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Treatment of Tanneries Waste Water by Ultrasound Assisted Electrolysis Process

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Summary: The leather industry is a major producer of wastewater and solid waste containing potential water and soil contaminants. Considering the large amount and variety of chemical agents used in skin processing, the wastewaters generated by tanneries are very complex. Therefore, the development of treatment methods for these effluents is extremely necessary. In this work the electrochemical treatment of a tannery wastewater by ultrasound assisted electrochemical process, using stainless steel and lead cathode and titanium anodes was studied. Effect of ultrasound irradiation at various ultrasonic intensities 0, 40, 60 and 80% on electrochemical removal of chromium was investigated. Experiments were conducted at two pH conditions of pH 3 and 9. Significant removal of chromium was found at pH 3 and it was also noticed that by increasing ultrasonic intensities, percentage removal of chromium and sulfate also increases. The optimum removal of chromium and sulfate ions was observed at 80% ultrasonic intensity. The technique of electrolysis assisted with ultrasonic waves can be further improved and can be the future waste water treatment process for industries.

Keywords: Ultrasound assisted electrochemical process, chromium removal, sono-electrochemical process.

Introduction

The uncontrolled release of tannery effluents in natural water bodies increases the environmental pollution and the health risks. Tannery Wastewater treatment represents a serious environmental and technological problem. In fact, after conventional treatment (i.e., chromium precipitation–primary sedimentation–biological oxidation–secondary sedimentation), effluents still do not meet the required limits [1-6]. Considering the large amount and variety of chemical agents used in skin processing, the wastewaters generated by tanneries are very complex. Therefore, the development of treatment methods for these effluents is extremely necessary. Conventional biological treatment methods are often inadequate for complet removal of pollutants in tannery wastewater [7-11]. Furthermore, biological treatment of wastewaters containing persistent and toxic compounds requires a long retention time in order to remove the pollutants.

Due to the limitations of the primary and biological wastewater treatment processes, alternative processes have been pursued. Amongst them, electrochemical processes have been proposed and it has received increasing attention in the last years. The kinetics of the electrochemical process are about 100-fold faster than biological oxidation process [10-13]. Electrochemical treatment seems to be a good prospect since the discharge flow from most tannery plants is not large; hence it is worth exploring the application of this method as an alternative to the conventional biological processes. Compared to traditional methods, electrochemical processes offer the treatment of liquid and solid waste by direct and indirect organic compound oxidation, metal reduction and electrodeposition, electro-coagulation and electro-flotation processes. Since current and electric potential are parameters that are easily acquired and controlled, the treatment process can also be automated easily. Moreover, the electrochemical processes are mediated by electron exchange with the electrode surface, dismissing the need for the addition of other chemical agents.

The electrochemical processes have limitations of metal removal if the concentrations of metals are reduced to certain limit. The electrochemical double layer is widened and the

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barrier between the bulk liquid and electrode surface is created due to which the metal ions require more energy in the form of agitation, stirring or some other mechanical methods to break the electrical double layer [2]. In order to facilitate the ions to cross this barrier at low energy consumption, ultrasound is coupled with electrochemical process in the current research.

The electrochemical deposition in the presence of ultrasound is a unique research area and work has been done to recover many metals like copper, lead, nickel from model solutions [10-15]. The intensity of ultrasound can induce a wide range of chemical and physical consequences in a chemical reaction. The high-intensity ultrasound has the ability to enhance mass transport, emulsification, bulk thermal heating, and a variety of effects on solids.

During sonication, liquids under irradiation produce cavitational, bubbles which collapse in nanoseconds and produces intense local heating & high pressures. The temperature inside the collapsing bubbles sometimes reaches to 5000°C, pressures of about 1000 atm, and heating and cooling rates above 1010 K/s [16]. Due to these characteristics, the current research was undertaken in order to reduce sulfates, TDS and chromium by coupling electrochemical and sonication processes. The main objective was to derive the metal ions on the collapsing cavitations which take them from bulk of the solution to the surface of electrodes and thus enhance electrochemical deposition and increase the removal percentage.

