



Kinetics of electrooxidation of landfill leachate in a three-dimensional carbon bed electrochemical reactor

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ABSTRACT

The electrooxidation of high strength leachate from an industrial solid waste landfill site was carried out in a three-dimensional carbon bed electrode reactor (TDR). This paper discusses the kinetics and mechanism of electrooxidation on the basis of time course variation of COD, TOC and TKN (total Kjeldahl nitrogen) from the raw leachate. The batch experiments were run at different applied currents (1–3 A) for a period of 6 h. A two-stage pseudo-first order reaction kinetics model was developed based on the initial rapid removal of pollutants (Phase I) followed by slow oxidation kinetics (Phase II). About 60–64% COD was removed within 1 h with a rate constant $5.83 \times 10^{-3} \text{ min}^{-1}$ in Phase I, which was near 5–7 times greater than that of Phase II ($0.81\text{--}1.03 \times 10^{-3} \text{ min}^{-1}$). The mineralization efficiency was found to be significant in the range 0.83–0.84. The apparent faradic efficiency and specific energy consumption for COD removal were also estimated. The mechanism of electrooxidation was discussed with the help of adsorption, kinetic and SEM results.

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1. Introduction

Electrochemical methods have been projected to have potential application in wastewater treatment (Chen, 2004; Deng and Englehardt, 2007). The secondary reagents that can be produced in an electrochemical reactor are clean and powerful redox reagents (hydroxyl radicals, hypochlorite, ozone, and metal redox couples). Thus, these methods, particularly electrooxidation, can be used for degrading or reducing the concentration of toxic pollutants in wastewater. The technique has been widely applied for the treatment of textile wastewater (Naumczyk et al., 1996a), tannery wastewater (Rao et al., 2001), coke plant wastewater (Chiang et al., 1995a), coffee curing wastewater (Bejankiwar et al., 2003), and other wastewaters containing cyanides (Lanza and Bertazzoli, 2002) and phenol (Canizares et al., 2002). The method was also applied for treatment of landfill leachate (Deng and Englehardt, 2007).

Although the electrooxidation of pollutants in bipolar cell (Chiang et al., 1995b; Cossu et al., 1998, 2007; Chen, 2004; Moraes and Bertazzoli, 2005; Cabeza et al., 2007; Deng and Englehardt, 2007) was the most studied system, the use of three-dimensional carbon bed (packed) cell (Tissot and Fragniere, 1994; Tennakoon et al., 1996; Xiong et al., 2001, 2003a; Zhou et al., 2007; Wu

et al., 2008) has been emphasized as it can yield higher treatment efficiency due to higher surface area-to-volume ratio. The three-dimensional carbon bed electrode reactors have been employed for degrading Acid Orange II (Xiong et al., 2001), formic acid (Xiong et al., 2003a), phenol (Xiong et al., 2003b), reactive brilliant red X-3B (Wu et al., 2008), aniline (Chun et al., 2002), municipal solid waste landfill leachate (Cossu et al., 2007) and Acid Orange 7 (Xu et al., 2008). Wang et al. (2007) proposed kinetic modeling of electrochemical degradation of phenol in a three-dimensional electrode reactor and presented a theoretical model for energy calculations.

In this paper, we investigated the electrooxidation of leachate from an industrial solid waste landfill site using three-dimensional carbon bed reactor. The study interested us for three reasons: (i) unlike municipal solid waste landfill leachate, the leachate from an industrial solid waste landfill site has very high concentrations of pollutants, (ii) detailed kinetics of electrooxidation of pollutants at carbon particle bed were seldom reported and (iii) the role of surface area and microporosity of carbon on the kinetics of electrooxidation of pollutants was not implicated previously.

2. Experimental section

2.1. Leachate

Leachate was obtained from a treatment storage and disposal facility (TSDF) at Ankleshwar, Bharuch district, India. Toxic organic

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wastes/solid wastes/incinerable aqueous waste from about 378 heterogeneous chemical industries are disposed at this facility. The dark brown leachate with pH 8.9 contained high COD in the range $17.1\text{--}18.4\text{ g L}^{-1}$, $2.00\text{--}2.24\text{ g L}^{-1}$ TKN (Total Kjeldahl Nitrogen) and $1.20\text{--}1.32\text{ g L}^{-1}$ ammonia nitrogen ($\text{NH}_4^+\text{-N}$). The landfill leachate also contained $52.30\text{--}54.28\text{ g L}^{-1}$ chloride. The concentrations of some heavy metals viz., Mn and Fe are high, 42.75 ± 1.00 and $19.75 \pm 0.50\text{ mg L}^{-1}$, respectively. The leachate used for the present study may be regarded as highly non-biodegradable (BOD/COD = 0.05) high strength wastewater.

2.2. Granular activated carbon

Two types of granular activated carbon (GAC-Indcarb-30 and 60) were purchased from Industrial Carbons Private Limited, Baroda, India. The average carbon particle size was 2–3 mm, and their surface areas were 600 and $1100\text{ m}^2\text{ g}^{-1}$, respectively.

