Mechanism of Electro-Coagulation with Al/Fe Periodically Reversing Treating Berberine Pharmaceutical Wastewater

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Abstract. The method of treating pharmaceutical wastewater by electro-coagulation with Al/Fe periodically reversing (ECPR) was proposed based on traditional electrochemical method. The principle of ECPR was generalized. Mechanism of ECPR to treat berberine pharmaceutical wastewater was investigated. Treatability and mechanism studies were conducted under laboratory conditions. For berberine wastewater (800 mg/L), decolourization efficiency and COD removal efficiency were highest to 98% and 95% respectively when voltage was 8V, reaction time was 60 min, alternating period was 10 S electrolyte concentration was 0.015 mol/L, stirring speed was 750 r pm, pH value was 3-10 and distance between two plates was 0.6 cm. For removal berberine, flocculation, floatation and oxidation provided 73%, 8% and 18% removal efficiency, which can be inferred by analysing UV-visible absorption spectrum, acidification experiment, EDTA shielding experiment, structure-activity relationship, oxidation and floatation. Meanwhile decolourization and COD removal conformed to apparent pseudo-first order and zero-order kinetics for 200mg/L and 400-1000 mg/L berberine wastewater respectively.

1. Introduction
Berberine is an important alkaloid, and traditional Chinese medicine applied long in China, which has a significant inhibitory effect. Its structure is shown in Table 1. Berberineis producted using natural plant extracts and chemical synthesis, through relatively mature technology of sulfuric acid and lime method [1].The mother liquor of berberine contains a high concentration of berberine which has strong antibacterial. Duo to it can’t be directly treated by biochemical methods, some pretreatment methods are needed like coagulation, membrane filtration or chemical before biochemical treatment. Electro-coagulation has been used to treat dyeing wastewater [2-3], papermaking wastewater [4], the coking wastewater [5], pharmaceutical wastewater [6], oily wastewater [7-8], heavy metal wastewater [9] and other wastewater. But traditional electro-coagulation technology uses of unidirectional power and one kind anode, which easily lead to extreme concentration and polarization plate passivation. And then treatment efficiency is reduced, power consumption will be increased. With regards to these, power supply was improved on the basis of traditional electrochemical, berberine wastewater was treated using homemade periodically reversing power [10] and aluminium and iron as electrodes. The mechanism of ECPR treating wastewater under the optimal conditions was investigated. Flocculation,
electric floatation and oxidation for berberine removal were quantified, which had guided significance to improve treating efficiency and reduce power consumption through adjusting reaction factors.

**Table 1.** The characteristics of berberine

| Name   | Structure | Molecular weight (g/mol) | Molecular formulae (nm) |
|--------|-----------|--------------------------|-------------------------|
| Berberine | ![Berberine Structure](image) | 373 | C20H18ClN O4 | 344 |

2. Materials and procedure

2.1. Principle of ECPR

In the process of treating organic wastewater by Fe/Al ECPR, Fe and Al plates as anode in turn dissolved and released Fe$^{2+}$, Fe$^{3+}$ and Al$^{3+}$ under commutation current function. And then these ionic are formation of various hydroxyl complexes, multi-core hydroxy complex and even hydroxides via a series of hydrolysis, polymerization and ferrous oxidation process, which could separate suspended and colloidal impurities by cohesion precipitation. Meanwhile charged pollutant particles moving in an electric field, could be destabilized and removed though part of charges neutralized. Moreover pollutant can directly be oxidized and reduced like ·OH and Fe$^{2+}$ on surface of anode and cathode in ECPR process. And the principle can be shown in Figure 1.

![Figure 1. Basic principle of ECPR with Al/Fe](image)
2.2. Materials
The berberine was obtained from a pharmaceutical factory in northeast China. The main characteristics of this organic substance and its structure are shown in Table 1. The simulated concentration of the berberine wastewater was 800 mg/L. The other agents were of analytical grade.

