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Optimization modeling and mechanism discussion on specific industrial coal-washing wastewater treatment

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Abstract

Coal-washing wastewater is the residual produced by the coal industry, which may represent a high risk of serious environmental problems worldwide. However, prevailing coal-washing treatment processes are hardly ideal for achieving the goal of solid–liquid separation due to the wastewater's extremely stable physicochemical properties. This research treats the coal-washing wastewater produced by a plant in Northeast China by means of the coagulation–flocculation process. The sedimentation ability of different coagulant choices and flocculant dosages is tested and analyzed through pseudo-first-order reaction kinetics. Scanning transmission electron microscopy is used to account for the settlement mechanism of flocs, which not only explains the characterized effect of coagulants and the flocculant but also demonstrates the advantage of using combined coagulates. Using the three-dimensional response surface method, an optimized treatment condition of 1.20 g $m(FeCl_3)$: $m(CaO) = 1:3$ mixed coagulants + 2.00 mL 0.13% polyacrylamide flocculant is proposed for 100 mL of selected wastewater. Additionally, the relationships between the optimal treatment conditions and the properties of wastewater obtained from X-ray energy-dispersive analysis are determined for future practical optimization needs.

Keywords Coagulant · Flocculant · Optimization modeling · Pseudo-first-order regression · Sedimentation mechanism

Introduction

China is a country which produces and consumes large amounts of coal (Gai et al. 2020). As an important by-product of the coal industry, the volume of coal-washing wastewater generated annually exceeds 2.8×10^7 tons (Li et al. 2002; Liu and Gao 2013). The inappropriate disposal of this black, colloid-characterized wastewater with a pungent odor is not only a waste of resources but also a significant potential source of pollution (Ma et al. 2021; Shi et al. 2021b; Tu et al. 2019), making its treatment and recycling crucial. However, high-concentration coal-washing wastewater has

extremely stable chemical and physical properties, helping it remain non-stratified for months (Li et al. 2002), which greatly enhances the difficulty with the sedimentation of this specific wastewater (Li et al. 2020). Its stability can be explained by the extended Deijaguin–Landau and Verwey–Overbeek (XDLVO) theory (Lin and Zhang 2021), which states that, firstly, coal-washing wastewater contains negatively charged small particles which repel each other under electrostatic repulsion, creating a stabilized dispersion colloid system (Peydayesh et al. 2021; Yan et al. 2012). Secondly, the particles exhibit Brownian motion. This non-stop irregular movement can make sedimentation harder since the particles are also small and near neutrally buoyant (Feng et al. 2010), and thirdly, the charged particles can attract the polarity of water molecules to form elastic membranes covering them over, thus lowering the probability of effective collisions and increasing resistance to sol polymerization (Li et al. 1999; Liu and Gao 2013).

At present, the most widely applied industrial treatment method for coal-washing wastewater is coagulation–flocculation (Duong et al. 2000; Jiang 2015; Lee et al. 2014; Maria et al. 2021; Teh et al. 2016), a flowchart of which is provided in Fig. 1. This method can achieve solid–liquid separation

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Fig. 1 Coagulation–flocculation process in coal-washing wastewater treatment
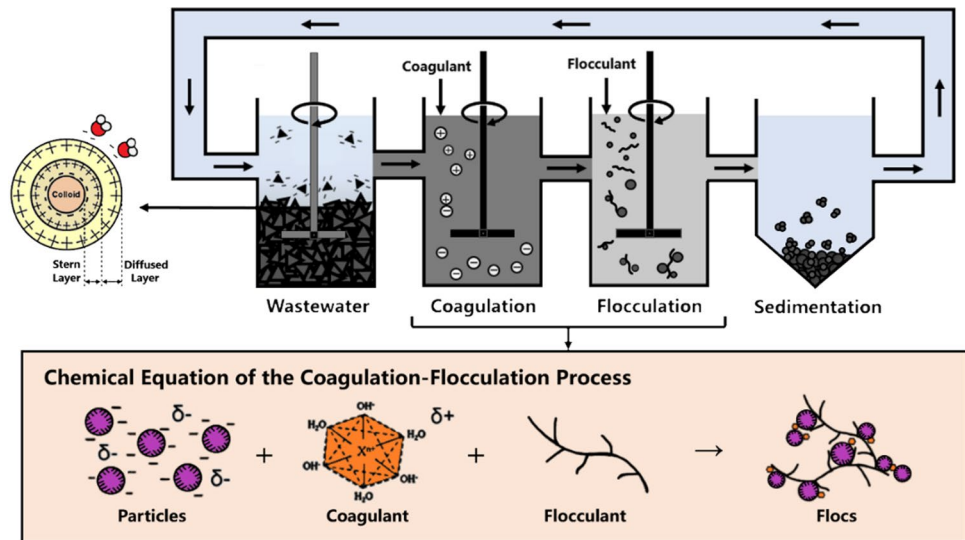
by destabilizing the charged particles and increasing their gravity–buoyancy ratio (Li et al. 2007, 1999; Semerjian and Ayoub 2003). Sedimentation involves two processes of coagulation and flocculation (Chen et al. 2010). Coagulation refers to the addition of inorganic salts with high cationic valence or inorganic high molecular polymers to reduce the particles' mutual repulsion (Zhao et al. 2021) and reduce the stability of the hydration membrane (Li et al. 2007), thereby providing possibilities for sedimentation to begin. Meanwhile, flocculation involves the addition of organic polymer flocculants to promote the aggregation of fine particles through dehydration (Li 2006) and adsorption bridging processes (Semerjian and Ayoub 2003; Zhang et al. 2003), which increases the chances of particle collisions and the volume of flocs, speeding up the settling rate and thus greatly enhancing the removal effect (Kooijman et al. 2020). Currently, high-quality coal can already be processed using this method in a closed circulation system where clarified supernatant is reused in washing the coal again. But for coal-washing wastewater with a high impurity content, the sedimentation speed is generally too slow to facilitate industrial recycling processes due to its complex chemical composition (Yang et al. 2014). The main strategy to improve sedimentation efficiency is to adjust the choice of coagulant and dosage of flocculant, and these two factors have the most significant impact on the settling effect according to the relevant literature (Li 2006; Zhao et al. 2021).

