UDC 66.067.17:628.4:547.475.2 *original scientific paper*
ISSN 1330-9862

(FTB-1293)

Nanofiltration of a Landfill Leachate Containing Pharmaceutical Intermediates from Vitamin C Production

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Received: December 15, 2003
Accepted: April 15, 2004

Summary

The main landfill of the city of Zagreb generates several hundreds of cubic meters of heavily contaminated leachate per day. The organic composition of the leachate is particularly peculiar because, besides common macromolecular humus-like dissolved organic carbon, it encompasses a number of specific compounds of pharmaceutical origin, including a suite of by-products deriving from the production of vitamin C. Since both macromolecular humic organic matter and vitamin C intermediates are rather resistant to microbial degradation, leachate treatment procedures using simple retention lagoons or conventional bioreactors are not very effective in reducing their levels before the discharge into the receiving waters. An attractive alternative is the application of membrane technology. The efficiencies of three different types of nanofilters for the purification of leachates from the Jakuševec landfill were examined. It was shown that both complex humic-like dissolved organic matter and anthropogenic compounds of pharmaceutical origin can be eliminated at high efficiencies, mostly above 90 %.

Key words: nanofiltration, landfill leachate, organic matter, pharmaceutical chemicals

Introduction

Landfill leachates are heavily loaded with different types of organic and inorganic contaminants and represent a major risk with respect to contamination of natural water resources (*1*). In unprotected landfills, leachates infiltrate vertically through the vadose soil zone below the landfill and eventually reach groundwater aquifer forming anaerobic plumes (*2*) that can pose a serious threat to drinking water resources (*1,3*). In landfills, which include a leachate collection system, it is mandatory to treat the collected leachate before its release into ambient surface waters.

It was estimated that the main landfill of the city of Zagreb (Jakuševec landfill) produces about 350 000 m^3 of leachate per year (*4*). Since the Jakuševec landfill contains waste from both domestic and industrial origin (*5,6*), the composition of leachate formed in the landfill is very complex and includes a wide spectrum of organic and inorganic contaminants having both biogenic and anthropogenic origins (*7*). Like in many other municipal solid waste landfills, the main inorganic constituents are ammonia and chloride, while in the organic fraction macromolecular humus-like materials dominate (*7*). However, some xenobiotic organic compounds of pharmaceutical origin were also found in rather high concentrations (*5,8*). Among these compounds the most abundant ones were isopropylidene derivatives of monosaccharides (*5*), which originate from the production of vitamin C.

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Both macromolecular humic organic matter, determined as chemical oxygen demand (COD), and vitamin C intermediates were detected in high concentrations in the adjacent groundwater aquifer (*7*), indicating that these constituents were rather resistant to microbial degradation. Therefore, the removal of these compounds from the leachate by conventional biological treatment is expected to be very difficult. In the last few years, wastewater treatment using membrane processes was gaining importance, and several papers demonstrated successful application of nanofiltration for the treatment of landfill leachates (*9–12*). Regarding the removal of specific micropollutants from polluted waters, the focus was on pesticide and herbicide residues (*13–15*). Recently, there has been an increasing number of reports on the application of pressure-driven membrane processes for the removal of various organic contaminants, including pharmaceutical and endocrine-disrupting chemicals, from wastewaters (*16,17*).

This paper examined the applicability of nanofiltration as an attractive alternative to biological treatment to remove specific class of pharmaceutical chemicals from a heavily loaded landfill leachate.

Materials and Methods

Field site and landfill leachate sampling

Landfill leachate was collected from the retention basin at the Jakuševec landfill during spring 1999. Samples of 50 L of leachate were transported to the laboratory and stored at 4 °C until processing. The main characteristics of the collected leachate are shown in Table 1.

