

Mediated electrochemical oxidation process for destruction of TOC in a batch recirculation reactor

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Abstract: Electro oxidation processes are developed throughout the world for ambient temperature destruction of organic wastes. Several of these processes are based on Mediated Electrochemical Oxidation (MEO). This article presents the experimental results of electro chemical study based on MEO process conducted for synthetic organic ion exchange resin materials. Investigation was carried out using the traditional noble metal oxide coated anode, RuO₂/Ti and the mediator used for the experiment was FeSO₄, with NaCl as supporting electrolyte. The concentration of NaCl was maintained at 5, 8, 12 gm/l.

The experiment was carried out in batch recirculation reactor with current densities 1.25, 2.50, 3.75, 5.00, 6.25, 7.50, 8.75, 10.00 A/dm² for various flow rates 20, 40, 60, 80, 100 l/h. The study highlighted that in batch reactor set up the best effect of TOC reduction was found to occur at 3.75 A/dm² with flow rate of 20 l/h. The simulated studies were carried out for different volumes of effluent and current densities. A graphical analysis was made between the experimental and simulated values and it was found that both the values are very close.

Key Words: Mediated electrochemical oxidation, Resin Effluent, Batch Recirculation reactor, Fenton's Mediator

1 Introduction

Hazardous wastes are a continuous problem in today's world, increasing in both quantity and toxicity. Besides inorganic materials industrial effluents also contain organic pollutants and also radioactive chemical toxic materials. Many treatment technologies are in use and have been proposed for recovery or destruction of these pollutants. These include activated carbon adsorption, solvent extraction for recovery of chemical, electrochemical oxidation for destruction, direct incineration, chemical destruction and even direct immobilization in matrix like cement, polymer etc. In addition management of hazardous organic mixed wastes can be done by employing techniques like wet oxidation, photochemical oxidation, and electrochemical oxidation. Of the techniques mentioned above, electrochemical oxidation offers an attractive way of treating solid or liquid organic waste as it uses electron as a reactant. The electrochemical destruction of organic wastes could be carried out by direct electrochemical oxidation (DEO) or by mediated electrochemical oxidation (MEO) for the treatment of hazardous and mixed wastes. The range of organic materials which can be destroyed by this

technique is very wide. The process is extensively employed for nuclear industry application, rubber, some plastics, poly urethane, ion exchange resins of various types and hydraulic and lubricating oils, aliphatic and aromatic compounds, chlorinated aliphatic and aromatic compounds etc.

Mediated electrochemical oxidation (MEO) is a rising and one of the most promising technologies extensively used for the destruction of organics since it is capable of mineralizing the organics into carbon dioxide and water completely, without emission of any toxic materials like dioxins¹⁻⁸. DEO processes have been carried out for a variety of organic compounds⁹. In these processes the organic compounds are oxidized to CO₂ and H₂O at the anode surface. The MEO process is an emerging technology for the destruction of various kinds of toxic and refractory organic pollutants¹⁰. This process employs an electrochemical cell to generate the oxidizing species and uses the same to destroy the organics at ambient temperatures (below 373 K) and at atmospheric pressure^{1,2,11,12}. The oxidizing species (mediator ions) are produced at the anode in an acidic medium and are used to destroy the organic compounds into CO₂ and water. Since the mediated metal ions have a strong potential to

oxidize, high temperature is not required for organic oxidation, and as a consequence, less volatile and off gases are produced. Several metal oxidizing agents like Ag(II)/Ag(I), Ce(IV)/Ce(III), Co(III)/Co(II), etc., have been tested previously in the MEO process both in pilot and commercial scale systems^{5,6,13,14}.¹⁵ studied the MEO process taking 0.5 M Ag(II) as mediator in sulphuric acid medium for the destruction of a number of organic compounds.¹⁶ in their work used Ag(II)-MEO system for the destruction of hydrocarbons and pesticides in sulphuric acid medium. Research studies provide evidence that Phenol is one of the most common pollutants found in the effluents of many industries such as pharmaceuticals, dyes, synthetic chemical plants, petroleum refineries, pesticides and herbicides, and treated by several technologies^{17,18,19,20,21}.

