

# Fe-doped carbon aerogels from sodium alginate for the removal of methylene blue

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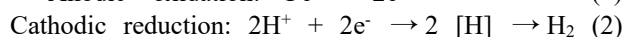
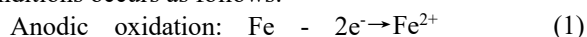
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**Abstract.** In this article, Fe-doped carbon aerogels from sodium alginate were used for the removal of methylene blue (MB) in water. Under acidic condition, the sample carbonized at 700 °C (T700) undergoes Fe-C micro-electrolysis to produce highly chemically active Fe<sup>2+</sup> and [H] to degrade MB. Under neutral or alkaline conditions, Fe<sup>2+</sup> produced by Fe-C micro-electrolysis become Fe(OH)<sub>3</sub>, which can effectively adsorb MB. In addition, when T700 combines with H<sub>2</sub>O<sub>2</sub> to form Fenton system, the MB removal efficiency was significantly improved. The Fe-doped carbon aerogels can be used in wastewater treatment and when combine the materials with H<sub>2</sub>O<sub>2</sub> can greatly improve the MB removal efficiency.

## 1 Introduction

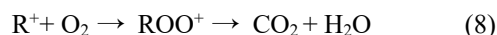
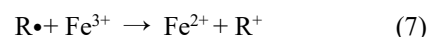
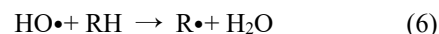
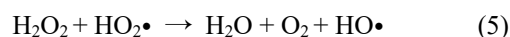
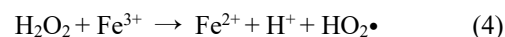
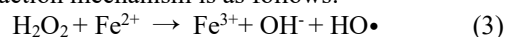
MB is a commonly used dye which is widely used in industrial and medical fields. However, the extensive application of MB produced a large amount of industrial wastewater. High concentrations of MB can poison or even die animals. Therefore, MB treatment is one of the current research focuses in the field of wastewater treatment. MB treatment includes biological [1,2], physical [3,4] and chemical [5,6] methods. Chemical method includes chemical oxidation, electro-oxidation, photo-oxidation, and ultrasonic oxidation, etc., which is a hot research for MB wastewater treatment.

Fe-C micro-electrolysis is an economical and environmentally friendly wastewater treatment technology, which is widely used in the treatment of high-concentration organic wastewater [7-10]. When iron filings and carbon particles are immersed in acidic wastewater, numerous micro-galvanic cells are formed in the wastewater due to the electrode potential difference between iron and carbon (1.2V). Low-potential iron becomes the anode, and high-potential carbon becomes the cathode. The electrochemical reaction under acidic conditions occurs as follows:



The Fe<sup>2+</sup> and [H] produced by the reaction have high chemical activity can change the structure of organic substances in wastewater. However, the reaction time of Fe-C micro-electrolysis is long. Fenton reaction is a simple and efficient wastewater treatment technology [11-13]. This process is based on the reaction of H<sub>2</sub>O<sub>2</sub> and Fe<sup>2+</sup> to produce highly oxidizing hydroxyl radicals (•OH) to degrade organics in wastewater.

The reaction mechanism is as follows:



Therefore, the combine of Fe-C micro-electrolysis and Fenton reaction will effectively improve their respective problems.

In this paper, The Fe-doped carbon aerogels were employed to treat MB in wastewater. The materials have broad application prospects in the field of wastewater treatment because they use environmentally friendly sodium alginate as raw material, the preparation process is simple, and the MB removal efficiency in wastewater is high.

## 2 Materials

Sodium alginate, Fe(NO<sub>3</sub>)<sub>3</sub>, was purchased from Aldrich Co. MB was purchased from Damao Chemical Reagent Factory. H<sub>2</sub>SO<sub>4</sub> and NaOH were purchased from Tianjin Fengchuan Chemical Reagent Technologies Co., Ltd.

