## Scale-Up of Self-Regenerating Semi-Batch Adsorption Cycles through Concurrent Adsorption and Reduction of Cr(VI) on Sheep Wool

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Keywords: industrial wastewater, semi-batch adsorption cycles, Adsorption, wool, hexavalent chromium

#### Abstract:

A previous publication by our group reported that adsorption of Cr(VI) on sheep wool reached 99% when allowed a long residence time, with concurrent reduction to Cr(III). In this study, the process was scaled up by optimizing a pilot plant based on semi-batch adsorption cycles. This yielded Cr(III), which is about 300 times less toxic than Cr(VI), and can be precipitated using lime at high pH. Since the reduction step is slower than the adsorption one, an adsorption column was designed to perform semi-batch operation cycles, whereby the extended "off cycle" allows reduction to take place. Since reduction of Cr(VI) frees active sites on wool, the plant acts in lieu of in situ regeneration, accompanied by additional adsorption of Cr(VI). The results show that 97% of the column efficiency can be recovered within 24 h of "off cycle". Wastewater from a local electroplating industry was treated by this method with high removal of Cr(VI), reaching the limit permitted by environmental standards. This study also reveals that typical concentrations of heavy metals, present in wastewater produced from electroplating, had no substantial antagonistic interference with Cr(VI) adsorption.

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Article

# Scale-Up of Self-Regenerating Semi-Batch Adsorption Cycles through Concurrent Adsorption and Reduction of Cr(VI) on Sheep Wool

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**Abstract:** A previous publication by our group reported that adsorption of Cr(VI) on sheep wool reached 99% when allowed a long residence time, with concurrent reduction to Cr(III). In this study, the process was scaled up by optimizing a pilot plant based on semi-batch adsorption cycles. This yielded Cr(III), which is about 300 times less toxic than Cr(VI), and can be precipitated using lime at high pH. Since the reduction step is slower than the adsorption one, an adsorption column was designed to perform semi-batch operation cycles, whereby the extended "off cycle" allows reduction to take place. Since reduction of Cr(VI) frees active sites on wool, the plant acts in lieu of in situ regeneration, accompanied by additional adsorption of Cr(VI). The results show that 97% of the column efficiency can be recovered within 24 h of "off cycle". Wastewater from a local electroplating industry was treated by this method with high removal of Cr(VI), reaching the limit permitted by environmental standards. This study also reveals that typical concentrations of heavy metals, present in wastewater produced from electroplating, had no substantial antagonistic interference with Cr(VI) adsorption.

**Keywords:** hexavalent chromium; wool; adsorption; semi-batch adsorption cycles; industrial wastewater

#### 1. Introduction

Trace concentrations of chromium are essential for metabolism in the human body, with a recommended 50–200  $\mu$ g daily diary intake for Cr(III) [1]. At higher concentrations, however, chromium has high toxicity and epidemiological studies show evidence of carcinogenic potential in the case of inhaled Cr(VI). Other adverse health impacts to chronic and acute exposure include ulcerations, bronchitis, and decreased pulmonary function, as well as damage to liver, kidney, and immune systems [2].

Chromium and chromium containing chemicals are used in a host of chemical industries [3]. Chromium compounds are present in natural and synthetic pigments [4]. The name chromium is from the Greek "chroma", meaning color [5]. Cr(VI) is used as a corrosion inhibitor for aluminum alloys [6]. Such industrial applications raise concerns about environmental contamination from waste effluents containing toxic chromium compounds.

