Nitrogen recovery from a stabilized municipal landfill leachate

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A B S T R A C T

The present paper reports the results of an investigation aimed at evaluating the effectiveness of magnesium ammonium phosphate precipitation (MAP), commonly called struvite, for removing ammonia from a mature municipal landfill leachate. MAP precipitation was carried out at laboratory scale by adding phosphoric acid and magnesium oxide as external sources of phosphorus and magnesium, respectively, and regulating the pH at 9.0. The effect of Mg:NH\textsubscript{4}:PO\textsubscript{3} molar ratio was studied. Due to the low solubility of MgO, a low ammonia removal efficiency (i.e. 67%), with a rather high residual concentration, was obtained when the stoichiometric molar ratio was applied. However, by doubling the amount of magnesium oxide (i.e. by using a molar ratio of 2:1:1), ammonia removal efficiency increased up to 95% with a residual concentration compatible with a successive biological treatment. The struvite produced in the present study showed a composition close to the theoretical one. Furthermore, the precipitate was characterized by a heavy metal content much lower than that of typical raw soil, excluding any concern about heavy metal contamination in the case of its use as a fertilizer. The economic analysis of the process showed that ammonia can be removed at a cost of 9.6 €/kg NH\textsubscript{4}–N\textsubscript{removed}. This value can be greatly reduced, however, if the value of the struvite produced is considered.

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1. Introduction

Municipal landfill leachates, resulting from the percolation of rainwater through solid waste, are considered one of the types of wastewater with the greatest environmental impact because of high concentrations of ammonium, salts and organic matter. Usually, ammonia removal represents the step of greatest concern because of its high concentration and the salinity of leachate wastewater. The conventional nitrification–denitrification biological process, widely used for ammonium removal from municipal and industrial wastewater, is not very suitable for treating leachates. Since the latter are characterized by high levels of ammonia, they require high hydraulic residence times (and thus large reaction volumes), in order to reduce the toxicity due to ammonia to a low level. Furthermore, the high salinity and lack of sufficient electron donors, especially in stabilized leachates, are additional obstacles to nitrification–denitrification biological treatment. In a previous study aimed at evaluating the effectiveness of biological nitrogen removal for treating a mature municipal landfill leachate, the authors obtained a low ammonia removal efficiency (i.e. 20%) even given a long hydraulic residence time (20 days) (Di Iaconi et al., 2006).

Due to its high effectiveness, reaction rate, simplicity and environmental sustainability, the precipitation of ammonium by struvite formation is a valid alternative for the removal of high ammonium concentrations from leachates. Struvite is a white crystalline compound composed of magnesium, ammonium and phosphorus in an equal molar ratio (i.e. MgNH\textsubscript{4}PO\textsubscript{3}.6H\textsubscript{2}O; magnesium ammonium phosphate hexahydrate). Moreover, struvite is a valuable fertilizer since it is a slow release source of nitrogen, magnesium and phosphorus (Booker et al., 1999; Caterell et al., 2000).

Ammonia removal by struvite precipitation has been widely applied for the pre-treatment of various wastewaters such as tannery effluents (Kabdasli et al., 2003; Tunay et al., 1997; Zengin et al., 2002), supernatants from anaerobic sludge digestion (Battistoni et al., 2001; Maqueda et al., 1994; Munch and Barr, 2001; Ohlinger et al., 1998; Siegrist, 1996), coking and nitrogen processing effluents (Zdybiewska and Kula, 1991), piggery effluents (Nelson et al., 2003; Webb and Ho, 1992; Wrigley et al., 1992), agro-industrial effluents (Altnbas et al., 2002) and human urine (Maurer et al., 2006). In contrast, few studies have addressed ammonia removal from landfill leachates by means of struvite precipitation (Güny et al., 2008; Kabdasli et al., 2000; Li et al., 1999; Zhang et al., 2009). This is probably due to the high operative costs of the process, which requires the addition of relatively expensive chemicals. In fact, leachates are characterized by low concentrations of magnesium and phosphorus and therefore external sources of these compounds are required. Nevertheless, in the case

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of stabilized leachates, characterized by high ammonium concentrations and very low BOD/COD ratios, the process could potentially compete even with the cheapest existing method (i.e. biological removal) since in the latter a huge amount of carbon from an expensive external source is required.