### 2.1 Materials preparation

Fe-doped carbon aerogels were synthesized as followings: sodium alginate was dissolved in H<sub>2</sub>O (solution A) and Fe(NO<sub>3</sub>)<sub>3</sub> was dissolved H<sub>2</sub>O (solution B). Solution A and solution B were mixed to obtain sodium alginate hydrogels. The hydrogels were placed in a freeze dryer

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obtain aerogels. Then the aerogels were transferred in a carbonization furnace at 500, 600, 700, 800, and 900 °C (the corresponding sample is named as T500, T600, T700, T800, and T900, respectively).

## 2.2 Characterization

The XRD patterns of the carbon aerogels were monitored by an Ultima X-ray diffractometer under copper K $\alpha$  radiation at 40 kV and 40 mA. A TU-1900 UV-vis spectrometer was used to measure the concentration of MB at 665 nm. The total iron content was measured using the TU-1900 UV-vis spectrometer at 510 nm according to iron-phenanthroline spectrophotometry.

## 2.3 Removal experiments

In the Fe-C micro-electrolysis experiments, 50 mg Fe-doped carbon aerogels were added to 50 ml MB aqueous solution (50 mg L<sup>-1</sup>) at 25 °C, pH=2.5. The pH was selected as the variable operating parameter to investigate the removal efficiency of MB. The pH was adjusted by H<sub>2</sub>SO<sub>4</sub> and NaOH. The MB removal efficiency was calculated using the following equation:

$$D(\%) = (C_0 - C_t) / C_0 \times 100 \quad (9)$$

where C<sub>0</sub> is the initial MB concentration (mg L<sup>-1</sup>) and C<sub>t</sub> is the MB concentration at time t (mg L<sup>-1</sup>).

In the Fenton experiments, 12 mg T700 was added to 40 ml MB aqueous solution (50 mg L<sup>-1</sup>) with H<sub>2</sub>O<sub>2</sub> was added at 25 °C, pH=2.5.

## 3 Result and Discussion

The MB removal efficiency of Fe-doped carbon aerogel samples are shown in Fig 1. After 9 h, the MB removal efficiency of T500, T600, T700, T800 and T900 is 20.1%, 25.4%, 96.0%, 94.7% and 93.0%, respectively. It can be seen that the MB removal efficiency of T500 and T600 is significantly lower than other samples. And the MB removal efficiency of samples T700, T800 and T900 are higher than 92% after 9 h. In addition, T700 has the best MB removal efficiency that can reach 96.0% after 9 h.

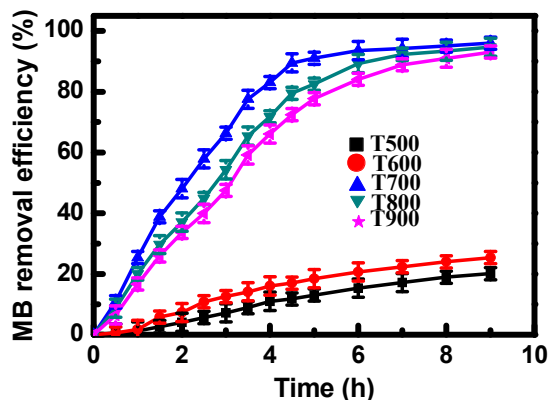


Figure 1. The MB Removal efficiency of Fe-doped carbon aerogels.

pH has a significant effect on Fe-C micro-electrolysis, so pH was selected as the operating parameter to investigate the MB removal efficiency of T700. As shown in Fig. 2, T700 has substantial MB removal efficiency under different pH conditions. This may be due to under acidic conditions, T700 produces highly chemically active Fe<sup>2+</sup> and [H] by Fe-C micro-electrolysis. Fe<sup>2+</sup> and [H] have strong oxidizing properties which can destroy the molecular structure of MB. And the stronger the acidity, the better the MB removal efficiency of T700. Under neutral or alkaline conditions, precipitation occurs in the MB solution as shown in the illustration in Fig. 2. And as the pH increases, the amount of precipitation increases. It is due to that Fe<sup>2+</sup>/Fe<sup>3+</sup> formed by iron-carbon micro-electrolysis react with OH<sup>-</sup> in the solution to form Fe(OH)<sub>2</sub>/Fe(OH)<sub>3</sub> precipitate. MB can form monovalent cationic quaternary ammonium groups in solution, while the Fe(OH)<sub>3</sub> colloid is negatively charged, so the material can effectively adsorb MB under neutral or alkaline conditions.

