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Application of polymeric aluminum salts in remediation of soil contaminated by Pb, Cd, Cu, and Zn

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Abstract: Soil contaminated with typical heavy metals (Pb, Cd, Cu, and Zn) was remedied by using the polymeric aluminum salt coagulants including polyaluminum chloride (PAC) and polyaluminum sulfate (PAS). The remediation efficiencies are influenced by reaction time, water amount, and dosage of remediation agent. The optimal remediation conditions are as follows: 6 h of reaction time, 1 kg/kg of water addition amount, and 0.25 kg/kg of remediation agent dosage. After PAC addition, the remediation efficiencies of diethylenetriamine-pentaacetic acid (DTPA)-extractable Pb, Cd, Cu, and Zn reach 88.3%, 85.1%, 85.4%, and 73.7%, respectively; and those for PAS are 89.7%, 88.7%, 83.5%, and 72.6%, respectively. The main remediation mechanism of the polymeric aluminum salt may contribute to the ionization and hydrolysis of PAC and PAS. H^+ released from ionization of polymeric aluminum salt can cause the leaching of heavy metals, while the multinuclear complex produced from hydrolysis may result in the immobilization of heavy metals. For PAC, the immobilization of heavy metals is the main remediation process. For PAS, both leaching and immobilization are involved in the remediation process of heavy metals.

Key words: heavy-metal pollution; soil remediation; immobilization; coagulant (coagulating agent); polyaluminum chloride (PAC); polyaluminum sulfate (PAS)

1 Introduction

With the development of mining and smelting industries, large areas of soil are contaminated by heavy metals. It is estimated that 20% of the total arable soil in China is contaminated with heavy metals. Consequently, grain yields decrease with 10^6 t due to contaminated soil. The concentration of heavy metals in 1.2×10^6 t of grains exceed the Standard of Chinese Food Security, and the direct economic loss is over 20 billion [1].

The remediation of soil contaminated with heavy metals is a hot issue all over the world [2−3]. Many remediation methods are available, including engineering, biological, agricultural, physicochemical, and chemical measures. Engineering methods include excavation, replacement with other soil, and deep fallowing of soil. There are more or less disadvantages among the above remediation methods. For instance, engineering method is laborious and it is difficult to store and treat the scooped soil. Biological measures are hard to be implemented in plant or microbe identification and low remediation rates. Agricultural measures need the long plant cycle and have low remediation efficiency. Chemical measures such as reacting the heavy metals with remediation agents make the metals be leached from or immobilized in the soil. The advantages of this approach are the high remediation rate and efficiency. Numerous remediation agents have been previously tested. For example, lime [4], phosphates [5], hydroxyapatite [6], ferrous salt [7], zeolite [8], oyster shells [9], manure [10], humic acid [11], chitosan [12], and biochar [13] can all be used as remediation agents to immobilize heavy metals in soil. Chelators (e.g., EDTA-Na_2 [14]) and acids (e.g., hydrochloric acid, citric acid [15]) can be used as remediation agents to leach heavy metals from soil. The selection of cost-effective and eco-friendly remediation agents is important in the remediation of heavy-metal-contaminated soil.

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Coagulants are substances that can precipitate small solid particles dispersed in liquid. Polymeric aluminum salts are efficient synthetic-coagulants due to their large number of active groups that enable particle precipitation via adsorption bridging and charge neutralization. Thus, coagulants have been used to remove heavy metals, turbidity, chromaticity, and a small amount of organic matters from wastewater [16]. However, the use of polymeric aluminum salts in the remediation of soil contaminated with heavy metals has not been reported.

Baiyin City in Gansu Province is located in Northwest China on the upper reaches of the Yellow River valley. This city is known as "copper city" rich in silver and copper. This city is one of the most important industrial centers of non-ferrous metals in China, with developed industries such as mining, mineral processing, smelting, plating, battery manufacture, and chemical production. Thus, Baiyin is the main area of heavy-metal pollution in the Yellow River valley. Many kinds of heavy metals are discharged into the soil, leading to severe pollution. Baiyin is currently one of the heavy-metal-pollution prevention and control zones in China. The treatment and remediation of soil contaminated with heavy metals are extremely urgent.