Some researchers have developed jar tests of the sedimentation of this specific coal-washing wastewater, in which calcium, aluminum, and iron salts are normally used as coagulants (Lee et al. 2014; Yang et al. 2016). These inorganic

reagents unite the slime in a similar mechanism by either neutralizing charged particles or enmeshment sweep floc in a precipitate (Jiang et al. 2007; Li et al. 2006). However, there is conflicting evidence of their actual coagulation effect. Li Mei et al. (Li et al. 2002) showed that polyaluminum chloride (PAC) has a positive effect in the treatment of coal-washing wastewater, and experiments by Fu et al. (Fu and Hu 2013) also proved that both PAC and ferric chloride (FC) are effective sewage treatment reagents. But Li Yafeng (Li 2006) found that PAC has poor performance in the coagulation and sedimentation of high-concentration coal-washing wastewater and FC was even worse since the supernatant could barely be separated, while cheap quicklime (Calcium Oxide, CaO) has a surprisingly good sedimentation effect. As for flocculants, only polyacrylamide (PAM) is extensively used (Lapointe et al. 2020; Wang et al. 2021; Yang et al. 2014), but its dosage can significantly influence the treatment's efficiency (Fu and Hu 2013; Li 2006; Suopajärvi et al. 2013). According to Huang Tinglin et al. (2002), more flocculant could obviously accelerate sedimentation, while Chen and Ji's (1998) results indicate that excessive flocculant cannot necessarily increase the sedimentation rate but may decrease it. Therefore, the amount of flocculant added is likely to have a certain range of adaptation (Lapointe et al. 2020), and the physical and chemical mechanisms behind the process remain unknown.

This work evaluates the effectiveness of the use of different coagulants and flocculant dosages on the sedimentation of inferior coal-washing wastewater provided by the North Industrial Treatment Plant, China. Coagulation–flocculation sedimentation was simulated under laboratory conditions,

and the 60-min settlement effect through pseudo-first-order regression was selected as an indicator of efficiency. Scanning transmission electron microscopy (STEM) and X-ray energy-dispersive analysis (EDAX) were also employed in the experiment to detect the details of aggregation for mechanism exploration. From the resulting understanding of the sedimentation processes of flocs, an optimal sediment condition is proposed. Finally, this study generalizes the optimized results for industrial use, which could add to the understanding of coal-washing wastewater sedimentation. The whole study started in 2021 at Xiamen University, China.

Materials and methods

Materials

The experiment takes high-impurity coal-washing wastewater from North Industrial Coal Washing Plant as a wastewater sample (suspended solids (ss): $(7.3 \pm 1.7) \times 10^4$ mg/L; chemical oxygen demand (COD_{Mn}): $(4.3 \pm 0.1) \times 10^4$ mg/L; pH: 8.11 ± 0.48; ζ: $(-6.5 \pm 0.1) \times 10^{-2}$ V) to conduct coagulation–flocculation treatment. The analytical reagents CaO, PAC, calcium chloride ($CaCl_2$), ferric chloride ($FeCl_3$), and titanium dioxide (TiO_2) were tested as possible coagulant choices. Flocculants with different concentrations were prepared by dissolving cationic PAM (molecular weight: 8–10 million, ionization degree: 30–50%, analytically pure) to deionized water. The equipment used to determine the sedimentation mechanisms of the flocs included a STEM (Phenom Scientific, China), EDAX (MIRION Technologies (CANBERRA), China), and pH meter (ThermoFisher Scientific, United States).

Coagulation–flocculation process

In order to ensure that the coal-washing wastewater used in the experiments had roughly consistent particulate size, as well as to remove cinder which had already settled at the bottom, the separated bottling wastewater was firstly coarsely filtered using medical gauze. Then, basic water quality parameters were measured and the suspended particulate matter was extracted and scanned using STEM and EDAX (Table S1, Figure S1). After the determination of these properties, coagulants and flocculants were added to the water sample successively according to Table 1 followed by stirring with a glass rod at a speed of 60 r/min until the reagents were fully mixed, and changes in volume for the

Table 1 Three experimental variables for the coagulation–flocculation sedimentation

Group	Coagulant	Coagulant dosage (g)	Flocculant concentration (%)
A1	$CaCl_2$	1.00	0.10
A2	$FeCl_3$	1.00	0.10
A3	TiO_2	1.00	0.10
A4	CaO	1.00	0.10
A5	PAC	1.00	0.10
A6	–	1.00	0.10
A7	–	–	–
B1	$FeCl_3$ + CaO	1.00 + 0.20	0.10
B2	$FeCl_3$ + CaO	0.80 + 0.40	0.10
B3	$FeCl_3$ + CaO	0.60 + 0.60	0.10
B4	$FeCl_3$ + CaO	0.40 + 0.80	0.10
B5	$FeCl_3$ + CaO	0.20 + 1.00	0.10
C1	$FeCl_3$ + CaO	0.30 + 0.90	–
C2	$FeCl_3$ + CaO	0.30 + 0.90	0.02
C3	$FeCl_3$ + CaO	0.30 + 0.90	0.05
C4	$FeCl_3$ + CaO	0.30 + 0.90	0.10
C5	$FeCl_3$ + CaO	0.30 + 0.90	0.15
C6	$FeCl_3$ + CaO	0.30 + 0.90	0.20
D1	$FeCl_3$ + CaO	0.30 + 0.90	0.13

solid–liquid separation boundary were then documented. When the sedimentation was completed, flocs and supernatant were analyzed using STEM and the pH meter.

In the experiment for the choice of coagulant, 7 groups of water samples were placed in measuring cylinders at 100 mL each according to previous research (Yan et al. 2012), and 1.00 g $CaCl_2$, $FeCl_3$, TiO_2, CaO, PAC were added to the first five. After stirring, 2.00 mL of 0.1% PAM was also added using a pipette, and the wastewater was stirred again and left to settle. The other two samples were control groups where only 2.00 mL of 0.10% PAM and 2.00 mL of deionized water were added. Then, changes in floc volume over time in all of the groups were recorded, and further analysis of the characteristics of the flocs and supernatant was conducted.

In the experiment varying the coagulant mixing ratio, 5 groups of water samples (100 mL each) were put into measuring cylinders, and each was dosed with 1. 20 g of coagulants with mixing ratios of m($FeCl_3$):m(CaO) = 5:1, 2:1, 1:1, 1:2, 1:5. Then, 2.00 mL 0.1% PAM solution was added after stirring before the subsequent analysis as described above for the first experiment.

In the experiment varying the coagulant mixing ratio, 6 groups of water samples (100 mL each) were put into measuring cylinders, 1.20 g 1:3 mixing coagulants and 2.00 mL of

0%, 0.02%, 0.05%, 0.10%, 0.15%, 0.20% PAM, respectively, were added to each group, prior to the same analysis as for the previous two sample groups.

In the experiment to determine the best sedimentation conditions, a 100-mL water sample was placed in a measuring cylinder and the theoretical best settlement results (1.20 g m(FeCl$_3$): m(CaO) = 1:3 + 2.00 mL 0.13% PAM) were added. Then, changes in floc volume over time were recorded, and values of ss and COD$_{Mn}$ of the supernatant after full sedimentation were measured.