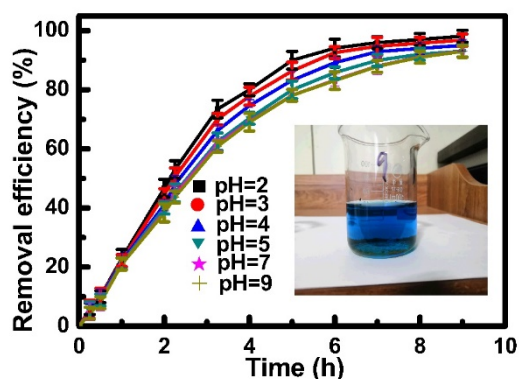
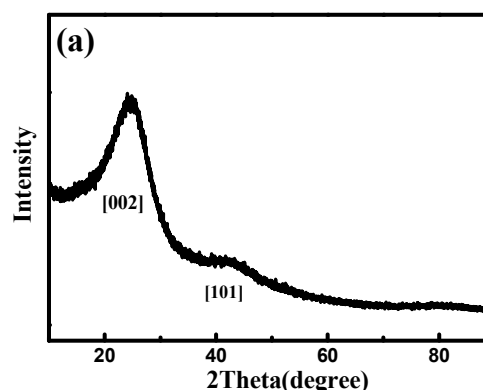
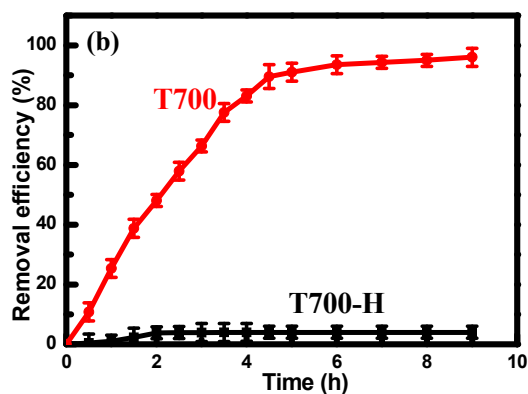


Figure 2. The pH effect on MB removal efficiency of T700.

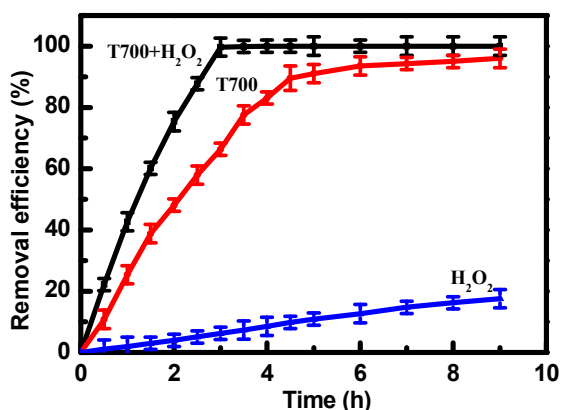
In order to confirm that the removal of MB by the sample is mainly caused by Fe-C micro-electrolysis, T700 was washed by HCl (named as T700-H). Fig. 3a shows the XRD pattern of T700-H. It can be seen that the peaks of Fe in the sample have disappeared, and only the peak of graphitic carbon remains. Fig. 3b shows the MB removal efficiency of T700 and T700-H. The MB removal efficiency of T700-H is only 4.1% while the MB removal efficiency of T700 is 96.0% after 9 h. It can be concluded that the removal of MB by T700 is mainly caused by Fe-C micro-electrolysis.





