

Research Article

Chemical Investigation and Separation of Chromium from Chrome Cake of BSCIC Tannery Industrial Estate at Hemayetpur, Dhaka, Bangladesh

Md. Ashraful Alam, Ajoy Kanti Mondal , Md. Tushar Uddin , Md. Abdur Razzaq, Murshid Jaman Chowdhury, and Madhu Sudan Saha

Leather Research Institute, Bangladesh Council of Scientific and Industrial Research, Savar, Dhaka 1350, Bangladesh

Correspondence should be addressed to Md. Tushar Uddin; tusarlr@yahoo.com

Received 14 January 2023; Revised 30 March 2023; Accepted 4 April 2023; Published 30 May 2023

Academic Editor: Afzal Khan

Copyright © 2023 Md. Ashraful Alam et al. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

Leather tanning mainly depends on chrome tanning. A huge amount of basic chromium sulfate (BCS) is used in leather tanning. About 60–70% of BCS has been taken by leather and the rest of the amount is discharged as effluent and solid waste. In the Common Effluent Treatment Plant (CETP) of BSCIC Tannery Industrial Estate (Hemayetpur, Savar, Dhaka), the effluent which contained a high concentration of chromium is precipitated as solid chromium hydroxide with other elements which is called a chrome cake. Chrome cake is not exposed directly in the open space due to its toxic effect on human health as well as the environment. Human occupational experience distinctly indicates that, when inhaled, chromium compounds are respiratory tract irritants, resulting in airway irritation, airway obstruction, and lung, nasal, or sinus cancer. It is strongly suggested to extract Cr from the chrome cake before dumping it; otherwise, it will be a potential hazard to the environment. Herein, the chrome cake is characterized by inductively coupled plasma-optical emission spectroscopy (ICP-OES), X-ray fluorescence (XRF), UV-visible spectrophotometer, etc., and develops a method to separate chromium from chrome cake. ICP-OES and XRF analyses show that the total chromium contained in chrome cake is ~17.45% and 20.7%, respectively. UV-visible spectrophotometer indicates that ~0.04% of chromium is hexavalent. Afterward, chromium has been separated by using H_2SO_4 where the optimized concentration was found to be 7%. The separation efficiency of chromium from the chrome cake for optimized condition is obtained at ~95%.

1. Introduction

In Bangladesh, leather or leather products are a high-priority industrial sector and footwear exports. A lot of animal (cow, goat, buffalo, and sheep) skins are produced all around the year, especially during Eid-ul-Azha in Bangladesh [1]. A tannery is a place where animal skins are processed. Bangladesh Small and Cottage Industries Corporation (BSCIC) established large units of tannery industries at Hemayetpur, Savar, which is the outskirts of the capital city of Bangladesh [2]. Leather is a strong, flexible, and durable material obtained from tanning, or chemical treatment, of animal skins and hides to prevent decay [3, 4]. Turning of skins and hides into leather requires the use of a number of chemicals. After

tanning, high concentrations of the used chemicals as well as compounds coming from the skin and hides can be found in the wastes generated in tannery processes including wastewater effluent, solid waste, and hazardous waste [5–9].

From raw hide to final leather, there are several steps that have to be processed and one of them is tanning [10]. Tanning is essentially the reaction of collagen protein in the hide with tannins, chromium, alum, or other chemical agents [11]. The common tanning agents used in the tannery are trivalent chromium in the form of basic chromium sulfate (BCS) [12]. After tanning, a significant amount of chromium is discharged which induces environmental pollution [13]. High levels of even Cr (III) in the discharged tannery wastewaters supplemented by the dynamic

interconversion among Cr (III) and Cr (VI) in aqueous environments may pose a health risk [14]. The pollution from chromium can have dangerous consequences for water and the soil environment. Chronic exposure and bioaccumulation of chromium, as a heavy metal, can cause toxicity and many pathophysiological defects, including allergic reactions, anemia, burning, and sores, particularly in the stomach and small intestine, and damage to sperm along with the male reproductive system and affect various biological systems [15]. Due to the opposing (essentiality and carcinogenicity) consequences of chromium compounds, speciation and determination of each species play a significant role in biochemical and toxicological investigations. It is therefore preferable to minimize the exposure because any amount of Cr (VI) entering cells can induce potentially toxic effects in humans and animals. Spectroscopic techniques are the most reported techniques used for the speciation and determination of chromium in real samples such as discharged tannery effluents and solid waste [16–18].

For the treatment of effluent and waste, the Common Effluent Treatment Plant (CETP) was commissioned by the government of the people's republic of Bangladesh. CETP has two different inlet lines from tannery: one is for the chrome recovery plant which line contains the effluent of the chrome tanning process, and another inlet line is called the general line which discharges all other effluents, except the chrome tanning process [19]. The collected effluent from the chrome tanning process is treated with alkaline oxide. After that, the chromium of the effluent is precipitated as chromium hydroxide with other solid sediments which is known as chrome cake. These chrome cakes are not exposed to open land because they contain highly concentrated chromium. Hence, the precipitation procedure for the separation of Cr has attracted a great deal of attention.

