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Kinetic study on the electrodecolorization of C.I. Acid Yellow 23

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ABSTRACT

The electrocoagulation (EC) is a simple and efficient method for the treatment of many water and wastewaters. The kinetics of decolorization of Acid Yellow 23 by EC using iron electrodes was studied. The electrodecolorization rate follows pseudo-first order kinetic with respect to the AY23 concentration having k_{app}= 5.65 cm min^{-1} at T= 295 K. The rate equation is as follows:

$$\ln [AY23]_t - \ln [AY23]_0 = -k_{app}\frac{36\,cm^2}{250\,cm^3}t$$

The pseudo-first order rate constant (k_{app}) is sensitive to the operational parameters. The k_{app} is low in both highly acidic and basic conditions. For the optimum operating conditions in electrodecolorization of AY23, the activation energy was 41.15 kJ mol^{-1}, sludge volume was about 8 ml from 250 ml of the original AY23 solution. The electrical energy consumption required for this treatment was 7.74 × 10^{-4} kW h and the electrode consumption was 37.4 mg.

Keywords: Electrodecolorization ; Electrocoagulation; Kinetic ; Acid Yellow 23 ; Tartrazine ; Iron electrode

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INTRODUCTION

Azo dyes are characterized by the presence of one or more azo bonds (-N=N-) in association with one or more aromatic systems, which may also carry auxochromes groups (-OH, $-SO_3$, etc.). Because of the variability of organic dyes and resultant waste solution, wastewater containing dyes is difficult to treat using traditional methods. Many kinds of bio-refractory and soluble dyes render traditional bio-chemical process and coagulant processes are inadequate. The cost of treatment by active carbon adsorption is high. Ozone and hypochlorite oxidation are efficient decolorization methods, but they are not desirable because of the high cost for equipment, operating costs and the secondary pollution arising form the residual chlorine[1]. One of the promising methods for treating wastewater streams is electrocoagulation. It is a simple and efficient method for the treatment of many water and wastewaters [2]. Electrocoagulation has been applied successfully to treat various industrial wastewaters[3]. Indeed it has been proposed as an effective method to treat wastewater streams from dyeing factories in recent years. The electrogenerated flocs separate rapidly and move color and turbidity from wastewaters[2]. Electrocoagulation (EC) is a complicated process involving many chemical and physical phenomena that use consumable electrodes to supply ions into the wastewater stream. In an EC process the coagulating ions are produced 'in situ' and involves three successive stages: (i) formation of coagulants by electrolytic oxidation of the 'sacrificial electrode', (ii) destabilization of the contaminants, particulate suspension, and breaking of emulsions and (iii) aggregation of the destabilized phases to form flocs [4].

The mechanism of EC is highly dependent on the chemistry of the aqueous medium, especially conductivity. In addition, other characteristics such as pH, particle size, and chemical constituent concentrations will also influence the EC process [5].

The electrochemical reactions with metal M as anode may be summarized as follows [4]:

- At the anode:

$M_{(s)} \rightarrow M_{(aq)}^{n+} + ne^{-}$ (1)

$2H_2O_{(l)} \rightarrow 4H^{+}_{(aq)} + O_{2(g)} + 4e^{-}$ (2)

- At the cathode:

$M_{(aq)}^{n+} + ne^{-} \rightarrow M_{(s)}$ (3)

$2H_2O_{(l)} + 2e^{-} \rightarrow H_{2(g)} + 2OH^{-}$ (4)

If iron or aluminum electrodes are used, the generated $Fe_{(aq)}^{3+}$ or $Al_{(aq)}^{3+}$ ions will immediately undergo further spontaneous reactions to produce corresponding hydroxides and/or polyhydroxides. For example, Al^{3+} ions on hydrolysis may generate $Al(H_2O)_6^{3+}$, $Al(H_2O)_5OH^{2+}$, $Al(H_2O)_4(OH)^{2+}$ and the hydrolysis products may form many monomeric and polymeric species such as, $Al(OH)^{2+}$, $Al_2(OH)_2^{4+}$, $Al(OH)^{-4}$, $Al_6(OH)_{15}^{3+}$, $Al_7(OH)_{17}^{4+}$, $Al_8(OH)_{20}^{4+}$, $Al_{13}O_4(OH)_{24}^{7+}$, $Al_{13}(OH)_{34}^{5+}$ over a wide pH range. Similarly, ferric ions generated by electrochemical oxidation of iron electrode may form monomeric ions, $Fe(OH)_3$ and polymeric hydroxy complexes, namely: $Fe(H_2O)_6^{3+}$, $Fe(H_2O)_5(OH)^{2+}$, $Fe(H_2O)_4(OH)^{2\ +}$, $Fe_2(H_2O)_8(OH)_2^{4+}$ and $Fe_2(H_2O)_6(OH)_4^{4+}$ depending on the pH of the aqueous medium. These hydroxides/polyhydroxides/polyhydroxymetallic compounds have strong affinity for dispersed particles as well as counter ions to cause coagulation. The gases evolved at the electrodes may cause flotation of the coagulated materials [4].

