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Preparation of a novel inorganic polymer coagulant from oil shale ash

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ABSTRACT

In this paper, a novel inorganic polymer coagulant was prepared from oil shale ash, and was adopted to treat municipal sewage. Effect of coagulants dosage on the turbidity and Chemical Oxygen Demand (COD) removal were examined. In addition, the structure and morphology of the prepared coagulants were characterized by transmission electron microscopy (TEM), X-ray diffraction (XRD) and infra-red spectra (FTIR), furthermore, the zeta potential of the sewage and the microscopic images of flocks were measured. The results indicate that the characterization and coagulation performance of the samples are affected by Al/Fe mole ratios and the type of lixiviant. The most of Fe^{3+} is not turned into the crystals, which means that the samples are not simple mixtures of raw materials but inorganic polymer compounds with iron, aluminum, silicon and other ions. When Al/Fe mole ratio is 0.71 or the $2HCl/H_2SO_4$ mole ratio of the lixiviant is 1:1, the coagulation performance of the sample is better than that of the others. The integrated analysis suggests that the entrapment, adsorption and complexation abilities play important roles in coagulation process although the charge neutralization is weak. Also, the chain-net structure and the suitable size of polymer group are favorable for the entrapment, adsorption and complexation ability of the samples.

1. Introduction

Shale oil is a type of alternative energy and possesses expanded potential under energy crisis. For this reason, more and more shale oil have been mined and applied for several decades. The exploration indicates that China is rich in shale oil resources, the mined reserves are 2432 million tons, and the refined shale oil is 120 million tons [1]. After shale oil is refined, a large amount of oil shale ash is abandoned. Generally, oil shale ash mainly consists of aluminum, iron and silicon compounds and less calcium, magnesium, sodium, potassium and titanium compounds. In order to reduce the accumulation and explore the application of oil shale ash, many application methods have been reported such as producing nanoscale gamma-alumina powder, silica powders, silica aerogel, zeolite, filter media, building material [2–7]. However, higher valued products are desirable.

Coagulation is an essential method in water and wastewater treatment, and the coagulant plays an important role in this process. The coagulant includes two kinds, even as inorganic coagulant and organic one. Inorganic coagulants are widely applied due to low price. Most of conventional common coagulants used in the treatment water or wastewater are aluminum and iron slats, such as aluminum sulfate, ferric sulfate, aluminum chloride and ferric chloride [8–12]. However, the formation of metal hydrolysis species of them is uncontrolled, and the dose of the coagulant is large. To avoid the drawbacks and improve the coagulation efficiency, several polymer inorganic coagulants have been developed, such as poly-aluminum sulfate, poly-ferric sulfate and poly-aluminum chloride [13–17], and moreover, the coagulation performance of polymer inorganic coagulants is generally better than that of conventional coagulants in the same dosage and a similar pH value. Both iron and aluminum-based coagulants have obviously merits and demerits for water and wastewater treatment. Therefore, a novel inorganic coagulant composed of both iron and aluminum is ideal, for that it possesses the merits of both coagulants, and their demerits can be avoided or reduced. In recent years, more and more novel polymer inorganic coagulants have been researched, which are modified by poly silicate (PS), such as poly-silicate-ferric, poly-aluminum-silicate-chloride, poly-zinc-silicate-sulfate, and poly-aluminum silicate-sulfate. Due to carrying a negative charge, PS is a better modifier of new composite coagulants in improving the coagulation performance. Therefore, the main goals of adding it are to enlarge the molecular size and enhance the aggregating ability of the coagulant, as well as increasing their stability and durability [18–22]. At the same time, many factors should be considered in preparing the coagulants, such as charge-

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neutralization, destabilization, bridging, sweeping and stability and so on. All the macroscopic behavior depends on the characteristics of the coagulants. Therefore, the characteristics of the coagulant should be considered in preparing the coagulants.

As mentioned before, oil shale ash is rich in aluminum, iron and silicon oxides, all of which are the appropriate raw materials for producing inorganic polymer coagulant. It makes it possible to utilize oil shale ash for producing a novel inorganic coagulant. There is a promising market, however, very few studies on this issue have been done until now.

The characterization and performance of the coagulant prepared from oil shale ash are affected by different factors. This study focused on Al/Fe mole ratio and type of leaching acid, and moreover the coagulation performance was evaluated through the treatment sewage. Firstly, the structure of prepared coagulant was analyzed by obtaining X-ray diffraction (XRD) and infra-red spectra (FT-IR), and morphology analysis of those were displayed by transmission electron microscopy (TEM) microphotographs, and turbidity and COD removal of the sewage were measured as evaluation indicator of the coagulation performance. Meanwhile, the zeta potential of pro- and last-treatment sewage and the microscopic images of the flocks formed in coagulation process were measured.

2. Materials and methods

2.1. Materials

All the chemical reagents were analytically pure and de-ionized water was used to prepare all the solutions. The oil shale ash was obtained from Fushun Mining Group Co., Ltd. (China), and the manufacturer provided the chemical properties of the oil shale ash is that 64.8% (*w*/*w*) SiO_2, 20.6% (*w*/*w*) Al_2O_3, 8.20% (*w*/*w*) Fe_2O_3 and less MgO, K_2O, CaO, TiO_2, etc. The sewage used in the coagulation experiments was obtained from main sewer of Bohai University (Liaoning Province, China), COD of the raw water is 302 mg/L, and the turbidity is 352 NTU.

2.2. Experimental

2.2.1. Preparation of the complex coagulants

In this paper, the influences of Al/Fe mole ratio and type of leaching acid on the characterization and performance of the novel inorganic coagulants were studied. Preparing the coagulants was followed three steps and had slight differences.

