



Efficient Removal of Chromium and Lead from Tanneries Effluent of Korangi Industrial Area Karachi Using Rotating Disk Mesh as Anode Electrode Electrocoagulation

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Abstract

The aim of this study was to examine the best electrode design for the electrocoagulation process with the best removal performance, reduced passivation on the electrode surface, and lower energy consumption requirements for removing Chromium (Cr) and Lead (Pb) from leather tannery effluent. Three different electrodes were compared: non-rotating disk electrode (NRDE), rotating disk electrode (RDE) and rotating disk mesh electrode (RDME). All electrodes were used to observe a reduction in passivation on the electrode surface and its effects on the removal performance of Cr and Pb. The material used for the electrodes was iron. The maximum removal efficiency obtained was Cr = 87.9% and Pb = 97.5% under the following operating conditions: pH = 7, treatment time = 90 min, current density = 6.57 mA/cm², and RPM = 80. The results show that the electrical energy requirement for treating chromium and lead using RDME was 4.5 kWh/m³, which was found to be lower than the energy requirement observed in various other studies for treating tannery effluent. According to the results, RDME shows the highest removal performance with lower specific energy consumption compared to NRDE and RDE. RDME can be efficiently employed at a larger scale for treating leather tannery effluent.

Keywords: Rotating disk mesh electrode, Rotating disk soled electrode, Nonrotating disk electrode, Passivation and specific energy consumption.

Introduction

The leather industry is considered one of the key exporting industries in Pakistan second only to the textile sector. This sector contributes more than 20% to GDP and holds significant potential for attracting foreign exchange through improvements in quality and diversification of leather products [1]. Leather manufacturing is a substantial manufacturing process in the Pakistan, with 700 tanneries located in major three cities Sialkot, Karachi and Lahore [2]. Many small-scale leather industries in Pakistan lack proper wastewater remediation facilities leading them

to discharge effluent into land and sewage lines [3]. Pb and Cr are two common elements found in leather tannery effluent, originating from various chemicals used in the processing of hides into leather products. Tannery effluent containing chromium and lead has a significant negative impact on the environment, including drinking water contamination, air pollution, and land pollution. The pollution generated by the tanneries has contaminated underground water at various locations in the Korangi industrial area of Karachi and the concentration of Cr

and Pb has been found to exceed the safe standard limits set by the Environmental Protection Agency Pakistan (EPA) and the World Health Organization (WHO) [4]. Cr and Pb contribute to environmental contamination and have adverse effects on human health. Many diseases, including dysentery, lung infections, typhoid, skin ulceration, lung cancer, and respiratory disorders, are frequently observed in local residents and industry workers [4, 5]. Hence, the removal of these pollutants is a requirement for leather tanneries to meet the standards set by international environmental regulating organizations and to compete in the international leather goods market. Many researchers have applied various treatment technologies for the removal of heavy metals, such as adsorption [6], ion exchange [7], membrane separation [8], chemical precipitation [7] and electrodialysis [9]. The chemical precipitation method provides good metal removal efficiency; however, the main limitation of this method is the large amount of sludge generation [10]. In the adsorption process, the preparation of adsorbent is often a tedious task and adsorbent regeneration is also a limiting factor in its application [11]. During the ion exchange process, a huge quantity of chemicals is consumed, while the membrane separation method works properly only when a limited amount of metal pollutants is present in water and wastewater [12]. Overall, the treatment methods discussed above are costly, less environmentally safe, and less efficient compared to the electrocoagulation technique. Hence, an advanced separation technique is required to address these problems [11-13]. Electrocoagulation offers several advantages, including simplicity, dependability, cost-effectiveness, low sludge volume, ease of maintenance, and environmental safety, making it one of the most effective technologies [14]. Researchers have shown significant interest in electrocoagulation for

treating wastewater from leather tanneries [15]. However, passivation and the formation of metal oxide layers on electrode surfaces are among the limitations of the electrocoagulation process. The primary objective of this study was to minimize passivation and the formation of metal oxide layers on the electrode surface, enhance the removal efficiency of Cr and Pb, reducing specific energy consumption and the generation of less hazardous sludge by implementing a novel anode electrode design for the electrocoagulation process, suitable for large-scale applications.