2.3. Reactor setup and experimental procedure

The schematic of the one compartment three-dimensional carbon bed reactor (TDR) was shown in Fig. 1. A quadrangular 2.6 L tank ($18\text{ cm} \times 12\text{ cm} \times 12\text{ cm}$) was fabricated using 6 mm thick Perspex® sheet. In this reactor, two stainless steel plates ($14 \times 10\text{ cm}$) were used as cathode situated 12.0 cm apart on opposite sides, and a 12 mm thick carbon plate anode was kept in the middle of the reactor. The carbon anode was perforated (2 mm diameter holes) to allow free flow of liquid across the anode. Approximately 1.16 kg granular activated carbon was packed into space between the electrodes up to a height of approximately 10 cm. A fine polyethylene net separated the carbon bed and the stainless steel cathodes on either side. Although this prevented direct electrical contact of cathodes and carbon bed, it allowed electrolytic contact. The drainable pore volume was approximately 0.85 L. Air was sparged to mix the effluent via an air distribution manifold situated at the bottom of the reactor. The air was supplied by a diaphragm pump at a rate of 1.0 L min^{-1} .

Approximately 1.10 L raw leachate was taken into TDR during each run as an influent and electric potential was applied using a Testronix 34-D DC power supply (Mumbai, India). The reactor was operated in batch mode. Addition of supporting electrolyte (NaCl) was not required due to high electrical conductivity and high concentration of chloride in the leachate. Based on separate adsorption experiments, a 1-h contact time was allowed initially for the establishment of adsorption equilibrium prior to supplying DC power. The electrooxidation experiments were run at constant current mode and the cell voltage was $3.25 \pm 0.15\text{ V}$ at 1 A, $4.30 \pm 0.20\text{ V}$ at 2 A and $5.90 \pm 0.20\text{ V}$ at 3 A. Several test samples were collected initially after every 15 min for 1 h and then hourly for 6 h. The variation in concentrations of COD, TOC and TKN was determined as a function of reaction time. Since free ammonia in the leachate was quickly removed during electrooxidation in the TDR, its concentration was not monitored. At the end of each run, the carbon bed was cleaned and reused. The carbon was thoroughly washed with hot water ($80 \pm 2\text{ }^\circ\text{C}$) by heating over a heating mantle for 8 h, intermittently flushed with fresh water, until no colour was found in the washings.

2.4. Analyses

The leachate was analyzed for various parameters according to standard methods (APHA, 2005). Since the samples contained higher concentration of chloride which is known to effect the COD determination, the samples were adequately diluted to obtain the concentration of chlorides $<2.0\text{ g L}^{-1}$ prior to COD determination by using open reflux method. The observed error in the determination of COD in duplicate tests was about 2–3%. The heavy metal analysis was done by Inductively Coupled Plasma-Atomic Emission Spectrometer (Jobin Yvon JY-24). Total organic carbon (TOC) analysis was carried out on a Shimadzu OCT-1 TOC- V_{CPH} analyzer. Average concentration of heavy metals and TOC was reported from duplicate test results. The surface morphology and pore structures of GAC particles were examined using JEOL JXA-840A scanning electron microscope (SEM).

