



Application for acrylonitrile wastewater treatment by new micro-electrolysis ceramic fillers

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ABSTRACT

A new kind of micro-electrolysis ceramic fillers (MCF) used to deal with acrylonitrile simulation wastewater was investigated. Scrap iron, powdered activated carbon (PAC), and clay were employed as raw materials to produce the raw MCF. The raw MCF was calcined at 500–600°C for 20–30 min in anoxic condition. The raw materials mass ratio of MCF was determined as 60% clay, 32% scrap iron, and 8% PAC. The microstructure and physical properties which include bulk density (997.2 kg/m³), grain density (1675.0 kg/m³), water absorption (18.0%), porosity (41.3%), and specific surface area (30.52 m²/g) were determined. The effects of pH value, hydraulic retention time (HRT), and aeration on COD_{Cr} and acrylonitrile removal efficiency were studied. The results showed that the optimal conditions were influent pH of 3, HRT of 6 h, and aeration-liquid ratio (A/L) of 10. And the removal efficiency of COD_{Cr} and acrylonitrile was 68.8 and 73.9% under the optimal conditions. When micro-electrolysis reactor ran 40 d continuously, the removal efficiency of COD_{Cr} and acrylonitrile was stable and the fillers did not become hardened. The system still had a good capacity for wastewater treatment.

Keywords: Micro-electrolysis; Scrap iron; Ceramic fillers; Acrylonitrile wastewater

1. Introduction

As an important chemical raw material, acrylonitrile has been widely used in synthetic fiber industry, synthetic rubber, synthetic plastic industry, synthetic resin, and other areas [1,2]. During the production and application processes of acrylonitrile, wastewater is produced, which is a kind of high concentrated organic wastewater and cannot be treated directly by microbes because of its toxicity. In this kind of wastewater, the

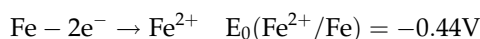
pollutions which are the most difficult to be removed by biological treatment are acrylonitrile, low polymer, and copolymer of acrylonitrile and nitriles. Acrylonitrile, with reproductive effects and cancer risk, can damage water ecosystem and do harm to human health [2]. Recently, the main ways to treat acrylonitrile are incineration treatment and pressurized hydrolysis—biochemical treatment [3]. However, there are very few studies about using micro-electrolysis technology to treat acrylonitrile wastewater.

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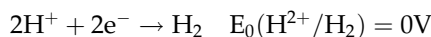
Scrap iron, a kind of common solid waste, is mainly generated from mechanical manufacturing industry and has a high production. What's more, scrap iron cannot only occupy the valuable land resources, but also lead to environmental pollution. Thus, how to decrease the environmental pollution of the iron scrap and reuse the iron scrap are widely studied [4–7].

The technology of micro-electrolysis, which is also called internal-electrolysis, is a kind of new process based on the electrochemistry. It was introduced into China in 1980s [8]. And in recent years, micro-electrolysis technology has been widely used in the wastewater treatment [9], such as electroplating wastewater [10], petrochemical industry wastewater [11], printing and dyeing wastewater [12,13], and other unmanageable industry wastewater. The construction of some nonbiodegradable organic pollutants can be broken by the micro-electrolysis process [14]. Therefore, the ratios of BOD₅ and COD_{Cr} can increase and color of wastewater can decrease, which has benefit to biological treatment and standards emissions [15]. Nonbiodegradable organics are degraded by the potential difference which is produced by the micro-electrolysis fillers in the wastewater. The basic electrode reactions can be represented as follows [16]:

Anode reaction:



Cathode reaction:

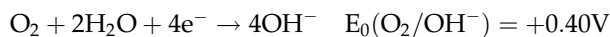


When the oxygen is presented:

Acid conditions:



Neutral or alkaline conditions:



During the running of traditional micro-electrolysis process, the contact area between the sewage and the padding could be reduced due to the fillers hardening, which decreased the removal efficiency of wastewater and even stopped the micro-electrolysis reaction [17,18]. As a result, it is necessary to study deeply on a new kind of unhardened micro-electrolysis fillers. Calcinations technology has been widely used in the

construction area, chemistry industry, agriculture area, and environment area [19,20]. In our previous study, the ceramic-corrosion-cell fillers, synthesized from a cathode and an anode ceramic-corrosion-cell filler, were applied for the treatment of wastewater in the cyclohexanone industries [15]. But in this study, a new kind of micro-electrolysis ceramic filler (MCF) which is made from iron scraps, clay, and activated carbon with calcinations technology not only solved the problem of easy-harden in the running of micro-electrolysis process and conversion of scrap iron into useful resources, but also achieved the integration of cathode and anode and made the use more convenient.

