Decoloration behavior of hydrolyze sediment of ferric salt doped with magnetite on dye wastewater

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Abstract. Based on the strong adsorption capacity of colloidal precipitate formed by hydrolysis of iron salts (FHCP), a kind of composite material of FHCP/Fe3O4 was prepared and used in the decoloration of dye wastewater. The results showed that FHCP/Fe3O4 had high decolorization efficiency for anionic dyes. FHCP/Fe3O4 was more suitable for the decolorization of anionic dyes in acidic environment. The impact order of foreign ions on the decolorization performance of FHCP/Fe3O4 was as follows, that is HCO3- > SO42- > Cl-. The fitting of adsorption kinetic of anionic dyes on FHCP/Fe3O4 matched with the pseudo-second-order kinetic equation.

1. Introduction
Iron salt is a commonly used coagulant in water treatment. The reason why iron salts are popular, in addition to their good coagulation effects, the convenient preparation and low cost of the products are also important factors. When iron salt is added to water, iron ions will hydrolyze rapidly to form a series of metal complexes containing hydroxyl groups. Because these hydrolyzates are charged positively, they have strong affinity for the anions and negatively colloidal particles in water.

As the coagulant, there are some problems in the practical application of ferric salt, such as the difficult control of hydrolysis speed, the inadaptability to low temperature conditions, and the strong acid corrosion to equipment and pipelines. Based on these problems, in recent years, many researchers have focused on the colloidal precipitates formed by the hydrolysis of iron salts. The results show that the hydrolytic colloidal precipitate of ferric salt (FHCP) still has good adsorption performance. Gao et al.[1] used iron precipitates arising from drinking water treatment process as phosphorus removal reagent, and found that these precipitates had strong adsorption for orthophosphate, polymerized phosphorus and organic phosphorus. In addition, Wang et al.[2] compared the phosphorus removal efficiency of iron-rich water treatment sediment with natural adsorbents (zeolite and diatomite), and confirmed that the phosphorus adsorption capacity of iron rich sediment was much larger than that of natural adsorbent. In addition to phosphate, FHCP also showed a good adsorption effect on some other oxygen-containing anions such as trivalent arsenic, pentavalent arsenic, tetravalent tin, pentavalent vanadium and hexavalent chromium[3-6]. Compared with the original ferric salt products, FHCP used as coagulation reagent is easier to control the reaction conditions and helps to overcome the strong acid corrosion problem. In the past reports on coagulation reaction of dye wastewater, it is rarely mentioned the application of FHCP.

In order to further explore the adsorption characteristics of FHCP, we have carried out some adsorption experiments for the simulation of soluble dye wastewater in the early stage. The preliminary results showed that the colloidal precipitate formed by ferric chloride solution at pH
4.0-4.5 has high decoloration efficiency for anionic dye, but unfortunately, the settling performance of flocs is not ideal. Therefore, we adjusted the experimental method and doped a small amount of magnetite into the colloidal precipitate. It was found that the composite colloidal precipitate showed good solid-liquid separation characteristics in the external magnetic field (figure 1). There have some reports about the compound usage of adsorbents with magnetite in dye wastewater, such as graphite[7], wheat straw[8] and montmorillonite[9]. In these studies, magnetite mainly played the role of high-efficiency magnetic separation. Up to now, there are few reports about the compound usage of magnetite and FHCP.

In order to better promote the actual industrial application of FHCP, this paper conducts the study of the coagulation of FHCP/Fe$_3$O$_4$ composite. The main goal is to investigate its adsorption performance for dye wastewater, including the main factors affecting the decoloration efficiency and the adsorption kinetics behavior.

2. Experimental materials and methods

2.1. Reagents and drugs
The reagents used in the experiment are all analytically pure grade. FeCl$_3$.6H$_2$O and NaOH were purchased from Sinopharm Chemical Reagent Co., Ltd. Fe$_3$O$_4$ was purchased from Tianjin Zhiyuan Chemical Reagent Co., Ltd; KH$_2$PO$_4$ was purchased from Shanghai Guangnuo Chemical Technology Co., Ltd.