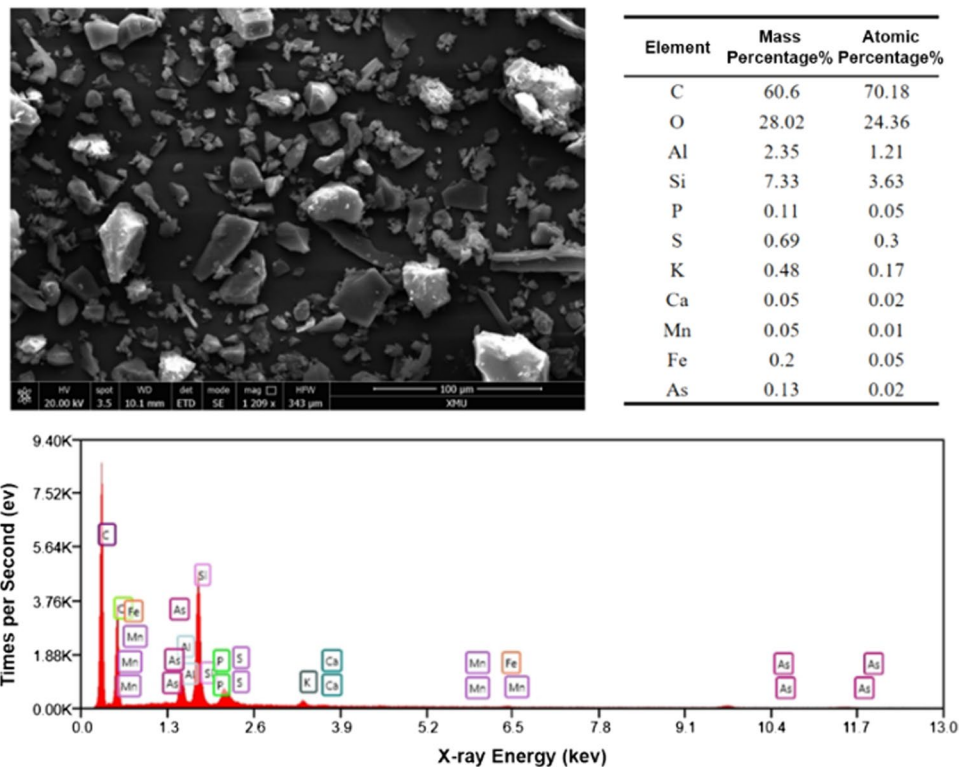# Results and discussion

Characteristics of wastewater sample

Compared to general coal-washing wastewater, the specific high-concentration sample had a much higher values of ss and CODMn, and its value of ζ was more negative as well (Huang et al. 2002), thus greatly increasing the difficulty of treating it (Feng et al. 2010; Sun et al. 2021). The results of the STEM and EDAX analysis of the physical morphology and chemical composition of the particulates showed that the wastewater sample contained a large number of scattered particles with smooth surfaces and diameters less than 10 μm. Their chemical composition consisted of mainly carbon and carbon compounds

with some silicate (silt) and alumina (mines), and small amounts of inorganic pollutants and heavy metals. Previous research has shown that silicate and alumina are the main sources of coal-washing wastewater's negative charge (Jiang et al. 2007; Li et al. 1999) and form colloids when reaching certain water systems. The presence of elements such as sulfur, manganese, iron, and arsenic implies that pollution could be caused if this wastewater was freely discharged (Shi et al. 2021a) (Fig. 2).

Coagulant choice

The coagulation–flocculation reaction (Fig. 1) shows that the sedimentation of wastewater can be expressed as a chemical equation. Given that the concentration of waste particles was significantly larger than the amount of coagulant or flocculant added, the reaction could be regarded as pseudo-first order (Benjamin and Lawler 2013; Yang et al. 2019) under the experimental conditions of full stirring which provides the same fluid shear (Benjamin and Lawler 2013; Mooyoung Han 1992). Moreover, because the changes in reactant concentration are approximately proportional to the depth of the supernatant (He et al. 2015), pseudo-first-order reaction kinetics can be used to describe adsorption and sedimentation in the solid–liquid phase by fitting the floc volume against time (Huang et al.

Fig. 2 Results of STEM (100 μm scale) and EDAX scanning of particles suspended in coal-washing wastewater samples. The larger particles were nearly 40 μm and the fine particles less than 10 μm, and the particles were mainly made of carbon, oxygen, aluminum, and silica

Element	Mass Percentage%	Atomic Percentage%
C	60.6	70.18
O	28.02	24.36
Al	2.35	1.21
Si	7.33	3.63
P	0.11	0.05
S	0.69	0.3
K	0.48	0.17
Ca	0.05	0.02
Mn	0.05	0.01
Fe	0.2	0.05
As	0.13	0.02

2019; Yuh-Shan 2004). The calculation processes are as follows:

$$\frac{dV}{dt} = k \cdot [(V_s - V_0) - (V_s - V_t)] \tag{1}$$

where V_s represents the total volume of wastewater (mL), V_t represents the volume of flocs at t minutes (mL), V_0 represents the volume of flocs at the end of sedimentation (mL), and k represents the quasi-first order reaction kinetic rate constant (t^{-1}). If $V_s - V_0 = V_r$, the integration of Eq. 1 gives:

$$\ln(V_t - V_0) = \ln V_r - kt \tag{2}$$

Take the natural base e to the power on the both sides of Eq. 2:

$$V_t = V_r \cdot e^{-kt} + V_0 \tag{3}$$

By fitting the data points to Eq. 3, a coagulation–flocculation sedimentation adsorption kinetic model can be established (Fig. 3, Table S2). In the fitting equation $(V = V_0 + V_r \cdot e^{-kt})$, V_0 is related to the choice of coagulant showing the completion of sedimentation, that is, the volume of flocs when the reaction reaches equilibrium. Meanwhile, k is controlled by both the choice of coagulant and flocculant dosage, and the reaction rate is also proportional to the settling speed of the flocs.

$CaCl_2$, $FeCl_3$, and CaO are effective coagulants for this coal-washing wastewater with a clear sedimentation effect as shown in Fig. 3a. High water separation rates of about 16% within 1 h were achieved, which is significantly statistically different ($p < 0.01$) from the control group (Figure S2). This indicates that suitable coagulants could speed up the sedimentation rate of coal-washing wastewater considerably. However, TiO_2 and PAC failed to show any significant coagulation effect, as their sedimentation rates were only slightly different from those of the controls.

