ICMERE2017-PI-123

CHROMIUM REMOVAL FROM THE TANNERY WASTEWATER EQUIPPED *MANGIFERA INDICA* BARK CHARCOAL

Md. Abul Hashem*, Md. Abdul Momen, Mehedi Hasan, Aishorjo Paul Bablee

Department of Leather Engineering, Khulna University of Engineering & Technology, Khulna-9203, Bangladesh
mahashem96@yahoo.com, motahirmomen@gmail.com, mehediashzad9040@gmail.com,
aishorjo95@gmail.com

Abstract- *Leather processing involves a series of chemical treatments and mechanical operations to attain the prescribed characteristics of the final leather. In tanning, basic chromium sulfate is used as a tanning agent to obtain better quality leather where pickled pelt up takes only 60% of the used chromium and remaining 40% of chromium is remained in the liquid waste. In this study, an investigation was made to remove chromium from the tannery wastewater using equipped charcoal of Mangifera indica bark. The charcoal was directly mixed with chromium containing wastewater, stirred and chromium content in the decanted aqueous was determined by following the Society of Leather Technologists and Chemists official method of analysis. Chromium removal effectiveness was examined investigating different parameters: charcoal dose, contact time, pH effect, etc. Results show the excellent chromium removal efficiency (99.9%) at optimized conditions. Application of equipped Mangifera indica bark charcoal to remove chromium from the tannery wastewater could be a better option.*

Keywords: Tannery, Wastewater, Chromium, Environment, Charcoal

1. INTRODUCTION

Tanning industries strengthen the economy for the country but it is facing severe challenges due to its environmental pollution caused by the wastes produced during leather processing. Leather processing involves a series of chemical treatments and mechanical operations to attain the prescribed characteristics. Inapt disposal of wastewater and solid waste from the tannery cause a serious environmental pollution.

During leather processing, huge amount of wastewater is generated. Since soaking to finishing operations, each chemical operation generate extensive amount of wastewater. Chromium containing wastewater is generated from chrome tanning operation, which are the most hazardous pollutants released to the environment from the tannery. Tanning especially chrome tanning is the subsequent operation of pickling that is the most common technique in leather processing. In tanning, 90% tanneries use basic chromium sulfate as tanning agent to obtain better quality leather [1]. The basic chromium sulfate binds with collagen to make it stabilize against biodegradation [2]. On average, the pickled pelt up takes only 60% of the chromium and the remaining 40% chromium remains in the solid/liquid wastes, especially as spent chrome liquor [3]. In conventional chrome tanning, wastewater contains 1500-3000 mg/L chromium [4].

Discharging of high chromium containing tanning wastewater is a major concern in leather processing. It is also a potential pollutant to soil, water, and air under definite conditions. A fraction of discharged spent chrome liquor is directly mixed with the water body, which causes serious environmental pollution; another fraction of chromium is settled in the lagoon or adsorbed by sediment/soil. Chromium has toxicity to humans at high doses. It exists in several oxidation states, with trivalent chromium and hexavalent chromium species being the most common forms [5]. The occupational exposure of chromium has been widespread and it is shown that chromium (III) under certain ligand conditions in environments leads to cell death and structural modification of proteins [6]. Removal of the chromium present in the wastewater is necessary for human and environmental causes.

Many researches have been carried out to recovery or remove chromium from the tannery wastewater using stone cutting solid waste [7], bone charcoal [8], natural marl [9]; but most of the techniques approached by treating mixed tannery wastewater. On the other hand, chemical precipitation and electrochemical precipitation are used for heavy metals removal [10, 11] but techniques are complicated.

In this study, an approached was made to remove chromium from the chrome tanning wastewater using equipped charcoal of *Mangifera indica* bark. The use of low cost charcoal could be a preferable option to remove chromium instead of conventional methods.

