Study on Decolorization of Methylene Blue by H_2O_2 Catalyzed with Iron-loaded Hydrated Cement Particles

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Abstract. In this study, a new type of heterogeneous catalyst based on cement matrix composite was developed. Hydrated cement particles (HCP) were used as the carrier material to immobilize the ferric iron produced by Fe^{2+}/H_2O_2 system. Iron load bearing by new catalyst was calculated to be about 130.5mg/g. The formation of iron compounds were verified by scan electron microscopy and energy dispersive spectroscopy. Due to there was no thermal treatment, the main constituents of iron phases were estimated to be the amorphous ferric hydroxide or hydrated ferric oxide. On this basis, the catalytic performances of new catalyst on methylene blue were investigated. Results showed that, for 50mg/L methylene blue solution, when the adding dosage of the catalyst and peroxide were of 100g/L and 100mM, the catalytic decolorization rate at room temperature on 9h reached 90.4%. The decolorization rate increased with the increase of the dosage of hydrogen peroxide. When the dosage of hydrogen peroxide was 250mM, the highest decolorization rate on 9h reached 98.7%. This result was about 74% higher than the catalytic efficiency of only peroxide. In addition, the new catalyst showed strong adaptability to pH value. On the whole, the decolorization efficiencies of MB at the acid conditions were superior to at the alkaline conditions. Circulating decolorization results demonstrated that the catalytic performance of iron-loaded HCP could keep relatively stable at original pH conditon of MB mixture solution.

Introduction

Fenton process has been successfully put into use for removal of recalcitrant organic contaminants [1]. However, there are some drawbacks encountered by this process, for example, pH-dependence of the system and formation of ferric hydroxide sludge. To solve these problems, several heterogeneous catalysts have been employed in Fenton reactions such as iron pillared clays [2], iron containing zeolites [3] and iron minerals [4]. A large number of studies have shown that heterogeneous Fenton reactions could overcome the shortcomings of homogeneous catalysis.

  Ordinary Portland cement (OPC) is widely used building material, and it is a complex mixture of tricalcium silicate (C_3S), dicalcium silicate (C_2S), tricalcium alumiunate (C_3A), tetracalcium aluminoferric (C_4AF), gypsum, and other minor phases. It's well known that OPC owns excellent chemical activities and could initiate hydration reaction with water. During hydration process, some new products formed, including calcium-silicate-hydrate (C-S-H) gel, portlandite, ettringite and calcium monosulfate (Afm). Portlandite still can react with CO_2 to form calcium carbonate. In recent years, more and more attentions have been paid to the application of cement hydration products in environmental pollution control. To sum up, most of reports mainly focus on two aspects. One is as adsorbents to remove the inorganic anion of wastewater, such as floride, phosphate and nitrate [5-6]. Another is used as fixing agent for heavy metals to limit them further migration and transformation in nature [7]. There are seldom mentions about adopted hydrated cement products as carrier to prepare catalyst. Taking into account the cement hydration products of portlandite and calcium carbonate can play buffer roles at acid conditions, we believe iron ion in solution are much easier to form ferric hydroxide and then deposite on the solid surface. So, in this study, a novel composite hydrated cement particle（HCP）was prepared and used as the carrier

material to immobilize the ferric iron produced by Fe^{2+}/H_2O_2 system.

The mian purposes of this study were，(1) to study the load charateristics of iron upon HCP；(2) to investigate the catalytic performance of load-iron HCP by the decolorization test of methylene blue.

Materials and Methods

Preparation of Iron-loaded Hydrated Cement Particles (IHCP)

Main raw materials for the preparation of cement particles include ordinary Portland cement clinker, calcium base bentonite, quartz sand and water. Among them, the doping ratio (mass) of cement clinker, Ca-bentonite and quartz sand is 4:2:1. The mass ratio of water and total solid materials is 1:2. Detailed processing steps are as follows, mixed materials added with water be stirred evenly, and then extruded into round bars with 3mm in diameter. After dried 72h at room temperature, round bars are cut into cylinder particles of length 0.5-2cm. Afterwards, the particles are soaked with tap water twenty days. In order to lower the alkalinity of particles, the water be replaced one time every day. Twenty days later, particles are taken out, and dried forty days at room temperature again. Finally, solid particles become hydrated cement particles (HCP). 50g of HCP are immersed into 50mL ferrous sulfate solution (0.2mM), and 1mL hydrogen peroxide (mass fraction 30%) be added. After soaked 12h, the particles be taken out and leached with distilled water 3 times. Through 48h natural dry, that is to get iron-loaded hydrated cement particles (IHCP). Appearances of HCP and IHCP are shown in Fig.1.

