 °C.

**Table 1: Chemical analysis of clays.**

<table>
<thead>
<tr>
<th>Sample</th>
<th>LOI*</th>
<th>SiO(_2)</th>
<th>Al(_2)O(_3)</th>
<th>TiO(_2)</th>
<th>FeO(_2)</th>
<th>CaO</th>
<th>MgO</th>
<th>Na(_2)O</th>
<th>K(_2)O</th>
<th>MnO</th>
<th>P(_2)O(_5)</th>
<th>Sum</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bofe raw</td>
<td>7.09</td>
<td>70.10</td>
<td>13.64</td>
<td>0.63</td>
<td>5.44</td>
<td>0.31</td>
<td>2.08</td>
<td>0.58</td>
<td>0.16</td>
<td>0.01</td>
<td>0.03</td>
<td>100.06</td>
</tr>
<tr>
<td>Bofe calc.</td>
<td>3.77</td>
<td>69.03</td>
<td>14.28</td>
<td>0.57</td>
<td>6.94</td>
<td>0.24</td>
<td>4.50</td>
<td>0.15</td>
<td>0.24</td>
<td>0.01</td>
<td>0.04</td>
<td>100.00</td>
</tr>
</tbody>
</table>

*LOI: loss on ignition

**Figure 1:** TG, DTG and DTA curves of Bofe raw clay.
The second endothermic peak, observed at the temperature of 488 °C, is due to clay dehydroxylation after the calcination. From this analysis a temperature of 500 °C was chosen for calcination of the clay, since dehydroxylation of raw clay was observed below this temperature. The occurrence of dehydroxylation is beneficial to the adsorption process of removing metals, since clays acquire an acidic character, avoiding the chemical precipitation of the metals.

The results of cation exchange capacity (CEC) of raw and calcined Bofe are 93 and 56 meq for 100 g of clays, respectively. The smectite clays of Paraíba (Brazil) typically have CEC values between 50 and 90 meq for 100 g of clay (Grim, 1968). The relatively high values of CEC of raw clays indicate that clays have a high level of isomorphic substitutions. Furthermore, the smectite calcined at 500 °C had its cation exchange capacity drastically reduced compared to the CEC of raw clays.

**Metal Speciation**

The diagrams of speciation in Figure 2 show the distribution of metal species of Ni and Cu in aqueous solution as a function of pH, respectively. According to the diagram of nickel, the chemical species Ni^{2+} is constant up to pH 6.0 and, while for the diagrams of copper, the chemical species Cu^{2+} appears at pH values up to 5.0.

**Adsorption Tests**

Tests were performed by fixed bed adsorption using calcined clay, calcined acid-activated clay and calcined Na-treated. The comparison between the behavior of the kinetics (breakthrough curves) of nickel and copper, as well as their respective calculated values of MTZ, the useful and total adsorbed amount and the removal percentage are shown in Figure 3 and Table 2.
Table 2: Values of MTZ, $q_0$, $q$ and removal to the breakthrough of adsorption of nickel and copper on calcined, acid-activated and sodic treated in bed Bofe clay.

<table>
<thead>
<tr>
<th>System</th>
<th>MTZ (cm)</th>
<th>$q_0$ (mmol.g$^{-1}$)</th>
<th>$q$ (mmol.g$^{-1}$)</th>
<th>%RT</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni/Bofe calcined</td>
<td>9.78</td>
<td>0.046</td>
<td>0.152</td>
<td>31.43</td>
</tr>
<tr>
<td>Ni/Bofe acid activated</td>
<td>12.47</td>
<td>0.007</td>
<td>0.067</td>
<td>24.30</td>
</tr>
<tr>
<td>Ni/Na-Bofe calcined</td>
<td>2.92</td>
<td>0.12</td>
<td>0.152</td>
<td>69.96</td>
</tr>
<tr>
<td>Cu/Bofe calcined</td>
<td>10.74</td>
<td>0.013</td>
<td>0.057</td>
<td>29.52</td>
</tr>
<tr>
<td>Cu/Bofe acid activated</td>
<td>12.17</td>
<td>0.009</td>
<td>0.067</td>
<td>31.27</td>
</tr>
<tr>
<td>Cu/Na-Bofe calcined</td>
<td>3.68</td>
<td>0.151</td>
<td>0.205</td>
<td>60.27</td>
</tr>
</tbody>
</table>

Breakthrough curves obtained by Gupta et al. (2009) on the adsorption of Cu and Ni ions presented similar behaviors, but with a higher time of saturation of the bed (48 hours).

