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Pretreatment of ammonium removal from landfill leachate by chemical precipitation

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ABSTRACT

Chemical precipitation is a useful technology to remove ammonium (NH_4^+) from landfill leachate. In this paper, the removal of ammonium from landfill leachate was studied. The objective of this study was to investigate optimum pH, optimum molar ratio, and different kinds of chemicals combinations for magnesium ammonium phosphate (MAP) precipitation. Furthermore, the kinetics of MAP formation and surface characterization were analyzed. The results indicated that ammonium in landfill leachate could be removed with the optimum pH of 9.5. The Mg^{2+}:NH_4^+:PO_4^{3-} molar ratio was practically controlled at 1.15:1:1 to remove ammonium effectively and avoid higher concentration of PO_4^{3-} in the effluent. Highest salt concentration was generated by using $MgCl_2{\cdot}6H_2O$ plus $Na_2HPO_4{\cdot}12H_2O$. Compare to $MgCl_2{\cdot}6H_2O$ and $Na_2HPO_4{\cdot}12H_2O$, adding MgO and 85% H_3PO_4 could significantly minimize the salt concentration, although ammonium removal ratio was 9 percents lower. The lowest ammonium removal ratio was generated by adding $Ca(H_2PO_4)_2{\cdot}H_2O$ and $MgSO_4{\cdot}7H_2O$. Moreover, the kinetics experiment shown that the rate of reaction was closer to the first-order kinetic model. Fourier transform infrared spectroscopy (FTIR) and X-ray diffraction (XRD) analysis indicated that MAP was the main composition of the precipitates. Scanning electron microscopy with energy dispersive X-ray (SEM–EDX) analysis indicated that the unshaped crystal was coarse and its size was irregular, the surface composition of the precipitates contains a great deal of O, P, Mg and trace of C, K, Na, Cl.

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1. Introduction

One of the major environmental concerns associated with municipal landfills is related to the landfill leachate into the environment. As a consequence, people have suffered a great deal from landfill leachate. Leachates generated from municipal landfills can be considered complex effluents that often contain organic compounds, heavy metals, ammonium (NH_4^+), chloride and many other soluble compounds. The type of waste and the age of landfill influence the composition and concentration of contaminants [1].

Treatment of landfill leachate is very complicated and generally requires various process applications that due to high concentrations of COD and ammonium. Anaerobic biological treatment systems are efficient to treat high concentrations of COD, but high concentrations of ammonium inhibit biological treatment systems. As a result, pretreatment of ammonium is very important.

Many physico-chemical processes which have widely been used can be applied in the pretreatment of ammonium from landfill leachate, such as air stripping [2,3], membrane separation processes [4,5], chemical precipitation [6,7]. Recently, chemical precipitation of ammonium by forming magnesium ammonium phosphate (MAP) precipitation has been studied widely [8,9]. It is a useful technology to remove ammonium from landfill leachate.

MAP is a white crystalline substance consisting of magnesium, ammonium and phosphorus in equal molar concentrations. The basic chemical reaction to form MAP has been expressed in Eq. (1) [10–12]:

$$Mg^{2+} + NH_4^+ + PO_4^{3-} + 6H_2O \rightarrow MgNH_4PO_4{\cdot}6H_2O \downarrow \quad (1)$$

$$pK_s = 12.6 \ (25^\circ C) \quad (2)$$

The kinetics of chemical reactions can be written as

$$-\frac{d[C]}{dt} = k[C]^n \quad (3)$$

where C is the molar concentration of reactant, t is the reaction time, k is the rate constant and n is the order of reaction [13]. The equation yields the following integrated equations respectively when it is integrated for the first, second, and third order.

$$\ln [C] = \ln [C]_0 - kt, \quad \text{for first order} \quad (4)$$

$$\frac{1}{[C]} = \frac{1}{[C]_0} + kt, \quad \text{for second order} \quad (5)$$

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$$\frac{1}{2[C]^2} = \frac{1}{2[C]_0^2} + kt, \quad \text{for third order} \tag{6}$$

In this paper, the objective of this study was to investigate optimum pH, optimum molar ratio, and different kinds of chemicals combinations in laboratory scale experiments. Furthermore, the kinetics of MAP formation and surface characterization were analyzed.

