Electrochemical oxidation of polyethylene glycol in electroplating solution using paraffin composite copper hexacyanoferrate modified (PCCHM) anode

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Abstract: Electrochemical oxidation of polyethylene glycol(PEG) in an acidic (pH 0.18 to 0.42) and high ionic strength electroplating solution was investigated. The electroplating solution is a major source of wastewater in the printing wiring board industry. A paraffin composite copper hexacyanoferrate modified(PCCHM) electrode was used as the anode and a bare graphite electrode was used as the cathode. The changes in PEG and total organic carbon (TOC) concentrations during the course of the reaction were monitored. The efficiency of the PCCHM anode was compared with bare graphite anode and it was found that the former showed significant electrocatalytic property for PEG and TOC removal. Chlorides present in the solution were found to contribute significantly in the overall organic removal process. Short chain organic compounds like acetic acid, oxalic acid, formic acid and ethylene glycol formed during electrolysis were identified by HPLC method. Anode surface area and applied current density were found to influence the electro-oxidation process, in which the former was found to be dominating. Investigations of the kinetics for the present electrochemical reaction suggested that the two stage first-order kinetic model provides a much better representation of the overall mechanism of the process if compared to the generalized kinetic model.

Keywords: polyethylene glycol(PEG); paraffin composite copper hexacyanoferrate modified(PCCHM) electrode; electroplating solution; two stage first-order kinetic model; generalized kinetic model

Introduction

A highly acidic electroplating solution (pH 0.18 to 0.42) with high ionic strength is a major wastewater source in the printing wiring board (PWB) industry. The chemical composition of the recipe solution (sulfuric acid of 60 g/L, $CuSO_4 \cdot 5H_2O$ of 200 g/L and 0.03 g/L of chlorides) makes it difficult to treat with conventional treatment processes (Suzuki, 1976; Andreozi, 1996a). Also, the chemical coagulation method, presently adopted by the industries is not a viable method due to a large amount of hazardous chemical sludge (containing very high concentration of Cu^{2+} ions) produced during the treatment. Recycling or reuse of the solution is inhibited because of the low quality of organics present after electroplating and electrophoresis. Therefore, removal of spent organics in order to add new additives is one of the very important steps for the neutralization process (Chang, 2001).

Polyethylene glycols (PEG: $H-(OCH_2CH_2)_n-OH$) are major organic compounds used as brightening and stabilizing agent during electroplating process (Fang, 1996). It is an important group of non-ionic synthetic water-soluble polymers of ethylene oxide. Several studies have been performed on the biodegradability of PEG's in water since biological oxidation is generally considered the most environmentally friendly and cheapest method of wastewater treatment (Haines, 1975; Watson, 1976, Dwyer, 1983). However, as mentioned earlier, biological treatment cannot work in such highly acidic and high ionic strength solutions.

Decomposition of PEG in electroplating solution by ozone/UV radiation has been reported (Chang, 2001), but this method appears to be uneconomical in both installation and operation. Also, other advanced oxidation processes (AOP's) like Fenton's reagent, H_2O_2/O_3 and H_2O_2/UV oxidation, photocatalytic oxidation, gamma irradiation and ultrasound technique though scientifically feasible are not economically suitable for wastewater treatment (Gulyas, 1997). The limiting factors for using conventional treatment methods, namely, high acidity and ionic strength can be advantageous for the electrochemical oxidation method. In such situations electrochemical oxidation technique appears to be an ideal method for decomposition of PEG in electroplating solution. A high salinity wastewater with 5% w/v chlorides was treated electrochemically to remove organic pollutants (Sheng, 1998). Also, high strength wastewaters from different industries were treated successfully at lab scale by many researchers(Vlyssides, 1997; Canozares, 2002; Bejankiwar, 2003; Bunce, 2003)

