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Design and optimization of a batch sequential contactor for the removal of chromium(VI) from industrial wastewater using sheep wool as a low-cost adsorbent

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ABSTRACT

Cr(VI) removal from wastewater streams using sheep wool in sequential batch contactors (SBC) mode was investigated. The influence of the number of contactors on removal efficiency was also studied. SBC was carried out in tanks containing 100 and 1000 mL solutions. Four SBC runs ensured complete removal of Cr(VI) whereas three runs reduced its concentration from 100 to 0.06 mg/L. Experiments in both tanks gave similar results, thus permitting scalability to a pilot plant and eventual industrial scale utilization. Regeneration studies were carried out using KCl. The optimum parameters in terms of time, concentration and temperature were 25 min, 0.10 m and 50.0°C. Simultaneous adsorption-desorption cycles showed that sheep wool can be regenerated several times with no discernible change in removal efficiency.

Keywords: Hexavalent chromium; Sheep wool adsorbent; Sequential batch contactors; Adsorption-desorption cycles; Regeneration

1. Introduction

Chromium is a heavy metal with oxidation states ranging from +2 to +6. Cr(III) and Cr(VI) are the most stable forms in aqueous systems [1–3]. The physiochemical properties, chemical and biochemical reactivity and health effects of these two forms differ markedly. Cr(III) is relatively water-insoluble and a vital micro nutrient [1–4] but Cr(VI) is toxic, a known carcinogen [2], water soluble and thus a potential soil, surface and groundwater contaminant. Cr(VI) accumulation in water bodies poses a serious threat to the ecosystem and adversely affects human health. Its health effects include, but are not limited to, skin irritations, cancer (lung, nasal, sinus), genetoxicity, respiratory effects such as airway irritation and airway obstruction, reversible renal tubular damage, liver abnormalities, cardiovascular collapse and hematological toxicity [2,5,6]. Chromium compounds are extensively used in industrial applications. These include anti-corrosion coatings (spray or chrome coatings), production of corrosion-resistant alloys such as stainless steel, mordants, tanning agents, plating, inks, paints and pigments, fungicides and wood preservatives [2,3,7]. The extensive industrial use of chromium generates large amounts of wastewater containing Cr(VI). A typical electroplating company generates around 150 m^3/month[1]. This environmental hazard has led to substantial research on Cr(VI) reduction and sequestration from wastewater streams. A number of physical and chemical processes have been adapted to ensure its complete and efficient removal from these streams. Methods include reduction, ion exchange, chemical and electrochemical precipitation, membrane separation, evaporation, solvent extraction, cementation, freeze and foam separation, reverse osmosis, adsorption and biosorption [4,8–16].

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Adsorption has been referred to as an effective and versatile technique for the removal of heavy metals, including Cr(VI), from aqueous solutions. A number of inexpensive adsorbents such as inorganic substance and agricultural byproducts, activated carbon, waste materials, biosorbents (e.g. almond shell, banana skin) and keratinous materials have been used for Cr(VI) removal [17–19]. Wool was found to be effective for complete removal of Cr(VI) from aqueous solutions. The optimum parameters for Cr(VI) adsorption and reduction into Cr(III) using wool in batch mode have been reported [2,20–21].

In this study, the effectiveness of batch and sequential batch contactors in tanks containing 100 and 1000 mL solutions was investigated for Cr(VI) removal from synthetic wastewater streams.

2. Experimental

2.1. Materials

Potassium dichromate and 1,5 diphenyl carbazide (analytical grade) were from SD Fine Chemicals, India. All other chemicals were reagent grade and were used without further purification.

2.2. Instrumentation

A Cary-A50 UV-Visible spectrophotometer and an axial sequential inductively coupled plasma-atomic emission spectrometer (ICP-AES), both from Varian, Australia, were used for Cr(VI) and total Cr analysis, respectively. Adsorption experiments were performed using a thermostated compact shaker (KS-15A) coupled with a rack system (Combifix KS) and incubator hood (TH-15, Edmund Buhler GmbH, Germany). pH measurements were performed on a Thermo-Orion 210A+ pH meter (USA).

2.3 Adsorbent preparation

Sheep wool was obtained from the Sharjah animal market. It was intensively cleaned using detergent, rinsed with distilled water, then allowed to dry in the open air. It was then riffled, sized to *ca*. 2 cm fiber length then stored in a sealed container.

