Performance of Egg-Shell and Fish-Scale as Adsorbent Materials for Chromium (VI) Removal from Effluents of Tannery Industries in Eastern Uganda

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Abstract

The performance of egg-shells and fish-scales biomaterials in separating chromium (VI) ions from tannery effluents obtained from tannery industries in Jinja town of Eastern Uganda was investigated. Using crushed egg-shell and fish-scales as adsorbents, sorption tests were carried out to determine the effects of bio-sorbent concentration and particle size on chromium (VI) removal. The adsorbate concentration in the tannery effluents before and after adsorption was analyzed using the UV-vis Spectrophotometer at wavelength of 540 nm. The adsorbent concentration was calculated from concentration change in aqueous solution before and after equilibrium sorption. Results showed that chromium (VI) ions adsorb on the surfaces of both biomaterials. The optimum conditions for chromium (VI) removal were found at pH of 6.8, particle size of 300 µm and bio-sorbent concentration of 0.5 g. The correlation coefficient (R²) showed that chromium (VI) adsorption fitted Langmuir adsorption isotherms. It was concluded that the adsorption process of chromium (VI) on the fish-scales and egg-shells was highly feasible.

Subject Areas
Analytical Chemistry, Environmental Chemistry

Keywords
Tannery Effluents, Chromium (VI) Removal, Egg-Shell, Fish-Scales, Biomaterials

1. Introduction

Leather tanning is important for converting hides and skins into usable materials
for production of leather based products. The tannery industry is one of the most chemical and water intensive industries [1]. The industry is also associated with a number of environmental and human health risks, including cancer among tannery workers [2]. In Uganda, working in a leather tanning industry involves exposure risks to a wide range of chemicals, some of have carcinogenic and mutagenic properties.

A significant number of operations within a tannery industry are wet operations that consume large amounts of water, chemicals and energy, and resulting in production of large amounts of polluted effluents. The effluents often contain considerable amounts of heavy metals that endanger public health and the environment if discharged without adequate treatment [3]. This happened to be a common practice in tannery industries found in Jinja town, eastern Uganda. One of the heavy metals that have generated international concern is chromium generated from the chrome based tannery industries. Chromium exists in several chemical forms and oxidation states ranging from (0) to (VI). However, only two forms, chromium (III) and chromium (VI) are stable enough to occur in the environment [4]. Chromium compounds in the form of Chromium (III) are used in the tanning process; mainly because chrome tanned leather possess top handling quality, high hydrothermal stability and other excellent user properties [5]. Despite these advantageous, there are several challenges associated with chromium removal from tannery wastes causing environmental pollution.

It has been reported that conventional chromium removal methods are not environmentally friendly due to the increased level of chemical sludge; energy inputs; and nutrient requirements from the removal processes; making the conventional processes expensive because of the implementation of large infrastructure [6] [7]. Consequently, biosorption offers better alternative to the conventional chromium removal methods because of limited chemical sludge making them environmentally friendly and non-expensive. This is great practical significance to the tannery industry in the region.

Several studies have shown that many materials of bio-origin are effective in adsorbing Chromium from its wastes. For example, Sumathi [8] employed sawdust; rice husk and charcoal as adsorbents for removal of Chromium from tannery effluents. The biosorbents were found to be effective in removing Chromium, implying that the bio-wastes were potential adsorbents for reduction of Cr from wastewater. Preethi [9] used extracts of various plants for chromium (CrVI) removal from its wastes. Results showed that some plant extracts reduced the CrVI. This suggested a possible application of plant extracts as eco-friendly materials for wastewater treatment. Jain [10] used nitrogen-enriched nano-bio-polymer for the removal of Cr(VI) from tannery effluent. Results showed maximum removal efficiency. Elabbas [11] employed egg-shell and marble to remove Cr(III) ions from chrome tanning wastes. Results showed that powdered marble adsorbed a larger amount of Cr (III) than egg-shell. Jadhav [12] used Tectona-Grandies leaves as ecofriendly and low-cost adsorbents for Chromium
VI) removal from wastewater. Results showed effective removal of the chromium. In this study, egg-shells and fish-scales of Nile perch (Lates niloticus sp.) were investigated as biosorbents for chromium sorption capabilities under different biosorbent-to-chromium mass ratios and contact times.