2. Materials and methods

2.1. Raw wastewater

The raw wastewater used in the experiments was collected from the landfill near Nanjing and stored in an icebox prior to the experiments. Table 1 shows some parameters of the wastewater sample.

2.2. Experimental procedures

Three factors affecting MAP formation were evaluated, including pH, molar ratio of Mg^{2+}:NH_4^+:PO_4^{3-}, different chemicals combinations of magnesium salt and phosphate. Ammonium removal ratio was used as the indicator for selecting optimum MAP sedimentation conditions.

Experiments for MAP precipitation were performed as follows. Firstly, add magnesium salt and phosphate to raw wastewater. Secondly, agitate the reaction solution by magnetic stirrers for 30 min, and then adjust pH, settle for 30 min. Thirdly, filter the reaction solution first with filter paper and then with 0.45 μm membrane filter. Lastly, after filtration, collect the supernatant to measure Mg^{2+} and NH_4^+ and collect the precipitates for surface characterization analysis.

2.3. Experimental procedures for kinetic study

Kinetic studies of MAP formation were performed with 200 mL wastewater at 25 °C. Firstly, $Na_2HPO_4{\cdot}12H_2O$ dissolved in wastewater was used as PO_4^{3-} sources. Then, the condition of pH was adjusted to 9.5 and pH was not adjusted during the course of the reaction, because the reaction was very fast. The Mg^{2+}:NH_4^+:PO_4^{3-} molar ratio was controlled at 0.2:1:1. The reaction started after adding $MgCl_2{\cdot}6H_2O$ as Mg^{2+} sources. 10, 20, 30 and 40 s later samples were taken and filtered with 0.45 μm membrane filter to determine the concentrations of Mg^{2+} remaining in the wastewater.

2.4. Analytical methods

The concentration of NH_4^+ was measured according to Standard Methods [14]. The concentration of Mg^{2+} was determined using an atomic absorption spectrophotometer (M6, Thermo, USA). The collected precipitates were washed with deionized water for three times, and then dried in an oven at 40 °C for 48 h [15], and then analyzed by Fourier transform infrared spectroscopy (FTIR, NEXUS870, USA), X-ray diffraction (XRD, X/TRA, ARL, Switzerland), scanning electron microscopy with energy dispersive X-ray analysis (SEM–EDX, S-3400N, Hitachi, Japan).

Table 1
Characteristics of raw wastewater.

Parameter	Unit	Concentrations
COD	mg/L	7200 ± 300
NH_4^+	mg/L	2520 ± 100
pH	–	8.10 ± 0.20
BOD_5	mg/L	1340 ± 100
Color	–	4000 ± 200
SS	mg/L	680 ± 50

3. Results and discussion

3.1. Optimum pH experiment

An important factor for MAP formation is pH. This experiment was to study the optimum pH for MAP formation in landfill leachate. This was tested by adding $MgCl_2{\cdot}6H_2O$ and $Na_2HPO_4{\cdot}12H_2O$ into the samples, and the molar ratio of Mg^{2+}:NH_4^+:PO_4^{3-} was 1:1:1. The pH range was 8.5–11.0.

As shown in Fig. 1, the maximum removal ratio of ammonium for the raw wastewater was 9.5. When the pH was lower than the optimum point, hydrogen ion in reaction solution would inhibit MAP formation. As a result, the removal ratio of ammonium was lower. When the pH was higher than the optimum point, $Mg_3(PO_4)_2$ was formed instead of MAP along with pH raising, which lead to the decrease of ammonium removal ratio. The optimum pH for ammonium removal of the raw wastewater was 9.5.

In the literature, there are some papers dealing with the optimum pH for ammonium removal. Buchanan et al. [16] reported that MAP could be precipitated out of solution at pH 9.0. Booker et al. [17] also reported the optimum pH for MAP formation was 9.0–9.4. These results are in similar range as our results.

