# Assessment of metal removal, biomass activity and RO concentrate treatment in an MBR–RO system

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## ABSTRACT

This work investigated the removal of metals from wastewater using a combined Membrane Bioreactor-Reverse Osmosis (MBR–RO) system. The concentrate produced by the RO system was treated by a fixed bed column packed with zeolite. The average metal removal accomplished by the MBR treating municipal wastewater was Cu(90%), Fe(85%), Mn(82%), Cr(80%), Zn(75%), Pb(73%), Ni(67%), Mg(61%), Ca(57%), Na(30%) and K(21%), with trivalent and divalent metals being more effectively removed than monovalent ones. The metal removal achieved by the MBR system treating wastewater spiked with Cu, Pb, Ni and Zn (4–12 mg L$^{-1}$ of each metal) was Pb(96%) > Cu(85%) > Zn(78%) > Ni(48%). The combined MBR-RO system enhanced metal removal from municipal wastewater to the levels of >90.9->99.8%, while for wastewater spiked with heavy metals the removal efficiencies were >98.4%. Fixed bed column packed with zeolite was effective for the removal of Cu, Pb and Zn from the RO concentrate, while Ni removal was satisfactory only at the initial stages of column operation. The presence of heavy metals increased inorganic fouling.

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## 1. Introduction

Membrane Bioreactors (MBRs) are successfully employed for the biological treatment of municipal wastewater. Their advantages include the production of high quality treated effluent, good disinfection capability, compactness and flexibility in operation. MBRs do not allow suspended solids to penetrate into the final effluent and thus metals attached to sludge flocs are effectively rejected. Santos and Judd [1] compared metal removal in MBRs and conventional activated sludge systems and found that MBRs achieved relatively higher metal removal efficiencies. Higher Solids Retention Times (SRTs) and Mixed Liquor Suspended Solids (MLSS) concentrations favoured heavy metal removal.

MBRs also constitute an effective pre-treatment step for Reverse Osmosis (RO). The integration of an MBR with RO for the treatment of wastewater produces very high water quality. Tam et al. [2] found that the adoption of an MBR–RO system for wastewater treatment produced high water quality which satisfied the drinking water requirements of the US EPA and WHO guidelines. MBR removed organic matter, ammonia, nitrogen and suspended solids, while the subsequent application of RO improved water quality, especially with respect to the aesthetical and microbial parameters.

Dialynas and Diamadopoulos [3] found that Pb and Ni were completely removed by an MBR system, indicating that these metals were in particulate form, while Cr and Cu were removed by 89% and 49% respectively. The combined use of MBR–RO provided high water quality which was essentially free of heavy metals. In some cases it has been reported that the increase of SRT results in an increase of the metal removal of the MBR system. For example, Fatone et al. [4] observed that the increase of SRT from 11 to >1000 d caused an increase of Ni removal from 40 to 89% and of Pb from 50 to >98%. Other studies have shown that an increase in SRT has little or no influence in metal removal by the MBR system [5,6].

The adoption of RO for the treatment of wastewater containing high concentration of heavy metals is limited by the significant volume of the contaminated concentrate that is produced. The concentrate can be toxic since it contains higher concentration of pollutants compared to the feed RO stream. Kalderis et al. [7] reported that an RO unit achieved 89%, 93% and 97.5% removal of As, Sb and Ni respectively from hydrometallurgical wastewater and investigated the combined use of RO and lime precipitation for the treatment of the resultant concentrate, achieving 97.5% removal of metals. Dialynas et al. [8] examined the treatment of concentrate produced from an MBR–RO system treating municipal wastewater. The researchers applied coagulation and activated carbon adsorption, electrochemical treatment, photocatalysis and sonolysis; adsorption using granular activated carbon exhibited the highest dissolved organic carbon (DOC) removal. Pérez et al. [9] investigated the application of an electro-oxidation system for the

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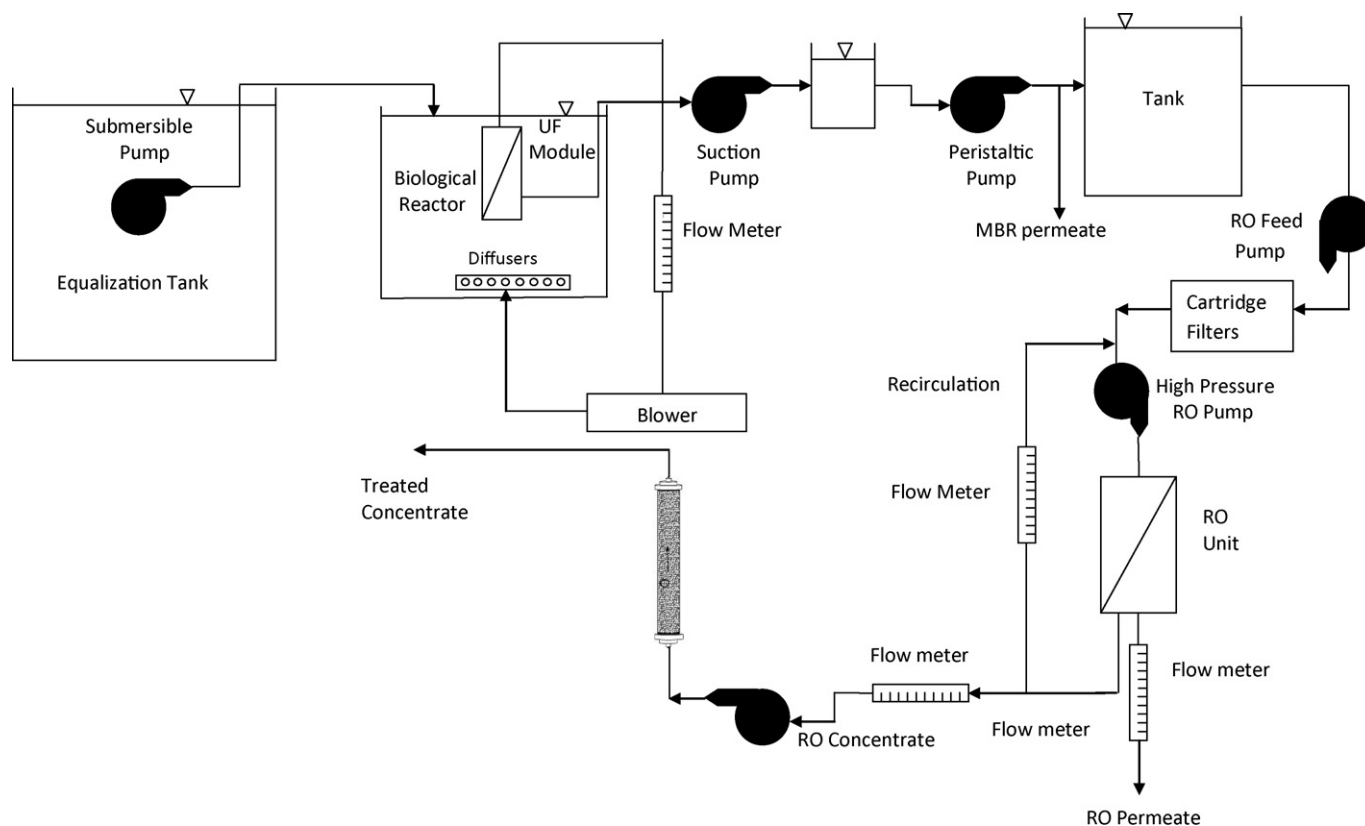
Fig. 1. MBR–RO and fixed bed column configuration.

