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COD Removal and Biodegradability Enhancement of Pharmaceutical Wastewater Using a Multilayer Internal Electrolysis Reactor

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A multilayer internal electrolysis reactor treating actual pharmaceutical wastewater was established to evaluate the ecological safety and feasibility of internal electrolysis processes. Our findings showed that about 20 % COD of the pharmaceutical wastewater was removed by the internal electrolysis reactor. The COD removal efficiencies increased initially and then decreased with the increase in influent concentrations. The best COD removal was observed at pH 4. Additionally, injection of air into the reactor can promote COD removal compared with non-aeration conditions. All $\eta_{B/C}$ and η_{ROUR} values under every condition were positive, which indicated the enhancement effects on the wastewater biodegradability after treatment. The effects of influent COD concentrations on $\eta_{B/C}$ and η_{ROUR} showed a similar trend with that of COD removal, suggesting that the biodegradability enhancement was mainly caused by COD removal in wastewater. High pH helped to improve the wastewater biodegradability while aeration lowered the biodegradability enhancements.

Key Words: Internal electrolysis, Pharmaceutical wastewater, COD removal, Biodegradability.

INTRODUCTION

Pharmaceutical wastewater is a big challenging task to human health and the environment because it often contains toxic and non-biodegradable organic compounds[1-3]. A wide variety of chemical compounds in pharmaceutical wastewater such as benzene, PAHs (polycyclic aromatic hydrocarbons) and heterocyclic compounds are carcinogens. Therefore, to conduct treatment on these contaminants is necessary[4,5]. Among various technologies treating pharmaceutical wastewater, the internal electrolysis technology has been widely applied due to its low operating cost and simple construction of the reactor[6].

The internal electrolysis is widely employed in the reduction of aromatic compounds[7,8], removal of polycyclic aromatic hydrocarbons[6-9] and decolorization of dyes[10,11], which has shown great potential to remove recalcitrant compounds. The filling materials in internal electrolysis reactors are composed of a mixture of iron scraps and inert carbon particles, such as graphite, active carbon or coke, which are cheap and easily available materials. Numerous electric cells are formed between iron with low potential and carbon with high potential in wastewater acting as electrolyte. The electrode reactions and their consequent electrochemical redox, electrophoretic deposition and electrochemical coagulation actions occur[12]. As a result of these reactions, the recalcitrant contaminants in pharmaceutical wastewater are reduced.

Most of the previous work on the internal electrolysis technology has focused on COD removal and destruction of organic compounds. There are only a few researches using internal electrolysis as a pretreatment to transfer some recalcitrant compounds to more degradable compounds aiming to improve subsequent biological treatment[13,14]. In this research, the ratios of BOD_5 and COD of wastewater (B/C) are made to evaluate the biodegradability of the wastewater. However, the B/C values cannot reflect the inhibition and toxicity effects of wastewater on active sludge in subsequent biological reactors. Therefore, the relative oxygen uptake rate (ROUR) is utilized to evaluate wastewater biodegradability in this study. The ROUR was determined by measuring the dissolved oxygen concentrations in an airtight vessel filled with active sludge[15]. Higher ROUR values meant that the wastewater was easier to be degraded by active sludge. Such data has been reported rarely in previous literatures and is essential for evaluating the effects of internal electrolysis on the subsequent biological treatment.

In this paper, a multilayer internal electrolysis reactor treating actual pharmaceutical wastewater was established. The COD removal and biodegradability changes (expressed by both B/C and ROUR) of the reactor have been investigated. The effects of the primary operating factors including influent COD concentrations, pH and aeration on the reactor performance have been evaluated systematically.

EXPERIMENTAL

The schematic diagram of the experimental apparatus is shown in Fig. 1. A multilayer internal electrolysis reactor was made of three layers of iron-coke with an internal diameter of 10 cm, an effective height of 25 cm and a capacity of 7.85 L. Iron scraps were thoroughly mixed with coke in a desired proportion (2:1, w/w) and the diameters of both iron scraps and coke were less than 2 cm.