3.2. Optimum molar ratio experiment

This experiment was to study the optimum molar ratio of Mg^{2+}:NH_4^+:PO_4^{3-} for ammonium removal. The experiments tested by adding $MgCl_2{\cdot}6H_2O$ and $Na_2HPO_4{\cdot}12H_2O$ into the samples, and the pH was 9.5.

Fig. 2 is the relationship between Mg^{2+} concentration and ammonium removal ratio. When Mg^{2+}:NH_4^+:PO_4^{3-} molar ratio increased from 1:1:1 to 1.15:1:1, ammonium removal ratio increased from 79.2 to 85.5%. However, any excess dose application for Mg^{2+} did not provide significant increase in ammonium removal. In separate consideration of Mg^{2+}, the optimum Mg^{2+}:NH_4^+:PO_4^{3-} molar ratio for ammonium removal was 1.15:1:1.

Fig. 3 is the relationship between PO_4^{3-} concentration and ammonium removal ratio. When Mg^{2+}:NH_4^+:PO_4^{3-} molar ratio increased from 1:1:0.9 to 1:1:1.1, ammonium removal ratio increased from 68.5 to 83.4%. And then any overdosing of PO_4^{3-} was not economical for additional ammonium removal. In separate consideration of PO_4^{3-}, the optimum Mg^{2+}:NH_4^+:PO_4^{3-} molar ratio for ammonium removal was 1:1:1.1.

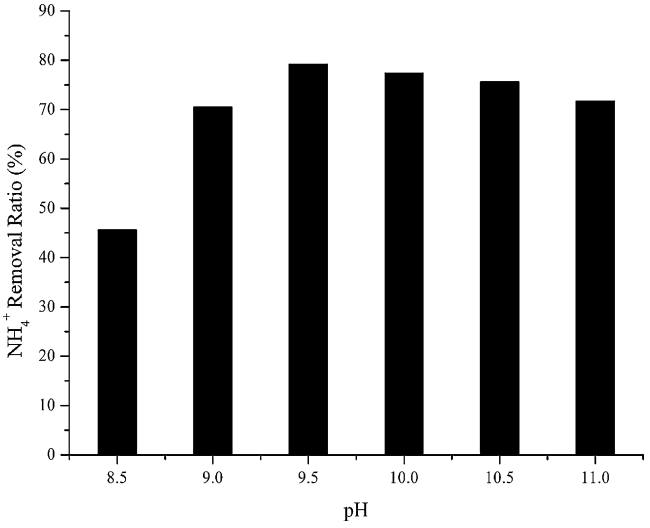

Fig. 1. NH_4^+ removal ratio at different pH.

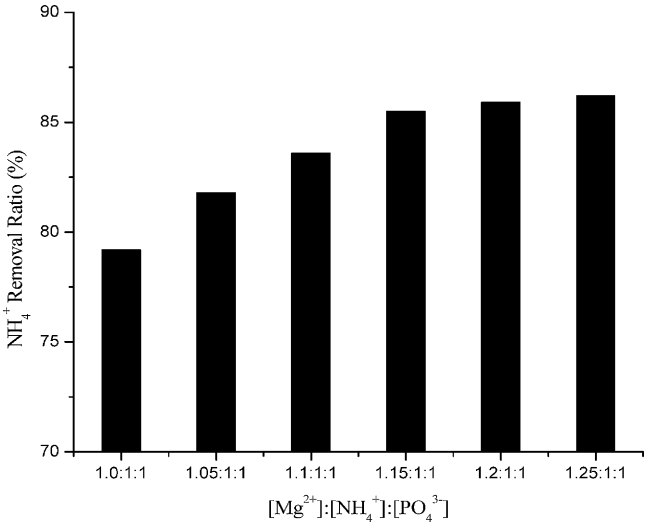

Fig. 2. NH_4^+ removal ratio at different molar ratio of Mg^{2+}.

Overdosing either Mg^{2+} or PO_4^{3-} can further lower the remaining ammonium concentration. However, from the environment point of view, overdosing PO_4^{3-} will generate higher concentration of PO_4^{3-} in the effluent. As a result, the removal efficiency Mg^{2+}:NH_4^+:PO_4^{3-} molar ratio in case control at 1.15:1:1 in order to remove ammonium effectively from landfill leachate as well as avoid higher concentration of PO_4^{3-} in the effluent.

