Removal of COD in wastewater by magnetic coagulant prepared from modified fly ash

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Abstract
In this paper, magnetic coagulants (Fe-AFA, Fe-BFA) were prepared, by mixing acid-modified fly ash (AFA) and base-modified fly ash (BFA) with magnetic components, as adsorbents for chemical oxygen demand (COD) in desulfurization wastewater and their adsorption kinetics and mechanism are reported. BET, SEM, EDS, FTIR, XPS, magnetization intensity, and batch experiments on coagulation kinetic and adsorption isothermal characteristics of magnetic coagulants were carried out. The results show that Fe-AFA has the best COD adsorption performance and superparamagnetism, and the COD removal amounts can reach 5.69 mg/g, which is 112.43% higher than the raw fly ash. It was also found that the quasi-second-order kinetic and Langmuir equation could well describe the COD coagulation process. Thermodynamic tests results showed that the COD removal was a spontaneous, endothermic, and irreversible process. Reusability of magnetic coagulants was investigated. After five cycles, the COD removal amount of Fe-AFA was 2.74 mg/g. These findings provide a feasible method for environmental-benign utilization of fly ash as low-cost adsorbents in wastewater treatment.

Keywords Fly ash · Acid–base modification · Mixed magnetic · Coagulant · COD · Kinetic

Introduction
With the deepening of industrialization and urbanization, the increasingly prominent problem of water pollution has become a constraint on the social and economic development of China. The chemical oxygen demand (COD) value as one of the important indicators to evaluate the sewage discharge; the higher the COD value, the more serious the water pollution. Without effective treatment, a large amount of organic pollutants can be adsorbed and deposited by the sediment, which can cause lasting toxicity on aquatic organisms within several years, and then damage to the ecological environment (Zhang et al. 2021; Wang et al. 2017). The effectiveness of the COD removal process and the extent need for effective materials are the focus of current research (Badawi et al. 2021a; Badawi et al. 2021a, 2021b). Badawi et al. (2021a, 2021b) used ferric chloride (FeCl₃) as coagulant, nano-zero-valent iron (nZVI) as adsorbent, and micro-zeolite (MZ) as filter medium for the removal of COD from raw textile effluents. The achieved results revealed the COD removal efficiency by using hybrid treatment system reaching 97.5% and at low cost for real textile effluent remediation.

Magnetic coagulation technology is currently one of the main technologies for treating desulfurization wastewater. This technology adds magnetic powder to the ordinary coagulation and sedimentation process, which makes coagulants, pollutants, and magnetic powder floculate together to form a high dense floc, thus improving the effect of coagulation and sedimentation (Karam et al. 2020a, 2020b; Katriina et al. 2020). At the same time, the added magnetic powder can be recovered and recycled (Wang et al. 2016; Zhang et al. 2017). Extensive research has shown that the magnetic $\zeta$ potential on the surface of magnetic powder is negatively charged (Amiralian et al. 2020; Scardigli et al. 2021) the positive ions generated by the aqueous solution of coagulant gather around the negatively charged colloidal particles and magnetic powder under the effect of electric neutralization. As the static electromagnetic force disappears, the colloidal particles and magnetic
powder particles are aggregated under the effect of van der Waals force, and then, the flocs are further agglomerated and enlarged by the adsorption bridging effect of flocculant, which finally makes the pollutants and water departed from wastewater (Lin et al. 2021; Hamoud et al. 2017; Sherman et al. 2019).

As the main solid contaminant wastes emitted from coal-fired power plants, fly ash often causes pollution to the surrounding environment without effectively disposed (Liu et al. 2018; Renew et al. 2021). The use of fly ash as adsorbent and flocculant in water treatment can effectively solve the recycling problem of solid waste from coal-fired power plants, and realize the sustainable use of resources (Swarnalakshmi et al. 2018; Trang et al. 2021). The raw fly ash has limited ability to remove pollutants. Therefore, the current research has focused on modification of fly ash, so as to improve its ability to remove pollutants from wastewater (Gao et al. 2021; Hussain et al. 2021). Chen et al. (2020) used HCl and NaOH for acid–base modification of fly ash to remove norfloxacin from water. The results showed that after the modification, the specific surface area of fly ash increased and the removal effect of norfloxacin was significantly enhanced. At the optimal reaction conditions, the maximum norfloxacin removal of acid-modified and base-modified fly ash were increased by 109% and 171%, respectively. In order to obtain fly ash with better performance, two or more modification methods are usually combined to modify fly ash (Jin et al. 2018; Sroka et al. 2017; Teng et al. 2019). Qi et al. (2020) used base co-roasting to modify fly ash and applied it to the treatment of desulfurization wastewater, the results showed that when the adsorbent dosage of 10 g/L, the reaction pH = 8.0 and the reaction temperature of 333 K, the removal rate of Cl− from simulated wastewater reached 68.1%.

