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Effect of Ultrasound and Electrode Material on Electrochemical Treatment of Industrial Wastewater

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Abstract: *The effect of ultrasound (US) and electrode material on electrochemical treatment of industrial wastewater was studied. Samples were taken from three industries i.e. battery, ghee and tannery. Treatment efficiency was monitored by comparing the results of electrochemical and sonoelectrochemical processes in terms of metals and chemical oxygen demand COD removal. Experiments were performed in ultrasonic bath. In sonoelectrochemical process concentration of Pb decreased from 11.5 to 0.6 ppm at 80 kHz form battery industry. Similarly about 95 % removal of Cr (III) was observed from tannery wastewater using lead cathode. Titanium anode was found best counter electrode in metals removing. High COD removal was obtained by using steel anode at 80 kHz. Use of ultrasound is very effective in removing heavy metals and organic pollutants from industrial wastewater.*

Keywords: Ultrasound, electrodes, electrochemical treatment, wastewater.

1. INTRODUCTION

Battery, leather and ghee (clarified butter) manufacturing industries, are the largest foreign exchange generators in Pakistan. The extremely high level of consumption of fresh water by these industries has resulted in generation of large volume of wastewater. Battery industries discharge mostly inorganic pollutants containing heavy metals like lead. Concentration of lead varies with the industrial operations and depends upon the amount of water discharge. In Pakistan the tanning industry is concentrated in Karachi (Korangi), Kasur, Lahore, Multan and Sialkot. More than 200 hundred tanneries are located in Kasur. As a result of tanning activities about 9,000 m^3 of heavily polluted wastewater is discharged daily into water bodies. Their effluents are characterized by high COD, BOD and Cr^{+3} concentrations. Tanneries utilize large quantity of water, roughly between 15 and 20 m^3 per tonnes of raw skin [1]. It is also observed that tannery wastewaters have COD and SS contents approximately five times higher than municipal wastewaters and high salt concentrations similar to brackish waters. Wastewater generated from ghee industry contains mostly organic compound like fats, oil and grease.

Various physical, chemical and biological techniques are applied to treat different types of industrial effluents. Each process has its own constraints in terms of cost, feasibility, practicability, reliability, stability, environmental impact, sludge production, operational difficulty, pretreatment requirements, extent of organic matter removal and potential toxic byproducts generation. Tannery wastewater treatment by biological processes may be difficult because of the presence of a broad spectrum of biocides used in the leather industry to prevent fungal attack [2].

The use of an electrochemical process for treatment of wastewater can be considered a relatively simple and clean method. Electrochemical treatment of wastes can results in partial or complete decomposition of the pollutants. Complete mineralization of or-

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ganic material refers to their oxidation to carbon dioxide. Organic pollutants during electrochemical oxidation treatment are either directly oxidized at the anode or indirectly oxidized by the anodically formed oxidants such as Cl_2 or hypochlorite, ozone, hydroxyl radicals and H_2O_2 [3-5]. For the direct oxidation, anodes of high oxidation potential are required. The pollutants are first adsorbed on the anode surface and then destroyed by the anodic electron-transfer reaction.

The wider uses of ultrasound (US) in environmental remediation have been reviewed Mason [6]**.** The combination of ultrasound and electrochemistry is termed `sonoelectrochemistry' [7, 8]. Generation of sonochemical reaction conditions in wastewater treatment processes provides contaminant annihilation either directly via activating thermal decomposition reactions, or indirectly by the production and/or enhancement of hydroxyl radical yield in advanced oxidation processes [9].

The aim of this research was to study for the first time the treatment of battery, leather, and ghee wastewater using electrochemical oxidation coupled with ultrasound to develop a treatment system for wastewater reuse.

2. EXPERIMENTAL

All experiments were performed in a rectangular Perspex vessel (14 cm × 6 cm × 14 cm) placed in a Digital Ultrasonic Bath at silent and at ultrasonic frequency of 80 kHz. The ultrasonic bath had four transducers each emitted Ultrasonic waves with 80 kHz frequency. Sonication was produced parallel to the liquid surface and electrodes were suspended vertically in the solution [10]. The electrodes were connected to a DC power supply with digital current and voltage display.

To remove Pb from battery effluent stainless steel cathode and titanium anode were used. Lead cathode was used to remove Cr^{+3} from tannery industry. Stainless steel and titanium were used as anode for the removal of COD from tannery and ghee industry.

2.1. Sampling

Samples from battery and ghee industry were taken from the discharge point. Samples from the tannery were collected after chrome recovery unit and equalization tank. Samples were preserved at 4 °C in a refrigerator before analysis.

2.2. Analysis

TDS, conductivity and pH were determined on site. Conductivity and TDS were determined by a conductivity meter (HANNA of model HI 9835) and pH was determined by a pH meter (HANNA of model HI 99003). Atomic Absorption Spectrophotometer (PerkinElmer) was used for the determination of metal concentrations. COD of the samples was determining by the Closed Reflux Colorimetric Method, according to [11].