In this study, we have carried out the electrochemical oxidation of PEG in a simulated solution(similar to the recipe of electroplating solution of PWB industry) using paraffin composite copper hexacyanoferrate modified (PCCHM) electrode. PCCHM anode has been used extensively in electrochromic devices, power sources, ion-selective electrodes and electro catalysis. Composite electrodes comprising of graphite powder and paraffin along with metal hexaferrocyanoferrates have also been used for the selective determination of alkali metal ions, thallium ions, nickel ions and for pH measurements. Narayanan and Deepa (Narayanan, 2001) have explained in detail the widespread use of PCCHM

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electrode. So far, there is no report on the use of this anode for electro-catalytic oxidation of organics presented in the wastewater. The main reason for selecting PCCHM anode for the present study is because of the fact that this electrode is relatively insoluble on redox cycling as charge neutrality is always maintained via the diffusion of electrolyte ions through the zeolytic structure(Scoltz, 1996).

The main objective of the present study is to evaluate the efficiency of paraffin composite copper hexacyanoferrate modified electrode for oxidation of PEG and to study the kinetics of the process. Measuring PEG concentration and total organic carbon(TOC) concentration during the course of reaction enabled the monitoring of the process efficiency. The experimental TOC concentration data was correlated to the two different kinetic models to establish the kinetics of the process. Kinetic rate constants were evaluated by non-linear regression method using Polymath software and energy consumption was evaluated in terms of kWh energy consumed per kg of TOC removed.

1 Materials and methods

1.1 Electrode preparation

Graphite powder(LOBA Chemicals Ltd., India) was mixed with a precipitate of copper hexaferrocyanate(Merck, Germany) in the ratio of 12:1(Narayanan, 2001) and was then added uniformly to melted paraffin to form a paste-like consistency. This paste was then packed into a plastic mould, which was removed after few minutes to get paraffin composite electrode of the required size. Similar procedure was followed, except for the addition of hexaferrocyanate to get bare graphite electrode.

1.2 Electrochemical reactor

Schematic of a single cell electrochemical reactor used in the study is shown in Fig. 1. The reactor was a 500 ml capacity Plexiglas container with a sampling port at the bottom of reactor. A Testronix 35D Model Dual DC power unit(Muropye, India) equipped with digital current-voltage meter was used as power supply source. A copper wire was used for all electrical circuits. All the experiments were conducted at room temperature with the exception of those for the kinetic study, which were conducted at 25℃, 35℃, 45℃ and 55℃.

1.3 Analysis

Samples were collected at different time intervals and analyzed for PEG and TOC concentration. PEG concentration was determined by conventional HPLC (Beckman, USA) method(Aquagel-OH 40, 300 × 7.5 column) using pure water as mobile phase at 1 ml/min. Detection was done by using a Shimatzu refractive index detector at high sensitivity range of 2×10^{-6} refractive index(Mantzavinos, 1997). A calibration curve was plotted using standard PEG samples. The intermediates (short chain organic compounds) formed during the electrolysis were separated on a Hamilton PRP X-300, 7 m. 250 × 4.1 column using 95:5 water(buffered with
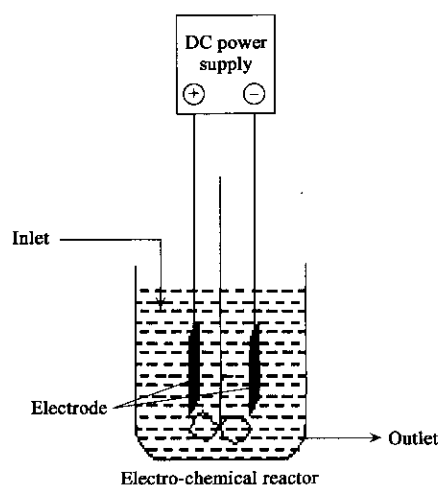

Fig. 1   Schematic diagram of electron-chemical reactor set-up

H_3PO_4): acetonitrile as an isocratic mobile phase at 1 ml/min and their detection was through a diode array detector at 200 nm. Injecting standards of the suspected compounds and comparing their chromatograms to those of the unknown compounds with respect to peak retention times and spectral characteristics, the unknown compound is identified. OIC 700 TOC analyzer (0.1. Corp., Tex.) was used for determination of TOC concentration. The instrument uses the UV-persulfate technique to convert the organic carbon for the subsequent analysis by an infrared carbon dioxide analyzer calibrated with potassium hydrogen phthalate standards. All the samples were analyzed in triplicates to get reproducible results of replication was found to be below 5% in all analyses.

