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Biodegradability and Acute Biotoxicity Assessment of Pharmaceutical Wastewater by Fe-C Internal Electrolysis Process

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In order to evaluate the ecological safety and feasibility of internal electrolysis processes for the treatment of pharmaceutical wastewater, the biodegradability and acute biotoxicity were investigated. The results showed that the internal electrolysis did not have a high efficient ability to remove the chemical oxygen demand, but biodegradability of the wastewater was enhanced remarkably and the toxicity was also reduced. Aeration could enhance the removal of chemical oxygen demand, however, the results indicated that biodegradability was enhanced more under anaerobic circumstances besides the biotoxicity. Acidification showed no enhancement on the reduction. The acute biotoxicity increased linearly with the logarithm of wastewater's chemical oxygen demand value, The effluent acute biotoxicity was less than 5 mg Zn^{2+} L^{-1} and an average acute biotoxicity cut rate could achieve 35 % no matter the influent chemical oxygen demand.

Keywords: Internal electrolysis, Pharmaceutical wastewater, Biodegradability, Acute biotoxicity.

INTRODUCTION

Many pharmaceutical firms are located in Jinan in Shandong Province of China in recent years, simultaneously so much pharmaceutical wastewater is produced but over 18 % can not meet the State's discharge standard (GB18918) after being treated. Pharmaceutical wastewater is an important source of environmental contamination, but it is very difficult to deal with the pharmaceutical wastewater[1,2]. The effective removal of substances included in pharmaceutical residual effluents is a challenging task due to the wide variety of chemicals produced in drug manufacturing plants, which lead to wastewater of variable compositions. There are benzene, polycyclic aromatic hydrocarbons (PAHs), heterocyclic compounds, *etc.* in the pharmaceutical wastewater and many of them are carcinogens, So, it is necessary to conduct pretreatment before conventional bioprocess[3]. The removal of the recalcitrant is extensively studied by the processes such as anaerobic pretreatment[4], advanced oxidation technologies[5] and membrane bioreactor[6]. However, current technologies focus on the removal of chemical oxygen demand and do not study the acute biotoxicity assessment of pharmaceutical wastewater. Some researches have been proved that the removal of chemical oxygen demand can not decrease the biotoxicity of wastewater[7]. Meanwhile many of the treating methods are not cost-effective, which limit their wide-spread application. Therefore, it is necessary to explore a pretreatment both feasible in economy and effective in technology for improving the biotoxicity so as to promote the efficiency of subsequent biochemical treatment process.

Over the last decade, a great deal of interest is focused on the degradation of organic compounds and groundwater remediation with the new treatment methods by zero-valent iron metal (Fe^0)[8,9]. For example, zero-valent iron is employed in the reduction of aromatic compounds[10] removal of PAHs[11] and decolourization of dyes[12]. In addition, Fe-C pretreatment process is widely used to improve subsequent biological treatment. There are two types of filling materials in such reactors, one is composed only of iron scraps and the other is of a mixture of iron scraps and inert carbon particles such as graphite, active carbon or coke. Numerous electric cells are formed between Fe with low potential and C with high potential in wastewater acting as electrolyte, electrode reactions and their consequent electrochemical redox, electrophoretic deposition, electrochemical coagulation actions occur[13], as the result of these reactions, chemical oxygen demand and biotoxicity are reduced, the biodegradability of wastewater is enhanced. The reaction process can be expressed figuratively: when a mixture of iron scraps and coke particles is in contact with wastewater (electrolyte solution), numerous microelectrolytic cells are formed between the particles of iron and carbon. The half-cell reactions can be represented as:

Anode (oxidation):

$$2Fe \rightarrow 2Fe^{2+} + 4e^{-} \quad (1)$$

Cathode (reduction). Acidic:

$$4H^{+} + 4e^{-} \rightarrow 2H_2 \rightarrow O_2 + 4H^{+} + 4e^{-} \rightarrow 2H_2O \quad (2)$$

Neutral to alkaline:

$$O_2 + 2H_2O + 4e^{-} \rightarrow 4OH^{-} \quad (3)$$

These cell reactions occur at microscopic scales, but simultaneous occurrences of these reactions on the surfaces of a large number of iron chips and coke particles can result in significant electron flows in the system, so substances included in the wastewater can be degraded. Because of the concomitant occurrences of many physical and chemical processes in internal electrolysis (IE), many factors may affect its treatment performance.

