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Electrochemical Treatment of Synthetic Wastewater Containing Paracetamol and Pseudoephedrine

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The electrochemical treatment of wastewater from pharmaceutical industry is a promising technique for substances which are widely used in medicinal materials. This paper deals with the electrochemical treatment of synthetic solutions containing paracetamol and pseudoephedrine. The changing of turbidity, oxidation reduction potential and chemical oxygen demand was investigated by varying the operating conditions. The results showed that turbidity, oxidation reduction potential and chemical oxygen demand which are eliminated by coagulation process and depends principally on aluminum concentration. All the results were obtained with the use of both cathode and anode made of aluminum (Al-Al system). With this system, optimal values of current density, initial pH and electrolysis time were 45 A/m^2, 6.8 and 300 min, respectively. For these optimal parameter values, the synthetic wastewater treatment of paracetamol data are better than the synthetic wastewater containing pseudoephedrine.

Keywords: Electrochemical treatment, Wastewater, Paracetamol, Pseudoephedrine.

INTRODUCTION

In the last few decades thousands of tons pharmaceutical drugs are consumed per year worldwide[1]. The contamination can arise from many sources, including excretion of ingested pharmaceuticals, improper disposal at the consumer level, intensive animal husbandry and inadequate treatment of manufacturing waste[2-5]. In the pharmaceutical drugs a high number of anti-inflammatory, analgesics, betablockers, lipid regulators, antibiotics, antiepileptics and estrogens has been found as minor pollutants[6-8]. These types of pharmaceutical compounds have been identified as contaminants in sewage effluents[9-13], surface and groundwater[14-21] and even drinking water[22-24]. Therefore the society has become increasingly sensitive towards the protection of the environment[25].

To prevent the toxic effect of drugs in the aquatic environment, there are many efforts to develop more powerful oxidation process than those currently applied in wastewater treatments for realizing their destruction. Ozonation and some advanced oxidation processe, such as O_3/H_2O_2, H_2O_2/UV and H_2O_2/Fe^{2+}/UV, have been successfully used to remove several common pharmaceuticals in aqueous media[26-31]. Furthermore, recent researchers have been investigated different way to eliminate pharmaceutical drugs is through the use of the electrochemical oxidation method. Electrocoagulation technique has been applied to treatment of water containing suspended solid[32]; fats, oils and greases[33-35]; color and dyes[36,37]; heavy metals[38]; landfill leachates[39] and phosphate[40], pharmaceutical pollutants.

During the application of electrochemical oxidation processes to eliminate pharmaceutical compounds does not require the use of chemicals, only a back ground electrolyte, already present in most effluents[1,41-43]. The electrocoagulation technique is one of the processes which offer high removal efficiencies in compact reactors, with simple equipments for control and relatively moderate operating cost[44].

The electrochemical reactions involving metal aluminum as anode can be summarized as follows: At the anode eqn. 1:

$$Al_{(s)} \rightarrow Al^{3+}_{(aq)} + 3e^{-} \quad (1)$$

The reaction occurring at the cathode is dependent on pH. At neutral or alkaline pH, hydrogen is produced through eqn. 2, whereas under acidic conditions eqn. 3 describes better hydrogen evolution at the cathode:

$$2H_2O_{(l)} + 2e^{-} \rightarrow H_{2(g)} + 2OH^{-}_{(aq)} \quad (2)$$

$$2H^{+}_{(aq)} + 2e^{-} \rightarrow H_{2(g)} \quad (3)$$

The generated metal ions [$Al^{3+}_{(aq)}$] immediately undergo further spontaneous reactions to produce corresponding hydroxides and/or polyhydroxides. The prevalence of the ionic or amorphous species is governed by operating conditions such as temperature, pH and the presence of other chemical species[44].

For practical applications, common electrolytes such as NaCl, Na_2SO_4 or KCl are most often added at low to moderate concentrations to obtain a sufficient electrical conductivity of the fluid to be treated, thereby increasing the efficiency of the process.

The main subject of the present study which is electrochemical treatment of wastewater containing of acetaminophen (also named as paracetamol or *N*-(*p*-hydroxyphenyl)acetamide) (Fig. 1) and pseudoephedrine ((*S,S*)-2-methylamino-1-phenylpropan-1-ol) (Fig. 2) may also discharge in to the sewage from manufacturing wastes[45].

