

BATCH ELECTROCOAGULATION PROCESS FOR REMOVAL OF CHROMIUM FROM TANNERY WASTEWATER

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Received: 19 June 2019

Accepted: 12 November 2020

ABSTRACT

This study was aimed to investigate the chromium removal from the tannery wastewater through electrocoagulation. The zinc and copper plates were used as electrodes for the electrocoagulation process. The effectiveness of the electrocoagulation for chromium removal efficiency was examined investigating various parameters: applied voltage, time, and current density. In batch experiment, 500 mL chromium-containing wastewater was used for electrocoagulation. Chromium content in the raw wastewater and after treatment at optimized conditions was 340.1 and 6.9 mg/L, respectively. The efficiency of chromium removal and reduction of biochemical oxygen demand (BOD) was at 98.0 and 64.6%, accordingly. Although total dissolved solids (TDS) was slightly increased. The increment of current density enhances forming zinc hydroxide which causes the damage of electrodes. Electrocoagulation is an effective technique to remove chromium from the wastewater especially from the tannery wastewater.

Keywords: Chromium; Current density; Electrocoagulation; Electrodes; Tannery effluent.

1. INTRODUCTION

Although the contribution of the tanning industry to the world economy is meritorious, it consistently envisaged criticisms due to a remarkable contribution to environmental pollution (Pal *et al.*, 2020). The global leather market is about US \$80 billion in 2018 and expected it will extend to US \$128 billion by 2022 (Sivaram and Banik, 2019). Eventually, tanneries discharge 30-35 m³ wastewaters during processing 150kg of hide/skin. These large volumes of wastewater contain a high amount of chromium, sodium, chloride, total dissolved solids (TDS), sulfide, nitrogen, biochemical oxygen demand (BOD), chemical oxygen demand (COD), dyes which are far above from the acceptable range (Chowdhury *et al.*, 2015). Kothai *et al.* (2019) have investigated that tannery wastewater contains different types of heavy metals like chromium (Cr), zinc (Zn), lead (Pb), nickel (Ni) which are nonbiodegradable and carcinogenic. Wastewater containing toxic heavy metals and dyes creates an adverse effect on the ecosystem as well as human health (Kamaraj *et al.*, 2020).

Tannery effluent contains the highest amount of pollutants comparing with all other industrial wastes. Especially, tanneries are a large contributor to chromium pollution (Belay, 2010). Statistics show around 90% tanneries are using basic chromium sulfate as a basic chemical in tanning operation and only tanning wastewater contains around 4000mg/L chromium which is much higher than the maximum permissible limit set by WHO (Saravanabhavan *et al.*, 2004). The tannery wastewater decreases the quality of water bodies into which they are discharged. The result of the disposition of chromium-containing tanning effluent into the environment is much serious as the Cr ion leached out from the effluent and pollute soil and water body then finally enters into the human body via food chain (Sarker *et al.*, 2013). How the physiochemical properties of groundwater, surface water, and soil are changes with the contamination of chromium is demonstrated and the final effect of chromium contamination on aquatic and terrestrial life is also observed e.g., trivalent chromium is harmful to aquatic life and fish at excess level (>5.0 mg/L) (Overah, 2011). Chromium exists in the natural environment in two forms: trivalent, Cr(III), and hexavalent, Cr(VI), tannery wastewater contains both the form. Based on toxicity Cr(VI) is more toxic and shows more mobility compare to Cr(III) (El-Taweel *et al.*, 2015). Like other heavy metals, chromium shows a nonbiodegradable character that can accumulate itself in the human body and causing serious health damage like hemorrhaging, lung malignancy, itching, chest pain, ulceration, profuse sweating, and skin irritation (Yahya *et al.*, 2020; Mohan *et al.*, 2006). Problems caused by chromium could be minimized if the chromium-containing tannery wastewater is treated before discharge to the environment.

