Removal of Cr(VI) by Used Cigarette Filters Column

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Abstract. The removal of chromium (VI) from water with used cigarette filters was studied by column experiments. The effects of flow rate, input Cr(VI) concentration, and column depth on the yield of Cr(VI) removal were investigated. The results reveal that the yield of Cr(VI) removal rises with bed depth as well as initial Cr(VI) concentration, but changes little with flow rate. The results contradict known column adsorption models, which imply that the mechanism of Cr(VI) removal by cigarette filters is not adsorption-dominated but reduction dominated.

Introduction

In our previous article [1], we reported Cr(VI) removal by used cigarette filters in batch contact manner, and the background and meaning were also mentioned. In this part, we provided the experimental results about Cr(VI) removal by used cigarette filters in continuous mode.

Materials and method

Cigarette butts and reagents
The cigarette butts used in this study all came from a student dormitory, the road, or from local garbage. Before the experiments, the remnant tobacco and paper were removed and the filters were cut and weighed. Chemical reagents were all analytical grade and were bought from a local chemical reagent company. The stock of aqueous Cr(VI) solution was prepared by dissolving potassium chromate in double-distilled water and was diluted before use.

Equipments and procedures
The column was made up of a 30 cm long PVC pipe of 2.5 cm internal diameter. A rubber plug was provided at the bottom to support the filters. Three outlets were created at 15, 20, and 25 cm from the inlet to change the height of the filter bed. Column experiments were conducted at flow rates of 3, 6, and 10 mL/min with 10, 50, and 100 mg/L of Cr(VI) solution (pH 1) using bed depths of 15, 20, and 25 cm. The samples (effluent solutions) were collected at regular time intervals, until the effluent Cr(VI) concentration was approximately equal to the initial (influent) concentration. The effluent concentration was measured using the same method as before.

Results and discussion
Column experimental results are shown in Fig. 1(a)–(i): Fig. 1(a)–(c), (d)–(f), and (g)–(i) represent the breakthrough curves for three different flow rates (3, 6, and 10 mL/min) and three different bed depths (Z = 15, 20, and 25 cm) at three constant initial Cr(VI) concentrations (10, 50, and 100 mg/L), respectively. It was concluded that under the conditions of identical bed depth, the higher the bed and the lower the flow rate, the longer the time needed to saturate the bed; for the same bed depth, the lower the initial concentration of Cr(VI) and flow rate, the longer the time needed to saturate the bed; as for the same flow rate, the lower the initial concentration of Cr(VI) and the higher the bed depth, the longer the saturation time. A higher bed depth meant that more filters were used and the bed had greater adsorption and reduction capacities. A lower flow rate and Cr(VI) concentration implied that
less Cr(VI) entered the bed per unit time, therefore, saturation of the column took longer at the same
bed depth. Equation 1 was used to calculate the saturated amount (Q (mg/g)) of Cr(VI) removal of the
column: the results are presented in Table 1. The Cr(VI) removal capacity of the filters increased with
increasing influent Cr(VI) concentration. The average increased from 1.1 mg/g at $C_0 = 10$ mg/L to 3.3
mg/g at $C_0 = 100$ mg/L. Moreover, the Cr(VI) removal capacity of the filters increased with increasing
bed depth. The average increased from 2.1 mg/g at 15 cm to 2.5 mg/g at 25 cm. Nevertheless, the
capacity changed little with flow rate, which may be attributed to the small spatial and temporal
difference. Although the flow rate tripled, the time difference was only 10 min which was much less
than the equilibrium contact time (120 min) deduced from earlier batch experiments.

$$Q = \frac{V_0 C_0}{1000 m} \int_0^t \left(1 - \frac{C_t}{C_0}\right) dt$$  (1)

where $Q$ (mL/min) is the flow rate, $V_0$ (mL) is the initial volume, $C_0$ (mg/L) is the influent
concentration of Cr(VI), $C_t$ (mg/L) is the effluent concentration of Cr(VI) at time $t$ (min), and $m$ (g) is
the mass of filter medium in the column.

![Graphs A, B, C, D showing the relationship between $C_t / C_0$ and time for different flow rates and bed depths.](image)
Figure 1. Relationship between $C_t/C_0$ and time.
Table 1. Cr(VI) removal capacity of filters in column, Q (mg/g).