In the present paper, the degradation of chemical oxygen demand and the enhancement of BOD_5/COD by Fe-C internal electrolysis is studied, simultaneously the acute biotoxicity assessment of pharmaceutical wastewater of internal electrolysis process is investigated. Effect of aeration, pH and influent chemical oxygen demand as factors of internal electrolysis are discussed in the paper. The results might provide a theoretical and practical guidance whose potential usage is high owing to its low cost and operational simplicity for enhancing the removal rate of toxic compounds and promoting efficiency of the subsequent biochemical treatment process.

EXPERIMENTAL

Operating conditions: The schematic diagram of experimental apparatus is shown in Fig. 1. The Fe-coke reactor was divided to three parts, which was made of organic glass with an external diameter of 12 cm, an internal diameter of 10 cm, an effective length of 25 cm and a capacity of 7.85 L. Iron scraps thoroughly mixed with coke were padded in the reactor. The mixture in a desired proportion (2:1, w/w) was then placed in the reactor to form a fixed Fe-C bed. The Fe-C reactor was operated continuously for about 2 months with 3.2 h of hydraulic retention time (HRT).

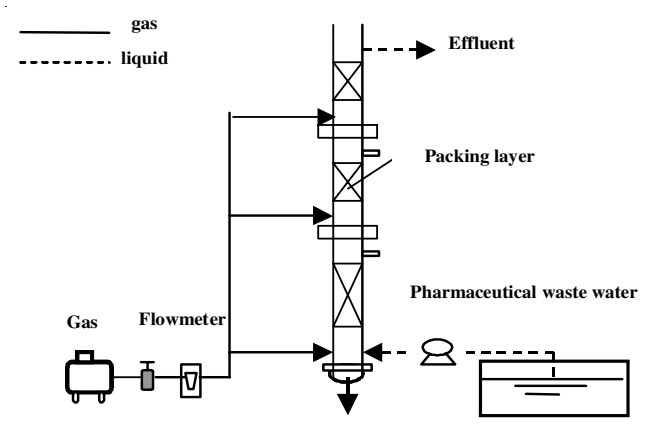

Fig. 1. Experimental setup for internal electrolysis

Characterization of wastewater: Pharmaceutical wastewater samples were collected from a pharmaceutical firm in Jinan city (in northern China) before being subjected to an anaerobic-aerobic biological treatment. Some characteristics of influent quality are given in Table-1.

Analytical methods: Chemical oxygen demand, BOD_5 were determined using standard methods[14]. pH was measured using a pH/ISE with a HACH sure-flow pH electrode.

Acute biotoxicity assessment of internal electrolysis products: The acute biotoxicity measurements were measured using a photo-bacterium bioassay method, which is widely used to evaluate the acute toxicity. The principle of the method quantifies the decrease in light emission from the bioluminescent bacteria, *Photo-bacterium phosphoreum*, resulting from exposure to pollutants. The extent of luminescence inhibition after 5 min of exposure was standardized into an equivalent concentration of Zn^{2+}, which was used to express the degree of the pollutants' effects on the test bacteria[15]. Thus, greater luminescence inhibition corresponded to a higher equivalent concentration of Zn^{2+}.

RESULTS AND DISCUSSION

Effect of the reactor for a long time: Fig. 2 showed the effect of chemical oxygen demand removal by the internal electrolysis process during 40 days. The results showed that the internal electrolysis did not have a high efficient ability to remove the chemical oxygen demand of pharmaceutical wastewater, in the operating time, an average chemical oxygen demand removal rate of 15 % was achieved. Consequently, biodegradability of the wastewater was enhanced, which created favorable conditions for the subsequent biological treatment. The ratio of BOD_5/COD and oxygen uptake rate (OUR) were used as a reference to assess biodegradability of the wastewater before and after treatment by the internal electrolysis process. BOD_5/COD and oxygen uptake rate were measured and calculated several times, when the system was in operation. The