Unlike the case with other heavy metals, chromium toxicity depends on valence, the most stable states being Cr(III) and Cr(VI) [7], with the latter being more toxic [1]. The most toxic route of exposure to Cr(VI) is inhalation. Cr(VI) in compounds such as chromate  $(CrO_4^{-2})$ , dichromate



 $(Cr_2O_7^{-2})$ , and chromium trioxide  $(CrO_3)$  are known carcinogens when inhaled [8]. They are strictly regulated by occupational safety authorities worldwide. The toxicity of Cr(VI) is attributed to its water solubility and permeability through cell membranes [9]. Absorption of water-soluble chromates in the blood is high, whereas insoluble chromates have lower absorption and longer residence time in lungs. The established exposure limit for inhaled Cr(VI) is 5 mg/m<sup>3</sup> for an 8-h time-weighted average [10]. Chromium is also toxic to marine organisms, but, in contrast with the case in humans, Cr(III) is more toxic for these organisms than Cr(VI) [11]. Both Cr(III) and Cr(VI) are toxic to microorganisms used in wastewater treatment [12].

Cr(VI) can be treated by reduction to the less toxic Cr(III), or by removal using ion exchange [13], nanofiltration [14], reverse osmosis [15], and phyto-remediation [16]. After reduction, Cr(III) can be precipitated by raising the pH in order to favor precipitation of chromium compounds containing  $S^{-2}$  or OH<sup>-</sup> [17]. Biosorption, in which biomass is used to adsorb chromium, has also been used, with reported removal efficiencies in excess of 90% [18]. However, the fate of the highly toxic Cr(VI) remains a serious concern after its adsorption.

Keratin based natural adsorbents, found in animal horns and wool, have the capacity to adsorb heavy metals such as mercury, copper, cadmium, zinc, arsenic, lead, and chromium [19]. For chromium, previous studies show very high removal efficiencies on wool when compared to other natural adsorbents such as olive cake, sawdust, pine needles, almond shells, cactus leaves, and coal [20]. Removal efficiencies ranging between 80 and 99% for Cr(VI) on wool have been demonstrated in a batch sequential reactor study, with the wool exhibiting no decline in removal efficiency even when regenerated with KCl in repeated cycles [21]. Another study reported up to 99% removal after a long residence time on sheep wool. Furthermore, Cr(VI) is not only adsorbed on wool but is also reduced to Cr(III) [22]. For short-term studies, external mass transfer controls adsorption, whereas intra-particle diffusion controls diffusion at later stages [23].

Reduction is a key feature of sheep wool when used as adsorbent for Cr(VI). Other adsorbents may have high adsorption capacity that could reach values as high as five times that with sheep wool [24]. However, in absence of accompanying reduction, the process will require regeneration and further treatment of effluent. A material that is reported to exhibit similar reduction behavior to sheep wool is activated carbon, with which 30% of Cr(VI) in the feed can be reduced to Cr(III) [25]. However, that observation has not been utilized to decrease the need for regeneration.

This study aimed at optimizing residence time in a semi-continuous adsorption column in which reduction occurs at values sufficient to permit operation without regeneration. With optimum adsorption/reduction cycles, an auto-regenerated column is shown to be effective. The product from such a column is Cr(III), which is about 300 times less toxic than Cr(VI) and can be precipitated using lime at high pH [26], or adsorbed efficiently by modified adsorbents [27].

#### 2. Materials and Instrumentation

#### 2.1. Materials

All chemicals were of analytical grade and were used without further purification. Solutions were prepared using distilled deionized water (DDW) and their concentrations determined spectrophotometrically. Potassium dichromate, used as a source of Cr(VI), was from Riedel De-Haen (Seelze, Germany). Acetone and 5-di-phenyl carbazide were from Sigma Aldrich (St. Louis, MO, USA). Sheep wool (Sharjah animal market) was trimmed, riffled, and then washed with water and detergent for two days.

#### 2.2. Instrumentation

Cr(VI) concentrations were determined on an Evolution 220 spectrophotometer (ThermoFischer Scientific, Waltham, MA, USA) at 540 nm, using the 1,5 diphenyl carbazide method. Total Cr was measured using inductively coupled plasma (ICP) (VARIAN, LIBERTY AX Sequential-ICP-OES,

coupled with SPS3 sample preparation system, and LYTRON cooling system). The difference between total Cr and Cr(VI) was taken to be Cr(III). ICP was also used to measure concentrations of Cu, Mn, Ni, Pb, and Zn in electroplating wastewaters. Columns were manufactured in our lab. Masterflex L/S dosing pump with four channels was used to supply feeds at the desired flow rate.

