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Preparation and Performance of Inorganic Coagulant for Landfill Leachate Pretreatment

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Landfill leachates are often defined as hazardous and heavy polluted wastewaters. It may contain large amount of organic matter, ammonia-nitrogen, heavy metals, chlorinated organics and inorganic salts (Wang et al. 2002). Proper treatment of leachate has therefore been a challenging problem confronting the local authorities. Anaerobic digestion or/and aerobic activated sludge methods are the most popular treatments for leachate in the past years because of simple technology and economical reasons (Lema et al. 1988). But for complex composition and toxicity of leachate, these methods along were known to be inadequate in handing such a difficult treatment task. Therefore, a combination of physical-chemical (pretreatment process) and biological methods is often required for the efficient treatment of this heavily polluted wastewater (Rautenbach and Mellis, 1994; Lin and Chang, 2000). Coagulation is often the most popular alternative method as pretreatment process (Tatsi et al. 2003; Uygur and Kargi, 2004). The principal benefits of this approach are simplicity of operation, low capital and operating costs. Coagulation is also a necessary pretreatment of membrane process for leachate disposal (Trebouet ea al. 2001; Amokrane et al. 1997). Several studies have been reported on the examination of coagulation for the treatment of leachates, aiming at performance optimization (Tatsi et al. 2003; Amokrane et al., 1997), however, limited information is available in literature about the development of new coagulation and its behaviour.

Traditional coagulants such as aluminum，iron salts，and its polymer flocculants are widely used for water and wastewater treatment. Coagulant based on aluminium can form large but weak and light flocs, so that breakage of flocs occurs readily, while flocs of coagulant based on iron are small, but compact and settleable (Liu et al. 1995). Coagulant with complex composition may have advantages of both, and has been the subject of much research in recent years(Liu et al. 1995; Jiang and Graham, 2003). Magnesium salts were found to be effective to treat wastewater as well (Boon et al. 2000; Ozkan and Yekeler, 2004). The purposes of this study were to develop, based on $FeSO_4 \cdot 7H_2O$、$MgSO_4 \cdot 7H_2O$ and $Al_2(SO_4)_3 \cdot 18H_2O$, a new structure of inorganic polymer coagulant for leachate treatment. The composition of the coagulant was analyzed, and optimum experimental conditions for leachate treatment with this coagulant were determined as well.

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MATERIALS AND METHODS

Leachate for test in this paper was sampled from a sanitary landfill site of Beijing(capital of P. R. China), which has been operated since 1994. The landfill site is located northeast of Beijing, and covers a surface of 60 ha. It receives 1700 tons of domestic solid waste per day, about 1000 $m^3 d^{-1}$ leachate is produced. The leachate is collected through a drainage network. At the lowest point of landfill, leachate exits to the surface, forming an artificial pond. Samples was collected from the artificial pond, and stored at 4 ℃. Characteristics of the sampled leachate are presented in Table 1.

Table 1. Average physical-chemical leachate parameters.

Parameters	COD(mg L^{-1})	BOD(mg L^{-1})	SS(mg L^{-1})	NH_3-N(mg L^{-1})	pH
Values	233380	12408	240	813	7.6

Preparation of coagulant was undertaken on a laboratory scale. $FeSO_4 \cdot 7H_2O$, $MgSO_4 \cdot 7H_2O$ and $Al_2(SO_4)_3 \cdot 18H_2O$ were dissolved in a predetermined water, preparing a stock solution. Certain amount H_2SO_4 was added to the stock solution when the solution was stirring and heated on a hot plate stirrer (SW-600H, Japan) at 80 ℃. H_2O_2 was thereafter titrated into the stock solution slowly until all Fe(II) turn into Fe(III). A brown liquid (coagulant named PFMAS) was obtained after keeping the solution under ambient temperature 30min for reaction. Solid PFMAS was obtained after the brown liquid was dried. Series of coagulants were prepared when the molar ratio of n(Fe):n(Al) :n(Mg) in PFMAS was changed. All the reagents used in this study were of analytical reagent grade except those being pointed out. The following coagulants were tested here: PFMAS, PFS (polyferric sulfate) and PAS (polyaluminium sulfate). Concentrated stock solutions of these coagulants were prepared by dissolving PFMAS (dried), PFS (commercial grade) and PAS (commercial grade) in deionized water at a concentration of 10% (by weight), respectively.

