

## ORIGINAL RESEARCH PAPER

# A Study on removal of chromium from tannery effluent treatment of chrome tanning waste water using tannery solid waste

A. Rahaman<sup>1,\*</sup>, Md. R. Hosen<sup>1</sup>, M. A. Hena<sup>1</sup>, U. H. B. Naher<sup>1</sup>, M. Moniruzzaman<sup>2</sup>

<sup>1</sup>Institute of Leather Engineering and Technology, University of Dhaka, Dhaka-1209, Bangladesh

<sup>2</sup>Soil, Environment and Agronomy Section, Bangladesh Council of Scientific and Industrial Research, Dhanmondi, Dhaka-1205, Bangladesh

Received 1 July 2016; revised 20 August 2016; accepted 29 September 2016; available online 1 October 2016

**ABSTRACT:** This study illustrates the process of removal of chromium from chrome tanning waste-water by fly ash which was drive from chrome shaving dust. This experiment was carried out in a batch process with laboratory prepared adsorbent samples and chrome tanning water collected from local tanneries. The influence of various factors likes adsorbent doses, contact time, and initial concentration of chromium on the removal of chromium from effluent was investigated. FTIR analysis was done to identify the functional groups presents in the fly ash. The maximum removal of chromium and absorption capacity was found to be 97.86%. And 23.11 mg/g at chromium concentration of 1000.3mg/l and 1291 mg/l respectively. Total dissolve solid, turbidity, and conductivity were reduced significantly. Waste water samples containing several interfering ions like Na, Fe, Ca, Zn, Mn etc. The langmuir absorption isotherm was also used to explain the nature of adsorption. This result indicates that chrome shaving dust ash can be successfully used to treat chrome tanning wastewater.

**KEYWORDS:** Adsorption; Chromium; Removal; Fly ash; Tannery effluent; Total dissolve solid (TDS)

## INTRODUCTION

Chromium is the 7<sup>th</sup> most abundant metal on the earth, which present in the environment, mainly two oxidation states Cr<sup>3+</sup> and Cr<sup>6+</sup> having average concentration 100 mg/kg (Stępniewska *et al.*, 2007, Apte *et al.*, 2005). Chromium is normally present in rocks, soil, volcanic and combustion dust (Pandhram and Nimbalkar, 2013). The major source of chromium in industrial waste water is electroplating aluminium conversion, cooling operating, metal finishing, pigments, leather fungicides, photographic materials and wood preservatives (Losi *et al.*, 1994, Kowalski, 1994). The global production of chromium is 10<sup>7</sup> tonnes per year among them 60-70% is used in alloys, including stainless steel and 15% in various chemical processes (Cervantes *et al.*, 2001, Polti *et al.*, 2011). The permissible limit of chromium in drinking water is 0.1

mg/L and in waste water is 5 mg/L for trivalent chromium and 0.05 mg/L for hexavalent chromium (Greenberg Arnold and Clesceri Lenore, 1992; Acar and Malkoc, 2004). Leather is tanned with chromium because of hydrothermal stability and excellent physical properties. Leather uptakes only 60-70% of chromium used in tanning process and untreated waste water contain 1500-3000mg/L of chromium (Aravindhan *et al.*, 2004). A very little amount of chromium is essential for glucose, lipid and amino acid metabolism but long time exposure causes skin disorders, lung carcinoma, kidney damage, dermatitis ulcers and skin lesions (Aravindhan *et al.*, 2004; Sekhar *et al.*, 2012). There are several traditional methods to remove chromium from industrial waste water Such as ion-exchange, membrane separation, Electroplating bioaccumulation, precipitation and modified zeolites etc. These methods suffer from various problems like costly, generation of

\*Corresponding Author Email: [ashik.shomik@gmail.com](mailto:ashik.shomik@gmail.com)  
Tel.: +8801 681 563 383

secondary sludge, incomplete metal removal, creation of toxic waste products and high reagent cost etc. In this study we utilise fly ash drive from chrome-tanning solid waste to remove chromium from liquid waste water. Researchers from around the world use various fly ash hevea brasiliensis sawdust activated carbon, Rice husk silica, phosphate removed using fly ash, coconut jute charcoal, and activated carbon from different materials to remove heavy metal and pollutants from aqueous solution (Karthikeyan *et al.*, 2005, Sivakumar 2015; Ragheb, 2013; Samadi *et al.*, 2009, Dias *et al.*, 2007). The aim of this study is to management both liquid and solid waste of tannery industries at a time.

