

## Removal of Chromate in Trace Concentration Using Ion Exchange From Tannery Wastewater

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**ABSTRACT:** The removal of chromate ions in trace concentration from tannery wastewater effluent using Ion exchange technique was carried out by varying parameters such as Chromate concentration and contact time. A maximum of 99% removal efficiency in the batch Ion exchange process was achieved over an equilibrium contact time of 20min. The equilibrium uptake of chromate was constant at average 9.8mg/L for initial chromate concentration of 10mg/L irrespective of the high concentration of chloride and sulphate ions in the wastewater. This inferred that the interference of these co-ions have no significant effect on the chromate uptake by the ions exchange resins used in this study. While, in the column experiments high effectiveness in the removal of chromate ions in trace concentration was observed. A removal efficiency of 98% of chromate removal was achieved even in the presence of high concentration of competing Ions. Obviously, this has shown the selectivity of the resin towards the chromate uptake. The ion-exchange technique was found to be appealing for the removal of trace concentration of chromate when in the background there is high concentration of chloride and sulphate co-ions present in the tannery wastewater.

**Key words:** Chromate, Wastewater, Ion exchange, Uptake, Pollution

### INTRODUCTION

Leather industries require large volume of water in the various tanning processes (Buljan, *et al.*, 2002; Ashraf and Shazad, 2003). Wastewater generated is characterize by it rich in suspended, dissolve impurities and toxic chemical has been discharged either to open land or onto surface waters, if not treated before discharge will eventually cause serious environmental pollution (Trumble and Jensen, 2004). Nowadays, the use of chrome salt ( $\text{Na}_2\text{Cr}_2\text{O}_7$ ) tanning is widely favoured by majority of leather Industries (Ashraf *et al.*, 1998). The salts when applied to a treated animal skin form a protective barrier, which prevents penetrating water into the leather pores. Low cost of applications, colour of the leather and resulting stability are added advantages of using chrome tanning (Hafiz *et al.*, 2002). In tanning processes a significant

amount of chromate sulphate of about 19000mg/L is applied in tanning of animal skin, only about 60%-70% of the chromate salt reacts with the skin. The remaining amount is discharge into the effluent (Mant *et al.*, 2005). Hence, this wastewater is an important source of chromate pollution to the environmental (Abass *et al.*, 2005). In order to comply with the strict legislation on total chromate content present in wastewater for discharge into open land and waterways, chromate removal and re-use has become necessary (Vilsmier *et al.*, 1999). In addition, Chromium is an expensive metal it cost implication on the leather industries and environmental effect are another reasons (Kocaoba and Akcin, 2002). In solution, chromium can exist in two-oxidation state namely Cr (VI) ions as chromate ( $\text{CrO}_4^{2-}$  and  $\text{Cr}_2\text{O}_7^{2-}$ ) and Cr (III) ions with contrasting toxicities, mobility and biodiversity. Cr (VI) has high tendency to bind with oxygen, so it can

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exist as an anion ( $\text{CrO}_4^{2-}$  and  $\text{Cr}_2\text{O}_7^{2-}$ ) of high solubility. Trace concentration of Cr (III) ions is beneficial to humans as food supplement especially in glucose metabolism (Park and Jung, 2001). Conversely, depending on the solution PH Chromate species  $\text{CrO}_4^{2-}$  and  $\text{Cr}_2\text{O}_7^{2-}$  are the most toxic to humans, animals and plants (Camargo *et al.*, 2003). The maximum concentration level permitted in wastewater is 5mg/L for Cr (III) and 0.05mg/L for Chromate ( $\text{Cr}_2\text{O}_7^{2-}$ ) taken into consideration of chromate species (Dahbi and Guardia de la, 1999).

