



Utilization of landfill leachate parameters for pretreatment by Fenton reaction and struvite precipitation—A comparative study

J. Kochany^{a,*}, E. Lipczynska-Kochany^b

^a Conestoga-Rovers & Associates, 111 Brunel Road, Mississauga, ON L4Z 1X3, Canada

^b Environmental Consultant, 30 Elm Dr. East, Suite #918, Mississauga, ON L5A 4C3, Canada

ARTICLE INFO

Article history:

Received 25 June 2008

Received in revised form 9 November 2008

Accepted 10 November 2008

Available online 17 November 2008

Keywords:

Landfill leachate
Struvite precipitation
Fenton reagent
Respirometry

ABSTRACT

This paper reports results of laboratory studies on two pretreatment methods, struvite precipitation using aeration with H_3PO_4 and Fenton oxidation. These methods utilized specific properties of the leachate: high magnesium content (172 mg L^{-1}) for struvite precipitation and a high iron concentration (56 mg L^{-1}) for Fenton treatment. Struvite precipitation (H_3PO_4 , 700 mg L^{-1}) removed 36% of $\text{NH}_3\text{-N}$ and 24% of SCOD. Fenton treatment (at pH 3.5) required 650 mg L^{-1} of H_2O_2 and removed 66% of SCOD. The effect of each pretreatment on the returned activated sludge (RAS) was evaluated using respirometry. Both methods reduced the inhibitory effect of the leachate and substantially increased biokinetic parameters. The BOD_5/SCOD ratio increased from 0.63 for raw leachate to 0.82 (struvite) and 0.88 (Fenton). Estimation of capital and operational costs of the total leachate treatment indicated that aeration with struvite precipitation, followed by biological treatment, would be the preferred option.

© 2008 Elsevier B.V. All rights reserved.

1. Introduction

Leachates are generated at any landfill by the contact of water with wastes and they create a great potential for an environmental harm. Their quantity and quality depends on a number of factors: the type of deposited wastes, hydrogeologic conditions, as well as the age of the landfill and the phase of waste decomposition. Leachates are characterized by a high content of organic matter (expressed as COD, BOD_5 and TOC), a high concentration of ammonia ($\text{NH}_3\text{-N}$) and inorganic salts [1–4].

Due to the weather conditions and a combination of physical, chemical and biological processes in the landfill, the composition of a leachate, particularly that from an active landfill, can fluctuate over both short and long term [3,4]. Therefore the leachate treatment system must be flexible enough to produce the same quality effluent despite the variations in the strength of the leachate. Such flexibility can be achieved using a combination of physical, chemical and biological methods [5–10].

Advanced oxidation processes (AOPs) have been the subject of a growing attention as attractive means to reduce organic load and to improve the biodegradability of recalcitrant organic contaminants in the mature leachate [8–10]. Fenton and Fenton like processes generating hydroxyl radicals ($\cdot\text{OH}$) via reaction of Fe^{2+}

(or Fe^{3+}) ions with H_2O_2 , have been used for the past 10–15 years for the oxidation of organic contaminants of wastewater [11–13]. However, this approach to the leachate treatment is relatively new. Recently, the Fenton reaction and its modifications have been studied for their application as a pretreatment or a post-treatment step in biological treatment or as a separate leachate treatment [8,9,14–19].

Struvite (magnesium ammonium phosphate hexahydrate ($\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$) precipitation was originally perceived as a phenomenon to be controlled or eliminated because it can be a nuisance during the operation of sewage treatment plants and other processes where high concentrations of ammonium, phosphate and magnesium ions occur. However, in the past 10 years the struvite precipitation has gained a considerable amount of interest as an attractive method of removing and recovering phosphorus from wastewater [20,21].

It has recently been proposed that the $\text{NH}_3\text{-N}$ concentration in leachate can be significantly reduced by struvite precipitation and a number of reports on the application of the struvite precipitation as a leachate pre- or post-treatment [7,10,22] have been published.

This paper describes results of treatability studies on the applicability of the Fenton reaction (to reduce organic load) and precipitation of struvite (to remove ammonia) as pretreatment steps before the subsequent biological (aerobic) treatment of a leachate from an active municipal landfill. The effect of both methods on the activity of the activated sludge (RAS) has been studied using respirometry.

* Corresponding author. Tel.: +1 905 712 0510; fax: +1 905 712 0515.
E-mail address: jkochany@crowworld.com (J. Kochany).

2. Materials and methods

2.1. Materials

Leachate samples for the studies were collected from an old cell and new cell collection system and were mixed in the ratio to be representative for the influent to the leachate treatment plant.

Biomass for respirometric studies was the returned activated sludge (RAS) from a local municipal treatment plant. RAS was acclimatized for three weeks to a mixture of leachate and sewage before biological tests. Sewage for the leachate dilution in respirometric tests was collected from the same municipal treatment plant. Samples of the leachate and sewage were analyzed for parameters which are shown in Table 1.

All chemicals used in this study were analytical grade and purchased from Anachemia Science, Lachine, QC, Canada. Oxygen for respirometric tests was medical grade from Proxair, Mississauga, ON, Canada. Cationic polyacrylamide flocculant (Nalcolyte 8105) was from Nalco Canada (Burlington, ON).

2.2. Methods

2.2.1. Precipitation and aeration

Precipitation tests were carried out at room temperature (22 °C) in 1-liter beakers equipped with stone aerators connected to a laboratory air-pump (ELITE 803, Rolf C. Hagen, Montreal, QC, Canada). Air flow to the treated leachate was adjusted at 400 mL per min (air/water ratio ~50:1). 500 mL samples of leachate were treated with the pre-determined doses of 10% H₃PO₄ and aerated for 60 min. Then the aeration was discontinued and solids were allowed to settle for 30 min. The amount of NH₃-N removed by the air stripping was determined in the same way, except that no H₃PO₄ was added. Samples of the supernatant were analyzed for pH, phosphate, soluble carbon oxygen demand (SCOD) and NH₃-N.