## MATERIALS AND METHODS

### Sample collection

The samples were collected in February 2016 from Ruma, Samina, and Chowdhury the local tannery in Dhaka. The PVC zip bag and high-density 1-liter PVC bottles were used to collect leather chrome shaving solid waste and the effluents from these tannery. Each bottle was cleaned thoroughly by rinsing with dilute HNO<sub>3</sub> followed by washing with distilled water (Nixon *et al.*, 1989). The collected samples were then filtered and preserved with Conc. HNO<sub>3</sub> for analysis (APHA, 1998; USEPA, 1979).

### Adsorbent preparation

Chrome shaving dust was incinerated in closed ..... °C for two hours. The combustion ash was collected from furnaces. The combustion ash was washed with 2M Nitric acid to remove chromium from ash. Nitric acid not only removes the chromium from ash but also active it for removal of chromium.

### Batch experiments for chrome removal

Batch experiments were carried out to evaluate the effect of contact time, adsorbent dose, and initial concentration of chromium on the removal of chromium from Tannery effluent. All the experiments were performed in 500ml Erlenmeyer flask containing 250ml of effluent with an adsorbent at room temperature. The influence of adsorbent dose on chromium removal form effluent was assessed by using 5 grams to 20 grams of adsorbent. The effect of contact time on the removal of chromium from effluent was determined by using 3 hours to 12 hours of contact time. In order to examine the effect of initial chromium concentrations on removal

of chromium we used the effluent of three different tanneries. Chromium ion concentration varying from tannery to tannery because of their own tanning method. The level of pH in tannery effluent ranges from 2.5 to 3.5 because of penetration of chromium in tanning better suited in this pH range (Mella *et al.*, 2015). After treatment all the samples were filtered through what man filter paper and the filtrate were analysed using AAS atomic Absorption Spectrophotometer. Normally, mixture of adsorbent and effluent was filtered after 12 hours of time except the experiments of the influence of contact time. To explain the nature of Langmuir isotherm we used 20 grams of adsorbent to remove chromium from different initial concentration of tannery effluents.

### Adsorption studies

Removal Percentage and adsorption capacity of adsorbents were calculated according to the expression (Eqs. 1 and 2)

$$\frac{C_0 - C_c}{C_0} \times 100 \quad (1)$$

$$Q_{max} = \frac{C_0 - C_c}{M} \times V \quad (2)$$

Here, Q<sub>max</sub> is absorption capacity, C<sub>0</sub> and C<sub>c</sub> are initial and equilibrium concentration of chromium m and V are mass of adsorbent in gram and volume of effluent in liter.

## RESULTS AND DISCUSSION

### Nature of adsorbents

The FTIR Spectrum as shown in Fig. 1 indicates the nature and functional groups present in the adsorbent. The absorption band range at 3800-2900 cm<sup>-1</sup> is indicating the -OH and -NH Group Present in the adsorbent. The spectrum band at 767.67cm<sup>-1</sup> represents the C-Cl group.

The absorption band 2927.91 cm<sup>-1</sup> represents C-H Stretching from polysaccharides. However, the absorption band range between 1421.1cm<sup>-1</sup> to 1616.35 cm<sup>-1</sup> is due to C=C vibration in the aromatic ring. On the other hand, band 1064.71 cm<sup>-1</sup> may be due to C-H stretching bond in acid alcohol and phenolic compound. The absorption band ranging from 632.65 cm<sup>-1</sup> to 518.85 cm<sup>-1</sup> may represent alkynes C-H bond.

