

Electrochemical degradation of pulp and paper industry waste-water

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Abstract

BACKGROUND: Conventional biological waste-water treatment techniques are insufficient to degrade large quantities of dissolved lignin discharged by small-scale paper mills. The current investigation is aimed at comparing the overall performance of basic electrochemical reactor configurations such as batch, batch recirculation, recycle and single pass systems, in removing the organic part of waste-water from a small-scale, agro-based paper industry. The effect of current density, supporting electrolyte concentration, duration of electrolysis, specific electrode surface and fluid flow rate on the removal of pollutants and energy consumption are critically evaluated. The improvement in biodegradability of the effluent during treatment is also noticed.

RESULTS: The batch recirculation mode of operation was found to be superior in comparison with a batch system using the same specific electrode surface for both COD removal (73.3 vs. 64%) and capacity utilization (rate constant 1.112×10^{-3} vs. $1.049 \times 10^{-3} \text{ cm s}^{-1}$). The pollutant removal performance of the batch recirculation system improved considerably with increase in the circulation flow rate. At the best operating point in the recycle system, 59% of COD was removed, corresponding to a current efficiency of 68.9% and specific energy consumption of $18.46 \text{ kWh kg}^{-1}$. The biodegradability index of the waste-water was improved from 0.18 ± 0.01 to 0.36 ± 0.01 .

CONCLUSION: A recycle reactor was the best configuration, because of its flexibility of operation. Circulation flow rate and withdrawal flow rate enable the control of transfer coefficients and treatment duration respectively. Electrochemical treatment not only removes the bulk of the organic matter, but also makes the remaining pollutants more easily biodegradable.

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Keywords: electrochemical degradation; pulp and paper waste-water; COD removal; batch recirculation; recycle

INTRODUCTION

The pulp and paper industry is one of the oldest and a core industrial sector in India. It is a high capital, high energy, and water intensive industry that is also highly polluting and requires substantial investment in pollution control equipment. India produces six million tons of paper per year in approximately 311 mills. Of these about 270 small paper mills (capacity $\leq 10\,000 \text{ tons year}^{-1}$, having a total installed capacity of $1.47 \text{ Mtons year}^{-1}$) do not have chemical recovery units.¹ In India, around 900 million m^3 of water is consumed and 700 million m^3 of waste-water is discharged annually by this sector. India's current average fresh specific water consumption for a large-scale wood based pulp and paper mill, of about $150 \text{ m}^3 \text{ ton}^{-1}$ of product is far above the global best specific water consumption of $28.66 \text{ m}^3 \text{ ton}^{-1}$. This large gap is primarily attributed to the use of obsolete technology and poor water management practices. The large water requirements and consumption by the Indian pulp and paper industries has led to water becoming a scarce commodity.

Among the various operations in the pulp and paper industry the most significant sources of pollution are wood preparation, pulping, pulp washing, bleaching and paper machine operations. Common pollutants include suspended solids, oxygen demanding wastes, colour, basicity, heavy metals, alkali and alkaline earth metals, phenols, chloro-organics, cyanide, sulfides and other

soluble substances.² The resultant effects on the environment are slime growth, thermal impact, scum formation and colour problems. They increase the amount of toxic substances in water, causing death to zooplankton and fish, as well as profoundly affecting the terrestrial ecosystem.³

Conventionally, pulp and paper industry waste-water has been treated by chemical coagulation followed by biological treatment. Although coagulation is efficient in removing waste-water contaminants, it is a simple physico-chemical process of phase transference. Sludge resulting from such treatment, placed in landfill, can cause soil, ground and underground water pollution by the leaching of contaminants. In the most common biological treatment system, i.e. the activated sludge process, considerable removal of biological oxygen demand (BOD), chemical oxygen demand (COD), adsorbable organic halides (AOX) and chlorinated phenolics can be achieved.⁴ However, the

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brownish colour of the effluent is not completely removed by this treatment. The waste-water components causing colour (lignin and its derivatives) are difficult to degrade naturally because of strong linkages in their molecular structure (especially the biphenyl type of carbon-carbon bond). The presence of such difficult-to-biodegrade and refractory materials in the waste makes the process very slow. The technical and economic feasibility of large-scale operations using other treatment alternatives such as adsorption,⁵ wet oxidation,⁶ ozone treatment,⁷ fractional precipitation,⁸ ultrafiltration,⁹ combined biological and membrane based treatments,¹⁰ etc., are questionable.

Over the past two decades there has been a growing interest in the use of electrochemical techniques such as electro-coagulation, electro-flotation and electro-oxidation for the treatment of organic effluents. The technical feasibility of treating various industrial effluents such as electroplating waste-water,¹¹ oil mill waste-water,¹² heavy metal laden waste-water,¹³ nitrite effluent,¹⁴ defluoridation,¹⁵ arsenic removal,¹⁶ textile dyes,¹⁷ landfill leachate,¹⁸ restaurant waste-water,¹⁹ laundry waste-water,²⁰ surfactants,²¹ agro industry waste-water,²² etc., has been studied.

Electrochemical degradation of pulp and paper waste-water has been reported by few researchers. Ugurlu *et al.*²³ studied electro-coagulation as a post-treatment of pulp and paper effluent using aluminium anodes in a batch electrochemical cell and reported removal capacities of 80% for lignin, 98% for phenol, 70% for BOD and 75% for COD. Mahesh *et al.*¹ studied the electrochemical degradation of pulp and paper mill effluent by electro-coagulation in a batch cell followed by chemical flocculation and reported an overall COD removal of 91% and almost complete colour removal. Mansour *et al.*²⁴ studied the treatment of waste-water in the paper industry by coagulation followed by electro-flotation and reported more than 95% removal of suspended solids. Patel *et al.*²⁵ studied the electrochemical treatment of 10 mg L⁻¹ of pentachlorophenol in pulp bleaching effluent and reported almost complete removal in less than 10 min at a current density of 6 mA cm⁻².

Electrochemical degradation on noble metal oxide anodes, a non-sacrificial anode process, eliminates the generation of chemical sludge and thus is attractive in operating cost and simplicity of operation. The economic viability of the complete mineralization of a large volume of such a heavily loaded organic effluent is questionable. But the possibility of integrating electrochemical with conventional methods for an improved, economically viable overall performance is still under examination.²⁶ In the current study, the performance of electrochemical degradation of the combined stream discharged from Sun Paper Mills Ltd., Cheranmahadevi, Thirunelveli district, Tamilnadu, India, a small-scale agro-based pulp and paper industry, is investigated using a RuO₂ coated titanium electrode in various types of reactor arrangements such as batch, batch recirculation and recycle reactors. The mechanism of the electrochemical degradation process and the effect of important operating parameters such as current density, supporting electrolyte concentration and electrolysis time on pollutant removal and energy consumption of these systems are studied. Improvement in the biodegradability of the effluent during the treatment was also studied.

MATERIALS AND METHODS

The effluent, 200–350 m³ ton⁻¹ of paper, was sampled from the equalization basin of the existing waste-water plant. For economic reasons this small-scale agro-based industry does not own a black liquor recovery unit. The physicochemical characteristics of the

Table 1. Characteristics of the small-scale agro-based pulp and paper industry waste-water

Parameter	Value
Colour	Dark brown
pH	6.8–8
Conductivity (mS cm ⁻¹)	2.1
Salinity (mg L ⁻¹)	320
Chloride (mg L ⁻¹)	200
Sulfate (mg L ⁻¹)	954
COD (mg L ⁻¹)	1669 ± 23
BOD (mg L ⁻¹)	300 ± 12
Suspended solids (mg L ⁻¹)	750–1140
Dissolved solids (mg L ⁻¹)	280–410
BI	0.18 ± 0.01

effluent were determined before treatment (Table 1). The waste was colored and contained slowly biodegradable organic matter and salts. The biodegradability index, defined as the ratio of BOD to COD, was found to be low, 0.18 ± 0.01.

All the chemicals used in the study were of analytical reagent (AR) grade. The sample COD was determined using the dichromatic open reflux method and BOD by Winkler's method, strictly following the APHA.²⁷ Experiments were repeated until the error was less than 3%. Electrochemical experiments were carried out using a RuO_x-IrO_x-TiO_x coated²⁸ titanium substrate insoluble anode (TSIA) and a stainless steel cathode.

