

## Feasibility of fly ash-based composite coagulant for coal washing wastewater treatment

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### ABSTRACT

In this study, several fly ash (FA)-based composite coagulants, leached by hydrochloric acid, were prepared to treat coal washing wastewater. The concentrations of  $\text{Al}^{3+}$  and  $\text{Fe}^{2+}/\text{Fe}^{3+}$  in the leachates and coagulants were analyzed, and optimal experimental conditions, including coagulant dosage and initial pH, were determined using various analytical techniques (scanning electron microscopy, energy dispersive spectrometry, X-ray diffraction (XRD), X-ray fluorescence (XRF), particle-size analysis, zeta potential, pH and conductivity measurements). A suspended solids (SS) and chemical oxygen demand (COD) removal efficiency from the effluent treated by one of the coagulants reached 99.61% and 96.48%, respectively, at dosages of  $10 \text{ g l}^{-1}$  (initial pH of 9, adjusted by CaO). This indicates that the coagulant was an effective agent for coal washing wastewater treatment, and that the leached  $\text{Al}^{3+}$  and  $\text{Fe}^{3+}$  and introduced  $\text{Ca}^{2+}$  may have improved the coagulation process. Analysis of the dry sludge composition and slurry particle size distribution of the coal washing wastewater showed that charged colloidal particles and the fine particle distribution in the coal washing wastewater make the wastewater treatment a difficult process. Results from this study could provide a novel approach for the treatment of coal washing wastewater and coal fly ash utilization.

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### 1. Introduction

The production of large effluent volumes by coal washing is a significant problem in the preparation of coal for coal-fired power plants [1,2]. The wastewater usually has a characteristic of dark black color and nauseating odor. Moreover, organic and inorganic matters, such as phenols, polycyclic aromatic hydrocarbons and humic substances, have also been detected in the effluent [3]. These contribute to chemical oxygen demand (COD) [4]. An aqueous suspension of coal and clay increases wastewater turbidity and color. Particles in the suspension do not undergo gravitational sedimentation at acceptable rates, owing to their surface charge and small particle size, which also cause the formation of a stable colloidal suspension [5]. The disposal of coal washing wastewater is therefore an expensive process. A potential method for reducing the

volume of effluent discharged to the environment is to recycle and reuse the effluent after treatment.

The coagulation process has attracted considerable attention, as it can yield high removal efficiencies in wastewater treatment. Coagulation not only removes organic compounds together with suspended solids, but may also decolorize waste streams [6,7]. Several coagulants have been used for wastewater treatment in laboratory- and pilot-scale experiments over recent years, predominantly aluminum and iron-based coagulants, including aluminum sulfate (AS), aluminum chloride (AC), poly-aluminum sulfate (PAS), poly-aluminum chloride (PAC), ferric chloride (FC), ferric sulfate (FS), poly-ferric sulfate (PFS) and poly-alumino-iron sulfate (PAFS) [8]. However, most coagulant manufacturers use ores or chemical salts of iron and aluminum as raw materials. These are not only costly, but also consume large quantities of the earth's limited mineral resources [9,10]. Although coagulation/flocculation with PAC (dosage: 80–240  $\text{mg l}^{-1}$ , 5–10% solution) and anionic polyacrylamide (A-PAM) (molecular weight: more than 3,000,000, dosage: 1.0–4.0  $\text{mg l}^{-1}$ , 0.1–0.26% solution) can be favorable in reducing the suspended solids concentration and COD in coal washing wastewater, the coagulant dosage and concentration are proportional to the waste materials in the water [11,12]. Furthermore, conventional coagulants including PAM and PAC are expensive and corrosive, and PAM monomers are strongly neurotoxic, thereby endangering

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the environment. Based on these problems, an effective, chemically non-invasive and low-cost coagulant should be developed to meet stringent environmental regulations placed on the quality of effluent discharged.

Fly ash (FA) is a solid waste residue produced from coal combustion in coal-fired power plants. It is estimated that the annual production of fly ash is more than 500 million tons throughout the world [13]. Traditionally, the majority of coal fly ash has been dumped into landfills, which could have harmful effects on the use of land and its maintenance [14]. In addition, as it is small and light, it is easily airborne by wind [15]. Untreated, fly ash may cause serious environmental problems by polluting the water, atmosphere, soil and landscapes through dust generation [16]. As a result, there has been an increased interest in the utilization of fly ash in recent years. Some fly ash is recycled in civil construction materials, but overall, the global recycling rate of coal ash is only approximately 15% [17]. Some researchers have tested the utilization of coal fly ash as a coagulant to treat sewage sludge, because fly ash is rich in iron oxides and aluminum, with the weight ratio of these substances appropriate for producing complex coagulants [18–20]. Fly ash could therefore be converted into a valuable coagulant for wastewater treatment, which could not only be helpful in solving the solid waste disposal problem, but could also reduce costs [21].

On the basis of the above discussion, in this study, several composite coagulants were prepared by leaching of fly ash in hydrochloric acid. The feasibility of using the resulting coagulants in coal washing wastewater treatment was assessed by evaluating the settling characteristics and reduction in COD and suspended solids (SS) after coagulation. The coal washing wastewater, synthesized coagulants and sludge slurry after treatment were examined by scanning electron microscopy (SEM), energy dispersive spectrometry (EDS), X-ray fluorescence (XRF), X-ray diffraction (XRD), particle-size analysis and zeta potential determination, and the metal ion concentration in the supernatant was also analyzed. Coagulant dosage and pH were also investigated to optimize conditions for treatment of coal washing wastewater.

## 2. Experimental details

### 2.1. Materials

Coal washing wastewater and a sample of raw fly ash were collected separately from a coal washing plant and power plant in Yulin, Shaanxi province of China, which is the location of one of the world's seven largest coalfields. The chemical properties of the fly ash as determined by XRF by the fly ash supplier are listed in Table 1. Analytical reagent grade hydrochloric acid (HCl), calcium oxide (CaO) and sodium carbonate ( $\text{Na}_2\text{CO}_3$ ) were purchased from Chemicals Ltd, Xi'an (China).

### 2.2. Experimental procedure

Three composite coagulants were prepared using three different fly ash samples (100 g) reacted with 4 M HCl solution (300 ml) at 80 °C in a 500 ml three-necked glass reactor to which a straight condenser was connected (Fig. 1). The first coagulant (FA-HCl-Y1) was prepared by treating raw FA with the HCl solution, the second coagulant (FA-HCl-Y2) was obtained by first calcining the raw FA at 800 °C for 2 h using a conventional oven before treatment with

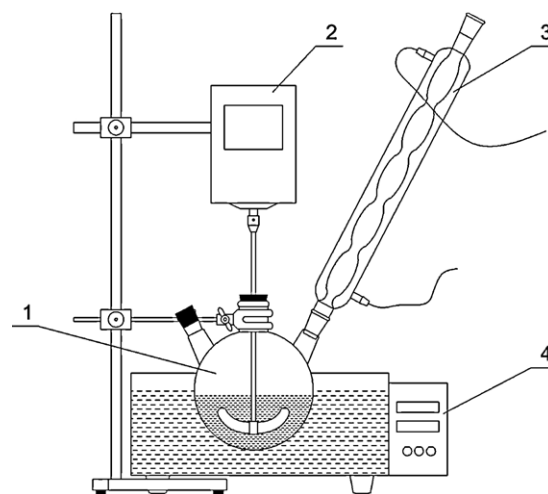


Fig. 1. Experimental setup (1 – three-necked glass reactor, 2 – stirrer, 3 – condenser, 4 – water bath).