At present, much of the research on fly ash has described the removal of heavy metals and salts, while there are less published data on the removal of COD from water. In order to simplify the technological process of magnetic coagulation and reduce the cost, this study used H2SO4 and NaOH to modify fly ash with acid and base, and prepared a magnetic coagulant by mixed magnetic treatment. Microstructure analysis of the prepared coagulants was performed by SEM, EDS, FTIR, XPS, and vibrating sample magnetometer (VSM) techniques. The mechanisms of COD removal and maximum uptake have been thoroughly discussed by different isotherm models. Different kinetic models were performed to accurately specify the rate and equilibrium time of reaction for the coagulants. This study provided a feasible method for the preparation of efficient COD-trapping magnetic coagulant, and a new insight for the treatment of COD wastewater by magnetic coagulation.

### Materials and methods

#### Materials

**Reagents and instruments**

Reagents: Potassium hydrogen phthalate (purity 99.9%) was purchased from Aladdin Reagent (Shanghai) Co., Ltd.; H2SO4, NaOH, and NaCl were all analytical pure.

Instruments: XCSQ50 × 70 magnetic separator (Jiangxi Hengcheng Mineral Processing Equipment Co., Ltd., China); H1850 high-speed desktop centrifuge (Shanghai Anting Scientific Instrument Factory, China); PHS-3C pH measuring instrument (Shanghai Precision Scientific Instrument Co., Ltd., China), HZQ-X300C porous physisorption apparatus (Beishide Instrument Technology Co., Ltd., China) SS-550 scanning electron microscope (Shimadzu Corporation, Japan). IRTracer-100 infrared spectrum (Shimadzu Corporation, Japan); 250XI X-ray photoelectron spectrometer (Thermo ESCALAB, USA); SQUID-VSM magnetic measurement system (Quantum Design, USA).

#### Selection of original fly ash

The original fly ash used in this experiment is taken from Datang Baoding Thermal Power Plant, China, and the chemical composition of the original fly ash is shown in Table 1.

The sum of SiO2, Fe2O3, and Al2O3 in the original fly ash reaches up to 83.2 wt% (Table 1). We can use this property to modify the original fly ash and thus improve its ability to remove pollutants. The original fly ash has a high content of iron, so more magnetic fly ash can be screened out using the magnetic separator. As fly ash contains a large number of irregular and closed pores, there are a large number of Si and Al active sites. The active Si and Al sites in fly ash can be altered by chemical modification, which generates not only compounds with flocculation effect but also increases its specific surface area, so that chemically modified fly ash has better ability to remove pollutants (Chen et al. 2020).

#### Preparation of COD standard solution

Accurately weighted 0.8502 g of potassium hydrogen phthalate and dried at 378 K for 2 h was dissolved in distilled water, then transferred to a 1000-mL volumetric flask and fixed the volume to the mark. The COD concentration was 1000 mg/L.

### Table 1 Chemical composition of fly ash

| Compound | SiO2 | Fe2O3 | Al2O3 | CaO | K2O | MgO | Others |
|----------|------|-------|-------|-----|-----|-----|--------|
| Content (wt%) | 54.12 | 17.48 | 11.63 | 11.27 | 1.18 | 0.19 | 4.13 |
Preparation of coagulants

Magnetic fly ash: The dried original fly ash was placed in a magnetic separator and scanned under 1500 Gs magnetic field to obtain magnetic fly ash with iron content more than 30%. The magnetic fly ash was ball milled and then magnetically sorted in 1000 Gs magnetic field to remove the strongly magnetic fly ash with iron content greater than 40%. The magnetic fly ash with iron content between 30 and 40% was marked as Fe.

Fly ash: The non-magnetic fly ash, remaining in the strong magnetic field, was sifted through a 200-mesh sieve. The sample was marked as FA.

Base modified fly ash: FA was mixed with 2.0 mol/L NaOH solution at a solid–liquid ratio of 1:3. After continuous electric stirring at 80 r/min for 30 min in a constant temperature water bath at 323 K, the mixture was washed with distilled water until neutral, and then dried. The sample was marked as BFA.

Acid modified fly ash: FA was mixed with 2.0 mol/L H2SO4 solution at a solid–liquid ratio of 1:3, and 1.0 g NaCl was added. After 30 min of continuous electric stirring at 80 r/min in a 323-K constant temperature water bath, the mixture was washed with distilled water until neutral, and then dried. The sample was marked as AFA.