The present paper reports the results of an investigation aimed at evaluating the effectiveness of ammonia removal via struvite as a pre-treatment stage of mature municipal landfill leachates, by adding phosphoric acid and magnesium oxide as external sources of phosphorus and magnesium, respectively. An economic evaluation of the applied process is also reported.

2. Methods

2.1. Leachate composition

The study was carried out using the leachate (the composition of which is reported in Table 1) from a mature municipal landfill located in Apulia, a region of southern Italy.

2.2. Chemicals for struvite precipitation

Magnesium ammonium phosphate (MAP), commonly called struvite, forms according to the following reaction:

\[
\text{Mg}^{2+} + \text{PO}_4^{3-} + \text{NH}_4^+ + 6\text{H}_2\text{O} \rightarrow \text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O} \tag{1}
\]

Taking into account the very low solubility of struvite (pKs = 12.6), it can be completely separated from the liquid phase.

Looking at Eq. (1), a Mg:\text{NH}_4:PO_4 stoichiometric molar ratio of 1:1:1 results. Municipal landfill leachates generally contain a low concentration of both magnesium and phosphorus (see also Table 1) so that an external source of these compounds must be added. Three types of magnesium sources are usually used in the precipitation of MAP: MgSO_4, MgCl_2 and MgO. MgSO_4 and MgCl_2 are more widely used than MgO, because of their lower cost, faster dissociation and shorter reaction time. However, since MgCl_2 and MgSO_4 release huge amounts of salts (chlorides and sulphates, respectively), had they been used in the present study, they would have made the subsequent biological treatment impossible. Therefore, MgO was used, since it does not cause any increase in wastewater salinity. As for the phosphorus source, H_3PO_4 was used because of its low cost in comparison with phosphorus salts such as Na_2HPO_4 or Ca(H_2PO_4)_2.

2.3. Experimental set-up and operative conditions

The success of the struvite precipitation process depends mainly on two factors: pH value of the precipitation and the molar ratio of Mg:NH_4:PO_4.

MAP precipitation was carried out at pH 9.0, taking into consideration not only the high alkalinity value typical of aged leachates (which makes it difficult to vary the pH), but also the pH range required to obtain minimum struvite solubility (i.e. 9.0–10.7) (Booker et al., 1999; Nelson et al., 2003; Ohlinger et al., 1998) and to carry out the subsequent biological treatment (i.e. 7.5–8.5).

As for the Mg:NH_4:PO_4 molar ratio, a series of batch investigations was conducted. In particular, four molar ratios (i.e. 1.1.1, 1.5:1:1, 2.1:1 and 2.5:1:1) were investigated. MgO (technical grade) in fine powder form and H_3PO_4 (75%) were used as magnesium and phosphorus sources, respectively; NaOH (30%) was added to control the pH value. The MAP precipitating tests were carried out at laboratory scale by means of the experimental set-up consisting in 1 L beaker, a magnetic stirrer, a pH control and a double-channel pump for dosing NaOH and H_3PO_4, respectively.

First the required amount of MgO was slowly added to the leachate in the beaker under mixing while the pH increased from 8.5 (i.e. the natural value) up to 9.2–9.5 as result of the alkaline properties of magnesium oxide. Successively, the required volume of H_3PO_4 was dosed by means of a peristaltic pump at a flow rate of 30 mL/h with consequent decrease in pH value; NaOH solution was added when the pH dropped to a value of 9. Once the whole volume of phosphoric acid had been added, the content of the beaker was stirred slowly until equilibrium was achieved (i.e. for 30 min) after which the mixing was stopped and the contents allowed to settle for 60 min. Finally, the composition of the supernatant and precipitate were determined after filtration on filter paper and drying in an oven at 40 °C (in order to minimize ammonia loss) until a constant weight was obtained (i.e. for 48 h), respectively.