Considering the sedimentation mechanisms involved, the main role of coagulants is to provide positively charged metal cations as 'counterions' to neutralize the particles' surface potential (Sun et al. 2015). But coagulants with the same cations, such as $CaCl_2$ and CaO, for instance, could still have quite different treatment effects. CaO worked more effectively, which may be due to the precipitation reaction of CaO and SiO_2 (Eq. 4) (Li et al. 2007) or the co-precipitation effect of $Ca(OH)_2$ in adsorbing suspended particles (Jiang et al. 2007). This difference illustrates the fact that pH is an important factor to be considered when Ca^{2+} is selected as the coagulant, and an alkaline was a better choice. $FeCl_3$ was another effective coagulant, and its strong sedimentation effect could be explained by the Schultz–Hardy rule which states that the coagulation capacity of electrolytes is proportional to the sixth power of the valence state of oppositely charged ions. As a high-valence cation, Fe^{3+} would undergo a certain degree of hydrolysis during aggregation and positively charged Fe(OH)3 colloid (Eqs. 5) at pH = 5.35 (its supernatant measurement result) would form which has high
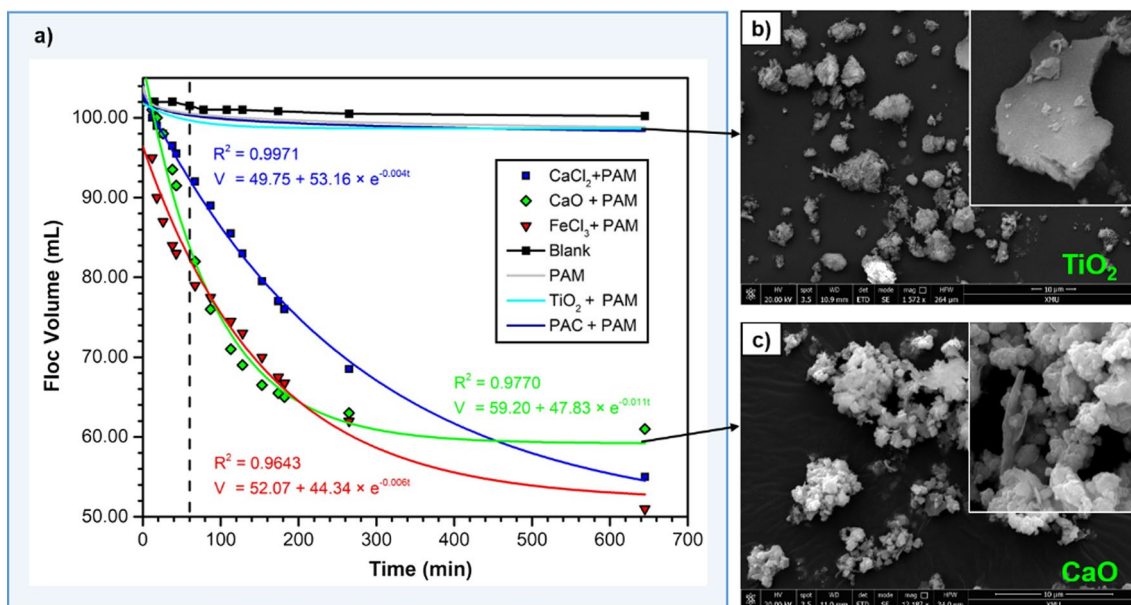

Fig. 3 **a** Changes in floc volume with time when different coagulants are added and the fitting effect of the quasi-first-order reaction kinetics model; **b** and **c** STEM images (10 μm scale) of flocs treated with TiO_2 and CaO, respectively, as coagulants

affinity toward contaminants (Agbovi and Wilson 2017). This process might thus stimulate the formation of flocs by eliminating the surface charge (Benjamin and Lawler 2013) and directly wrapping the sticky waste particles.

$$Ca(OH)_2 + 5SiO_2 \rightarrow CaO \cdot 5SiO_2 \cdot H_2O \tag{4}$$

$$Fe^{3+} + 3OH^- \rightarrow Fe(OH)_3(\text{colloid}) \tag{5}$$
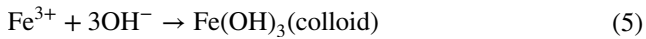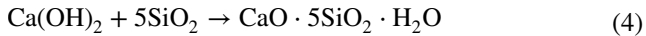
PAC also contains the high-valence cation Al^{3+} and is a high molecular polymer, which leads to a good theoretical sedimentation effect (Fu and Hu 2013; Guo et al. 2022; Jiang 2015; Yan et al. 2012). However, probably due to its limited solubility in the sample water, the experimental results show that PAC was a much worse coagulant compared to Fe^{3+} and even Ca^{2+}. It barely showed any ability in the destabilization of particles or condensing fine particles during the treatment process. TiO_2 performed to a similar degree. Although titanium is tetravalent, it was hard to ionize in wastewater for negative charges combining, leading to a poor aggregation effect.

The STEM results show the same trends in terms of the sedimentation effect. Figure 3b presents the flocs processed with TiO_2. It can be seen that many fine debris particles are visible, many of which still have retained smooth surfaces. This indicated that they have not been encapsulated effectively, which corresponds to the experimental observation of slow sedimentation. On the other hand, flocs treated with CaO (Fig. 2c) were

fully encapsulated by flocculant, and large aggregations with rough surface were formed which led directly to the improvement in particulate collision frequency and treatment efficiency (Lee et al. 2014) as well as the adsorption effect (Chen et al. 2010). Scattered particles disappeared, corresponding to the faster sedimentation rate for CaO shown macroscopically.

To some extent, CaO and $FeCl_3$ were suitable coagulants with regard to the specific coal-washing wastewater samples selected in this experiment, since the particles settled quickly. But the mechanisms involved were somewhat different. The CaO could provide Ca^{2+} to compress the colloid's double layer (Li et al. 2007; Yan et al. 2012), neutralize negative charges, and generate $Ca(OH)_2$ to participate in the sedimentation of the waste particles (Jiang et al. 2007; Semerjian and Ayoub 2003). Meanwhile, $FeCl_3$ could assist in sedimentation through hydrolysis and $Fe(OH)_3$ positive colloids formation to act directly on the negative particles (Agbovi and Wilson 2017), in addition to providing the Fe^{3+} cation. In order to further optimize sedimentation efficiency, it may be possible to mix CaO and $FeCl_3$ at different ratios to determine the best combination. The existence of CaO could offer $FeCl_3$ a more advantageous environment in terms of pH, which might further accelerate sedimentation by promoting the formation of $Fe(OH)_3$ colloid while alleviating the problems of high expense and equipment corrosion when $FeCl_3$ is used alone (Xiao et al. 2003).
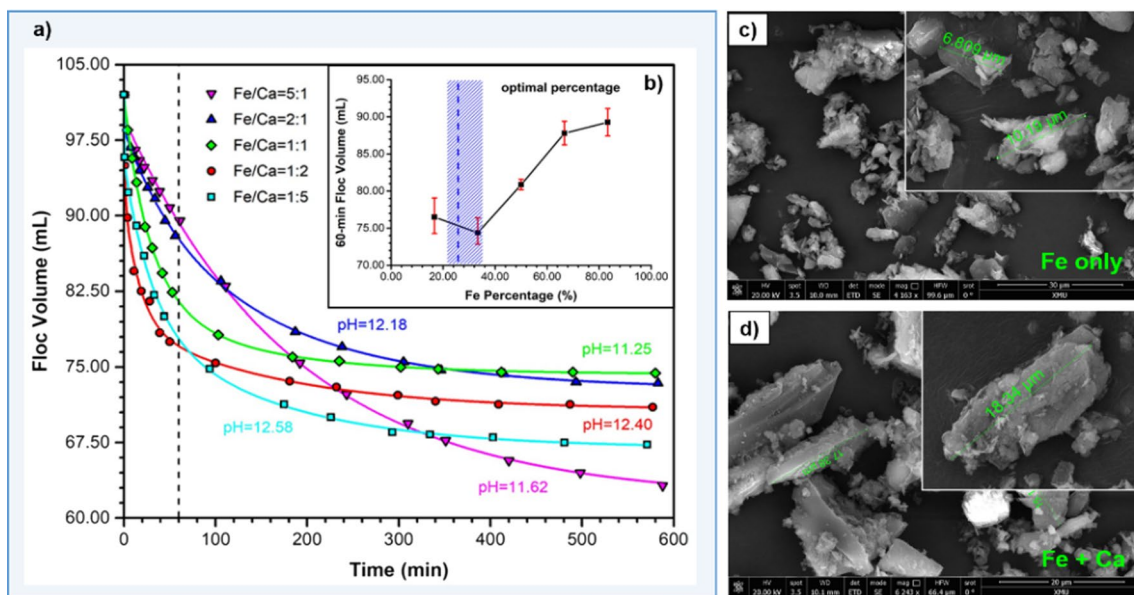