2.4. Chromium analysis

An aqueous stock potassium dichromate solution containing 100 mg/L Cr(VI) was prepared and used to make standard Cr(VI) solutions in the range 0.2–1.0 mg/L. Solutions with these concentrations were used to obtain the calibration curve for the determination of Cr(VI) by the colorimetric method [20,22]. The ligand solution was prepared by dissolving 250 mg 1,5 diphenylcarbazide in 500 mL acetone.

Cr(VI) concentrations were determined using method 7196A [20,22]. In this method, a predetermined volume of sample was mixed with 0.2 mL aliquot following addition of 2 drops of 6.0 M HCl and the final volume adjusted to 10 mL. The solution was then allowed to stand for 5–10 min in order to achieve full color development. Absorbance was measured at 540 nm. Total Cr concentrations were determined using ICP.

2.5. Chromium removal

2.5.1. Adsorption steps

In each experiment, 8 g of 2 cm long wool fibers was added to a known volume of synthetic wastewater containing 100 mg/L Cr(VI) and stirred at 150 rpm. pH and temperature were fixed at 2.0 ± 0.05 and 25.0 ± 0.1°C, respectively. pH adjustments were done using either 0.10 m NaOH or HCl. Procedures followed in studying the effect of contact time, adsorbent dosage, temperature, pH and KCl concentration have been described previously [20]. Experiments were performed using 100 and 1000 mL scale synthetic wastewater solutions in a sequential batch mode. The adsorption efficiency was calculated using Eq. (1)

$$Cr(VI)removal\ \% = \frac{C_o - C_i}{C_o} \times 100 \quad (1)$$

where C_o and C_i are the initial and equilibrium Cr(VI) concentrations, respectively (mg/L).

In the sequential batch mode, four sequential batch contactors (i.e. four stages) were employed. After adsorption in the first SBC the supernatant was transferred to the second SBC. Fresh adsorbent (8.0 g wool) was added to the second SBC and stirred at 150 rpm, after which the supernatant was transferred to the third SBC, and so on. A schematic representation of sequential batch contactors is shown in Fig. 1.

2.5.2. Regeneration steps

Known amounts of used wool were placed in conical flasks containing KCl solutions of known molarity then agitated for 25 min at 150 rpm and 25.0°C. The % desorption efficiency was calculated using the equation

$$\%desorptionefficiency = \frac{\text{Amount of Cr desorbed (desorption step)}}{\text{Amount of Cr adsorbed (adsorption step)}} x100 \quad (2)$$

The same procedure was followed for determining the effect on desorption efficiency of contact time, temperature and KCl concentration.

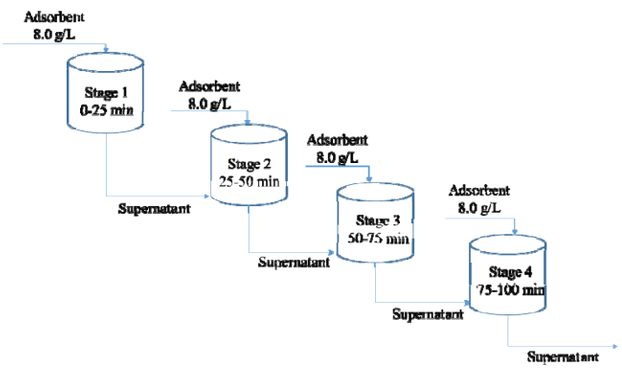

Fig. 1. Representation of sequential batch contactors.

3. Results and discussion

3.1. Cr(VI) removal using sequential batch contactors (SBC)

Table 1 gives chromium concentrations at the end of each stage for 100 mL and 1000 mL synthetic wastewater solutions. For the first solution, total chromium concentration decreased from 100 to 14.74 mg/L in the first stage, 14.74 to 4.64 mg/L in the second, and 4.64 to 2.41 mg/L in the third. Similar trends were observed for Cr(VI). Cr(VI) decreased from 100 to 13.66, 1.55 and 0.06 mg/L in the first, second and third stages, respectively. Analogous results were observed with the 1000 mL solutions (Table 1). Here, Cr(VI) decreased from 100 to 11.98 mg/L in the first stage, from 11.98 to 1.45 mg/L in the second and from 1.45 to 0.04 mg/L in the third. For both solutions, Cr(VI) concentrations were below the detection limit in all attempted fourth stages.