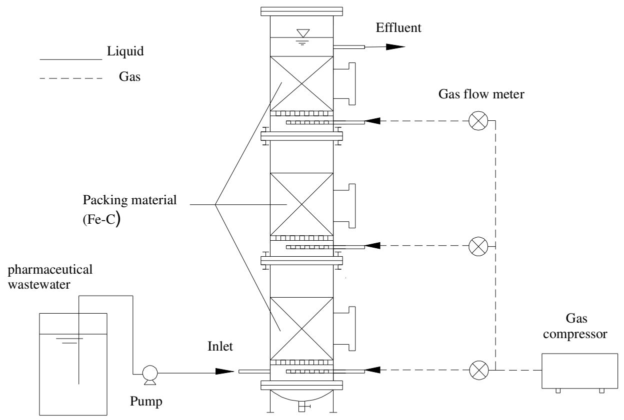

Fig. 1. Experimental setup for internal electrolysis reactor

Operating conditions: The multilayer internal electrolysis reactor was operated continuously for about 2 months. The hydraulic retention time was 190 min. The detailed operating conditions were divided into three phases as shown in Table-1.

TABLE-1
OPERATING CONDITIONS IN VARIOUS PHASES

Phase No.	Running days	Operating conditions
1	1-8	Influent COD = 6000 mg/L, pH = 4, non-aeration
	9-15	Influent COD = 7000 mg/L, pH = 4, non-aeration
	16-20	Influent COD = 8000 mg/L, pH = 4, non-aeration
2	21-24	pH = 2, influent COD = 6000 mg/L, non-aeration
	25-29	pH = 3, influent COD = 6000 mg/L, non-aeration
	30-36	pH = 4, influent COD = 6000 mg/L, non-aeration
	37-40	pH = 5, influent COD = 6000 mg/L, non-aeration
3	41-44	Influent COD = 5000 mg/L, pH = 4, aeration
	45-48	Influent COD = 7000 mg/L, pH = 4, aeration
	49-52	Influent COD = 8000 mg/L, pH = 4, aeration

Water quality: Pharmaceutical wastewater was collected from a pharmaceutical firm in Tianjin city, China. The characteristics of influent quality are given in Table-2.

TABLE-2
WASTEWATER CHARACTERISTICS

Parameters	COD (mg/L)	BOD_5 (mg/L)	B/C	Temp. (ºC)	pH
Values	5000-8000	1050-1350	0.21-0.23	15-30	4-5

Detection method: The B/C ratio and ROUR were used to evaluate the biodegradability of the wastewater.

B/C measurements: COD value was applied to reflect the content of organic compounds in wastewater and the BOD_5 represented the biodegradable organic compounds in wastewater. Therefore, the index of B/C was widely used to assess the biodegradability of wastewater.

A new index of B/C enhancement efficiency $\eta_{B/C}$ was defined as follows:

$$\eta_{B/C} = \frac{B/C_{in} - B/C_{out}}{B/C_{in}} \times 100\ \% \quad (1)$$

where B/C_{in} and B/C_{out} are the B/C values of influent and effluent, respectively.

Relative oxygen update rate (ROUR) measurements: The oxygen uptake rate (OUR) was determined by measuring the dissolved oxygen concentration in the airtight vessel filled with active sludge. The ratio of the OUR values of wastewater and sludge in endogenous respiration gave the ROUR:

$$ROUR = \frac{R_s}{R_0} \quad (2)$$

where R_s is the OUR value of wastewater and R_0 is the OUR value of sludge in endogenous respiration.

The ROUR values were made to assess the inhibition effects of wastewater on sludge. Higher ROUR values meant that the wastewater was easier to be degraded.

A new index of ROUR enhancement efficiency η_{ROUR} was defined as follows:

$$\eta_{ROUR} = \frac{ROUR_{in} - ROUR_{out}}{ROUR_{in}} \times 100\ \% \quad (3)$$

where $ROUR_{in}$ and $ROUR_{out}$ are the ROUR values of influent and effluent, respectively.

RESULTS AND DISCUSSION

Performance of the multilayer internal electrolysis reactor: Fig. 2 shows the COD removal performance of the multilayer internal electrolysis reactor. For the first 20 days, the reactor was examined under various influent COD concentrations. Present findings showed that the COD removal efficiencies increased initially and then decreased with the increase in influent concentrations. From day 20 to day 40, the influent pH was changed within the pH range of 2-5. The best COD removal was observed at pH = 4 (days 30-36). From day 41, air was injected into each iron-coke layer. The reactor was operated under aeration conditions at influent concentrations of 6000, 7000 and 8000 mg/L to compare the performance with that under non-aeration conditions (phases 1). Throughout the whole operation, the reactor presented about 20 % COD removal of pharmaceutical wastewater.

