Removal of Pyrogallol from Drinking Water by Alternating Current Electrocoagulation Technique

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Abstract: In this work, the feasibility of pyrogallol removal from an aqueous solution was investigated in an electrochemical cell equipped with aluminum plates by using alternating current (AC) in electrocoagulation processes. The electrodes were connected as bipolar mode and a power supply was used for supplying alternating current. Several parameters, such as current density, initial metal ion concentration, contact time, inter-electrode distances, solution pH variation, applied voltage and solution conductivity were investigated. The best removal efficiency obtained was 100% using an aluminum electrode, the initial pH was 6.30, the cell operation time was 100 min from the initial concentration of 0.5 mg L^{-1} of pyrogallol and current density was 0.04 A m^{-2} at 50V. A pseudo-second-order kinetic model provided a good fit to the experimental results of the adsorption process at various applied voltages, indicating that pyrogallol precipitation in an aqueous solution was attributable to the alternating current electrocoagulation (ACE) process. Considering the obtained efficiency in the present study, under the studied operational conditions, AEC may be suggested as an effective alternative technique for pyrogallol removal.

Key words: Electrocoagulation · Alternating current · Pyrogallol removal · Adsorption kinetics

INTRODUCTION

Currently, pyrogallol is used for dying of wool, staining leather and manufacturing various dyes [1]. Pyrogallol is also used as a developer in photography [1] and holography [2]. A chemical reagent for antimony and bismuth; and as an active reducer for gold, silver and mercury salts [1]. It is used for making colloidal solutions of metals, process engraving [3] and in the manufacture of pharmaceuticals and pesticides [4]. Due to its antioxidant properties, pyrogallol is used as a corrosion inhibitor (i.e. oxygen scavenger) in boilers [5, 6].

In nature, pyrogallol is incorporated in tannins, anthocyanins, flavones and alkaloids [4]. Pyrogallol may be released into the environment during its manufacture, transport, disposal and industrial use. Pyrogallol is a byproduct of the decomposition of humic substances and may be present in the water supply of geographic regions rich in organic matter such as coals and shales [7].

Long-term drinking of water containing high pyrogallol content can result ingastrointestinal tract irritation, hemolysis, renal injury, uremia, methe moglobinemia and death.With the realization that pollutants present in water adversely affect humanand animal life, domestic and industrial activities pollution control and management is now a highpriority area. As a result of the serious efforts of researchers all over the world in the field of pollution control and management, a number of methodologies with varying degrees of success have been developed to manage water pollution. Some of them involve coagulation, foam flotation, filtration, ion exchange, sedimentation, solvent extraction,

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adsorption, electrolysis, chemical oxidation, disinfection, chemical precipitation and membrane process. However, these methods have their own shortcomings and limitations.

Among various available technologies for water pollution control listed above, Direct current electrocoagulation (DCE) is considered better as compared to other methods because of high particulate removal efficiency, a compact treatment facility, relatively low cost and the possibility of complete automation. This method is characterized by reduced sludge production, a minimum requirement of chemicals and ease of operation [8, 9]. Electrocoagulation technique for wastewater is already used with high efficiency in removing heavy metal pollutants like Cu, Cr, Ni, Zn, Ag and As [10-12] and organic removals in bilge water [13].

However, direct current electro-coagulation processes may result in the formation of an impermeable oxide layer on the cathode as well as corrosion on the anode. These prevent the effective current transport between the anode and cathode, so the efficiency of electro-coagulation processes declines. These disadvantages have been overcome by adopting alternating current electro-coagulation processes (AEC). In this process electro-chemically generated metallic ions from the anode can undergo hydrolysis to produce a series of activated intermediates that are able to destabilize the dispersed particles present in the water to be treated. The destabilized particles then aggregate to form flocks.