treatment of RO concentrate, achieving removal higher than 92% of several emerging pollutants.

The studies assessing the performance of the MBR–RO system have focused on municipal wastewater. Further insight is required with respect to heavy metal removal from industrial wastewater and the effective treatment of the produced RO concentrate. It is important to examine the MBR–RO performance when it is subjected to shock loads of wastewater containing significant heavy metal concentrations. The aim of this work is to investigate heavy metal removal in an MBR–RO system treating municipal wastewater and wastewater spiked with heavy metals and to evaluate the use of fixed bed columns to treat the concentrate produced by the RO unit.

## 2. Materials and methods

### 2.1. MBR–RO configuration

The MBR–RO configuration is given in Fig. 1, while the MBR and RO characteristics are summarized in Table 1. Municipal wastewater was pumped from a primary sedimentation tank to a 2 m$^3$ equalization tank and then fed to a pilot scale MBR which treated approximately 450 L d$^{-1}$ of wastewater. The MBR operated at an SRT of 15 d and at a Hydraulic Retention Time (HRT) of 11.2 h. The permeate was filtered at a 10 min period during which filtration took place for 9 min and 40 s, while backwash lasted 20 s. Transmembrane pressure (TMP) was continuously recorded using a digital recorder (Easylog 40KH) having an accuracy of $\pm 0.25$ kPa which was connected to a pressure transducer (S-10 Wika). Temperature was recorded using a data logger (Easylog 40NSW) having an accuracy of $\pm 0.1$ °C. The membrane module of the MBR was chemically cleaned approximately every 3 months using 1000 mg L$^{-1}$ (as Cl$_2$) NaOCl solution and afterwards with 4000 mg L$^{-1}$ citric acid solution. Coarse bubble aeration was supplied to the membrane module to minimize membrane fouling. Fine bubble aeration was also provided to maintain the dissolved oxygen (DO) concentration in the biological reactor higher than 2 mg L$^{-1}$. Fine bubble aeration was accomplished using suitable diffusers placed at the bottom of the biological reactor. MBR permeate was occasionally collected, stored in a 200 L tank and periodically fed using a high pressure pump to a pilot scale RO unit. The RO operated in a single-pass mode producing permeate at a rate of ~2.36 L min$^{-1}$ for an influent rate of ~5.9 L min$^{-1}$. Very small part of the concentrate was recirculated to the RO unit and the system recovery was approximately 40%. The membrane module of the RO unit was cleaned prior to each filtration experiment using

**Table 1**
MBR and RO characteristics.

| Membrane parameters | MBR | RO | Pilot parameters | MBR | RO |
|---|---|---|---|---|---|
| Manufacturer | GE-W&PT[a] | DOW | Manufacturer | GE-W&PT[a] | Chemitec |
| Module type | One (1) ZW-10 | Four TW30-4021 | Configuration | Submerged hollow fibre | Spiral wound |
| Nominal pore size (μm) | 0.04 | – | Operation mode | Continuous | – |
| Surface area (m$^2$) | 0.93 | 3.3 (per element) | Permeate volume (m$^3$ d$^{-1}$) | 0.43 | 3.4 |
| Material | PVDF | Polyamide thin-film composite | Coarse bubble aeration rate (m$^3$ h$^{-1}$) | 4.0 | – |
| Salt rejection (%) | – | >99.5% | Operating pressure (bar) | 0.10–0.55 | 14–16 |

[a] GE Water & Process Technologies.

the chemical Kathon WTE of Rohm and Haas at a concentration of $20 \, mg \, L^{-1}$.

