

Degradation of 4-CP in an internal electrolysis system

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Abstract: The characteristic and mechanism of parachlorophenol (4-CP) degradation in an internal electrolysis system were investigated. The degradation rate of 4-CP was higher in acid solution than that of in neutral or alkaline solution. Addition of activated carbon could make 4-CP easier be degraded by the surface contact catalysis. The dissolved oxygen in solution could take part in the electrode reaction and intensify the degradation of 4-CP. By the analysis of intermediates of degradation of 4-CP, it could be conferred that 4-CP was broken through the bond beside hydroxy firstly, then the bond beside chloride was broken and the chloride was dechlorinated simultaneously. Most intermediate products were glycerine, ethane diacid and acetic acid, while very few 1, 4-butanediol and alcohols were found.

Keywords: internal electrolysis; degradation; wastewater

Introduction

Micro electrolysis based on cell reaction of galvanochemistry was developed as a new method to dispose wastewater in 1970s (Chen, 2000; Leah, 1994). In the system, metal particles as the anode contact with the negative electrode materials and all of them are submerged in an electrolyte solution, forming a lot of micro-cells. The series of micro-cells can induce electrified effects making the charged particles in the solution move to antipole. The intermediates of the cell reaction are more active in oxidation-reduction process and can break the construction of refractory organic pollutants. The technique of iron-carbon micro-cells used to treat wastewater will generate active species, such as nascent hydrogen, ferrous irons and oxygen. After aeration and neutralization to alkalinity, ferrous irons are further oxidized to form colloid of $\text{Fe}(\text{OH})_3$, it has a stronger absorbability than that of general flocs.

Chlorophenols (CPs) as a group of phenolic compounds are very important chemical compounds and intermediates for pesticide and dyes production in chemical industry. Phenolic compounds are characteristic of high hazardous and toxic, and many of them are known or suspected as human carcinogens (Slein, 1980; HEW, 1976). Therefore, the removals of them from aqueous field have been an important task for wastewater treatment. 4-CP is one of the toxic hazardous and refractory organic compounds. Such treatment methods as biological treatment (Kabbalo, 1995), activated carbon adsorption (Gonzin, 2002), solvent extraction and catalytic wet oxidation (Qin, 2001) were tried to remove 4-CP since 1990s. Because the method of iron-carbon electrolysis is highly efficient, cost-effective and easy to be magnified, this paper reports a successful degradation of 4-CP in an aqueous solution. The characteristic and mechanism of the

degradation are also analyzed and discussed.

1 Experimental

1.1 Apparatus and reagent

Particles of cast iron are soaked in hydrochloric acid solution (2%) to be activated for 2 h before each experiment, and activated carbons are soaked in 4-CP solution (1 g/L) for 12 h to obtain absorption saturation.

The analysis apparatus list as follows: Trace 2000 series GC-MS (FID, DB-5); Metrohm 792 Basic Ion Chromatograph; 722s Spectral Photometer; pHs-25 pH Meter; Electric Agitator (6000/min); Air Blast (60 L/min).

1.2 Experimental procedure

The system of internal electrolysis is shown in Fig. 1. In each experiment, 4-CP of 300 ml solution is poured into a reactor. Some activated cast iron particles and activated carbon particles after absorption saturation are then added. When the experiment begun, a little air blast and an electric agitator are used to fill in oxygen and to make the particles fluidizing. The pH of the solution is adjusted by adding sulfuric acid and sodium hydroxide.

Samples are taken at appropriate time intervals from the reactor with an addition of some sodium hydroxide following to make iron ions to precipitate before analysis. The total phenol concentration is determined by a spectral photometer; free chloride concentration is determined by a Metrohm 792 Basic Ion Chromatograph equipped with a Metrosep A supp 4 column (250 × 40 mm), a Metrosep A supp 4/5 Guard column, and a conductivity detector. Sodium carbonate and sodium bicarbonate are used as an fluent; and intermediates are analyzed by a trace GC-MS (Initial temperature: 50°C, initial time: 3.00 min, rate: 15.0 deg/min, final temperature: 240°C, GC interface temperature: 260°C, source temperature: 200°C).

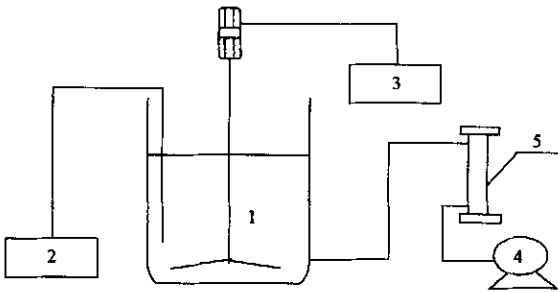


Fig.1 The system of internal electrolysis
1. reactor; 2. pH-meter; 3. electric agitator; 4. air blast; 5. flowmeter

2 Results and discussion

2.1 Effect of pH value

pH value is an important factor determining the degradation rate of 4-CP. To obtain the variation on the degradation of 4-CP by different pH, the investigation was carried out at various pH values, the results are shown in Fig.2.