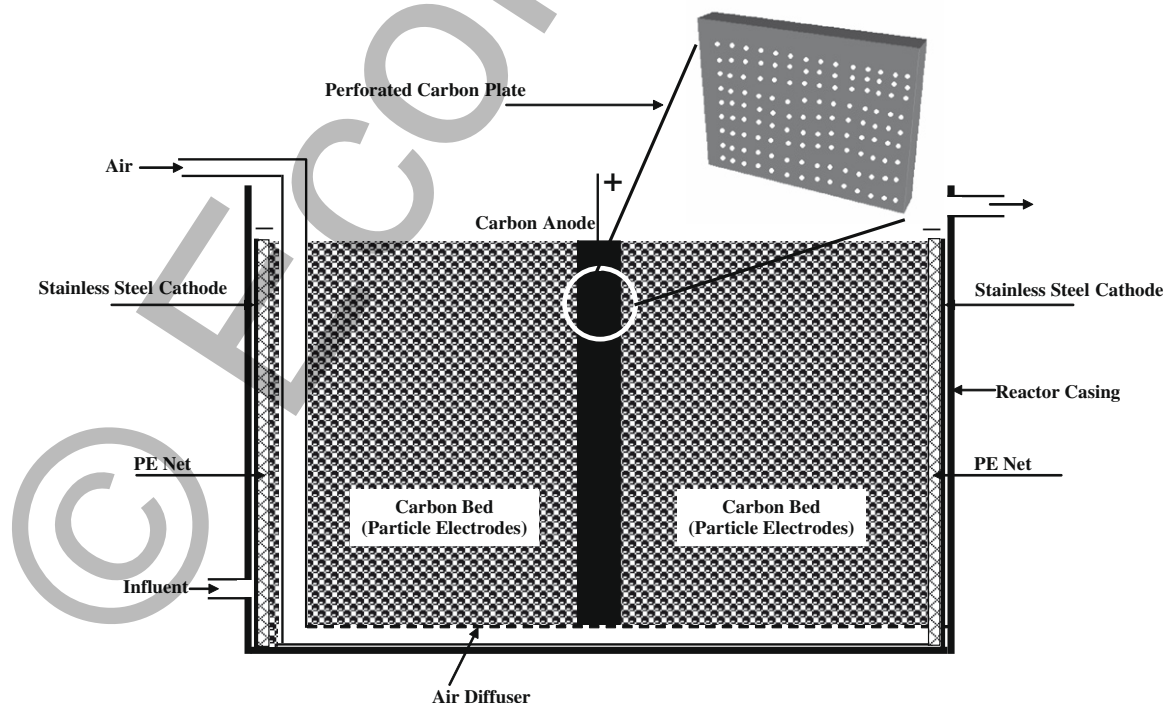


Fig. 1. Schematics of the three-dimensional carbon bed electrochemical reactor (TDR).

3. Results and discussion

Initially, it was necessary to attain adsorption equilibrium between pollutants in the leachate and activated carbon before commencing the electrooxidation experiments. This minimizes the contribution from adsorption by activated carbon. It was found that the carbon in TDR adsorbed pollutants from the leachate and the observed saturation adsorption removals during 1 h equilibrium contact time were approximately 10–11% COD, 12% TOC, 11–12% TKN.

Evolution of tiny gas bubbles was noticed at both carbon anode and steel cathodes as soon as DC current was applied. After 10–15 min, the typical smell of gaseous chlorine was noticed which became stronger with the time of electrolysis. Formation of foam was noticed particularly during initial 1–2 h, indicating presence of some surfactant compounds in the leachate. The pH of the leachate sample after 6 h electrooxidation was observed to become slightly alkaline (pH = 9.0–9.1) compared to initial pH.

3.1. Electrooxidation kinetics-removal of COD, TOC, and TKN

The time course variation in normalized concentration of COD, TOC and TKN and its dependence on applied current was illustrated in Figs. 2a–4a. Figs. 2a and 3a display two distinct linear regions identified as Phase I and Phase II. About 60–64% COD and 66–73% TOC were reduced during one-hour electrooxidation treatment (Phase I) at the applied currents. The removal of COD and TOC gradually increased with treatment time, and 76–80% COD and 83–85% TOC removals were achieved at the end of 6 h (Phase II).

The concentration of TKN decreased exponentially with time as expected for a typical first order reaction (Fig. 4a). About 57–64% TKN was removed during 1-h electrooxidation treatment at all the applied currents. Approximately 91% and 94% TKN was removed at 1 A and 2 A during 6 h and near complete removal (97%) was achieved in 6 h at 3 A.

Based on the concentration data in Figs. 2a–4a, the pseudo first order rate constants (k , min^{-1}) with respect to removal of COD, TOC and TKN were deduced for the process representing Phase I and II from the corresponding first-order kinetic plots shown in Figs. 2b–4b. The apparent rate constants, including those of some control experiments that will be described elsewhere in this paper, are presented in the Table 1. Regression coefficient (R^2) was often >0.92 suggesting that the electrochemical reaction of removal of COD, TOC and TKN follows pseudo-first order kinetics in their concentrations. The pseudo-first order rate constant for COD removal (k_{COD}) at 1.0, 2.0 and 3.0 A within Phase I regime was about $5.83 \times 10^{-3} \text{ min}^{-1}$ and the corresponding values for k_{COD} under Phase II were $0.81\text{--}1.03 \times 10^{-3} \text{ min}^{-1}$. The k_{COD} (Phase I) is 5–7 times greater than k_{COD} (Phase II). Similarly, the k_{TOC} under Phase I regime ranges from 7.00×10^{-3} to $8.10 \times 10^{-3} \text{ min}^{-1}$, while k_{TOC} was an order of magnitude less under Phase II. Both k_{COD} and k_{TOC} showed little dependence on the applied current. A possible explanation is: although increasing current would enhance chlorine generation, the pollutants were actually removed in subsequent reactions involving hypochlorite, etc. i.e., indirect oxidation (Chiang et al., 1995b). Cossu et al. (1998) reported electrochemical treatment of sanitary landfill leachate at catalytic anodes viz., Ti/PbO₂ and Ti/SnO₂, and found that k in the final stage of the reaction was one order of magnitude lower than k in the first part of the reaction. They attributed this to the presence of more easily oxidizable compounds initially in the leachate. Similarly, Xiong et al. (2001, 2003a) presented kinetic curves that describe time course variation of COD in a three-dimensional carbon bed reactor. In both cases, an initial sharp decrease in COD (about 40%) can be found