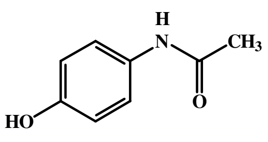

Fig. 1. Paracetamol

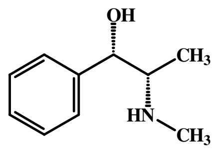

Fig. 2. Pseudoephedrine

Literature survey reports that there is no studies comparison of electrochemical application with paracetamol and pseudoephedrine solutions. In this paper, experimental conditions of laboratory-scale were performed for two different synthetic wastewater containing 1 g L^{-1} of paracetamol and 1 g L^{-1} pseudoephedrine respectively in batch scale made using aluminum electrodes as anode and cathode. The different parameters effects of electrolysis time, current density, initial pH have been investigated.

EXPERIMENTAL

Paracetamol and pseudoephedrine were supplied from Merck. Anhydrous sodium sulfate used as an electrolyte was analytical grade from Fluka. All waters which used to prepared solutions were obtained from Millipore Milli-Q system (Conductivity < 6×10^{-8} Scm^{-1}). 0.1 M NaOH and 0.1 M HCl were used to adjust the pH of solution, both of analytical grade from Aldrich.

Electrolysis cell was made of glass having dimensions 10, 18, 10 cm. The anode and cathode electrodes were a pair of Al plate electrodes of 5×10 cm^2 size. Power of the electrochemical treatment was performed by a DC Power Supply RXN_305D (Ztiaoxin) (Fig. 3). The electrical circuit were obtained from wires which made of copper. All sample extract from taking the electrolysis cell were filtred using filter paper from whatman before analysis.

Analytical procedures: Chemical oxygen demand levels were determined using standardized calorimetric technique with an excess of hexavalent chromium and subsequent measurement of the optical density[45]. Turbidity as measured by WTW Turb 550IR turbidimeter. The pH was measurement using a WTW series/ pH 720 pH-meter.

Evaluation: The electrochemical treatment's efficiencies of synthetic wastewater solutions of paracetamol and pseudoephedrine were evaluated by measuring the changes in terms of turbidity, oxidation reduction potential and chemical oxygen demand[46]. Turbidity, oxidation reduction potential and chemical oxygen demand were calculated as follow:

$$A \text{ removal} = [(A_0 - A)/A_0] \times 100$$

A: turbidity, oxidation reduction potential, chemical oxygen demand.

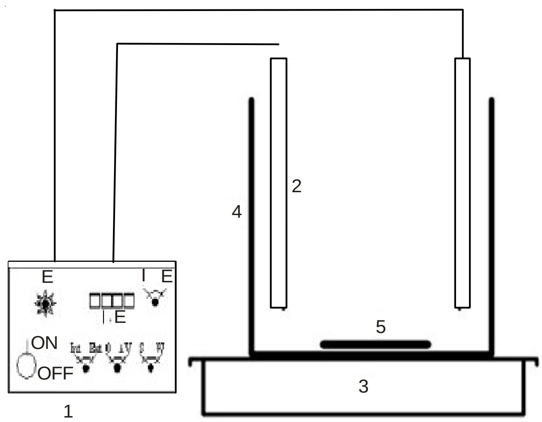

Fig. 3. Experimental devices for electrochemical treatment: (1) power supply; (2) Al plate electrodes; (3) magnetic stirrer; (4) electrolysis cell; (5) magnetic stir bar

RESULTS AND DISCUSSION

Two different solutions which are contained, respectivelly 1 g L^{-1} paracetamol and 1 g L^{-1} pseudoephedrine of pH 6.8 were initially electrolyzed at 45 A/m^2 and at room temperature *i.e.* at 25 ± 2 °C for 300 min to test its comparative degradation using a Al-Al system.

Effect of electrochemical operating time and current density: For three current densities, from 15 to 45 A/m^2 and with aluminum electrodes (anode and cathode), electrochemical experiments have been run with 1 g L^{-1} paracetamol and 1 g L^{-1} pseudoephedrine wastewater solutions.

