Removal performance of heavy metals in MBR systems and their influence in water reuse

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ABSTRACT

The removal performance of heavy metals by two experimental full-scale membrane bioreactors (microfiltration and ultrafiltration) and the influence of activated sludge total suspended solid (TSS) concentration were studied under real operational conditions. Influent and effluent Be, Sc, V, Cr, Mn, Co, Ni, Cu, Zn, As, Mo, Cd, Ba, Sn, Sb, Pb and U concentrations were analysed by inductively coupled plasma-mass spectrometry. An average contamination rate for most of the analysed heavy metals was observed in raw wastewater, resulting in effluents without limitation for reuse in agricultural destinations according to Spanish law. Removal efficiencies up to 80% were obtained regardless of whether microfiltration or ultrafiltration membranes were used, except for As, Mo and Sb. The removal yields of different heavy metals can be strengthened by increasing the activated sludge TSS concentration, mainly at concentrations above 10 g/L.

Key words | heavy metals, microfiltration, ultrafiltration, water reuse

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INTRODUCTION

Heavy metals are considered to be elements with a density higher than 5 g/cm^3, which are present in the environment mainly via human activity such as traffic or industrial activities (Sörme & Lagerkvist 2002). Some of these elements cause acute or chronic toxicity to higher organisms, including humans, microorganisms and plants, which has led to increasing their regulation in water and sludge reuse, also, given its tendency to bioaccumulate (Chipasa 2003).

In this regard, wastewater treated by a conventional process might present problems due to the excessive presence of heavy metals in treated water, both in the liquid phase or associated with suspended solids (Karvelas *et al.* 2003). Membrane bioreactor (MBR) technology has proved its ability to provide high quality water for reuse (Arévalo *et al.* 2012), due in part to the total retention capacity of the suspended solids generated in the biological process, increasing the heavy metal removal capacity to between 5 and 13% compared with conventional processes (Santos & Judd 2010).

The reuse in agriculture of treated water or sewage sludge with heavy metals can lead to problems of accumulation in soils and its passage to plants, and entry into the trophic pyramid (Chipasa 2003). This has motivated an increase in the regulatory processes related to the control of heavy metals in the environment, prominent among which is the Water Framework Directive (2000/60/EC) which indicates the need to control certain metals as major priority pollutants. The Spanish legislation for water reuse (RD 1620/2007) determined as a control parameter for agricultural reuse the concentration of As, Be, Cd, Co, Cr, Cu, Mn, Mo, Ni, Se and V.

Heavy metal removal by MBR systems presents changing yields depending on the conditions which have been used to carry out the study. Several investigations have been developed with synthetic wastewater enriched with heavy metals, with high concentrations, and specific conditions of inlet concentration, sludge retention time (SRT), hydraulic retention time (HRT), pH, addition of reagents, etc. (Nakhla *et al.* 2008; Katsou *et al.* 2011). The removal of heavy metals in MBR systems is determined mainly by biosorption (Fatone *et al.* 2005; Santos & Judd 2010) and next to other mechanisms such as chemical precipitation (Chipasa 2003).

Heavy metals that are less frequent or have lower natural concentrations have escaped the study of their evolution and fate in wastewater treatment plants. Studies have focused on the key elements, such as Cu, Cd, Hg, Pb, Zn,

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As and Ni (Chipasa 2003; Karvelas *et al.* 2003) while a wide range of metals that can cause toxicity problems have been omitted from study. These compounds have also tended to be evaluated in laboratory-scale plant or on a small scale, with synthetic wastewater, while there is a great lack of knowledge of the processes and results expected in large-scale MBR systems treating real urban wastewater.

In view of this, the objectives of this paper are to compare the heavy metal removal performance of two MBR systems (microfiltration and ultrafiltration) working under real operational conditions. The concentrations of heavy metals in the influent and effluent and the influence of the concentration of activated sludge total suspended solid (TSS) concentration were analysed.

METHODS

Two full-scale MBRs configured in pre-denitrification mode and equipped with microfiltration and ultrafiltration membranes were used for the experiment (Figure 1) during a period of 475 days. Both installations running in parallel were located at the wastewater treatment plant (WWTP) of Granada (Spain). The ultrafiltration MBR system was equipped with hydrophilicised hollow-fibre submerged ultrafiltration membranes (0.034 μm nominal pore size) made of polyvinylidenefluoride (PVDF) with a maximum treatment capacity of 120 m^3/d. The microfiltration MBR system was equipped with hydrophilicised submerged plane microfiltration membranes (0.4 μm nominal pore size) made of polyethylene (PE) with a maximum treatment capacity of 36 m^3/d. Influents to installations were pre-treated raw wastewater. The sludge purge was carried out from the aerated reactor from both installations as a function of the selected SRT, varying between 20 and 45 days. Membranes were chemically cleaned using NaClO (100 mg/L) in scheduled procedures if the trans-membrane pressure (TMP) became excessively high.