Treatment in batch mode

The experimental set-up of the batch reactor used for electrochemical degradation studies consisted of a 500 mL capacity Perspex cylinder (diameter 8 cm, height 11 cm) with a PVC lid with facilities to fit a pair of electrodes and withdraw samples periodically. A rectangular, stainless steel flat plate cathode and a rectangular flat expanded mesh of titanium catalytic oxide coated anode. The plates (4 cm × 7.5 cm) were parallel to each other with a 10 mm inter-electrode gap. The void fraction of the mesh anode was 22%, which resulted in an effective area of 18 cm² (dipped area: 4 × 5.75 cm). The electrodes were connected to a 5 A, 10 V DC regulated power supply, through an ammeter and a voltmeter. Preliminary batch experiments of COD removal were conducted to find the influencing parameters and their experimental domains. The ionic conductivity of the waste-water was increased by adding an appropriate amount of sodium chloride. Since the pH of the effluent was found to have less influence on the response during the preliminary runs, no adjustment was made. The electrode plates were cleaned manually by washing in distilled water prior to every run. The electrodes were placed in the required volume of waste-water in the cell such that 18 cm² of active surface of the anode was immersed. The solution was constantly stirred at 200 rpm using a magnetic stirrer to maintain uniform concentration. DC power was supplied to the electrodes according to the required current density and the experiments were carried out under constant current conditions. The efficiency of the electrochemical reactor was studied under various conditions of current density, supporting electrolyte concentration, and reactor hold-up. The effluent was treated at two different current densities, 2.5 and 5.0 A dm⁻² and the hold-up volume was 200, 325, and 450 mL. The supporting electrolyte concentration was varied (1, 2, 3, 4, 5 g L⁻¹ at 2.5 A dm⁻²

and 5, 6, 7, 9 g L⁻¹ at 5.0 A dm⁻²). Progress of pollutant removal was measured by COD determination at regular intervals over 5 h.

Treatment in batch recirculation mode

The experimental set-up of the batch-recirculation/recycle/once-through mode of operation is schematically represented in Fig. 1. By adjusting the valves the same set-up can be operated either in batch recirculation, recycle, or once-through modes (i.e. for batch recirculation mode, streams 10 and 12 are closed). The electrolytic flow reactor consisted of a cylindrical stainless steel cathode (20 cm long and 7.8 cm diameter) and a catalytic expanded mesh cylindrical (surface void fraction 0.22) anode of RuO_x-IrO_x-TiO_x coated titanium, measuring 15.2 cm long and 3.7 cm diameter (active anode area: 138 cm²). The anode was held co-axially with the cathode with a constant 2.05 cm inter-electrode gap. Provisions were made for electrical connections to constitute an electrolytic cell. The cell had one inlet in the bottom cover and an outlet in the top cover. The electrodes were connected to a 6 A, 15 V DC regulated power supply, an ammeter and a voltmeter. The other components of the set-up were a 3.0 L reservoir, a magnetically driven self-priming centrifugal pump and a rotameter, connected using silicone rubber tubes. The reservoir was filled with 2.5 L of waste-water containing 3 g L⁻¹ sodium chloride. The required flow rate through the reactor was established by pumping and adjusting the valves. DC power was supplied to the electrodes keeping a constant current of 3.44 A, corresponding to a current density of 2.5 A dm⁻². The liquid flow rate into the reactor was varied (20, 40, 60, 80, or 100 L h⁻¹) measured using a calibrated rotameter. Every experiment was run for 6 h and samples were collected every hour from the reservoir and kept under acidic conditions for the determination of COD.

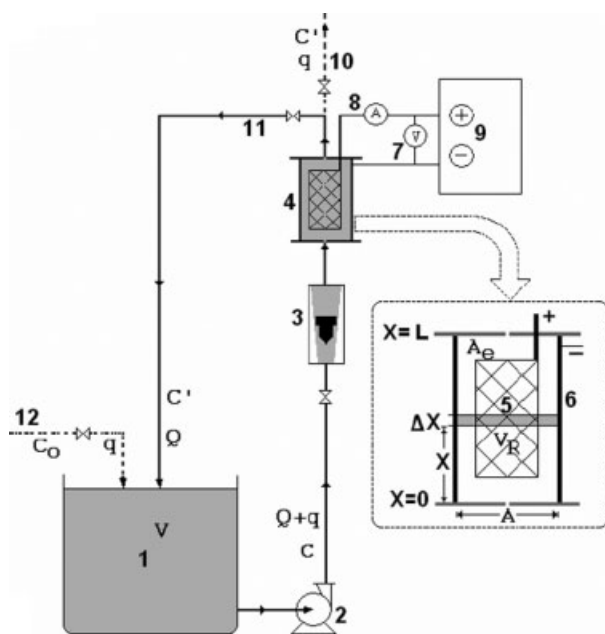


Figure 1. Experimental set-up of flow reactor: 1. reservoir, 2. pump, 3. rotameter, 4. cylindrical flow cell, 5. anode, 6. cathode, 7. digital voltmeter, 8. digital ammeter, 9. d.c. regulated power supply, 10. treated waste-water outlet, 11. recirculation stream, 12. waste-water inlet reactor. (For batch recirculation system stream 10 and 12 will be absent and for once-through operation stream 11 will be absent).

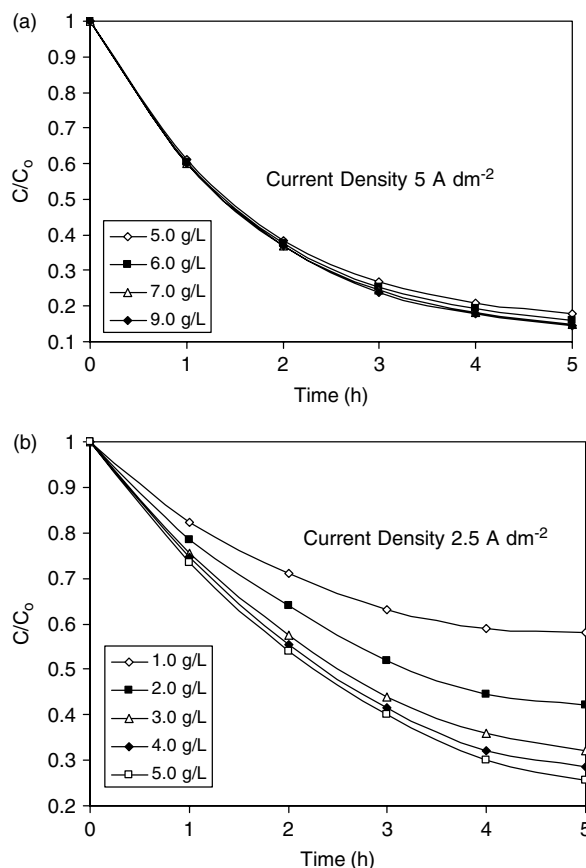


Figure 2. Effect of electrolysis time and supporting electrolyte concentration on percentage removal of COD in the batch system. Conditions: volume 200 mL; initial COD 1669 ± 23 mg L⁻¹; specific electrode surface 0.09 cm⁻¹. (a) Current density 5.0 A dm⁻²; (b) Current density 2.5 A dm⁻².

Treatment in recycle mode

Figure 2 shows the experimental set-up of the recycle mode of operation. Waste-water containing 3 g L⁻¹ sodium chloride was placed in the reservoir. The required recycle flow rate Q and flow rate through the reactor ($Q + q$) was established by pumping and adjusting the valves. A DC power supply was connected to the electrodes keeping a constant current of 3.44 A, corresponding to a current density of 2.5 A dm⁻². Maintaining the required discharge flow rate, the waste-water inlet flow rate was adjusted to reach steady state reservoir level. The recycle flow rate (Q) was varied (20, 40, 60 L h⁻¹) and for each Q , the inlet/discharge flow rate (q) was varied (0.21, 0.37, 0.55, 0.73 or 1.0 mL s⁻¹). Samples were collected from the exit stream for each experiment for COD determination.