2. MATERIALS AND METHODS

2.1 Sample collection

Chromium containing wastewater was collected from the tannery at Jessore, Bangladesh. Just after completing chrome tanning operation, the wastewater was collected into polyethylene container that was pre-washed with diluted nitric acid, and immediately transported to the laboratory for experimentation. The *Mangifera indica* bark was collected from the local saw mills Khulna, Bangladesh

2.2 Materials

The reagents: perchloric acid (Merck, India), sulphuric acid (Merck KGaA, Germany), nitric acid (Merck KGaA, Germany), ammonium ferrous sulphate (Merck, India), *N*-phenylanthranilic (Loba Chemie, India), glass bed (Loba Chemie, India), and filter paper (Whatman No. 1) were purchased from a local scientific store, Khulna, Bangladesh.

2.3 Charcoal preparation

The collected *Mangifera indica* bark was cut into small pieces and sun-dried. Then, the sun-dried bark was burnt at 450-550°C, cooled and grinded with mortar. The grinded charcoal was sieved on 80-mesh and preserved for the experiment.

2.4 Treatment of wastewater

Batch-wise chromium removal test was performed. The scheme for the treatment of chrome tanning wastewater is shown in Fig. 1.

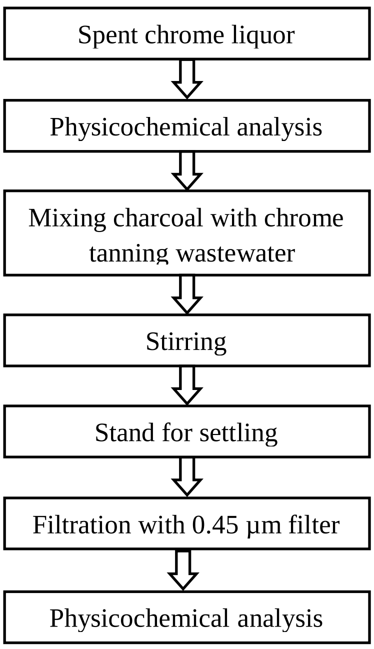

Fig. 1: Scheme for chromium removal treatment process

Firstly, physicochemical parameters of the untreated chrome tanning wastewater were analyzed and filtered through 0.45 µm pore size filter. Secondly, 75 mL filtrate wastewater was mixed with the prepared charcoal. The charcoal mixed wastewater was stirred over a fixed period of time and the mixture was allowed settling for a fixed time of period. After settling, the mixture was filtered through 0.45 µm pore size filter. Chromium and physicochemical parameters of the supernatant were analyzed.

2.5 Determination of pH

pH was measured by the digital pH instrument (UPH-314, UNILAB, USA). Before measuring pH, the instrument was calibrated in the two points with standard solutions of pH 4.01 and pH 7.00, respectively.

2.6 Chromium determination

Chromium content in the untreated chrome tanning wastewater and after treatment in the filtrate was performed by the titrimetric method following the official methods of analysis of Society of Leather Technologist and Chemists [12] official method of analysis (SLC 208). A 50 mL sample volume was taken in 500 mL conical flask. 20 mL concentrated nitric acid was added followed by 20 mL perchloric acid/sulphuric acid mixture; the flask was gently heated and boiled until the mixture had become a pure orange-red color and continue boiling for one minute. The flask was removed from the heating source and as soon as ebullition has ceased; rapidly the flask was cooled by swirling in cold water bath. Carefully, 100 mL distilled water was added with a few glass beads and boiled for 10 minutes to remove free chlorine. Then, 10 mL 30% (v/v) sulphuric acid was added and cooled to room temperature. The mixture was titrated with freshly prepared 0.1N ferrous ammonium sulfate solution with six drops of *N*-phenyl anthranilic acid as an indicator. The end color was indicated by a color change from the violet to green.

2.7 Process optimization

Bath-wise examinations were carried out to optimize the chromium removal parameters: charcoal dose, and contact time. Optimized conditions were established by investigating the chromium removal efficiency of the wastewater.