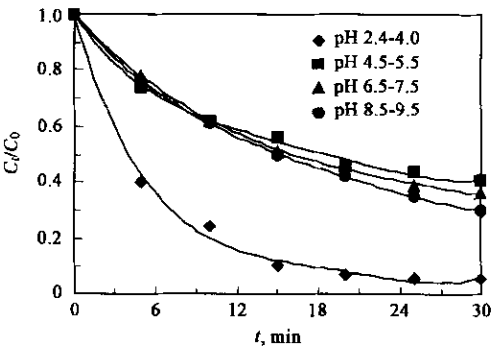
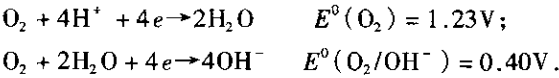


Fig.2 Degradation of 4-CP as a function of the pH value
 C_t : 4-CP concentration at various reaction time; initial 4-CP concentration (C_0): 100 mg/L; aeration flux: 24 L/h; Fe/C ratio: 30:1; temperature: 298K

It is seen that the degradation rate is higher in acid solution than that of in neutral or alkaline solution, because the electrode reaction is different in an acid solution compared with that in a neutral or alkaline solution (Lu, 2001):



From above electrode reaction, it is shown that the electrode voltage is higher in an acid solution than that in a neutral or alkaline solution. As a result, more energy can be provided and the electrode reaction can be strengthened, which leads to speed up the degradation rate of pollutants. Experimental results are shown that most of iron ions generating from electrode reaction are ferrous ions, and no visible flocculent species are produced in acidity. Contrast to in neutrality or alkalinity, ferrous ions are oxidized to ferric ions promptly, which further reacted with OH^- in the solution to generate flocculent of $\text{Fe}(\text{OH})_2$ or $\text{Fe}(\text{OH})_3$ in

alkaline. During the series of reaction, it can be identified with flocculate and adsorption for the organic pollution in neutrality or alkalinity (Lu, 2001), but ferrous ions will contend for ion acceptors, which decrease the removal rate of 4-CP. At last, the total amount of 4-CP removal is decreased. Two groups of data are shown in Table 1, it can be used to illustrate the behavior.

Table 1 Phenol concentration before and after iron ions precipitation

C_t , mg/L	t , min					
	5	10	15	20	25	30
Before precipitated	56.88	42.3	34.45	30.53	27.2	17.7
After precipitated	52.15	37.26	28.3	23.8	19.87	14.83

Notes: Initial 4-CP concentration(C_0): 100 mg/L; pH: 2.4—4; aeration flux: 24 L/h; Fe/C ratio: 30:1; temperature: 291 K

After the solution in the reactor is kept in acidic, at different time intervals, the sample is then moved and divided each of them into two and separate all of them into two groups. The phenol concentrations of one group are determined at once and the other are added sodium hydroxide to adjust pH value higher than 10 to make the iron ions precipitating with OH^- before determining. From Table 1, it is seen that the removal of 4-CP is mainly due to the degradation; the removal by degradation is 47.8% and by flocculate and adsorption is only 4.7% at 5 min.

2.2 Effect of Fe/C ratio

The effect of ratio of Fe to C is shown in Fig.3. It is seen that the degradation rate is increased significantly when a small quantity of activated carbon added after adsorption saturation(soaking in 4-CP solution of 1 g/L for 12 h and air dry in dorm-temperature before experiments). From the principle of internal electrolysis, iron will form much more cells with activated carbon in addition of the cells constructed by irons and carbons in cast iron(because cast iron is often constructed by iron and carbon mainly), the electrode reaction is strengthened and more energy is provided for the degradation. In addition, activated carbon has very large specific surface and can adsorb organics on its surface, so that the pollutants are easier to be degraded because of decrease of the activation energy in the contact catalysis of the surface(John, 1974). When the pollutants on the surface are degraded, the other organics are adsorbed in turn. The addition of activated carbon thus promotes the degradation of pollutants. However, when the Fe/C ratio is up to 30:1, the rate is not increased with the increase of the amount of the addition. It is perhaps because there are already certain carbons in particles of cast iron, which constitute micro cells with irons. When the two counterparts are matched with each other, the increase of the addition will have no effect on the rate.

