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Study on the Effect of Potassium on Struvite Precipitation in Synthetic Landfill Leachate

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Abstract: Struvite precipitation (MAP, $MgNH4PO_4.6H_2O$) is a common method for the treatment of ammonium-nitrogen (NH_4-N) in wastewater. Landfill leachate, one of the most hazardous waste streams, contains different pollutants (e.g. potassium (K)) that could affect the process of MAP recovery. This study investigated the effect of K on NH4-N recovery by struvite precipitation from landfill leachate. Bench-scale experiments were carried out using synthetic landfill leachate, by varying N:K molar ratio from 0.0 to 1.0, in which the results illustrated that increasing the molar ratio of K:N from 0.0 to 1.0 lowered the recovery of NH_4-N from 88% to 77%. Additionally, the precipitation of K compounds was confirmed by Scanning Electron Microscope/Energy Dispersive X-ray analysis (SEM-EDX). Finally, this study concluded that only high concentrations of K could affect the purity of struvite recovered from landfill leachate.

Key words: Struvite, magnesium, ammonium, potassium, landfill leachate.

Introduction

Landfill leachate (LL) is one of the most hazardous wastewaters with the greatest environmental impact because of high concentrations of different pollutants such as ammonium-nitrogen (NH_4-N), salts and organic matter. Being disposed without proper treatment, LL can cause eutrophication in natural water bodies, as well as contamination of groundwater and soil (Alslaibi et al., 2011; Yusof et al., 2009).

Since the organic matter contained in LL is usually stabilized, especially in old-aged one, it is difficult to remove NH_4-N directly by conventional nitrification-denitrification technique (Di Iaconi et al., 2010), which makes it worthy to reduce NH_4-N through a pretreatment process. One of the most effective methods is chemical precipitation of NH_4-N in the form of magnesium ammonium phosphate hexahydrate ($MgNH_4PO_4.6H_2O$; MAP). Generally, this method is simple, environmental friendly and can selectively remove NH_4-N with high efficiencies (Li et al., 2012). In addition, the resulted product, well-known as "Struvite", is an efficient slow-release fertilizer, which showed high efficiency in growing different types of plants (Rahman et al., 2014).

$$Mg + NH_4 + PO_4 \rightarrow MgNH_4PO_4.6H_2O \quad (1)$$

Struvite precipitation process is known to be influenced by several factors, including pH, molar ratio

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of constituents and foreign elements. A wide range of pH values (7.5-10.5) were reported as optimum for struvite crystallization. The presence of elements like Ca and K could result with the formation of other compounds that consume Mg and/or PO_4 ions. As noticed from literature, many studies reported that the concentration of Ca in LL was low, compared to NH_4-N (Huang et al., 2014), while high concentrations of K were reported in other studies (Xiu-Fen et al., 2011). In the same context, several researchers declared that K could affect MAP precipitation and purity to some extent. However, these studies focused on specific cases of K concentration. Moreover, to the best of our knowledge, no study had analyzed the relationship between K and N in terms of molar ratio. Therefore, the main goal of this study is to investigate the effect of K on MAP precipitation in LL.

Materials and Methods

Experimental Setup

The study was carried out using synthetic leachate that has the recipe shown in Table 1. This recipe was adapted from Rowe et al. (2002). The obtained synthetic leachate has values of chemical oxygen demand (COD) and total organic carbon (TOC) of 10,500±200 mg/l and 3,350±150 mg/l, respectively.

The experiments of struvite precipitation were carried out in 500-ml batch samples contained in 800-ml beakers. $MgCl_2.6H_2O$ and $NaH_2PO_4.2H_2O$ were applied as the sources of Mg and PO_4, respectively. To study the effect of K, the molar ratio of N:K was increased systematically from 0 to 1 (11 samples). After adding the required amounts of chemical reagents, pH was adjusted to 9.0±0.05 by adding 10M NaOH solution. Each sample was mixed for 30 min by a jar tester, and then allowed to settle for another 30 min. Supernatants were filtered through 0.45µm Whatmann GF/C filter, and NH_4-N was measured by Nessler Method using UV-spectrophotometer (DR6000, HACH Inc., USA). The harvested precipitates were separated, washed with de-ionized water and dried at ambient room temperature. Three samples with different N:K molar ratios (0.0, 0.5 and 1.0) were chosen to be analyzed by Scanning Electron Microscopy-Energy Dispersive X-ray spectroscopy (SEM-EDX; Gemini, Zeiss Supra Series, Germany), in order to verify the effect of K.

Results and Discussion

Effect of Potassium

Figure 1 illustrates the effect of K on the efficiency of NH_4-N removal. When K:N molar ratio was increased from 0.0 to 1.0, NH_4-N removal was gradually decreased from 88% to 77%. Precisely, NH_4-N removal started to decrease sharply at K:N > 0.2, which indicates that high purity struvite was obtained with low K concentrations. This obviously reveals that increasing K concentration could, to some extent, lower the efficiency of NH_4-N recovery by MAP precipitation technique.