In the present work, heavy-metal-contaminated soil in Baiyin City was used to assess the feasibility and performance of a new chemical remediation method using polymeric aluminum salt coagulants.

2 Experimental materials and methods

2.1 Heavy-metal-contaminated soil

Soil contaminated with the heavy metals Pb, Cd, Cu and Zn was collected from suburban of Baiyin City (35°33′–37°38′ N and 103°3′–105°34′ E). The soil samples were collected at a depth of 0–20 cm, air dried, ground and passed through a 2 mm sieve. The physical and chemical characteristics of the soil are presented in Table 1. The characteristics were mainly measured by the following methods [17−18]. The soil pH in a 1:2.5 (m/V) soil-water suspension was measured by using a pH meter. Organic matter was analyzed by oxidation with potassium dichromate and titration with ferrous ammonium sulphate. The cation exchange capacity (CEC) was detected by an EDTA–ammonium acetate method. The maximum water-holding capacity was determined by the ring sampler. The total heavy-metal concentrations of Pb, Cd, Cu and Zn in soil were analyzed by digestion with aqua regia using an inductively coupled plasma emission spectrometer.

2.2 Remediation agents

The soil remediation agents were polymeric aluminum salt coagulants polyaluminum chloride (PAC) and polyaluminum sulfate (PAS). PAC $\{[Al_2(OH)_n Cl_{6-n}]_m$ (m≤10, 1≤n≤5)} and PAS $\{[Al_2(OH)_n(SO_4)_{3-n/2}]_m$ (m≤10, 1≤n≤5) were from Shanxi Province and Beijing City, China, respectively. The products met the national standards, i.e., ≥29% Al_2O_3 purity (product purity is usually indicated by the mass fraction of Al_2O_3).

2.3 Remediation processes

2.3.1 Remediation time

To determine the optimal remediation time, the following experiments were designed. 0.2 kg/kg of PAC or PAS (was added to soils with 100% maximum water-holding capacity (0.31 kg/kg). The samples were oscillated for 6 h at 180 r/min using a horizontal oscillator under 25 °C, and then kept in room temperature for 6 h, 12 h, 24 h, 48 h, and 96 h, respectively. The samples were air dried, ground, blended, and stored for measuring available Pb, Cd, Cu, and Zn in the treated soils by the DTPA extraction method. The experiments were performed in triplicate.

2.3.2 Treatment with different amounts of water

To determine the optimal water amount, the following experiments were designed. 0.2 kg/kg of PAC or PAS was added to soils with six levels of water amounts: 0.18 (60% of the maximum water-holding capacity), 0.31 (100% of the maximum water-holding capacity), 1, 2, 3, and 5 kg/kg. The treated samples were oscillated for 6 h at 180 r/min under 25 °C. After 6 h, further treatments were required according to the presence of liquid in the samples. When liquid was present in the treated samples, the suspensions were vacuum filtered, and the filtrates was used to measure the leaching amount of heavy metals. The residues were air

Table 1 Physical and chemical characteristics of soil sample

pH	Organic matter/ %	CEC/ (cmol·kg^{-1})	Maximum water-holding capacity/(mL·kg^{-1})	Total Pb/ (mg·kg^{-1})	Total Cd/ (mg·kg^{-1})
6.52±0.12	1.4±0.18	18.2±0.3	312±8	598.2±21.8	39.55±1.12
Total Cu/ (mg·kg^{-1})	**Total Zn/ (mg·kg^{-1})**	**DTPA-extractable Pb/ (mg·kg^{-1})**	**DTPA-extractable Cd/ (mg·kg^{-1})**	**DTPA-extractable Cu/ (mg·kg^{-1})**	**DTPA-extractable Zn/ (mg·kg^{-1})**
253.6±5.2	742.2±7.9	132.0±3.5	11.82±0.43	86.1±1.5	160.2±2.1

dried, ground, blended, and stored for measuring available Pb, Cd, Cu, and Zn by the DTPA extraction method. When liquid was absent, the treated samples were directly air dried, ground, blended, and stored for measuring available Pb, Cd, Cu, and Zn by the DTPA extraction method. The experiments were performed in triplicate.