#### 3. Methods

#### 3.1. Sample Preparation

Wool was soaked in water for one day to loosen debris and then washed with detergent to remove lipids. This was followed by air drying at 40 °C for 6 h. Wool was cut in ca. 2 cm long strips for packing columns. Stock Cr(VI) solutions were prepared from potassium dichromate and used in feed solutions for preliminary column studies. The pH of the feed solution was adjusted to 2.0 using HCl. Wastewater from a local electroplating company was diluted and adjusted to this pH. After dilution, the solution had the composition shown in Table 1. This solution was used to assess the performance of the semi-continuous column in presence of other heavy metals.

Heavy Metal	Concentration, mg/L
Cr (Total)	$8.6 \times 10^{2}$
Cr(VI)	$6.2 \times 10^{2}$
Cr(III)	$2.3 \times 10^{2}$
Cu	14
Mn	0.30
Ni	32
Pb	0.90
Zn	3.2

Table 1. Electroplating waste composition (after dilution and pH adjustment).

#### 3.2. Continuous Flow Experiments

A fixed bed column packed with sheep wool was prepared with inner and outer diameters of 32 and 40 mm. It had a packing height of 106 mm and a packing density of 100 g/L. The layout of the process is shown in Figure 1. The column was washed with HCl and the pH brought down to 2.0. Prepared feed was then passed through the column. Samples were collected at time intervals and analyzed for Cr(III) and Cr(VI). Wastewater was fed to the column for 5 min at a flow rate of 200 mL/min. The column was then left undisturbed for 55 min and the cycle repeated several times. The column was finally left for 24 h, labeled as a dark interval. Following this interval, the column was operated again using the same cycles.



Figure 1. Packed column experimental setup.

#### 4. Results and Discussion

The following conditions from our previous work on batch sequential reactors [21] were used: Wool dosage = 8.0 g/L, contact time = 25 min, pH = 2.0, T = 25.0 °C, initial Cr(VI) concentration = 100 mg/L, and regeneration using 1.0-m KCl. For the first semi-continuous column trial shown in Figure 2, 100 mg/L Cr(VI) was fed into the adsorption column at pH 2.0. A volume of 12.0 L was processed in the first cycle and a breakthrough time was observed at 60 min with 6.0 L feed. The column was left idle for 24 h in the off cycle. The break in the horizontal axis in Figure 2 corresponds to the dark period. At the end of this period, a relatively high Cr(III) concentration of 70 mg/L was observed in the eluent (red circle). The results indicate that for a 6.0 L feed of 100 mg/L Cr(VI), Cr(III) is produced at ca. 5 mg/L after 70 min of operation. This indicates that reduction is simultaneous with adsorption, but it occurs at a slower rate. The 24-h dark period allows for reduction of additional adsorbed Cr(VI).

In the second run, the same feed concentration was used, the breakthrough time from the previous run was taken as a rough guideline, and the column was allowed a dark period after only 60 min. The cycle was repeated by leaving the column idle for 24 h so as to permit reduction to proceed. After this dark period, Cr(III) spiked as expected, reaching a concentration of 130 mg/L. In the second ON cycle, the column processed another 6.0 L of feed, giving Cr(III) concentrations below 5.0 mg/L. This indicates that ca. 97% of column efficiency was recovered. The breakthrough curve for the two cycles is shown in Figure 3. The results from this run clearly point to the possibility of running the column without the need for regeneration if extended idle/dark periods are incorporated in operation cycles.