In Figure 3, an accentuated difference was observed in behavior between the breakthrough curves. After acid activation, the clay reduced its adsorptive properties with regard to nickel ion, presenting a pronounced Mass Transfer Zone, which represents a greater resistance to saturation as well as lower levels of useful and total amount adsorbed, and a smaller total removal. In the case of copper, acid activation was less significant. Regarding the treatment with sodium in bed, there was a noticeable improvement in the adsorption of nickel and copper ions by modified clay, with 70% and 60% removal at approximately 12 and 8 hours, respectively. Moreover, the Mass Transfer Zone was drastically reduced to 30% of the values obtained for the calcined clay.

Therefore, it appears that, amongst the processes for clay modification, the treatment with sodium seems to be an alternative to improve the adsorptive properties of clay. This may be related to the phenomenon of ion exchange. There is an increased amount of exchangeable cations (Na$^+$) in the clay galleries. These ions in turn are replaced by nickel or copper ions during the adsorption.

The treatment of clays in order to transform them into sodium clays can occur through a chemical reaction of double reversible exchange, using the increasing concentration of sodium salt in the displacement. The transformation of clays into sodium smectite clays can be done in polycationic clays no matter what the exchangeable cations. This cation exchange for sodium should not be called "activation" because it does not affect the octahedral sheet; however, it can affect the intrinsic specific area of the monocation clay.

The surface area obtained by EGME and N$_2$ adsorption analysis of the clays studied is presented in Table 3. It is observed that the area of the sodium clay obtained by N$_2$ adsorption is about half of the value presented by the clay after the calcination process, but the area obtained by the EGME method is very large comparing these clays. The increase in the surface area has a positive influence on the removal process of metals. This result is a strong indication that the adsorption is also occurring sharply in this removal process.

Figures 4 and 5 show the SEM images and mapping of Na$^+$ species on calcined clay without chemical treatment and calcined clay treated with NaCl, respectively. From the micrographic analysis, the distribution and relative local concentrations of Na$^+$ species can be observed.

Comparing Figures 4 and 5 it can be observed that, with the treatment performed in the fixed bed, the concentration of sites containing sodium is uniformly distributed, while for calcined clay the concentration of sodium was not detected. From the image of Figure 4 it is not possible to see if the sites containing sodium correspond to the precipitates containing sodium chloride, or other species. Due to these facts, an XDR analysis of the clay treated with NaCl in the bed was performed to identify characteristic peaks of other non-clay solids such as sodium chloride. Figure 6 presents the results of X-ray diffraction of the calcined Bofe sample and treated with NaCl.

Table 3: Correlation Matrices between Specific Surface Area Estimates of Clays.

<table>
<thead>
<tr>
<th></th>
<th>EGME method (m$^2$.g$^{-1}$)</th>
<th>N$_2$ Adsorption (m$^2$.g$^{-1}$)</th>
<th>$V_{mi}$ (cm$^3$.g$^{-1}$)</th>
<th>$V_{mes}$ (cm$^3$.g$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Raw</td>
<td>376</td>
<td>79</td>
<td>19.725</td>
<td>24.560</td>
</tr>
<tr>
<td>Calcined</td>
<td>663</td>
<td>90</td>
<td>21.660</td>
<td>31.945</td>
</tr>
<tr>
<td>Calcined/sodic</td>
<td>817</td>
<td>47</td>
<td>10.891</td>
<td>22.815</td>
</tr>
</tbody>
</table>

Brazilian Journal of Chemical Engineering
The three clays have a peak corresponding to the $d_{(001)}$ lattice constants, whose spacing in the samples calcined at 500°C is on average 0.996 nm. In comparison to the raw sample (Figure 6), the calcined samples showed a reduction of $d_{(001)}$, indicating that the calcination causes a partial collapse of the layered structure of clay. In all clays, we could observe the presence of other peaks in the ranges: 0.45 and 0.41 nm corresponding to smectite, 0.32 and 0.25 nm corresponding to quartz and 0.15 nm corresponding to the basal spacing $d_{(060)}$, showing that the smectites are bi-octahedrons (Brindley and Brown, 1980). From Figure 6 it is observed that the XRD with calcined Na-Bofe looks more amorphous. The treatment with NaCl causes no significant changes in the structure of the sample of calcined Bofe and there are no peaks of solid NaCl. Moreover, the chemical composition obtained by EDX did not reveal the presence of chlorine in the samples. Thus, the increase in sodium as exchangeable cation is probably the main factor responsible for the increased removal of nickel and copper.

Chen et al. (2007), investigating the removal of Cu$^{2+}$ by a palygorskite, stated that the cationic exchange would induce an increase in the solution pH since the hydrolysis constant (Kps) of Cu$^{2+}$ is lower.
than that of the exchangeable cations in the palygorskite.

