REMOVAL OF HEXAVALENT CHROMIUM FROM AQUEOUS SOLUTIONS BY ADSORPTION ON PEACH KERNEL AND NUTSHELL

Cristina Modrogan, Cristina Costache, Daniela Oanamari Orbulet
University Politehnica of Bucharest, str. Polizu, nr. 1-7, sector 1, Bucharest, Romania
c_modrogan@yahoo.com

Abstract

A new process for the hexavalent chromium removal from aqueous solutions is described. The paper intend to present, on a hand how to obtain an adsorbant using unconventional materials (peach kernel and nutshell), and on the other hand the study of hexavalent chromium removal from wastewater of different industries using this adsorbant. The paper has a double purpose. In the first part, was obtained from nonconventional materials: coconut bark and peach kernel an adsorbant mass. In the second part of the paper, was studied the hexavalent chromium removal from wastewater proceeding from different industries. The authors studied the influence of the following parameters: the initial pH of solution, the contact time on the adsorption capacity. The adsorbent efficiency to the chromium removal was also studied using chromium-plating wastewater.

Key words

Hexavalent chromium, nutshell, aqueons solutions

1 INTRODUCTION

Chromium can be acutely toxic to both plants and animals. To develop effective remediation plans for contaminated sites, it must understand the processes governing the transport and fate of chromium in the environment. Since both the mobility and toxicity of Cr depend on its oxidation state, redox reactions involving Cr are extremely important in determining its fate in the environment and its risk to human health (12). Until a few years ago, it also was the favored corrosion control agent in cooling towers whose water blow down (waste) was dumped into rivers, pits, lakes, and oceans. Cr occurs in wastewaters resulting from these operations in both trivalent [Cr(III)] and hexavalent [Cr(VI)] forms. The hexavalent form is more hazardous to animals than the trivalent form.
The metals requiring careful control include cadmium, zinc, copper, chromium, mercury, lead, and cyanide complexes of these metals. Their limits depend somewhat on the plant size, flow rate, and nature of the process, but the ultimate goal is zero discharge and complete control of the toxic metals.

While Cr oxidation states range from –2 to +6, the +3 and +6 states are most prevalent in the environment. Cr$^{6+}$ is more toxic and generally more mobile than Cr$^{3+}$. The Cr(VI) anions as chromate and dichromate are not strongly adsorbed on some soils under alkaline to slightly acidic conditions, thus they can be very mobile in the subsurface environment. In contrast, Cr$^{3+}$ readily precipitates as Cr(OH)$_3$ or as the solid solution FexCr1-x(OH)$_3$ under alkaline to slightly acidic conditions (12).

Chromium compounds are widely used by modern industries, resulting in large quantities of this element being discharged into the environment. Some of the main uses for chromium compounds are as follows: (a) plastic coating of surfaces for water and oil resistance, (b) electroplating of metal for corrosion resistance, (c) leather tanning and finishing, and (d) in pigments and for wood preservative.

A wide range of technologies is available for the removal of Cr(VI) from wastewaters, some of which are well-established methods that have been in practice for decades such as precipitation, coprecipitation (11), and concentration (U.S. EPA, 1980). These processes simply remove Cr from wastewaters by reduction (Shen and Wang, 1995), coagulation, and filtration. Although these technologies are quite satisfactory in terms of purging chromium and other heavy metals from water, they produce solid residues (sludge) containing toxic compounds whose final disposal is generally by landfilling with related high costs and still a possibility of groundwater contamination. From the environmental point of view, removing pollutants from liquid wastewater does not solve the problem but transfers it from one phase (usually liquid) to another phase (usually solid). Leather industry provides the necessities, such as leather shoes and garments, while using the by-products of the meat industry. However, the leather-making process, in turn, generates by-products and wastes. It is known that only 20% of wet salted hides/skins are converted into commercial leather, while 25% becomes chromium-containing leather waste (CCLW), and the remainder becomes non-tanned waste or is lost in wastewater as fat, soluble protein and solid suspended pollutants (1). Environmental pollution is a difficult problem for world leather industry (3,5). In past decades, a lot of effort has been made to study the solid collagenous wastes, including isolation of protein products from CCLW. Unfortunately, most of these processes reported bring about new residues during treatment.

In some studies, Babel S, Kurniawan TA investigated the technical feasibility of coconut shell charcoal (CSC) and commercial activated carbon (CAC) for Cr(VI) removal in batch studies using synthetic electroplating wastewater. Both granular adsorbents are made up of coconut shell (Cocos nucifera L.), an agricultural waste from local coconut industries. Surface modifications of CSC and CAC with chitosan and/or oxidizing agents, such as sulfuric acid and nitric acid, respectively, are also conducted to improve removal performance. The results of their Cr removal performances are statistically compared. It is evident that adsorbents chemically modified with an oxidizing agent demonstrate better Cr(VI) removal capabilities than as-received adsorbents in terms of adsorption rate.