**Figure 2.** Chromium concentrations in the eluent. Initial Cr(VI) feed concentration = 100 mg/L; flow rate = 200 mL/min; operation time = 2 h, followed by dark interval of 24 h, and then terminated by 2-h operation; and T =  $25.0 \degree$ C.



**Figure 3.** Chromium concentrations in eluent. Initial Cr(VI) feed concentration = 100 mg/L; flow rate = 200 mL/min; operation time = 1 h, followed by dark interval of 24 h, and then terminated by 1-h operation; and T = 25.0 °C.

Now that a self-regenerating adsorption column has been demonstrated, the next step was to investigate its effectiveness in treating real wastewater containing Cr(VI). Other chemicals present in wastewater may interfere with adsorption or reduction, or may compete with Cr(VI) and adsorb on the

wool surface. To investigate the possibility of antagonistic interactions with other metals, wastewater from a local electroplating company was analyzed for total Cr, Cr(VI), Cu, Mn, Ni, Pb, and Zn. As the concentrations of total Cr and Cr(VI) were high, the wastewater was diluted to obtain concentrations ca. 600 mg/L for Cr(VI), so that 1.0 L of feed can be processed in the column in accordance with the previous results.

Table 1 lists the heavy metals concentrations. The column processed 6.0 L of 100 mg/L Cr(VI) in the previous run before the breakthrough concentration of 1.0 mg/L was exceeded, as shown in Figure 2. The column was therefore expected to process only 1.0 L of 600 mg/L Cr(VI). Hence, an additional interval of 55 min, during which the flow was interrupted, was introduced to maintain a comparable load per unit time on the adsorbent. Figure 4 shows that with ca. 6-fold higher concentration of Cr(VI), 5.0 L of feed was processed before the breakthrough concentration was reached. Moreover, the other metals present in the wastewater had no effect on adsorption. The concentrations of these metals remained at values around the original feed concentrations (Figure 5), with slight fluctuations resembling a sine wave when examined closely. This pattern is consistent with repeated cycles of adsorption.



**Figure 4.** Chromium concentrations in the eluent. Initial Cr(VI) feed concentration (from electroplating wastewater) = 620 mg/L, flow rate = 200 mL/min, operation time = 5 min followed by dark interval of 55 min, and T = 25.0 °C.

Reduction of Cr(VI) is due to cysteine in wool. Cysteine thiols can be oxidized to produce sulfur-containing acids, namely sulfenic [R-S-O-H], sulfinic [R-S=O(OH)] and sulfonic  $[S(=O)_2(OH)]$  [28], in addition to disulfides and persulfides [29]. In a previous study from this lab, FTIR analysis of wool used to adsorb Cr(VI) showed that S=O bonds were affected, indicating that cysteine was involved in adsorption as an electron donor [22]. It is noteworthy that, in the presence of oxidants such as hydrogen peroxide, cysteine can be oxidized to sulfinic and sulfonic acids [30].

Concentration, mg/L

35

30

25

20

15





Time, min

**Figure 5.** Heavy metal concentrations in the eluent. Initial feed is electroplating wastewater, flow rate = 200 mL/min, operation time = 5 min followed by dark interval of 55 min, and T =  $25.0 \degree$ C.

Extension to additional cycles was also tested. In Figure 6, each point represents 2.0 L of processed wastewater, with a total of 8.0 L in each cycle. The first break denotes the first 24-h dark time, followed by a spike in Cr(III). After an additional 8.0 L of wastewater was processed, a second 24-h dark period was initiated, after which another spike in Cr(III) was observed, with the concentration of Cr(VI) remaining below 5.0 mg/L The slope observed in the first cycle is due to the effect of dilution, as experiments were carried out using an initially water filled column.



**Figure 6.** Chromium concentrations in the eluent for three consecutive cycles. Initial Cr(VI) feed concentration (from electroplating wastewater) = 620 mg/L, flow rate = 200 mL/min, operation time = 5 min followed by a dark interval of 55 min, and T =  $25.0 \degree$ C.