In recent times, tannery wastewaters treatment presents a serious environmental and technology problem (Ramasani and Rao., 1991). The conventional methods for removing toxic  $\text{Cr}_2\text{O}_7^{2-}$  include chemical reduction followed by precipitation (Abass *et al.*, 2005), adsorption on activated carbon (Dhabi *et al.*, 1999) and Biological reduction (Fude *et al.*, 1994). These methods are effective when the chromate concentrations are relatively high (>25mg/L) but a draw back has been reported when the chromate concentrations are in traces (<25mg/L). The removal of trace concentrations of these metal ions is often complex and complicated (Lloyd-Jone *et al.*, 2004). In the past, Chromate discharged as effluent of less than 25mg/L concentration are recovered and recycled back into the tanning process by chemical precipitation method. This involves Chromate to be reduced to Cr (III) by reducing agent then precipitated by an alkali as  $\text{Cr}(\text{OH})_3$ . This method cannot adequately remove trace concentration of chromate from tannery effluent directly (Ashraf and Shazhad, 2003). Ion exchange a physico-chemical process is an economic and convenient method that can directly and adequately removes heavy metals ions in trace concentration from industrial solutions and wastewater. Arup, *et al.*, 1988, reported the mechanism and some properties of Chromate Ion exchange. The uptake of these metal ions on the resins is a reversible reaction and can be regenerated and re-use for several cycles of operations (Elshazly and Konsowa, 2003).

The capacity of Ion exchange method for removal of toxic heavy metal ions in wastewater and industrial solutions has been investigated

by (Erdem *et al.*, 2004; Lloyd-Jones *et al.*, 2004 and Elshazly and Konsowa, 2003). In the studies of (Anuradha and Arup, 1992; Arup *et al.*, 1988 and Lloyd-Jones *et al.*, 2004) investigates the capacities of different Ion exchange resins in batch and column reactors and reported an encouraging conclusion with regard to the extent of removal of different heavy metal ions. Poor selectivity for competing ions is a common problem with the method. The selectivity of different Ion exchange resins toward removal of trace concentration of chromate in the background of high concentration of co-ions was demonstrated by Arup *et al.*, 1988. Also, (Anuradha and Arup, 1992 and Vilsmeier *et al.*, 1999) reported that the modification of the Ion exchange surface of resins for removal of heavy metal ions can improve on the selectivity toward particular metal ions. The affinity of the resins for various ions depended on the charge density of the ions bonding effect. This implies that the extent to which exchange occur between the ions depend on the affinity of the resins for each ions concentration in the solution and on the resins. These resins have widely developed pore structure. That can be filled with solution of the ions for uptake at active sites. The reaction between the resins and dissolved ions is also diffusion controlled (Perry, 1997). The characteristics of tannery wastewaters vary widely depending on the tanning process adopted and the type of animal skin used (Javeed and Mobeen, 1997). The quantity of water used depends on the method of hide preservation and processing together with the in-plant measures adopted in minimization of water used to reduce pollution (Tunay *et al.*, 1995). The work presented by (Oke *et al.*, 2006 and Lofrano *et al.*, 2006) outline the result of tannery wastewater characterization in Nigeria and Italy. The wastewaters have been reported to contain very high pollution load including toxic chromate and exhibiting toxicity. The purpose of the study was to investigate the possibility of using Ion exchange resin to make certain it's selectively toward the uptake of trace concentration of chromate from tanning wastewater effluent and synthetic solution. The inference of most common ions (chloride and sulphate ions) present in the Tannery

wastewater on the uptake of chromate was additionally investigated.