(a) Acid leaching

First, the oil shale ash used were attrited to particle size lower than 120 meshes, and were calcined at 650 °C for 3 h. The ratio of leaching acid solution to oil shale ash was based on the stoichiometry of reactions between acid and the iron and aluminum oxides in oil shale ash. Second, exact 120 g of oil shale ash and 240 mL of sulfuric acid, hydrochloric acid or the mixed acid which contains 8 mol/L H^+ were added in 3 mouths flask in each acid leaching. The oil shale ash slurry was stirred and heated to slight boiling for 4.5 h and was separated by filtration. Third, the solid residue was washed for three times following this: the insoluble oil shale ash particles and 150 mL water were mixed into 3 mouths flask and heated to 100 °C for 15 min under stirring. The slurry was filtered after cooling. Finally, the mixed solution of mother and washing solution were heated to concentrate at different degree, after filtering the precipitation crystals the iron and aluminum solution were obtained with different Al/Fe mole ratio. The concentration of iron and aluminum was measured using VISTA-MPX ICP-OES spectroscopy (VARIAN, American), and the concentration of Fe^{3+} and Fe^{2+} were measured by oxidation–reduction titration method.

(b) Alkali leaching

After acid leaching and washing, the remaining oil shale ash was dried at 110 °C for 2 h, and then 45 g dried oil shale ash and 180 mL of 5 mol/L sodium hydroxide solution were mixed and heated to slight boiling for 4 h under stirring, it was filtered afterward. Finally, the residue was washed for three times like acid leaching. The water glass solution contained 1.65 mol/L silicon, which were mixed by mother and washing solution. The concentration of silicon was measured by back titration method.

(c) Polymerizing

First, the PS solution was prepared following this: the water glass solution was dropped slowly into 1.6 mol/L sulfuric acid solution at 20 °C to pH 4.0 under magnetic stirring, and then it was aged under stirring rapidly for 20 min. Second, exact 100 mL of iron and aluminum solution was held at 50 °C under vigorous magnetic stirring, meanwhile, quantitative PS solution was titrated at a flow rate of 1.0 mL/min into it. Afterwards, 4 mol/L sodium hydroxide solutions were added dropwise at a flow rate of 0.4 mL/min into the above solution under rapid magnetic stirring, the solutions were aged under normal stirring at 50 °C for 3 h and a novel inorganic coagulant was made. Finally, the coagulant solutions were dried at 50 °C and attrited to obtain the powder samples.

2.2.2. Coagulation experiments

The coagulation experiments were carried out using a jar test apparatus with six paddles (Qianjiang Meiyu Co., China) at room temperature (about 20 °C). During the rapid stir (200 rpm), a measured amount of coagulant was added into 1.0 L sewage, and the samples were mixed rapidly at 200 rpm for 1 min, and mixed slowly at 40 rpm for 5 min. After slow mixing, the mixtures were kept for 20 min for separation of the flocks. Finally, the unfiltered supernatant was withdrawn 3.0 cm below the water surface to analyze the residual turbidity, COD and zeta potenial. Turbidity of sewages was measured by 2100AN turbidimeter (HACH, American), and COD was measured by closedreflux method using dichromate as oxidant (GB11984-89, China). Also, the zeta potentials of pre- and past-treatment sewage were measured by ZS90 laser particle analyzer (Malvern Instruments Ltd., Britain). For observing the structure of the flocks, 1–2 drops of the coagulated water sample was placed on a microscope slide using suction tubes with a large tip to minimize breakage of the flocks during transfer. The microscopic of the flocks were examined by BK-POLR transmitting and reflecting polarizing microscope (Chongqin Optec Instrument Co., Ltd., China).

2.2.3. Characterization of the complex coagulants

The morphology of the coagulant was examined by TEM. The liquid samples were adsorbed onto the copper net, and then dried at room temperature, after that it was loaded to transmission electron microscope (Philips EM400T, Holland) to be observed. XRD were measured for the determination of crystalline phases in the solid coagulant, using D/MAX-RB X-ray diffractometer (Rigaku, Japan) with Cu K-radiation in the 2θ range of 5–65° at a scan rate of 4°/min. Meanwhile, the powder samples were mixed with potassium bromide and the pellets were prepared, respectively. FT-IR spectroscopy was recorded with the Scimitar 2000 Near FT-IR Spectrometer (Thermo electron, USA) and the spectra were recorded in the range of 4000–400 cm^{-1}.

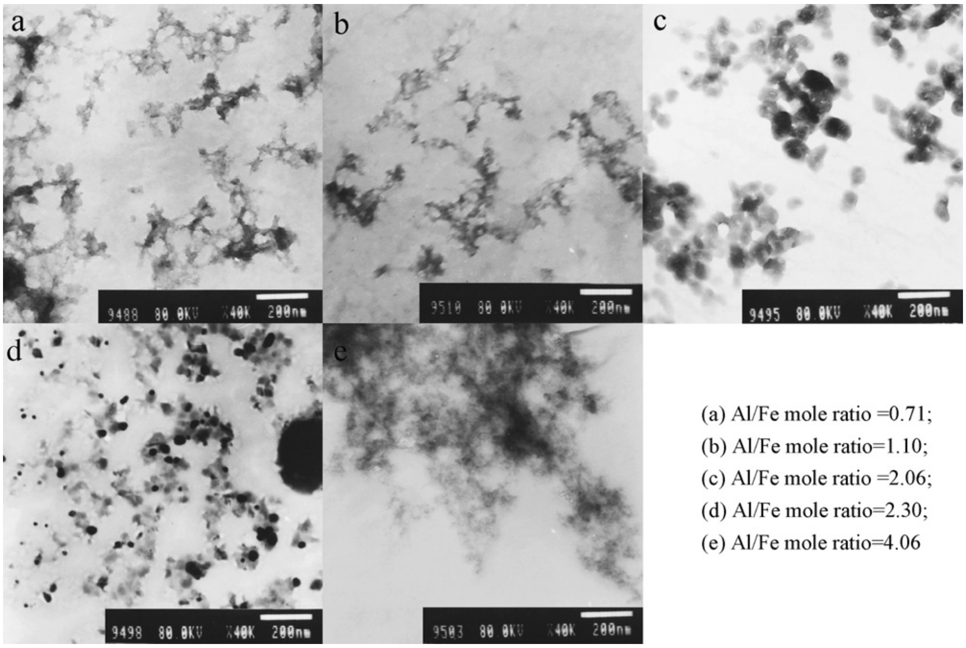


Fig. 1. TEM microphotographs of the novel inorganic polymer coagulants with different Al/Fe mole ratio.