Consequently, some aspects were explored in this study as follows: (i) the feasibility of using calcined iron-carbon-ceramic as micro-electrolysis fillers and raw materials mass ratio of MCF; (ii) the optimal parameters (including pH, hydraulic retention time (HRT), and the aeration rate) were determined through the removal efficiency of COD_{Cr} and acrylonitrile when MCF was used as fillers to treat simulated acrylonitrile wastewater and (iii) the treatment efficiency of acrylonitrile wastewater was studied when the MCF worked for a long time.

2. Materials and methods

2.1. Raw materials

Clay, scrap iron, and powdered activated carbon (PAC) were utilized to produce MCF. Clay was taken from a brickfield of Shandong Province, China. Scrap iron was obtained from Jinan Machinery Plant in Shandong and PAC was purchased from Kermel Company in Tianjin. The clay and scrap iron were dried for 4–5 h at 105 °C, and then crushed through 100 mesh sieves. In order to prevent pretreated materials from moisture, polyethylene containers were used to store materials.

The acrylonitrile sample was obtained from Qilu Petro Chemical Company. And the acrylonitrile simulation wastewater was prepared as acrylonitrile aqueous solutions (1,600 mg/L). The water quality parameters of acrylonitrile simulation wastewater are shown in Table 1.

2.2. Preparation of MCF

The preparation of MCF was divided into three parts as follows.

Step 1: Mixing and granulating. Scrap iron, PAC, and clay were completely mixed according to a certain mass ratio. The mixture was made into pellets in a

Table 1
Water quality parameters of acrylonitrile simulation wastewater

Acrylonitrile (mg/L)	COD _{Cr} (mg/L)	TOC (mg/L)	TN (mg/L)
1,600.2	2,054.8	687.6	422.5

pelletizer (QJ300, China), the speed of electromotor was about 600–700 rpm, and about 8.00 wt.% binder solution was added during this step. The pellets which have a diameter of 5–6 mm were selected and then dried at room temperature (20–25°C) for 24 h.

Step 2: Calcining in anoxic condition. The dried pellets were put into muffle furnace (SX2-4-13, made in China) and calcined at 500–600°C for 20–30 min without oxygen.

Step 3: Cooling and storage. After calcining process, the pellets cooled down to room temperature (20–25°C) in anoxic conditions to prevent oxidation, and stored into polyethylene containers.

2.3. Characterization of MCF

Bulk density, grain density, water absorption, and porosity were determined according to GB/T 17431.2-2010 [21]. Specific surface area of MCF was determined by a specific surface area and pore size analyzer (JW-BK122W, China). The MCF was kept in 105°C for 4 h to be dehumidified before the tests. The pellets were put into a 250 mL measuring cylinder. The scale reading was the volume of these pellets. These pellets were soaked into water for 1 h and wiped. Then, these soaked pellets were put into a 500 mL measuring cylinder which contained 250 mL water. Grain density was calculated according to the actual particle volume which determined by Archimedes' principle. These physical parameters can be calculated by Eqs. (1–4):

$$\text{Bulk density (m}^3/\text{kg)} = \frac{M}{V} \quad (1)$$

$$\text{Grain density (m}^3/\text{kg)} = \frac{M}{V' - 250} \quad (2)$$

$$\text{Water absorption} = \frac{M' - M}{M} \times 100\% \quad (3)$$

$$\text{Porosity} = \left(1 - \frac{\text{Bulk density}}{\text{Grain density}}\right) \times 100\% \quad (4)$$

where V is the volume of these pellets (mL), M is the mass of these pellets (g). M' is the mass of soaked

pellets (g), and V' is the scale reading of liquid level in the 500 mL measuring cylinder (mL).

