Removal of Heavy Metals with Membrane Bioreactor Combined with Activated Carbon

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Abstract

In this study, the removal of selected heavy metals (nickel (Ni), lead (Pb), arsenic (As) and zinc (Zn)) by a lab-scale submerged membrane bioreactor (MBR) combined with a granular activated carbon (GAC) system was investigated. Different membrane fluxes (16, 20 and 24 L m^{-2} h^{-1}) and hydraulic retention times (HRTs: 12.8 h, 10.4 h and 9.2 h) were applied as variable parameters to examine how they influence removal efficiency. Synthetically prepared wastewater was pre-treated in the MBR. Then, the efficiency of GAC adsorption applied as post-treatment was additionally examined in the current study. Chemical oxygen demand (COD), ammonium (NH_4-N) and phosphates (PO_4-P) were measured in two phases: first, after the MBR treatment step and, secondly, after the GAC post-treatment. The highest heavy metal removal efficiency after the 1st treatment stage (i.e. MBR effluent) was obtained at the lowest flux value (i.e. 16 L m^{-2} h^{-1}). Ni, Pb, Zn and As removals were measured as equal to 96.9, 98.3, 98 and 8.5%, respectively. Under the lowest applied flux value, COD, NH_4-N and PO_4-P removals were also found to be the highest (96.8, 98.9 and 46%, respectively) for the MBR effluent due to minimized heavy metal toxicity. More importantly, heavy metal concentration was under the limit of detection after the GAC post-treatment; over 99% removal was achieved for all heavy metals.

Keywords: Heavy metal removal, membrane bioreactor, granular activated carbon, adsorption, flux

Nomenclature	
CAS	Conventional Activated Sludge
COD	Chemical Oxygen Demand
GAC	Granular Activated Carbon
ICP-MS	Inductively Coupled Plasma Mass Spectrometry

HRT	Hydraulic Retention Time
MBR	Membrane Bioreactor
MLSS	Mixed Liquor Suspended Solids
MLVSS	Mixed Liquor Volatile Suspended Solids
PES	Polyethersulfone
SRT	Sludge Retention Time
TSS	Total Suspended Solids

1. Introduction

Water resources are becoming increasingly scarce. Thus, wastewater treatment is needed to enable water reuse in line with the concept of sustainable water resources management. More importantly, water quality standards in recent years are following highly stringent laws and regulations [1-2]. Heavy metals such as lead (Pb), nickel (Ni), arsenic (As) and zinc (Zn) traced in surface and underground waters are of the utmost importance due their impact on ecosystems and human health [3-4]. They are considered pollutants with significant direct and indirect effects even at very low concentrations [2-5].

Heavy metal discharge occurs through effluents originating from various industrial sectors such as metallurgy, mining, electroplating plants, leather, nuclear and electronic industries, etc. [4, 6-7]. Living beings need a certain concentration of heavy metals to survive and perform their essential vital activities [8-10]. Even the low concentration of heavy metals existing within organisms is hardly biodegradable via natural processes and can only converted to less toxic forms [5, 11]. If the heavy metal discharge to the receiving environment exceeds a certain concentration, it affects the food chain, the living beings and, thus, part or the whole ecosystem [12]. Hence, it is necessary that effluents including significant heavy metal concentration undergo a certain pretreatment prior to being discharged to the ecosystem. Domestic and industrial wastewaters are treated together in many wastewater treatment plants [13]. More effective and economical treatment alternatives have been developed, but the biological treatment has gained ground amongst them [14]. In terms of heavy metal removal from wastewater, various alternatives exist including ion exchange, adsorption [15], coagulation/flocculation [16], flotation [17], electrochemical precipitation [18], and membrane bioreactors (MBRs) [19].

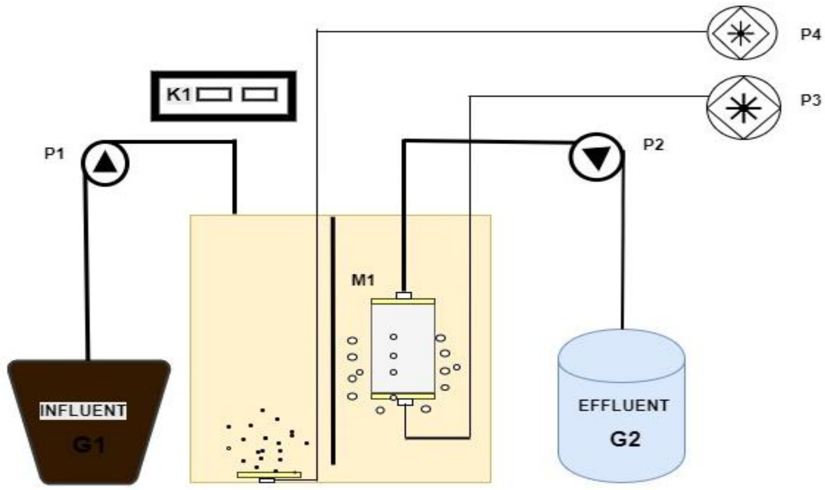
MBRs are an attractive option widely applied both in industrial and municipal wastewater treatment as a very effective and successful technology [20]. Small carbon footprint, superior effluent quality, high biomass retention at high organic loading rates and high organic removal when compared to conventional activated sludge (CAS) systems are among their advantages [21-22]. They can also be used for the treatment of specific industrial wastewaters such as textile, leather etc. [23-25]. Heavy metal removal from wastewater by MBRs is usually associated with high Mixed Liquor Suspended Solids (MLSS) content and solid retention time (SRT) [13, 26-27]. Heavy metal removal by microorganisms is called biosorption [28]. During the biosorption, heavy metals are bound by living cells, dead biomass and extracellular polymeric substances [29]. However, the bounding occurs randomly. Moreover, heavy metal removal depends on the metal type and concentration. Binding heavy metals to biopolymers through biosorption can reduce toxicity and increase biological activity [30-31].