Fig.1 Appearances of HCP and IHCP

By detected the concentration of iron ion in ferrous sulfate solution before and after immersion, iron load could be calculated. Specific calculation method sees equation (1).

$$M_{Fe} \ (\mathrm{mg/g}) \ = \frac{C_0 \times V_0 - C_1 \times V_1}{50} \tag{1}$$

Where, M_{Fe} represents the load of iron, mg/g; C_0, V_0 and C_1, V_1 represent the concentrations (mg/L) of iron ion and volumes (L) of ferrous sulfate solution corresponding before and after immersion. The concentration of iron ion is determined by Ortho-phenanthrene molecular absorption spectroscopy.

Characterization

The morphological features and surface characteristics of samples were obtained from scanning electron microscopy (SEM)（Hitachi SU-70，Japan). Elements composition of samples were examined by Energy Dispersive Spectrometer（EDS）（HORIBA EX250，Japan）.The samples were coated with gold by electro-deposition under vacuum prior to analysis.

Decloriztion Performance Test

In this experiment, cationic dye methylene blue (MB) was selected as treat object. The molecular formula of MB is $C_{16}H_{18}N_3SCl$. During the whole experiment, the initial concentration of methylene blue solution was 50mg/L (pH=6.7). The adding dosage of IHCP was 100g/L. The

temperature and time of reaction were controlled at 25℃ and 9h.

The first phase of the experiment was to investigate the effect of adding dosage of H_2O_2 on decolorization efficiency. The initial concentration range of hydrogen peroxide of solution was 100-250mM. In the second stage, the effect of pH value on decolorization efficiency was studied. The range of pH value was controlled between 3 and 13. 1M HCl and 1M NaOH were used to adjust pH value. The third stage mainly focused on determines the ability of IHCP on continuous catalytic decolorization. Under the condition of no adjust pH value, IHCP needed to treat MB solution 6 times continuously, and the change of the efficiency of decolorization was observed.

MB concentration in the solution was determined by measuring the absorbance of the solution at 665 nm (λmax for MB), using a UV–vis spectrophotometer (UVT6, Beijing Purkinje General Instrument Co. Ltd, China). The color removal rate was calculated based on the following equations (2).

$$Color\ removal\ (\%) = \frac{C_0 - C_t}{C_0} \times 100\%$$

.   (2)

Where, C_0 (mg/L) and C_t (mg/L) are MB concentrations at the initial time and time t (h).

