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Preparation and performance of fly ash-based coagulants in chemically enhanced primary treatment of domestic wastewater

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ABSTRACT

Fly ash was adopted to prepare a composite coagulant containing Al and Fe salts by acid leaching. The concentrations of Al and Fe salts in the coagulant and the conversion efficiencies of Al and Fe oxides in fly ash are strongly affected by L/S ratio (defined as the ratio of volume of acid solution to mass of fly ash, ml/g), reaction temperature, and H_2SO_4 concentration. At L/S ratio of 3 ml/g, H_2SO_4 concentration of 4 mol/L, the prepared fly ash-based coagulant after heating and cooling of 0.5 h achieves maximum concentrations of 0.137 mol/L Al^{3+} and 0.0464 mol/L $Fe^{3+} + Fe^{2+}$. At a dosage of 3.2 ml/L, coagulation of domestic wastewater results in removal efficiencies of 92% SS, 65% COD, and 98% PO_4^{3-}-P. The prepared coagulant proves to be an effective agent in terms of pollutant removal and exhibits comparable performance with conventional and polymer Al and Fe coagulants. This could be ascribed to charge neutralization by Al and Fe salts, and bridging effect with the aid of solubilized silicic acid and residual particles.

Keywords: Composite coagulant; Fly ash; Chemically enhanced primary treatment; Domestic wastewater

1. Introduction

Chemically enhanced primary treatment (CEPT) is a relatively simple and efficient process for water treatment [1,2] in removing disinfection byproduct precursors and inorganic, particulate, and color-causing compounds [3]; for example, suspended solid (SS) and total phosphorus (TP) removal efficiencies could reach up to 90 and 80–90%, respectively [4]. CEPT is also considered as a cost-effective method possessing advantages of low-energy requirement and easy operation and maintenance [5,6] when compared with the conventional primary sedimentation plus activated sludge process, of which the construction and operation costs save 45 to 42.9%, respectively [7]. Therefore, it is recommended to be adopted in rapidly growing megacities and developing countries [8,9]. However, this

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method unavoidably presents certain disadvantages in most cases such as the production of excessive sludge volumes and the cost of coagulants [10].

Coal is an important energy resource (accounted for around 25% of total global primary energy) [11]. Coal firing inevitably results in the generation of substantial amount of coal ash (fly and bottom ash accounted for 80–90 and 10–20% of the combustion residues, respectively). In the USA, about 131 million tons of fly ash are produced annually by 460 coal-fired power plants. At 2008, industry survey estimated that 43% was reused [12]. In China, coal combustion produced approximately 200 million tons of fly ash in 2009, of which only a part was utilized, the rest was disposed of by landfills [13]. Efficient fly ash disposal poses a worldwide issue as a result of its massive volume and deleterious effect on the environment [14].

Traditionally, fly ash is widely used in construction areas. Despite the positive uses, the production rate clearly far outweighs consumption [15]. To increase the recycling rate, fly ash is viewed as an untapped resource of marvelous potential. At present, researches on application focused on the modification of fly ash to improve the adsorption capacity [16,17]. These utilizations are confronted with problems including difficult separation of fly ash from treated water, adsorbent regeneration, and condensed structure (low pore volume) of prepared zeolites [18].

However, a survey [18] on the composition of fly ash from different countries indicates the abundance of Al and Fe oxides in fly ash, which are the two major ingredients for inorganic coagulant production. Moreover, the weight ratio of Fe to Al oxides in fly ash is appropriate for producing composite coagulants [19]. While fly ash is recognized to have such value-added potential, few studies [13,19,20] were carried out besides certain commercial exploitations, such as producing adsorbents, glass-like materials, mullite, and zeolites. A direct acid leaching process was revealed as an effective way to recover Al and Fe components [19] so as to produce polymeric coagulants through various complicated processes. Li et al. [21] prepared polymeric ferric sulfate (PFS) and polymeric aluminum sulfate coagulants from fly ash with concomitant flue gas scrubbing. Sun et al. [13] prepared poly-ferric-aluminum-silicate-sulfate coagulant by making full use of Al, Fe, and Si components in fly ash, which involved an additional alkali leaching process.

This study aimed at attaining high conversion efficiencies of Al and Fe components by optimizing acid leaching conditions to produce fly ash-based coagulant and applying the product in CEPT process, for the purpose of reducing the coagulant cost and integrating solid waste disposal into wastewater treatment by fly ash reutilization. However, no investigation has been reported on the roles of acid concentration and dosage during the process. In particular, the feasibility and mechanism of CEPT technology to treat domestic wastewater using produced fly ash-based coagulant were discussed.