Table 1. Composition of the leachate from the Jakuševec landfill (Zagreb, Croatia)[a]

pH	7.39–7.84	γ (Mn)/(mg/L)	0.71
Conductivity/(µS/m)	7560–9690	γ (Li)/(µg/L)	5–12
γ (TDS)/(mg/L)	4170–5270	γ (Cd)/(µg/L)	<5
γ (Na)/(mg/L)	649–655	γ (Pb)/(µg/L)	70
γ (K)/(mg/L)	381–387	γ (Cu)/(µg/L)	189
γ (Ca)/(mg/L)	52–55	γ (Zn)/(µg/L)	220
γ (Mg)/(mg/L)	59–64	γ (Cr)/(µg/L)	33
γ (F^-)/(mg/L)	0.02–0.03	γ (Ni)/(µg/L)	119
γ (Cl^-)/(mg/L)	975–1253	γ (Ag)/(µg/L)	<1
γ (NO_3^-)/(mg/L)	6.4–6.9	γ (Hg)/(µg/L)	<1
γ (HCO_3^-)/(mg/L)	2981–5120	COD/(mg/L)	574–803
γ (SO_4^{2-})/(mg/L)	18–29	TOC/(mg/L)	519–633
γ (Fe)/(mg/L)	5.4	Pharm./(mg/L)[b]	27–55

[a] Sample collected from the retention basin
[b] Pharm. = sum of intermediates from the vitamin C production – di(isopropylidene) sorbose (DAS), di(isopropylidene) α-ketogulonic acid (DAG) and di(isopropylidene) xylose (DAX)

Nanofiltration unit

Nanofiltration was performed on a pilot-scale unit, consisting of a membrane pressure vessel, centrifugal pump and corresponding pipes, valves, manometers and flow meters. No pH adjustment was made before the process. However, in order to minimize fouling of the nanofilters, prior to nanofiltration particles were removed from the feed by a replaceable 5-µm microfiltration cartridge. The original sample was diluted by a factor of 3 with deionized water to lower the osmotic pressure and allow higher water recoveries and then passed through nanofilters. All of the experiments were conducted as once-through system without recirculation of the concentrate. The rejection (expressed as percentage) was calculated from the decrease of concentration of individual contaminants in the permeate as compared to their concentration in the feed. The membranes used in these experiments were NF 45, NF 70 and NF 200B polyamide spiral wound membranes (Film Tec, Dow Chemical USA). Membrane characteristics and experimental conditions are given in Table 2.

Table 2. Nanofiltration membrane characteristics and experimental conditions

Membrane	Nominal MMCO	Membrane area	Applied pressure	Water recovery	Permeate flux
	Da	m^2	bar	%	L/(m^2h)
NF 70	200	2.2	6.5	50	9.1
NF 200B	300	2.6	6.5	50	11.5
NF 45	400	6.5	6.0	75	20.8
			5.0	50	20.0
			4.0	25	11.8

MMCO – molecular mass cut off

Analyses

Common water contaminants such as major cations and anions, chemical oxygen demand (COD) and total organic carbon were determined using standard methods (*18*).

Identification and quantitative analysis of pharmaceutical intermediates from the vitamin C production were performed using gas chromatography – mass spectrometry. Briefly, the 300-mL sample aliquots were extracted with 2 portions (50+30 mL) of dichloromethane at the original pH (7.2–7.8). The combined extracts were dried with anhydrous sodium sulphate and evaporated to a small volume (approx. 1 mL). A known amount of deuterated phenanthrene was added into the extract as an internal standard prior to GC/MS determination. The gas chromatographic separation was carried on a fused-silica capillary column (20 m × 0.2 mm i.d.) coated with 0.33 µm of HP-5. Temperature programming was performed from 70 to 290 °C at 5 °C/min. Samples were injected in splitless mode and the chromatograms were acquired in full scan mode (m/e 50–450). Based on the recorded mass spectra, the most prominent compounds deriving from the vitamin C production were identified as diacetone xylose (DAX, M_r=230 Da), diacetone sorbose (DAS, M_r=260 Da) and two isomers of diacetone α-ketogulonic acid (DAG, M_r=274 Da). The concentration of the target compounds was determined in relation to deuterated phenanthrene as internal standard, assuming relative response factors of 1 for all analytes.