The objective of this research was to determine the feasibility of using AEC as a pretreatment method of wastewater with an emphasis on removal of effluent organic materials such as pyrogallol. In order to achieve the goals of study, there was a plan to study a batch process by changing initial pH, current density, reaction time, initial concentrations, solution conductivity and inter-electrode distance to get optimum conditions of these parameters. It is decided to use pyro gallol concent rationas parameters of range of treatment. These parameters indicate the effective process of AEC in water treatment when comparison is made after and be fore treatments. The research had three stages: synthetic wastewater preparation, AEC treatment and sample analyzing.

MATERIALS AND METHODS

All reagents including pyrogallol, sodium chloride, ammonium hydroxide, ammonium chloride, ethylenediaminetetraacetic acid and Eriochrome Black T indicator were purchased from Merck, Germany and used without purification. Deionized water was used in all preparations.

Desired concentrations of pyrogallol were prepared by mixing proper amount of pyrogallol with deionized water for the required concentration. In order to increase the conductivity of the solutions to 1.06mS/cm, sodium chloride (0.250 mg/L) was added to the solution before injecting it into the apparatus. The chloride salt added to the solution can also prevent the formation of the oxide layer on the anode and therefore reduce the passivation problem of the electrodes.

AEC treatment: Alternating current electrocoagulation (AEC) was carried out in batch reactor consisting of a 5.0-L Plexiglas container with a 5 L capacity. The AEC reduction was performed with a bipolar mode and with aluminum-aluminum anode-cathode electrodes. The electrodes were connected to a regulated alternating current (AC) power supply (0-5 A, 0-270 V, 50 Hz; AMETEK Model: EC1000S). The Aluminum electrodes with a surface area of $0.8 dm^2$ acted as the anode and the cathode, respectively, were placed vertically at a fixed inter-electrode distance of 0.01 m.

The contents of the EC reactor were gently aerated with a magnet rotator (Alfa, HS-860). In this study, both low and high currents were investigated. The currents were fixed at 4, 5 and 6 A. The temperature of the electrolyte has been controlled to the desired value with a variation of ±2 K by using a Thermo Scientific HAAKE Refrigerated Circulating Water Bath. Before starting-up the process, the electrodes were cleaned with 1 M H_2SO_4 and rinsed with de-ionized water to eliminate impurities from the surface of the electrodes.

In order to determine the effect of voltage on process efficiency in this study, the efficiency of contaminant removal in different electrical potentials, reaction times, applied currents and the pH were investigated. Voltage and current were measured by a digital voltameter (max 12) and digital ammeter (DT9201A). The conductivity of the solutions was measured by means of Philips digital conductivity meter (PW 9526). The pH was measured using a Hanna Instrument Check Temp (HI8314) pH meter.

Sample analyzing: Samples of 5 mL were drawn periodically during the experimentations, filtered through a Whatman filter paper no. 40 to separate the sludge from the supernatant.

Absorbance measurements of the residual pyrogallol were carried out on a Perkin Elmer Lamda 35 UV-VIS spectrophotometer. First order derivative spectra of the
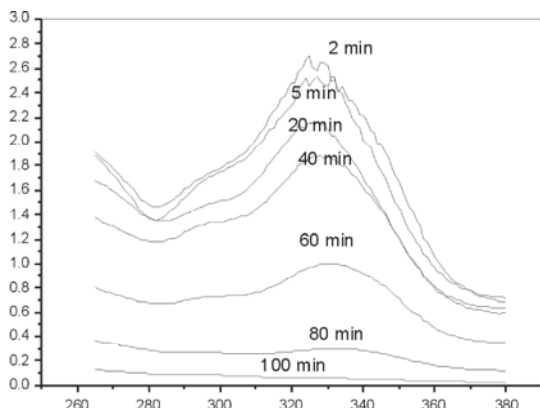
Fig. 1: First-order derivative spectra of pyrogallol.

pyrogallol were recorded in the wavelength region 200-400 nm. These first-order derivative spectra showed a maximum derivative amplitude at 275 nm (Figure 1).

