REMOVAL OF FORMIC ACID FROM WASTEWATER USING THREE-PHASE THREE-DIMENSIONAL ELECTRODE REACTOR

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Abstract. A new electrochemical reactor, three-phase three-dimensional electrode reactor, was designed and used to investigate the removal of formic acid from simulated wastewater. The experimental results were assessed in term of Chemical Oxygen Demand (COD) removal efficiency. The results showed that the three-phase three-dimensional electrodes could effectively remove formic acid. Its COD removal efficiency was much higher than those of two-dimensional electrodes and common three-dimensional electrodes, respectively. The COD removal efficiency of the three-phase three-dimensional electrodes using air as a sparge gas increased 13.5% relative to that using nitrogen as a sparge gas. The observation indicated that the sparged air in the three-phase three-dimensional electrodes not only participated in some physical processes but also played an important role in electrochemical reactions to assist COD removal.

Keywords: COD removal, electrochemical method, formic acid, three-phase three-dimensional electrodes, wastewater

1. Introduction

The presence of harmful organic species in water supplies and in the wastewater discharge from chemical industries, power plants and agricultural sources is of global concern (Legrini *et al*., 1993; Hoffmann *et al*., 1995). A variety of physical, chemical and biological techniques and their combinations have been employed to remove organic pollutants. However, all existing wastewater treatment processes have their inherent limitations in applicability, effectiveness and cost (Bandara, 1996; Matatov-Meytaland and Sheintuch, 1998; Ray, 1998). These limitations have spurred an effort to develop new and effective technologies for detoxification and removal of undesirable organic substances (Simonsson, 1997).

Recently, interest in environmental electrochemistry, an emerging technology, has increased and possible application to the treatment of effluents from industrial or municipal plants can be envisaged (Rajeshwar *et al*., 1994; Coin *et al*., 1996; Simonsson, 1997). In particular, the electrochemical technologies based on three-dimensional electrodes for wastewater treatment have attracted more atten-

tion (Brown *et al.*, 1994; Tissot and Fragniere, 1994; Rajeshwar *et al.*, 1994; Tennakoon *et al.*, 1996; Bockris and Kim, 1997; Simonsson, 1997) because the electrodes are characterized by large specific surface area and high performance in comparison with conventional two-dimensional electrodes (Bockris and Kim, 1997; Simonsson, 1997). However, most of the researches about the three-dimensional electrode are mainly focused on organic electrosynthesis (Pasquini and Tissot, 1996; Dieckmann and Langer, 1997; Simonsson, 1997; Belmant *et al.*, 1998; Scott *et al.*, 1998; Szanto *et al.*, 1998) and removal of metal ions from wastewater streams (Walsh and Reade, 1994; Grau and Bisang, 1998; El-Deab *et al.*, 1999; Ragnini *et al.*, 2000). Our work will be devoted to extend the application of the three-dimensional electrodes to the treatment of organic wastewater.

Formic acid exists in some actual industrial wastewater such as effluents from tanners, dye workshops, and printed fabrics mills (Claudel *et al.*, 1984). And it is also one of stable intermediates in the complete mineralization of many organic pollutants (Chou *et al.*, 1998; Davis and Green, 1999; Hwang *et al.*, 1999; Dinsdale, 2000), which is resistant to further oxidation (Ogata *et al.*, 1981; Harmsen *et al.*, 1997). Hence it is frequently used as a model organic pollutant in the study of organic wastewater (Kawaguchi, 1993; Kim and Anderson, 1994; Hidaka *et al.*, 1996; Kim and Anderson, 1996; Butterfield *et al.*, 1997; Candal *et al.*, 1997; Miller *et al.*, 1999). The aim of the present work was to probe the removal efficiency of formic acid from synthetic wastewater using a new kind of electrochemical reactor, three-phase three-dimensional electrode reactor.

2. Experimental Section

2.1. MATERIALS

A commercial vegetable-based granulated activated carbon (GAC) from KEBO AB Company, Sweden, was used as the working electrode materials in this study. It has an average particle size of 3–5 mm and a specific weigh of 0.2727 kg L^{-1}. Formic acid (80–100%) was obtained from Merck KGaA Company, Germany, and other regents were of analytical-reagent grade. All solutions were prepared with deionized water.