Results and Discussion

As can be seen from Table 1, the leachate from the Jakuševec landfill contained rather high concentrations of various contaminants, including common cations and anions, organic carbon, and some specific toxic pollutants such as heavy metals. The organic matter in the leachate was composed mainly of recalcitrant macromolecular organic matter (Table 1). As revealed by ultrafiltration (UF hollow fibre membrane PM10, Romicon, USA), molecules smaller than 10 kDa strongly dominated (90 %) the composition of the organic matter in the leachate. The concentration of the organic matter, expressed as COD, is somewhat lower than that reported for the raw leachate (*7*), indicating that some degradation of the labile portion of organic matter occurred in the retention basin. However, the concentration of COD was still too high and could not be considered suitable for the release into the recipient ambient waters without further treatment.

Moreover, the landfill leachate from the Jakuševec landfill was heavily contaminated with pharmaceutical chemicals. The most abundant individual anthropogenic constituents in the leachate collected from the retention basin were the diacetonated (di-isopropylidene) intermediates from the vitamin C synthesis, DAS, DAG and DAX, reaching the total concentration in the range of 27–55 mg/L. This represented about 3–5 % of the total organic carbon. Very little is known, so far, about the ecotoxicological properties of these diacetonated compounds. Our study of the groundwater contamination near the Jakuševec landfill indicated their biorefractory behaviour in the aquifer (*5,6*). As to their biological effects, sodium salt of DAG is used as a plant growth regulator, which can remarkably influence the germination of seeds kept under adverse storage (*19*).

The removal of common wastewater contaminants using 3 different nanofilters is presented in Fig. 1. High rejection rates were obtained for the organic load (COD and TOC) on all of the examined membranes, while for the collective inorganic parameters (conductivity and total dissolved solids) the rejection rate was lower than 60 %. Moreover, for inorganic constituents, the membrane NF 70 was significantly more efficient than the other two membranes. The removal of the total hardness varied from 62 % for NF 45 to about 90 % for NF 70 (Fig. 2).

It should be noted that magnesium was removed much more efficiently than calcium. Rejection of chloride by membranes NF 45 and NF 200B was very low, which can probably be explained by the Donnan exclusion model since feed water contains high salt concentration in which most abundant cations are monovalent sodium and potassium. A much higher chloride rejection was obtained by the membrane NF 70 with the smallest pore size, which was designed by the manufacturer for high salt rejection.

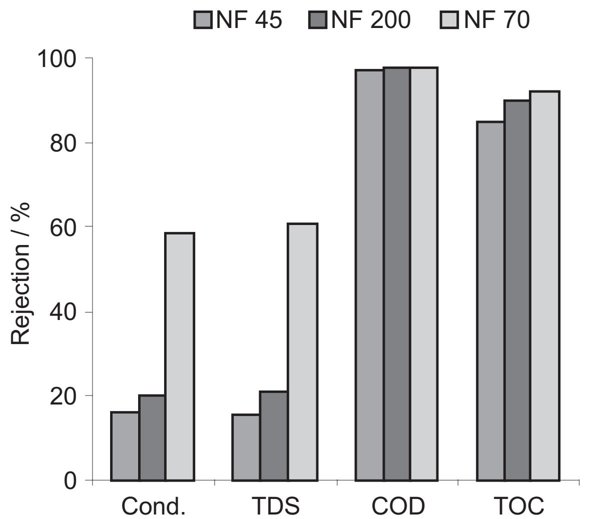

Fig. 1. Comparison of the rejection rates of some general inorganic and organic constituents from the leachate collected from the retention basin of the Jakuševec landfill using different nanofilters (WR=50 %); Cond.=conductivity; TDS=total dissolved solids; COD=chemical oxygen demand; TOC=total organic carbon

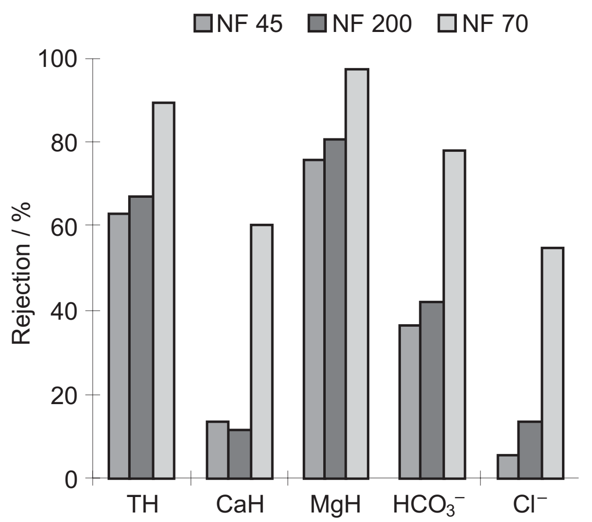

Fig. 2. Comparison of the rejection rates of inorganic constituents from the leachate collected from the retention basin of the Jakuševec landfill using different nanofilters (WR=50 %); TH=total hardness; CaH=calcium hardness; MgH=magnesium hardness