Treatment in once-through mode

Waste-water containing 3 g L⁻¹ sodium chloride filled the reservoir. The required flow rate through the reactor was established by pumping and adjusting the valves (i.e. stream 11 in closed condition). A DC power supply was connected to the electrodes keeping a constant current of 3.44 A, which corresponds to a current density of 2.5 A dm⁻². The recycle mode of operation was changed over to the once-through mode by closing the recirculation valve. The flow of the make-up stream was increased to maintain a steady state reservoir volume. The liquid flow rate through the reactor (Q) was varied (20, 25, 30 or 35 L h⁻¹) and each experiment was run for 15 min (more than three times the

residence time of the reservoir) before sampling the outlet stream for COD determination.

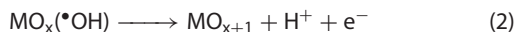
ELECTRO-OXIDATION – THEORETICAL APPROACH

Pulp and paper mill waste-waters contain lignin, sulfides, sulfur compounds, chlorinated compounds, and various inorganic salts. Lignin is an amorphous, branched, poly-dispersed macromolecular substance, having several functional groups, notably phenolic, hydroxyl, benzylic, carbonyl and aliphatic carboxylic groups. Catechols which contain ortho-substituted dihydroxyl groups, are known to form stable complexes with multivalent metal cations. During the cooking operation lignin is partly degraded, becomes water soluble, and also remains in a colloidal form. As the pH is lowered (in the acidic region), lignin, which behaves as a hydrocolloid, precipitates with simultaneous production of acidic groups in the liquor. Electrochemical degradation of waste-water occurs via oxidation. Since pulp and paper mill effluent used in the present study contains a small amount of chloride ($\text{Cl}^- \sim 200 \text{ mg L}^{-1}$) to improve its ionic conductivity and promote oxidation sodium chloride was added. The mechanism of electrochemical oxidation of waste-water is a complex phenomenon involving the coupling of an electron transfer reaction with a dissociate chemisorption step. Basically two types of oxidative mechanism may occur at the anode; in the case of an anode with high electro-catalytic activity, oxidation occurs at the electrode surface (direct electrolysis); in other instances, for example with a metal oxide electrode, oxidation occurs via the surface mediator generated continuously on the anodic surface (indirect electrolysis). In direct electrolysis, the rate of oxidation depends on electrode activity, diffusion rate of pollutants and current density. The electrochemical conversion/combustion of organics on a noble oxide coated catalytic anode (MO_x) can be explained as follows.

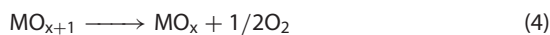
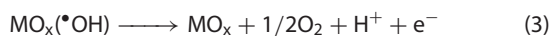
In the first step, H_2O is discharged at the anode to produce adsorbed hydroxyl radicals according to the reaction:



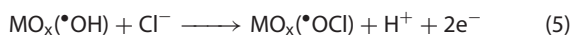
In the second step, the adsorbed hydroxyl radicals may interact with the oxygen already present in the oxide anode with possible transition of oxygen from the adsorbed hydroxyl radical to the oxide to form a higher oxide MO_{x+1} :



At the anode surface, active oxygen can be present in two states, either as physisorbed hydroxyl radicals, ($\bullet\text{OH}$) and/or chemisorbed (oxygen in the lattice, MO_{x+1}). In the absence of oxidizable organics, the active oxygen produces dioxygen according to the following reactions:

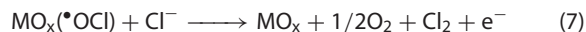
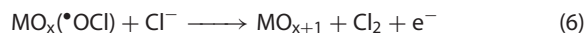


When NaCl is used as supporting electrolyte, chloride ions may anodically react with $\text{MO}_x(\bullet\text{OH})$ to form adsorbed -OCl radicals according to the following reaction:

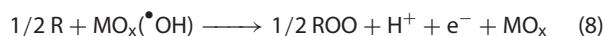


Further, in the presence of chloride ion, the adsorbed hypochlorite radicals may interact with the oxygen already present in the oxide

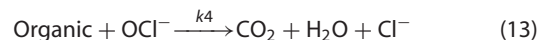
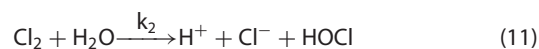
anode with the possible transition of oxygen from the adsorbed hypochlorite radical to the oxide, to form a higher oxide MO_{x+1} according to the reaction given below. Simultaneously $\text{MO}_x(\bullet\text{OCl})$ can react with the chloride ion to generate active oxygen (dioxygen) and chlorine according to the following reactions:



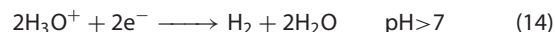
In the presence of oxidizable organics, the physisorbed active oxygen ($\bullet\text{OH}$) can predominantly cause complete oxidation of organics and will participate in the formation of selective oxidation^{29,30} products according to the following reactions:



The physisorbed route of oxidation is preferable for waste treatment since the organic hydrogen peroxides formed are relatively unstable and their decomposition will lead to molecular breakdown and the formation of subsequent intermediates with lower carbon numbers. These sequential reactions will continue until carbon dioxide and water are formed.^{31,32} In this case the diffusion rate of organics on the anode area controls the rate of decomposition.^{33,34} On the other hand in indirect electrolysis, temperature, pH and the diffusion rate of generated oxidants determine the rate of oxidation. An indirect electrochemical oxidation mechanism has been proposed for waste-water treatment using a metal oxide anode with chloride supporting electrolyte.^{35–37} Anodic oxidation of chloride ions to form chlorine in the bulk solution as given by Equations (6) and (7) further proceeds as follows:



Since organic compounds in the effluent are electrochemically inactive, the primary reaction occurring at the anodes is chloride ion oxidation (Equations (6) and (7)) with the liberation of Cl_2 , a robust oxidizing agent. As regards the reactions in the bulk, gaseous Cl_2 dissolves in the aqueous solutions as indicated in Equation (11). At the cathode the following reactions takes place:



The rate of the bulk reaction is lower in acidic solution due to the instability of OH^- and considerably higher in basic solution due to the ready formation of the OCl^- ion ($\text{p}K_a$ 7.44) (Equation (12)) implying that basic or neutral pH conditions are more favorable for reactions involving chlorine. The rate of direct electro-oxidation of organic pollutants depends on the catalytic activity of the anode, the diffusion rate of the organic compounds to the active points of anode and the applied current density. The indirect electro-oxidation rate of organic pollutants depends on the diffusion

rate of the oxidants into the solution, flow rate of the effluent, temperature and pH. In moderate alkaline solutions, a reaction cycle of chloride–chlorine–hypochlorite–chloride takes place, which produces OCl^- . The pseudo-steady state theory can be applied to each of the intermediate products (HOCl and OCl^-) in the bulk solution. The rate of reaction of the components can be written as:

$$-r_{\text{Cl}_2} = k_2[\text{Cl}_2] \quad (16)$$

$$r_{\text{HOCl}} = k_2[\text{Cl}_2] - k_3[\text{HOCl}] + k'_3[\text{H}^+][\text{OCl}^-] = 0 \quad (17)$$

$$r_{\text{OCl}^-} = k_3[\text{HOCl}] - k'_3[\text{H}^+][\text{OCl}^-] - k_4[\text{organic}][\text{OCl}^-] = 0 \quad (18)$$

$$-r_{\text{organic}} = k_4[\text{organic}][\text{OCl}^-] \quad (19)$$

Then using the above equations we can easily deduce the following expression:

$$-r_{\text{Cl}_2} = -r_{\text{organic}} = k_4[\text{organic}][\text{OCl}^-] \quad (20)$$

Finally as regards the bulk solution it can be noted from Equation (11) that $-r_{\text{Cl}_2} = r_{\text{Cl}^-}$ that is:

$$-r_{\text{Cl}_2} = r_{\text{Cl}^-} = k_2[\text{Cl}_2] = -r_{\text{organic}} = k_4[\text{organic}][\text{OCl}^-] \quad (21)$$

where the rate of reaction r_i and the rate constants k_i ($i = 2, 3$ and 4) are defined with respect to the bulk. The rate expression for the main electrode reaction (Equation (10)) can be written as:

$$-r'_{\text{Cl}^-} = r'_{\text{Cl}_2} = k_1[\text{Cl}^-] \quad (22)$$

where k_1 is the heterogeneous electrochemical rate constant.

