Efficiency and Mechanism of Low-Cost Coal Fly Ash Magnetic Beads Enhanced Coagulation for Treating Relatively High-Turbidity and Low-Organic Wastewater

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Abstract. The resource utilization of coal fly ash solid waste has become a research hotspot. In this work, magnetic beads were separated from industrial waste fly ash by wet magnetic separation and used as magnetic seeds (MS-CFA) in magnetic coagulation (MC). The superiority of MC was evaluated by comparison with traditional coagulation (TC). Meanwhile, The potential and feasibility of MS-CFA were evaluated by also employing Fe_3O_4 in the MC process. MS-CFA was characterized by SEM, XRD, VSM, and XPS. The results showed that MS-CFA was a composite microsphere crystal with a saturation magnetization of 33.71 emu/g. The addition of MS-CFA reduced the residual turbidity from 10.87 NTU to 3.27 NTU and increased the chemical oxygen demand (COD) removal rate from 42.92% to 64.24%. MS-CFA achieved water treatment performance comparable to or even better than Fe_3O_4, especially in organic matter removal. As a waste-derived material, MS-CFA not only reduces costs but also provides stronger adsorption for organic pollutants. This study provides a reference route for developing low-cost and high-efficiency magnetic coagulation technology.

1 Introduction

Coagulation represents one of the most essential procedures in water treatment[1]. However, this process has two main drawbacks. First, the formed flocs have low density and slow settling velocity, usually requiring more than 30 minutes[2], which limits treatment capacity. Second, it shows poor removal efficiency for hydrophilic dissolved organic matter (DOM)[3,4]. Therefore, conventional coagulation remains challenging for treating wastewater with high turbidity and low organic pollutants[5].

In recent years, adding magnetic particles during coagulation has become a research focus. Magnetic particles can promote floc growth and increase compactness, thus improving solid–liquid separation[6]. Nevertheless, practical applications reveal that magnetic seeds used in magnetic coagulation are costly[7]. A major barrier to the widespread adoption of magnetic coagulation is its high operational cost. Most existing investigations fail to address this economic challenge adequately, making cost reduction for magnetic seeds an immediate priority.

MS-CFA is the magnetic component in fly ash. It features high wear resistance and compressive strength[8], and can serve as an alternative to Fe_3O_4. MS-CFA is a byproduct of coal combustion in thermal power plants. As an industrial waste, it is low-cost and readily available. Current studies on MS-CFA in wastewater treatment mainly focus on its adsorption performance[9,10]. Few studies have clarified the synergistic mechanism of MS-CFA combined with coagulants such as polyaluminum chloride (PAC) in magnetic coagulation.

In this paper, MS-CFA obtained by wet magnetic separation was used as a magnetic seed to treat simulated high-turbidity and low-organic wastewater. Its performance was compared with PAC-only coagulation and Fe_3O_4-enhanced systems to demonstrate the superiority of MS-CFA. The material was characterized by SEM, XRD, and VSM. The magnetic coagulation mechanism was systematically explained using zeta potential, floc particle size, and XPS. This work aims to replace Fe_3O_4 with waste-derived fly ash magnetic beads to reduce the cost of magnetic seeds, and provide a theoretical basis for developing low-cost magnetic seeds in magnetic flocculation technology.

2 Materials and Methods

2.1. Materials and Chemicals

Kaolin, polyaluminum chloride (PAC, Al_2O_3: 32%, basicity: 80%-85%), and Fe_3O_4 were obtained from Tianjin Kaimate Chemical Co., Ltd. Humic acid (HA) was sourced from Shanghai Yuanye Bio-Technology Co., Ltd., while Fe_3O_4 functioned as the conventional magnetic particle in experiments. All reagents were of analytical grade. Raw fly ash was provided by a thermal power plant in Tianjin.

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Simulated wastewater was prepared as follows: 2 g kaolin powder and 0.1 g humic acid powder were dissolved in an appropriate amount of 0.01 mol/L NaOH solution, then diluted to 500 mL with tap water. The mixture was stirred continuously for more than 10 minutes. The simulated wastewater had a turbidity of 450 ± 10 NTU, COD of 90 ± 1.5 mg/L.

2.2 Separation of MS-CFA

MS-CFA was separated by a wet magnetic separation process. A certain amount of raw fly ash was dispersed in deionized water to form a suspension with a solid-liquid ratio of 1:60 g/mL. The suspension was stirred, and a NdFeB permanent magnet (magnetic field intensity = 0.3 T) was placed close to the outer wall of the container for 5-10 minutes. The supernatant and non-magnetic particles were slowly poured out. The remaining solid attached to the wall was rinsed 2-3 times with deionized water, collected, and dried at 60 °C for 12 h to obtain gray-black MS-CFA. The obtained MS-CFA was ground and sieved before use.