Numerous techniques have been employed to remove such toxic metal from the tannery wastewater like ion exchange, coagulation/flocculation, membrane filtration, adsorption, reverse osmosis, and precipitation (Kusku *et al.*, 2014; Obayomi *et al.*, 2020; Koushkbaghi *et al.*, 2018). Among them, the coagulation/flocculation method has achieved much popularity because of its simplicity but the main disadvantages of this technique are it causes secondary pollution due to the use of the excess amount of chemicals (Lefebvre and Moletta, 2006; Kumer *et al.*,

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2018). Recently many researchers have shown their interest in electrocoagulation technology for the treatment of wastewater, the reason behind that compared to other technology it has some attractive advantages like environmental friendliness, cost-effectiveness, simple in application, have the ability to reduce the possibility of secondary pollution (Ghernaout *et al.*, 2011). In the recent past, the electrocoagulation technique has been applied for the treatment of different industrial wastewater, municipal wastewater (Makwana and Ahammed, 2016), Dairy wastewater (Aitbara *et al.*, 2014), Pharmaceutical wastewater (Khaldi *et al.*, 2017), and Distillery wastewater (Thakur *et al.*, 2009). Mavrov *et al.* (2006) have also investigated that the electrocoagulation technique can remove 90% selenium from the copper industry.

The goal of the present study is to utilize the electrocoagulation process to remove tannery chromium from industrial wastewater. The performance of the electrocoagulation process was determined to investigate different parameters: applied voltage, current, and time using zinc (Zn) and copper (Cu) electrodes. Besides different water quality parameters: pH, turbidity, conductivity, TDS, and BOD has also been investigated.

2. EXPERIMENTAL PROCEDURE

2.1 Collection of Wastewater

Wastewater sample from chrome tanning operation was directly accumulated from SAF Industries Ltd. Situated in Noapara, Jashore, Bangladesh. Sampling was conducted in a plastic vessel after washing with nitric acid and rinsing with a wastewater sample. The wastewater was stored in the laboratory immediately after collection.

2.2 Chemicals

The reagents utilized in this experiment were of analytical grade. The chemicals were obtained from a local scientific shop in Khulna, Bangladesh.

2.3 Physico-chemical Parameter

The untreated and treated spent chrome liquor as characterized through the following parameters: chromium content, pH, turbidity, electrical conductivity (EC), total suspended solids (TSS), TDS, BOD, and COD, and compared with a standard value. All measurement was maintained in triplicate.

2.3.1 Chromium Analysis

SLC 208 titrimetric method of SLTC (Society of Leather Technologist and Chemists) (SLTC, 1996) was carried out to determine chromium concentration in initial and final treated liquor. The experiment was initiated with a 50 mL wastewater sample in a conical flask of 500 mL volume. After mixing 20 mL nitric acid and 20 mL of concentrated sulphuric acid and perchloric acid mixture, the flask was heated until the solution turned into red brick colour. Extra 1-minute continued heating and quickly cooled down in a water bath. Distilled water (100 mL) and few glass beads were mixed with the solutions and boiled for 10 minutes for chlorine removal. 10 mL of 30% concentrated sulphuric acid was added after cooling and took for titration with ferrous ammonium sulfate. Few drops (5-6) of indicator (*N*-phynylanthralinic acid) were used and the green color denoted the endpoint of the titration.

2.3.2 pH Measurement

The pH meter (UPH-314, UNILAB, USA) at first was calibrated with a two-point standard solution at pH 4.01 and pH 7.00, respectively. Then it was used for pH determination during the experiment.

2.3.3 Determination of TSS, TDS, EC, and turbidity

APHA-2540D method was carried out for TDS and TSS analysis of chromium-containing wastewater and treated liquor. The wastewater sample was filtered through weighed filter paper (Whatman No. 1) and the filtrate was dried at $105 \pm 2^\circ\text{C}$ until a constant weight was gained. TSS was calculated from the suspended dry matter on the filtered paper and TDS from the dried filtrate. EC and the turbidity were measured by a conductivity meter (CT-676, BOECO, Germany) and a portable turbidity meter (Hach 2100Q, 2100Q, Germany) respectively.