*Characterization of tannery effluents*

Characterization of samples was completed to measure the level of Total dissolve solid (TDS), Turbidity conductivity and several other cation present

in the effluents. According to Figs. 2 and 3 the amount of cation and TDS, Turbidity, and Conductivity was higher in Chowdhury tannery effluents among the three tanneries.

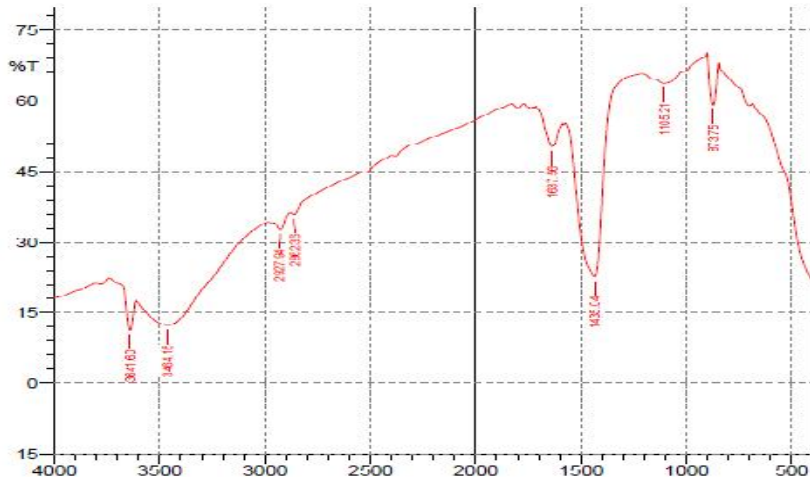


Fig. 1: FTIR analysis of fly ash

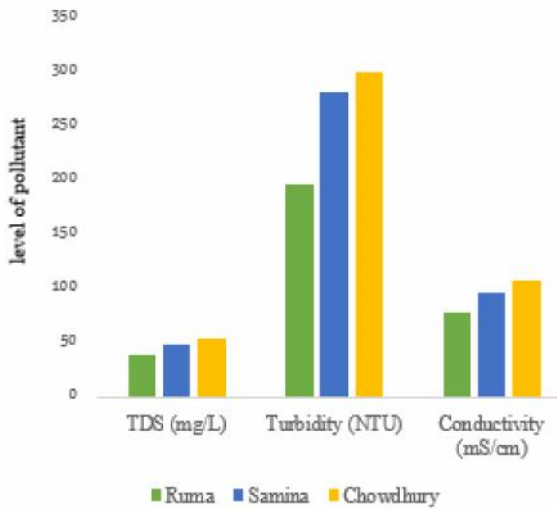


Fig. 2: Level of TDS, Turbidity and conductivity in tannery effluents

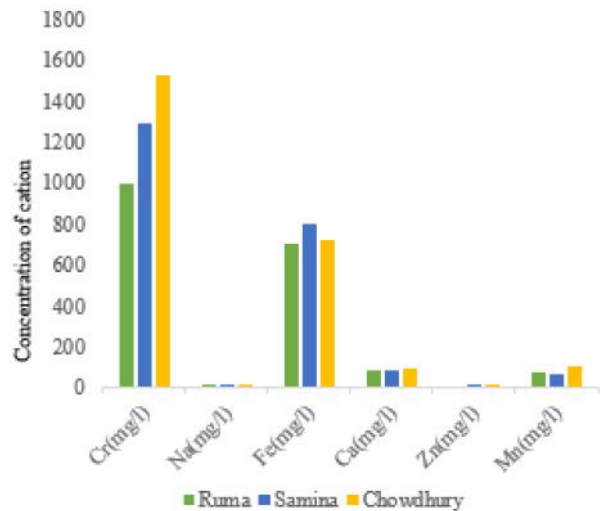


Fig. 3: Cations present in tannery effluents

*The effect of initial chromium concentration*

The above [Tables 1 and 2](#) show the removal percentage and absorption capacity of chromium ion depending on its initial concentration in tannery effluents. Remove percentage decreases with the increase of initial metal ion concentration. This is due to lesser availability of adsorbent active site are left for the absorption of fresh chromium ion which is similar to the study of [Modak and Natarajan \(1995\)](#).

