

Removal of pharmaceuticals from wastewater by electrochemical oxidation using cylindrical flow reactor and optimization of treatment conditions

B. RAMESH BABU, P. VENKATESAN, R. KANIMOZHI and C. AHMED BASHA

Pollution Control Division, Central Electrochemical Research Institute, Karaikudi, Tamil Nadu, India

This paper examines the use of electrooxidation for treatment of wastewater obtained from a pharmaceutical industry. The wastewater primarily contained Gentamicin and Dexamethasone. With NaCl as supporting electrolyte, the effluent was treated in a cylindrical flow reactor in continuous (single pass) mode under various current densities (2–5 A/dm²) and flow rates (10–40 L/h). By cyclic voltammetric (CV) analysis, the optimum condition for maximum redox reaction was determined. The efficiency of chemical oxygen demand (COD) reduction and power consumption were studied for different operating conditions. From the results it was observed that maximum COD reduction of about 85.56% was obtained at a flow rate of 10 L/h with an applied current density of 4 A/dm². FT-IR spectra studies showed that during electrooxidation, the intensities of characteristic functional groups such as N-H, O-H were reduced and some new peaks also started to appear. Probable theory, reaction mechanism and modeling were proposed for the oxidation of pharmaceutical effluent. The experimental results demonstrated that electrooxidation treatment was very effective and capable of elevating the quality of treated wastewater to the reuse standard prescribed for pharmaceutical industries.

Keywords: Pharmaceutical effluent, removal efficiency, NaCl, electrochemical oxidation, Ti/RuO₂ anode.

Introduction

Pharmaceutical residues have been detected in many environmental matrices worldwide (e.g., in waters, wastewaters, sediments and sludge). Depending on hydrophilicity, those compounds can enter the aquatic environment or remain adsorbed on solid particles. Households, wastewater treatment plants, hospitals, industrial units and intensive animal-breeding farms are the most important sources of such compounds in the environment.^[1] The main sources of pharmaceutical contamination in natural water systems are human and veterinary drugs which represent more than 4,000 molecules and 1,000 specialized products.^[2,3] Contamination of waterways by pharmaceuticals is widely documented: hormones, beta-lactamides, anti-inflammatories, analgesics, lipid regulators, anti-depressants, antibiotics, cytostatic agents have been found in small creeks, lakes, rivers, estuaries and rarely in groundwater, drinking water and marine water.^[4–7] Groundwater contamination is primarily due to infiltration of surface water containing

pharmaceutical residues as well as by leaks in landfill sites and sewer drains.^[8] It is well known that the main route for human pharmaceuticals into the aquatic environment is through sewage treatment plants (STP) receiving wastewater from households and hospitals.^[9–12] The release of pharmaceuticals from sewage effluents to rivers and lakes is turning out to be an alarming issue. Drugs are frequently detected in effluents at levels ranging from below 1 ng/L up to a few µg/L.^[13]

Biological treatments are the most efficient and cost-effective way of reducing the environmental impact of civil and major industrial effluents containing organic pollutants.^[14] However, many industries including oil refineries, coke, chemical, plastic and food processing plants (tannery, edible-oil manufacturing, etc.), produce wastewaters containing appreciable content of organics (e.g., complex phenolic compounds) and are not suitable for conventional biological oxidation.^[15–17] In this context, many alternative processes have been proposed for the degradation of organic compounds, ranging from wet air oxidation^[18] to ozonization, from electrochemical to photocatalytic oxidation often combined with biological processes as pre- or, more frequently, post-treatments.^[19] The increase in biodegradability is crucial in most of the wastewater treatment systems, especially for pharmaceutical effluents that are otherwise commonly resistant to biological

Address correspondence to B. Ramesh Babu, Pollution Control Division, Central Electrochemical Research Institute, Karaikudi, Tamil Nadu, India. E-mail: akbabu_2001@yahoo.com
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treatment. Electrochemical treatment is an alternative technology, attempted by many researchers of late, for the removal of organic and inorganic impurities from water and wastewater.^[20] The electrochemical oxidation is a promising treatment route for organic pollutants (e.g., polyphenols), which are recalcitrant to biological degradation^[21,22] and is the cost-effective and most widely used technology to abate organics from civil and industrial effluents. Several studies have been performed on the kinetics of the electrochemical oxidation processes, the selection of anodic material (e.g., SnO₂, PbO₂, and Pt) and the sub products obtained. The tests were generally carried out in pollutant concentrations ranging from 1 to 100 mM with electrolyte salt concentrations (e.g. NaCl, Na₂SO₄, and H₂SO₄) equal to 0.2–2 M.

The main scope of this paper is to demonstrate the pilot-scale reactor study for the treatment of pharmaceutical wastewater in NaCl medium in which Cl⁻ ions plays a vital role in indirect oxidation. Effluent for the study was collected from a pharmaceutical plant mainly containing gentamicin and dexamethasone. During the electrolysis on a continuous single-pass process, COD reduction, energy consumption and mass transfer coefficient were investigated under different flow rates and current densities.

