Optimization of physicochemical parameters used in the removal of zinc and copper from aqueous solutions by the sugarcane bagasse

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Abstract: The present study was carried out to optimize the various physicochemical parameters (the size of particles of the material, the initial pH of the aqueous solutions, the mass of material used and the equilibrium time) used in the removal of the metal ions of Zn\(^{2+}\) and Cu\(^{2+}\) from aqueous solution by the sugarcane bagasse (SCB). The trading volume for each metal solution is 100 ml. The results show that, for completely purify a metal solution of Cu\(^{2+}\) or Zn\(^{2+}\) of concentration equal to 20ppm by the SCB requires a initial pH equal to 7.2, the diameter (D) of particles of the SCB is of the order 50µm< D <100µm, the mass of the SCB is equal to 0.75g and the optimal equilibrium time of removal of metal ions is equal to 60min.

Keywords: Removal, copper, zinc, sugarcane bagasse, optimization

1-Introduction

The water pollution by the heavy metals, remains today one of the major problems to solve in the industrialized countries and the countries in developing. Although they are of trace elements grace the important roles they play in different biological systems, the metal ions such as Mn\(^{2+}\), Zn\(^{2+}\), Cu\(^{2+}\) and Fe\(^{2+}\) can produce toxic effects when present in large quantities. Other heavy metals such as cadmium, mercury, chromium and lead are toxic even in very contrast to trace. In order to cure this plague, of the specific and effective techniques were employed for the removal of toxic metals from aqueous solutions such as: the extraction liquid-liquid [1-4], the extraction liquid-freezing [5-12], the membrane separation[13-16], the exchange of ions [17-20], the extraction liquid-solid[21-25] which still one of the most used methods seen the various advantages it offers, such as the reusability of the solid phase, the non-use of toxic solvents and the fact that it generates little waste. During these last years, many works were focused on the use of resins of natural origins to depollute the solutions loaded with industrial effluents of efficiently manner and economically [26-33].

The objective of this work is to improve and optimize the parameters affecting the removal efficiency of metal ions of Cu\(^{2+}\) and Zn\(^{2+}\) from aqueous solutions by the sugarcane bagasse.
2-Materials and Methods

2-1-Choice of material
We have chosen sugarcane bagasse (SCB) as material to remove the heavy metals from the aqueous solutions for the following reasons:

- Its high content of cellulose, hemicellulose and lignin, which are contained in their structures of the groupings hydroxyls and phenol hydroxides, which play an important role at the level of extraction mechanisms of heavy metals.
- Another essential reason, it is that the sugarcane bagasse is available and less expensive.
- Also, grace to the mechanical properties of bagasse, we can regenerate this material in several cycles of extraction - deextraction of heavy metals, and in wastewater treatment in general [34].

2-2 - Chemical composition of material
The sugarcane bagasse is made up mainly by natural polymers (biopolymers) such as, the cellulose whose monomer is the glucose, the hemicellulose which is a copolymer whose principal reason is composed of xylose connected with glucose and arabinose [35], and the lignin which is a three-dimensional polymer, its pattern is constituted mainly by three different monomers such as, coniferyl alcohol, paracoumaryl alcohol and sinapyl alcohol [36]. The table (1) summarizes the percentage of cellulose, hemicellulose and lignin in the sugarcane bagasse.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Percentage (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cellulose</td>
<td>43.6</td>
</tr>
<tr>
<td>Hémicellulose</td>
<td>33.5</td>
</tr>
<tr>
<td>Lignin</td>
<td>18.1</td>
</tr>
<tr>
<td>Ash</td>
<td>2.3</td>
</tr>
<tr>
<td>Wax</td>
<td>0.8</td>
</tr>
<tr>
<td>Other</td>
<td>0.7</td>
</tr>
</tbody>
</table>

2-3-Preparation of the sugarcane bagasse (SCB)
The sugarcane bagasse (SCB) was dried with the air, under the action of the solar rays, then crushed and tamised so as to obtain homogeneous materials for the experimental achievements, and the diameter size (D) of particles of material is of the order: 50 µm < D <100µm, 100 < D < 250µm, 250 < D < 500µm and 500 < D < 2000µm.

2-4- Choice of metals
We have chosen the zinc and the copper as metals to remove from aqueous solutions for the following reasons:
- Its uses in many industrial fields, we find the zinc in the rubber industry, paints, pigments, copiers, agricultural products and some cosmetics and medical products. Also the copper is widely used in various alloys, in the electrical industry, the construction industry, in gas lines and dyes [37]
- Its high toxicities and its harmful for the environmental [38, 39]
2-5. **Preparation of metal solutions**

The metal solutions of copper and zinc were prepared by dissolving of salts in the form of chloride in distilled water. The pH of each solution was adjusted with the hydrochloric acid and the sodium hydroxide (NaOH) using a combined glass electrode with pH-meter of EUTECH type, instrument pH 510.