*The effect of adsorbent dose on the removal of chromium:*

The effect of adsorbent dose on the removal of chromium from effluent also represent by the above [Tables 1 and 2](#). Removal of chromium increases with the increase of adsorbent dose but absorption capacity decreases. Absorption capacity or metal ion absorbed per gram of

adsorbent is higher for lower adsorbent dose. Although, the percentages of chromium removal increases at higher adsorbent dose because of available adsorbents active sites pre chromium ion increases. In a previous study similar result was founded by [Molkoc et al. \(2006\)](#).

*The effect of contact time on removal of chromium*

For this study we use Ruma (1000.3mg/L) Tannery effluent and 20g of adsorbent. The effect of contact time on the removal of chromium was established by using four different time intervals ranging from 3 hours to 12 hours. The bellows [Table 3](#) shows removal percentage and absorption capacity increase with the increase of contact time. The maximum amount of absorption done in initial stage because in initial period the maximum amount of active sites are available. Our findings are similar to study of ([Sharma and Goyal 2011](#)).

Table 1: Removal Percentage of chromium

Name of Tannery	5g	10g	15g	20g
Ruma (1000.3 mg/L)	40.63%	70.87%	85.66%	97.86%
Samina (1291 mg/L)	35.80%	59.95%	72.33%	92.17%
Chowdhury (1524 mg/L)	21.7%	47.2%	65.3%	86.8%

Table 2: Absorption capacity of adsorbent.

Name of Tannery	5g	10g	15g	20g
Ruma (1000.3 mg/L)	20.32 mg/g	17.72mg/g	14.28mg/g	12.24 mg/g
Samina (1291 mg/L)	23.11 mg/g	17.15mg/g	16.23mg/g	14.87mg/g
Chowdhury (1524 mg/L)	16.5 mg/g	18.07 mg/g	16.23mg/g	16.53mg/g

Table 3: Removal percentage and absorption capacity at various times interval.

Time	3 hour	6 hour	9 hour	12 hour
Removal percentage	45.69%	64.20%	89.20%	97.86%
Absorption capacity	5.71 mg/g	8.07 mg/g	11.16 mg/g	12.24 mg/g

*Effect of pH and Interfering ion*

Most of the tanneries in tanning process maintain pH ranging from (2.5 to 3.5) because of better chrome penetration. In generally, lower pH is suitable for absorption of chromium from aqueous solution. Interfering ions also have a positive effect on absorption. The interfering ion likes Na, Fe, Ca, Zn, Mn, etc. are very common in tanning effluents.

*Others parameters of tannery effluents*

We measure the level of TDS, Turbidity and conductivity before and after treatment with 20 grams of adsorbent. The below (Table 4) shows the reduction level of TDS, Turbidity and conductivity from this Table Tannery effluent contain lower concentration of chromium shows better rate of reduction than others.

*Adsorption studies*

Isotherm models are widely used to establish a relationship between absorbed ( $q_e$ ) and aqueous

concentration at equilibrium. In this study we use Langmuir absorption model. As shown in Fig. 4, the Langmuir isotherm has been used to discuss the absorption quality of Chromium from aqueous solution (Eq. 3).

$$\frac{1}{q_e} = \frac{1}{q_0} + \frac{1}{C_c} \cdot \frac{1}{kq_0} \quad [Linear\ form] \quad (3)$$

Where,  $q_e$  is the chromium absorbed per unit mass of adsorbent  $q_0$  represents the capacity of the adsorbent  $C_c$  concentration of chromium at equilibrium.  $K_L$  is Langmuir constant and  $q_0$  and  $K_L$  is calculated by using the intercepts and slope of the plot. The main characteristics of the isotherm can be expressed in terms of a dimensionless constant separation factor  $R_L$ . This  $R_L$  value indicates the nature of adsorbent unfavourable ( $R_L > 1$ ), linear ( $R_L = 1$ ), irreversible ( $R_L = 0$ ) or favourable ( $0 < R_L < 1$ ). In this study the value of  $R_L$  was from 0.3411 to 0.513 which remarks that this experiment was favorable.

