Detoxification of Cr(vi) from Tannery Effluents by Natural Adsorbents

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Abstract - Researches aimed at remedying our environment from unwanted pollutants have been on the increase with the hope of finding cost effective and efficient methods to replace the existing expensive ones. In this work three natural adsorbents; maize (Zea mays) cob, hardwood sawdust from Khaya senegalensis and coal (letter coded MC, SD and CO respectively) were tested for the detoxification of chromium from tannery effluents. Sorption experiments were carried out using static adsorption process in which changes in concentration of the adsorbate were monitored by the use of Shimadzu AA650 Double Beam Atomic Absorption/Flame spectrophotometer. Results indicated a wider applicability of MC with % removal of the adsorbate varying from 53.8% to 20% in the five different effluents analysed. While CO showed a promising performance of 76.9% to 40% between three effluent samples analysed. However, it shows no effects in the remaining two effluent samples. SD was found to have least performance in the detoxification of the effluents analysed compared to MC and CO. This suggested that the adsorbents can be employed for the detoxification depending on the applicability needs.

Keywords: Adsorbate, Adsorbent, Coal, Maize cob, % Removal and Sawdust

1. Introduction

The presence of heavy metals in the environment is of major concern because of their extreme toxicity and tendency for bioaccumulation in the food chain even in relatively low concentrations. They are highly toxic as ions or in compound forms; they are soluble in water and may be readily absorbed into living organisms. These are facts that necessitate the present work such that cheap and easily available means of removing heavy metals from waters in our environment would be obtained.

Cr(VI) compounds are usually highly soluble, mobile and bioavailable compared to the sparingly soluble trivalent chromium species (Nriagu and Nioboer, 1988). Cr(VI) is a strong oxidizing agent and therefore harmful to biological systems in that it is toxic and carcinogenic (Ackerley et al., 2004; Florence, 1982; and Zhitkovich, 2005). This fact warrants its regulation in the environment. According to European (1980) and Polish (2000) regulations, the maximum allowable concentration of total chromium in drinking water is 50 μgL⁻¹. Additionally, Polish regulations distinguish between total chromium and Cr(VI), whose concentration cannot exceed 3 μgL⁻¹.

Chromium (III) sulphate salt used as tanning agent is transformed into Cr (VI), resulting in severe groundwater contamination around tanneries, (Thakur et al., 2001). Hafez et al., (2002) and Ashraf et al., (1998), reported that Cr ions concentration in the tanning wastewater varies from 2500 to 8000 mg/L and 1300 to 2500 mg/L, respectively. The highest concentrations of chromium are found in sludge and as a result the terrestrial disposal of this material has attracted most environmental concern (Conrad et al., 1976; Bartlett, 1991). On the average, it has been reported that 40 million m³ of chromium containing tannery wastewater is discharged each year to the world's waterways (Macchi et al., 1991). The introduction of treatment processes has considerably reduced the chromium content of the effluent in many modern tanneries. However, many older tanneries still incorporate little or no treatment of the effluent prior to discharge, which leads to substantial chromium contamination of the receiving waters (Smilie et al., 1981; Aboul Dahab et al., 1990; Fuller et al., 1990).

Several methods; such as solvent extraction, reverse osmosis, precipitation, ion exchange, etc. have been employed for the treatment of wastewaters contaminated with heavy metals (Bansal et al., 2009; Gupta and Mohapatra, 2003). However, these techniques have certain disadvantages, such as high capital and operational costs of treatment and disposal of the residual metal sludge. Therefore the aforementioned methods are not economically feasible for small and medium scale industries. Hence an efficient and competitively economical means for the treatment of heavy metals containing wastewaters have been sought for. Adsorption compared with other methods appears to be an attractive process due to its efficiency and ease with which it can be applied in the treatment of heavy
metal containing wastewater (Vołesky and Holan, 1995). In recent years, a number of adsorptive materials, such as aquatic plants (Axteill et al., 2003), clay (Marquez et al., 2004), zeolite (Alvarez-Ayuso et al., 2003) and microorganisms (Dilek et al., 2002) have been used in heavy metal removal from wastewaters. Also researches into the utilization of agricultural byproducts as adsorbents for the removal of heavy metals from aqueous solutions have been on the increase. This is because these agricultural byproducts are naturally occurring; hence they are available at little or no cost. They also have advantage over the conventional adsorbents such as activated carbon particularly because of their low cost and high availability. There is also no need for complicated regeneration processes when using agricultural by-products and they are capable of binding to heavy metals by adsorption, chelation and ion exchange (Gardea-Torresdey et al., 1996; Gang and Weixing, 1998; Argun and Dursun, 2006).