2. Material and methods

2.1. Characterization of fly ash

Raw fly ash collected from Harbin Third Power Plant was used. The size distribution indicated that the particles were mostly in the range of 15–75 μm. The value of loss of ignition was very low (2.79 wt.%).

The major components in fly ash sample were determined by using a Axios pw4400 X-ray fluorescence spectrograph. Results are presented in Table 1. Raw fly ash was characterized by high contents of $Al_2O_3 + SiO_2$ (76 wt.%) and $Al_2O_3 + Fe_2O_3$ (24.2 wt.%), which can be classified as Class F as defined in ASTM C618. The elemental analysis shows a potential for mineral extraction.

2.2. Preparation of fly ash-based coagulant

The amorphous Si and Al components in fly ash resist to acid leaching under the prevailing conditions. To facilitate the reactions, 100 ml of H_2SO_4 with different concentrations (calculated as H^+ concentration, mol/L) was used to extract the metals at different L/S ratios (defined as the ratio of volume of acid solution to mass of fly ash, ml/g). Acid solution was added into and well mixed with fly ash at ambient or boiling temperature. The reactions were conducted for 0.5 h with refluxing. The slurry was then allowed to cool

Table 1
Chemical composition of fly ash[a]

Component	wt.%	Component	wt.%
Na_2O	0.154	Fe_2O_3	3.282
MgO	0.248	ZnO	0.035
Al_2O_3	20.932	Rb_2O	0.014
SiO_2	55.682	SrO	0.058
P_2O_5	0.237	Y_2O_3	0.006
SO_3	0.196	ZrO_2	0.058
K_2O	2.426	Nb_2O_5	0.009
CaO	3.671	BaO	0.062
TiO_2	0.729	PbO	0.015
MnO	0.076		

[a] Element concentrations of C, N, B, He, Li, and Be were not able to detect using XRF method.

for another 0.5 h to prepare the fly ash-based coagulant. The salts in the coagulant were determined. All studies were conducted in laboratory glassware.

2.3. Jar tests

Coagulation experiments were carried out by jar testing on a six-paddle gang stirrer (C6F, VELP® SCIENTIFICA). About 250 ml domestic wastewater was stirred at first to minimize the heterogeneity of water sample. Then, a required dosage of fly ash-based coagulant was injected into the test water, followed by a rapid stirring at 200 rpm for 5 min and a slow stirring at 60 rpm for 10 min. After the completion of coagulation, the water sample was allowed to settle for 30 min. Finally, supernatant was withdrawn for measurement. Jar tests were conducted at 18–21℃. For experiments on the effect of pH, the pH value of wastewater was adjusted with 2 mol/L H_2SO_4 and 2 mol/L NaOH.

2.4. Analytical methods

The concentrations of Fe^{3+} and Fe^{2+} in the coagulant were measured using the 1,10-Phenanthrolene colorimetric method [22]. The concentrations of Al^{3+} in the coagulant were measured using the EDTA titration method with NaF as the masking agent [23]. Determination of the sample was done in triplicate. Therefore, each reported result represented an average of three determinations.

Domestic wastewater was collected from urban drainage systems. The COD, SS, and PO_4^{3-}-P of the wastewater before and after treatment were measured using Chinese standard analysis methods [22]. The pH was monitored by a pHS-3C digital pH meter (Wei-ye, Shanghai).

The characterization of the wastewater is listed in Table 2.

3. Results and discussion

3.1. Factors affecting solubilization of Al and Fe contents of fly ash

At preliminary studies, orthogonal experiment (data not shown for brevity) was conducted at boiling temperature with H_2SO_4 leaching to determine the effects of various conditions of H^+ concentration (0.5, 1, and 4 mol/L), L/S ratio (1.5, 5, and 10 ml/g), leaching time (0.5, 1, and 2 h), and particle size (coarse and fine ashes) on the conversion efficiencies of Al and Fe contents. The results calculated through range analysis showed that the relative importance were H^+ concentration > L/S ratio > particle size of fly ash > leaching time for leaching behavior of Al component and H^+ concentration > L/S ratio > leaching time > particle size of fly ash for leaching behavior of Fe component. Both H^+ concentration and L/S ratio were identified as the key factors for the Al or Fe leaching behavior and therefore, examined carefully in our study.

Table 2
Characterization of domestic wastewater for experiments

Parameter	Value	Parameter	Value
COD (mg/L)	349–641	NH_4^+-N(mg/L)	30–59
SS (mg/L)	102–162	pH	7–8
PO_4^{3-}-P (mg/L)	3.12–3.59	*T* (℃)	9–19

3.1.1. Effect of L/S ratio

The study was at first conducted at ambient temperature and at 100 ml of H_2SO_4 (2 mol/L H^+ concentration) with various amounts of fly ash. The concentrations of $Fe^{3+} + Fe^{2+}$ and Al^{3+} in the prepared coagulant and corresponding conversion efficiencies are indicated in Fig. 1. The conversion efficiency is defined as the ratio of the mass of $Fe^{3+} + Fe^{2+}$ or Al^{3+} in the product to the mass of Fe or Al in fly ash [21].

