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EXTRACTION OF TRIVALENT CHROMIUM FROM TANNERY EFFLUENT BY ION EXCHANGE WITH INDION 790 RESIN

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ABSTRACT

Extraction of chromium(III) from a model tanning effluent has been studied by ion exchange using Indion 790 resin. The resin has been found to be selective for the sorption of chromium(III) in the pH range 0.5-3.5 from a model solution containing 500 ppm chromium(III). Beyond pH 3.5 extraction of chromium(III) drastically decreases from 92% to 76.5%. Sorption of chromium(III) on Indion 790 follows Freundlich isotherm indicating strong chemical interaction of the metal ion with the resin. Desorption of chromium(III) from the loaded resin increases with the increase in concentration of eluant (5-20% H_2SO_4). With 20% sulfuric acid solution 89% chromium(III) was eluted in two stages. The bench scale results are also validated in continuous mode in a fixed bed column for the recovery of chromium(III) from tannery effluent.

INTRODUCTION

Tanning is the main process that protects leather against some environmental effects such as microbial degradation, heat, sweat or moisture, etc. In the tanning process, chromium(III) salts are widely used as tannage materials because of the excellent properties of the chromium compounds in the tanning. In the chromium tanning process, the leather takes up only 60–80% of applied chromium, and the rest is usually recycled into the hides. After recycling, the solution becomes unacceptable for tanning and the it is discarded as spent solution which is discharged for treatment. The waste water so obtained from the treatment contains some chromium causing serious environmental impact. The traditional technique used for chromium control in the waste water involves chemical precipitation of chromium(III) as $Cr(OH)_3$ and secure dumping. But, experimental evidences show that the kinetics of the transformation of chromium(III) to chromium(VI) is rapid enough in presence of even mild oxidants [1], and chromium(VI) is highly toxic as a potential carcinogenic agent [2] due to its high oxidation potential and relatively smaller size, which enables it to penetrate through biological cell membranes. Therefore, the land fills of chromium may be considered as potential hazard to the environment. However, some studies related to recovery or recycling of chromium from spent tanning liquors have been made [3–7]. Out of several options for removing chromium from wastewaters, ion exchange is considered to be quite promising. Several studies considering the chromium removal by ion exchange resins have been reported in the literature [8-9].

In the present work the removal of chromium(III) from aqueous solutions using a cationic resin (Indion 790) was investigated. The main objective of the study was to evaluate the sorption equilibrium for this resin at temperature and to understand the dynamic behaviour of the process in a column test.

EXPERIMENTAL

A synthetic stock solution containing 1000 ppm chromium(III) was prepared by dissolving 5.12g of $CrCl_3.6H_2O$ in 1000 mL distilled water. Chromium(III) solutions of desired concentrations were prepared by diluting the stock solution with distilled water and used to investigate the extraction of chromium(III) by ion exchange using Indion 790. The resin Indion 790 was obtained from Ion Exchange, India. The resin is a strongly acidic cation exchanger with styrene-DVB and sulfonic acid as the functional group. The particle size is in the range 0.3-1.2 mm with 51-55% moisture content.

To study the extraction of chromium(III) by ion exchange, 50 mL of the aqueous solution of known concentration and pH was taken in a conical flask of 250 mL capacity and weighed amount (0.5g) of dry resin was added in the flask so as to maintain the A/R ratio of 50. [A=Volume of the aqueous feed in mL and R= Amount of resin in g]. The contents of the flasks were equilibrated by a wrist action shaking machine for certain length of time at room temperature. The speed of shaking was fixed at 250 oscillations/min. The equilibrated solution was filtered by filter paper (Whatman 41) to separate it from the resin.

The loaded resin was washed thoroughly with distilled water and then chromium was eluted with 50 mL of sulphuric acid solution of a known strength. All the extraction and elution studies were carried out at room temperature. The raffinate and the eluted solutions were analyzed by Atomic Absorption Spectrometer ECIL, India and the material balance was checked.

