Degradation of Painting Ink Wastewater in a Tubular Reactor with Electrochemical Treatment

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In the present study, electrochemical treatment experiments were conducted to degrade water-based printing ink wastewater. It was performed with ruthenium oxide coated titanium acting as anode and stainless steel tube as cathode. Electrolyses carried out in batch under steady conditions and operating at constant flow velocity between 0.538×10^{-3} and 6.129×10^{-3} m/s. The evolution of color and COD removal, the value of pH were found to be inter-related. The kinetics for the concentration decays of the wastewater pseudo first-order reaction that is characteristic for a mass transfer controlled operation. The mass transfer coefficient kc increased with increasing flow velocity and Reynolds number. The evolution of color and COD removal, the value of pH were found to be inter-related. The effect of the parameters on current efficiency and energy cost has also been investigated. The tubular electrochemical reactor could be considered a feasible and an effective alternative system for the electrochemical treatment of water-based printing ink wastewater.

1. Introduction

Water-based ink as the environmental-friendly material has been widely used in printing the packaging of food, drug, toy, wine product and so on. One of the main problems generated from the printing process is the production of wastewater. Painting ink wastewater contains a large number of compounds, such as pigments, binders, carriers and additives (Gecol et al., 2001). The wastewater is intensely colored, with high organic concentration due to the above-mentioned compounds, and therefore, cannot be directly discharged into receiving streams or onto land without any treatment due to its deleterious effect on human health and the environment (Metes et al., 2001)..

A large range of conventional treatment methods have been proposed: coagulation, fenton process, bacteria (Roussy et al., 2005). Many researchers had investigated the coagulation of printing ink wastewater with polyaluminum chloride, zeolite, magnesium chloride (Metes et al., 2004). In the sense, electrochemical technologies have been proposed for the treatment of various effluents. Their main advantages are practically no consumption of chemicals and no production of slugde during the process. On the other hand, commonly the processes are carried out at room temperature and atmospheric pressure, thus reducing the possibility of volatilization and discharge of untreated residues. In the sense, electrochemical technologies have been proposed for the treatment of various effluents. Their main advantages are practically no consumption of chemicals and no production of slugde during the process. On the other hand, commonly the processes are carried out at room temperature and atmospheric pressure, thus reducing the possibility of volatilization and discharge of untreated residues.

An electrochemical procedure has been found to be the most suitable because of the economics and scale of wastewater purification operations. There are different configurations of electrochemical reactors employed for the electrochemical oxidation of various types of wastewater. The tubular electrochemical reactor has been developed in recent years. It has a large length-diameter ratio and little distance between electrodes to enhance mass transfer and reduce cell voltage. The fluid in the reactor presents plug flow. Synthetic wastewaters contaminated with a wide variety of organic pollutants such as olive oil, phenol, paint were investigated by the tubular electrochemical reactor (Korbahti and Tanyolac, 2009).

In this work, the study is focused on degradation studies of water-based printing ink wastewater for removal of chemical oxygen demand (COD) and color using tubular electrochemical reactor. The various factors affecting the electrochemical degradation are studied using catalytic anode of titanium mesh coated with ruthenium oxide. With this study, application of the tubular reactor for electrochemical oxidation of water-based painting ink wastewater was realized for the first time in literature.

2. Material and method

The water-based printing ink wastewater was obtained from an ink chemical company located in Hangzhou, China. The main components of the wastewater sample were water, acrylics, ethanolamine, phthalocyanine blue, phthalocyanine green, azo dyes. This wastewater was neutral (pH 7.3-8.0) and intense black in color. Its concentration of COD ranged 600-1600mg/L. The efficiency of wastewater treatment process was mainly evaluated in terms of the color and COD removal. The tube wall was constructed of organic glass, $\Phi 65 \times 608$ mm, effective volume was 2 L. The Ti/RuO_2 electrode was used as the anode material, $\Phi 25 \times 500$ mm. It was originally designed and manufactured for DC electric motors to endure high voltage and current loads. The stainless steel wall of the reactor was used as cathode, $\Phi 63 \times 500$ mm. The anode and cathode were placed coaxial shaft, the distance between electrodes was 19 mm.