2 Results and discussion

Current density below 0.4 A/cm^2 was found to be too low to give detectable results. Therefore, preliminary electrolysis experiments were conducted at a higher current density of 0.5 A/cm^2 (anode surface area of 8 cm^2), to optimize the electrolysis time, using both bare graphite anode and PCCHM anode. The variations of PEG and TOC concentration during the course of electrochemical oxidation process for both the anodes are depicted in Fig. 2. It is evident from the figure that, with PCCHM anode around 78% of PEG and 79% of TOC removals were achieved after 45 min of electrolysis, while only 35% of PEG and 24% of TOC removals were observed with that of bare graphite anode. This can be attributed to the electro-catalytic oxidation of PEG in solution by hexacyanoferrate. It is worth to note that the concentration of PEG and TOC at different time intervals (for PCCHM anode) was equivalent. This suggested that PEGs are converted into highly unstable intermediates, which further rapidly get oxidized to CO_2 and H_2O. This was supported by the presence of short chain organic compounds such as acetic acid, oxalic acid, formic

acid and ethylene glycol formed during electrolysis as identified by HPLC method.
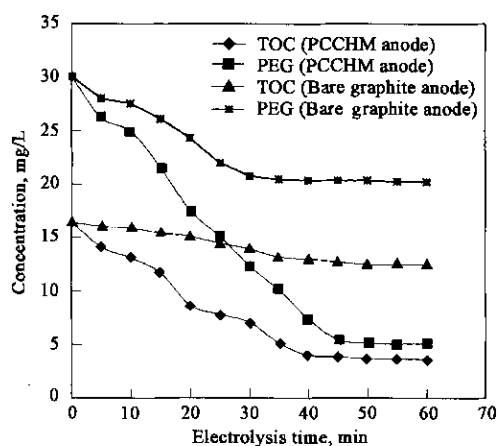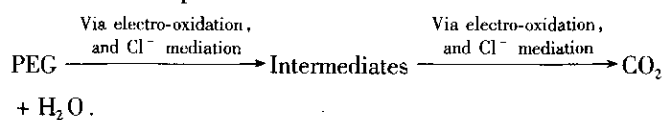

Fig.2 Variation of PEG and TOC during the electrolysis of electroplating solution

Since the electroplating solution was rich in chloride concentration, the indirect oxidation route in which chloride ions take part in oxidation cannot be denied. Therefore, electrolysis experiments were conducted in a simulated electroplating solution of similar composition without any chloride ions. Fig. 3 shows the variations of PEG and TOC concentration during the course of electrolysis in electroplating solution without chlorides. It was observed that around 59% of PEG and 44% of TOC removals could be achieved in chloride-less electroplating solution after 45 min of electrolysis. This suggested that indirect oxidation by chloride ions contribute to around 24% in PEG removal and 44% in TOC removals in the overall electrochemical oxidation removal process. It is also noted that during electrolysis in chloride-less solution the TOC removal obtained was lesser than that of PEG removal. This overrules the possibility of direct oxidation of PEG into CO_2 and H_2O; rather it suggested the simultaneous double route oxidation, which can be represented as follows:

PEG $\xrightarrow[\text{and } Cl^- \text{ mediation}]{\text{Via electro-oxidation,}}$ Intermediates $\xrightarrow[\text{and } Cl^- \text{ mediation}]{\text{Via electro-oxidation,}}$ CO_2
+ H_2O.

