USE OF CHEMICALLY ACTIVATED BIOMASS IN REMOVAL OF SOME TOXIC IONS FROM WASTE SOLUTIONS.

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INTRODUCTION

Waste water discharged by industrial activities are often contaminated by a variety of hazardous toxic metals. Elevated environmental levels of some heavy metal ions namely, lead, copper and zink, come from many sources such as; metal plating,
industrials mining, fertilizers and alloys (Low and Lee, 1991). These metals find their way to the aquatic environment.

Conventional methods for removing heavy metals from industrial effluent e.g.; precipitation, sludge separation, chemical oxidation or reduction, ion exchange, membrane separation, electro-chemical treatment, evaporation and ion-exchange resins, are often ineffective and costly when applied to dilute effluents (Macias-Garcia et al., 1993; Okutani and Uzawa, 1995; Meyer and Lieser, 1995; Bolto and Pawlowski, 1987).

Therefore, there is a need to look for alternative to investigate a low cost method which is effective and economic.

Many agricultural byproducts of cellulosic origin are available at very little cost and have been successfully utilized for metal ion adsorption by many workers (Shukla and Sakhardande, 1991; Moloukhia, H., 2004).

The use of the agricultural byproducts, as corn cobs (after chemical activation with 20% HNO₃ for 24 hours), is important from the economic point of view in treatment of heavy metals. In the present work, studies have been carried out to examine its sorption capacity towards the removal of Pb(II), Cu(II) and Zn(II) ions from aqueous solutions.

EXPERIMENTAL.

Chemical activation of sorbent material

Corn cobs were cut into small pieces and crushed in a mortar then immersed in 20% HNO₃ solution for 24 hours, then washed thoroughly with distilled water and dried for 24 hours.

The produced sorbent was sieved into various grain size ranges and kept in a desiccator over silica gel. The best mesh size used was 0.2 mm.

Sorption experiments

These experiments were carried out using a batch technique with V/m=200 where 10 ml aliquots of the metal ion containing 50 ppm of Pb(II), Cu(II) and Zn(II) unless otherwise stated were contacted with 0.05 g of chemically activated corn cobs powder in stoppered glass bottles. The condition were adjusted and the bottles were shaken using a thermostat shaker, kottermann D-1362, Germany, till equilibration time. Each mixture was filtered throughout 0.454 µm filter paper. The samples were analyzed using atomic absorption spectrophotometer, model Z-6100, Hitachi, Japan.
The capacity of the sorbent may be expressed in terms of the following equation:

\[ \text{Percentage uptake} = \frac{C_o - C_e}{C_o} \times 100 \quad (1) \]

The amount of metal ions sorbed \((q_e) = \frac{(C_o - C_e) \times V}{m} \quad (2)\)

- where \(C_o, C_e\) are the initial and final concentrations of \(\text{Pb(II)}, \text{Cu(II)}\) and \(\text{Zn(II)}\) in solutions, respectively.
- where \(v\) and \(m\) are the volume of solution (ml) and weight of sorbent material (gm), respectively.

Desorption process:

Dried sorbents obtained from sorption experiment were placed into 30 ml stoppered bottles and 10 ml of distilled water were added to calculate the percentage desorption by the same manner.

RESULTS AND DISCUSSION

Chemical analysis of adsorbent

Chemical constituents of raw corn cobs as shown in table (1) were determined in faculty of Agriculture, Ain shams University, Cairo

Table (1): Proximate analysis of raw corn cobs as dry matter basis.

<table>
<thead>
<tr>
<th>Ash content 5.7%</th>
<th>Organic content (94.3 %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crude protein</td>
<td>Cellulose hemicelluloses and lignin (crud fibers)</td>
</tr>
<tr>
<td>4.30</td>
<td>36.3</td>
</tr>
</tbody>
</table>

Physical Characteristics:

The specific surface area and pore-size determination were measured with the help of Nova 3200 BET Instrument (Quantachrome corporation, USA) and Mercury porosimeter apparatus (Model 9320) respectively. The BET Specific surface area of the sample is \(87.0886 \text{ m}^2/\text{g}\) while the total pore area obtained from pore-size is \(36.285 \text{ m}^2/\text{g}\). The difference between the two values could be attributed to the
difference in two instrument technique where the BET concerned with micro pores and mesopores while pore size depends on macro pores and meso pores. The average pore diameter, bulk density, apparent density and porosity were determined with Pore size analysis. Table (2) summarizes the obtained results.