By comparison with the work reported by Jumean et al. [20], which was confined to single run short term, batch experiments, it can be deduced that three SBCs with adsorbent dosage of 8.0 g/L and 25 min contact time are sufficient to lower the initial Cr(VI) concentration in synthetic wastewater from 100 to 0.06 mg/L, i.e. to within the regulatory permissible discharge limit. This eliminates the need for large contact times (5 or more days) in order to attain complete removal of Cr(VI) from wastewater streams.

Table 1 also shows that there is a negligible effect of volume change, from 100 to 1000 mL, on removal efficiency. Changes in the stage wise removal efficiencies of Cr(VI) and total Cr points to the reduction of Cr(VI) to Cr(III) on the wool surface.

3.2. Regeneration studies

3.2.1. Effect of contact time

Table 2 gives the effect of contact time on chromium desorption from wool. The maximum desorption efficiency occurs at 25 min. After this time, no appreciable efficiency increase is observed. Hence, 25 min was selected as optimal contact time for wool regeneration. The maximum desorption efficiencies for Cr(VI) and total Cr are *ca.* 60 and 52%, respectively.

3.2.2. Effect of temperature

The effect of temperature on wool regeneration is shown in Table 3 for the short-term mode. The results indicate that wool regeneration is favored at elevated temperatures. The maximum desorption efficiency for Cr(VI) and total chromium is about 50% in both cases. Analogous results for other keratinous adsorbents have been reported [23].

3.2.3. Effect of KCl

Table 4 shows that varying KCl concentration in the range 0.1–1.0 m has little effect on desorption efficiency.

Table 2
Effect of contact time on chromium desorption. [KCl] = 0.10 m, volume of solution = 100 mL, adsorbent dosage = 8.0 g/L, pH = 2.0, T= 50.0°C, shaking speed = 150 rpm

Time, min	[Cr (VI)], mg/L	% desorption efficiency of Cr(VI)	Total [Cr], mg/L	% desorption efficiency of total Cr
2	26.1 ± 2.2	31.4 ± 2.1	27.9 ± 1.9	33.1 ± 1.9
5	33.9 ± 0.3	40.9 ± 1.0	40.2 ± 2.5	45.4 ± 2.2
10	38.4 ± 1.6	46.3 ± 1.0	47.7 ± 1.1	51.0 ± 0.3
15	42.8 ± 1.6	51.6 ± 0.5	50.8 ± 1.7	51.3 ± 1.2
25	49.8 ± 1.1	60.0 ± 2.3	55.1 ± 1.4	52.4 ± 0.4

Table 3
Effect of temperature on % desorption efficiency. Initial [KCl] = 0.10 m, volume of solution = 100 mL, adsorbent dosage = 8.0 g/L, shaking speed = 150 rpm, contact time = 25 min

T, °C	Final [Cr(VI)], mg/L	% desorption efficiency of Cr(VI)	Final total [Cr], mg/L	% desorption efficiency of total Cr
25.0	20.7 ± 3.2	22.5 ± 4.4	30.2 ± 1.8	34.4 ± 2.7
35.0	24.7 ± 0.9	27.1 ± 1.0	35.9 ± 0.4	40.6 ± 1.1

Table 1
Final concentration and % removal of chromium in sequential batch contactor during the three stages using 100 and 1000 mL synthetic wastewater solutions. Initial concentration of chromium = 100 mg/L, adsorbent dosage = 8.0 g/L, pH = 2.0, T = 25.0°C, shaking speed = 150 rpm. Stage 1: 0–25 min, stage 2: 25–50 min, stage 3: 50–75 min

Volume	Stage	Cr(VI)			Total Cr		
		Final concentration, mg/L	Cumulative % removal	Stagewise % removal, mg/L	Final concentration, mg/L	Cumulative % removal	Stagewise % removal, mg/L
100 mL	1	13.7 ± 1.9	85.8 ± 1.5	85.8 ± 1.8	14.7 ± 2.5	85.2 ± 2.5	85.3 ± 2.5
	2	1.55 ± 0.3	98.7 ± 0.2	90.7 ± 0.8	4.64 ± 0.4	96.1 ± 0.4	72.9 ± 2.3
	3	0.06 ± 0.05	100 ± 0.01	97.5 ± 1.1	2.41 ± 0.9	98.2 ± 0.7	54.4 ± 5.9
1000 mL	1	12.0 ± 0.3	88.0 ± 0.3	88.0 ± 0.4	12.8 ± 1.2	87.2 ± 1.2	87.2 ± 1.2
	2	1.45 ± 0.2	98.6 ± 0.2	88.3 ± 1.7	3.64 ± 0.4	96.4 ± 0.4	71.8 ± 0.5
	3	BDL*	100 ± 0.01	98.3 ± 0.7	1.39 ± 0.6	98.8 ± 0.5	66.8 ± 1.1