The anode surface area and the applied current density are very important factors in any electrochemical oxidation processes; their significant effects on process efficiency have been reported by many researchers (Biwyk, 1980; Matis, 1980; Cenkin, 1985; Lin, 1994; Awad, 1997; Gennaro, 1997). Therefore, experiments were conducted to examine the effect of applied current density and surface area on removal of PEG and TOC. Table 1 gives the summery of results obtained and the conditions maintained during different runs. It is evident from the table that there was a significant enhancement in the rate removal of PEG with increasing current density. The trend is expected based on the greater ability of anodic electro-catalytic surface sites to mineralize, or at least partially oxidize substrate organic to CO_2. This can be also attributed to the fact that the increase in current density increases the ionic transport that in turns increases the rate of electrode reactions. This trend is particularly evident on comparing the oxidation profiles at current density of 0.5 A/cm^2, 1.0 A/cm^2, and 2.0 A/cm^2. By increasing current density from 0.5 A/cm^2 to 2.0 A/cm^2, the electrolysis time required was found to reduce from 45 min to 15 min and TOC removal was found to increase from 79% to 91%. The energy consumption for 1 kg of TOC removal was found to increase from 7.476×10^{-3} kWh to 9.655×10^{-3} kWh. However, the removal efficiency was found to be influenced by more surface area of anode rather than the current density. This can be seen by comparing the PEG removals at anode surface areas of 8 cm^2 and 34 cm^2. The reason is that the graphite surface area rather than the applied current, limits oxidation reactions. Increase in surface area also increases the mass transport, which facilitates the oxidation process. Increase in surface area from 8 cm^2 to 34 cm^2 was found to increase TOC removal from 79% to 93%, and also decreases the electrolysis time from 45 min to 10 min. In this context, it is important to mention that the increase in energy consumption is less in case of increase in surface area rather than the increase in current density.

3 Kinetic studies

Referring to Fig.2, it is evident that at the initial stage

Table 1 Results of electrochemical oxidation of PEG during different experimental runs

| Runs	Anode surface area, cm^2	Current density, A/cm^2	Electrolysis time required, min	PEG, mg/L		Removal, %	TOC, mg/L		Removal, %	Energy consumption, kWh/kg TOC, $\times 10^{-3}$
				Initial	Final		Initial	Final		
1	8.0	0.5	45	30	6.58	78.06	16.3	3.28	79.26	7.476
2	8.8	0.75	30	30	6.50	78.33	16.3	3.28	79.26	7.419
3	8.0	1.0	20	30	6.50	78.33	16.3	3.28	79.88	6.529
4	8.0	1.25	20	30	6.46	78.47	16.3	3.24	80.12	8.134
5	8.0	1.50	20	30	6.32	78.93	16.3	1.54	90.55	9.406
6	8.0	2.0	15	30	6.52	78.27	16.3	2.96	81.84	9.655
7	14.0	0.75	30	30	4.98	83.40	16.3	2.54	84.42	12.44
8	22.0	0.75	15	30	5.55	81.50	16.3	2.96	81.84	9.955
9	28.0	0.75	15	30	3.86	87.13	16.3	1.92	88.22	11.77
10	34.0	0.75	10	30	2.08	93.07	16.3	1.12	93.13	8.653
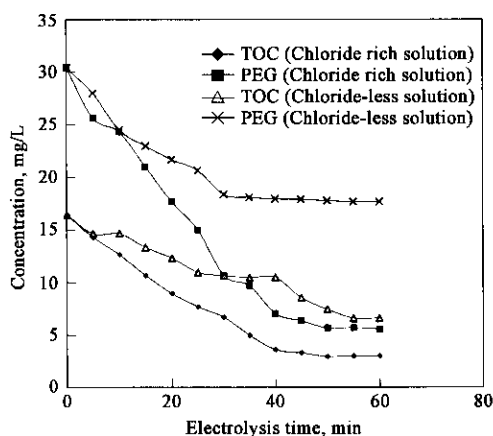
Fig. 3   Variation of PEG and TOC during electrolysis at PCCHM anode in chloride rich and chloride less solution

Fig. 4   Arrhenius plots of kinetic rate coefficients of two-stage first order kinetics

of electrolysis, the change in PEG and TOC concentration is very fast. This pattern of PEG removal suggested the first order kinetics. The intermediates formed during the course of the reaction are identified as acetic acid, oxalic acid, formic acid and ethylene glycol. Therefore, the experimental PEG concentration data is correlated to two different kinetic models based on first order kinetics namely, two-stage, first-order kinetic model and a generalized kinetic model.