In Fig. 1, the concentrations of $Fe^{3+} + Fe^{2+}$ and Al^{3+} in the product decrease sharply with an increase in L/S ratio. However, the conversion efficiencies of metal contents slightly change with L/S ratio. Since the addition of fly ash increased as a result of decreasing L/S ratio, more interface was created for the interactions between particles and acid solution, resulting in an increase in the $Fe^{3+} + Fe^{2+}$ and Al^{3+} concentration. Regarding the conversion efficiency, it was influenced

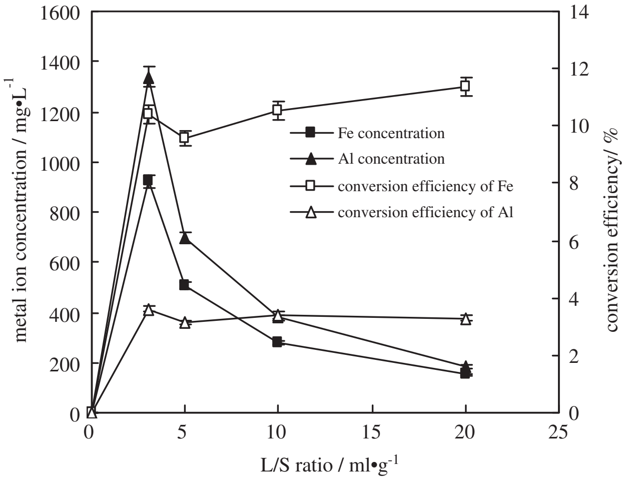

Fig. 1. Effect of L/S ratio on conversion efficiencies of Fe and Al at ambient temperature.

by dissolved metal ions and fly ash dosage. Generally, fly ash was easily available at low price, and a full utilization of sulfuric acid should be taken for granted. Therefore, a low L/S ratio was preferred. In our study, a too much lower L/S ratio led to thickened slurry which was difficult to mix and separate from the liquid. So in the further study, L/S ratio was chosen as 3 ml/g.

As for the Al content, the conversion efficiency was not above 4% at various L/S ratios. This result was possibly due to the mineral phase of fly ash. The overall low conversion efficiencies of Fe and Al at ambient temperature required a higher reaction temperature as satisfied in the following study.

3.1.2. Effects of H_2SO_4 concentration and reaction temperature

At L/S ratio of 3 ml/g, various H_2SO_4 concentrations were investigated at boiling and ambient temperatures.

In Fig. 2, a positive linear relationship is observed between the metal ion concentrations and H_2SO_4 concentration when H_2SO_4 concentration is below 2 mol/L. Then, the increase in $Fe^{3+} + Fe^{2+}$ and Al^{3+} concentrations gradually reached the plateau. At 4 mol/L of H_2SO_4 concentration, the concentrations of $Fe^{3+} + Fe^{2+}$ and Al^{3+} in the coagulant reached 2,588–3,779 mg/L, respectively, which was increased by a factor of 2.8 and 2.5 compared with the concentrations obtained at ambient temperature (Fig. 3). The effect of temperature on conversion efficiencies of Fe and Al was remarkable. Increments in conversion efficiencies by 21.91–6.18% for Fe and Al (Figs. 2 and 3) at higher temperature demonstrate that the leaching reactions favor relatively high temperature. This result is consistent with other research [20]. It is obvious that the dissolution of Fe and Al oxides with sulfuric acid are endothermic reactions [19]. And the result is in agreement with reaction rate theory, which holds that the rate of a chemical reaction increases with reaction temperature [19].

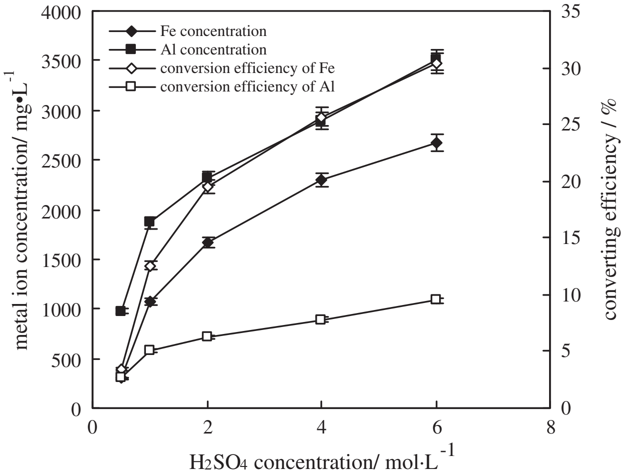

Fig. 2. Effect of H_2SO_4 concentration on conversion efficiencies of Fe and Al at boiling temperature.