Additionally, final total chromium and Cr(VI) concentrations are very close, indicating that the solution contains essentially Cr(VI). These results indicate that reduction of adsorbed Cr(VI) to Cr(III) did not take place during the short contact time of these experiments (25 min). This is in agreement with previous findings that short term exposure does not result in reduction of Cr(VI) to Cr(III) [20].

Fig. 2. Shows the colors of wool samples following adsorption and regeneration. Used wool samples are dark yellow due to adsorbed Cr(VI) whereas the color of regenerated samples is close to that of native wool, indicating highly effective regeneration.

3.2.4. Adsorption-desorption cycle

Wool was subjected to three adsorption-desorption cycles. Fig. 3 is a schematic diagram of these cycles. The experimental conditions were maintained at optimum parameters. Fig. 4 summarizes the effect of time on Cr(VI) concentration during each cycle. The maximum Cr(VI) concentration at complete regeneration is *ca.* 50 mg/L (100 mg/L initially), indicating that adsorption on wool is followed by significant reduction of Cr(VI) into Cr(III). The finding that wool is regenerated by desorption of Cr(VI) is supported by the reaction between KCl and the wool-Cr(VI) complex, in which Cr(VI) is released into the regenerating solution.

Tables 5 and 6 summarize the adsorption efficiency of Cr(VI) by wool in three consecutive adsorption-desorption cycles. The results indicate that removal efficiency of chromium (hexavalent and total) over these cycles remains essentially constant. This is indicates highly effective wool regeneration.

Table 4
Effect of KCl concentration on % desorption efficiency. Volume of solution = 100 mL, adsorbent dosage = 8 g/L, shaking speed = 150 rpm, T =50.0°C, contact time = 25 min

[KCl], m	Final [Cr(VI)], mg/L	% desorption efficiency of Cr(VI)	Final total [Cr], mg/L	% desorption efficiency of total Cr
0.1	49.3 ± 1.1	48.4 ± 2.2	51.2 ± 1.4	49.1 ± 0.3
1.0	46.3 ± 0.5	52.8 ±0.8	47.8 ± 1.0	51.5 ± 0.7

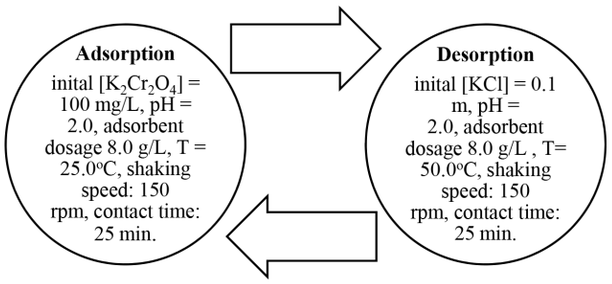

Fig. 3. Schematic representation of consecutive adsorption desorption cycles.

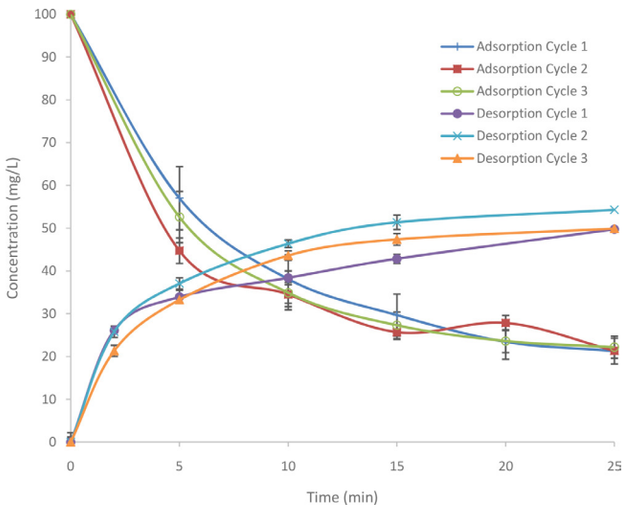

Fig. 4. Variation of Cr(VI) concentration with time over three adsorption-desorption cycles.