HCl, and the third coagulant (FA-HCl-Y3) was obtained by first calcining the raw FA mixed with  $\text{Na}_2\text{CO}_3$  (100:6 weight ratio of raw FA: $\text{Na}_2\text{CO}_3$ ) at 800 °C for 2 h before treatment with HCl solution. All of the experimental conditions were based on the orthogonal test except that calcination temperature and time are from literature [21,22]. The three coagulants were dehydrated using a rotary evaporator under a vacuum of  $-0.085$  MPa.

The coagulation experiments were performed in beakers containing 100 ml wastewater according to the National Standard and relative literature [8,23]. The initial wastewater pH was adjusted (using concentrated HCl or CaO solution to minimize the volume change) as it plays an important role in the treatment efficiency. Agitation by magnetic stirrer commenced after a designated dosage of FA-HCl-Y coagulant was added to the water samples. The coagulation experiments proceeded with rapid agitation at 500 rpm for 5 min to guarantee thorough mixing between effluent and coagulant followed by slow agitation at 60 rpm for 30 min. After settling, aliquots of supernatant fluid were periodically extracted from the system and collected in a receiving flask at 1, 2, 5, 10, 20 and 40 min after the agitation had stopped. The pH, COD, SS and conductivity of these samples were analyzed, with data reported as the average of three trials. All experiments were carried out at room temperature (33–35 °C) and compared to a control in which no coagulant was used.

The wastewater-coagulant mixture was stirred to produce a uniform suspension before the settling characteristics of the flocs/solids were studied in a 100 ml graduated cylinder. The effect of different coagulants on the settling characteristics was observed.

### 2.3. Analytical methods

Standard methods (APHA, 2005) [24] were used to measure the value of the COD and SS of the raw and treated wastewater. The COD was determined using potassium dichromate as oxidant, after which the free potassium dichromate was titrated with a standard ferrous ammonium sulfate solution. The SS was determined as the ratio of the mass of residue on the filter paper to the volume of filtered wastewater. The COD and SS removal efficiencies  $R$  ( $R_{\text{COD}}$  and  $R_{\text{SS}}$ ), at time  $t$ , were calculated as follows:

$$R = \frac{c_0 - c_t}{c_0} \times 100\% \quad (1)$$

$c_0$  ( $\text{mg l}^{-1}$ ) is the initial COD or SS value of the raw wastewater and  $c_t$  ( $\text{mg l}^{-1}$ ) the concentration in the effluent at time  $t$  (min).

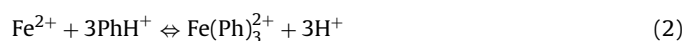
Table 1  
Composition of fly ash.

Elements as oxides	$\text{SiO}_2$	$\text{Al}_2\text{O}_3$	$\text{Fe}_2\text{O}_3$	CaO	$\text{TiO}_2$	$\text{Na}_2\text{O}$	$\text{SO}_3$
wt%	45.51	21.38	19.36	3.24	0.74	1.32	0.97

The pH and conductivity of the effluent were monitored by pH (pHS-3C, China) and conductivity meter (DDS-11A, China), respectively. The dry sludge composition of the coal washing wastewater and the slurry particle size distribution were studied by EDS (with SEM attachment, EDAX genesis xm-2, USA) and particle-size analyzer (BI-90Plus, USA), respectively, dry sludge and coagulants by SEM (Philips-FEI Model Quanta 200, USA), coagulant elemental concentration by XRF (S4 PIONEER, Germany), coagulant precursors and sludge slurry phase composition after treatment by XRD (XRD-7000, Japan), and wastewater zeta potential before and after treatment using a Zetasizer Nano Instrument (Delsa Nano C, USA).

A replacement complexometric titration method was used to determine the  $\text{Al}^{3+}$  concentration in the leachates. Excess EDTA solution was added to chelate  $\text{Al}^{3+}$ , and the free EDTA titrated with a standard zinc chloride solution [25].

The phenanthroline spectrophotometry method was used to determine the  $\text{Fe}^{2+}/\text{Fe}^{3+}$  concentration in the leachates with a spectrophotometer at 510 nm (721, China) [26]. Samples were diluted 100,000 times prior to analysis. Hydroxylamine hydrochloride was added to the diluted samples to reduce the ferric iron to ferrous iron, which reacts with orthophenanthroline to form an orange-red  $\text{Fe}(\text{II})$ -orthophenanthroline complex as described by Eq. (2). The instrument was calibrated with standard  $\text{Fe}(\text{II})$ -orthophenanthroline complex solutions at 1, 2, 5, 8, 10 ppb prior to each analysis. An instrument blank was run before each sample set.



### 3. Results and discussion

#### 3.1. Analysis of coal washing wastewater

The major characteristics of the coal washing wastewater are presented in Table 2. High COD and SS values were found to be characteristic of the wastewater, possibly owing to the argillization of coals in the washing process. This results in the production of many sludge particles, which contribute to the dark black color of the wastewater and long slurry settling times. Treatment of wastewater of this type depends significantly on sludge properties and particle size distributions [27].

##### 3.1.1. SEM of the dry sludge

Dry sludge was obtained after drying the coal washing wastewater at  $80^\circ\text{C}$ . The surface of the dry sludge is uneven, and contains some white floc deposits (Fig. 2), which may result from the presence of colloidal particles in the coal washing wastewater.

##### 3.1.2. EDS of the dry sludge and colloid formation

EDS data (Fig. 3) shows that the dry sludge consists of clay mineral particles, mainly comprised of silica, aluminum and oxygen. This suggests that the dry sludge mineral composition is  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$ , which could be responsible for its colloidal nature. Owing to their high concentration, some  $\text{SiO}_2$  molecules on the slurry particle surface react with water to generate silicic acid, which then dissociates into  $\text{H}^+$  and  $\text{SiO}_3^{2-}$  (Eqs. (3) and (4)).  $\text{SiO}_2$  colloidal

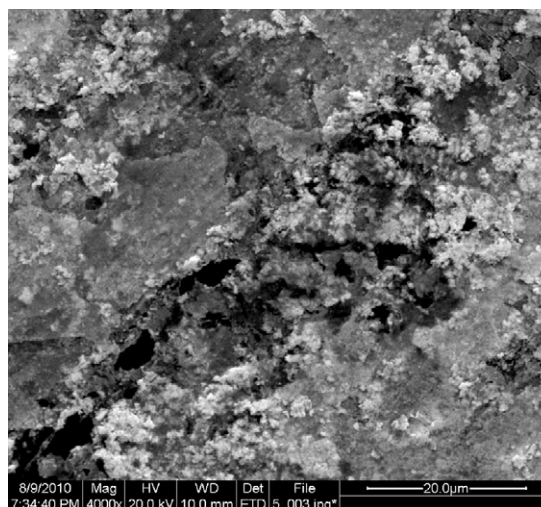


Fig. 2. SEM of the dry sludge. (Note that the surface of the dry sludge is uneven, and contains some white floc deposits.)

nuclei adsorb the common component  $\text{SiO}_3^{2-}$ , resulting in negatively charged colloidal particles,  $\{[\text{SiO}_2]_m \cdot n\text{SiO}_3^{2-} \cdot 2(n-x)\text{H}^+\}^{2x-}$ .