Table 4: Removal of TDS, Turbidity and Conductivity.

Name of parameters	Ruma		Samina		Chowdhury	
	Initial	Final	Initial	Final	Initial	Final
TDS (gm/l)	38.7	3.2	481	6.12	54.3	8.3
Turbidity (NTU)	197	1	281	0.9	300	1.2
Conductivity(mS/cm)	77.5	6.25	96.3	11.25	107.1	17.15

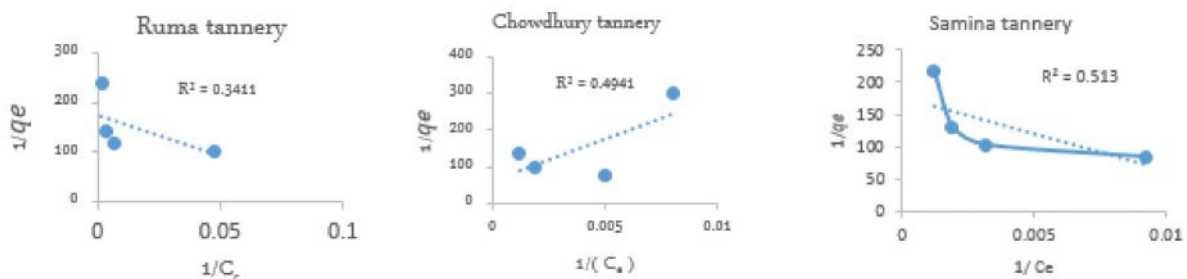


Fig. 4: Langmuir isotherm

## CONCLUSION

In this study we real tannery effluent. Chrome shaving dust ash was used to remove chromium from Tannery effluent. Influence of initial metal ion. Contact time and adsorbent dose on the removal of chromium also determined. Chrome shaving dust ash remove more than 97% Chromium from Tannery effluent. Removal of chromium increases with the increase of connection adsorbent dose but decreases with the increase of initial chromium concentration. The amount of ash required to perform a chromium removal above 90% is about 80 g/l. TDS, Turbidity and conductivity of effluent also reduced significantly. Chrome shaving dust ash can be successfully used for the treat of tannery effluents.

## ACKNOWLEDGEMENT

First and second author had equally been contributed this study. Special thanks to scientists of Environment and Agronomy Section, Bangladesh Council of Scientific and Industrial Research (BCSIR) for their cordial help to finish this research.

## CONFLICT OF INTEREST

The authors declare that there are no conflicts of interest regarding the publication of this manuscript.