2. Literature Review

Many types of biomass materials have been investigated as adsorbents for removal of heavy metals from waste waters [13] [14] [15] [16]. Also, fish-scales in fishery waste management have been reported as adsorbents in adsorption processes due to the high binding capacities [17] [18].

Chicken egg-shells as well as fish-scales have also been used as low cost adsorbent of several heavy metal ions [19]. Egg-shell is mainly composed of calcium carbonate and it should behave as other adsorbents that contain this compound, i.e., calcite and calcareous soils. On the other hand fish-scales are a by-product of fishery; the scales are composed of hydroxyapatite and collagen, forming a natural composition with a large specific surface area that intensifies the adsorption process [20]. Adsorption using natural materials can be an efficient technology compared to that which employs synthetic substances. In particular, egg-shells and fish-scales natural materials are reported to contain high adsorptive properties for the removal of metallic ions from water [21].

However little information is available on how effective the egg-shells and fish-scales are in removing chromium from polluted effluents. This study was intended to evaluate the effectiveness of egg-shells and fish-scales in removing chromium from tannery effluents. Additionally, tannery effluents contain large quantities of organic and inorganic compounds including toxic substances such as chromium salts. Poorly treated tannery effluents leads to wide spread contamination of food chains, sharp decline in productivity of food crops, soil, vegetables, livestock and even milk production.

One of the most widely used synthetic adsorbents is activated carbon since it offers fast kinetics and low cost. Others include silica gel and alumina which have enormous surface areas per unit weight [22].

Adsorption is one of the promising physical processes that can remove heavy metals from water. The process is suitable even when the metal ions are present in concentration as low as 1 mg/L [23]. Activated carbon has been used for the removal of Pb, Cd and other heavy metals especially when associated with organic particulates in water [24]. Hydroxides of Alumina and Iron have also been used as adsorbents for the removal of heavy metals [16]. Unfortunately, the cost of these synthetic adsorbent is high. There is, therefore, an increasing trend for substituting the pure synthetic adsorbents with naturally occurring bio-materials in order to make the adsorption process economically feasible.

The bio-materials or biosorbents include algal biomass, fungi, and peat moss among others. The advantages of biosorbents are: low cost, high efficiency of heavy metal removal from dilute solutions, regeneration and possible metal recovery [16]. It has been reported that the algal biomass of the Sargassum family
possesses a metal binding capacity superior to inorganic adsorbents [25]. Consequently, brown marine macro-algae were used to remove Cd (II) [26]. However, the direct application of live biosorbents for heavy metal removal is unfavorable due to the resistance of living cells to metal ions.

3. Materials and Methods

The two different adsorbents used in this study were low-cost powdered egg-shells and fish-scales. The egg-shells were collected from hotels around Kampala, while the waste fish-scales were collected from a fish processing plant. These adsorbents were washed with tap water several times to remove adhering dust and soluble impurities from their surface and rinsed with de-ionized water. The materials were dried in an oven at temperature of 40˚C to a constant weight. The dried materials were then converted to 300 - 600 µm mesh powder by grinding in a mechanical grinder and preserved in polythene containers for subsequent use as adsorbents.

Chrome effluents containing chromium (VI) was obtained from two different tannery industries and collected in plastic containers. The effluent samples from the two tannery industries were labeled as effluent-1 (from Leather Industries of Uganda) and effluent-2 (from Sky Fat Tannery). The samples were collected from predefined sites using grab method. Three samples were collected at different time intervals (in the morning, midday and in the afternoon) from each industry giving a total of six samples per day. Sampling time was synchronized with the discharging time of the tannery effluents from the industries. The three samples collected for each industry per day were mixed in equal proportions in a 2000 mL high density polyethylene bottle. The pH was recorded and the samples were transferred to the laboratory in plastic bottles and preserved with 2 mL of nitric acid and stored at 4˚C.