Zhang et al. [18] reported that ammonium in coking wastewater could be treated by chemical precipitation and the optimum molar ratio of Mg^{2+}:NH_4^+:PO_4^{3-} was 1.1:1:1.

3.3. Experiments for compare with different chemicals combinations

Different chemicals combinations could have different ammonium removal ratio because of the complicated of the landfill leachate. The three combinations of chemicals $MgCl_2{\cdot}6H_2O + Na_2HPO_4{\cdot}12H_2O$, $MgO + 85\%\ H_3PO_4$, $Ca(H_2PO_4)_2{\cdot}H_2O + MgSO_4{\cdot}7H_2O$ were employed and the precipitation experiments were carried out under similar experimental conditions with the molar ratio of 1.15:1:1 and the pH of 9.5.

As shown in Fig. 4, the experimental results by comparing the removal ratio of ammonium with the additions of different chemicals combinations were that the combination of $MgCl_2{\cdot}6H_2O$ plus $Na_2HPO_4{\cdot}12H_2O$ was the most efficient for ammonium removal, but generated the highest salt concentration in the effluent. In theory, each mole of ammonium removed will produce 2 mol of NaCl. The high salt concentration will inhibit the following biological treatment process. Compare to $MgCl_2{\cdot}6H_2O$ and $Na_2HPO_4{\cdot}12H_2O$, adding MgO and 85% H_3PO_4 could significantly minimize the salt concentration, although the ammonium removal ratio was 9% lower. Thus the combination of MgO plus 85% H_3PO_4 would be a new choice in future instead of the traditional chemicals combination of $MgCl_2{\cdot}6H_2O$ plus $Na_2HPO_4{\cdot}12H_2O$. Compare to $MgCl_2{\cdot}6H_2O$ and $Na_2HPO_4{\cdot}12H_2O$, adding $Ca(H_2PO_4)_2{\cdot}H_2O$ and $MgSO_4{\cdot}7H_2O$ could also significantly minimize the salt concentration, but the removal ratio of ammonium was 24% lower. As a result, this kind of chemicals combination would not be applied to removing ammonium from landfill leachate.

In the literature, there are some papers dealing with comparing different chemicals combinations. Zhang et al. [18] did some research for coking wastewater on this aspect. Li et al. [19] did some study for landfill leachate on this aspect. These papers also made the conclusion that the combination of $MgCl_2{\cdot}6H_2O$ plus $Na_2HPO_4{\cdot}12H_2O$ generated the highest salt concentration in the effluent.

3.4. Kinetics of MAP formation

Kinetic studies of MAP formation are important. This experiment was to study the kinetics of MAP formation in landfill leachate. The Mg^{2+}:NH_4^+:PO_4^{3-} molar ratio was controlled at 0.2:1:1, the concentrations of NH_4^+ and PO_4^{3-} were sufficient compared to the contents of Mg^{2+}, so Mg^{2+} was choose to study the kinetics of the reaction. The reaction was very fast and completed in about 50 s. The course of the reaction is given in Table 2 as the average of three sets of experimental data. The constants of the kinetic model obtained are presented in Table 3.

According to Eqs. (4)–(6), C is the concentration of Mg^{2+}, C_0 is the initial concentration of Mg^{2+}, t is the reaction time, and k is the rate constant. Integrated forms of the first-, second- and third-order kinetic models were fitted to the experimental data. The first-order kinetic model was fitted to the experimental data with the good R-square value of 0.99 as shown in Fig. 5. The second-order kinetic model and the third-order kinetic model were fitted to the experi-