2.3 Effect of aeration

The effect of aeration on 4-CP degradation is shown in Fig.4. The results indicated that the degradation rate is highest when pure oxygen is aerated. It is known from the

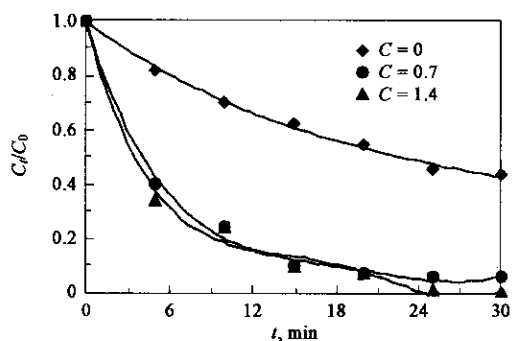
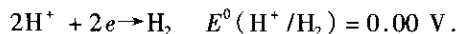


Fig. 3 The effect of Fe/C ratio

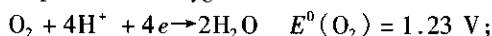
C_t : 4-CP concentration at different reaction time; initial 4-CP concentration(C_0): 100 mg/L; pH: 2.4–4; aeration flux: 24 L/h; temperature: 298 K

principle that the reactions of electrode are different whether there is oxygen or not. In the absence and presence of oxygen, the electrode reactions are shown as following respectively(Lu, 2001):

In the absence of oxygen:



In the presence of oxygen:



From above electrode reaction, it is obvious that oxygen in solution is able to take part in the electrode reaction and makes the voltage higher than that in the absence of oxygen, therefore the cell reaction is more violent and the degradation of 4-CP is intensified. Contrast to oxygen added, the nitrogen in solution maybe cover the surface of some particles (as electrodes), so as to make the total interface between liquid and oxygen decreasing, the rate will then decrease instead of increase.

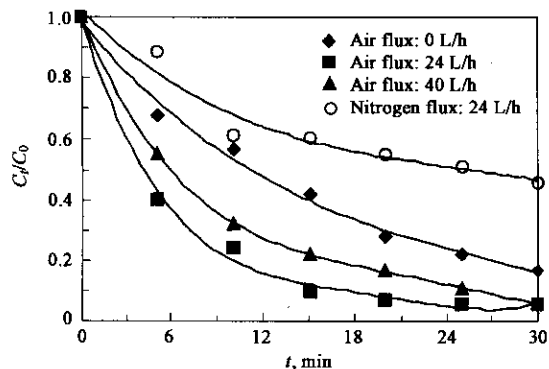


Fig. 4 The effect of aeration

C_t : 4-CP concentration at different reaction time; initial 4-CP concentration(C_0): 100 mg/L; pH: 2.4–4; Fe/C ratio: 30:1; temperature: 298 K

2.4 Variation of free chloride and COD

The free chloride concentration and chemical oxygen demand(COD) can manifest the degree of 4-CP degradation. They are determined under the condition of pH 3, air aeration

flux of 24 L/h and Fe/C ratio of 3:1. The results are shown in Fig. 5. From Fig. 5, it is shown visibly that the concentration of free chloride is enhanced during the process of degradation. This means that the free chloride is resulted from dechlorinating from degradation of 4-CP. COD value is also decreased during the experiment and it remains 23% removal rate at 60 min. That means most of 4-CP can be finally mineralized in the system.

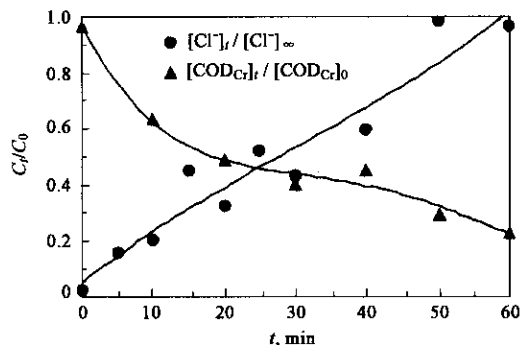


Fig. 5 Variation of free chloride concentration and COD during experiment

$[Cl^-]_t$: free chloride concentration at t time; $[Cl^-]_\infty$: total chloride concentration in 4-CP of 100 mg/L; $[COD_{Cr}]_t$: chemical oxygen demand at t time; $[COD_{Cr}]_0$: initial COD of 4-CP; initial 4-CP concentration(C_0): 100 mg/L; pH: 2.4–4; aeration flux: 24 L/h; Fe/C ratio: 30:1; temperature: 298 K

3 The degradation pathway of 4-CP

In the electrolysis system, the organics can be oxidized as well as be deoxidized. In order to determine the process of the degradation, the intermediates at 18 min on the same condition as (2.4) are analyzed. The sample is determined by GC-MS after making iron ions precipitation by adding ammonia(5 mol/L), and the precipitates are filtrated by microporous filtering film. The results are shown in Figs.6–8.

Excluding the background, the results indicated that most intermediates are glycerine, ethane diacid and acetic acid, and a few of 1,4-butanediol and alcohols are found. In addition, there are very few chloro-hydrine and chloric ether such as CCl_3CHO and $CHCl_2-O-CHCl_2$. From the determined results, it can be conferred that the benzene ring is broken through the bond beside hydroxy firstly, then the bond beside chloride is broken and the chloride is dechlorinated simultaneously. As the results of intermediates analysis, 4-CP degradation mainly pathway maybe take place as Fig.9.

4 Conclusions

The experiments in electrolysis indicated that internal electrolysis system made 4-CPs degraded and mineralized almost completely at last through optimizing experimental condition. The degradation rate was higher in acid solution than that in neutral or alkaline solution. Addition of activated

