Application research of internal electrolysis as pre-treatment for berberine wastewater biodegradation

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Abstract. The composition of the berberine wastewater is complicated with high concentration of chemical oxygen demand (COD). Because it is hard to be degraded by traditional biochemical treatment and causes serious environmental pollution. The applicability of internal electrolysis to improve the biodegradability of berberine wastewater to be treated biologically was investigated. The wastewater was originated from a factory producing berberine. Treatability studies were conducted under laboratory conditions in order to determine the operational conditions to enhance the biodegradation of the wastewater. The major operational conditions, such as the initial pH, the second stage pH, the volume ratio of iron-carbon micro-electrolysis filler to wastewater and aeration time were investigated in the paper. The result of the experiment shows that the initial pH 2.0-2.5, second stage pH 9, the best volume ratio of iron-carbon micro-electrolysis packing and wastewater is 1:1 and the residence time control in 120 minutes are the best operating parameters on the berberine wastewater treatment.

1. Introduction
Berberine is an alkaloid found in plants and is a broad-spectrum antibacterial agent[1]. Berberine hydrochloride, also known as Berberine, formula C20H18NO4Cl, Berberine production is the traditional method of plant extraction, from Coptis Chinensis, Phellodendron amurense and three needles obtained. The molecular structure is shown in Fig.1. Berberine has effects on staphylococcus, streptococcus, streptococcus pneumoniae, shigella, escherichia coli, typhoid, bordetella pertussis and amoeba. It is effective for acute conjunctivitis, aphtha, acute shigelliosis, enterocolitis, etc. At present, the more mature process is sulfuric acid method and lime water method, but this method is long time, high cost, the purity of the product is low, the yield is small. The main pollutants in berberine mixed wastewater are berberine, berberine hydrochloride, toluene, methanol, alkali, ammonium bromide and so on. At present, biochemical method is used to treat the mixed wastewater of berberine production by chemical synthesis method, but the mixed wastewater contains more bio-toxic substances, high alkalinity and poor biodegradability. The water quality indexes of typical berberine wastewater samples are shown in Tab.1. Berberine wastewater treatment needs a large number of water dilution, wastewater treatment costs increased, increased the burden on enterprises. In recent years, the electrochemical method, especially the internal electrolysis, otherwise known as the iron-carbon micro-electrolysis method, has been paid attention to and gradually stepped onto the stage of wastewater treatment. The method has been successfully applied to the treatment of arsenic and fluorine containing wastewater[2], printing and dyeing wastewater[3,4], dye wastewater[5], electroplating wastewater[6-8] and petrochemical industry[9,10]. The specific reaction principle of iron-carbon micro-electrolysis is the synthesis of flocculation, adsorption, sweeping, coprecipitation, electrodeposition and electrochemical oxidation-
reduction. The present paper is basically about the treatability studies carried out adopting the internal electrolysis oxidation process to the berberine wastewater of concern.

Fig.1 Molecular structure of berberine

Tab.1 Table of the berberine raw water

| Water quality objectives | value   |
|--------------------------|---------|
| pH                       | 2.5     |
| Chromaticity             | 304     |
| COD(mg/L)                | 5855    |
| BOD₅(mg/L)               | 200     |
| berberine(mg/L)          | 529     |
| SS(mg/L)                 | 750     |
| NH₃-N(mg/L)              | 95      |
| TN(mg/L)                 | 100     |
| TP(mg/L)                 | 1.5     |
| TOC(mg/L)                | 1600    |

2. Related work
A. Reaction principle of internal electrolysis

2.1 Electrochemistry
The basic principle of internal electrolysis is the use of iron and carbon (or the addition of inert electrodes) in iron filings to form the positive and negative electrodes of the tiny primary battery, with the waste water charged as the electrolyte solution, it redox to form a galvanic cell. The electrode response is as follows:

Anode Fe-2e → Fe²⁺
E⁰(Fe²⁺/Fe) = -0.4V

Cathode 2H⁺+2e → 2[H] → H₂
E⁰(H⁺/H) = 0.00V

When there’s oxygen, O₂+4H⁺+4e → 4H₂O
E⁰(O₂) = 1.23V
O₂+2H₂O+4e → 4OH⁻
E⁰(O₂/OH⁻) = 0.40V

A myriad of microbattery systems are formed within the device, creating an electric field in the space in which they operate. The new ecology, such as [H⁺], Fe²⁺, can redox with many components in the waste water, and can destroy the chromophore or auxiliary chromophore of the colored substance in the colored waste water, even break the chain, to achieve the role of degradation decolorization.