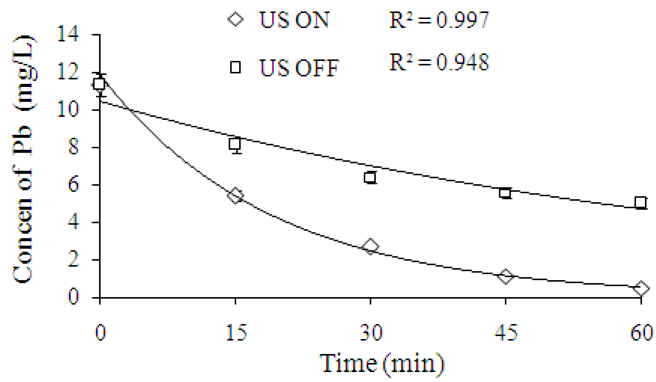

Figure 1. Concentration of lead from battery industry effluent during electrolysis (US OFF) and sonoelectrolysis (US ON) process

3. RESULTS AND DISCUSSION

3.1. Characterization of wastewater

Before treatment, each industrial effluent was characterized. Table 1 shows the concentration of different parameters for Battery, Ghee and Tannery industry wastewaters. Concentration of Ni was near to National Environmental Quality Standards (NEQS) level of Pakistan and value of COD was 300 ppm in the effluent due to the presence of fats. Sirajuddin et al. [12] found 200 ppm of nickel in the solid waste of ghee industry. As sample from tannery was collected after chromium recovery plant and equalization tank, so the value of Cr (III) was low as compared to effluent discharge from tanneries. Similar value of chromium was found by Apaydin et al [13]. Sirajuddin et al. [14] studied the high Cr^{+3} values of 2550 mg/ L average contents in a 5-times analyzed sample of untreated effluent discharge from tannery in Peshawar. Battery industries discharged mostly metallic ions containing heavy metals like Pb and Cu. Concentration of Pb was found 10-12 ppm and Cu was 0.01 ppm.

3.2. Heavy metals removal

3.2.1. Effect of Ultrasound (US) and Electrodes materials

Table 1. Characteristics of industrial wastewater and NEQS limits

	Concentration (mg/L)					
	Cr^{3+}	Cu	Pb	Ni	Cl^-	COD
NEQS* limits	1	1	0.5	1	1000	150
Battery industry	-	0.01	10-12	-	-	-
Ghee industry	-	-	-	2.5-3.0	-	300
Tannery	25	-	-	-	5820	1500

*NEQS: National Environmental Quality Standards of Pakistan

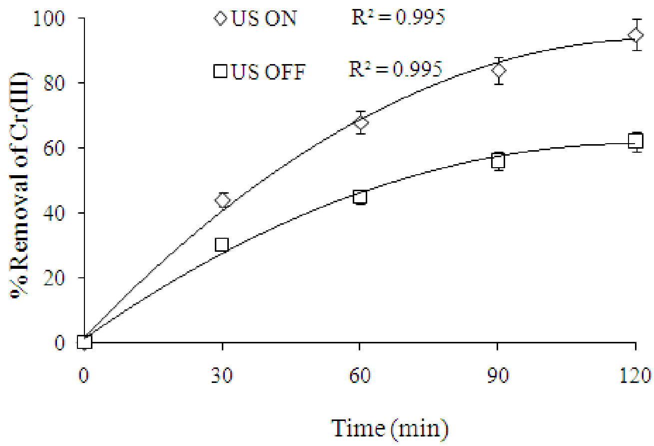

Figure 2. Removal of Cr (III) during electrolysis (US OFF) and sonoelectrolysis (US ON)