C.I. Acid Yellow 23 (AY23) is a synthetic yellow azo dye often used in textile and foodstuff and pharmaceutical industries [6-8]. Therefore wastewaters from these industries must be treated to remove AY23 before being discharged in receiving water bodies.

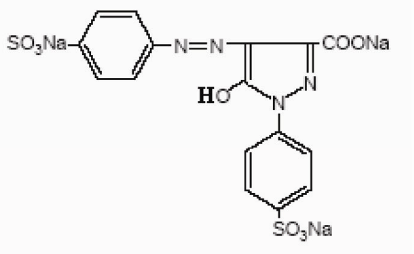
In our previous work the effect of operational parameters on the removal efficiency of AY23 from aqueous solutions by electrocoagulation was reported [3]. In the present work a kinetic analysis of removal AY23 by EC using iron electrodes was carried out and the kinetic parameters were also obtained.

EXPERIMENTAL

Materials and methods

The experiments were performed on AY23 (Acros-USA) solutions with concentrations of 40 mg l^{-1}. The chemical structure and other characteristics of AY23 are listed in table 1. At the beginning of a run, 250 ml solution of the desired concentration of the dye was fed into the reactor and NaCl salt (Merck-Germany) as electrolyte was added to the solution, since NaCl is used mainly as an electrolyte to increase the conductivity and adjust a fixed ionic strength of the solution. The iron electrodes are placed inside a Pyrex glass reactor at a distance of 1.5 cm from each other. All experiments were performed in the above batch reactor as shown in Fig.1, and a DC power supply (REC-P-6, 0-50 V, 0-5 A), magnetic stirrer, flat-plate anode and cathode were employed. The total submerged surface area of each electrode was 18 cm^2 and there was a 2 cm distance between the bottom of the electrodes and the bottom of the cell which allowed easy stirring. Before each experiment, the electrodes were abraded with sand-paper to remove scale and then cleaned with successive rinses of water, 0.1 N NaOH (Merck-Germany), HNO_3 (Merck-Germany) solution (10%) and distilled water. After electrolysis of dye solution, it was allowed to settle for 20 min in a 250 ml graduated cylinder. The dye concentration was determined with UV/vis spectrophotometer (Ultrospec 2000, Biotech Pharmacia England) at $\lambda_{Max} = 428$ nm. A calibration plot based on Beer – Lambert΄s law was established by relating the absorbance to the concentration.

Table 1. Characteristics of Acid Yellow 23

Absorption Maximum (*nm*)	Formula Weight (gr mol^{-1})	Physical State	Other names	Empirical Formula	Structural Formula
428	534.385	Orange Powder	Tartrazine E 102 or FD&C Yellow 5	$C_{16}H_9N_4O_9S_2Na_3$	

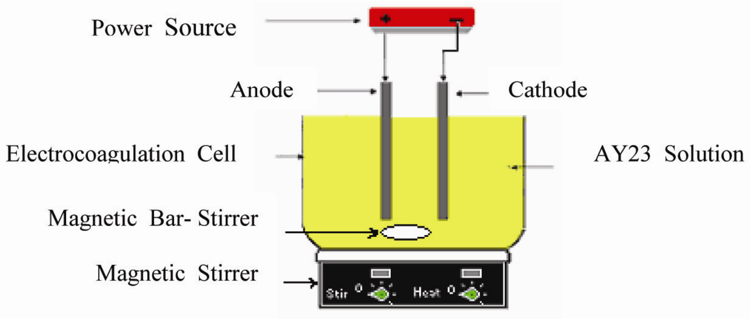


Fig.1. The experimental EC reactor.