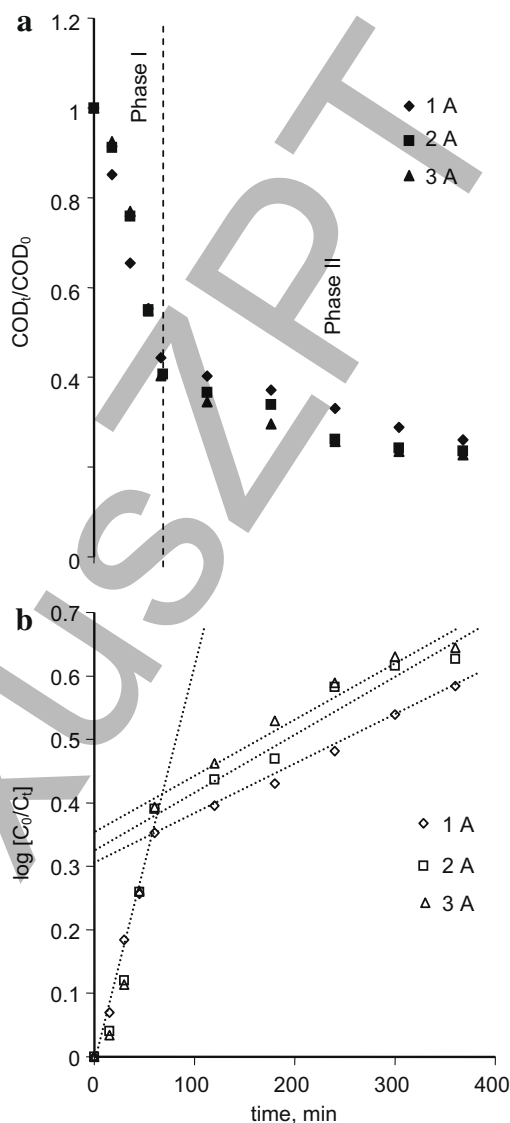


Fig. 2. (a) Time course variation of normalized COD concentration as a function of treatment time and (b) logarithm of normalized COD concentration as a function of treatment time illustrating two-stage pseudo-first order kinetics (c_0 17.1 g L^{-1} for 1 A, 18.4 g L^{-1} for 2 A and 18.2 g L^{-1} for 3 A).

from the plots and the average rates in the first part of the reaction were higher. Although Xiong et al. (2001, 2003a) reported that the initial rate of reaction was not influenced by airflow rates (sparging-rate), they did not reason this behavior.

The mineralization efficiency was estimated using $(\text{TOC}_0 - \text{TOC}_t)/\text{TOC}_0$, and the values are given in Table 1. The ratio of $k_{\text{TOC}}/k_{\text{COD}}$ which can be considered to represent mineralization rate, was also calculated and included in Table 1. The mineralization efficiency was highest (0.71–0.72) in the initial 1 h at all the applied currents in this study. It increased gradually to 0.83–0.84 at the end of 6 h. Further, the mineralization rate was found to be in the range 0.79–0.90 (Table 1, for Phase II) indicating effective removal of organic carbon from the leachate sample. The ratio of $k_{\text{TOC}}/k_{\text{COD}}$ for Phase I regime is >1 , implying faster mineralization than COD removal. This apparent discrepancy may be attributed to possible interference from free ammonium and hypochlorite ions in the determination of COD. It may be expected that free ammonium, hypochlorite and some organic byproducts build up during the electrooxidation process (Naumczyk et al., 1996b).

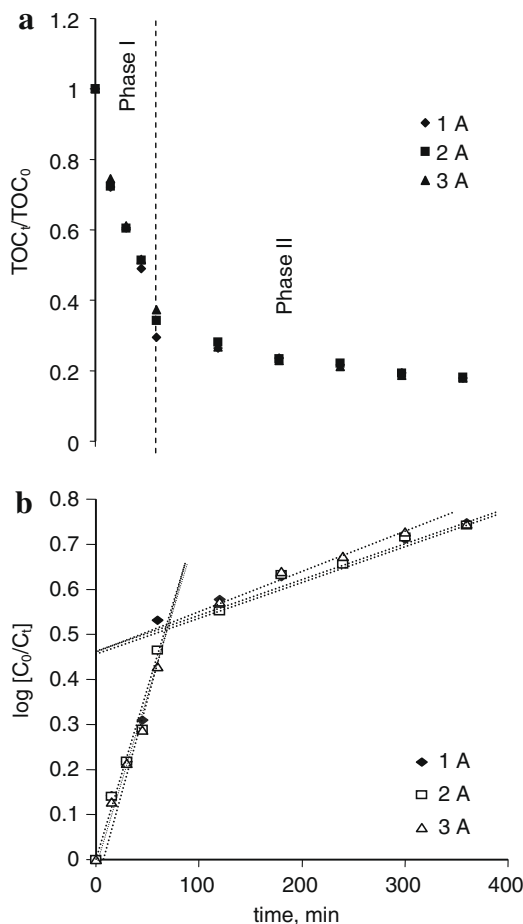


Fig. 3. (a) Time course variation of normalized TOC concentration as a function of treatment time and (b) logarithm of normalized TOC concentration as a function of treatment time illustrating two-stage pseudo-first order kinetics (c_0 5.71 g L⁻¹).