In the following section an attempt is made to establish a relationship between the reacting species in bulk and at the electrode surface. The basic relationship applicable to all electrochemical reactions is Faraday's law that relates to the amount of substance reacted on the surface to the charge ($I_A t$) passed, $M_A I_A t / nF$ (assuming 100% current efficiency) and the characteristic measurable parameter, current density, i_A (defined as I_A / A_e). Thus, the electrochemical reaction rate (for the disappearance of reactant A) can be expressed as:

$$-\left(\frac{V_R}{A_e}\right) \frac{d[A]}{dt} = \frac{i_A}{nF} \quad (23)$$

where I_A is the current passed in time t , M_A is the molecular weight, n is the number of electrons transferred per mole of reaction, A_e electrode area, V_R reactor volume and F is the Faraday constant (96 485.3 coulomb mol^{-1}); note that $-r_A = -d[A]/dt = i_A a / nF$, where a is specific electrode area (A_e / V_R); assuming the main electrode reaction is governed by a simple Tafel type expression:

$$-\left(\frac{V_R}{A_e}\right) \frac{d[A]}{dt} = \frac{i_A}{nF} = k'[A] \exp(bE) \quad (24)$$

or:

$$-r'_{\text{Cl}^-} = r'_{\text{Cl}_2} = k_1[\text{Cl}^-] = k'_1 a [\text{Cl}^-] \exp(bE) \quad (25)$$

The reaction may be assumed to be under diffusion control as the reacting species, Cl^- in the electrolyte is dilute. The reactant Cl^- is transported from the bulk to electrode surface where it undergoes

electrochemical oxidation to Cl_2 and it may be transported back to the bulk by diffusion reaction in the bulk. Then:

$$\frac{i_A}{zF} = k_L([\text{Cl}^-] - [\text{Cl}^-]_s) \quad (26)$$

Eliminating $[\text{Cl}^-]_s$ using Equations (16) and (17):

$$\frac{i_A}{zF} = k_1[\text{Cl}^-] \quad (27)$$

where

$$\frac{1}{k_1} = \frac{1}{k_L} + \frac{1}{k'a \exp(bE)} \quad (28)$$

From a material balance of species Cl^- by taking note of Equations (12) and (13) one can write:

$$\frac{i_A}{zF} = k'[\text{Cl}_2] \quad (29)$$

$$\frac{i_A}{zF} = k''[\text{organic}][\text{OCl}^-] \quad (30)$$

During electrolysis, if a constant current is applied, the rate of generation of $[\text{OCl}^-]$ will remain constant under a given set of experimental conditions, but will vary if the applied current is altered. Then:

$$\frac{i_A}{zF} = k_{\text{obs}}[\text{organic}] = k[\text{COD}] = kC \quad (31)$$

Batch Reactor

Adopting the same classification for the reactors as for conventional reactors, the electrochemical reaction rate (for removal of COD) in a batch reactor can be expressed as:

$$-\left(\frac{V_R}{A_e}\right) \frac{dC}{dt} = \frac{i_A}{zF} = kC \quad (32)$$

$$C = C_0 \exp(-kat) \quad (33)$$

or in an integrated form $-\ln\left[\frac{C}{C_0}\right] = kat$

In electrochemical conversion, the high molecular weight aromatic compounds and aliphatic chains are broken to intermediate products for further processing. In electrochemical oxidation, the organics are completely oxidized to CO_2 and H_2O . The progress of organic pollutant destruction was monitored by COD determination. The potentials required for oxidation of organic pollutants are generally high and the production of oxygen from the electrolysis of water molecules may determine the reaction yield. The current efficiency of the electrolysis can be calculated using the following expressions:

For batch reactor:

$$\text{Current Efficiency (CE)} = \frac{V_R \Delta C}{\left(\frac{16It}{2F}\right)} \times 100$$

For flow reactor:

$$\text{Current Efficiency (CE)} = \frac{Q \Delta C}{\left(\frac{16I}{2F}\right)} \times 100 \quad (34)$$

where ΔC is the difference in COD in mg L^{-1} , due to passing current I (A) for t (s); V_R is volume of the reactor (L); Q is the volumetric flow rate (L s^{-1}) and F is Faraday's constant.

While current efficiency indicates the fraction of the total current passed for the targeted reaction, the term (E), the power consumption ($k \text{ Wh kg}^{-1}$) is the quantity of energy consumed in the process for a kg of COD to be digested and can be obtained using the equations:

For a batch reactor:

$$\text{Power consumption, } E = \frac{Vt}{3600 \times 10^3} \times \frac{1}{\Delta \text{COD} \times V_R \times 10^{-6}} \quad (35)$$

For flow reactor:

$$\text{Power consumption } E = \frac{VI}{3600 \times 10^3} \times \frac{1}{\Delta \text{COD} \times Q \times 10^{-6}}$$

where V represents the applied cell voltage in volts and the remaining terms are defined above.

Batch reactor with recirculation mode

In the current flow reactor system, the flow in the reactor is axial. Thus for the batch recirculation system streams 10 and 12 will be absent. An approximate model which represents the given system in which the reactions take place can be described by a plug flow reactor (PFR). A dynamic material balances of each of component or species in the reactor can be written as:

$$\left[\begin{array}{c} \text{rate of change mass of} \\ \text{species in the reactor} \end{array} \right] = \left[\begin{array}{c} \text{rate of mass} \\ \text{input} \end{array} \right] - \left[\begin{array}{c} \text{rate of mass} \\ \text{output} \end{array} \right] \mp \sum \left[\begin{array}{c} \text{rate of mass of species disappeared} \\ \text{or generated physico chemical phenomena} \end{array} \right]$$

The concentration variation of the organics in the differential volume of reactor (Fig. 1) can be written as:

$$-A \Delta x \left(\frac{\partial C'}{\partial t} \right) = Q \left(\frac{\partial C'}{\partial x} \right) \Delta x + A \Delta x k_L a C' \quad (36)$$

The LHS represents the rate of change of COD in the differential volume of reactor, $A \Delta x$, where A is the cross sectional area of the reactor. The first term of the RHS is the net rate of change of COD due to the bulk flow in the differential volume and Q is the volumetric flow rate through the reactor. The last term in the right-hand side represents the rate of degradation of organic contaminants in the solution due to the reaction.

The reservoir always provides a perfectly back-mix system. The mass balance for the effluent reservoir is:

$$V \left(\frac{dC}{dt} \right) = QC' - QC \quad (37)$$

Furthermore it can be assumed that the reactor is under steady state conditions as $dC'/dt = 0$, and Equation (36) can be rewritten as:

$$C' = C \exp(-k_L a \tau_R) = C \exp \left(-\frac{k_L A_e}{Q} \right) \quad (38)$$

where a is specific electrode area (A_e/V_R) and τ_R is the residence time in the reactor (V_R/Q). The mass balance equation can be

solved after substitution of the expression for C' knowing the initial COD, the resultant equation can be written as:

$$\begin{aligned} \frac{C}{C_0} &= \exp \left[-\frac{t}{\tau} (1 - \exp(-k_L a \tau_R)) \right] \\ &= \exp \left[-\frac{t}{\tau} \left\{ 1 - \exp \left(-\frac{k_L A_e}{Q} \right) \right\} \right] \end{aligned} \quad (39)$$

where C_0 is the initial value of COD of waste-water and τ is the residence time (V/Q) in the reservoir.

It should be noted that the extent of degradation is defined as $X = (C_0 - C)/C_0$. The unconverted species ($1 - X$), (or C/C_0), decreases exponentially with time. According to Equation (39), the slope of the plot of $-\ln(1 - X)$ versus t , gives the value $\{1 - \exp(-\frac{k_L A_e}{Q})\}/\tau$ from which the value of k_L , the rate transfer coefficient, may be computed.