2.4. Micro-electrolysis reactor

A micro-electrolysis reactor was installed as shown in Fig. 1. The reactor was a cylinder which made by polymethyl methacrylate. It had a 20 L total volume with a diameter of 160 mm and a height of 1 m. The reactor was filled with MCF and the fillers had a height of 800 mm with effective volume of 16 L. Water and air distribution plate was set up at the place which had a distance of 100 mm from the bottom of the reactor. Air was fed into the reactor by an air pump and distributed equally by the plate. Raw wastewater entered the reactor through a peristaltic pump. Treated effluent was discharged at the top of the reactor and collected by an effluent tank.

2.5. Starting and running

Adjustment stage: Acrylonitrile aqueous solutions (1,600 mg/L) were used as acrylonitrile simulation wastewater. In order to reduce the influence of PAC adsorption on the experiment, the wastewater was fed into the reactor through a peristaltic pump under a condition of HRT of 4 h and no aeration. COD_{Cr} of treated effluent was measured every 12 h until the value of COD_{Cr} was basically stable, which meant that

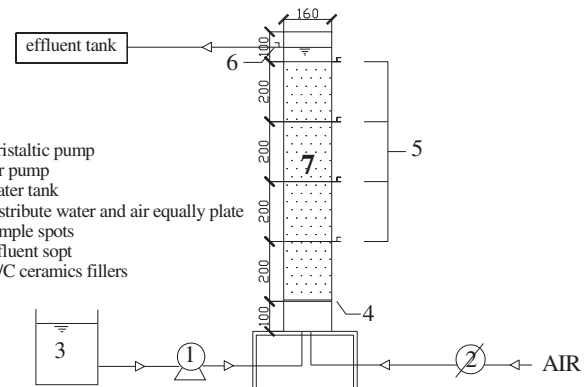


Fig. 1. Schematic diagram of experiment (dimensioning unit: mm).

the PAC of the MCF was saturated by acrylonitrile. And then formal experiment could be started.

Experimental stage: The concentration of acrylonitrile simulation wastewater was 1,600 mg/L and the water quality parameters are shown in Table 1. The basic factors of the experiment were as follows: pH 4, HRT=8 h, and no aeration. And then, the operation parameters were determined by single factor experiment at room temperature (20–25°C). In addition, as the reactor running, the hardened effects of the MCF were studied.

2.6. Analytical methods

The influent and effluent samples were collected immediately and the parameters of pH, total organic carbon (TOC), COD_{Cr} , and acrylonitrile concentration were determined. The solution pH was measured by a pH meter (PHS-3CW, China). And then, each sample was adjusted to pH 9–10 and passed through 0.22 μm filter membrane before measuring other parameters. TOC was determined by a TC/TN analyzer (Shimadzu TOC-V CPH, Japan). COD_{Cr} was measured using COD heating device (JH-12, China) according to GB11914-89 [22]. The concentration of acrylonitrile was analyzed by a HPLC (Shimadzu SPD-20A, Japan) with an octadecylsilane (ODS, C-18) reverse phase HPLC column. The HPLC conditions were as follows: mobile phase, degassed organic-free reagent water; flow rate, 1.0 mL/min; detector UV wavelength, 195 nm.

The system was operated at room temperature (20–25°C). All parameters of each sample were measured for three times, and then the average was taken from two nearly values as the result.

3. Results and discussion

3.1. Determination of raw materials mass ratio

3.1.1. Determination of clay mass fraction of MCF

Clay was rich in SiO_2 and Al_2O_3 which could reach 85% mass ratio in total. In the appropriate proportions, SiO_2 and Al_2O_3 played a role of framework and supported Fe and C after calcining. Thus, clay was an important material of MCF.

In the calcining process, the optimum mass ratios of SiO_2 , Al_2O_3 and fluxing medium (Fe_2O_3 , K_2O , Na_2O , CaO , MgO and other metal oxides) were determined as 53–79, 11–25, and 13–26% according to Riley phase diagram [23]. Therefore, MCFs were prepared at different clay mass fractions (40, 50, 60, and 70%) and Fe/C mass ratio was selected as 3:1 initially.

