Removal of COD in Wastewater By Magnetic Coagulant Prepared From Modified Fly Ash

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Research Article

Keywords: Fly ash, Acid-base modification, Mixed magnetic, Coagulant, COD, Kinetic

Posted Date: December 6th, 2021

DOI: <https://doi.org/10.21203/rs.3.rs-1078441/v1>

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Version of Record: A version of this preprint was published at Environmental Science and Pollution Research on March 8th, 2022. See the published version at <https://doi.org/10.1007/s11356-022-19540-0>.

Abstract

In order to investigate the effective method of COD removal from desulfurization wastewater, acid-modified fly ash (AFA) and base-modified fly ash (BFA) were prepared by impregnation method. Then, magnetic coagulants (Fe-AFA, Fe-BFA) were prepared by mixing the modified fly ash with magnetic components. The structural characterization results showed that the specific surface area and the porosity of fly ash were obviously increased after modification. Fe-AFA magnetic coagulant has the best performance and superparamagnetism. Under the same experimental conditions, the maximum COD removal amounts of FA, BFA, AFA, Fe-BFA and Fe-AFA were 2.180, 3.209, 4.631, 3.710 and 5.687 mg/g, respectively. The COD removal amount of Fe-AFA was increased by 112.43% compared with the raw FA. The quasi-second-order kinetic and Langmuir equation could well fit the COD coagulation process of five coagulants. After five cycles, the COD removal amount of Fe-AFA was 2.735 mg/g, and the removal rate still reached 67.53%. These findings provide a feasible method for the treatment of fly ash from coal-fired power plants and the preparation of highly efficient COD trapping magnetic coagulants.

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 (Gao 2018). The 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).

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 flocculate together to form a high dense floc, thus improving the effect of coagulation and sedimentation. 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 ζ 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, Finqueneisel and Azambre 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, Ho and Babel 2021). The primitive 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, Zhang and Qi 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 333K, the removal rate of Cl^- from simulated wastewater reached 68.1%.

At present, much of the research on fly ash has been describe the removal of heavy metal and salt, while little published data on the removal of COD in water. In order to simplify the technological process of magnetic coagulation and reduce the cost, this study used H_2SO_4 and NaOH to modify fly ash with acid and base, and prepared a magnetic coagulant by mixed magnetic treatment. Through the characterization analysis and mixed magnetic treatment of coagulant, the removal mechanism of COD in water was studied, which provides 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.

Experimental Section

Experiment materials

Reagents: glucose standard product (purity 99.9%) was purchased from Aladdin Reagent (Shanghai) Co., Ltd.; H_2SO_4 , NaOH, and NaCl were all analytical pure.

Instruments: XCSQ50×70 magnetic separator (Jiangxi Hengcheng Mineral Processing Equipment Co., Ltd., China); 6B-12 COD intelligent digestion instrument, 6B-80 intelligent water quality analyzer (Jiangsu Shengao Hua Environmental Protection 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 a power plant in North China, and the chemical composition of the original fly ash is shown in Table 1.

Table 1 Chemical composition of fly ash								
Compound	SiO ₂	Fe ₂ O ₃	Al ₂ O ₃	CaO	K ₂ O	MgO	MnO	Others
Content(%)	54.1	17.5	11.6	11.3	1.18	0.192	0.126	4.002

What stands out in the table is the content of SiO₂, Fe₂O₃ and Al₂O₃ in the original fly ash is as high as 83.2%. As fly ash contains a large number of irregular and closed pores, there are a large number of Si and Al active points. The active using Al and Si in fly ash can be released by chemical modification, which can not only generate compounds with flocculation effect, but also increase its specific surface area, so that fly ash has both flocculation and adsorption in solution.

Coagulant preparation

Magnetic fly ash: Firstly, put the dried original fly ash into the magnetic separator and scan the fly ash under strong magnetic field to obtain magnetic fly ash with iron grade more than 30%. Subsequently, the magnetic fly ash was ball milled and then magnetically sorted in a weak magnetic field to remove the strongly magnetic fly ash with an iron grade greater than 40%, and finally obtain medium to strong magnetic fly ash with iron grade between 30% and 40%. The magnetic fly ash obtained by magnetic separation was marked as Fe.

Fly ash: Take the non-magnetic fly ash remaining in the strong magnetic field, and through 200 mesh to obtain the non-magnetic fly ash, which was sealed and stored for later use. The sample was marked as FA.