2.3.4 Determination of BOD

APHA method 5210 B (APHA, 2012) as carried out for BOD determination. The wastewater was diluted at the desired level and the BOD bottle was filled with the diluted sample (300 mL). 1 mL of manganoussulfate, alkaline azide solution, and concentrated sulphuric acid were added with the sample avoiding any form of air bubbles, and shaken. Then the sample was titrated with sodium thiosulfate (0.02 N) to find out the initial dissolved oxygen

(DO). Another BOD bottle containing a diluted sample was kept in an incubator at $20 \pm 1^\circ\text{C}$. After 5 days the BOD was taken out from the incubator and the same process was followed as described earlier to measure the final DO. Finally, BOD_5 was calculated from the initial DO and finally DO by using the following formula

$$\text{BOD}_5 = (\text{DO}_i - \text{DO}_f) \times \text{D.F}$$

Where DO_i is the initial DO, DO_f is the final DO and D.F is the dilution factor.

2.4 Batch-wise electrocoagulation test

Fig. 1 represents the schematic illustration of the electrocoagulation process. The experiment was conducted in a round shape glass beaker (height 14.5 cm diameter 11 cm) with a volumetric capacity of 1000 mL. A zinc plate (13.20 cm \times 5.30 cm) and copper plate (13.20 cm \times 5.30 cm) acted as anode and cathode respectively. During the batch experiment, 600 mL chromium-containing wastewater was used in the coagulation cell where two electrodes were set down vertically and parallel in the wastewater. Direct current (DC) was supplied to the electrodes and at different time intervals, 50 mL supernatant was taken from the top of the reactor for chromium measurement.

