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Detergent Removal from Rinsing Water by Peroxi Electrocoagulation Process

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***Abstract*—**Among the various methods of treatment, advanced oxidation processes (AOP) are the most promising ones. In this study, Peroxi Electrocoagulation Process (PEP) was investigated for the treatment of detergent wastewater. The process was compared with electrooxidation treatment. The results showed that chemical oxygen demand (COD) was high 7584 $mgO_2.L^{-1}$, while the biochemical oxygen demand was low (250 $mgO_2.L^{-1}$). This wastewater was hardly biodegradable. Electrochemical process was carried out for the removal of detergent using a glass reactor with a volume of 1 L and fitted with three electrodes. A direct current (DC) supply was used. Samples were taken at various current density (0.0227 A/cm^2 to 0.0378 A/cm^2) and reaction time (1-2-3-4 and 5 hour). Finally, the COD was determined. The results indicated that COD removal efficiency of PEP was observed to increase with current intensity and reached to 77% after 5 h. The highest removal efficiency was observed after 5 h of treatment.

***Keywords*—**Advanced oxidation processes, chemical oxygen demand, COD, detergent, peroxi electrocoagulation process, PEP, wastewater

I. Introduction

AMONG the emerging contaminants investigated in urban water systems and water bodies since the beginning of the 2000s, detergents and biocides are of growing concern due to their ubiquist presence and contributions to impacts on ecosystems, ecotoxicity, and difficulty in treatment and removal [1]. Detergents are composed of various compounds such as surfactants, anti-redeposition agents, water softeners, bleaching agents, brightening pigments, perfumes and so on [2]. Washing detergents are getting attention as serious pollutants of the environment, particularly water [2]. It can cause serious environmental problems including the eutrophication phenomenon. Also, detergent decomposition process will generate residual benzene that could become a meaningful environmental problem [3].

Methods for removal of surfactants involve processes such as biological methods [4], phytoremediation [5], adsorption [6], coagulation [7], and membrane technology [8]. Actually, much research has focused on a new class of oxidation technique: advanced oxidation processes (AOPs).

The AOPs are effectively degrading recalcitrant components without generating a secondary waste stream. Moreover, in most cases the formation of hazardous species in the effluent is limited [9]. These processes are based on the *in situ* formation of hydroxyl •OH radicals, which have a higher oxidizing power than traditional oxidants [10]. The complete mineralization of pollutants was observed non-selectively with the help of hydroxyl radicals.

Organic pollutants are degraded via dehydrogenation, redox reaction and hydroxylation reactions [11]. Advanced oxidation processes are performed for benzene removal [12], textile wastewater [13], tannery wastewater [14], and pharmaceutical wastewater [15]. AOPs are also found to be effective for reducing arsenic toxicity by oxidizing arsenite to arsenate [10].

Assadi et al. studied the possibility of removal of phenol from the solution model with PEP method with iron anodes. In these tests, the efficiency of phenol removal with a concentration of surfactant of 50 mg/L was reached to 100% in the presence of 0.025M H_2O_2 at pH 3. It was found that the proper voltage and electrolysis time was 10 volts and 10 min [16].

Yazdanbakhsh et al. achieved a removal efficiency of 98% in the removal of humic acid from synthetic wastewater by the peroxi electrocoagulation method. The study has shown that under the optimum operating range for the process (current density = 1 A/cm^2, hydrogen peroxide concentration = 150 mg/L, reaction time = 20 minutes and pH = 3.0), humic acid removal efficiency reached 98% [17].

The aim of this study is to evaluate the performance of PEP for detergent removal from manufactory wastewater at different operating conditions.

II. Experimental

Industrial wastewater samples were collected from manufacturing process located in Algiers, Algeria. The samples were collected in plastic bottles pre-served at 4 °C before analysis. Table I shows the characteristics of wastewater.