## REFERENCES

- Acar, F.N.; Malkoc, E., (2004). The removal of chromium (VI) from aqueous solutions by *Fagus orientalis* L. *Bioresource Technol.*, 94(1): 13-15 (3 pages).
- Apte, A.D.; Verma, S.; Tare, V.; Bose, P., (2005). Oxidation of Cr (III) in tannery sludge to Cr (VI): field observations and theoretical assessment. *J. Hazard. Mater.*, 121(1): 215-222 (8 pages).
- American Public Health Association (APHA), (1998). Standard methods for the examination of water and wastewater (20th). Washington, D.C, American Public Health Association, p. 2-24 to 2-26.
- Aravindhan, R.; Madhan, B.; Rao, J.R.; Nair, B.U.; Ramasami, T., (2004). Bioaccumulation of chromium from tannery wastewater: an approach for chrome recovery and reuse. *Environ. Sci. Technol.*, 38(1): 300-306 (7 pages).
- Cervantes, C.; Campos-García, J.; Devars, S.; Gutiérrez-Corona, F.; Loza-Tavera, H.; Torres-Guzmán, J.C.; Moreno-Sánchez, R., (2001). Interactions of chromium with microorganisms and plants. *FEMS Microbiol. Rev.*, 25(3): 335-347 (13 pages).
- Dias, J.M.; Alvim-Ferraz, M.C.; Almeida, M.F.; Rivera-Utrilla, J.; Sánchez-Polo, M., (2007). Waste materials for activated carbon preparation and its use in aqueous-phase treatment: a review. *J. Environ. Manage.*, 85(4): 833-846 (14 pages).
- Greenberg Arnold, E.; Clesceri Lenore, S., (1992). Standard methods for the examination of water and wastewater. American public health association, USA.
- Karthikeyan, T.; Rajgopal, S.; Miranda, L.R., (2005). Chromium (VI) adsorption from aqueous solution by Hevea Brasilinesis sawdust activated carbon. *J. Hazard. Mater.*, 124(1): 192-199 (8 pages).
- Kowalski, Z., (1994). Treatment of chromic tannery wastes. *J. Hazard. Mater.*, 37(1): 137-141 (5 pages).
- Losi, M. E.; Amrhein, C.; Frankenberger, Jr., (1994). Environmental biochemistry of chromium. In G. V. Ware (ed.), *Reviews of environmental contamination and toxicology*, Springer, New York, 136: 91-121 (31 pages).
- Malkoc, E.; Nuhoglu, Y.; Dundar, M., (2006). Adsorption of chromium (VI) on pomace—an olive oil industry waste: batch and column studies. *J. Hazard. Mater.*, 138(1): 142-151 (10 pages).
- Mella, B.; Glanert, A. C.; Gutterres, M., (2015). Removal of chromium from tanning wastewater and its reuse. *Process Saf. Environ. Prot.*, 95: 195-201 (7 pages).
- Modak, J.M.; Natarajan, K.A., (1995). Biosorption of metals using nonliving biomass-A review. *Miner. Metall. Proc.*, 12(4): 189-196 (8 pages).
- Nixon, D.E.; Moyer, T.P.; Squillace, D.P.; McCarthy, J.T., (1989). Determination of serum nickel by graphite furnace atomic absorption spectrometry with Zeeman-effect background correction: values in a normal population and a population undergoing dialysis. *Analyst*, 114(12): 1671-1674 (4 pages).
- Pandhram, P.; Nimbalkar, S., (2013). Adsorption of chromium from industrial waste water by using neem leaves as a low cost adsorbent. *Int. J. Chem. Phys. Sci.*, 2: 149-158 (10 pages).
- Polti, M.A.; Atjián, M.C.; Amoroso, M.J.; Abate, C.M., (2011). Soil chromium bioremediation: synergic activity of actinobacteria and plants. *Int. Biodete. Biodegr.*, 65(8):1175-1181 (7 pages).
- Ragheb, S.M., (2013). Phosphate removal from aqueous solution using slag and fly ash. *Hous. Buil. Natl. Res. Cent. J.*, 9(3): 270-275 (6 pages).
- Samadi, M.T.; Rahman, A.R.; Zarrabi, M.; Shahabi, E.; Sameei, F., (2009). Adsorption of chromium (VI) from aqueous solution by sugar beet bagasse based activated charcoal. *Environ. Technol.*, 30(10):1023-1029 (7 pages).
- Sekhar, K.P.C.; Babu, R.V.; Srividhya, D.; Ravindhranath, K., (2012). Removal of Chromium (VI) from Waste Waters Using Leaves Powders of *Justicia adhatoda*, *Cissus quadrangularis*, *Soapnut Acacia*. *Phar. Chem.*, 4(2): 664-673 (10 pages).
- Sharma, I.; Goyal, D., (2011). Chromium removal from industrial effluent by *Eucalyptus tereticornis* bark. *Asian J. Exp. Sci.*, 25(1): 29-35 (7 pages).
- Sivakumar, D., (2015). Hexavalent chromium removal in a tannery industry wastewater using rice husk silica. *Global J. Environ. Sci. Manage.*, 1(1): 27-40 (14 pages).
- Stępniewska, Z.; Wolińska, A.; Pióro, W., (2007). Chromium migration in the vicinity of a tannery waste lagoon. *Pol. J. Soil Sci.*, 2: 139-145 (7 pages).
- U. S. environmental protection agency (USEPA), (1979). Methods for chemical analysis of water and wastes. US Rep. EPA 600/4-79-020. USEPA, EMSL, Cincinnati, OH.