Results and Discussions

Effect of pH and Ultrasonic Irradiation on Chromium Removal

The effect of ultrasonic irradiation for percentage removal of chromium at lead cathodes during electrolysis process is shown in Fig. 1 and 2. The results show that by increasing the ultrasonic intensities, removal rate of chromium is also increased. Maximum removal of 76.44% was found at frequency of 40 kHz, 60% ultrasonic intensity and at pH 3 after two hours of process. It was also observed that during first hour the removal rate was more as compared to second hour at different ultrasonic intensities. This enhancement of chromium removal is due to increase in mass transport and creation of turbulences and acoustic streaming in the bulk liquid which assists to transport ions towards the electrode surfaces by breaking electrochemical double layer.

Similarly the effect of pH on removal of chromium was also studied, it was observed from the Fig. 1 and 2 that the removal of chromium ion was more at pH 3 as compared to pH 9. The maximum removal of chromium was found to be 72.3 % at pH 3 which is less at pH 9 and was found to be 51.99 % at 80% ultrasonic intensity.
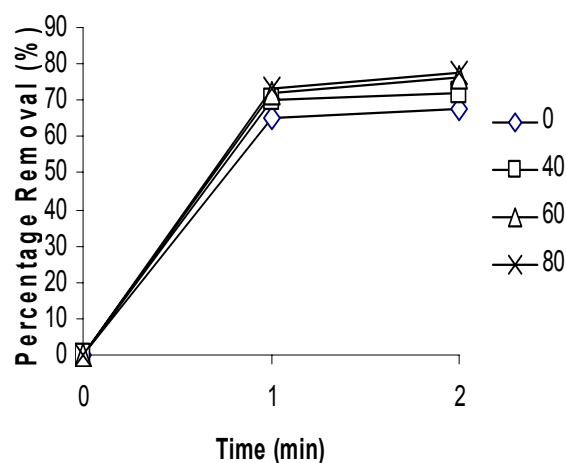

Fig. 1:   The percentage removal of Chromium at pH 3 at 40kHz and at different ultrasonic intensities during electrochemical process.
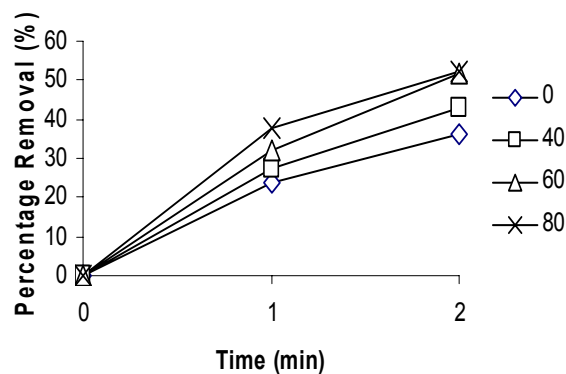

Fig. 2:   The percentage removal of Chromium at pH 9 at 40 kHz and at different ultrasonic intensities during electrochemical process.

Effect of Ultrasonic Intensities on Conductivity and TDS Removal

The effect of ultrasonic frequencies on the conductivity and TDS at pH 3 and 9 was studied (Tables-1 and 2). As conductivity of solution is directly proportional to the concentration of TDS, by increasing ultrasonic intensities, rate of chromium deposition was increased. The numbers of total dissolve solids were also decreased. At pH 3, 13.8 % decrease in conductivity and TDS was found at 80 %

ultrasonic frequency. At pH 9, 10.1 % of decrease is observed in conductivity and 9.8% decrease in TDS was found.