**Figure 3.** (a) XRD pattern of T700-H and (b) the MB removal efficiency of T700 and T700-H.

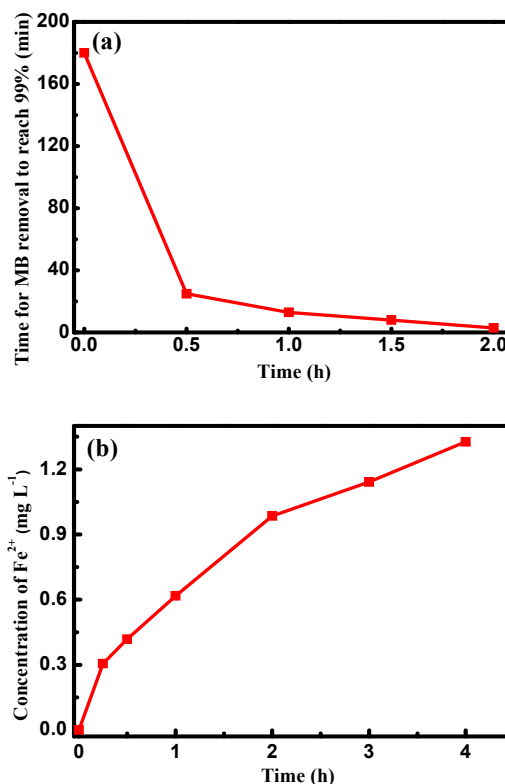
$Fe^{2+}$  produced by Fe-C micro-electrolysis can form a Fenton system with  $H_2O_2$  to improve the MB removal efficiency. In order to confirm the efficient removal efficiency of the Fenton system, a comparative experiment was performed. Fig. 4 shows the result of the comparative experiment. It can be seen that the MB removal efficiency of T700+ $H_2O_2$  can reach 99.7% after 3 h while the MB removal efficiency of T700 and bare  $H_2O_2$  are 66.3% and 6.3%, respectively. It can be concluded that adding  $H_2O_2$  to T700 can effectively improve MB removal efficiency.



**Figure 4.** The MB removal efficiency of T700+ $H_2O_2$ , T700 and  $H_2O_2$ .

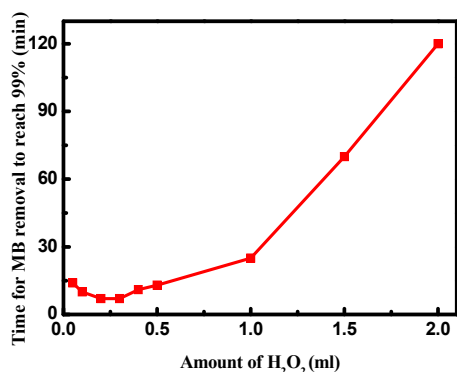
The addition time of  $H_2O_2$  is a key factor affecting the Fenton reaction. Figure 5a shows the time required for sample T700 to remove more than 99% MB by adding 0.5 ml  $H_2O_2$  after Fe-C micro-electrolysis at different times. Figure 5a shows that the longer the time of the Fe-C micro-electrolysis reaction, the higher MB removal efficiency after adding  $H_2O_2$ . The removal rate of MB reached 99% in 180 min when  $H_2O_2$  and T700 were added at the same time, but reached 99% in only 3 min when  $H_2O_2$  was added after 2 hours of T700 added. This result may be because the concentration of  $Fe^{2+}$  produced by Fe-C micro-electrolysis gradually increases with time, which promotes the Fenton reaction and improves the MB removal efficiency. To further prove this speculation, the concentration of  $Fe^{2+}$  in solution was determined at different times during Fe-C micro-electrolysis. Figure 5b shows that the concentration of  $Fe^{2+}$  in the solution

increases with increasing Fe-C micro-electrolysis time. With increased Fe-C micro-electrolysis time, the MB removal efficiency is better after adding  $H_2O_2$ . But adding  $H_2O_2$  after 0.5 hours of T700 added shows the shortest total time of MB removal to 99%.