2.4. Analytical methods

Chemical oxygen demand (COD), biochemical oxygen demand (BODs), total Kjeldahl nitrogen (TKN), total suspended solids (TSS), volatile suspended solids (VSS), ammonia, pH, total phosphorus (P-tot), phosphate (PO_4^{3-}), alkalinity, sulphates and chlorides were determined according to standard methods (APHA, 1999). Dissolved organic carbon (DOC) was measured by means of a carbon analyzer Shimadzu Co., Japan (model 5050). Absorbable organic halogen compounds (AOX) were measured according to the method ISO/FDIS 9562 “Determination of adsorbable organically bound halogens (AOX), 2004”. Volatile organic compounds (VOCs) were measured by head-space solid phase micro extraction coupled with gas chromatography–mass spectrometry (HS-SPME/GC/MS). Linear alkylbenzenesulfonate (LAS) was measured by means of the methylene blue method (APHA, 1999). Metal concentrations were measured by inductively coupled plasma optical emission spectroscopy (ICP-OES) analysis, using an Optima 3000 instrumentation (Perkin–Elmer). In the case of struvite, the metals were determined after acidic digestion.

3. Results and discussion

Fig. 1 reports the residual ammonia concentration in the supernatant as well as its removal efficiency as a function of the Mg:NH_4:PO_4 molar ratio. It can be seen that using the stoichiometric molar ratio an ammonia removal efficiency of 67% was obtained, with a residual concentration in the supernatant of

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Table 1

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>COD</td>
<td>9.7 g/L</td>
<td>AOX</td>
<td>6 mg/L</td>
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<td>CODsol^a</td>
<td>9.1 g/L</td>
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<tr>
<td>DOC</td>
<td>2.8 g/L</td>
<td>Chlorides</td>
<td>6.0 g/L</td>
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<tr>
<td>BODs</td>
<td>1.5 g/L</td>
<td>Cadmium</td>
<td>0.1 g/L</td>
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<td>BODs/COD</td>
<td>0.15</td>
<td>Copper</td>
<td>1.0 g/L</td>
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<tr>
<td>TSS</td>
<td>390 mg/L</td>
<td>Nickel</td>
<td>0.6 mg/L</td>
</tr>
<tr>
<td>VSS</td>
<td>220 mg/L</td>
<td>Lead</td>
<td>0.7 mg/L</td>
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<tr>
<td>TKN</td>
<td>2.7 g/L</td>
<td>Potassium</td>
<td>1.8 g/L</td>
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<tr>
<td>NH(_4)-N</td>
<td>2.6 g/L</td>
<td>Manganese</td>
<td>0.2 mg/L</td>
</tr>
<tr>
<td>P-tot</td>
<td>2.5 g/L</td>
<td>Zinc</td>
<td>0.5 mg/L</td>
</tr>
<tr>
<td>Conductivity</td>
<td>21 mS/cm</td>
<td>Magnesium</td>
<td>212 mg/L</td>
</tr>
<tr>
<td>pH</td>
<td>8.5</td>
<td>Chromium</td>
<td>1.2 mg/L</td>
</tr>
<tr>
<td>Alkalinity (as CaCO(_3))</td>
<td>16.1 g/L</td>
<td>Calcium</td>
<td>290 mg/L</td>
</tr>
<tr>
<td>VOCs</td>
<td>1.5 mg/L</td>
<td>Sulphates</td>
<td>1.8 g/L</td>
</tr>
<tr>
<td>LAS</td>
<td>11 g/L</td>
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</table>

^a Filtered on 0.45 µm filter.
830 mg/L. This limited removal efficiency value, however, could be ascribed to the low dissolution of MgO in the leachate leading to low MAP precipitation efficiency.

This is confirmed by the data shown in Fig. 2, which shows the residual magnesium and phosphate concentrations in the supernatant at each molar ratio. In fact, it can be observed that at the stoichiometric molar ratio, the magnesium concentration measured in the supernatant was very low (lower than 2 mg/L), while the phosphorus concentration was as high as 2274 mg/L, indicating a deficiency of magnesium only.

By doubling the magnesium dose (i.e. changing the molar ratio from 1:1:1 to 2:1:1), an increase in ammonia removal efficiency was achieved, passing from 67% to 95% efficiency. Moreover, it can also be seen from Fig. 2 that, at this molar ratio range, the residual magnesium concentration in the supernatant remained very low, indicating that the efficiency of the struvite precipitation depended on the amount of MgO added, at least up to a molar ratio of 2:1:1.