A high level of  $\text{Al}_2\text{O}_3$  also contributes to colloid formation. Some  $\text{Al}_2\text{O}_3$  combines with water molecules to form  $\text{Al}(\text{OH})_3$ , which then dissociates into  $\text{H}^+$  and  $\text{AlO}_2^-$  in a suitable pH range (Eqs. (5) and (6)). Negatively charged colloidal particles,  $\{[\text{Al}(\text{OH})_3]_m \cdot n\text{AlO}_2^- \cdot (n-x)\text{H}^+\}^{x-}$ , were formed from the absorption of  $\text{AlO}_2^-$  by the absorbed  $\text{Al}(\text{OH})_3$ .



The two negatively charged colloids interact with the sludge and maintain the stability of the coal washing wastewater, which is detrimental in coal washing wastewater treatment.

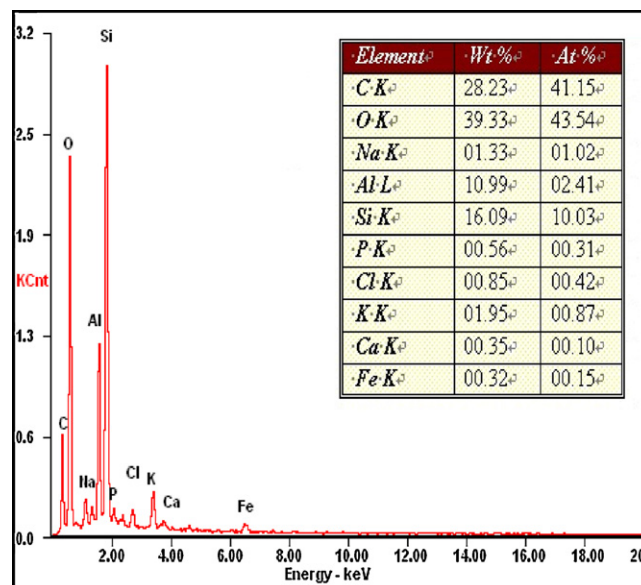


Fig. 3. EDS of the dry sludge. (Note that the dry sludge mainly comprised of silica, aluminum and oxygen besides carbon.)

Table 2  
Major characteristics of coal washing wastewater.

Parameter	Value	Parameter	Value
Density	$1.138 \text{ g cm}^{-3}$	Color	Dark black
pH	4.72	Conductivity	$944 \mu\text{S cm}^{-1}$
COD	$7480 \text{ mg l}^{-1}$	SS	$12,445 \text{ mg l}^{-1}$
Kinematic viscosity	$0.045 \text{ cm}^2 \text{ s}^{-1}$	Zeta potential	$-0.063 \text{ V}$



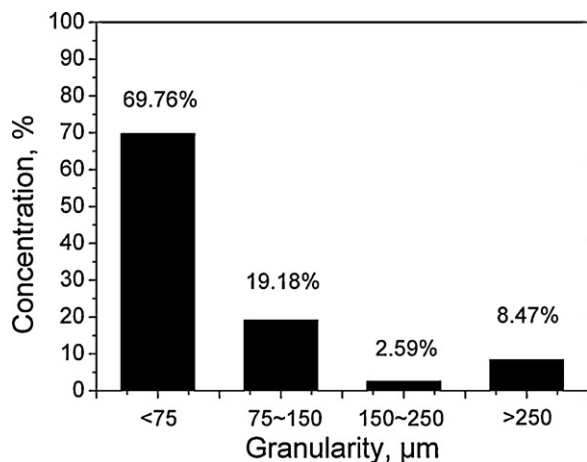


Fig. 4. Slurry particle size distribution. (Note that mostly particles in coal washing wastewater are less than  $75 \mu\text{m}$ .)

### 3.1.3. Slurry particle size distribution in the wastewater

Fig. 4 shows the slurry particle size distribution of the coal washing wastewater, where 69.76% of the particles are less than  $75 \mu\text{m}$ , 19.18% are  $75\text{--}150 \mu\text{m}$  in size, 2.59% occur in the range of  $150\text{--}250 \mu\text{m}$ , and 8.47% are larger than  $250 \mu\text{m}$ . According to the Stokes formula (Eq. (7)), where  $V$  ( $\text{m s}^{-1}$ ) is the settling velocity of particles,  $\delta$  ( $\text{kg m}^{-3}$ ) is the particle density,  $\rho$  ( $\text{kg m}^{-3}$ ) is the fluid density,  $g$  ( $9.8 \text{ m s}^{-2}$ ) is the gravitational acceleration,  $\mu$  ( $\text{Pa s}$ ) is the fluid viscosity and  $d$  ( $\text{m}$ ) is the particle diameter, the settling velocity of particles is proportional to the square of the particle diameter:

$$V = \frac{(\delta - \rho)g}{18\mu} d^2 \quad (7)$$

The smaller the particle size, the slower the settling velocity, and the more difficult it is to separate the particles from the supernatant. The slurry particle size distribution in the wastewater therefore has an important impact on the coal washing process; a high concentration of mostly fine particle clays ( $<75 \mu\text{m}$ ) is problematic in coal washing wastewater treatment, as these particles form a stable coagulation. The SEM results together with the coagulation stability of these particles provide insight into the difficulty of washing wastewater treatment

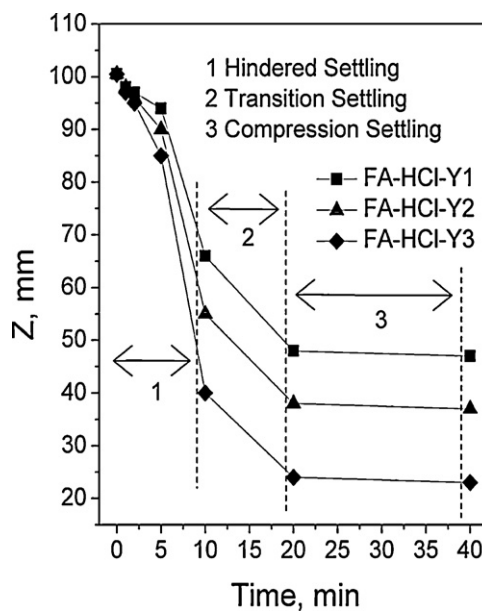


Fig. 5. Settling characteristics with different coagulants. (Note that the coagulants dosage is  $10 \text{ g l}^{-1}$ , and FA-HCl-Y3 has better settling characteristics than FA-HCl-Y1 or FA-HCl-Y2 in wastewater treatment.)

### 3.2. Effect of three coagulants in wastewater treatment

The aim of the coal washing wastewater treatment is to accelerate the particle settling rate and reduce contaminants in the wastewater. Parameters used for evaluating the extent of wastewater treatment therefore include settling characteristics and the measurement of COD and SS.

#### 3.2.1. Effect of different coagulants on settling characteristics

Good settling parameters imply a high level of purification. The settling characteristics of the wastewater treated with three FA-HCl-Y coagulants (dosage  $10 \text{ g l}^{-1}$ ) are compared in Fig. 5, which depicts the change in height of the suspension-supernatant interface ( $Z$ ) with time ( $t$ ). No settling occurred in the absence of a coagulant.