Recycle reactor

For the recycle reactor system, streams 10 and 12 will be present and the material balance around the reservoir will give the concentration of the reactant entering the reactor as:

$$C = \frac{qC_0 + QC'}{q + Q} = \frac{RC_0 + C'}{R + 1} \quad (40)$$

where q is the volumetric inlet/discharge flow rate, and R is the ratio, defined as $R = q/Q$, and Q , the bulk flow rate of the effluent circulating and entering the reservoir all the time. The material balance around the reactor is:

$$C' = C \exp(-k_L a \tau_R) = C \exp \left(-\frac{k_L A_e}{Q + q} \right) \quad (41)$$

where $Q + q$ is the total flow of effluent passing through the reactor. In Equation (39) substituting for C' from the above expression, we get:

$$C = \frac{RC_0 + C \exp \left(-\frac{k_L A_e}{Q(1 + R)} \right)}{R + 1} \quad (42)$$

The above equation can be rearranged as:

$$\left(\frac{k_L A_e}{Q(1 + R)} \right) = \ln \left(\frac{1 - X}{(R + 1)(1 - X) - R} \right) \quad (43)$$

According to Equation (43), the slope of the plot

$$\ln \left(\frac{1 - X}{(R + 1)(1 - X) - R} \right) \text{ versus } 1/(1 + R)Q$$

gives the value $k_L A_e$ from which the value of k_L , the rate transfer coefficient, may be computed for the given conversion in the recycle reactor.

Single pass flow reactor

The expression for outlet concentration in the flow reactor (single pass or once-through mode of operation) is obtained as:

$$C' = C_0 \exp(-k_L a \tau_R) = C_0 \exp \left(-\frac{k_L A_e}{Q} \right) \quad (44)$$

Hence:

$$\left(\frac{k_L A_e}{Q} \right) = \ln \left(\frac{1}{1 - X} \right) \quad (45)$$

According to Equation (45), the slope of the plot $-\ln(1 - X)$ versus $1/Q$ gives the value from which the value of k_L , the rate transfer coefficient, may be computed.

RESULTS AND DISCUSSION

The results of the experiments carried out are presented in Figs 2–5 and Tables 1–5.

Treatment in batch mode

Preliminary batch experiments show that the electrolysis time, supporting electrolyte concentration, current density and reactor hold-up considerably influence the performance of the process. Process performance is defined in two ways, one with respect to the extent of reaction completion (X or COD removal) and the other with respect to the energy consumption, E (kW h kg^{-1}). The rate of the process, determined by the current density (Equation (31)), is evaluated in terms of the heterogeneous rate constant k_L (cm s^{-1}) by monitoring the extent of COD removal. The energy consumption is also defined in two ways. Computation of the current efficiency (CE) indicates the path and course of the targeted reaction by monitoring the extent of COD removal (Equation (34)). The actual utilization of energy in processing a unit quantity of the targeted reaction (power consumption E ($\text{kW h (kg COD)}^{-1}$)) is found by monitoring the cell voltage and extent of COD removal (Equation (35)). The results of the batch experiments are reported in Figs 2(a), 2(b), 3 and Tables 2 and 3. Batch studies were useful in determining operating parameters such as electrolysis time, supporting electrolyte concentration, current density and reactor hold-up giving better reactor performance.

Figure 2(a) and 2(b) indicate the variation of the extent of unconverted organic contaminants (in terms of COD, $C/C_0 = 1 - X$) with electrolysis time for various supporting electrolyte concentrations at two different current densities (2.5 and 5.0 A dm^{-2}). It can be seen in both cases that the unconverted fraction of organic matter (C/C_0) decreases exponentially as the process progresses. The expected increase in pollutant removal beyond 5 h of treatment is marginal. It can also be seen that the supporting electrolyte plays a major role in the degradation of the organic matter in the waste-water. Even though the pollutant removal increases with increase in salt levels, the change in performance decreases as the salt concentration increases. Thus increasing the supporting electrolyte concentration from 1–2 g L^{-1} resulted in an improvement in COD removal from 41.92–57.97% after 5 h of treatment (Table 2), but the improvement was much less

Table 2. Effect of supporting electrolyte concentration and current density on the performance of the batch electrochemical reactor. Initial COD $1669 \pm 23 \text{ mg L}^{-1}$; electrolysis time 5 h; specific electrode surface 0.0551 cm^{-1} ; volume 200 mL

Current Density A dm^{-2}	[NaCl] (g L^{-1})	Cell voltage (V)	COD removal X (%)	Current efficiency CE (%)	Power consumption E (kW h kg^{-1})	$k_L \times 10^4$ (cm s^{-1})
2.5	1	5.1	41.92	20.84	82.01	3.39
	2	4.5	57.97	28.81	52.32	5.51
	3	3.8	67.99	33.79	37.67	7.22
	4	3.4	71.50	35.54	32.05	8.03
	5	3.1	74.50	37.03	28.05	8.66
5.0	5	5.2	82.00	20.38	85.49	10.73
	6	4.8	84.00	20.87	77.04	11.45
	7	4.5	85.00	21.12	71.37	11.86
	9	4.3	85.50	21.25	67.81	12.08

Table 3. Effect of reactor hold-up on the performance of the batch electrochemical reactor. Initial COD $1669 \pm 23 \text{ mg L}^{-1}$; electrolysis time 5 h; active electrode area 18 cm^2 ; current density 2.5 A dm^{-2} ; supporting electrolyte concentration 3 g L^{-1}

V_R mL	Cell voltage (V)	COD removal X (%)	Current efficiency CE (%)	Power consumption E (kW h kg^{-1})	$k_L \times 10^4$ (cm s^{-1})
200	3.9	68.00	33.81	38.66	5.94
325	3.7	64.00	51.69	23.98	10.49
450	3.6	61.00	68.22	17.68	16.24

(71.5–74.5%) when the supporting electrolyte concentrations were increased to higher levels, i.e. 4–5 g L^{-1} .

The process performance due to salt concentration was found to improve only marginally beyond 3 g L^{-1} . Comparing Fig. 2(a) and 2(b), it can be seen that the process improvement due to the combined effects of increased salt levels and current density is not considerable. While 68% COD removal is achieved after 5 h treatment at a current density of 2.5 A dm^{-2} and supporting electrolyte concentration of 3 g L^{-1} , only 85.5% removal was achieved under the extreme conditions of current density, 5 A dm^{-2} , and supporting electrolyte concentration, 9 g L^{-1} . Since post-treatment for removal of the dissolved inorganic substances is cumbersome, the salt level in the waste-water has to be limited. Moreover, current density is a direct measure of the energy consumption of the process and thus has to be limited for better overall economics.

The effect of specific electrode surface on COD removal was studied by a batch process with various treatment volumes, but with the same electrode area. The results (Fig. 3) show that COD removal decreases as the specific electrode area decreases. Table 3 shows the improvement in pollutant removal performance is not considerable (61–68%) following increase in the specific electrode surface A_e/V_R from 0.04–0.09 cm^{-1} .

The trend of heterogeneous rate constant k_L (cm s^{-1}) with respect to the variation of current density, supporting electrolyte concentration and reactor hold-up (V_R) was also studied in the batch operation (Tables 2 and 3). In Table 2, a marked

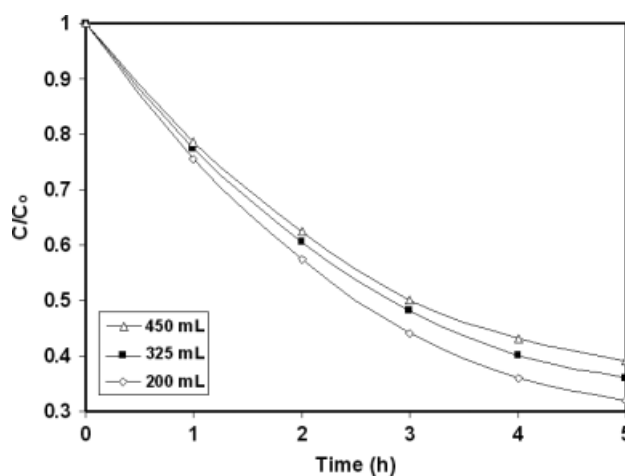


Figure 3. Effect of electrolysis time and effluent volume on percentage removal of COD in the batch system. Conditions: active electrode area 18 cm^2 ; current density 2.5 A dm^{-2} ; initial COD $1669 \pm 23 \text{ mg L}^{-1}$; supporting electrolyte concentration 3 g L^{-1} .

improvement is seen in the value of k_L with increase in salt concentration, especially at lower salt levels, probably due to the generation of more oxidizing agents from the additional amount of salt added. With the addition of extra salt, the controlling step of the process might have changed from a condition of limiting oxidizing agents to another limiting condition, such as limiting organic species. As can be seen in Table 3, decrease in the specific electrode surface causes a predominant increase in the value of k_L (cm s^{-1}). This may be because of the availability of a larger amount of reactants (organic matter) when the specific electrode surface is low. Even though the amount of reaction was larger, the extent of reaction was poor.

