The Effect of Initial pH on Pistachio Processing Industrial Wastewater Pre-treatment by Electrocoagulation Method

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***Abstract*—In this study, removal of chemical oxygen demand (COD) and total phenols (TP) from pistachio processing industry wastewater was investigated using electrocoagulation method. COD and TP removal efficiencies were compared considering wastewater initial pH by using stainless steel cathodes and aluminum anodes. To determine the effect of initial pH on removal efficiency, 4, 5.2 (original wastewater pH), 6 and 7 pH were investigated. Results showed that optimum values of operating variables wastewater initial pH was 5.2 for COD removal efficiency and 7 for TF removal efficiency. Removal of COD of pH 5.2 up has increased. Removal of COD began to decrease at higher pH values than the original pH value. TF removal efficiency increased with increasing pH. The pH values at the obtained the highest energy consumption value was the original pH. The energy consumption value were decreased above and below the original pH value. The highest removal efficiencies for COD and TF were %60 and %95, respectively under operating conditions as 25 ml/min flow rate and 20 A current intensity.**

Keywords-electrocoagulation; ınitial pH; removal efficiency; aluminum anode

I. INTRODUCTION

Pistachio processing is a rapidly developing industry in Turkey. In 2012, Turkey ranked third among the world's exporters of pistachio products (1). Wastewaters from the pistachio processing industry (PPI) are characterized by high chemical oxygen demand (COD), total organic carbon (TOC), and total phenol (TP) due to their high level of organic contents. Pistachio is processed in a wet system in Turkey. In 2012, Turkey produced 120,000 tons of pistachio and the processing industry of pistachio produces approximately 6 m3 of wastewater per ton of pistachio, which is directly discharged to the sewage system.

EC has been proved to be an efficient method for the treatment of wastewater containing high amounts of organic matter (such as PPIW). It was tested successfully to treat textile wastewater (2), polyvinyl alcohol (3, 4), laundry wastewater (5), chemical mechanical polishing wastewater (6), arsenic removal (7), soluble oil wastewater (8), salicylic acid (9), and indium ions (10). EC has also been proposed to treat various food industry wastewaters such as yeast wastewater (11), restaurant wastewater (12), poultry slaughterhouse (13), and olive mill wastewater (14).

Electrochemical methods appear to be effective for the treatment of different effluents compared with conventional methods. Electrocoagulation has many advantages over conventional chemical coagulation, such as simple equipment, easy operation and automation, a short retention time, low sludge production, and no chemical requirement; therefore, it does not produce secondary pollution. Electrocoagulation is the process of destabilizing suspended, emulsified, or dissolved contaminants in an aqueous medium by introducing an electric current ninto the medium (15). Several materials can be used for the anodes, such as Al and Fe electrodes in the electrocoagulation process. For example, aluminum anodes have the same effect as the addition of Al based coagulants in conventional treatment systems (16).

The most widely used electrode materials in the electrocoagulation process are aluminum and iron. In the case of aluminum, the main reactions are as follows:

Ανοδε: $A\lambda_{(\sigma)} \rightarrow A\lambda_3{}^{+}{}_{(\alpha\theta)} + 3\varepsilon^{\updownarrow}$ (1)

Cathode: $3H_2O + 3e^- \rightarrow 3/2H_{2(g)} + 3OH^-_{(aq)}$ (2)

On the other hand, at higher pH values, both cathode and anode may be chemically attacked by OH^- ions:

$$2A\lambda_{(\sigma)} + 6H_2O + 2OH^{\updownarrow}{}_{(\alpha\theta)} \rightarrow 2A\lambda(OH)_4{}^{\updownarrow}{}_{(\alpha\theta)} + 3H_{2(\gamma)} \quad (3)$$

$Al_3{}^{+}$ and OH^-ions generated by electrode reactions (1) and (2) react to form various monomeric species such as $Al(OH)_2{}^{+}$, $Al(OH)_2{}^{+}$, $Al_2(OH)_2{}^{2+}$, $Al(OH)_4{}^{-}$, and polymeric species such as $Al_6(OH)_{15}{}^{3+}$, $Al_7(OH)_{17}{}^{4+}$, $Al_8(OH)_{20}{}^{4+}$, $Al_{13}O_4(OH)_{24}{}^{7+}$, $Al_{13}(OH)_{34}{}^{5+}$, which transform finally into $Al(OH)_3$(s) according to complex precipitation kinetics (17).

$$A\lambda_3{}^{+}{}_{(\alpha\theta)} + 3H_2O \square A\lambda(OH)_{3(\sigma)} + 3H^{+}{}_{(\alpha\theta)} \quad (4)$$

Freshly formed amorphous $Al(OH)_{3(s)}$ "sweep flocks" have a large surface area which is beneficial for a rapid adsorption of soluble organic compounds and trapping of colloidal particles.