3.2. Apparent faradic efficiency and specific energy consumption

The apparent faradic efficiency (η_F) of COD removal was calculated using the following formula (Szpyrkowicz et al., 1995):

$$\eta_F = \frac{(\Delta\text{COD} \times V \times F)}{8 \times I \times \Delta t} \quad (1)$$

where ΔCOD is the net COD removed (g L⁻¹) after a treatment time t , V is the volume of treated leachate (L), F is Faraday's constant (96487 C equiv⁻¹), 8 is the equivalent weight of oxygen, I is the applied current and Δt is the treatment duration (s). The η_F for COD removal was 8.00, 4.45 and 2.94% at 1.0, 2.0 and 3.0 A, respectively. Similar current efficiency for COD removal was obtained by Cossu et al. (1998) during electrochemical treatment of sanitary landfill leachate at Ti/PbO₂ and Ti/SnO₂ anodes.

Specific energy consumption (E_{sp}), the electric energy in kilowatt-hours required to degrade a kilogram of a pollutant in water, was calculated using the formula for batch operation (Bolton et al., 2001):

$$E_{sp} = \frac{P \times t \times 10^6}{V(c_0 - c_t)} \quad (2)$$

where P is the rated power (kW) of the reactor, V is the volume (L) of water treated in the time t (h), c_0 and c_t are the initial and final concentrations (mg L⁻¹) of a pollutant, and the factor of 10⁶ converts mg to kg. The E_{sp} for the removal of COD, TOC and TKN during 6 h at 1 A are 1.33 kW h kg⁻¹ COD, 3.64 kW h kg⁻¹ TOC and

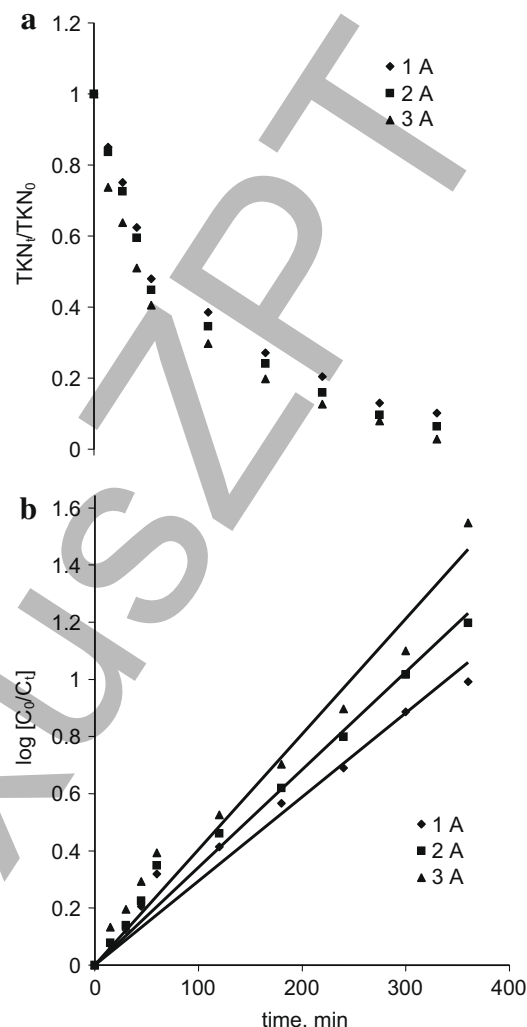


Fig. 4. (a) Time course variation of normalized TKN concentration as a function of treatment time and (b) logarithm of normalized TKN concentration as a function of treatment time (c_0 2.0 g L⁻¹).

9.59 kW h kg⁻¹ TKN. The result indicates that electrooxidation of organic nitrogen (TKN) is relatively more energy consuming. This may be due to more complex heterocyclic molecules having C–N and C=N bonds which account for TKN. The TDR employed in this study registered lower E_{sp} for COD removal compared to previously reported bipolar cells (Vlyssides et al., 1999; Rao et al., 2001; Cossu et al., 2007).

3.3. Degradation mechanism

The removal of COD, TOC and TKN in the three-dimensional carbon bed electrochemical reactor used in the present study may be very complex, involving adsorption, water electrolysis, chloride ion discharge and electrooxidation processes. It is known that the carbon particles that constitute bed in the three-dimensional electrode reactor, by virtue of contact resistance, polarize under the influence of electric field in between the feeder electrodes and function as microelectrodes (Xiong et al., 2001; Wang et al., 2007). Some of the important reactions that may be taking place at main feeder electrodes as well as at the polarized carbon particles may be written as follows:

Adsorption at carbon:

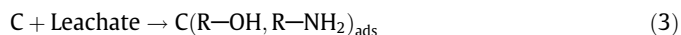


Table 1
Pseudo-first order rate constants (k) for the removals of COD, TOC and TKN and mineralization data.