Materials and Methods

Characterization and Collection of Sample

The effluent sample was obtained from a combined channel for the drainage of effluent from various tanneries in the Korangi Industrial Area, Karachi, Pakistan. It was placed in a polyethylene bottle, preserved with the addition of two to three drops of Nitric acid (Reagent grade 98% pure, Merck) and kept refrigerated at 4°C. The sample was analyzed for chromium and lead before and after electrocoagulation using ICP-MS (Shimadzu ICPMS-2030). pH and electrical conductivity (EC) were measured by a multi-meter (PHS-3BW). Biochemical oxygen demand (BOD), Total dissolved solids (TDS), and Total suspended solids (TSS) were measured by the dilution method or the standard methods, 2540D and 2540C, respectively as given in the Annual Book of Standard Methods for Examination of Water and Wastewater [17]. Chemical oxygen demand (COD) was determined using the closed reflux method (D1252-95, ASTM 1995) [16, 17]. The results of the characterization are shown in Table 2. The surface of the electrode was examined using SEM and EDX by (JEOL-6490LV).

Experimental Assembly of Rotating Disk Mesh Electrode Electrocoagulation Reactor

The cylindrical electrocoagulation cell has a 6.5 cm diameter and a 22.5 cm height. It was made of acrylic material. Table 1 provides precise measurements and it can hold 1 litre of effluent. The electrodes used were made of iron material and the initial pH of the tannery wastewater was set by adding 2% Sulfuric acid (H_2SO_4 reagent grade 98% pure, Merck) solution and 5% Sodium hydroxide solution (NaOH pellets, Merck). The electrode plates were cleaned with diluted 2% Hydrochloric acid (HCl reagent grade = 37 %, Merck) solution and de-ionized water following the completion of each experiment. They were oven-dried at 105 °C. Four plates were utilized in each batch of the electrolytic

reactor to serve as the anode and cathode for NRDE. Four disc electrodes were used in the design of RDE and RDME as anode and four circular rings as cathode. A DC supply (TITAN TN305D) with a range of 0–30 volts and 0–5 amps was employed. In order to observe the effects of the electrodes, 10 mL of the sample was taken from the electrocoagulation cell after 15 min and filtered using Whatmann filter paper no. 42 to separate the effluent from the sludge. The concentration of the filtrate used for the removal of lead and chromium was discovered using ICP-MS. The leftover filtrate residue was dried in an oven at 105 °C to remove the water. Table 1 provides comprehensive dimensions of the electrocoagulation experimental setup and Fig. 1 shows the electrocoagulation cell experimental setup.