3.1. Sample Characterization

The collected raw effluent samples had a dark green color. This indicated the presence of chromium (III). It was therefore necessary to convert the chromium (III) to chromium (VI). This was accomplished by oxidation with potassium permanganate using APHA method and the color intensity was measured spectrophotometrically using a UV-1700 Spectrophotometer.

3.2. Determination of Adsorbent Particle Size

The influence of adsorbent particle size on the chromium adsorption was studied using 300, 425 and 600 µm particle sizes. These particle sizes were found to be more efficient from preliminary experimentation.

3.3. Adsorbent Dose

The mass of the dry adsorbent (egg-shells and fish-scales) were varied from 0.05 to 1.0 g. The desired mass was placed in a flask with 100 mL of effluent at pH 6.8
for 6 hours. The mixture was shaken using flask shaker at 300 rpm and 25°C. The uptake of chromium (VI) was determined from residual concentration of chromium (VI) in the supernatant.

3.4. Contact Time

A 0.5 g portion of dry adsorbent was placed in each flask containing 100 mL of effluent at pH 6.8. The contents of the flasks were equilibrated on the flask shaker at 300 rpm for 20, 40, 60, 80, 100, 120, 140, 160, 180, 200, 220 and 240 minutes. The treated effluent was filtered and the chromium (VI) concentration was determined.

3.5. Initial Concentration of Chromium (VI)

Portions of 0.5 g dry adsorbents (egg-shells and fish-scales) were placed in a series of flasks containing 100 mL of prepared effluent samples of different initial concentrations at pH 6.8. The contents of the flasks were shaken at 300 rpm and 25°C for 6 hours. At equilibrium, the residual concentration of chromium (VI) was determined and the amount adsorbed was computed.

4. Results and Discussion

The data was collected from runs for each of the adsorbents and the effluents; followed by plots for percent removal. Using chromium standard solutions, a calibration curve was obtained with the help of the Spectrophotometer.

4.1. Effect of Adsorbent Particle Size on Chromium Removal

The data for effect of different adsorbent particle sizes on percentage removal of chromium (VI) is shown in Table 1. The data shows that adsorption of chromium (VI) on egg-shell and fish-scale powder decreased with the increase in particle size for all initial concentrations. The level of adsorption was generally proportional to specific surface area. This result was consistent with that reported by Aliabadi et al., [27], where the chromium (VI) removal at different particle sizes increased with decrease in particle size of adsorbent.

4.2. Effect of pH

Data for effect of pH on the adsorption of chromium (VI) ions is shown in Figure 1. The data shows that adsorption capacity of chromium (VI) ions on

<table>
<thead>
<tr>
<th>Adsorbent plus effluent sample</th>
<th>Particle size (±0.5 µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>300</td>
</tr>
<tr>
<td>Effluent-1/Egg-shell</td>
<td>54.43</td>
</tr>
<tr>
<td>Effluent-1/Fish-scale</td>
<td>51.89</td>
</tr>
<tr>
<td>Effluent-2/Egg-shell</td>
<td>14.46</td>
</tr>
<tr>
<td>Effluent-2/Fish-scale</td>
<td>13.25</td>
</tr>
</tbody>
</table>
Figure 1. The effect of pH on Chromium (VI) adsorption.

egg-shells and fish-scale powder was maximum at pH 2.0 and decreases with increase in pH up to 8.9. At pH values of 2 and 8.9, corresponding uptake yield values were found to be 60.12% and 48.1%, respectively, for egg-shell powder; and 50.63% and 40.51%, respectively, for fish-scale powder.

The metal adsorption dependence on pH can largely be attributed to the type and ionic state of the functional group present in the adsorbent and also to the metal chemistry in the solution [28]. High adsorption of chromium (VI) at low pH can be attributed to particular chromium species and the adsorbent surface. At low pH, the predominant chromium species are $\text{Cr}_2\text{O}_7^{2-}$, $\text{HCrO}_4^{-}$, $\text{Cr}_2\text{O}_7^{2-}$ and $\text{Cr}_2\text{O}_{13}^{3-}$ [29]. Above pH of 8, only $\text{CrO}_4^{2-}$ is stable and as the pH decreases it changes to the dichromate. On the other hand, under low pH values, the adsorbent surface becomes highly protonated and favors the uptake of chromium (VI) in the anionic form. With increase in pH, the degree of protonation of the surface reduces gradually, resulting in decreased adsorption [30]. As the pH is increased further, there is competition between OH$^-$ and chromate ions ($\text{CrO}_4^{2-}$), the former being the dominant species at higher pH values. The net positive surface potential of the adsorbent decreases, resulting in the weakening of electrostatic forces between adsorbent and adsorbate, which ultimately leads to reduced sorption capacity.