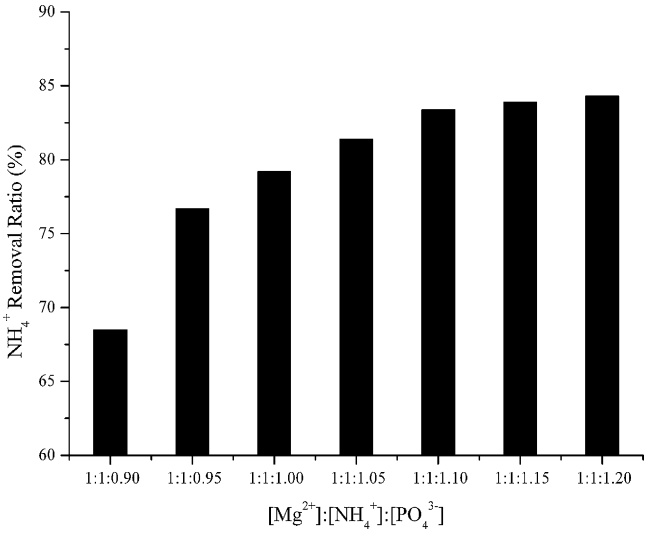

Fig. 3. NH_4^+ removal ratio at different molar ratio of PO_4^{3-}.

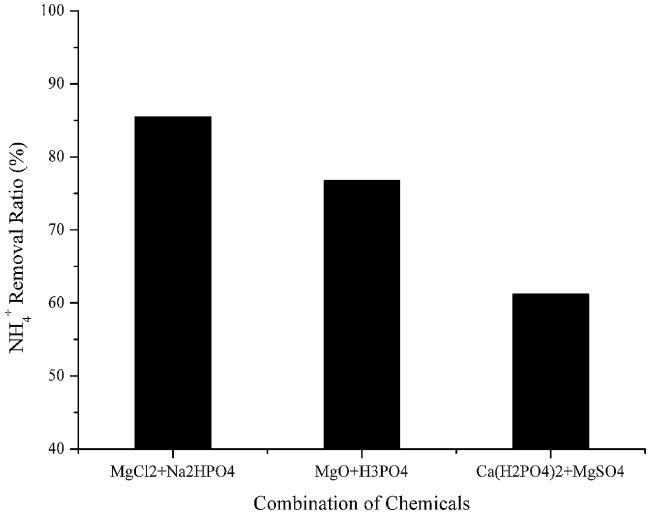

Fig. 4. NH_4^+ removal ratio at different combinations of chemicals.

Table 2
Changes of Mg^{2+} concentrations with time during MAP formation.

Time (s)	Mg^{2+} (mg L^{-1})	Percent of Mg^{2+} in supernatant (%)
0	988.8	100.0
10	504.0	51.0
20	235.2	23.8
30	132.9	13.4
40	81.9	8.3

Table 3
Estimation of kinetic parameters in kinetic model.

Order	R^2	k	Fit line approach
First	0.9918	230 h^{-1}	$\ln[Mg^{2+}] = -0.065t - 3.2$
Second	0.9385	24.2×10^3 L/mol h	$1/[Mg^{2+}] = 6.709t - 4.64$
Third	0.7941	3.62×10^6 L^2/mol^2 h	$1/2[Mg^{2+}]^2 = 1005.7t - 6928.4$

mental data with the *R*-square value of 0.93 and 0.79, respectively. As a result, this experiment shown that the rate of reaction was closer to the first-order kinetic model.

In the literature, some papers reported MAP kinetics. Nelson et al. [20] reported MAP formation fit to the first-order kinetics with the rate constants 3.7 h^{-1} at pH 8.4, 7.9 h^{-1} at pH 8.7 and 12.3 h^{-1} at pH 9.0. Ohlinger et al. [21] reported that MAP precipitate obeyed the first-order kinetics with the rate constant 4.2 h^{-1}. They all used Mg^{2+} to study the kinetics reaction. The reason of the differences between our results and the others is that the complicated element in landfill leachate could result in different MAP sedimentation kinetics.