<table>
<thead>
<tr>
<th>BD(^a) [cm]</th>
<th>15</th>
<th>20</th>
<th>25</th>
<th>3</th>
<th>6</th>
<th>10</th>
<th>3</th>
<th>6</th>
<th>10</th>
<th>3</th>
<th>6</th>
<th>10</th>
</tr>
</thead>
<tbody>
<tr>
<td>FR(^b) [mL/min]</td>
<td>10</td>
<td>1.10</td>
<td>1.19</td>
<td>1.16</td>
<td>1.12</td>
<td>1.20</td>
<td>1.11</td>
<td>0.85</td>
<td>1.08</td>
<td>1.29</td>
<td>1.12</td>
<td></td>
</tr>
<tr>
<td>C(_0) [mg/L]</td>
<td>50</td>
<td>2.97</td>
<td>2.73</td>
<td>1.92</td>
<td>3.11</td>
<td>2.71</td>
<td>2.82</td>
<td>2.38</td>
<td>2.70</td>
<td>2.65</td>
<td>2.67</td>
<td></td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>2.46</td>
<td>2.86</td>
<td>2.87</td>
<td>3.38</td>
<td>3.46</td>
<td>2.48</td>
<td>3.90</td>
<td>4.58</td>
<td>3.26</td>
<td>3.25</td>
<td></td>
</tr>
<tr>
<td>Q</td>
<td>Average</td>
<td>2.18</td>
<td>2.26</td>
<td>1.98</td>
<td>2.54</td>
<td>2.46</td>
<td>2.14</td>
<td>2.38</td>
<td>2.79</td>
<td>2.40</td>
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<td>2.52</td>
<td></td>
<td></td>
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</tbody>
</table>

\(^a\) BD-Bed depth, \(^b\) FR-Flow rate

The Thomas model and the Yoon–Nelson model are commonly used to represent the adsorption-breakthrough behaviour of columns [2,3]. In terms of these two models, the plot of \(\ln(C_0/(C_0 - C_t))\) versus time \(t\) should be linear. These equations were used to model the present experimental column data. However, no good correlations were found. As an example: the plot of \(\ln(C_0/(C_0 - C_t))\) versus \(t\), based on the data in Fig. 1(a) is shown in Fig. 2. There were substantial discrepancies between the line and the data points. The Bohart–Adams equation is another model used to portray the performance of adsorption columns. According to this model, bed depth and the time at a given breakthrough percentage are linearly related. Three representative data points are shown in Fig. 3(a)-(c): Fig. 3(a) and 3(c) indicate good agreement between the model and the experimental data points. Nonetheless, Fig. 3(b) exhibits an obvious bias. These examples implied that Cr(VI) removal by used cigarette filters is not dominated by adsorption. In fact, the filters have a low specific surface area (of the order of × 0.1 m\(^2\)/g [4]. The filters detain tar and particulates in the smoke by collision, condensation, and binding to complex flow channels [5]. On the other hand, many of the chemicals detained on such filters can reduce Cr(VI) to Cr(III). Measurements of total chromium in effluents proved that chromium adsorbed — the difference of total Cr remaining in solution and the initial Cr(VI) concentration — accounted for less than 50% of the Cr(VI) removal.

\[\ln(C_0/(C_0 - C_t))\]

Figure 2. Relationship between \(\ln(C_0/(C_0 - C_t))\) and \(t\) (corresponding data: Fig. 1(a)).
Figure 3. Relationship between 90% breakthrough time (T$_{90}$) and bed depth.

Conclusions

The removal of Cr(VI) from water by used cigarette filters is affected mainly by solution pH. In column, and flow, modes, the capacity of Cr(VI) removal of the filters increases with increasing influent Cr(VI) concentration and bed depth. The average changes from 1.1 mg/g at 10 mg/L to 3.3 mg/g at 100 mg/L and from 2.1 mg/g at 15 cm to 2.5 mg/g at 25 cm, respectively. The results of the column experiments are not represented adequately by the Yoon–Nelson model, the Thomas model, or the Bohart–Adams equation, which, combined with the determination of total chromium, indicates that the removal of Cr(VI) from water by used cigarette filters is dominated by chemical reduction, and not by adsorption.

References