Base modified fly ash: Prepare 2.0 mol/L NaOH solution, mixed it with FA according to a solid-liquid ratio of 1:3, stirred continuously electrically at 298K in a constant temperature water bath at 80r/min for 30 min, filtered, dried, ground and set aside. The sample was marked as BFA.

Acid modified fly ash: Prepare 2.0 mol/L H₂SO₄ solution, mixed with FA according to the ratio of solid-liquid ratio of 1:3, and add 1.0 g NaCl, other operations were the same as BFA preparation process. The sample was marked as AFA.

Mixed magnetic base modified fly ash: Fully mix the BFA with Fe in the ratio of 10:3 to obtain the magnetic coagulant. The sample was marked as Fe-BFA.

Mixed magnetic acid modified fly ash: Fully mix the AFA with Fe in the ratio of 10:3 to obtain the magnetic coagulant. The sample was marked as Fe-AFA.

Characterization of coagulants

The specific surface area and pore volume of coagulants were determined by porous physisorption apparatus (EVO) (Li et al. 2020). 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. 2021; Abdelmaksoud et al. 2021; Lee et al. 2021). 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. 2020).

Experimental design

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 298K. After shaken and stirred for 60 min, the samples were taken at 0, 1, 3, 5, 10, 15, 30, 45, 60, 120, 240 and 360 min, respectively, to study the coagulation kinetic process. COD concentration of 100, 200, 300, 400, 500, 600, 700, 800, 900 and 1000 mg/L, respectively, to study the coagulation isothermal process. On the basis of coagulation isothermal experiments, the temperature was assessed at 288, 298, and 308 K, respectively, to study the coagulation thermodynamic process. Repeatability experiments were performed five times. After shaking and stirring for 60 min, the solution was left for 60 min and the COD concentration of the upper clear layer was measured.

All the above experiments were performed with 3 groups of duplicates, and the data were fitted and analyzed using Origin.

Data analysis processing

Removal amount

Eq. (1) is the calculation formula of COD removal amounts Q_t at time t :

$$Q_t = \frac{(C_0 - C_t)V}{m} \quad (1)$$

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; m is the sample weight, g.

Coagulation kinetic analysis

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

$$\frac{dQ_t}{dt} = k_1(Q_\infty - Q_t) \quad (2)$$

$$\frac{dQ_t}{dt} = k_2(Q_e - Q_t)^2 \quad (3)$$

Where Q_e is the removal amounts of COD at equilibrium, mg/g; k_1 is the quasi-first-order rate constant, h^{-1} ; k_2 is the quasi-second-order rate constant, $g/(mg \cdot h)$.

Coagulation isothermal analysis

The isothermal experiments were performed by fitting the data with Freundlich equation (4) and Langmuir equation (5) to analyze the removal process of COD by FA, BFA, AFA, Fe-BFA and Fe-AFA. The equations are as follows.

$$\ln Q_e = \ln K_f + \frac{1}{n} \ln C_e \quad (4)$$

$$\frac{1}{Q_e} = \frac{1}{Q_m} + \frac{1}{K_L Q_m C_e} \quad (5)$$

Where C_e is the mass concentration of COD in the solution system at equilibrium, mg/L; K_f is the Freundlich equilibrium constant; n represents the constant of reaction strength; Q_m is the theoretical maximum removal, mg/g; K_L is the affinity coefficient, L/mg.

Thermodynamic analysis of coagulation

The Gibbs free energy equations (6) and (7) were used to calculate the thermodynamic parameters (enthalpy change ΔH , entropy change ΔS) of the coagulation process and analyze the effect of temperature on COD removal.

$$\Delta G = -RT \ln K \quad (6)$$

$$\Delta G = \Delta H - T \Delta S \quad (7)$$

Where ΔG 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·K); T is the reaction temperature, K; ΔH is the standard enthalpy change, kJ/mol; ΔS is the standard entropy change, kJ/(mol·K); make a relation straight line of $\Delta G - T$, whose slope and intercept correspond to the values of ΔS and ΔH , respectively.

Results And Discussion

Characterization analysis of coagulant

BET specific surface area and pore volume analysis

Table 2
Specific surface area and pore volume analysis

Sample	Specific surface area (m ² /g)	Pore volume (cm ³ /g)
FA	2.220	0.004
BFA	11.767	0.011
AFA	22.218	0.016
Fe-BFA	20.325	0.018
Fe-AFA	28.636	0.022

Table 2 shows the specific surface area and pore volume of FA, BFA, AFA, Fe-BFA and Fe-AFA. What stands out in the table is the specific surface area and the porosity of fly ash were obviously increased after modification. The specific surface areas of BFA and AFA were 11.767 and 22.218 m²/g, respectively, which were 4.30 and 9.01 times higher than FA, and the pore volume were 1.75 and 3.00 times that of FA. However, in comparison, the specific surface area and pore volume of the AFA were better than that of the BFA, which indicated that acid modification was more helpful to the formation of pore structure. 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 20.325 and 28.636 m²/g, respectively.