Coagulation and precipitation studies were performed in a conventional jar-test apparatus, using a six paddle stirrer (JMD-6, Japan). The samples volume were 400 mL respectively, agitation rate was 220 rpm for one minute, followed by a rate of 48 rpm for 20 minutes. A settling period of 30 minutes for all coagulation was adopted, and samples of the supernatants were collected for parameter analysis. A series of experiments were performed varying the kind of coagulant, dosage of coagulant and pH of leachate. The pH was adjusted by adding HCl (1N) or $Ca(OH)_2$ (1N) to the samples before rapid mixing stage.

Samples of water were collected at the same depth (5 cm below the surface of the supernatant). pH of leachate was measured with a pH meter (Benchtop, U.S.A.). COD was determined with a quick COD meter (Lovibond-ET99732, German), and an infrared spectroscope (Nicolet 5PC, U.S.A.) was used for chemical structure analysis of the coagulant.

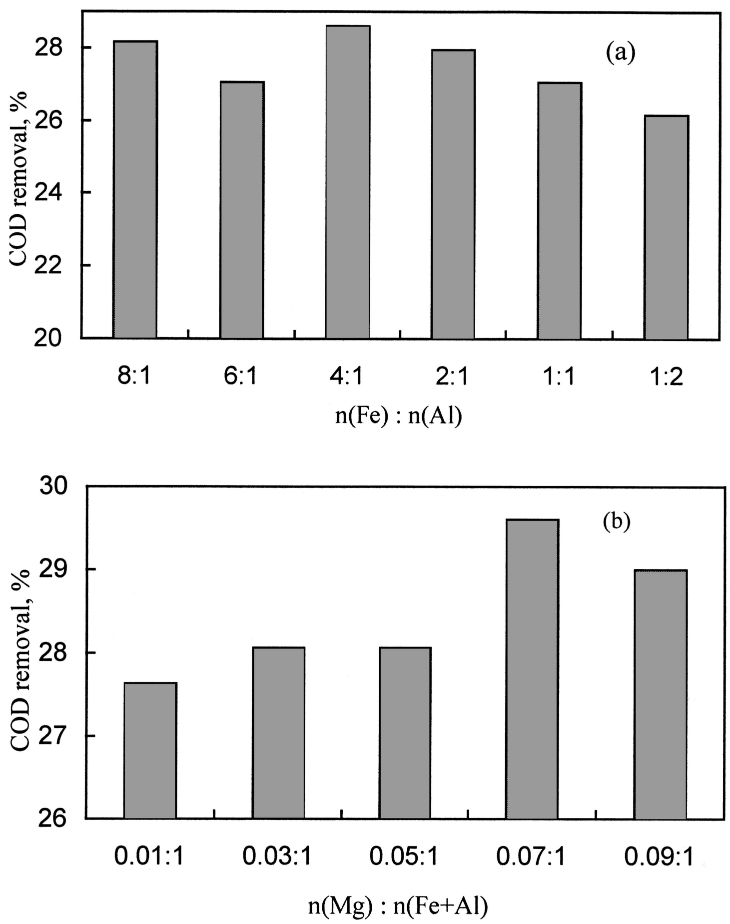

Figure 1. COD removal by PFMAS with different composition.

RESULTS AND DISCUSSION

A series of coagulants was prepared with n(Fe):n(Al) ratio decreasing in coagulants. Their efficiencies for treating leachate are presented in Figure 1(a). It can be seen form Figure 1(a) that most COD can be removed by the coagulant with n(Fe):n(Al) ratio 4:1. Furthermore, coagulants based on more Fe may result in flocs precipitation more rapidly and less volume of flocs within the same time of precipitation. These results agree with works of Diamadopoulos (1994), who demonstrated that iron salts were proved to be more efficient than aluminum ones in terms of COD removal from leachate.

