Magnetic FeS$_2$/Fe$_3$O$_4$ composites as adsorbents for chromium (VI) removal from aqueous solution

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Abstract. In this study, novel magnetite composites FeS$_2$/Fe$_3$O$_4$ were facilely synthesized by a one-pot hydrothermal method. It is applied as an adsorbent for chromium (VI) removal from aqueous solution. The pyrite (FeS$_2$) and the magnetite (Fe$_3$O$_4$) were also synthesized and compared. The analysis results of XRD, SEM and XPS confirmed the formation of FeS$_2$/Fe$_3$O$_4$ composite. The magnetic characterization revealed that the saturation magnetization value for FeS$_2$/Fe$_3$O$_4$ was 50.89 emu/g, which is helpful for the separation. The effects of the initial pH values, adsorbent dosage, contact time and reaction temperatures on the Cr (VI) removal by various materials were studied and contrasted in detail through experiments. It is found that the composite FeS$_2$/Fe$_3$O$_4$ had high removal ability for Cr (VI) at high pH. 86.1% of Cr (VI) removal efficiency was obtained when the pH value is at 12.0, the contact time is 3h and the temperature is controlled at 35°C. FeS$_2$ component was inferred as the major contribution for the composite to the Cr (VI) removal. FeS$_2$/Fe$_3$O$_4$ displayed a promoted Cr (VI) removal efficiency with the increasing temperature and its absorption process is proved spontaneous.

1. Introduction
Chromium is one of the most common heavy metal pollutants in wastewater, industrial waste and polluted soil. It usually exists in form of the hexavalent chromium (Cr (VI) or trivalent chromium (Cr (III)). The allowable concentration of total chromium in drinking water was 50 μg L$^{-1}$ by WHO [1]. However, the concentration of chromium (VI) in polluted wastewater always far exceeds the safety level [2]. Compared with chromium (III), the toxicity of chromium (VI) is nearly one hundred times higher than that of chromium (III), which due to the formation of insoluble species for Cr (III) such as Cr(OH)$_3$ or Cr$_x$Fe$_{1-x}$(OH)$_3$ [3]. Chromium (VI) is soluble in a wide range of pH environments and can diffuse rapidly in liquid environments. Therefore, it is imperative to develop an effective method to remove Cr (VI) in water.

Reduction and / or adsorption Cr (VI) from the aqueous solution is generally considered as an environmentally friendly and economical technology [4]. Among the various adsorbents, Fe$_3$O$_4$ has been paid special attention in water purification, due to its simple magnetic separation process and mild reaction conditions [5]. Feng et al. [6] synthesized Fe$_3$O$_4$ nanoparticles and studied the effects of various conditions for the removal of Cr (VI) in aqueous solution. The maximum adsorption capacity was 56.625 mg/g at 35°C and the pH value was controlled at 2.0. From the previous reports, the reduction ability of Fe$_3$O$_4$ is quite weak and hardly to apply, its adsorption capacity also exhibits
comparatively low. Therefore, in order to successfully remove Cr (VI) using magnetic particles, functionalization and modification of Fe₃O₄ is a practicable strategy.

Natural sulfides are always abundant and can be used as reductants. Amorphous iron sulfides FeS₂ and FeS have been evaluated the remediation performance toward hexavalent chromium (Cr (VI)) [7]. Theoretically, Cr (VI) reduction reactions occurred on the surface of Fe₅S₇ and formed the product. The polysulfide is presumed to be better electron donor and more effective to remove Cr (VI) from solution. In this work, using one-pot hydrothermal method, novel magnetic adsorbent FeS₂/Fe₃O₄ were synthetized for the removal of Cr (VI) from aqueous solution. In order to compare the adsorption efficiency, Fe₃O₄ and FeS₂ were also prepared as the adsorbents. The X-ray diffraction, morphology, X-ray photoelectron spectroscopy, and magnetic characterizations were employed to reveal the structure and physical difference among the various materials. The influence of pH value, time and temperature on the adsorption efficiency of Cr (VI) removal were also investigated in detail.