The pH at the top of the column was measured in all removal trials. The pH decreased during the removal, within the range pH indicated in the study of speciation of the species Ni$^{2+}$ and Cu$^{2+}$.

**Modification System**

The Bofe clay was also treated with sodium chloride in batch to be used in a fixed bed as adsorbent. The results of copper ion removal in a fixed bed obtained with this material were compared to the results of calcined Bofe clay previously treated with 1% NaCl (pH 3) in a fixed bed. Figure 7 presents the breakthrough curves obtained under the operating conditions of room temperature, particle size of 0.855 mm, flow rate of 4 mL.min$^{-1}$, Cu$^{2+}$ concentration of 2.36 mmol.L$^{-1}$ for samples of each sodium and calcined clay. The breakthrough curves present different behaviors, indicating the influence of chemical modification on diffusional resistance. The breakthrough curve of the modified Bofe clay in a fixed bed was a step function, suggesting less diffusional resistance and a more favorable removal process. This result indicates that all exchange sites are located in an area readily accessible to the copper ions.

![Figure 7: Breakthrough curves of the chemical modified clays.](image)

The sodium Bofe clay modified in batch showed a curvilinear behavior for the breakthrough curve with higher resistance to saturation compared with the Bofe clay treated with NaCl in the fixed bed. This result indicates that all exchange sites of sodium clay modified in batch are located in a more intrinsic area. Comparing both results, the modification performed in the bed is a more attractive process than the modification of raw clay.

**CONCLUSIONS**

The results of thermal analysis indicated mass losses in the range expected for raw Bofe clay and showed that the temperature of 500 °C is best suited for the calcination of that clay. Bofe clay presented the predominance of smectite clay in its composition and its CEC value (93.33 ± 5.74 meq.(100g)$^{-1}$) is in the range of clays of this type.

The acid activation of Bofe clay presented no significant removal results, reducing the removal of the metals studied when compared to the clay without modification. The treatment of clay with sodium presented relevant results for removal of nickel and copper. Comparing both treatments of clay with sodium applied in this study, the modification system in the bed offers higher performance for the removal of copper ion.

**ACKNOWLEDGMENTS**

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**NOMENCLATURE**

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>ion concentration, mmol.L$^{-1}$</td>
</tr>
<tr>
<td>$C_0$</td>
<td>initial concentration of the metal in the liquid phase, mmol.L$^{-1}$</td>
</tr>
<tr>
<td>CEC</td>
<td>Cation Exchange Capacity, meq.(100g)$^{-1}$</td>
</tr>
<tr>
<td>$C_{Na^+}$</td>
<td>ion concentration Na$^+$ measured by atomic adsorption, mg.L$^{-1}$</td>
</tr>
<tr>
<td>$C_{\mid z=L}$</td>
<td>ion concentration in the outflow, mmol.L$^{-1}$</td>
</tr>
<tr>
<td>$f$</td>
<td>conversion factor of sodium to equivalents, 23 grams of Na$^+$ for equivalent</td>
</tr>
<tr>
<td>Ht</td>
<td>bed height, cm</td>
</tr>
<tr>
<td>$m$</td>
<td>mass of adsorbent, grams</td>
</tr>
<tr>
<td>MTZ</td>
<td>Mass Transfer Zone, cm</td>
</tr>
<tr>
<td>$q$</td>
<td>total amount of metal ion adsorbed per gram of adsorbent, mmol.g$^{-1}$</td>
</tr>
<tr>
<td>$q_u$</td>
<td>useful amount of metal ion adsorbed per gram of adsorbent, mmol.g$^{-1}$</td>
</tr>
<tr>
<td>SSA</td>
<td>area for EGME, m$^2$.g$^{-1}$</td>
</tr>
<tr>
<td>$t$</td>
<td>time, minutes</td>
</tr>
<tr>
<td>$t_b$</td>
<td>breakthrough time, minutes</td>
</tr>
<tr>
<td>$V$</td>
<td>flow, mL.min$^{-1}$</td>
</tr>
<tr>
<td>$V_{mes}$</td>
<td>mesoporous volume, cm$^3$.g$^{-1}$</td>
</tr>
<tr>
<td>$V_{mi}$</td>
<td>microporous volume, cm$^3$.g$^{-1}$</td>
</tr>
<tr>
<td>$V_{NH_4^+}$</td>
<td>volume of ammonium acetate 3 mol.L$^{-1}$, mL</td>
</tr>
<tr>
<td>$W_a$</td>
<td>weight of EGME retained by the sample, grams</td>
</tr>
<tr>
<td>$W_S$</td>
<td>weight of clay, grams</td>
</tr>
<tr>
<td>%RT</td>
<td>percentage of total removal</td>
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REFERENCES