Series of standard solutions of pyrogallol were prepared and the absorbance of each solution was measured at 320nm. The results obtained show a linear relationship between absorbance and concentration in the range of 2.0×10^{-6}-1.2×10^{-5} M. The molar absorptivity as calculated from the linear part of Beer's law plots was 1.52×10^4 $L^{-1}mol^{-1}cm^{-1}$. The calibration curve obtained was used to determine the concentration of pyrogallol in sample solution.

The calculation of % removal efficiency of pyrogallolafter ACE treatment was performed using the equation:

$$\% \ RE = [C_0 - C/C_0] \times 100$$

where, Co and C concentration of dissolved pyrogallol before and after ACE process in mg L^{-1}, respectively. The pK values of electrolytic solutions were calculated using the following equation:

$$pH = pK + \log C/C_0$$

where, C, is the concentration of solution in each run and Co is the initial concentration. The effects of the reaction time, the applied current density, initial pollutant concentrations and inter-electrode distances were investigated.

RESULTS AND DISCUSSION

Initial Pyrogallol Concentrations: To demonstrate the effect of initial organic pollutants concentration and the time required for their quantitative removal, a set of

experiments were conducted with three different aliquot solutions containing same concentrations of 0.1, 0.3 and 0.5 mg/L of pyrogallol. The solutions were treated at a constant current density of 0.04 (A/m^2) at different voltages and different times of electrolysis. Figures 2-4 show the variations of percentage removal of pyrogallol with time.

The three different initial concentrations of 0.1, 0.3 and 0.5 mg/L of pyrogallol in the aliquots were reduced to acceptable levels after 30 min. According to Figures 2-4, no direct correlation exists between pyrogallol concentration and removal efficiency. Certainly, for higher concentrations longer time for removal is needed, but lower initial concentrations were reduced significantly at higher voltage in relatively less time than higher concentrations. The ACE process is more effective at the beginning when the concentration is higher than at the end of the operation when the concentration is low.

Effect of pH on Pyrogallol Removal: It has been established that pH is an important parameter influencing the performance of the EC process [14]. To examine its effect, the sample was adjusted to a desired pH for each experiment by using potassium hydroxide. Figures 5-7 show variation of pH pyrogallol wastewater with time at different initial concentrations and at different voltages using a constant current density of 0.04 (A/m^2). The removal efficiency of pyrogallol as a function of pH is shown in Figure 7. pH of the medium increased during the process with time.

The solution pH stabilizes at nearly constant value around 8.7, which may be ascribed to the buffering capacity of complex nature of aqua Al^{3+}/Al(OH)$_3$ system [15]. The maximum removals of pyrogallolwere observed at pH around 6-7. Best removal results for 20 min electrolysis duration were observed at a pH of 6-7. However, as shown in Figure 7, at 50 V and initial concentration of 0.1 mg/L, the process is clearly more efficient from pH 6 to 7 for only 20 min of electrolysis. The removal (%) of pyrogallol in this pH region was 98-99%.

Effect of Conductivity: Electricalconductivity is the ability of the mediato conduct electricalcurrent between two electrodes. It appears that pollutant removal efficiency was not significantly affected by the wastewater conductivity over the range investigated, as shown in Figure 8. One explanation for such an observation is that destabilization ofdispersed particles is primarily accomplished through the mechanism of adsorption and charge neutralization ofelectrochemically produced

