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Treatability of resin effluents by electrochemical oxidation using 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. This article presents the experimental results of electro chemical study based on mediated electrochemical oxidation process conducted for synthetic organic ion exchange resin materials. Investigation was carried out using the traditional noble metal oxide coated anode, ruthenium oxide-titanium and the mediator used for the experiment was ferrous sulphate, with sodium chloride as supporting electrolyte. The concentration of sodium chloride was maintained at 5, 8, 12 gm/L. The experiment was carried out in batch recirculation reactor with varied current densities for various flow rates. The study highlighted that in batch reactor set up the best effect of total organic content 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.

Keywords: Electro chemical regeneration; Fentons' mediator; Organic compounds; Simulation; Total organic content

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 these 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.

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 dioxins (Chiba et al., 1995; Farmer et al., 1991; 1992; Nelson, 2001; Steele et al., 1992). DEO processes have been carried out for a variety of organic compounds. 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 pollutants (GEF, Report of UNEP, 2004). 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 (Galla et al., 2000;

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Turner, 2002). The oxidizing species (mediator ions) are produced at the anode in an acidic medium and are used to destroy the organic compounds into CO, 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 (Farmer et al., 1992). Chiba (1993) 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. Bringmann et al. (1998) 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 treated by several technologies (Comninellis and Pulgarin, 1991; Esplugas et al., 2002; Feng and Li, 2003; Lippincot, 1990; Pifer et al., 1999). Ince (1999) found that the Fenton's reagent and the photo-oxidation using UV/H₂O₂, UV/TiO₂ or $UV/H_2O_2/Fe^{3+}$ systems were effective in the elimination of organic compounds dissolved or dispersed in aqueous media. Boye et al. (2002) and Oturan (2000) established that the electro-Fenton process was effective in the elimination of synthetic dye mixture from water and the strong odour and ecotoxicological consequences. Raju and Basha (2005) 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 MEO has been identified as one of the most promising future technologies by the United Nations Environmental Programme (GEF, 2004) for the ambient temperature destruction of toxic organic pollutants and waste streams, including persistent organic pollutants and dioxins (Balaji et al., 2007a, b, c; Kokovkin et al., 2007; Matheswaran et al., 2007). In particular, the Ag (II)/ Ag (I) based MEO system has been widely studied to destroy hazardous industrial waste (Bringmann et al., 1995; Farmer et al., 1992; Galla et al., 2000; Sequeira et al., 2006) and to decontaminate plastic waste (Fourcade et al., 2003), 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 (Beauchesne et al., 2005; Chen and Lim, 2005; Hwang et al., 1987; Kusakabe et al., 1986), 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. Since the MEO process minimizes additional treatment of the effluents, this study used the MEO process and attempted to identify the best way to reduce Total organic content (TOC) for resin effluents using batch recirculation method. The current study was carried out at Central Electrochemical Research Institute, Karaikudi, India during the period August 2008 to December 2008.

MATERIALS AND METHODS

The synthetic resin effluent was prepared by dissolving an appropriate amount of cationic resin (Amberlite strong acid styrene based cation exchange resin - functional group - SO₃H) in water in presence of ferrous sulphate (Fe²⁻/Fe³⁻) as catalyst, with drop wise addition of H₂O₂ by maintaining temperature of the reaction mixture at 95-100 °C.

Experimental setup

Experiments were carried out under galvanostatic condition at different current densities and flow rates using RUO, coated Titanium expanded mesh anodes

and stainless cathodes. The electrolyser was of filter press type reactor (Fig. 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 are connected in parallel to the reactor.

Experimental procedure

All experiments were carried out under batch recirculation conditions, first treating 2 L 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 1h interval. Based on the results obtained it was decided to continue the investigation using FeSO₄ as the mediator along with NaCl as the supporting electrolyte with only 500 mL of the electrolyte at a flow rate of 20 L/h in order to provide a good conductivity conc. H₂SO₄ (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/dm². 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/h.

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 L
Flow rate	20 L/h
Duration of electrolysis	8 h

By taking 10 A/dm^2 as the opinion current density, experiments were carried out with different flow rates such as 20, 40, 60, 80, 100 L/h.

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 50/100 µL. 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.



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

Treatability of resin effluents

RESULTS AND DISCUSSION

Influence of anode material

The presence of NaCl in electrolyte catalyses the oxidation of organic resins only in case of inactive anode, Ti/RUO_2 . 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/RUO_2 , a traditional anode material, give relatively low current efficiency.

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 (Figs. 2-4). 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 wastewater.

Influence of current density

Figs. 5 and 6 show the effect of current density on % 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 % 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 fairy 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.

Effect of applied current

Fig. 7 shows the effect of applied current on the % reduction of TOC of the organic ion exchange resins as a function of time. The time efficiency for complete oxidation of organic resins for 8 h run changes from 5.31 % to 3.48 %, 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











Fig. 4. Percentage reduction of TOC Vs Charge for different current densities at flow rate 20 L/h

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 90 % conversion for the higher currents.

Effect of flow rates

Figs 8 and 9 show the effect of flow rates on the % reduction of TOC removal. % 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







Fig 6: Current density vs percentage reduction of TOC for flow rate 20 L/h







Fig. 8: Percentage reduction of TOC vs flow rate for current density 10 (A/dm²)



Fig. 9: Experimental percentage reduction of TOC vs simulated percentage reduction of TOC

cell, the % removal of TOC of the organic ion exchange resin was found to be decreased with high flow rates.

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



Fig. 10: Current efficiency Vs Flow rate for 10 (A/dm²)



Fig. 11: Experimental current efficiency vs simulated current efficiency

of Fe (II). The data from the sets of experiments revealed that TOC removal was found to be very low (about 25 % reduction was only achieved) in the absence of Fenton's mediator.

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 coloumbic efficiencies at the dimensionally stable anodes (DSA).

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 thereby creates over voltage which automatically gives high energy consumption.

Simulated results

The experimental data were used to develop neural networks using general regression neural network (GRNN) model. Figs. 10 and 11 brings out the experimental and simulated graphs.

CONCLUSION

This study focused on using electro chemical treatment based on MEO as a potential candidate to achieve mineralization of organic resins. The process was 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 (Fe²⁺/Fe³⁺ + H₂O₂),OH^o. Thus, NaCI 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.

In nuclear power plants uranium wastes that are obtained could be initially removed by cold combustion process later followed by electrochemical treatment reduces the organic resin wastes to a higher extent when compared to other processes. 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 % only in the absence of Fenton's mediator, which implied the catalytic action of Fenton's mediator. The study aligned with the earlier studies of Beauchesne et al. (2005); Chen and Lim (2005); Hwang et al. (1987) that the electro chemical oxidation method is advantageous and efficient for the removal of resin effluents which predominantly contain metal ions. 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.

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