Theoretical approach

In electrochemical processes, the pollutants are destroyed either by direct or indirect oxidation process. In direct anodic oxidation process, pollutants are first adsorbed on the surface of anode and then destroyed by anodic electron transfer reaction whereas in indirect oxidation process, strong oxidants such as hypochlorite ion/chlorine, ozone and hydrogen peroxide are generated electrochemically^[23] and then the pollutants are destroyed in bulk solution by oxidation reaction of the generated oxidant. All the oxidants are generated in situ and are utilized immediately.^[24] Among the oxidants, generation of hypochlorite ion is cheaper and most of the effluents have a certain amount of chloride. Though direct electrolysis of organic compounds at the anode surface is also possible, a major portion of oxidation is mediated by active chloro species when electrochemical oxidation is conducted in the presence of chloride using an undivided cell.

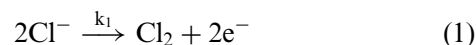
The mechanism of electrochemical oxidation of wastewater is a complex phenomenon involving coupling of electron transfer reaction with a dissociate chemisorption step. Basically two different processes occur at the anode: on anode having high electrocatalytic activity, oxidation occurs at the electrode surface (direct electrolysis) whereas on metal oxide electrode, oxidation occurs via surface mediator on the anodic surface, where they are generated continuously [indirect electrolysis]. In direct electrolysis, the rate of oxidation is dependent upon the electrode activity, pollutants diffusion rate and current density. On the other hand, tem-

perature, pH and diffusion rate of generated oxidants determine the rate of oxidation in indirect electrolysis. In indirect electro-oxidation, chloride salts of sodium or potassium are added to the wastewater for better conductivity and generation of hypochlorite ions/chlorine.^[25,26]

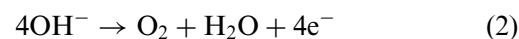
Anodic reactions

In electrochemical conversion, the high molecular weight aromatic compounds and aliphatic chains are broken to intermediate products for further processing. In electrochemical combustion the organics are completely oxidized to CO₂ and H₂O. A brief explanation of the reaction mechanism taking place at the metal oxide electrode is enumerated next:

The generation of chlorine from chloride ion in anodic oxidation is given in Equation 1 (Main reaction):

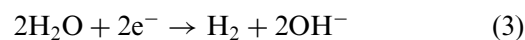


Supplement reaction is given in Equation 2:



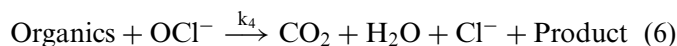
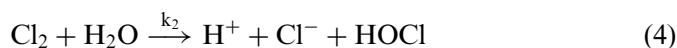
Cathodic reactions

Cathodic reaction is given in Equation 3:



Reaction in bulk solution

The role of hypochlorite in the electrochemical treatment of pharmaceutical effluent by means of chloride ion generation is given here:



The hypochlorite ion acts as the main oxidizing agent for the degradation of organic pollutants present in pharmaceutical wastewater.

The pseudo-steady-state theory can be applied to each of the intermediate products (HOCl and OCl⁻) taking part in the bulk solution. Considering the fact that all other reactions are irreversible processes, the rates of reactions r_i for the sequence are:

$$-r_{\text{Cl}_2} = k_2[\text{Cl}_2] \quad (7)$$

$$r_{\text{HOCl}} = k_2[\text{Cl}_2] - k_3[\text{HOCl}] + k'_3[\text{H}^+][\text{OCl}^-] = 0 \quad (8)$$

$$r_{\text{OCl}^-} = k_3[\text{HOCl}] - k'_3[\text{H}^+][\text{OCl}^-] - k_4[\text{Organics}] \times [\text{OCl}^-] = 0 \quad (9)$$

$$-r_{\text{Organics}} = k_4[\text{Organics}][\text{OCl}^-] \quad (10)$$

Using Eqs. (8) and (9) the following expression can be made:

$$-r_{Cl_2} = -r_{Organics} = k_4[Organics][OCl^-] \quad (11)$$

Finally with regard to bulk solution, it should also be noted that $-r_{Cl_2} = r_{Cl^-}$ from material balance of Equation 4 is:

$$-r_{Cl_2} = r_{Cl^-} = k_2[Cl_2] = -r_{Organics} = k_4[Organics][OCl^-] \quad (12)$$

where the rate of reaction r_i and the rate constants k_i ($i = 2, 3$ and 4) are defined with respect to bulk and the rate expression for main electrode reaction as per Equation 1 can be written as:

$$-r'_{Cl^-} = r'_{Cl_2} = k_1[Cl^-] \quad (13)$$

where k_1 is heterogeneous electrochemical rate constant. Hence, in the following section a relation between the reacting species in bulk and at the electrode surfaces has been established. The basic relationship applicable to all electrochemical reactions is Faraday's law that relates to the amount of substance reacted at the surface to the charge ($I_A t$) passed is $M_A I_A t / nF$ (assuming 100% current efficiency) and the characteristic measurable parameter is current density, i_A , which is I_A / A_e . Thus, the electrochemical reaction rate (for the disappearance of reactant A) can be expressed as:

$$-\left(\frac{V_R}{A_e}\right) \frac{d[A]}{dt} = \frac{i_A}{nF} \quad (14)$$

where I_A is the current passed in time t , M_A the molecular weight, n the number of electrons transferred per mole of reaction, A_e electrode area, V_R reactor volume and F the Faraday (96,500 C or A·s/mol). It has to be noted $-r_A = -d[A]/dt = i_A a / nF$, where a is specific electrode area (A_e / V_R). Assuming that the main electrode reaction is governed by a simple Tafel type expression, then:

