Pulse Electrocoagulation Applied on Dyeing Wastewater Decoloration Treatment

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Abstract. This study examined the possibility to remove color causing-compounds from effluent by pulse electrocoagulation. For better result, this work is focused on the comparison of energy saving effect at different current density, pulse frequencies. During the pulse electrocoagulation experiment using sacrificial aluminium electrodes operated at an electrical potential of 30 V. A factorial design was applied for optimization of working conditions of the pulse electrocoagulation experiments. In all tested cases, a decrease of the color removal time was observed with the increase of current density, it depends very much upon the pulse frequency. The energy consumption during electrocoagulation process were also discussed. The results indicated that the optimum conditions for the treatment of dyeing wastewater were achieved at temperature:25℃, and inter-electrode distance:5 cm, voltage is 30V, the initial PH is about 8,pulse frequency is 1000Hz,Operating time is 20min.Finally, the technical-economical analysis results have clearly shown that the pulse electrocoagulation method is very promising for dyeing wastewater treatment.

Introduction

Recently, there has been a concerted effort from both the government and academia towards recognition of the importance of water and the severity of pollution problems, as well as the need for preservation and development of water resources.

Dyeing wastewater has been one of the most difficult problems for prevention of water pollution. Dye stuff is the major contaminant in the textile effluent and must be removed before discharging the effluent into an aqueous ecosystem, because the polluted effluent seriously affects both the aesthetic quality and water transparency even at low concentrations[1].It`s a significant source of environmental pollution. Such as high chemical oxygen demand (COD) concentration, strong color, highly fluctuating pH and low biodegradability. The dyeing industry utilizes about 10,000 different dyes and pigments[2]. As much as 20–50% of reactive dyes used in dyeing fabrics can be released into waterways[3].Colour usually appears as the result of the presence of low concentrations of specific compounds, such as azo dyes, which is the most common group of dyes used[4].There are dyes which are recalcitrant and toxic substances, they are resistant to biological degradation. Moreover, dyes molecules are highly structured molecules that are potentially toxic to organisms[3]. Therefore, it is difficult to degrade them biologically.

The main techniques available in the literature for the decolorization of wastewaters involve adsorption, precipitation, chemical degradation, electrochemical, photochemical, enzymatic biodegradation processes includes biological aerobic or anaerobic treatments, membrane separation, chemical coagulation/flocculation and electrolytic treatments, which include electrooxidation, electroflocculation, and/or electrocoagulation[5, 6, 7, 8].

Although above 90% of COD removal for dyeing industry wastewater can be achieved using usual wastewater processes, the color removal is not so effective and has become a big challenge over the last decades[9]. The primary treatment or second treatment holds the important status in the entire process, which will affect the biochemical process effect directly. Energy consumption is an important factor influencing the cost of dye wastewater treatment. It has been indicated that the pulse current could decrease the energy consumption during pulse electrocoagulation dye wastewater treatment. Compared with other methods, there were a few advantages for the treatment of dyeing wastewater by pulse electrocoagulation for the primary treatment or second treatment[10]. The pulse electrocoagulation is considered to be an effective tool for the treatment of dyeing wastewater with high decolorization efficiency and with the formation of relatively low amount of sludge. It has been successfully employed for the removal of dyes[1]. The electrocoagulation is considered to be an effective tool for the treatment of textile wastewater with high decolorization efficiency and with the formation of relatively low amount of sludge[11].What`s more, pulsed electro-coagulation technology has the advantage of lower energy consumption and apply the pulse power electrolysis can eliminate the behavior of anode passivation in the process of electro-coagulation[12]. According to the character of dyeing wastewater from a dyeing plant, the pulsed electro-coagulation is chosen to do the experiment. Key factors affecting on the treatment effect of pulsed electro-coagulation including electrode material, electrolytic time, applied voltage and pulse frequency of dyeing wastewater are investigated.

Pulse electrocoagulation equipment is simple and easy to operate[13]. The pulse Electrocoagulation is a process sacrificial anodes (aluminium or iron electrodes) corrode to creating a floc insoluble of metallic hydroxides within the effluent to be cleaned by electrodissolution of soluble anodes and pollutants are removed by surface complexation or electrostatic attraction, at an appropriate pH value.