The elimination of isopropylidene intermediates from the vitamin C production was rather high for all of the examined membranes. The concentration of these compounds after nanofiltration was reduced from the original several tens of mg/L to less than 1 mg/L. The rejection rates of individual compounds ranged from 92–97 % for diacetone xylose (M_r=230 Da) to 97–99 % for diacetone sorbose (M_r=260 Da) and diacetone α-ketogulonic acid (M_r=274 Da (Fig. 3). A slightly lower efficiency was observed for the smallest intermediate diacetone xylose (M_r=230 Da). In fact, a highly significant statistical correlation (r^2=0.9665) was observed between the molecular mass of the individual intermediate and the »break-through rate« (equal to 100 % – rejection rate). This regularity indicated that the size of the mole-

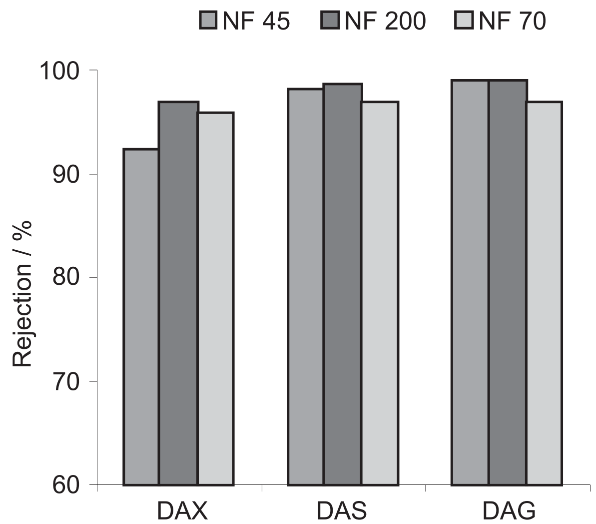

Fig. 3. Comparison of the rejection rates of some specific organic constituents of pharmaceutical origin from the leachate collected from the retention basin of the Jakuševec landfill using different nanofilters (WR=50 %); DAX=diacetone xylose; DAS=diacetone sorbose; DAG=diacetone α-ketogulonic acid

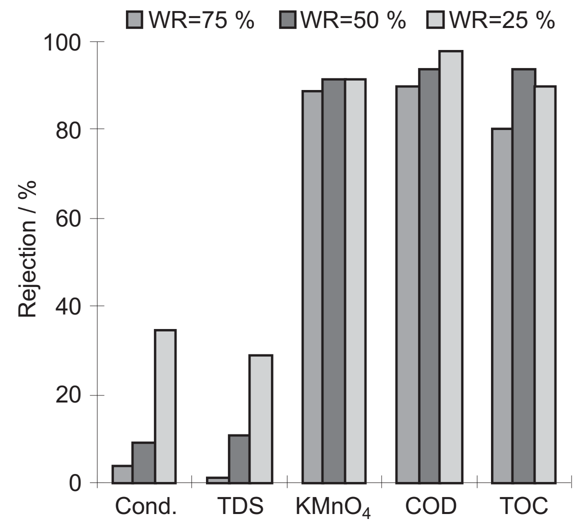

Fig. 4. Comparison of the rejection rates of some general inorganic and organic constituents of the leachate collected from the retention basin of the Jakuševec landfill at different water recoveries (nanofilter NF 45); Cond.=conductivity; TDS=total dissolved solids; COD=chemical oxygen demand; TOC=total organic carbon

cule rather than their polarity determined the efficiency of the removal of vitamin C intermediates by nanofiltration.