2. Experimental

2.1. Preparation of Fe₃O₄, FeS₂/Fe₃O₄ and FeS₂ materials

The preparation of magnetic nanoparticles was according to the procedures reported in previous researches [2]. FeS₂ materials were synthesized by using a solvothermal method in our previous report [8]. The preparation process of FeS₂/Fe₃O₄ materials is similar to the above FeS₂ synthesis procedures. The appropriate amount of as-prepared Fe₃O₄ was dispersed in the solvent ethylene glycol, then Fe(NO₃)₃•9H₂O and NH₂CSNH₂ were added and dissolved in turn. The following operation was the same as described in the above pyrite preparation. The mole ratio of FeS₂ to Fe₃O₄ was controlled at 1:1.

2.2. Adsorption experiments

The synthetic Fe₃O₄, FeS₂/Fe₃O₄ and FeS₂ particles were applied to remove Cr (VI). The Cr (VI) solution (100 mg/L) was prepared by dissolving 0.2827 g of stock K₂Cr₂O₇ with 1000 mL deionized water and kept away from sunlight. The reaction volume of Cr (VI) solution was 50 mL for all the experiments. The desired adsorption conditions, such as initial pH value, adsorbent dosage, contact time and temperature were researched in detail. The initial pH value were ranged from 2.0 to 12.0, and the adjustment reagent was 0.5M H₂SO₄ or 0.5M NaOH. The desired adsorbent dosages were performed at 0.2, 0.3, 0.4, 0.6 and 0.8 g/L, respectively. The contact times of various materials were conducted at 1, 2, 3, 4, 5 and 6 hours, respectively. The desired temperature were changed from 25°C to 45°C. After adsorption finished, Fe₃O₄ and FeS₂/Fe₃O₄ materials were removed from the solution by magnetic separation, the pyrite were separated centrifugally.

3. Results and discussion

XRD patterns of the different powders were shown in Figure 1. The Bragg diffraction peaks of FeS₂ and Fe₃O₄ can be perfectly confirmed as one single phase (JCPDS card No. 42-1340 and 88-0315), no peaks of other iron sulfides and oxides, are observed in XRD patterns. It is obviously noted that the observable reflections of FeS₂/Fe₃O₄ contained has the strong and sharp diffraction peaks for both FeS₂ and Fe₃O₄. Thus, it is inferred that the novel FeS₂/Fe₃O₄ has been successfully synthetized. The hydrothermal synthesis process was proved to be a reliable method to prepare the pure iron sulfide or oxide.
The morphology and the change of detailed microstructure for the three materials are illustrated by SEM images, as shown in Figure 2. From Fig. 2a, Fe₃O₄ particles exhibits the morphology of regular octahedra with a particle size range about 1-5 μm. SEM image of FeS₂ in Fig. 2b indicated that the synthetic pyrite material was composed of particle agglomeration, the small first particle was all irregular sphere with 1-2 μm in diameters. It is interesting to learn that the composite FeS₂/Fe₃O₄ presents the mixed characteristics of the former two materials. The structure of particle agglomeration and regular octahedra are both maintained in the novel material, indicating that the formation of pyrite in the Fe₃O₄ suspension does not influence its morphological characteristics critically.

Figure 3 shows the magnetic property of different samples. Saturation magnetization (M), showing in the hysteresis loop of magnetic material, demonstrates the complete magnetizability of test materials. It is apparently found that the FeS₂ has no magnetic property. The saturation magnetization value for FeS₂/Fe₃O₄ was 50.89 emu/g. The decrease is about 37% comparing to the saturation magnetization of Fe₃O₄. This is caused by the less concentration of magnetite in the composite. Even so, the separation process of FeS₂/Fe₃O₄ from the solution can be finished successfully and quickly.
The as-prepared materials were used for the removal of aqueous Cr (VI) at various pH values range from 2.0 to 12.0. Figure 4 shows experimental data for the influence of pH value on Cr (VI) adsorption. It was observed that the Cr (VI) removal efficiency with FeS₂ fell down quickly from the initial 96.9% with the increasing pH value. The lowest Cr (VI) removal efficiency reached to 34.1% for pyrite material when the pH was controlled at 12.0. In the previous researches, different reaction mechanism have been proposed to understand the Cr (VI) removal process. The consensus view is that Cr (VI) is reduced to Cr (III) by pyrite, Fe (II) and S²⁻ are oxidized to Fe (III) and SO₄²⁻, respectively. Besides, some intermediate products such as elemental sulfur can formed during the reaction:

$$3\text{FeS}_2 + 3\text{HCrO}_4^- + 21\text{H}^+ = 3\text{Fe}^{3+} + 6\text{S}_0 + 3\text{Cr}^{3+} + 12\text{H}_2\text{O} \quad (1)$$

$$3\text{FeS}_2 + 15\text{HCrO}_4^- + 57\text{H}^+ = 3\text{Fe}^{3+} + 6\text{SO}_4^{2-} + 15\text{Cr}^{3+} + 36\text{H}_2\text{O} \quad (2)$$