Mechanism of the electrocoagulation using aluminium electrodes. Energy consumption could be decreased for the better conductivity due to the masses of salt and the reaction conditions could be easily controlled by changing the electro cell current or voltage, even pulse frequency. The fine bubbles and poly-nuclear hydroxy complexes produced by the electrocoagulation were effective to float and coagulate the dyes[14]. Pulse Electrocoagulation has the advantage of removing small colloidal particles which have a larger probability of being coagulated due to the electric field that sets them in motion as compared with coagulation. The electrical current causes the dissolution of metal into wastewater, and this can form wide ranges of coagulated species and metal hydroxides that destabilize and aggregate the suspended particles or precipitate and adsorb dissolved contaminants.

There several main processes occur during electro-coagulation[14, 15, 16]: electrolytic reactions at the surface of electrodes, formation of coagulants in aqueous phase, adsorption of soluble or colloidal pollutants on coagulants, and removal by sedimentation and floatation. In the case of aluminum, main reactions are as:

$$2H_2\mathrm{O} + 2e^- \rightarrow H_2 + 2OH^- \quad (1)$$

$$2\mathrm{Al} + 6H_2O + 2OH^- \rightarrow 2\mathrm{Al(OH)}^- + 3H_2 \quad (2)$$

Precipitation:

$$\mathrm{Dye} + \mathrm{monomeric\ Al} \rightarrow [\mathrm{Dye} - \mathrm{monomeric\ Al}](\mathrm{s}) \quad (3)$$

OR

$$\mathrm{Dye} + \mathrm{polymeric\ Al} \rightarrow [\mathrm{Dye} - \mathrm{polymeric\ Al}](\mathrm{s}) \quad (4)$$

Adsorption:

$$\mathrm{Dye} + \mathrm{Al(OH)}_3(s) \rightarrow\rightarrow [\mathrm{particle}] \quad (5)$$

$$[\mathrm{Dye} - \mathrm{polymeric\ Al}](\mathrm{s}) + \mathrm{Al(OH)}_3(s) \rightarrow\rightarrow [\mathrm{particle}] \quad (6)$$

These flocs polymerise as :

$$\mathrm{n\ Al(OH)}_3 \rightarrow \mathrm{Al}_n\mathrm{(OH)}_{3n} \quad (7)$$

Hence, soluble and insoluble pollutants can be coagulated by aluminium hydrates or hydroxide aluminium, and effectively removed from effluent[17].

The purpose of this study is to conduct an experimental investigation on the removal of a reactive dyeing dye from real dyeing wastewater solution using a plus electrocoagulation process method in different experimental conditions. In order to obtain optimal reactor performance for a pollutant removal, a statistical design was applied. The effects of current density, pulse frequency, and electrolysis time on pollutant removal efficiency have been investigated. The costs of pulse EC treatment were evaluated and compared with different research parameters.

Materials and methods.

Samples. The wastewater was collected from an equalization tank of a wastewater pretreatment, which is a by-product of textile factory located in a typical dyeing and finishing industry cluster in zhejiang province, China. The plant is responsible for the centralized treatment of wastewater from more than one hundred mills in this industry cluster. The plant employed a typical secondary treatment process including primary sedimentation, hydrolytic acidification, oxidation ditch and secondary sedimentation in sequence. After sampling a mixture of all samples was collected in order to obtain a homogenized wastewater pre-treatment. The characteristics of dyeing wastewater are displayed in Table 1 below.

Table.1 Characteristics of tested wastewaters

Tested wastewater	pH	Temperature (℃)	Color (°)	COD(mg/L)
pretreatment wastewater	8	25	500	800

Before the pulse electrocoagulation treatments, all dyeing wastewater effluent samples were preserved at 6℃once received at the laboratory, and were brought to room temperature prior to pulse electrocoagulation testing.

The optimum conductivity was adjusted by current, which was adjusted using proper amount of NaCl. For pulse electrocoagulation experiments, the optimal working pH values are suggested to be in the range of pH from 7.5 to 9.0[18]. The PH of pretreatment wastewater is about 8, therefore, the initial pH of the effluent was left unaltered.

Experimental apparatus. In the present study, a laboratory-scale pulse electrocoagulation reactor consisting of 8L container was built from polyethylene material and used.