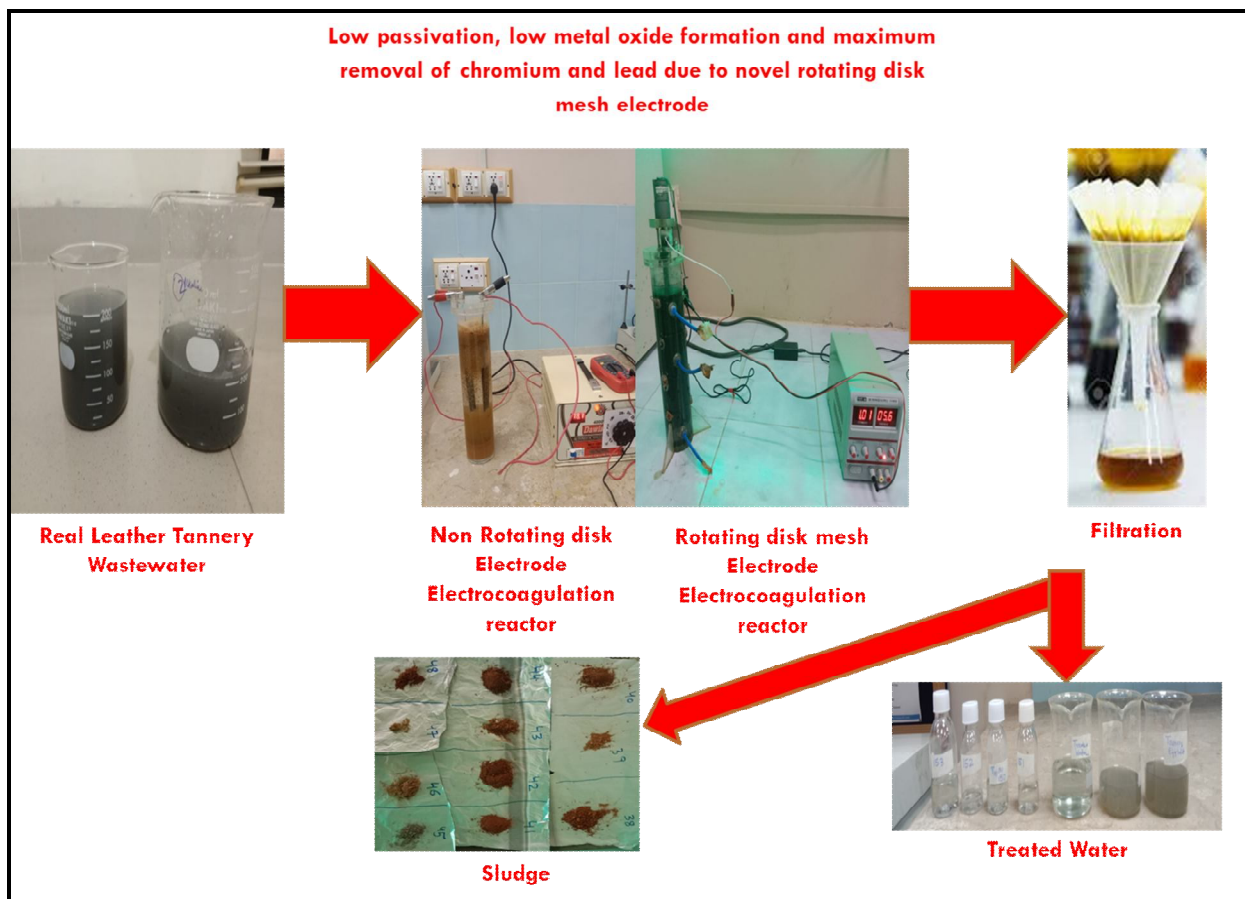


Figure 1. Process flow diagram of experimental setup for treatment of leather tannery effluent

Specific energy consumption for elimination of Cr and Pb was determined by Eq. 1 and Eq.2, respectively.

$$\text{Removal efficiency (\%)} = \frac{C_o - C_t}{C_o} \times 100 \quad (1)$$

$$\text{Specific energy consumption} \left(\frac{\text{kWh}}{\text{kg.m}^3} \right) = \frac{VIt}{(C_o - C_t)v} \quad (2)$$

Where C_o (mg/L) represents concentration of pollutant before electrocoagulation and C_t (mg/L) is concentration of pollutant after electrocoagulation, V (volt) is voltage and I (Amp) is current, v (m^3) is volume of wastewater treated and t (h) is treatment time.

$$\text{Energy Consumption} \left(\frac{\text{kWh}}{\text{m}^3} = \frac{VIt}{v} \right) \quad (3)$$

Table 1. Geometrical dimension of electrocoagulation reactor.

Electrodes	
Material (anode and cathode)	Iron
Shape	Circular (rotating disk and mesh electrodes) and rectangular (for non-rotating)
Diameter of disk anode electrode	3.2 cm
Size of nonrotating electrode	9.5 cm x 0.6 cm x 0.4 cm
Plate arrangement	Parallel
Effective one electrode Surface area rectangular and disk	19 cm^2
Thickness of anode electrode	3 mm
Diameter of ring cathode	6.4 cm
Thickness of ring cathode	1mm
Number of anode electrodes	4
Number of cathode electrode	4
Total Effective surface area	76 cm^2
Reactor characteristics	
Material	Acrylic
Shape	Cylindrical
Reactor Type	Batch Mode
Dimension	22.5 cm height and 6.5 cm diameter
Volume	1 L
Electrode gap	5 cm
Power supply	DC
Voltage	0-30 volt
Current	0-5 Amp