TABLE I
The Composition of Detergent Wastewater

Parameter	Value
pH	9.5
Conductivity ($mS.cm^{-1}$)	2.5
Turbidity (FNU)	297
Chloride ($mg.L^{-1}$)	851
COD ($mgO_2.L^{-1}$)	7584
BOD_5 ($mg\ O_2.L^{-1}$)	250
Suspended Matters *($mg.L^{-1}$)*	0.34

Batch treatment of 1000 ml wastewater was carried out in an electrolytic cell. The PEP unit with bipolar electrodes in

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parallel connection consists of an electrolytic cell, a DC power supply and electrodes. The cell reactor was equipped with a magnetic stirrer using a constant speed of 400 rpm in order to get a correct homogenization of the wastewater mixture. The cathode and anode consist of pieces of graphite electrodes dipped in the wastewater (Fig. 1).

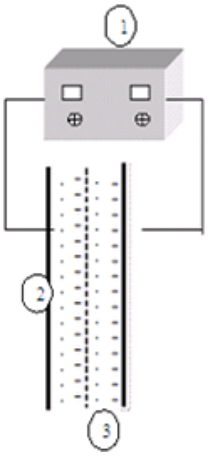

Fig. 1 Schematic diagram of the electrolysis cell; 1: D.C. power; 2: electrode, 3: additive electrode

The effects of the main operational variables including pH of solution (3 or 9.5), current density (0.0227- 0.0378 A/cm^2) and reaction time (1–5 h) on the electrochemical process in treating detergent wastewater were investigated in various runs.

The experiments were compared with electrooxidation (EO) process using two electrodes on graphite. This process was conducted at pH of 9.5 (initial pH of wastewater without adjustment). Tests were conducted with 0.15 A current intensity during 2 h.

pH and COD were determined. pH measurements were done by pH 210 *HANNA* and a closed reflux colorimetric method [18] was used for COD analysis. Chloride ions were measured by argentometric titration [19]

III. Results and Discussion

The applied process was examined for their ability to remove organic compounds. A graphite cathode was used in order to provide hydrogen peroxide production.

A. Comparison of Detergent Removal in Different Processes: EO and PEP

The applied processes were examined for their ability to remove organic compounds. The experiments were firstly conducted at pH of 9.5, a current intensity of 0.15 A and 2 h of electrolysis treatment.

Table II shows chloride and COD removal from detergent wastewater using different electrochemical processes.

We found that EO could eliminate COD about 49% during 2 h. The presence of an additional electrode between the anode and the cathode increases COD removal until 70%. Furthermore, we have observed that chloride ions were more consumed in PEP system. The PEP decreases chloride ion concentration until 92%. These ions can induce the generation of active chlorine species in the solution destructing the organic compounds [20]. Also, radical or hydroxyl radical generated during electrochemical treatment can degrade organic pollutants [11]. These results indicated that the presence of the third electrode improved the performance of electrochemical process to decrease COD and chlorine concentration within 2 h of treatment at pH solution of 9.5.

TABLE II
Characteristics of Treated Detergent Wastewater

Parameters	Graphite/graphite system	Graphite/Iron/graphite system
pH	7.9	9.18
Conductivity (mS.cm^{-1})	4.2	4.4
Turbidity (FNU)	317	379
Chloride (mg.L^{-1})	1134.45	70.90
COD (mg O_2.L^{-1})	3840	1728

Initial pH= 9.5, current intensity = 0.15 A and 2 h

B. Effect of pH

In this work the electrochemical degradation of detergent was carried out at different pH values. For this purpose, PEP experiments were conducted at pH 3 and the natural pH of the solution (pH = 9.5).

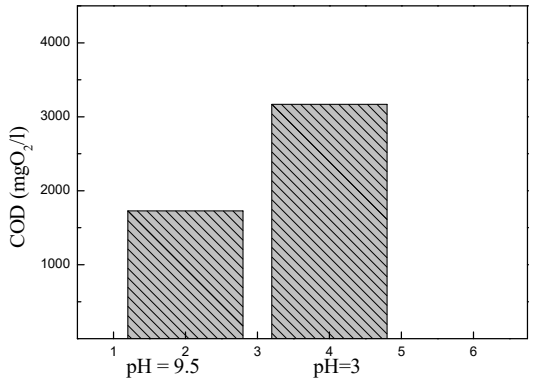

Fig. 2 Effect of pH on COD value of treated wastewater (current density = 0.0227 A/cm^2, electrolysis time = 2h)

As shown in Fig. 2, the COD reduction was increased with the increase of initial pH. Thus, the solution at pH 9.5 attained COD reduction of 77.21% after 2 h, while only around 58.22% was achieved for the solution at initial pH of 3.