²² in their study identified that the mediated metal ions have a strong potential to oxidize, and a high temperature is not required for organic oxidation and therefore, less volatile and off gases are produced. The organic destruction in the MEO process can be carried out in either a batch or in a continuous feeding mode. In the case of batch type reaction, the organic is added at one time (zero time) in the reactor, and the process is carried out with or without Ce(IV) regeneration. However, in real applications, the continuous organic addition is used mainly for minimizing the oxidant usage by simultaneous regeneration, and by this way more quantity of the organic materials can be destructed than in the batch process. Usually, in the continuous process, an organic substance is added for a long time (e.g. hours, days etc.) at a particular flow rate and the oxidant concentration is maintained nearly at the same level by in situ electrochemical regeneration. However, it is also possible to predict the course of the destruction process by simulation based on simple kinetic models.

The mediated electrochemical oxidation (MEO) has been identified as one of the most promising future technologies by the United Nations Environmental Programme¹⁰ for the ambient temperature destruction of toxic organic pollutants and waste streams including persistent organic pollutants and dioxins^{1,5,16,11,23,24,25,26,27,14,28,29,30}. In particular, the Ag(II)/Ag(I) based MEO system has been widely studied to destroy hazardous industrial waste^{1,5,16,11,23,14}. It may be mentioned here that the advantages of electrochemical approach, compared to several other chemical tools, have been well recognized for the recovery of metals in their metallic form from metal ion pollutants^{31,32}, because the electrochemical methods are relatively simple and clean; moreover, as the conversion of the response of a chemical reaction or a process into a measurable electronic signal is direct and precise in electrochemical methods (as current or potential), regulation and automation are easier to achieve with them in comparison to the chemical techniques.

MEO process offers a number of advantages namely, the oxidation reaction takes place at ambient

temperatures and pressures, the products of destruction are contained in the reaction vessel itself with the exception of gases and the production of secondary waste is minimized which avoids additional treatment methods. Hence a study was conducted to identify the best way to reduce TOC using electrochemical treatment method for resin effluents using batch recirculation method.

2 Materials and methods

2.1 Materials: The synthetic resin effluent was prepared by dissolving an appropriate amount of cationic resin (Amberlite strong acid styrene based cation exchange resin - functional group – SO_3H) in water in presence of ferrous sulphate ($\text{Fe}^{2+}/\text{Fe}^{3+}$) as catalyst, with drop wise addition of H_2O_2 by maintaining temperature of the reaction mixture at 95-100°C

2.2 Experimental setup: Experiments were carried out under galvanostatic condition at different current densities and flow rates using RuO_2 coated Titanium expanded mesh anodes and stainless cathodes. The electrolyser was of filter press type reactor (figure 1). The fluid flow circuit consists of a reservoir, a magnetically driven self priming centrifugal pump, a flow meter and the electrolytic cell. The electrical circuit consists of a regulated D.C. Power supply, ammeter and the cell with the voltmeter connected in parallel to the reactor.

2.3 Experimental procedure: All experiments were carried out under batch recirculation conditions, first treating 2 liters of the solution per batch of electrolysis by passing a quantity of electricity corresponding to the current densities. The process of electrolysis was followed by continuous monitoring of variation of pH, cell voltage and TOC values. For the purpose of determination of TOC, samples were drawn at predetermined intervals and the estimation was carried out using TOC analyzer.

NaCl was used as a supporting electrolyte with various concentrations and tried it in the oxidative destruction of the organic compounds. The electrolysis was carried out at different flow rates of 20, 40, 60, 80, 100 l/h.

TOC was determined at 1hr interval. Based on the results obtained it was decided to continue the investigation using FeSO_4 as the mediator along with NaCl as the supporting electrolyte with only 500ml of the electrolyte at a flow rate of 20 l/h. in order to provide a good conductivity conc. H_2SO_4 (0.025 N) was added and these experiments were carried out again in batch recirculation at different current densities such as 1.25, 2.50, 3.75, 5.00, 6.25, 7.50, 8.75, 10.00 A/dm^2 . The concentration of the mediator was maintained at 0.37 g/l and for the purpose of generation of OH free radical H_2O_2 was added at the rate of 1ml/hr.

The conditions are given below:

Type of mediator : FeSO_4 with 0.37 g/l

Type of supporting electrolyte : NaCl with 5 g/l

Volume of the electrolyte : 0.5 litre

Flow rate : 20 l/h

Duration of electrolysis : 8 hrs

By taking 10 A/dm² as the opinion current density, experiments were carried out with different flow rates such as 20, 40, 60, 80, 100 l/h.