Results and Discussion

Surface analysis of different electrodes

SEM results revealed that all three electrodes RDE, RDME, and NRDE have a layer of sludge and oxide fouling film on their

surfaces. Fig. 2(a) shows SEM image of electrode before experiment. Fig. 2(b) and 2(c) shows SEM images of NRDE and RDE after experiment having a greater metal oxide layer on surface of electrode compared with RDME Fig. 2(d). In Fig. 3(a,b,c) EDX also shows the same observation as shown by SEM images. Fig. 3(a) depicts the results of an electrocoagulation experiment using a RDME, showing that 11.45% of the elemental weight was oxygen, 0.41% was Cr, 17.19% was Pb, sodium (Na) was 2.6 % and Iron (Fe) is 67.91%. In contrast to RDME designs, RDE and NRDE designs exhibit higher weight percentages of oxygen, chromium and lead after the electrocoagulation process, as shown in Fig. 3(b) and 3(c). According to EDX studies, RDME designs for electrocoagulation reactors have less metal oxide layer on their surfaces than RDE and NRDE designs. At the same time in Fig. 3(d) the sludge formed after electrocoagulation shows the removal of Cr, Pb, Fe, Si, Ca, S, Cl, and Al.

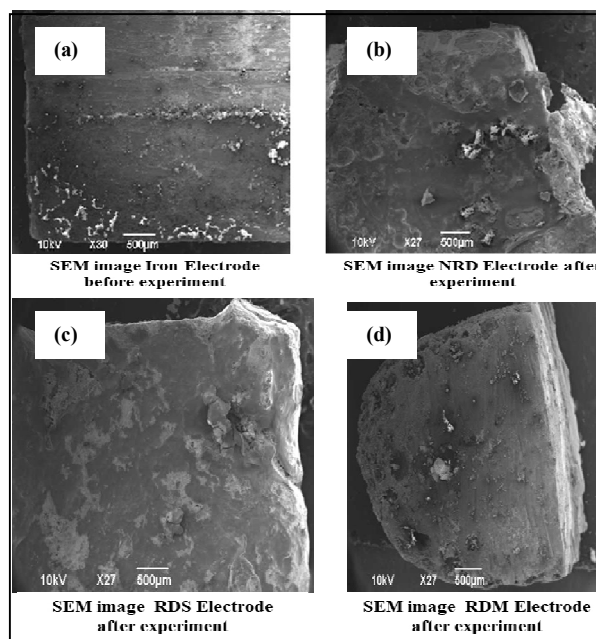


Figure 2. SEM images of (a) disk electrode before experiment (b) non-rotating disk electrode (c) rotating disk electrode (d) rotating disk mesh electrode