A total of 2 L of printing ink wastewater was poured into the reservoir and fed to the column to fill it completely and then recycled with the application of the specified current and voltage. To investigate the efficiency of electrochemical activities, galvanostatic electrolysis was performed in the wastewater. To study the effect of flow velocity of the electrochemical cycling process on printing ink wastewater viability, the solution was exposed to the flow velocity ranging from 0.538×10^{-3} to 96.8×10^{-3} m/s. The oxidation experiments were performed at a current density of 20.000 mA/cm^2, and imposing sodium sulphate as the supporting electrolyte with a concentration of 4.5 g/L. At appropriate time intervals, 20 mL samples were taken from the reservoir for analysis to determine the rate of COD and color removal, pH of the reaction medium during electrochemical conversion. The initial samples of 100 mL without any treatment were taken from the reservoir as the control samples. It is also important to know how electrochemical oxidation affects the composition of the wastewater. Analyses were undertaken in triplicates. Absorbance spectra of printing ink wastewater were analyzed using the UV-2910 spectrophotometer (Shanghai, China). COD was determined in accordance with the fast digestion-spectrophotometric method (HJ/T 399-2007). The pH was measured using PHS-25C meter. The electrical conductivity was measured using the conductivity meter (Seven Easy).

3. Result and discussion

3.1 Degradation behavior of printing ink wastewater in the flow plant

To elucidate the degradation behavior of water-based printing ink wastewater in the electrochemical tubular reactor, the removal efficiencies of color and COD of real wastewater were conducted under different flow velocities with a constant current density of 20.000 mA/cm^2 and an electrolyte concentration of 4.5 g/L. Experimental results were presented in Figure 1

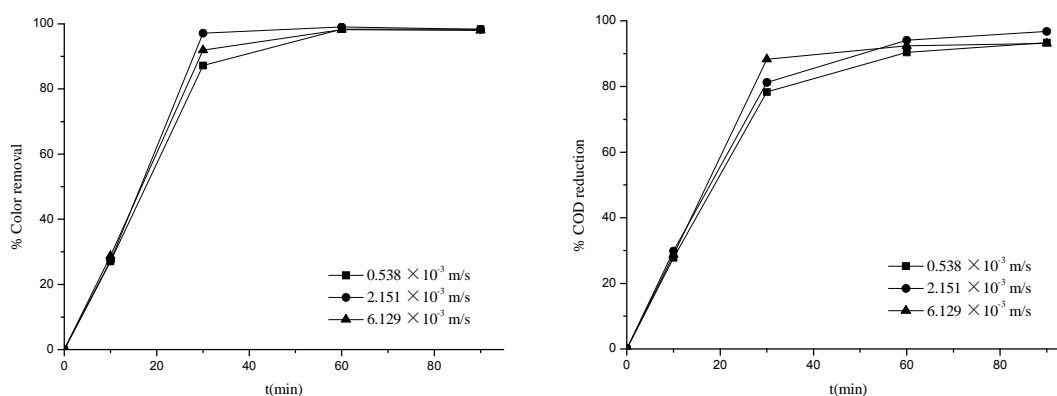
Figure 1: Effect of flow velocity and electrolysis time on color and COD removal by electrochemical process; (b) Symbols: (■) 0.538×10^{-3} m/s; (●) 2.151×10^{-3} m/s; (▲) 6.129×10^{-3} m/s.

As shown in Figure 1, for an initial absorbency of 2.09~2.24, the color removal increased rapidly in proportion with the electrolysis time, and reached gradually a nearly constant value of 97.9~99.0% after the electrolysis time of 60 minutes. The influence of flow velocity on the color removal was small. When the flow velocity increased from $0.538×10^{-3}$ to $6.129×10^{-3}$ m/s, the color removal efficiency increased accordingly from 87.2% to 97.1% for an electrolysis time of 30 minutes. However, the differences were indistinct as the flow velocity was over $6.129×10^{-3}$ m/s, which indicated that when the liquid flow was higher than $96.8×10^{-3}$ m/s, the color removal was no longer mass-transfer controlled (Zhou et al., 2004).And the COD removal under different flow velocities during the electrooxidation of water-based printing ink wastewater. For an initial COD concentration of 600~1600 mg/L, the COD removal efficiency increased and reached a constant value of 90.4%~94.1% after the same electrolysis time of 60 minutes. The COD removal influenced by the flow velocity was similar to decolorisation. The COD removal efficiency increased from 78.4% to 88.3% for an electrolysis time of 30 minutes as the flow velocity increased from $0.538×10^{-3}$ to $6.129×10^{-3}$ m/s, which indicated that most organic substrates in the wastewater have been mineralized in treatment. Only after that, the aromatic rings are prone to be degraded, thus contributing to the continuation of the COD removal.