2.2.2. Fenton treatment

Fenton treatment was conducted at room temperature (22 °C) using a six paddle mixer (Phipps & Bird, Model 7790, Richmond, VA, USA). Initially the pH of the leachate was adjusted to 3.5 using 1.0 N H₂SO₄. It was monitored using a laboratory pH meter with a combination electrode (ThermoOrion Model 5625, Cole-Parmer, Vernon

Hills, IL). Then predetermined volumes of 20% H₂O₂ were added and mixing was continued for 60 min. After the reaction was completed, the mixture was neutralized using 10% of NaOH and 5 mg L⁻¹ of flocculant was added. Solids were allowed to settle for 30 min. Samples of the supernatant were analyzed for SCOD and NH₃-N. Optimum H₂O₂ dose was determined based on the efficiency of SCOD removal.

2.2.3. Analyses

Tests (with the same dose of each chemical) were conducted in triplicate, analyses of the supernatant were duplicated and the results were averaged. All analyses of leachate samples, during the studies reported in this paper, were conducted according to Standard Methods procedures [23]. Experimental error (%) was in the following ranges: pH: 2–3, NH₃-N: 4–7.5, phosphate: 8–12, struvite: 7–12, SCOD: 5–8, TSS: 6–11, and TDS: 3–5.

2.2.4. Respirometric tests

The respirometric system used in the study included Comput-OX, N-CON 12 channel respirometer connected to a PC with CTOX computer program (N-CON Systems Co., Crawford, GA, USA) and 12 reactors, each 1-liter volume, connected to a pure oxygen supply system. Reactors were kept in a water bath with a precision temperature control ±0.5 °C, set up at 22 °C. The content of respirometric reactors was mixed with magnetic mixers to ensure their homogeneity. The system recorded mass and volume of oxygen as well as the time when it was delivered to each reactor.

During each respirometric test 10 reactors contained 10 mL of RAS and various concentrations (2–100%) of investigated leachate in sewage. Two control reactors contained RAS in sewage without leachate and leachate without RAS, respectively. Two tests were conducted for raw leachate and for the leachate pretreated with H₃PO₄ and H₂O₂. Averaged results from two tests with the same set up were used for biokinetic calculations. Reactor contents were analyzed for TSS, VSS, SCOD and NH₃-N. Respirometric data were analyzed using the procedure developed by Rozich and Gaudy [24].

2.2.5. Statistical analysis of the biochemical data fitting

Non-linear regression and biokinetic constants were calculated using Mathcad 2001 computer program (MathSoft Inc. Cambridge, MA). Statistical analysis of the biokinetic data fit to the Monod and Haldane models was conducted applying the *F*-test (variance analysis) at 5% significance level. The upper critical value of *F* distribution (3.726) was obtained from the e-Handbook of Statistical Methods [25].

3. Results and discussion

3.1. Leachate characteristics

Leachate samples were collected from an active municipal landfill, expected to operate for the next 15 years. They were generated from old and new cells and were mixed in the ratio to be representative for the influent to the leachate treatment plant. The mixed leachate samples will be hereafter called the leachate.

As shown in Table 1, the leachate contained high concentrations of organic (SCOD = 5700 mg L⁻¹; TOC = 1650 mg L⁻¹) and inorganic substances, mainly sodium, potassium, calcium and magnesium chlorides as well as ammonia (NH₃-N = 530 mg L⁻¹). Based on these parameters and on results of respirometric experiments, which suggested that the leachate had an inhibitory effect on RAS, it was expected that a biological treatment should be preceded by a chemical pretreatment. The purpose of the pretreatment was to mitigate the inhibition of biological processes (described in section 3.5 herein) and to reduce the organic and/or ammonia load. At the

Table 1
Leachate parameters and discharge limits.

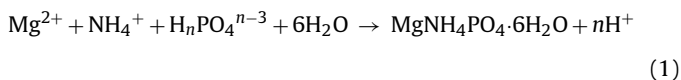
Parameter (mg L ⁻¹)	Leachate	Sewage	Limit ^a
pH (St. Units)	7.8 ± 0.3	7.3 ± 0.2	6.5–9.0
Alkalinity (mg CaCO ₃ L ⁻¹)	2800 ± 00	180 ± 5	–
TDS	9600 ± 200	360 ± 10	–
TSS	105 ± 5	18 ± 2	10
VSS	70 ± 5	12 ± 2	–
BOD ₅	3600 ± 200	138 ± 10	20
SCOD	5700 ± 300	162 ± 10	50
TOC	1650 ± 50	56 ± 5	–
TKN	590 ± 10	16 ± 2	2.0
NH ₃ -N	530 ± 10	12 ± 2	1.0
NO ₃ -N	0.8 ± 0.2	0.6 ± 0.1	–
T-Phosphorus	8.5 ± 0.5	3.2 ± 0.2	0.5
Phenols	2.6 ± 0.4	<0.05	0.5
Calcium	520 ± 20	54 ± 0.5	–
Iron	56 ± 2	2.3 ± 0.5	0.1
Magnesium	172 ± 5	14 ± 2	–
Manganese	8.8 ± 0.3	<0.02	–
Potassium	710 ± 10	8 ± 2	–
Sodium	1300 ± 50	26 ± 3	–
Chloride	1360 ± 60	34 ± 3	–
Sulfate	280 ± 5	10 ± 1	–

^a Ontario Ministry of the Environment Water Quality Objectives www.ene.gov.on.ca/envision/techdocs—accessed August 2008.

same time the addition of chemicals during the pretreatment had to be limited.