The principle behind exploring agricultural by-products in this work is the fact that most agricultural by-products are composed of cellulose in the plant cell walls. Cellulose (C_{6}H_{10}O_{5})_{n} is a large chain polymeric polysaccharide carbohydrate of beta-glucose. The principal functional groups in pure cellulose are hydroxy (-OH) making cellulose a polyol with primary and secondary alcohol functional groups (-CH$_{2}$OH, -CHOH). As reported by Abdel-Ghani et al., (2007) infrared spectrum of maize cobs shows two strong bands at 3479.3 and 3413.8 cm$^{-1}$ which were attributed to stretch (N-H) of amide. The medium band at 3556.5 cm$^{-1}$ and that at 2920 cm$^{-1}$ assume the existence of H-bridges and some crystal water. The strong band observed at 1041.5 cm$^{-1}$ indicates the stretching of the many C-OH and C-O-C bonds. However, sawdust was found to show weak band at 2125.4 cm$^{-1}$ which may be attributed to (C=CH) and a band at 1639.4 cm$^{-1}$ which was believed to be due to (C=C). On the other hand, FT-IR studies of coal sample conducted by Saikia et al., (2007) shows the presence of aliphatic -CH, -CH$_{2}$ and -CH$_{3}$ groups, aliphatic C-O-C stretching associated with -OH and -NH stretching vibrations and HCC rocking (single and condensed rings).

2. Materials and Methods Adsorbents

The adsorbents employed in this research were Maize cob (MC), Sawdust (SD) and Coal (CO). Hardwood sawdust from Mahogany (Khaya senegalensis) tree was collected from a local sawmill, and maize cob was collected from local farm in Minjibir Local Government are of Kano state, Nigeria, while Coal was obtained from the Kano Railway Station. They were air dried in sunlight until almost all the moisture evaporated. The sawdust was washed several times with distilled water in order to remove the water soluble tannins, after which it was dried in air and then oven dried at 80°C. The materials were then allowed to cool, ground and sieved to obtain the working particle size (850μm), and kept in a plastic container for subsequent use.

2.1. Preparation of Reagents

The water used throughout this work was initially distilled and then passed through a deionizer. AnalR grade reagents were employed for the preparation of all stock solutions, which were refrigerated thereafter. Fresh working standards were prepared daily by appropriate dilution of the stock solutions. All glasswares and plastic containers were washed with detergents, rinsed with distilled water and then soaked in a 10% HNO$_{3}$ solution for 24 hrs. They were later washed with deionised water and dried in an oven for 24hrs at 80°C (Todorovi et al., 2001).

a) Sampling

Triplicate effluents samples were collected at points of discharge from the runway of five different tanneries situated at Challawa and Sharada Industrial Estates of Kano state, Nigeria. The collection was done by dipping the washed plastic container into the flowing effluent and then stopped when filled. The samples were labeled GltD, IttD, AyfD, UnqD and FtD respectively and were transported to the laboratory and allowed to settle. Samples where fine particles persist were centrifuged with a Hermle z200A Labnet Centrifugal Machine at 2500rpm for a period of 30 minutes and in either case the clear supernatant solution was used for the various analyses.

b) Spectroscopic Measurements

All AAS measurements for this work were carried out using Shimadzu AA650 Double-Beam Digital Atomic Absorption/Flame Spectrophotometer using a chromium hollow-cathode lamp and an air/acetylene flame (Svehla, 2006). Blank solution was prepared by diluting 10 cm$^{3}$ of 6M HNO$_{3}$ solution to mark in a 100 cm$^{3}$ standard volumetric flask and was used to flush the spectrophotometer by aspirating between the standard and sample measurements.

c) Static Adsorption Studies

Eight grams (8.0g) of the adsorbents were weighed separately into 250 cm$^{3}$ screw capped conical flasks. Each of the adsorbent was contacted with 100 cm$^{3}$ of the tannery effluent. The mixture was agitated on a mechanical shaker (model: Innova 4000, from New Brunswick Scientific) at a speed of
290rpm for an equilibrium period of one hour (Ibrahim, 2011). Thereafter, the samples were separately filtered using Whatman number 1 filter paper, and the filtrates collected were taken for AAS measurements for the residual level of Cr(VI). In all cases the sorption analyses were carried out at room temperature, i.e 30 ± 2 °C.

d) Control Analysis

The same weight (8.0g) of each adsorbent was soaked separately in 100cm³ of deionised water in a screw capped conical flask and shaken for an hour and then filtered using Whatman number 1 filter paper. The different filtrates were analysed for the presence of Cr(VI).