The time of electrochemical treatment is one of the important parameter which effect the efficiency of electrochemical process. It is the time provided to the system to generate $Al(OH)_3$ and to complete flocculation of the pollutions[47]. Normal application time is from 240 min[1,46] to 400 min[5] for highest possible removal of some pharmaceutical materials. In the present work electrochemical treatment time used was from 20 to 300 min.

The experimental results showed that for higher current densities (45 A/m^2), the treatment can be carried out with high efficiency of turbidity for two different solution (Fig. 4) and (Fig. 5). Beside of this, the highest removal efficiency has been achieded in 300 min as optimum value for chemical oxygen demand and oxidation reduction potential (Figs. 6 and 7).

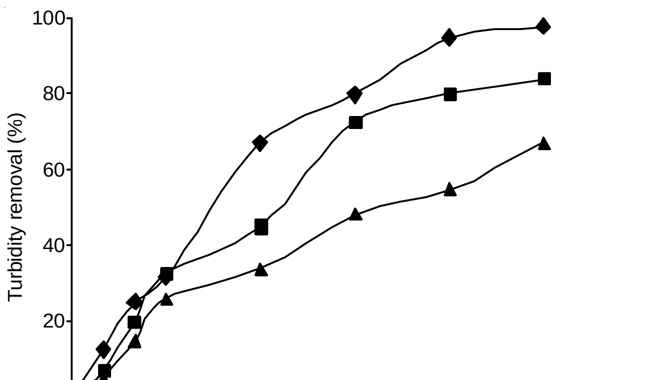

Fig. 4. Turbidity removal, depending on current density and electrolysis time (pH 6.8; C = 1 g L^{-1} paracetamol; Al-Al electrodes). 15 A/m^2 (▲), 25 A/m^2 (■), 45 A/m^2 (◆)

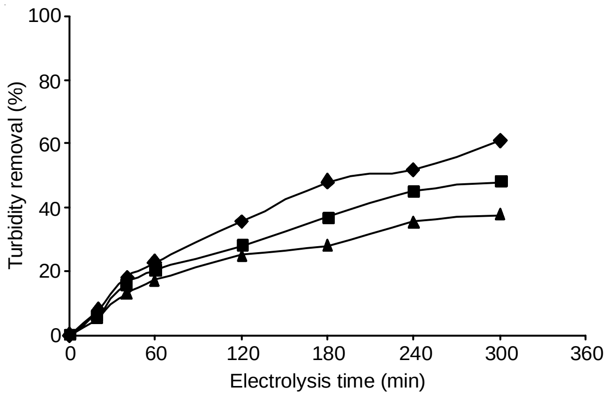

Fig. 5. Turbidity removal, depending on current density and electrolysis time (pH 6.8; C = 1 g L^{-1} pseudoephedrine; Al-Al electrodes). 15 A/m^2 (▲), 25 A/m^2 (■), 45 A/m^2 (◆)

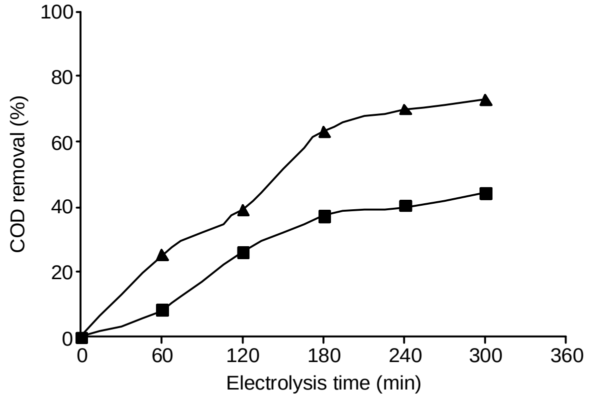

Fig. 6. Chemical oxygen demand removal, depending on wastewater type and electrolysis time (pH 6.8; Al-Al electrodes). 1 g L^{-1} paracetamol (▲), 1 g L^{-1} pseudoephedrine (■)