2.3. Procedure
Self-designed batch-type electrolytic reactor [10] was applied to the experiment, which was shown in Figure 2. Reactor is made of Plexiglas column with the effective volume of 400 mL. Aluminium and iron plates (80 mm × 60 mm × 2 mm, adjustable distance between the electrode plates) were used as electrodes in turn. And the solution was mixed by a heating magnetic stirrer to ensure a constant concentration of ions. The simulated wastewater was prepared with pure berberine (800 mg/L), and Na₂SO₄ was added as the supporting electrolyte.

3. Results and discussion
For berberine wastewater (800 mg/L), decolourization efficiency and COD removal efficiency were highest to 98% and 95% respectively when voltage was 8V, reaction time was 60 min, alternating period was 10 S electrolyte concentration was 0.015 mol/L, stirring speed was 750 rpm, pH value was 3-10 and distance between two plates was 0.6 cm. Validity and stability of treating berberine wastewater by ECPR under optimal conditions had been verified [11]. The mechanism of ECPR treating berberine wastewater was investigated in next experiments.

3.1. Analysis of UV-visible absorption spectrum
Changes process of berberine molecules were researched through analysing UV – visible absorption spectrums after treating at different reaction time. Figure 3 shown that characteristic absorption peaks of berberine (228 nm, 263 nm and 344 nm) were significantly reduced as the reaction proceeding, the absorption peaks disappeared at 60 min, and there weren’t new absorption peaks appeared in the whole reaction process. Yellow bubble layer was found on the uppermost layer of the solution, which due to the gas adsorbent berberine molecules. Yellow-green bubble layer was under yellow bubble layer, which formed because of divalent iron ion complex and aluminium ionic flocculants berberine molecules. Therefore it can be inferred that most berberine molecules were removed directly by floatation of gas and flocculation of forming inorganic salt flocculants with aluminium ions and metal ions. Through further analyzing, the reason may be that berberine molecules dissolved in water and dissociated into colloid charging positively and chloride ions, and the hydroxide flocculants forming of the iron ion and aluminium ion usually charge negatively. Two oppositely charged colloidal occurs electroluminescence, so most berberine molecules were directly flocculating removed. Meanwhile Chloride ions can be formed to Cl₂ near the anode, and further generating strong oxidizing ClO⁻ and ClO₄⁻ can oxidize berberine molecules, but the oxidation product needed to further proof.
3.2 Analysis of flocculation of mental ions by acidification

The process of treating barberry wastewater by ECPR, may include flocculation of Fe (OH)_3, Fe (OH)_2 and Al (OH)_3 and adsorption of metal hydroxy complex. The pH value of solution had important impact on precipitation of Fe^{2+}, Fe^{3+}, Al^{3+} and formation of complex. Fe^{3+} began to precipitate at pH value of 2 and Fe (OH)_3 formed. Fe^{2+} and Al^{3+} successively precipitate with the pH value increasing. If the pH value of solution was adjusted to 2 or less, then metal ion flocculants dissolved, which will course flocculated berberine molecules re-released back to solution. The following experiment was designed to further study flocculation of metal ions in the process of ECPR.

| pH value | COD of berberine (mg/L) | COD of Na_2SO_4 (mg/L) | Difference COD (mg/L) | Decolorization rate | Reaction 60 min | Acidification after reaction 60 min |
|----------|------------------------|------------------------|----------------------|--------------------|-----------------|-----------------------------------|
| pH=10.73 | 1023.8                 | 0                      | 1023.8               | 58.6               | 1085.6          | 1098.2                            |
| pH=2     |                        |                        |                      |                   |                 |                                   |
| pH=1.5   | 1023.8                 |                        | 1023.8               | 38.1               | 1006            | 1010.5                            |

Figure 4 shown that the decolourization rate was up to 99% when wastewater (800mg/L) reacted 60 min under optimal conditions. When the pH value of the solution was reduced to 2 or less, flocculation and flotation were eliminated, and then the decolourization rate dropped to 18%. As seen from Table 2, when the pH value was 1.5, the COD value of the solution was close to the COD value of the berberine dope. It can be inferred that 19% berberine molecules were bleaching via oxidation or reduction, but formed intermediate molecules still remained in solution. And 80% berberine molecules redissolved with the dissolution of the metal flocculants, which indicated that flocculating and floatation of the metal ions was dominant in the process of treating berberine wastewater by ECPR.