Mise SR, Rajamanya VS studied in the work deals with the adsorption of Cr(VI) on activated carbon derived from Sorghum vulgare. The activated carbons were prepared by physical and chemical activation using H$_2$SO$_4$, H$_3$PO$_4$ activating agents of different impregnation ratio (I.R.). The effect of adsorption of Cr(VI) on pH, particle size concentration, contact time and dosage has been studied. The Cr(VI) removal...
attained in equilibrium maximum of 50 minutes and slightly decreases with increasing I.R. Adsorption increases with decrease in pH, is maximum at pH 2. Increase in impregnation ratio also increases surface area of *Sorghum vulgare* carbons.

Saifuddin M. Nomanbhay, Kumaran Palanisamy in the present investigation an attempt was made to overcome these mass transfer limitations by synthesizing a biosorbent by coating chitosan on the surface of palm oil shell charcoal and evaluating its equilibrium adsorption properties. The combination of the useful properties of oil palm shell char and that of natural chitosan, could introduce a composite matrix with many application and superior adsorption capabilities. Using synthetic wastewater, the chromium removal by oil palm shell charcoal coated with chitosan and acid treated oil palm shell charcoal adsorbents were compared. Oil palm shell has been successfully used to produce high quality activated carbon because of their inherent high densities and carbon content. In this work char from oil palm shell was prepared according to the method described by Guo and Lua, 2000. No attempt was made to determine the solid density and apparent densities of both the starting material and the char.

Erhan Demirbas et. all. (2004) used a low-cost adsorbents such as cornelian cherry, apricot stone and almond shell under different experimental conditions for removal of hexavalent chromium from aqueous solution. The influences of initial Cr$^{6+}$ concentration (20 to 300 mg/l), pH (1 to 4) and particle size (1.63 to 2.5 mm) have been reported. Adsorption of Cr(VI) is highly pH-dependent and the results indicate that the optimum pH for the removal was found to be 1 for all types of carbon.

2 EXPERIMENTAL

The subject of this paper is extremely typical, because there are a lot of interest in studying this issue. The complexity of leaking-infiltration phenomena, their evolution in time influenced both by natural and anthropogenic factors gives to the Cr reduction a new perspective in our days (although this subject was intensely studied in the literature).

2.1 The adsorbent mass preparation

Peach kernel and nutshell were obtained from Rm. Valcea county. The materials are waste released from agriculture. These materials are low-value agricultural waste products. Each material was ground in a micro-hammer cutter mill and sieved to a 2.0 mm x 0.5 mm particle size prior to activation. Chemical activation using H$_2$SO$_4$ at moderate temperatures produces a high surface area and high degree of microporosity (6). The materials were mixed in a 1:1 wt ratio with concentrated H$_2$SO$_4$ and allowed to soak for 24 h at room temperature. The samples were placed in an oven and heated to 200°C where they were held for 24 h. After this, the samples were allowed to cool back to room temperature. Then, the samples were washed with distilled water and soaked in 1% NaHCO$_3$ solution to remove any remaining acid. The samples were then washed with distilled water until pH of the activated carbon reached 6, dried at 24°C for 72 h (6). Characteristics of the carbon were presented in Table 1.
Table 1 The characteristics of the mass adsorbents

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Peach kernel</th>
<th>Nutshell</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bulk density (g/ml)</td>
<td>0.58</td>
<td>0.47</td>
</tr>
<tr>
<td>Ash content (%)</td>
<td>2.28</td>
<td>2.12</td>
</tr>
<tr>
<td>pH</td>
<td>6.2</td>
<td>5.8</td>
</tr>
<tr>
<td>Solubility in water (%)</td>
<td>0.8</td>
<td>0.79</td>
</tr>
<tr>
<td>Solubility in 0.25 MHCl (%)</td>
<td>1.20</td>
<td>1.22</td>
</tr>
</tbody>
</table>

2.2 The study of the adsorption

The adsorption isotherms are determined at the equilibrium conditions. All reagents used were of AR grade (Merck, Germany). The Cr samples were prepared by dissolving a known quantity of potassium dichromate (K₂Cr₂O₇) in distilled water and used as a stock solution and diluted to the required initial concentration. The model of water had 1g Cr/l concentration as the wastewater concentration from galvanization. 50 ml water model was in contact mass of 1 g of adsorbent. After 48 h (contact time), the sample was filtrated and then in the presence of 2.5 ml diphenilcarbazide, the remnant Cr was analyzed (spectrophotometer Cintra 5 at λ 545 nm (STAS 7884-91). The quantity of adsorbed chromium is expressed as follows:

\[ a = \frac{(C_0 - C_e) \cdot V}{m} \]  

Where:

C₀ and Cₑ represent respectively Cr (VI) concentration initially and at the equilibrium, mg/