Table 2

The relationship between clay mass fraction and strength of MCF

Clay mass fraction (%)	40	50	60	70
Strength	Shapeless	Fragile	Solid	Solid

The relationship between clay mass fraction and strength of MCF is shown in Table 2. MCF should possess a certain strength level because of the need of wastewater treatment. And the content of Fe should be high to ensure the wastewater treatment efficiency. As a result, clay mass fraction was determined as 60% from Table 2.

3.1.2. Determination of Fe/C mass ratio

Fe/C mass ratio was determined by the removal efficiency of acrylonitrile (concentration 1,600 mg/L). The influence of Fe/C mass ratio on removal efficiency of COD_{Cr} and acrylonitrile of acrylonitrile simulation wastewater was studied at pH of 4, HRT of 8 h, and without aeration. Five kinds of MCF which were prepared at different Fe/C mass ratios (5:1, 4:1, 3:1, 2:1, and 1:1) and contained 60% clay were selected.

Fig. 2 illustrates the COD_{Cr} and acrylonitrile removal efficiency by the micro-electrolysis system at different Fe/C mass ratios. When Fe/C mass ratio was 1:1, the removal efficiency of COD_{Cr} and acrylonitrile was the lowest in five ratios. Removal efficiency increased as Fe/C mass ratio increased from 1:1 to 4:1 and reached the highest (33.9 and 39.2%, respectively)

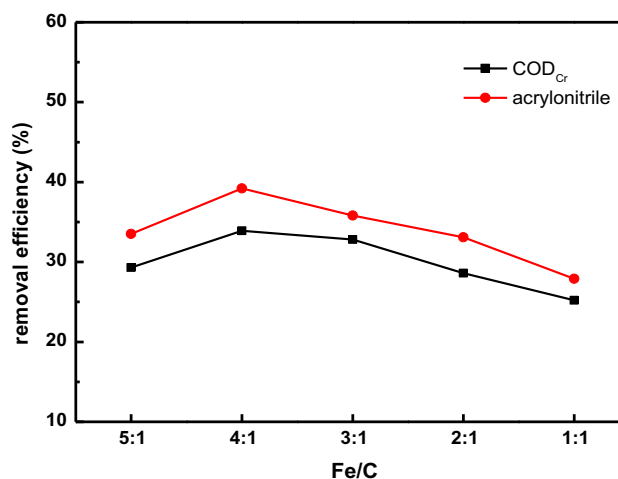


Fig. 2. The removal efficiency of COD_{Cr} and acrylonitrile at different Fe/C mass ratios (pH of 4, HRT of 8 h, and without aeration).

with Fe/C mass ratio of 4:1. When Fe/C mass ratio increased over 4:1, removal efficiency began to decline, instead.

Electrochemical reaction between the iron and carbon in the simulated wastewater is an electrochemical corrosion process. When the MCF was soaked into the wastewater, numerous macroscopic galvanic cells in which Fe was the anodic metal formed between the iron and carbon. Thus, the number of macroscopic galvanic cells which was mainly determined by Fe/C ratio has an important influence on removal efficiency of wastewater. When Fe/C mass ratio was low, increasing mass of iron means increasing the number of macroscopic galvanic cells. Thus, more acrylonitrile was degraded. The removal efficiency reached the highest when Fe/C mass ratio was at 4:1 (volumetric ratio probably was 1:1). Equaling the volume of similar-sized iron and carbon particles will maximize the number of macroscopic galvanic cells, for the number of anode and cathode will be the same [24]. But when iron was too much, the electrode reaction of galvanic cell was suppressed. Therefore, Fe/C mass ratio of 4:1 was selected as the optimum mass ratio and the raw materials mass ratio of MCF was determined as 60% clay, 32% scrap iron, and 8% PAC in the following studies.