$$-\left(\frac{V_R}{A_e}\right) \frac{d[A]}{dt} = \frac{i_A}{zF} = k'[A] \exp(bE) \quad (15)$$

or

$$-r'_{Cl} = r'_{Cl_2} = k_1[Cl^-] = k'_1 a [Cl^-]_s \exp(bE) \quad (16)$$

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

$$\frac{i_A}{zF} = k_L ([Cl^-] - [Cl^-]_s) \quad (17)$$

Elimination of $[Cl^-]_s$ using Equations 16 and 17 results as:

$$\frac{i_A}{zF} = k_1[Cl^-] \quad (18)$$

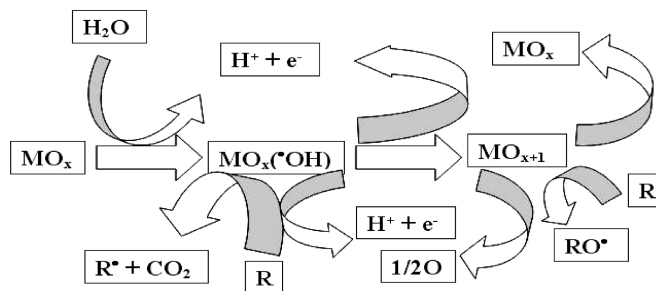


Fig. 1. Representation of indirect oxidation of pollutant.

where

$$\frac{1}{k_1} = \frac{1}{k_L} + \frac{1}{k'a \exp(bE)} \quad (19)$$

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

$$\frac{i_A}{zF} = k'[Cl_2] \quad (20)$$

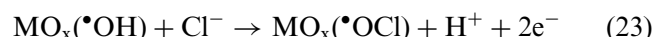
$$\frac{i_A}{zF} = k''[Organics][OCl^-] \quad (21)$$

Since constant current is applied, the rate of generation of $[OCl^-]$ will remain constant during electrolysis under a given set of experimental condition but varies when the applied current is altered. Then:

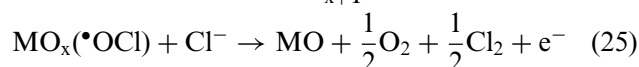
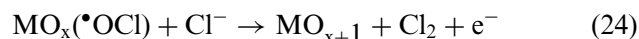
$$\frac{i_A}{zF} = k_{obs}[Organics] \quad (22)$$

A schematic diagram of indirect oxidation of pollutant is presented in Figure 1, which shows a generalized scheme of the electrochemical conversion/combustion of organics on noble oxide coated catalytic anode (MO_x).

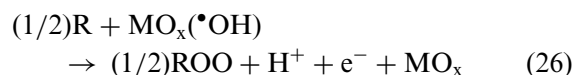
In the presence of NaCl as supporting electrolyte, the chloride ion may also interact with active hydroxyl radical and give adsorbed hypochlorite radical (Equation 23):



The excess of chloride ion interacts with hypochlorite radical to form chlorine and oxygen molecules (Equations 24 and 25).

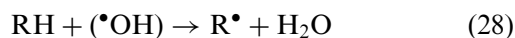


In the presence of oxidizable organics, the physisorbed "active oxygen" ($\bullet OH$) should cause predominantly complete combustion of the organics. Chemisorbed oxygen will participate in the formation of selective oxidation products.



The physisorbed route of oxidation is the preferable way for wastewater treatment. It is probable that dioxygen also

participates in the combustion of organics according to the following reaction schemes: (i) Formation of organic radicals by a hydrogen abstraction mechanism (Equation 28):



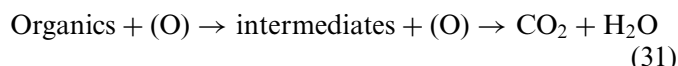
(ii) Reaction of organic radical with dioxygen formed at the anode (Equation 29):



and (iii) further abstraction of a hydrogen atom with formation of an organic hydrogen peroxide (ROOH) and another radical (Equation 30):



These sequential reactions continue until the formation of carbon dioxide and water.



The cylindrical electrochemical flow reactor can be considered as a plug flow reactor (PFR) and its material balance equation is given by:

$$U \frac{d[\text{Organics}]}{dx} + (-r_{\text{Organics}}) = 0 \quad (32)$$

where U is the average velocity of trough the reactor at a distance x from the leading edge and $-r_{\text{Dye}} = k_{\text{obs}}a[\text{organics}]$ and in the integrated form:

$$[\text{Organics}]_x = [\text{Organics}]_0 \exp\left(\frac{-k_{\text{obs}}ax}{U}\right) \quad (33)$$

The rate of COD reduction in the effluent depends upon the concentration of Gentamicin and Dexamethasone.

For this reaction kinetics by assuming steady-state condition in cylindrical flow cell, the expression can be derived assuming plug flow:

$$[\text{COD}]_L = [\text{COD}]_0 \exp\left(\frac{-k_{\text{obs}}aL}{U}\right) \quad (34)$$

where k_{obs} is the mass transfer coefficient with respect to COD removal, $a = A_e/V_R$, a the specific electrode area, L the length of electrode area, $[\text{COD}]_0$ the concentration of dyestuff in terms of COD at the reactor inlet and $[\text{COD}]_L$ at the reactor exit, A_e the area of electrode and V_R the volume of the reactor. If q is the volumetric flow rate, then U is the superficial velocity, defined as q/A , where A is the cross sectional flow area.