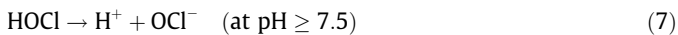
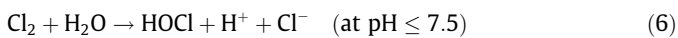
Current	Phase	$k_{\text{COD}} (\text{min}^{-1})$		$k_{\text{TOC}} (\text{min}^{-1})$		$k_{\text{TKN}} (\text{min}^{-1})$		Mineralization data	
		$\times 10^{-3}$	R^2	$\times 10^{-3}$	R^2	$\times 10^{-3}$	R^2	Mineralization efficiency (%)	$k_{\text{TOC}}/k_{\text{COD}}$ (mineralization rate)
1 A	I	5.83	0.99	8.12	0.96	2.91	0.96	–	–
	II	0.81	0.99	0.73	0.99	–	–	0.83	0.90
2 A	I	5.82	0.93	7.32	0.97	3.39	0.98	–	–
	II	1.03	0.96	0.93	0.96	–	–	0.83	0.90
3 A	I	5.84	0.92	7.04	0.98	4.03	0.96	–	–
	II	0.91	0.96	0.72	0.97	–	–	0.84	0.79
<i>Blank experiments</i>									
Indcarb-30	I	5.8	0.92	–	–	–	–	–	–
	II	0.9	0.98	–	–	–	–	–	–
Indcarb-60	I	6.6	0.92	–	–	–	–	–	–
	II	1.2	0.97	–	–	–	–	–	–
Parallel plate ^a		0.3	0.88	–	–	–	–	–	–

^a Without carbon bed.

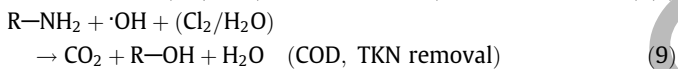
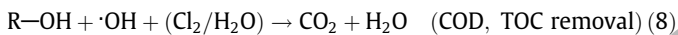
Water and chloride oxidation at anode:



Disproportionation of electrogenerated molecular chlorine:



Oxidation of organic compounds:



As mentioned earlier, the adsorption accounted for 10–12% removal of COD, TOC and TKN from the leachate. It may be assumed that electrochemical mineralization of organic compounds in the leachate occurs with concomitant evolution of oxygen and chlorine at anode. At the operating voltage (4.5 V), both the reactions (4)

and (5) may occur at the carbon anode. The counter reactions at the cathode would be the reduction of water and other reducible species, viz., Fe and Mn metal ions present in the leachate. However, due to prevailing alkaline pH, these metals ions can form corresponding hydroxides flocs. It is believed that these metal oxide flocs floated to the top along with foam and formed scum. Alternatively, they may remain attached to the surface of carbon. Since the TDR was sparged with air, we might also expect reduction of molecular oxygen to H_2O_2 at stainless steel cathodes, which might oxidize organic compounds. However, in a separate experiment in TDR using Indcarb-30 at 1 A without air-sparging, we found that the overall percent COD removal was only slightly less by 3–4% when compared to 76% obtained under air-sparging. Thus, the oxidation of organic compounds in the leachate using in situ generated H_2O_2 is less significant. Some authors (Xiong et al., 2001; Chun et al., 2002) have earlier reported that H_2O_2 is generated at SS cathodes under air-sparging and suggested that a specific air-flow rate is required to be maintained to realize higher removal efficiencies.