2.3 Coagulation Beaker Tests

Coagulation experiments were conducted in six 1.0 L beakers using a six-unit stirrer (JJ-4, Guohua Instrument Manufacturing Co., Ltd.). Rapid stirring at 300 rpm for 2 min and slow stirring at 60 rpm for 10 min were applied to the water samples. Turbidity and UV_{254} of the supernatant were measured at intervals. Settling performance was compared between traditional coagulation and magnetic coagulation.

2.4 Analytical Methods

Turbidity and COD were measured using a multi-parameter analyzer (LH-3BA, Lianhua Yongxing Technology Co., Ltd., China) and a UV/Vis spectrophotometer (LH-S700, Lianhua Yongxing Technology Co., Ltd., China). The morphology and surface characteristics of MS-CFA were observed by scanning electron microscopy (SEM, Sigma 360, Germany). Phase analysis was performed by X-ray diffraction (XRD, Rigaku SmartLab SE, Japan). Saturation magnetization was measured using a vibrating sample magnetometer (VSM, LakeShore 7404, USA). Zeta potential and floc particle size before and after coagulation were determined by dynamic light scattering (DLS, Malvern Zetasizer Nano ZS90, UK).

3 Results and Discussion

3.1 Characterization of MS-CFA

The morphology and structure of MS-CFA were analyzed by SEM. As shown in Figure 1a, MS-CFA existed as dispersed particles, mainly regular spherical or near-spherical. At high magnification (Figure 1b), the particle surface was generally smooth and dense, with an average particle size of approximately 9.76 μm. Although a small part of the magnetic core was slightly exposed, which might slightly affect magnetic stability, subsequent magnetic tests and experiments indicated that this effect was negligible.

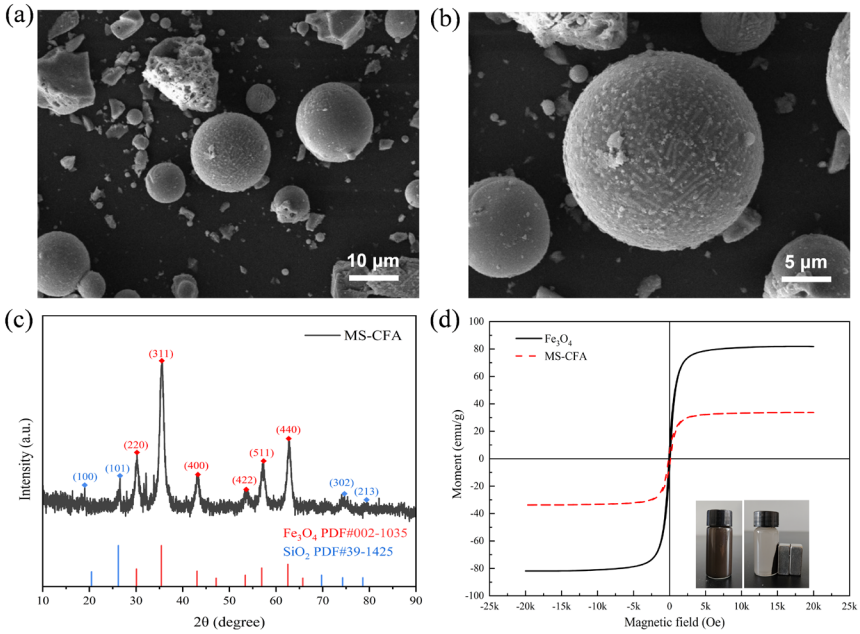

Figure 1. Characterization of the MS-CFA composite: (a, b) SEM images at different magnifications; (c) XRD pattern; (d) VSM hysteresis loops of MS-CFA.

The crystal structure was characterized by XRD (Figure 1c). The diffraction peaks of MS-CFA matched well with the (111), (220), (311), (222), (400), (422), (511), and (440) planes of magnetite Fe_3O_4 (PDF#002-1035). Clear diffraction peaks of SiO_2 were also observed, confirming that MS-CFA was a composite crystal composed of SiO_2 and Fe_3O_4.