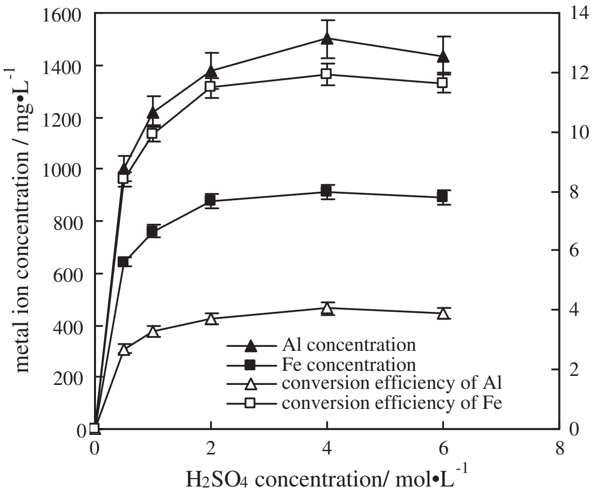

Fig. 3. Effect of H_2SO_4 concentration on conversion efficiencies of Fe and Al at ambient temperature.

Thermodynamical comparison of standard-state Gibbs function changes between reaction of Fe_2O_3 and H_2SO_4 and reaction of Al_2O_3 and H_2SO_4 indicates that Fe_2O_3 is more readily to solubilize into sulfate by acid solution. At ambient temperature, conversion efficiency of Fe shows very little response to acid concentration indicating the easy solubilization of Fe content in fly ash. A higher conversion efficiency of Fe is, therefore, observed. In order to improve the conversion efficiency of Al, an elevated reaction temperature was demanded. Al oxides in fly ash appear more vulnerable to temperature than Fe oxides in the acid leaching process, as can be seen in Figs. 2 and 3. In the further study, boiling temperature was adopted to facilitate the leaching process.

According to the chemical composition of tested fly ash (Table 1), based on the stoichiometric amounts of metal oxides and sulfuric acid, the calculated H_2SO_4 concentration should exceed 1.7 mol/L. This means, a low acid concentration (such as 0.5 and 1 mol/L) is insufficient to react, while a high concentration (such as 6 mol/L) definitely led to an excess volume of acid solution. So, 4 mol/L is recognized as an appropriate acid concentration in this study.

On the result of above experiments, we conclude the conditions for producing fly ash-based coagulant as follows: L/S ratio of 3 ml/g, H_2SO_4 concentration of 4 mol/L, heating for 0.5 h with refluxing, and cooling for 0.5 h. The prepared coagulant is gray slurry with density of 1.22–1.24 g/ml approximately. It contains $Fe^{3+} + Fe^{2+}$ of 2.6 g/L and Al^{3+} of 3.7 g/L, which correspond to $Al_2(SO_4)_3$ of 19.3 g/L and $Fe_2(SO_4)_3$ of 7.5 g/L, respectively.

3.2. Coagulation performance of fly ash-based coagulant

The produced coagulant was tested for performance at various pH and coagulant dosages.

3.2.1. Effect of pH

The impact of coagulation pH on the pollutant removal has been examined and the results are presented in Fig. 4. The ranges of pH investigated were from pH 2.75 to 11.77 with coagulant dosage of 20 ml/L (3.7×10^{-3} mol/L as Al + Fe).

In the pH range of 5–9, which represents slight acidic to slight alkaline conditions, the removal rates are generally satisfactory in terms of SS and orthophosphate (PO_4^{3-}-P) removal; while COD removal is lower and deficient at operating pH values, due to the large part of soluble COD in the total COD which was unable to eliminate by coagulation process.

The SS and PO_4^{3-}-P removals are strongly affected by the pH changes of the suspension. At low influent pH side, adding acidic coagulant decreases pH values to 2.75–4.53. A notable enhancement of PO_4^{3-}-P removal occurs when coagulation pH rises from 2.75 to 4.53. When the coagulant is used at pH 5.36, effluent SS and PO_4^{3-}-P are 8 and 0.005 mg/L, respectively. At higher pH (>9), the SS and PO_4^{3-}-P removal efficiencies decrease with increasing pH. However, the difference in COD removal efficiency at various pH values is unremarkable, probably due to the high dosage.

3.2.2. Effect of dosage

Experiments were conducted using dosages of 0.4–20 ml/L for a wastewater of COD 424 mg/L, SS 175 mg/L, and PO_4^{3-}-P 3.12 mg/L at coagulation pH of 7–8.