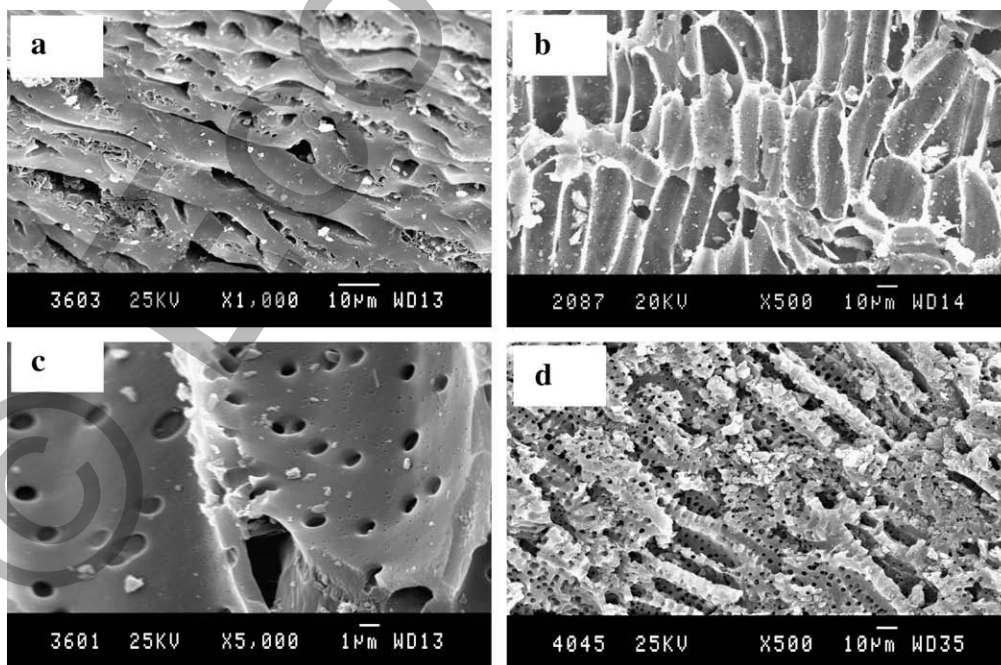


Fig. 5. Photomicrographs (SEM) showing pore structures in granular activated carbon.

The discharge of chloride ions at the carbon particle electrodes as per the reaction step (5) appears predominant due to the presence of more than one mole per liter of chloride ($>52 \text{ g L}^{-1}$) in the leachate sample. The observation of chlorine gas evolution during the electrooxidation experiments in TDR was identified by its typical smell and supports this mechanism. The chlorine gas thus formed may undergo disproportionation into hypochlorous acid or chlorite ions as shown in reaction steps (6) and (7). Since the initial pH of the leachate was about 8.9 which became slightly alkaline during electrooxidation, we may expect formation of OCl^- ions ($\text{pK}_a = 7.44$) to dominate in the reactor. Thus, the observed electrochemical oxidation can be attributed to indirect oxidation utilizing chlorine/hypochlorite formed by anodic oxidation of chloride. The chloride-mediated electrochemical mineralization of organics has been discussed by many authors (Comninellis, 1994; Comninellis and De Battisti, 1996; Panizza et al., 2000) and important mechanistic interpretations have been proposed. A number of related studies have also reported indirect oxidation to prevail under high Cl^- concentration (Chiang et al., 1995; Moraes and Bertazzoli, 2005; Cabeza et al., 2007; Deng and Englehardt, 2007).

It was observed that faster removal of pollutants occurs initially followed by slow oxidation kinetics that could be described by two-stage linear first-order plots (Figs. 2b and 3b). It can be seen from the Figs. 2a and 3a, that the Phase I lasted for about 1 h. In this time, the contribution from adsorption to COD removal was not more than 12%, which occurred at a rate of $30\text{--}34 \text{ mg L}^{-1} \text{ min}^{-1}$. In the parallel plate configuration, about $<5\%$ COD was removed during 1 h ($6.6 \text{ mg L}^{-1} \text{ min}^{-1}$). In the TDR, we obtained 60–64% COD removal during 1 h ($155 \text{ mg L}^{-1} \text{ min}^{-1}$), which is higher than the sum of COD removals due to adsorption and two-dimensional electrode system. This result suggests that the efficiency of TDR under applied current is higher than that can be accounted for considering adsorption and reactions at parallel plate feeder electrodes. Thus, saturation adsorption over GAC may not be the cause for the observed lower rate of removal under Phase II. It was predicted initially that the faster removal under Phase I may be due to enhanced adsorption capacity of GAC under the electrochemical conditions and removal through electrosorption may be dominant. Since electrosorption can be expected to be dependent on the applied current (electrical field) the slopes of linear plots under Phase I must be different (Figs. 2b and 3b and Table 1). However, we found that the slopes are independent of applied current, implying that electrosorption also may not be contributing significantly for the observed pollutant removal. Alternatively, the lower rate of electrooxidation under Phase II may be attributed to build up of intermediates through reactions under Phase I, and those intermediates may be inhibiting the electrooxidation under Phase II. Some authors reported passivation of main anodes [Pt, SS (Stainless Steel), etc.] due to polymer film formation, although Xiong et al. (2003b) found that polymers are not formed at GAC anodes. Moreover, the build up of intermediates may be possible particularly when mineralization efficiency is low. Although the nature of intermediates could not be assessed in the present context mainly because of the complex nature of leachate, the intermediate build up may be considered to be less because of the high mineralization efficiency obtained in the present study (0.79–0.90).