3. Results and discussion

3.1. Structure and morphological analysis of the coagulants

TEM, XRD and FT-IR were carried out to identify the structure of a novel inorganic polymer coagulant and to elucidate whether Al/Fe mole ratio and the type of acid lixiviant affect the structure and morphology of those.

3.1.1. TEM microphotographs analysis

The coagulants with different Al/Fe mole ratio were prepared with sulfuric acid as leaching acid, and they mainly contained iron, aluminum and silicon, so they could be named poly-ferric-aluminum-silicate-sulfate (PFASS). (Al + Fe)/Si mole ratio of the samples is 12:1 and (Al + Fe)/NaOH volume ratio is 10:1. Fig. 1 shows TEM images of PFASS, it can be seen that the morphologies of PFASS are different due to various Al/Fe mole ratios. It is obvious that when Al/Fe mole ratio is 0.71, there is some imperfect chain-net structure with three dimensions and there is an aggregation trend between the chain-nets. Meanwhile, as Al/Fe mole ratio is 1.10, the structure of the coagulant has a slight transformations, the group of chain-net becomes little. Furthermore, when Al/Fe mole ratio increases continually, there is a distinct change, the chain-net structure disappears and the agglomeration particles appear. The particles of the PFASS become small and there exists many short branches around the particles at 2.30 Al/Fe mole ratio. However, when Al/Fe mole ratio increases to 4.60, the PFASS is fluffy flocculent.

Fig. 2 is TEM microphotographs of the novel inorganic polymer coagulants which were prepared by different acids as lixiviants at 12:1 (Al + Fe)/Si mole ratio and 10:1 (Al + Fe)/NaOH volume ratio, and the leaching acid is a simplex hydrochloric acid or the mixture of sulfuric acid and hydrochloric acid, so they could be named poly-ferric-aluminum-silicate-chloride (PFASC) or poly-ferric-aluminum-silicate-chloride-sulfate (PFASCS). The leaching efficiency of iron and aluminum is different due to the component of leaching acid, and when $2HCl/H_2SO_4$ mole ratios are 1:3, 1:1, 3:1 and ∞:1, Al/Fe mole ratio of the coagulants are 3.33, 5.12, 3.04 and 2.10, respectively. Above results indicate that the component of acid lixiviant affects the metal leaching efficiency of oil shale ash. Fig. 2 shows that when $2HCl/H_2SO_4$ mole ratio is 1:3, the structure of the sample is nearly ideal net, however, when $2HCl/H_2SO_4$ mole ratio increases to 1:1, the microstructure of the coagulant is turned into porous aggregate, and the net is small which only consists in agglomerated particles. Meanwhile, at 3:1 $2HCl/H_2SO_4$ mole ratio, there are a compact chain-net structure and many big particles appearing. When the leaching lixiviant is hydrochloric acid, the chain and net disappear and the microstructure of PFASC is compactly porous. For this reason, it is suggested that the microstructures of the novel inorganic polymer coagulants are affected by Al/Fe mole ratio and the type of acid lixiviant.

3.1.2. XRD analysis

XRD spectra of the novel inorganic polymer coagulants powder are shown in Fig. 3, Fig. 3(a) is XRD spectra of the coagulants with different Al/Fe mole ratios which were prepared with sulfuric acid as a lixiviant and Fig. 3(b) is XRD spectra of the coagulants which were prepared with different acid lixiviant. It is obvious that a series of characteristic diffractive peaks of crystal materials can be observed at certain 2θ. As shown in Fig. 3(a), when the coagulants were prepared with sulfuric acid as a lixiviant, the samples contain $FeSO_4{\cdot}H_2O$, $NaAl(SO_4)_2{\cdot}(H_2O)_6$ and other crystals, and moreover, the intensity of the peaks changes slightly according to Al/Fe mole ratios. With Al/Fe mole ratio increasing, the amount of $FeSO_4{\cdot}H_2O$ in the samples decreases and the amount of $NaAl(SO_4)_2{\cdot}(H_2O)_6$ increases gradually. Also, when the coagulants were prepared with mixed acid or hydrochloric acid as lixiviant, the crystal formation changes. The XRD spectra indicate that when $2HCl/H_2SO_4$ mole ratio is 1:3, there still exist $FeSO_4{\cdot}H_2O$, $NaAl(SO_4)_2{\cdot}(H_2O)_6$ and other crystals in the coagulant, however, as $2HCl/H_2SO_4$ mole ratio increases to 1:1, there are $FeCl_2{\cdot}H_2O$, NaCl and other crystals, at the same time, the peaks of $FeSO_4{\cdot}H_2O$ and $NaAl(SO_4)_2{\cdot}(H_2O)_6$ disappear. Meanwhile, when $2HCl/H_2SO_4$ mole ratio is 3:1, the main crystals become NaCl, the intensities of other peaks get weak. It is noteworthy that when the acid lixiviant is hydrochloric acid, there are NaCl, $FeCl_2$, $FeCl_3{\cdot}6H_2O$ and other crystals. Moreover, a detailed study of the peaks reveals that there are some peaks which are not attributed to any standard crystal, it indicates that