## **MATERIAL & METHODS**

Commercially available weak base Ion exchange resins Rohm & Haas Amberlite IR-45 (Containing Polyamine Functionality) was used to remove chromate from tannery wastewater because of its outstanding selectivity to particularly chromate. The resins used in the Chromate-Ion exchange operation was at its fullest capacity at low pH of 4.0. The resins were conditioned following standard procedures of cyclic exhaustion with 2N Sulphuric acid and regeneration with 2N Sodium Hydroxide. Subsequently, the resin was converted to chloride form with 2N Sodium Chloride and was rinsed with distilled deionized water and dried for 48 hrs. The resin particles were screened to particles in the range of 250  $\mu$  m to 500  $\mu$  m. All inorganic chemicals were supplied by BDH; Chemical, UK as analytical grade reagents and distilled deionized water was used. The metal ions studied were  $\text{Cr}_2\text{O}_7^{2-}$  as Chromate. We prepared a synthetic stock solution of Potassium dichromate as Chrome salt in distilled deionized water as a source of chromate. Series of solution containing different chromate concentration were prepared. Raw wastewater samples were collected in Kano a city in the Northern Nigeria. The Tannery factories mostly produce leather from goat and cattle skin. The sample was delivered to the laboratory under 5hrs for chemical analysis. The sample was kept refrigerated at 20°C during the analysis. In situ measurement of PH was carried out using a conductivity meter (HACH, Co.150). Determination of TSS, Sulphate and Chloride ions concentrations were carried out using Colorimeter (HACH, DR890). Chromate ( $\text{Cr}_2\text{O}_7^{2-}$ ) concentration was determined using Atomic Absorption spectrophotometer (HACH, DR2000). Also, COD and BOD concentrations were determined according to the standard prescribed by APHA, 2005. The results were presented in Table 1. Synthetic wastewater was prepared using stock solutions of Potassium dichromate salt ( $\text{K}_2\text{Cr}_2\text{O}_7$ ), Sodium Sulphate ( $\text{Na}_2\text{SO}_4$ ) and Sodium Chloride ( $\text{NaCl}$ ). Different concentrations were

prepared to mimic a typical wastewater from a tannery factory effluent in Nigeria. Similar procedures as in the case of raw wastewater were used to determine the concentrations of the wastewater parameters to make certain their toxicity.

A 2g preconditioned resin (dry weight) was added to a 2L Erlenmeyer flask containing 500mL potassium dichromate ( $\text{K}_2\text{Cr}_2\text{O}_7$ ) solution of known concentration maintained at pH 4.0. Samples were agitated using a stirrer rotating at 160rpm. The solution pH was adjusted by adding 1M NaOH solution until a constant pH was attained. The sample pH attained equilibrium when no significant change in pH was observed after some time. The equilibrated samples were filtered using 0.2 $\mu$ PTFF Syringe top filters to remove the resin particles and analyzed for chromate using atomic absorption spectrophotometer. While, Sulphate and Chloride ions were analyzed using Colorimeter (HACH, DR890) to determine their concentrations. The experiments were performed for 30min and the temperature was maintained at 32°C using a temperature controller unit. The chromate concentration was kept at trace concentrations many folds less than the co-ions and 10% chromate reduction was considered. A 2g of preconditioned resins (dry weight) was placed in a 2L Erlenmeyer flask. Prior to the start of the experiment, the resins were placed in distilled deionised water in order to expel any trapped air and to allow swelling to take place. In the flask, 1L sample of Chromate solution of known initial concentration and the resin was agitated using a stirrer rotating at 160rpm using a motor. Inside the flask, pH 4.0 and reaction temperature of 32°C were maintained constant. Series of 1mL samples were drawn at certain time intervals and analyzed for chromate, sulphate and chloride ions respectively. The percentage uptake of chromate was calculated using the equation.

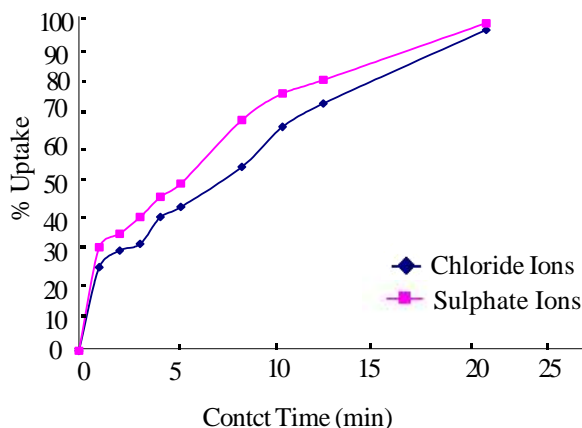
$$\% \text{ Uptake} = \left( \frac{C_i - C_f}{C_f} \right) \times 100$$