4.3. Effect of Dosage

The effect of adsorbent dosage on sorption of chromium (VI) is shown in Figure 2. When adsorbent dosage was increased from 0.05 to 0.5 g, as determined from preliminary experimentation; at constant pH of 6.8 the chromium (VI) adsorbed increased from 48.1% to 60.1% for egg-shell and from 55.96% to 60.1% for fish-scale in effluent-1. While for Sky fat it increased from 7.23% to 15.66% for egg-shell and from 8.43% to 15.45% for fish-scale powder. This implied that adsorbent dosage enhanced chromium (VI) removal from tannery effluents. The increase in chromium (VI) adsorption with adsorbent dosage could be attributed to increased surface area and also availability of more binding sites. When the
adsorbent powders were mixed with the effluent solution, the calcium salts in the adsorbent partially dissolved and released Ca$^{2+}$, HCO$_3^-$, CO$_3^{2-}$ and OH$^-$ ions causing the solution to become basic and forming negative charges on adsorbent surfaces. As the egg-shell dosage was increased, the solution became more basic and the surface area together with negative charge increased, thus, adsorption of chromium (VI) decreased. This was in agreement with literature findings by Arunlertaree et al., [31].

The percentage removal decreased slightly at higher dosage (up to 1 g/100 mL) of the adsorbent. It could be attributed to the fact that at higher dosage the particles aggregate, overlapping and overcrowding, resulting in a decreased surface area as well as decreased adsorption capacity. The effect of diverse ions commonly present in industrial effluents was studied by El-Sheikh and Sweileh [32]. Results revealed a 10% to 15% drop is percent recovery of analytes in the presence of certain inorganic and organic anions. Compared to this, it was possible that effluent-2 samples contained more inorganic and organic anions that lowered adsorption due to precipitate or chelate formation with different adsorption sites on the adsorbents. The increase in percent removal was also consistent with results by Kara and Demirbel [33]; and Govindarajan et al., [34] who reported that the percentage removal increased with increasing adsorbent dosage.

4.4. Effect of Initial Chromium Concentration

The removal of chromium (VI) was determined at 25°C for different concentrations in the range from $7.0 \times 10^{-2}$ mg·L$^{-1}$ to $30 \times 10^{-2}$ mg·L$^{-1}$ for effluent-1 and from $6.0 \times 10^{-2}$ mg·L$^{-1}$ to $14 \times 10^{-2}$ mg·L$^{-1}$ for effluent-2 at constant pH of 6.8 and 150 min contact time. The data is shown in Figure 3. The data showed that adsorption decreased to a certain level, remained almost constant and finally decreased further with increasing initial chromium (VI) concentration. This could be attributed to formation of monolayer followed by multilayer. The intermediate flat regions in the curves correspond to layer formation. This can be ex-
Figure 3. Effect of metal concentration on adsorption of chromium (VI)

explained on the basis of a possibility of the adsorbate getting taken up in the tiny capillary pores of adsorbent at a concentration below saturation of the adsorbate. It was also observed that percentage adsorption removal rapidly decreased with increase in adsorbate concentration. This could be explained by the fact that further increase in the concentration of chromium (VI) ion could lead to a decrease in the percentage removal as the active sites were already occupied, hence more metal ions remained in solution after adsorption. Similar results were observed by Dawodu et al. [35].

4.5. Effect of Contact Time

The data for effect of contact time on adsorption of chromium (VI) is shown in Figure 4. The data showed that adsorption of chromium (VI) gradually increased with contact time. Also, the time required to reach equilibrium conditions appeared to be independent of initial chromium (VI) concentrations. In addition, it can be seen that the percentage adsorption of chromium (VI) from effluent-2 was much lower than that for effluent-1. This was probably due to the presence of other inorganic and organic anions in effluent-2. El-Sheikh and Sweileh [32] noted that there is usually a 10% to 15% drop in recovery of analytes in the presence of certain inorganic and organic anions that may cause formation of precipitates and/or chelates with the adsorbent materials.