According to the above equations, acidic conditions are considered to favor the Cr (VI) reduction by pyrite. The higher pH could induce the Fe- or Cr- hydroxides precipitate on FeS₂ material and lead to surface passivation. Furthermore, since the product Fe (III) is a strong oxidizing agent, it would be expected to expedite the pyrite dissolution in lower pH values. The solution pH also can influence the existence of Cr species. CrO₄²⁻ is the major Cr (VI) state under the alkaline condition and the dominant reduction product is Cr (III)-OH [9]. It was evident that the removal ratio of Cr (VI) was lowly pH dependent for Fe₃O₄. This could be attributed to weaker reductivity comparing to the pyrite. Another reason could be that the surface of regular octahedral magnetite particles are smoother and less micro-pore structure, as shown in Fig. 2. The removal efficiency of Cr (VI) from aqueous solution ranged from only 17.3% to 24.2% for the whole pH values, much lower than that applying FeS₂. It was worth noting that the solution pH has been observed as one of the important parameters affecting the Cr (VI) removal. It is interesting to find that Cr (VI) removal efficiency dramatically enhance from 22.4% to 86.1% when the pH value increased from 8.0 to 12.0. The reason could be explained as follows: the presence of Fe₃O₄ decreased the formation of Fe-Cr hydroxides at higher pH values and the formed discontinuous intermediate products on the composite surface such as elemental sulfur, Fe-S and Fe-OH may owe strong adsorption capacity of CrO₄²⁻ under alkaline conditions.

The effect of adsorbent dosage on Cr (VI) removal with Fe₃O₄, FeS₂/Fe₃O₄ and FeS₂ were displayed and the results were shown in Figure 4. The adsorption capacity of Cr (VI) for the three synthetic materials declined rapidly with the augment in adsorbent dosage from 0.2 to 0.4 g/L. The highest adsorption capacity of Cr (VI) for Fe₃O₄, FeS₂/Fe₃O₄ and FeS₂ were 82.0, 130, 141 mg/g,
respectively. With further increase the adsorbent dosage from 0.4 to 0.8 g/L, the change of Cr (VI) removal capacity became slow. FeS₂ and Fe₃O₄ obtained the max and the min Cr (VI) removal capacity respectively for the same adsorbent dosage. This is in agreement with the above analysis.

![Graph](image)

**Figure 4.** Effect of pH value and on Cr (VI) removal with Fe₃O₄, FeS₂/Fe₃O₄ and FeS₂ (Contact time = 3 h, initial Cr (VI) concentration = 100 mg/L, T = 35°C).

### 4. Conclusion

In summary, Fe₃O₄, FeS₂, and FeS₂/Fe₃O₄ have been successfully synthesized for removal of Cr (VI) from water solution. The obtained FeS₂/Fe₃O₄ includes a composite morphological characteristics for both Fe₃O₄ and FeS₂. It also exhibits the strong magnetism as fabricated and easily separated from the solution after adsorption. The adsorption capacities for Fe₃O₄, FeS₂, and FeS₂/Fe₃O₄ were 82.0, 141, and 130 mg/g, respectively, showing that FeS₂/Fe₃O₄ have both high adsorption capacities and convenient magnetic separation. The optimal conditions for FeS₂/Fe₃O₄ to remove Cr (VI) were that the contact time is 3 h and the pH value is 12. The kinetics of adsorption indicate that the adsorption process of Cr (VI) using either FeS₂ or FeS₂/Fe₃O₄ is spontaneous and the high the temperature can enhance the adsorption reaction. The study will provide a basis for designing composite of sulfide and magnetic Fe₃O₄ with controlled morphology and porous structures for practical environmental applications.

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