Many attempts have been made to the selective separation of Cr by using different chemicals [20–22] and different techniques [23, 24]. Some antioxidant compounds and substances are used that can reduce Cr (VI) to a lower oxidation state of enzymatic and nonenzymatic pathways that detoxify the chromium-induced oxidative damage in organisms [25–28]. Specific bacteria are effective in the treatment of organic waste or industrial effluent [29, 30]. Cr is separated using bacteria from tannery industry sediment to detoxify Cr (VI) by reducing the oxidation state [31]. The use of expensive and harmful organic solvents has limited the broad range of applications contemplating their high selectivity and recovery efficiency. Various treatment procedures such as adsorption, electrocoagulation, chemical precipitation, electrodialysis, ion exchange, and membrane separation are well known for the removal of Cr from wastewater [32]. Among them, chemical precipitation is the common way where NaOH, Ca(OH)₂, MgO, or CaMg(CO₃)₂ is generally used for the precipitation of chromium [32].

In this study, the chrome cake was analyzed by ICP-OES, XRF, UV-visible spectrophotometer, Karl-Fischer titrator, pH meter, and so on. Total chromium, Cr (VI), Cr (III), water content, and pH of the chrome cake were determined. Furthermore, a chemical separation method was proposed

for the treatment of this chrome cake. To the best of our knowledge, no study has been reported for the separation of chromium using the similar method from chrome cake. This separation method of chromium from chrome cake will be a potential process for the reuse of chromium in tanneries and minimization of health risks as well as environmental pollution.

2. Experimental

The solid effluent discharged from the CETP of BSCIC Tannery Industrial Estate at Hemayetpur, Dhaka, Bangladesh, contained a high concentration of chromium known as chrome cake. Chromium from chrome cake reacts with H₂SO₄ and precipitates as Cr₂(SO₄)₃, which is the main purpose of this study.

2.1. Description of the Study Area. In this study, the sample “chrome cake” was collected from the chrome recovery plant of CETP at BSCIC Tannery Industrial Estate, which is located at Hemayetpur, Savar, Dhaka, Bangladesh. It is situated on the bank of the Dhaleshwari River. Six sampling sites of the different portions of the chrome recovery plant of CEPT were selected and the sample from each site was collected daily for three consecutive days using 2000 mL polyethylene bags. Then, six samples were mixed up thoroughly and a composite sample was made. The initial chrome cake was ground and sieved (<0.5 mm) to be homogenized for analysis.

2.2. Chemicals and Apparatus. In this study, nitric acid (70%), perchloric acid (70%), sulfuric acid (98%), sodium hydroxide, potassium dichromate, 1,5-diphenylcarbazide were used (98%, Hightech Health Care) (DPC). Distilled deionized water (DDW) was also used throughout the study. All the reagents were of analytical grade and were used without prior treatment. A UV-visible double beam spectrophotometer (LAMBDA 365, PerkinElmer) and inductively coupled plasma optical emission spectrometer (5110 ICP-OES, Agilent) were used for the determination of the hexavalent and total chromium levels in the chrome cake collected from the selected sampling sites, respectively. X-ray fluorescence spectroscopy (XRF, Bruker AXS, S8 Tiger) was used to determine total chromium. A microwave digestion machine (SCP-Science, MiniWave) was used to prepare the sample for analysis. A Karl-Fischer titrator (Metrohm, Switzerland) and pH meter (HM-40X, DKK-TOA, Japan) were used to determine the water content and pH of the chrome cake, respectively.

2.3. Characterization of Chrome Cake. Before starting the chemical separation, it is essential to characterize the raw material. Here, chrome cake is the main raw material that is collected from the tannery, and then the chrome cake is characterized in terms of physical appearance and chemical parameter, as well as spectroscopic method.

2.3.1. Physical Appearance, pH, and Water Content of the Chrome Cake. The physical appearance of the chrome cake is gray. It is a soil-like solid material. Before determining the pH, the chrome cake was sun-dried and then dispersed in DDW. Then, the pH value is determined by a pH meter. The water content of the chrome cake is analyzed by a Karl-Fischer titrator. About 0.1 g of solid chrome cake was taken to determine the water content.

2.3.2. Analyses of Total Chromium in the Chrome Cake by ICP-OES. Before the determination of chromium in chrome cake by ICP-OES, 1000 ppm standard chromium stock solution was prepared by dissolving 0.2829 g of $K_2Cr_2O_7$ in a 100 mL volumetric flask with DDW. Furthermore, working solutions of desired concentrations were prepared from the stock solution by serial dilution. In order to determine the total chromium content in the chrome cake using the ICP-OES instrument, the samples were digested using a microwave digestion procedure (USEPA 3015) with minor modifications [33].