2.3.3 Treatment with different dosages of remediation agent

To determine the optimal dosage of remediation agent, the following experiments were designed. PAC and PAS were added to soils at eight levels: 0, 0.005, 0.01, 0.05, 0.1, 0.15, 0.2, and 0.25 kg/kg. The amount of water added was 1 kg/kg. The experiments were performed in triplicate. The subsequent processes were the same as in Section 2.3.2.

2.3.4 Contributions of leaching and immobilization to remediation of heavy metals

To obtain the contributions of leaching and immobilization to the remediation of heavy metals, the Pb, Cd, Cu, and Zn contents in the filtrates obtained from Sections 2.3.2 and 2.3.3 were measured.

2.4 Assessment of remediation efficiency

The remediation effects were assessed by the removal of available heavy metals measured by the diethylenetriaminepentaacetic acid (DTPA) extraction method. Many methods for measuring the available heavy metals have been established, including the HCl and DTPA extraction methods [19]. In the present work, the DTPA extraction method was used because the amount of heavy metals extracted by DTPA are directly related with the metal adsorption capacities of crops [20−21]. DTPA extraction method was described as follows: DTPA solution (containing 0.005 mol/L DTPA, 0.01 mol/L $CaCl_2$, and 0.1 mol/L triethylamine; pH 7.3 was added into soil at a 5:1 solution-to-soil ratio. The samples were then oscillated for 2 h at 180 r/min on a horizontal oscillator under 25 °C. After vacuum filtering the samples, the filtrates were stored for analyzing the concentrations of Pb, Cd, Cu and Zn by using ICP-AES.

The removal (or remediation) amount and efficiencies of the available heavy metals were calculated according to the formulae:

$$\Delta X = X_0 - X_1 \tag{1}$$

$$Y = (X_0 - X_1)/X_0 \tag{2}$$

where X_0 and X_1 are the available heavy metal amounts in untreated and treated soils, respectively; ΔX and Y are the removal (or remediation) amount and efficiency of the available heavy metals in treated soil, respectively.

3 Results and discussions

3.1 Remediation time

The variation in the amount of DTPA-extractable heavy metals with the addition of PAC and PAS are shown in Fig. 1. The remediation reactions between the heavy metals (Pb, Cd, Cu, and Zn) and PAC or PAS can be achieved within 6 h. The reduction amount of DTPA-extractable Pb, Cd, Cu, and Zn in the PAC-treated soils are 109.5, 9.3, 67.6, and 103.1 mg/kg, respectively, with the remediation efficiencies of 85.8%, 79.6%, 78.5%, and 64.4%, respectively. In the PAS-treated soils, the reduction amounts are 118.9, 9.78, 72.8, and 19.6 mg/kg, respectively, with remediation efficiencies for Pb, Cd, and Cu reaching 90.1%, 83.0%, and 84.7%, respectively.

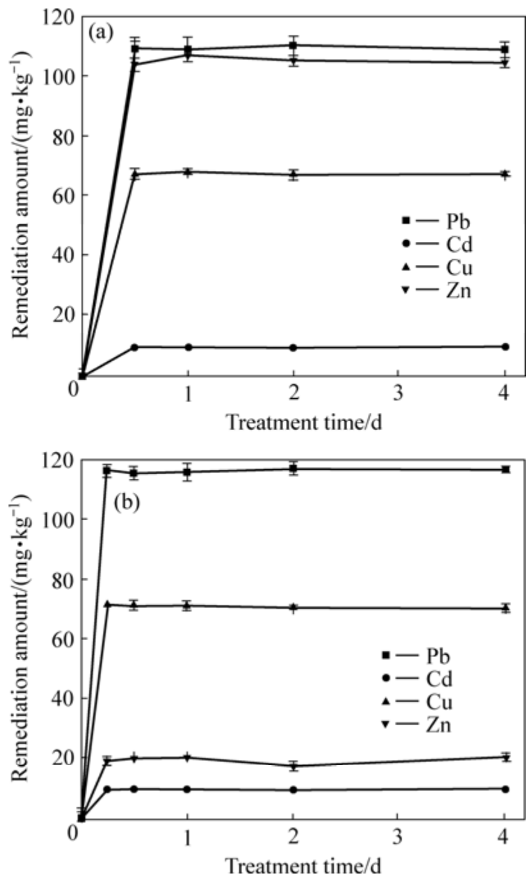

Fig. 1 Variation in amount of DTPA-extractable heavy metals with remediation time: (a) PAC; (b) PAS