2.2 Coagulation of iron ion
Iron-carbon micro-electrolysis technology integrates the functions of activated carbon adsorption, iron/carbon micro-electrolysis, iron oxidation-reduction, coagulation and precipitation. After the
wastewater was pretreated by iron-carbon micro-electrolysis technology, the structure of the bio-toxic Berberine was destroyed, and a large amount of COD was removed through the adsorption of activated carbon and flocculation and precipitation, thus improving the biodegradability of the wastewater, the impact on the subsequent biochemical treatment unit is reduced. In order to degrade organic pollutants, the 1.23 v potential difference produced by the micro-electrolysis material filled in the wastewater is used to treat the wastewater without electricity.

For the wastewater produced in the process of synthetic berberine, using copper chloride as a catalyst, the composition of waste water contains a large number of copper ions, the berberine wastewater containing copper was pretreated by pilot scale Fe-C microelectrolysis reactorion exchange combined process[11]. In this paper, the iron-carbon micro-electrolysis pretreatment technology for the wastewater from the extraction of Berberine from natural products is studied, and a set of pretreatment technology is obtained.

3. materials and methods

3.1. Wastewater
The wastewater used is from a medium scale pharmaceutical intermediate roughing plant in Sichuan province producing berberine hydrochloride. Typically, the total number of products amount to 10 ton per year. The intermittent cleaning of the tanks used in the production processes and soaking of raw materials and extraction of berberine make up the wastewater coming out of the plant. The company decided to construct a wastewater treatment plant that will satisfy the discharge limits stated by the Chinese integrated wastewater discharge standard (GB8978-1996). The regulation requires that COD of the wastewaters should be reduced down to 500 mg/L in order to discharge to a receiving water body.

3.2. Methodology
The general approach in the treatability studies was to optimize the operational conditions in the internal electrolysis unit to achieve maximum treatment efficiency while minimizing the use of chemicals (acid and base for pH adjustment, iron-carbon microelectrolytic filler, Polyacrylamide, Aluminium chlorohydrate and lime milk as the flocculating precipitant) and hence minimizing operation costs of the treatment plant. The main idea was to maximize the overall treatment efficiency considering units, internal electrolysis treatment. Therefore, improved biodegradability after internal electrolysis was as important as reduction in waste load in internal electrolysis oxidation. As part of the treatability studies, analyses of COD was carried out to investigate biodegradability of the pharmaceutical effluents from the plant.

3.3. Experimental procedure
The major operational conditions that would affect the treatment of the pharmaceutical effluents from the plant using internal electrolysis reagent are initial pH, the second stage pH, the volume ratio of iron-carbon microelectrolysis filler to waste water and aeration time. The effects of these parameters on treatment efficiency were investigated. The experiments were conducted in batch reactors and 100–200 mL wastewater samples were used in the experiments. The pH of the sample was adjusted to the required value with lime milk. Required amounts of iron-carbon microelectrolysis filler were added to the sample. The solution was aerated. Three hundred minutes were allowed for the completion of the reaction. Then, another 30 min were allocated for precipitation. The supernatant was then decanted. The pH of the decanted supernatant was then adjusted to the desired value to initiate coagulation. Two hours were allowed for precipitation. After precipitation, the supernatant was decanted for COD measurement for the selected samples.

All the experiments conducted were carried out in duplicates. All measurements were performed in parallels in each set. The removals reported are the average of the parallel measurements of the duplicate sets and the parallel measurements.
3.4. Materials
Polyacrylamide, Aluminium chlorohydrate, which were used during experiments, were purchased from Henan Gongyi Huaming water treatment materials Co., Ltd. (China), iron-carbon microelectrolysis filler was provided by Shandong Senyang Environmental Technology Co., Ltd and possessed the technical parameters as specific gravity of 1.0t/M$^3$, specific surface area of 1.2M$^2$/g, void rate of 65%, physical intensity of 1000 Kg/cm$^2$, particle size of 2.54cm. The Composition of filler is fine iron powder 80%, carbon 15%, catalyst 5%, activator 3%. Lime milk was added to the system in liquor form.

3.5. Analytical methods
COD of the samples were measured according to an EPA approved reactor digestion method (for a COD range 0–1500 mg/L with a HACH DR2000 instrument). pH measurements were performed using a pH meter (Model PHS-3C, Shanghai Yidian Scientific Instrument Co., Ltd, China).

4. results and discussion

4.1. Treatability studies with internal electrolysis

4.1.1. Effect of initial pH and the second stage pH
The effect of initial pH on COD removal efficiency was tested. When tested with the initial pH range 1.0–3.5, no significant differences in treatment efficiency were observed though pH 2.0 produced slightly better results (Fig. 1). This finding is in line with recent research findings that suggest that the optimum pH for internal electrolysis is independent from the nature of wastewater and at around 2.0–2.5.