Another important finding of the study was the current efficiency CE and the power consumption E . Table 2 shows that an increase in salt concentration improves the energy of the process, especially at lower salt concentrations. This is because of the improved ionic conductance of waste-water. The highest current efficiency and lowest power consumption after 5 h of treatment, was 37.03% and 28.05 kWh kg^{-1} , respectively, at a current density 2.5 A dm^{-2} and supporting electrolyte concentration 5 g L^{-1} . Another noticeable result in Table 2 is the fact that an increase in current density decreases the current efficiency and increases power consumption. The possibility of loss of electrical energy in the form of heat and unwanted reactions is greater at higher levels of current density. Thus, in general, a higher current density operation will give high capacity utilization, at the expense of higher energy loss.

The relationship between specific electrode surface and energy is presented in Table 3. The table shows that the operation is more energy efficient when the specific electrode surface is low. As reported above, this may be because of the availability of higher amounts of reactants (organic matter). In general, operation with a lower specific electrode surface is advantageous either because of the high capacity of operation or degradation of higher amounts of pollutants at better energy figures, but with poor extent of completion of the process. Moreover, the batch study showed that improvement in voltage was almost linear from 5.1–3.1 V as the supporting electrolyte concentration varied from 1–5 mg L^{-1} at the end of 5 h of treatment at a current density of 2.5 A dm^{-2} . The effect of influent COD variation from 1646–1692 mg L^{-1} was studied and the variation was found less than 2% on all the four performance terms.

Batch reactor with recirculation mode

Dynamic response of the COD removal performance of the system was studied at various flow rates Q at constant current density (2.5 A dm^{-2}), supporting electrolyte concentration (3 g L^{-1}) and initial COD (1669 \pm 23 mg L^{-1}) (Fig. 4). This shows there is an increase in percentage of COD removal with respect to time. The improvement in performance after 6 h operation is marginal. It can also be seen in the figure that the pollutant removal improves considerably with increase in flow rate. Table 4 shows the COD removal after 6 h of operation to be 56 and 73.3% at circulation flow rates of 20 and 100 L h^{-1} respectively. This may be because of the enhancement of the transfer coefficient at higher flow rates. Pollutant removal and energy consumption was studied with respect to the variation of flow rates over 6 h at constant conditions as explained above (Table 4).

The improvement in voltage (3.9–3.6V) and in COD removal (56–73.3%) resulted in considerable improvement in current efficiency (37.89–49.59%) and power consumption (34.485–24.32 kWh kg^{-1}) when the flow rate (Q L h^{-1}) increased from 20 to 100 L h^{-1} .

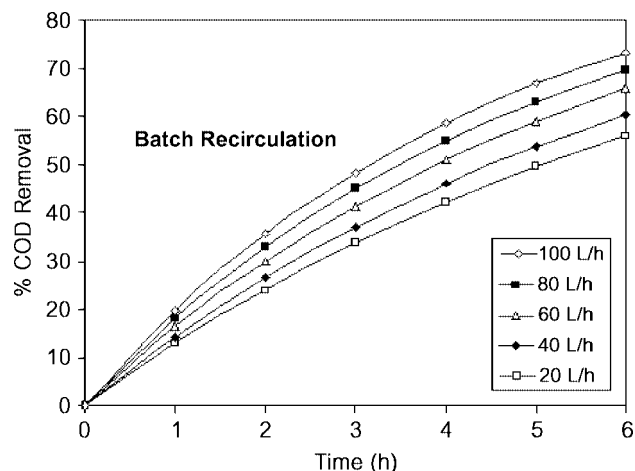


Figure 4. Effect of electrolysis time and flow rate on percentage removal of COD in the batch recirculation system. Conditions: active electrode area 138 cm^2 ; current density 2.5 A dm^{-2} ; initial COD 1669 \pm 23 mg L^{-1} ; supporting electrolyte concentration 3 g L^{-1} .

Table 4. Effect of flow rate on the performance of the batch recirculation electrochemical reactor. Initial COD 1669 \pm 23 mg L^{-1} ; electrolysis time 6 h; current density 2.5 A dm^{-2} ; supporting electrolyte concentration 3 g L^{-1} ; active electrode area 138 cm^2 ; reactor volume 955.2 mL; reservoir volume 2.5 L

Flow (L h^{-1})	Cell voltage (V)	COD removal X (%)	Current efficiency CE (%)	Power consumption E (kWh kg^{-1})	$k_L \times 10^4$ (cm s^{-1})
20	3.9	56.0	37.89	34.49	6.96
40	3.8	60.0	40.59	31.36	7.78
60	3.8	65.6	44.38	28.68	9.01
80	3.7	69.6	47.08	26.33	10.03
100	3.6	73.3	49.59	24.32	11.12

$$k_L = au^b \text{ where } a = 0.001253, b = 0.2903$$

h^{-1} . This may be because of the improved ionic conductivity by bulk movement and reduction of resistance on the electrode surface. The quantity of pollutant removed by this change in flow rate is expected to be almost 1.6 times as indicated by the values of heterogeneous rate constant k_L (6.96×10^{-4} to $11.12 \times 10^{-4} \text{ cm s}^{-1}$). Comparing the batch recirculation system with a circulation flow rate 100 L h^{-1} , with the batch system with the same specific electrode surface, 0.055 cm^{-1} (batch case: reactor volume: 325 mL), it can be observed that the batch recirculation system is superior in both completion of COD removal (73.3 vs. 64%) and rate constant (1.112×10^{-3} vs. $1.049 \times 10^{-3} \text{ cm s}^{-1}$). Thus even though the energy figures are marginally lower, the overall performance of the batch recirculation system (rate, quantity and completion of pollutant removal) is superior to the batch system.

Correlation of the mass transfer coefficient with the velocity of effluent flowing through the reactor has been attempted:

$$k_L = au^b \quad (46)$$

Graphical solution of the above equation gave values of a and b of 0.00125 and 0.29, respectively. The R^2 value of the model (0.957) is quite good and shows the ability to predict the rate constant. The Reynolds Number as found to vary from 90.7 to 453.6 as the

flow rate varied from 20 to 100 L h⁻¹ indicating a laminar regime. The value of the exponent (0.29) of u in Equation (46) supports the above. This correlation indicates that there is a lot of scope for augmentation of mass transfer of the system by improved turbulence.

Recycle reactor

Pollutant removal and energy consumption of the recycle reactor was studied for various influent/withdrawal flow rates (q) and recycle flow rates (Q) (Table 5). As for the batch recirculation reactor a higher circulation flow rate appears to improve all aspects of the process. This may be because of better mixing and in turn, better transfer coefficients. An increase in withdrawal flow rate decreases the COD removal. The percentage of COD removal at 0.4 and 2.9 L h⁻¹ for a recycle flow rate of 60 L h⁻¹, are 65.3 and 61.3% respectively. This may be due to the shorter residence time at a higher withdrawal flow rates. The improvement in the power consumption at higher withdrawal flow rates can be seen in Table 5. There is considerable increase in the value of k_L as the withdrawal flow rate increases for all cases. In general, the operation of the reactor at higher withdrawal flow rates provides better capacity utilization with better energy figures, but at the expense of poor completion of the process.