2.2. CHEMICAL OXYGEN DEMAND (COD) ANALYSIS

The COD was determined using a LP1W spectrophotometer and a commercial Dr-Lange standard procedure (Dr Bruno Lange Gmbh, Düsseldorf, Germany). It reflects the amount of formic acid in the sample. The experimental results were assessed with COD removal efficiency (%), i. e., the ratio of the COD removal after treatment to the initial COD concentration of formic acid solution.
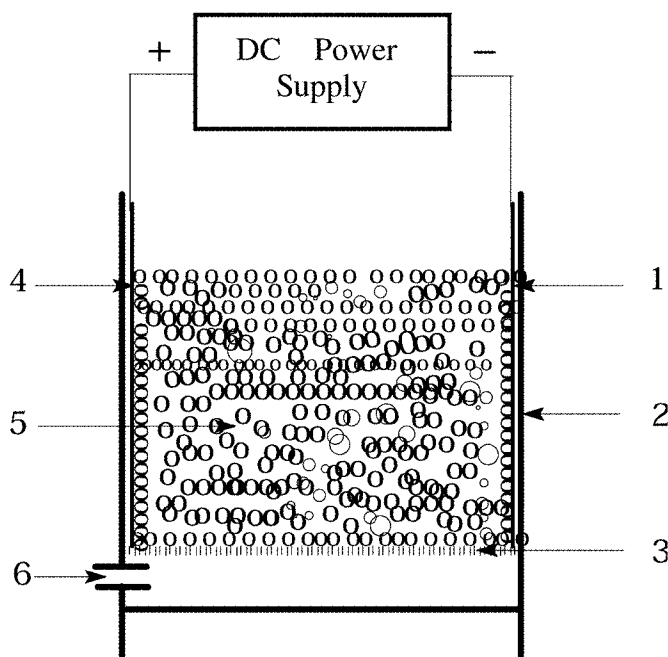
Figure 1. Schematic diagram of three-phase three-dimensional electrode reactor (1: cathode; 2: support; 3: micropore plate; 4: anode; 5: particle electrodes; and 6: inlet of compressed-air).

2.3. EXPERIMENTAL SET-UP

The experimental apparatus is a batch rectangular undivided three-phase three-dimensional electrode reactor as shown in Figure 1. The reactor mainly consists of four parts, support, anode and cathode, GAC packed bed and provision for compressed air. The support was made from plastic with a size of $(11 \times 4 \times 20)$ cm^3. The anode and cathode (main electrodes) were two stainless steel plates situated 11 cm apart from each other. The 60 g GAC was packed between the two main electrodes, forming a cubic packed-bed three-dimensional electrode with a bed height of 5 cm. The effective volume of the three-dimensional electrodes was $11 \times 4 \times 5$ cm^3. The compressed air was sparged into the particle electrodes by a micopore plate from the bottom of the reactor. The sparging of the compressed air into the reactor will cause an increase in the height of the packed-bed, such as, for airflow of 7.0 L min^{-1}, the height about 1 cm. The electric power was supplied with regulated DC power supply, PAC 30–6, Kenwood, Japan.

2.4. EXPERIMENTAL METHOD

A simulated organic wastewater containing formic acid was prepared to a COD concentration of 364.2 ppm. The pH was adjusted to a requred value using NaOH or H$_2$SO$_4$ in order to investigate the effect of pH value on COD removal efficiency.

And pH value was not adjusted and no electrolyte was also added in all other experiments.

A 130.0 mL simulated wastewater was fed into the three-dimensional electrode reactor prior to each electrolysis. The reactor was timed starting when the DC power and compressed-air supply were switched on. The resulted solution was analyzed for COD. In order to ensure that the used electrodes were of the same state as possible, the virgin GACs were employed as the working particle electrodes in each run. General treatment conditions were 28.0 V applied cell voltage, 7 L min^{-1} airflow and 60.0 min treatment time unless otherwise stated.