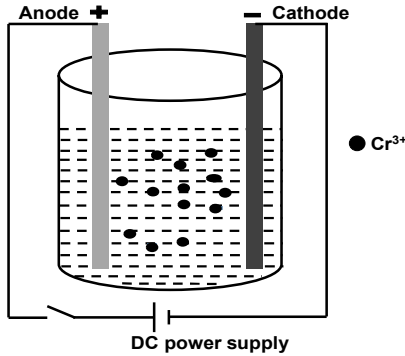


Figure 1: Electrocoagulation process

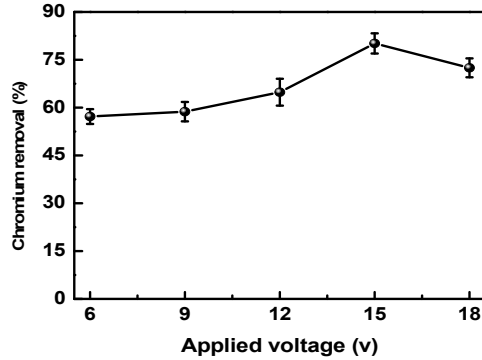


Figure 2: Effect of applied voltage on chromium removal efficiency

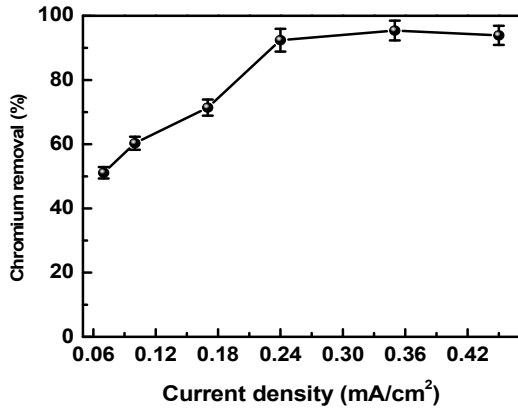


Figure 3: Effect of current density on chromium removal efficiency

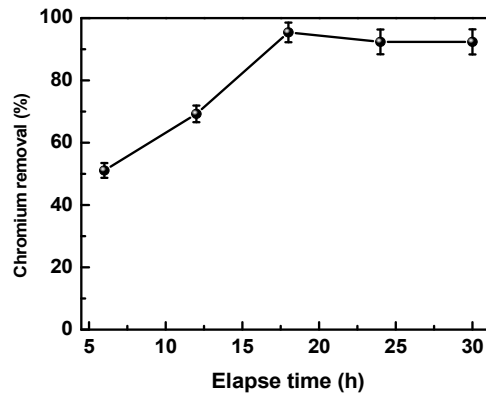
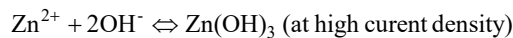
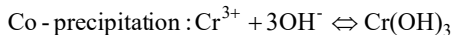
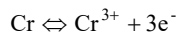
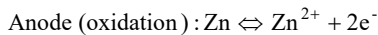
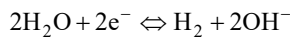


Figure 4: Effect of time on chromium removal efficiency

The Electrocoagulation process involves the generation of coagulants and form co-precipitation. Water is ionized by DC supply and produce hydroxyl radical and hydrogen gas. In the cell, the following reactions occur:



2.5 Optimization of the Batch Experiment

The electrocoagulation process was optimized in a batch-wise experiment to obtain the optimum conditions viz. applied voltage, time, and the current density. The chromium removal percentage was considered during optimization.

2.5.1 Voltage Optimization

A predefined voltage was applied during the electrocoagulation process and the voltage was controlled by using a digital multimeter (CD 800, Japan). A 600 mL wastewater sample was poured into the electrocoagulation chamber and applied 6, 9, 12, 15, and 18V, respectively. After treatment, supernatant was restocked for chromium measurement. For each applied voltage, a triplet batch experiment was conducted.

2.5.2 Time Equilibrium

For time optimization, predefined time e.g., 6, 12, 18, 24, and 30h, 600 mL of sample was treated in the electrocoagulation chamber and then repeated with a new wastewater sample. To obtain the optimal time, chromium content was measured of the supernatant. The experiment was continued in a triad.

2.5.3 Optimizing Current Density

For optimum current density, defined current 0.07, 0.10, 0.17, 0.24, 0.36 and 0.46 mA/cm² was passed through the electrocoagulation process after defined time interval and sample was withdrawn and refilled with untreated wastewater. The withdrawn samples were examined for Cr content and the procedure was continued in a triad. A digital multimeter (CD 800, Japan) was used to monitor the current density.

3. RESULTS AND DISCUSSION

3.1 Optimal Voltage

Applied voltage plays a significant role in the electrocoagulation process as total energy consumption depends on it. In batch experiment, the chromium removal efficiency was observed at different voltages: 6, 9, 12, 15 and 18 V by the electrocoagulation process. It is clear from Fig. 2 that applied voltage has a positive effect on the chromium removal efficiency as chromium removal efficiency was increased with the increase of applied voltage. For applied voltage 6, 9 and 12V chromium removal efficiency was obtained by 57.2, 58.7 and 64.8%, respectively. It seems that by increasing the applied voltage up to 12V, the chromium removal efficiency was increased very slightly. In case of applied voltage 15V, the chromium removal efficiency was maximum (80.1%). Bhatti *et al.*, (2011) observed the same phenomena and they found maximum chromium efficiency at 12 V. Unfortunately, above-applied voltage >15V, the chromium removal efficiency was decreased (72.5%). Therefore, the applied voltage was selected 15V for chromium removal through the electrocoagulation process.

3.2 Optimal Current Density

Electrocoagulation process was significantly affected by the current density as it has a great effect on the pollutant removal rate and it is considered as one of the most important parameters (Aoudj *et al.*, 2012). With applied current density viz. 0.07, 0.10, 0.17, 0.24, 0.36 and 0.46 mA/cm²; chromium removal efficiency was found 51.1, 60.3, 71.4, 92.4, 95.4 and 93.9%, respectively. It is quite clear that with the increase the current density chromium removal also increased. According to Faraday's law, this type of phenomena was observed due to anodic dissolution (El-Taweel *et al.*, 2015). It is obvious from Fig. 3 that there was a good linear relationship between current density (0.07, 0.10, 0.17, 0.24 mA/cm²; correlation coefficient ($R^2=0.983$) and chromium removal efficiency. The chromium removal efficiency for the current densities 0.24, 0.36, and 0.46 mA/cm² was almost same (92.4, 95.4 and 93.9%).