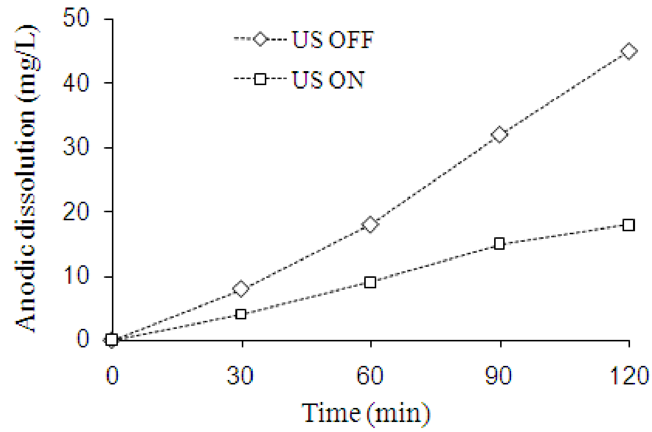

Figure 3. Dissolution of steel anode during electrolysis and sonoelectrolysis

Samples from battery industry were treated at their original pH 6.0 by electrochemical process and by using ultrasound at a frequency of 80 kHz. At voltage of 10 volts flow of current varies between the electrodes 0.3 to 0.5 A. Fig. 1. Shows the decrease in concentration of lead during electrolysis (US OFF) and sonoelectrolysis (US ON) from battery industry effluent. It is clear from Fig 1 that, from initials Pb concentration of 11.5 ppm electrochemical process was able to reduce the concentration to 5 ppm in 1 hour, where as ultrasound with electrochemical process reduce to further to 0.6 ppm in 1hr. Similar Cr^{+3} removal was 95 % at 80 kHz of US frequency and 62 % at US OFF shown in Fig 2. In simple electrochemical process the rate of mass transport strongly decreases at extremely low concentrations. US waves generated within the solution affect the mass transport process towards the electrode from bulk solution and reduce the diffusion layer thickness [10, 15, and 16].

Reaction for removal of metals at Cathodes

$$Pb^{2+} + 2e^{-} \rightarrow Pb(s) \quad (1)$$

$$Cr^{3+} + 3e^{-} \rightarrow Cr(s) \quad (2)$$

Lead cathodes were used to remove Cr (III) instead of steel cathode because Pb shows more reactivity for Cr than steel. In case of metal removal cathode material also affects the process. Anode material plays an important role in deposition of metals; insoluble anodes like titanium result in smooth flow of current within the bulk solution. As the concentration of Ni was near NEQS level, therefore more attention should be paid to reducing COD values.

3.2.2 Effect of US on anodic dissolution

The electrode material plays a very important role in the electrodeposition of metal or compounds. In this study two types of anodes were used i-e steel and titanium anodes. Anodic dissolution of steel also affects the removal of heavy metals and adds Fe (III) contamination to water. It was also observed that during electrochemical reaction Fe (III) was released into the water from the steel anode. This Fe (III) coagulates the suspended and dissolves solids and settled down as sludge. Comparison between ultrasound and silent condition on steel dissolution is shown in Fig 3. Less anodic

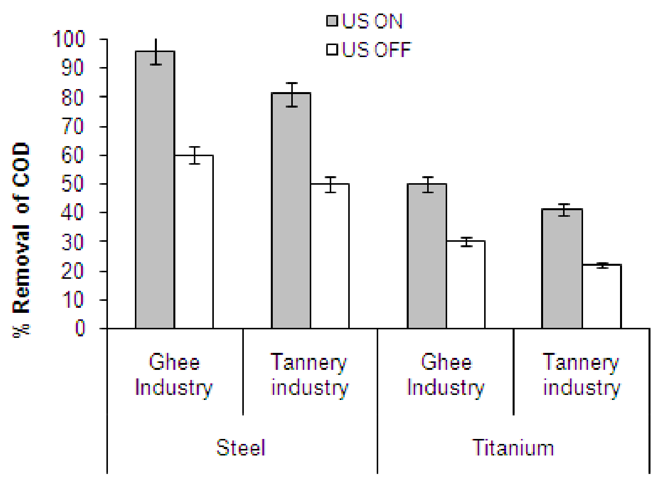

Figure 4. Percentage removal of chemical oxygen demand using steel and titanium anode

dissolution was found with steel when ultrasound was applied with frequency of 80 kHz on same reaction conditions. Ti anode was found very effective in combination with steel cathode, for the removal of metals because no dissolution of titanium anode was observed. Anodic dissolution also affects the conductivity of final effluent. Low rate of TDS and conductivity was observed during the electrochemical process. This has two reasons: (i) when current flows through the solution, the surface of colloides or suspended particles becomes charged [10] and (ii) many charged species are generated at the surface of electrodes.

3.3. COD removal

For chemical oxygen demand (COD) removal, samples of tannery industry were treated for 60 min by electrochemical process with ultrasonic frequency of 80 kHz. Samples were treated at their original pH values. High percentage removals of COD were found using steel anode in the presence of ultrasound for both ghee (96 %) and tanneries (81%) industries.

Besides ultrasound, other parameters also affect the removal of COD e.g. anode material. Anode with higher oxidation potential may affect the decrease in COD value. Fig. 4 shows the comparison between the percentage removal of COD at steel and titanium anode. Steel anode showed higher efficiency in both electrolysis and sonoelectrolysis because of its higher oxidation potential than titanium. The results from this study are in agreement with the work of Lidia et al [17] who showed that the rate of pollutant removal was significantly influenced by the type of anode material and electrochemical parameters.

4. CONCLUSION

Use of ultrasonic waves with electrochemical process provides a good option for the removal of metallic ions from industrial wastewater and can be beneficial in terms of a reduction in cost of chemicals used for the precipitation. Stainless steel anode also increases the degradation rate of organic pollutants compared to titanium anode.

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