3. Results and Discussion

3.1. EFFECT OF CELL VOLTAGE

The unifying feature for three-dimensional electrodes is that the cell chamber is filled or partly filled with needed working electrode materials depending on the aims of researches. In aqueous medium, activated carbon has considerable electrochemical activity (Putzien, 1984; Kastening *et al.*, 1997a, b), in addition to its strong adsorption capability. Therfore it has attracted considerable attention recently for its utilization as an electrode material (Card *et al.*, 1990; Goodridge *et al.*, 1977; Canizares *et al.*, 1999). In this study, the GAC packed bed was employed as a working electrode. The instantaneous current-voltage curves for the GAC packed bed are presented in Figure 2. They show approximate linear current-voltage graphs, similar to the current-potential curve of the reported activated carbon electrode (Canizares *et al.*, 1999). It can be seen from the figure that the order of current is C > B > A at same cell voltage, suggesting that the current was increased not only by the addition of formic acid but also by the sparging of air. The enhancement effect of formic acid can be attributed to the increase in the solution conductivity due to the addition of formic acid as an electrolyte and the increase in the number of transferred electrons with the oxidation of formic acid while the enhancement effect of the sparged air indicates the sparged air may have a positive role for the oxidation of formic acid. The experimental results encouraged us further to investigate the role of the sparged air in the reactor.

The dependence of COD removal efficiency on applied cell voltage at a constant airflow of 7.0 L min^{-1} was illustrated in Figure 3. It can be seen from the figure that the COD removal efficiency increases from 37.9 to 73.4%, that is, has an absolute increase of 36.5% with increasing the applied cell voltage from 0.0 to 30.0 V although the change is not in a linear fashion like the current-voltage curve. The adsorption of GAC is reponsible for the removal efficiency at 0.0 V, i.e., open circuit while the increase in COD removal efficiency can be simply attributed to the increasing in the driving force of electrode reaction as increase in the cell voltage because potential is the major driving force for the respective phenomena of interest in electrochemical reactors (Card *et al.*, 1990).
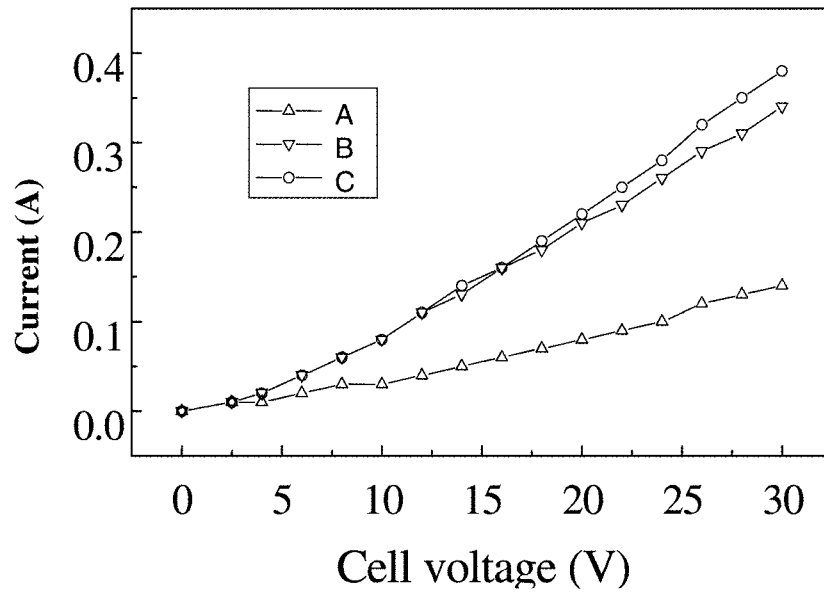
Figure 2. Dependence of current on cell voltage of three-dimensional electrodes (A: in the absence of formic acid solution and sparged air; B: in the presence of 300 mL formic acid, no sparged air; C: in the presence of 130.0 mL formic acid and a airflow of $7.0 \ L \ min^{-1}$).
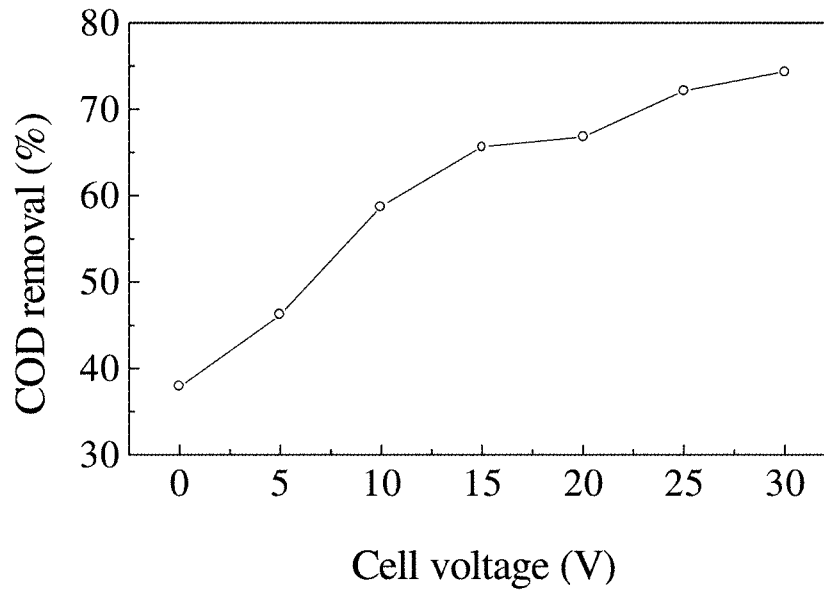

