ELECTROCHEMICAL TREATMENT OF STARCH EFFLUENT USING RuO$_2$/ Ti AND PbO$_2$/ Ti ELECTRODES

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The wastewater generated from Sago factories which cultivates Tapioca contains starch in both the suspended and dissolved forms. The starchy waste is very difficult to degrade by the conventional activated sludge process. In this paper the starch effluent (real and synthetic) was treated by an electrochemical method with the principal aim of eliminating COD using RuO$_2$/ Ti and PbO$_2$/ Ti anodes. Experiments were conducted to examine the effects of the operating parameters such as current density and concentration of NaCl on the COD removal efficiency. For the starch effluent containing high biodegradable organic content the current density of 7.5 A.dm^{-2} was required for both types of anodes to achieve a maximum removal of COD. The pseudo first order kinetics was found to be maintained throughout the reaction. Comparing the results of the electrooxidation of the starch effluent at the above two electrodes, the RuO$_2$/ Ti anode proved to be very effective than PbO$_2$/ Ti.

INTRODUCTION

More than thousands of Sago industries cultivate Tapioca in Tamilnadu and Kerala due to which 100 million liters of wastewater are generated every day which have high. Organic content. These organic matters consume the dissolved oxygen in water and eventually destroy the ecosystem of the hydrosphere. This is the main content of not only food processing waste but also the industrial wastewaters such as those from chemical. pulp and leather and the municipal wastewater. In the case of starch producing, super refining and brewing industries, the BOD level of wastewater is especially high and causes environmental pollution. Due to its environmental impact, this waste requires treatments before being released. The starch processing wastewater usually contains high concentration of organic substances such as carbodydrates, protein, fats and a mixture of them and it also produces obnoxious fouling odour if the wastewater suffers from anaerobic conditions or during fermentation. Biological treatment of this kind of wastewater does not always ensure satisfactory efficiency and it is a time consuming process. Hence the electrochemical process can be applied as an alternative route to a traditional biological process.

Electrochemical methods have been applied in the treatment of the wastewater since the early 1960s [1]. This method has been successfully tested to various industrial wastewaters such as metal plating industries in silver recovery from photographic baths and in other process of metal recovery [2], in the purification of wastewater containing cyanides [3], and phenols [4], waste water from dye production [5], tannery [6], and others [7]. However no attempt has been made till date dealing with starch by electrochemical method. The present study demonstrates the treatment of the starch effluent by electrochemical method.

EXPERIMENTAL DETAILS

Investigations on the electrochemical treatment of synthetic starch effluent and real effluent were carried out galvanostatically in a batch static condition. The synthetic starch effluent was prepared by dissolving an appropriate amount of atta flour in water and kept for fermentation for about 4-5 days. Real effluent was collected from a SAGO factory near Rasipuram Industrial Area, Salem, India. Tapioca is employed as the raw material here. Batch electrolyte cell used in the electrooxidation process is shown in Fig. 1. The cell consists of a glass beaker of 250 ml capacity closed with a PVC lid having provision to fit a
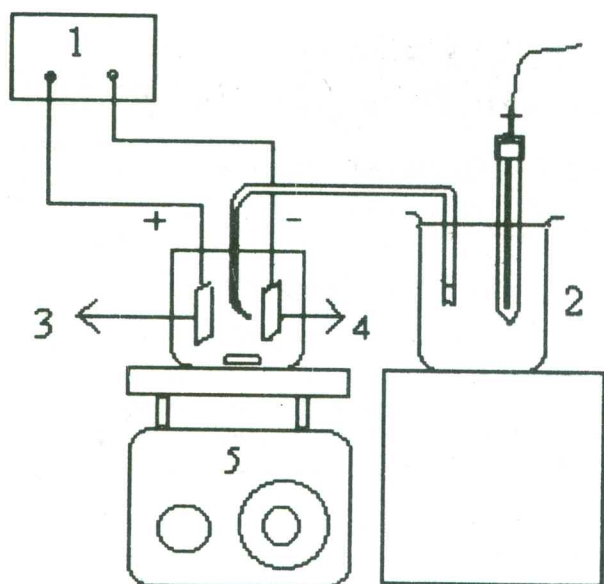
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Fig. 1: Schematic diagram of experimental setup used for the galvanostatic oxidation of starch
(1) Power supply   (2) Reference electrode
(3) Anode   (4) Cathode   (5) Magnetic stirrer