Where  $C_i$  and  $C_f$  are the initial and final concentrations of Chromate at time  $t = 0.0$  min and time  $t = t$  min respectively. An Ion exchange

column fitted with glass wool to support a known weight preconditioned resins was used in this experiment. The column was filled with the resin to a particular height. Distilled water was thoroughly passed through the column until the effluent is neutral. Several solutions of chromate ions at an optimum pH of 4.0 were made to flow across the resins bed using a pump at a flow rate of 2.0m<sup>3</sup>/mm. Effluents were collected and analyzed for chromate. The experiment was repeated for certain resins mass.

### RESULTS & DISCUSSION

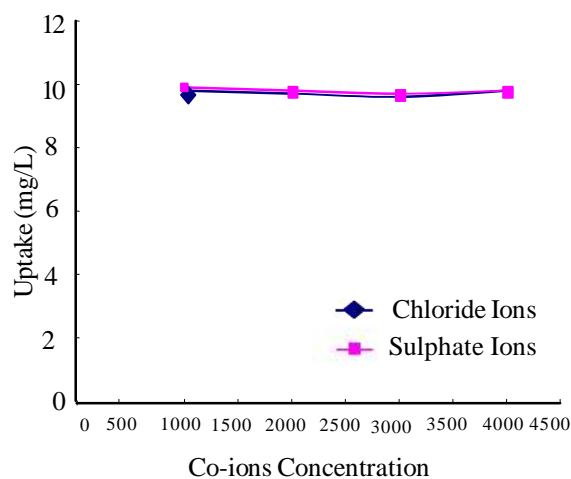
In order to understand the effect of contact time on the uptake of chromate on the resins (Amberlite IR45), series of experiments were carried out at optimal pH, agitation speed of the stirrer, and resin dose. The results were presented in the plot (Fig.1).



**Fig. 1. Percentage Uptake of Chromate from Tannery Wastewater by Ion-exchange**

It was observed that chromate removed increased with increasing contact time. The kinetics of chromate removal by the resins was relatively fast, which within 15min, uptake of 67% was achieved and the equilibrium uptake of 99% was achieved at about 20min. The increased uptake of chromate with contact time can be due to the decreased mass transfer coefficient of the diffusion controlled reaction between the resins and chromate. This equilibrium time is the optimal time to achieve 99% removal of chromate. This is a crucial parameter for an optimal removal of chromate in the wastewater.

Sulphate and chloride ions are the major co-ions that are in many folds higher than chromate ions in tannery wastewater. Their effect on the uptake of Chromate by the resin was investigated. Several batch experiments were conducted using concentrations of chloride and sulphate ions in the range of 1000 mg/L and 40000 mg/L at constant Chromate concentration of 10 mg/L. The result presented in (Fig. 2).



**Fig. 2. Effect of Interference of Co-ions on the Uptake of Chromate**

Depicted that the presence of this ions (chloride and sulphate ions) have no significant effect on the removal of chromate by the resins. The uptake for chromate on the resins was found to be at a constant concentration at 9.8mg/L irrespective of the chromate concentrations. The extent by which the competing ion interfered with the uptake of chromate is important for the choice of resins that will selectively remove chromate contaminants from tanning wastewater. This study can justify the use of Amberlite IR45 to selectively remove chromate from industrial wastewaters that have similar content of sulphate and chloride ions in concentrations many folds higher than the chromate concentration. Several Experiments were carried out to investigate the extent of removal of chromate by ion-exchange resins in vertical cylindrical column. Two different concentrations of 5mg/L and 25 mg/L were prepared as the synthetic wastewater. The extent of removal was characterized based on the effluent concentration of chromate that passed through the resins bed.