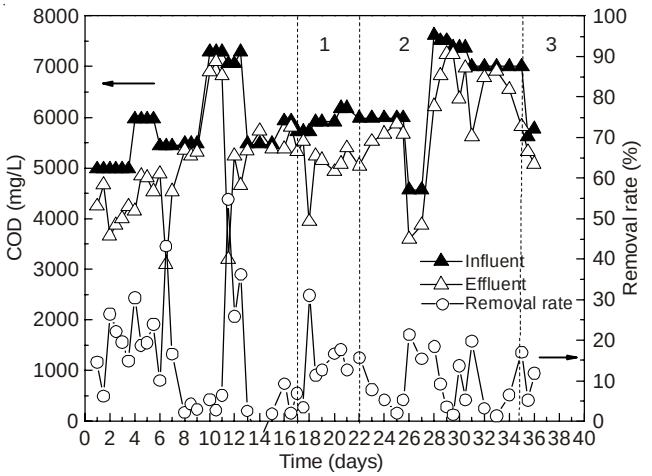

Fig. 2. Chemical oxygen demand removal by the internal electrolysis process

TABLE-1
CHARACTERISTICS OF INFLUENT OF THE INTERNAL ELECTROLYSIS PROCESS

Parameters	Chemical oxygen demand (mg/L)	BOD_5 (mg/L)	BOD_5/COD	Acute biotoxicity (mg-Zn^{2+}L-liquid)	pH
Influent	5000-9000	1050	0.21	4.5-7.1	4-5

results indicated that the ratio of BOD_5/COD increased from 0.21 to a range of 0.34-0.39 after the treatment, the average enhancement rate is 75 %. Oxygen uptake rate increased from a range of 1.2-3.4 to a range of 1.5-4, the average enhancement rate is 20 %.

An average acute biotoxicity cut rate was 45 % (Fig. 3). The results indicated that internal electrolysis was an efficient method to reduce the acute biotoxicity of pharmaceutical wastewater on condition that low removal of chemical oxygen demand. The mechanism by the internal electrolysis process was discussed to the changes of chemical composition. Some reactions occurred during the internal electrolysis process, such as hydrolytic reaction, cracking and redox reaction. Thus, the cyclic structure opened and changed into chains and the macromolecular compounds were spilt to small molecule substances. All these reactions tended to simplify the structure of molecules so as to improve the biodegradability and reduce the biotoxicity. For example, some chromophoric groups like $-NO_2$, -NO were reduced to $-NH_2$, which could change the colour intensity and improve the biodegradability. Some unsaturated chromophoric groups could be destroyed by newly formed Fe^{2+}, such as double bond of -C=O and -N=N-, which could make the colour decrease. Some compounds with cyclic or long carbon chain could be decomposed by newly formed Fe^{2+} into small molecule substance, which could reduce the acute biotoxicity.

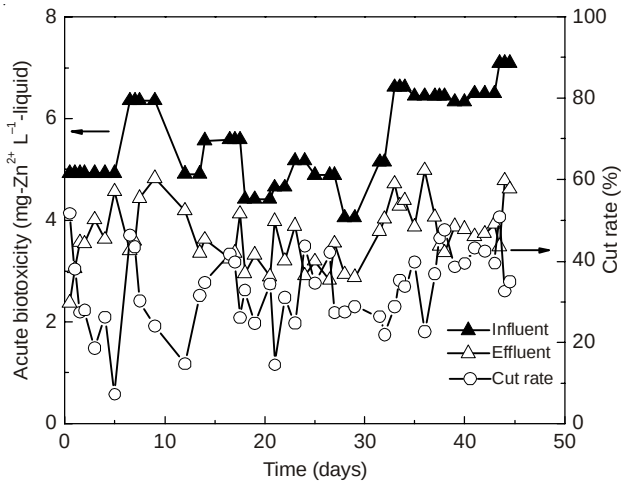

Fig. 3. Acute biotoxicity assess by the internal electrolysis process

Effect of aeration on the results of internal electrolysis: Fig. 4 showed that the results of effect of aeration as a factor of internal electrolysis. In the aeration condition, a chemical oxygen demand removal rate of 24 % was achieved, but it was 14.5 % under anaerobic circumstances. Aeration could achieve a higher chemical oxygen demand removal rate. However, the results indicated that biodegradability of the wastewater was enhanced more under anaerobic circumstances besides the biotoxicity. Under anaerobic circumstances the ratio of BOD_5/COD was 0.40 but it was 0.37 in the aeration condition. The acute biotoxicity of effluent was less than that in the aeration condition.