3.2 Influence of water amount on remediation effect

The water amount greatly influences the remediation efficiencies (Fig. 2). Amount for the soil treated with 0.2 kg/kg PAC, when the water addition amount are lower than 1 kg/kg, the remediation efficiencies of heavy metals slowly decline with increased water addition amount. The maximum remediation efficiencies of heavy metals is obtained at

1 kg/kg of water amount. However, when the water amounts are higher than 1 kg/kg, the remediation efficiencies rapidly decline with increased water amount.

In the soil treated with 0.2 kg/kg PAS, the change trends of Pb and Cu remediation efficiencies in relation to the water amount are similar with those using PAC. However, the remediation efficiencies of Cd and Zn remediation in relation to the water amount are different from those using PAC. The remediation efficiencies of Cd reach the maximum value at the water amount of higher than 0.31 and 1 kg/kg, respectively. When the water amount are lower than 0.19 kg/kg, the remediation efficiency is negative, which indicates that Zn in the soil is activated and the DTPA-extractable Zn in the soil increases. Taking the remediation efficiencies of Pb, Cu, Cd into account, a water addition amount of 1 kg/kg is the optimal value.

3.3 Influence of remediation agent dosage on remediation effect

The relationship between the remediation efficiencies and the agent dosages are described in Fig. 3. The agent dosages remarkably influence the remediation effects.

When low PAC and PAS (≤0.01 kg/kg) dosages are

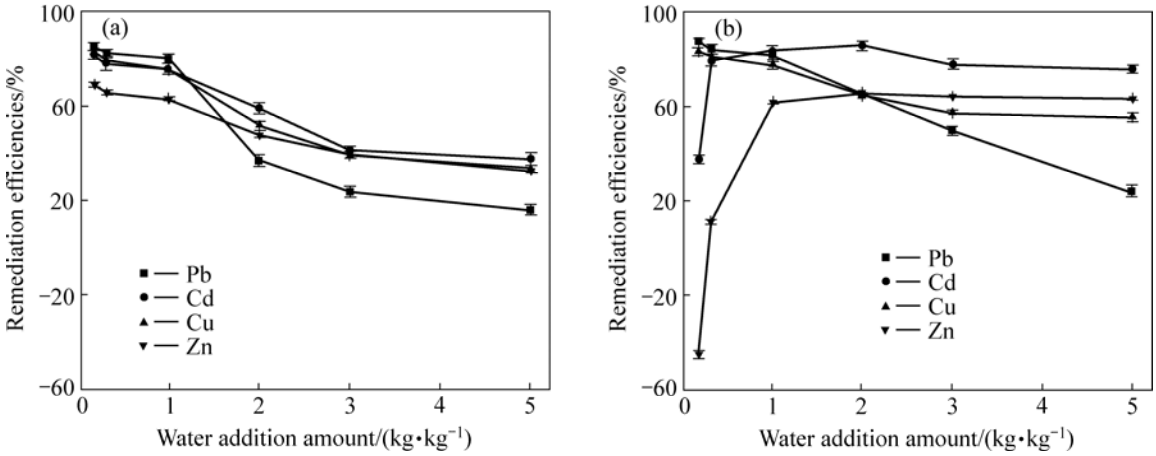

Fig. 2 Variation in remediation efficiencies with water amount using PAC(a) and PAS(b)