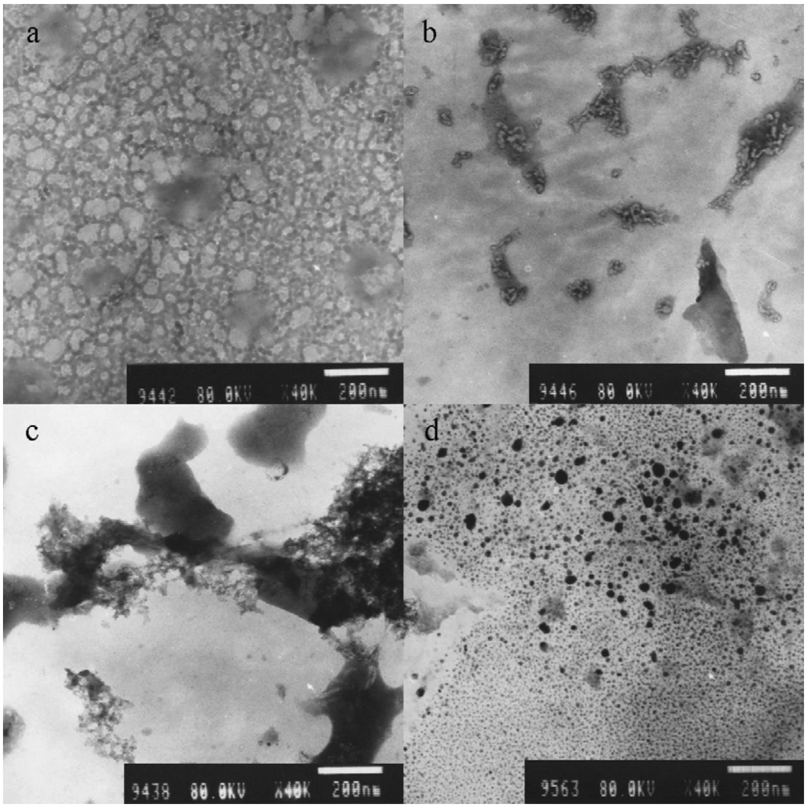


Fig. 2. TEM microphotographs of the novel inorganic polymer coagulants prepared with different lixiviant. (a) 2HCl/H_2SO_4 mole ratio is 1:3; (b) 2HCl/H_2SO_4 mole ratio is 1:1; (c) 2HCl/H_2SO_4 mole ratio is 3:1; (d) HCl.

a new compound has been formed in the novel inorganic polymer coagulants. In order to study the form of iron ion, Fe^{2+} mole percent in total iron ion is measured, and the results are shown in Table 1.

Table 1 illustrates that more than 95% iron ion is Fe^{3+}, and Fe^{2+} is less. However, above results imply that most iron crystals contain Fe^{2+} rather than Fe^{3+} in the samples, materials such as Fe^{3+}, Al^{3+}, $SO_4{}^{2-}$ and Si have been polymerized to form a new compound. As

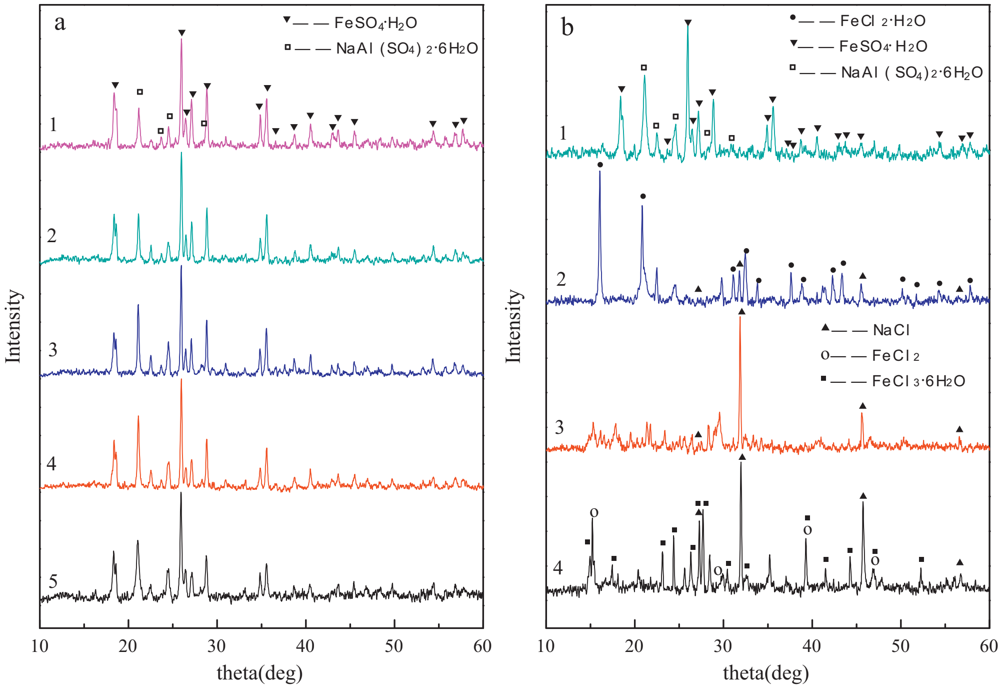


Fig. 3. XRD spectra of the inorganic polymer coagulants. (a) The coagulants with different Al/Fe mole ratio: (1) Al/Fe mole ratio is 0.71; (2) Al/Fe mole ratio is 1.10; (3) Al/Fe mole ratio is 2.06; (4) Al/Fe mole ratio is 2.30; (5) Al/Fe mole ratio is 4.06. (b) The coagulants prepared with different lixiviant: (1) 2HCl/H_2SO_4 mole ratio is 1:3; (2) 2HCl/H_2SO_4 mole ratio is 1:1; (3) 2HCl/H_2SO_4 mole ratio is 3:1; (4) HCl.

Table 1
Fe^{2+} mole percent in total iron ion.