Briefly, 0.5 g of each sample was taken in a 50 mL Quartz digestion tube and 15 mL of HNO_3 , $HClO_4$, and H_2SO_4 mixture (1 : 1 : 1) was added to the sample and made up to the mark with DDW and then digested at 170°C. Each digested outcome was allowed to cool, filtered, and diluted to 100 mL with DDW. Unlike the others, 5 mL of the digestion outcome of chrome cake was diluted to 50 mL with DDW for the original sample forming an intense green color indicating a relatively high chromium concentration. The instrumental operating conditions for ICP-OES are presented in Table 1.

2.3.3. Analyses of Total Chromium in the Chrome Cake by XRF. Total chromium in the chrome cake was determined by XRF analysis by following the instrumental operating conditions (Table 1). About 4 g of fine chrome cake powder was taken and mixed with 2 g of binder (Boreox). Then, the mixture was poured into a pressing die, and the sample was pressed to make a pellet. Then, the resulting pellet or tablet is used for XRF analysis.

2.3.4. Analyses of Cr (VI) in the Chrome Cake by UV-Visible Spectrophotometer. Standard solution of different concentrations of $K_2Cr_2O_7$ was prepared from the 100 ppm of intermediate standard solution using serial dilution. 5 mL of all standards and a blank in a 25 mL volumetric flask were taken. DPC reagent was prepared by first dissolving a 0.25 g of DPC in 5 mL acetone and then diluting to 100 mL with DDW. 1.0 mL of DPC solution was added to each working solution including the blank for complexing chromium (VI) [34, 35]. Then, pH of each solution was adjusted by 5 mol/L of H_2SO_4 until a pink color was observed, except in the blank. After 15 min, the absorbance of the solutions was measured using the UV-visible spectrophotometer at a wavelength of 540 nm. Afterward, Cr (VI) was extracted from the chrome cake by following the published method with minor modifications [36]. Briefly, 1.0 g of chrome cake

TABLE 1: The optimized operating conditions for ICP-OES and XRF instruments.

Parameter	Condition
<i>ICP-OES</i>	
Power	1100 W
Nebulizer flow rate	0.65 L/min
Nebulization pressure	1.75 ber
Pump speed	20 rpm
Plasma flow	15 L/min
Auxiliary flow	0 L/min
Sheath flow	0.2 L/min
Wavelength	267.716
<i>XRF</i>	
X-ray tube	Rh
Rating	60 kV, 1 mA
Detector	Flow proportional and scintillation
Working environment	Air

was taken in a 100 mL beaker and then 50 mL of 0.1 M sodium hydroxide was added to the mixture. Afterward, the solution mixture was placed on a hot plate for 60 min at 90–95°C, with sporadic shaking [36]. Later, the final volume of the solution was made to 100 mL and the solution was filtered. 5 mL of the abovementioned solution was taken in a 25 mL volumetric flask, and then a similar procedure was followed as in the blank and standard analysis.

2.4. Chemical Treatment for Separation of Chromium from the Chrome Cake. The chromium from the chrome cake was separated by batch method using H_2SO_4 . At first, different concentrations of sulfuric acid (1.0%, 3.0%, 5.0%, 7.0%, 9.0%, 11.0%, 13.0%, 15.0%, 17.0%, and 19.0% (V/V)) were prepared for optimization of the process by dilution of concentrated sulfuric acid (98%). Then, 10 g of chrome cake was taken in a 250 mL beaker and 100 mL of prepared 1% H_2SO_4 solution was added and stirred for 3 h with a magnetic stirrer. After that, the solution was kept overnight. Then, the solution was filtered with Whatman filter paper and washed with DDW. The solid retained on filter paper was dried in an oven for 3 h at 105°C. The same procedure was followed for the preparation of all the concentrations mentioned above for optimization.

The solid retained on the filter paper was analyzed by ICP-OES for the determination of total chromium by following the method mentioned in Section 2.3.2, and recovery percentage was calculated. XRF and UV-visible analyses of the retained solid were performed after chromium separation from the chrome cake in optimized conditions.

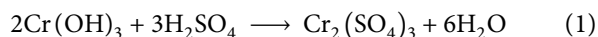
For all the analysis processes, three parallel samples were examined and the average test results were presented.