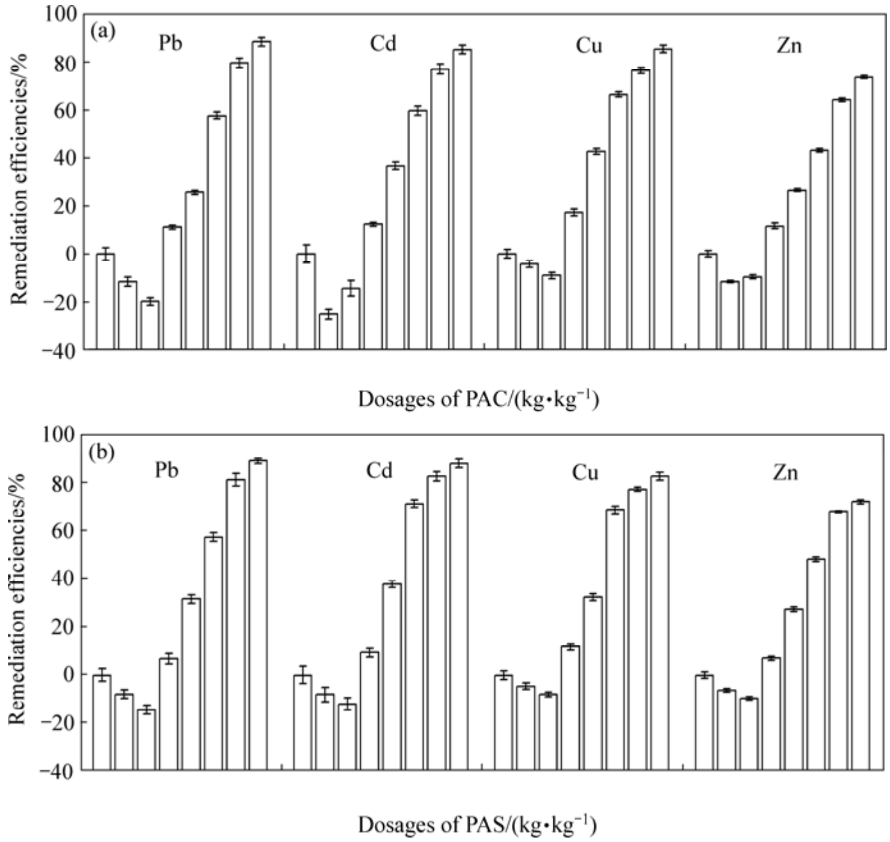

Fig. 3 Variation in remediation efficiencies with agent dosages using PAC(a) and PAS(b) (Dosages of PAC and PAS are 0, 0.005, 0.01, 0.05, 0.1, 0.15, 0.2, and 0.25 kg/kg, respectively)

added to the soils, heavy metals are activated by PAC and PAS, resulting in increased concentrations of DTPA-extractable Pb, Cd, Cu, and Zn and the calculated remediation efficiencies are negative. When PAC and PAS dosages varies from 0.01 to 0.05 kg/kg, low remediation efficiencies of Pb, Cd, Cu, and Zn are obtained. The remediation efficiencies of the above heavy metals for PAC and PAS are 10%–18% and 9%–11.8%, respectively. With further increasing dosage of polymeric aluminum salt to 0.25 kg/kg, the remediation efficiencies of Pb, Cd, Cu, and Zn for PAC treatment reach 88.3%, 85.1%, 85.4%, and 73.7%; and those for PAS reach 89.7%, 88.7%, 83.5%, and 72.6%, respectively. The results indicate that the remediation efficiencies of heavy metals are dependent on its pollutant species since polymeric aluminum salt had higher remediation efficiencies for Pb, Cd and Cu than that for Zn. Moreover, there is no significant difference of remediation efficiencies of above four heavy metals between PAC and PAS.

3.4 Contributions of leaching and immobilization to remediation of heavy metals

Generally, remediation of heavy-metal-contaminated soil includes two situations: One is the removal of heavy metals from soils, such as leaching and flushing; Another is immobilization of heavy metals. In the first situation, heavy metals are transformed into ions and they are leached from the soil. In the second situation, heavy metals are transformed into residual forms and they are immobilized in the soil.

The leaching amount of heavy metals in different treatments are described in Fig. 4. In the soil treated with PAC with different dosages and water amounts, the leaching amounts of Pb, Cd, Cu, and Zn are all less than 5 mg/kg. This finding indicates that the transportation amount of the heavy metals from soil to solution and the contributions of leaching to the remediation are very small. Thus, most of the heavy metals are immobilized in the soil and immobilization is the predominant remediation process.