2.4 TOC Analyses: TOC was used to verify that no organics remained in the spent electrolytes. To determine the quantity of organically bound carbon, the organic molecules must be broken down to single carbon units and converted to a single molecular form that can be measure quantitatively. Toc measurements were carried out by using TOC analyzer formacs^{HT}. Samples were withdrawn from the electrolysis solution at different intervals. They were filtered and acidified by HCl and brought to pH 2 prior to analysis. The injection volumes were 50/100μ L. The temperature in the oven was 680°C in combustion with a Pt catalyst. Calibration of the analyzer was achieved with potassium hydrogen phthalate standards (Merck).

Total organic carbon = Total carbon – inorganic carbon.

2.5 Reactor Modelling: The concentration of organic ion-exchange resins varies due to the various reactions. The pseudo-steady state theory, which is based on the concept of no accumulation of the intermediates in the reactor helps to obtain the rate of the reaction in this reactor.

Further it can also be assumed that the reactor is under steady state condition, hence assuming the reactor is ideal CFSTER (continuous flow stirred tank electrochemical reactor), and the performance equation can be written as

$$T_{CFSTR} = V_R / Q$$

$$= (C - C') / (-r)$$

where

-r = the rate of degradation of organic pollutants.

-r = k C'

Q = Volumetric flow rate

$$T_{CFSTR} = (-1/k) [(C/C') - 1] \text{ ---- (1)}$$

Where

-r = k C' = rate of degradation of organics in the reactor

k = electro chemical reactor rate constant.

V_R = active volume of reactor

-r = k₂ [S] C

The disappearance is directly proportional to the concentration of organic pollutants. C is multiplied by the concentration of active sites [S], which is essentially a constant. Hence,

-r = kaC' is a pseudo first order kinetic equation

$$\tau_R = (C - C') / kaC' \text{ ----- (2)}$$

-r = kaC' = rate of disappearance of organic resins in the reactor by reactions

k = electro chemical rate constant

V_R = active volume of the reactor

Q = volumetric flow rate

A = active total electrode area

τ_R = space time for the reactor = V_R/Q

C' = concentration of organic pollutants in leaving stream of the reactor

C = concentration of organic pollutants in the entering stream of the reactor

a = specific electrode area = A/V_R

Then rewriting equation (2) as,

$$V_R / Q = (C - C') / [k(A/V_R)C'] = V_R (C - C') / KAC'$$

$$kA/Q = (C - C') / C' = C/C' - 1$$

$$C'/C = (kA/Q) + 1$$

$$C'/C = 1 / [(KA/Q) + 1] \text{ ----- (3)}$$

In batch recirculation system, the mass balance can be written as

$$V_m dC/dt = -Q (C' - C) \text{ ----- (4)}$$

Substituting for C' from equation (3)

$$V_m dC/dt = \{Q C / (1 + [kA/Q])\} - C$$

$$V_m dC/dt = \{Q C [1 - (1 + 1[kA/Q])]\} / (1 + [kA/Q])$$

$$V_m dC/dt = Q C [kA/Q] / (1 + [kA/Q]) \text{ ----- (5)}$$

On integrating,

$$C_1/C_0 = \exp(-t/\tau_m) [kA/Q] / (1 + [kA/Q]) \text{ ---- (6)}$$

Where,

V_m = volume of the reservoir

T_m = space time of the reservoir = (V_m / Q)

Q = volumetric flow rate

C₀ = initial concentration of organic pollutants in reservoir

C_t = concentration of organic pollutants at time t in the reservoir

Equation (6) can be written by taking logarithm on both sides

$$\ln C_1/C_0 = (t/\tau_m) [kA/Q] / (1 + [kA/Q]) \text{ ----- (7)}$$

From the above equation (7) the rate constant k, can be calculated, from the slope of the graph by plotting

-ln C_t/C₀ = t. for the given A and Q.

3 Results and discussion

3.1 Influence of anode material: The presence of NaCl in electrolyte catalyses the oxidation of organic resins only in case of inactive anode, Ti/RuO₂. The catalytic action NaCl has been attributed to the participation of electro generated ClO⁻ in the oxidation of organics near the anode or/and in the bulk of electrolyte. Being Ti/RuO₂, a traditional anode material, it gave relatively low current efficiency.