Proper ratio of Fe(III):Al(III) may achieve best result, which indicates that coagulant based on Fe(III) or Al(III) along may not be the optimum coagulant for leachate treatment, and a coagulant with complex composition will be potentially

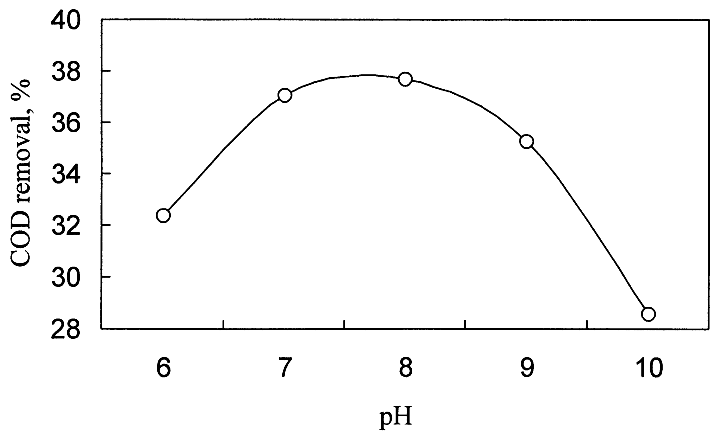

Figure 2. COD removal by PFMAS under different pHs.

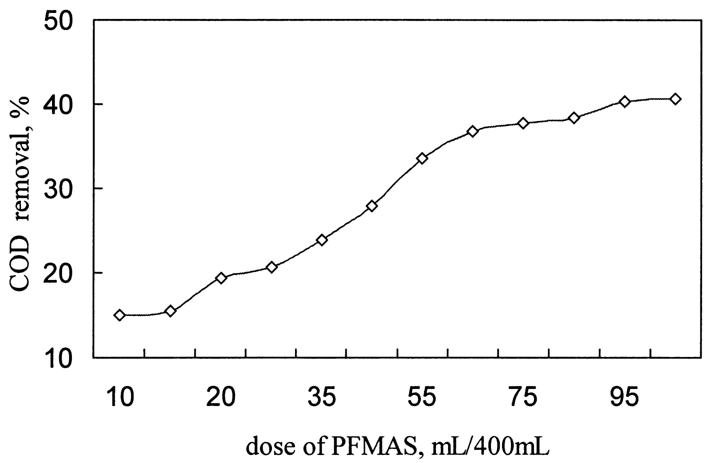

Figure 3. COD removal under different coagulant dosages.

better effective. Since the charge of Fe(III) is the same as Al(III), the mechanism of COD removal with PFMAS must not be charge neutralization only, there maybe some reactions taken place between Fe(III) and the organic matters in leachate.

A series of coagulants was prepared with different n(Mg):n(Fe+Al) after n(Fe):n(Al) was determined. Effects of them for treating leachate are presented in Figure 1(b). Most COD can be removed from leachate by the coagulant with n(Mg):n(Fe+Al) ratio 0.07:1 (Fig. 1b), which indicates that n(Fe):n(Al):n(Mg) 4:1:0.07 was the optimum composition for PFMAS compound in this paper.

To study the possible effect of initial pH of leachate, a series of experiments was

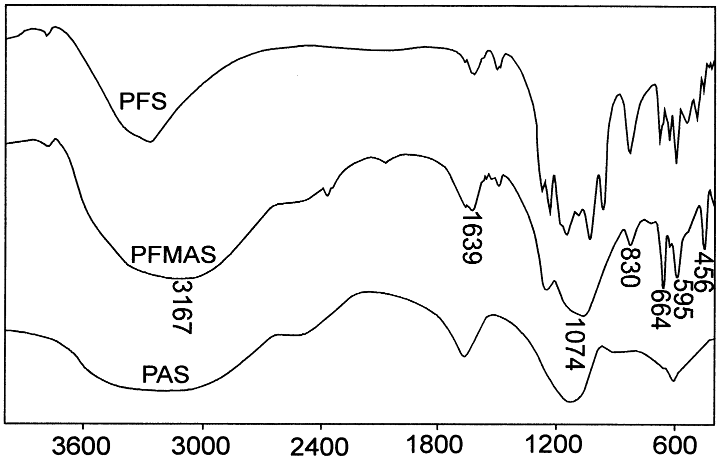

Figure 4. Infrared spectral analysis of polyferric sulfate (PFS), polyaluminium sulfate (PAS) and PFMAS.

performed with PFMAS of the optimal composition. The pH values were between 6-10, and the results obtained on effectiveness in terms of COD removal are presented in Figure 2. It can be seen clearly from Figure 2 that COD removal from leachate with PFMAS were low in both low pH and high pH. The highest COD removal rate took place at pH value around 8.0. The colour of flocs was changed with the pH value of leachate. Floc turned from dark brown to yellow, then, clear yellow, when pH value increased from 6.0 to 8.0. Flocs turned from clear yellow to brown, then olive-drab when pH value continued to increase from 8.0 to 10.0, indicating $Fe(OH)_3$ beginning to form at this period.