In the soil treated with PAS ≤0.1 kg/kg dosages, the leaching amounts of Pb, Cd, Cu, and Zn are all less than 1 mg/kg, with very low remediation efficiencies. However, with increased dosage to 0.15 kg/kg, the leaching amounts of Pb, Cd, Cu, and Zn rapidly increase. When the dosage exceeds 0.25 kg/kg, the leaching amounts of Pb, Cd, Cu, and Zn reach 8.42, 12.14, 33.58, and 137.65 mg/kg, respectively. Meanwhile, at 0.25 kg/kg of PAS dosage, the remediation efficiencies also rapidly increase (Fig. 3). This finding indicates that some heavy metals are transported from soil to solution and the leaching is involved in the remediation process. Comparing leaching amount of heavy metals with its removal percentage, it is found that leaching amount is less than removal percentage, implying that one part of heavy metals is immobilized in soils. Therefore, both immobilization and leaching contribute to the remediation process for PAS treatment.

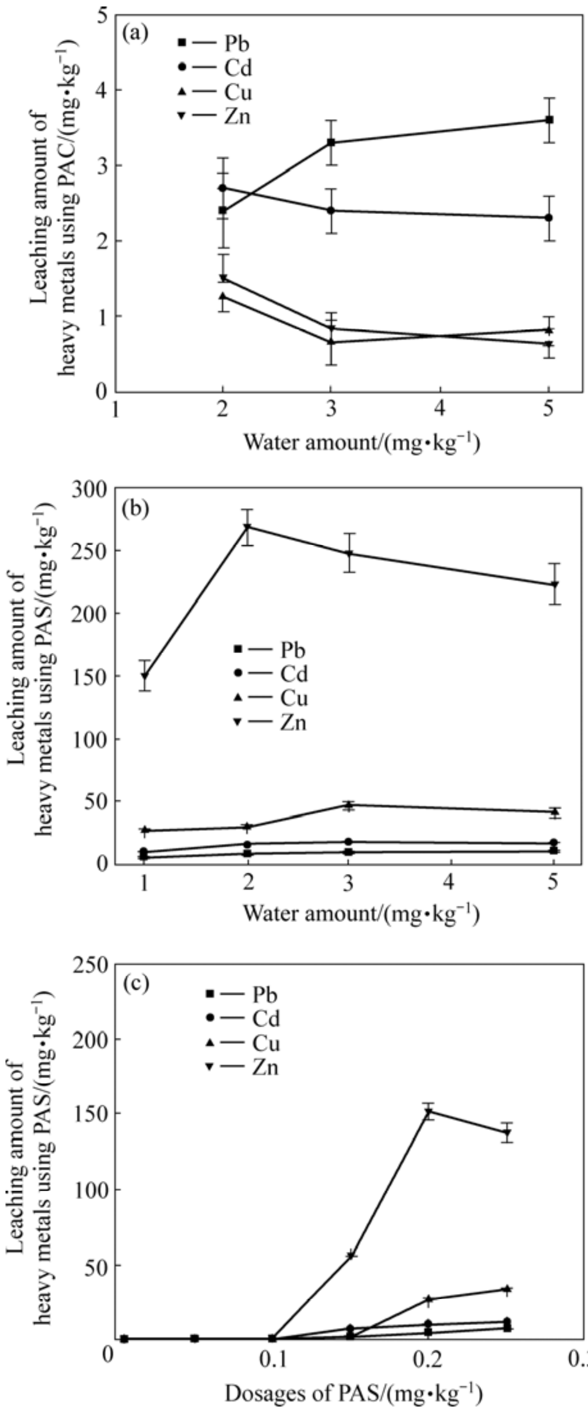

Fig.4 Leaching amounts of heavy metals in different treatments: (a) PAC at different water amounts; (b) PAS at different water amounts; (c) PAS dosage

