Preparation of iron-modified portland cement adsorbent and the investigation of its decolorization performance

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Abstract. The ordinary portland cement was modified by ferric salt impregnation method. Through the technologies of x-ray diffraction, scanning electron microscope and energy dispersive spectroscopy, the physicochemical properties of modified cement were detected and analyzed. It was found that after the modification, the main constituents of raw cement, tricalcium silicate and dicalcium silicate had been depleted, and the new crystal mineral of antarcticite replaced them. The iron precipitates and cement hydration products calcium silicate hydrate gel mainly existed in the form of amorphous on modified cement. The results of BET specific surface determination showed that the modified cement particles had mesoporous distribution. The results of adsorption experiment revealed modified cement exhibited excellent adsorption performance on reactive brilliant blue KNR. The combination mechanism between modified cement and adsorbate was mainly electrostatic interaction. The adsorption process satisfied with the pseudo-second order kinetics model, and the adsorption reaction was a spontaneous endothermic process.

1. Introduction
Portland cement (PC) is a widely used building material. The main components of PC consists of tricalcium silicate (3CaO·SiO₂), dicalcium silicate (2CaO·SiO₂), tricalcium aluminate (3CaO·Al₂O₃), Tetracalcium aluminoferrite (4CaO·Al₂O₃·Fe₂O₃), gypsum and a small amount of other mineral phase composition [1]. It well known that the chemical property of cement is very active, and the hydration reaction occurs in the case of meeting water. During the hydration reaction process, some new phase components will form such as calcium silicate hydrate gel (CSH), portlandite, ettringite, monosulfoaluminate hydrate (AfM) etc. Portlandite can further react with CO₂ in air to form the calcium carbonate. CSH is the general name of the ternary compound of CaO·SiO₂·H₂O formed in the cement hydration reaction, and it’s also the main source of the solidification strength of cement. Seen from the material structure, CSH is similar to the mixture of tobermorite and Jennite, and its layer structure contains Ca-O octahedral and [SiO₄] tetrahedron [2]. According to relevant report, CSH has a very high specific energy and ion exchange capacity, and it can immobilize foreign ions by adsorption, symbiosis and chemical replacement [3]. Zhang [4] reported that organic macro-molecules of the carboxylic acids and the aliphatic can be physically adsorbed and enter into the inner layer of CSH structure to conduct intercalation reaction. Beaudoin [5] found that the calcium ion on the surface of cement could conduct ion-exchange reaction with the monomer and dimer of the methylene blue.
cations, and then realize the decolorization. In addition to CSH, ettringite, monosulfoaluminate hydrate and calcium carbonate could also exhibit certain affinity on foreign ions. It should be said that the cement as adsorbent for waste-water treatment has great potential for development. In spite of that, considering the hydration reaction of cement will be accompanied by the release of a large amount of alkalinity (Ca (OH)$_2$), and then lead to a sharp increase in pH value of the solution, there are seldom report about directly application of cement on the disposal of wastewater.

In this paper, we tried to use impregnation method of iron salt solution to modify portland cement. On the one hand, by the neutralization of acidity of ferric salt solution and alkalinity released in the hydration reaction of cement, the hydration process of cement could be accelerated. On the other hand, utilize the morphological changes of ferric ion and its interaction with cement particles, a new type of cement composite materials contains iron precipitate could be obtained. For the new material of modified cement, some detection technologies including x-ray diffraction, BET specific surface analysis, scanning electron microscope and energy dispersive spectroscopy were used to characterize its physico-chemical properties. On the basis of it, the adsorption performance of modified cement on the reactive blue KNR of anthraquinone dye was investigated. The main purpose of this study is to provide reference for the further amplified application of cement materials in the field of waste-water treatment.