As shown in Fig. 5, the removal efficiencies of COD, SS, and PO_4^{3-}-P increase with an increase in dosage. With dosage higher than 3.2 ml/L, the removal efficiencies reach plateau values, and the enhancement by dosage increment is negligible. Meanwhile, effluent COD, SS, and PO_4^{3-}-P are 147–126 mg/L, <14, and <0.045 mg/L, respectively, within removal efficiencies reaching at least 65, 92, and 98%, respectively. The effluent concentrations of SS and TP meet the Class IB criteria of the Discharge Standard of Pollutants for Municipal Wastewater Treatment Plant (GB18918-2002) in China, whereas it has been exceeded for COD concentration. This requires further biological treatment for COD reduction.

From an economic point of view, 3.2 ml/L is identified as an optimum dosage when treating domestic wastewater. At this dosage, corresponding to 62 mg $Al_2(SO_4)_3$, 24 mg $Fe_2(SO_4)_3$ with 4.82 g fly ash residual are applied together to treat 1 L wastewater.

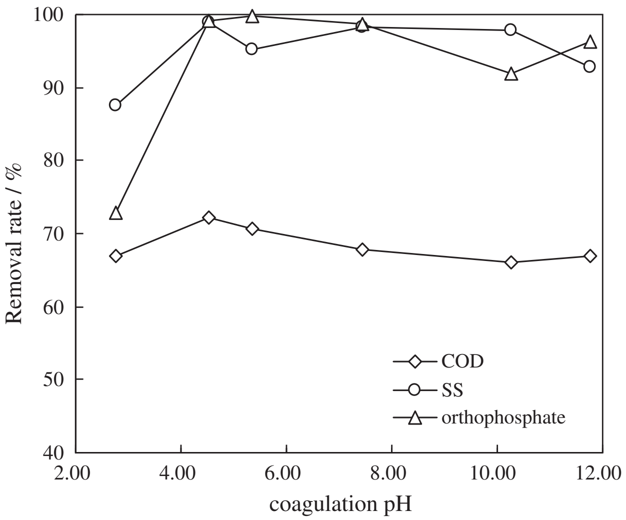

Fig. 4. Effect of coagulation pH vs. removal rate.

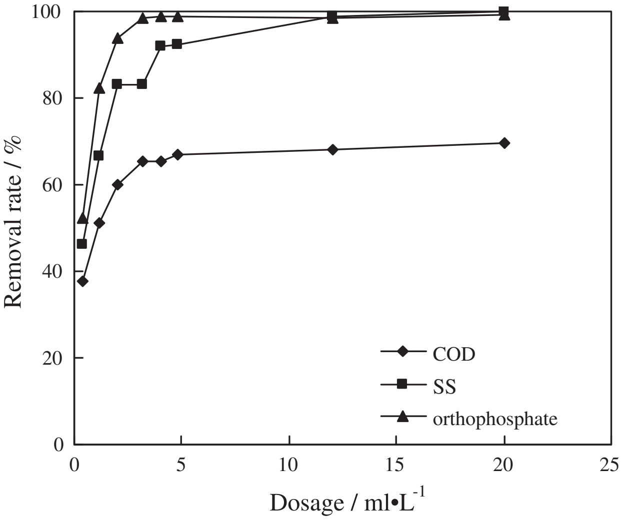

Fig. 5. Effect of dosage vs. removal rate.

3.2.3. Comparison of treatment performance with other coagulants

Coagulation experiments were also conducted to assess the produced coagulant in comparison with other commercial types (i.e. $Al_2(SO_4)_3$, $Fe_2(SO_4)_3$, polyaluminum chloride, and PFS) regarding the pollutant removal. The coagulant dosage was 4 ml/L, corresponding to 7.3×10^{-4} mol/L as Al + Fe concentration for fly ash-based coagulant; for commercial coagulants, the same dosage of 7.3×10^{-4} mol/L was applied as Al + Fe or Al/Fe alone concentration.

As shown in Fig. 6, the results from fly ash-based coagulant become comparable with those from commercial types. Apparently, the cost of solid waste is far less than that of natural ores considering the raw material for preparation; moreover, a direct acid leaching process can be applied readily to practice. Thus, optimizing the beneficial use of fly ash for Al and Fe elements recovery could reduce the cost of coagulant while improving its overall performance.

The pollutant removal in the study resulted from the solubilizing and hydrolyzing of various metal salts associated with fly ash, including Fe^{3+}, Al^{3+}, Ca^{2+}, Fe^{2+}, and Mg^{2+}; the adsorption capacity of chemically treated fly ash and the rapidly developed large flocs with the involvement of ash residual and H_2SiO_3. The satisfactory performance of product demonstrates the process of CEPT as an efficient domestic wastewater treatment method to remove most SS, PO_4^{3-}-P, and partial COD to reduce the influent loading of subsequent biological treatment.