Mixed magnetic base/acid modified fly ash: Magnetic coagulants Fe-BFA and Fe-AFA were obtained by mixing BFA or AFA with Fe in a ratio of 10:3.

Characterization of coagulants

The specific surface area and pore volume of coagulants were determined by porous physisorption apparatus (EVO) (Li et al. 2020a, 2020b). The scanning electron microscopy energy dispersive spectroscopy analysis (SEM–EDS), Fourier Transform infrared spectroscopy (FTIR), and X-ray photoelectron spectroscopy (XPS) were used to characterize the particle size distribution, microstructure morphology, functional groups, and chemical state of coagulants, respectively (Lee et al. 2021a, 2021b; Abelmaksoud et al. 2021; Lee et al. 2021a, 2021b). A physical property measurement system-vibrating sample magnetometer (PPMS-VSM) was used to measure the magnetism of coagulants (Dennis et al. 2015; Li et al. 2020a, 2020b).

Methodology

A total of 10.00 g of FA, BFA, AFA, Fe-BFA, and Fe-AFA were taken into 250-mL conical flasks, and 100 mL of simulated wastewater with COD concentration of 400 mg/L was added. The initial pH of the solution was adjusted to 7.0 ± 0.2, and the test temperature was 298 K. After shaking and stirring for 60 min, the coagulation kinetic process was studied by sampling the solution at standing for 0, 1, 3, 5, 10, 15, 30, 45, 60, 120, 240, and 360 min. COD concentrations of 100, 200, 300, 400, 500, 600, 700, 800, 900, and 1000 mg/L were used to study the coagulation isothermal process. On the basis of coagulation isothermal experiments, the temperature was assessed at 288, 298, and 308 K to study the coagulation thermodynamic process. Repeatability experiments were performed five times. After shaking and stirring for 60 min, the solution was settled for 60 min, and a spectrometer (HACH DR/2000) with wavelengths of 620 nm was utilized to analyze the COD concentration of the upper clear layers.

All experiments were repeated three times, and the data were fitted and analyzed using Origin.

Data analysis

Removal amount

The removed COD amount $Q_t$, at time $t$ was calculated by Eq. 1:

$$Q_t = \frac{(C_0 - C_t)V}{m}$$

where $C_0$ and $C_t$ are the mass concentration of COD in the flocculation system at the initial and time $t$, respectively, mg/L; $V$ is the volume, L; and $m$ is the sample weight, g.

Coagulation kinetic analysis

The coagulation kinetics experiments were fitted and analyzed by the quasi-first-order (Eq. 2) and quasi-second-order kinetic equations (Eq. 3):

$$\frac{dQ_t}{dt} = k_1(Q_e - Q_t)$$

$$\frac{dQ_t}{dt} = k_2(Q_e - Q_t)^2$$

where $Q_e$ is the removed amount of COD at equilibrium, mg/g; $k_1$ is the quasi-first-order rate constant, h$^{-1}$; and $k_2$ is the quasi-second-order rate constant, g/(mg · h).

Coagulation isothermal analysis

The isothermal experiments were estimated by fitting the data with the Freundlich adsorption isotherm (Eq. 4) and the Langmuir adsorption isotherm (Eq. 5) to analyze the removal process of COD by fly ash samples. The equations are as follows:
where \( C_e \) is the mass concentration of COD in the solution at equilibrium, mg/L; \( K_f \) is the Freundlich equilibrium constant, mg\((1−1/n)/(g \cdot L^{1/n})\); \(1/n\) represents the constant of reaction strength; \(Q_m\) is the theoretical maximum removal capacity, mg/g; and \( K_L \) is the affinity coefficient, L/mg.

**Thermodynamic analysis of coagulation**

The Gibbs free energy relationships (Eqs. 6 and 7) were used to calculate the thermodynamic parameters (enthalpy change \( \Delta H \), entropy change \( \Delta S \)) of the coagulation process and analyze the effect of temperature on COD removal.

\[
\Delta G = -RT \ln K
\]

(6)

\[
\Delta G = \Delta H - T \Delta S
\]

(7)

where \( \Delta G \) is the Gibbs free energy change, kJ/mol; \( K \) is the thermodynamic equilibrium constant, which can be fitted by the Langmuir equation, L/mol; \( R \) is the ideal gas constant, 8.314 J/(mol \cdot K); \( T \) is the reaction temperature, K; \( \Delta H \) is the standard enthalpy change, kJ/mol; and \( \Delta S \) is the standard entropy change, kJ/(mol\cdotK). The values of \( \Delta G \) at different temperatures were derived according to Eq. 6. With \( \Delta G \) as the vertical coordinate and temperature as the horizontal coordinate, made a relation straight line of \( \Delta G \) vs \( T \), according to Eq. 7, its slope and intercept corresponded to the values of \( \Delta S \) and \( \Delta H \), respectively.