The increase in removal efficiency in alkaline pH is probably due to the formation of ferrous species which amplify the production of hydroxyl radicals and so increase the efficiency of removal. Eryuruk et al. reported that there was minor removal at an acidic pH because of collapsing hydroxide ions generated at the cathode by protons which caused an insufficient formation of iron hydroxide [21].

Vasudevan et al. [22] studied the removal of copper by electrochemically- assisted coagulation. Their results showed that the optimum removal efficiency of 96.6% was achieved at a current density of 0.05 A/dm^2 and a pH of 7.0.

Zhou et al. [23] reported that the pH did not dramatically

influence the yields of H_2O_2 generated at the cathode.

C. Effect of Current Density and Time

The current density affects the removal of the organic composes. For this reason the effect of current density on the removal of the detergent was studied under the following operating conditions: 7584 mgO_2/L initial COD and pH of 9.5.

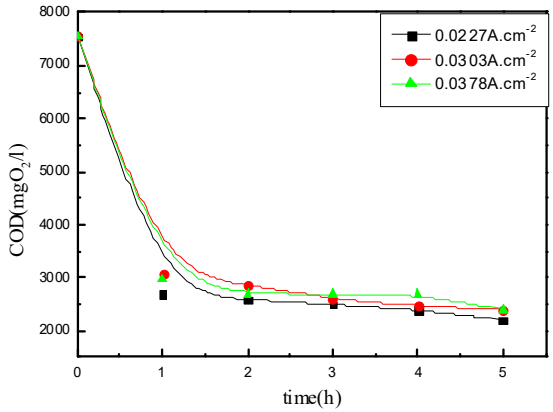

Fig. 3 Effect of current density and electrolysis time on COD value of wastewater (pH of 9.5)

We found that the lowest COD value is obtained when applying a low current density. That is, COD was reduced by 77% and 86 % 0.0227A/cm^2 and 0.0378 A/cm^2respectively.

Removal efficiency of detergent at natural pH for 5 h at a current intensity of 0.0227A/cm^2 was nearly 77%. According to the result of our study, increasing the intensity of the current was not affecting the treatment efficiency of detergent.

The current density would lead to higher production rate of hydrogen peroxide on the cathode surface. As a result, more free hydroxyl radicals would accumulate in the bulk solution, leading to a greater degradation of pollutants [24].

Increasing current, due to producing more iron and hydrogen peroxide of oxygen, increases removal efficiency relatively. In a study by Assadi et al., using electrocoagulation proxy on phenol, increasing potential current from 10 V current to 20 V then 30 V, increased phenol removal efficiency from 99.7%, 99.4% and 100% [16].

Ghanbari et al. [25] found that higher current density can result in the side reactions in electrochemical cell in which cathodic reactions for hydrogen peroxide generation would be disturbed. H_2 evolution competes with the main reaction of hydrogen peroxide generation. Thusly, hydrogen peroxide was oxidized to hydroperoxyl ($HO_2^{\cdot}$) and oxygen (O_2) at the anode in higher current density (40 mA/cm^2) [25], [26]. As a result, Fenton reaction was reduced.

$$2H_2O \rightarrow 4H^+ + O_2 + 4e- \quad (1)$$

$$2H^+ + 2e- \rightarrow H_2 \quad (2)$$

As shown in Fig. 3, early on, the pollutant decomposition rate was very high, and increasing reactive time did not significantly affect the removal of COD. The decrease of COD removal as a function of elapsed time might be caused by the production of Fe^{3+} ions from iron. When using iron electrode, the PEP generates Fe(II) or Fe(III) on the surface. And in the presence of H_2O_2 generated in the solution, Fenton reaction takes place to produce hydroxyl radicals to attack organic compounds.

IV. Conclusion

PEP was found very effective to treat detergent wastewater than EO process. COD removal was found as pH dependent and increased with current density. The process reduced to COD 250 mgO_2/L from 7584 mgO_2/L (77% COD reduction) at 0.0227A/cm^2, pH 9.5 and 5 h.

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