When compared with the batch recirculation reactor, recycle reactor performance is found to be attractive on power consumption figures and rate constant. Thus the recycle reactor is better

Table 5. Effect of discharge flow rate and recycle flow rate on the performance of the recycle electrochemical reactor. Initial COD 1669 ± 23 mg L⁻¹; current density 2.5 A dm⁻²; supporting electrolyte concentration 3 g L⁻¹; active electrode area 138 cm²; reactor volume 955.2 mL; reservoir volume 2.5 L

Q (L h ⁻¹)	q (L h ⁻¹)	Cell voltage (V)	COD removal X (%)	Power consumption E (kW h kg ⁻¹)	k_L (cm s ⁻¹)
20	0.4	3.7	57.0	37.20	0.0010
	0.7	3.8	53.9	20.20	0.0018
	1.1	3.8	52.9	13.72	0.0027
	1.4	3.8	51.1	10.65	0.0034
	1.8	3.9	48.5	9.22	0.0039
	2.2	3.9	47.1	7.91	0.0045
	2.5	3.9	45.7	6.99	0.0051
	2.9	3.9	44.7	6.25	0.0057
40	0.4	3.7	59.2	35.82	0.0011
	0.7	3.7	58.4	18.16	0.0021
	1.1	3.7	57.6	12.27	0.0031
	1.4	3.7	56.8	9.33	0.0041
	1.8	3.7	56.0	7.57	0.0050
	2.2	3.7	55.2	6.40	0.0059
	2.5	3.8	54.4	5.72	0.0067
	2.9	3.8	53.7	5.07	0.0075
60	0.4	3.6	65.3	31.60	0.0014
	0.7	3.6	64.7	15.94	0.0027
	1.1	3.6	64.3	10.70	0.0041
	1.4	3.6	63.7	8.10	0.0053
	1.8	3.7	63.1	6.72	0.0066
	2.2	3.7	62.5	5.65	0.0078
	2.5	3.7	61.9	4.89	0.0089
	2.9	3.7	61.3	4.32	0.0100

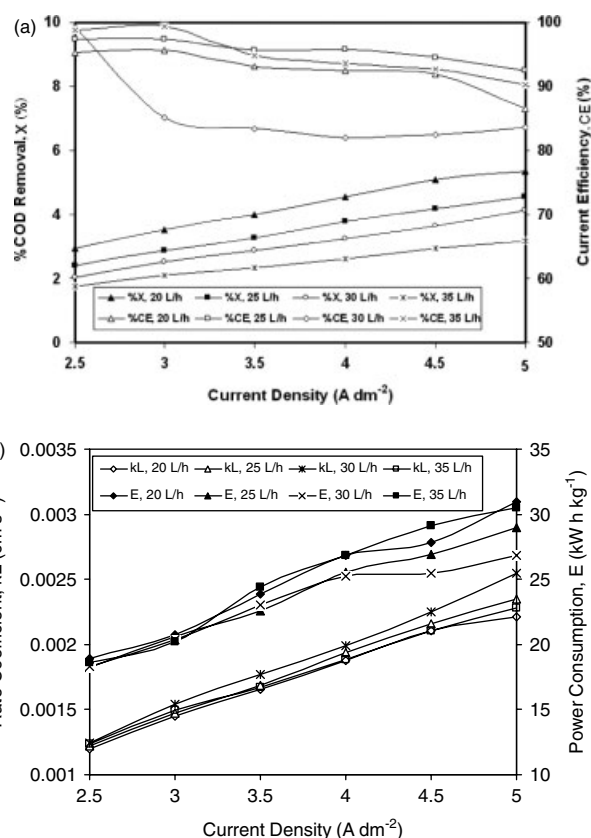


Figure 5. Effect of flow rate on current density on (a) the percentage removal of COD and CE (%) and (b) k_L (cm s⁻¹) and E (kW h kg⁻¹) in the single pass system. Conditions: active electrode area 138 cm²; current density 2.5 A dm⁻²; initial COD 1669 ± 23 mg L⁻¹; supporting electrolyte concentration 3 g L⁻¹.

for commercial applications. The biodegradability index was estimated, at the best operating point of the recycle system (Q 60 L h⁻¹, q 2.9 L h⁻¹) as 0.36 ± 0.01. This shows that electrochemical oxidation does not only remove COD but also makes the effluent more biodegradable. The improvement in biodegradability of the effluent indicates the possible advantage in the reactor volume required in the biological treatment step if followed.

Single pass flow reactor

Pollutant removal and energy consumption of the single pass flow reactor were studied by varying the current density (2.5–5 A dm⁻²) and flow rate (20–35 L h⁻¹) (Fig. 5(a) and 5(b)). Increase in the current density improves both the pollutant removal parameters, while the energy terms are in the other direction. In other words, operation of the cell at a higher current density level enables higher COD removal at an improved rate at the expense of more energy wastage and more unwanted side reactions. As seen in Fig. 5(a), the amount of COD removal in the reactor is much less (1.73–5.33%) probably due to the lower residence time. The decrease in current efficiency due to the increase in current density is 99.3–82.0%. The current efficiency of recycle reactor is far higher than the efficiency reported in any of the other reactors considered. In Fig. 5(b), both the rate of the process and power consumption are not affected significantly by the flow rate at lower current density operation, while, there is a marked difference in the reaction rate due to variation of the flow rate at high current density levels. This may

be because of a changeover of the controlling mechanism of the process as current density increases.

CONCLUSIONS

Electrochemical degradation of waste-water from a small-scale, agro-based pulp and paper industry was investigated using a RuO₂ coated titanium electrode in various types of reactor configurations, i.e. batch, batch recirculation, recycle and single pass systems. Theoretical models for these systems and mechanism of the electrochemical degradation of the waste-water are proposed. The effect of important operating parameters such as current density, electrolysis time, supporting electrolyte concentration and specific electrode surface on the pollutant removal and energy consumption of these systems are critically examined.

Batch studies show the operating parameters of current density: 2.5 A dm⁻², electrolysis duration: 5 h, supporting electrolyte concentration: 3 gm L⁻¹, as optimal for the overall system performance. Batch operation at varied reactor hold-up (specific electrode surface) showed that the capacity utilization and required energy improve considerably with a decrease in the specific electrode surface, with little effect on process completion. Batch recirculation mode of operation was superior for COD removal (73.3 vs. 64%) and capacity utilization (rate constant 1.112 × 10⁻³ vs. 1.049 × 10⁻³ cm s⁻¹) when compared with the batch system with the same specific electrode surface, but with little reduction in energy figures (power consumption: 24.32 vs. 23.98 kW h kg⁻¹). The pollutant removal performance of the batch recirculation system improved considerably with increase in the circulation flow rate. The improvement in voltage (3.9–3.6 V) and in COD removal (56–73.3%) resulted in considerable improvement in current efficiency (37.89–49.59%) and power consumption (34.5–24.3 kW h kg⁻¹) as the circulation flow rate increased from 20 to 100 L h⁻¹.

Continuous systems were found superior to batch systems in energy utilization with comparable COD removal. The COD removal was limited to around 65% in the case of a continuous system at the maximum circulation flow rate of 60 L h⁻¹ and lowest withdrawal flow rate of 0.4 L h⁻¹ studied. Operation of the continuous recycle system at conditions of moderately higher withdrawal flow rates (2.9 L h⁻¹) was found to give better COD removal (61.3%) with good energy figures (power consumption: 4.3 kW h kg⁻¹) and capacity utilization (rate constant: 0.01 cm s⁻¹) than the batch recirculation system.

Single pass operation was found to give very much less completion of the process due to the lower residence time. In order to get a comparable residence time as the recycle system, either the feed rate has to be considerably reduced or the reactor volume has to be considerably increased or both. While the reduction in flow rate limits the process by the reduction in transfer coefficients, an increase in reactor volume causes greater capital investment. Thus the recycle system of operation has the best performance of the four conventional reactor configurations studied. The capacity utilization of the system improved considerably under continuous recirculation condition than the batch recirculation.