3.2 Influence of NaCl concentration: NaCl was used as the supporting electrolyte for providing good conductivity to the electrolyte and also a good mediator in producing OCL⁻ ion for the oxidation of organics. Some tests were run at different NaCl concentrations using Ti/RuO₂ anode, keeping other condition constant. The results reported that TOC reduction is almost independent of NaCl and has only very little effect on TOC elimination. NaCl concentration should be kept minimum, because anodic oxidation of organics in presence of NaCl lead to the chlorination of some organics. This can potentially increase the toxicity and the environmental hazard associated with waste water (figure 2, 3, 4).

3.3 Influence of current density: Figure 5 and 6 shows the effect of current density on percentage reduction of TOC and current efficiencies. Experiments were done by changing the current densities from 1.25 A/dm² to 10.00 A/dm². By increasing the current densities, the

percentage reduction of TOC also gets increased and current efficiencies were almost same for all current densities. The electron transfer mediator must be continuously generated at fairly high current densities so that a steady state concentration available to bring about oxidation of the organic compounds present. Under these conditions, the overall current efficiency can be expected to be very low.

3.4 Effect of applied current: Figure 7 shows the effect of applied current on the percentage reduction of TOC of the organic ion exchange resins as a function of time. The time efficiency for complete oxidation of organic resins for an eight hours run changes from 5.31percentage to 3.48percentage, for various current passed. The lower current efficiency at high current results from greater O_2 evolution, which also may contribute to the reduced by-product. In addition, greater evolution of O_2 on the electrode surface may cause improved mass transfer rates, which could affect the by-product formation. The improved current efficiency which applied current is a consequence of the shorter time required to achieve a 90percentage conversion for the higher currents.

3.5 Effect of flow rates: Figure 8 and 9, shows the effect of flow rates on the percentage reduction of TOC removal. Percentage reduction of TOC was found to be high for very slow flow rates, since the residence time of the electrolyte solution inside the electrolytic cell was very high. Thus for low residence time of the electrolyte solution inside the cell, the percentage removal of TOC of the organic ion exchange resin was found to be decreased with high flow rates.

3.6 Electrolysis in the absences of Fenton's mediator ($Fe^{2+}/Fe^{3+} + H_2O_2$): Electrolysis was carried out in the flow cell with various flow rates and current densities in the absence of Fe (II). The data from the sets of experiments revealed that TOC removal was found to be very low (about 25 percentage reduction was only achieved) in the absence of Fenton's mediator (figure 10).

3.7 Electrolysis in the presence of Fenton's mediator ($Fe^{2+}/Fe^{3+} + H_2O_2$): When the electrolysis was repeated with the addition of Fenton's mediator, it has shown a marked increase in the rate of reaction. The presence of mediator ions enhances both the conversion and coulombic efficiencies at the DSA (Dimensionally Stable Anodes) (figure 11).

3.8 Influence of electro chemical cell (divided or undivided): The type of electro chemical cell (divided or undivided) can influence the current efficiency especially for the treatment of benzene derivatives or aromatics.

Very low current efficiency was achieved in the case of divided cell due to the generation of over potential in the electrolyte contrary to the undivided cell. Though, in the divided cell, cathodic reduction was avoided, which promotes anodic oxidation of the organic pollutants, it provides high resistance and there by creates over voltage which automatically gives high energy consumption (figure 12, 13).

4. Simulated Results

The experimental data were used to develop neural networks using general regression neural network (GRNN) model. Figure 14 to 18 brings out the experimental and simulated graphs at various flow rates.

5. Conclusion

This study focused in using electro chemical treatment based on MEO as a potential candidate to achieve mineralization of organic resins. The process is conducted for synthetic ion exchange resin materials by constant stirring batch reactor process. The experimental study was carried out in batch setup at different current densities 1.25, 2.5, 3.75, 5.00 A/dm² for various flow rates 20, 40, 60, 80, 100 l/h using RuO₂/Ti as anode and stainless steel as cathode in the electrolyser. The mediators used for this process are in situ generated OCI^- ion and the Fenton's reagent ($Fe^{2+}/Fe^{3+} + H_2O_2$), OH° . Thus NaCl acts not only as supporting electrolyte as well as enhances the anodic oxidation of organics. The study highlighted that in batch reactor set up the best effect of TOC reduction was found to occur at 3.75 A/dm² with flow rate of 20 l/h. The results of the study reported that TOC reduction is almost independent of NaCl and has only very little effect on TOC elimination and NaCl concentration should be kept minimum since anodic oxidation of organics in presence of NaCl leads to the chlorination of some organics.