**Results and discussion**

**Characterization analysis of coagulant**

**BET specific surface area and pore volume analysis**

Table 2 shows the specific surface area and pore volume of FA, BFA, AFA, Fe-BFA, and Fe-AFA. It can be seen from Table 2 that the specific surface area and porosity of fly ash increased after modification. The specific surface areas of BFA and AFA were 11.77 and 22.22 m\(^2\)/g, respectively, which were 4.30 and 9.01 times higher than FA, and pore volumes were 1.75 and 3.00 times that of FA. However, in comparison, the specific surface area and pore volume of AFA were larger than those of BFA, which indicated that acid modification was more efficient in the formation of pore structure (Wang et al. 2019). The specific surface areas of the coagulants were increased further after mixing magnetization, and the specific surface areas of Fe-BFA and Fe-AFA were 20.33 and 28.67 m\(^2\)/g, respectively.

**SEM and EDS energy spectrum analysis**

Figure 1 shows SEM images of FA, BFA, AFA, Fe-BFA, and Fe-AFA. It can be seen from Fig. 1 that the surface of FA was smooth and its specific surface area was small. After the modification, due to the corrosive effect of NaOH and H\(_2\)SO\(_4\), the original surface morphology of fly ash was greatly changed. The surface of BFA and AFA was rougher than FA, and their specific surface area and porosity were significantly improved (Dmitry et al. 2020). Moreover, compared with BFA, the surface of AFA was rougher and more porous, and corroded to a greater extent. After the addition of magnetic powder, a large number of particles were attached to the surface of Fe-BFA and Fe-AFA, and the coagulants pores were more abundant.

In order to analyze whether the particles attached to the surface of Fe-BFA and Fe-AFA are doped with magnetic powders, EDS analysis was used to determine the approximate chemical composition of the coagulants. Figure 2 and Table 3 show EDS spectra and normalized mass percentage of chemical elements for FA, BFA, AFA, Fe-BFA, and Fe-AFA, respectively. The five coagulants contained mainly O, Al, and Si. The absorption peaks of Fe only appeared in the EDS energy spectra of Fe-BFA and Fe-AFA, while the content of Fe in FA, BFA, and AFA did not reach the detection limit of the instrument, and it was tentatively inferred that the magnetic powder successfully adhered to the surface of fly ash after acid–base modification. Another important finding was that after acid–base impregnation, FA reacted chemically with used acid–base solutions, which led to decrease of O content in modified fly ashes.

**FTIR analysis**

The changes of the main functional groups of the coagulant before and after the modification were analyzed by FTIR. Figure 3 shows FTIR spectra of FA, BFA, AFA, Fe-BFA, and Fe-AFA. As can be seen in Fig. 3, the five coagulants...
showed distinctive peaks near 1095 cm\(^{-1}\) and 464 cm\(^{-1}\), which were identified as Si--O bending vibration and stretching vibration peaks (Liu et al. 2020). The adsorption peak at 800 cm\(^{-1}\) is assigned to the Si--O-Si stretching vibration peak, and the adsorption peak at 557 cm\(^{-1}\) is assigned to the Al-O stretching vibration peak (Wang et al. 2015).

Compared with FA, the intensity of the characteristic peaks of Si–O and Al–O bonds in BFA and AFA were significantly weakened after the modification. It indicated that the modification produced changes to the chemical structure of the fly ash, and Si–O and Al–O bonds in FA were broken, which led to decrease of response values. Compared with BFA, the characteristic peak response values of AFA were further reduced. This result shows that the acid modification contributed more to the breakage of Si–O and Al–O bonds, which led to a stronger ability of AFA to remove pollutants (Sroka et al. 2017; Chen et al. 2020). It can also be seen from Fig. 3 that after the modification, Si–O–Si, Si–O, and Al–O bonds were redshifted to different degrees. The reason for this result is that the acid–base modification had a corrosive effect on the fly ash, which led to the expansion of Si–O, Al–O, and Si–O–Si bonds to different degrees, and to increase in the crystal spacing. Therefore, van der Waals and intermolecular forces were weakened and the absorption peaks were shifted to the long wavelength direction (Jhang et al. 2017). Compared with BFA and AFA, the characteristic peaks of Fe-BFA and Fe-AFA after mixing magnetization did not change much, indicating that the mixing magnetization only changed the physical properties of fly ash and did not change the chemical structure of fly ash.