The electro-oxidation of wastewater in the presence of a supporting electrolyte is influenced by various operating parameters. The progress of destruction of the organic pollutant has been monitored by COD estimation. 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

Table 1. Characteristics of pharmaceutical effluent.

Parameter	Pharmaceutical effluent
pH	7.6
Conductivity (mS)	14.69
COD (mg/L)	1365
TOC (mg/L)	22.1
TN (mg/L)	4.7
TDS (ppm)	3550

instantaneous current efficiency (ICE) may be defined as:

$$\text{ICE} = \left[\frac{\Delta_{\text{COD}} \text{FV}}{8I\Delta t} \right] \quad (35)$$

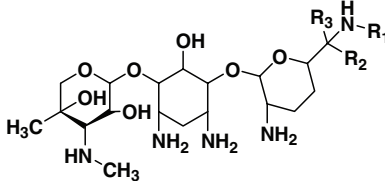
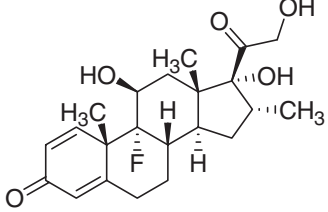
where F is the faraday constant; Δ_{COD} the difference in COD between initial and final in mg/L; V the volume of reactor in litre; I the current passed in ampere and Δt the time interval in seconds.

The instantaneous current efficiency is a measure of efficiency of electro-oxidation. The ICE has been estimated for all experimental runs in the present investigation and critically examined.

Materials and methods

The experiments were performed on effluent (wash water) collected from an industrial pharmaceutical plant which mainly contained gentamicin and dexamethasone. The effluent characteristics are presented in Table 1. All the reagents used were of AR grade. NaCl was used as supporting electrolyte. The structure of gentamicin and dexamethasone is presented in Table 2.

Table 2. Structures of gentamicin and dexamethasone.

Name	Structure
Gentamicin	
Dexamethasone	

Cyclic voltammetry studies

The analysis was performed using a standard three-electrode cell and the waveforms were generated by IM6, controlled by BAS software. The 10 ml of wastewater was taken in the cell in different concentrations of NaCl electrolyte medium. The working electrode for the controlled potential was a platinum foil of surface area of 1 cm², the reference electrode was a saturated calomel electrode and the counterelectrode a platinum wire. The electrodes were immersed in the pharmaceutical wastewater.

Cyclic voltammetry (CV) scans were taken with decreasing potential from 1.0 V to -0.75 V and at a scan rate of 100 mV/s. The cyclic voltammetry studies were used to find out the medium (and its optimum conditions) in which effective indirect oxidation of organics can take place. Hence readily available Pt electrode was used for the experiments and CV was studied in different concentrations of NaCl medium. All the experiments were performed at room temperature and the electrochemical cell was kept open.

Analytical measurements

The solution pH, total dissolved solids (TDS) and conductivity were determined using standard procedures. Total organic carbon (TOC) and total nitrogen (TN) were measured using a flow injection analyzer (SKALAR). Chemical oxygen demand (COD) of all the samples was determined by dichromate reflux method using Merck Thermoreactor TR620. From the values of COD, the % reduction of COD was calculated by using the following formula:

$$\% \text{ COD reduction} = 100 \times \frac{[\text{COD}]_0 - [\text{COD}]_L}{[\text{COD}]_0} \quad (36)$$

Electrolytic cylindrical flow reactor

Figure 2 depicts a schematic diagram of flow reactor set-up. Experiments were conducted in electrolytic flow reactor consisting of a cathode made up of stainless-steel pipe of 110 cm height and 7 cm diameter and Ti/RuO₂-coated expanded mesh cylinder as a catalytic anode measuring 100 cm long and 5 cm diameter, which was held axially inside the cathode in such a way to have 1 cm as inter-electrode distance. Provisions were made for electrical connections so as to constitute an electrolytic cell. The capacity of the cell was 4.5 L. The cell had one inlet at the bottom cover and one outlet at the top cover. It was connected to 100 A and 50 V DC regulated power supply. Reservoir, pump, flow meter and electrolytic flow reactor were connected using silicone rubber tubes.