It is interesting to observe, however, that at a molar ratio of 2:1:1, the whole amount of MgO and H₃PO₄ which had been added was completely consumed during the precipitation process. This is very important in cases where enhanced phosphorus removal in the subsequent biological treatment is not foreseen.

Two other important aspects of the MAP precipitation process are the amount of struvite formed and the chemicals consumed.

As regards the amount of MAP precipitated, Fig. 3 shows the theoretical and experimental amount of dried struvite produced per m³ of leachate at each investigated molar ratio value. Theoretical struvite is the amount of precipitate that one would expect on the basis of ammonia removals shown in Fig. 1, whereas the experimental struvite is the amount of precipitate actually weighed during the tests. Looking at Fig. 3, it is possible to note that the amount of struvite produced increases with the increase in the molar ratio (i.e. from 30 kg at the stoichiometric molar ratio to 60 kg/m³ of leachate at a molar ratio of 2.5:1:1.1) because of the increased quantity of removed ammonia. In addition, this figure highlights a difference between the theoretical and experimental struvite values, probably due to the presence in the latter of other precipitates. The data regarding excess MgO, also reported in Fig. 3, confirm this hypothesis; in fact, the difference between the amounts of experimental and theoretical struvite increases with the increase in molar ratio, almost in direct proportion with the amount of magnesium oxide overdosed. Therefore, as the molar ratio increases, the degree of pureness of the struvite decreases, as a result of undissolved MgO. The pureness can be improved, however, by dissolving the precipitate in acid conditions (the impurities and MgO remaining undissolved can be removed by centrifugation) and then precipitating it again by raising the pH.
As for the amount of chemicals consumed, Fig. 4 shows the chemical consumption at each investigated molar ratio. It can be seen that the MgO and NaOH consumptions show opposite trends. In particular, an increase in the amount of magnesium oxide results in a decrease in NaOH volume. This is simply due to the alkaline properties of magnesium oxide, which consequently reduce the NaOH volume needed for fixing the pH at 9.0. However, at molar ratio values higher than 2:1:1, the saving in NaOH volume becomes smaller in proportion compared with the increase in the amount of MgO added. In fact, Fig. 4 clearly shows that the slope of the NaOH line decreases for molar ratio values higher than 2:1:1.

On the basis of the data reported in Figs. 1 and 4, and considering that the residual ammonia concentration in the supernatant at a molar ratio of 2:1:1 (i.e. about 130 mg/L) is compatible with a successive biological treatment, there is a strong indication that this molar ratio should be chosen for MAP precipitation. Chemical characterization of the struvite obtained was also carried out in order to evaluate its possible utilization as a fertilizer. Therefore, Table 2 reports the chemical composition of the struvite obtained at a molar ratio of 2:1:1.

In general, struvite is a white crystalline powder. However, in the present experiment, the MAP precipitate generated from the leachate was light brown in colour (see Fig. 5). This could be due to the co-precipitation of some organic compounds present in the leachate. The analysis of the COD content in the MAP precipitate confirmed this hypothesis; a content of 12 mg COD/gstruvite was obtained.

The analytical results reported in Table 2 indicate that the struvite obtained had a composition of 16.8% Mg, 4.6% N and 10.7% P. This composition, which is not far from the theoretical one (i.e. 9.9% Mg, 5.7% N and 12.6% P), is coherent with the mass balance of magnesium, ammonia and phosphorus. The higher magnesium content confirms the presence of MgO in the precipitate due to the limited solubility in water of this compound. The presence of potassium in the precipitate can be ascribed to MgKPO4 usually present during struvite precipitation (Lind et al., 2000; Wilsenach et al., 2007) whereas the low content of calcium excluded the formation of representative amounts of calcium phosphates that usually occurs when the precipitation is carried out at pH value above 9.5 (Doyle and Parsons, 2002).