It has been reported that the adsorption of hydrophobic contaminants on the nanofiltration and reverse osmosis membranes may lead to an overestimation of rejection rates if the membranes were not previously saturated with the contaminants to be eliminated (*16,17*). However, DAG, DAS and DAX with the log K_{ow} values of 1.35, 2.34 and 2.65, respectively (*20*), can be regarded only as slightly to moderately lipophilic compounds. Therefore, it is not very likely that the adsorption of DAG, DAS and DAX on nanofiltration membrane substantially influences the estimation of their rejection.

The removal of contaminants from the leachate using the membrane NF 45, which was selected because it allows operation at the highest flow rates and/or the lowest pressure, was examined at different water recoveries, ranging from 25 to 75 %. The impact of higher water recoveries on the rejection rate for organic parameters (COD, $KMnO_4$, TOC) was relatively small (Fig. 4).

The rejection rate at the 25 % water recovery was 90–98 %, while at the yield of 75 % the rejection rate dropped down to 80–90 %. The impact was, however, very pronounced for general inorganic parameters such as electric conductivity and total dissolved solids. The rejection rate for these constituents decreased from about 29–33 to only 2–4 % when the recovery increased from 25 to 75 % (Fig. 4).

The specific inorganic constituents also showed a conspicuous dependence of the rejection rates on the applied recoveries (Fig. 5). At the highest recovery (75 %), the total hardness was reduced by only 35 %, while the rejection rates of hydrogen carbonate and chloride were even lower (<20 %).

In contrast, the rejection rate for most of the intermediates from the vitamin C production was affected very little by the changes in water recovery (Fig. 6).

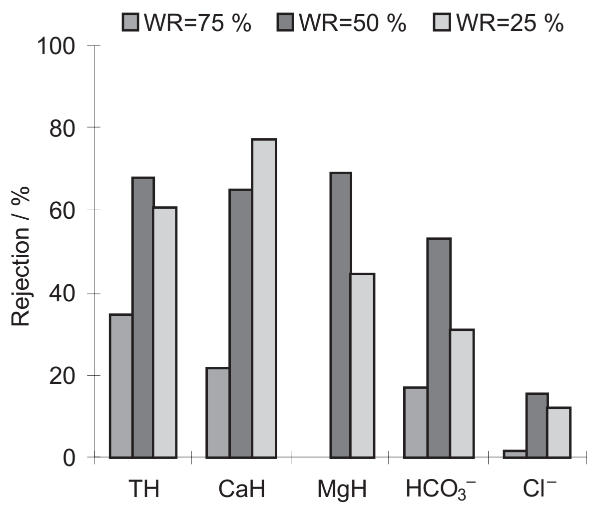

Fig. 5. Comparison of the rejection rates of inorganic constituents from the leachate collected from the retention basin of the Jakuševec landfill at different water recoveries (nanofilter NF 45); TH=total hardness; CaH=calcium hardness; MgH=magnesium hardness

Nevertheless, some effect could be observed for the diacetone xylose, which is the smallest intermediate. At the highest water recovery examined (75 %), the rejection rate dropped down below 80 %, while for all other intermediates the removal remained above 90 %.

Due to the high rejection of the organic load, including both macromolecular organic matter as well specific pharmaceutical compounds, the leachate purified by nanofiltration is suitable for discharge into the river Sava. The nanofiltration concentrate contained very high concentrations of COD (>1000 mg/L) and vitamin C intermediates (>50 mg/L). Possible solutions for the concentrate treatment and disposal are already reported in the literature (*21,22*) and applied in practice. In the case of landfill leachate, the concentrate could be recirculated

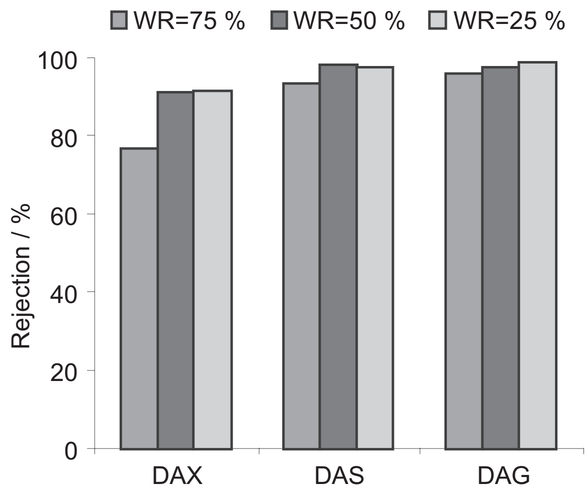

Fig. 6. Comparison of the rejection rates of some specific organic constituents of pharmaceutical origin from the leachate collected from the retention basin of the Jakuševec landfill at different water recoveries (nanofilter NF 45); DAX=diacetone xylose; DAS=diacetone sorbose; DAG=diacetone α-ketogulonic acid