2. Materials and methods

2.1. Materials
Portland cement (Grade 32.5) was purchased from market. The elements constitution of portland cement was as follows, CaO 48.47%; SiO$_2$ 26.13%; Al$_2$O$_3$ 12.17%; SO$_3$ 4.73%; MgO 3.17%; Fe$_2$O$_3$ 2.99%; K$_2$O 0.96%;TiO$_2$ 0.64%; Na$_2$O 0.27%;MnO 0.15%;P$_2$O$_5$ 0.14%;SrO 0.10%;Cl 0.03%;ZrO$_2$ 0.03%. Chemical reagents employed in modification experiment including FeCl$_3$.6H$_2$O, NaOH and HCl were all analytical pure. Reactive blue KNR of anthraquinone dye (Industrial grade) was purchased from Shanghai Jia Ying Chemical Co.Ltd. Its chemical formula is C$_{22}$H$_{16}$N$_2$Na$_2$O$_{11}$S$_3$.

2.2. Methods

2.2.1. Preparation of ferric-salt modified portland cement (FMPC) Firstly, 0.5mol/L of ferric chloride solution was prepared. Then weighed 10g of raw cement and added it into 50ml 0.5mol/L of ferric chloride solution. The mixture liquid was stirred in water bath at 25°C for thirty minutes. After the settling of twenty minutes, the mixture liquid was directly put into the oven for drying at 100°C for twelve hours. The residue solid was cooled and grinded to small particles (Particle size, 80-150 mesh). The final product of FMPC was obtained.

2.2.2. Physico-chemical characterization of FMPC The surface morphology of the sample was observed by field emission scanning electron microscopy (SU-70, Hitachi, Japan). The surface elements were detected by X-ray energy dispersive spectroscopy (EX-250, HORIBA, Japan). The specific surface area and pore size distribution was checked by surface analyzer (V-Sorb 2800P, GAPP, Beijing), and the results was analyzed by the calculation method of the BET (Brunauer-Emmett-Teller). The crystal structure of the material was determined by poly-crystalline powder diffraction XRD (Empyrean, PANalytical, Holland), The main parameters of XRD equipment are as follows, the diffraction angle range of 2θ is 3°-80°, scanning speed is 4°/min, the voltage is 40KV and the current is 40mA. Quantitative of constitute of crystal phase was calculated by the XPert HighScore Plus software package.

2.2.3. Investigation of adsorption performance First of all, the decolorization efficiency of FMPC under the conditions of different concentrations of reactive brilliant blue solution was investigated. Set the dosage of cement as 1g/L. The initial concentrations of reactive brilliant blue KNR solution were
50mg/L, 75mg/L, 100mg/L, 135mg/L and 170mg/L, respectively. The mixture liquid was put into the constant temperature magnetic stirrer, and reacted in water bath of 25°C for six hours. The changes of dye concentration were detected at certain time intervals. The adsorption capacity and decolorization rate were calculated. Calculation methods of equilibrium adsorption amount and decolorization rate referred to equation (1) and (2).

\[ R = \frac{(C_i - C_e)}{C_i} \times 100\% \] (1)

\[ q_e = \frac{(C_i - C_e)V}{m} \] (2)

In which, \( R \) is the decolorization rate (%), \( C_i \) is the initial concentration of reactive brilliant blue solution (mg L\(^{-1}\)), \( C_e \) is the adsorption equilibrium concentration (mg L\(^{-1}\)), \( q_e \) is the equilibrium adsorption capacity (mg g\(^{-1}\)), \( V \) is the volume of solution (mL), \( m \) is the quality of adsorbent (g). In order to evaluate the change of the adsorption properties of cement before and after modification, the parallel experiments were carried out on the raw materials.

Secondly, the effect of cement dosage on decolorization efficiency was investigated. When the concentration of reactive brilliant blue solution was as 170mg/L, the temperature and time of reaction were as 25°C and 6h, the dosage of cement was increased to 2g/L, 4g/L, 6g/L, 8g/L, 10g/L, respectively. The decolorization efficiency at adsorption equilibrium under the conditions of different dosage was examined. Finally, the effects of the initial pH value and temperature on the decolorization efficiency were detected. When the dosage of cement was as 1g/L and the reaction time was as six hours, the initial pH value and temperature of the solution were regulated to 3, 5, 7, 9, 12 and 25°C, 35°C, 45°C, 55°C respectively. The adsorption capacity and decolorization rate at adsorption equilibrium were detected and calculated. Considering the change of the pH value of the solution may affect the stability of the metal oxide on cement sample, the concentration of calcium and ferric ions in the solution were checked.