Fig. 4 **a** Changes in floc volume with time when Fe and Ca coagulants were mixed at different ratios and pH values of supernatants; **b** short-term sedimentation effect (after 60 min) with different mixing ratios to find a suitable stoichiometry; **c** and **d** STEM images (10 μm scale) of flocs treated by $FeCl_3$ exclusively and $FeCl_3$/CaO combined

Coagulant mixing ratio

The significant influence of iron–calcium stoichiometry (Fe/Ca) on the coagulation effect is represented in Fig. 4a. When Fe/Ca = 5:1, the sedimentation was complete later, which corresponds to the observation when $FeCl_3$ was used alone in previous experiments. But the average sedimentation rate of this group was slower, making it a poor choice for efficient industrial use especially when the time available is limited. On the other hand, the sedimentation effect was better over a short time period when Fe/Ca = 1:2 and 1:5. Their one-hour water separation rate was close to 22%, exceeding the results when CaO and $FeCl_3$ were dosed alone and therefore meeting the criterion for optimization.

The improved settling effect using mixed coagulants might be related to the pH changes in the supernatant systems. When the two reagents were used together, the pH ranged between 11 and 13, which is not only the most suitable adsorption environment for $Ca(OH)_2$ (Sabah and Erkan 2006) but also an appropriate condition for the formation of the iron hydroxide colloid whose point of zero charge (PZC) is over 8.5 (Dayarathne et al. 2021; Kosmulski 2020). Therefore, when the coagulants were mixed, both substances could react to the waste particles in the most effective forms, in turn providing better conditions for the formation of large neutral particles (Yu et al. 2010) and thus resulting in a better sedimentation effect. The STEM photograph in Fig. 4c and d supports this conjecture by demonstrating the role

$Ca(OH)_2$ and $Fe(OH)_3$ played in the coagulation process. When Fe^{3+} was the only coagulant, the pH of wastewater was not alkaline enough for $Ca(OH)_2$ to co-precipitate more particles and generate sufficient ferric hydroxide colloids. The diameter of the fine flocs ranged between 5 and 10 μm, which is not ideal for precipitation. But when the mixed iron–calcium coagulant was used, most flocs had a diameter greater than 10 μm. Some even reached 20 μm, at which size natural particle sedimentation can begin on a large scale (Benjamin and Lawler 2013). Stray particles were also effectively removed, showing a much better sedimentation effect.

To explore the relationship between the short-term sedimentation effect and Fe/Ca for practical use, the mass percentage of $FeCl_3$ in the mixed coagulant can be taken as the abscissa, with the 60 min floc volume as ordinate to determine changes in sedimentation effect with increasing iron percentage. The results shown in Fig. 4b show that the floc volume over 60 min increased with the proportion of Fe in the coagulant in an 'S'-shaped plot. Obviously, for short-term sedimentation, a lower Fe^{3+} percentage would be a better choice. From an optimization perspective, when combined with the 15% water separation rate after one hour when using CaO alone, the fastest sedimentation rate could be expected with a proportion of Fe between 20 and 30%.
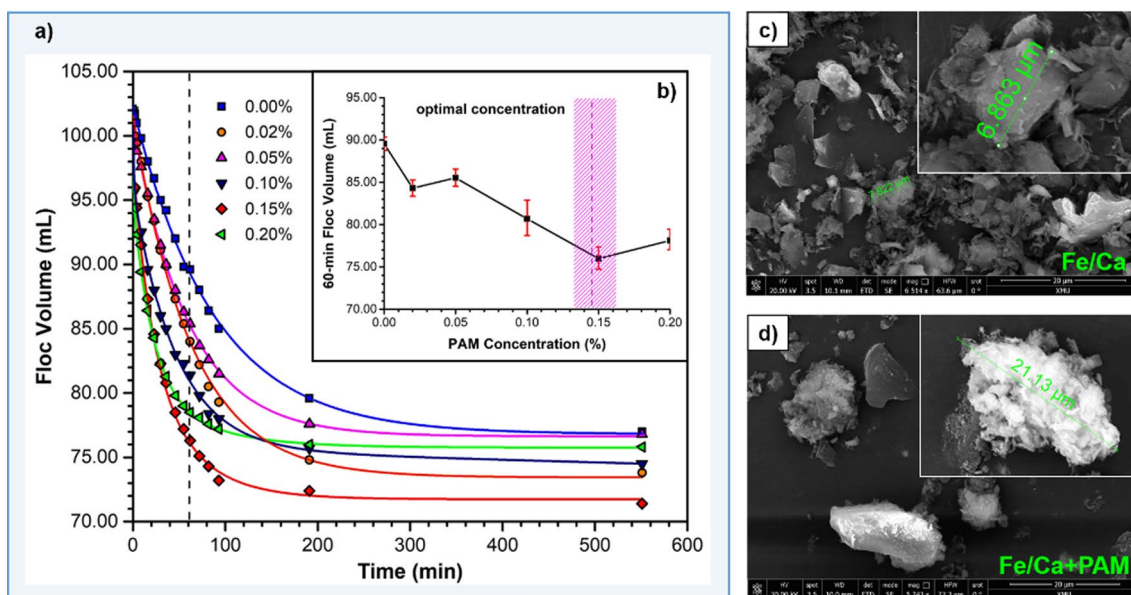

Fig. 5 **a** Changes in floc volume with time at different PAM concentrations; **b** short-term sedimentation effect (60-min) with different flocculant dosage to find the optimal concentration; **c** and **d** STEM scanning results (10 μm scale) of flocs treated by coagulants only (Fe/Ca) and coagulants and flocculant, respectively

Flocculant dosage

When PAM was not added or its dosage was very small, floc volume decreased approximately linearly with time over the 60 min (Fig. 5a), indicating a nearly unchanged settling velocity throughout the sedimentation process. As PAM concentration increased, the sedimentation rate changed with time, showing obvious pseudo-first-order reaction kinetic characteristics (Benjamin and Lawler 2013). This demonstrates the importance of the addition of PAM in the coagulation–flocculation reaction in speeding up the short-term settlement effect by changing the sedimentation kinetics toward being first-order in nature. According to the regression using Eq. 3, the higher the amount of flocculant PAM added to the coal-washing wastewater, the higher the sedimentation rate constant k the group has (Table S2). However, perhaps due to the completion limit (V_0) of the sedimentation process, the final floc volume of the 0.2% PAM samples was overtaken by those of the 0.15% group at 60-min control.