3.2. Properties of MCF

The specific properties of MCF are shown in Table 3. It indicated that MCF with a low bulk density (997.2 kg/m^3) could be regarded as light-weight aggregate. The high porosity and relatively low bulk density of MCF could provide favorable hydraulic conditions and delay the hardening of the fillers during the process of wastewater treatment. Therefore, the life of fillers will be longer. And physical properties had benefits to the backwashing of fillers as well.

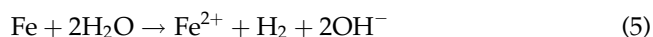
The appearance and microstructure of MCF ((A-1) surface of MCF with $200\times$ magnification, (A-2) surface of MCF with $700\times$ magnification, (B-1) section of MCF with $200\times$ magnification, and (B-2) section of MCF with $700\times$ magnification) are shown in Fig. 3. It can be seen from Fig. 3(A-1, A-2) that the surface of MCF is rough and has irregular shape because there are many small apertures on the surface, which could enhance

the specific surface area. Fig. 3(B-1, B-2) shows that the section of MCF is rougher and has more and larger apertures than surface. Owing to the internal and external structure, specific surface area of MCF could increase and the probability of contacting between wastewater and fillers would increase as well, which means improving treatment efficiency and reducing treatment time. The calcined surface structure of MCF could be destroyed in the wastewater treatment process. As the consumption of iron on the surface, the surface of MCF fell off and renewed. As a result, the hardening and service cycle of fillers were delayed and extended, respectively, and the frequency of backwashing reduced obviously as well.

3.3. Effect of influent pH on COD_{Cr} and acrylonitrile removal efficiency

In micro-electrolysis process, pH played a key role in affecting the kinetics [25]. The influence of pH on removal of COD_{Cr} and acrylonitrile was investigated at HRT of 8 h and without aeration. And nine different pH values of influent (2–10) were selected.

Influence of influent pH on COD_{Cr} and acrylonitrile removal efficiency is shown in Fig. 4. It is illustrated that the removal efficiency of both COD_{Cr} and acrylonitrile gradually increased as pH decreased. When pH was less than 3, the removal efficiency of COD_{Cr} and acrylonitrile was almost constant which over 35 and 40%, respectively. When pH increased from 4 to 9, the removal efficiency reduced obviously. And when pH reached 10, the removal efficiency was lower than 10%. Different reaction rates were presented with different pH of influent, which were shown as follow equations:



Reduction potential increased with the increase in hydrogen ion concentration according to Nernst Equation. As a result, micro-electrolysis reaction worked better in acidic condition and more and more acrylonitrile was removed with the decrease in pH. However,

Table 3
Specific properties of MCF

Bulk density (m^3/kg)	Grain density (m^3/kg)	Water absorption (%)	Porosity (%)	Specific surface area (m^2/g)
997.2	1,675.0	18.0	41.3	30.52