## 2.2. Experimental periods

Two experimental periods were conducted at steady-state conditions. In the first experimental period (74 days - control period) the MBR–RO system treated municipal wastewater, while in the second period (150 days) municipal wastewater was spiked with Cu, Pb, Ni and Zn. These metals were selected because they are present in several industrial wastewater streams. Sulphate salts of the above metals were supplied by Merck [$CuSO_4$, $NiSO_4 \cdot 6H_2O$, $ZnSO_4 \cdot H_2O$] and Sigma–Aldrich [$PbSO_4$]. The periodic spiking of influent wastewater with heavy metals took place in an equalization tank ($2 \, m^3$) where the influent wastewater was temporarily stored and was kept under continuous agitation. Wastewater having significant heavy metal concentrations was periodically fed into the biological reactor for 6 h in order to avoid excessive heavy metal accumulation inside the reactor resulting from the long-term system operation. To avoid dilution effects and to achieve similar metal concentrations inside the reactor with those of influent wastewater, it was usually necessary to add metals directly inside the reactor, depending on their concentrations in the mixed liquor at the initiation of the 6-h experimentation period. In order to assess MBR performance for the treatment of various influent metal concentrations, a concentration range of $4–12 \, mg \, L^{-1}$ was employed for each metal. The sampling procedure for the measurement of the parameters took place at the end of the 6-h period. During the remaining time period the MBR was fed with municipal wastewater. The pH of the mixed liquor was maintained above 6.9 using NaOH when necessary in order to ensure effective biological treatment. The MBR permeate was collected in a 200 L tank and was periodically fed to the RO system. During the 2nd period, the RO was fed with MBR permeate collected during the 6-h heavy metal addition period.

## 2.3. Fixed bed column

The concentrate produced by the RO unit was fed to a fixed bed column packed with natural zeolite (clinoptilolite) in order to reduce the heavy metal concentrations (Fig. 1). Zeolite was obtained by S&B Industrial Minerals S.A. and its chemical composition was determined by X-ray Fluorescence (XRF) analysis [10]. Zeolite was sieved to the desired size (1.0–1.4 mm), rinsed with distilled water, dried at 80 °C for 24 h and stored in a desiccator until its use. The column had an internal diameter of 2.0 cm and a length of 70 cm. The bed volume (BV) is defined as the volume of liquid equal to the volume of the empty bed. The concentrate was pumped through the column at a constant flow rate of $14.7 \, BV \, h^{-1}$ ($53.9 \, mL \, min^{-1}$), using a peristaltic pump (Heidolph PD5006) in an up-flow mode to ensure complete wetting of the mineral particles, avoid channelling due to gravity and enhance uniform distribution of solution throughout the column. The duration of each experiment was 60 min. The treated samples were collected from the column outlet at specified time intervals (10, 20, 40 and 60 min), filtered and measured for their Cu, Pb, Ni and Zn content. The concentrate treatment was performed only during the 2nd period when significant heavy metal concentrations were detected in the RO feed. In each experiment the fixed bed column was packed with new zeolite in order to obtain comparable results among the various trials. The used zeolite was regenerated by passing 1 M KCl desorbing solution through the column at a rate of $1.0 \, BV \, h^{-1}$ for a period of 4 h. Then the regenerated zeolite was washed by passing deionised water through the column and the same RO concentrate solution was treated by passing it through the fixed bed column packed with regenerated zeolite. Treated samples were collected

at the time intervals of 10 and 60 min, filtered and measured for their metal content.

## 2.4. Analytical methods

Laboratory analyses were conducted to determine the characteristics of influent wastewater, activated sludge, MBR permeate, RO permeate, RO concentrate and column outflow. COD, ammonium nitrogen ($NH_4$-N) and nitrate nitrogen ($NO_3$-N) were determined photometrically using the Spectroquant Nova 60 photometer and suitable Spectroquant Merck kits. The parameters of Total Suspended Solids (TSS), Volatile Suspended Solids (VSS), Total Dissolved Solids (TDS) and pH were determined using Standard Methods [11].

For the determination of metals the samples (all except sludge samples) were digested by adding $3 \, mL \, 5 \, M \, HNO_3$ and $5 \, mL \, 6 \, M \, HCl$ in 100 mL sample volume. A more effective digestion procedure was employed for sludge samples: 2 mL of liquid sludge sample was placed in a Hach digestion device (model 23130-20,-21) and 4 mL of concentrated (98%) $H_2SO_4$ was added. The temperature increased to 440 °C and after 5 min 10 mL of $H_2O_2$ (30 wt%) was added. The digestion procedure lasted for 15 min. Then the liquid was allowed to cool down and was filtered through GF/C Whatman filers. The metals Cu, Pb, Ni, Zn, Mn, Fe, Cr, Ca, Mg, Na and K were determined using the Atomic Absorption Spectrometer Varian AA240FS. A graphite furnace (GTA120 graphite tube atomizer) was used when the samples had low metal concentrations.

## 2.5. Biomass inhibition experiments

The specific Oxygen Uptake Rate (sOUR) of activated sludge was determined using wastewater as substrate. The experimental protocol is described in the work of Katsou et al. [12]. The average inhibition of heterotrophic biomass growth (HI) was determined using the following equation:

$$(\%) \, HI = \frac{sOUR_1 - sOUR_2}{sOUR_1} \times 100 \tag{1}$$

where $sOUR_1$ and $sOUR_2$ $[mgO_2 \cdot (gVSS \, h)^{-1}]$ are the average specific oxygen uptake rates of activated sludge without any heavy metal addition and with the spiking of heavy metals respectively (i.e. 1st and 2nd period respectively). The inhibition of autotrophic biomass was determined through the determination of the specific Ammonium Uptake Rate (sAUR). The experimental protocol is described in the work of Katsou et al. [12]. The average inhibition of autotrophic biomass growth (AI) was determined using the following equation:

$$(\%) \, AI = \frac{sAUR_1 - sAUR_2}{sAUR_1} \times 100 \tag{2}$$

where $sAUR_1$ and $sAUR_2$ $[mgNO_3-N \, (gVSS \, h)^{-1}]$ are the average specific ammonium uptake rates of activated sludge without any heavy metal addition and with the spiking of heavy metals (i.e. 1st and 2nd period) respectively. At least ten repetitions of sOUR and sAUR experiments were conducted in each period.