Experimental procedure

Samples to be treated were taken in the reservoir and fed into the reactor, NaCl salt was added as electrolyte medium

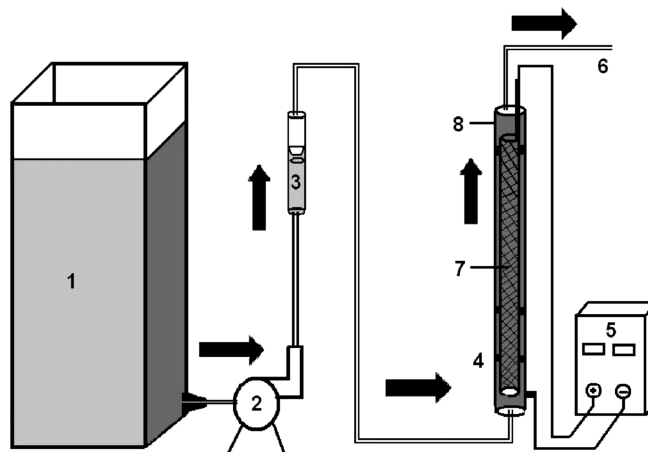


Fig. 2. Schematic diagram of flow reactor set-up: (1) reservoir; (2) pump; (3) rotameter; (4) electrolytic cell; (5) DC power supply; (6) treated effluent; (7) Ti/RuO₂ coated expanded mesh-anode; (8) stainless-steel-cathode.

for adjusting to a fixed strength ionic solution. The flow rate was determined by calibrating the rotameter. The current required was passed using a regulated power supply and cell voltage was noted for each flow rate. The effluent was allowed to flow in a single pass from the bottom of the cell. After attaining steady-state, the outlet samples were collected and subjected to COD, FT-IR analysis. Various experimental conditions and parameters were studied at different current densities such as 2, 3, 4 and 5 A/dm². For each current density, the experiment was repeated for different flow rates of effluent to the reactor i.e., 10, 20, 30, and 40 L/h.

Results and discussion

Cyclic voltammetry studies

To understand the electrochemical behaviour of the electrolytic medium, cyclic voltammetry (CV) studies were carried out. CV studies were also carried out to compare the electrochemical behavior of pharmaceutical effluent at different concentrations of NaCl (Fig. 3). In the case of 3 g/L, the oxidation and reduction of pharmaceuticals occur at -0.5 V and 0.1 V, respectively. Gentamicin and dexamethasone undergoes oxidation at the peak potential of background response which indicates that gentamicin and dexamethasone is indirectly oxidized by some reactive species in the background electrolyte. This suggests that the oxidation of pharmaceuticals occur through indirect oxidation by hydroxyl or other oxidant reagent electro-generated from the electrolyte (mainly OCl⁻ ions in NaCl). Among all the results, the redox behavior of pharmaceuticals in NaCl was good in 3 g/L concentration. With respect to 2, 4 and 5 g/L, the intensity of oxidation and reduction peaks did not appear within the range as in the case of 3 g/L. It

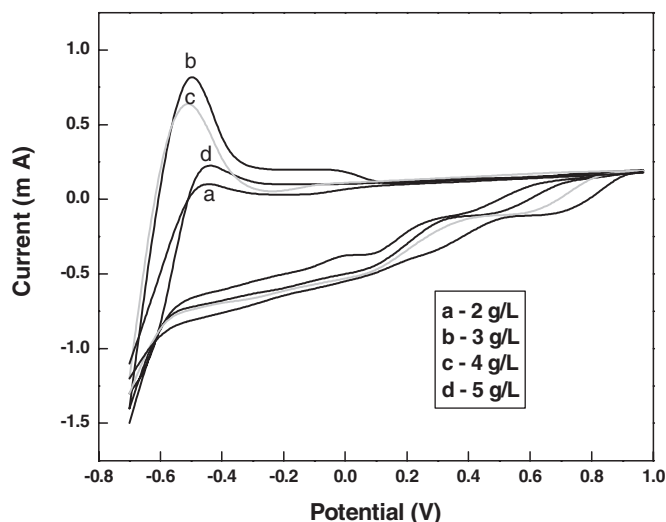


Fig. 3. Cyclic voltammogram studies of pharmaceutical effluent under different NaCl concentrations: (a) 2 g/L; (b) 3 g/L; (c) 4 g/L; (d) 5 g/L; current density (4 A/dm²).

indicates that the increase of NaCl beyond 3 g/L will not enhance the oxidation of organic compounds present in the effluent. This reflects the feasibility of the electrochemical oxidation of pharmaceuticals.

Effect of current density and flow rate on COD removal

An increase in flow rate resulted in a decrease in the removal efficiency as shown in Figure 4. Experiments were conducted at 4 different current densities from 2 to 5 A/dm². COD reduction efficiency increases with increase in current density and decreases with increase in flow rate. When the current density was increased, the rate of generation

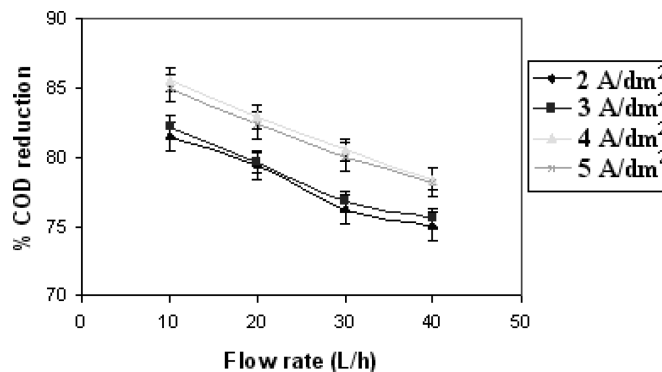


Fig. 4. Effect of COD reduction on flow rate at different current densities: (NaCl: 3 g/L).

of hypochlorite ion increased. The increase in hypochlorite ions approaches equilibrium with degradation of organics. Results showed that higher COD reduction occurred at higher charge input and electrolysis (residence time) time (Table 3). A high detention time resulting from a low flow rate has caused an increase in the removal efficiency. The easily oxidizable organics present in the effluent contribute to the decrease in the COD at low flow rate.