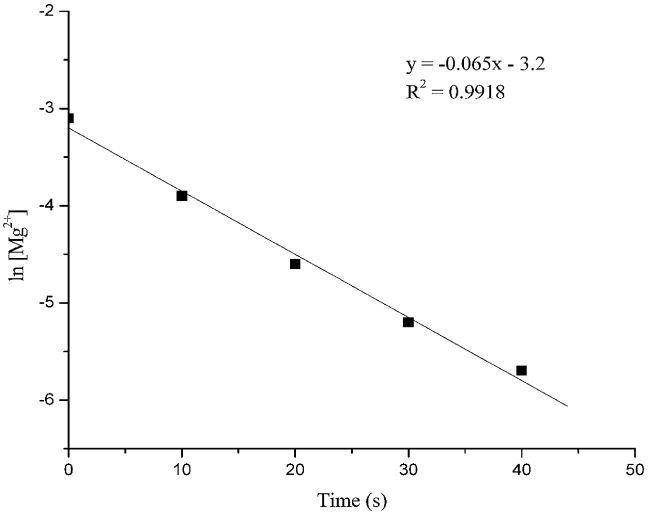

Fig. 5. Time versus ln [Mg^{2+}] for first-order reaction.

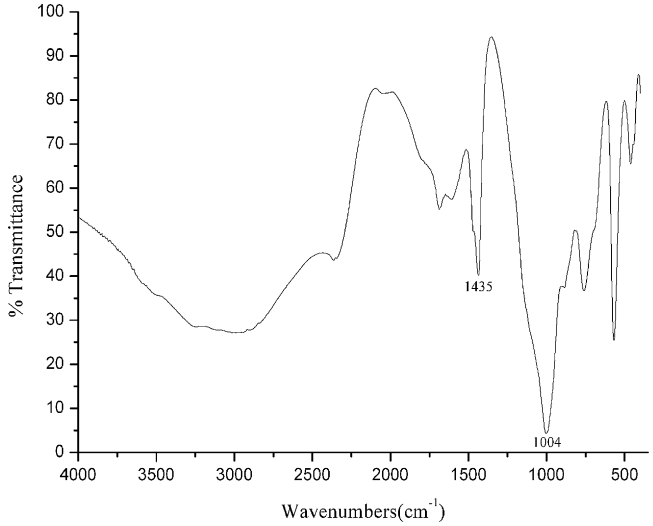

Fig. 6. Fourier transform infrared spectroscopy analysis of MAP.

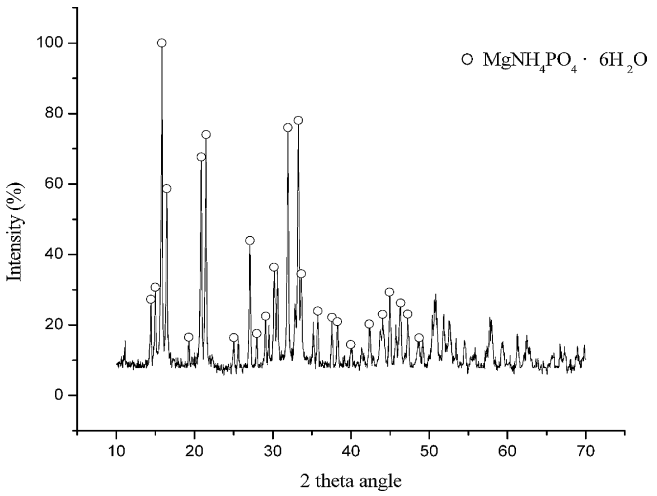

Fig. 7. X-ray diffraction analysis of MAP.