3. Results and Discussion

Leather tanning is an industrial process used for the conservation of raw hides by binding different chemicals comprising chromium salts to enhance the leather quality [37]. Naturally, chromium exhibits different oxidation states, but Cr (III) and Cr (VI) are of noteworthy concern

biologically, especially since their hexavalent form is highly toxic and carcinogenic [38]. The requirement of Cr is increasing day by day because of its extensive use in numerous industries, not only in tanning industries but also in other chemical processes such as film and photography, plating and electroplating, galvanometric and electrical procedures, metal cleaning, and mining [39]. These industrial processes generate toxic waste in large amounts that consists of different forms of chromium with concentrations ranging from 10–100 mg/L [40]. Chromium is frequently found in soil and ground water because of its wide spread industrial use in various process industries including tannery [41].

The effluent from the chrome tanning method in tannery industries is treated with alkaline oxide and precipitated as chromium hydroxide with other solid sediments which is known as chrome cake. This hazardous chromium element is of great concern for Bangladesh in terms of environmental load and health effects. So, it is essential to separate chromium from the chrome cake. H_2SO_4 reacts with chromium hydroxide to form chromic sulfate. Herein, chromium is separated from the chrome cake using H_2SO_4 by following reaction (1).



Chrome cake is a solid material that is gray. The water content of the chrome cake is ~25.1%. The pH value of the chrome cake is ~7.4, which is slightly basic. This is due to the alkaline treatment of chrome tanning effluents.

Table 2 represents the ICP-OES analysis results of the chrome cake. It shows that before treatment, the total chrome content in the chrome cake is ~17.45 (%w/w). Similarly, XRF analysis shows the total chromium content ~20.70 (%w/w). Hexavalent chromium in the chrome is 0.04 (%w/w) determined by a UV-visible spectrophotometer. Trivalent chromium is calculated by simple subtraction of hexavalent chrome from total chrome found in ICP-OES analysis, and the value is obtained at 17.41 (%w/w) in the raw chrome cake.

Then, the chromium is separated by the chemical separation method using H_2SO_4 . Different concentrations of H_2SO_4 were used to optimize the maximum separation performances (Figure 1). Figure 1 shows that when the concentrations of H_2SO_4 increase, then the separating performances also increase gradually. At about ~7% H_2SO_4 concentration, the separating performance is maximum. Further increasing the acid concentration, the separation rate is insignificant, indicating most of the chromium from the chrome cake is separated in this optimized concentration (Figure 1).

Kokkinos and Zouboulis separated chromium from tannery waste using three acids parallelly, namely, H_2SO_4 , HNO_3 , and HCl [42]. They found that the maximum percentage of Cr(III) extraction (93%) was obtained by using 1 N H_2SO_4 , compared with similar concentrations of HNO_3 (73%) or HCl (65%). In this study, only H_2SO_4 was selected to separate the chromium from the chrome cake due to its maximum separating performance compared with other acids [42]. In CETP, the chrome cake is formed due to the

TABLE 2: Chromium content determination (before and after treatment) in chrome cake by ICP-OES, XRF, and UV-visible spectrophotometer.

Total chromium		Cr (VI) UV-Vis	Cr (III)
ICP-OES	XRF		
<i>Before treatment of chrome cake</i>			
17.45	20.7	0.04	17.41
<i>After treatment of chrome cake</i>			
0.71	0.88	0.01	0.70

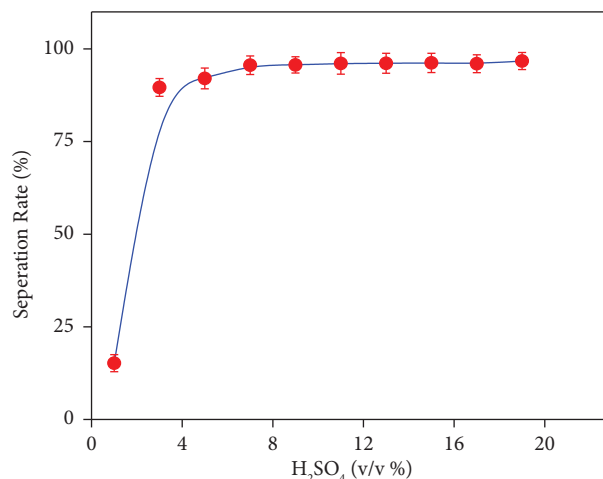


FIGURE 1: Separation rate of chromium against different concentrations of H_2SO_4 .

alkaline treatment, where maximum chromium is found in Cr^{3+} forms as $Cr(OH)_3$. When H_2SO_4 is used for separation, the maximum amount of chromium is obtained as $CrSO_4^+$, which has a higher solubility than Cr^{3+} [43–45]. In addition, H_2SO_4 is chosen for the separation of chromium which is due to the reuse of chromium as chromium sulfate in the further retanning process.