Figure 3. Effect of cell voltage on COD removal efficiency (airflow: $7.0 \ L \ min^{-1}$ and treating time: 60 min).

3.2. Effect of airflow

The three-phase three-dimensional electrode reactor used in this study is a kind of undivided electrochemical reactor based on the combination of a GAC packed-bed electrode and air-fed gas-diffusion electrodes, differing from the reported three-dimensional electrode (only solid and liquid phases) (Brown *et al.*, 1994; Tissot and Fragniere, 1994; Tennakoon *et al.*, 1996; Bockris and Kim, 1997). The compressed air was uniformly sparged into the cell by a micropore plate. The sparged air serves two purposes. One is to agitate in order to speed mass transfer. Another is to supply the essential oxygen for electrochemical reactions because some authors reported that the oxygen could be changed into a stronger oxidizing agent H_2O_2 on activated carbon electrode by the two-electron reduction of oxygen (Yeager, 1984; Tatapudi and Fenton, 1993; Foller and Bombard, 1995; Alverez-Gallbergos and Pletcher, 1999). It was found in our study that about 10^{-5} mol L^{-1} H_2O_2 could be electrogenerated by three-phase three-dimensional electrode reactor (Chen and Zhu, 1998). The three-phase three-dimensional electrodes could simultaneously make use of direct anodic oxidation and cathodic electrogenerated H_2O_2 to degrade organic pollutants. As a result, it was expected that the sparged compressed air would play an important role in the degradation of formic acid.

The COD removal efficiencies for different airflow are shown in Figure 4. It indicates that increasing the sparging rate of air from 0.0 to 7.0 L min^{-1} resulted in an increase in COD removal efficiency from 49.7 to 73.1% during a 60 min electrolysis. A maximum enhanced COD removal efficiency of 23.4% is observed. Although no well-defined plateau in the curve is observed in this experimental range, it is found that the curve rises rapidly up to 1.0 L min^{-1} airflow and changes slowly over 1.0 L min^{-1}, specially, 5.0 L min^{-1} airflow. The experimental results suggests that the rate-determining step of the COD removal is mass transfer when air is sparged with smaller airflow; the COD removal rate is mainly controlled by electrochemical reaction when air is sparged with greater airflow.