2-6. **Experimental protocol**

The removal metal ions of Zn\(^{2+}\) and Cu\(^{2+}\) from aqueous solutions by the sugarcane bagasse (SCB) was carried out by contacting a volume of 100 ml of each metal solution of concentration and pH are known with a mass of SCB in stirred beakers at 25 °C until the extraction equilibrium. The extractant support was previously introduced into a small sachet of filter paper closed by a wire. The homogenisation of the aqueous solutions is ensured by an agitator magnetic with a constant agitation. Each sample was diluted with distilled water, and assayed to determine the final concentration of metal remaining at the extraction equilibrium, and calculated the removal yield.

2-7. **Analysis method**

In this work, the dosage of metal solutions of zinc and copper is realized by the technique of the Atomic Absorption Spectrometry with flame (AAS), the spectrometer used is the type Unicam 929 AA.

2-8. **The removal yield of metal ions**

The evaluation of the effectiveness of removal of heavy metals from aqueous solutions is carried out by determining the removal yield, denoted R%, it is defined by the following formula:

\[
R\% = \left( \frac{C_o - C_e}{C_o} \right) \times 100
\]

Co: initial concentration of metal ion (ppm).
Ce: residual concentration of metal ion at the equilibrium extraction (ppm).

3. **Results and discussions**

3-1. **Optimization of the particle size of material**

The main objective of this study is to determine the optimal size of grains of sugarcane bagasse (SCB) which enabled us to provide of better removal yields of metal ions of Zn\(^{2+}\) and Cu\(^{2+}\). To realize this study, we prepared of samples of the sugarcane bagasse (SCB), where the diameter (D) of the particles is of the order: 50\(\mu\)m \(\leq D < 100\mu\)m, 100\(\leq D < 250\mu\)m, 250\(\leq D < 500\mu\)m and 500 \(\leq D < 2000\mu\)m. A mass of 0.5 g of each sample is contacted with aqueous solutions of zinc and copper of concentrations equal to 20ppm. The volume treated of each solution is equal to 100ml, and the initial pH of each solution was fixed to 5.5.

The results of variations of removal yields of Cu\(^{2+}\) and Zn\(^{2+}\) as a function of particle diameter of the sugarcane bagasse (SCB) are summarized in the Table (2). From these results it is found that the removal yields of Zn\(^{2+}\) and Cu\(^{2+}\) increases with the decreasing of the grain size of the sugarcane bagasse. This is signified by the increased of contact surface between the aqueous phase and the solid phase, which is enable to facilitate the diffusion of metal ions in the solid phase. Therefore it can be concluded that the optimal diameter (D) of particle of the sugarcane bagasse to remove the metal ions Cu\(^{2+}\) and Zn\(^{2+}\) is of the order 50 \(\mu\)m \(\leq D < 100\mu\)m.
Table (2): Optimization of the particle size of the SCB ([Zn$^{2+}$] = [Cu$^{2+}$] = 20 ppm, 0.5g, pH= 5.5, $V_{aq}$ = 100ml)

<table>
<thead>
<tr>
<th>Diamter (D) (µm)</th>
<th>50 µm &lt; D&lt;100µm</th>
<th>100 µm &lt; D&lt;250µm</th>
<th>250 µm &lt; D &lt;500µm</th>
<th>500 µm &lt; D &lt; 2000µm</th>
</tr>
</thead>
<tbody>
<tr>
<td>R% Zn$^{2+}$</td>
<td>65.5</td>
<td>62.25</td>
<td>60.84</td>
<td>56.58</td>
</tr>
<tr>
<td>R% Cu$^{2+}$</td>
<td>63.75</td>
<td>61.5</td>
<td>59.65</td>
<td>54.96</td>
</tr>
</tbody>
</table>

3-2- Optimization of initial pH of metal solutions

The initial pH of aqueous solution is an important controlling parameter in the removal process because it affects the solubility of the metal ions, concentration of counter ions on the surface functional group of the material and degree of ionization of the aqueous solution during reaction.

To optimize the initial pH ($pH_i$) of the metal solutions of Zn and Cu, we have prepared aqueous solutions for each metal at different pH: 3.5; 4.5; 5; 5.5; 6; 6.5; 6.7; 6.8; 6.9; 7; 7.1; 7.2; 7.3; 7.4; 7.5 where we dove the same amount of the SCB (m = 0.5g). The grain diameter of the sugarcane bagasse is in the order 50µm$<D<100µm$.

The table 3 summarizes the results of evolution of removal yields of metal ions of Cu$^{2+}$ and Zn$^{2+}$ versus initial pH. These results show that, for a mass of 0.5g of the SCB, the removal yield of each metal increases with the increasing of pH initially imposed at each aqueous solution. A better removal yield of metal ions of Cu$^{2+}$ and Zn$^{2+}$ by the SCB is reached at pH 7.2. It can be concluded that, the optimal initial pH for have of maximum removal yields of the metal ions Zn$^{2+}$ and Cu$^{2+}$ by the SCB is about 7.2. To improve the removal yield of these metals, we proceed by an increase of the mass of the SCB.