4.6. Comparison with Other Adsorbents

The adsorption capacities of the prepared adsorbents were compared with other adsorbents reported in the literature and shown in Table 2. Data from the present study was not different from literature values. This comparison established the validity and applicability of the powdered egg-shells and fish-scales as potential low-cost adsorbents in removing of chromium (VI) from tannery effluents. The adsorption capacities varied and depended on the properties of in-
Figure 4. Effect of contact time on adsorption of chromium (VI).

Table 2. Comparison of chromium (VI) adsorption with other adsorbents in literature.

<table>
<thead>
<tr>
<th>Adsorbents</th>
<th>Adsorption capacity (mg/g)</th>
<th>Initial chromium conc mg/L</th>
<th>pH</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Synthetic nano size zero valent iron</td>
<td>17.240</td>
<td>1 to 30</td>
<td>7.0</td>
<td>Rahmani, Samadi and Noroozi [36]</td>
</tr>
<tr>
<td>Saw dust</td>
<td>0.198</td>
<td>1 to 10</td>
<td>5.0</td>
<td>Aliabadi, Morshedzadeh &amp; Soheyli [27]</td>
</tr>
<tr>
<td>Pine leaves</td>
<td>0.470</td>
<td>1 to 10</td>
<td>5.0</td>
<td>Aliabadi, Morshedzadeh &amp; Soheyli [27]</td>
</tr>
<tr>
<td>Activated spent Pleurotus</td>
<td>50.470</td>
<td>5</td>
<td>2-11</td>
<td>Carol, Kingsley &amp; Vincent [37]</td>
</tr>
<tr>
<td>Tea factory waste</td>
<td>27.240</td>
<td>2.0</td>
<td></td>
<td>Malkoc and Nuhoglu [38]</td>
</tr>
<tr>
<td>Polyaniline with rice husk</td>
<td>4.739</td>
<td>3.0</td>
<td></td>
<td>Kanwal et al., [39]</td>
</tr>
<tr>
<td>Polyaniline with rice saw dust</td>
<td>5.128</td>
<td>3.0</td>
<td></td>
<td>Komal et al., [39]</td>
</tr>
<tr>
<td>Fish-scales</td>
<td>27.270</td>
<td>0.158</td>
<td>2.0</td>
<td>This study</td>
</tr>
<tr>
<td>Egg-shells</td>
<td>10.300</td>
<td>0.158</td>
<td>2.0</td>
<td>This study</td>
</tr>
</tbody>
</table>

dividual adsorbents, initial adsorbate concentration and other factors.

5. Conclusion

A number of conclusions were arrived at from the study. It was concluded that the adsorption of chromium (VI) on egg-shell and fish-scale powder decreased with the increase in particle size for all initial concentrations. Also, the adsorption of chromium (VI) ions on egg-shells and fish-scale powders decreases with increased pH up to 8.9. The adsorbent dosage enhances chromium (VI) removal from tannery effluents. Furthermore, it was concluded that the adsorption of chromium (VI) on egg-shell and fish-scale adsorbents increases with contact time. Additionally, the percentage adsorption of chromium (VI) from effluent-2 was much lower than that for effluent-1. Powdered egg-shells and fish-scales can be applied as low-cost adsorbents in treating and removing of chromium (VI) from tannery effluents. Furthermore, the adsorption capacity of chromium (VI) ions on egg-shells and fish-scale powder was favored by acid conditions. This
idea could be adopted for large scale chromium removal from its wastes. Also, the adsorbent dosage enhances chromium (VI) removal from tannery effluents. It was therefore concluded that chromium removal can be highest with increase in adsorbate concentration. Since contact time also enhanced adsorption of chromium (VI) gradually, it was concluded that to achieve sufficient removal of chromium, the effluent should be left in contact with the adsorbent material long enough to guarantee maximum chromium removal.

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