SEM and EDS energy spectrum analysis

Figure 1 shows the SEM images of FA, BFA, AFA, Fe-BFA and Fe-AFA. It can be seen from Figure 1 that the surface of FA was smoothly and the specific surface area was small. After the modification, due to the corrosive effect of NaOH and H₂SO₄, the original surface morphology of fly ash was greatly changed. The surface of BFA and AFA was rougher than FA, and the specific surface area and porosity have been significantly improved. Moreover, compared with BFA, the surface of AFA was rougher and more porous, and the surface was 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, which made the surface of the coagulant show "flocculence". and the coagulants porosity were more abundant.

In order to analyze whether the particles attached to the surface of Fe-BFA and Fe-AFA are doped magnetic powders, EDS analysis was used to determine the elements of the coagulants. The Fig. 2 and Table 3 shows the EDS spectra and elemental normalized mass percentage of FA, BFA, AFA, Fe-BFA and Fe-AFA, respectively. From Fig. 2 and Table 3, it can be seen that the five coagulants are mainly based on O, Al and Si elements. The absorption peaks of Fe element only appeared in the EDS energy spectra of Fe-BFA and Fe-AFA, while the content of Fe element 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, the FA reacted chemically with the acid-base solution, which leads to a reduction of O element content in the modified fly ash.

Table 3
The normalized mass percentage of elements (wt%) of 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

FTIR analysis

The changes of the main functional groups of the coagulant before and after the modification were analyzed by FTIR. Fig. 3 shows the 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 the FTIR of the FA, the intensity of the characteristic peaks of the 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 the Si-O and Al-O bonds in the FA were broken, which led to decrease of response values. Compared with BFA, the characteristic peak response values of AFA were further reduced. This results was shown that the acid modification contributed more to the breakage of Si-O and Al-O bonds, which made the acid-modified coagulant have stronger coagulation and adsorption ability. It can also be seen from Fig. 3 that after the modification, the Si-O-Si, Si-O, and Al-O bond were redshifted to different degrees. The reason for this result is that the acid-base modification will have a corrosive effect on the fly ash, which leads to the expansion of Si-O, Al-O and Si-O-Si bonds to different degrees, and an increase in the crystal spacing. Therefore, the van der Waals and intermolecular forces were reduced 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, indicated 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 the XPS spectra of FA, BFA, AFA, Fe-BFA and Fe-AFA. It can be seen from Figure 4(a) that the characteristic peaks of O1s, C1s, Si2p and Al2p appeared in the five kinds of coagulants. Due to the erosion effect of NaOH and H_2SO_4 , the intensity of the O1s characteristic peaks on the BFA and AFA was significantly weakened, which was the same as that determined by EDS in 3.1.2. After the mixing of

modified fly ash, both Fe-BFA and Fe-AFA had Fe2p characteristic peaks on the XPS curves, which indicated that the magnets had been successfully mixed with fly ash. The Fe2p characteristic peaks on Fe-BFA and Fe-AFA were further analyzed, and Figure 4(b) showed the fine mapping of the Fe2p region. The peak values of Fe2p_{3/2} and Fe2p_{1/2} in Figure 4(b) are 712.4 and 725.8 eV, respectively, which coincided with the Fe2p peak in Fe₃O₄ standard (Im et al. 2015). Further analysis showed that the magnetic material in Fe-BFA and Fe-AFA was Fe₃O₄.

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 12.46 emu/g. Both Fe-BFA and Fe-AFA exhibited superparamagnetism (Li et al. 2020). Since FA, BFA and AFA were magnetically separated, the change of VSM curve were not obvious, and the saturation values of magnetization were 1.56, 1.42, and 1.29 emu/g, respectively. It can be seen from Figure 5 that the prepared Fe-BFA and Fe-AFA magnetic coagulants have higher magnetic induction intensity after magnetic mixing.