Table 3: Optimization of $pH_i$ of metal solutions ([Zn$^{2+}$]$_i$ = [Cu$^{2+}$]$_i$ =20ppm , $pH_i$=7.2, m(SCB) = 0.5g, 50µm$<D<100µm$)

<table>
<thead>
<tr>
<th>pH</th>
<th>3.5</th>
<th>4.5</th>
<th>5</th>
<th>5.5</th>
<th>6</th>
<th>6.5</th>
<th>6.7</th>
<th>6.8</th>
<th>6.9</th>
<th>7</th>
<th>7.1</th>
<th>7.2</th>
<th>7.3</th>
<th>7.4</th>
<th>7.5</th>
</tr>
</thead>
<tbody>
<tr>
<td>R% Zn$^{2+}$</td>
<td>52</td>
<td>55</td>
<td>61</td>
<td>64</td>
<td>65</td>
<td>67</td>
<td>68</td>
<td>69</td>
<td>70</td>
<td>71</td>
<td>72</td>
<td>73</td>
<td>73</td>
<td>73</td>
<td>73</td>
</tr>
<tr>
<td>R% Cu$^{2+}$</td>
<td>50</td>
<td>54</td>
<td>60</td>
<td>63</td>
<td>64</td>
<td>66</td>
<td>67</td>
<td>68</td>
<td>69</td>
<td>70</td>
<td>71</td>
<td>72</td>
<td>72</td>
<td>72</td>
<td>72</td>
</tr>
</tbody>
</table>

3-3- Optimization of the mass of the SCB

To realize this study, we introduced of increasing masses of the SCB in of volumes of 100 ml of metal solutions of Zn$^{2+}$ and Cu$^{2+}$ of concentrations equal to 20 ppm. The $pH_i$ of each solution was fixed at 7.2 because the latter
as we offer a better removal efficiency, and the diameter of the material used is of the order of 50\mu m < D < 100\mu m.

The results of variations of removal yields of the metal ions in function of mass of the sugarcane bagasse are summarized in Fig.1. The analysis of this obtained curve shows that the removal efficiency of metal ions increases with the increasing of the mass of the SCB. The bearing of saturation corresponding at removal equilibrium of two metals are achieved has a mass of 0.75g, and the removal yields for this mass for the two metals are of the order of 100%. It can be concluded that a mass of 0.75g of the SCB is sufficient to completely purify of metal solutions of Cu and Zn of concentration equal to 20 ppm.

![Graph showing the variation of removal yield of Cu$^{2+}$ and Zn$^{2+}$ versus the mass of SCB ([$M^{2+}$]$_i$ = 20 ppm, pH = 7.2, 50\mu m < D < 100\mu m)](image)

**Fig 1:** Variation of the removal yield of the Cu$^{2+}$ and Zn$^{2+}$ versus the mass of SCB ([$M^{2+}$]$_i$ = 20 ppm, pH = 7.2, 50\mu m < D < 100\mu m)

### 3-4- Optimization of removal time of metal ions

To optimize the removal time of metal ions of Cu$^{2+}$ and Zn$^{2+}$ by sugarcane bagasse, the initial pH of each metal solution was adjusted at 7.2 (optimum pH), the diameter (D) of SCB is about 50\mu m < D < 100\mu m, the concentration of each metal solution is 20 ppm, and the trading volume for each solution is 100 ml and the mass of material equal to 0.75g (optimum mass). The study of the removal of metal ions is followed on each system by performing of levies of the each samples of the aqueous phase at of regular time intervals.

The effect of contact time on removal of copper and zinc from aqueous solutions by SCB was studied, and the results were shown in Fig.2. The data obtained showed that the removal yield for the two metals increases with increase in contact time. The removal of metal ions was rapid for the first 15 min and equilibrium was nearly reached after 60 min for Cu$^{2+}$ and Zn$^{2+}$, and the removal yields corresponding at this time are of the order of 100%. Therefore, the optimal time to reach equilibrium of complexation between the metal ions Cu$^{2+}$ and Zn$^{2+}$ and sugarcane bagasse is equal to 60 min of system stirring.
Fig.2: Variation of the removal yields of the Cu$^{2+}$ and Zn$^{2+}$ versus time ([M$^{2+}$]$_i$ = 20ppm, pH =7.2, 50µm<D<100µm, m(SCB) = 0.75g )

Conclusion
The work that we have presented is the optimization of physicochemical parameters (the particle diameter of SCB, the initial pH of the metal solutions, the mass of material used and the equilibrium time) used in the elimination process of metal ions of Cu$^{2+}$ and Zn$^{2+}$ from aqueous solutions by the complexing matrix which is the sugarcane bagasse (SCB). The trading volume for each metal solution is 100 ml. The results show that for completely purify a metal solution of Cu$^{2+}$ or Zn$^{2+}$ of concentration equal to 20ppm by the sugarcane bagasse require the following optimal operating conditions:
✓ The particle size of the SCB is of the order of 50µm<D<100µm.
✓ The initial pH of the metal solutions is equal to 7.2.
✓ The mass of the complexing matrix is equal to 0.75g.
✓ The contact time between the aqueous phase and the solid phase equal to 60 min.

References