V represents volume of Cr (VI) solutions, l

m represents the weight of the adsorbent mass, g

3 RESULTS AND DISCUSSIONS

![Figure 1 - The isothermes of reaction at 20°C](image1)

![Figure 2 - The influence of mass adsorbent on chromium removal](image2)

The removal of Cr (VI) by adsorption on peach kernel and nutshell was shown to increase with time and get the maximum value after 48 h. Starting with a 1g/l initial
solution concentration, the amount adsorbed raises up to 47.5 mg/g carbine for nutshell and up to 46.64 mg/g in the case of adsorbent mass proceeding from peach kernels. The figure 2 shows that the Cr (VI) amount rises proportionally with the amount of adsorbent mass used. When the nutshell is used, the amount of Cr (VI) restraint is greater comparative to the amount restraint when are used peach kernels.

3.1 Effect of pH

The Cr (VI) removal by two types of mass adsorbent (peach kernel and nutshell) at different values of pH when the initial Cr (VI) concentration is 1000 mg/l, the temperature is 20ºC and agitation speed 200 rot/minute are shown in figures 4 and 5. The Cr (VI) adsorption occurred in two steps. In the first place, the adsorption takes place in proportion of 90% in the very first minutes. The second step is very slow and may be for a long period of time. For the adsorbent mass proceeding from nutshell, the neutral value of pH is optimum in order to restrain chromium from wastewater. Different values of pH were studied (2.5, 6 and 10.5) in order to demonstrate the adsorbent mass behaviour in restraint of Cr (VI) being in different oxidation stages, is reported in diagram from figure 3.

Figure 3 - Stability diagram $E_{\text{r}}$-pH for chromium compounds

Figure 4 - The pH influence on Cr(VI) restraint onto nutshell

Figure 5 - The pH influence on Cr(VI) restraint onto peach kernel
3.2 Adsorption dynamics

The study of adsorption dynamics describes the solute uptake rate and evidently this rate controls the residence time of adsorbate uptake at the solid-solution interface. The kinetics of Cr (VI) adsorption on the activated carbons was analyzed using pseudo first-order (10), kinetic models. The conformity between experimental data and the model predicted values was expressed by the correlation coefficients ($r^2$, values close or equal to 1). A relatively high $r^2$ value indicates that the model successfully describes the kinetics of Cr (VI) adsorption (6).

The pseudo first-order equation

The pseudo first-order equation (10) is generally expressed as follows:

$$\frac{dq_t}{dt} = k(q_e - q_t)$$

(2)

Where:

$q_e$ and $q_t$ are the adsorption capacity respectively at equilibrium and at time $t$, mg/g,

$k$ is the rate constant of pseudo first-order adsorption, 1/min,

The initial conditions are $t=0$ si $t=t$; $q_t=q_e$. This equation becomes:

$$\log(q_e - q_t) = \log(q_e) - \frac{k}{2.303}t$$

(3)

The values of $\log (q_e - q_t)$ were linearly correlated with $t$. The plot of $\log (w_e - q_t)$ vs. $t$ should give a linear relationship from which $k$ and $w_e$ can be determined from the slope and intercept of the plot, respectively.

Table 2 - The adsorption kinetic model rate constants for the Peach kernel and nutshell at different values of pH

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Initial pH</th>
<th>Pseudo first order</th>
<th>$R^2$</th>
<th>$k$</th>
</tr>
</thead>
<tbody>
<tr>
<td>peach kernel</td>
<td>2.5</td>
<td>0.95</td>
<td>13.38</td>
<td></td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>0.98</td>
<td>10.78</td>
<td></td>
</tr>
<tr>
<td></td>
<td>10.5</td>
<td>0.97</td>
<td>11.49</td>
<td></td>
</tr>
<tr>
<td>nutshell</td>
<td>2.5</td>
<td>0.9881</td>
<td>11.47</td>
<td></td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>0.991</td>
<td>8.98</td>
<td></td>
</tr>
<tr>
<td></td>
<td>10.5</td>
<td>0.99</td>
<td>10.161</td>
<td></td>
</tr>
</tbody>
</table>

In order to find the optimal adsorbent mass that may be used for the Cr (VI) optimum removal, a series of experiments were done by contacting different quantities of adsorbent and 50 ml Cr (VI) solution. After 48 h (contact time), the sample was filtrated and the Cr (VI) concentration in the solution is analysed.

4 CONCLUSIONS

1. The Cr (VI) removal from aqueous solution is possible using several abundantly available low-cost adsorbents.
2. The Cr (VI) adsorption depends of pH and the results demonstrates that the optimum value pH is 6.
3. The kinetics of Cr (VI) adsorption on the different adsorbents was found to follow a pseudo first-order rate equation.
4. One g of adsorbent mass may adsorbs 47.5 mg/g hexavalent chromium those results are obtained when teh adsorbant mass is made up from nutshell and 46.64 mg/l those results are obtained when the adsorbant mass is made up from peach kernel.

REFERENCES