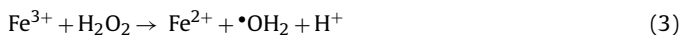
3.2. Selection of pretreatment methods

Two chemical treatment methods were selected for further testing: struvite [26,27] precipitation (using aeration with H_3PO_4) and the Fenton reaction. The first method could use high concentration of magnesium ($Mg = 172 \text{ mg L}^{-1}$) to partially remove $NH_3\text{-N}$ in the form of struvite [Eq. (1)]:



where $n = 0, 1$ and 2 , as a function of pH.

The Fenton oxidation [11,13] could utilize iron ($Fe = 56 \text{ mg L}^{-1}$) present in the leachate mostly ($\sim 80\%$) in the dissolved, ferrous (Fe^{2+}) form. The general classic procedure of the Fenton reaction consists of the addition of hydrogen peroxide (H_2O_2) to a treated solution or a suspension, containing Fe^{2+} ions. The mechanism of the reaction includes many steps during which iron cycles between its $+2$ and $+3$ oxidation states [Eqs. (2) and (3)] and hydroxyl radicals ($\cdot OH$), electrophilic oxidants reacting with most organic contaminants at near diffusion-controlled rates [11,13], are generated [Eq. (2)].



The overall reaction (3) is several orders of magnitude slower than the step (2), and thus the step (3) is the rate-limiting step [13]. Chemistry of the Fenton and Fenton-like systems is strongly dependent on the pH and Fe/H_2O_2 ratios [11,13]. Under real environmental conditions it is also influenced by many other factors, including the presence of anions [28], chelating agents [13] and humic substances [29].

The efficiency of both selected methods, the struvite precipitation and the Fenton reaction, depends on many factors including the initial concentrations of the reagents, pH, and the presence of inorganic and organic substances [13,21,28,29]. Thus, treatability studies were necessary to determine the optimum condition of each pretreatment and its potential effect on the subsequent biological process.

3.3. Struvite precipitation (aeration with H_3PO_4)

Struvite precipitation occurs when concentrations of magnesium, ammonium and phosphate ions exceed the solubility product K_{sp} [26,27,30]. Since the molar ratio of $Mg : NH_4 : PO_4$ in struvite is $1 : 1 : 1$, the component existing at the lowest concentration decides about the removal of two others. Concentrations of Mg and PO_4 in the leachate were much lower ($Mg \sim 172 \text{ mg L}^{-1}$, $T\text{-P} \sim 8.5 \text{ mg L}^{-1}$) than the $NH_3\text{-N}$ content (530 mg L^{-1}). An addition of phosphate could not be avoided because, based on $BOD_5 = 3600 \text{ mg L}^{-1}$, 36 mg L^{-1} of P (or 110 mg L^{-1} PO_4) was necessary to meet the biological treatment requirement. Thus the Mg concentration limited removal of $NH_3\text{-N}$ as struvite. Theoretical phosphate demand for the struvite precipitation from the leachate, calculated from the equation (1) was 673 mg L^{-1} . H_3PO_4 doses in the range of $400\text{--}1000 \text{ mg L}^{-1}$ were therefore tested.

Struvite precipitation is strongly pH dependent, being effective at pH values from 8 to 10.7 [26]. As it can be seen from Eq. (1), formation of struvite leads to the pH decrease. The investigated leachate had a high buffering capacity (alkalinity $\sim 2800 \text{ mg CaCO}_3 \text{ L}^{-1}$) but it was not sufficient to compensate for the addition of H_3PO_4 . In order to keep the pH in the desired range, aeration was

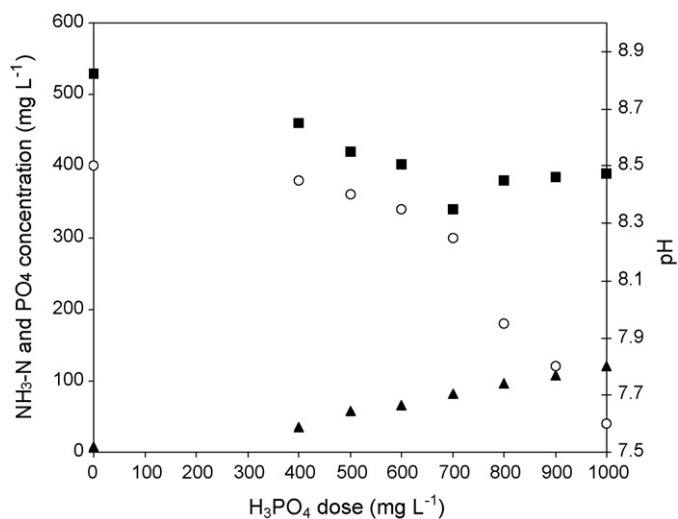


Fig. 1. Impact of H_3PO_4 dose on the pH (○) as well as on the $NH_3\text{-N}$ (■), and the residue phosphate (▲) concentration after 60 min of aeration.

applied. During the aeration, dissolved carbon dioxide was stripped out from the leachate, increasing pH. Aeration also provided mixing of the leachate and oxidation of iron Fe^{2+} to iron Fe^{3+} which precipitated as ferric species, removing some co-precipitated and adsorbed organics, decreasing SCOD.

The initial tests indicated that the optimum aeration time was 60 min. Longer aeration had a negligible effect on $NH_3\text{-N}$ and SCOD removal, while after a shorter aeration the precipitated solids did not settle well and a flocculent addition was necessary. Fig. 1 demonstrates that, after 60 min of aeration, the leachate pH was in the range of 8.7–8.3 when the H_3PO_4 doses were lower than 700 mg L^{-1} .

As shown in Fig. 2, about 5% of $NH_3\text{-N}$ was removed by aeration alone, due to air-stripping. The SCOD level was reduced by about 18% what probably resulted from a combination of air stripping and removal of organic pollutants together with precipitated iron/calcium oxides and carbonates.