At elevated current density, there is a strong possibility to form a high amount of hydrogen bubbles in the cathode that will cause the uphill movement of the sludge (Sengiland Ozakar, 2006). At higher the current density e. g., 0.42 mA/cm² amount of co-precipitation forming of Zn(OH)₂ was so high. It is observed that with increasing the current density, the turbidity of wastewater was also increased. Thus, 0.36 mA/cm² considered the favourable current density for the electrocoagulation technique.

3.3 Optimal Time

Time is important parameters in the electrocoagulation process as it has a profound effect on energy consumption as well as pollutant removal efficiency (Gholami *et al.*, 2019). In Fig. 4 we have represented the relationship between chromium removal efficiency and the processing time. The relationship shows that at the initial stage of the processing time chromium removal efficiency was gradually increased. For 6, 12 and 18h removal efficiency of chromium was observed 27.8, 63.4 and 98.0%, respectively and after that, the removal efficiency was decreased as the increased in time. This phenomenon was observed due to rapid oxidation of Cr³⁺ and formation of Cr(OH)₃. At the beginning of electrocoagulation process, tiny particles tend to form floc but with the increase of process time, particle size turns into muscular form due to this tendency latter part of the electrocoagulation process chromium removal efficiency start to decrease (Moradi *et al.*, 2020). A possible explanation is that after 18h the

precipitated chromium returns to the aqueous phase. For this reason, the removal efficiency of chromium by the electrocoagulation process decline and increased the TDS simultaneously. Therefore, 18h was decided as the optimum time for chromium removal for the electrocoagulation process.

3.4 Removal Efficiency at Optimal Conditions

Table 1 represents the optimum data for the electrocoagulation process before and after treatment. To assess the quality of the treatment, several physicochemical parameters like pH, TDS, BOD, chromium, turbidity, and EC were determined after all stages of treatments. It was found that after treatment the pH, TDS, BOD, chromium, turbidity, and EC were 7.0, 2756mg/L, 780mg/L, 6.9mg/L, 57 NTU, and 8.7 mS, respectively. The value of pH, TDS, and conductivity was higher in the treated sample compared to the raw sample. The possible explanation behind this is the rapid production of hydroxyl ion during the treatment process (Lakshmi and Sivashanmugam, 2013). The obtained removal efficiency for BOD, chromium, and turbidity was 64.6, 98.0 and 75.5%, respectively. Mella *et al.*, (2015) have observed maximum removal efficiency of chromium was 97.8% which is lower than this study. Table 1 shows that although there was a significant reduction of chromium in the wastewater but still higher according to ECR standard. The treatment process achieved a higher efficiency of chromium removal, along with BOD and turbidity reduction.

Table 1: Data comparison between raw sample and treated sample

Parameters	Raw sample	Treated sample	ECR (1997)
pH	4.8±1.7	7.0±1.9	6-9
TDS (mg/L)	2248±39	2756±47	2100
BOD(mg/L)	2200±27	780±14	250
Cr (mg/L)	340.1±9	6.9±1.8	2.0
Turbidity (NTU)	233±7	57±3	-
Conductivity (mS)	7.5±1.3	8.7±2.4	-

4. CONCLUSIONS

The batch-wise electrocoagulation process is a feasible solution for removing chromium from tannery wastewater. The process shows superior removal efficiency of pollutants in comparison with other techniques. Chromium from wastewater was co-precipitated with zinc oxides and removed from the water body and at optimized conditions removal efficiency was of 98.0%. The biological oxygen demand and turbidity were removed 64.5% and 75.5%, respectively. Total dissolved solids were slightly increased due to the generation of ZnO(OH) in the sludge sample as a zinc plate was used as the anode. This process could reduce pollution load at a significant level and chromium could be recovered at a large scale from the co-precipitation of zinc oxide for reuse.