**XPS analysis**

Figure 4 shows XPS spectra of FA, BFA, AFA, Fe-BFA, and Fe-AFA. The characteristic peaks of O1s, C1s, Si2p, and Al2p appeared in the five types of coagulants (Fig. 4a). Due to corrosive effect of NaOH and H\(_2\)SO\(_4\), the intensity of the O1s characteristic peaks on BFA and AFA was significantly weakened, which was the same as determined by EDS. After the mixing of modified fly ash, both Fe-BFA and Fe-AFA had Fe2p characteristic peaks on XPS curves. The Fe2p characteristic peaks on Fe-BFA and Fe-AFA were further analyzed, and Fig. 4b shows the fine mapping of the Fe2p region. The peak values of Fe2p\(_{3/2}\) and Fe2p\(_{1/2}\) in Fig. 4b are 712.4 and 725.8 eV, respectively, which coincided with the Fe2p peak in Fe\(_3\)O\(_4\) standard (Im et al. 2015). Further analysis showed that the magnetic material in Fe-BFA and Fe-AFA was Fe\(_3\)O\(_4\).

**Magnetization intensity analysis**

Figure 5 shows the variation curves of magnetization intensity with magnetic field for FA, BFA, AFA, Fe-BFA, and Fe-AFA. The VSM curves showed that the magnetization intensity of Fe-BFA and Fe-AFA increased with the increase of magnetic field, and the magnetization intensity finally reached the saturation values of 10.38 emu/g and
Fig. 2 EDS spectra of FA, BFA, AFA, Fe-BFA, and Fe-AFA
12.46 emu/g. Both Fe-BFA and Fe-AFA exhibited super-paramagnetism (Li et al. 2020a, 2020b). Since FA, BFA, and AFA were magnetically separated, the change of VSM curve was not obvious, and the saturation values of magnetization were 1.56, 1.42, and 1.29 emu/g, respectively. It can be seen from Fig. 5 that the prepared Fe-BFA and Fe-AFA magnetic coagulants have higher magnetic induction intensity after magnetic mixing.

Coagulation kinetic analysis

The prepared Fe-BFA and Fe-AFA magnetic coagulants have higher magnetic induction intensity after magnetic mixing. The coagulation kinetics experiment clearly demonstrated the significant change of removed COD amounts after the fly ash modification. This was due to the corrosive effect of base and acid, which increased the surface defects of fly ash.

Table 3 The normalized mass percentage of chemical elements (wt%) in FA, BFA, AFA, Fe-BFA, and Fe-AFA

| Sample | C   | O    | Al   | Si   | K    | Fe     | Others |
|--------|-----|------|------|------|------|--------|--------|
| FA     | 5.34| 33.86| 24.40| 30.58| 1.53 | Not detected | 4.29 |
| BFA    | 5.16| 28.72| 31.53| 29.36| 1.27 | Not detected | 4.96 |
| AFA    | 5.97| 25.23| 31.74| 29.19| 1.22 | Not detected | 6.65 |
| Fe-BFA | 4.75| 26.25| 30.73| 28.11| 1.01 | 3.23   | 5.92   |
| Fe-AFA | 5.05| 23.59| 30.25| 27.90| 0.92 | 3.77   | 8.52   |

Figure 6 shows the curves of COD removal by FA, BFA, AFA, Fe-BFA, and Fe-AFA with time. When the coagulant dosage was 100 g/L and the initial concentration of COD was 400 mg/L, the coagulation kinetic processes of FA, BFA, AFA, Fe-BFA, and Fe-AFA on COD were divided into the rapid phase and equilibrium phase. Within the first 30 min, which is the rapid coagulation stage, the removal of COD by all five coagulants exceeded 70% of the total removal, reaching 1.18, 1.48, 2.45, 2.43, and 3.53 mg/g for FA, BFA, Fe-BFA, AFA, and Fe-AFA, respectively. After 30 min of reaction time, the removal rates of COD by FA, BFA, AFA, and Fe-BFA gradually slowed down. Among them, FA and BFA reached equilibrium after 120 min, and the equilibrium removal amounts of COD were 1.67 mg/g and 2.04 mg/g, respectively. The equilibrium coagulation time of AFA and Fe-BFA was 60 min, and the removal amounts of COD at equilibrium were 2.79 mg/g and 2.58 mg/g, respectively. The results of the coagulation kinetic analysis showed that the removal of COD by coagulants could be further improved and the flocculation time shortened through the mixing magnetic operation of the acid modified fly ash.