Results and Discussion

Loading Characteristics of Iron

Surface morphology and elemental analysis about HCP were shown in Fig.2 and Fig. 4(a) (b). It could be observed that, through 63 days hydration, calcium carbonate had occupied the majority surface area of HCP. Calcium carbonate was the main transformation products of portlandite. In additon to Ca, C and O, some other elements such as Al, Mg and Si were also being detected, but there was no iron element be found. After the load, the surface morphology of HCP became much smoother, and there was a large number of spherical and ellipsoidal substances formed (Fig.3). EDS checking results could testify these substances were ferric compounds (Fig. 4(a) (b)). It's worth noted that, after the load, the calcium carbonate of HCP were converted to calcium sulfate.
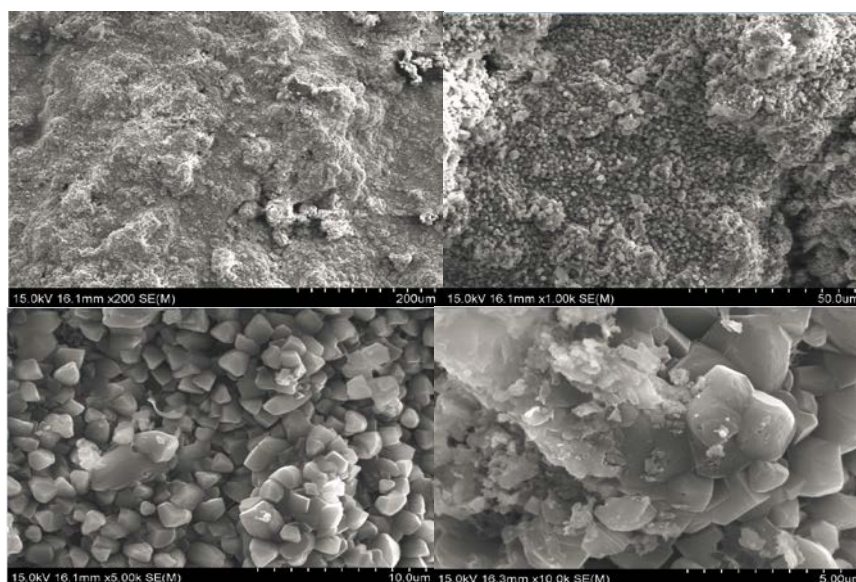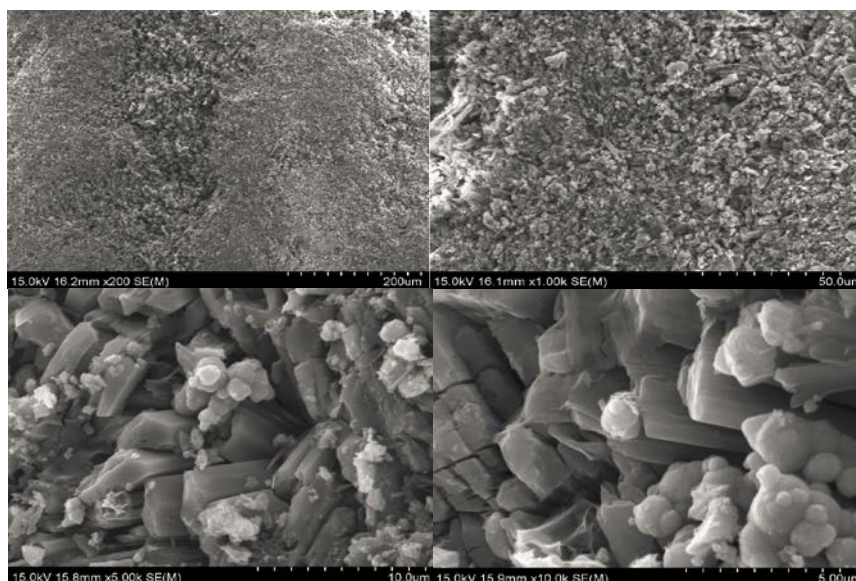