The concentration of reactive brilliant blue KNR solution was checked by UV-vis spectrophotometer (T6, Purkinje general, Beijing). The maximum absorption wavelength (\( \lambda_{\text{max}} \)) was determined as 595nm. The ion concentrations of calcium and ferric were tested by atomic absorption instrument (A3AFG, Purkinje general, Beijing). The pH values of mixture liquid were recorded by digital pH meter (PHS-25, Leici, Shanghai). Based on the experimental data, the adsorption kinetics and thermodynamic model were calculated.

The adsorption kinetics models mainly referred to the formulas of the pseudo-first-order and pseudo-second-order [6-7].

The expression of pseudo-first-order kinetic model was as follows,

\[ \frac{1}{q_t} = \frac{1}{q_e} + \frac{1}{k_1 q_e t} \] (3)

The expression of pseudo-second-order kinetic model was as follows,

\[ \frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \] (4)

In which, \( q_e \) and \( q_t \) represent the adsorption capacity at equilibrium and time \( t \), respectively (mg g\(^{-1}\)). \( k_1 \) is the reaction rate constant of pseudo-first-order, (min\(^{-1}\)). \( k_2 \) is the reaction rate constant of pseudo-second-order, (g mol\(^{-1}\) min\(^{-1}\)).

The calculations of key parameters on thermodynamic model included Gibbs free energy (\( \Delta G^0 \)), standard enthalpy change (\( \Delta H^0 \)) and standard entropy change (\( \Delta S^0 \)). The calculation of \( \Delta G^0 \) referred to formula (5) and (6).

\[ \Delta G^0 = -RT \ln K_c \] (5)
In which, \( K_c \) is the equilibrium constant, \( R \) is the ideal gas constant (J mol\(^{-1}\) K\(^{-1}\)), \( T \) is the reaction temperature (K), \( C_{AE} \) is the amount of dye adsorbed on adsorbent at equilibrium per litre solution (mg L\(^{-1}\)), \( C_{SE} \) is the equilibrium concentration of dye solution (mg L\(^{-1}\)).

The calculations of \( \Delta H^0 \) and \( \Delta S^0 \) referred to Van’t Hoff equation (7).

\[
\ln K_c = -\frac{\Delta H^0}{RT} + \frac{\Delta S^0}{R}
\]

(7)

3. Results and discussion

3.1. Physico-chemical characteristics of FMPC

3.1.1. XRD The test results of crystal phase XRD of cement materials before and after modification were shown in Figure 1. It can be seen that, before the modification, the main crystal minerals of cement included tricalcium silicate (PDF\# 49-0442, \( d_{001}=2.78\AA \), \( 2\theta=32.21^\circ \)), dicalcium silicate (PDF\# 24-0034, \( d_{001}=2.74\AA \), \( 2\theta=32.63^\circ \)), calcite (PDF\# 47-1743, \( d_{001}=3.04\AA \), \( 2\theta=29.41^\circ \)) and quartz (PDF\# 65-0466, \( d_{001}=3.35\AA \), \( 2\theta=26.63^\circ \)). The total mass fraction of these four crystal minerals was about 95%. In addition, there was a small amount of tetracalcium aluminoferrite, gypsum and monosulfoaluminate hydrate be detected. After the modification, Quartz and calcite still existed, and the sum of their mass fraction was about 40%. However, tricalcium silicate and dicalcium silicate had not been detected. A new crystal mineral of antarcticite (CaCl\(_2\)·6H\(_2\)O, PDF\# 26-1053, \( d_{001}=2.16\AA \), \( 2\theta=41.80^\circ \)) replaced them. The mass fraction of antarcticite in FMPC was about 56%.