2.8 Adsorption kinetics

Adsorption kinetics is very important because it defines the rate of adsorption process as well as adsorption dynamics. Adsorption mechanism depends on the physical and chemical properties of adsorbent.

To decide the adsorption kinetics, pseudo-first and pseudo-second order kinetic model were examined. The linear form of the pseudo-first-order kinetic model can be expressed as:

$$\ln(a-x) = \ln a - K_1 t$$

Where,

a = adsorption capacity at equilibrium (mg/g)

x = adsorption capacity at time t (mg/g)

K_1 = constant rate for adsorption process (min^{-1})

The value of K_1 and correlation co-efficient (R^2) can be obtained from the linear plot of ln {(a-x)/a} versus t.

Pseudo-second-order kinetic was analyzed based on the equation as:

$$x = \frac{a^2 K_2 t}{1 + K_2 at}$$

$$\text{Or, } \frac{a}{a(a-x)} = K_2 t$$

Where,
x = adsorption capacity at time t (mg/g)
a = adsorption capacity at equilibrium (mg/g)
K_2 = equilibrium constant rate for adsorption process (g/mg/min)
The value of K_2 can be calculated from the slope and the intercept of the plots of x/a(a-x) versus t.

2.9 Adsorption isotherm

Adsorption isotherm describes the way of interactions between adsorbent and adsorbate. It determines the adsorbent capacity and elevating adsorbent consumption [13]. In this study, Langmuir isotherm and Freundlich isotherm were studied to elucidate the adsorbent characteristics of bark charcoal.
Langmuir model assumes the uniform energy of adsorption onto the solid surface [14]. Langmuir isotherm describes a single layer adsorption that means adsorption in the homogenous sites and the homogenous structure of the adsorbent. It also focuses the limited capacity for adsorption [13]. The following equation signifies the Langmuir model:

$$Q=(Q_m K_L C_e)/(1+ K_L C_e)$$

The linearized form of this equation is that

$$1/Q= 1/C \times 1/(Q_m K_L) + 1/Q_m$$

Where,
Q = is the sorption capacity at equilibrium (mg/g),
C_e = is the final equilibrium concentration (mg/L)
Q_m = is the maximum bio-sorption capacity (mg/g)
K_L = is the Langmuir constant related to the free energy of biosorption (L/mg).

Freundlich isotherm is an empirical equation, which expresses the multi-layers adsorption on heterogeneous surfaces among the adsorbed molecules, which is mainly used for studying experimental data in the liquid phase (Gimbert et al. 2008). It assumes that increasing the concentration of the adsorbed mass, there is more amount of adsorption, which can result in unlimited amount of adsorption (Allen et al. 2004). Freundlich isotherm equation express as:

$$Q_e = K_f \, Ce^{\frac{1}{n}}$$

The linear form of the equation is as follows:

$$\text{In}Q_e = \text{Ink}_f + 1/n\,(\text{InC}_e)$$

Where,
Q_e= is the sorption capacity at equilibrium (mg/g)
C_e= is the final equilibrium concentration (mg/L)
K_f = is the Freundlich adsorption model constant (L/g)
n= is Freundlich adsorption model exponent
K_f and n is calculated from the intercept and slope of the plot ln Q_e versus ln C_e. Where, K_f shows the quantity of adsorbate adsorbed onto the adsorbent for a unit equilibrium concentration [13]. Unit value of 1/n represents linear adsorption. The adsorption process will be chemical for the values less than 1, and when it is more than one, physical adsorption process takes place [13]. The most surface heterogeneity occurs when the value of 1/n is near to zero [15].

3. RESULTS AND DISCUSSION

3.1 Optimal charcoal dose

The charcoal dose is the most important parameter in the treatment process. The effect of charcoal dose on the efficacy of chromium removal from the wastewater is depicted in Fig. 2.