3.3 Analysis of flocculation by EDTA shielding experiment

Flocculation in the process of ECPR was further analyzed through shielding flocculation utilized EDTA. The results were shown in Table 3. Decolorization rate gradually decreased with addition of EDTA increasing, indicating EDTA could constant shield flocculation. Decolorization rate descended to constant 25% when addition of EDTA was up to 5000 mg/L or more. Decolourisation rate difference (about 73%) can be considered contribution rate of flocculation.
Table 3. The effect of EDTA addition

| Addition of EDTA (mg/L) | 1000 | 2000 | 3000 | 4000 | 5000 | 6000 | 7000 |
|------------------------|------|------|------|------|------|------|------|
| Decolorization rate (%)| 90.7 | 72.3 | 60.2 | 38.66| 25.41| 23.8 | 26.8 |

3.4. Analysis of structure-activity relationship
Metal ions of solution exist in the form of structural states polyhydroxy complexes in the process of ECPR. Figure 5 showed coordination number of Polyhydroxy complexes was higher, the complex ion charging negatively electricity tariff was higher, and the adsorption ability of the outer attracting opposite charged ions was stronger. So berberine dissolved in solution could be occur electrical hop reaction with polyhydroxy complexes of metal ions. Otherwise berberine molecule can replace the hydroxyin polyhydroxy complexes and coordinate with metal ions by N atom in the molecule structure of berberine, which made berberine firmly adsorbed with complexes of the metal ions.

![Figure 5. Diagram of ferrous hydroxyl complex](image)

3.5. Analysis of electric floatation
As the principle of ECPR known, O$_2$ generated on the anode and H$_2$ generate on cathode when the reaction was carried out. Electric floatation cannot be ignored in the electro-coagulation process. The following two groups were carried out under optimal conditions to research floatation to remove berberine. The first group was contrast: absorbance and COD value of filtrate were directly measured after reaction ending. And the second group: the power was turned off and the plates were removed, but stirring was continued. Stirring was stopped when the bubble layer on solution surface. And then absorbance and COD value of filtrate were measured. The results were shown in Table 4.

Table 4. The effect of floating on treating efficiency

|                        | Decolourization rate (%) | Removal rate of COD (%) |
|------------------------|--------------------------|-------------------------|
| First group            | 99.21                    | 94.5                    |
| Second group           | 91.34                    | 88.4                    |
| Difference             | 7.87                     | 6.1                     |

In the second group, decolourisation rate and removal rate of COD declined, indicating berberine molecules adsorbed on yellow bubble layer re-dissolved to solution with bubble layer disappearing. Therefore difference (about 8%) between two groups was roughly understood as floating occupied proportion. But re-dissolved berberine molecules may be removed through the flocculation of metal ions complex, so practical proportion of floating should be higher than experimental date (8%).

3.6. Analysis of oxidation
Structure of berberine molecule showed Cl$^-$ existed in berberine solution, and Cl$^-$ converted into Cl$_2$ by anodic chlorine evolution. Cl$_2$ converted into reactive oxidants HClO via hydrolysis. While HClO
participated in sires of main and side reactions and generated Cl\(^-\). Therefore recycling mechanism of Cl\(^-\) existed, which was favorable to HOCl playing oxidation.

3.7. Analysis of reaction kinetics
Berberine pharmaceutical wastewaters (200--1000mg/L) were treated under optimal conditions, and removal kinetics of berberine molecules were researched through investigating the changes of decolourisation rate and COD removal rate. The results showed that decolourisation and COD removal rate conformed to apparent pseudo-first order kinetics while 200 mg/L berberine wastewater was treated by ECPR. And decolourisation and COD removal rate conformed to apparent zero-order kinetics while 400--1000 mg/L berberine wastewater was treated by ECPR.

4. Conclusions
The principle of ECPR with Fe/Al was generalized. And through a series of designed experiments, flocculation, floatation and oxidation were quantified in process of treating berberine wastewater by ECPR, which provided 73%, 8% and 18% removal efficiency. Meanwhile decolorization and COD removal conformed to apparent pseudo-first order and zero-order kinetics for 200mg/L and 400-1000 mg/L berberine wastewater respectively.

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