2.2. Preparation of FHCP/Fe$_3$O$_4$
500mL 0.1mol/L FeCl$_3$ solution was prepared at room temperature and 5g of Fe$_3$O$_4$ was added. After rapid stirring uniformly, 1.0mol/L NaOH solution (120mL) was used for titration. The stirring intensity was set to medium speed and the titration speed was controlled to 5mL/min. After titration, the mixed solution of colloidal precipitate was obtained. The pH value of the solution was detected as 4.58. The supernatant was removed after sedimentation for 3 hours, and the final volume was controlled at 250 mL. Store the prepared solution in polyethylene bottle for standby. By differential weight method, it can be determined the wet solid content of FHCP/Fe$_3$O$_4$ solution was 0.22g/mL.

2.3. Phosphorus adsorption experiment
The experimental apparatus of adsorption is shown in figure 2. The main reactor is a 1L covered polyethylene bottle. The supporting equipment includes liquid adding funnel, siphon and agitator.

![Figure 1. Magnetic separation of colloidal precipitate](image)

![Figure 2. Adsorption experimental apparatus](image)

Prepared 10mg/L of dye solution, and injected 500mL of dye solution into the reactor through the feeding funnel, then added 5mL FHCP/Fe$_3$O$_4$ solution, start the stirring device, and set the stirring speed to low speed. Through the constant temperature water bath control system, the reaction temperature is 20℃. The reaction time was set at 90 minutes. During the reaction, 50 mL of the mixture was extracted from the siphon every 10 minutes, and the supernatant was taken to measure the
pH value and absorbance. In order to avoid the interference of fine particles, the supernatant should be filtered with 0.45μm membrane when measuring the absorbance. After the detection, all the remaining mixture was poured back to the reactor to continue to participate in the reaction.

Based on the above operation steps, we firstly investigated the decolorization effect of FHCP/Fe₃O₄ on four different dyes including reactive brilliant blue KNR, acid black 10B, acid red B and methylene blue. After that, we selected the best decolorization dye as the object to further investigate the effect of pH value and foreign ions on the decoloration performance of FHCP/Fe₃O₄. During the experiment, the dosage of FHCP/Fe₃O₄ was set as 1.0% (volume ratio), the pH value was set as 3-12, and the dosage of foreign ions was set as 1mmol-10mmol.

The absorbance of the solution was determined by visible spectrophotometer (model, T6 new century, general analysis), and the pH value of the solution was recorded by digital pH meter (model, pHs-25, Shanghai Leici). The maximum absorption wavelengths of reactive brilliant blue KNR, acid black 10B, acid red B and methylene blue are 595nm, 620nm, 514nm and 665nm, respectively.

The calculation formula of dye decolorization rate is as follows,

\[ R = \frac{C_0 - C_t}{C_0} \times 100\% \]  

Where, \( C_0 \) is the initial concentration of dye, mg/L; \( C_t \) is the concentration of dye at time t, mg/L.

2.4. Adsorption kinetics model
The adsorption kinetics mainly referred to the pseudo-first-order and pseudo-second-order model [9].

The formula of pseudo-first-order model is as follows,

\[ \ln (q_e - q_t) = \ln q_e - \frac{k_1}{2.303}t \]  

Where, \( q_e \) and \( q_t \) are the adsorption capacity at equilibrium and time t, mg/g; \( k_1 \) is the first order adsorption rate constant, min⁻¹.

\[ \frac{t}{q_t} = \frac{1}{(k_2 \cdot q_e^2)} + \frac{t}{q_e} \]  

Where, \( k_2 \) is the second order adsorption rate constant, g/(mg·min).