REFERENCES

- Aitbara A., Cherifi M., Hazourli S., and Leclerc J.P., 2014. Continuous treatment of industrial dairy effluent by electrocoagulation using aluminum electrodes. *Desalin. Water Treat.* 57(8), 3395-3404.
- Aoudj S., Khelifa A., Drouiche N., and Hecini M., 2012. HF wastewater remediation by electrocoagulation process. *Desalin Water Treat.* 51, 1596-1602.
- APHA, American Public Health Association, 2012. *Standard Methods for the Examination of Water and Wastewater*
- Belay A. A., 2010. Impacts of chromium from Tannery effluent and evaluation of alternative treatment options. *J. Environ. Prot.* 1, 53-58
- Bhatti M. S., Reddy A. S., Kalia R. K., and Thukral A. K., 2011. Modeling and optimization of voltage and treatment time for electrocoagulation removal of hexavalent chromium. *Desalination* 269(1-3), 157-162.
- Chowdhury M., Mostafa M. G., Biswas T. K., Mandal A., and Saha A. K., 2015. Characterization of the Effluents from Leather Processing Industries. *Environ. Process* 2(1), 173-187.
- El-Taweel Y. A., Nassef E. M., Elkheriany I., and Sayed D., 2015. Removal of Cr(VI) ions from wastewater by electrocoagulation using iron electrode. *Egypt. J. Pet.* 24(2), 183-192
- Environmental Conservation Rules, ECR 1997. Ministry of Environment & Forest (MoEF) Government of the People's Republic of Bangladesh
- Ghernaout D., Naceur M. W., and Ghernaout B., 2011. A review of electrocoagulation as a promising coagulation process for improved organic and inorganic matters removal by electrophoresis and electroflotation. *Desalin Water Treat.* 28(1-3), 287-320.
- Gholami P., Dinpazhoh L., Khataee A., and Orooji Y., 2019. Sonocatalytic activity of biochar-supported ZnO nanorods in degradation of gemifloxacin: Synergy study, effect of parameters and phytotoxicity evaluation. *Ultrason. Sonochem.* 55, 44-56.