With regard to the formation mechanism of antarcticite, its analyzed to be related with the cement’s hydration reaction and the chemical reaction of ferric chloride. When raw cement is contact with the solution of ferric chloride, tricalcium silicate and dicalcium silicate firstly react with water to form calcium silicate hydrate gel (CSH), and to release the strong alkali substance calcium hydroxide. Subsequently, ferric chloride reacts with calcium hydroxide to form calcium chloride and ferric hydroxide precipitate. In the later drying process, soluble calcium chlorides in solution crystallize and form antarcticite. Specific reaction processes see chemical equation (8) - (11).

\[
\begin{align*}
2(3CaO \cdot SiO_2) + 6H_2O &\rightarrow 3CaO \cdot 2SiO_2 \cdot 3H_2O(CSH) + 3Ca(OH)_2 \quad (8) \\
2(CaO \cdot SiO_2) + 4H_2O &\rightarrow CaO \cdot SiO_2 \cdot 3H_2O(CSH) + Ca(OH)_2 \quad (9) \\
3Ca(OH)_2 + 2FeCl_3 &\rightarrow 3CaCl_2 + 2Fe(OH)_3 \quad (10) \\
CaCl_2 + 6H_2O &\rightarrow CaCl_2 \cdot 6H_2O(Crystallize) \quad (11)
\end{align*}
\]

Besides the tricalcium silicate and dicalcium silicate, there was also no CSH and iron-containing crystal mineral to be detected in FMPC. It was speculated that the newly formed CSH and iron precipitates mainly exist in the form of amorphous.

3.1.2. FESEM and EDS The surface morphology and elements analysis of cement before and after modification were shown in Figure 2.

In which, figure 2((a)-(d)) were the surface morphology of the sample observed by field emission scanning electron microscopy. Before the modification, raw cement was mainly composed of irregular massive particles. The surface of particles was smooth, the edge was clear and the three-dimensional structure was prominent. After the modification, the surface of the particles was covered with flake sediments. The volume of particles became greater and the surface became rougher. The analyzing result of energy dispersive spectroscopy (Figure 2((e)-(f))) showed that the mass fraction of iron and chlorine on the surface of the modified cement increased obviously. It was thought that the increase of chlorine was related to the crystallization of calcium chloride on the surface of the particles. This was
consistent with the results of XRD. The increase of iron could further confirm that the ferric of solution had deposited on the surface of the particles.

![XRD diagram](image)

**Figure 1.** Crystal phase XRD of cement materials before and after modification.

### 3.1.3. Specific surface area and porosity
Nitrogen adsorption and desorption isotherm data were shown in Figure 3. Seen from the figure, there existed a hysteresis loop in the region of 0.4-1.0 (P/P₀). According to the report of Liu [8], it can be judged that the modifying cement owns the characteristic of mesopore distribution. By the calculation, the total specific surface area of the modifying cement was determined as 4.08 m²/g, and its total pore volume and average pore size was 0.168 cm³/g and 165.2 nm, respectively.