cathode and an anode. Salt bridge with reference electrode was inserted through the holes provided in the lid. The cathode was a stainless steel plate and the anode taken was a $RuO_2/$ Ti of area 0.2304 dm^2 or a $PbO_2/$ Ti of area 0.192 dm^2. The current was supplied by an electric power source (Aplab 7771). Stirring was done with a magnetic stirrer. The effluent volume of 200 ml was taken

for all the experiments. Electrolysis were carried out at different current densities viz 2.5, 5 & 7.5 $A.dm^{-2}$ and NaCl concentrations viz 10, 20, 30 gl^{-1}. During the electrolysis, samples were collected at different time intervals and the COD concentration was measured by the standard method (APHA 1992) [8].

RESULTS AND DISCUSSION

The data showing the results of investigations on the electrooxidation of the starch (synthetic & real) effluents carried out galvanostatically at $RuO_2/$ Ti and $PbO_2/$ Ti anodes are summarized in Table I.

Effect of current densities

The conductivity of the synthetic effluent strongly depends on the salinity [9]. The present electrochemical treatment is no exception. First the experiments were carried out in synthetic effluent on $PbO_2/$ Ti anode (Table expts [1-3] at different current densities viz 2.5, 5 and 7.5 $A.dm^{-2}$ keeping the NaCl concentration (10 gl^{-1}) constant. As the COD removal efficiency is a function of time the variation of COD on PbO_2/Ti at different current densities with respect to time were observed and is presented in Fig. 2. From the figure and table it is observed that COD removal efficiency increases with increase of current densities. The maximum COD removal efficiency of 63.79% and CE. of 34.35% are obtained at a current density of 7 $A.dm^{-2}$. The energy consumption increases with increase in current density. The electrolytes were carried out on $RuO_2/$ Ti (Table expts 4 -6a, Fig. 3) under

TABLE I: Electrochemical data on the galvanostatic oxidation of starch at different anode in NaCl media

Exp no	Current density $A.dm^{-2}$	[NaCl] gl^{-1}	Anode type	Electrolysis time hrs	Cell voltage V	COD reduction %	Current efficiency %	Energy consumption Kwh/Kg COD
1	2.5	10	$PbO_2/$ Ti	12.5	4.88-4.98	45.2	26.0	63.5
2	5.0	10	"	6.3	6.49-6.39	61.8	31.6	68.3
3	7.5	10	"	4.2	9.74-7.80	63.8	34.4	85.5
4	2.5	10	$RuO_2/$ Ti	10.4	5.12-4.95	56.3	17.4	97.1
5	5.0	10	"	5.2	7.63-6.31	75.0	26.1	89.5
6a	7.5	10	"	3.4	11.50-8.35	80.0	34.5	140.1
6b	7.5	20	"	3.4	3.59-3.05	86.1	35.4	31.4
6c	7.5	30	"	3.4	5.18-4.99	91.9	43.1	39.5
7	7.5	30	"	4.2	4.95-4.22	75.8	65.7	23.4
8	7.5	30	$PbO_2/$ Ti	4.2	6.68-5.96	50.5	47.3	44.8

Synthetic effluent expt no: 1-6c   Real effluent expt no: 7 & 8

identical condition to that of $PbO_2/$ Ti. Here also, the COD removal efficiency is found to be dependent on current density. At current density 7.5 A.dm^{-2} the CE. of 26.09% was obtained for the maximum COD removal of 80% at low NaCl conc. of about 10 gl^{-1}. When compared to $PbO_2/$ Ti, the energy consumption was also significantly found to be higher at $RuO_2/$ Ti and it may be probably in part because of the marked Joule effect (high temperature rise for higher currents is noticed at $RuO_2/$ Ti than $PbO_2/$ Ti).
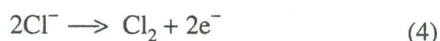
During the electrooxidation process the overall possible reactions taking place at the electrodes are given as follows.