With the assumption of direct electrochemical reaction and mass transport limitations, a valid equation for describing the COD changes during electrochemical oxidation was presented as following.

$$\ln\left(\frac{C_{org}}{C_{org,0}}\right) = -\frac{k_c A}{V} t \tag{1}$$

where C_{org} is the concentration of the pollutants at time t, $C_{org,0}$ is its initial concentration, A is the area of the anode, V is the volume of the printing ink wastewater in the tank, and k_c is the value of the apparent reaction rate constant.

According the equation, the concentration of the pollutants (e.g. COD) was related to A/V value, electrolysis time and mass transfer coefficient. As a given experimental set, the A/V value was fixed, the concentration of the pollutants was only related to t and k_c. A semi-logarithmic representation of COD concentration decays via t (electrolysis time) was listed in Figure 2.
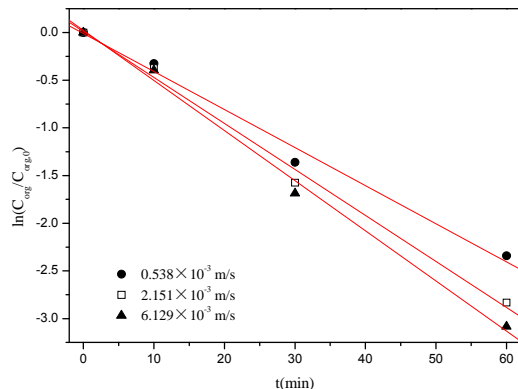

Figure 2: A semi-logarithmic representation of concentration decays
Symbols: (■) $0.538×10^{-3}$ m/s; (●) $2.151×10^{-3}$ m/s; (▲) $6.129×10^{-3}$ m/s.

As shown in Figure 2, the COD concentration decays fit well with a pseudo-first-order kinetic pattern, which is characteristic for a mass transfer controlled operation. The apparent reaction rate constants of water-based ink printing wastewater during electrooxidation were in Table 1.

Table 1: The apparent reaction rate constant of water-based ink printing wastewater during electrooxidation

flow velocity	K_{obs}/min^{-1}	R^2
$0.583×10^{-3}$m/s	0.03994	0.9897
$2.151×10^{-3}$m/s	0.04828	0.9936
$6.129×10^{-3}$m/s	0.05258	0.9945

From Table 1, it indicated that the flow velocity enhanced the transport of pollutants and its products to the Ti/RuO$_2$ anode surface, which was benefit for the reaction occurring on the anode surface. Under the tested conditions of relatively high current density and low compound concentrations, kc in Eq.(1) actually represents the average mass-transfer coefficient of the target compound over the electrochemical cell and the reservoir (Santos et al, 2010). The kc increased from 0.03994 min^{-1} to 0.05258 min^{-1} as the flow velocity increased from 0.538×10^{-3} to 6.129×10^{-3} m/s. In an electrochemical reactor, mass transfer coefficient is related to the physical properties and hydrodynamics of flow.

At a given flow, the flow velocity made significantly influences on mass transfer, which in turn affect the electrochemical oxidation, adsorption and desorption (Zhou and Lei, 2006). The mass transfer coefficient in engineering literature was generally express as Sherwood number in terms of Schmidt and Reynolds numbers. Reynolds number is known as the ratio of the inertial force to the viscous force and can be defined with the tube linear velocity and its diameter. In this experiment, the density of water-based printing ink wastewater was 0.9955×10^3 kg/m^3, and its kinematic viscosity was 0.8036×10^{-6} m^2/s. For the tubular electrochemical reactor, the Re was in the range from 25.4 to 289.8 at the flow velocity varying from 0.538×10^{-3} to 6.129×10^{-3} m/s, known as laminar flow.