3.3. Effect of pH

Formic acid is a weak organic acid. Its existing forms are dependent on pH value of solution. HCOOH is a main form at low pH value while $HCOO^-$ is one at high pH. It was expected that pH value of solution possibly affected electrochemical reaction on electrode surface. Therefore the influence of initial pH value for formic acid solution on COD removal efficiency was also investigated in this work. Nine experiments were carried out corresponding to the initial pH values ranging from 1.0 to 12.0 at a constant cell voltage of 28.0 V and airflow of 7.0 L min^{-1}. As can be seen from Figure 5, the increase in the initial pH of the solution from 1.0 to 12.0 decreases in COD removal efficiency from 75.7 to 69.2%. The decrease, at least, may be explained from the following two facts. One is that the oxidation of $HCOO^-$ ion, existing mainly in the solution with high pH value, is slower than that of HCOOH that exists in the solution with low pH value (Harmsen *et al.*,
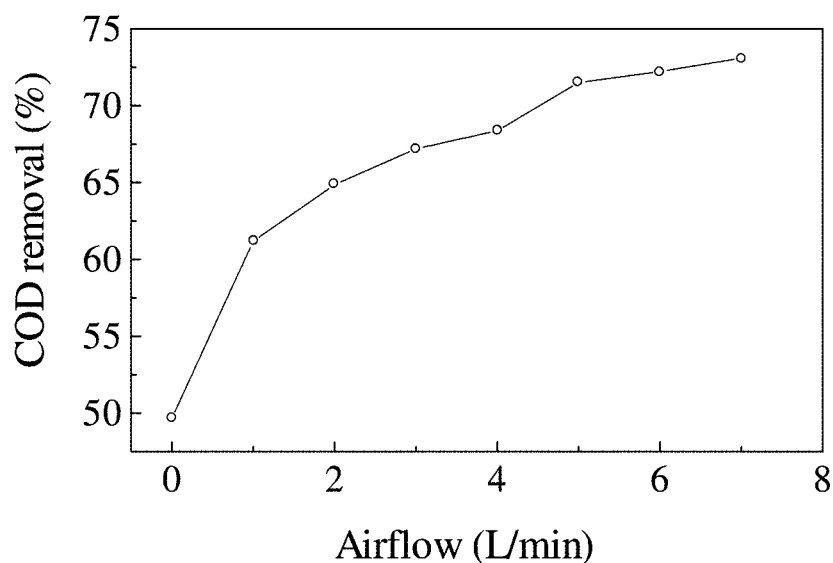
Figure 4. Dependence of COD removal efficiency on airflow (cell voltage: 28.0 V and batch treating time: 60 min).

1997). The second is that carbonate and bicarbonate, the final oxidized products of formate at high pH value, are two well-known ·OH radical scavengers. The ·OH radical is an active species for the degradation of organic compounds in a carbon electrode cell (Boncz *et al.*, 1997; Brezonik *et al.*, 1998).

Harmsen *et al.* (1997) investigated the influence of pH value on the disappearance rate of formic acid in wet air oxidation using carbon supported platinum catalyst. They found that the disappearance rate decreased with either decreasing or increasing pH value from about pH 4, appearing an optimal pH range near 4 for removing formic acid. The phenomenon was not observed in our present experiment. The discrepancy between Harmsen *et al.*'s and our experimental results may be attributed to the different removing mechanisms for formic acid. The removal of formic acid in the present research is based on electrochemical oxidation while Harmsen *et al.* removed formic acid by chemical catalytic oxidation.

3.4. KINETICS OF COD REMOVAL

The kinetic curves of COD removal at three experimental conditions are presented in Figure 6. The curve A shows the dependence of COD removal on reaction time using the GAC packed-bed at an airflow of 7 L min^{-1} and open circuit (0.0 V cell voltage). It is mainly an adsorption curve of formic acid by the GAC at the condition of air-bubble. The curve B presents the change of COD removal efficiencies with reaction time at a constant cell voltage of 28.0 V and in the absence of sparged air. It is kinetic curve of COD removal common in batch three-dimensional
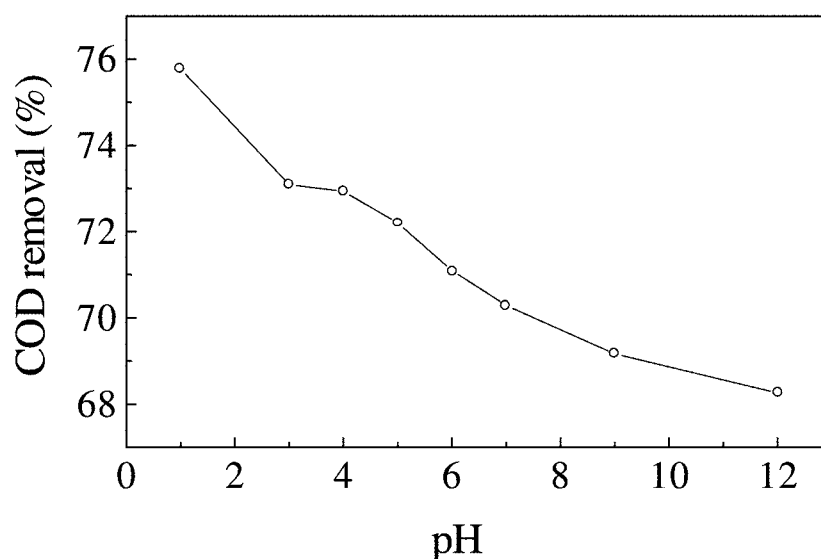
Figure 5. Dependence of COD removal efficiency on initial pH value of the wastewater (cell voltage: 28.0 V; airflow: 7.0 L min^{-1} and reaction time: 60 min).