$$NaCl \longrightarrow Na^+ + Cl^- \qquad (1)$$

Anode

$$2Cl^- \longrightarrow Cl_2 + 2e^- \qquad (2)$$

$$NaCl \longrightarrow Na^+ + Cl^- \qquad (3)$$

Anode

$$2Cl^- \longrightarrow Cl_2 + 2e^- \qquad (4)$$

$$H_2O + Cl_2 \longrightarrow HOCl + HCl \qquad (5)$$

Cathode

$$2H^+ + 2e^- \longrightarrow H_2 \qquad (6)$$

Bulk

$$Organic\ matter + OCl^- \longrightarrow$$

$$CO_2 + H_2O + Cl^- + product \qquad (7)$$

In addition to the generation of OCl⁻ ions there are many other side reactions taking place apart from the COD removal. This may be the reason for low current efficiency observed at these electrodes. The maximum COD removal efficiency was achieved for $RuO_2/$ Ti electrode at 7.5 A.dm^{-2} than $PbO_2/$ Ti. Plotting the removal of COD vs COD concentration, a linear relationship was obtained for all the runs indicating that probably a pseudo first order kinetics was maintained. The corresponding plots for the two different electrodes at different current densities are shown in Fig. 4.

Effect of NaCl concentration

In order to improve the conductivity and also enhance the COD removal efficiency the NaCl concentration was increased. Among the two electrodes $RuO_2/$ Ti & $PbO_2/$ Ti, the maximum COD removal was obtained for $RuO_2/$ Ti at 7.5 A.dm^{-2}. So in this electrode the effect of NaCl concentrations have been studied by keeping the optimum current density (7.5 A.dm^{-2}) as constant. From table expts 6a- 6c, it was observed that the maximum COD removal of 91.8% and CE of 43.11% were achieved for NaCl concentration of 30 gl^{-1}.
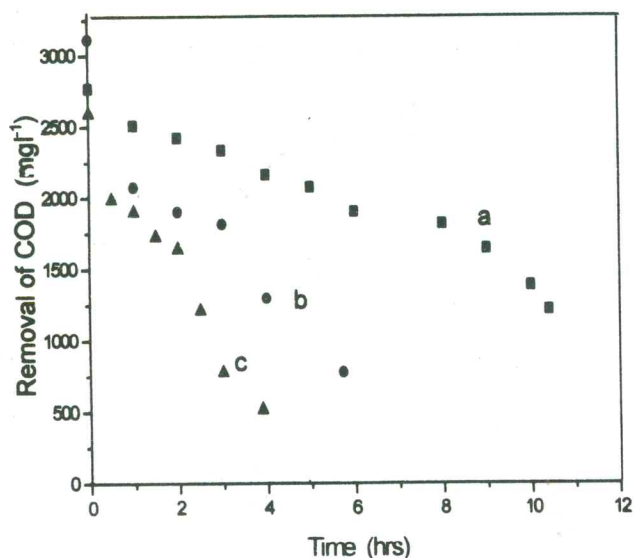
Fig. 2: Progress of COD removal from the synthetic starch effluent on $PbO_2/$ Ti at current density A.dm^{-2}
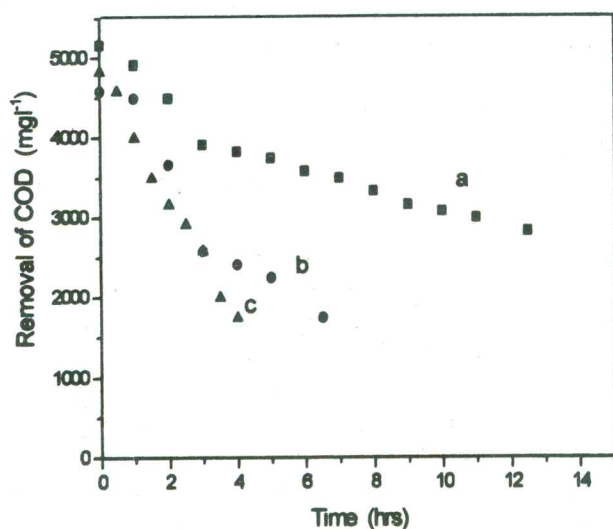(a) 2.5   (b) 5.0   (c) 7.5 concn NaCl 10 g.l^{-1}