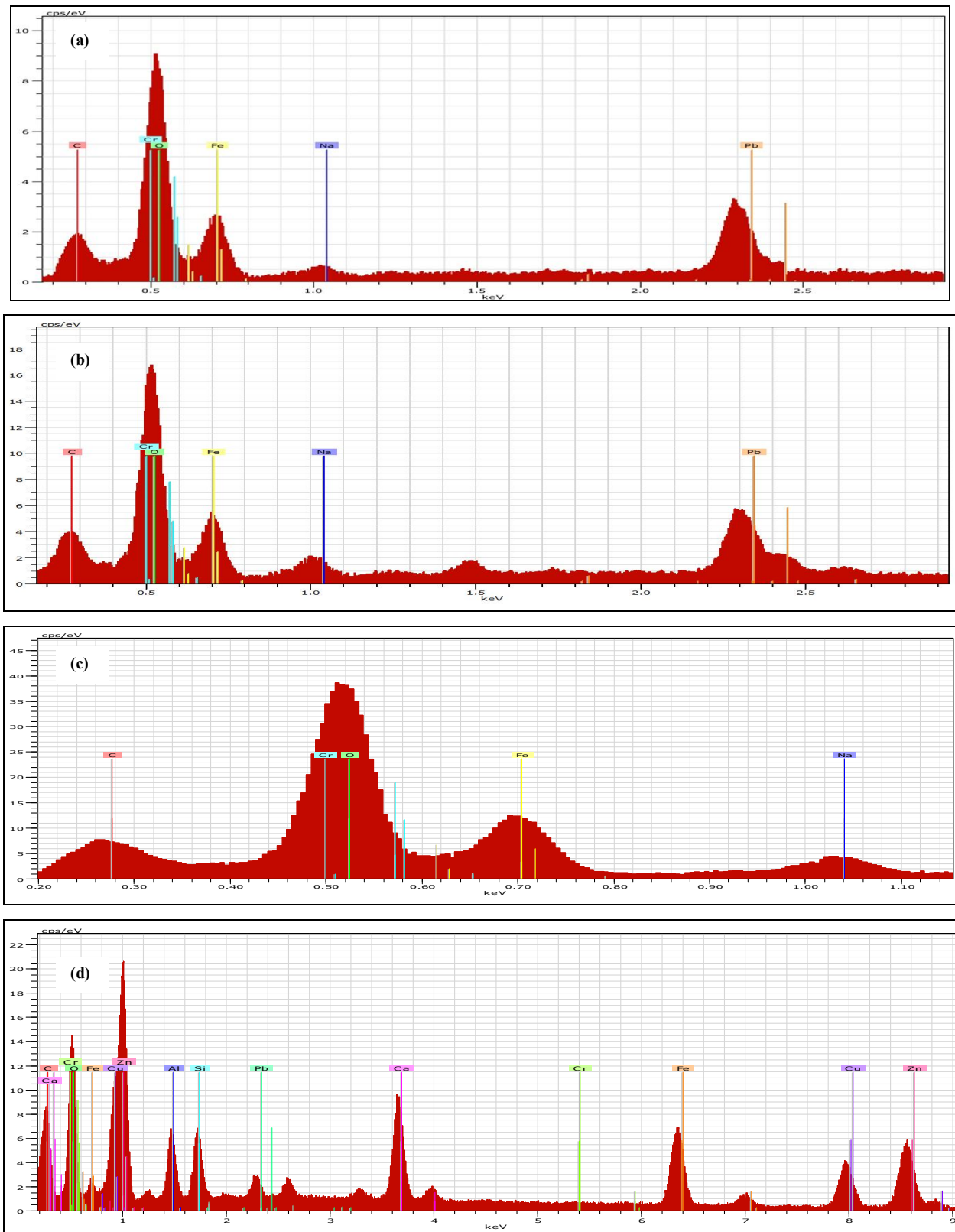


Figure 3. EDX analysis of (a) Rotating disk Mesh Iron Electrode (b) Rotating disk Iron Electrode (c) Non- Rotating Iron disk Electrode (Operating condition pH=7, Current density=6.57 milliamp/cm², RPM=80, Real Tannery Effluent) (d) sludge formed by rotating disk mesh electrode after treatment

Comparison of removal performance and specific energy consumption of rotating disk mesh electrode with conventional electrodes

The performance of NRDE and RDE was compared with RDME electrocoagulation reactor (operating condition of pH=7, current density=6.57 milliamp/cm², RPM=80 and material of electrode iron). The initial concentration of chromium and lead were 110 ppm and 20 ppm and detailed characterization of leather tannery effluent is given in Table. 2. The NRDE reactor decreases concentration of Cr and Pb from 110 ppm to 83.1 ppm and 20 ppm to 3.1 ppm, respectively, from leather tannery effluent at above mentioned operating conditions. The RDE electrocoagulation reactor decreased the concentration of Pb Cr from 20 ppm to 0.6 ppm and Cr from 110 ppm to 31.3 ppm. The RDME decreased Cr concentration from 110 ppm to 83.1 ppm and Pb from 20 ppm to 3.1 ppm. It had been determined that removal efficiency of Cr for NRDE was 24.45 %, RDE 71.54% and RDME 87.90% during electrocoagulation process. The removal efficiency of Pb for NRDE was 84.5%, RDE 97% and RDME 97.5% as shown in Fig. 4.

Table 2. Characterization of leather tannery effluent.