In this study, the increase in flow rate from 10 to 40 L/h leads to gradual decrease in the COD removal at 40 L/h. The maximum possible COD reduction was 85.56% at 10 L/h and 4 A/dm². At higher flow rates (40 L/h) and lower current density (2 A/dm²), the COD reduction was found to be low (74.94 %).

FT-IR spectral studies

The FT-IR spectra for untreated and treated pharmaceutical effluent were recorded on Thermo Nicolet Nexus

Table 3. Effect of current density and flow rate on power consumption, mass flux and mass transfer coefficient.

Current density (A/dm ²)	Flow rate (L/h)	Voltage (V)	Retention time (hr)	COD (mg/L)		Power consumption (kWh/g COD)	Mass flux (g COD/h dm ²)	Mass transfer coefficient (cm/s)
				Initial	Final			
2	10	1.7	0.44	1365	253	1.9968	0.2012	0.0041
	20		0.21	1365	282	0.9785	0.4106	0.0077
	30		0.14	1365	325	0.6793	0.5914	0.0105
	40		0.10	1365	342	0.4933	0.8144	0.01351
3	10	2.4	0.44	1365	244	2.7964	0.2028	0.0042
	20		0.21	1365	278	1.3764	0.4121	0.0078
	30		0.14	1365	317	0.9517	0.5959	0.0107
	40		0.10	1365	334	0.6910	0.8208	0.0137
4	10	3.7	0.44	1365	197	4.0515	0.2113	0.0047
	20		0.21	1365	234	2.0394	0.4287	0.0086
	30		0.14	1365	266	1.3991	0.6250	0.0119
	40		0.10	1365	295	1.0265	0.8519	0.0149
5	10	4.5	0.44	1365	205	4.9614	0.2099	0.0046
	20		0.21	1365	241	2.4438	0.4261	0.0085
	30		0.14	1365	273	1.6769	0.6210	0.0118
	40		0.10	1365	298	1.2258	0.8495	0.0149

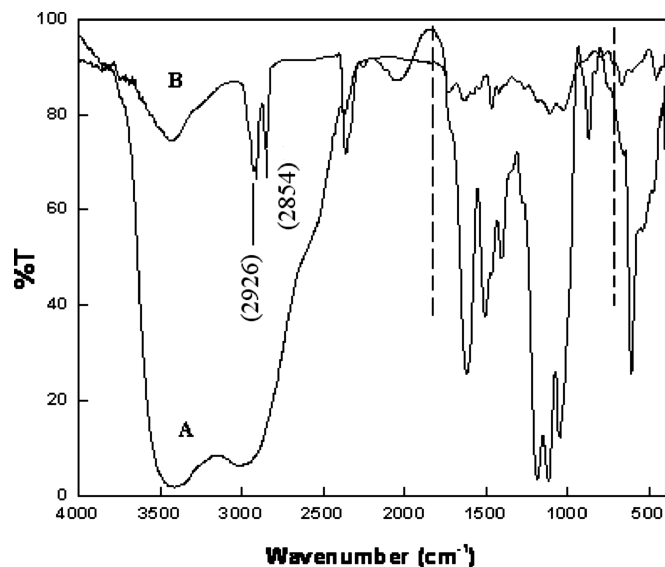


Fig. 5. FT-IR spectrum of: untreated (A); treated (B) pharmaceutical effluent (Current density 4 A/dm² at 10 L/h; NaCl: 3 g/L).

670 FT-IR spectrophotometer in the range between 400 and 4000 cm⁻¹. The samples were pressed with pure KBr crystals to prepare pellets and used for analysis. From the spectra (Fig. 5) it can be concluded that some structural changes might have occurred during the electrochemical oxidation process. The peaks covering the region 700–1800 cm⁻¹ (dashed lines) shows that most of the peaks of raw effluent were gone in the spectrum of treated effluent. Peaks at 3418, 1615, 1513, 1055 and 608 cm⁻¹ were due to the characteristic absorption peaks of N-H, C-N and carbonyl groups.

The characteristic absorption peaks of alcoholic O-H group were found at 3418 and 1398 cm⁻¹. The cyclic and acyclic ether linkage (C-O-C) absorbs at 1190 and 1118 cm⁻¹. After treatment, the intensities of amine and O-H groups got reduced. This is mainly due to the fact that the organics present in pharmaceutical wastewater are converted into other secondary products.

The reduction of peak intensity at 1190 cm⁻¹ and 1118 cm⁻¹ may be due to the breaking up of cyclic ether linkage (C-O-C) and tetrahydropyran and cyclohexane rings are formed. Appearance of new peaks at 2926 and 2854 cm⁻¹ and a low intense peak at 1445 cm⁻¹ proves the formation of cyclohexane and tetrahydropyran ring in effluent. From the results, all characteristic absorption peaks appear reduced in the spectra. This indicates that the organics present in the effluent may have converted into some other products like formic, oxalic and acetic acids. Further, these acids may get converted to CO₂ and water. The overall possible degradation pathways for gentamicin and dexamethasone by electrochemical oxidation are shown schematically in Figures 6 and 7, respectively.