As presented in Figs. 1 and 2, the minimum $NH_3\text{-N}$ concentration (the highest $NH_3\text{-N}$ removal, $\sim 36\%$) was achieved when H_3PO_4 dose 700 mg L^{-1} ($Mg/PO_4 \sim 1 : 1$), was applied. About 30% of this removal was related to the struvite precipitation. At higher H_3PO_4 doses the

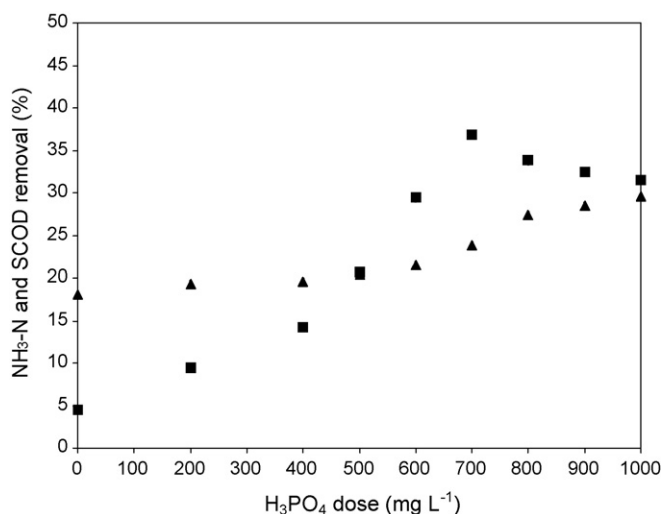


Fig. 2. Impact of the H_3PO_4 dose on the $NH_3\text{-N}$ (■) and SCOD (▲) removal after 60 min of aeration.

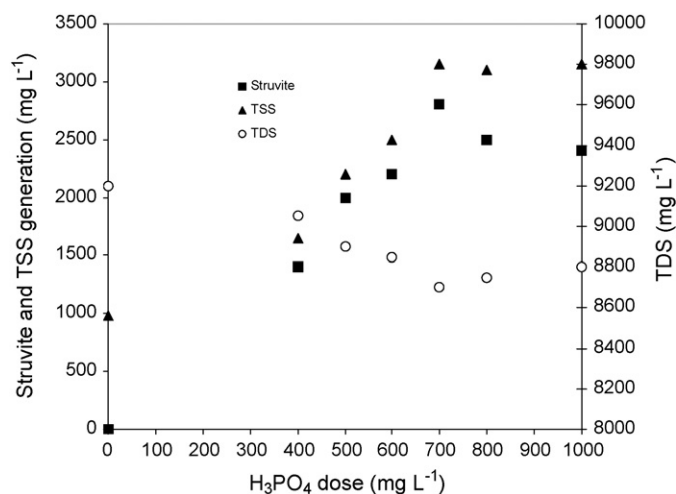


Fig. 3. Relation between the H₃PO₄ dose and TSS (▲), TDS (○) and struvite (■) generation after 60 min aeration.

pH value dropped to about 7.6 and the NH₃-N removal decreased, while SCOD removal (~24% at 700 mg L⁻¹) increased up to ~30% (at 1000 mg L⁻¹ H₃PO₄, Fig. 2).

The impact of the H₃PO₄ dose on the generation of struvite, total suspended solids (TSS) and total dissolved solids (TDS) is presented in Fig. 3. Struvite concentration in the precipitated solids was calculated based on the NH₃-N removal, subtracting the removal caused by air stripping. When the H₃PO₄ dose increased over 400 mg L⁻¹, struvite became the main component of TSS and reached the maximum at 700 mg L⁻¹ dose. At higher H₃PO₄ doses, struvite was predominant but not the only precipitated species. Fig. 3 shows that, while struvite concentration decreased, the TSS did not.

The investigated leachate had a high alkalinity (2800 mg L⁻¹) and it contained significant amount of calcium (520 mg L⁻¹) and iron (56 mg L⁻¹). Calcium ions react with phosphate or carbonate ions to form calcium phosphates or calcium bicarbonate [27], iron precipitates as oxides/hydroxides and/or phosphate. Formation of these species likely contributed to the observed TSS generation at H₃PO₄ doses higher than 700 mg L⁻¹ (Fig. 3). Co-precipitation of organic substances with iron and calcium phosphates was probably responsible for the enhanced SCOD removal on increasing the H₃PO₄ doses, shown in Fig. 2.

3.4. Fenton treatment

While Fe²⁺ salts are soluble at both acidic and neutral pH, as pH increases, Fe³⁺ ions undergo hydrolysis. The resulting oxides and hydroxides do not re-dissolve readily and do not participate in the reduction steps including the step (3). Soluble Fe²⁺ salts tend to co-precipitate with the Fe³⁺ oxy/hydroxides if both ions are present at neutral pH.

Degradation of pollutants by the Fenton reaction is therefore most effective in acidic solution (pH~3) which keeps Fe³⁺ species soluble [11,13].

Due to the high buffering capacity of the studied leachate, a large amount of acid was necessary to achieve the required pH 3.5, but no further pH adjustment during the reaction was necessary. The leachate contained significant amounts of anions (Table 1), known scavengers of •OH radicals [31] and inhibitors of the Fenton reaction [28]. The requirement for some excess of H₂O₂ was therefore expected and its dose had to be determined experimentally.