As far as heavy metal content is concerned, an important aspect if the struvite obtained were to be used as a fertilizer, the results reported in Table 2 show a low content of all metals. Moreover, by comparing these values with those typical of Italian soils (Cr: 70; Cd: 0.6; Cu: 50; Zn: 110; Ni: 50; Pb: 18 mg/kg; Leita et al., 1998), it can be observed that the struvite produced in this study was characterized by a metal content much lower than that of raw soil. Therefore, there would be no need for concern regarding heavy metal contamination if the struvite were applied to the soil.

The economic evaluation of ammonia removal by struvite precipitation was carried out taking into account only the costs of the chemicals (i.e. MgO, H3PO4 and NaOH) and without considering energy and investment costs. In particular, Table 3 reports the results of the economic evaluation for the struvite produced by using a molar ratio of 2:1:1; the input data are also reported in this table.

From the data reported in Table 3 a cost of about 24 €/m3 of leachate results for chemicals addition. Due to both the high price and the amount of H3PO4 added, the cost of this chemical represents approximately 50% of the overall costs. NaOH could be replaced, however, by a cheaper source, such as Ca(OH)2, although the biggest saving could be obtained by using a cheaper phosphate source. Taking into account the amount of ammonia removed in the process (i.e. about 2.5 kg NH3–N per m3 of leachate), a specific cost of 9.6 €/kg NH3–Nremoved is obtained. This value, in accordance with those reported in the literature for other kinds of wastewater (Celen and Turker, 2001; Günay et al., 2008; Siegrist, 1996), is almost double that of the external carbon sources used in nitrification–denitrification biological processes. In fact, taking into account the low biodegradable organic matter content of the investigated leachate, the addition of 5–6 kg of an external carbon source would probably be required per kg of ammonia, with a cost approximately of 5 €/kg NH3–Nremoved. However, if the value of the struvite produced is considered in the economic analysis, then, ammonia removal by struvite precipitation could compete with the biological process.

### Table 2

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value (mg/kg)</th>
<th>Parameter</th>
<th>Value (mg/kg)</th>
</tr>
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<tr>
<td>COD</td>
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<td>Cadmium</td>
<td>&lt;dl</td>
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<td>NH4–N</td>
<td>46,200</td>
<td>Copper</td>
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<tr>
<td>PO4 3–</td>
<td>107,200</td>
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<tr>
<td>Magnesium</td>
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<td>45</td>
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<tr>
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<td>Lead</td>
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<tr>
<td>Calcium</td>
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<tr>
<td>Chromium</td>
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</tr>
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</table>

<dl: Detection limit.

### Table 3

<table>
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<tr>
<th>Economic analysis of the ammonia removal process by struvite precipitation.</th>
<th>Value (€/m3 of leachate)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cost for MgO addition (€/m3 of leachate)</td>
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</tr>
<tr>
<td>MgO added (kg/m3 of leachate)</td>
<td>15</td>
</tr>
<tr>
<td>MgO price (€/kg)</td>
<td>0.6</td>
</tr>
<tr>
<td>Cost for H3PO4 (75%) addition (€/m3 of leachate)</td>
<td>12.3</td>
</tr>
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<td>H3PO4 (75%) added (L/m3 of leachate)</td>
<td>15.4</td>
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<tr>
<td>H3PO4 (75%) price (€/L)</td>
<td>0.8</td>
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<tr>
<td>Cost for NaOH (30%) addition (€/m3 of leachate)</td>
<td>2.8</td>
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<tr>
<td>NaOH (30%) added (L/m3 of leachate)</td>
<td>13.9</td>
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<tr>
<td>NaOH (30%) price (€/L)</td>
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<tr>
<td>Cost for chemicals (€/m3 of leachate)</td>
<td>24.1</td>
</tr>
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</table>

4. Conclusions

The results obtained during an investigation aimed at evaluating the effectiveness of ammonia removal by struvite precipitation as a pre-treatment stage of a mature municipal landfill leachate show that a Mg:NH4:PO4 molar ratio of 2:1:1 is required for a satisfactory ammonia removal (i.e. 95%). The struvite produced was
characterized by a heavy metal content much lower than that of typical raw soil, indicating that it could be used as fertilizer. Finally, the economic evaluation of ammonia removal by struvite precipitation showed that the process could compete with biological nitrogen removal if the struvite were used as a fertilizer.

Acknowledgements

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