3.5 Remediation mechanisms

The remediation of heavy metals by polymeric aluminum salts is related to their properties, such as ionization and hydrolysis. The remediation process may result from four synthesis reactions. The first stage is the polymeric aluminum salt-induced production of H^+ by ionization and multinuclear complex ions by hydrolysis. The second stage is the reaction of H^+ with heavy metals. H^+ results in the release of heavy metal from the un-dissolved form, such as carbonates-bonded and oxides-bonded forms, and then the dissolved heavy metal can be leached from soils. The third stage is the reaction of multinuclear complex ions with heavy metals. During this stage, multinuclear complex ions react with heavy metals via adsorption bridging and charge neutralization to produce flocculent or lumpish precipitates. The SEM images of soils treated with PAC show the presence of flocculent or lumpish precipitates in the remedied soils (Fig. 5). The fourth stage is the reaction of H^+ with the aluminide sediments. Due to the amphoteric characteristic of aluminides, the aluminide sediments can react with H^+ or OH^- in a strong acid medium or strong alkaline medium. When H^+ is in excess, the remaining H^+ can react with the aluminide sediments containing heavy metals, and the heavy metals can be released into the liquid phase as ions. Therefore, pH may be one of important factors to control the immobilization and leaching process. The hydrolysis degree of PAS is much higher than that of PAC. Within the dosage range used in the present work, the pH values of the PAC solutions are about 4.1−4.6, but the pH values of the PAS solutions are about 2.1−3.3.

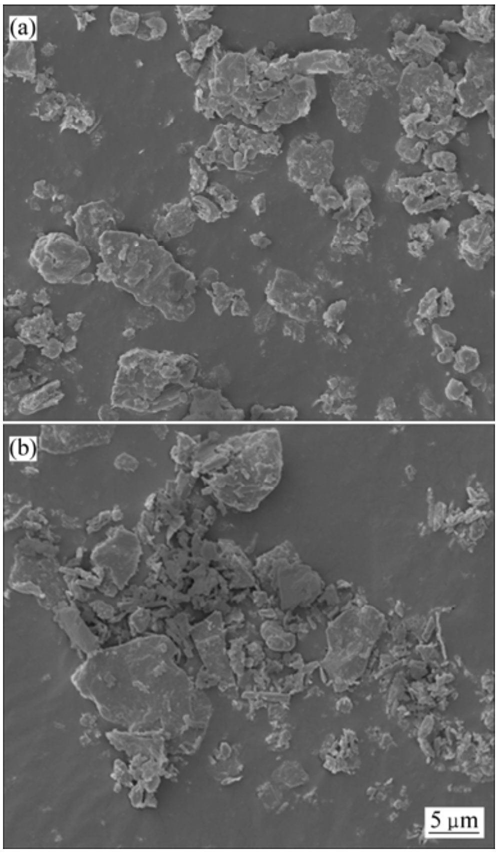

Fig. 5 SEM image of soils treated with PAC: (a) Untreated soil; (b) Treated soil

In the PAC-treated soil, the H^+ ions produced by ionization and hydrolysis are insufficient. The fourth reaction stage does not occur, and thus the leached heavy metal is less. The heavy metal immobilization by multinuclear complex ions is the dominant remediation process. However, in the PAS-treated soil, the H^+ ions are sufficient and all remediation reaction stages occur. Consequently, one part of heavy metals can be leached from soils by excess H+ and another part of heavy metal can be immobilized by multinuclear complex ions.

4 Conclusions

1) Polymeric aluminum salts can be used in the remediation of soil contaminated by Pb, Cd, Cu, and Zn. The remediation efficiencies are influenced by time, water amount, and remediation agent dosage. The optimal conditions are as follows: remediation time of 6 h, water amount of 1 kg/kg, and remediation agent dosage of 0.25 kg/kg. The remediation efficiencies of PAC to DTPA-extractable Pb, Cd, Cu, and Zn for PAC reach 88.3%, 85.1%, 85.4%, and 73.7%; those for PAS reach 89.7%, 88.7%, 83.5%, and 72.6%, respectively.

2) The main remediation mechanisms of heavy metals in soils by using PAC could be contributed to the production of multinuclear complex ions by PAC hydrolysis. The multinuclear complex ions can precipitate the heavy metals via adsorption bridging and charge neutralization. When PAS is used in the remediation of heavy metal contaminated soil, one part of heavy metal can also be leached from soil because of H^+ produced from PAS ionization and another part of heavy metals can be immobilized by multinuclear complex ions produced by PAS hydrolysis. The results imply that both leaching and immobilization are involved in the remediation process.

3) The ecological risk assessment of soil remediation by polymeric aluminum salts needs to be further investigated.

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