S. No.	Parameter	Quantity (ppm)	SEQs Limit
01	TDS	8450 ppm	3500 ppm
02	TSS	1370 ppm	400 ppm
03	pH	6.9	6.5-8.5
04	COD	941 ppm	400 ppm
05	Chromium	110 ppm	1 ppm
07	Lead	20 ppm	0.5 ppm
08	Sulfate	220.1 ppm	1000 ppm

RDME exhibits a greater removal efficiency compared to RDE because RDME provides a larger surface area of contact with pollutants in the effluent. The efficiency of the NRDE electrocoagulation reactor is lower

when compared to the RDE and RDME electrocoagulation reactor. This is because the rotation of the electrode reduces the passivation film, removes the metal oxide layer and sludge from the surface of the electrode, induces turbulence in the effluent, which exerts a force on the layer on the surface of the electrode, and facilitates proper diffusion of metal ions in the tannery effluent. According to Chen , periodic cleaning of electrodes is necessary to increase the efficiency of the electrocoagulation process [18].

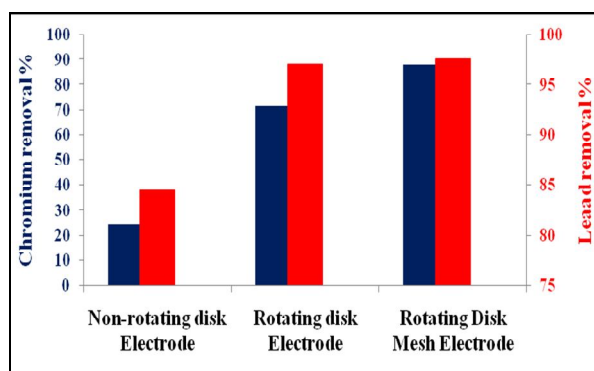


Figure 4. Performance of different electrocoagulation reactor

Nippatla et al. also observed similar behavior when treating textile wastewater using a rotating disk electrocoagulation reactor [19]. The specific energy consumption requirement for NRDE was 562.5 kwh/kg Cr and 569.6 kwh/Kg Pb, RDE was 120.6 kwh/kg Cr and 466.32 kwh/kg Pb and RDME was 98.14 kwh/Kg Cr and 463.9 kwh/Kg Pb as shown in Fig. 5. It was deduced from results that RDME is energy efficient electrode for removing of Cr and Pb because of high removal efficiency in less time due to less metal oxide and sludge layer on surface of electrode and maximum reaction of metal ions released from electrode with Cr and Pb. Similar specific energy consumption behavior was observed by Nippatla et al for the treatment of textile industry waste [19].

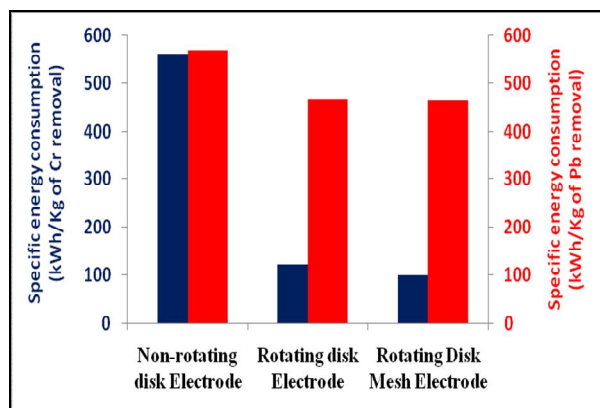


Figure 5. Specific energy consumption of various electrodes

Effect of treatment time on removal performance of chromium and lead by various electrodes

It is evident from Fig. 6 that RDME has greater performance than RDE and NRDE for removing Cr and Pb. Fig. 6 also illustrates that RDME has a greater removal efficiency for Pb compared to Cr due to its lower solubility, lower valence state and larger ionic radius. The reduced solubility of Pb ions in wastewater is responsible for the formation of larger flocs. Additionally, its lower valence state and larger ionic radius facilitate the development of more polarizable complexes with iron ions in aqueous form, which are released by the iron electrode during electrocoagulation. Pb removal is achieved in just 15 min, while Cr removal requires 90 min to reach equilibrium. Since Pb forms an insoluble iron hydroxyl-complex, it can be removed more rapidly from the solution compared to Cr during the electrocoagulation process. The iron electrode exhibits a stronger affinity for removing Pb in a shorter period than Cr, which exists in +3 and +6 oxidation states and necessitates a more negatively charged metal hydroxide complex for destabilization from wastewater. Given that electrocoagulation primarily depends on the response of metals discharged in the form of ions, lead high atomic radius and +2 charge simultaneously contribute to its quicker

removal compared to Cr. Additionally, it was found that the effectiveness of Cr and Pb removal was higher in the first 15 min, decreased for Cr removal and Pb removal because in accordance with the Faraday law iron dissolution in wastewater increases over time [20] and because initially the electrode has no external material on its surface, but later on, a layer forms on the electrode's surface, which reduces the electrode material's reaction with Cr and Pb [21].