Coagulation kinetic analysis

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 a rapid phase and an equilibrium phase. Within 0-30 min, which is the rapid coagulation stage, the removal of COD by all five coagulants exceeded 70% of the total removal, reaching 1.180, 1.475, 2.451, 2.425 and 3.527 mg/g, respectively. Among them, when the coagulation time was 30 min, the coagulation system of Fe-AFA to COD reached equilibrium. 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 of reaction, and the equilibrium removal amounts of COD were 1.665 mg/g and 2.039 mg/g. The equilibrium coagulation time of AFA and Fe-BFA was 60 min, and the removal amounts of COD at equilibrium were 2.786 mg/g and 2.582 mg/g, respectively. The results of the coagulation kinetic analysis were shown that the coagulant removal of COD can be further improved and the flocculation time shortened by mixing magnetic operation of the modified fly ash.

The coagulation kinetics experiment clearly demonstrates the significant change of the COD removal amounts after modification. This was due to the corrosive effect of base and acid, which increased the surface defects of fly ash, enriched the porosity, and increased the specific surface area. Therefore, the coagulation provided more adsorption sites, and the adsorption capacity were enhanced, which makes more COD enriched on the surface of coagulations and removed by sedimentation through the coagulation process (Wang et al. 2020). The magnetic mixing operation of the modified fly ash can further improve the coagulant's ability to remove COD and greatly reduce the time required for flocculation reaction. The coagulant Fe-AFA, prepared by acid modification of fly ash followed by mixing

magnetic process, showed the best removal effect. The removal of COD by Fe-AFA was increased 111.83% 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 were fitted using quasi-first-order and quasi-second-order kinetic equations, respectively. The correlation parameters were shown in Table 4. It is apparent from this table that the quasi-second-order kinetic equation model fitted well for the five coagulants to remove COD. The R^2 values of the fitted equations for FA, BFA, AFA, Fe-BFA and Fe-AFA were 0.9118, 0.8873, 0.9410, 0.9375 and 0.9417, respectively, which reached the highly significant correlation level. In summary, these results show that the quasi-second-order kinetic equations can better fitted the coagulation kinetic processes of FA, BFA, AFA, Fe-BFA and Fe-AFA on COD. Therefore, it was inferred that the process of COD removal by the five coagulants was not a single flocculation reaction, but the result of multiple mechanisms (such as surface adsorption, chemisorption, coagulation and precipitation, etc.) acting simultaneously (Folens et al. 2017).

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		
	$Q_{e,1}$	k_1	R^2	$Q_{e,2}$	k_2	R^2
FA	1.623	0.0558	0.8856**	1.761	0.0472	0.9118**
BFA	1.952	0.0670	0.8424**	2.111	0.0480	0.8873**
AFA	2.689	0.1441	0.9033**	2.868	0.0768	0.9410**
Fe-BFA	2.518	0.1835	0.9102**	2.661	0.1105	0.9375**
Fe-AFA	3.472	0.2915	0.9373**	3.643	0.1306	0.9417**
Note: ** indicates extremely significant correlation ($p \leq 0.001$).						

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 COD removal amounts of five coagulants showed a trend of increasing with the initial concentration and finally reached saturation. The maximum COD removal amounts of five coagulants were 2.180, 3.209, 4.631, 3.710 and 5.687 mg/g, respectively, and the removal capacity were order by Fe-AFA>AFA>Fe-BFA>BFA>FA. After modification by NaOH and H₂SO₄, 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 flocculant, the COD removal ability of the new flocculant is further enhanced. Compared with FA, the removal of COD by Fe-

BFA and Fe-AFA has 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 isothermal of COD removal by FA, BFA, AFA, Fe-BFA and Fe-AFA were fitted using Freundlich and Langmuir equations, respectively, 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 0.8857, 0.9703, 0.9876, 0.9660 and 0.9794, respectively, which were higher than the fitted values of the Freundlich equation and showed good correlation. The isothermal curve of coagulation in Fig. 7 also showed that the Langmuir model curve fits better with the measured values, so the Langmuir equation can better reflect the COD removal process of the five coagulants at 298 K. The correlation coefficients R^2 has reached a extremely significant correlation. This indicated that the COD removal process of the five coagulants mainly occurs 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 determines 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 the removal capacity of the coagulant for the pollutant (Wang et al. 2019). In Table 5, the K_L values of the five coagulants were 0.0041, 0.0045, 0.0075, 0.0070, and 0.0232, respectively, and the K_L value obtained by Fe-AFA fitting was the highest and the theoretical removal capacity is the strongest, which was consistent with the results of isothermal experiment. The $K_L>0$, indicated that the COD removal process of five coagulants can be carried out spontaneously at room temperature (Graouerbacart, Sayen and Guillon 2015).