The unity effect of flocculants can be explained by referring to the microscopic views from the STEM results shown in Figs. 5c and d. It can be seen that, when no flocculant was added, the flocs contained a large number of fine particles with diameters less than 10 μm, which is only slightly larger than their untreated size (Fig. 5c). This indicates that, when the coagulant was the only reagent added, the main reason for the settling of flocs was the neutralization of negatively charged colloid by the metal cations. This provides only the necessary conditions for sedimentation to happen, but does not necessarily lead to the settling of flocs, and it was still difficult for the destabilized particles to settle naturally since they were so small and their collision frequency depended only on Brownian motion which is relatively weak. Thus, the 0% control group settled quite slowly compared to the PAM additional ones (Figure S3). After the addition of flocculants, stray particles were effectively removed due to the dehydration and intermolecular bridging processes initiated by PAM, and the particle diameter rose to about 20 μm (Fig. 5d). Since the density of flocs (Jiang 2015) and wastewater viscosity did not change appreciably throughout the process, the existence of flocculants could greatly enhance the gravity-buoyancy ratio and promote rapid settlement (Eq. 6). That accords with the macroscopic observation of accelerating sedimentation and confirms the importance of adding an appropriate amount of PAM to treat coal-washing wastewater rapidly.

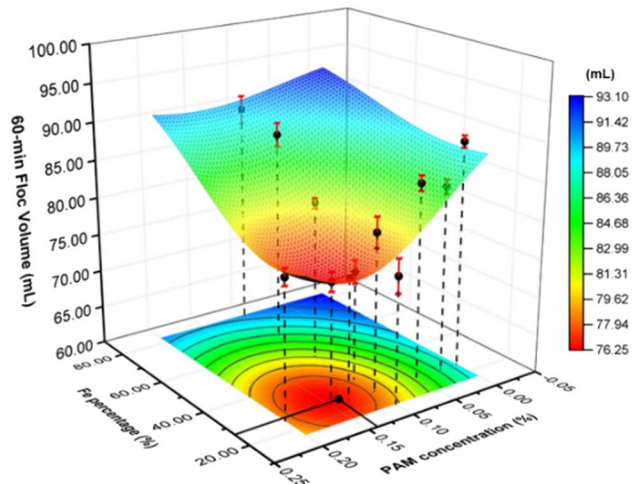$$V_p = \frac{(\rho_p - \rho_l) \cdot d_p^2 \cdot g}{18\mu} \tag{6}$$

Fig. 6 3D-RSM Fitting surface of the 60-min sedimentation effect result from different coagulation mixture ratios and PAM dosage

In order to find the most suitable PAM dosage and to explore the influence on the short-term sedimentation effect of changes in PAM dosage, PAM concentration and the floc volume at 60 min were taken as the abscissa and ordinate, respectively, to plot the experimental data and perform curve-fitting. The results indicate that the sedimentation volume at 60 min decreased with PAM concentration at first and then increased with PAM dosage (Fig. 5b), which means that excessive flocculant may not be an ideal choice for rapid sedimentation. That may be because extra multiple polymers could wrap the surface of particles and reform poly-membranes (Zhang et al. 2010), thus affecting the flocculation kinetics and protecting the waste particles again by lowering collision efficiency (Blanco et al. 2005). In the light of both sets of experimental results, 2 mL of 0.15% PAM is likely to give the optimal sedimentation effect.

Optimum sedimentation conditions

To obtain the best sedimentation conditions for the specific coal-washing wastewater, the three-dimensional response surface method (3D-RSM) as shown in Fig. 6 was used to model the orthogonal simulations against two factors that influence the sedimentation: the mass percentage of Fe in the mixed coagulant and the PAM dosage (Agbovi and Wilson 2017; Kumar and Venugopal 2017). Floc volume at 60 min according to pseudo-first-order regression was chosen as the response variable on the contour.

The theoretical optimal sedimentation conditions were determined according to the orthogonal simulation results as follows: 1.20 g Fe/Ca = 1: 3 mixed

coagulants + 2.00 mL 0.13% PAM flocculant. Under this condition, the flocs could settle down at a higher speed and the completion ratio was good, which led to the best water separation rate of nearly 25% within one hour (Figure S4). In addition, the supernatant was high in quality. Not only did it appear to be colorless and transparent but also had low values of ss and COD_{Mn} (15.9 mg/L), where the latter is far below the national first-level discharging standard of 100 mg/L in China (Anonymous 1996). This result fully achieves the goal of industrial cycling and proves the proposed method to be practical in coal-washing wastewater treatment.

However, previous experimental results have shown that the same coagulation choice and flocculant dosage could have different treatment effects when dealing with different examples of coal-washing wastewater due to differences in chemical composition. Therefore, the optimal sedimentation conditions obtained might lack universality because of variations in location and the coal-washing method used. To help resolve this issue, an attempt was made to determine the relationship between the original composition of the wastewater and the optimal sedimentation conditions and to integrate previous research findings, resulting in the following propositions:

Cations in the coagulants could be preferentially selected from elements with low original content in the wastewater. Taking the present experiments as an example, the wastewater has low Ca^{2+} and Fe^{3+} concentrations, while they both exhibited a good neutralizing effect when used as coagulants. Meanwhile, the wastewater had a high original concentration of Al^{3+}, but when it was treated with PAC which also contained a large amount of Al^{3+}, the results turned out to be poor. Experiments by Gou et al. (2009) have also proved that when there is a large amount of Fe^{3+} in the waste treated, the sedimentation effect of $FeCl_3$ is poor. That may be due to the dissolution of metal ions in the coal-washing wastewater. If the dissolved ions are continually added to the wastewater, more of the same ions will be adsorbed on the surfaces of the coal particles (Li 2006), thus increasing the amount of attachment and changing the electrical properties of the particles and thereby stabilizing the colloids again (Li et al. 2007). However, if a mixture of coagulants was to be selected, the optimal ratio of these elements would preferably by the inverse of their original content ratio in the wastewater. For instance, in this experiment, the optimal conditions were Fe/Ca = 1:3, and the original mass ratio of Fe/Ca was 4:1, showing an approximately inverse relationship. So, when the wastewater contains a large number of certain elements, smaller amounts of them will be needed as coagulants, which is consistent with the above argument. On the other hand, there is a certain proportional relationship between the optimal flocculant dosage and the amount of coagulant added. Based on the results of previous experiments and these suggested best conditions, it can be found that the concentration ratio of flocculant and coagulant (F–C ratio) is nearly the same (Table 2), with a statistical 95% confidence interval of [2.01, 6.56], within which the sedimentation effect will be expected to improve. This relationship may hold due to the positive correlation between coagulant dosage and the negative charge content in wastewater. Because of the relatively stable charge carried by a single particle, the coagulant dosage is also proportional to particulate concentration (Yan et al. 2012). Since the concentration of particles can determine how much flocculant needs to be added (Liu et al. 2018), the mass ratio of flocculant and coagulant comes to a relatively stable number.