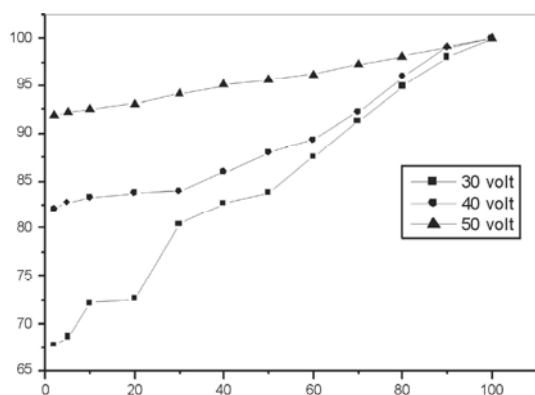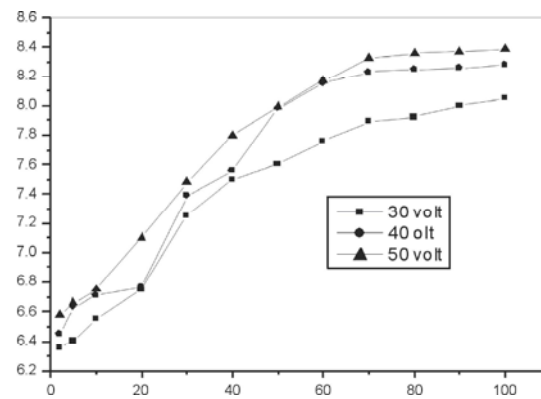Fig. 2: % Removal efficiency of Pyrogallol (0.1mg/L) versus Time.

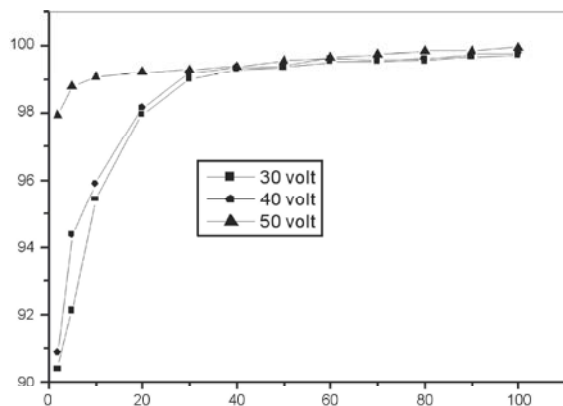Fig. 5: Variation of pH of pyrogallolwith time. [Pyrogallol]: 0.10 mg/L

Fig. 3: % Removal efficiency of Pyrogallol(0.3 mg/L) versus Time.

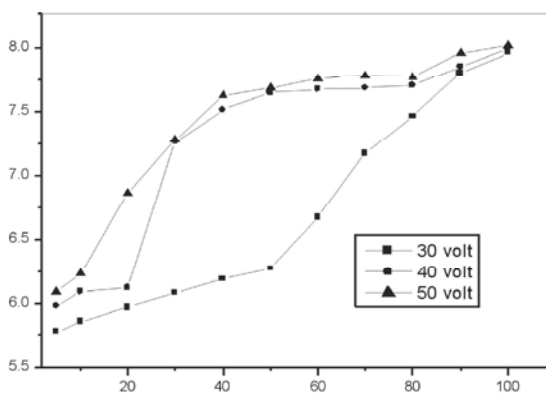

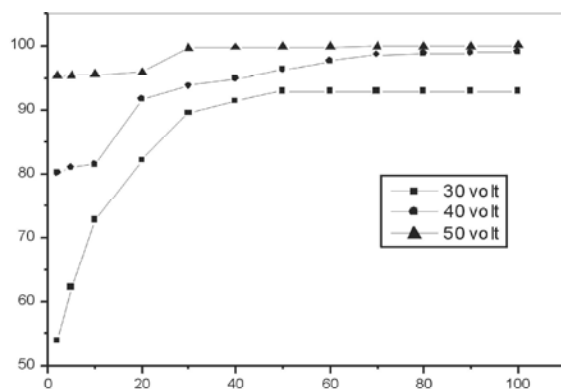Fig. 6: Variation of pH of pyrogallol with time. [Pyrogallol]: 0.30 mg/L

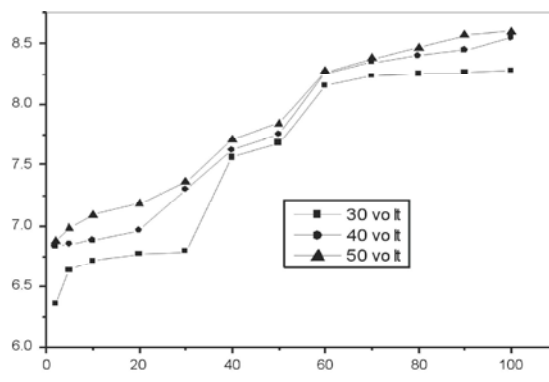Fig. 4: % Removal efficiency of Pyrogallol(0.5 mg/L) versus Time.