Effect of current density and flow rate on power consumption

Electrochemical treatment is undoubtedly an energy-intensive process and its efficiency is usually assessed in terms of specific energy consumption (SEC). This is defined as the amount of energy consumed per unit mass of organic load (e.g., COD) removed. Energy consumption is directly affected by the current density applied to the system. To enumerate the effects of current density and flow rate on power consumption, the current was varied from 2 to 5

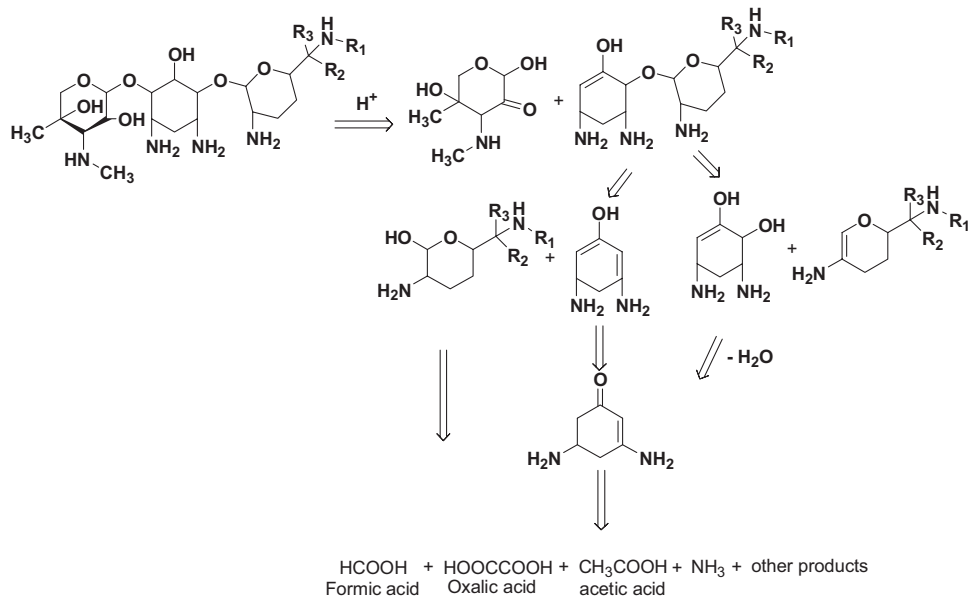


Fig. 6. Possible degradation pathway for gentamicin.

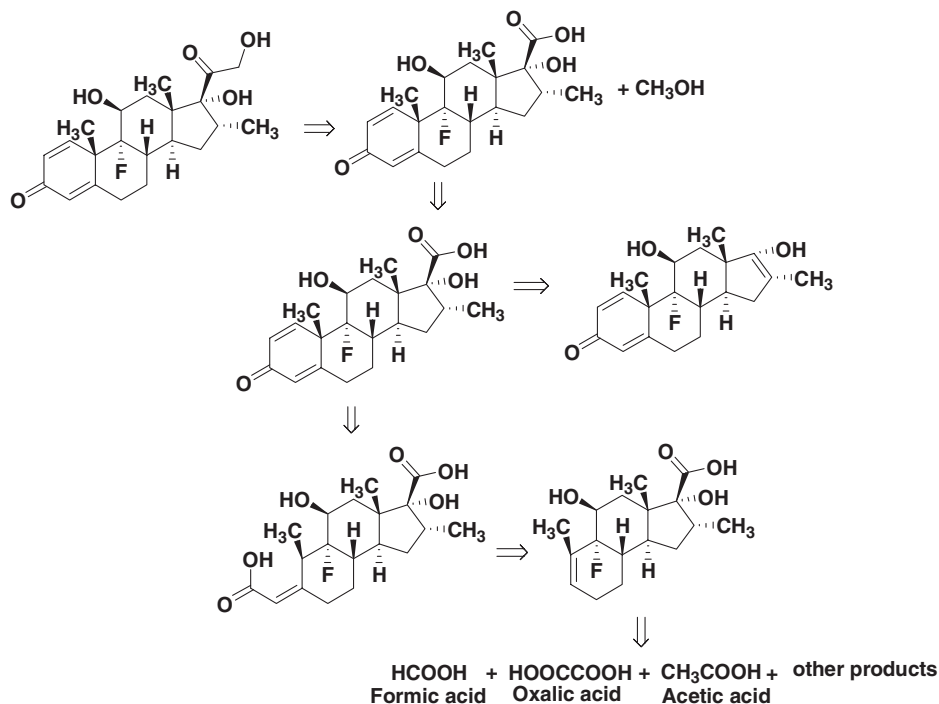


Fig. 7. Possible degradation pathway for dexamethasone.

A/dm². The SEC is expressed in kWh/kg of COD removal and is given as:

$$\text{Energy Consumption} = ((IVt/vol)/\Delta_{\text{COD}}) \quad (37)$$

where Δ_{COD} is difference in COD between initial and final in g/L, vol is the volume of reactor in litre, I the current passed in Ampere, t the retention time in hour, V the cell voltage in Volt.