Effects of influent COD concentrations: Fig. 3 shows the effects of influent COD concentrations on COD removal efficiency [Fig. 3(a)], B/C enhancements efficiency $\eta_{B/C}$ [Fig. 3(b)] and ROUR enhancements efficiency η_{ROUR} [Fig. 3(c)].

As shown in Fig. 3(a), when the average influent COD concentrations were about 6000 mg/L, the removal efficiencies fluctuated around 17 %. Notably, increasing the influent concentrations to 7000 mg/L did not decrease the removal efficiencies but instead, it increased to about 20 %. Similar results were also reported in a previous study[15]. However, when influent concentrations were increased higher than 8000 mg/L, the

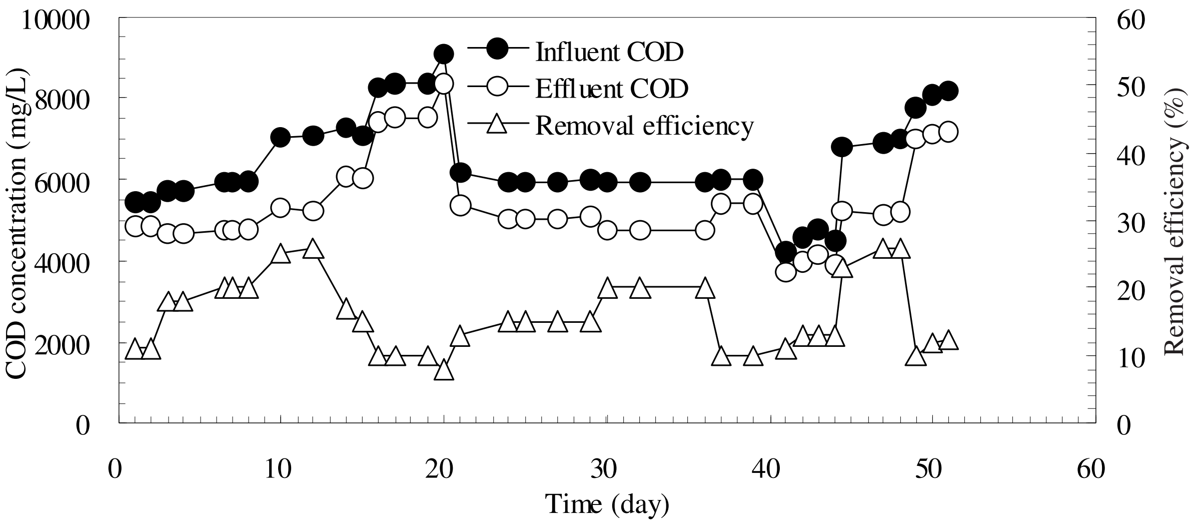

Fig. 2. COD removal performance by a multilayer internal electrolysis reactor

removal efficiencies remarkably declined to around 10 %. Probably, the presence of organic compounds in wastewater accounted for the corrosion of iron[16]. High concentration influent organic compounds enhanced iron corrosion and produced more ferric oxyhydroxide, which promoted the removal of COD content in wastewater. However, superfluous organic compounds would result in a decrease of the COD removal efficiencies.

Figs. 3(b) and 3(c) show the changes of $\eta_{B/C}$ and η_{ROUR} under various influent COD concentrations. All the values of B/C and ROUR in effluent at every concentration were higher than those in influent, suggesting prevalent enhancement effects on wastewater biodegradability after treatment. The maximum enhancement efficiencies of $\eta_{B/C}$ and η_{ROUR} could reach 65 and 16 %, respectively, creating favorable conditions for the subsequent biological treatment. However, both the $\eta_{B/C}$ and η_{ROUR} declined when the influent COD concentrations were higher than 7000 mg/L. These results show that the biodegradability of wastewater has a similar trend with that of COD removal, suggesting that the biodegradability enhancement was mainly caused by COD removal in wastewater.

Effects of influent pH: Fig. 4(a) shows the effects of influent pH on COD removal efficiencies. About 13 % of COD content was removed at the influent pH of 2. When the influent pH was increased to 4, the average COD removal efficiencies reached the maximum value of 20 %. The further increase in pH to 5 resulted in a decrease of COD removal efficiencies to 10 %. As reported in previous researches[7,13], COD removal was mainly due to the reduction of atomic hydrogen produced on the carbon surface as well as the coagulation of Fe $(OH)_2$ and Fe $(OH)_3$ formed by the corrosion product of iron:

$$4H^+ + 4e \rightarrow 4H$$

$$4H + \text{organic compounds} + O_2 \rightarrow 2H_2O + \text{Products}$$

$$Fe - 2e \rightarrow Fe^{2+} - e \rightarrow Fe^{3+}$$

$$Fe^{3+} + 3OH^- \rightarrow Fe(OH)_3$$

Therefore, the extreme low pH (pH 2-3) delayed the rate of ferric hydroxide colloid flocculation [$Fe(OH)_3$)] and reduced the co-precipitation of organic compounds. On the other hand, fewer electrons transported from iron to carbon were accepted by H^+ in a weak acidic condition (pH 5-6), resulting in less atomic hydrogen production on carbon that relied in the reduction of organic compounds. Therefore, the best COD removal was obtained at pH = 4.

As shown in Figs. 4(b) and 4(c), the influent pH has distinct effects on the biodegradability changes from COD removal. Both the B/C and ROUR values in effluent increased with the rise of influent pH. Under the condition of influent pH = 5, the enhancement efficiency of $\eta_{B/C}$ and η_{ROUR} reached 77 and 15 %, respectively. Therefore, the high pH contributed to improve the biodegradability of pharmaceutical wastewater by internal electrolysis.

Comparing the results of COD removal and biodegradability enhancement, the biodegradability data demonstrated more remarkable changes than COD removal. These results indicate that the organic compounds were not degraded completely by internal electrolysis but were transformed to other less toxic compounds. The atomic hydrogen produced by internal electrolysis opened the cyclic structure of organic compounds. Therefore, the macromolecular compounds such as aromatic carbonyl compounds were split to small molecule substances by atomic hydrogen and these reactions tend to simplify the structure of molecules and increase the donating electron groups to improve the biodegradability.

Effects of aeration: As shown in Fig. 5(a), the average COD removal efficiencies under aeration of 20, 25 and 13 % were achieved at influent concentrations of 6000, 7000 and 8000 mg/L, respectively, while they were 17, 20 and 10 %, respectively, under non-aeration conditions. These results demonstrate that aeration can promote COD removal performance by the internal electrolysis reactor because air inflow (mainly oxygen) helped to form $Fe(OH)_3$ having good flocculation, which can precipitate dispersive molecule substance and reduce COD content.