As it can be seen from Fig. 4, the highest SCOD removal/H₂O₂ ratio was observed when ~650 mg L⁻¹ H₂O₂ (mass ratio Fe/H₂O₂

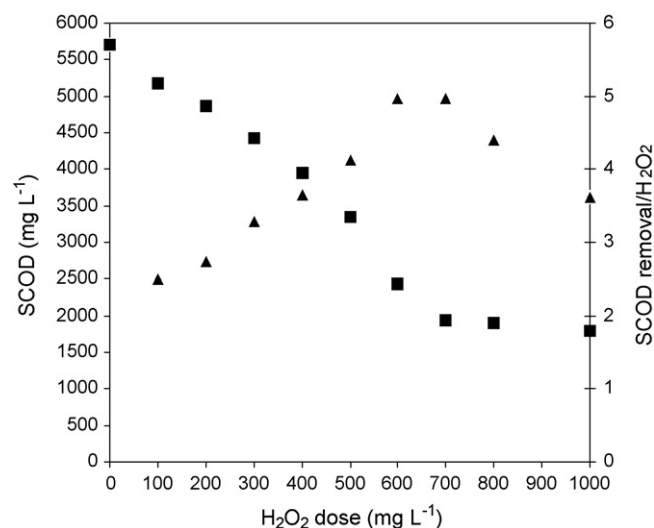
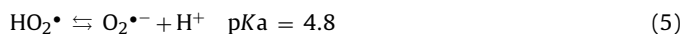
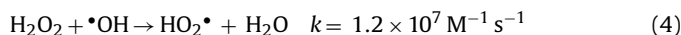


Fig. 4. Impact of the H₂O₂ dose on the SCOD (■) concentration and on the ratio of the SCOD removed/H₂O₂ (▲), 60 min, pH 3.5.

~1: 12; molar ratio ~1:19) was applied. It corresponded to the H₂O₂/SCOD and Fe/SCOD mass ratios of ~1:9 and ~1: 100, respectively. Under this condition, the SCOD level was reduced by ~66%, but no NH₃-N was removed (Fig. 5). On further increasing the H₂O₂ doses (>700 mg L⁻¹) the ratio of the SCOD removed to H₂O₂ applied decreased (Fig. 4). This effect was related to the reaction [Eq. (4)] between H₂O₂ and •OH (oxidizing radicals formed in the Eq. (2)) and in the change of the mechanism [11,13], resulting in the removal of both reagents in step (4) and in the production of reducing agents: superoxide anion O₂^{•-} [Eq. (5)] and hydroxyperoxide anion HO₂⁻ [Eq. (6)]:



3.5. Respirometric tests

The rate of aerobic respiration is directly related to the substrate removal and the biomass growth. Measurements and interpretation of biological oxygen consumption under well-defined conditions

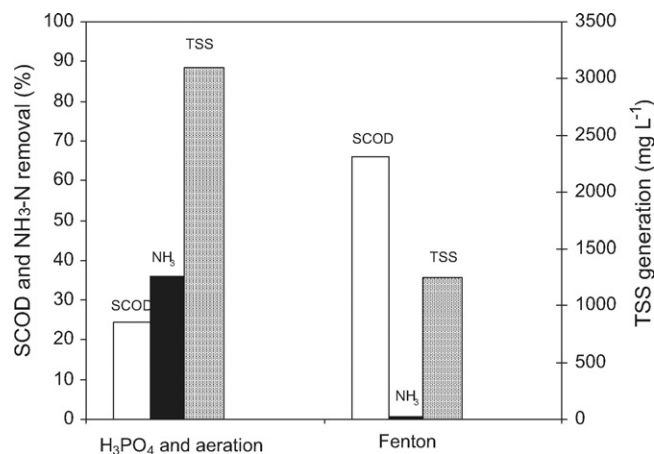


Fig. 5. Comparison of the removal of SCOD (1) and NH₃-N (2) and generation of TSS (3) during aeration with H₃PO₄ (700 mg L⁻¹) and the Fenton reaction (650 mg L⁻¹ H₂O₂, pH 3.5), time 60 min.