It was found that SEC was at highest at lower flow rates at all current densities studied. A significant reduce in SEC was observed when flow rate was increased in the electrochemical system. As seen from Table 2, SEC reduced from 4.0515 to 1.0265 kWh/g of COD removed at 4 A/dm² in 0.44 hr duration. Increase in the current density increases the power consumption at flow rates. Furthermore, higher current density could bring high electric energy consumption and operating cost. This may bring a certain industrial application prospect.

It is also interesting to note that the mass flux of the system decreases linearly with the decrease in flow rate (Table 3). At 5 A/dm², the mass flux was found to be 0.2099 g COD/h dm² at flow rate of 10 L/h and mass flux of 0.8495 g COD/h dm² at flow rate of 40 L/h. As mass flux depends on the time of operation, the effect of residence time plays an important role in the process. The current density is directly proportional to the mass flux. These results are shown in Table 3. At current density of 2 A/dm² and flow rate of 10 L/h, the mass flux was 0.2012 g COD/h dm², but at high current density (5 A/dm²) with

same flow rate, mass flux increased to 0.2099 g COD/h dm².

Mass transfer coefficients increase with increase in flow rate as well as with increase in current density. The mass transfer coefficient 0.015 cm/s was found to be high in the case of 40 L/h and 5 A/dm². As time of operation reduces, mass transfer coefficient increases steadily. It has a direct relation to the current density and flow rate, as indicated in the table. It increases with increases in flow rate at all current densities, which are due to rapid reaction that is followed by a slow reaction at high current density. Results

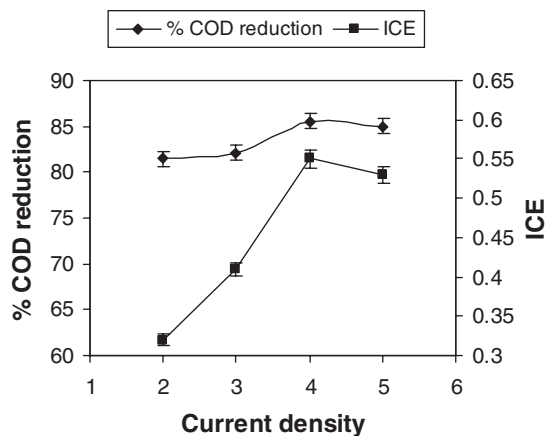


Fig. 8. Variation of percentage COD reduction and instantaneous current efficiency (ICE) at different current density (Time: 0.44 h).

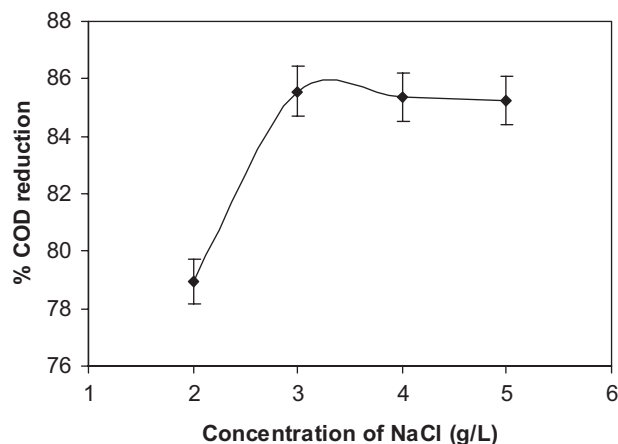


Fig. 9. Variation of percentage COD reduction with different concentration of NaCl (Current density: 4 A/dm²).

clearly indicate that current density and flow rate strongly influences the rate of reaction.

Percentage of COD reduction and ICE

The Instantaneous current efficiency (ICE) was calculated for all the experiments in the present investigation. The variation of ICE along with percentage of COD reduction with current density is given in Figure 8. It can be noticed from the figure that the percentages of COD reduction and ICE increase in current density initially and decrease beyond 4 A/dm².

Effect of the electrolyte concentration

NaCl can enhance the degradation efficiency and shorten reaction time which may be due to the reaction between the generated chlorine/hypochlorite and organic molecule. When the concentration of NaCl increases, solution conductivity was improved which leads to less power consumption. Increasing the concentration of NaCl up to 3 g/L accelerated the removal rate, enabling complete mineralization of organics to an extent of 85.56% COD reduction efficiency in 0.44 hr (Fig. 9). A further increase in NaCl concentration (up to 5 g/L) did not bring about any improvement in COD reduction efficiency, so the optimal NaCl concentration used in the successive experiments was 3 g/L.

Conclusion

In the present study, the feasibility of an electrochemical oxidation process for pharmaceutical effluent treatment was investigated. The experimental results of the lab-scale setup indicated that the cylindrical flow reactor was very effective and reliable for treating pharmaceutical effluent. Un-

der the most favorable treatment conditions, COD removal was 85.56% at 4 A/dm² in the flow rate of 10 L/h in 3 g/L NaCl. COD reduction performance was affected by flow rate. Both mass flux and mass transfer coefficient (0.8495 g COD/h dm² and 0.0149 cm/s) are higher in the case of high flow rate (40 L/h) and current density (5 A/dm²). The results of this study are unique and could provide important information for practical applications. This method can be utilized for the treatment of other organic pollutants and help to meet the requirements for treatment of wastewater discharged to environment. For the industrial application, flow cell method can be recommended with two or more reactors in series. The process should be made according to the demand and effluent quality.

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