Fig. 7: Variation of pH of pyrogallol with time. [Pyrogallol]: 0.50 mg/L

Al^{3+} and its hydrolysis products, whereas the contribution from Na^+ through double-layer compression is insignificant.

The conductivity can strongly affect the electrolysis voltage, as shown in Table 1. At constant current density and at electrolysis time, as the appliedvoltage between electrodes increased the conductivity increased for the electrocoagulation cell. As it has been established forrestaurant wastewater [16], the removal efficiency foroil and grease, COD and suspended solids was notsignificantly affected byvariation in conductivity,but in electrolysis voltage, the higherthe conductivity,
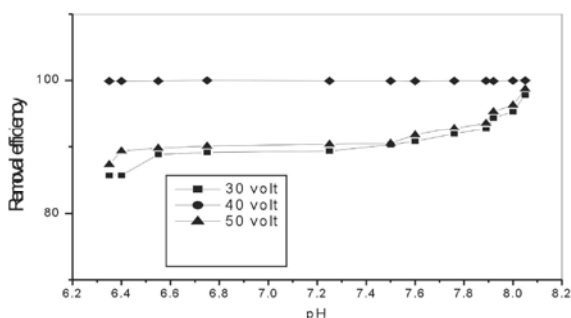
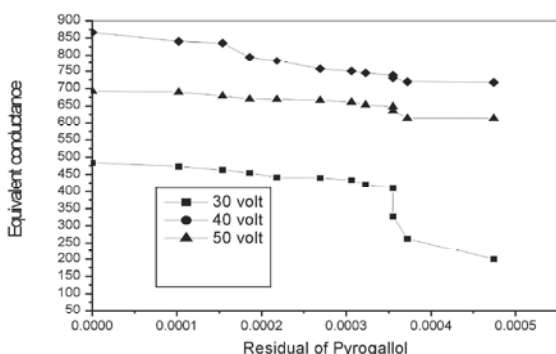Fig. 8%: Removal efficiency of pyrogallol versus pH at initial concentration of 0.1 mg/L

Fig. 9: Equivalent conductance versus residuals of 0.1 mg/L pyrogallol

Table 1: Equivalent conductance of pyrogallol solutions

Time (min)	Equivalent conductance (cm²/ Ù eq)		
	30 V	*40 V*	*50 V*
2	200	613.8	717.54
5	263.1	614.1	719.54
10	327.4	635.9	729.99
20	410.1	647.8	738.46
30	420.3	652.9	745.04
40	433.4	661	750.48
50	439.7	665.7	757.31
60	441.6	668.8	782.14
70	454.8	669.5	794.39
80	463.2	678.7	835.6
90	473.5	689.9	840.8
100	483.6	692.4	866.4

Current density: 0.04 A/m², voltage: 30, 40 and 50 V, [Pyrogallol]: 0.10 mg/L

the lower the electrolysis voltage.This feature of the conductivity is used to lowerthe powerused inthe treatment,and consequently,to lower the operation costs.

Pyrogallol Removal Kinetics: In the electrocoagulation process, the removal rate of pyrogallol is proportional to the amount of hydroxyl cationic complexes (e.g. $Al(OH)_3$), which can effectively remove pyrogallol. Further, the
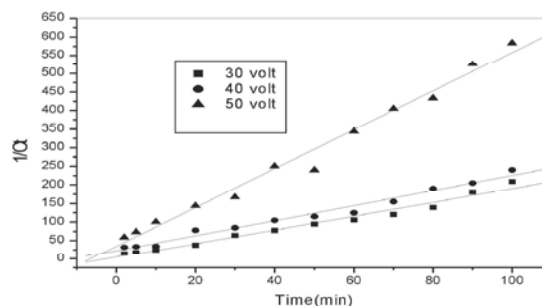