When the flow presented laminar flow, the hydrodynamic entrance length for the channel of relatively small distance between electrodes was calculated from the equation

$$L_h/d_e = 1.12×10^{-2}Re \tag{2}$$

The flow at l(l < L$_h$) was considered to the unfolding flow, and the flow at l(l > L$_h$) was considered to the unfolded flow. In our study, the length of the reactor l was less than the hydrodynamic entrance length L$_h$ indicating that it presents the unfolding flow. For the unfolding flow, the laminar flow mass transfer equation can be written as:

$$Sh_{av} = 0.96(L/d_e)Re^{1/2}Sc^{1/3} \tag{3}$$

According to Eq.(3), the diffusion coefficient of water-based ink printing wastewater can be calculated as 5.85×10^{-8} m^2/s. The flow velocity was varied in the range of 0.538×10^{-3} to 6.129×10^{-3} m/s, corresponding to a mass-transfer coefficient in the cell, of about 2.03×10^{-5} to 2.68×10^{-5} m/s. It indicated that mass-transfer coefficient increased with increasing flow velocity and Reynolds number. The film resistance i.e. stagnant film thickness around the electrodes proportionally decreases with increasing flow rate within the reactor resulting in enhanced mass transfer rate.

3.2 The effect of solution pH during electrolysis of printing ink wastewater
The initial pH of the wastewater was appreciably different because the water-based ink printing wastewater was real wastewater, with the fluctuant range of 7.5 to 8. The pH change profile of the outlet of tubular reactor via time during the electrolysis process was shown in Figure 3 as the flow velocities were varied from 0.538×10^{-3} to 6.129×10^{-3} m/s.
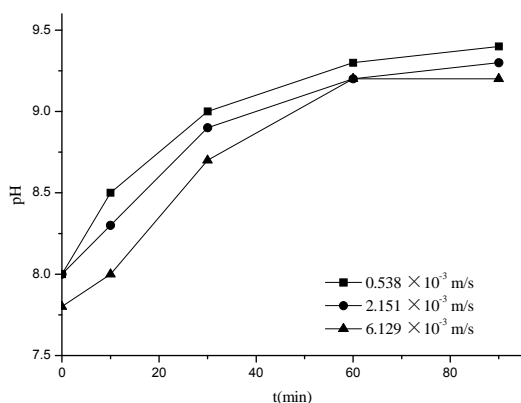

Figure 3: Effect of flow velocity and electrolysis time on pH of the solution by electrochemical process
Symbols: (■) 0.538x10^{-3} m/s; (●) 2.151x10^{-3} m/s; (▲) 6.129x10^{-3} m/s.

As the settling time increased, the pH value raised from an average value of 7.5 to 9.4. The trend in pH can be explained by the products formed on both electrode surfaces. There was an occurrence of the water reduction with the consequent hydrogen evolution and an increase of the pH due to the formation of hydroxyl anions on

the cathode. In opposition to the hydroxyl formation in the cathodic side, the formation of different organic acids resulted in the pH drop. This variation on the pH to lower values has not the same magnitude of the pH increasing in the cathodic side (Motheo and Pinhedo, 2000).

3.3 Current efficiency and energy cost for the electrooxidation process

Measurements of instantaneous current efficiency (ICE), defined as the current efficiency measured at a particular time or at constant time intervals during the treatment of wastewater, give information about the electrochemical oxidation process. ICE was calculated by the COD method as the following relation:

$$ICE = \frac{COD_t - COD_{t+\Delta t}}{8I\Delta t} \times FV_s \qquad (4)$$

where COD_t and $COD_{t+\Delta t}$ are the chemical oxygen demands at times t and t $+\Delta$t (in g/L), respectively, I is the current (A), F is the Faraday (96487 C/mol) and V is the volume of electrolyte (L).