Composition	Fe^{2+} mole percent in total iron ion (mole%)
Al/Fe mole ratio is 0.71 (acid lixiviant is sulfuric acid)	4.54
Al/Fe mole ratio is 1.10 (acid lixiviant is sulfuric acid)	3.49
Al/Fe mole ratio is 2.06 (acid lixiviant is sulfuric acid)	2.72
Al/Fe mole ratio is 2.30 (acid lixiviant is sulfuric acid)	2.53
Al/Fe mole ratio is 4.06 (acid lixiviant is sulfuric acid)	4.06
$2HCl/H_2SO_4$ mole ratio is 1:3 (acid lixiviant)	4.55
$2HCl/H_2SO_4$ mole ratio is 1:1 (acid lixiviant)	2.20
$2HCl/H_2SO_4$ mole ratio is 3:1 (acid lixiviant)	2.35
HCl (acid lixiviant)	1.61

Fu [19] suggests that the reaction rate of Fe^{2+} with PS is very slow, so the reaction between Fe^{2+} and Si can be neglected here, for this reason, the mode of Fe^{2+} is $FeSO_4{\cdot}H_2O$, $FeCl_2$, $FeCl_2{\cdot}H_2O$ crystals in the samples, which means that the novel inorganic polymer coagulants contain new chemical species rather than a simple mixture of the raw materials.

3.1.3. *FTIR spectra analysis*

Fig. 4(a) presents the FTIR spectra of the novel inorganic polymer coagulant with various Al/Fe mole ratio, and Fig. 4(b) presents the FTIR spectra of those which were prepared with various acid as lixiviant. Both spectra exhibit two characteristic bonds at 3500–3300 cm^{-1} and 1641 cm^{-1}, which can be attributed to the stretching vibration of –OH and to the bending vibration of water absorbed, polymerized or crystallized in the coagulants [18,20]. Meanwhile, the peaks at 578, 456 cm^{-1} are associated with winding vibration of Fe–O and Al–O, respectively, and the bonds around 2500 cm^{-1} are probably related to chemical bonding of iron or aluminum and oxide [23–25]. However, the peaks at 667 cm^{-1} and 604 cm^{-1} are regarded as bending vibration of Fe–OH and Al–OH, at the same time, the peaks at 1017 cm^{-1} are attributed to the stretching vibrations of those [26,27], and the bonds at 889 cm^{-1} and 851 cm^{-1} attributed to the bending vibration of Fe–OH–Fe or Al–OH–Al, respectively [27,28]. In addition, the strong absorption peaks at 1095 cm^{-1} and 1178 cm^{-1} are due to Si–O–Si and Si–O, respectively [29,20], and moreover, the peaks at 1284 cm^{-1} are due to Fe–O–Fe or Al–O–Al. At the same time, 1322 cm^{-1} are related to the stretching vibration of Fe–O–Si or Al–O–Si bonds, and 947 cm^{-1} are attributed to the winding vibration of those [23,30].

It can be seen from Fig. 4(a) that the intensity of the bonds rise with Al/Fe mole ratio, which are attributed to Al–O, Fe–O, Si–O, Fe–OH, Al–OH–Al, Fe–OH–Fe, Al–O–Al and Fe–O–Fe; the intensity of the bonds relating to Al–OH and Si–O–Si change little. The peaks of Al–O, Fe–OH–Fe disappear nearly with large Al/Fe mole ratio, however, the peaks of Al–O–Si and Fe–O–Si increase with Al/Fe mole ratio. Above results suggest that the bonds in the coagulant is influenced by Al/Fe mole ratio, more aluminum are favorable to forming Al–O–Si and Fe–O–Si, but the formation of Si–O–Si is hardly related to Al/Fe mole ratio, also, less iron leads to the peaks of Al–O, Fe–OH–Fe disappearing, which probably indicates that Al and Fe link O to form Al–O–Si and Fe–O–Si at first. In addition, the peaks varying with the leaching acid can be observed from Fig. 4(b). It is obviously that the peaks around 3500–3300 cm^{-1} blue shift gradually with the increase of hydrochloric acid in leaching acid, which are probably attributed to the appearance of H–Cl bonds. Meanwhile, the wave number or intensity of almost all bonds has changed with various lixiviants. A lot of HCl leads to decreasing or disappearing of Al–O, Fe–O, Si–O, Al–OH, Fe–OH, Al–OH–Al, Fe–OH–Fe, Al–O–Al, Fe–O–Fe, Al–O–Si, Fe–O–Si, etc., which suggests that more and more HCl is unfavorable to form above bonds. To sum up, the results of FT-IR analysis probably demonstrate that new chemical species are formed which consist of iron, aluminum and silica, and the polymerization degree of the coagulant is affected by Al/Fe mole ratio and the type of leaching acid. Furthermore, the results of TEM, XRD and FTIR all suggest that the coagulant prepared from oil shale ash are not simple mixture of raw materials but inorganic polymer compound by iron, aluminum, silicon and other ions.

3.2. *Evaluation of coagulation efficiency*

3.2.1. *Coagulation efficiency*

The coagulation efficiencies of the coagulants by treating sewage on turbidity and COD were evaluated, and the results are given in Fig. 5. As revealed in Fig. 5, the coagulation efficiency is affected by the dosage (mg/L as Fe + Al + Si) and characteristic of the coagulants. Fig. 5(a) shows that the turbidity removal enhances with