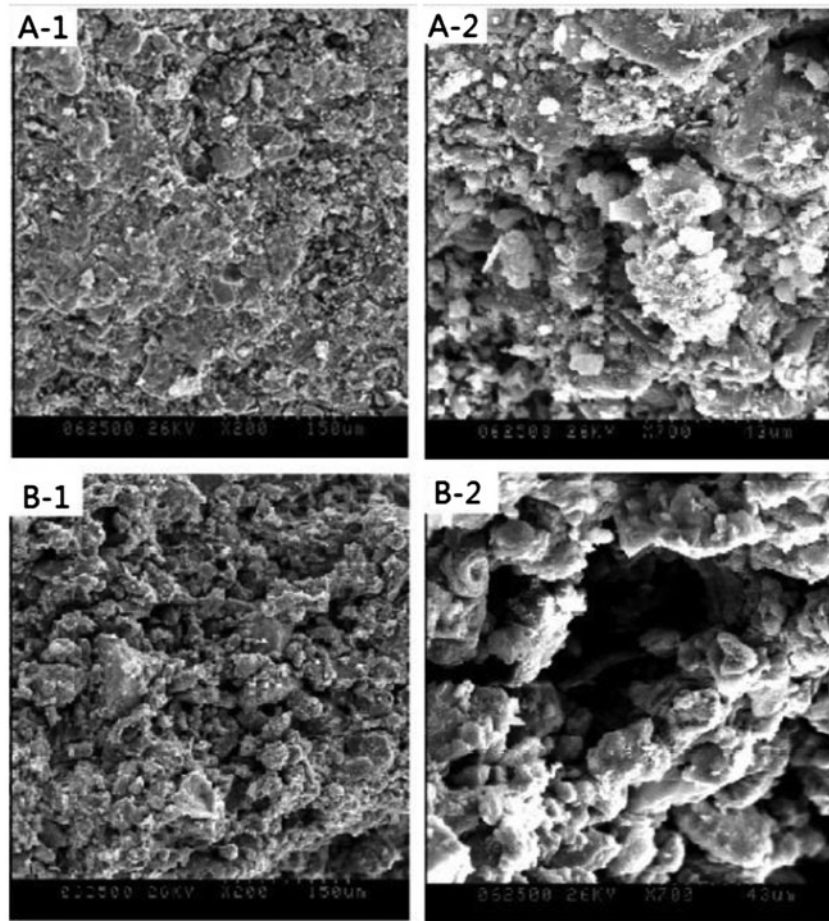


Fig. 3. The appearance and microstructure of MCF ((A-1) surface of MCF with 200 \times magnification, (A-2) surface of MCF with 700 \times magnification, (B-1) section of MCF with 200 \times magnification, and (B-2) section of MCF with 700 \times magnification.

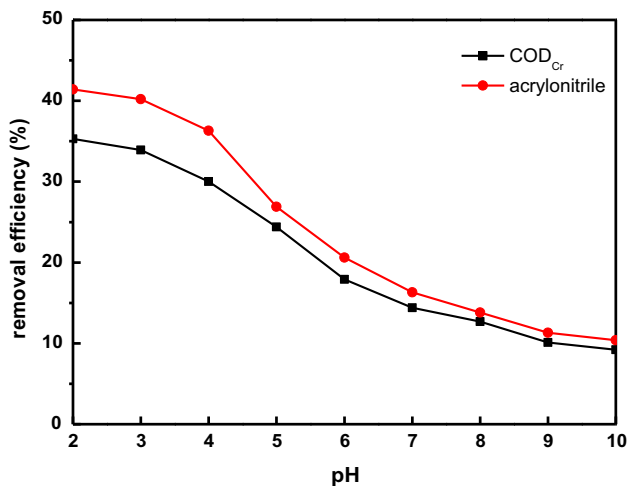


Fig. 4. Effect of influent pH on COD_{Cr} and acrylonitrile removal efficiency (HRT of 8 h and without aeration).

the removal efficiency of acrylonitrile which reached up to 40% was higher than COD_{Cr} removal efficiency in each different pH. It indicated that only the key functional groups, such as C≡N and C=C, in acrylonitrile molecule could be destroyed by the micro-electrolysis process, but some functional groups were too stable to break such as -C-C- [26]. It is the reason that COD_{Cr} removal efficiency is lower than acrylonitrile. The surface of MCF had negative charge with pH of operating condition, which was determined by zeta potential. Therefore, lots of H⁺ ions were attracted by MCF on the surface and received the electrons which came from carbon (cathode of the galvanic cells) to generate [H] which could react with acrylonitrile molecule. In other word, acrylonitrile was removed by [H] which produced from electrochemical reaction. Although zeta potential decreased from -5.265 to -28.723 mV with pH increased from 2 to 10, the numbers of H⁺ ions were few when pH was high. Thus,

the concentrations of H^+ ions have intimate relation with the removal efficiency of COD_{Cr} and acrylonitrile. But dosage of acid to adjust pH and erosion of iron would increase when pH was too low, which would increase the cost of wastewater treatment. As a result, the optimum pH was selected as 3–4 in the following studies.

3.4. Effect of HRT on COD_{Cr} and acrylonitrile removal efficiency

HRT was a necessary influence factor in micro-electrolysis process. Ten different HRTs (0.5, 1, 2, 3, 4, 5, 6, 8, 10, and 12 h) were selected to investigate the removal efficiency of COD_{Cr} and acrylonitrile. Other operating conditions were as follows: influent initial pH of 3 and without aeration.