Table-1: The comparison of percentage decrease in conductivity and TDS at pH 3 by ultrasound assisted electrochemical process at different ultrasonic intensities at 40kHz

Experimental parameters	Ultrasonic intensities			
	0%	40%	60%	80%
Decrease in Conductivity	7	9.5	10	13.8
Decrease in TDS	6.5	9.3	11	13.8

Table-2: The comparison of percentage decrease in conductivity and TDS at pH 9 by ultrasound assisted electrochemical process at different ultrasonic intensities at 40 kHz

Experimental parameters	Ultrasonic intensities			
	0%	40%	60 %	80 %
Decrease in Conductivity	2.8	6.27	7.47	10.1
Decrease in TDS	3.3	6.3	7.01	9.8

Removal of Sulfates

Table-3 and 4 show the decrease in concentration of SO_4 at pH 3 and 9. By increasing the ultrasonic intensities, there is a decrease in concentration of SO_4 ions. The Table-3 shows that maximum decrease in sulfate ion concentration was found at 80% intensities. It was decreased from 250 ppm to 113 ppm at pH 3. Similarly, it's concentration was decreased from 250 ppm to 172 ppm at pH 9 which shows that at pH 3 the removal of sulfate ions is more as compared to pH 9 during electrochemical process.

Table-3: The comparison of percentage decrease in SO_4 ions at pH 3 by ultrasound assisted electrochemical process at 40kHz and at different ultrasonic intensities

Time (h)	Ultrasonic intensities			
	0%	40%	60%	80%
0	250	250	250	250
1	170	151	125	220
2	149.17	135	127	113

Table-4: The comparison of percentage decrease in SO_4 ions at pH 9 by ultrasound assisted electrochemical process at 40kHz and at different ultrasonic intensities

Time (h)	Ultrasonic intensities			
	0%	40%	60%	80%
0	250	250	250	250
1	220	212	198	189
2	207	196	184	172

Energy Consumption

High removal rate of chromium ions effects the energy consumption during electrolysis process.

Table-5 shows the energy consumption (EC) during sonoelectrolysis process. The results show that by increasing ultrasonic intensities, the removal rate of chromium ions increases with decrease of energy consumption. At 0% ultrasonic intensity (electrochemical process without ultrasound), total energy consumption is 0.075 kWhL^{-1} for removing 36.16% removal of chromium after two hours which is reduced to 0.034 kWhL^{-1} for the same percentage removal of chromium in half time i.e., after one hour and at 60% intensity of ultrasound. It is observed that increase in ultrasonic intensity, removal of chromium is increased with decrease in energy consumption.

Effect of Cathodes on Chromium Removal

The cathode material plays a very important role in the electrodeposition of metals or compounds. Both the steel and lead cathodes were used to remove Cr^{+3} metals from the solution. Table-6 shows the comparison between percentage removal of Chromium at steel and lead cathode. It is observed that percentage removal with lead cathode is more as compared to the steel cathode. Maximum percentage removal of chromium was 41.56 % at 40 kHz and at 80% ultrasonic intensity, with steel cathode and 77.37 % with lead cathode. It was due to reactivity of the cathode material towards the chromium ions and the electrode potential depends upon the position of metals in standard electrochemical series. The electrode potential of Chromium is -0.74V, whereas the electrode potentials of steel (iron) and lead electrodes are -0.44V and -0.13V respectively. As lead is below iron in the electrochemical series so it shows more reactivity towards chromium as compared to steel.

Effect of Concentration on Percentage Removal of Chromium

The effect of ultrasonic intensities on percentage removal of Chromium was observed by varying the concentration. Three concentrations 2.5, 5 & 10mgL^{-1} were used during analysis. At concentration of 5mgL^{-1}, ultrasound showed the best removal percentage as compared to 2.5 and 10mgL^{-1}. In concentrated solution there are plenty of ions approaching the electrode surface but in dilute solution there are few ions reaching the electrode surface. Therefore the removal of chromium at 2.5 mgL^{-1} is less as compared to higher concentrations. During electrolysis process, the transports of ions from the bulk of solution to the surface of electrode are very low which are enhanced by increasing ultrasonic frequencies [15]. At 10mgL^{-1} of chromium, high concentration of ions are present in the solution so ultrasound is not effective to further bring them towards the electrode as the collision between the ions themselves inside the bulk of liquid hinder their movement towards the electrodes.