On the other hand, in view of the extensive pore structures comprising of large tubular pores, macro and micro pores in carbon particles, at least two reaction zones, namely electrooxidation on the external surface of carbon particles and that in the pores may be expected. The SEM photomicrographs of GAC prior to and after use in TDR are shown in Fig. 5. Prior to use, it revealed extensive pore structures comprising of large tubular pores (micrographs a and b) and macro pores within each tube ($10 \mu\text{m}$, micrograph b) and also micro pores ($0.1\text{--}1.0 \mu\text{m}$, micrograph c). The SEM photomicrograph d of carbon recovered from TDR after electrooxidation

experiments at 3 A for 6 h displayed surface erosion and apparently no extraneous metal/metal oxide deposits were found on the surface. The following two experiments were performed to ascertain the role of GAC in the TDR: (i) testing the performance of the reactor in parallel plate (without carbon bed) and (ii) testing the performance of the reactor using higher surface area GAC. The Indcarb-30 ($600 \text{ m}^2 \text{ g}^{-1}$) carbon bed in TDR was replaced with Indcarb-60 which has higher surface area ($1100 \text{ m}^2 \text{ g}^{-1}$). The comparison of COD removals under these test conditions is presented in Fig. 6. The rate constant data is given in Table 1. The parallel plate configuration resulted in a maximum removal of 28% COD in 6 h at 3.0 A and 5.9 V at a rate of $6.6 \text{ mg L}^{-1} \text{ min}^{-1}$ ($k = 3.0 \times 10^{-4} \text{ min}^{-1}$), as against 78% using three-dimensional configuration (Indcarb-30) at a rate of $155 \text{ mg L}^{-1} \text{ min}^{-1}$ ($k = 5.83 \times 10^{-3} \text{ min}^{-1}$), after accounting for 10% COD removal due to adsorption on carbon bed. This result confirms that GAC in TDR has significant beneficial effect. On the other hand, in experiments replacing the Indcarb-30 ($600 \text{ m}^2 \text{ g}^{-1}$) carbon bed in TDR with GAC-Indcarb-60 which has higher surface area ($1100 \text{ m}^2 \text{ g}^{-1}$), $>12\text{--}15\%$ increase in the overall COD efficiency was observed, leading to higher COD removal

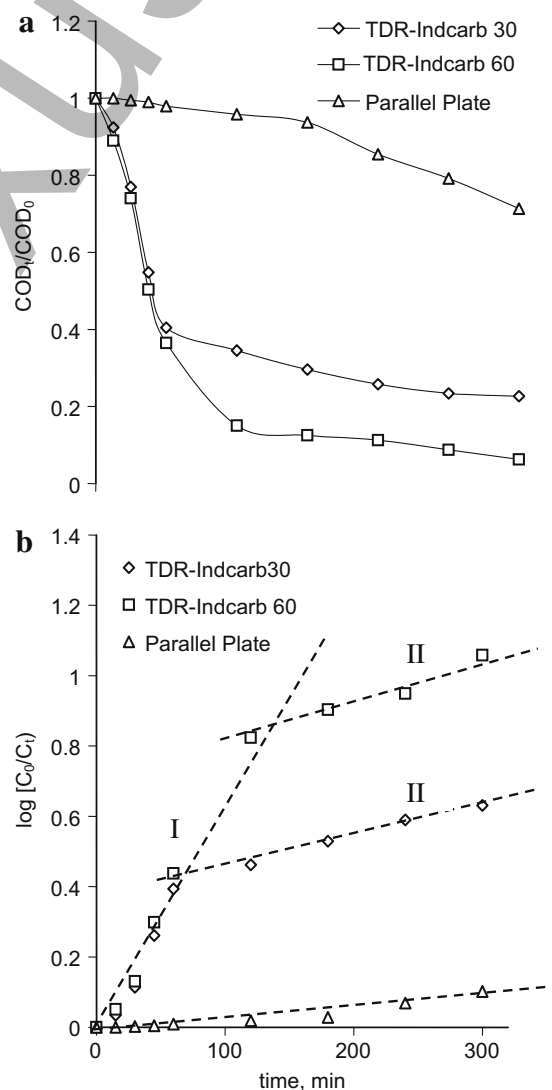


Fig. 6. (a) Time course variation of normalized COD concentration as a function of treatment time using the parallel plate reactor and using two different GACs viz., Indcarb-30 and 60, and (b) logarithm of normalized COD concentration as a function of treatment time illustrating two-stage pseudo-first order kinetics ($c_0 = 17.1 \text{ g L}^{-1}$).

(>80%) during Phase I. The k value was $6.60 \times 10^{-3} \text{ min}^{-1}$ when Indcarb-60 was used. These results support that the faster kinetics under Phase I is due to greater availability of adsorbed reactants and high rate of generation of chloride based secondary oxidants initially on the surface of GAC particles. The low rates of oxidation under Phase II may be due to reactions within the pores, although surface erosion of carbon in TDR may be also responsible partly. However, the presently available data are insufficient to clearly distinguish between these two possibilities. Thus, a two-stage pseudo-first order reaction kinetics model satisfactorily explains the electrochemical oxidation of pollutants at carbon particle bed electrodes.

4. Conclusions

The electrochemical oxidation of pollutants from the leachate in TDR proceeds with high mineralization efficiency and low consumption of electrical energy. The reaction is chloride-mediated and follows a two-stage pseudo-first order reaction kinetics model. The use of higher surface area GAC may be beneficial as it can lead to higher pollutant removal from the leachate.

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