3. Results and Discussion

The physical characteristics of the chrome-tannery wastewater samples were as presented in Table 1, from which it can be observed that all the samples have basic pH values having a mean value of 8.935. This, according to Michalski, 2004; and Cotton et al., 1995, points to the fact that the Cr(VI)

<table>
<thead>
<tr>
<th>Sample</th>
<th>pH</th>
<th>Cond.</th>
<th>Density(ρ)</th>
<th>Viscosity (η)</th>
<th>Cr(VI)Conc (mg/L)</th>
<th>Θ</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>(g/cm³)</td>
<td>( x10⁻⁴ kgm⁻¹s⁻¹)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>GltD</td>
<td>8.98</td>
<td>24.0</td>
<td>0.9961</td>
<td>11.102</td>
<td>2.1667</td>
<td>0.7692</td>
</tr>
<tr>
<td>IttD</td>
<td>10.01</td>
<td>23.8</td>
<td>0.9873</td>
<td>9.641</td>
<td>2.3333</td>
<td>0.8572</td>
</tr>
<tr>
<td>AyfD</td>
<td>9.59</td>
<td>24.5</td>
<td>0.9882</td>
<td>8.733</td>
<td>2.5000</td>
<td>0.4667</td>
</tr>
<tr>
<td>UnqD</td>
<td>8.83</td>
<td>38.4</td>
<td>0.9902</td>
<td>9.802</td>
<td>2.1667</td>
<td>0.8462</td>
</tr>
<tr>
<td>FtD</td>
<td>8.96</td>
<td>36.2</td>
<td>0.9902</td>
<td>8.775</td>
<td>1.6667</td>
<td>0.7000</td>
</tr>
</tbody>
</table>

**Table 1:** Physical Characterization of the Tannery Effluents

**Figure 1**: Variation of % Removal of Chromium from Tannery Effluent using 8g of the Different Adsorbents
ion is existing in the form of a tetrahedral yellow chromate ion, \( \text{CrO}_4^{2-} \). In an earlier work by Ibrahim and Jimoh, (2011) it has been observed that the optimum pH value for the adsorption of Cr(VI) onto the three adsorbents was pH 2, due to the positive nature of the surface charge of the adsorbents at lower pH which subsequently enhanced the binding of the adsorbate more than at higher pH. The Cr(VI) level in the effluents ranges from 1.6667 mg/L to 2.5000 mg/L with a mean value of 2.1667 mg/L, which agree closely with that reported by Dan’azum and Bichi, (2010) in their work for the heavy metals profile of Challawa river, a river which receives all the discharges from tanneries situated at the Challawa industrial area of Kano, Nigeria.

The results for the control analyses generally showed absence of Cr(VI) from the filtrates obtained for the agitation of the separate adsorbents with the deionised water. From Fig. 1 for sample GlD, a 76.9% removal of Cr(VI) was observed by the use of coal adsorbent, while a 53.8% was observed with maize cob and lastly a 23% with sawdust. However, for FtD the efficiency reduced to 50% and FtD whereas that of maize cob the % efficiency was almost maintained throughout the samples. These observed trends may likely be linked to the variation in the nature and number of functional groups associated with each adsorbent, such that amide functional group in MC have higher tendencies of being protonated compared to other functional groups in SD and CO which may lead to a better chances of complexing with the \( \text{CrO}_4^{2-} \) ion. The results of fractional surface coverage (\( \theta \)) of the adsorbate onto the different adsorbents as computed from the relation:

\[
\theta = 1 - \frac{C_e}{C_o}
\]

where \( C_o \) and \( C_e \) are the initial and equilibrium concentration of the Cr(VI) ion in the different effluents also suggested a more delocalized distribution of the adsorbate onto coal material in relation to the other adsorbents employed.

4. Conclusion

The agro adsorbents tested in this work have varied ability for removing the toxic metallic ion component of the different tannery effluents investigated with coal being a better choice compared to the other adsorbents because of the over 50% removal realized with coal among three of the five tanneries studied. However, where wide range of applicability is required, one may opt for using maize cob over the coal adsorbent.

References