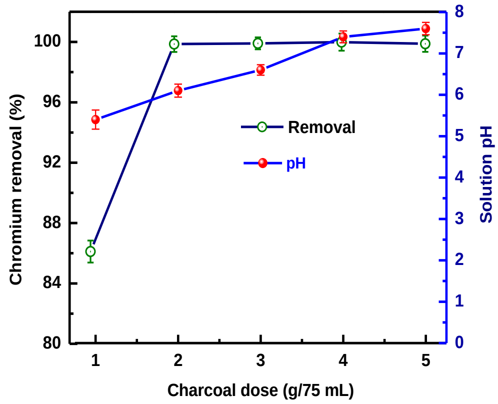

Fig. 2: Charcoal dose and pH effect on chromium removal

It is clear from Fig. 1 that charcoal has a significant effect on the removal of chromium. It was perceived that with increasing charcoal dose, chromium removal percentage was gradually increased to 3 g per 75 mL wastewater. Subsequently, with increasing charcoal dose, chromium removal percentage was slightly increased.

3.2 Optimal contact time

Chromium removal efficiency was observed at regular time intervals to determine the optimal contact time.

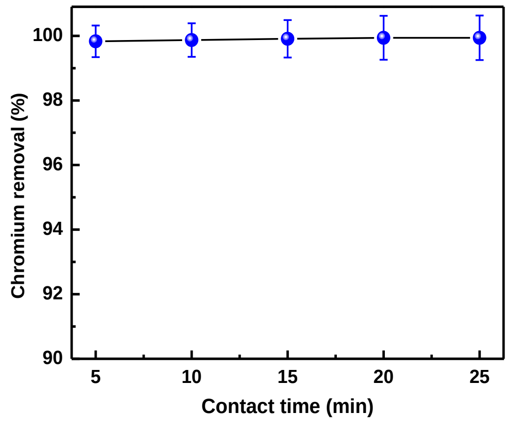

Fig. 3: Effect of contact time on chromium removal

[Fig. 3](#) shows that with interval of time, there was a steady increase the percentage of chromium removal. With contact time 15 min, the chromium removal efficiency was maximum (99.9%) and after that percentages of chromium removal was almost unchanged. Therefore, it was decided that contact time was 15 min.

3.3 Efficiency of the treatment process

The results of the treatment process with optimum conditions are represented in Table 1. The optimized treatment conditions were: adsorbent dose 3 g/75 mL wastewater and contact time 15 min. The initial concentration of chrome tanning wastewater was 2920.01 mg/L and after treatment at optimised conditions chromium concentration was 4.2 mg/L. Therefore, it could be concluded that maximum chromium removal was attained 99.9%.

Table 1: Data comparison with ECR standard

Parameters	Raw sample	This study	ECR [16]
pH	3.7±0.3	8.2±0.1	6–9
TDS (mg/L)	44.3±0.6	48.9±0.2	2100
EC (mS)	73.7±0.7	80.5±0.4	1.20
Salinity (ppt)	44.9±0.5	50.0±0.6	–
Cr (mg/L)	2920.1±0.7	4.2±0.4	2.0

3.4 Adsorption kinetics

Fig. 4a, the correlation coefficient values of R_1^2 (0.9102) and R_2^2 (0.9312) are obtained for pseudo-first-order and pseudo-second-order kinetics, respectively.

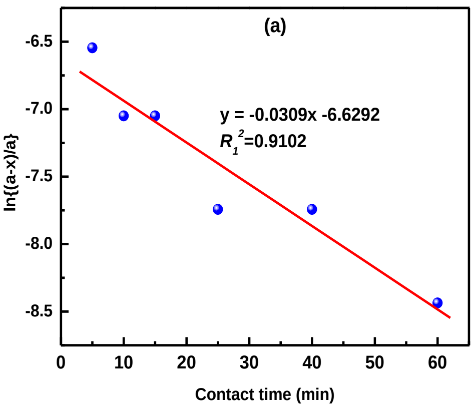

Fig. 4a: Pseudo first order kinetic of adsorption

It could be evidently described that the pseudo-second-order kinetic did not provide a good description for the adsorption of the Cr (III) onto charcoal rather pseudo-first-order kinetic equation can, as the plot of x/a(a-x) against *t* provided a good fit (R_2^2 = 0.9312) as depicted Fig. 4b. The pseudo-first-order model suggests that the biosorption process follows a 1st order mechanism, which is the rate of adsorption is proportional to the number of unoccupied sites of charcoal.