The best operating point (Q 60 L h⁻¹, q 2.9 L h⁻¹) of the best reactor configuration (recycle reactor) was further investigated by estimating the biodegradability index, resulting in a considerable improvement to 0.36 ± 0.01. This shows that the remaining 40% of the COD can be easily digested biologically. Thus, the advantage of the process is two-fold; it not only removes the bulk quantity of organic matter (60%), but also makes the remaining

matter more easily biodegradable. The conventionally practised biological treatment for the removal of dissolved organic matter (including the slowly biodegradable lignin, hemicelluloses, etc.) of such a waste stream (BI: 0.18 ± 0.01) is much less attractive because of the requirement for a large equipment footprint. The improvement in biodegradability of the effluent resulting from the treatment indicates possible advantage in the reduction of reactor volume of the following biological treatment step.

REFERENCES

- 1 Mahesh S, Prasad B, Mall ID and Mishra IM, Electrochemical degradation of pulp and paper mill wastewater. Part 1. COD and color removal. *Ind Eng Chem Res* **45**:2830–2839 (2006).
- 2 Achoka JD, The efficiency of oxidation ponds at the Kraft pulp and paper mill at Webuye in Kenya. *Water Res* **36**:1203–1212 (2002).
- 3 Pokhrel D and Viraraghavan T, Treatment of pulp and paper mill wastewater – a review. *Sci Total Environ* **333**:37–58 (2004).
- 4 Tsang YF, Hua FL, Chua H, Sin SN and Wang YJ, Optimization of biological treatment of paper mill effluent in a sequencing batch reactor. *Biochem Eng J* **34**:193–199 (2007).
- 5 Shawwa AR, Smith DW and Sego DC, Color and chlorinated organics removal from pulp wastewater using activated petroleum coke. *Water Res* **35**:745–749 (2001).
- 6 Verench S, Laari A and Kallas J, Wet oxidation of concentrated waste water of paper mills for water cycle closing. *Waste Manage* **20**:287–293 (2000).
- 7 Kreetachat T, Damrongsri M, Punsuwon V, Vaithanomstat P, Chiemchaisri C and Chomsurin C, Effects of ozonation process on lignin-derived compound in pulp and paper mill effluents. *J Hazard Mater* **142**:250–257 (2007).
- 8 Run Cang Sun and Tomkinson J, Fractional separation and physico-chemical analysis of lignins from the black liquor of oil palm trunk fibre pulping. *Sep Purif Technol* **24**:529–539 (2001).
- 9 Chiranjib Bhattacharjee and Bhattacharya PK, Ultrafiltration of black liquor using rotating disk membrane module. *Sep Purif Technol* **49**:281–290 (2006).
- 10 Bhattacharya PK, Jayan R and Chiranjib Bhattacharjee, A combined biological and membrane-based treatment of prehydrolysis liquor from pulp mill. *Sep Purif Technol* **45**:119–130 (2005).
- 11 Adhoum N, Monser L, Bellakhal N and Belgaid EJ, Treatment of electroplating waste water containing Cu²⁺, Zn²⁺ and Cr (VI) by electrocoagulation. *J Hazard Mater* **112**:207–213 (2004).
- 12 Giannis A, Kalaitzakis M and Diamadopoulos E, Electrochemical treatment of olive mill wastewater. *J Chem Technol Biotechnol* **82**:663–671 (2007).
- 13 Lai CL and Lin SH, Electrocoagulation of chemical mechanical polishing (CMP) wastewater from semiconductor fabrication. *Chem Eng J* **95**:205–211 (2003).
- 14 Koparal AS and Ogutveren UB, Removal of nitrate from water by electroreduction and electrocoagulation. *J Hazard Mater* **89**:83–94 (2002).
- 15 Zhu J, Zhao H and Ni J, Fluoride distribution in electrocoagulation defluoridation process. *Sep Purif Technol* **56**:184–191 (2007).
- 16 Ahmed Basha C, Josephine Selvi S, Ramasamy E and Chellammal S, Removal of arsenic and sulphate from the copper smelting industrial effluent. *Chem Eng J* **141**:89–98 (2008).
- 17 Dogan D and Turkdemir H, Electrochemical oxidation of textile dye indigo. *J Chem Technol Biotechnol* **80**:916–923 (2005).
- 18 Tsai CT, Lin ST, Shue YC and Su PL, Electrolysis of soluble organic matter in leachate from landfills. *Water Res* **31**:3073–3081 (1997).
- 19 Chen X, Chen G and Yue PL, Separation of pollutants from restaurant wastewater by electrocoagulation. *Sep Purif Technol* **19**:65–76 (2000).
- 20 Ge J, Qu J, Lei P and Liu H, New bipolar electro coagulation–electro flotation process for the treatment of laundry wastewater. *Sep Purif Technol* **36**:33–39 (2004).
- 21 Onder E, Koparal AS and Ogutveren UB, An alternative method for the removal of surfactants from water: electrochemical coagulation. *Sep Purif Technol* **52**:527–532 (2007).
- 22 Drogui P, Asselin M, Brar SK, Benmoussa H and Blais J-F, Electrochemical removal of pollutants from agro-industry wastewaters. *Sep Purif Technol* **61**:301–310 (2008).

- 23 Ugurlu M, Gurses A, Dogar C and Yalcin M, The removal of lignin and phenol from paper mill effluents by electrocoagulation. *J Environ Manage* **87**:420–428 (2008).
- 24 Ben Mansour L, Ksentini I and Elleuch B, Treatment of wastewaters of paper industry by coagulation–electroflotation. *Desalination* **208**:34–41 (2007).
- 25 Patel UD and Suresh S, Electrochemical treatment of pentachlorophenol in water and pulp bleaching effluent. *Sep Purif Technol* **61**:115–122 (2008).
- 26 Mantzavinos D and Psillakis E, Review – Enhancement of biodegradability of industrial wastewaters by chemical oxidation pretreatment. *J Chem Technol Biotechnol* **79**:431–454 (2004).
- 27 Clesceri LS, Greenberg AE and Eaton AD, *Standard Methods for the Examination of Water and Wastewater*, 20th edn. APHA, Washington DC (1998).
- 28 Subbiah P, Krishnamurthy S, Asokan K, Subramanian K and Arumugam V, An improved process for the preparation of insoluble non-precious metal oxide anode doped with platinum group metal oxide to be used in electrochemical processes. Indian Patent 178184 (1990).
- 29 Panizza M, Michaud AP, Cerisola G and Comninellis Ch, Electrochemical treatment of wastewater containing organic pollutants on boron doped diamond electrode: prediction of specific energy consumption and required electrode area. *Electrochem Commun* **3**:336–339 (2001).
- 30 Simond O, Schaller V and Comninellis C, Theoretical model for the anodic oxidation of organics on metal oxide electrodes. *Electrochim Acta* **42**:2009–2012 (1997).
- 31 Malpass GRP and Motheo AJ, Electro-oxidation of formaldehyde methanol solutions on Ti/Ru_{0.3}Ti_{0.7}O₂ electrodes using a filter-press cell. *J Appl Electrochem* **31**:1351–1357 (2001).
- 32 Bindu K, Velusamy S, Basha CA and Vijayavalli R, Mediated electrochemical oxidation of organic pollutants in wastewater treatment. *Indian J Environ Health* **42**:185–191 (2000).
- 33 Raghu S and Basha CA, Electrochemical treatment of procion block 5B using cylindrical flow reactor- a pilot plant study. *J Hazard Mater* **139**:381–390 (2007).
- 34 Buso A, Balbo L, Giomo M, Farnia G and Sandona G, Electrochemical Removal of Tannins from Aqueous Solutions. *Ind Eng Chem Res* **39**:494–499 (2000).
- 35 Comninellis Ch and Pulgarin C, Electrochemical oxidation of phenol for wastewater treatment using SnO₂ anodes. *J Appl Electrochem* **23**:108–112 (1993).
- 36 Miwa DW, Malpass GRP, Machado SAS and Motheo AJ, Electrochemical degradation of carbaryl on oxide electrodes. *Water Res* **40**:3281–3289 (2006).
- 37 Malpass GRP, Miwa DW, Mortari DA, Machado SAS and Motheo AJ, Decolorisation of real textile waste using electrochemical techniques: effect of the chloride concentration. *Water Res* **41**:2969–2977 (2007).