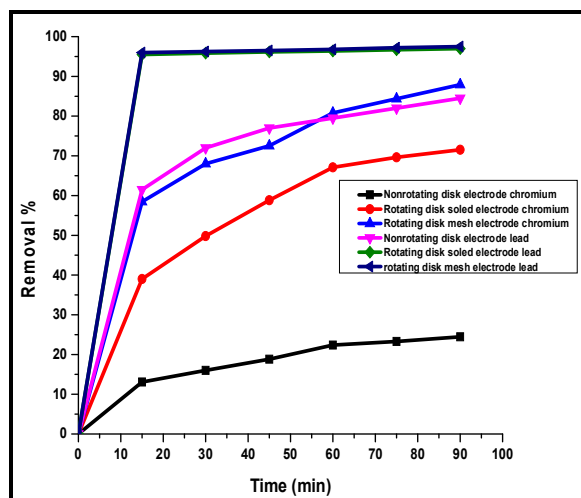


Figure 6. Effect of treatment time on removal of chromium and lead from leather tannery effluent

Comparison of previous studies with current study for treatment of leather tannery effluent

Table 3 shows the related studies for removal of Cr and Pb from leather tannery wastewater with removal performance and energy consumption requirements. It was obtained from the results that RDME used in this study has best removal performance of Cr=87.90% and Pb=97.5% simultaneously within 90 min. The energy requirement in this process was less than the energy used by other researchers for the treatment of leather tannery effluent for Cr and Pb removal and it was 4.5 kWh/m³.

Table 3. Comparison of removal performance Cr and Pb with previous studies.

Initial Conc. of pollutant	Operating conditions	Pollutant removal	Energy consumption (kWh/m ³)	Ref
Cr=50 mg/L, Pb=20 mg/L, pH=6.5, Conductivity=2.4 ms/cm	Aluminum, Volume of wastewater handled 1.4 dm ³ , DC supply 0-30 volts, 0-5 amp, RPM=180, treatment time=90 min and surface area=272 cm ²	Cr=55.2%, of Pb=58.3%	24.96	[13]
Cr=30 mg/L	Aluminum, pH 3, current density 40 mA/cm ² , Treatment time =30 minutes, capacity of reactor 0.7 litre, surface area 60 cm ²	Cr=84.2 %	30	[22]
Cr=7000 mg/L	Aluminum plate electrode, Current density 400 A/m ² , 6 h, surface area 210 cm ²	Cr=87%	35	[23]
Cr=120 ppm, Pb=20 ppm	Iron rotating disk mesh electrode, surface area 76 cm ² , treatment time=90 min, current density=6.57 mA/cm ² , initial pH=7, RPM=80	Cr=84.5%, Pb=97.5%	4.5	This study

Conclusion

The RDME exhibits less passivation and metal oxide layer formation on the surface compared to the RDE and NRDE. Simultaneously, it demonstrates higher removal efficiency for chromium and lead from leather tannery effluent when used as an anode for electrocoagulation. This superior performance was observed under operating conditions of pH=7, current density=6.57 mA/cm², RPM=80, and treatment time=90 minutes, resulting in Cr removal of 87.9% and Pb removal of 97.5%. SEM and EDX results further confirm the reduced presence of metal oxide layers and passivation on the surface of the RDME, as compared to the RDE and NRDE. These findings highlight the

superiority of RDME over conventional designs for large-scale electrocoagulation of leather tannery effluent, offering benefits such as reduced surface passivation, lower energy consumption and environmental friendliness. This study paves the way for the widespread adoption of RDME as a replacement for traditional electrodes, thereby enhancing the efficiency of Pb and Cr removal while conserving energy.

Conflict of Interest

The authors declare that there is no conflict of interest.

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