electrodes. The curve C gives the kinetic profile of COD removal using the three-phase three-dimensional electrodes. The three curves all rise rapidly during first 10 min and change slowly after the time. Although they are characterized by the similar shape, their corresponding rates of COD removal are apparent different. The average rates of COD removal in 60 min for curve A, B and C are calculated to be 2.3 ppm min^{-1}, 3.0 ppm min^{-1} and 4.4 ppm min^{-1}, respectively. The last are 1.9 and 1.5 times of the first two rates, indicating that either cell voltage or sparged-air considerably speeds up the degradation of formic acid. It is also observed that the average COD removal rate in first 10 min for curve A (16.0 ppm min^{-1}) is close to that in curve B (16.5 ppm min^{-1}), showing that sparged-air did not change basically the kinetic nature of COD removal in the three-dimensional electrodes during the first 10 min. The above-mentioned kinetic difference of COD removal between the three-phase three-dimensional electrodes and common three-dimensional electrodes originated from the post-10 min electrolysis.

3.5. COMPARISONS OF TWO- AND THREE-DIMENSIONAL ELECTRODE REACTORS

A series of comparable experiments was performed for the same wastewater, in order to further analyse the COD removal efficiency of the three-phase three-dimensional electrodes. These experimental results are presented in Figure 7. As can be clearly seen from the figure, the COD removal efficiencies of various reactors are in the following order: three-phase three-dimensional electrodes (Bar 3(b))
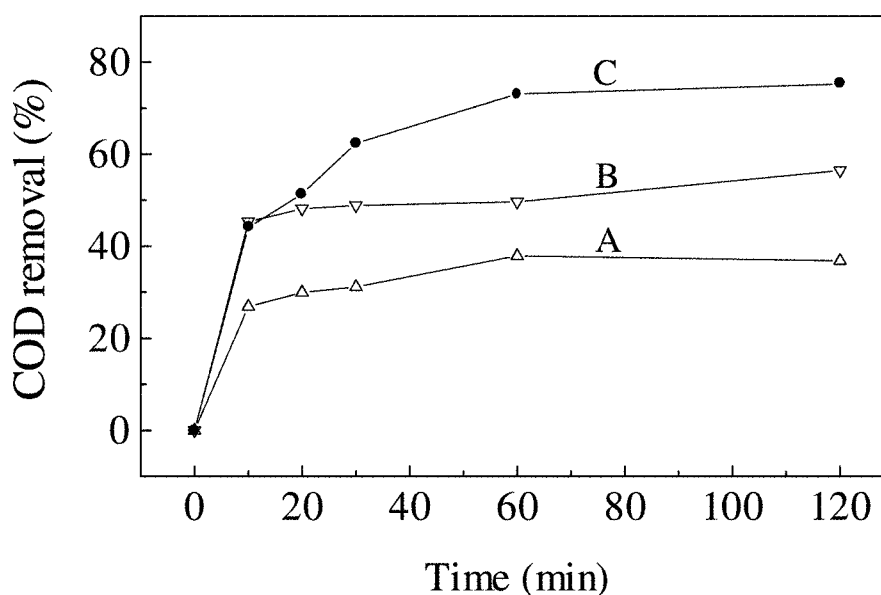
Figure 6. Kinetic curves of COD removal efficiency (A: 7.0 L min^{-1} airflow, open circuit; B: 28.0 V cell voltage, no sparged air; C: 28.0 V cell voltage and 7.0 L min^{-1} airflow).

> three-dimensional electrodes (Bar 2(b)) > GAC packed-bed (Bar 1(b)). And these COD removal efficiencies are all much higher than those of classical two-dimensional planar electrodes. For example, the COD removal efficiencies of three-phase three-dimensional electrodes (Bar 3(b)) is found to be 13.7 times as that of the corresponding two-dimensional planar electrodes under identical experimental conditions.