Fig.2 Surface morphology of HCP

Fig.3 Surface morphology of IHCP

According to these results, we can deduce the loading mechanism of iron on the HCP in Fe^{2+}/H_2O_2 system. That is, calcium carbonate reacted with H^+ of the solution firstly, and then, following the increase of the pH value around the interface of solid-liquid, the ferric ions produced by the fenton reaction were induced to form hydroxide ferric in the surface of the calcium carbonate. Due to there exist a lot of SO_4^{2-} within the acid solution, calcium carbonate inclined to be replaced by the calcium sulfate. With regard to the compositions of ferric compounds, we speculated amophous ferric hydroxides or hydrated ferric oxides were the main constituents because there was no thermal treatment during dry process. By the calculation of equation (1), it was determined that the iron load on HCP was 130.5 mg/g.
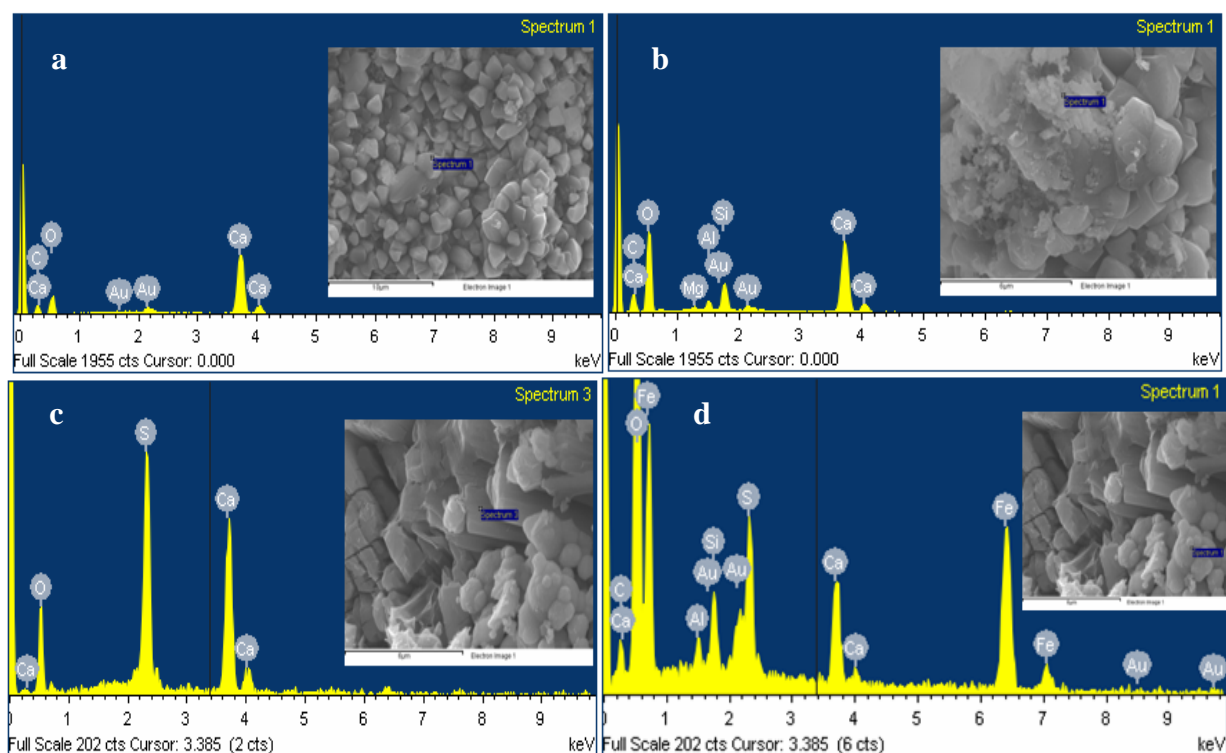

Fig.4 Energy spectrum analysis of HCP and IHCP (a, b HCP c, d IHCP)

Effects of Peroxide Dosage on Decolorization

The decolorization profile of MB on the different peroxide dosage was shown in Fig.5. It can be seen that，for the range of peroxide dosage from 100mM to 250mM, the decolorization efficiency of MB show the tendency of increase. When the dosage of peroxide was 250mM, the decolorization rate of MB on 3h reached 88.5%, and the highest decolorization rate on 9h could reach 98.7%. This result was much higher than the decolorization efficiency of only peroxide (The highest decolorization rate was only 25%, data not show). The buildup of decolorization efficiency should be attributed to the catalytic decompose roles of ferric compounds on the peroxide. Much more hydroxyl radicals were produced from IHCP/H_2O_2 system and this could enhance the attack efficiency on methylene blue.