From Fig. 5 it can be seen that all settling curves exhibit the same trend: fast settling in the hindered zone (Zone 1), followed by

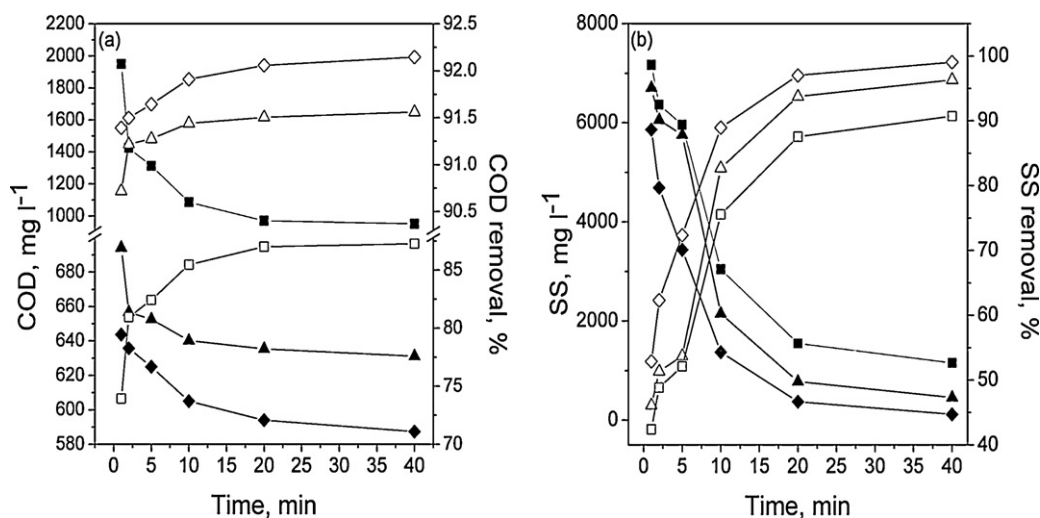


Fig. 6. COD and SS variation with different coagulants. (a) COD variation, (b) SS removal.  $\blacksquare$  FA-HCl-Y1,  $\blacktriangle$  FA-HCl-Y2,  $\blacklozenge$  FA-HCl-Y3. (Note that the coagulants dosage is  $10 \text{ g l}^{-1}$ , and FA-HCl-Y3 has better COD and SS removal as compared with the two other coagulants.)

slower settling in the compression zone (Zone 3). These two major zones are separated by a transition zone (Zone 2). These results are similar to previously reported results [28–30]. An increase in settling velocity after the start for the sedimentation run occurs as a result of the rapid aggregation of flocs [31]. Wastewater treated with FA-HCl-Y3 showed better settling characteristics as compared with the FA-HCl-Y1 and FA-HCl-Y2 treated wastewater. However, the wastewater treated with FA-HCl-Y2 resulted in a much faster settling rate than that with FA-HCl-Y1. Furthermore, the hindered zone was much larger for the wastewater treated with FA-HCl-Y3 than that for the other two suspensions.

### 3.2.2. Effect of different coagulants on COD and SS of coal washing wastewater

The effect of the three FA-HCl-Y coagulants (dosage  $10 \text{ g l}^{-1}$ ) on the COD and SS removal was investigated with results shown in Fig. 6. The COD and SS removal increases with time with removal efficiencies by the different coagulants after 40 min decreasing as follows: FA-HCl-Y3 > FA-HCl-Y2 > FA-HCl-Y1. A COD removal of 87.28%, 91.56% and 92.14% resulted for the FA-HCl-Y1, FA-HCl-Y2 and FA-HCl-Y3 systems, respectively, with an SS removal of 90.72%, 96.34% and 99.07% for the FA-HCl-Y1, FA-HCl-Y2 and FA-HCl-Y3 systems, respectively. This indicated that all FA-HCl-Y coagulants, particular the FA-HCl-Y3 coagulant, positively affect the wastewater treatment process.

Although the three FA-HCl-Y coagulants affect the wastewater treatment positively, the COD and SS values are still high after treatment and do not meet the discharge water standard in China [32]. After 10 and 20 min, respectively, the COD and SS values began to stabilize. The COD value of the effluent was reduced to 951, 631 and  $587 \text{ mg l}^{-1}$  in the FA-HCl-Y1, FA-HCl-Y2 and FA-HCl-Y3 systems, respectively, after 40 min treatment. The SS value decreased from 12,445 to 1154, 455 and  $115 \text{ mg l}^{-1}$ , for the three systems, respectively. The efficiency of FA-HCl-Y3 in removing COD and SS was found to be marginally lower as compared with the other coagulants.

### 3.3. Analysis of the coagulants and study of the coagulation mechanism

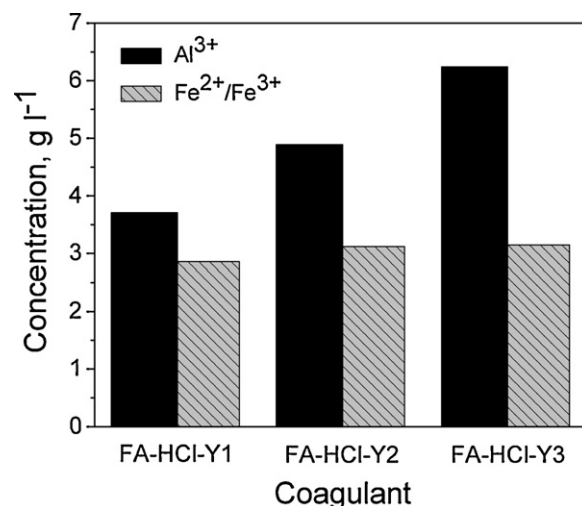
The coagulant XRF analysis, solution metal ion concentration after leaching and XRD analysis of the coagulant precursors were studied to explain the observed reduction in COD and SS.

From the XRF analysis (Table 3) it can be seen that the concentration of Al and Fe is highest in the FA-HCl-Y3 coagulant. The advantage of using this coagulant for coal washing wastewater treatment must occur because Al and Fe are leached from the fly ash by the HCl, so the metal ion concentrations in the supernatant and the FA samples before acid treatment were also examined.