Thereafter, the effect of the second stage (i.e. coagulation) pH on treatment efficiency was searched. The pH of the solution, after oxidation at pH 7.5, was varied from 7 to 9 and the effect on the residual COD was searched. This pH did not seem to affect the treatment efficiency as long as it was equal to or greater Fig. 1. Effect of first stage pH on removal efficiency than 7. Therefore, the pH was adjusted to 9 before coagulation.

![Fig.2 Effect of initial pH on COD removal efficiency](image1)

![Fig.3 Effect of the second stage of pH on COD removal efficiency](image2)
4.1.2. Effect of volume ratio of iron-carbon micro-electrolysis packing and wastewater

It can be seen from Fig. 4 that higher iron-carbon micro-electrolysis packing doses generated more oxidants, which, in turn, improved the COD removal efficiency.

![Fig.4 Effect of volume ratio of iron-carbon micro-electrolysis packing and wastewater treatment](image.png)

The removal rate of COD increases with the increase of the ratio of iron-carbon micro-electrolysis filler to the treated wastewater. In the presence of iron, the main reactions occur as follows.

\[
\text{Anode: } \text{Fe} - 2\text{e}^{-} \rightarrow \text{Fe}^{2+} \\
E^\circ(\text{Fe}^{2+} / \text{Fe}) = -0.4\text{V}
\]

When the amount of iron is appropriate, the reaction is promoted and the rate of active hydrogen production is fast. At the same time, the ferric iron produced by the reaction has a certain flocculation effect, and some COD can be removed by precipitation filtration, which enhances the removal function of iron-carbon micro-electrolysis, but when it is too high, the precipitation produced can cover and encase the original filler, thus preventing the further reaction, reducing the reaction efficiency and increasing the cost of reagent, increasing the amount of sludge and causing secondary pollution. Through the experiment, the best volume ratio of iron-carbon micro-electrolysis packing and wastewater is 1:1.

4.2. Effect of aeration reaction time

Other conditions do not change, change the reaction residence time to carry out the experiment, experimental results can be seen in Fig. 5.

![Fig.5 Effect of Aeration reaction time on removal rate of COD](image.png)

As can be seen from Fig.5, the removal rate of COD increases with the increase of the reaction residence time. But with 120 minutes as the time node, the increasing trend was obvious before this point, and after that the increasing trend tended to smooth. In addition, when the residence time is more than 150 minutes, the color of the effluent tends to deepen, which may be caused by too much iron dissolving into the wastewater. Therefore, comprehensive consideration, the residence time control in 120 minutes is the best.
4.3. Optimum process parameters
Based on the results from the above summarized treatability studies, the internal electrolysis unit of the treatment plant was operated under the following conditions: initial pH 2.0-2.5, second stage pH 9, the best volume ratio of iron-carbon micro-electrolysis packing and wastewater is 1:1 and the the residence time control in 120 minutes is the best. The treatment plant established was monitored for a period of 2 months and the following general performance was observed.

In general, treatment with internal electrolysis was found to improve the biodegradability of the wastewater. The COD removal efficiency attained in this unit was between 75% and 80%. After internal electrolysis, the BOD5/COD ratio of the wastewater was increased by about 3–5 times and concurrently an average COD removal efficiency of 90% was achieved. This was well below the discharge limit of 500mg/L set in the discharge standards.

5. Conclusions
(1) Berberine wastewater is a kind of organic wastewater with high concentration which is difficult to be biotreated. The pretreatment of berberine wastewater by iron-carbon micro-electrolysis method has a good effect.
(2) The experimental results show that under suitable reaction conditions, the removal rate of COD is as high as 90% in the pretreatment of berberine wastewater by iron-carbon micro-electrolysis, and the BOD5/COD of the wastewater increases from 0.08 to 0.41, which greatly improves the biodegradability of the wastewater. The effluent can be directly bio-treated in the deep well aeration tank of a pharmaceutical general factory wastewater treatment workshop.
(3) Pretreatment of berberine wastewater by iron-carbon micro-electrolysis method has the advantages of simple raw material, low consumption, low operation cost and simple operation.
(4) Treatment with iron-carbon micro-electrolysis oxidation improved the biodegradability and reduced the toxicity of the pharmaceutical wastewaters. Iron-carbon micro-electrolysis oxidation was an effective pretreatment method for the non-biodegradable portions of the pharmaceutical wastewater, which makes it easier to be biodegraded for subsequent biological process.

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