Finally, these flocks are removed easily from aqueous medium by sedimentation or H_2 flotation.

The objective of the present study is to investigate the efficiency of electrocoagulation pre-treatment of PPIW using aluminum electrode. The effects of operational parameters, namely initial pH of wastewater, was examined on COD and TP removal efficiency.

II. MATERIAL AND METHODS

A. PPIW Effluent

Wastewater samples used in the present study were obtained from a local pistachio processing plant with the daily capacity of 13 tons and producing approximately 80 m3 of wastewater a day in the city of Gaziantep (Turkey). Wastewater was filtered using a screen filter to remove large suspended solids before being used for the subsequent studies. Results of the chemical analysis of PPIW are given in Table 1. The pH of the wastewater was adjusted to the required value using concentrated nitric acid and sodium hydroxide. All chemicals were at analytical grade and supplied by Merck. COD and TP were determined as proposed by standard methods (18).

The removal efficiency and energy consumption (4, 25) in PPIW treated by electrocoagulation is calculated as follows:

$$\%\ Removal\ efficiency = \frac{C_0 - C_t}{C_0} * 100 \quad (5)$$

where C_0 is the initial COD and TP value (mg L^{-1}), C_t is the COD and TP value at time.

$$Energy\ consumrtion\ (W) = \frac{V * I * t}{v} \quad (6)$$

where W is the energy consumption (kW-h m^{-3}), V is the average cell voltage (V), I is the current density (A), t is the electrolysis duration (h), and v is the volume of the wastewater (m^3).

B. Electrocoagulation Procedure

The electrocoagulation cell was constructed from stainless steel having an inner diameter of 6 cm and height of 65 cm. The experimental equipment schematically was shown in Figure 1. The total volume of wastewater used in each experiment was approximately 500 mL. Aluminum (Al) electrode an inner diameter of 5 cm and height of 70 cm was used for the sacrificial electrode. The distance between electrodes was fixed at approximately 5 mm. Aluminum electrode had approximately 1130 cm2 of effective surface. The current was maintained to be constant by means of a precision DC power supply characterized by the ranges from 0 to 40 A for current and 0 to 120 V for voltage. Two digital multimeters (Brymen Bm-201; one as ampermeter and the other as voltmeter) were used to measure the current passing through the circuit and the applied potential, respectively. The temperature, conductivity, and pH of the wastewaters were measured by a multi-parameter (WTW Multiline P-4 F-Set-3) during the experiments. Treated wastewater was collected over a desired period of time from the reactor and the collected samples were filtered by the cellulose acetate membrane filter with the pore diameter of 0.45 μm (Schleicher and Schuell) before the analysis. The reactor was operated in continuous and galvanostatic mode.

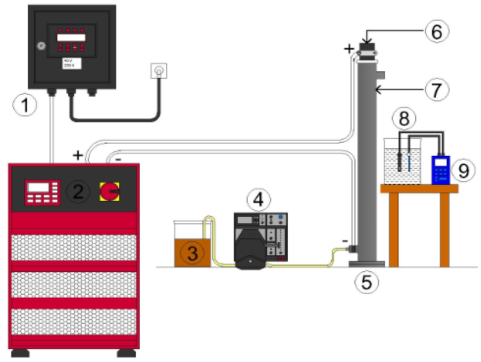

FIGURE I. SCHEMATIC VIEW OF THE EXPERIMENTAL SYSTEM (1: CONTROL PANEL 2: POWER SUPPLY 3: WASTEWATER INLET CHAMBER 4: PERISTALTIC PUMP 5: REACTOR 6: ANODE ELECTRODE 7: CATHODE ELECTRODE 8: WASTEWATER OUTLET CHAMBER 9: PH CONTROL UNIT)

III. RESULTS AND DISCUSSIONS

Initial pH of wastewater is one of the most important process parameters in electrocoagulation (19, 20). Since the pH of untreated wastewater can affect the stability of hydroxide types, this effect can also be seen on pollutant removal efficiency negatively or positively. Anode and cathode reactions in aqueous solutions can result in alterations of pH values in solutions. Therefore, electrolytic soluble metal ions depending on wastewater pH (such as Al^{+3} and Fe^{+2}) can form different hydroxide types with different pH values (21). In addition, changes in pH can alter the surface load of particles and this can affect the removal of organic materials dispersed in wastewater (22).

Wastewater with the initial pH values in the range of 3.0 to 8.0 was used in order to investigate the effect of initial pH in wastewater on the removal efficiency of COD and TP using aluminum electrode. Experiments were carried out without intervening pH values during reaction. Throughout the experiment period, constant current intensity was 15 A, flow rate was 100 ml/min and the temperature was 293 K. Figure 2-3 represents graphically the results obtained for the removal efficiency of COD and TP.