### 3.2. Adsorption properties on reactive brilliant blue KNR

#### 3.2.1. Adsorption efficiency
The profiles of adsorption and decolorization on reactive brilliant blue KNR by cement were shown in Figure 4. It can be seen from the figure, for 50 mg/L initial concentration of the reactive brilliant blue solution, as reached equilibrium, the adsorption capacities of PC and FMPC on the adsorbate were 34.5 mg/g and 33.7 mg/g, respectively. Compared with raw cement, the equilibrium adsorption capacity of modified cement was slightly decrease. With regard to the higher efficiency of raw cement, it was analyzed that this mainly related with the charge characteristics of CSH. Reactive brilliant blue KNR was an anionic dye, and its chromogenic group charged negatively in aqueous solution. As the main active component of adsorption reaction, the properties of surface charge of CSH were being influenced by the change of calcium concentration of the solution. Nachbaur [1] found that, with the increase of calcium concentration in the solution, the surface charge of CSH will be changed from negative to positive. The concentration of calcium in the solution as reaching to the isoelectric point on the surface of CSH was about 4 mM (80 mg/L). In this experiment, the change range of calcium concentration in solution on PC during the course of thirty to three hundred minutes’ reaction time was 108.57 - 162.86 mg/L. So, it can be concluded that the combination of CSH and reactive brilliant blue KNR was mainly electrostatic interaction. In addition, it’s worth note that the pH value of mixture solution of PC was as high as 12.3. This means large amount of hydroxyl ion of the solution might compete with the chromogenic group of active brilliant blue for the active site of CSH. After the modification, the pH value of mixture liquid of cement decreased to 10.3, but it was still alkaline. The initial pH value of reactive brilliant blue solution was 7.4. It’s believed that the excess alkalinity still originated from cement materials. This phenomenon
maybe due to that calcium hydroxide had not been completely transformed into antarcticite, and there might have some residues of calcium hydroxide in modified samples. The decrease of alkalinity is helpful to alleviate the competition between the hydroxyl ion and chromogenic group on the active site of CSH. In spite of it, considering the calcium concentration in the mixture liquid of modified cement maybe limit to the dissolution rate of antarcticite (See Table 1, the concentration of calcium on FMPC liquid after reaction was 106.75mg/L), we speculated that this might impose some negative impact on the electrostatic interaction of CSH.

Figure 2. The surface morphology and element composition of cement before and after modification (a,b pre-modified SEM, c, d modified SEM; e, pre-modified EDS, f, modified EDS).
Figure 3. Adsorption and desorption isotherm.

Figure 4. Comparison of adsorption properties of cement on reactive brilliant blue KNR before and after modification.

Figure 5 revealed the profiles of adsorption and decolorization of modified cement materials under different initial concentration and dosage. It can be seen from figure 5(a), within the initial concentration range of 50-170mg/L, the adsorption capacity of modified cement on reactive brilliant blue increased with the increase of concentration of adsorbate. When the concentration of solution as 170mg/L, the equilibrium adsorption capacity of FMPC on reactive brilliant blue could reach to 135.4mg/g and the corresponding solution decolorization rate was 79.2%. Increasing the dosage of reagent can further improve the decolorization efficiency. Figure 5 (b) showed that, same as the solution of 170mg/L, when the dosage of FMPC increased to 4g/L, the decolorization rate of active brilliant blue could reach to 95.5%. Then to continue increasing the dosage, the solution decolorization rate basically remained stable. In addition, the initial pH value of solution also had a great influence on the adsorption properties of the modified cement. As can be seen from Table 1, when the initial pH value of solution was 3, the equilibrium adsorption capacity of FMPC on 50mg/L of reactive brilliant blue solution increased to 40.9mg/g. This results demonstrated that, compared with the alkaline environment, acidic environment was more conducive to improve the adsorption effect of FMPC on
reactive brilliant blue. Meanwhile, it was noticed that the concentrations of calcium and ferric also reached to the highest value at acidic condition. Here, the increase of calcium in acidic solution should play the key role on the higher adsorption efficiency of reactive brilliant blue. Additionally, by observing the change of calcium and ferric concentrations on the different pH value, it was found that the release of calcium on the modified cement be limited by the iron precipitates. This phenomenon could be explained that, during the course of crystallization of calcium chloride, there had a considerable number of crystals were coated or covered with iron precipitate. Due to the precipitate of iron at the alkaline condition was relatively stable, thus the dissolution of antarcticite would be inhibited, and the release amount of calcium in cement would be decreased. In contrast, with the rapid dissolution of iron precipitate in the acidic conditions, much more calcium could be released into the solution.