Magnetic properties were tested by VSM (Figure 1d). MS-CFA showed a typical ferromagnetic curve with a saturation magnetization (Ms) of 33.71 emu/g, lower than pure Fe_3O_4 (81.86 emu/g). Nevertheless, the material exhibited good magnetic responsiveness. Under an external magnetic field (0.3 T), MS-CFA particles dispersed in water could be rapidly attracted and separated within 30 s (inset of Figure 1d).

3.2 Coagulation Performance of MS-CFA

Figure 2(a) and (b) show the changes in residual turbidity and COD removal efficiency with settling time for TC and MC systems. Overall, magnetic coagulation with Fe_3O_4 and MS-CFA resulted in lower final turbidity and higher COD removal efficiency than traditional coagulation. In the magnetic coagulation process, PAC interacts effectively with the magnetic particles, leading to the formation of composite Al species-magnetic particle aggregates. Subsequent to the addition of MS-CFA and PAC into the kaolin suspension, a significant proportion of the magnetic material is incorporated into the developing floc structure. Thus, flocs formed in MC were easily separated by solid–liquid separation.

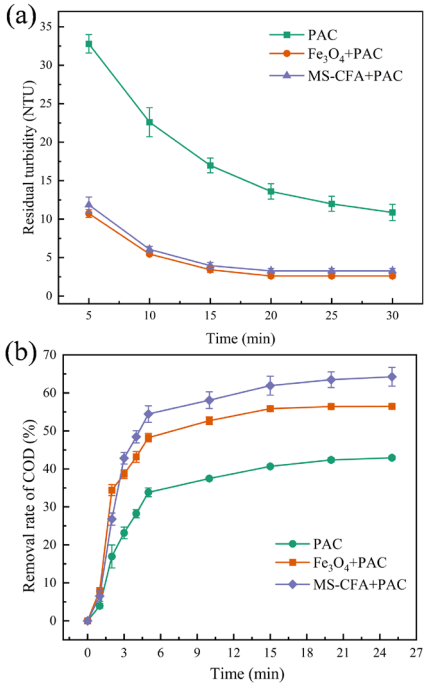

Figure 2. Variations of (a) residual turbidity and (b) COD removal efficiency with reaction time for PAC, Fe_3O_4+PAC and MS-CFA+PAC coagulation systems.

As shown in Figure 2a, after 15 min of settling, the addition of magnetic particles reduced residual turbidity from 16.97 NTU to 3.6 NTU. MC with MS-CFA achieved similar removal efficiency to MC with Fe_3O_4. However, large-scale application of Fe_3O_4 would significantly increase costs compared with traditional coagulation. For COD removal, adding Fe_3O_4 increased COD removal from 42.92% to 56.46%, while MC with MS-CFA reached 64.24%, indicating high adsorption capacity of MS-CFA.

3.3 Magnetic Coagulation Mechanism of MS-CFA

To better understand the enhanced coagulation effect of magnetic flocculation, zeta potentials of each system were measured. Increasing zeta potential weakens electrostatic repulsion between colloidal particles and promotes aggregation[11]. As shown in Figure 3a, the zeta potential of raw water particles was -15.38 mV, indicating strong electrostatic repulsion. After adding PAC, the zeta potential of flocs increased significantly to -4.47 mV. Cations generated by PAC hydrolysis effectively compressed the electric double layer on particle surfaces via charge neutralization, reducing the electrostatic repulsion barrier and causing particles to destabilize and aggregate[12].

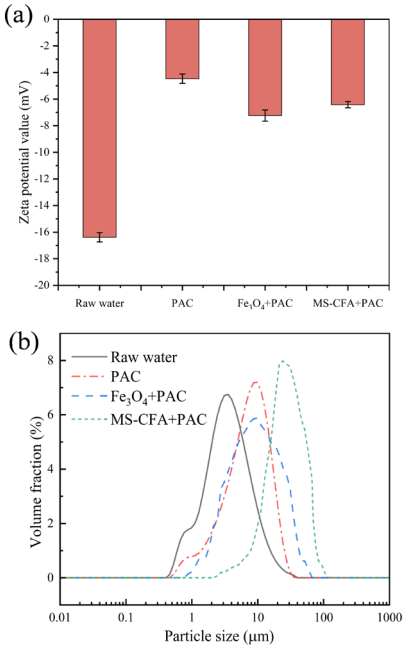

Figure 3. (a) Zeta potential and (b) particle size distribution of flocs in different coagulation systems.