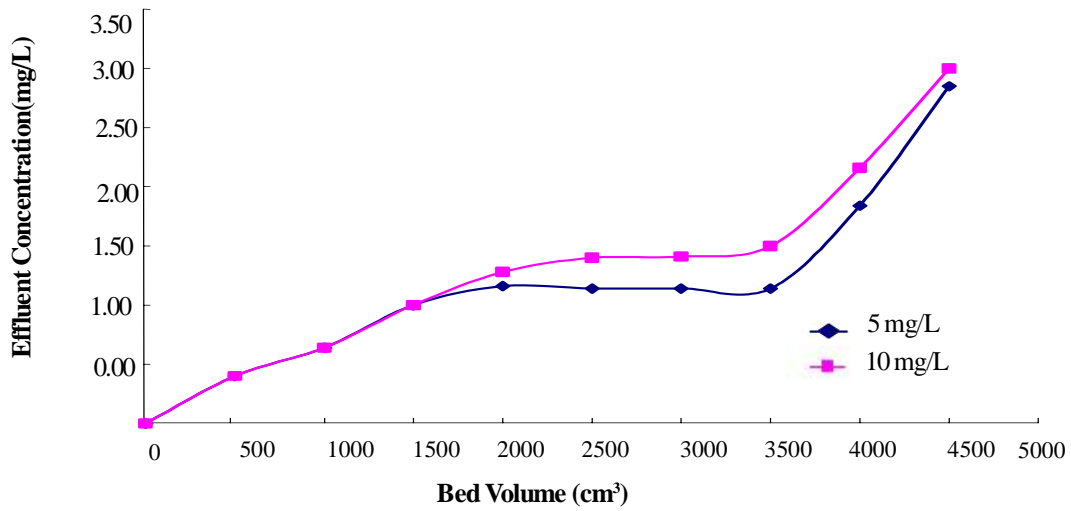


Fig. 3. Effluent charateristic of Fixed Bed Ion-exchange Column for Removal of Chromate

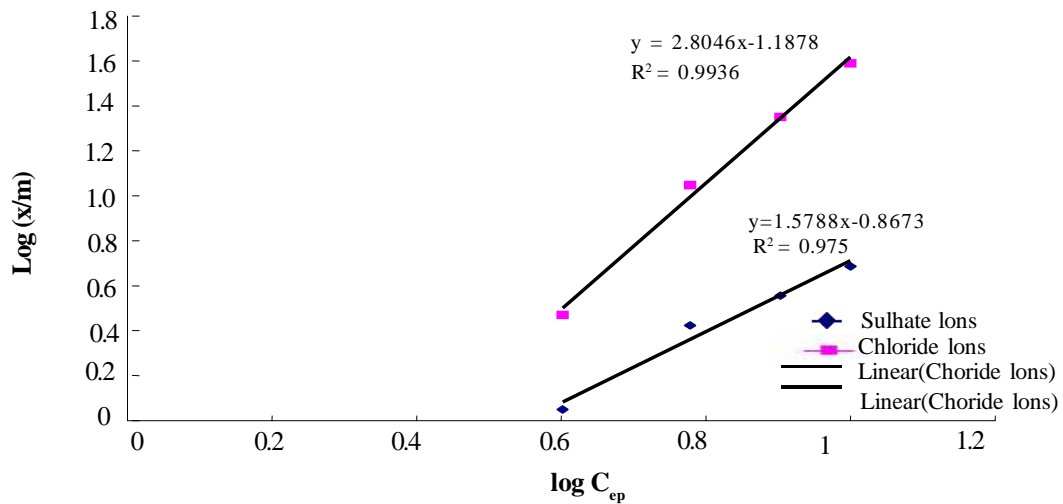


Fig 4. Freundlich Adsorption Model for Chromete uptake on Ion-exchang Resins System