- Kamaraj M., Srinivasan N. R., Assefa G., Adugna A. T., and Kebede M., 2020. Facile development of sunlit ZnO nanoparticles-activated carbon hybrid from pernicious weed as an operative nano-adsorbent for removal of methylene blue and chromium from aqueous solution: Extended application in tannery industrial wastewater. *Environ. Technol. Innov.* 17, 100540. doi:10.1016/j.eti.2019.100540
- Khalidi S., Lounici H., Drouiche M., and Drouiche N., 2017. Treatment of ointment pharmaceutical wastewater by electrocoagulation process. *Desalin Water Treat.* 71, 152-158.
- Kothai P., Meena A., Meenaloshini E., Revathy A., and Kumar N.V., 2019. Treatment of tannery effluent using groundnut shells. *Int. Res. J. Eng. Tech.* 6(3), 2395-0072.
- Koushkbaghi S., Zakialamdari A., Pishnamazi M., Ramandi H. F., Aliabadi M., and Irani M., 2018. Aminated-Fe₃O₄ nanoparticles filled chitosan/PVA/PES dual layers nanofibrous membrane for the removal of Cr(VI) and Pb(II) ions from aqueous solutions in adsorption and membrane processes. *Chem. Eng. J.* 337, 169-182.
- Kumar D., Singh J., and Baleanu, D., 2017. A new numerical algorithm for fractional Fitzhugh–Nagumo equation arising in transmission of nerve impulses. *Nonlinear Dyn.* 91(1), 307-317.
- Kusku O., Rivas B. L., Urbano B. F., Arda M., Kabay N., and Bryjak M., 2014. A comparative study of removal of Cr(VI) by ion exchange resins bearing quaternary ammonium groups. *J. Chem. Technol. Biotechnol.* 89(6), 851-857.
- Lefebvre O., and Moletta R., 2006. Treatment of organic pollution in industrial saline wastewater: A literature review. *Water Res.* 40(20), 3671-3682.
- Lakshmi M., and Sivashanmugam P., 2013. Treatment of oil tanning effluent by electrocoagulation: Influence of ultrasound and hybrid electrode on COD removal. *Sep. Purif. Technol.*, 116, 378-384.
- Makwana, A. R., and Ahammed M. M., 2016. Continuous electrocoagulation process for the post-treatment of anaerobically treated municipal wastewater. *Sep. Purif. Technol.* 102, 724-733.
- Mavrov V., Stamenov S., Todorova E., Chmiel H., and Erwe T., 2006. New hybrid electrocoagulation membrane process for removing selenium from industrial wastewater. *Desalination* 201(1-3), 290-296.
- Mella B., Glanert A. C., and Gutterres M., 2015. Removal of chromium from tanning wastewater and its reuse. *Process Saf. Environ.* 95, 195–201.
- Mohan D., 2006. Trivalent chromium removal from wastewater using low cost activated carbon derived from agricultural waste material and activated carbon fabric cloth. *J. Hazard. Mater.* 135, 280-295
- Moradi M., Vasseghian Y., Arabzade H., and Khaneghah, A.M., 2020. Various wastewaters treatment by sono-electrocoagulation process: A comprehensive review of operational parameters and future outlook. *Chemosphere* 263, 128314.
- Obayomi K. S., Auta M., and Kovo A. S., 2020. Isotherm, kinetic and thermodynamics studies for adsorption of lead(II) onto modified Aloji clay. *Desalin Water Treat.* 181, 376-384.
- Overah L. C., 2011. Biosorption of Cr (III) from aqueous solution by the leaf biomass of *Calotropis procera* ‘Bombom’. *J. Appl. Sci. Environ.* 15(1), 87-95
- Pal M., Malhotra M., Mandal M. K., Paine T. K., and Pal P., 2020. Recycling of wastewater from tannery industry through membrane-integrated hybrid treatment using a novel graphene oxide nanocomposite. *J. Water Process. Eng.* 36, 101324, doi:10.1016/j.jwpe.2020.101324
- Saravanabhavan, S., Thanikaivelan P., Rao J. R., Nair B. U., and Ramasami T., 2004. Natural Leathers from Natural Materials: Progressing toward a New Arena in Leather Processing. *Environ. Sci. Technol.* 38(3), 871-879.
- Sarker, B. C. Basak, B., and Islam, M. S., 2013. Chromium effects of tannery wastewater and appraisal of toxicity strength reduction and alternative treatment. *Int. J. Agric. Res.* 3(11), 23-35
- Sengil, I.A., and Ozacar, M., 2006. Treatment of dairy wastewaters by electrocoagulation using mild steel electrodes. *J. Hazard. Mater.* 137:1197-1205.
- Sivaram N. M., and Barik D., 2019. Toxic Waste from Leather Industries, Energy from Toxic Organic Waste for Heat and Power Generation, 55-67.
- Society of Leather Technologist and Chemists, SLTC, 1996. Official Methods of Analysis, Northampton, UK.
- Thakur C., Srivastava V. C., and Mall I. D., 2009. Electrochemical treatment of a distillery wastewater: Parametric and residue disposal study, *Chem. Eng. J.*, 148(2-3), 496-505.
- Yahya M. D., Abubakar H., Obayomi K. S., Iyaka Y. A., and Suleiman B., 2020. Simultaneous and continuous biosorption of Cr and Cu (II) ions from industrial tannery effluent using almond shell in a fixed bed column, *Results in Engineering* 6, 100113, doi:10.1016/j.rineng.2020.100113.