The coagulation kinetics experiment clearly demonstrated the significant change of removed COD amounts after the fly ash modification. This was due to the corrosive effect of base and acid, which increased the surface defects of fly ash.
ash, enriched the porosity, and increased the specific surface area. Therefore, the BFA and AFA provided more free sites, and make more COD enriched on the surface of coagulants and removed by sedimentation through the coagulation process (Wang et al. 2020). The magnetic mixing operation of the chemically modified fly ash could further improve the coagulant’s ability to remove COD and greatly reduce the time required for flocculation reaction. The coagulant
Fig. 5 VSM curves of FA, BFA, AFA, Fe-BFA, and Fe-AFA

Fig. 6 Coagulation kinetics curves of COD removal by FA, BFA, AFA, Fe-BFA, and Fe-AFA
Fe-AFA, prepared by acid modification of fly ash followed by mixing magnetic process, showed the best removal efficiency. The removal of COD by Fe-AFA was approximately 2 times higher than that of FA, and the time to reach the best coagulation effect was shortened by 4 times.

The coagulation kinetics of COD removal by FA, BFA, AFA, Fe-BFA, and Fe-AFA was fitted using quasi-first-order and quasi-second-order kinetic equations. The correlation coefficients and residuals are listed in Table 4. Compared with quasi-first-order kinetic equations, the $R^2$ values of quasi-second-order kinetic equation for FA, BFA, AFA, Fe-BFA, and Fe-AFA were 0.92, 0.89, 0.94, 0.94, and 0.94, respectively, which reached the highly significant correlation level. Meanwhile, the residual values of quasi-second-order kinetic equation were 0.26, 0.45, 0.42, 0.36, and 0.60, respectively, and the fitted data were more reliable than quasi-first-order kinetic equations. In summary, the quasi-second-order kinetic equation fitted well the removal kinetics of COD by five coagulants. Therefore, it was inferred that the process of COD removal by the five coagulants was not a single coagulation reaction, but the result of multiple mechanisms (such as surface adsorption, chemisorption, coagulation, and precipitation) acting simultaneously (Folens et al. 2017; Karam et al. 2020a, 2020b).

Coagulation isothermal analysis

Figure 7 shows the curves of COD removal by FA, BFA, AFA, Fe-BFA, and Fe-AFA with the initial concentration at 298 K. When the coagulant addition was 100 g/L, the removed COD amounts of five coagulants showed an increasing trend with the initial concentration and finally reached saturation. The maximum COD amounts removed by FA, BFA, AFA, Fe-BFA, and Fe-AFA were 2.18, 3.21, 4.63, 3.71, and 5.69 mg/g, respectively, and the removal capacity was in the order; Fe-AFA > AFA > Fe-BFA > BFA > FA. In comparison with FA, after modification by NaOH and $\text{H}_2\text{SO}_4$, the maximum removal of COD by BFA and AFA increased by 47.20% and 112.43%, respectively. Moreover, through the magnetic mixing operation of the modified coagulant, the COD removal ability of the new coagulant is further increased. Compared with FA, the COD removal of Fe-BFA and Fe-AFA increased by 70.18% and 160.87%, respectively. The experimental results showed that the new coagulant prepared from fly ash by acid–base modification and mixing magnetic process could significantly improve the removal ability of COD. Li et al. (2017) also showed that acid–base modification of biochar from potato stem and leaf could improve its adsorption capacity for sulfathiazole.

The coagulation isotherm curves of COD removal by FA, BFA, AFA, Fe-BFA, and Fe-AFA were fitted using the Freundlich and Langmuir equations, and the specific parameters are shown in Table 5. The fitted correlation coefficient $R^2$ values of the Langmuir equation for FA, BFA, AFA, Fe-BFA, and Fe-AFA were 0.89, 0.97, 0.99, 0.97, and 0.98, respectively, which were higher than the fitted values of the Freundlich equation. Meanwhile, the residual values of the Langmuir fitted data were lower than those of the Freundlich fitted data. The coagulation isotherm curves in Fig. 7 also showed that the Langmuir isotherm equation fitted better the measured data, so the Langmuir equation could better reflect the COD removal process of the five coagulants at 298 K. This indicated that the COD removal process using the five coagulants mainly occurred in the single molecular layer on the surface of fly ash (Zhu et al. 2018), and the number of adsorption sites on the surface of coagulants determined the strength of their removal ability of COD. In the Langmuir equation, $K_L$ represented the affinity constant, and the larger the value, the stronger association between the coagulant and the pollutants (Wang et al. 2019). In Table 5, the $K_L$ values of FA, BFA, AFA, Fe-BFA, and Fe-AFA were 0.004, 0.005, 0.008, 0.007, and 0.023, respectively. The $K_L$ and $Q_m$ values for Fe-AFA were the highest, consistent with the results of isothermal experiment. The $K_L > 0$ indicated that the COD removal process of five coagulants was spontaneous at room temperature (Graouerbacart et al. 2015).

