Multipurpose Utilization of Lixivium Obtained in Removing Iron from Quartz Sand

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Abstract-This paper reported the visible light decoloration rate of the solution, mixed methylene blue with the lixivium obtained in removing iron from quartz sand by ultrasonic treatment. The effect of the concentration of ethanedionic acid, time of treatment by ultrasound, the initial concentration of methylene blue and the volume of lixivium were investigated in details. The primary result showed that it was apparent improved in decoloration efficiency after mixed. And the decoloration rate improved more highly after visible light irradiation. The decoloration rate of mixed solution containing 20 ppm methylene blue got to 99.5% under the condition of $[H_2C_2O_4]$ 5g/L, treating by ultrasonic for 2.5h, using 30mL lixivium. It also had certain affection for the CODCr of lixivium. This process realized the multipurpose utilization of liquid waste.

Keywords-methylene blue; quartz sand; lixivium; removing iron; multipurpose utilization

I. INTRODUCTION
Quartz sand, which is called silica sand, is widely used in construction, glass ceramic and foundry industry, is a common nonmetallic mineral materials. It also plays an important role in many new and high technology industries, such as semiconductor technology, SiO2 thin-film material, atomic energy, optical fiber communication cable material and national defense science technology and so on [1-2]. According to the former researches, oxalic acid with ultrasonic wave for removing iron and aluminum from silica sand has a very good effect [1-5], avoids the high cost and harm to the environment. However, the soluble complex in lixivium, the possible composition, doing harm to the environment, is an environmental problem badly needed treatment.

Dye wastewater with deep chromaticity and high COD, is one of industrial wastewater which is difficult to deal. Thus the elementary task is decoloration. However, owing to the second pollution caused by the physicochemical and the biochemical methods, we should not abuse it. Actually the multistage series-connection dealing method of flocculent condensed precipitation-biological oxidation cannot meet the emission standard. Therefore, it seems a worthful issue to try to put forward a economical, efficient and effective treatment.

The experiment investigated decoloration rate of the mixed solution under visible light, which was consisted of lixivium and dye solution. The lixivium was got through the process of purifying silica sand by means of ultrasonic treatment. Then, our research work had focused on influence factors. The successful conclusion will provide a reference for making use of waste circularly for environment comprehensive management.

II. EXPERIMENTAL
A. Instruments and Reagent
CQ-500 ultrasonic cleaner, 721 spectrophotometer, electronic balance, centrifuge, magnetic stirrer, quartz sand, oxalic acid, methylene blue, silver sulfate, mercuric sulfate, sulfuric acid, potassium dichromate solution (0.250 mol/L), ferrous ammonia sulfate (0.010 mol/L).

B. Experimental Procedure
1) Preparation of Lixivium
To weight 10g silica sand, put 25mL 5g/L $H_2C_2O_4$, treat 2.5h with ultrasonic waves and filter.

2) Decolouration of Methylene Blue
The mixed solution made up of 60mL methylene blue (20ppm), 20mL lixivium and 20mL oxalic acid (5g/L), reacted 45min in the dark, 2h under visible light. Then, centrifuge and measure the absorbance of upper clear liquid at 665nm wavelength. Finally, the factors that influenced decolouration of methylene blue, including oxalic acid concentration, time of treatment by ultrasound, the initial concentration of dye solution and the volume of lixivium were studied in details.

3) Determination of Solution's CODCr
Measure the changes of solution’s CODCr before and after treatment by the method of $K_2Cr_2O_7$ [10].

III. RESULTS AND DISCUSSION
A. Decolouration of Methylene Blue by Lixivium

Fig.1 Decolouration of the Methylene Blue (20ppm) by Lixivium
Fig. 1 showed that it was apparent in decoloration efficiency of the new solution after 15min reaction in the dark. The decolouration rate had achieved more highly after irradiation. This indicated that lixivium of removing iron could decolour the solution obviously. In combination with the relevant literatures [7-9], oxalic acid with ultrasonic wave mainly removed FeOOH film from the surface of silica sand and when the added oxalic acid was excessive, Fe(II)-oxalic acid was the main product, which was high efficiency of photodissociation. Hydroxyl radicals (·OH), the photodissociation product of Fe(III)-oxalic acid, was a strong oxidizer, which could damage conjugate system of chromophores molecules to lead to fracturing double bond of dye molecules, so dye solution was decoloring.

B. Decolouration of Methylene Blue by Oxalic Acid

From Fig. 2, only oxalic acid, decolouration of mixture increased first and reduced later with the increasing of irradiation time. The maximum decolouration was about 20%. It maybe because methylene blue and oxalic acid formed a new compounds or occurred others reaction, such as tautomerism and so on to cause the change of absorbance [11].