The concentration of  $\text{Al}^{3+}$  and  $\text{Fe}^{2+}/\text{Fe}^{3+}$  in the leachates of the FA-HCl-Y coagulants is depicted in Fig. 7. It can be seen that the concentration of  $\text{Al}^{3+}$  increases more than that of  $\text{Fe}^{2+}/\text{Fe}^{3+}$  and decreases according to FA-HCl-Y3 > FA-HCl-Y2 > FA-HCl-Y1. Equal concentrations of  $\text{Fe}^{2+}/\text{Fe}^{3+}$  occur in the leachates of FA-HCl-Y3 and FA-HCl-Y2, and this concentration is higher than that in the leachate of FA-HCl-Y1. These results correspond to the COD and SS removal, indicating that adding  $\text{Na}_2\text{CO}_3$  and calcining can enhance the leaching of  $\text{Al}^{3+}$  and  $\text{Fe}^{2+}/\text{Fe}^{3+}$ . The high COD and SS removal efficiency

**Table 3**  
XRF analysis of FA-HCl-Y coagulants (wt%).

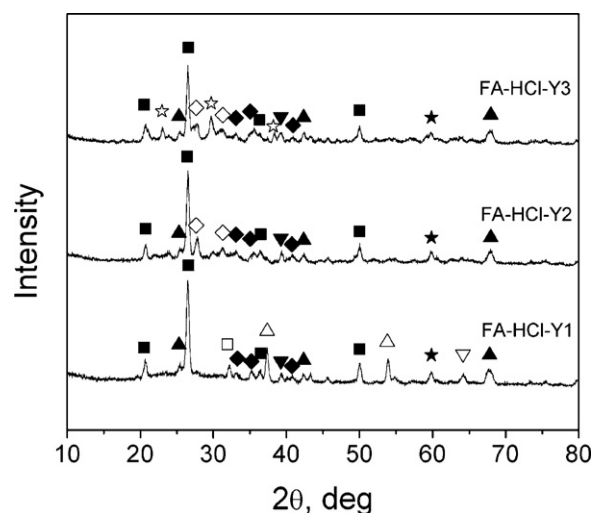
Element	Si	Al	Fe	Ca	Na	O	Cl	Others
FA-HCl-Y1	16.39	4.986	2.541	7.121	0.535	41.1	23.11	4.217
FA-HCl-Y2	15.4	5.857	2.676	6.799	0.521	39.2	25.2	4.347
FA-HCl-Y3	17.19	6.464	2.708	7.41	0.574	43.8	17.95	3.904



**Fig. 7.** Concentration of  $\text{Al}^{3+}$  and  $\text{Fe}^{2+}/\text{Fe}^{3+}$  in the leachates of FA-HCl-Y coagulants. (Note that the concentration of  $\text{Al}^{3+}$  and  $\text{Fe}^{2+}/\text{Fe}^{3+}$  in the leachate of FA-HCl-Y3 is higher than that in the leachates of FA-HCl-Y1 or FA-HCl-Y2.)

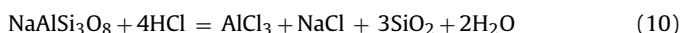
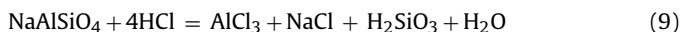
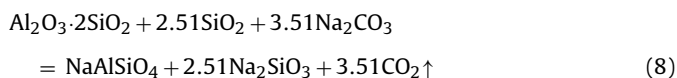
can be attributed to the fact that  $\text{Al}^{3+}$  and  $\text{Fe}^{3+}$  are leached from the fly ash, converting FA-HCl-Y into aluminum and iron-based coagulants.

To explain why the concentration of  $\text{Al}^{3+}$  and  $\text{Fe}^{2+}/\text{Fe}^{3+}$  is different in the leachates of the FA-HCl-Y coagulants, the XRD analysis of the coagulant precursors (fly ash samples before acid treatment) is shown in Fig. 8. The FA-HCl-Y1 precursor is the raw fly ash sample, the FA-HCl-Y2 precursor is the fly ash sample after being calcined and the FA-HCl-Y3 precursor is the fly ash sample after adding  $\text{Na}_2\text{CO}_3$  and calcining. The FA-HCl-Y1 precursor is complex and contains many mineral phases, such as  $\text{SiO}_2$ ,  $\text{Al}_6\text{Si}_2\text{O}_{13}$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{Fe}_3\text{O}_4$ ,  $\text{Ca}_2\text{Al}_2\text{SiO}_7$  and  $\text{Ca}_3\text{Fe}_2\text{Si}_3\text{O}_{12}$ . Some glass phases can be found in the raw fly ash although no sodium compounds were detected in FA-HCl-Y1. When sintered at  $800^\circ\text{C}$ , several mineral phases disappear, and the  $\text{NaAlSi}_3\text{O}_8$  phase appears in the FA-HCl-Y2 precursor. In addition to the  $\text{NaAlSi}_3\text{O}_8$  phase, a  $\text{NaAlSiO}_4$  phase exists in the FA-HCl-Y3 precursor as compared with the FA-HCl-Y2 precursor. This may result from the low  $\text{Na}_2\text{O}$  concentration in the fly ash, which disperses in the mineral and glass phases of the



**Fig. 8.** XRD patterns of FA-HCl-Y precursors. ■  $\text{SiO}_2$  ◆  $\text{AlSi}_2\text{O}_{13}$  ▲  $\text{Al}_2\text{O}_3$  ▼  $\text{Fe}_2\text{O}_3$  ★  $\text{Fe}_3\text{O}_4$  □  $\text{Ca}_2\text{Al}_2\text{SiO}_7$  ◇  $\text{NaAlSi}_3\text{O}_8$  △  $\text{Ca}_3\text{Fe}_2\text{Si}_3\text{O}_{12}$  ▽  $\text{Fe}_3\text{Al}_2(\text{SiO}_4)_3$  ☆  $\text{NaAlSiO}_4$ . (Note that there is  $\text{NaAlSi}_3\text{O}_8$  phase in the FA-HCl-Y2 precursor, and there are  $\text{NaAlSi}_3\text{O}_8$  phase and  $\text{NaAlSiO}_4$  phase in the FA-HCl-Y3 precursor as compared with the raw fly ash sample.)

fly ash. For this reason, the sodium compound is not found in the FA-HCl-Y1 precursor. When it is calcined at 800 °C, the Na<sub>2</sub>O will react with SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> and a phase transformation takes place. Na<sub>2</sub>CO<sub>3</sub> reacts with the fly ash according to Eq. (8) in the 800 °C sintered case, explaining the presence of the sodium compound in the FA-HCl-Y2 and FA-HCl-Y3 precursors. The diffraction intensity of the Fe<sub>2</sub>O<sub>3</sub> peaks is enhanced in the FA-HCl-Y2 and FA-HCl-Y3 precursors. Fe<sub>2</sub>O<sub>3</sub>, NaAlSi<sub>3</sub>O<sub>8</sub> and NaAlSiO<sub>4</sub> will react with HCl and generate Al<sup>3+</sup> and Fe<sup>2+</sup>/Fe<sup>3+</sup> according to Eqs. (9)–(11). Calcination and Na<sub>2</sub>CO<sub>3</sub> addition can therefore increase the concentration of Al<sup>3+</sup> and Fe<sup>2+</sup>/Fe<sup>3+</sup> in the coagulants.



In addition to Fe<sup>2+</sup>/Fe<sup>3+</sup> and Al<sup>3+</sup>, the FA-HCl-Y3 coagulant contains a multi-component multi-phase mixture of Ca<sup>2+</sup>, H<sub>2</sub>SiO<sub>3</sub> and undissolved fly ash particles. Fe<sup>2+</sup>, Fe<sup>3+</sup> and Al<sup>3+</sup> hydrolyzed and polymerized to form polynuclear hydroxy polymers, which not only play a role in electric double layer compression to reduce the ζ potential (from −63.98 to −8.34 mV), but also bridge the adsorption in the coagulation process. As seen from Eq. (9), some dissolved silicic acid generated from the coagulant allows for the adsorption of impurity particles onto the surface to form large, heavy alum, which enhances the coagulation process to some extent. Furthermore, the presence of fly ash particles will improve the alum structure and increase its weight, thus speeding up the formation of alum. Besides, fly ash itself is also a good adsorbent; its surface area increases with increasing particle surface roughness, and its adsorption capacity increases when treated with acid, allowing it to remove COD and SS to some degree. Fig. 9 shows SEM images of the raw fly ash and FA-HCl-Y3 coagulant samples. As shown in Fig. 9b, the strong reactive capacity of HCl changes the surface of the coal fly ash microspheres, and the FA-HCl-Y3 coagulant surface becomes rough after treatment with HCl, this implies that the coal fly ash specific surface area increases significantly. The factors described above result in the FA-HCl-Y3 coagulant having a more effective treatment effect as compared with the two other coagulants, and the possible mechanisms are also consistent with reported literature [18,33].