In the internal electrolysis process, when the influent was acidic, many ferric ions were produced in the system because of the existence of O_2. These ions formed $Fe(OH)_3$ which had

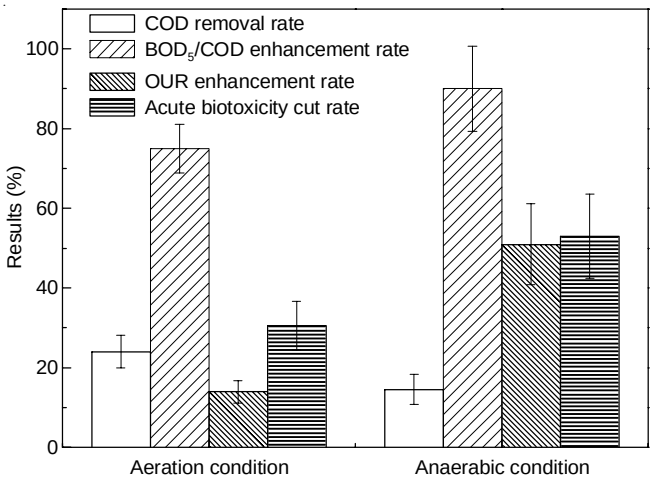

Fig. 4. Effect of aeration on the results of internal electrolysis

good flocculation, so dispersive molecule substance could be precipitated and the chemical oxygen demand was removed, oxidation and coagulation were the principal reaction in the aeration condition. However, atomic [H] was produced under anaerobic circumstances in the internal electrolysis process, it was much active and could reduce the complicated compounds of wastewater. As a result, structure of molecules was simplified so as to improve the biodegradability and reduce the biotoxicity.

Effect of acid addition on internal electrolysis: It had been established that pH had great influence on contaminant reduction by internal electrolysis and due to the increased release of electron and generation of H_2, yet the pH influence was not precisely in accordance with the increase in degradation. The pH rose to around 6 in the effluent, which indicated that the H^+ in solution was consumed by the corrosion of iron. As shown in Fig. 5, the results were somewhat lowered compared with that lower pH. In the condition around pH 5, there was a good results of internal electrolysis, thus, it could be concluded that the lower pH did not contribute to pharmaceutical wastewater treatment by internal electrolysis. The reason was probably due to the entering of O_2 and escape of H_2 during the addition process. Both processes enhance the loss of reductants, especially atomic H. Some researchers demonstrated that the hydrodegradation was proportionally related to the

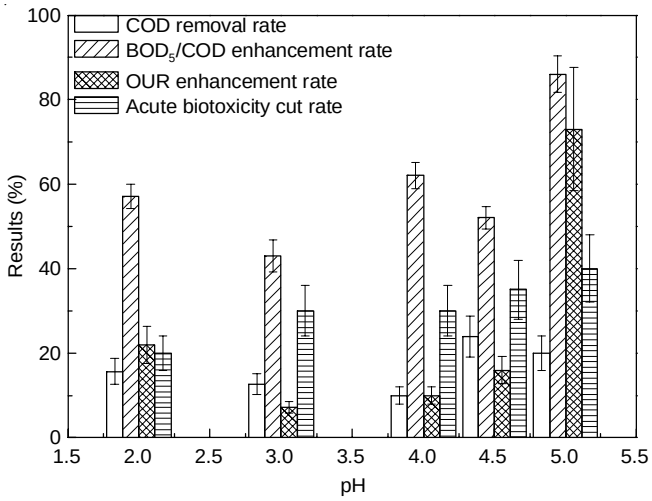

Fig. 5. Effect of acid addition on the results of internal electrolysis

hydrogen activity (or concentration) at the particles surface (rather than to the rate of hydrogen production). Acidification showed no enhancement on the reduction regardless of increased iron corrosion and H_2 production. As a result, acid addition was not active to the results and the major mechanism of catalytic hydrogenation by Fe could be proposed for internal electrolysis process, because acid addition lowered the rate of Fe precipitation and reduced organic substance adsorption and co-precipitation.

Effect of influent chemical oxygen demand internal electrolysis: Fig. 6 showed the results of effect of influent chemical oxygen demand of internal electrolysis. When the influent chemical oxygen demand was around 5500 mg/L, the ratio of BOD_5/COD increased from 0.21 to 0.37, but when the influent chemical oxygen demand was around 9000 mg/L, the ratio of BOD_5/COD increased from 0.21 to 0.24. It was indicated that influent chemical oxygen demand was effected on the wastewater biodegradability of internal electrolysis.