The study further reported that the percentage reduction of TOC gets increased and current efficiencies were almost the same for all current densities. The percentage reduction of TOC was found to be high for very slow flow rates since the residence time of the electrolyte solution inside the electrolytic cell was very high. The study further revealed that the TOC removal was very low about 25 percentage only in the absence of Fenton's mediator, which implied the catalytic action of Fenton's mediator. The simulated studies were carried out for different volumes of effluent and current densities. A graphical analysis was made between the experimental and simulated values and it was found that both the values are very close.

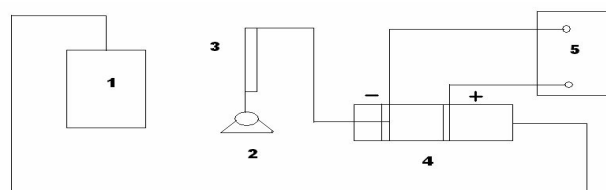


Figure 1: Filter press type of reactor (continuous batch recirculation)

1= Reservoir, 2= Pump, 3= Flow meter, 4= Filter press type reactor, 5= DC power supply

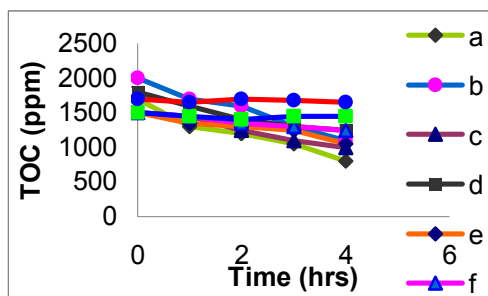


Figure 2: TOC concentrations Vs time of electrolysis for various current densities.

h.1.25A/dm², g.2.50A/dm², f.3.75A/dm², e.5.00A/dm², d.6.25A/dm², c.7.50A/dm², b.8.75A/dm², a.10.00 A/dm²

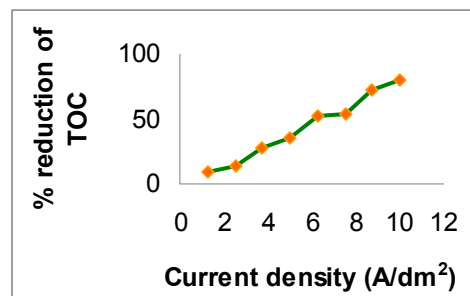


Figure 6: Current density Vs Percentage reduction of TOC for flow rate 20 l/h

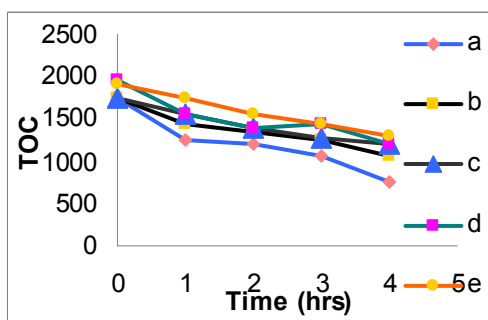


Figure 3: TOC concentration Vs time of electrolysis for various flow rates.

a. 20 l/h, b. 40 l/h, c. 60 l/h, d. 80 l/h, e. 100 l/h

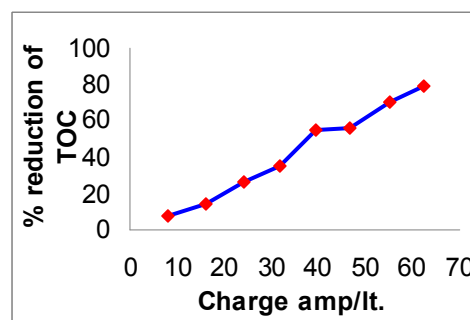


Figure 7: Percentage reduction of TOC Vs Current for flow rate 20 l/h.