3.1 Two stage, first-order kinetic model

This kinetic model can be represented by,

$$\ln\left[\frac{PEG_t}{PEG_0}\right] = - kt , \qquad (1)$$

where PEG_0 and PEG_t are the initial PEG concentration and that at time t respectively, and k is the kinetic rate coefficient which is related to the reaction temperature according to the Arrhenius equation,

$$k = A \times \exp\left[\frac{-\Delta E}{RT}\right], \qquad (2)$$

where A is the frequency factor, E is the activation energy, R is the gas constant and T is the reaction temperature. The observed data of the electrochemical treatment could be represented by a two stage, first-order reaction kinetics represented by Equation (2). The two kinetic rate constant k_1 and k_2 were calculated from the slopes of the straight lines plotted (not reported) according to Equation (1) for each temperature and are given in Table 2. From the table we can see that the first kinetic rate constant k_1 increases with increase in reaction temperature, while second kinetic rate constant k_2 decreases. It means the increase in temperature favors the oxidation of PEG to intermediates and inhibits the conversion of intermediates to final products. The two kinetic rate constants vs. the reciprocal of temperature in semi-logarithmic scale are shown in Fig. 4. The straight lines obtained for both kinetic rates constants are standard Arrhenius plots according to Equation (2). The regression coefficient for the straight line of first reaction constant is 0.988 and that of the second is 0.998.
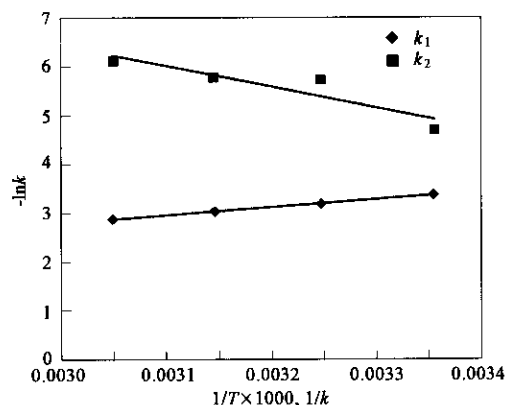
3.2 Generalized kinetic model

This model is based on the assumption that some of the organic pollutants are directly oxidized to the end products (CO_2 and H_2O) in the electrochemical oxidation process, while the rest is firstly converted into intermediate products that are then further oxidized to the final products. This model was proposed by Li *et al* . (Li, 1991) for the wet air oxidation of organics and supported by Lin *et al* . (Lin, 1998) for electrochemical oxidation of saline wastewater. The model can be represented by following reaction sequence:

$$A + O_2 \xrightarrow{k_1} D ,$$

$$A + O_2 \xrightarrow{k_2} B + O_2 ,$$

$$B + O_2 \xrightarrow{k_3} D .$$
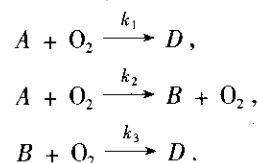
In the above reaction pathway, A represents the PEG and other unstable intermediate organic compounds, B is the refractory intermediate product and D is the end products (CO_2 and H_2O). Assuming a first order kinetics for all reaction paths, the generalized kinetic model is given by

$$\left[\frac{[A + B]}{[A + B]_0}\right] = \frac{k_2}{k_1 + k_2 - k_3}\exp(- k_3 t) +$$