Fig. 10: Variation of $1/C_t$ with t at 30, 40 and 50 V using initial pyrogallol concentration of 0.5 mg/L and AC source.
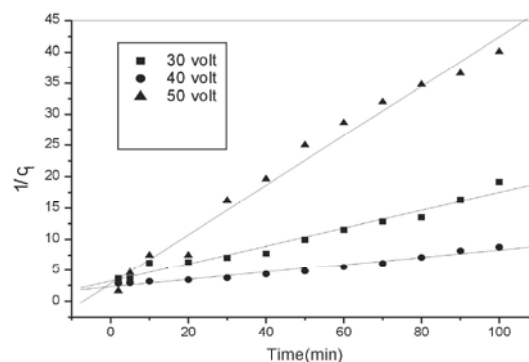

Fig. 11: Variation of $1/C_t$ with time at 30, 40 and 50 V using initial pyrogallol concentration of 0.3 mg/L and AC source.
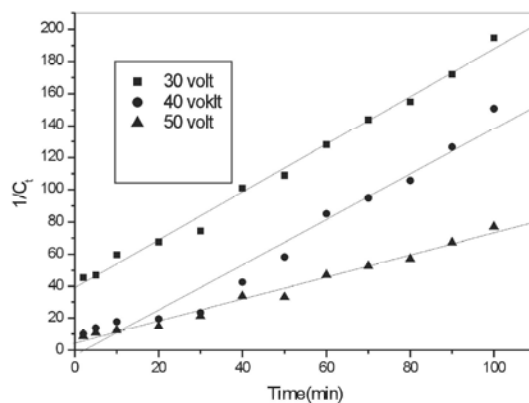

Fig. 12: Variation of $1/C_t$ with t at 30, 40 and 50 V using initial pyrogallol concentration of 0.1 mg/L and AC source.

applied current density determines the rate of aluminum hydroxide production. The overall electrocoagulation process in terms of the apparent kinetics of pyrogallol removal is described by a pseudo kinetic model in which the rate constant depends on the current density. In order

Table 2: Pseudo-kineticrateconstantswith second-ordermodelsfor pyrogallol removalatconstantcurrentdensity of 0.04 A/m^2

Voltages (V)	k_2(L/mg min)	R^2
	0.1 mg/L	
30	0.06043±0.00352	0.9962
40	0.14313±0.0082	0.9822
50	0.3963±0.00170	0.9915
	0.3 mg/L	
30	1.85732±0.00893	0.9313
40	1.41373±0.0855	0.9835
50	1.48762±0.04115	0.9903
	0.5 mg/L	
30	1.85732±0.00893	0.9885
40	2.02941±0.09397	0.9844
50	5.23567±0.21542	0.9916

to investigate the adsorption processes of pyrogallolon hydroxyl cationic complexes, a second order kinetic model were used. For a pseudo-second-order kinetic model, the integrated rate law is:

$$1/C_t = k_2t+1/C_0$$

As seen in Figure 9-12, a pseudo-second-order kinetic model provided a good fit to the experimental results for various initial pyrogallol concentrations and various voltages. It can be ascertained that a higher value of regression coefficient of R^2 (~0.99) for the pseudo- second order kinetics confirms that the adsorption process of pyrogallol on hydroxyl cationic complexesis more appropriately followed by the pseudo– second-order kinetic model. The values of k_2 obtained from the slope are shown in Table 2.

CONCLUSIONS

The best removal efficiency obtained was 100% using an aluminum electrode, the initial pH was 6.30, the cell operation time was 100 min from the initial concentration of 0.5 mg L^{-1} of pyrogallol and current density was 0.04 A m^{-2} at 50V. A pseudo-second-order kinetic model provided a good fit to the experimental results of the adsorption process at various applied voltages, indicating that pyrogallol precipitation in an aqueous solution was attributable to the alternating current electrocoagulation (ACE) process.

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