Conclusion

We performed the coagulation–flocculation process to speed up the sedimentation rate of high-concentration coal-washing wastewater under laboratory conditions. The sedimentation effect revealed pseudo-first-order patterns of kinetics and revealed the molecular working mechanisms of coagulant and flocculant, respectively. A combination of CaO and $FeCl_3$ coagulants can neutralize the wastewater's electricity, decrease the

Table 2 Best coagulant–flocculant ratio in former studies

Flocculant (mg/L)	Coagulant (g/L)	F–C ratio (10^{-3})	Scholars
26.00	12.00	2.17:1	This study
40.00	6.00	6.67:1	Jiang, B.; Dai, J.; Zhang, P. (Jiang et al. 2007)
6.25	0.72	8.68:1	Jia, F. et al. (Jia et al. 2011)
20.00	5.00	4.00:1	Li, Y.; Liu, T.; Cao, L. (Li et al. 1999)
40.00	15.00	2.67:1	Li, Y.; Su, Y.; Zhu, L. (Li et al. 1995)
5.00	2.00	2.50:1	Li, Y.; Chen, J.; Ban, F. (Li et al. 2006)
20.00	6.00	3.33:1	Li, Y. et al. (Li et al. 2004)

electrostatic repulsion between particles, and encourage particles to adhere to each other through the synergetic effect of $Ca(OH)_2$ and positive colloid $Fe(OH)_3$ formation, which makes the sedimentation process possible. The appropriate input of the PAC flocculant led to an effective increase in floc diameter due to dehydration and intermolecular bridging processes and thus increased the frequency and efficiency of inter-particulate collisions, leading to faster settlement. The optimization of coagulant choice and flocculant dosage revealed that the combination of 1.20 g $m(FeCl_3):m(CaO) = 1:3$ mixed coagulants + 2.00 mL 0.13% PAM flocculant provides the best sedimentation conditions for 100 mL of the chosen wastewater over 60 min. The optimal model also indicates two possible processing characteristics for coal-washing wastewater. The first is that coagulants are preferable when high-valence metal cations are present with a lower original concentration, and the second is that the optimal flocculant dosage falls within the range of coagulant: flocculant = 1000: 2.01–6.56. Overall, this study has proposed a unique approach to understanding the sedimentation mechanism of coal-washing wastewater and offers possible optimizations to speed up the floc settlement rate. We expect these results to be helpful and to be of practical use in the design of industrial coal-washing wastewater treatments.

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Data availability All data generated or analyzed in the study have been included in this published article.

Declarations

Conflict of interest The authors declare that they have no conflict of interest.

Ethical approval This article does not contain any studies with human participants or animals performed by any of the authors.

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References

Agbovi HK, Wilson LD (2017) Flocculation optimization of orthophosphate with FeCl3 and alginate using the box-behnken response surface methodology. Ind Eng Chem Res 56:3145–3155

Anonymous (1996): Integrated Wastewater Discharge Standard. In: China SEPAo (Hrsg.). Polices, Regulations, and Rules, pp. 9–12

Benjamin MM, Lawler DF (2013) Water quality engineering: physical/chemical treatment processes. John Wiley & Sons

Blanco A, Negro C, Fuente E, Tijero J (2005) Effect of shearing forces and flocculant overdose on filler flocculation mechanisms and floc properties. Ind Eng Chem Res 44:9105–9112

Chen J, Ji Y (1998) Reasonable Application of Flocculant in the Treatment of Slime Water in Coal Preparation Plant Coal. Process Compr Util 5:17–20

Chen C, Zhang P, Zeng G, Deng J, Zhou Y, Lu H (2010) Sewage sludge conditioning with coal fly ash modified by sulfuric acid. Chem Eng J 158:616–622

Dayarathne HNP, Angove MJ, Aryal R, Abuel-Naga H, Mainali B (2021) Removal of natural organic matter from source water: Review on coagulants, dual coagulation, alternative coagulants, and mechanisms. J Water Process Eng 40:101820

Duong C, Choung J, Xu Z, Szymanski J (2000) A novel process for recovering clean coal and water from coal tailings. Miner Eng 13:173–181

Feng L, Liu J, Zhang M, Song L (2010) Analysis on influencing factors of sedimentation characteristics of coal slime water. J China Univ Min Technol 39:671–675

Fu JJ, Hu MZ (2013) Coagulation experimental study of coal washing wastewater treatment. Appl Mech Mater 361–363:705–708

Gai H, Zhang X, Chen S, Wang C, Xiao M, Huang T, Wang J, Song H (2020) An improved tar–water separation process of low–rank coal conversion wastewater for increasing the tar yield and reducing the oil content in wastewater. Chem Eng J 383:123229

Gou P, Ye X, Lv Y, Wang Z (2009) The water quality characteristics and treatment technology of coal slurry. Industrial Water Treatment 29:53–57

Guo J, Zhou Z, Ming Q, Huang Z, Zhu J, Zhang S, Xu J, Xi J, Zhao Q, Zhao X (2022) Recovering precipitates from dechlorination process of saline wastewater as poly aluminum chloride. Chem Eng J 427:131612

He Z, Zhang Y, Wang H, Qi L, Yin X, Zhang X, Wen Y (2015) A novel method to compute the flocculation sedimentation rate of activated sludge. Environ Pollut Cont 37:35–40

Huang T, Li M, Gao X (2002) Study on the perfect coagulation process in treating coal-washing wastewater. Ind Water Wastewater 33:23–25

Huang Y, Wang Q, Tang Q, Liu J, Chen C, Liu S (2019) Removal of cadmium ion from aqueous solution by nano zero-valent iron: Kinetics, equilibrium and impact factors. Ecol Environ Sci 28:2053–2061

Jia F, Li D, Zhang M, Jiang J, Suen Y (2011) Experiment study on the coagulation and flocculation treatment of the coal dressing water. Energy Environ Prot 25:21–24

Jiang J-Q (2015) The role of coagulation in water treatment. Curr Opin Chem Eng 8:36–44

Jiang B, Dai J, Zhang P (2007) Study on the effect and action mechanism of coal-washing wastewater treatment with carbide slag and PAM. J Shenyang Jianzhu Univ Nat Sci 23:1009–1011

Kooijman G, de Kreuk MK, Houtman C, van Lier JB (2020) Perspectives of coagulation/flocculation for the removal of pharmaceuticals from domestic wastewater: a critical view at experimental procedures. J Water Process Eng 34:101161

Kosmulski M (2020) The pH dependent surface charging and points of zero charge. VIII. Update. Adv Colloid Interface Sci 275:102064