Wilsenach et al. (2007) reported the co-precipitation of $MgKPO_4.6H_2O$ (Struvite-K) crystals, in parallel with MAP, in human urine, especially at low NH_4-N concentration. Similarly, a research done by Xu et al. (2011) demonstrated that ammonium-struvite ($MgNH_4PO_4.6H_2O$) had more tendency to precipitate

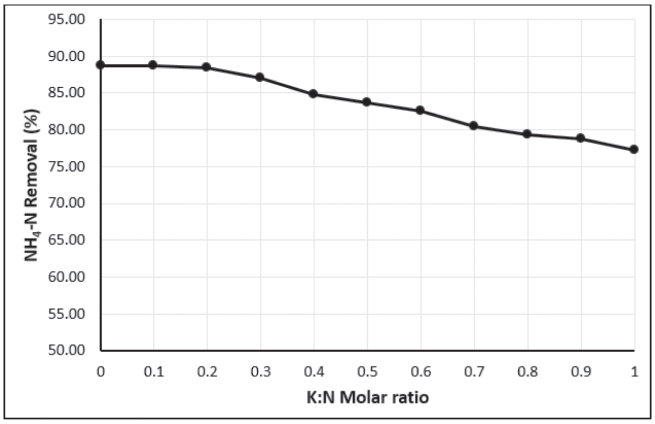

Figure 1: Effect of K on NH_4-N removal (pH = 9.0).

Table 1: Synthetic leachate recipe

Component	*Concentration (per L)*	*Component*	*Concentration (per L)*
Acetic acid	2,000 mg	Na_2CO_3	120 mg
Propionic acid	500 mg	K_2HPO_4	100 mg
Butyric acid	500 mg	$Ca(NO_3)_2$	50 mg
Humic acid	200 mg	NH_4Cl	Varied according to desired concentrations
$(NH_2)_2CO$	700 mg	KCl	

Table 2: EDX analysis results

Element	*K:N molar ratio*			
	0.0	*0.5*	*1.0*	*Standard struvite*
	(Weight %)			
C	29.44	30.34	26.22	-
O	45	39.26	40.5	-
Mg	8.5	10.17	11.65	9.9
N	4.67	3.82	3.58	5.7
P	11.88	14.54	14.88	12.6
K	-	1.57	2.7	-
Na	0.51	0.3	0.47	-

than struvite-K. Apparently, the current results match well with previous studies.

SEM-EDX Analysis

The samples with K:N molar ratio of 0.0, 0.5 and 1.0 were analyzed by SEM-EDX. The SEM images (Figures 2a-c) showed elongated crystals in Figure 2a (K:N = 0), while crystals were needle-shaped in Figures 2b and 2c (K:N = 0.5 and 1.0 respectively). In addition, crystals in Figure 2a has smoother surface, indicating that more pure struvite was probably crystallized. It is worth mentioning that struvite crystals could have different shapes such as cube granules (Cho et al., 2009), rod shaped (Hutnik et al., 2013), needle shape (Zhang et al., 2016) and irregular shape (Zhang et al., 2009). The results of EDX presented in Table 2 indicate that N content was reduced in the precipitates obtained with K:N molar ratio of 0.5 and 1.0, which means that struvite purity was quite lowered. Obviously, this was probably due to the formation of K compounds such as $MgKPO_4.6H_2O$ besides $MgNH_4PO_4.6H_2O$, which competed with MAP formation.

Conclusion

Recovery of NH_4-N through MAP crystallization technique is a wide-spread approach that could achieve high efficiencies. However, the presence of foreign elements is a significant factor that should be considered while applying the process. Potassium can be found with high concentrations in different types of wastewater, such as landfill leachate. The current study investigated the effect of K on NH_4-N recovery from landfill leachate, and demonstrated that co-precipitation of K compounds could notably occur if K:N molar ratio

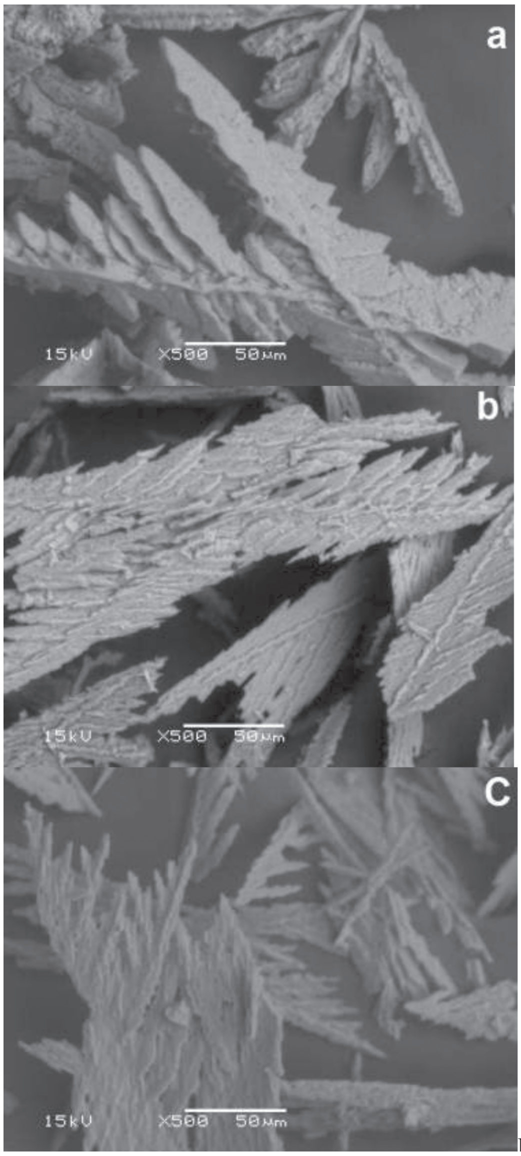

Figure 2: SEM images of the precipitates obtained with K:N molar ratios of 0.0 (a), 0.5 (b) and 1.0 (c).

is higher than 0.2. In addition, SEM-EDX analysis results showed that K was co-precipitated in parallel with struvite.

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