RESULTS AND DISCUSSION

Effect of mixing time

Aqueous feed solutions containing 500 and 1000 ppm chromium(III) were contacted with Indion 790 at A/R ratio of 50 and 2.74 pH for various time intervals and the results are depicted in Fig. 1. It was found that the extraction of chromium(III) increased with increase in contact time. Within 12 min of contact, 92.5% chromium(III) was extracted from 500 ppm solution, although major extraction was achieved in 8 min. However, from 1000 ppm chromium(III) solution only 78% chromium(III) was extracted when contacted with Indion 790 for 16 min. Thus, extraction of chromium(III) increased with the decrease in chromium(III) concentration in the aqueous solution. This is due to the fact that for dilute solution amount of active sites available in the resin is higher as compared to that of concentrated solutions, resulting in higher level of extraction from the dilute solution.

Effect of pH on the extraction of chromium(III)

Extraction of chromium(III) from 500 ppm chromium(III) solutions of various pH was studied using Indion 790 at A/R ratio of 50. It was observed that (Fig. 2) extraction of chromium(III) remain almost constant (92%) within the pH range 0.5 – 3.5. However, beyond pH 3.5 chromium(III) extraction decreased. At pH 5.0 only 65.4% chromium(III) was extracted. Decrease in chromium(III) extraction beyond pH 3.5 may be due to hydrolysis of chromium(III) ion forming $Cr(OH)_3$.

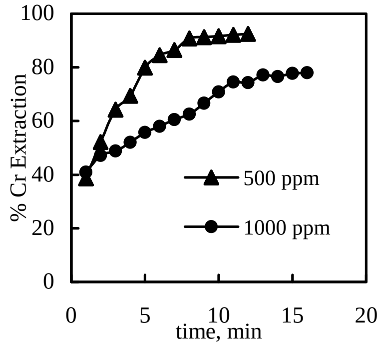

Fig. 1. Effect of mixing time on extraction of chromium(III) with Indion 790. pH = 2.74, A/R = 50.

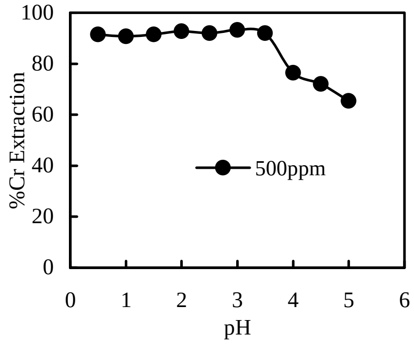

Fig. 2. Effect of pH on extraction of chromium(III) with Indion 790; A/R = 50.

Sorption isotherm

Maximum loading capacity of Indion 790 was determined by repeatedly contacting 1 g of the resin with fresh 500 ppm chromium(III) solution. It was observed that a saturation loading of 69.224 mg Cr/g resin was attained in eight stages. In order to determine the nature of sorption of chromium(III) on the resin, the data so obtained while determining loading capacity were fitted into Freundlich (Eq. 1) and Langmuir (Eq. 2) isotherms and the plots depicted in Figs. 3 and 4.

$$q = K_f (C_e)^{1/n} \qquad \text{or} \qquad \log q = (1/n)\log C_e + \log K_f \tag{1}$$

$$q = (q_m K_l C_e)/(1 + K_l C_e) \tag{2}$$

where q = amount of chromium(III) loaded on resin (mg/g)

C_e = the equilibrium concentration of chromium(III)

q_m = Loading capacity of Indion 790

K_f/K_l = Freundlich/Langmuir csonstant

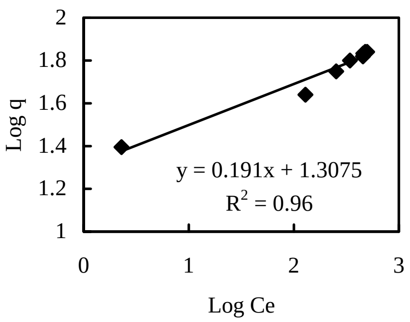

Fig. 3 Freundlich isotherm for sorption of chromium(III) with Indion 790

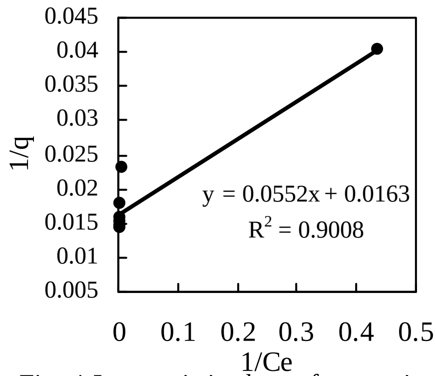

Fig. 4 Langmuir isotherm for sorption of chromium(III) with Indion 790

Higher R^2 value obtained for Freundlich model as compared to Langmuir model show that the system so developed with Indion 790 follows Freundlich isotherm. Freundlich and Langmuir constants were found to be 20.267 and 0.295. Higher value of Frundlich constant indicates strong chemical interaction between the resin and chromium(III).