In order to access the effect of electrocoagulation, at the lower part of the reactor, two active identical Al electrode plates (9cm width×20cm length×0.2cm thick, 99.5% purity, China) were firmly assembled in an upright position and arranged parallel to each other with a gap between the anode and cathode plates using a non-conducting horizontal adjustable support to avoid any short-circuits. That were installed at 2 cm from the bottom of the cell and were situated 5 cm apart. The electrodes were operated in mono-polar mode and connected to terminals of direct current power supply (Instrutemp DC Power Supply, containing internal digital ammeter and voltmeter), which provided stabilized currents and voltages in the range from 0 to 10 A, and from 0 to 60 V, respectively. Figure 1 showes the schematic diagram of used experimental set up. A potential of 30 V was held constant during the treatment at room temperature of 25℃.

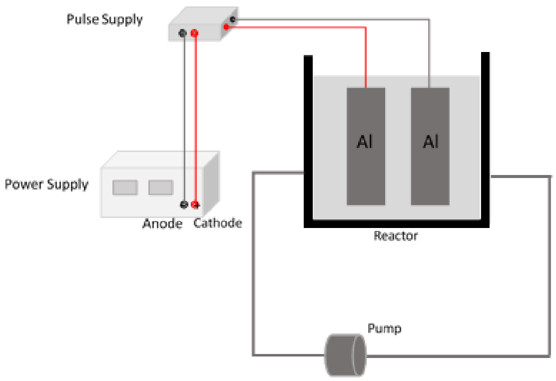

Fig.1 Experimental set-up used for pulse electrocoagulation

Table.2 The parameter of pulse electrocoagulation

pulse frequency(Hz)	current A	current density(mA/cm^2)
100	0.935	5
500	1.87	10
1000	2.805	15
1500	3.74	20
2000	4.675	25

Experimental procedure. Based on the factorial design, different pulse electrocoagulation experiments were performed, where the electrolysis time was a control parameter and the following conditions were applied: initial pH equals to 8, 5.0 cm internal electrode distance, and 180cm^2 plate area. The parameter of pulse electrocoagulation are displayed in Table 2 below.

At the beginning of the experiment, the electrocoagulation cell was thoroughly washed and rinsed with deionized water followed by rinsing with the sample solution. To achieve a better mass transfer in the electrochemical reactor, a peristaltic pump (Model MN2 type) was used to circulate the electrolyte. The current density（voltage and current）was adjusted to a desired value.

The samples were taken at every 5min up to 60 min for color analyses, such as at 5 min,10 min,15 min,20 min,25 min. At the end of each run, all samples were filtered with 0.45 mm filter paper (China) and then the filtrate was used for colority determined by dilution method[19]. All the procedure were carried out with ultrapure water.

All the experiments were repeated, and the experimental error was below 3%. And all analytical measurements were done in triplicate.

Result and discussion.

Results from effects of operating parameters including pulse frequency, current density and electrolysis time to obtain the optimum conditions for the decoloration were presented and discussed in this section. The significance of the pulse frequency and current density values effects and their combined actions on final color and energy consumption values were confirmed by the application of ANOVA analysis. The energy consumption values for pulse electrocoagulation reactor working also shown in figure 2 and figure 3.

Effect of current density on decoloration of dyeing wastewater. The current density is one of the main operating parameters which affect performance of the pulse electrocoagulation process and operating cost. It was needed to limit the current density in order to avoid excessive oxygen evolution as well as to eliminate other adverse effects, like heat generation [11].

Therefore, 25 mA/cm^2 was chosen as the highest current density in our experiments. Figure 2 shows energy consumption when cell current density was varied from 5mA/cm^2 to 25mA/cm^2 at five different density currents. A decrease of the color removal time was observed with the increase of current density. The color removal process may involve electrochemical oxidation and adsorption by electrostatic attraction and physical entrapment[20].The highest cell current produced the quickest treatment reduction occurring after 20 min when the pulse frequency was 1000Hz.

In pulse electrocoagulation it is the current density (mA/cm^2) that determines dosage rate for the release of aluminum ions required to form Al-hydroxide. Equally, cathode hydrogen evolution increase proportional to the electric field strength, driven also by the current density. Moreover, the rate of bubble-generation increases and the bubble size decreases with increasing current density; both of these trends are beneficial in terms of high pollutant-removal efficiency by H_2 flotation[21].

Effect of pulse frequency. Figure 3 shows the change in energy consumption during the reaction period at various pulse frequency. An inverse response of energy consumption with pulse frequency during the electrochemical experiment was observed, this being characteristic behavior of complex processes[22]. what`s more[23], because at the beginning of the process the electrode surface is smooth and the energy supplied is directly proportional to the amount of metal ion generation, which in turn is related to floe formation.