Measurements of instantaneous current efficiency (ICE), defined as the current efficiency measured at a particular time or at constant time intervals during the treatment of wastewater, give information about the electrochemical oxidation process. ICE was calculated by the COD method as the following relation, the result was shown in Figure 4,
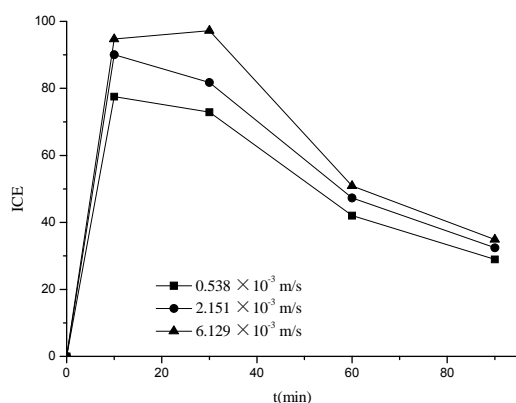

Figure 4: Variation of ICE values with time during the electrochemical process
Symbols: (■) 0.538×10-3 m/s; (●) 2.151×10-3 m/s; (▲) 6.129×10-3 m/s.

As shown in Figure 4, the ICE values increases with raising liquid flow velocity, enhancing the transport of organics to the Ti/RuO$_2$ anode. The maximum value of ICE occurred at the earlier stages of the treatment, but decreased as the treatment proceeded. The ICE value increased to 97.3% at 30 min of the treatment at 6.129×10^{-3} m/s, but it drops up to 72.91% at 0.538×10^{-3} m/s. A dramatic decay in ICE can be explained that the pollutant concentration decreased with increasing the electrolysis time, and then the driving force of mass transfer dropped.

Electrochemical reaction is non-homogeneous reaction occurring on the anode surface. Energy consumption was related to electrolysis process condition and reactor structure. In theory, the energy consumption of 1.204×10^7 C i.e. 3344 Ah, is required to decompose 1 kg COD. In this study, for a water-based printing ink wastewater in 4.5 g/L Na$_2$SO$_4$ at current density of 20.000 mA/cm^2 and the electrode potential of 7.0 V, the actual energy consumption was 38.4 kWh/kg COD within 90min under a flow velocity of 0.538×10^{-3} m/s, higher than the theoretical energy consumption of 23.4 kWh/kg COD. The energy usage ratio of the tubular reactor was 39%, a higher value. In the literature (Raghu and Basha, 2007), the mean energy consumption was determined as 0.2480-16.3034 kWh/g COD removed for the electrochemical treatment of Procion Black 5B in a cylindrical flow reactor consisted of 304 stainless steel cathode and Ti/RuO$_2$ anode placed at the center of the reactor.

Therefore, to enhance the efficiency of tubular reactor, better electrode materials and reactor configuration such as decrease in electrode spacing, should be attempted before industrial applications.

4. Conclusion

The electrochemical treatment of water-based printing ink wastewater in an electrochemical tubular reactor constructed from a stainless tube with a Ti/RuO$_2$ anode at the center was investigated. The oxidation experiments were performed at a current density of 20.000 mA/m^2, and imposing sodium sulphate as the supporting electrolyte with a concentration of 4.5 g/L. Water-based printing ink wastewater was electrolyzed with flow velocity ranging from 0.538×10^{-3} to 96.8×10^{-3} m/s in an electrolysis time of 90 min. The variation of COD and color removal, pH of the reaction medium were examined during electrochemical oxidation. When the flow velocity increased from 0.538×10^{-3} to 6.129×10^{-3} m/s, the color and COD removal efficiency increased from 87.2%, 78.4% to 97.1%, 88.3% for an electrolysis time of 30 minutes. The experimental results indicate that the influence of flow velocity on the color removal was small. The concentration decays of the wastewater fit well with a pseudo-first-order kinetic pattern that is characteristic for a mass transfer controlled operation. The flow at Reynolds number in the range of 25.4 to 289.8, is known as laminar flow. As a general trend, k_c increased with increasing flow velocity and Reynolds number. As the settling time increased, the pH value raised from an average value of 7.5 to 9.4. The ICE values increases with raising liquid flow velocity, the maximum value of ICE occurred at the earlier stages of the treatment, but decreased as the treatment proceeded. The actual energy consumption was 38.4 kWh/kg COD within 90min under a flow velocity of 0.538×10^{-3} m/s. The results indicated that the electrochemical tubular reactor could be a feasible and an effective alternative system for the electrochemical treatment of water-based printing ink wastewater.

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