3. Experimental results and discussion
3.1. Decolorization of different dyes
The decolorization of four dyes by FHCP/Fe₃O₄ was shown in figure 3. It can be seen that the decolorization effect of FHCP/Fe₃O₄ on anionic dyes is obviously better than that of cationic dyes. Among the three anionic dyes, anthraquinone reactive brilliant blue KNR has the best decolorization efficiency. Its highest decolorization rate reached 99.4% in 90 min. Acid black 10B and acid red B are both azo dyes. In contrast, the decolorization effect of acid black 10B was better, and the highest decolorization rate reached 96.8%. The highest decolorization rate of acid red B was 96.1%. Methylene blue belongs to cationic dye. Its molecular structure is positively charged in aqueous solution. So there has strong electrostatic repulsion between methylene blue and FHCP/Fe₃O₄ surface active sites. As shown in Figure, the decolorization rate of methylene blue in the first 60 minutes was low and had a large fluctuation. It was relatively stable in the later 30 minutes and the highest decolorization rate was about 60%.

3.2. Kinetic calculation
The adsorption processes of FHCP/Fe₃O₄ for three anionic dyes were fitted by pseudo-first-order and pseudo-second-order kinetic model (Table 1). By comparing the \( R^2 \) value of correlation coefficient, it can be judged that the adsorption process was more in line with pseudo-second-order kinetic model. This also means that the adsorption processes of FHCP/Fe₃O₄ for these anionic dyes are controlled by chemical adsorption[10].
Table 1. Kinetic parameters of the fitting of adsorption process

| Dye name                  | Pseudo-first-order | Pseudo-second-order |           |
|---------------------------|--------------------|---------------------|-----------|
|                           | $q_e$ (mg/g)       | $k_1$ (min$^{-1}$) | $R^2$     | $Q_e$ (mg/g) | $k_2$ (g/(mg·min)) | $R^2$ | $q_{de}^a$ (mg/g) |
| Reactive brilliant blue KNR | 0.8358             | 0.0287              | 0.3366    | 34.12        | 0.0366              | 0.9996 | 33.87 |
| Acid black 10B            | 0.2039             | 0.0111              | 0.2967    | 48.10        | 0.5820              | 1.0000 | 48.16 |
| Acid red B                | 0.0905             | 0.0120              | 0.2768    | 41.96        | 0.1416              | 0.9998 | 42.34 |

$q_{de}^a$ is the equilibrium adsorption capacity determined by experiment

In view of the best decolorization effect of FHCP/Fe$_3$O$_4$ on reactive brilliant blue KNR, we selected reactive brilliant blue KNR as the object to further investigate the influences of pH value and foreign ions on the decolorization performance of FHCP/Fe$_3$O$_4$.

3.3. Influence of pH value

The background pH value of reactive brilliant blue KNR solution (100mg/L) was 5.73. After added 5mL of FHCP/Fe$_3$O$_4$ solution, the pH value of the mixture solution decreased to 5.27. On this basis, we regulated the initial pH value of the dye solution with 1 mol/L HCl and 0.75 mol/L NaOH. As shown in figure 4(a), when the initial pH value of the solution was regulated to 2.98, the highest decolorization rate of FHCP/Fe$_3$O$_4$ was 99.5%. This result was almost not different from the original pH value (pH = 5.73) (99.4%). It can be seen that increasing the acidity of the solution had no negative effect on the dye adsorption. As the initial pH value of the solution was further increased to 7.20 and
9.93, the decolorization were also basically uneffected, and the highest decolorization rate could reach more than 99% (figure 4(a)). By recording the change of pH value of the mixture solution during the reaction, we found that the mixture still maintained acidity under the two initial pH values. When the initial pH values were 7.20 and 9.93, the corresponding highest pH values of the mixture solution were 5.51 and 5.83. The slight change of pH value demonstrated that FHCP/Fe₃O₄ solution had a certain buffer capacity for alkalinity. Despite of it, as the pH value of the initial solution was regulated to 12.01, excessive alkalinity would still break down the buffer capacity of FHCP/Fe₃O₄ and elevated the pH value of mixed solution to a much high level. During this reaction period, the pH value of mixed solution varied in the range of 11.43-11.78, and the decolorization rate declined to less than 15% rapidly. On the whole, the influence of pH value on the decolorization efficiency of FHCP/Fe₃O₄ is mainly related to the change of surface charge characteristics of colloidal precipitates. With the increase of solution alkalinity, the number of positive charges on the surface of FHCP/Fe₃O₄ decreases, and thus leads to the decline of adsorption efficiency. This also demonstrated that the adsorption of anionic dye by FHCP/Fe₃O₄ might be more suitable to the acidity conditions.