## 2.6. Membrane fouling

Membrane fouling was assessed by calculating the membrane permeability reduction with time. Membrane permeability is given by:

$$L_{20} = \frac{J_{20}}{TMP} \tag{3}$$

where $J_{20}$ ($L \, m^{-2} \, h^{-1}$) is the filtration flux corrected to the reference temperature of 20 °C, TMP (bar) is the transmembrane pressure and $L_{20}$ ($L \, m^{-2} \, h^{-1} \, bar^{-1}$) is the membrane permeability corrected to

**Table 2**
MBR system operating characteristics.[a]

| Parameter | 1st period | 2nd period |
|---|---|---|
| SRT (d) | 15 | 15 |
| HRT (h) | 11.2 | 11.2 |
| Mixed liquor pH | 7.33 (6.92–7.57) | 7.41 (6.97–7.72) |
| MLSS (g L$^{-1}$) | 5.91 (5.33–6.48) | 5.44 (4.60–6.41) |
| MLVSS (g L$^{-1}$) | 4.77 (4.25–5.51) | 4.26 (3.57–4.92) |
| Filtration flux (L m$^{-2}$ h$^{-1}$) | 22.3 | 22.3 |
| Backwash flux (L m$^{-2}$ h$^{-1}$) | 26.8 | 26.8 |
| Aeration rate (m$^3$ h$^{-1}$) | 4.0 | 4.0 |
| F M$^{-1}$ [mg COD (mg MLVSS d)$^{-1}$] | 0.24 | 0.26 |

[a] Variation is given in parenthesis.

20 °C. The temperature correction factor employed was the following [13]:

$$J_{20} = J_T \times 1.025^{(20-T)} \tag{4}$$

The contribution of the membrane material, the suspended solids (SS), the colloidal-soluble organics and the colloidal-soluble inorganics to the total resistance to filtration flow $R$ was determined in clean water. This was accomplished by consecutively removing the influence of each type of foulant that was attached to the membrane and calculating each time the resistance to filtration. Initially, the clean membrane resistance was determined, corresponding to the resistance of the membrane material. At the end of each experimental period, the fouled membrane module resistance was determined in clean water. The influence of SS was removed through an 8-h aeration of the module in clean water. Then the impact of soluble and colloidal organics was removed by placing the module into NaOCl solution (1000 mg L$^{-1}$ Cl$_2$) for 8 h. Then the membrane module was placed in 4000 mg L$^{-1}$ citric acid solution for 4 h to remove colloidal-soluble inorganics. The resistance to filtration $R$ (m$^{-1}$) is given by:
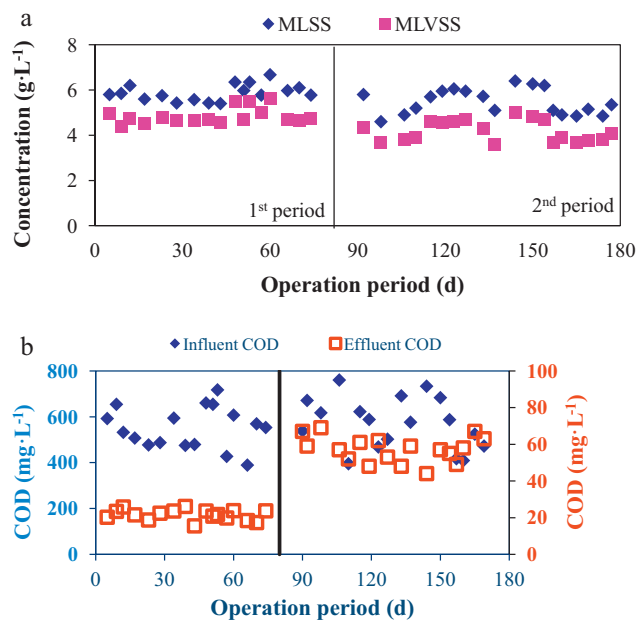
$$R = \frac{TMP}{\mu \times J} \tag{5}$$

where $\mu$ (kg m$^{-1}$ s$^{-1}$) is the permeate viscosity.

## 3. Results and discussion

### 3.1. MBR–RO performance for municipal wastewater treatment

The system operating characteristics are shown in Table 2. The removal of TSS by the MBR was complete, indicating that the membranes were in good condition. Fig. 2a shows the variation of

**Fig. 2.** Variation of (a) MLSS and MLVSS concentration and (b) influent and permeate COD with time for the MBR system.

the MLSS and MLVSS concentration where it is seen that biomass development was stable. In the first period the MLSS concentration ranged from 5.33 to 6.48 g L$^{-1}$ with an average of 5.91 g L$^{-1}$. Fig. 2b shows the influent and treated effluent COD variation where it is seen that the permeate COD was very low (<25 mg L$^{-1}$). The COD removal efficiency achieved by the MBR system was high (95–97%). Complete nitrification of ammonia occurred and since denitrification did not take place in the biological reactor the permeate was characterized by high concentration of nitrate.

The pH in the mixed liquor ranged from 6.9 to 7.6 with an average value of 7.3. The feed wastewater and MBR permeate characteristics are summarized in Table 3. This Table shows the metals' concentration in influent municipal wastewater, MBR permeate, RO permeate and concentrate. Influent wastewater was characterized by high zinc concentrations (on average >400 μg L$^{-1}$) and significant concentration of iron. Copper, chromium and nickel had low average influent concentrations (<50 μg L$^{-1}$). Metal removal achieved by the MBR was on average 90% for Cu (76–99%), 85% for Fe (62–98%), 82% for Mn (64–93%), 80% for Cr (66–92%), 75% for

**Table 3**
Performance of the MBR–RO system for the treatment of municipal wastewater[a] (1st period).

| Parameter | MBR influent | MBR permeate | RO permeate | RO concentrate |
|---|---|---|---|---|
| TSS (mg L$^{-1}$) | 231 (87–380) | <0.5 | – | – |
| VSS (mg L$^{-1}$) | 185 (65–307) | <0.5 | – | – |
| TDS (mg L$^{-1}$) | Not measured | 667 (547–753) | 21 (13–32) | 1073 (885–1233) |
| COD (mg L$^{-1}$) | 551 (389–717) | 21 (18–24) | <4 | 35 (27–42) |
| NH$_4$–N (mg L$^{-1}$) | 53 (39–64) | <0.5 | <0.5 | <0.5 |
| NO$_3$–N (mg L$^{-1}$) | <0.5 | 48 (38–56) | 3.8 (1.8–6.7) | 75 (52–91) |
| Conductivity (μS cm$^{-1}$) | Not measured | 1071 (881–1177) | 36 (21–51) | Not measured |
| Cr (μg L$^{-1}$) | 19.9 (<0.08–54.5) | 4.2 (<0.08–17.0) | <0.08 | 7.2 (<0.08–30.5) |
| Cu (μg L$^{-1}$) | 39.9 (4.2–87.3) | 2.8 (0.6–7.1) | <0.5 | 4.7 (1.1–11.6) |
| Mn (μg L$^{-1}$) | 123.6 (19.2–400) | 16.6 (6.8–50) | 0.7 (<0.5–2.1) | 28.6 (10.8–92.0) |
| Fe (μg L$^{-1}$) | 234.8 (46–582) | 40.4 (1.0–155) | <1 | 66.4 (1.7–241.6) |
| Ni (μg L$^{-1}$) | 10.2 (<0.9–35.8) | 3.7 (<0.9–15.1) | <0.9 | 6.3 (<0.9–26.9) |
| Pb (μg L$^{-1}$) | 97.6 (9.3–329) | 24.9 (0.9–87) | <0.25 | 40.5 (1.8–132.9) |
| Zn (μg L$^{-1}$) | 411.1 (117–940) | 117.8 (3.0–435) | 1.3 (<0.05–5.3) | 195.3 (5.7–721.2) |
| K (mg L$^{-1}$) | 30.9 (7.2–65.4) | 24.3 (6.1–48.5) | 1.8 (0.2–3.7) | 39.6 (12.9–74.6) |
| Na (mg L$^{-1}$) | 232.3 (115.1–387.3) | 162.7 (59.1–321.3) | 9.3 (5.4–15.0) | 268.9 (92.1–538.0) |
| Ca (mg L$^{-1}$) | 243.1 (112.4–415.9) | 101.0 (43.4–156.8) | 2.1 (0.02–4.2) | 166.9 (68.4–265.3) |
| Mg (mg L$^{-1}$) | 40.7 (11.2–59.3) | 16.5 (4.2–29.4) | 0.6 (0.2–1.6) | 28.1 (7.1–52.5) |

[a] The variation of each parameter is given in parenthesis.

**Table 4**
Comparison of MBR and MBR–RO metal removal for municipal wastewater.

| MBR | MBR–RO | Reference |
|---|---|---|
| Cu(90%), Fe(85%), Mn(82%), Cr(80%), Zn(75%), Pb(73%), Ni(67%), Mg(61%), Ca(57%), Na(30%), K(21%) | Cu(>97.1%), Fe(>99.3%), Ni(>90.9%), Pb(>99.2%), Cr(>99.0%), Mn(>99.1%), Zn(>99.8%), Na(95.7%), K(94.1%), Ca(99.1%), Mg(98.5%) | Present study |
| Cu(95%), Zn(94%), Ni(86%), Cr(75%), Pb(74%) | – | [14] |
| Cr(72%), Ni(72%), Pb(74%), Zn(83%), Cu(90%) | – | [15] |
| Cd(>50%), Cu(90%), Pb(88%), Ni(50%), Zn(51%) | – | [16] |
| Pb(>99.9%), Ni(>99.9%), Cu(49%), Cr(89%) | Cu(>99.9%), Cr(>99.9%) | [3] |
| Fe(99%), Mn(92%) | – | [17] |
| Cr(>99%), Cu(94%), Fe(90%), Mn(77%), Ni(48%), Pb(88%), Zn(77%) | – | [18][a] |
| Cr(>99%), Cu(49%), Fe(94%), Mn(84%), Ni(65%), Pb(16%), Zn (77%) | – | [18][b] |

[a] The MBR operated at MLSS = 9.2 g L$^{-1}$.
[b] The MBR operated at MLSS = 16.6 g L$^{-1}$.

Zn (49–99%), 73% for Pb (50–98%), 67% for Ni (51–86%), 61% for Mg (47–73%), 57% for Ca (34–79%), 30% for Na (12–53%), 21% for K (8–39%). Thus, significant variation in the removal efficiencies of all metals occurred. This work demonstrates that divalent and trivalent metals were more effectively removed than monovalent ones. This happened probably because divalent and trivalent metals were more easily attached to activated sludge than monovalent ones. It seems that activated sludge is more selective towards the former metal ions. The metal removal order is in agreement with that reported in the review of Santos and Judd [1]. The obtained Cu, Pb and Cr removal was similar to that of previous works [14,15], while Zn and Ni removal was higher than that reported by Cecchi et al. [16] and lower than the one reported by Fatone et al. [14]. Yang et al. [17] obtained higher Fe and Mn removal than that of the present study (Table 4). These variations can be attributed to differences in activated sludge characteristics, operating conditions, influent metal concentrations as well as the membrane pore size.

As mentioned, the metal removal achieved by the MBR was variable. This can be attributed to fluctuations in influent metal concentration, MLSS concentration, pH and metal competition. In most cases, low metal removal was associated with low mixed liquor pH (7.0–7.1), low influent metal concentrations, low MLSS concentrations (5.4–5.7 g L$^{-1}$) and/or with the presence of competitive metal cations. For example, very high (>96%) removal efficiencies were obtained for Cu on days 17 and 51. On day 17, high mixed liquor pH (7.4) and high influent Cu concentration were observed, which seem to result in high copper removal, despite the relatively low MLSS concentration. On day 51, the MLSS concentration (5.97 g L$^{-1}$) and the pH (7.3) were high and this probably resulted in high copper and manganese removal. On day 48, the high MLSS concentration (6.35 g L$^{-1}$) seems to be related to the high removal of copper, chromium and iron. However, a clear trend could not be identified due to the interaction and fluctuation of these parameters and particularly due to the low influent metal concentrations. Bolzonella et al. [18] operated two MBR systems treating municipal wastewater at MLSS concentrations of 9.2 and 16.6 g L$^{-1}$ respectively and found that the metal removal efficiencies in the two cases were similar. On the contrary, Santos and Judd [1] mentioned that the increase in MLSS resulted in an increase of heavy metal removal.

The RO unit was evaluated in terms of its ability to remove TDS, organic matter, nitrate and metals (Table 3). TDS removal efficiencies were 95–99% with the TDS in the RO permeate being very low (on average 21 mg L$^{-1}$). RO effectively removed organic matter, since the COD concentration in the RO permeate was below the detection limit (<4 mg L$^{-1}$). RO could remove nitrate at an average efficiency of 92%. However, NO$_3$–N was detected in the RO permeate and on average it was 3.8 mg L$^{-1}$. Thus, complete removal of nitrates did not usually occur. Other studies have also shown that it is not possible to eliminate nitrates. Dialynas and Diamadopoulos [3] treated MBR permeate with RO and found significant concentrations of nitrogen in the RO permeate (17–21 mg L$^{-1}$). Comerton et al. [19] concluded that despite the high nitrate removal efficiency achieved by RO membranes (>90%), the RO permeate had nitrogen concentrations up to 3.6 mg L$^{-1}$.

The RO system achieved complete removal (i.e. below the detection limit) of Cu, Fe, Ni, Cr and Pb. The average removal of the other metals was Mn(>95.3%), Zn(>99.0%), Na(93.7%), K(92.4%), Ca(97.8%), Mg(96.1%). The adoption of the integrated MBR–RO system provided excellent water quality (Table 4), with the complete removal (i.e. below the detection limit) of Cu, Fe, Ni, Pb and Cr, of Zn >99.8%, of Ca 99.1% and of Mg 98.5%. The monovalent cations Na and K were less effectively removed (95.7% and 94.1% respectively).

### 3.2. MBR–RO performance for the treatment of wastewater spiked with heavy metals

The MBR–RO performance was assessed for the treatment of wastewater which was occasionally spiked with significant concentrations of Cu, Pb, Ni and Zn. This experiment aimed to test the system response at significant influent heavy metal concentrations. The influent municipal wastewater was periodically spiked with heavy metals, each time for a period of 6 h (Table 5). The addition of heavy metals resulted in a reduction of the MLSS and MLVSS concentration compared to that of the 1st period due to partial inhibition of biomass. In particular, MLVSS reduction was approximately 11% (Fig. 2a). Despite this reduction, the biomass concentration was relatively stable. COD removal efficiency was satisfactory (86–94%), but lower than that of the first period. The COD concentration of the MBR permeate was higher compared to that of the 1st period and ranged from 44 to 69 mg L$^{-1}$, due to partial inhibition of heterotrophic biomass. Nitrification efficiency ranged from 28 to 58% depending on the influent metal concentration, showing that significant inhibition of autotrophic biomass occurred. The average nitrification efficiency observed in the second period was 40%.

The Cu, Pb, Ni and Zn concentration in influent industrial wastewater, MBR permeate, RO permeate and RO concentrate during the 2nd period are given in Table 5. The metal removal achieved by the MBR followed the order: Pb(96%, 92–99.7%) > Cu(85%, 76–96%) > Zn(78%, 68–92%) > Ni(48%, 38–59%). Comparing the metal removal accomplished by the MBR system for municipal wastewater and wastewater containing significant heavy metal concentrations it is observed that Cu and Zn had similar behaviour, while Pb was less effectively removed from municipal wastewater. On the contrary, Ni removal was much higher in the case of municipal wastewater. It seems that at lower influent concentrations, it is easier for nickel to be adsorbed on activated sludge. Nevertheless, in both cases Ni was the metal exhibiting the lowest removal compared to the other three metals.

Several mechanisms are involved in metal removal. These include metal precipitation, with the metals precipitating either independently or due to their entrapment in the sludge floc matrix, the adsorption of metals on extracellular polymeric substances, the uptake of metals by the biomass cells [20,21] and the retention of particulate metal forms by the membranes. Intracellular accumulation of heavy metals is conducted by living cells and its contribution to metal removal is considered to be limited [22–25].

**Table 5**
Performance of the MBR–RO system for the treatment of wastewater spiked with heavy metals[a] (2nd period).

| Parameter | MBR influent | MBR permeate | RO permeate | RO concentrate |
|---|---|---|---|---|
| TSS (mg L$^{-1}$) | 241 (113–525) | <0.5 | – | – |
| VSS (mg L$^{-1}$) | 187 (74–451) | <0.5 | – | – |
| TDS (mg L$^{-1}$) | Not measured | 743 (609–870) | 26 (14–39) | 1203 (833–1576) |
| COD (mg L$^{-1}$) | 570 (395–733) | 57 (44–69) | <4 | 92 (67–117) |
| NH$_4$–N (mg L$^{-1}$) | 47 (36–60) | 24 (11–32) | 1.1 (<0.5–2.1) | 39 (17–57) |
| NO$_3$–N (mg L$^{-1}$) | <0.5 | 17 (8–32) | 2.2 (<0.5–5.2) | 31.4 (16.6–51.7) |
| Conductivity (μS cm$^{-1}$) | Not measured | 1181 (1055–1310) | 40 (23–58) | Not measured |
| Cu (mg L$^{-1}$) | 6.36 (4.28–9.11) | 0.95 (0.19–1.38) | 0.02 (<0.00005–0.08) | 1.60 (0.28–2.21) |
| Pb (mg L$^{-1}$) | 8.78 (5.75–11.58) | 0.35 (0.02–0.76) | 0.003 (<0.00025–0.02) | 0.60 (0.03–1.25) |
| Ni (mg L$^{-1}$) | 9.94 (6.21–12.03) | 5.17 (2.73–7.34) | 0.15 (<0.0009–0.34) | 8.60 (4.90–12.92) |
| Zn (mg L$^{-1}$) | 8.54 (4.34–11.33) | 1.86 (0.55–3.45) | 0.04 (<0.00005–0.12) | 3.17 (0.87–5.99) |

[a] The variation of each parameter is given in parenthesis.

In the second part of this study where influent wastewater is spiked with significant heavy metal concentrations and some biomass was actually dead, biosorption is considered to be much more important than intracellular accumulation. The extent of metal solubility dictates whether the metals will penetrate into the MBR permeate. Ni was mainly in soluble form at the mixed liquor pH range and was not effectively retained by the UF membranes. On the other hand, Pb was mainly removed due to precipitation. As a result, the MBR permeate was always characterized by low Pb concentrations (<0.8 mg L$^{-1}$) irrespective of the MLSS concentration and the influent Pb concentration. Zn, Cu and Ni concentrations in the MBR permeate exhibited fluctuations due to changes in mixed liquor pH, influent metal concentration and MLSS concentration. Copper also formed insoluble compounds to some extent and was thus rejected by the membranes. Adsorption was an important removal mechanism since in most cases an increase in MLSS resulted in an increase of metal removal, which was more evident for Cu and Zn. For example, on days 144 and 150 when high MLSS concentrations were measured (6.3–6.4 g L$^{-1}$) the removal of copper (7.9–8.2 mg L$^{-1}$) and zinc (7.8–8.6 mg L$^{-1}$) was very high. This removal is calculated as the difference between the influent and effluent metal concentrations.

The adsorption capacity of sludge depends on the pH, the metal type, the influent metal concentration, the presence and concentration of competitive ions and the MLSS concentration. In Table 6 the amount of metal that is adsorbed and that precipitates per sludge MLSS at the end of the 6-h period is given for all four metals (i.e. amount of particulate metal in the mixed liquor). Lead exhibited the highest removal since the vast majority of lead precipitated. The metal exhibiting the lowest amount of removal was nickel. The pH range of the mixed liquor did not favour nickel precipitation; also activated sludge selectivity towards nickel was limited.

The RO unit resulted in the production of high quality treated water. The treated water could easily meet the US EPA reclaimed water recommended limits for agricultural irrigation [26]. Effective COD removal was accomplished by the RO system since its concentration was below the detection limit of 4 mg L$^{-1}$. Nevertheless, RO produced a waste stream with significant metals and organic content, which had to be treated prior to its disposal. The average heavy metal removal achieved by the RO unit was Cu(98.1%), Pb(99.3%), Ni(97.1%) and Zn(97.5%). The combined MBR–RO system accomplished average removals of 99.7% for Cu, >99.9% for Pb, 98.5% for Ni and 99.5% for Zn.

### 3.3. Assessment of biomass growth inhibition

As it has been mentioned in Section 2.2 the addition of heavy metals in the influent wastewater was only conducted for a specific time period (6 h) and thus heavy metal accumulation inside the biological reactor was limited. Nevertheless, partial inhibition of biomass growth occurred since the influent heavy metal concentrations were significant. Fig. 3a shows the variation of sOUR with time for both the 1st and the 2nd periods. A significant decrease of the heterotrophic biomass activity was observed when heavy metals were introduced into the system. The average inhibition of heterotrophic biomass growth was found to be 49%. Inhibition of heterotrophic biomass growth resulted in a reduction of the MLVSS concentration and an increase of the permeate COD concentration in the 2nd period compared to the values obtained in the 1st period.

Fig. 3b illustrates the measured sAUR for the two experimental periods showing the significant reduction of autotrophic biomass activity occurring in the 2nd period due to the presence of heavy metals inside the biological reactor. The average inhibition of autotrophic biomass growth was found to be 66%.

**Table 6**
Amount of particulate metal in the mixed liquor at the end of the 6-h heavy metal addition (2nd period).

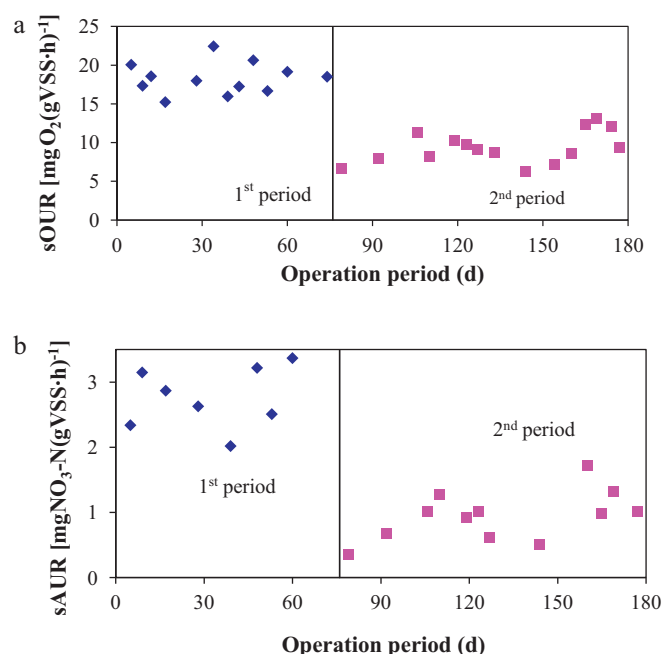| Metal | Amount of metals adsorbed and precipitated (mg metal) (g MLSS)$^{-1}$ | | |
|---|---|---|---|
| | Average | Variation | St. deviation |
| Cu | 1.51 | 1.04–2.00 | 0.27 |
| Pb | 2.39 | 1.57–3.56 | 0.55 |
| Ni | 1.36 | 0.87–2.19 | 0.30 |
| Zn | 1.87 | 0.97–2.51 | 0.43 |



**Fig. 3.** Variation of the (a) sOUR and (b) sAUR of activated sludge with time.

**Table 7**
Heavy metal concentrations of the RO concentrate (i.e. inflow to fixed bed column) and the treated stream (i.e. outflow from the fixed bed).

| Sample | Zeolite | Cu | Ni | Pb | Zn |
|---|---|---|---|---|---|
| RO Concentrate (Inflow) (mg L$^{-1}$) | – | 1.440 (0.18–2.212) | 8.255 (5.210–12.920) | 0.700 (0.034–1.250) | 2.340 (0.657–5.990) |
| Outflow $t = 10$ (mg L$^{-1}$) | New | 0.019 (<0.0005–0.063) | 0.549 (0.101–0.921) | 0.008 (<0.00025–0.031) | 0.030 (0.003–0.087) |
| Outflow $t = 20$ (mg L$^{-1}$) | New | 0.068 (0.001–0.201) | 1.268 (0.489–1.982) | 0.017 (<0.00025–0.042) | 0.091 (0.009–0.255) |
| Outflow $t = 40$ (mg L$^{-1}$) | New | 0.106 (0.004–0.254) | 2.728 (1.523–4.171) | 0.042 (<0.00025–0.112) | 0.166 (0.013–0.703) |
| Outflow $t = 60$ (mg L$^{-1}$) | New | 0.163 (0.004–0.399) | 3.885 (2.654–5.168) | 0.066 (<0.00025–0.174) | 0.254 (0.013–0.992) |
| Outflow $t = 10$ (mg L$^{-1}$) | Regenerated | 0.025 (0.001–0.094) | 0.759 (0.148–1.330) | 0.010 (<0.00025–0.026) | 0.035 (0.007–0.077) |
| Outflow $t = 60$ (mg L$^{-1}$) | Regenerated | 0.178 (0.005–0.451) | 4.129 (2.383–5.368) | 0.076 (0.009–0.189) | 0.301 (0.029–1.252) |

### 3.4. Fixed bed columns for the treatment of RO concentrate

The concentrate produced by the RO unit was treated using a fixed bed column packed with natural zeolite in order to reduce heavy metal concentrations to acceptable levels for safe discharge. Table 7 shows the metal concentration in the untreated RO concentrate and in the column outflow after certain time intervals of column operation. This system could effectively remove Cu, Pb and Zn, since after 60 min of column operation their concentrations in the treated effluent did not exceed 0.4 mg L$^{-1}$, 0.2 mg L$^{-1}$ and 1.0 mg L$^{-1}$ respectively. This system was not effective for Ni removal for the same time period. When the column was operated up to 10 min the removal of all four metals was satisfactory, since the metal concentration of the treated effluent was lower than 1 mg L$^{-1}$. The inferior performance of nickel was attributed firstly to the low selectivity of clinoptilolite for this metal and secondly to the higher Ni concentration in the column inlet.

The regeneration of used zeolite with 1 M KCl solution proved to be effective. The results of Fig. 3 show that regenerated zeolite usually performed well compared to the new zeolite. In some cases the regenerated zeolite exhibited inferior performance, while in some cases it resulted in higher metal removal than new zeolite. The latter could be possibly attributed to the modification of the mineral structure caused by the regenerating solution. Natural zeolite could also partially remove the organic matter of the concentrate since 17.5–28.4% of COD removal was observed.

### 3.5. Membrane fouling

When the MBR treated municipal wastewater the rate of membrane permeability reduction with time was 1.48 L m$^{-2}$ h$^{-1}$ bar$^{-1}$ d$^{-1}$, while this rate increased to 1.68–1.79 L m$^{-2}$ h$^{-1}$ bar$^{-1}$ d$^{-1}$, when heavy metals were introduced (i.e. 2nd period). Heavy metal addition increased inorganic fouling since metals deposited on the membrane surface and interior. Table 8 shows the contribution of the membrane material and of the deposited substances to the total resistance to filtration flow. In the case of industrial wastewater the contribution of colloidal and soluble inorganics to resistance was higher compared to that obtained for municipal wastewater (10.4% against 2.3%).

**Table 8**
Contribution of membrane material and deposited substances to the total resistance to filtration for (a) municipal wastewater and (b) wastewater spiked with heavy metals.

| Membrane material and foulants | Contribution to filtration resistance (%) | |
|---|---|---|
| | 1st period (Municipal wastewater) | 2nd period (Wastewater-heavy metals) |
| Membrane material | 14.4 | 13.8 |
| Colloidal and soluble organics | 68.5 | 62.1 |
| Soluble inorganics | 2.3 | 10.4 |
| Suspended solids | 14.8 | 13.7 |

## 4. Conclusions

The metal removal of the MBR system treating municipal wastewater followed the order Cu(90%) > Fe(85%) > Mn(82%) > Cr(80%) > Zn(75%) > Pb(73%) > Ni(67%) > Mg(61%) > Ca(57%) > Na(30%) > K(21%). For wastewater containing significant heavy metal concentrations the order was Pb(96%) > Cu(85%) > Zn(78%) > Ni(48%). The variability in metal removal efficiencies was attributed to fluctuations in influent metal concentrations, metal competition, changes in pH and MLSS concentration. In the case of municipal wastewater, the RO achieved complete removal of Cu, Fe, Ni, Cr and Pb while the removal of the other metals was Mn(>95.3%), Zn(>99.0%), Na(93.7%), K(92.4%), Ca(97.8%) and Mg(96.1%). When wastewater containing significant heavy metal concentrations was treated, the heavy metal removal achieved by the RO unit was Cu(98.1%), Pb(99.3%), Ni(97.1%) and Zn(97.5%). The combined MBR–RO system effectively treated both municipal and industrial wastewater, accomplishing metal removal higher than 90%. Fixed bed column packed with zeolite was effective for the removal of Cu, Pb and Zn from the RO concentrate, while Ni removal was satisfactory only at the initial stages of column operation. Finally, heavy metals increased inorganic fouling of the MBR system.

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