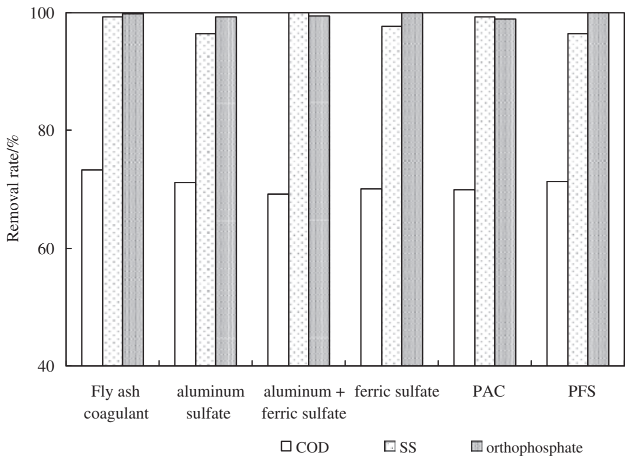

Fig. 6. Treatment performance of fly ash-based coagulant compared with other coagulants.

3.3. Mechanism of coagulation performance with fly ash-based coagulants

The prepared coagulant contains Al and Fe salts and other inorganic solutes in the liquid and residual particles. The performance is, therefore, derived from the integration of different behaviors of above-mentioned contents in coagulation.

3.3.1. Hydrolyzing metal salts as coagulants

For hydrolyzing coagulants, such as alum or ferric, organic matter is removed through mechanisms of charge neutralization, entrapment, adsorption, and complexation with metal hydrolysis species into insoluble particulate aggregates [24]. The coagulation performance is dependent on concentration and species distribution of Fe^{3+}/Fe^{2+} and Al^{3+}. Unlike inorganic polymer coagulant, the highly acidic coagulant of pH <1 led to the only existence of monomeric ions of Fe and Al. In this case, charge neutralization through compressing electrical double layer turned out to be the dominant mechanism. Since zeta potential is widely used for quantification of the magnitude of the electrical charge at the double layer, its value was determined within domestic wastewater before and after adding fly ash-based coagulant produced at ambient temperature (Zetasizer Nano Z, Malvern). The result is shown in Fig. 7.

The zeta potential of raw wastewater was around −18 mV, indicating an incipient instability of the colloid. Then, its value increased with an increase in dosage as a function of neutralizing the electrical charge of the interacting particles, which led to further destabilization of colloidal particles to aggregation. Removal rates of COD and SS were correspondingly raised (Fig. 5). At dosage of 60 ml/L, a maximum value of −6.15 mV was attained which implied an optimum dosage for fly ash-based coagulant. The greater dosage here (60 ml/L) is owing to the lower concentrations of metal ions solubilized at ambient temperature. It is obvious that the concentrations of Al and Fe ions solubilized at reflux boiling temperature were much greater, and therefore, a smaller dosage (3.2 ml/L) was demanded. When dosage was above 60 ml/L, zeta potential gradually decreased with decrement of pollutant removal rates. Consequently, effluent concentrations were strongly related to the zeta potential during coagulation.

Normally, the slope of zeta potential curve is important in evaluating the charge neutralization capacity of an inorganic coagulant. As seen in Fig. 7, the slope showed a trend of initially increasing and then decreasing, indicating that at neutral pH, lower

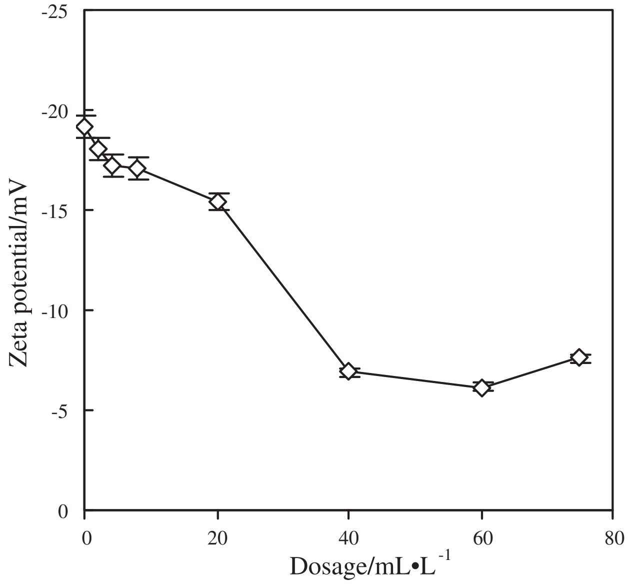

Fig. 7. Effect of dosage on zeta potential.

dosage exhibited a stronger capacity of charge neutralization than higher dosage did. Noteworthily, when added thoroughly washed and dried fly ash particles with and without acid leaching to distilled water, zeta potential of the slurry also decreased from −9.59 to −29.77 mV, which proved the solubilization of metal oxides.