Coagulation thermodynamic analysis

Table 6 shows the coagulation thermodynamic fitting parameters of COD removal by FA, BFA, AFA, Fe-BFA, and Fe-AFA at different temperatures. The Gibbs free energy

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### Table 4 Coagulation kinetic fitting parameters of COD removal by FA, BFA, AFA, Fe-BFA, and Fe-AFA

| Sample  | Quasi-first-order kinetic | Quasi-second-order kinetic |
|---------|---------------------------|---------------------------|
|         | $Q_e$ (mg/g) | $k_{1h} (1/h)$ | $R^2$ | Residual | $Q_e$ (mg/g) | $k_{2h} (1/(mg · h))$ | $R^2$ | Residual |
| FA      | 1.62         | 0.056         | 0.89** | 0.33 | 1.76         | 0.047         | 0.92** | 0.26 |
| BFA     | 1.95         | 0.067         | 0.84** | 0.62 | 2.11         | 0.048         | 0.89** | 0.45 |
| AFA     | 2.69         | 0.144         | 0.90** | 0.69 | 2.87         | 0.077         | 0.94** | 0.42 |
| Fe-BFA  | 2.52         | 0.184         | 0.91** | 0.52 | 2.66         | 0.111         | 0.94** | 0.36 |
| Fe-AFA  | 3.47         | 0.292         | 0.94** | 0.64 | 3.64         | 0.131         | 0.94** | 0.60 |

** Extremely significant correlation ($p < 0.001$)
The change $\Delta G$ of FA, BFA, AFA, Fe-BFA, and Fe-AFA at different temperatures were less than 0, consequently indicating spontaneous coagulation (Zhai and Li 2019). The enthalpy change values of FA, BFA, AFA, Fe-BFA, and Fe-AFA are 24.26, 11.98, 11.46, 33.60, and 25.26 kJ/mol, respectively. On the one hand, with $\Delta H > 0$, indicated that their coagulation is an endothermic process. On the other hand, the $|\Delta H| < 40$ kJ/mol, suggested that the coagulation process of COD occurred through van der Waals forces and hydrogen bonding (Taha et al. 2021). The entropy change values $\Delta S$ of the five coagulants were all greater than 0, indicating that the removal of COD by coagulants was an irreversible process (Toumi et al. 2015). In summary, the COD removal of FA, BFA, AFA, Fe-BFA, and Fe-AFA was a spontaneous, endothermic and irreversible process.

Table 5  Coagulation isotherm fitting parameters of COD removal by FA, BFA, AFA, Fe-BFA, and Fe-AFA

| Sample | $T$/K | Freundlich | | | Langmuir | |
| --- | --- | --- | --- | --- | --- | --- | --- |
| | | $K_f$ | $n$ | $R^2$ | Residual | $Q_m$(mg/g) | $K_L$(L/mg) | $R^2$ | Residual |
| FA | 298 | 0.13 | 0.45 | 0.77** | 0.81 | 3.09 | 0.004 | 0.89** | 0.41 |
| BFA | 298 | 0.17 | 0.47 | 0.90** | 0.74 | 4.56 | 0.005 | 0.97** | 0.22 |
| AFA | 298 | 0.35 | 0.43 | 0.92** | 1.16 | 6.09 | 0.008 | 0.99** | 0.19 |
| Fe-BFA | 298 | 0.30 | 0.41 | 0.87** | 1.19 | 4.81 | 0.007 | 0.97** | 0.32 |
| Fe-AFA | 298 | 0.96 | 0.31 | 0.85** | 3.76 | 6.57 | 0.023 | 0.98** | 0.50 |