When magnetic seeds were introduced, the zeta potential decreased slightly but remained higher than that of raw water. The zeta potential was -7.23 mV for the Fe_3O_4+PAC system and -5.22 mV for the MS-CFA+PAC system. The lower absolute zeta potential of the MS-CFA+PAC system indicated fewer net negative charges on floc surfaces. Combined with its best flocculation performance and largest floc size, the dominant mechanism of MS-CFA in flocculation may go beyond the classical charge neutralization mechanism.

Particle size distribution of flocs was analyzed to evaluate the enhancement of floc aggregation and growth (Figure 3b). Most colloidal particles in raw water were 1-10 μm with an average size of 4.6 μm, showing no aggregation. After PAC treatment, fine colloids aggregated, and the average size increased to 8.49 μm. This was likely because PAC promoted particle aggregation through charge neutralization and bridging[13]. Adding Fe_3O_4 further increased the average floc size to 17.03 μm. The average floc size in the MS-CFA system reached 43.49 μm. Under the action of coagulants, magnetic particles aggregated to form magnetic nuclei

and further captured colloidal particles[14]. The size distribution curve of magnetic flocculation shifted toward larger particles, helping shorten settling time.

In general, although adding magnetic particles weakened charge neutralization to some extent, the coagulation effect of magnetic flocculation was still stronger than conventional coagulation in terms of floc size. This further confirms that magnetic particle-enhanced coagulation relies on the synergistic effect of charge neutralization, adsorption bridging, and magnetic agglomeration.

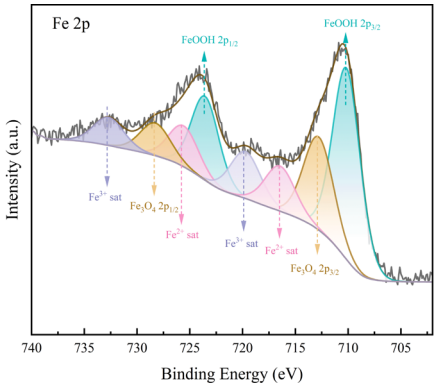

Figure 4. High-Resolution XPS Spectra of Fe in Coagulated Flocs.

Figure 4 presents the high-resolution Fe 2p XPS spectrum of the flocs after MS-CFA magnetic coagulation. The distinct Fe_3O_4 characteristic peaks confirm that the magnetic seeds act as the core of the flocs, effectively anchoring pollutants on their surfaces. Furthermore, the spectrum reveals the coexistence of a certain amount of FeOOH. As a proven high-efficiency adsorbent, the presence of FeOOH endows the material with abundant surface active sites, which mechanistically accounts for its superior COD adsorption performance.

3.4 Preliminary Cost Analysis of MS-CFA

From an economic perspective, MS-CFA is an extracted byproduct of industrial solid waste with near-zero raw material costs. Its primary production expenses are limited to electricity consumption and equipment depreciation during the wet magnetic separation process. Preliminary estimates indicate that the comprehensive production cost of MS-CFA is approximately 200-300 RMB/ton. In contrast, the market price for industrial-grade commercial Fe_3O_4 used in water treatment typically ranges from 2,500 to 4,000 RMB/ton. Consequently, the cost of MS-CFA is only about 10% of that of commercial magnetic powders. Given that its magnetic coagulation performance is comparable to Fe_3O_4-and even superior in terms of organic matter removal-MS-CFA can potentially serve as an alternative magnetic seed for application in magnetic coagulation technology.

4 Conclusions

In conclusion, magnetic beads derived from coal fly ash (MS-CFA) were successfully prepared via wet magnetic separation and used as low-cost magnetic seeds for enhanced coagulation of high-turbidity and low-organic wastewater. Compared with conventional coagulation and Fe_3O_4-enhanced magnetic coagulation, MS-CFA composite particles significantly improved the treatment performance. The residual turbidity decreased from 10.87 NTU to 3.27 NTU, and the COD removal efficiency increased from 42.92% to 64.24%. MS-CFA exhibited comparable or even better purification effect than Fe_3O_4, especially in organic matter removal. Mechanism investigations revealed that MS-CFA served as magnetic cores to form larger and denser flocs, which accelerated solid–liquid separation. Meanwhile, MS-CFA acted as an adsorbent to strengthen interparticle binding and improve organic removal. The enhanced coagulation was attributed to the synergistic effects of charge neutralization, adsorption bridging and magnetic agglomeration. This study demonstrates that waste-derived MS-CFA can serve as a low-cost, sustainable alternative to Fe_3O_4 in magnetic coagulation. The findings provide a feasible route for resource utilization of fly ash and offer a promising strategy for high-efficiency treatment of high-turbidity and low-organic wastewater.

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