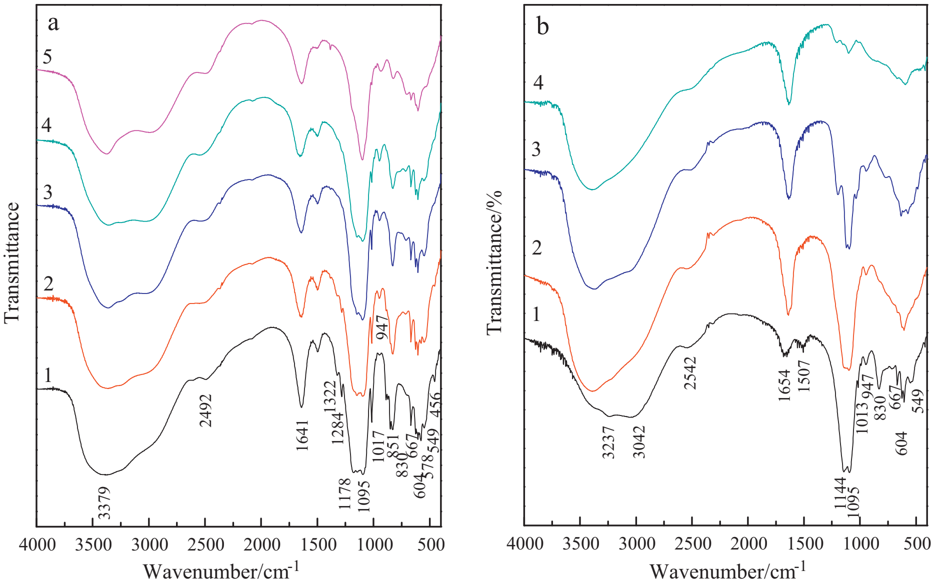


Fig. 4. FTIR spectra of the inorganic polymer coagulants. (a) The coagulants with different Al/Fe mole ratio: (1) Al/Fe mole ratio is 0.71; (2) Al/Fe mole ratio is 1.10; (3) Al/Fe mole ratio is 2.06; (4) Al/Fe mole ratio is 2.30; (5) Al/Fe mole ratio is 4.06. (b) The coagulants prepared with different lixiviant: (1) $2HCl/H_2SO_4$ mole ratio is 1:3; (2) $2HCl/H_2SO_4$ mole ratio is 1:1; (3) $2HCl/H_2SO_4$ mole ratio is 3:1; (4) HCl.

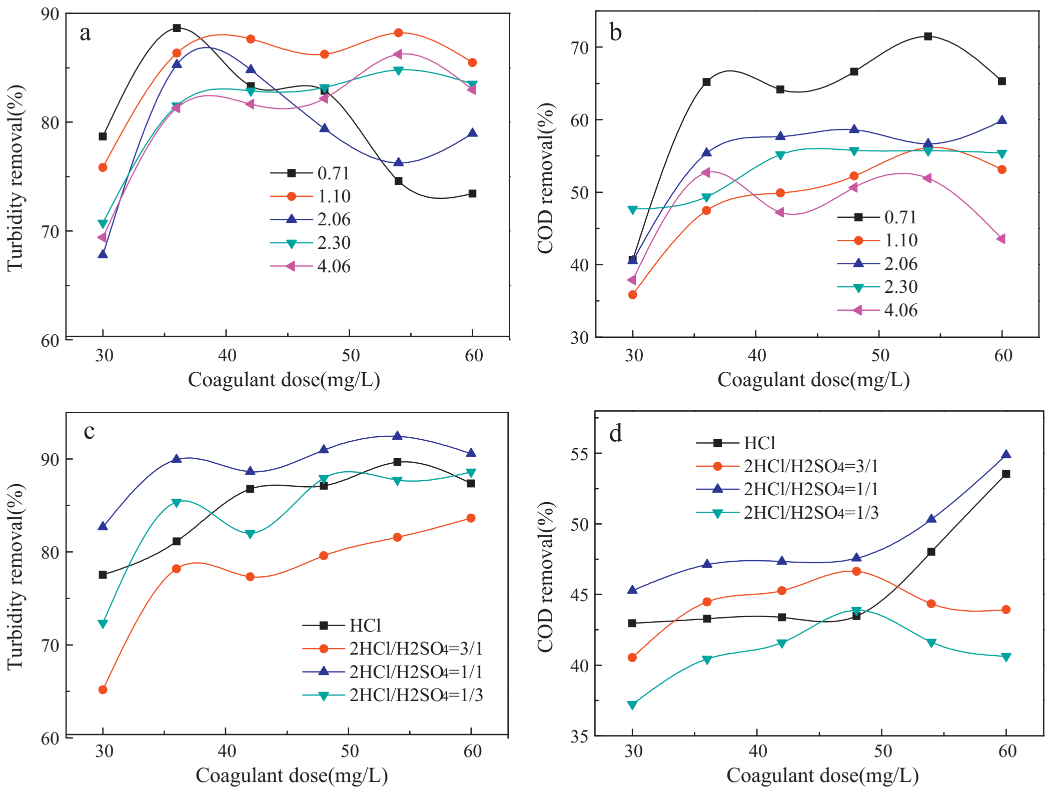


Fig. 5. Coagulation efficiency of the coagulants on turbidity and COD. (a) The turbidity removal by the coagulants with different Al/Fe mole ratio; (b) COD removal by the coagulants with different Al/Fe mole ratio; (c) the turbidity removal by the coagulants prepared with different lixiviant; (d) COD removal by the coagulants prepared with different lixiviant.

the coagulant dosage, and then it is in decline when the coagulant dosage is above the suitable, and moreover, the turbidity removal increases with Al/Fe mole ratio. It is mentionable that the turbidity removal by 0.71 Al/Fe mole ratio coagulant is the best in lower dosage, however, it decreases rapidly with the coagulant dosage increasing. Fig. 5(b) implies that COD removal by 0.71 Al/Fe mole ratio coagulant is the best. Fig. 5(c and d) illustrate that the coagulation performances of 1:1 2HCl/H_2SO_4 mole ratio coagulant is better than the others.

3.2.2. *Zeta potential of the sewage*

The zeta potential values of colloid microflocs are generally used to evaluate the destabilization ability of coagulant, so the variations of zeta potential values against coagulant dosage were shown in Fig. 6. It can be seen from Fig. 6(a) that the zeta potential decreases with the increase of Al/Fe mole ratio and Fig. 6(b) shows that the zeta potential raises sharply with the coagulant dosage increasing which is prepared with 1:1 2HCl/H_2SO_4 mole ratio as lixiviant. Figs. 5 and 6 illustrate that the variational degree of zeta potential is related to the coagulation performance of the samples, the zeta potential following the coagulant dosage increase faster, the coagulation performance of the sample is the better.