Table-5: The energy consumption at different ultrasonic intensities.

Time (h)	0 %		40 %		60 %		80 %	
	EC kWhL⁻¹	Removal (%)	ECkWhL⁻¹	Removal (%)	EC kWhL⁻¹	Removal (%)	EC kWhL⁻¹	Removal (%)
1	0.039	23.65	0.036	27.41	0.034	32.12	0.034	37.67
2	0.075	36.16	0.069	42.78	0.064	51.51	0.052	55

Table-6 The comparison of steel and lead cathodes for percentage removal of Chromium

Time (h)	Steel Cathode			Lead Cathode		
	0%	40%	80%	0%	40%	80%
1	2.87	18.31	19.64	65.37	69.25	72.25
2	28.11	34.34	41.56	67.5	71.87	77.37

Experimental

All experiments were performed using Digital Ultrasonic Bath (Cleaner Model UTECH PRODUCTS, INC) at ultrasonic frequency of 40 kHz at different ultrasonic intensities of 0, 40, 60, 80% in a rectangular Perspex glass vessel. Couple of electrodes hung up vertically into the solution. The stainless steel and lead electrodes were used as cathode for deposition of metallic ions and titanium was used as anode. Surface Area of the electrodes dipped into 1 Liter of solution was 102 cm². Electrodes were connected to the DC power supply (DAZHENG PS-305D) with digital current and voltage display. The experiments were conducted for 2hr at 10 volts.

Model solutions were prepared in de-ionized water with lab analytical grade salts of chromium sulfate and 0.1 molar sulfuric acid was used to adjust the pH. Solutions of 0.05 and 0.1 gm chromium sulfate were prepared in 1 liter of deionized water. Physical parameters i-e pH, TDS and conductivity were examined. Conductivity and TDS were determined by conductivity meter (HANNA of model HI 9835). pH was determined by pH meter (HANNA of model HI 99003).

Concentration of sulfate ions was quantified using spectrophotometer by turbid metric method. Sulfates were analyzed by spectrophotometer at 420 nm. [17].

Flame method and graphite furnace were used to determine the chromium concentrations at wave length of 357.9 nm [17].

Removal percentage of chromium and sulfate were determined by using following equation;

% Removal = $(1-C_t/C_o)$ x100

where C_t and C_o are the concentrations of chromium at reaction time t and 0, respectively

Conclusion

The electrochemical processes have limitations of metal removal if the concentrations of metals are reduced to certain limit. The electrochemical double layer is widened and the barrier between the bulk liquid and electrode surface is created due to which metal ions require more energy in the form of agitation, stirring or some other mechanical methods to break the electrical double layer

The current research was undertaken in order to reduce sulfates, TDS and chromium by coupling electrochemical and sonication processes. The main objective was to derive the metal ions on the collapsing cavitations which take them from bulk of the solution to the surface of electrodes and thus enhance electrochemical deposition and increase the removal percentage. The results show that by increasing the ultrasonic intensities, removal rate of chromium is also increased. Maximum removal of 76.44% was found at frequency of 40 kHz, 60% ultrasonic intensity and at pH 3 after two hours of process. Similarly the effect of pH on removal of chromium was also studied, it was observed from the Fig. 1 and 2 that the removal of chromium ion was more at pH 3 as compared to pH 9. The maximum removal of chromium was found to be 72.3 % at pH 3 which is less at pH 9 and was found to be 51.99 % at 80% ultrasonic intensity. The effect of ultrasonic intensities on percentage removal of Chromium was observed by varying the concentration. At Concentration of 5mgL⁻¹, ultrasound showed the best removal percentage as compared to 2.5 and 10mgL⁻¹. In concentrated solution there are plenty of ions approaching the electrode surface but in dilute solution there are few ions reaching the electrode surface. Therefore the removal of chromium at 2.5 mgL⁻¹ is leas as compared to higher concentrations.

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