Table (2) the physical characteristics of the sample

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specific surface area (BET)</td>
<td>87.0886 m²/g</td>
</tr>
<tr>
<td>Specific surface area (Pore size)</td>
<td>36.285 m²/g</td>
</tr>
<tr>
<td>Average pore diameter</td>
<td>0.2449 μm</td>
</tr>
<tr>
<td>Bulk density</td>
<td>0.2453 g/ml</td>
</tr>
<tr>
<td>Apparent density</td>
<td>0.5392 g/ml</td>
</tr>
<tr>
<td>Porosity</td>
<td>54.50 %</td>
</tr>
</tbody>
</table>

Table (2) shows the specific surface area measured by BET – instrument and specific surface area measured by Pore size instrument in addition to average pore diameter, bulk density, apparent density and porosity. The sample contains high percent of meso- pores with respect to macro- and micro pores as shown from incremental intrusion against diameter curve.

Factors affecting removal of Pb (II), Cu(II) and Zn(II) ions

Effect of contact time:

Uptake of 10 ml of Cu (II), Zn (II) and Pb (II) at concentration of 50 ppm using sorbent material as a function of contact time was illustrated in Fig.1. The results obtained cleared that, the percentage uptake was increased with the increase in time. Maximum uptake was 91.4%, 87.0% and 76.0% for Pb (II), Cu (II) and Zn (II), respectively. These results in agreement with those obtained by Moloukhia and Belacy (2005)
Effect of pH values:

Effect of pH on sorption of metal ions is shown in Fig.2. The results showed that, removal of ions was increased as the pH increased. The maximum sorption process reached a maximum value at pH 6-8 and then slightly decreased till pH 9 due to formation of hydroxo-complexes. The results agree with that of Moloukhia et al., (2006)

Effect of temperature:

The uptake of the investigated ions was increased with increasing in temperature as shown in figures (3-5) which indicated that the process was endothermic in nature. The concentration of adsorption sites may increase with rising temperature due to the breaking of some internal bonds near the edge of the particle as shown by Gupta et al (1997).
**Effect of sorbent mass:**

The effect of mass of sorbent material on the removal of Pb (II), Cu (II) and Zn (II) is showed in Fig.6. The results indicated that, the removal was increased gradually with increasing the sorbent mass from 0.02 g to 0.1 g, and maximum uptake was recorded at 0.05g. However, increasing the weight of sorbent material to 0.2g, lead to non significant increase in percentage uptake.

**Desorption studies**

Desorption studies were carried out on loaded sorbent material using distilled water as shown in fig. 7. The desorption of the investigated ions was increased with time reaching 48%, 41% and 38% for Pb ,Cu and Zn ions, respectively after 3 hours shaking time and stayed nearly constant till 24 hours contact time. This reveals that in addition to physical adsorption, chemical bonds are also formed between metal ions and active functional groups on the surface of the sorbent material.

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![Graph showing effect of temperature on the amount adsorbed (mg/ g) of Pb²⁺ by chemically activated corn cobs powder as a function of time.](image-url)

**Fig. (3):** Effect of temperature on the amount adsorbed (mg/ g) of Pb²⁺ by chemically activated corn cobs powder as a function of time.
Fig. (4): Effect of temperature on the amount adsorbed (mg/g) of Cu$^{2+}$ by chemically activated corn cobs powder as a function of time.

Fig. (5): Effect of temperature on the amount adsorbed (mg/g) of Zn$^{2+}$ by chemically activated corn cobs powder as a function of time.
Fig. (6) Effect of sorbent mass on removal of Pb$^{2+}$, Cu$^{2+}$ and Zn$^{2+}$ by chemically activated corn cobs powder.
CONCLUSION

On the basis of this data, it could be concluded that the available chemically activated corn cobs which is an agricultural byproduct, can be converted by a one-step activation technique into a valuable sorbent for toxic metals from aqueous solutions and can be utilized for waste treatment and environmental protection purposes.
REFERENCE: