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Compost leachate treatment using polyaluminium chloride and nanofiltration

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Abstract: Laboratory scale filtration tests utilizing leachate were conducted to investigate fouling and filtration performance of nanofiltration membranes. The work presented in this study is conducted on real samples rather than model water. Physico-chemical analyses showed that the leachate contained a lot of organic substances, exceeding 20000 mg/L O_2 expressed as chemical oxygen demand. Proper pre-treatment method must be chosen in order to reduce fouling index. Coagulation pre-treatment using poly-aluminium chloride was chosen. Two thin film polysulfone membranes were used, purchased by Osmonic Desal. The focus of this research is to assess the influence of the particle size and zeta-potential of the colloidal fraction in leachate on nanofiltration performance. The isoelectric point of both membranes was 4.7 and 4.3, respectively. The fouled membranes were negatively charged over the pH range with isoelectric point shifting to the left (lower pH) indicating the foulant material mainly not charged. It was confirmed by its zeta-potential, measured at -2 mV.

Keywords: compost leachate, coagulation, nanofiltration, zeta potential

1 Introduction

Compost will produce leachate if water is allowed to percolate through it. CompostThis leachate is a potentially polluting liquid, due to high organic and inorganic load, which may cause harmful effects on groundwater and surface water. Therefore, excess leachate must be removed and disposed of in a carefully controlled manner. The quality of the leachate is determined primarily by theits composition and solubility of the waste constituents. If waste changes in composition, due to biodegradation for example, the leachate quality will also change with time. Compost leachate contains high concentrations of dissolved organic matter (alcohols, acids, aldehydes, short chain sugars etc.), inorganic macro components (common cations and anions including sulphate, chloride, iron, aluminium, zinc and ammonia), heavy metals (Pb, Ni, Cu, Cd), and organic compounds such as pesticides [1]. Due to its complex composition, the treatment of compost leachate is a challenge.

The required values to oxidize soluble and particulate organic matter in leachate above 50000 mg/L O_2 were previously reported [1, 2]. As colloids are also present in high concentrations, a suitable combination of methods for their elimination has to be chosen. The treatment scheme comprises combinations of physical, biological and chemical treatment, with the key operational determination being organic loading rate. It is important to note that the mixed liquor generated from leachate is much less filterable compared to that produced by sewage or other industrial effluents, taking more than 10 min to filter 2 mL of leachate biomass [3]. Therefore, compost leachate could be treated with a Membrane Bio-Reactor (MBR) [2]. Although inorganic nitrogen is primarily removed through the nitrification–denitrification process, dissolved organic nitrogen (DON) becomes the main nitrogen component in the final effluent [4].

Fouling due to organic matter was previously observed to be strongly correlated with membrane hydrophobicity, charge effects and electro-kinetic phenomena. Streaming potential measurements are often used for the electro-kinetic characterisation of membrane surfaces, and is one of the more convenient techniques [5].

The aim of the present work is to purify compost leachate in such a manner that it could be released into the environment. The focus of this research is to assess the influence of the zeta-potential of the colloidal fraction in leachate on nanofiltration performance. The work presented in this study is conducted on real samples rather than model water. According to the research, the following procedures are proposed for leachate treatment: coagulation using Polyaluminium Chloride (PACl) followed by nanofiltration. By applying the suggested procedures,

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it is possible to reduce the chemical oxygen demand (COD) by 75%.

2 Methodology

2.1 Standard methods

Physico-chemical analyses of compost leachate were performed following standard methods, as displayed in Table 1.

Table 1: Standard methods.

Parameter	Apparatus	Standard
pH	pH meter MA 5740	SIST ISO 10523
Tur (NTU)	Turbidity-meter HACP 2100P	SIST ISO 7027
κ (μS/cm)	Conductivity-meter WTW LF 537	EN (DIN) 27 888
COD (mg/L)	LOVIBOND ET 108 Thermo-block	SIST ISO 6060

2.2 Jar-test

Jar tests were performed on a home made flocculator (R-vizija, Slovenia) with 4 stirrers (Fig.1). The compost leachate was first mixed in a series of 4 jars at 100 rpm for 2 min. Varying amounts of PACl (Kemiclar 200, Kemira, Slovenia) were then added into each jar and the solutions were mixed for 10 min. During this time period, flocculant Magnaflock was added (1 drop of 1% solution). The flocks were then allowed to settle for a maximum of 20 mins. From Fig.1 the obtained leachate samples are visible.

Table 2: Overview of the used NF membranes with manufacturer's specification.

Membrane	DL	DK
Manufacturer	Osmonics Desal, USA,	Osmonics Desal, USA
$MgSO_4$ rejection, %	96	96
Pressure, bar	0.5-28	0.5-28
Max. temp (°C)	50	50
pH range	2-11	2-11
Morphology	thin film composite	thin film composite
Support	Polyester	Polyester
Composition top layer	polyamide/ polysulfone	polyamide/ polysulfone

2.2.1 Nanofiltration (NF) trials

After coagulation and filtration using glass fibre filter (1.2 μm), the NF experiments were carried out with a Stirred cell unit, Model 8200, in which membrane was installed. Two thin film polysulfone NF membranes (DL and DK) were used, as purchased by Osmonic Desal. The membrane area of each membrane sheet was 29 cm^2 and molecular weight cut-off (MWCO) was determined at 340 Da for DL and 230 Da for DK membrane. The pH range for both membranes was specified from 2-11, max. temperature 50 °C and max. pressure 50 bar.

The experiments were performed at 3 different transmembrane pressures with milli-Q water. Further, the treated and untreated compost leachates were filtered through both membranes, under the same conditions as with milli-Q water.

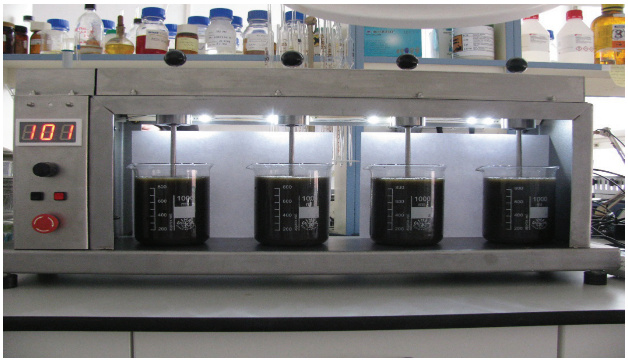

Figure 1: Flocculator (R-vizija, Slovenia).

2.3 Leachate samples

Slovene firm Kogal collect, handle and compost biowaste. Water passed from the compost pile into the stabilization ponds, where the compost leachate samples were collected. Since last years' monitoring showed high COD values, pretreatment is needed before nanofiltration. High concentration of organic substances, especially colloids, would foul the nanomembrane immediately.

2.4 Particles and membrane characterisation

The streaming potential of membranes was measured using an EKA electrokinetic Paar analyzer, SurPASS. The solution for the streaming potential cell contained 0.001 M KCl as a background electrolyte at pH range of 2-10 (pH was changed using 0.1 M HCl). The pH was set to 11 with 0.1 M NaOH and changes of approximately 1 pH unit value were recorded automatically by dosing 0.1 M HCl to electrolyte. The analyser automatically calculated zeta potential.

The particle size distribution and zeta potential of the particles were measured using a Zeta sizer Nano ZS instrument (Malvern Instruments, UK) equipped with dynamic light scattering and laser Doppler microelectrophoresis. Both parameters were measured in compost leachate and in supernatant obtained after the jar test was done.

3 Results and discussion

Jar tests were performed with coagulants, as reported in section 2.2. The optimum amount of PACl was 10 mL per 1 L of compost leachate. Although the optimum concentration of PACl was high, it should be noted that the COD value in the compost leachate sample was determined to be 31.0 g/L O_2. The quantities of precipitate in each jar after 10 min of settlement are seen in Fig. 2. The 4 jars in Fig. 2 represent (from left to right); compost leachate containing 0, 20, 15 and 10 ml of PACI respectively. In jars 2 to 4, a drop of 1% polyelectrolyte was also added. It was observed that the amount of sludge was linear with the PACl dose. In jar 2, more than half of the leachate amount represented the sludge. After coagulation and flocculation, the COD was reduced down to 7.7 g/L O_2 in jar 4. Turbidity was reduced from 1970 NTU down to 208 NTU, which represents a removal of 89%. The supernatant of jar 4 was collected for the nanofiltration.

Due to the decrease of COD value (jar 4), we assumed that the substantial share of colloids was removed from compost leachate. Therefore, particle size distribution analysis of the compost leachate and of the supernatant solution obtained after the jar test was performed (Fig. 3). It was observed that, after coagulation, the average particle size decreased to 1.5 nm. The average size of particles in the leachate prior to coagulation was larger, mostly 254 nm (75%), but also 1420 nm (25%).

The results show that the majority of larger particles were removed after coagulation, and consequently the membrane is expected to be fouled at much lower rate.

3.1. Results of membrane trials

Firstly, the permeability of each membrane was determined. Table 2 presents the milli-Q water fluxes, *J*, at different transmembrane pressures, *P*.

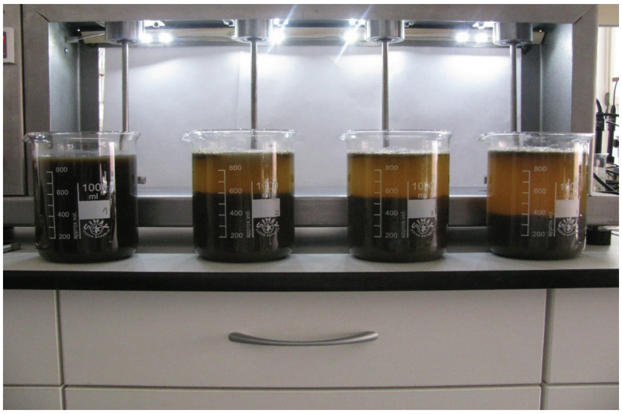

Figure 2: Jar test using different volumes of PACl.

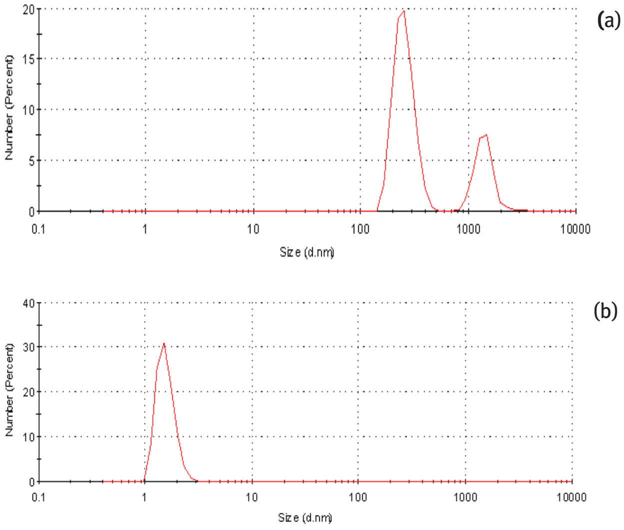

Figure 3: Particle size distribution in compost leachate (a) and after jar test (b).

Table 2: Millipore water fluxes.

P (bar)	J_{DK} (LMH)	J_{DL} (LMH)
2.5	22.2	26.9
3.5	29.7	35.6
4.5	38.8	46.8

Fig. 4 presents the flux dependence on pressure. Permeability was calculated at 8.3 L/h · m^2 · bar for DK membrane and at 9.95 L/h · m^2 · bar for DL membrane. The values are comparable with the literature data [5].

The leachate wastewater flux for both membranes is presented in Table 3. The flux without pre-treatment (J_{DK} and J_{DL}) is presented in columns 2 and 4, whilst the PACl pre-treated wastewater flux (J_{DKP} and J_{DLP}) is seen in columns 3 and 5. The flux of the leachate wastewater without any pre-treatment was negligible, as seen from

Table 3. Compost leachate immediately fouled both nanofiltration membranes.

When the DK and KL NF membranes are brought into contact with an aqueous solution of an electrolyte, carboxyl groups are attached to the membrane surface. The presence of dissociated carboxyl groups on the membrane surface causes a membrane charge. As a result of cake deposition on the membrane, dissolved solutes might be entrapped in the cake, leading to a decline in solute rejection. Studies have shown that the hydrodynamic cake resistance can be very high compared to the enhanced build-up of solutes inside the cake [6]. The increased cake resistance observed when dosing PACl may therefore result in increased rejection of solutes. Thus, the build-up of an initial fouling layer, rich in suspensions is hypothesized. The visual data supports this behaviour for the treated samples as these layers were thick and were definitely enriched conglomerates. As the suspension was easily washed away with demineralized water, it is clear that the PACl does not foul the membrane initially.

These findings are particularly important when considering the effect of the operating condition of pH on natural organic matter (NOM). The influence of pH on NOM fouling was investigated and the fouling layer was found to be denser at low pH due to electrostatic repulsion between the membrane surface charge and NOM. At high operating pH, membranes DL and DK attracted positive feed constituents more strongly than other membranes. These observations are in agreement with other authors [6].

The carboxyl groups ($-COO^-$) which may be present on polyamide membranes are weakly acidic and cannot be dissociated at low pH. A polyamide membrane can also contain amino groups which can be positively charged depending on the pH of the environment, i.e. NH_3^+ is positively charged in acidic medium, whilst $-R_3N^+$ (R different than H) is positively charged over the entire pH range. The virgin DK NF was positively charged at low pH, with an isoelectric point around pH 4, and negatively charged at high pH. More specifically, the isoelectric points of the DK and DL membranes were 4.7 and 4.3 respectively. Virgin DL was slightly more negative than DK membrane. The DL membrane attained more negative zeta potential (approximately −60 mV at pH 9.0) than the DK membrane (approximately −58 mV at pH 9.0). Zeta potential curves of this shape are characteristic of surfaces with both acidic and basic functional groups. The fouled DK and DL membranes were negatively charged above pH 5, with the isoelectric point shifting slightly to the right (higher pH). This indicates that the foulant material was mainly neutral in charge. Indeed, the zeta potential of compost leachate after PACl treatment was determined at -2 mV. Particles from leachate tend to disperse at high charge density, resulting in a cake consisting of fine particles. Consequently, the cake

Table 3: Leachate waste water fluxes.

P (bar)	J_{DK} (LMH)	J_{DKP} (LMH)	J_{DL} (LMH)	J_{DLP} (LMH)
2.5	<0.1	1.7	<0.1	2.2
3.5	<0.1	4.8	<0.1	5.4
4.5	<0.1	7.5	<0.1	7.9

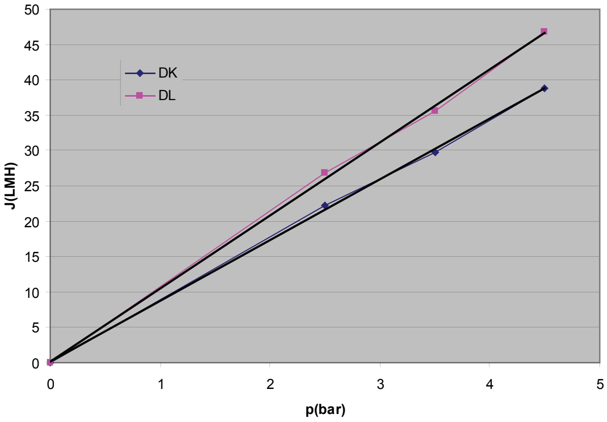

Figure 4: Millipore water flux as a function of pressure.

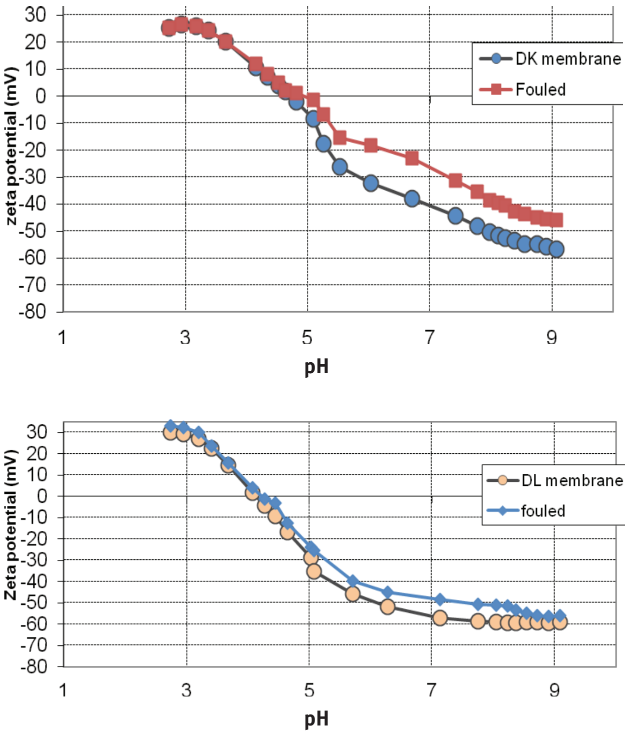

Figure 5: Zeta-potential as a function of pH (KCl = 0.001M) for DK membrane (above) and DL membrane (below), O -virgin, ☐-fouled.

Figure 6: Compost leachate (left), after the treatment with PACl (centre) and after NF (right).

resistance increased and the permeate flux decreased in the case of both membranes.

The main foulant material could be hydrophobic NOM, which was predominantly either very slightly negatively charged at -2 mV or without charge, due to the very small change in membrane potential after both membranes were fouled. The marked flux drop with more hydrophobic DL can be attributed to its strong hydrophobic interaction with organic foulants in the raw water, such as humic substances (HS) which are considered as the hydrophobic fraction in the NOM [7].

The denser NOM fouling layer would lead to cake-enhanced concentration polarisation. The specific cake resistances of high humic water were higher than those of low humic water. Fouling indices for high humic waters were also higher than those for low humic waters. These results suggest that the flocs formed from high humic water possess more significant membrane fouling potentials than those of low humic natural water. The SUVA index implies that the molecules contained in leachates resulting from pre-treated wastes would be more aromatic and hydrophobic. The SUVA index of compost leachate was around 58 L/cm/g (may be considered as high humic water) and, after treatment with PACl, decreased to around 15 L/cm/g (may be considered as low humic water). This means that the aromatic and hydrophobic character of leachate changed, becoming less aromatic and more hydrophilic. Therefore, the fouling was reduced [8]. A necessary condition for this phenomenon is that the membrane surface charge is large enough; otherwise hydrophobic forces overcome the electrostatic forces, resulting in more fouling of hydrophobic membranes [9].

Samples of the untreated compost leachate, the leachate after coagulation and the NF permeate are displayed in Fig. 6. The measurement of COD in the colourless NF permeate showed a decrease below 120 mg/L O_2.

4 Conclusions

Compost leachate with high organic load was treated with PACl and a dosage of 10 mL/L was found to result in a colloid removal of 75%. Particle size distribution analyses indicated the removal of colloids by the reduced average particle size from 1.4 µm to less than 0.1 µm. After coagulation, nanofiltration of the supernatant was performed using two nanomembranes, DK and DL. DK and DL membranes exhibit both negative and positive surface charge depending on pH. Streaming potential measurements showed that DL and DK membranes have a much stronger negative charge under alkaline conditions than positive charge under acidic conditions due to high carboxyl group density on membrane surface. The organic matter was removed below the statutory level of 120 mg/L using nanofiltration. However, pre-treatment using PACl was absolutely necessary to remove foulants and improve the flux performance from below 0.1 LMH up to 7.9 LMH. Hydrophobic foulants, such as humic acid, were also removed.

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