The heavy metals analysed were Be, Sc, V, Cr, Mn, Co, Ni, Cu, Zn, As, Mo, Cd, Ba, Sn, Sb, Pb and U. Samples were analysed by source mass spectrometry inductively coupled plasma technique (ICP-MS) over 24-hour composite samples from the influent and the effluent of each experimental plant. Samples were introduced into an ICP-MS Sciex Elan model Perkin Elmer 5000 using an internal calibration (Rhodium) and standard calibration multi-element for dilution with 10% HNO_3. The detection limit was 0.01 μg/L for the majority of analysed heavy metals, apart from Be and Cr with a detection limit of 0.1 μg/L. Activated sludge from each experimental installation was analysed daily for TSS concentration according to *Standard Methods* (APHA 1992).

Data obtained through this study were analysed by computer-assisted statistics, using STATGRAPHICS Plus for Windows 3.0 by Statistical Graphics Corp. (1997). An analysis of variance (ANOVA) test was used to assess homogeneity of variance with a significance level of 5% ($p < 0.05$).

RESULTS AND DISCUSSION

In accord with the experiences of Arévalo *et al.* (2012), both MBR systems produced effluent with a high degree of clarification, with physical and microbiological characteristics far better than the minimum standards set by Spanish law for wastewater reuse (RD 1620/2007).

The concentrations of the analysed heavy metals in the urban wastewater of Granada are shown in Table 1. With respect to heavy metal concentrations described in the literature, it is observed that input to the experimental installation has an average contamination degree in most of the analysed elements, while in some of them (Be, Sn, V and Sb) concentrations are greater than those observed in other scientific papers. However, Cd, Ni and Zn have concentrations lower than those usually observed in urban wastewater (Fatone *et al.* 2005; Santos & Judd 2010; Choubert *et al.* 2011).

MBR systems generally have a greater capacity for removing heavy metals from wastewater compared to conventional technologies due to physical separation of the membrane with a significant removal of suspended solids (Santos & Judd 2010). Effluent quality was high, regardless of whether microfiltration or ultrafiltration membranes were used with no statistical significant differences between the effluent concentrations of analysed heavy metals, according to the *p*-value registered in Table 1.

High heavy metals' removal efficiency yields were generally observed for both installations (Figure 2), with up to 13 of the 18 elements studied with yields above 80%. However, the yield for As was low both for microfiltration and ultrafiltration. The removal capacity of the facilities with respect to the performance data from the literature were usually similar (Battilani *et al.* 2010; Santos & Judd 2010), improving the percentages referenced for V, Mn, Co, Cu, Sn and Ba.

Recent work with the same installations showed no difference in biological activity between the two facilities (Ruiz *et al.* 2011) and both installations worked with very