The influence of HRT on removal efficiency of COD_{Cr} and acrylonitrile is shown in Fig. 5. It can be seen that the removal efficiency of COD_{Cr} and acrylonitrile increased as HRT increased. When the HRT increased from 0.5 to 6 h, the removal efficiency of both COD_{Cr} and acrylonitrile increased rapidly which could reach 33.9 and 40.1% at HRT of 6. When the HRT increased from 6 to 12 h, the removal efficiency of COD_{Cr} and acrylonitrile was almost stabilized which only increased by 2.4 and 2.8%, respectively.

According to Eqs. (5) and (6), pH which influenced the rate of micro-electrolysis reaction increased with the running of micro-electrolysis system. When HRT increased from 0.5 to 3 h, pH of effluent was lower than 4. It is the reason why the rate of reaction was high in the first 3 h. When pH of effluent changed from 4.67 to 7.55 as HRT increased from 4 to 6 h, Fe^{2+} and Fe^{3+} mainly existed in the form of $Fe(OH)_2$ and

$Fe(OH)_3$ which had a positive effect on flocculation precipitation to organic wastewater. Therefore, the removal efficiency of COD_{Cr} and acrylonitrile increased obviously when HRT increased from 4 to 6 h. However, the wastewater transformed from acidic condition to alkaline condition when HRT was too long, so the removal efficiency of COD_{Cr} and acrylonitrile was almost constant when HRT increased from 6 to 12 h. To consider the removal efficiency of COD_{Cr} and acrylonitrile, HRT of 6 h was chosen as the suitable operating condition.

3.5. Effect of aeration on COD_{Cr} and acrylonitrile removal efficiency

Aeration is also important to micro-electrolysis system. When experiment followed the optimum conditions (influent pH of 3 and HRT of 6 h), three different aeration–liquid ratios (A/L) (0, 5, and 10) were chosen to study the influence of aeration on the micro-electrolysis system.

The removal efficiency of COD_{Cr} and acrylonitrile in aerobic condition, which could reach 68.8, and 73.9%, respectively, was almost 30% higher than anaerobic condition, as shown in Table 4. It was because the oxidation potential in aerobic condition (0.4–1.23 V) was higher, and more energy was provided to destruct bonds of organic pollutant in wastewater [27]. When oxygen existed, Fe^{2+} also transformed to $Fe(OH)_3$ which was more effective in flocculation precipitation [28]. Aeration was helpful in falling off and refreshing of MCF surface, which made the cycle of backwashing longer. Therefore, the aeration had benefits to process of micro-electrolysis system and A/L of 10 was selected.

3.6. Successive run and backwashing of the micro-electrolysis reactor

The micro-electrolysis reactor ran 40 d continuously in optimum parameters (influent pH of 3, HRT of 6 h, and A/L of 10) and samples were taken according to the predetermined time.

The running state of micro-electrolysis reactor is shown in Fig. 6. At the first 10 d of micro-electrolysis reactor running, the removal efficiency of COD_{Cr} and acrylonitrile was very stable which could reach about 70 and 75%, respectively. Because of the consumption of Fe on the surface of MCF, the removal efficiency of COD_{Cr} and acrylonitrile decreased a little but still reached up to 65–70%, respectively, in the next 10 d. As the running time became longer (from 20 to 25 d), the removal efficiency reduced rapidly because of the

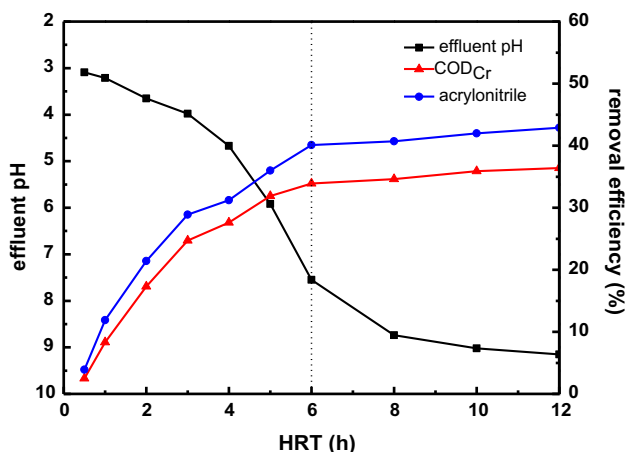


Fig. 5. Effect of HRT on COD_{Cr} and acrylonitrile removal efficiency (influent initial pH of 3 and without aeration).