It is considered that when pulse electrocoagulation effluent treatment is applied at industrial

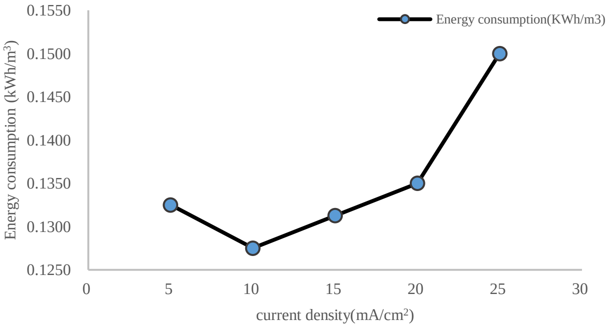

Fig.2 Effect of pulse frequency on the Energy consumption

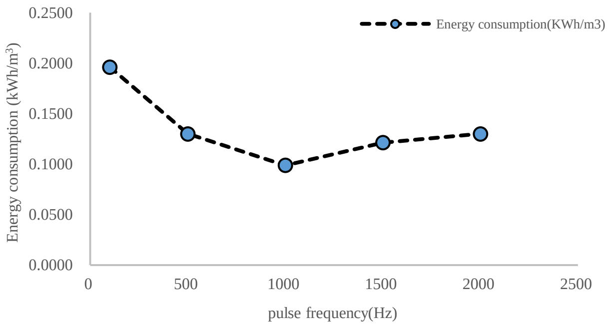

Fig.3 Effect of pulse frequency on the Energy consumption

scale the method is evaluated through the operational cost analysis. In the pulse electrocoagulation process, the amount of energy consumption and the amount of electrode material are two important parameters that should be taken into account to estimate the pulse electrocoagulation reactor operational costs such as RMB per m^3 of the treated dyeing wastewater. We just analysis the Energy consumption of per m^3. Equation (8) evaluates the electrical operational cost, where the electrical energy consumed is calculated in kWh per m^3 of the treated dyeing wastewater.

$$\text{energy consumption} = \frac{\text{UIT}}{V} \quad (8)$$

where: U, I, T, and V represent the applied voltage to the electrodes (V), the current passing through the electrodes (A), the electrocoagulation time (H) and the volume of the treated wastewater (L), respectively. The unit of energy consumption is Kwh^{-1} per m^3.

Conclusion

In this work, the decoloration removal efficiency of pulse electrocoagulation technique (aluminium electrodes) applied on a pretreatment wastewater was studied. What`s more, a factorial design was applied for optimization of working conditions of the pulse electrocoagulation experiments.

Pulse electrocoagulation is an efficient process, even at high pH, for the removal of color and total organic carbon in reactive dyes textile wastewater[24]. The efficiency of the process is influenced strongly by the current and the time of the reaction and pulse frequency. In all tested cases, a decrease of the color removal time was observed with the increase of current density, it depends upon the pulse frequency. In consideration of treatment effect and energy consumption, the optimum operation condition of the equipment are as follows: Al is used as the electrode material, voltage is 30V, the initial PH is about 8, pulse frequency is 1000Hz, Operating time is 20min.Optimal electrolysis time and current density were determined to achieve a decoloration yield between 90 and 95% removal, therefore, this can make the wastewater meet the discharge standards of dyeing wastewater.

From the results of these studies[25, 26, 27], electrocoagulation may prove to be not only feasible and environmentally-friendly, has advantages in decoloration efficiency and low energy consumption, but also more technical and economical superior to conventional technology[13].Moreover, test series must be performed using different configurations and settings before pulse electrocoagulation-technology become widely accepted for industrial applications. Therefore, testing and improvements involving continuous operation, for industrial and municipal wastewater treatment applications, will be the main research filed in the future. Since the advantages of this method are a low material and energy consumption. The amount of produced sludge was low[11]; sludge disposal and management costs would be reduced. This method should be used cautiously for treatment of textile wastewater due to the formation of intermediate compounds.

The pulse electrocoagulation method has shown a great potential in the decoloration from dyeing wastewater. Its advantages can be extended to many industrial applications. In the future, we will focus on using a pulse electrocoagulation treatment coupled with an adsorption in the batch system as well as a continuous wastewater treatment system. Consequently, this technology is suitable for the printing and dyeing wastewater`s treatment and its reuse.

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