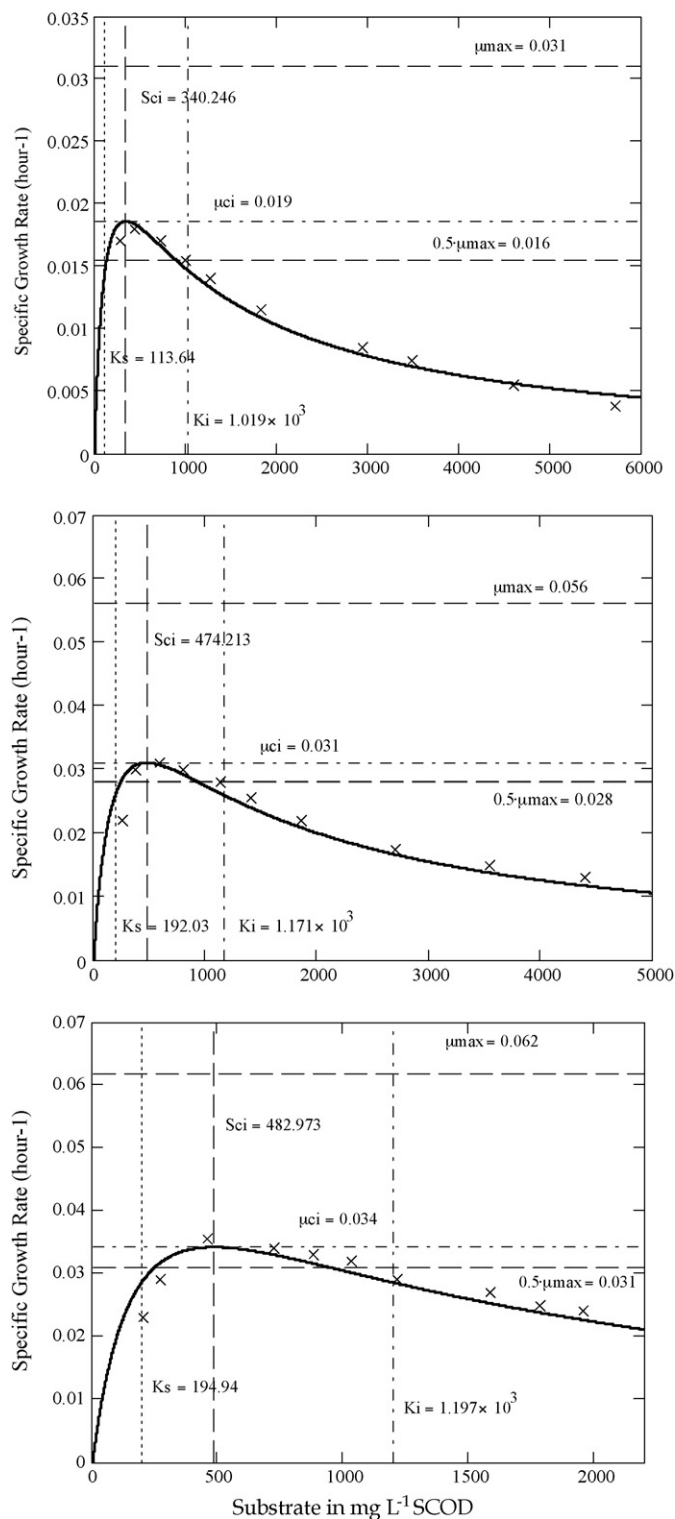


Fig. 6. Non-linear regression (Haldane) curves for the raw leachate (upper chart), leachate after aeration with 700 mg/L of H₃PO₄ (middle chart), and leachate after the Fenton (650 mg L⁻¹ H₂O₂, at pH 3.5) treatment (bottom chart).

are the basis of the aerobic respirometry [24]. This method was applied to evaluate the leachate effect on RAS. The respirometric oxygen uptake data obtained and the results of the chemical analyses of the reactors content were analyzed using the Monod and Haldane models and the following biokinetic parameters (shown in Fig. 6) were calculated using the procedure which has been

described in detail elsewhere [32]:

μ	specific growth rate calculated from respirometric data and chemical analyses
μ_{max}	maximum specific growth rate
μ_{ci}	critical rate constant, the practical maximum growth rate
Ks	saturation constant, SCOD concentration at $\mu = 0.5 \mu_{max}$
Ki	inhibition constant, SCOD concentration above which the system becomes upset
Sci	critical saturation constant, SCOD concentration for which μ_{ci} can be achieved

The results of the analysis did not comply with the Monod model for non-inhibitory wastes suggesting that, as in many other cases, the enzymatic transformations occurring in RAS were inhibited by the leachate contaminants. As it can be seen from Fig. 6 (upper chart) the non-linear regression curve obtained using data for the untreated leachate shows a very good fit ($F=415$, and residue sum of squares, $SS=6.3 \times 10^{-7}$) to the Haldane model, indicating an inhibitory effect of the raw leachate on RAS.

The critical saturation constant $Sci = 340.246 \text{ mg L}^{-1}$ SCOD, close to ~6% content of leachate means that a higher content would result in lowering the specific growth rate μ . Stronger inhibition was expected for the content of leachate of ~18%, corresponding to $Ki = 1019 \text{ mg L}^{-1}$ SCOD. These data suggested that for the biological treatment to be stable, a substantial dilution of the leachate (~6 times since leachate $SCOD = 5700 \text{ mg L}^{-1}$) would be necessary. Using the formula developed by Rozich and Gaudy [24] it was calculated that the required hydraulic retention time (HRT) of the biological system would be 5 days.

The next set of respirometric tests was conducted on the leachate aerated with 700 mg L⁻¹ of H₃PO₄ (struvite precipitation). Non-linear regression analysis of data from these tests is presented in Fig. 6 (middle chart). The biological system still complied with the Haldane model for inhibitory wastes ($F=41$, $SS=6.75 \times 10^{-6}$). However, the values of all the biokinetic parameters were higher than those for the non-pretreated leachate indicating that the inhibition was reduced. The critical growth rate $\mu_{ci}=0.031 \text{ h}^{-1}$ was higher than that for the raw leachate ($\mu_{ci}=0.019 \text{ h}^{-1}$). The critical saturation constant ($Sci = 474.213 \text{ g L}^{-1}$ SCOD) and the inhibition constant ($Ki = 1171 \text{ mg L}^{-1}$ SCOD) were also higher than those for the untreated leachate. It follows that for a stable operation of the biological system, less dilution of such pretreated leachate would be necessary, and the HRT would be 3.5 days.

Respirometric tests with the leachate pretreated with the Fenton reagent, which reduced the SCOD by 66% (Fig. 6, bottom chart) still complied with the Haldane model for inhibitory wastes ($F=28$, $SS=6.9 \times 10^{-6}$). The biokinetic parameters ($\mu_{ci}=0.034 \text{ h}^{-1}$, $Sci=482.973 \text{ mg L}^{-1}$ SCOD and $Ki=1197 \text{ mg L}^{-1}$ SCOD) were only slightly higher than those for the leachate aerated with H₃PO₄ ($\mu_{ci}=0.031 \text{ h}^{-1}$, $Sci=474.213 \text{ mg L}^{-1}$ SCOD and $Ki=1171 \text{ mg L}^{-1}$ SCOD), the SCOD of which was reduced by ~24%. It was likely related to the inhibitory effect of ammonia that was not removed by the Fenton pre-treatment.

Results of the BOD₅ and SCOD analyses indicated that BOD₅/SCOD ratio increased from 0.63 for raw leachate to 0.82 and 0.88 after aeration with H₃PO₄ and the Fenton treatment, respectively, which suggested that the removal of ammonia (and heavy metals) played an important role in the detoxification of the leachate.

3.6. Comparison of pretreatments

As it is shown in section 3.5, both pretreatments reduced the inhibitory effect of the leachate on RAS, increased BOD₅/SCOD ratio and they reduced the required HRT of biological systems from 5

Table 2
Estimation of annual operational costs (USD) of biological treatment without and with (struvite or Fenton) pretreatment.

Pretreatment	Operational cost (USD)			
	Energy (\$0.08/kwh)	Chemicals	Solids disposal (\$50.00/ton)	Total
None	30,900	28,500 ^a	45,000	104,400
Struvite	25,600	120,000 ^b	55,000	200,600
Fenton	20,800	430,000 ^c	32,000	482,800

^a Cost of phosphoric acid and flocculant.