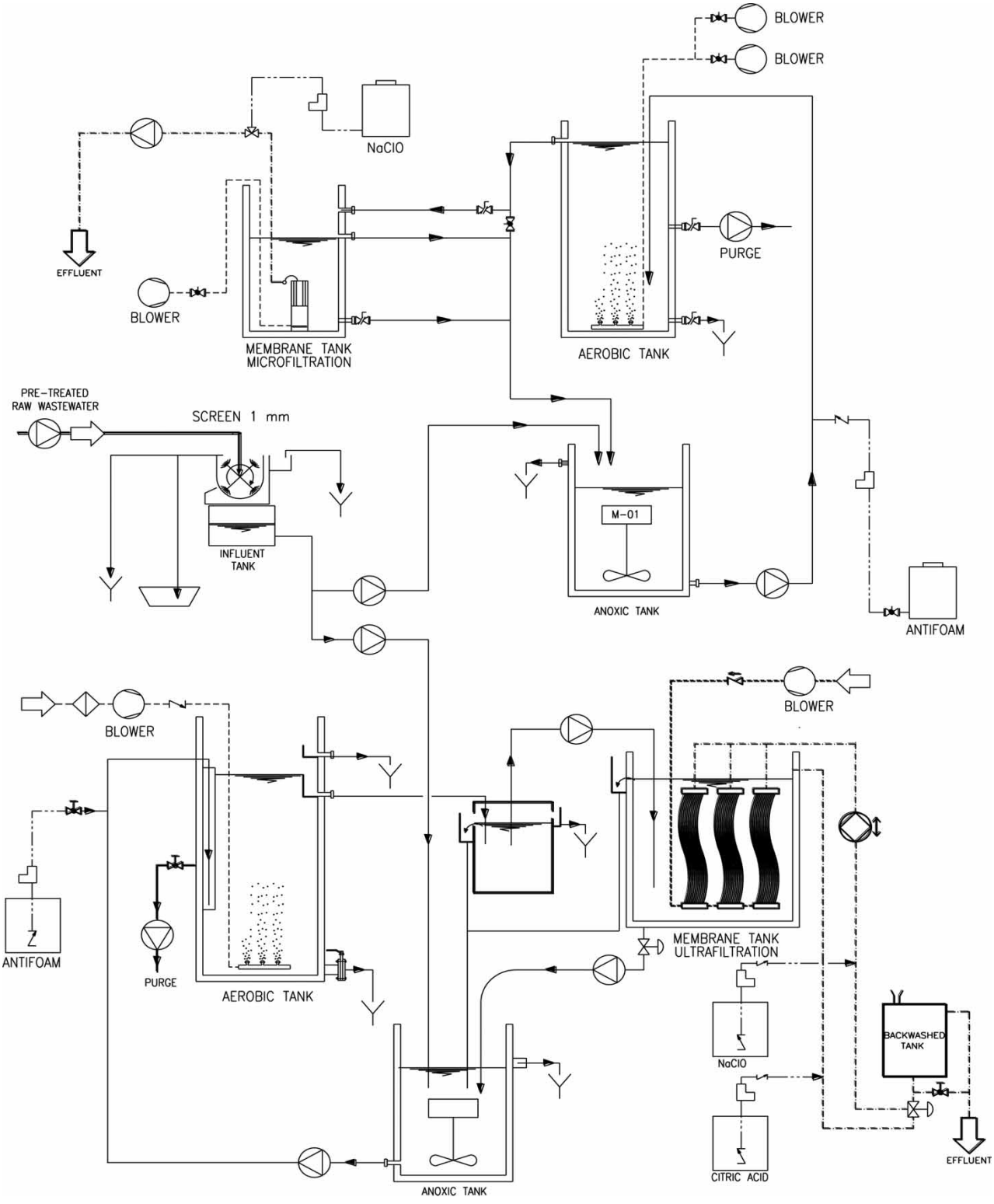

Figure 1 | Layout of experimental installations.

Table 1 | Concentrations of heavy metals obtained from influents and effluents (in μg/L)

	Influent	Microfiltration effluent			Ultrafiltration effluent			
	Avg.	Avg.	Max.	Min.	Avg.	Max.	Min.	*p*-value
Be	0.174	0.007	0.041	n.d.	0.012	0.086	n.d.	0.3602
Sc	8.391	1.8361	2.872	0.751	1.902	3.629	0.751	0.6245
V	14.685	1.530	3.028	0.514	1.557	2.402	0.580	0.2470
Cr	25.324	2.677	4.430	0.699	2.176	4.190	0.650	0.4305
Mn	62.182	0.411	1.050	n.d.	0.712	2.760	n.d.	0.4891
Co	1.774	0.229	0.380	0.127	0.221	0.303	0.127	0.5914
Ni	27.061	4.599	9.170	2.451	4.912	9.510	2.451	0.5556
Cu	152.908	3.474	6.340	0.002	2.773	7.150	0.498	0.3118
Zn	260.071	38.441	71.700	5.374	33.707	57.550	5.471	0.4266
As	2.401	1.832	2.866	0.919	1.982	3.569	0.832	0.4217
Mo	3.592	1.259	1.976	0.650	1.499	2.701	0.572	0.1224
Cd	0.384	0.016	0.040	n.d.	0.014	0.050	n.d.	0.7668
Sn	57.767	2.171	5.010	n.d.	1.450	4.700	n.d.	0.2697
Sb	6.171	2.469	5.420	0.327	2.099	6.110	0.326	0.5506
Ba	96.570	1.916	5.800	n.d.	1.199	4.610	n.d.	0.1943
Pb	70.174	0.477	0.951	0.052	0.437	1.186	0.037	0.6352
U	1.366	0.0389	0.160	n.d.	0.016	0.035	n.d.	0.0415

n.d. Not detected.