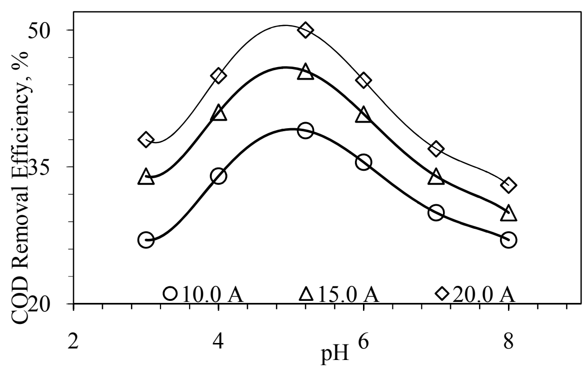

FIGURE II. THE EFFECT OF INITIAL PH ON COD REMOVAL, 30 ML/MIN FLOW RATE, 293 K WASTEWATER TEMPERATURE

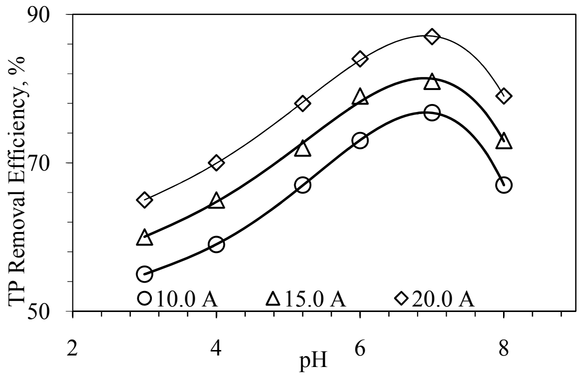

FIGURE III. THE EFFECT OF INITIAL PH ON TP REMOVAL, 30 ML/MIN FLOW RATE, 293 K WASTEWATER TEMPERATURE

COD removal efficiency values (η) obtained after 20 minute reaction period are 40%, 45%, 50%, 45%, 37%and 33% for initial pH values ranging from 3 to 8. The TP removal efficiency values (η) were found to be 65%, 70%, 77%, 83%, 88%and 77%.

When considering Figure 2, it can be seen that COD and TP removal efficiency in wastewater from the pistachio processing industry using the electrocoagulation process is associated strongly with the initial pH of wastewater. The COD removal efficiency increases when wastewater initial pH increases from 3 to 5.2. However, when the initial pH is higher than 5.2, the removal efficiency decreases consistently and when the initial pH is 7, COD removal efficiency reach the lowest value. TP efficiency was increased with increasing wastewater pH values. This situation depends on the type of phenol present in the solution. TP removal takes place in reaction the first time. When Figure 4 was investigated, it was seen that the initial pH changes during the reaction of waste water. The effluent pH is increased at the end of the reaction time for investigated all pH values. The reason of increase the TP removal efficiency by pH 7 was considered that formation of aluminum hydroxide until the pH range is to be the highest.

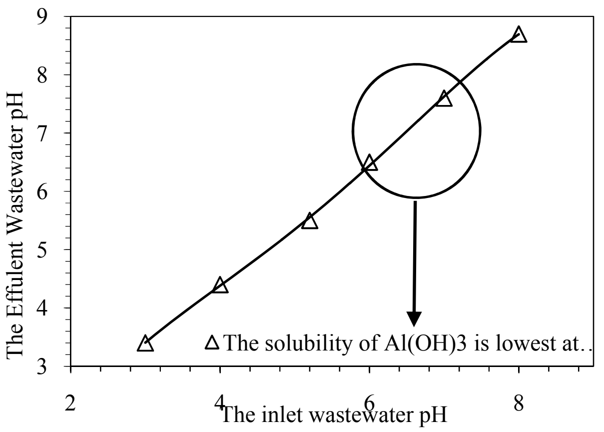

FIGURE IV. THE CHANGES OF PH OF THE WASTE WATER BY ELECTROCHEMICAL REACTION

IV. CONCLUSIONS

The present study showed the applicability of electrocoagulation method in the pre-treatment of COD and TP from PPIW. The following results were obtained:

Experiments were carried out under uncontrolled pH (not constant pH) conditions ranging from 3.0 to 8.0. The effect of initial pH on the system performance was evaluated based on the removal efficiency and energy consumption. From the results obtained in the experiments, low initial pH is suitable for removal efficiency when pH is not controlled because the solubility of Al(OH)3 is minimum in this pH interval which has a good flocking and weak solving feature. Under optimum conditions as 20 Amper current intensity, 293 K waste water temperature and 30 ml/min flow rate, 50% COD removal and 88% TP were achieved. The obtained values was indicated that electrocoagulation process was a suitable process for treatment of the pistachio processing industry wastewaters.

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