Table 4
Effect of aeration on COD_{Cr} and acrylonitrile removal efficiency

Aeration–liquid ratio (A/L)	COD _{Cr} removal efficiency (%)	Acrylonitrile removal efficiency (%)
0	34.2	40.2
5	60.3	66.4
10	68.8	73.9

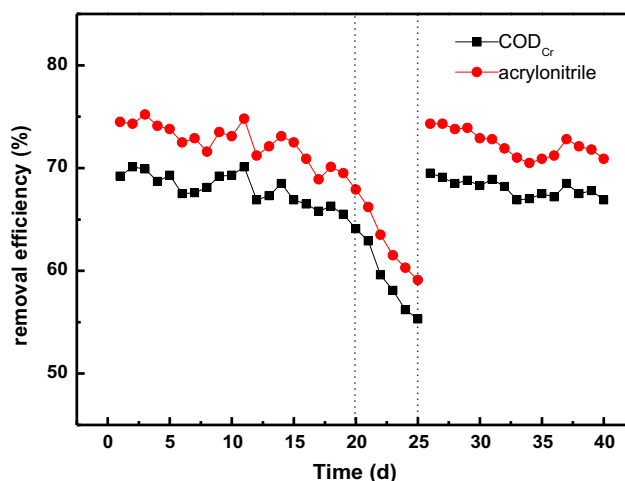


Fig. 6. Successive running of the micro-electrolysis reactor (influent pH of 3, HRT of 6 h, and A/L of 10).

passivation of surface of MCF. However, the fillers did not harden and hydraulic conditions of micro-electrolysis reactor were still well. The fillers were backwashed and lasted 20 min when the reactor ran 25 d continuously, and the intensity of backwashing was determined as 40.5 m/h. It can be seen from Fig. 6 that the removal efficiency of COD_{Cr} and acrylonitrile restored and stayed stable after backwashing. Therefore, MCF could be used as micro-electrolysis fillers. And the fillers should be backwashed every 20 d by considering the removal efficiency and cost of the micro-electrolysis reactor.

3.7. Analysis of operating cost

MCF would be consumed with the erosion of iron in acidic condition when the micro-electrolysis reactor treated wastewater. Therefore, the consumption of MCF led to the main cost of reactor running. The cost price of MCF was almost 2,000 CNY/m³. When the micro-electrolysis reactor continuous run (40 d) with optimal operating condition of Fe/C mass ratio of 4:1, influent pH of 3, HRT of 6 h, and aeration of 0.2 L/min, 1.05 m³ of wastewater was treated totally

and the consumption of MCF was almost 350 mL. As a result, the cost of fillers consumption was about 0.67 CNY/ton wastewater [29]. However, other cost of the micro-electrolysis reactor running should be investigated in detail in the future. Even so, the micro-electrolysis system using MCF was a suitable, economical, and effective way to treat acrylonitrile and some other toxic and refractory wastewater.

4. Conclusion

It is feasible to use scrap iron, PAC, and clay as raw materials to produce a new kind of MCF, and the raw materials mass ratio of MCF was determined as 60% clay, 32% scrap iron, and 8% PAC through analyzing the properties of MCF. MCF was effective on the treatment of acrylonitrile simulation wastewater with the optimal conditions of influent pH of 3, HRT of 6 h, and A/L of 10. The highest removal efficiency of COD_{Cr} and acrylonitrile could reach 68.8 and 73.9%, respectively. During the successive running period of the micro-electrolysis reactor, the removal efficiency was stable. The intensity and cycle of backwashing were determined as 40.5 m/h and 20 d. The cost of fillers consumption was only about 0.67 CNY to treat 1 ton of acrylonitrile simulation wastewater. Thus, micro-electrolysis reactor with MCF is a suitable, economical, and effective way to treat acrylonitrile wastewater.

Acknowledgments

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