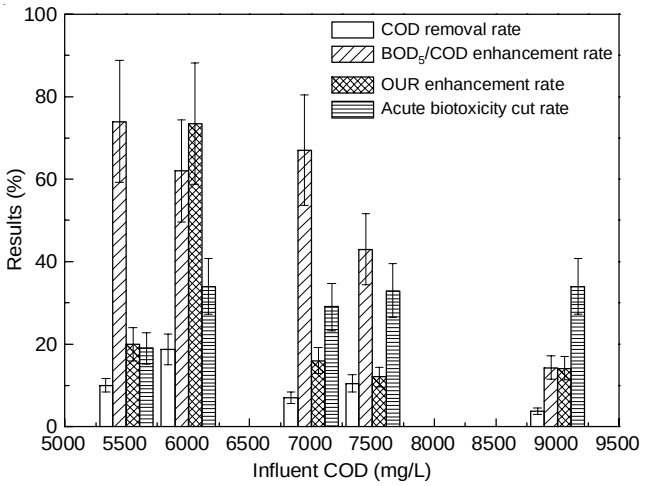

Fig. 6. Effect of influent chemical oxygen demand on the results of internal electrolysis

However, with the high influent chemical oxygen demand, the acute biotoxicity of wastewater was high. The acute biotoxicity increased linearly with the logarithm of wastewater's chemical oxygen demand value (Fig. 7). Acute biotoxicity was mainly dependent on chemical oxygen demand concentrations.

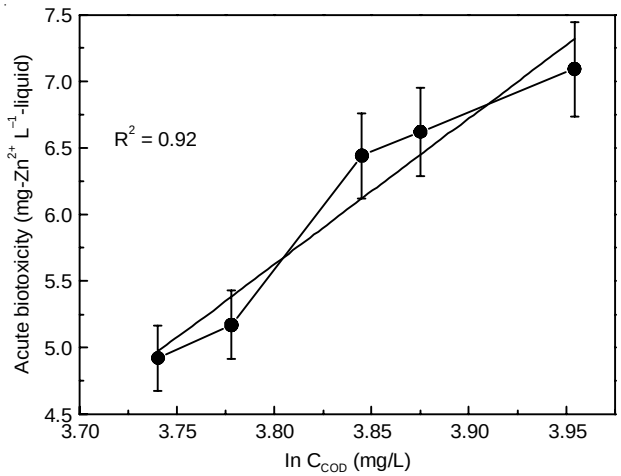

Fig. 7. Acute biotoxiciy at increasing chemical oxygen demand values of wastewater sample

In our study, a weak correlation between acute biotoxicity and biodegradability was detected. When the effluent acute biotoxicity was high, the ratio of BOD_5/COD was less. The effluent acute biotoxicity was less than 5 mg Zn^{2+}L-liquid and an average acute biotoxicity cut rate could achieve 35 % no matter the influent chemical oxygen demand. Thus, internal electrolysis was a useful method to reduce the toxicity of pharmaceutical wastewater.

Conclusions

Chemical oxygen demand, the ratio of BOD_5/COD, OUR and acute biotoxicity were used to analyze the changes in biodegradability and toxicity of raw water and effluent treated by internal electrolysis. The following conclusions were drawn from the experimental results:

• The internal electrolysis did not have a high efficient ability to remove the chemical oxygen demand of pharmaceutical wastewater in the operating time. However, biodegradability of the wastewater was enhanced remarkably and the toxicity was also reduced. By the internal electrolysis process, an average chemical oxygen demand removal rate of 15 % was achieved, but the average enhancement rate of the ratio of BOD_5/COD is 75 % and the average acute biotoxicity cut rate was 45 %.

• Aeration could achieve a higher chemical oxygen demand removal rate. However, the results indicated that biodegradability of the wastewater was enhanced more under anaerobic circumstances besides the biotoxicity. Acidification showed no enhancement on the reduction of internal electrolysis, in the condition around pH 5, there was a good results of internal electrolysis to teat the pharmaceutical wastewater.

• Acute biotoxicity was mainly dependent on chemical oxygen demand concentrations corresponded to the logarithm of wastewater's chemical oxygen demand value, a weak correlation between acute biotoxicity and biodegradability was detected.

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