After successful separation of chromium from chrome cake by using optimized H_2SO_4 , the solid retained or residue was characterized by ICP-OES and XRF and the maximum separating performances were calculated (Figure 1). Table 2 indicates the ICP-OES, XRF, and UV-visible results of the chrome cake after chemical separation. Results show that ~95.61% of total chromium is removed from the chrome cake analyzed by ICP-OES (Figure 2). Similarly ~95.75% of total chromium is removed from the chrome cake analyzed by XRF (Figure 2). Figure 2 shows that the maximum separation efficiency of chromium is ~96.75% by using 19% of H_2SO_4 . In the optimized concentration of H_2SO_4 (7%), the efficiency of separation is ~95.75% which may slightly improve by using a higher percentage of H_2SO_4 (19%). In that case, the use of H_2SO_4 is very high, but the separation efficiency is not significantly improved, so the optimized condition for H_2SO_4 is chosen at 7%. In the ICP-OES analysis method, the chrome cake is digested in the microwave to prepare the sample. Further dilution was made for analysis in ICP-OES. But, XRF analysis of the chrome cake sample is directly used to determine the total

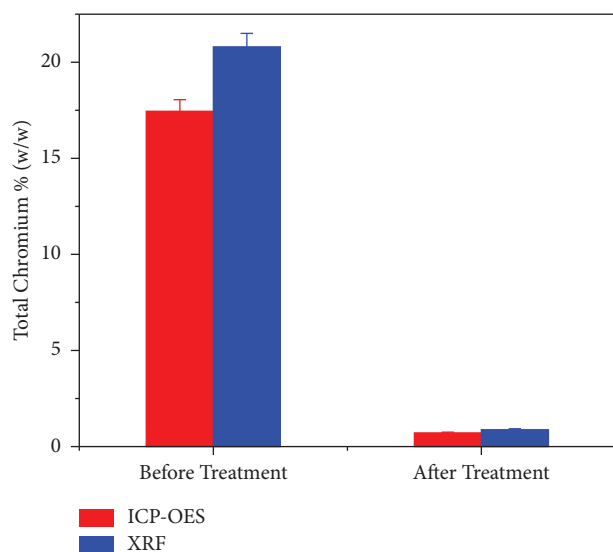


FIGURE 2: Total chromium contents in the chrome cake (before and after treatment) by ICP-OES and XRF analyzers.

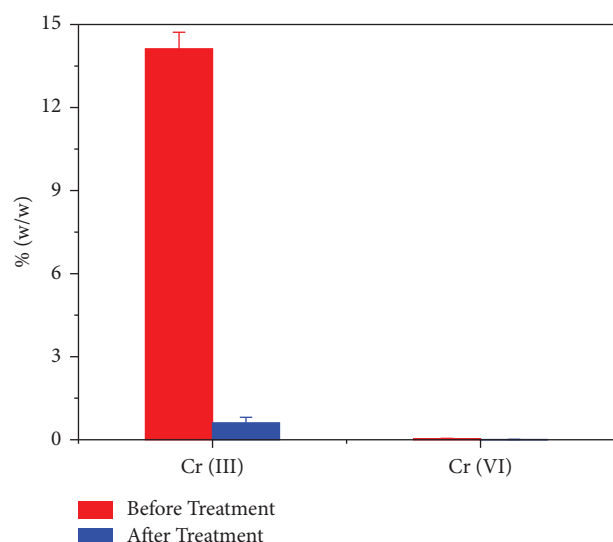


FIGURE 3: Trivalent and hexavalent chromium contents in the chrome cake (before and after treatment).

chromium. For this reason, the results varied slightly in these two analysis methods. A similar observation is found in previously reported literature [46].

Hexavalent chromium is more toxic than trivalent chromium. Here, we determined the hexavalent chromium by a UV-visible spectrophotometer after the chemical treatment of the chrome cake (Figure 3). Table 2 shows that after the chemical separation, the hexavalent chromium in the chrome cake is ~0.01%.

Chromium is a well-known corrosive, cytotoxic, and carcinogenic agent in humans. Basically, Cr (VI) is highly toxic and associated with some pathology by entering the human cell through the sulfate transport system as an oxy-anion at physiological pH. The toxicological effects of chromium on humans can be categorized as respiratory

effects, carcinogenic effects, genotoxic and mutagenic effects, cardiovascular effects, and reproductive and developmental effects. The tannery workers are under constant threat of chromium toxicity. At present, a huge amount of chromium containing chrome cake is usually stored beside the tannery estate. If proper steps are not taken immediately to separate or recover this toxic chrome cake, in the future, it would be a great threat to the fertile land, environment, and human health. According to the FAO/WHO, the permissible limit of chromium in soil is ~20 mg/kg [47], which is too low with respect to the chrome cake ($\sim 2.7 \times 10^5$ mg/kg).