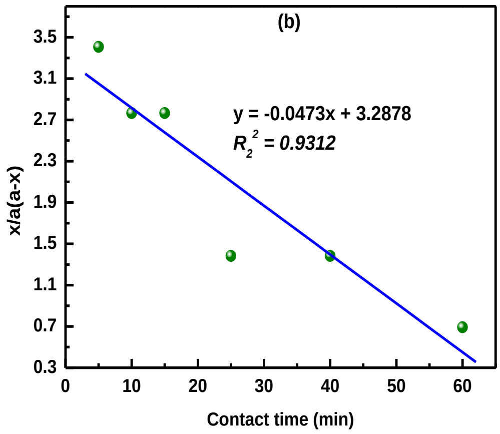

Fig. 4b: Pseudo second order kinetic of adsorption

3.5 Adsorption isotherm

Fig. 5 indicate that the Freundlich model were well fitted with the adsorption data, as well as the correlation coefficients (R_2^2=0.9945) of the Freundlich model was more suitable for chromium removal from the wastewater using *Mangifera indica* bark charcoal. The value of 1/n obtained from the Freundlich model was above 1 (1/n=3.0307), which indicates the favorable adsorption conditions for *Mangifera indica* bark charcoal adsorbent, and adsorption will be multi-layer adsorption on the heterogeneous surface by physical process.

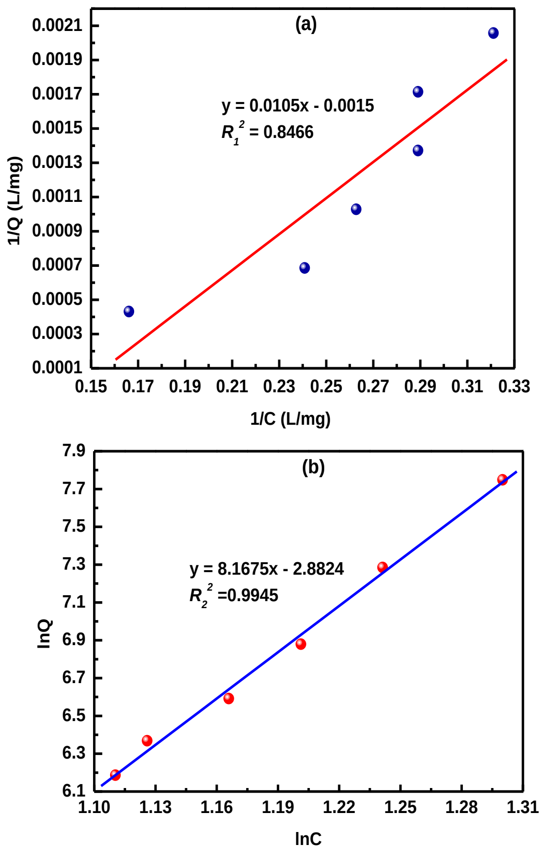

Fig. 5: Upper panel linearized Langmuir (a) and lower panel Freundlich (b) adsorption isotherms

4. CONCLUSION

Batch-wise spent chrome liquor was treated to remove chromium using *Mangifera indica* bark charcoal. The removal efficiency of chromium at optimized condition was 99.9%. The investigation indicates that it was an effective technique to remove chromium that will minimize pollution load from the spent chrome liquor. The study could be helpful to design the treatment of spent chrome liquor in house prior to discharge and the adsorbed chromium could recover by desorption.