$$O_2 + 4Fe^{2+} + 2H^+ \rightarrow 4Fe^{3+} + 2OH^-$$

$$Fe^{3+} + 3OH^- \rightarrow Fe(OH)_3$$

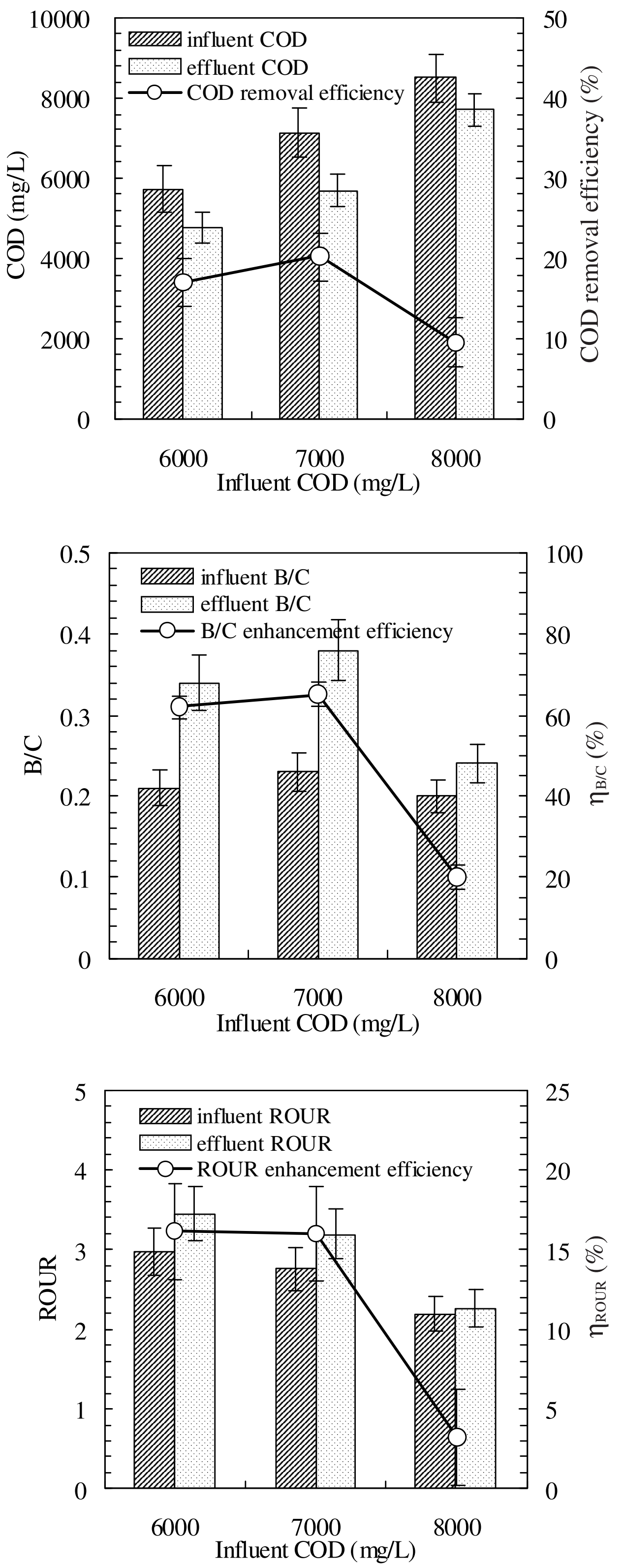

Fig. 3. Effects of influent COD: (A) COD removal; (B) B/C enhancement efficiency; (B) ROUR enhancement efficiency

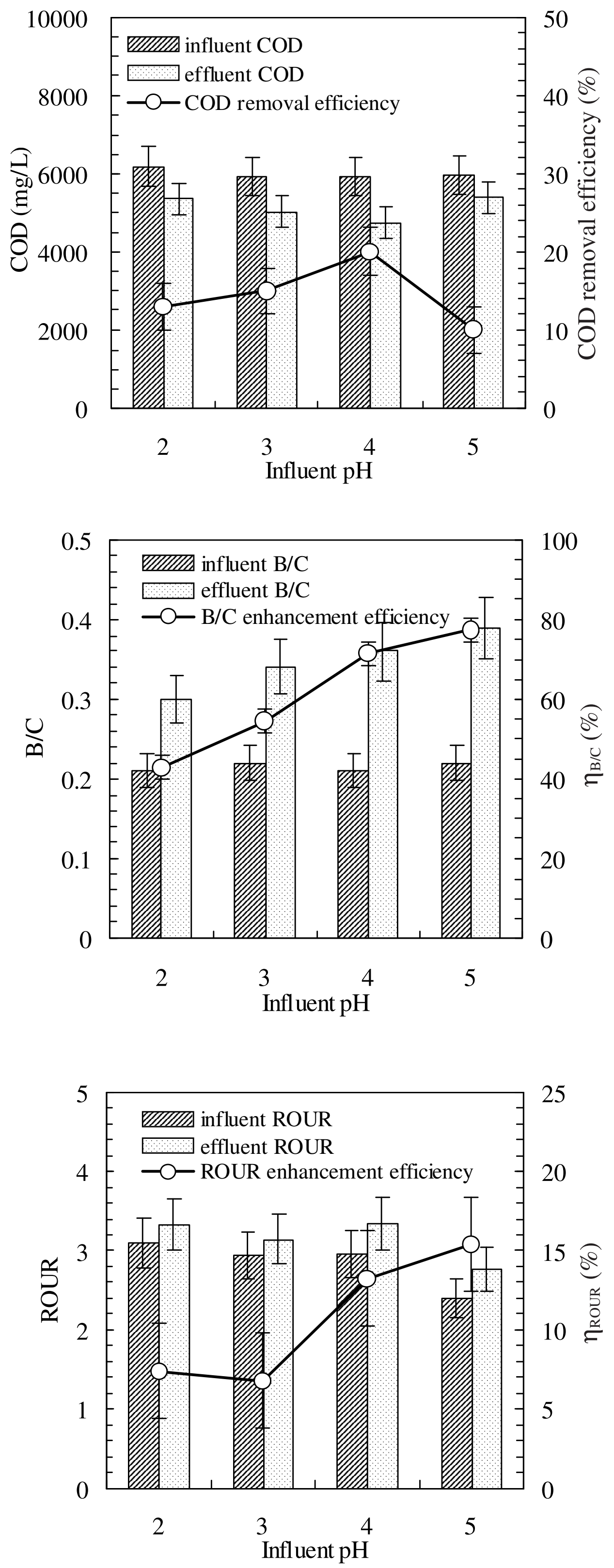

Fig. 4. Effects of influent pH: (A) COD removal; (B) B/C enhancement efficiency; (B) ROUR enhancement efficiency

In contrast with the aeration effects on COD removal, most $\eta_{B/C}$ and η_{ROUR} under aeration conditions were lower than those under non-aeration conditions. This was mainly due to the reaction of atomic hydrogen and oxygen. Additionally, atomic hydrogen was established to change significantly the structure of organic compounds to improve the biodegradability of wastewater. Therefore, O_2 inflow decreased the atomic hydrogen concentration, which lowered the biodegradability enhancements.