3.3.2. *Activated silica functions as coagulant aid*

The silicic acid solubilized from fly ash was activated at strong acid condition and used as a flocculent to promote the formation and strengthening of flocs. During the polymerization of silicic acid (H_4SiO_4), the presence of Al and Fe cations may interact with silica as already indicated by Farmer and Fraser [25]. Duan and Gregory [26] found increasing concentrations of dissolved silica required to prevent coagulation of kaolin suspensions by alum with decreasing pH values. Further researches on interactions among dissolved silica, aluminum, and ferric species are in progress. The concentrations of SiO_2 solubilized at various H_2SO_4 concentrations at L/S of 3 ml/g at reflux boiling temperature were determined (seen Fig. 8).

The dissolved SiO_2 decreased with an increase in H_2SO_4 concentration and afterward reached a constant level when H_2SO_4 concentration was greater than 4 mol/L. Flocculation can be carried out by bridging the colloidal particles with activated silica to form large, rapid-settling, dense flocs [27]. The activated

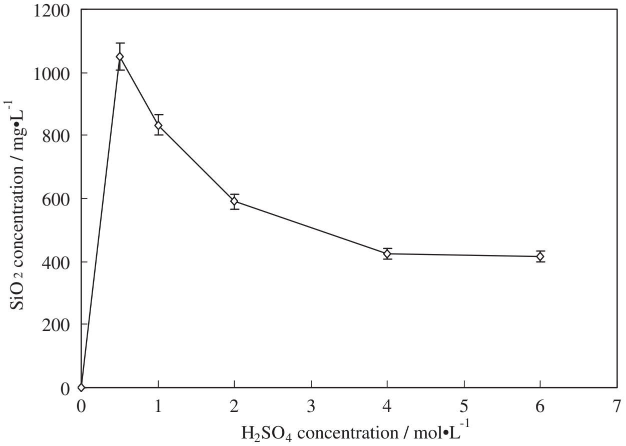

Fig. 8. SiO_2 concentration at various H_2SO_4 concentrations.

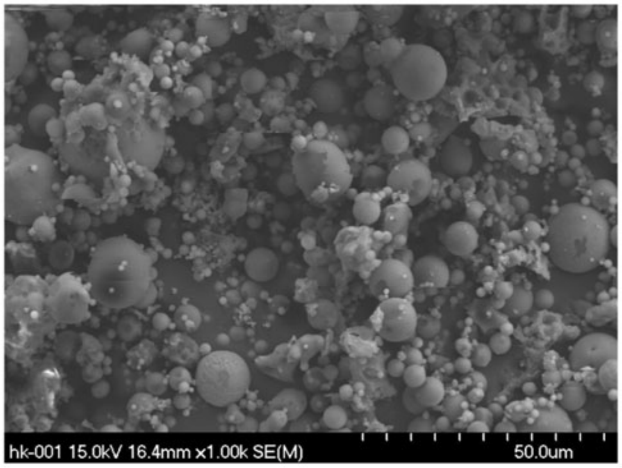

Fig. 9. SEM microphotographs of fly ash.

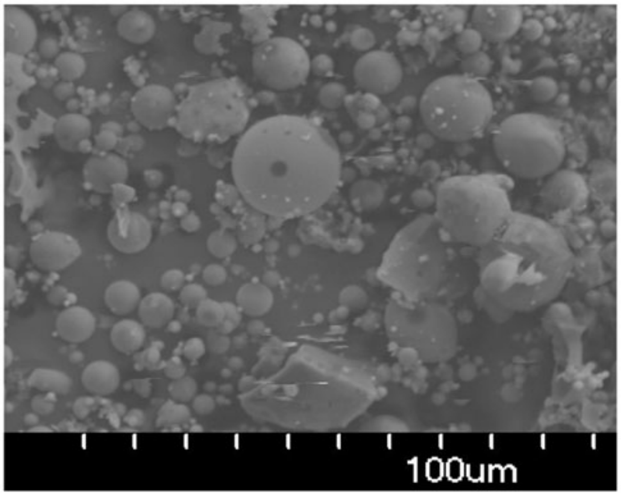

Fig. 10. SEM microphotographs of acid-leached fly ash.