Table 1. Characteristics of Tannery Wastewater

Parameters	Units	Value	
		Raw Wastewater	Treated Wastewater
Chromate	mg/L	87	0.06
TSS	mg/L	1976	13
BOD	mg/L	2978	37.6
COD	mg/L	4587	15
Sulphate	mg/L	8673	437.5
Chloride	mg/L	6854	283.4
pH	-	8.2	7.4
Color	-	Dark brown	Clear

The effect of resin dose on the effluent concentration of chromate was presented in the plot (Fig. 3). It was observed that between 0.00mg/L to 11.5mg/L of the chromate effluent concentration, the removal was found to be independent of the initial concentration of chromate. Also observed was a gradual breakthrough point for the two initial chromate concentrations. However, the gradual breakthrough points the effluent history curves diverge which suggested that the effluent concentration increased with increasing initial concentration. Conversely, in the report of Arup et al. (1988) the gradual breakthrough points were common to the two concentration curves. The Freundlich adsorption isotherm was used in this study to describe the experimental results on the uptake of chromate on the Ion-exchange resins. Over moderate range of concentrations, the model agreed quit well with the experimental results. The model can be represented by the equation shown below:

$$\log \left( \frac{x}{m} \right) = \log K + \left( \frac{1}{n} \right) \log C_e$$

Where  $C_{eq}$  = the equilibrium concentration (mg/L)

and  $\frac{x}{m}$  = the amount of uptake per unit mass of

the resins (mg/g). Plot of  $\log \frac{x}{m}$  versus  $\log C_{eq}$

gives a straight line with a slope  $\frac{1}{n}$  and intercept

$\log K$ . The plots were presented in (Fig. 4). The K value was found to be 7.37 for the uptake with Sulphate as co-ion and for uptake with chloride as co-ions were 15.41 for the resin. While, the values of 'n' were calculated to be 0.61 when the co-ions were Sulphate ions and 0.36 for when the co-ion was Chloride. The values of 'n' are generally not an integer's value that was used to correlate adsorption data on an adsorbent over a wide range of concentrations. This shows a favourable uptake of chromate on the ion-exchange resins that is consistent with the report of Lloyd-Jones *et al.*, 2004. The raw wastewater samples characterized were taken from the out let of

the equalization pond of a tannery industry. The parameters and toxicity results were presented in (Table 1). The chromate concentration was at 87 mg/L above 0.01 mg/L the limit in wastewater for discharge to surface water prescribed by FEPA (1991) in Nigeria. The wastewater was sequentially treated using coagulation-flocculation and biological treatment were a decreased concentration of chromate was observed due to the uptake by organic matter and reduction to Cr (III) by the existing colonies of microorganisms. Further treatment using precipitation technique to decreases the chromate concentration to 10 mg/L. The failure of the treatment techniques to meet the limit prescribed by FEPA (1991), ion-exchange resins in batch reactor was used to achieve a near to complete removal of chromate at 99% removal efficiency.

## CONCLUSION

The study shows that removal of Chromate by Ion exchange depends on the diffusion controlled reaction and physico-chemical characteristics of the resin. The resin operates best over wide range of trace Chromate concentrations at constant pH 4.0. The rapid uptake of Chromate in the background of high concentrations of co-ions and non interference of the co-ions on the Chromate uptake indicates the selectivity of the resin toward Chromate. This agrees well with the finding of Arup *et al.* (1988). The promising results obtained during batch and column experiments revealed that the method is technically feasible. The characterization of the tannery wastewater has shown a similar content of pollution load as it was in Italy presented in the report Lofrano *et al.* 2006. Primary and secondary treatments of the wastewater, the trace concentration of chromate remaining treated using Ion exchange resin in batch reactor the results revealed that the method can remove chromate in tannery wastewater to near to complete removal. Equally, these treatment methods using batch and Column process can be use to remove other heavy metal ions that may be present in the tannery wastewater and other Industrial solutions. The regeneration of the resins to be use for several cycle of operations and the high

selectivity toward chromate removal are the economic and environmental benefits of the treatment method.

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