3.2.3. *Microscopic analysis of the flocks*

In order to observe the microstructure of the flocks in the coagulation process, the microphotographs of them are illustrated in Figs. 7 and 8. It can be seen that the flocks with 0.71 Al/Fe mole ratio coagulant is big and compact, and it is formed more quickly in coagulation experiment, however, the flocks become thin and incompact with Al/Fe mole ratio increasing, which the flocks is formed slowly during the tests. In contrast, although the flocks become thick and dense when Al/Fe mole ratio keeps increasing to 4.06, some flocks are found floating on the water surface during the coagulation process, which means the coagulation performance becomes poor.

The flocks with the coagulants are shown in Fig. 8, which were prepared using various lixiviant in the acid leaching process, it is shown that the flocks is incompact with 1:3 2HCl/H_2SO_4 mole ratio lixiviant, meanwhile, the 2HCl/H_2SO_4 mole ratio of the lixiviant increases to 1:1, the flocks become thick and compact, and the flocks are found forming quickly in the test, which means the settlement performance becomes better. However, 2HCl/H_2SO_4 mole ratio of the lixiviant keeps raising, the flocks get fluffier which were watched forming and settling slowly in the coagulation test.

3.3. *Discussion*

The coagulation of the pollutant by hydrolyzing metal salts is generally described as a combination of charge neutralization, entrapment, adsorption and complexation with coagulant metal hydrolysis species into insoluble particulate aggregates [31]. In this study, the results imply that when the zeta potentials of the sewage reach the isoelectric points the coagulation efficiency is not ideal and it is different with the conclusion of the previously published studies [31,32], therefore the charge neutralization ability is weak in coagulation process. On the contrary, the entrapment, adsorption and complexation ability play important roles in coagulation process. Fig. 5 shows that neither too little nor too much coagulant is unfavorable for coagulation efficiency, which could probably be explained that the coagulant metal hydrolysis species is not enough at little dosage. However, at large dosage, there are no unoccupied surface to bridge due to every colloidal particle adsorbing redundant the coagulant, and in this case, the entrapment, adsorption and complexation ability become weak and the coagulation efficiency is lower.

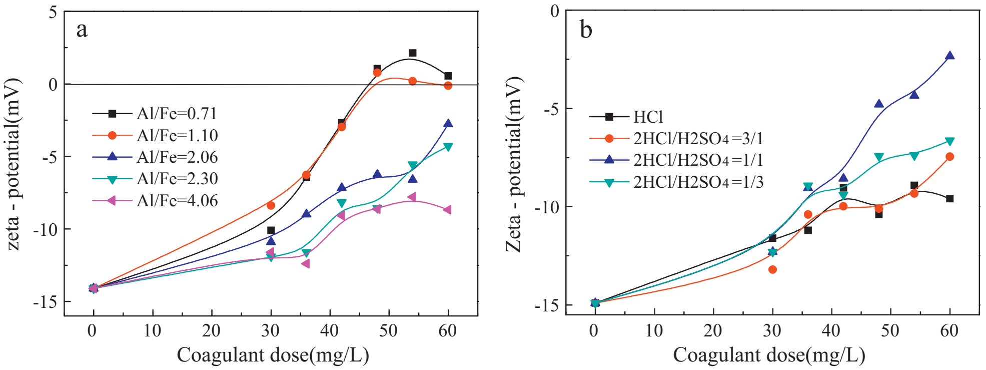
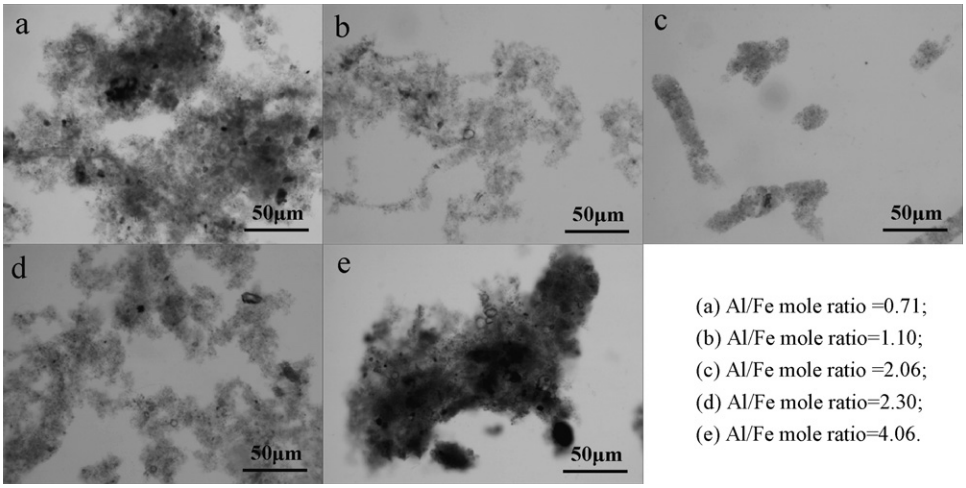


Fig. 6. Influence of coagulant dose on the zeta-potential of the sewage. (a) The coagulants with different Al/Fe mole ratio; (b) the coagulants prepared with different lixiviant.



(a) Al/Fe mole ratio =0.71;
(b) Al/Fe mole ratio=1.10;
(c) Al/Fe mole ratio =2.06;
(d) Al/Fe mole ratio=2.30;
(e) Al/Fe mole ratio=4.06.

Fig. 7. Microphotographs of the flocs formed by the coagulants with different Al/Fe mole ratio.