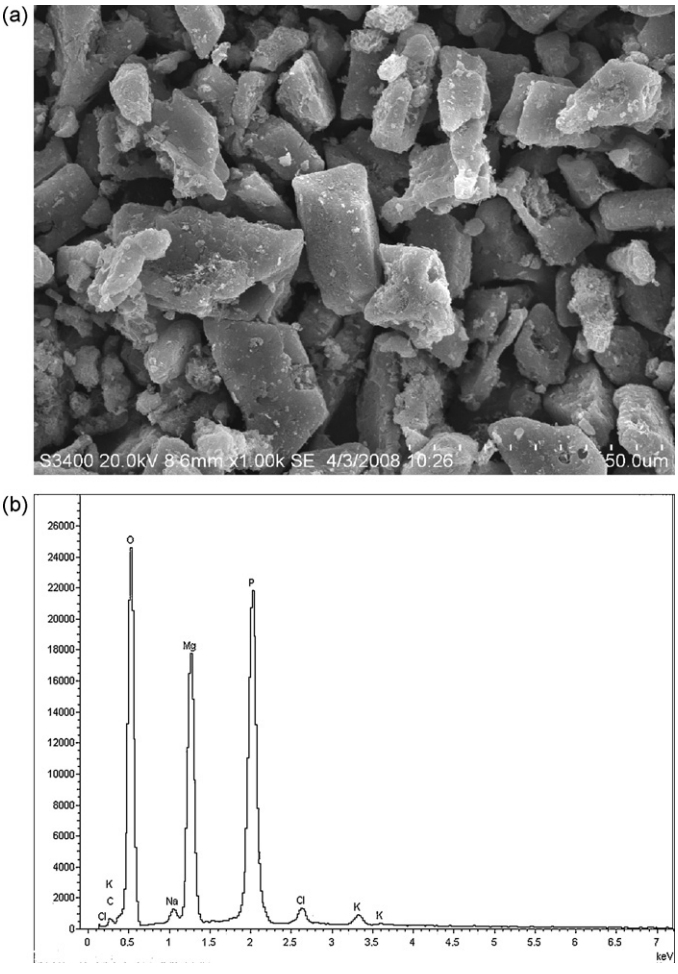

Fig. 8. Scanning electron microscopy with energy dispersive X-ray analysis of MAP: (a) scanning electron microscopy analysis of MAP and (b) energy dispersive X-ray analysis of MAP.

3.5. Surface characterization analysis

FTIR and XRD analysis indicated that the main composition of the precipitates was MAP (Figs. 6 and 7). Fig. 6 is FTIR analysis, which shown that the infrared spectrum of the precipitates was similar to that of MAP in Sastler infrared spectrum database. The characteristic Mg^{2+} band was at 1435 cm^{-1} and the characteristic PO_4^{3-} band at 1004 cm^{-1}. Fig. 7 is XRD analysis, which indicated that the characteristic peaks of the precipitates were close to that of the pattern for the MAP standard (JCPDS 15-0762) [22].

SEM–EDX analysis was performed to identify the surface characterization of the precipitates (Fig. 8a and b). Fig. 8a is SEM analysis, the surface of the unshaped crystal was coarse, and its size was irregular (15–40 μm length). Fig. 8b is EDX analysis, the surface composition of the precipitates contain a great deal of O, P, Mg and trace of C, K, Na, Cl.

4. Conclusions

As a pretreatment for ammonium removal of the landfill leachates, the chemical precipitation was investigated and the following conclusions could be obtained.

When $MgCl_2{\cdot}6H_2O$ and $Na_2HPO_4{\cdot}12H_2O$ were employed, the optimum pH of this treatment was 9.5 and the molar ratio of Mg^{2+}:NH_4^+:PO_4^{3-} was practically controlled at 1.15:1:1 in order to remove ammonium effectively and avoid higher concentration of PO_4^{3-} in the effluent.

Among the three chemicals combinations, $MgCl_2{\cdot}6H_2O$ plus $Na_2HPO_4{\cdot}12H_2O$ was the most efficient for ammonium removal, but generated the highest salt concentration in the effluent. Compare to $MgCl_2{\cdot}6H_2O$ and $Na_2HPO_4{\cdot}12H_2O$, adding MgO and 85% H_3PO_4 could significantly minimize the salt concentration and the ammonium removal ratio was 9% lower. Adding $Ca(H_2PO_4)_2{\cdot}H_2O$ and $MgSO_4{\cdot}7H_2O$ could also significantly minimize the salt concentration, but the removal ratio of ammonium was lowest.

Under the conditions studied, the rate of reaction was closer to the first-order kinetic model with a good *R*-square value of 0.99.

FTIR and XRD analysis indicated that MAP was the main composition of the precipitates. SEM–EDX analysis indicated that the unshaped crystal was coarse and its size was irregular, and the surface composition of the precipitates contains a great deal of O, P, Mg and trace of C, K, Na, Cl.

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