4. Conclusions

In this study, the chrome cake was collected from CETP of BSCIC Tannery Industrial Estate, Hemayetpur, Dhaka, Bangladesh. The chrome cake was characterized by ICP-OES, XRF, UV-visible spectrophotometer, and so on, and a method was developed to separate chromium from the chrome cake. Total chromium contained in the chrome cake was parallelly determined by ICP-OES and XRF analyses, and the results demonstrated that the total chromium contained in the chrome cake is ~17.45% and 20.7%, respectively. The UV-visible spectrophotometer showed that ~0.04% of chromium is hexavalent. Then, the chromium was separated by using H_2SO_4 where the optimized concentration was found as 7%. The separation efficiency of chromium from the chrome cake for optimized condition is obtained at ~95%. Some advanced technologies (phyto-remediation, bioadsorbent, and so on) may need further improvement to enhance the separation efficiency. To the best of our knowledge, no study has been reported for the separation of chromium using the chemical separation method from chrome cake. This study presents not only a simple and scalable platform for separating chromium from chrome cake but also an easy way to reuse chromium in tanning and other purposes.

Data Availability

All data presented or analyzed during this study are included in this article.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

Authors' Contributions

Md. Ashrafal Alam performed lab work. Ajoy Kanti Mondal developed methodology and curated the data. Md. Tushar Uddin conceptualized, supervised, and validated the study. Md. Abdur Razzaq did sampling. Murshid Jaman Chowdhury did sample analysis. Madhu Sudan Saha reviewed and edited the manuscript.

Acknowledgments

This work was supported by the Bangladesh Council of Scientific and Industrial Research as part of the Research and Development (R&D) project. The authors are grateful to

Dr. Shirin Akter Jahan, Sabrina Mostofa, Md. Lutfor Rahman, and Palash Kumar Das for their support during the performance of experiment and writing the manuscript.