$$\frac{k_1 - k_3}{k_1 + k_2 - k_3}\exp\{ - (k_1 + k_3)t\} , (3)$$

where $[A]$ and $[B]$ are the concentration of species A and B, respectively, in the reaction pathway. In terms of COD, concentrations $[A + B]$ and $[A + B]_0$ are the same as $[PEG]$ and $[PEG]_0$ respectively in Equation (1). The experimental PEG removal data are computed according to Equation (3) for four different reaction temperatures of $25\,℃$, $35\,℃$, $45\,℃$ and $55\,℃$. The fit seems to be quite good (not reported). The kinetic rate constants are calculated using the least square fitting method and shown in Table 2. It is observed that the first kinetic rate coefficient k_1 is increased with the increase in reaction temperature. This is an usual trend, also observed in previous studies (Li, 1999) and Lin *et al* . (Lin, 1998), while no order was observed in second kinetic rate coefficient k_2. It is also observed that

there was no significant change in the second kinetic rate coefficient with the change in reaction temperature.

Table 2　Kinetics rate parameters of the electrochemical oxidation of PEG

Reaction temperature, ℃	Kinetic rate coefficient, min⁻¹					
	k_1	R^2	k_2	R^2	k_3	R^2
Two-stage first order kinetic model						
25	0.0345	0.988	0.0091	0.988		
35	0.0408	0.978	0.0033	0.958		
45	0.0479	0.968	0.0031	0.966		
55	0.0571	0.955	0.0022	0.966		
Generalized kinetic model						
25	0.0197	0.968	0.0176	0.982	0.0019	0.987
35	0.0216	0.988	0.0183	0.984	0.0004	0.997
45	0.0244	0.994	0.0173	0.978	0.0003	0.994
55	0.0267	0.956	0.0174	0.955	0.0002	0.986

The Arrhenius plots for the two kinetic rate coefficients of generalized kinetic model are shown in Fig.5. It is evident that the straight line obtained for first kinetic rate coefficient k_1 is a standard Arrhenius plot as per Equation (2), while that of second kinetic rate coefficient is not. The regression coefficient values for the straight lines of k_1 and k_2 were 0.995 and 0.637 respectively. It is evident, from the Arrhenius plots of kinetic rate constants for both two-stage first-order kinetic model and generalized kinetic model, that the electrochemical oxidation of PEG can be well represented by the two stage first order kinetic model.
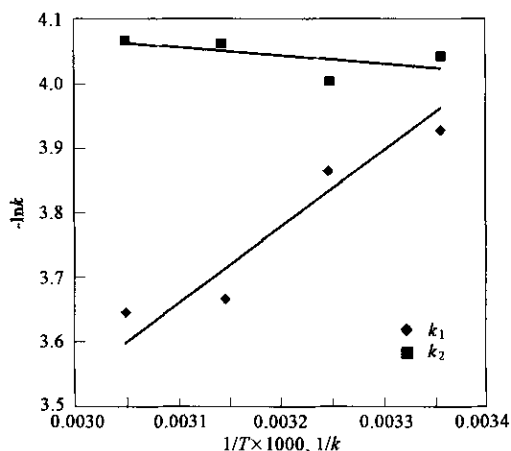

Fig.5　Arrhenius plots for kinetic coefficients of generalized kinetics

4　Conclusions

In this study, we have evaluated the efficiency of paraffin composite copperhexaferrocyanate modified anode for electrochemical removal of polyethylene glycol. The PCCHM anode was found efficient in PEG and TOC removals from electroplating solution of high acidity and ionic strength. PEG and TOC concentrations are found to be reduced to 2.08 mg/L and 1.18 mg/L respectively, after 10 min using 34 cm² anode and applying 0.75 A/cm² current density. Chlorides present in electroplating solution contribute to the removal of PEG and TOC concentrations in overall process via mediated

electro-oxidation mechanism. The electrochemical oxidation process was found to be influenced by applied current density and surface area of the anode; the latter is more dominant. Kinetic investigations (including computations of kinetic rate constants) using two different kinetics models suggest that both models provide reasonable fit to the experimental data. However, two-stage first-order kinetic model appears to be a much better representation of the overall reaction mechanism.

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