KINETIC INVESTIGATION

In the literature the coagulation rate of aqueous suspensions of ultrafine kaoline particles in a single stirred cell apparatus and in a continuously flowing system was described by a second- order rate equation[4]:

$$\frac{dC}{dt} = -\frac{4k_B T}{3\eta} C^2 (1 - e^{-\frac{u}{x}t})^2 \qquad (5)$$

in this equation k_B, T, η, u, x, t and C are Boltzman's constant, temperature, viscosity, electrophoretic velocity of the particles, geometric parameter of the electrode size, EC application time and concentration of iron ions produced in EC at t time, respectively. This second-order rate equation incorporates the electrophoretic migration of particles, and subsequent release of discharged particles into the bulk. The constant terms in this equation were derived from the basic electrophoretic and coagulation phenomenon, which is dependent on the zeta potential of the suspended particles, the applied voltage, the initial concentration of the particles and the electrode geometry. The authors conducted a number of EC experiments with ultrafine kaoline particles in a single stirred cell with electrodes in parallel connections and found reasonably good agreement with the theoretically predicted coagulated fraction.

Rate of consumption of organic species to be degraded at the electrode's surface, is given by [9]:

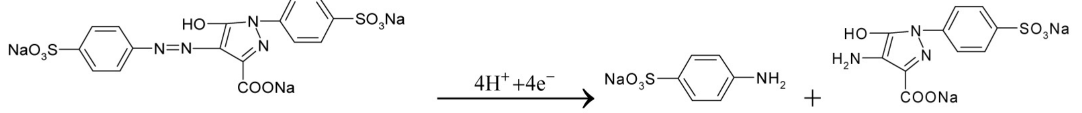
$$\text{Rate (mol s}^{-1}) = -V\frac{dC}{dt} = \frac{[i]A}{nF} \qquad (6)$$

in this equation [i], A, n, F are current density (A m^{-2}), the total active electrodes area (m^2), number of electrons transferred in the reaction and constant of Faraday (96485 C mol^{-1}), respectively. The macroscopic reduction rate in the reactor can be described using an empirical reaction rate equation with apparent reaction parameters[10]:

$$r = Kk_{app} C^{\alpha_{app}} \qquad (7)$$

in this equation k_{app} and α_{app} are apparent reaction rate constant and apparent reaction order, respectively. This equation combines the microscopic effects of mass transfer and electrochemical kinetics on the reduction into a macroscopic apparent reaction rate constant k_{app} and an apparent reaction order α_{app}. The parameter K is introduced as a constant, which has a value of 1 and a dimension of $mol^{1-\alpha_{app}}\ m^{3\alpha_{app}-3}$. Thus K only maintains the dimensional integrity of Eq. (7).

Based on the results of experiments [3], electrochemical processing removes color more rapidly. The EC reaction can be formulated as following:



(8)

$$\text{Hydroxides and/or Polyhydroxides + Intermediates} \xrightarrow{k_1} \text{Final products} \qquad (9)$$

The results obtained by electrochemical treatments allow for kinetic analyses and for the calculation of the apparent rate constant for degradation, which may be a useful tool for process scale up. However, degradation rate constant values are dependent on operational parameters such as current density and on the characteristics chosen for degradation (color).

Fig. 2 presents a plot of $\ln\frac{C_{(0)}}{C_{(t)}}$ versus time of electrolysis in which the slope is related to the apparent rate constant for AY23 decolorization.

From the plot, it is deduced that the decolorization kinetics can be described as a first order reaction with respect to the AY23 concentration. With substituting of α_{app}=1 and K=1 to Eq. (7) we obtain:

$$r = k'_{app}\ C\ ,\ k'_{app} = k_{app}\frac{A}{V} \qquad (10)$$

With integrating Eq. (10) we obtain:

$$\ln C_{(t)} - \ln C_{(0)} = -k_{app}\frac{A}{V}t \qquad (11)$$

$A = 36\ cm^2$, $V = 250\ cm^3$

In this equation $C_{(t)}$ and $C_{(0)}$ are concentration of AY23 at t time and initial concentration of

AY23. The fitted correlation coefficient was 0.948 and the resulting value of k_{app} was 5.65 cm min^{-1} (9.41×10^{-4} m s^{-1}).