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	$Q_m(\text{mg/g})$	$K_L(\text{L/mg})$	R^2
FA	298	0.1267	2.243	0.7725**	3.091	0.0041	0.8857**
BFA	298	0.1664	2.120	0.8988**	4.555	0.0045	0.9703**
AFA	298	0.3497	2.331	0.9246**	6.091	0.0075	0.9876**
Fe-BFA	298	0.2949	2.436	0.8736**	4.810	0.0070	0.9660**
Fe-AFA	298	0.9632	3.188	0.8461**	6.565	0.0232	0.9794**
Note: ** indicates extremely significant correlation ($p\leq0.001$).							

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 change ΔG 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 process is an endothermic process. On the other hand, the $|\Delta H| < 40$ kJ/mol, suggested that the coagulation process of COD was occurred through van der Waals forces and hydrogen bonding (Taha et al. 2021). The entropy change values ΔS of the five coagulants were all greater than 0, indicated 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 6
Thermodynamic parameters of COD removal by FA, BFA, AFA, Fe-BFA and Fe-AFA

Sample	T /K	K_L / L·mol ⁻¹	ΔG / kJ·mol ⁻¹	ΔH / kJ·mol ⁻¹	ΔS / kJ·mol ⁻¹ ·K ⁻¹
FA	288	522.46	-14.99	24.26	0.136
	298	738.66	-16.36		
	308	1008.90	-17.71		
BFA	288	756.67	-15.87	11.98	0.096
	298	810.72	-16.59		
	308	1044.93	-17.80		
AFA	288	1297.15	-17.16	11.46	0.099
	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		

Repeatability test analysis of coagulants

Figure 8 shows the effect of recovery 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 repetition 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 were order by 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). What is interesting about the data in Figure 8 is that the COD removal rate by Fe-AFA remained above 60% after five recycling.

Conclusions

In this paper, we have prepared five 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 BFA and AFA being 4.30 and 9.01 times that of FA, respectively. In addition, we successfully prepared magnetic coagulants Fe-BFA and Fe-AFA. After mixing the magnet, Fe existed in the form of Fe_3O_4 in the coagulant, and both Fe-BFA and Fe-AFA exhibited superparamagnetic.

The results of coagulation experiments showed that under the same experimental conditions, the removal ability of COD were order by Fe-AFA>AFA>Fe-BFA>BFA>FA. The maximum COD removal amounts of FA, BFA, AFA, Fe-BFA and Fe-AFA were 2.180, 3.209, 4.631, 3.710 and 5.687 mg/g, respectively, and the coagulation equilibrium times were 120 min, 120 min, 60 min, 60 min and 30 min, respectively. After modified-mixed magnetic, the performance of coagulant on COD removal was significantly improved. 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 3 times. The coagulation characterization showed that the quasi-secondary 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 disordered. Impressively, after five cycles, the COD removal amount of Fe-AFA was 2.735 mg/g, and the removal rate still reached 67.53%. Therefore, the coagulant Fe-AFA with highest specific surface area, stability and coagulation performance can be considered a good candidate for the removal of COD from desulfurization wastewater.

Declarations

Author contributions Wen Wang: Investigation, Formal analysis, Writing - original draft. Li-Qiang Qi: Conceptualization, Writing – review & editing, Supervision, Funding acquisition. Pan Zhang: Data curation, Methodology. Ji-Chen Luo: Investigation, Formal analysis. Jing-Xin Li: Resources, Methodology.

Funding This work was supported by Natural Science Foundation of Hebei Province [grant numbers B2019502067]; and the Fundamental Research Funds for the Central Universities [grant numbers 2020MS152].

Data availability Not applicable

Ethics approval and consent to participate Not applicable.

Consent to publish Not applicable.

Competing interests The authors declare no competing interests.

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Figures

Figure 1

SEM diagrams of FA, BFA, AFA, Fe-BFA and Fe-AFA

Figure 2

EDS spectra of FA, BFA, AFA, Fe-BFA and Fe-AFA

Figure 3

FTIR spectra of FA, BFA, AFA, Fe-BFA and Fe-AFA

Figure 4

XPS spectra of FA, BFA, AFA, Fe-BFA and Fe-AFA (a) and fine spectra of Fe2p peak (b)

Figure 5

VSM curves of FA, BFA, AFA, Fe-BFA and Fe-AFA

Figure 6

Coagulation kinetics curves of COD removal by FA, BFA, AFA, Fe-BFA and Fe-AFA

Figure 7

Coagulation isotherm curve of COD removal by FA, BFA, AFA, Fe-BFA and Fe-AFA

Figure 8

Effect of recovery times on COD removal efficiency by FA, BFA, AFA, Fe-BFA and Fe-AFA