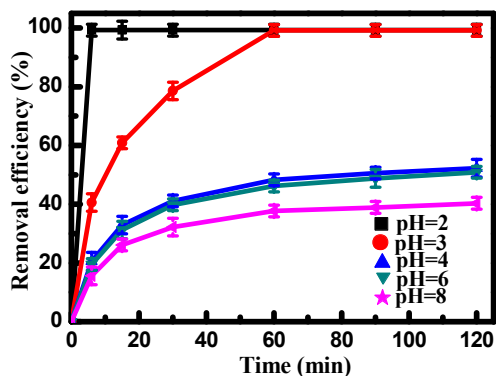
**Figure 5.** (a) The time of  $H_2O_2$  added after T700 added and (b) the concentration of  $Fe^{2+}$  produced by Fe-C micro-electrolysis.

The amount of  $H_2O_2$  added is an important factor affecting the Fenton reaction. Therefore, the experiment that investigated the effect of adding different amounts of  $H_2O_2$  on the MB removal efficiency after 0.5 hours of Fe-C micro-electrolysis was applied. As shown in Figure 6, with increased  $H_2O_2$ , the MB removal efficiency is increase. But the MB removal efficiency is decreased when the amount of  $H_2O_2$  is more than 0.4 ml. This difference may be because when the initial concentration of  $H_2O_2$  is low, increasing the amount of  $H_2O_2$  can effectively promote the Fenton reaction. However, when the concentration of  $H_2O_2$  is too high, the hydrogen peroxide will be invalid decomposed, which will inhibit the progress of the Fenton reaction. The Fenton reaction can efficiently degrade organic pollutants in wastewater due to the strong oxidation ability of  $\bullet OH$ . To determine the important role played by  $\bullet OH$ , a set of comparative experiments were conducted. After 0.5 hours of Fe-C micro-electrolysis,  $H_2O_2$  was directly added to sample 1, and two drops of isopropanol (a hydroxyl radical quencher) were added to sample 2, followed by  $H_2O_2$  added. The MB solution in sample 1 changed from blue to colourless in 7 min, and the MB solution in sample 2 did not change significantly even after 2 h. The comparative experimental results show that  $\bullet OH$  plays an important role in the MB removal.



**Figure 6.** Effect of the amount of H<sub>2</sub>O<sub>2</sub> on MB removal efficiency.

PH of the solution is another important factor affecting Fenton reaction. Figure 7 shows the effect of pH on the MB removal efficiency that adding H<sub>2</sub>O<sub>2</sub> after 0.5 hours of T700 added. It can be seen that the MB removal efficiency can reach 99% only in 6 min at pH=2. When the pH of the solution is greater than 4, the MB removal efficiency is much lower than 99% after 120 min. This is because Fe<sup>3+</sup> can generate Fe(OH)<sub>3</sub> precipitation at pH = 3.7 that leads to a decrease of Fe<sup>3+</sup> content in the solution. Thus Fe<sup>3+</sup> cannot be converted to Fe<sup>2+</sup>, resulting in a sharp decrease of Fe<sup>2+</sup> in the solution, thereby inhibiting the Fenton reaction.



**Figure 7.** Effect of pH on MB removal efficiency.

## 4 Conclusions

In summary, The Fe-doped carbon aerogel were used for the MB removal in wastewater. The MB removal efficiency of T700 could reach 96.0% after 9 h. T700 was selected for further research considering the energy consumption and the MB removal efficiency. Furthermore, the materials have good MB removal efficiency at different pH. T700 was also used in combination with H<sub>2</sub>O<sub>2</sub>. The MB removal efficiency can reach to 99% in 3 min under the conditions that pH=2 and 0.2 ml H<sub>2</sub>O<sub>2</sub> was added after 0.5 h of Fe-C micro-electrolysis reaction, These novel Fe-doped carbon aerogels will have broad application prospects in the field of wastewater treatment due to the environmentally friendly raw material, simple preparation process, and efficient removal of organics in wastewater.

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