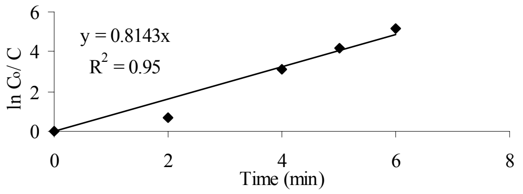


Fig.2. Logarithm of normalized AY23 concentration as a function of electrolysis time with Fe / Fe electrode pair. $C_{0[AY23]}$ =40 mg l^{-1}, C_{NaCl} = 400 mg l^{-1}, [i] =120 A m^{-2}, d= 1.5 cm, sedimentation time= 20 min, T= 295 K.

RESULTS AND DISCUSSION

Influence of operational variables on the pseudo-first order rate constant

Effect of the initial concentration of the dye

As shown in Fig. 3 k_{app} decreased with increasing initial concentration of AY23 when other parameters are kept unchanged. Decrease of the reaction rate with the increase in the initial concentration of dye could be due to the presence of intermediate products formed during the electrolysis process at higher concentrations, which then could compete with AY23 and water for the active sites on the electrode, or these intermediate products may be insoluble in water and would block the electrode active sites. On the other hand one of the most important pathways of color removal by EC process is adsorption on metallic hydroxide flocs and the adsorption capacity of flocs is limited [3].

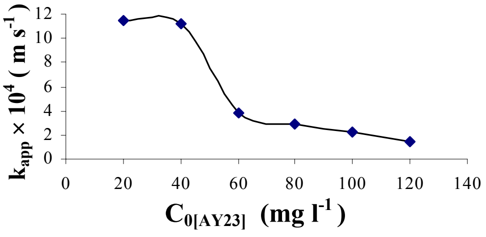


Fig.3. Plot of pseudo-first order rate constant against initial concentration of AY23 with Fe / Fe electrode pair. C_{NaCl} = 400 mg l^{-1}, $t_{elec.}$= 5 min,[i] =120 A m^{-2}, d= 1.5 cm, sedimentation time= 20 min, T= 295 K.

Effect of the electrolyte concentration

In order to increase the conductivity of the AY23 solution, NaCl was added to the solution. As shown in Fig. 4 an increase in the concentration of NaCl from 200 mg l^{-1} to 400 mg l^{-1} causes an increase in k_{app} and then had little effect on k_{app} value. For lower concentrations, there is a decrease of that rate, probably because there are not enough ions to conduct the current. Thus it may be concluded that increasing the electric resistance of the solution would decrease the efficiency of the process [3].

Effect of the current density

Current density directly determines both coagulant dosage and bubble generation rates, as well as strongly influencing both solution mixing and mass transfer at the electrodes [11]. However, the current density might not only have positive effect on the kinetics of surface electrochemical reactions, but also enhances the production of bulk chemicals, which may contribute, through parallel reaction schemes, to the degradation process [12]. As expected, current density plays an important role in the color degradation rate. Fig. 5 shows that k_{app} increased with increasing current density, because when the current density increases, the efficiency of ion production on the anode and cathode increases. Therefore, there is an increase in floc production in the solution and hence an improvement in the efficiency of color removal [3].

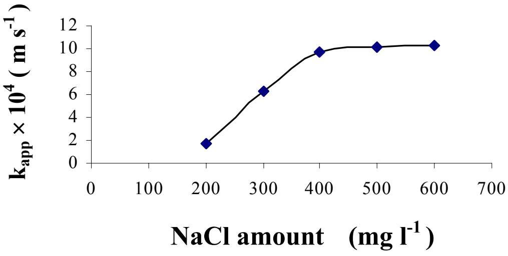


Fig.4. Effect of NaCl amount on the pseudo- first order rate constant with Fe/Fe electrode pair. $C_{0[AY23]}$ =40 mg l^{-1}, $t_{elec.}$= 5 min,[i] =120 A m^{-2}, d= 1.5 cm, sedimentation time= 20 min, T= 295 K.