Fig. 3: Progress of COD removal from the synthetic starch effluent on $RuO_2/$ Ti at current density A.dm^{-2}
(a) 2.5   (b) 5.0   (c) 7.5 concn NaCl 10 g.l^{-1}
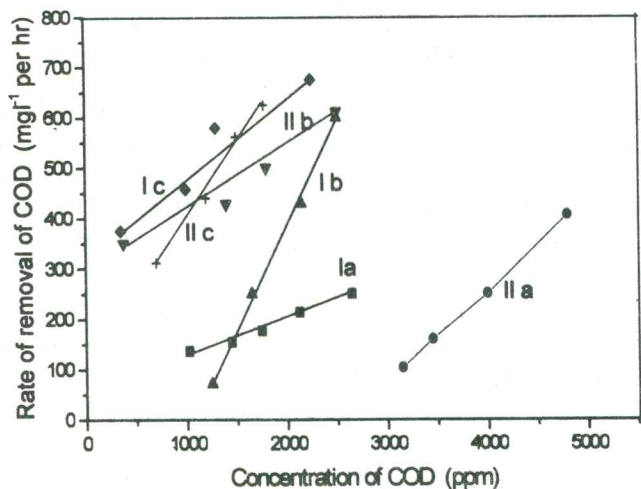
Fig. 4: COD removal rate vs concentration of COD at the synthetic starch effluent at $PbO_2/$ Ti (I) and $RuO_2/$ Ti (II) anodes at current density A.dm^{-2}
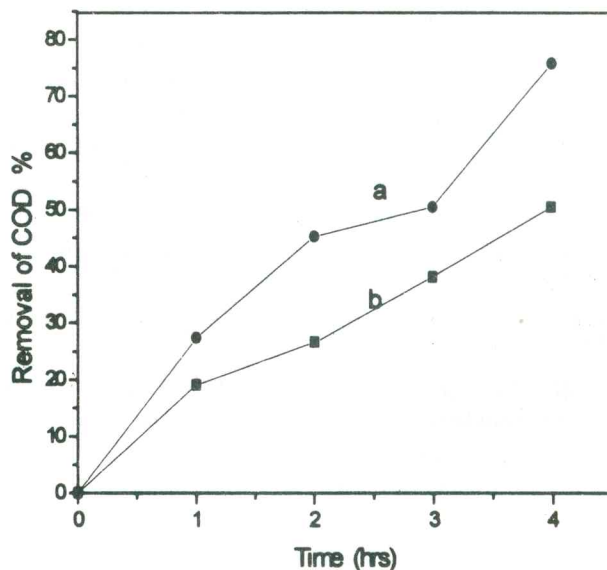(a) 2.5   (b) 5.0   (c) 7.5

Fig. 5: Variation of COD with respect to time during the electrolysis of real effluent at $RuO_2/$ Ti (a) and $PbO_2/$ Ti (b) anodes at current density 7.5 A.dm^{-2}; at NaCl concn of 30 gl^{-1}

Finally the electrolyses were also carried out in the real effluent both at $RuO_2/$ Ti & $PbO_2/$ Ti electrodes under best condition of c.d. 7.5 A.dm^{-2} and NaCl concentration of 30 gl^{-1} (Fig. 5 and Table expts 7 & 8). It was observed that 75.78% of COD removal and CE of 65.68% were achieved at $RuO_2/$ Ti with low energy consumption of 23.28kWh/Kg of COD whereas in the case of $PbO_2/$ Ti only 50.48% COD removal and 47.3% CE were obtained. Comparing the results obtained for the electrooxidation of the starch effluent at the above two electrodes, the $RuO_2/$ Ti anode proved to be very effective for the oxidation of starch effluent even in presence of a low concentration of NaCl 10 gl^{-1}, than $PbO_2/$ Ti anode.

CONCLUSION

Electrochemical method has been employed in the present study to treat the starch wastewater using catalytic anodes. Effects of current density and NaCl concentration on the treatment efficiency are studied. For the starch wastewater containing biodegradable organic content, the current density for both electrodes has to be high (7.5 A.dm^{-2}) to achieve a substantial removal of COD. Due to electrocatalytic nature of $RuO_2/$ Ti and $PbO_2/$ Ti anodes, the COD removal from the starch effluent with these electrodes in presence of NaCl is a combined effect of direct as well as indirect anodic oxidation. It is evident from the above results that

the process of COD removal proceeds to higher degree at a $RuO_2/$ Ti than at a $PbO_2/$ Ti. It is also observed that the pseudo first order kinetics was maintained during the process.

The experimental data presented here were only under batch conditions and the optimization of the results can be expected for dynamic conditions. For the practical application of the process, dynamic conditions would be suitable and the research is under progress to make the process possible to improve and rationalize the conditions.

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