![Figure 5](image)

**Figure 5.** Influence of initial concentration and dosage on adsorption efficiency (a, initial concentration, b, cement dosage).

| pH value | Before reaction | After reaction | Equilibrium adsorption capacity (mg g⁻¹) | Ion concentration (mg L⁻¹) | Ca²⁺ | Fe³⁺ |
|----------|----------------|---------------|------------------------------------------|---------------------------|------|------|
| 3.0      | 7.3            | 40.9          | 152.65                                  | 4.42                      |
| 5.5      | 9.8            | 33.8          | 122.18                                  | 1.27                      |
| 7.4      | 10.3           | 33.7          | 106.75                                  | 1.23                      |
| 9.5      | 10.3           | 31.8          | 98.28                                   | 1.12                      |
| 12.0     | 11.9           | 30.2          | 48.55                                   | 0.49                      |

3.2.2. Adsorption kinetics The adsorption process of FMPC was fitted by pseudo-first order and pseudo-second order kinetics model. The calculation results of main parameters were shown in Table 2. By comparing the R square value of correlation coefficient, it can be seen that the adsorption process of modified cement on reactive brilliant blue KNR was more satisfy with the pseudo-second order kinetics model.

![Table 1](image)

**Table 1.** Influence of initial pH value on adsorption efficiency.

| C₀ (mg/L) | Pseudo-first-order | Pseudo-second-order |
|-----------|---------------------|---------------------|
|           | qₑ (mg g⁻¹) | K₁ (min⁻¹) | R² | qₑ (mg g⁻¹) | K₂ (g mg⁻¹ min⁻¹) | R² |
| 50        | 35.6       | 13.4       | 0.8350 | 34.4       | 3.3×10⁻³       | 0.9983 |
| 100       | 67.9       | 23.6       | 0.6708 | 80.9       | 2.0×10⁻³       | 0.9836 |
| 135       | 125.1      | 65.3       | 0.9293 | 124.5      | 1.3×10⁻⁴       | 0.9883 |
3.2.3. **Thermal-dynamics**

The calculation results of thermal-dynamics parameters were shown in Table 3. The data of $K_c$ revealed that the adsorption equilibrium constant decreases with the increase of temperature. The Gibbs free energy $\Delta G^0$ were negative in the temperature range of 298-328K. This demonstrated that the adsorption process of FMPC on reactive brilliant blue KNR was spontaneity. Standard enthalpy change $\Delta H^0$ was 24.171kJ mol$^{-1}$ (>0), which means the adsorption process was endothermic. According to the report of Lian [9], when the value of $\Delta H^0$ was in the range of -20~40kJ mol$^{-1}$, the adsorption process was mainly physical in nature, while the value of $\Delta H^0$ was in the range of -400~80kJ mol$^{-1}$, the adsorption process was mainly chemical adsorption. The calculation of thermal-dynamics further confirmed the electrostatic interaction of FMPC on reactive brilliant blue KNR. In addition, Table 3 revealed that standard entropy change $\Delta S^0$ was 0.073kJ mol$^{-1}$. $\Delta S^0$ >0 means the randomness of the solid-liquid interface between modifying cement and reactive brilliant blue solution increased. It was analyzed that the increase of the randomness may be originated from the dissolution of FMPC on the antarcticite and iron-precipitate.

| Temperature (K) | $K_c$   | $\Delta G^0$ (kJ mol$^{-1}$) | $\Delta H^0$ (kJ mol$^{-1}$) | $\Delta S^0$ (kJ mol$^{-1}$K$^{-1}$) |
|----------------|--------|----------------------------|-----------------------------|------------------------------------|
| 298            | 2.478  | -2.249                     |                             |                                    |
| 308            | 1.774  | -1.467                     |                             |                                    |
| 318            | 1.382  | -0.857                     | 24.071                      | 0.073                              |
| 328            | 1.004  | -0.011                     |                             |                                    |

4. **Conclusions**

In this study, we had tried to use iron salt to modify portland cement and obtained the new type adsorbent of FMPC. There presented some new features on the physicochemical characteristics of FMPC. For example, appearance of new crystal mineral antarcticite, the mesoporous distribution, and amorphous iron species precipitated in the surface. It’s worthy to note that, the modification could effectively lower the alkalinity of hydrated cement, but show little effect on the enhancement of adsorption capacity. The combination mechanism of FMPC on reactive brilliant blue KNR was mainly physical in nature. The adsorption process of FMPC on reactive brilliant blue KNR was satisfied with the pseudo-second order kinetics model and the adsorption reaction was a spontaneous endothermic process.

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