to the landfill or evaporated and treated further as a solid waste. Alternatively, it could be treated in a bioreactor for the treatment of leachate. Such sequential treatment was shown to significantly increase biodegradation rate (*9*).

As to the practical technical aspects, no significant fouling of nanofilters was observed due to a short duration of the experiments. Nevertheless, the nanofilters were cleaned with mild alkaline solution between the experiments. Comparison of 3 different membranes indicated that the membrane NF 45 was the least efficient but at the same time it provided operation at significantly higher permeate flux (20.8 L/(m^2 h) at 6.5 bar for the NF 45 compared to 11.5 and 9.1 L/(m^2 h) for the NF 200B and NF 70, respectively. Since the rejection rate was sufficiently high even with the membrane NF 45, this membrane was considered suitable for practical applications, without sacrifying high rejection rate of organic contaminants. With a full-scale nanofiltration plant, having a filtration area of approximately 300 m^2, it is possible to achieve flows reaching 150 m^3/day, which is the approximate production rate of the leachate in the Jakuševec landfill. However, a careful planning of the procedures for the cleaning of membranes should be developed in order to allow stable conditions during the nanofiltration treatment.

Conclusion

Nanofiltration has been proven to be an attractive alternative for the treatment of landfill leachates contaminated with chemicals of pharmaceutical origin. The intermediates from the vitamin C production, with relative molecular mass in the range of 200–300 Da, can be efficiently removed from the leachates, containing up to 1 g/L of organic matter, expressed as COD. The efficiencies vary for different types of nanofilters but are, as a rule, better than 90 %. The rejection rate for individual ispropylidene compounds is correlated with molecular mass rather than with the polarity of the molecule. Considering the vicinity of vulnerable groundwater aquifer of the Črnkovec area, the advanced treatment of the leachate using nanofiltration seems to be economic and viable solution to minimize environmental risks.

Acknowledgements

This research was supported by the Ministry of Science and Technology of the Republic of Croatia through projects 00980120 and 0125016, as well as the project TP-B14/2002, which was carried out in the framework of the programme of Croatian Innovative Technological Development (HITRA). We thank Ivana Jeličić for the technical assistance.

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Nanofitracija procjednih voda odlagališta otpada onečišćenih intermedijerima iz proizvodnje vitamina C

Sažetak

Procijenjeno je da na glavnom odlagalištu grada Zagreba kod Jakuševca nastaje nekoliko stotina kubičnih metara procjednih voda dnevno. Sastav je organskog opterećenja procjednih voda odlagališta Jakuševec vrlo specifičan jer, uz kompleksnu visokomolekularnu organsku tvar humusnog karaktera, sadržava veliki udjel spojeva iz farmaceutske industrije među kojima ima najviše intermedijera iz proizvodnje vitamina C, diaceton sorboze, diaceton ksiloze i diaceton-α-ketogulonske kiseline. Budući da spomenuti sastojci pokazuju znatnu otpornost na mikrobiološku razgradnju, uobičajeni postupci za smanjivanje organskog opterećenja upotrebom retencijskih laguna i konvencionalnih bioreaktora ne predstavljaju učinkovit način za njihovu obradu prije ispuštanja u prirodne vode. Atraktivna alternativa biološkim postupcima su membranske tehnologije. U ovom je radu ispitana djelotvornost triju nanofiltracijskih membrana za pročišćavanje procjednih voda s odlagališta otpada Jakuševec. Rezultati pokazuju da se i kompleksna visokomolekularna tvar i intermedijeri iz proizvodnje vitamina C nanofiltracijom mogu vrlo učinkovito (>90 %) ukloniti iz procjednih voda.