Bars 1(a) and (b) indicate that formic acid is little removed from aqueous solution by air-strip, similar to the Kim *et al.*'s experimental observation (Kim and Anderson, 1994), while the GAC packed-bed can remove 37.9% COD from the solution at air-bubbling condition in 60 min. These results suggest the GAC packed-bed with air bubbling removed formic acid almost by GAC adsorption rather than by airstrip. Generally, the adsorption of target compounds on electrode is an indispensable step for the electrochemical reactions of the compounds on the surface. Hence above adsorption is beneficial to the electrochemical degradation of formic acid.

Comparing Bars 3(a), (b) and (c), it is found that COD removal efficiency of the three-phase three-dimensional electrodes using air as a sparge gas rises 13.5% relative to that using nitrogen as a sparge gas while the latter is 10.0% higher than that of common three-dimensional electrodes (Bar 3(a)). Nitrogen is a kind of inert gas and generally does not participate in chemical reaction. Therefore above observations indicate the sparged air in the three-phase three-dimensional
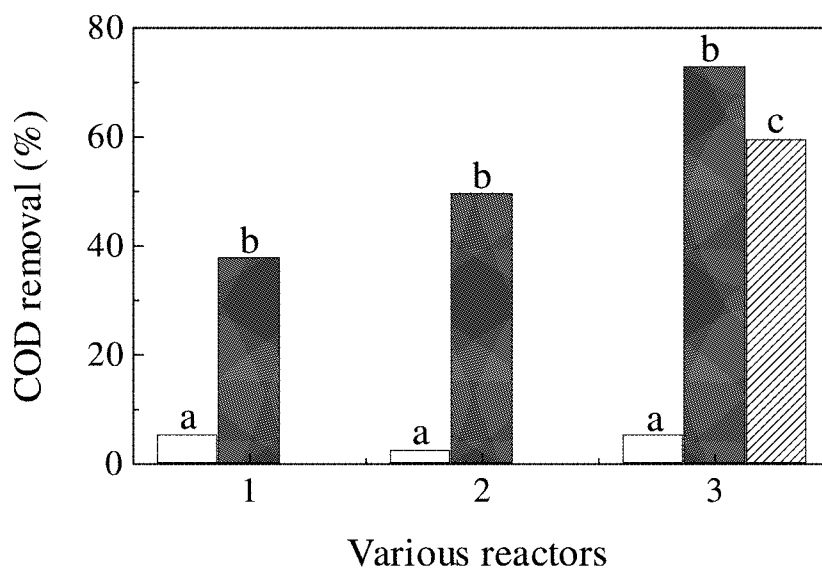
Figure 7. Comparison of COD removal efficiencies of various reactors (1a: bubbling reactor (7.0 L min^{-1} airflow and no GAC); 2a and 3a: two-dimensional electrode reactor (2a: 28.0 V and no sparged air, 3a:'28.0 V and 7.0 L min^{-1} airflow); 1b: GAC packed-bed; 2b and 3b, c: three-dimensional electrode reactor (2b: 28.0 V and on sparged air, 3b: 28.0 V and 7.0 L min^{-1} airflow, 3c: 28.0 V and 7.0 L min^{-1} N$_2$).

electrodes participated not only in some physical process, such as agitation, but also in electrochemical reaction to assist COD removal, as expected previously.

4. Conclusion

It has been confirmed that the formic acid can be effectively removed from the simulated wastewater with the three-phase three-dimensional electrode reactor using GAC as working electrode and compressed air as gas resource. The performance of the electrochemical reactor is considerably affected by applied cell voltage, airflow, pH value of wastewater and treatment time. It is also demonstrated that COD removal efficiency of the air-fed three-phase three-dimensional electrode reactor is much higher than that of two-dimensional electrodes and common three-dimensional electrodes, even nitrogen-fed three-dimensional electrodes. The removal of formic acid may be contributed to a combination of many factors, such as direct and indirect electrochemical oxidation, adsorption, electrochemical adsorption and air-strip etc. Further work is needed to test the electrode lifetime and other organic wastewater.

Acknowledgements

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