An increase in solution pH accompanies the reduction that takes place when wastewater is processed, particularly during the 24 h dark period. Adsorption is highly dependent on pH, as results from batch studies indicate [21,23]. The optimum pH of 2.0 has led to ca. 99% removal of Cr(VI). Thus, an increase wastewater pH will lead to a decrease in adsorption efficiency. To ensure that pH does not exceed the optimum value, two possible treatments can be made. The first is to start with a pH lower than the optimum. The second is to process HCl at low pH (1.0) immediately before the dark cycle. The second procedure was used, albeit the data were somewhat distorted as some Cr(VI) washes out, giving peaks at the beginning of Cycles 2 and 3. Whenever such peaks are observed, the eluent should be diverted to the feed for retreatment. The observed increase in pH is roughly one unit (from 1 to 2), with the higher pH being within the optimum range for adsorption, as shown in Figure 7. Wool is stable over a wide range of pH [31] and its high surface area facilitates absorption. The potential/pH (Pourbaix) diagrams for chromium in the pH 1–2 range show that at a redox potential of 1.1 V Cr(VI) is dominant, and below -1.0 V metallic Cr is dominant. Cr(III) exists between -1.0 and -0.1 V and Cr(II) between -0.1 and 1.1 V. Thus, Cr(III) is generally more stable at low pH and oxidizes to Cr(VI) at high pH [32]. Reduction of Cr(VI) to Cr(III) occurs at low pH, at which protonated active sites generate electrostatic attraction for Cr(VI). This is explained by H<sup>+</sup> causing reduction of Cr(VI) into Cr(III) [33] as shown below:

$$Cr_{2}O_{7}^{-2} + 14H^{+} + 6e^{-} \leftrightarrow 2Cr^{+3} + 7H_{2}O$$

$$CrO_{4}^{-2} + 8H^{+} + 3e^{-} \leftrightarrow Cr^{+3} + 4H_{2}O$$

$$HCrO_{4}^{-} + 7H^{+} + 3e^{-} \leftrightarrow Cr^{+3} + 4H_{2}O$$

$$H_{2}CrO_{4} + 6H^{+} + 3e^{-} \leftrightarrow Cr^{+3} + 4H_{2}O$$



**Figure 7.** Variation of pH in eluents for three consecutive operation cycles. Initial Cr(VI) feed concentration (from electroplating wastewater) = 620 mg/L, flow rate = 200 mL/min, operation time 5 min followed by dark interval of 55 min, and T =  $25.0 \degree$ C.

The mechanism proposed earlier [22] for adsorption and reduction of chromium on wool can be amended to accommodate the role of  $H^+$  in the process so that the mechanism can now be written as:

 $Cr^{+6} + wool \ + H^+ \rightarrow \left(Cr^{+6}\right) \cdots \left(wool \cdot H\right)^+ \rightarrow \left(Cr^{+3}\right) \cdots \left(wool \ \right) \rightarrow \ Cr^{+3} + wool \ + W^{+3} + W^{+$ 

#### 5. Conclusions

This work demonstrates the efficacy of a semi-continuous adsorption column for adsorption and reduction of Cr(VI) to Cr(III). This column can operate with reduced need for regeneration. A dark period of 24 h was found to be sufficient for regeneration of the packing for subsequent operation cycles as it allows for reduction of Cr(VI) to Cr(III). The presence of other heavy metals, in concentrations found in a typical electrochemical polishing facility waste, had no influence on the efficiency of the adsorption column. As pH highly affects adsorption efficiency, eluent pH was monitored. Measurements show that the operating pH does not increase above 2.0 for the chosen operating cycle periods. That pH was found to be optimal in previous batch adsorption experiments.

**Author Contributions:** M.B. performed most of the experiments. This research was led by T.H.I., M.I.K. and F.H.J. who were also instrumental in the initiation, conceptualization and planning of this work. All authors have read and agreed to the published version of the manuscript.

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