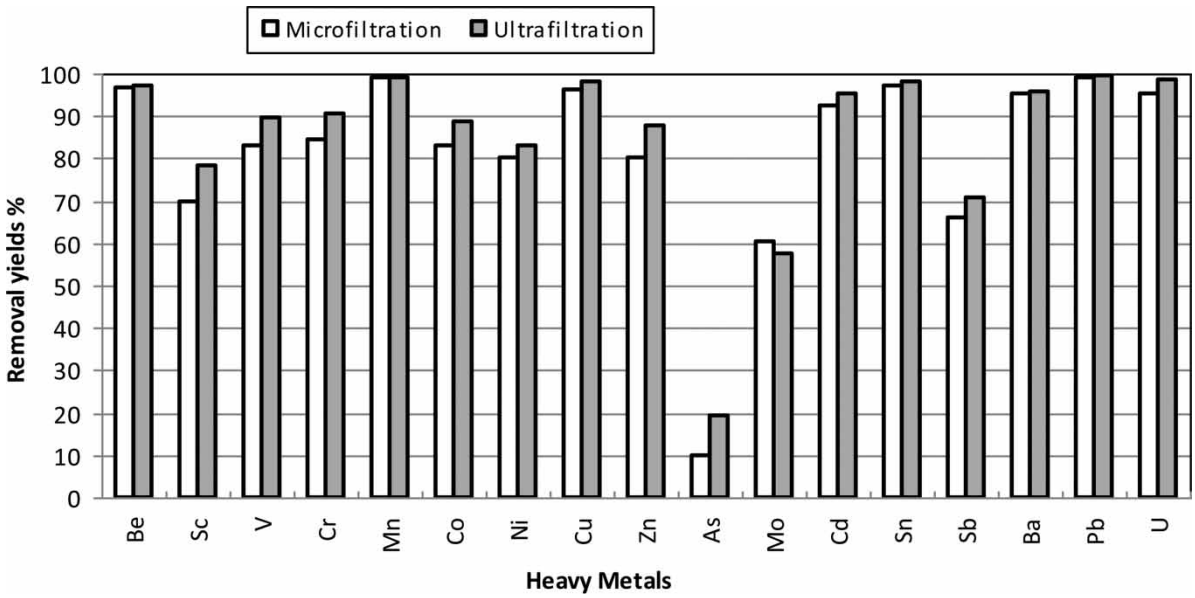

Figure 2 | Heavy metal yield removal in the facilities.

similar activated sludge TSS concentrations. Thus, the removal of heavy metals from the aqueous phase due to binding to sludge compounds should be similar. The two technologies have different pore sizes (ultrafiltration and microfiltration); however, effluent from both installations do not contain suspended solid. Membranes in MBR can increase their capacity to retain macromolecules due to the effect of the filter cake layer that adheres to the

membrane surface mainly in microfiltration (Tao *et al.* 2005), reducing the effective pore size range.

Comparing the results obtained in the effluent with the requirements set in RD 1620/2007 establishing the legal Spanish framework for the reuse of treated water, the effluent heavy metals' concentrations are lower than the limits established, so the presence of heavy metals in the effluent from MBR with ultrafiltration or microfiltration membrane would not present a limitation in the reuse of treated wastewater in an agricultural destination under our experimental conditions.

The removal of heavy metals in activated sludge systems is defined by several mechanisms, such as biosorption (Chipasa 2003). The sludge has negative charges on its surface, which interact with the positive charges of heavy metals and remove them from the water, being adsorbed to carboxylic, hydroxylic, phosphate and sulfonate groups of the lipids, proteins and polysaccharides found on the cell surfaces. Other mechanisms are bioaccumulation, sorption to extracellular biopolymers or particles, and chemical precipitation (Chipasa 2003).

Several heavy metals, such as Cr, Cd, Cu, Zn, Sn and Pb have a greater affinity for attachment to sludge compounds, so they are more effectively removed; the effluent concentrations are low whereas sludge concentration increases by accumulation. For Ni, Co, Ba and U, adsorption to sludge is possible but the velocity of adsorption is lower so that their elimination yields are usually lower, while there are some heavy metals, such as As or Mo, that remain in the aqueous phase (Choubert *et al.* 2011) for which removal yield is poor.

As presents the worst removal percentage of the analysed heavy metals. This element usually is present in the aqueous phase of activated sludge. The failure of the activated sludge to remove this metalloid is probably due to the particular chemistry in wastewater processes. Given the typical range of pH values (6–8) and redox values (from −100 to +300 mV), As will be present as a mixture of two forms: arsenate, As(V), and arsenite, As(III). Arsenate can be present as $H_2AsO_4^-$ and $HAsO_4^{2-}$, which are soluble and negatively charged, so they do not react with binding sites in the activated sludge. Arsenite is present as H_3AsO_3, a neutral molecule with low chemical reactivity (Bolzonella *et al.* 2010). Thus, biological treatment yields, without seeking specific removal of As, are generally between 8 and 55% (Shafer *et al.* 1998).