**Extremely significant correlation ($p \leq 0.001$)

Reuse test analysis of coagulants

Figure 8 shows the effect of reuse times on COD removal efficiency by FA, BFA, AFA, Fe-BFA, and Fe-AFA. When the coagulant dosage was all 100 g/L, and the initial concentration of COD was 400 mg/L, the COD removal rates of FA, BFA, AFA, Fe-BFA, and Fe-AFA decreased with the increase of the reuse times. At the first use, the COD removal rates of FA, BFA, AFA, Fe-BFA, and Fe-AFA were 41.63%, 51.02%, 70.05%, 64.78%, and 87.92%, respectively. After the 5th recycling, the COD removal rates of the five coagulants were 16.69%, 27.20%, 48.31%, 45.64%, and 68.37%, respectively. The COD removal capacity of the five coagulants was in the order: Fe-AFA > AFA > Fe-BFA > BFA > FA. Due to the limited adsorption performance of fly ash, the...
removal capacity of COD was gradually reduced after several coagulations. Through acid–base modification of fly ash and mixed magnetic operation, the surface of the new coagulant Fe-AFA was rougher, the adsorption sites were increased, thus enhancing the adsorption and flocculation capacity of the coagulant (Wang et al. 2020). It is worthy to note that the COD removal rate by Fe-AFA remained above 60% after five reuse steps.

### Conclusions

In this paper, we prepared five fly ash-derived coagulants: FA, BFA, AFA, Fe-BFA, and Fe-AFA. Through the acid–base modification, the Si–O-Si, Si–O, and Al-O bonds on the FA surface were broken, and the specific surface area and pore volume were significantly increased. The specific surface area of base (BFA) and acid (AFA) modified fly ashes was 4.30 and 9.01 times larger than that of original fly ash (FA), respectively. In addition, we successfully prepared magnetic coagulants Fe-BFA and Fe-AFA. After mixing the magnet, Fe existed in the form of $\text{Fe}_3\text{O}_4$ in the coagulant, and both Fe-BFA and Fe-AFA exhibited superparamagnetism.

The results of coagulation experiments showed that under the same experimental conditions, the removal ability of COD by five coagulants was in the order: Fe-AFA > AFA > Fe-BFA > BFA > FA. The maximum COD amounts removed by FA, BFA, AFA, Fe-BFA, and Fe-AFA were 2.18, 3.20, 4.63, 3.71, and 5.69 mg/g, respectively, and the coagulation equilibrium times were 120 min, 120 min, 60 min, 60 min, and 30 min, respectively. Fe-AFA showed the best coagulation performance, the COD removal increased by 112.43% compared with FA, and the time required for coagulation equilibrium was shortened by

![Fig. 8 Effect of recovery times on COD removal efficiency by FA, BFA, AFA, Fe-BFA, and Fe-AFA](image-url)

| Sample  | $T$ (K) | $K_L$ | $\Delta G$ (kJ/mol) | $\Delta H$ (kJ/mol) | $\Delta S$ (J/K mol) |
|---------|--------|-------|---------------------|---------------------|---------------------|
| FA      | 288    | 522.46| −14.99              | 24.26               | 0.136               |
|         | 298    | 738.66| −16.36              |                     |                     |
|         | 308    | 1008.90| −17.71              |                     |                     |
|         | 288    | 756.67| −15.87              | 11.98               | 0.096               |
| BFA     | 298    | 810.72| −16.59              |                     |                     |
|         | 308    | 1044.93| −17.80              |                     |                     |
|         | 288    | 1297.15| −17.16              | 11.46               | 0.099               |
| AFA     | 298    | 1351.20| −17.86              |                     |                     |
|         | 308    | 1765.57| −19.14              |                     |                     |
| Fe-BFA  | 288    | 900.80| −16.29              | 33.60               | 0.172               |
|         | 298    | 1261.12| −17.69              |                     |                     |
|         | 308    | 2233.98| −19.75              |                     |                     |
| Fe-AFA  | 288    | 2756.45| −18.97              | 25.26               | 0.153               |
|         | 298    | 4179.71| −20.66              |                     |                     |
|         | 308    | 5476.86| −22.04              |                     |                     |

![Table 6 Thermodynamic parameters of COD removal by FA, BFA, AFA, Fe-BFA, and Fe-AFA](image-url)
3 times. The coagulation characterization showed that the quasi-second-order kinetic equation and the Langmuir isotherm equation could better fit the process of COD removal by coagulants, and the thermodynamic analysis showed that the process was spontaneous, heat-absorbing, and disorder. Impressively, after five cycles, the COD removal amount of Fe-AFA was 2.74 mg/g, and the removal rate still reached 67.53%. Therefore, the coagulant Fe-AFA with the highest specific surface area, stability, and coagulation performance can be considered a good candidate for the removal of COD from desulfurization wastewater.

Author contribution Wen Wang: investigation, formal analysis, writing — original draft. Li-Qiang Qi: conceptualization, writing — review and editing, supervision, funding acquisition. Pan Zhang: data curation, methodology. Ji-Chen Luo: investigation, formal analysis. Jing-Xin Li: resources, methodology.

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Declarations

Ethics approval and consent to participate Not applicable.

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