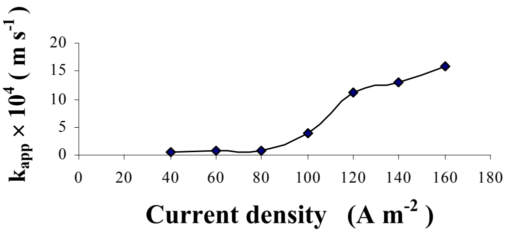


Fig.5. Plot of pseudo- first order constant against current density with Fe / Fe electrode pair. $C_{0[AY23]}$ =40 mg l^{-1},C_{NaCl} = 400 mg l^{-1}, $t_{elec.}$= 5 min, d= 1.5 cm, sedimentation time= 20 min, T= 295 K.

Effect of the temperature

In a range of 276 - 307 K a linear relationship between $\ln k_{app}$ and $\frac{1}{T}$ was observed. The slope of the straight line was 4950, which according to Arrhenius equation corresponds to an activation energy of 41.15 kJ mol^{-1} (Fig. 6) .

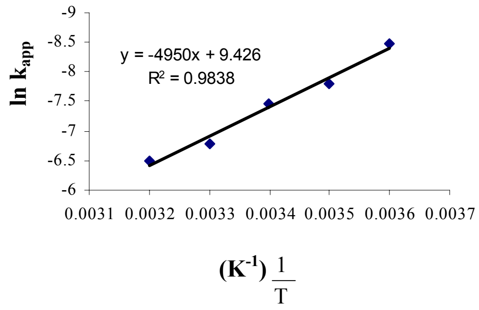


Fig.6. Effect of reaction temperature on the pseudo- first order rate constant with Fe / Fe electrode pair. $C_{0[AY23]}$ =40 mg l^{-1},C_{NaCl} = 400 mg l^{-1}, $t_{elec.}$= 5 min,[i] =120 A m^{-2}, d= 1.5 cm, sedimentation time= 20 min, T= 295 K.

Effect of the initial pH

It has been established that pH is an important operating factor influencing the performance of electrocoagulation process [2]. As shown in Fig. 7 the pH of the medium changes during the process. This change depends on the type of electrode material and on initial pH. To examine its effect, the sample was adjusted to a desired pH for each experiment by using sodium hydroxide or sulfuric acid. Results obtained from experiments with varying pH from 1.86 to 10.1 are illustrated in Fig. 8. From the plot, it is deduced that the pseudo-first order rate constant (k_{app}) increased with increasing pH until to reach a maximum at pH = 6.47 and then decreased with increasing pH. Because at too low pHs, the solution protons were reduced at the cathode to H_2 and the same proportion of hydroxide ions can not be produced and at too high pHs the amount of hydroxide ions in solution is increased. Consequently, some of hydroxide ions are probably oxidized at the anode. This action prevents the production of the same proportion of iron ions [3]. In addition too high pHs will increase iron hydroxide solubility which is useless for the treatment process.

Effect of the distance between the electrodes

Fig. 9 presents k_{app} versus distance between the electrodes. From the plot, it is deduced that the decolorization rate of AY23 decreases with an increase distance between the electrodes. This is because both local concentration and electrostatic attraction decrease with increasing distance between electrodes [3].

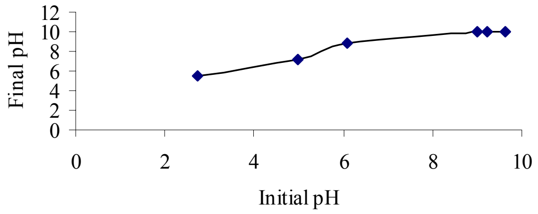


Fig.7. The pH change of AY23 solution after electrocoagulation as a function of initial pH with Fe/Fe electrode pair. $C_{0[AY23]}$ =40 mg l^{-1},C_{NaCl} = 400 mg l^{-1}, $t_{elec.}$= 5 min, [i] =120 A m^{-2}, d= 1.5 cm, sedimentation time= 20 min, T= 295 K.