References

- [1] B. A. Mollik, "Bangladesh's leather industry," 2022, https://papers.ssrn.com/sol3/papers.cfm?abstract_id=4044704.
- [2] M. S. Rahman, Z. Ahmed, S. M. Seefat et al., "Assessment of heavy metal contamination in sediment at the newly established tannery industrial Estate in Bangladesh: a case study," *Environmental Chemistry and Ecotoxicology*, vol. 4, pp. 1–12, 2022.
- [3] R. Duraisamy, S. Shamina, and A. K. Berekete, "A review of bio-tanning materials for processing of fish skin into leather," *International Journal of Engineering Trends and Technology*, vol. 39, no. 1, pp. 10–20, 2016.
- [4] K. M. Maraz, "Benefits and problems of chrome tanning in leather processing: approach a greener technology in leather industry," *Materials Engineering Research*, vol. 3, no. 1, pp. 156–164, 2021.
- [5] S. Dixit, A. Yadav, P. D. Dwivedi, and M. Das, "Toxic hazards of leather industry and technologies to combat threat: a review," *Journal of Cleaner Production*, vol. 87, pp. 39–49, 2015.
- [6] G. Saxena and R. N. Bharagava, "Persistent organic pollutants and bacterial communities present during the treatment of tannery wastewater," *Environmental Waste Management*, pp. 217–247, CRC Press, Taylor and Francis Group, Boca raton, FL, USA, 2015.
- [7] J. Kanagaraj, R. C. Panda, and V. Kumar, "Trends and advancements in sustainable leather processing: future directions and challenges—a review," *Journal of Environmental Chemical Engineering*, vol. 8, no. 5, Article ID 104379, 2020.
- [8] M. Nur-E-Alam, M. A. S. Mia, F. Ahmad, and M. M. Rahman, "An overview of chromium removal techniques from tannery effluent," *Applied Water Science*, vol. 10, no. 9, p. 205, 2020.
- [9] S. M. M. Hasan, M. A. Akber, M. M. Bahar et al., "Chromium contamination from tanning industries and phytoremediation potential of native plants: a study of savar tannery industrial estate in Dhaka, Bangladesh," *Bulletin of Environmental Contamination and Toxicology*, vol. 106, no. 6, pp. 1024–1032, 2021.
- [10] O. Tünay, I. Kabdaşlı, D. Orhon, and G. Cansever, "Use and minimization of water in leather tanning processes," *Water Science and Technology*, vol. 40, no. 1, pp. 237–244, 1999.
- [11] G. Krishnamoorthy, S. Sadulla, P. Sehgal, and A. B. Mandal, "Green chemistry approaches to leather tanning process for making chrome-free leather by unnatural amino acids," *Journal of Hazardous Materials*, vol. 215–216, pp. 173–182, 2012.
- [12] A. Fathima, J. R. Rao, and B. Unni Nair, "Trivalent chromium removal from tannery effluent using kaolin-supported bacterial biofilm of *Bacillus* sp isolated from chromium polluted soil," *Journal of Chemical Technology and Biotechnology*, vol. 87, no. 2, pp. 271–279, 2012.
- [13] A. Esmaeili and R. Vazirinejad, "Chromium (III) Removal and Recovery from Tannery Wastewater by Precipitation Process," 2005, <https://agris.fao.org/agris-search/search.do?recordID=AV20120161798>.
- [14] H. Zhang, "Light and iron (III)-induced oxidation of chromium (III) in the presence of organic acids and manganese (II) in simulated atmospheric water," *Atmospheric Environment*, vol. 34, no. 10, pp. 1633–1640, 2000.
- [15] H. Hossini, B. Shafie, A. D. Niri et al., "A comprehensive review on human health effects of chromium: insights on induced toxicity," *Environmental Science and Pollution Research*, vol. 29, no. 47, Article ID 70686, 70705 pages, 2022.
- [16] B. Dayananda and H. Revanasiddappa, "Spectrophotometric determination of chromium by oxidation of prochlorperazine dimaleate," *Oxidation Communications*, vol. 30, no. 1, pp. 197–205, 2007.
- [17] L. Hua, Y. C. Chan, Y. Wu, and B. Wu, "The determination of hexavalent chromium (Cr6+) in electronic and electrical components and products to comply with RoHS regulations," *Journal of Hazardous Materials*, vol. 163, no. 2–3, pp. 1360–1368, 2009.
- [18] H. Revanasiddappa and T. K. Kumar, "Rapid spectrophotometric determination of chromium with trifluoperazine hydrochloride," *Chemia Analytyczna*, vol. 47, no. 2, pp. 311–318, 2002.
- [19] H. Rahman, N. Hoque, P. K. Sarker, and A. Safa, "Assessment of hexavalent chromium pollution in buriganga and Dhaleshwari river waterbodies adjacent to tannery estates in Bangladesh," *MIST International Journal of Science and Technology*, vol. 8, no. 1, pp. 11–15, 2020.
- [20] A. Azizitorghabeh, F. Rashchi, A. Babakhani, and M. Noori, "Synergistic extraction and separation of Fe (III) and Zn (II) using TBP and D2EHPA," *Separation Science and Technology*, vol. 52, no. 3, pp. 476–486, 2017.
- [21] P. T. de Souza e Silva, N. T. De Mello, M. M. Menezes Duarte et al., "Extraction and recovery of chromium from electroplating sludge," *Journal of Hazardous Materials*, vol. 128, no. 1, pp. 39–43, 2006.
- [22] A. Senol, "Optimal extractive separation of chromium (VI) from acidic chloride and nitrate media by commercial amines: equilibrium modeling through linear solvation energy relation," *Industrial and Engineering Chemistry Research*, vol. 52, no. 46, 16334 pages, Article ID 16321, 2013.
- [23] K. Yan, Z. Liu, Z. Li, R. Yue, F. Guo, and Z. Xu, "Selective separation of chromium from sulphuric acid leaching solutions of mixed electroplating sludge using phosphate precipitation," *Hydrometallurgy*, vol. 186, pp. 42–49, 2019.
- [24] S. S. Goh, M. Rafatullah, N. Ismail, M. Alam, M. R. Siddiqui, and E.-K. Seow, "Separation of chromium (VI), copper and zinc: chemistry of transport of metal ions across supported liquid membrane," *Membranes*, vol. 12, no. 7, p. 685, 2022.
- [25] P. Ghosh, T. Dey, A. Chattopadhyay, and D. Bandyopadhyay, "An insight into the ameliorative effects of melatonin against chromium induced oxidative stress and DNA damage: a review," *Melatonin Research*, vol. 4, no. 3, pp. 377–407, 2021.
- [26] Q.-N. Liu, Y.-Y. Tang, J.-R. Zhao et al., "Transcriptome analysis reveals antioxidant defense mechanisms in the red swamp crayfish *Procambarus clarkia* after exposure to chromium," *Ecotoxicology and Environmental Safety*, vol. 227, Article ID 112911, 2021.
- [27] M. Qadir, A. Hussain, M. Hamayun et al., "Phytohormones producing rhizobacterium alleviates chromium toxicity in *Helianthus annuus* L. by reducing chromate uptake and strengthening antioxidant system," *Chemosphere*, vol. 258, Article ID 127386, 2020.
- [28] J. Yin, L. Wang, S. Li, F. Chen, A. M. Hegazy, and X. Zhang, "Accumulation and depuration of dissolved hexavalent chromium and effects on the antioxidant response in bighead carp (*Aristichthys nobilis*)," *Environmental Toxicology and Pharmacology*, vol. 80, Article ID 103465, 2020.
- [29] F. H. M. Nor, S. Abdullah, Z. Ibrahim et al., "Role of extremophilic *Bacillus cereus* KH1 and its lipopeptide in