^b Cost of phosphoric acid and flocculant.

^c Cost of sulfuric acid, sodium hydroxide, hydrogen peroxide and flocculant.

to 3.5 days and 3.2 days, for the struvite and the Fenton pretreatment, respectively. Struvite precipitation removed ~36% of NH₃-N, and ~24% of SCOD but it generated a large amount of sludge (TSS ~3000 mg L⁻¹). The Fenton reaction removed more SCOD (66%) but it did not reduce the NH₃-N concentration (Fig. 5). It did not require aeration, but the oxygen demand for nitrification after the Fenton pretreatment was practically the same as for the raw leachate. Therefore the oxygen requirement (and related power requirement for aeration) for the total treatment (organics and NH₃-N) of the leachate pretreated with both tested methods was similar.

The requirement for acidification is a serious drawback of the Fenton treatment. Application of acid, and subsequent neutralization after oxidation is completed, increases the salinity of the treated water. Since the investigated leachate had very high alkalinity, a large amount of H₂SO₄ (3100 mg L⁻¹) was necessary to reduce the pH to 3.5 and 1300 mg L⁻¹ of NaOH was required subsequently for the neutralization.

3.7. Evaluation of total cost of the leachate treatment

Total cost of the treatment was calculated based on 15 years of operation and flow rate of 150 m³ per day. The size of biological reactors was based on the results of the analysis of the respirometric tests: HRT = 5 days for the un-pretreated leachate and HRT = 3.5 and 3.2 days for the leachate pretreated by the struvite precipitation and the Fenton reaction, respectively. The capital cost of biological leachate treatment system without any pretreatment was ~12 million USD. The capital costs for the analogous systems with the struvite and the Fenton pretreatments were ~7 million USD, and ~8 million USD, respectively.

While an application of the Fenton pretreatment would substantially reduce the capital cost, due to a requirement of a large amount

of chemicals, the operating cost of such a system would be very high (Table 2, Fig. 7).

Comparison of the total costs (Fig. 7) indicated that the aeration with H₃PO₄ (struvite precipitation) followed by the biological treatment would be the most cost effective option for the treatment of the studied leachate.

4. Conclusions

The following conclusions can be drawn from the results of the treatability studies, conducted on the leachate from an active municipal landfill:

- 1) Respirometric tests indicated that biological treatment of the raw leachate would be strongly inhibited.
- 2) High magnesium content (172 mg L⁻¹) in the leachate allowed for a partial (36%) removal of NH₃-N by aeration with H₃PO₄ (700 mg L⁻¹). This pretreatment reduced the SCOD by 24% and it reduced the inhibition of RAS.
- 3) The elevated concentration of iron (56 mg L⁻¹) in the leachate was used to conduct the Fenton pretreatment by acidification and H₂O₂ addition. Using the optimum dose of H₂O₂ (650 mg L⁻¹), 66% of SCOD was removed and the inhibition of RAS was substantially reduced. However, the NH₃-N concentration was not reduced.
- 4) Evaluation of the capital and operational costs indicated that aeration with H₃PO₄ followed by biological treatment would be the more cost effective option.

Acknowledgements

Authors thank Mr. Andrew Lugowski of CRA and Mr. Wayne Smith of ALS Laboratories, Waterloo, ON, for help in some experiments and Dr. Alan Weston of CRA, Niagara Falls, NY, for his suggestions. Referees' comments are appreciated.

References

- [1] L.M. Lema, R. Mendez, R. Blazquez, Characteristics of landfill leachates and alternatives for their treatment: a review, *Water Air Soil Pollut.* 40 (1988) 223–250.
- [2] T.H. Christensen, P. Kjeldsen, H.-J. Albrechtsen, G. Heron, P.H. Nielsen, P.I. Bjerg, P.E. Holm, Attenuation of landfill leachate pollutants in aquifers, *Crit. Rev. Environ. Sci. Technol.* 24 (1994) 119–202.
- [3] P. Kjeldsen, M.A. Barlaz, A.P. Rooker, A. Braun, A. Ledin, T.H. Christensen, Present and long-term composition of MSW landfill leachate: a review, *Crit. Rev. Environ. Sci. Technol.* 32 (2002) 297–336.
- [4] J. Scott, D. Beydoun, R. Amal, G. Low, J. Cattle, Landfill Management, Leachate Generation, and Leach Testing of Solid Wastes in Australia and Overseas, *Crit. Rev. Environ. Sci. Technol.* 35 (2005) 239–332.
- [5] A. Marco, S. Esplugas, G. Saum, How and why combine chemical and biological processes for wastewater treatment, *Water Sci. Tech.* 35 (1997) 321–327.
- [6] A. Papadopoulos, D. Fattad, M. Loizidou, Treatment of stabilized landfill leachate by physico-chemical and bio-oxidation processes, *J. Environ. Sci. Health A33* (1998) 651–670.
- [7] J. Kochany, A. Lugowski, Multistage treatment of high strength leachate, *Environ. Technol.* 21 (2000) 623–629.
- [8] C. Di Iaconi, R. Ramadori, A. Lopez, Combined biological and chemical degradation for treating a mature municipal landfill leachate, *Biochem. Eng. J.* 31 (2006) 118–124.