TEM results show that there are some imperfect chain-net with three dimensions appearing and an aggregation trend between the chain-net at 0.71Al/Fe mole ratio, and the structure of this sample is more compact than the others. XRD and FT-IR results illustrate that the coagulants are not simple mixture of raw materials but inorganic polymer compound by iron, aluminum, silicon and other ions, meanwhile, zeta potential results indicate that the charge neutralization ability is stronger at lower Al/Fe mole ratio. Furthermore,

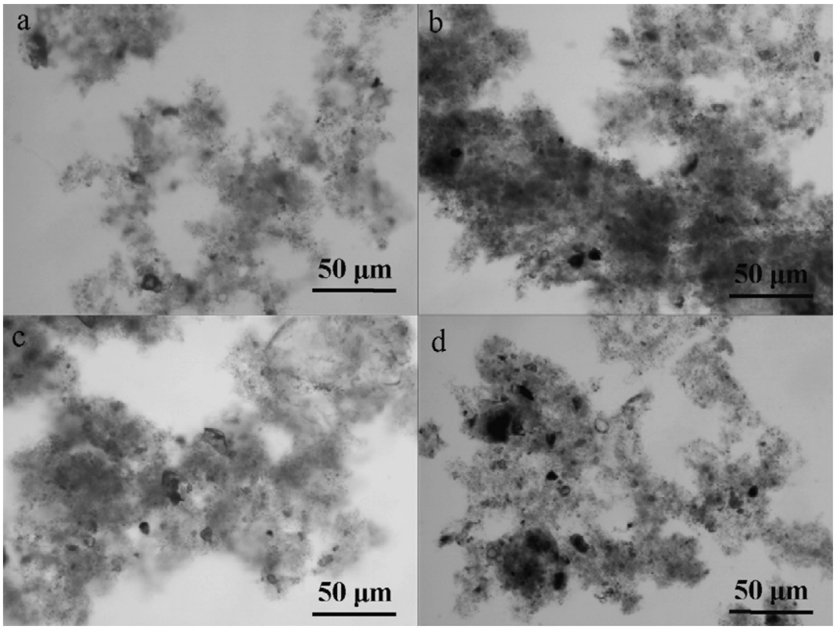


Fig. 8. Microphotographs of the flocs formed by the coagulants prepared with different lixiviant. (a) $2HCl/H_2SO_4 = 1:3$; (b) $2HCl/H_2SO_4 = 1:1$; (c) $2HCl/H_2SO_4 = 3:1$; (d) HCl.

the coagulation performance of 0.71 Al/Fe mole ratio sample is the best, which can be explained that the charge neutralization, entrapment, adsorption and complexation ability of it are stronger than that of the others. The coagulation experiment results indicate that the coagulation performance of the sample is better than that of the others, which was prepared by 1:1 $2HCl/H_2SO_4$ mole ratio as lixiviant, at the same time, TEM results illustrate that the structure of that is not the most perfect but the size of the chain-net structure group is opportune, and zeta potential results indicate that the charge neutralization ability is stronger than that of the others. As such, XRD and FT-IR results illustrate that the coagulants are inorganic polymer compound instead of a simple mixture of raw materials. For this reason, the suitable size polymer group and chain-net structure group cause the entrapment, adsorption and complexation ability of the samples to enhance, and charge neutralization ability is favorable for the coagulation efficiency, yet.

In addition, Fig. 5 shows that the coagulation efficiencies of various Al/Fe mole ratio coagulants are better than those prepared with different acid as lixivilant. It probably suggests that the Al/Fe mole ratio of the latter is not probable. Above results possibly imply that the suitable element mixture ratio and prepared method influence not only the structure of the inorganic polymer coagulant but also the coagulation efficiency of that.

4. Conclusions

The high-performance inorganic polymer coagulants were prepared from oil shale ash, and the main conclusions from this work were:

(1) The morphology of coagulants is affected by Al/Fe mole ratio and the type of lixiviant. The microstructure of PFASS is different with various Al/Fe mole ratios, and moreover, there are some imperfect chain-net structures with three dimensions appearing and an aggregation trend between the chain-net in 0.71 Al/Fe mole ratio coagulant, therefore, the structure of this sample is more compact than the others. In addition, the microstructure of PFASCS are porous aggregate structure, the net is small and only consists in agglomerated particles when the coagulant are prepared with 1:1 $2HCl/H_2SO_4$ mole ratios as lixiviant.

(2) The coagulants prepared using sulfuric acid as lixiviant contain $FeSO_4{\cdot}H_2O$, $NaAl(SO_4)_2{\cdot}(H_2O)_6$ and other crystals, and the amount of $FeSO_4{\cdot}H_2O$ in the samples decrease and the amount of $NaAl(SO_4)_2{\cdot}(H_2O)_6$ increase gradually with the increase of Al/Fe mole ratios. However, when the ratio of hydrochloric acid in the lixiviant increases, the type of crystals changes subsequently. Furthermore, the most of Fe^{3+} is not turned into the crystals, which means that the samples contain new chemical species rather than simple mixtures of the raw materials.

(3) FT-IR analysis probably demonstrate that new chemical species are formed which consist of iron, aluminum and silica, and the polymerization degree is affected by Al/Fe mole ratio and lixiviant. More aluminum are favorable to form Al–O–Si and Fe–O–Si, however, the formation of Si–O–Si is hardly related to Al/Fe mole ratio, also, a little iron leads to the peaks of Al–O and Fe–OH–Fe disappearing. More hydrochloric acid in the lixiviant leads to decreasing or disappearing of Al–O, Fe–O, Si–O, Al–OH, Fe–OH, Al–OH–Al, Fe–OH–Fe, Al–O–Al, Fe–O–Fe, Al–O–Si Fe–O–Si, etc.

(4) For the coagulation performance of the coagulants, the optimal Al/Fe mole ratio is 0.71 and the optimal $2HCl/H_2SO_4$ mole ratio as the lixiviant is 1:1.

(5) The microstructure of the flocks is related to Al/Fe mole ratio and the type of lixiviant acid, and moreover, the flocks is big and compact when Al/Fe mole ratio is 0.71 or $2HCl/H_2SO_4$ mole ratio of the lixiviant is 1:1, and it forms quickly in coagulation experiment.

(6) The analysis results imply that the charge neutralization ability is favorable for the coagulation efficiency, but it is weak in coagulation process. However, the entrapment, adsorption and complexation ability play important roles in the coagulation process, the suitable size polymer group and chain-net structure group make the entrapment, adsorption and complexation ability of the samples enhancing.

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