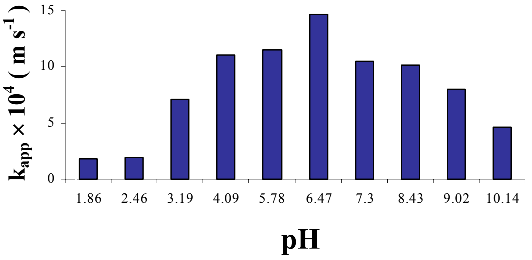


Fig.8. Effect of pH on the pseudo- first order rate constant with Fe/Fe electrode pair. $C_{0[AY23]}$ =40 mg l^{-1},C_{NaCl} = 400 mg l^{-1}, $t_{elec.}$= 5 min,[i] =120 A m^{-2}, d= 1.5 cm, sedimentation time= 20 min, T= 295 K.

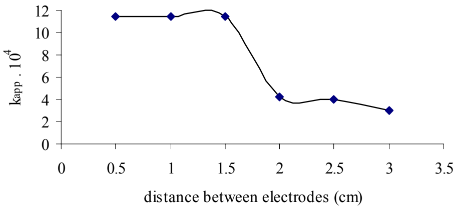


Fig.9. Plot of pseudo- first order constant against distance between the electrodes with Fe/Fe electrode pair. $C_{0[AY23]}$ = 40 mg l^{-1}, C_{NaCl} = 400 mg l^{-1}, $t_{elec.}$= 5 min, sedimentation time = 20 min, T= 295 K.

Effect of the sedimentation time

Fig. 10 shows that increasing sedimentation time to 15 min would increase the rate of color removal slightly but after 15 min, it is relatively constant, since the metallic hydroxide flocs can attract contaminate particles during settling, but after 15 min the adsorption capacity of flocs becomes exhausted [3]. It is noted that the sludge volume produced after sedimentation could be an important factor in assessing the electrocoagulation performances. At this experiment the sludge volume after 20 min of sludge settling was about 8 ml from 250 ml of original AY23 solution. This amount of sludge was not excessive and considered as acceptable.

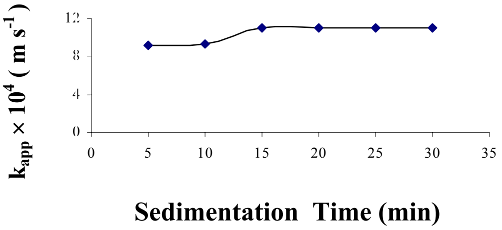


Fig.10. Plot of pseudo- first order constant against sedimentation time with Fe/Fe electrode pair. $C_{0[AY23]}$ =40 mg l^{-1},C_{NaCl} = 400 mg l^{-1}, $t_{elec.}$= 5 min, d= 1.5 cm, T= 295 K.

The cost of EC process

One of the most important parameters that affect the application of any method of wastewater treatment greatly is the cost. The cost of the process is determined by the consumption of the sacrificial electrode and the electrical energy which economically are the advantages of this method. In an EC experiment the electrode or electrode assembly is usually connected to an external DC source. The amount of metal dissolved or deposited is dependent on the quantity of electricity passed through the electrolytic solution. A simple relationship between current density and the amount of substances dissolved can be derived from Faraday's law [13]:

$$m = \frac{ItM}{nF} \qquad (12)$$

in this equation m and I are quantity of electrode material dissolved (g) and current intensity (A), respectively. The electrical energy consumption was calculated as a function of the applied cell voltage [14]:

$$E = UIt \qquad (13)$$

For the optimum operating conditions in decolorization of AY23 (I= 0.43 A, t = 300 s, U = 21.6 V) the electrical energy consumption required for this treatment was 7.74 × 10^{-4} kW h and the electrode consumption was found to be 37.4 mg.

CONCLUSIONS

On the basis of the kinetic study of electrodecolorization of AY23 the following aspects may be concluded:

1. Decolorization of AY23 is a first order reaction with respect to the AY23 concentration with k_{app} = 5.65 cm min^{-1}.

2. The activation energy of decolorization of AY23 by EC was 41.15 kJmol^{-1}. 3. k_{app} is sensitive to the operational parameters such as the current density, initial pH of solution, interelectrode distance, electrolyte concentration, AY23 concentration and solution temperature. 4. The k_{app} is a function of pH value and is lower in both highly acidic and basic conditions. 5. For the optimum operating conditions in decolorization of AY23, the sludge volume was about 8 ml from 250 ml of original AY23 solution, the electrical energy consumption required for this treatment was 7.74 × 10^{-4} kW h and the electrode consumption was found to be 37.4 mg.

Acknowledgements

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