C. Effect of Concentration of Oxalic Acid

Fig. 3 showed that the decolour rate was increased up to 98% and then tended to keep stable. So taking the economic benefit into consideration, the best concentration of oxalic acid was 5 g/L. The main reasons for the influence of oxalic acid concentration due to two aspects. On one hand, when the concentration increased, it was stronger to bonding “secondary iron” on the surface of silica sand with oxalic acid. In other words, it produced more Fe(III)-oxalic acid complexes. Under visible light, its photodissociation product (·OH), which has strong oxidizing activity, would be produced more and thus benifiting to decoloring. On the other hand, the concentration of oxalic acid decided the pH of the system. The competition direction on photochemical system was reaction of \( \text{H}_2\text{O}_2^-/\text{O}_2^- \) or reaction of Fe(III)/Fe(II), and that how about the production rate and the formation rate of activity species (·OH and \( \text{H}_2\text{O}_2^- \)) in system. Finally, it decided the oxidation.

D. Effect of Time of Treatment by Ultrasound

Fig. 4 showed that in the initial stages, the decolour rate increased with the increase of the time of ultrasound, while gently after the time of ultrasound was 2.5h.

Ultrasonic is a kind of high frequency vibration, it will make the internal pressure of liquid change while taking effect with liquid. It has two functions, stress and tension. When the pressure reached a certain value, it can make the liquid molecular rupture, produce cavitation effect, and cause millions of small bubbles at the same time. As the small bubbles burst, thousands even ten thousands of atmospheric pressure will be produced. The violent of atmospheric pressure against the solid particles in the liquid cause iron impurity being off from the surface of solid particles and into liquid to remove iron impurity [12]. In short, in a certain range of ultrasonic time, the longer ultrasonic time, the stronger shock wave, the better removal of iron impurity. The more Fe(III)-oxalic acid complexes, the better decoloration. However, when more than the range, it could not influence the amount of Fe(III)-oxalic acid any more for the fixed iron.
TABLE 1. THE CHANGE OF LIXIVIUM IN COD$_{Cr}$

<table>
<thead>
<tr>
<th>volume of lixivium (mL)</th>
<th>original COD$_{Cr}$ (mg/L)</th>
<th>final COD$_{Cr}$ (mg/L)</th>
<th>removal rate (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>609.0</td>
<td>168.4</td>
<td>72.4</td>
</tr>
<tr>
<td>30</td>
<td>609.0</td>
<td>258.3</td>
<td>57.6</td>
</tr>
</tbody>
</table>

impurity on the surface of silica sand. Neither could the decolouration [13, 14]

E. Effect of Initial Concentration of Dye Solution

The initial dye concentration is an important factor to the decolorization of dye. Fig. 5 showed that when the initial dye concentration ranged from 10 ppm to 50 ppm, the greater the initial concentration, the smaller the decolouration rate. This indicated that the system had a good bleaching, not to high concentration dye solution but to low concentration dye solution. However, combine used with other water treatment method, it is possibly to realize the deep treatment of high concentration dye wastewater [11, 12].

F. Effect of Volume of Lixivium

Fig. 6 showed the relationship between the volume of lixivium and its effect to the decoloration function of methylene blue. For the reason that the volume of lixivium influence the amount of oxalic acid complex directly and thus influencing the decoloration effect. When the volume is below 30 mL, the decolour rate increased obviously (takes on obvious increase) with the increase of volume, while flatten out if the volume reaches 30 mL. Therefore, we can draw a conclusion that the best volume of lixivium is 30 mL.

G. The Change of Lixivium in COD$_{Cr}$

According to table 1, after reaction under visible light, COD$_{Cr}$ of lixivium dropped from 609 mg/L to about 200 mg/L. That is to say, the removal rate for COD$_{Cr}$ of lixivium was significant. The highest removal rate could amount to 72.4%.

IV. CONCLUSION

In summary, after mixed the lixivium with dye solution, it was apparent in decoloration efficiency. The decoloration rate had achieved more highly after irradiation. Under the follow conditions, the concentration of H$_2$C$_2$O$_4$ is 5 g/L, treating by ultrasonic for 2.5 h, using 30 mL lixivium, the decoloration rate of mixed solution containing 20 ppm methylene blue was about 99.5%. And the highest removal rate for COD$_{Cr}$ of lixivium could be up to 72.4%. The results of this study have a good reference function, not only on performing energy conservation and emission reduction, but also on realizing to treat waste by waste.

ACKNOWLEDGEMENT

This work was financially supported by the Science and Technology Project of Fujian Province (No. CE0015) and Ningde Normal University projects on serving the western coast to the TW strait (No. 2010H103) and the Undergraduate Science and Technology Project of Fujian Normal University (No. BKL2010-037).

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