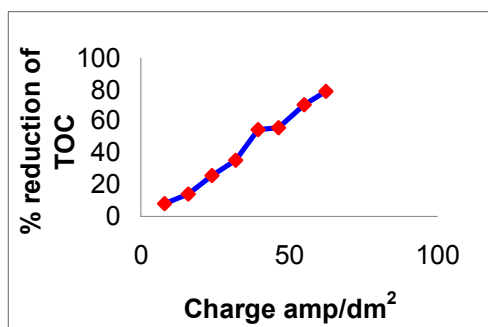


Figure 4: Percentage reduction of TOC Vs Charge for different current densities of flow rate 20 l/h

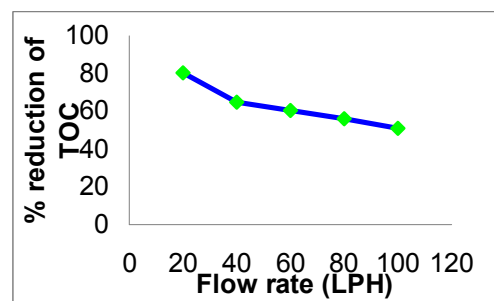


Figure 8: Percentage reduction of TOC Vs Flow rate for Current density 10 (A/dm²)

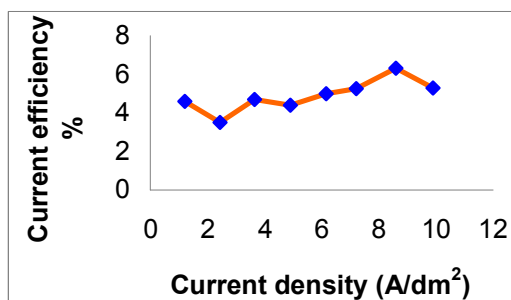


Figure 5: Current efficiency Vs Current densities for flow rate of 20 l/h

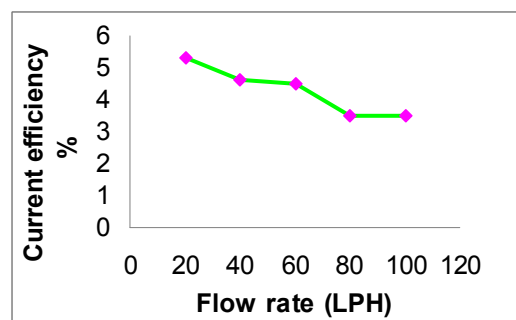


Figure 9: Current efficiency Vs Flow rate for 10 (A/dm²)

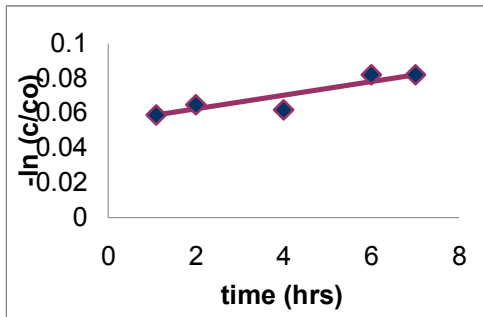


Figure 10: Plot of $-\ln(c/c_0)$ Vs time (hrs) for 2.5 (A/dm^2) and 20 l/h
Slope, $k = 2 \times 0.02 / 8 \times 1 = 0.1389 \times 10^{-5} (sec)$

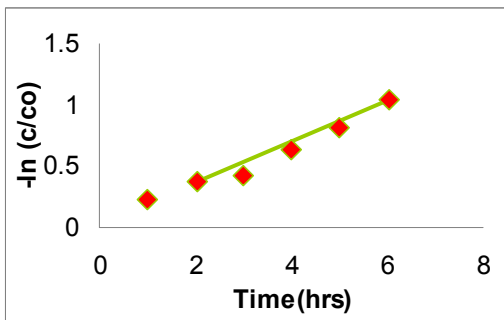


Figure 11: Plot of $-\ln(c/c_0)$ Vs time (hrs) for 10 (A/dm^2) and 20 l/h
Slope, $k = 6 \times 0.02 / 7 \times 1 = 4.762 \times 10^{-5} (sec)$

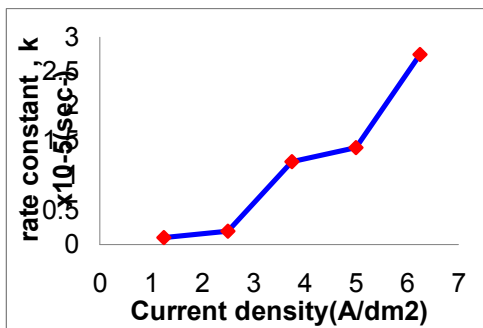


Figure 12: Current density Vs constant for Flow rate 20 l/h.