Both facilities worked with a similar TSS concentration, between 0.5 and 22 g/L. In order to evaluate the influence of activated sludge concentration on heavy metals removal, four comparison groups, from <5, 5–10, 10–15 and 15–20 g/L were obtained (Table 2). Statistically significant differences between TSS concentrations were obtained for 14 of the 18 elements studied and, in most of them, an improvement in heavy metal removal was observed when there was an increase in suspended solids' concentration. The lower removal yields were observed for activated sludge concentrations under 5 g/L whereas higher removal was observed for activated sludge concentrations over 20 g/L (Table 2). Due to its chemical characteristics, this behaviour was outlined for As.

No influence for activated sludge concentration was observed for Be, Mo and Ba, whereas for Cr, Ni, Sb, Cr or Zn the influence of activated sludge concentration was significant. The ionic forms of these metals at the usual activated sludge pH values have high affinity for the biomass flocs (Malamis *et al.* 2009) and these heavy metals are effectively retained by membranes. Thus, the increase in TSS concentration in the activated sludge increases the elimination yields. On the other hand, the usual small size of activated sludge flocs in the MBR increased the sludge surface and therefore increased the electrostatic binding of heavy metals to sludge compounds (Rossin *et al.* 1982).

High removal yield regardless of TSS concentration was observed for Mn, Cu, Cd, Sn, Ba, Pb and U. Mn is subjected

Table 2 | Heavy metals' removal efficiency (%) as a function of activated sludge TSS concentration

Heavy metal	<5 g/L (%)	5–10 g/L (%)	10–15 g/L (%)	15–20 g/L (%)	*p*-value
Be		96.98	93.44	97.84	0.5981
Sc	79.69	63.70	83.14	82.46	0.0078
V	87.19	81.41	90.11	96.18	0.0106
Cr	81.29	83.18	96.29	96.82	0.0067
Mn	96.58	98.96	99.60	99.51	0.0136
Co	86.44	82.01	90.34	92.22	0.0519
Ni	76.89	77.45	89.92	91.08	0.0046
Cu	96.71	95.47	99.51	99.74	0.0058
Zn	74.13	78.00	92.49	97.35	0.0001
As	−8.45	1.63	27.70	58.25	0.0197
Mo	70.11	58.52	56.57	56.68	0.3038
Cd	92.22	91.64	100	99.81	0.0140
Sn	94.95	96.57	100	99.96	0.0243
Sb	65.80	61.51	72.00	85.63	0.0040
Ba	93.27	95.68			0.3438
Pb	97.63	99.12	99.54	99.51	0.0642
U	97.48	94.10	99.80	99.91	0.0005

to oxidation during aerobic treatment, so soluble Mn(II) is transformed into insoluble Mn(IV) which is significantly removed independently of activated sludge TSS concentration (Karvelas *et al*. 2003). High removal capacity has been observed for Pb at 5 g/L of TSS concentration which was removed completely, indicating that Pb was present in particulate form (Dialynas & Diamadopoulos 2009).

Under our working conditions, the increase in the TSS concentration above 10 g/L allowed yields for the majority of heavy metals' removal from the effluent close to 100%. In other conditions, it may be necessary to apply specific tertiary treatment for heavy metals' removal, or the addition of reagents to the sludge to increase its binding capacity, such as activated carbon or vermiculite (Santos & Judd 2010).

CONCLUSIONS

We assessed the removal capacity of a wide range of heavy metals present in urban wastewater from the city of Granada (Spain) by two different MBR technologies (microfiltration and ultrafiltration), in order to reuse the treated wastewater. The conclusions that can be drawn are as follows.

Raw urban wastewater from Granada presents an average contamination rate for most of the analysed heavy metals, and resulting effluents from MBR technology are without limitation for reuse in agricultural destinations according to Spanish law. Heavy metal removal yields were high regardless of whether microfiltration or ultrafiltration membranes were used, except for As, owing to its particular chemistry in wastewater. The removal yields of different heavy metals such as Cr, Ni, Sb, Cr and Zn can be strengthened by increasing the concentration of TSS present in the sludge. At concentrations above 10 g/L, removal yields are higher than those obtained at lower concentrations, presenting significant differences in many of the analysed heavy metals.

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