Effects of pH Value on Decolorization

When the dosage of peroxide was 100mM, the initial pH value of MB mixture solution was about 6. By adjusting the pH value to 3, 5, 9, 11 and 13, the changes of decolorization rates of MB were recorded in Fig.5 (b). Obviously, the decolorization efficiencies of MB at the acid conditions were superior to at the alkaline conditions. When the pH value lowered to 3, the highest decolorization rate of MB on 9h increased to 97.6%. However, as the pH value rose to 13, the highest rate of MB reduced to 85.6%. For the range of pH value from 5 to 9, the decolorization rates of MB were maintained at 90% approximately. It was analyzed that the improvements of the decolorizaiton efficiency at acid conditions maybe originate from the dissolution of the ferric compounds. While at alkaline conditions, hydroxide ions incline to consume much more hydroxyl redicals, and lead to the decline of decolorizaiton efficiency.
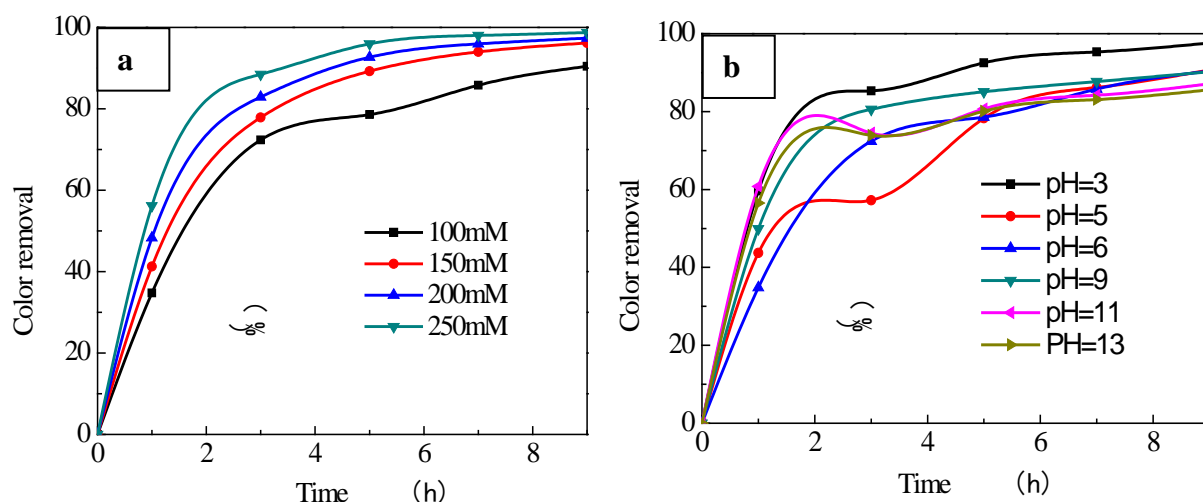

Fig.5 The change of decolorization rate follows H_2O_2 dosage and pH (a, H_2O_2 b, pH)

Effect of Continuous Operation on Decolorization

The decolorizaiton effects of the methylene blue under the conditions of continuous operation were shown in Fig.6. For the dosage of peroxide was 250mM and the initial pH value of MB mixture solution was 5.8, the decolorizaiton rates of the methylene blue reduced from 98.7% to 94.7% through 6 times continuous use of IHCP. On the whole, the catalytic performance of IHCP kept relatively stable at original pH conditon of MB mixture solution. About 4% of reduction of decolorizaiton rate was maybe caused by the loss of the ferric compounds. The oxygen produced by heterogeneous fenton reaction would scour the surface of IHCP and cause part of ferric compounds fall off.

Conclusions

Through this study, the following conclusions can be drawn:

(1) HCP as carrier material could efficiently load the ferric produced by Fe^{2+}/H_2O_2 system. The calucium carbonate formed by the surface of HCP play an important role on the load of iron. The constituents of ferric compounds are mainly amorphous iron phases.

(2) IHCP owns excellent performance of catalytic decomposition of peroxide. For the dosage of peroxide of 250mM, the highest decolorization rate of MB on 9h reached 98.7%. This result was about 74% higher than the catalytic efficiency of only peroxide.

(3) IHCP showed strong adaptability to pH value. On the whole, the decolorization efficiencies of MB at the acid conditions were superior to at the alkaline conditions.

(4) The catalytic performance of particles could keep relatively stable at original pH conditon of methylene blue mixture solution, but the oxygen produced by heterogeneous fenton reaction still has some certain negative impacts on the stability of catalyst.
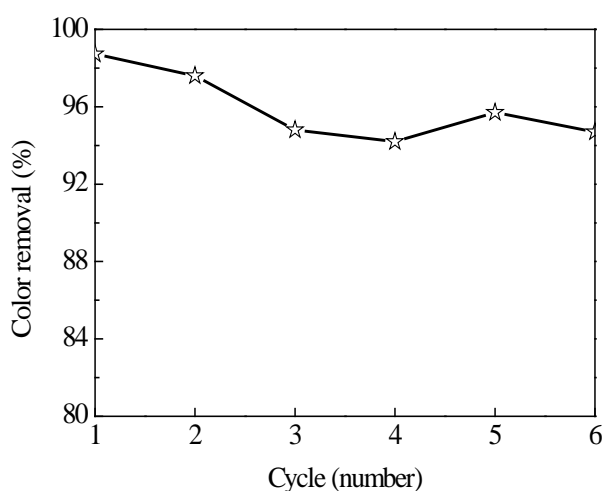

Fig.6 Change of decolorization rate under continuous operating conditions

Acknowledgements

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