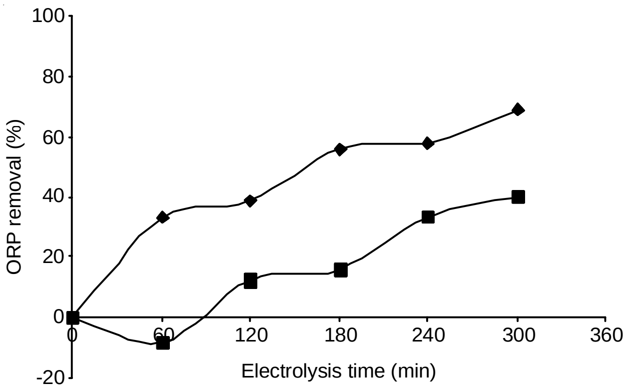

Fig. 7. Oxidation reduction potential removal, depending on wastewater type and electrolysis time (pH 6.8; Al-Al electrodes). 1 g L^{-1} paracetamol (◆), 1 g L^{-1} pseudoephedrine (■)

In the optimum experimental conditions; time (300 min), pH 6.8 and 45 A/m^2; chemical oxygen demand, turbidity and oxidation reduction potential removals attained, respectively for paracetamol; 74.58, 98.56 and 68.08; for pseudoephedrine; 42.43, 61.23 and 49.07 %.

Effect of initial pH: The beginning pH is considered as an important applying effect influencing the efficiency of electrochemical reactions[48]. To investigate its influence for electrochemical processes of paracetamol and pseudoephedrine wastewater, the pH of the solution to be considered was adjusted to the required amount for each experiment by addition of NaOH or HCl. The removal efficiency of turbidity, oxidation reduction potential and chemical oxygen demand as a effect of the beginning pH shows at (Table-1), after 300 min of electrolysis at 45 A/m^2 current density.

The maximal removal data were obtained at neutral pH (equal to 6.8) and these are in agreement with lots of previous works interested in electrochemical application using aluminum electrodes[44,47,49-51] as shown in (Table-1) very low range of pH is not desirable for two different solutions of paracetamol and pseudoephedrine. The parameters removal can be explained by amphoteric behaviour of aluminum hydroxide that precipitates at pH 6-7 and whose solubility increases when the solution becomes either more acidic or alkaline[44].

Conclusion

The present work reported that electrochemical application of synthetic wastewater contained paracetamol 1 g L^{-1} and pseudoephedrine 1 g L^{-1} with Al-Al electrodes influences of different parameters; initial pH, current density, electrolysis time; on paracetamol and pseudoephedrine wastewater treatment have been investigated. About 74.58 % paracetamol removal of chemical oxygen demand; turbidity and oxidation reduction potential have been reached using Al electrodes and supplied to be beter than pseudoephedrine, respectively 98.56 and 68.08 %. The optimum application parameters are electrolysis time of 300 min, current density of 45 A/m^2 and initial pH 6.8. It was observed that the synthetic wastewater treatment of paracetamol datas better than the synthetic wastewater of pseudoephedrine. The basic operating cost with Al-Al electrodes was observed to be more advantage than that of other pharmaceutical wastewater treatment system[44].

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TABLE-1
EFFECT OF FIRST pH ON ELECTROCHEMICAL WASTEWATER TREATMENT PROCESS EFFICIENCY C = 1 g L^{-1} PARACETAMOL AND C = 1 g L^{-1} PSEUDOEPHEDRINE; t = 300 min, CURRENT DENSITY = 45 A/m^2; Al-Al ELECTRODES

Initial pH	Parameter removal (%)						Final pH
	Chemical oxygen demand		Turbidity		Oxidation reduction potential		
	Paracetamol	Pseudoephedrine	Paracetamol	Pseudoephedrine	Paracetamol	Pseudoephedrine	
3.8	68.72	37.14	78.21	57.08	63.23	45.03	5.1
4.9	73.07	39.22	96.52	60.07	65.07	46.73	6.1
6.8	74.58	2.43	98.56	61.23	68.08	49.07	7.8
8.5	70.21	42.03	90.03	57.07	66.23	47.82	9.1
9.9	7.24	40.26	85.02	56.07	64.02	45.73	10.2
11.0	65.38	38.22	83.43	56.17	60.72	43.71	11.3

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