Kumar S, Venugopal R (2017) Performance analysis of jig for coal cleaning using 3D response surface methodology. Int J Min Sci Technol 27:333–337

Lapointe M, Farner JM, Hernandez LM, Tufenkji N (2020) understanding and improving microplastic removal during water treatment: impact of coagulation and flocculation. Environ Sci Technol 54:8719–8727

Lee CS, Robinson J, Chong MF (2014) A review on application of flocculants in wastewater treatment. Process Saf Environ Prot 92:489–508

Li Y, Su Y, Zhu L (1995) Study on the action mechanism of lime in the coal-washing wastewater treatment. Energy Environ Prot 10:25–27

Li M, Huang T, Wang G (2002) An experimental study on the high efficiency treatment of coal-washing wastewater. J Xian Univer Arch Technol Nat Sci Edit 34:38–41

Li Y, Hu X, Chen J, Zhang L (2004) Treatment technology and engineering practice on high-concentration coal-washing wastewater. Ind Water Treat 24:68–70

Li Y, Chen J, Ban F (2006) Effect of the chemical combiningly prepared by $CaCl_2$ and $MgSO_4$ on coal-washing wastewater treatment and its mechanism. Ind Water Treat 26:47–49

Li Y, Jin Y, Liu Y (2007) Study on the action mechanism of Ca^{2+} and two other components in coal slime coagulation. J Shenyang Jianzhu Univ Nat Sci) 23:473–477

Li D, Liu J, Wang S, Cheng J (2020) Study on coal water slurries prepared from coal chemical wastewater and their industrial application. Appl Energy 268:114976

Li Y, Liu T, Cao L (1999): Study on the Causes of the Difficulties in Coal Washing Wastewater Treatment and the Treatment Methods Mining Safety & Environmental Protection, 1–3+49

Li Y 2006: Study on Treatment and Reuse Technology of Concentrated Wastewater of Coal Washing, Ph.D. thesis, Northeastern University, Liaoning, China

Lin Z, Zhang W (2021) Flocculation process of coal slime water based on flocculation kinetics and its research methods: a critical review. China Min Mag 30:160–167

Liu C, Gao Y (2013) Common processes and coagulants for coal-washing wastewater treatment liaoning. Chem Ind 42:431–433

Liu C, Zhang Q, Wu X, Gao J, Zhang Y (2018) Experiment research on settlement of high concentration coal slurry water. Contemp Chem Ind 47:1370–1373

Ma H, Wang H, Tian C, Wang L, Yuan W, Qi Y, Ma H, Chao Z, Lv W (2021) An integrated membrane- and thermal-based system for coal chemical wastewater treatment with near-zero liquid discharge. J Clean Prod 291:125842

Maria A, Mayasari E, Irawati U, Zulfikurrahman (2021): Comparing the effectiveness of chitosan and conventional coagulants for coal wastewater treatment. IOP Conference Series: Materials Science and Engineering 980

Mooyoung Han DFL (1992) The (relative) insignificance of G in flocculation. J Am Water Works Assoc 84:79–91

Peydayesh M, Suta T, Usuelli M, Handschin S, Canelli G, Bagnani M, Mezzenga R (2021) Sustainable removal of microplastics and natural organic matter from water by coagulation-flocculation with protein amyloid fibrils. Environ Sci Technol 55:8848–8858

Sabah E, Erkan ZE (2006) Interaction mechanism of flocculants with coal waste slurry. Fuel 85:350–359

Semerjian L, Ayoub GM (2003) High-pH–magnesium coagulation–flocculation in wastewater treatment. Adv Environ Res 7:389–403

Shi J, Huang W, Han H, Xu C (2021a) Pollution control of wastewater from the coal chemical industry in China: Environmental management policy and technical standards. Renew Sustain Energy Rev 143:110883

Shi J, Xu C, Han Y, Han H (2021b) Case study on wastewater treatment technology of coal chemical industry in China. Crit Rev Environ Sci Technol 51:1003–1044

Sun W, Zhou S, Sun Y, Xu Y (2021) Synthesis and evaluation of cationic flocculant P(DAC-PAPTAC-AM) for flocculation of coal chemical wastewater. J Environ Sci 99:239–248

Sun Y, Min F, Chen C, Liu C, Chen S (2015) Research status about the adsorption characteristics of the metal cations of the coagulant in the coal slurry. Multipurp Util Miner Res 1:14–17

Suopajärvi T, Liimatainen H, Hormi O, Niinimäki J (2013) Coagulation–flocculation treatment of municipal wastewater based on anionized nanocelluloses. Chem Eng J 231:59–67

Teh CY, Budiman PM, Shak KPY, Wu TY (2016) Recent advancement of coagulation-flocculation and its application in wastewater treatment. Ind Eng Chem Res 55:4363–4389

Tu Y, Feng P, Ren Y, Cao Z, Wang R, Xu Z (2019) Adsorption of ammonia nitrogen on lignite and its influence on coal water slurry preparation. Fuel 238:34–43

Wang N, Sun X, Zhao Q, Wang P (2021) Treatment of polymer-flooding wastewater by a modified coal fly ash-catalysed Fenton-like process with microwave pre-enhancement: System parameters, kinetics, and proposed mechanism. Chem Eng J 406:126734

Xiao X, Zhang J, Li H (2003) Development of research on floculant in water treatment. Min Res Geol 17:90–95

Yan L, Wang Y, Ma H, Han Z, Zhang Q, Chen Y (2012) Feasibility of fly ash-based composite coagulant for coal washing wastewater treatment. J Hazard Mater 203–204:221–228

Yang X, Zhao T, Zhang Q (2014) Current status and development trend of coal washing wastewater treatment technology. Res Econ Environ Prot 07:163–164

Yang R, Li H, Huang M, Yang H, Li A (2016) A review on chitosan-based flocculants and their applications in water treatment. Water Res 95:59–89

Yang Y-J, Franses EI, Corti DS (2019) Effects of light dispersed particles on the stability of dense suspended particles against sedimentation. J Phys Chem B 123:922–935

Yu W-Z, Gregory J, Campos L (2010) Breakage and regrowth of al-humic flocs-effect of additional coagulant dosage. Environ Sci Technol 44:6371–6376

Yuh-Shan H (2004) Citation review of Lagergren Kinetic rate equation on adsorption reactions. Scientometrics 59:171–177

Zhang C, Zhang D, Luo Y (2003) Study on application of a PAMAM dendrimer in the coal washing wastewater. Energy Environ Prot 17:20–24

Zhang L, Yao R, Li C (2010) Preparation of polyacrylamide initiated by photoinitiator and its application characteristics to coal dressing wastewater. J Taiyuan Univ Technol 41(745–747):766

Zhao C, Zhou J, Yan Y, Yang L, Xing G, Li H, Wu P, Wang M, Zheng H (2021) Application of coagulation/flocculation in oily wastewater treatment: a review. Sci Total Environ 765:142795