- treatment of organic pollutant in wastewater,” *Bioprocess and Biosystems Engineering*, vol. 46, no. 3, pp. 381–391, 2023.
- [30] S. N. F. Moideen, S. Krishnan, Y.-Y. Li et al., “Performance evaluation and energy potential analysis of anaerobic membrane bioreactor (AnMBR) in the treatment of simulated milk wastewater,” *Chemosphere*, vol. 317, Article ID 137923, 2023.
- [31] G. Suresh, B. Balasubramanian, N. Ravichandran et al., “Bioremediation of hexavalent chromium-contaminated wastewater by *Bacillus thuringiensis* and *Staphylococcus capitis* isolated from tannery sediment,” *Biomass Conversion and Biorefinery*, vol. 11, no. 2, pp. 383–391, 2021.
- [32] M. Mia, A. Sayid, F. Ahmad, and M. Rahman, “An overview of chromium removal techniques from tannery effluent,” *Applied Water Science*, vol. 10, no. 9, pp. 1–22, 2020.
- [33] L. Collins, *Microwave Sample Preparation for Analysis of Metals in Environmental Samples*, American Chemical Society, Washington, DC, USA, 1996.
- [34] P. Lazo, “Determination of Cr (VI) in environmental samples evaluating Cr (VI) impact in a contaminated area,” *Journal of International Environmental Application and Science*, vol. 4, no. 2, pp. 207–213, 2009.
- [35] F. Zarghampour, Y. Yamini, M. Baharfar, G. Javadian, and M. Faraji, “On-chip electromembrane extraction followed by sensitive digital image-based colorimetry for determination of trace amounts of Cr (vi),” *Analytical Methods*, vol. 12, no. 4, pp. 483–490, 2020.
- [36] B. R. James, J. C. Petura, R. J. Vitale, and G. R. Mussoline, “Hexavalent chromium extraction from soils: a comparison of five methods,” *Environmental Science and Technology*, vol. 29, no. 9, pp. 2377–2381, 1995.
- [37] L. E. Lockman, “Case report: allergic contact dermatitis and new-onset asthma. Chromium exposure during leather tanning,” *Canadian family physician Medecin de famille canadien*, vol. 48, pp. 1907–1909, 2002.
- [38] R. Rahmaty and J. Khara, “Effects of vesicular arbuscular mycorrhiza *Glomus intraradices* on photosynthetic pigments, antioxidant enzymes, lipid peroxidation, and chromium accumulation in maize plants treated with chromium,” *Turkish Journal of Biology*, vol. 35, no. 1, pp. 51–58, 2011.
- [39] D. Ünal, N. O. Işık, and A. Sukatar, “Effects of chromium VI stress on green alga *Ulva lactuca* (L.),” *Turkish Journal of Biology*, vol. 34, no. 2, pp. 119–124, 2010.
- [40] Y. Cheng, F. Yan, F. Huang et al., “Bioremediation of Cr (VI) and immobilization as Cr (III) by *Ochrobactrum anthropi*,” *Environmental Science and Technology*, vol. 44, no. 16, pp. 6357–6363, 2010.
- [41] Z. Zhang, S. S. Leonard, S. Wang, V. Vallyathan, V. Castranova, and X. Shi, “CR (VI) induces cell growth arrest through hydrogen peroxide-mediated reactions,” *Molecular and Cellular Biochemistry*, vol. 222, no. 1/2, pp. 77–83, 2001.
- [42] E. Kokkinos and A. Zouboulis, “A step by step investigation of Cr (III) recovery from tannery waste,” *Multidisciplinary Digital Publishing Institute Proceedings*, vol. 48, no. 1, 2019.
- [43] D. R. Lide, *CRC Handbook of Chemistry and Physics*, CRC Press, Boca Raton, FL, USA, 2004.
- [44] E. Kokkinos, V. Proskynitopoulou, and A. Zouboulis, “Chromium and energy recovery from tannery wastewater treatment waste: investigation of major mechanisms in the framework of circular economy,” *Journal of Environmental Chemical Engineering*, vol. 7, no. 5, Article ID 103307, 2019.
- [45] S. Shen, R. D. Tyagi, and J.-F. Blais, “Extraction of Cr (III) and other metals from tannery sludge by mineral acids,” *Environmental Technology*, vol. 22, no. 9, pp. 1007–1014, 2001.
- [46] E. Marguí, J. Tapias, A. Casas, M. Hidalgo, and I. Queralt, “Analysis of inlet and outlet industrial wastewater effluents by means of benchtop total reflection X-ray fluorescence spectrometry,” *Chemosphere*, vol. 80, no. 3, pp. 263–270, 2010.
- [47] O. Kayode, E. Ogunyemi, A. Odukoya, and A. Aizebeokhai, “Assessment of chromium and nickel in agricultural soil: implications for sustainable agriculture,” in *IOP Conference Series: Earth and Environmental Science*, IOP Publishing, Bristol, United Kingdom, Article ID 12014, 2022.