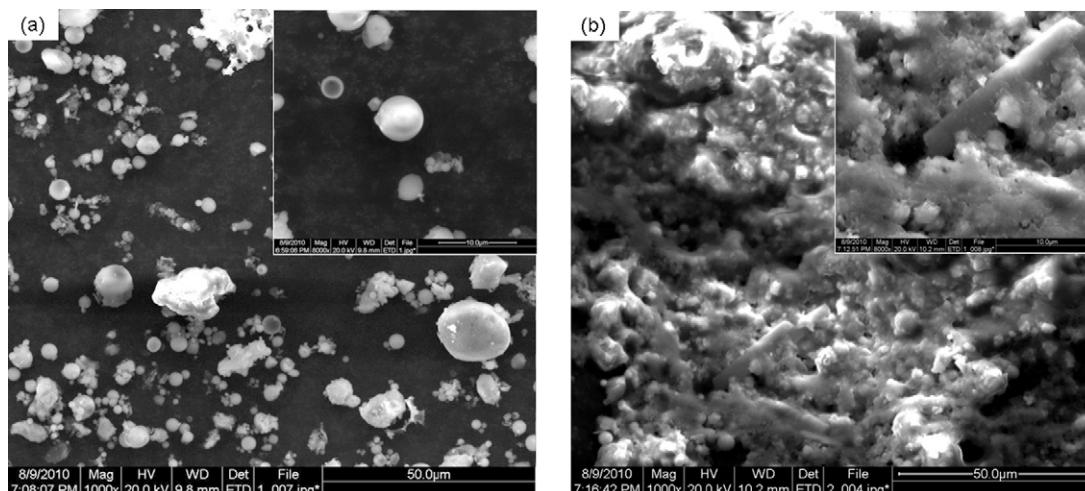


Fig. 9. SEM of (a) raw fly ash and (b) FA-HCl-Y3 coagulant. (Note that the FA-HCl-Y3 coagulant surface becomes rough after treatment with HCl.)

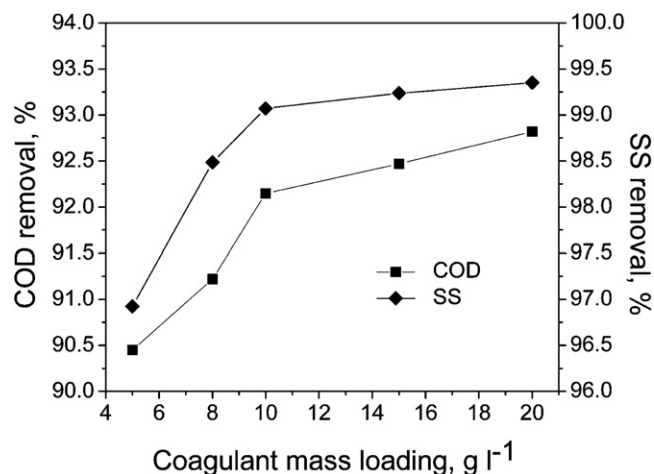


Fig. 10. Effect of coagulant dosage on COD and SS removal. (Note that an increase in FA-HCl-Y3 dosage helps to enhance COD and SS removal until dosage is over 10 g l<sup>-1</sup>.)

### 3.4. Optimization of experimental conditions

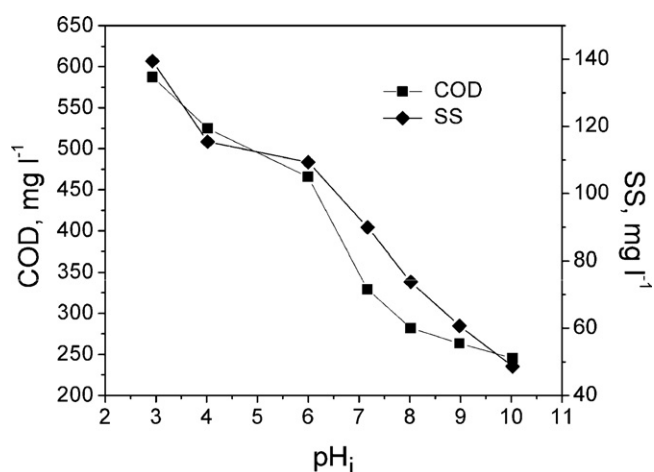
The performance of the FA-HCl-Y3 coagulant was tested in a beaker system with respect to the effect of coagulant dosage and pH on COD and SS removal.

#### 3.4.1. Effect of coagulant dosage

The effect of FA-HCl-Y3 coagulant mass loading (5–20 g l<sup>-1</sup>) on the COD and SS removal of coal washing wastewater was studied after 40 min of treatment (Fig. 10). A 96.92% SS removal is obtained at a dosage of 5 g l<sup>-1</sup>, which is marginally higher than that observed without the addition of a coagulant, because clear precipitation was observed at this time. With an increase of FA-HCl-Y3 dosage, SS removal is facilitated. At a dosage of 10 g l<sup>-1</sup>, the SS removal increases to 99.07% (SS concentration of 115 mg l<sup>-1</sup>) after which the increase in SS removal is slow and insignificant. Raising the dosage to 20 g l<sup>-1</sup>, resulted in a SS removal increase to only 99.35%, with a correspondingly high increase of sludge quantity and cost owing to the high FA-HCl-Y3 dosage.

COD removal shows a similar trend as that for SS removal. An increase in FA-HCl-Y3 dosage helps to enhance COD removal with a rapid increase to 92.14% at a FA-HCl-Y3 dosage of 10 g l<sup>-1</sup>, and only a slight increase thereafter. Taking cost into account, a suitable





**Fig. 11.** Effect of initial pH on COD and SS. (Note that the initial pH is 4.02 when only FA-HCl-Y3 coagulant is added; and COD and SS decrease with the increasing of  $pH_i$ , respectively.)

FA-HCl-Y3 dosage is  $10\ g\ l^{-1}$ , which results in a COD effluent decrease to  $587\ mg\ l^{-1}$ .