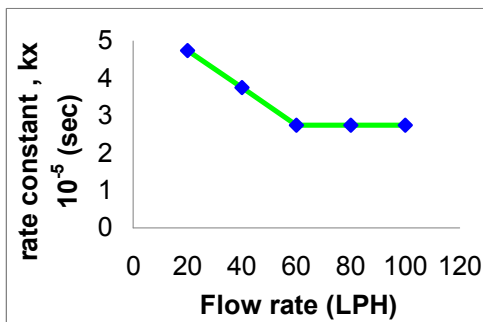


Figure 13: Flow rate Vs rate constant for Current density 10 (A/dm^2)

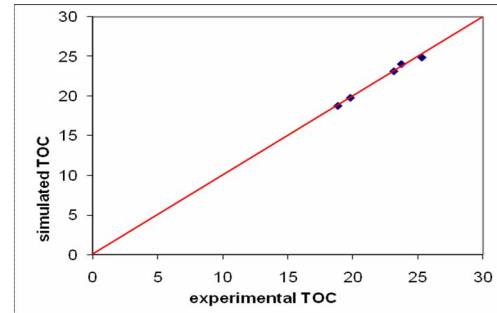


Figure 14: Experimental reduction of TOC vs Simulated reduction of TOC

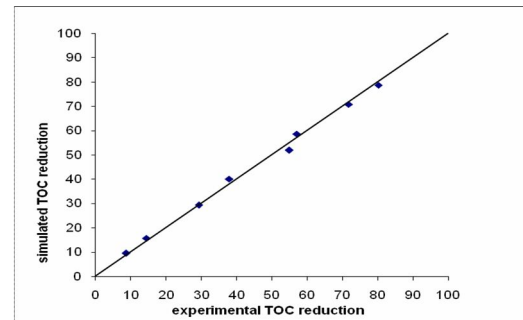


Figure 15: Experimental percentage reduction of TOC vs Simulated percentage reduction of TOC

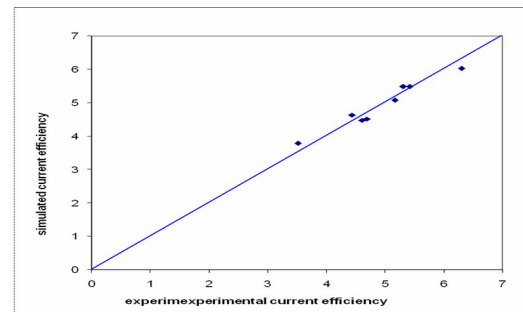


Figure 16: Experimental current efficiency vs Simulated current efficiency

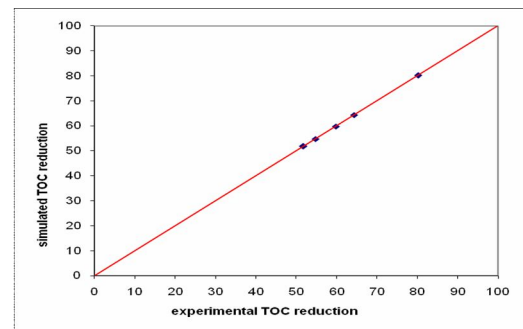


Figure 17: Experimental percentage reduction of TOC vs Simulated percentage reduction of TOC

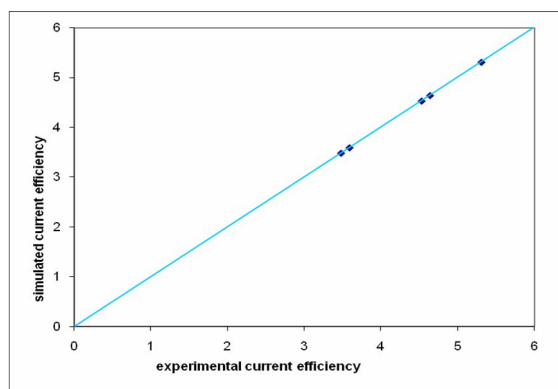


Figure 18: Experimental current efficiency vs Simulated current efficiency

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