5. REFERENCES

[1] R. Avindhan, B. Madhan, J. R. Rao, B. U. Nair, and T. Ramasami, "Bioaccumulation of chromium from tannery wastewater: an approach for chrome recovery and reuse", *Environ Science & Technology*, vol. 38, no. 1, pp. 300–306, 2004.

[2] M. A. Hashem, A. Islam, S. Mohsin, and M. S. Nur-A-Tomal, "Green environment suffers by discharging of high-chromium containing wastewater from the tanneries at Hazaribagh, Bangladesh", *Sustainable Water Resources Management*, vol. 1, pp. 343–347, 2015.

[3] C. Fabiani, F. Ruscio, M. Spadoni, and M. Pizzichini, "Chromium (III) salts recovery process from tannery wastewaters", *Desalination*, vol. 108, no. (1-3), pp. 183–191, 1997.

[4] V. Suresh, M. Kanthimathi, P. Thanikaivelan, J. R. Rao, and B. U. Nair, "An improved product-process for cleaner chrome tanning in leather processing", *Journal of Cleaner Production*, vol. 9, pp. 483–491, 2001.

[5] J. Kotas, and Z. Stasicka, (2000), "Chromium occurrence in the environment and methods of its speciation", Environ Pollution, vol. 107, pp. 263–283, 2000.

[6] K. Balamurugan, R. Rajaram, T. Ramasami, and S. Narayanan, "Chromim(III) induced apoptosis of lymphocytes: death decision by ROS and Src-family tyrosine kinases", *Free Radical Biology & Medicine*, vol. 33, no. 12, pp. 1622–1640, 2002.

[7] M. Al-Jabari, M. Abdulfailat, and S. Shaleen, ''Treating Leather Tanning Wastewater with Stone Cutting Solid Waste'', *Clean–Soil, Air, Water*, vol. 40, no. 2, 206–210, 2012.

[8] S. Dahbi, M. Azzi, N. Saib, M. de la Guardia, R. Faure, and R. Durand, ''Removal of trivalent chromium from tannery waste waters using bone charcoal'', *Analytical and Bioanalytical Chemistry*, vol. 374, pp. 540–546, 2002.

[9] M. Jabari, F. Aqra F, S. Shahin, and A. Khatib, ''The treatment of chromium tanning wastewater using natural marl'', *Chemical Speciation & Bioavailability*, vol. 21, no. 3, pp. 185-191, 2009.

[10] C. Ozdemir, M. Karatas, S. Dursun, M. E. Argun, and S. Dogan, "Effect of $MnSO_4$ on the chromium removal from leather industry wastewater", *Environmental Technology*, vol. 26, pp. 397–400, 2005.

[11] N. Meunier, P. Drogui, C. Montane, R. Hausler, G. Mercier, and J-F. Blais, "Comparison between electrocoagulation and chemical precipitation for metals removal from acidic soil leachate", *Journal of Hazardous Materials*, vol. 137, no. 1, pp. 581–590, 2006.

[12] Society of Leather Technologist and Chemists, Official Methods of Analysis. Northampton, UK, 1996.

[13] S. k. Ghorbani, and M. A. Behnajady, "Chromium (VI) adsorption from aqueous solution by prepared biochar from *Onopordom Heteracanthom*", *International Journal of Environmental Science & Technology*, vol. 13, pp. 1803–1814, 2016.

[14] R. S. Khoubestani, N. Mirghaffari, and O. Farhadian, "Removal of Three and Hexavalent Chromium from Aqueous Solutions Using a Microalgae Biomass-Derived Biosorbent", *Environmental Progress & Sustainable Energy*, vol.34, no.4, pp. 949-956, 2015.

[15] F. Gimbert, N. Morin-Crini, F. Renault, P. M. Badot, and G. Crini, "Adsorption isotherm models for dye removal by cationized starch-based material in a single component system: error analysis", *Journal of Hazardous Materials*, vol. 157, no. 1, pp. 34–46, 2008.

[16] Environment Conservation Rules, Ministry of Environment & Forests (MoEF), Government of the People's Republic of Bangladesh, 1997.