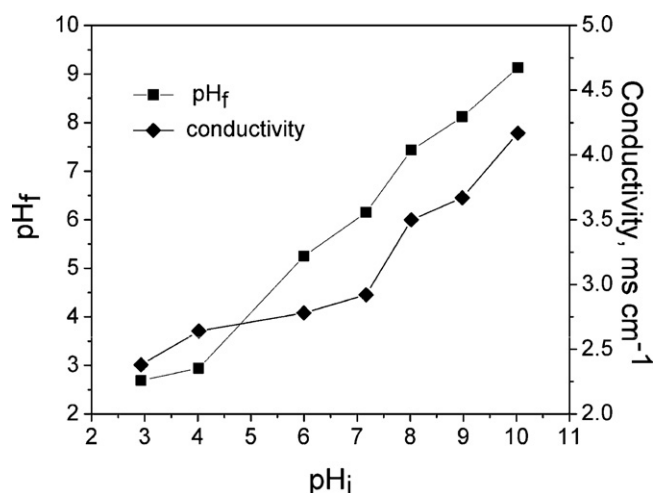
The final pH of the treated wastewater is reduced from 4.72 to 2.64. This decrease may be attributed to several hydrolytic reactions that take place during the coagulation process, resulting in the formation of multivalent charged hydroxide species and generating  $H_3O^+$  ions during each step [34].

#### 3.4.2. Effect of initial pH on COD, SS, final pH and conductivity

The initial pH of the wastewater plays an important role in the coagulation process. Concentrated HCl or CaO solution was used to adjust the wastewater pH to the desired level, because the initial pH was 4.02 with the addition of the FA-HCl-Y3 coagulant only.

The variation of COD and SS in the coal washing wastewater with initial pH ( $pH_i$ ) after addition of the FA-HCl-Y3 coagulant is shown in Fig. 11 (FA-HCl-Y3 dosage  $10\ g\ l^{-1}$ , 40 min treatment). When the  $pH_i$  value of the wastewater is adjusted to 2.93, the COD and SS values increase. This conflicts with some views that the addition of an acid with a coagulant favors the removal of COD and SS from wastewater [35]. An increase of  $pH_i$  from 4.02 to 10.03 results in a decrease of the COD and SS to  $245\ mg\ l^{-1}$  and  $48.60\ mg\ l^{-1}$ , respectively, and a  $\zeta$  potential reduction from  $-63.98\ mV$  to  $-0.84\ mV$ , which is close to the value of tap water ( $-0.34\ mV$ ). These results agree with previous findings [36]. The  $\zeta$  potential reduction occurs because of the increase in  $Ca^{2+}$  and  $Ca(OH)_2$  concentrations with the addition of CaO. Free  $Ca^{2+}$  is adsorbed, the electric double layer is compressed by electrostatic interaction, and the ions also react with  $H_2O$  to generate  $[Ca(H_2O)_6]^{2+}$ , which destroys the electric double layer. Furthermore,  $Ca(OH)_2$  can adsorb and precipitate Al-OH and Si-OH, which also promote the coagulation of solids in wastewater.

It is noticed from Fig. 12 that the final pH ( $pH_f$ ) and conductivity of the treated wastewater increased with increasing  $pH_i$ . This is because CaO dissolved into the wastewater and reacted with  $H_2O$  to generate  $OH^-$  and  $Ca^{2+}$ , which increased the  $pH_f$  and conductivity, separately. Although CaO addition can reduce the COD and SS, too much CaO may affect water quality. When the  $pH_i$  is 10.03, the  $pH_f$  value is in excess of 9, which is the minimum pH required according to the discharge water quality standard in China. Hence, the amount of CaO addition should be controlled by adjusting the  $pH_i$  to 9. At this point, the COD and SS of the effluent after 40 min treatment were  $263\ mg\ l^{-1}$  and  $60.75\ mg\ l^{-1}$ , and the removal reached 96.48% and 99.61%, respectively.



**Fig. 12.** Effect of initial pH on final pH and conductivity. (Note that the  $pH_i$  is 10.03, the  $pH_f$  value is in excess of 9.)

#### 3.5. Sludge treatment and practicability of the process

Although the effluent after treatment was clear with low pollutant concentrations, approximately 20 vol% of slurry was produced after treatment in our investigation (Fig. 5, Fig. 13). XRD analysis of the sludge (Fig. 14) shows that carbon is the main element present, suggesting that sludge slurry may have a high calorific value with potential applications in energy production. In fact, large amounts of coal sludge produced from coal washing wastewater treatment are produced currently in industry, for use as fuel after dewatering and drying [15,37].

The FA-HCl-Y3 coagulant preparation conditions were: 3:1  $ml\ g^{-1}$  ration of 4M HCl solution to fly ash, 2 h leaching time and  $10\ g\ l^{-1}$  coagulant dosage, which is lower than that reported by some researchers [18]. The COD and SS of the wastewater after 40 min treatment was reduced to  $245\ mg\ l^{-1}$  and  $48.60\ mg\ l^{-1}$  from  $7480\ mg\ l^{-1}$  and  $12,445\ mg\ l^{-1}$ , respectively, indicating that this process could be applied practically.



**Fig. 13.** Coal washing wastewater. (a) Before and (b) after treatment. (Conditions: 100 ml wastewater, adjusted the initial pH to 9 by CaO, FA-HCl-Y3 coagulant dosage  $10\ g\ l^{-1}$ , 40 min treatment.)

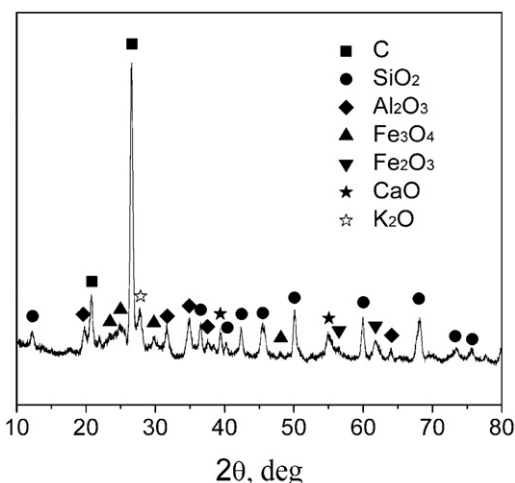


Fig. 14. XRD pattern of the dry sludge. (Note that carbon is the main element present in the sludge.)

#### 4. Conclusions

Based on the above discussion, FA-HCl-Y3 is an inexpensive coagulant, and it is at least as feasible as the coagulants used conventionally in coal washing wastewater treatment plants. The effluent after treatment was clear with low pollutant concentration. The COD and SS removal was up to 96.48% and 99.61%, respectively. Utilization of the fly ash and production of a valuable chemical reagent for the treatment of wastewater could not only be helpful to the environment in solving solid waste disposal problems, but could also be economically viable.