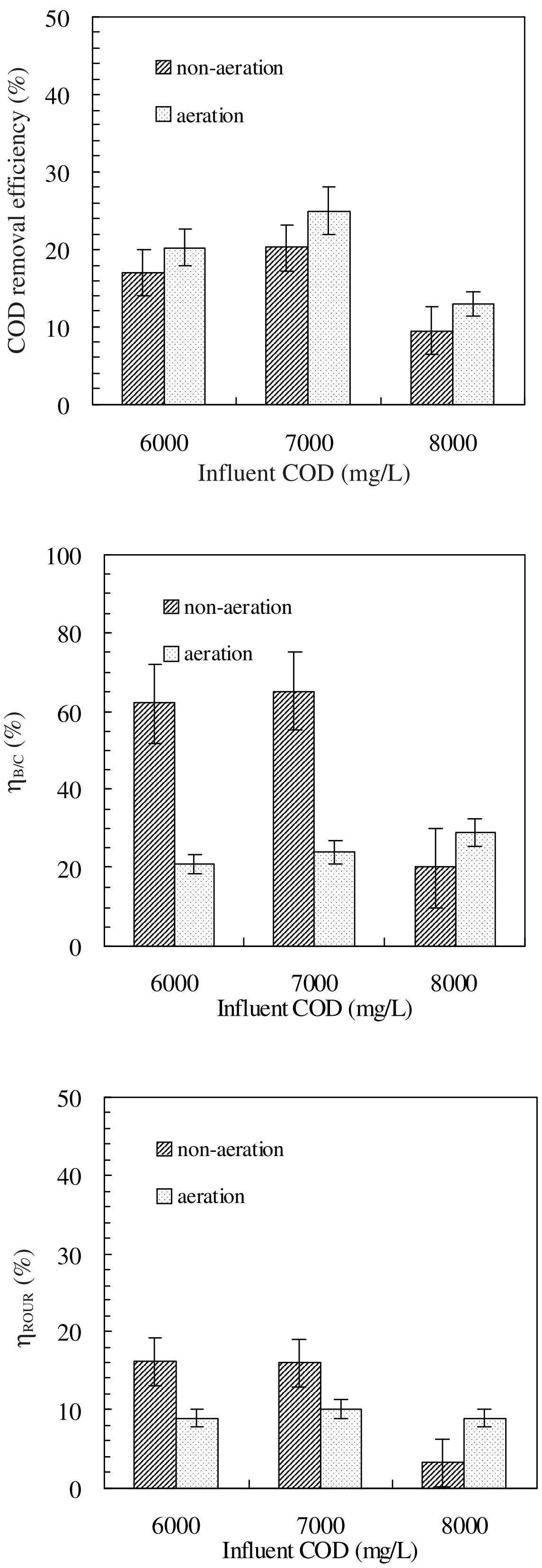

Fig. 5. Effects of aeration: (A) COD removal; (B) B/C enhancement efficiency; (B) ROUR enhancement efficiency

Conclusion

This study evaluated the COD removal and biodegradability changes including B/C and ROUR using a multilayer internal electrolysis reactor. Present findings showed that about 20 % COD of the pharmaceutical wastewater was removed by the internal electrolysis reactor. The COD removal efficiencies increased initially and then decreased with the increase in influent concentrations. The best COD removal was observed at pH 4. Moreover, injection of air into the reactor can promote COD removal compared with the non-aeration conditions.

All the values of $\eta_{B/C}$ and η_{ROUR} under every condition were positive, which indicates the enhancement effects on the wastewater biodegradability after treatment. The effects of influent COD concentrations on $\eta_{B/C}$ and η_{ROUR} showed a similar trend with that of COD removal, suggesting that the biodegradability enhancement was mainly caused by COD removal in wastewater. The influent pH showed distinct effects on the biodegradability changes from COD removal. The high pH helped to improve the wastewater biodegradability while aeration lowered the biodegradability enhancements.

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