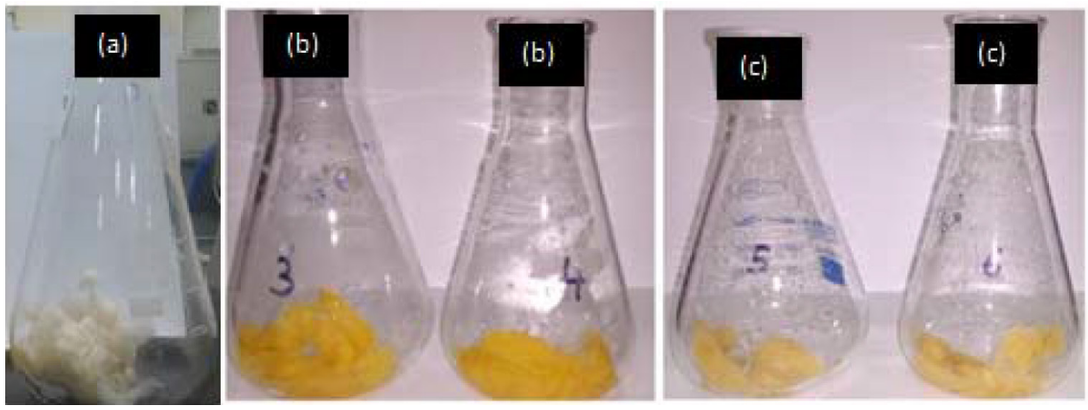

Fig. 2. Color of wool samples (a) before adsorption (b) after adsorption (c) after regeneration.

Table 5
Concentrations of Cr(VI) and total Cr at the end of each adsorption-desorption cycle

Cycle No	Final [Cr(VI)], mg/L	Final total [Cr], mg/L
Adsorption cycle 1	19.8 ± 1.8	21.3 ± 3.0
Desorption cycle 1	49.8 ±1.1	55.1 ± 1.4
Adsorption cycle 2	21.3 ± 0.7	25.9 ± 1.8
Desorption cycle 2	45.0 ± 3.9	54.3 ± 1.7
Adsorption cycle 3	22.2 ± 2.6	23.9 ± 3.9
Desorption cycle 3	49.9 ± 2.6	61.4 ± 1.6

Table 6
Final concentration and % removal efficiency of chromium during adsorption cycles. Initial chromium concentration = 100 mg/L, pH = 2.0, volume of solution =100 mL, adsorbent dosage = 8.0 g/L, T = 25.0°C, shaking speed = 150 rpm, contact time = 25 min

Cycle No	Final [Cr(VI)], mg/L	Adsorption efficiency of Cr(VI), mg/L	Final total [Cr], mg/L	% Adsorption efficiency total Cr
1	19.8 ± 1.8	84.2 ± 1.4	21.3 ± 3.0	83.0 ± 2.4
2	21.3 ± 0.7	82.9 ± 0.6	25.9 ± 1.8	79.3 ± 1.5
3	22.2 ± 2.6	82.3 ± 2.1	23.9 ± 3.9	80.9 ± 0.8

4. Conclusion

Cumulative removal of Cr (VI), using sheep wool as adsorbent, exceeded 99% in three sequential batch contactors (SBC). Regeneration of wool was successfully done with KCl solutions. Optimum parameters for regeneration in terms of temperature, contact time and KCl concentration were 50°C, 25 min and 0.10 M, respectively. No change in adsorption efficiency or wool affinity for Cr(VI) was observed in three consecutive adsorption-desorption cycles. Thus, a three step removal (SBC) is proposed. The high affinity of Cr(VI) for wool and complete regeneration of wool support the selection of SBC as a practical method for Cr(VI) removal from wastewater streams. Desorbed Cr(VI) can be stored and used in industrial applications. Pilot scale batch and continuous scale studies can be carried out to determine process feasibility. The novelty of the present study can be ascribed to the optimization of a sequential batch contactor, with low timing, for essentially complete removal of Cr(VI) from industrial wastewater. This work furnishes a basis for the installation of large scale Cr(VI) removal plants on sites of industrial establishments, such as electroplating industries. The wastewater generated from a medium size electroplating industry contains around 2500 mg/L Cr(VI). Application of the SBC method described in this work appears promising for treatment of this type of wastewater.

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