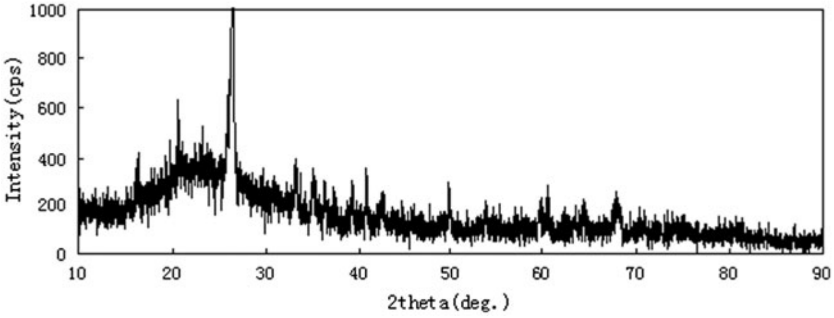

Fig. 11. XRD pattern of fly ash.

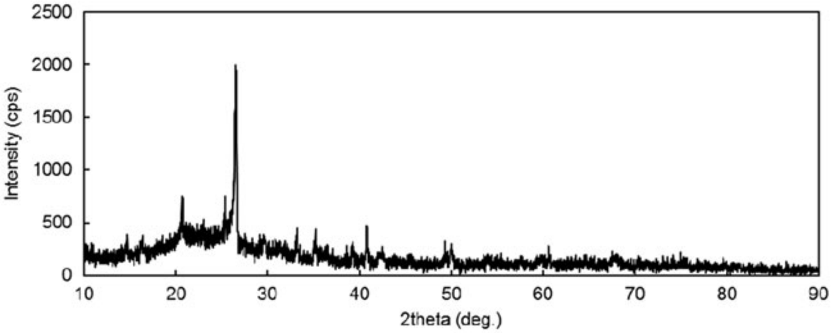

Fig. 12. XRD pattern of acid-leached fly ash.

silica serves to link the small flocs into substantially larger units and increases the rate of coagulation.

3.3.3. *Adsorption of fly ash residuals*

Fly ash has a hydrophilic surface [15] and is extremely porous as indicated by scanning electron microscope (SEM) photographs (Fig. 9). The specific surface area became larger as a result of leaching reaction with more micropores observed in SEM photos (Fig. 10). Adsorption is closely related to specific surface area and occurs during the coagulation to improve the performance. Furthermore, fly ash particles aided in forming and strengthening the flocs. In our study, it has been observed that flocs formed within fly ash residuals are larger and precipitate rapidly in 10 min in comparison with other commercial coagulants. More detailed studies on acid-altered surface of ash particles as adsorbents are undergoing.

Figs. 11 and 12 illustrate the XRD of raw material and fly ash specimens after acid leaching. The main crystalline phases of raw fly ash were quartz, mullite, and hematite. The diffraction peak profiles in the range of 22–35 ($2\theta_{\max}\mathrm{CuK}_{\alpha}$) suggested glass phases presented in raw material (Fig. 11). In Fig. 12, acid-leached fly ash showed peaks for quartz, indicating incomplete leaching reaction for various aluminosilicate phases which may need more rigorous treatment to be totally dissolved [28]. Comparing the X-ray diffractographs of unleached (Fig. 1) and leached residual fly ash (Fig. 12), the insoluble residue becomes the dominant phases consisting of mullite, while a portion of metal oxides in the mineral and glass phases have been solubilized [29].

4. Conclusions

Fly ash from coal-fired power plant was successfully explored for producing a composite coagulant containing metal salts by acid leaching. Factors that affected the conversion efficiencies of Fe and Al oxides in fly ash were discussed. Results show that the concentrations of $Fe^{3+} + Fe^{2+}$ and Al^{3+} in the coagulant increase with L/S ratio, reaction temperature, and H_2SO_4 concentration. At L/S ratio of 3 ml/g, H_2SO_4 concentration of 4 mol/L, heating of 0.5 h and cooling of 0.5 h, the prepared fly ash-based coagulant exhibits the following properties: Al^{3+} concentrations of 0.137 mol/L and $Fe^{3+} + Fe^{2+}$ concentrations of 0.0464 mol/L; 1 ml such coagulant contains 0.83 ml solution and 0.17 ml fly ash residual. Experiments on CEPT of domestic wastewater applying such coagulant, which favors at coagulation pH of 5–9 and optimum dosage of 3.2 ml/L, show high removal efficiencies of COD, SS, and PO_4^{3-}-P.

The satisfactory performance of fly ash-based coagulant is attributed to the following steps. Firstly, the stable colloidal particles were destabilized by charge neutralization of Al and Fe salts, and then these smaller destabilized particles agglomerated to larger and compact aggregates by bridging with the aid of solubilized silicic acid and residual particles.

Acknowledgments

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