Flocs were found to be difficult to settle when pH value was bigger than 8.0. The initial pH of raw leachate was 7.6, just locating within the optimal pH range for PFMAS operation. Therefore, the raw leachate can be treated with PFMAS without pH control. The optimum performance pH of PFMAS was 8.0 implies that the COD removal with PFMAS does not depend on the formation of $Fe(OH)_3$. Hydrolytic reactions of PFMAS should play an important role during coagulation according to Duan's et al. (2003).

Varying amount of PFMAS was used to treat leachate under the optimum pH range, the results are presented in Figure 3. It can be observed that when coagulant dosage increases, more COD is removed from leachte. However, COD removal rate increases quickly from coagulant dosage 10mL/400mL to 65mL/400mL leachate, but declines when the dosage was more than 65mL/400mL leachate. With coagulant dosage increasing, the dark brown colour of raw leachate turned to clear brown above sludge, then to yellow and clear yellow. For economic reasons, 65mL/400mL should be the most proper dosage for leachate treatment with PFMAS.

Results of infrared spectral analysis with PFS, PAS and PFMAS are presented in

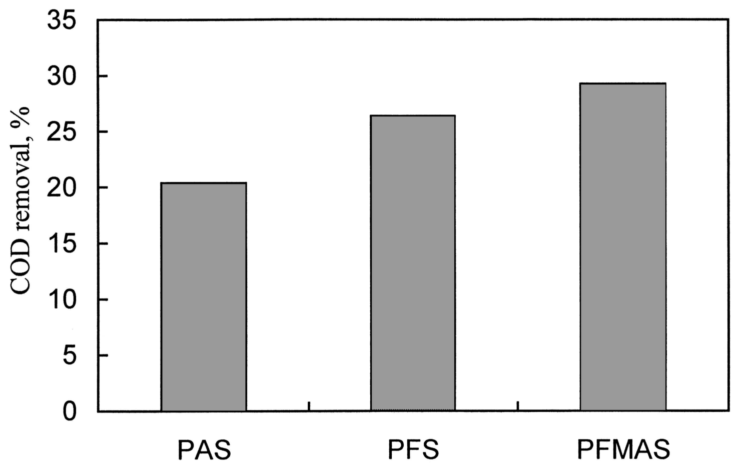

Figure 5. COD removal with different kinds of coagulants.

Figure 4. The three coagulants have the similar trend of spectrogram, all of them have adsorption peaks of hydroxyl at 3000-3700 cm^{-1}, 1620-1660 cm^{-1} and 1040-1130 cm^{-1} (Fig. 4). This may imply that PFMAS has the similar constitution with PFS and PAS. Compare with PAS, PFMAS has additional adsorption peaks at 830cm^{-1}, 664 cm^{-1} and 456cm^{-1}. This may result from the dissymmetric adsorption of atom O in OH^- by Fe(III), Al(III) and Mg(II), indicating Fe(III), Al(III) and Mg(II) may be connected by hydroxyl bond, and eventually attains long-range crystalline order, which suggests that PFMAS is another high molecule inorganic coagulant besides PFS and PAS. Abound of hydroxyl bond in PFMAS implies the mechanism of COD removal from leachate may include hydroxyl bond between coagulant molecules and contaminated matters. In this case, binding ('bridging') of particles by precipitated hydrolysing metal salts may result in stronger aggregates, thereafter, optimal removal of COD from leachate can be achieved (sweep coagulation) (Duan et al., 2003).

Chemical oxygen demand (COD) removal tests with equal mass of the three kinds of coagulants were conducted(Fig 5). Test results showed that PFMAS is more effective to remove COD from leachate than PFS and PAS. It could also be observed from the tests that flocs of PAS were large and loose, while flocs of PFS were small and compact. However, flocs of FMAS were comparative large, formed rapidly and settled easily. Better effectiveness of PFMAS for leachate treatment than PFS and PAS means PFMAS has better composition than PFS and PAS.

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