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#### References

- [1] S. Mohanta, B.K. Mishra, S.K. Biswal, An emphasis on optimum fuel production for Indian coal preparation plants treating multiple coal sources, *Fuel* 89 (2010) 775–781.
- [2] T. Nakajima, H. Hasegawa, S. Nakamata, H. Takanashi, A. Ohki, Mutagenicity of eluent by hot water extraction of various coals: effect of chlorination, *Fuel* 87 (2008) 3132–3136.
- [3] L.A. Berrueta, L.A. Fernández, F. Vicente, Fluorescence study of the solubilization of benzo[*a*]pyrene: application to its detection in coal washing waters, *Anal. Chim. Acta* 243 (1991) 115–119.
- [4] T. Nakajima, T. Kanda, T. Fukuda, H. Takanashi, A. Ohki, Characterization of eluent by hot water extraction of coals in terms of total organic carbon and environmental impacts, *Fuel* 84 (2005) 783–789.
- [5] T.J. Johnson, E.J. Davis, Electrokinetic clarification of colloidal suspensions, *Environ. Sci. Technol.* 33 (1999) 1250–1255.
- [6] L. Semerjian, G.M. Ayoub, High-pH-magnesium coagulation-flocculation in wastewater treatment, *Adv. Environ. Res.* 7 (2003) 389–403.
- [7] M.A. Aboulhassan, S. Souabi, A. Yaacoubi, M. Baudu, Improvement of paint effluents coagulation using natural and synthetic coagulant aids, *J. Hazard. Mater.* 138 (2006) 40–45.
- [8] J.C.S.S. Menezes, R.A. Silva, I.S. Arce, I.A.H. Schneider, Production of a poly-alumino-iron sulphate coagulant by chemical precipitation of a coal mining acid drainage, *Miner. Eng.* 23 (2010) 249–251.
- [9] A. Garg, I.M. Mishra, S. Chand, Thermochemical precipitation as a pretreatment step for the chemical oxygen demand and color removal from pulp and paper mill effluent, *Ind. Eng. Chem. Res.* 44 (2005) 2016–2026.

- [10] M. Fan, R.C. Brown, S. Sung, Y. Zhuang, A process for synthesizing polymeric ferric sulfate using sulfur dioxide from coal combustion, *Int. J. Environ. Pollut.* 17 (2002) 102–109.
- [11] C. Duong, J. Choung, Z. Xu, J. Szymanski, A novel process for recovering clean coal and water from coal tailings, *Miner. Eng.* 2 (2000) 173–181.
- [12] Z. Lin, C. Yang, Z. Shen, X. Qi, The properties and sedimentation characteristics of extremely sliming coal slime water, *J. China Coal Soc.* 2 (2010) 312–315.
- [13] H. Tanaka, S. Fujimoto, A. Fujii, R. Hino, T. Kawazoe, Microwave assisted two-step process for rapid synthesis of Na–A Zeolite from coal fly ash, *Ind. Eng. Chem. Res.* 47 (2008) 226–230.
- [14] S. Wang, Application of solid ash based catalysts in heterogeneous catalysis, *Environ. Sci. Technol.* 42 (2008) 7055–7063.
- [15] H. Liu, Z. Liu, Recycling utilization patterns of coal mining waste in China, *Resour. Conserv. Recycl.* 54 (2010) 1331–1340.
- [16] Z. Bian, J. Dong, S. Lei, H. Leng, S. Mu, H. Wang, The impact of disposal and treatment of coal mining wastes on environment and farmland, *Environ. Geol.* 58 (2009) 625–634.
- [17] M. Ahmaruzzaman, A review on the utilization of fly ash, *Prog. Energy Combust.* 36 (2010) 327–363.
- [18] C. Chen, P. Zhang, G. Zeng, J. Deng, Y. Zhou, H. Lu, Sewage sludge conditioning with coal fly ash modified by sulfuric acid, *Chem. Eng. J.* 158 (2010) 616–622.
- [19] A. Seidel, Y. Zimmels, Mechanism and kinetics of aluminum and iron leaching from coal fly ash by sulfuric acid, *Chem. Eng. Sci.* 53 (1998) 3835–3852.
- [20] M. Fan, R.C. Brown, J.V. Leeuwen, M. Nomura, Y. Zhuang, The kinetics of producing sulfate-based complex coagulant from fly ash, *Chem. Eng. Process.* 42 (2003) 1019–1025.
- [21] S. Wang, Y. Boyjoo, A. Choueib, Z.H. Zhu, Removal of dyes from aqueous solution using fly ash and red mud, *Water Res.* 39 (2005) 129–138.
- [22] Y.Q. Li, Preparation of coagulant from fly ash and its application in coagulation-constructed wetland (Dissertation for the Doctoral Degree), Harbin Institute of Technology, 2008, (in Chinese).
- [23] General Administration of Quality Supervision, Inspection and Quarantine of P.R.C. (AQSIQ), Water treatment chemical – Poly aluminium chloride (GB 15892-2003), General Administration of Quality Supervision, Inspection and Quarantine of P.R.C., Beijing, 2003.
- [24] American Public Health Association (APHA), American Water Works Association (AWWA), Water Environment Federation (WEF), Standard Methods for the Examination of Water and Wastewater, 21st ed., American Public Health Association, Washington, DC, 2005.
- [25] M. Fan, R.C. Brown, T.D. Wheelock, A.T. Cooper, M. Nomura, Y. Zhuang, Production of a complex coagulant from fly ash, *Chem. Eng. J.* 106 (2005) 269–277.
- [26] L. Li, M. Fan, R.C. Brown, J.A. Koziel, J.V. Leeuwen, Production of a new wastewater treatment coagulant from fly ash with concomitant flue gas scrubbing, *J. Hazard. Mater.* 162 (2009) 1430–1437.
- [27] Y. Chen, Y.S. Chen, G. Gu, Influence of pretreating activated sludge with acid and surfactant prior to conventional conditioning on filtration dewatering, *Chem. Eng. J.* 99 (2004) 137–143.
- [28] A. Garg, I.M. Mishra, S. Chand, Thermo-chemical precipitation as a pretreatment step for the COD and colour removal from pulp and paper mill effluent, *Ind. Eng. Chem. Res.* 44 (2005) 2016–2026.
- [29] T. González, J.R. Domínguez, J. Beltrán-Heredia, H.M. García, F. Sanchez-Lavado, Aluminium sulfate as coagulant for highly polluted cork processing wastewater: evaluation of settleability parameters and design of a clarifier-thickener unit, *J. Hazard. Mater.* 148 (2007) 6–14.
- [30] O. Larue, E. Vorobiev, Floc size estimation in iron induced electrocoagulation and coagulation using sedimentation data, *Int. J. Miner. Process.* 71 (2003) 1–15.
- [31] A. Garg, I.M. Mishra, S. Chand, Effectiveness of coagulation and acid precipitation processes for the pre-treatment of diluted black liquor, *J. Hazard. Mater.* 180 (2010) 158–164.
- [32] State Environmental Protection Agency (SEPA), General Administration of Quality Supervision, Inspection and Quarantine (AQSIQ), Emission standard for pollutants from coal industry (GB 20426-2006), China Environmental Science Press, Beijing, 2006.
- [33] P. Pengthamkeerati, T. Satapanajaru, P. Chularuengsoarn, Chemical modification of coal fly ash for the removal of phosphate from aqueous solution, *Fuel* 87 (2008) 2469–2476.
- [34] R.J. Stephenson, S.J.B. Duff, Coagulation and precipitation of amechanical pulping effluent—I. Removal of carbon, colour and turbidity, *Water Res.* 30 (1996) 781–792.
- [35] W.W. Eckenfelder Jr., *Industrial Water Pollution Control* (McGraw-Hill Series in Water Resources and Environmental Engineering), 3rd ed., McGraw-Hill, Singapore, 2000.
- [36] Y. Li, Study on treatment and reuse technology of concentrated wastewater of coal washing (Dissertation for the Doctoral Degree), Northeastern University of China, 2005, (in Chinese).
- [37] D. Fyttili, A. Zabanitou, Utilization of sewage sludge in EU application of old and new methods – a review, *Renew. Sustain. Energy Rev.* 12 (2008) 116–140.