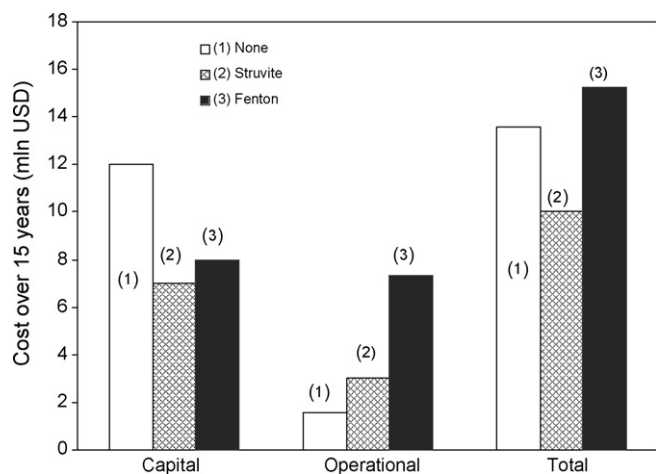


Fig. 7. Comparison of the costs (million USD, 15 years) of biological treatment of the raw leachate (1), and biological treatments of leachate with pretreatments using struvite precipitation (2) and the Fenton reaction (3).

- [9] J. Wiszniowski, D. Robert, J. Surmacz-Gorska, K. Miksch, J.V. Weber, Landfill leachate treatment methods: a review, *Environ. Chem. Lett.* 4 (2006) 51–61.
- [10] S. Renou, J.G. Givaudan, S. Poulain, F. Dirassouyan, P. Moulin, Landfill leachate treatment: review and opportunity, *J. Hazard. Mater.* 150 (2008) 468–493.
- [11] E. Lipczynska-Kochany, Degradation of aromatic pollutants by means of advanced oxidation processes in homogeneous phase: photolysis in the presence of hydrogen peroxide versus the Fenton reaction, *Chemical Oxidation. Technologies for the Nineties*, in: Proceedings of the 3rd International Symposium, Vanderbilt University, Nashville, TN, 1993, pp. 12–27.
- [12] E. Chamarro, A. Marco, S. Esplugas, Use of Fenton reagent to improve organic chemical biodegradability, *Water Res.* 35 (2001) 1047–1051.
- [13] J.J. Pignatello, E. Oliveros, A. MacKay, Advanced oxidation processes for organic contaminants destruction based on the Fenton reaction and related chemistry, *Crit. Rev. Env. Contr.* 36 (2006) 1–84.
- [14] A. Lopez, M. Pagano, A. Volpe, A.C. Di Pinto, Fenton's pretreatment of mature landfill leachate, *Chemosphere* 54 (2004) 1005–1010.
- [15] J. Lopes de Morais, P. Zamora, Use of advanced oxidation processes to improve the biodegradability of mature landfill leachates, *J. Hazard. Mater.* 23 (2005) 181–186.
- [16] H. Zhang, H.J. Choi, C.-P. Huang, Optimization of Fenton process for the treatment of landfill leachate, *J. Hazard. Mater.* B125 (2005) 166–174.
- [17] Y. Deng, J.D. Englehardt, Treatment of landfill leachate by the Fenton process. Review, *Water Res.* 40 (2006) 3683–3694.
- [18] O. Primo, A. Rueda, M.J. Rivero, I. Ortiz, An integrated process, Fenton reaction-ultrafiltration, for the treatment of landfill leachate: pilot plant operation and analysis, *Ind. Eng. Chem. Res.* 47 (2008) 946–952.
- [19] H. Zhang, H.J. Choi, P. Canazo, C.P. Huang, Multivariate approach to the Fenton process for the treatment of landfill leachate, *J. Hazard. Mater.* 161 (2008) 1306–1312, doi:10.1016/j.hazmat.2008.04.126.
- [20] J.D. Doyle, S.A. Parsons, Struvite scale formation and control, *Water Sci. Technol.* 49 (2004) 177–182.
- [21] L.E. De-Bashan, Y. Bashan, Recent advances in removing phosphorus from wastewater and its use as fertilizer (1997–2003), *Water Res.* 38 (2004) 4222–4246.
- [22] D. Kim, H.-D. Ryu, M.-S. Kim, J. Kim, S.-I. Lee, Enhancing struvite precipitation potential for ammonia nitrogen removal in municipal landfill leachate, *J. Hazard. Mater.* 146 (2007) 81–85.
- [23] APHA, AWWA, WPCF, Standard Methods for the Examination of Water and Wastewater, 20th ed., American Public Health Association, Washington, D.C., 1999.
- [24] A.F. Rozich, A.F. Gaudy, Design and Operation of Activated Sludge Process Using Respirometry, Lewis Publishers, Boca Raton, FL, 1992.
- [25] NIST/SEMATECH e-Handbook of Statistical Methods, <http://www.itl.nist.gov/div989/handbook> (accessed June, 2008).
- [26] J.D. Doyle, S.A. Parsons, Struvite formation, control and recovery, *Water Res.* 36 (2002) 3925–3940.
- [27] K.S. Le Corre, E. Valsami-Jones, P. Hobbs, S.A. Parsons, Impact of calcium on struvite crystal size, shape and purity, *J. Cryst. Growth* 283 (2005) 514–522.
- [28] E. Lipczynska-Kochany, G. Sprah, S. Harms, Influence of some groundwater and surface waters constituents on the degradation of 4-chlorophenol by the Fenton reaction, *Chemosphere* 30 (1995) 9–20.
- [29] E. Lipczynska-Kochany, J. Kochany, Effect of humic substances on the Fenton treatment of wastewater at acidic and neutral pH, *Chemosphere* 73 (2008) 745–750, doi:10.1016/j.chemosphere.2008.06.28.
- [30] N. Bouropoulos, P.G. Koutsoukos, Spontaneous precipitation of struvite from aqueous solutions, *J. Cryst. Growth* 213 (2000) 381–388.
- [31] J. Kochany, E. Lipczynska-Kochany, Application of EPR spin-trapping technique for the investigation of the reactions of carbonate, bicarbonate and phosphate anions with hydroxyl radicals generated by the photolysis of H₂O₂, *Chemosphere* 25 (1992) 1769–1782.
- [32] E. Lipczynska-Kochany, J. Kochany, Respirometric studies on the impact of humic substances on the activated sludge treatment. Mitigation of an inhibitory effect caused by diesel oil, *Environ. Technol.* 29 (2008) 1109–1118.