Kinetics of extraction

In order to determine the kinetics of sorption of chromium(III) onto the resin, kinetic data were fitted into Lagergren first and second order model. The rate constants and R^2 values obtained are shown in Table 1. The R^2 value of second order plot is more convincing than that of first order kinetics indicating sorption of chromium(III) follows second order kinetics. Further, negative rate constant value obtained for first order reaction model confirms that the sorption of chromium onto the resin follows second order kinetics.

Table 1: R^2 and rate constant values obtained for Ist and IInd order rate equations for different aqueous feed concentration.

[Cr(III)], ppm	IInd order			Ist order	
	R^2	k_2	h	R^2	k_1
500	0.9971	0.01336	11.905	0.9636	-0.2814
1000	0.9844	0.009	17.794	0.9773	-0.0712

Desorption study

Elution of chromium(III) from loaded Indion 790 was studied using various concentrations (5 – 20% w/v) of sulfuric acid solutions as eluant (Fig. 5). Desorption of chromium(III) increased with increase in sulfuric acid concentration. With 20% sulfuric acid solution 89.23% chromium(III) was eluted in two stages, whereas in the third stage no chromium was eluted. This may be due to formation of $Cr(OH)SO_4$ species, which is difficult to elute under normal condition.

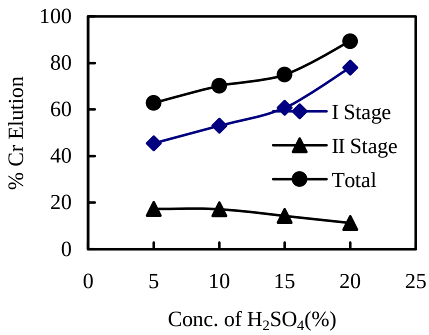

Fig. 5 Elution study for chromium(III) from loaded Indion 790 resin

Recovey of chromium(III) from tanning effluent

Experiments were carried out with a typical tannery effluent solution to know the effectiveness of Indion 790 for extraction of chromium(III). Results obtained are given in Table 2. A 95% chromium(III) was extracted by this resin under similar conditions stated earlier. From the loaded resin 93% chromium(III) was eluted with 20% sulfuric acid solution in single stage.

Table 2. Extraction of chromium(III) from tanning effluent in three stages. Resin: Indion 790; pH: 2.74; A/R: 50, mixing time: 15 min

[Cr(III)], ppm	% Extraction of chromium(III)			Elution with 20% H_2SO_4
	1st stage	2nd stage	3rd stage	93%
457.6	66.18	92.7	95.5	

CONCLUSION

Extraction of chromium(III) from model tanning solution has been studied by ion exchange using Indion 790. It has been observed that extraction of chromium(III) increases with the increase in time of contact between the resin and chromium solution. From 500 ppm chromium(III) solution 92.5% chromium is extracted onto the resin. However, from 1000 ppm chromium(III) solution only 78% chromium is extracted. It is also observed that in the pH range 0.5-3.5, extraction of chromium(III) remains almost constant, but beyond pH 3.5 extraction of chromium decreases due to hydrolysis of chromium(III). Sorption of chromium(III) on Indion 790 follows Freundlich isotherm indicating strong chemical interaction of the metal ion with the resin. Desorption of chromium(III) from the loaded resin increases with the increase in concentration of eluant (5-20% H_2SO_4). With 20% sulfuric acid solution

89% chromium(III) was eluted in two stages. Extraction of chromium(III) from a typical tannery effluent has also been carried out. From the tannery effluent 95.5% chromium(III) was extracted in three stages and 93% of chromium was eluted with 20% H_2SO_4 solution in single stage.

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