![Figure 4. The influence of initial pH value (a) and foreign ions (b) on
decoloration efficiency of FHCP/Fe₃O₄](image)

3.4. Influence of foreign ions
The influences of the foreign ions on the decolorization of FHCP/Fe₃O₄ were shown in figure 4(b). It can be seen that three kinds of ions (Cl⁻, SO₄²⁻, HCO₃⁻) all showed negative impacts on the decolorization of FHCP/Fe₃O₄. Among them, the impact of HCO₃⁻ was the strongest, followed by sulfate ion, the role of chloride ion was relatively small. In addition to extra added chloride ions, FHCP/Fe₃O₄ solution itself also contains a certain amount of chlorine (0.24mmol Cl⁻/mL). If only seen from the results mentioned above, the introduction of Cl⁻ by FHCP/Fe₃O₄ showed no adverse effect on the decolorization reaction. However, after added more Cl⁻ to the dye solution, the decolorization efficiency of FHCP/Fe₃O₄ began to decline. This means there still have competitive problem of adsorption between chloride ion and dye molecule. Figure 4(b) showed when added 1mmol Cl⁻ (1mL 1.0 mol/L NaCl solution), the decolorization rate of dye solution decreased from 99.4% to 71.8%. According to the relavant literature, the coordination of chloride with iron oxide (or hydroxyl oxide) mainly form outer-sphere complex[11]. The decline of decolorization rate illustrated the combination of dye molecule and FHCP/Fe₃O₄ might also form outer-sphere complex. After that, kept on increasing the dosage of sodium chloride, there was no further decline of the decolorization rate. On the contrary, the decolorization rate showed the trend of increase. As shown in figure 4(b), when added 10mL of sodium chloride solution, the decolorization rate of dye increased to 79% again. This phenomenon also showed that, in addition to competition, sodium chloride can also play a certain role in promoting the adsorption of dyes. It’s well known, sodium chloride as an electrolyte is very important to the dissolution of reactive dyes in water. But excessive sodium ions will inhibit the
ionization of sulfonic acid groups and reduce the solubility of dyes [12]. In addition, for the FHCP/Fe₃O₄, excessive chloride ion will lower the surface potential of colloidal particle by compressing the double layer, and then enhance the non-static contact between colloidal particles and dye molecules[11]. These should be the main reasons for the rebound of decoloration rate in this study. Compared with chloride ion, the competition between sulfate ion and dye molecule was more prominent. It is believed that the ionized sulfonic group should be the main contact site of active brilliant blue with FHCP/Fe₃O₄. Although the molecular structure of sulfonic acid group is similar to that of sulfate ion, the binding affinity of sulfonic acid group with FHCP/Fe₃O₄ is lower than that of sulfate ion due to the limitation of steric hindrance. For the bicarbonate, in addition to the competitive action itself, the hydroxy ion produced by hydrolysis of bicarbonate is another important factor lowering the decoloration rate seriously. The detection results showed that, after added 1mL, 5mL and 10mL of NaHCO₃ solution (1mol/L), the corresponding pH value of the dye solution increased to 8.02, 8.83 and 9.08 respectively. All the adsorption reactions were carried out in alkaline environment.

4. Conclusions
Based on the above study, we draw the following conclusions,
(1) The adsorption effect of FHCP/Fe₃O₄ for anionic dyes is much better than that of cationic dyes. (2) The adsorption kinetic of FHCP/Fe₃O₄ for anionic dyes can be described by pseudo-second-order kinetic equation. (3) FHCP/Fe₃O₄ is more suitable to adsorb anionic dye in acidic environment. (4) The impact order of foreign ion on decoloration performance of FHCP/Fe₃O₄ is HCO₃⁻ > SO₄²⁻ > Cl⁻.

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