In the current study, a lab-scale MBR (pre-treatment) combined with granular activated carbon (GAC) (post-treatment) was implemented to investigate the removal of selected heavy metals (nickel (Ni), lead (Pb), arsenic (As) and zinc (Zn)) from synthetic wastewater at 3 different flux values (16, 20 and 24 L m^{-2} h^{-1}) and hydraulic retention times (HRTs: 12.8 h, 10.4 h and 9.2 h).

2. Materials and Methods

2.1. MBR and GAC system

During the study, removal of selected heavy metals (Ni, Pb, As and Zn) by a MBR followed by GAC was investigated. The system was divided into two parts. The first part was the MBR as shown in Fig.1.



P1: feed pump	**G1:** influent
P2: vacuum pump	**G2**: effluent
P3: membrane blower	**M1**: fleet sheet membrane
P4: air pump	**K1**: conductor

Figure 1. Process diagram of the MBR applied for the pre-treatment of synthetic wastewater.

The MBR was used for the pretreatment of the synthetic wastewater. The total volume of the lab-scale MBR tank was 20L. The tank was designed according to the *principle of computational* and divided into two sections to enable water flow from the bottom. The first section was aerated with the aid of an air pump (P4). In the second section, there was a membrane aerated with the aid of a diffuser (P3) to prevent fouling. Both tanks were inoculated with activated sludge collected from a full-scale municipal CAS plant in Erzurum (Turkey). A flat sheet membrane (M1) was placed in the 8-L membrane chamber for solid-liquid separation. It was a plate and frame Polyethersulfone (PES) membrane with a pore size of 0.038µm (Fig. 1). The total area of each unit was 0.032 m^2. In each period, the membrane module was cleaned using 500 mg Cl_2 L^{-1} hypochlorite. The MLSS concentration in the membrane tank was approximately 4.5 g L^{-1} at the beginning of each cycle, and 12 g L^{-1} at the end of the cycle. Three different membrane fluxes were applied in the membrane unit by using a vacuum pump (P2); i.e. 16, 20 and 24 L m^{-2} h^{-1} for periods 1,2 and 3, respectively. Post treatment occurred by using GAC. Its properties are given below (Table 1).

Table 1. GAC properties.

Activated Carbon Powder	
Specification	
Density	1.8-2.1 g cm^{-2}
Solubility in water	Insoluble
Molarity	12.01 g mol^{-1}
pH	4-7
CTC absorption	62 min
Bulk density	0.42-0.52 g mL^{-1}
Moisture content	5% (max)
Ash content	4% (max)
Iodine number	1120 mg g^{-1} min^{-1}
Hardness	96% (min)

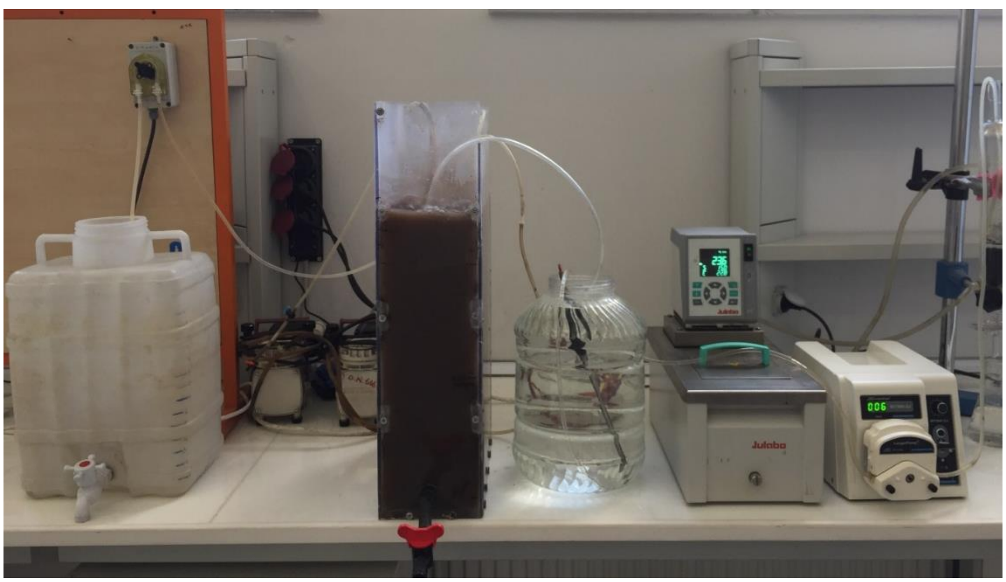


Figure 2. The whole lab-scale integrated treatment system used in the current study (MBR pre-treatment and GAC post-treatment).

2.2. Synthetic wastewater characteristics

COD in the influent ranged from 475.4 and 680.7 mg L^{-1} in all the runs. Table 2 shows the composition of the synthetic wastewater used in the current study. A stock solution containing the selected heavy metals (Ni, Pb, As and Zn) was prepared and added to the synthetic wastewater.

Table 2. Composition of the synthetic wastewater treated in the MBR.

Element	Concentration (mg L^{-1})
$CH_3COONa.3H_20$	500
NH_4Cl	80
KH_2PO_4	18
$NaHCO_3$	140
Pb	0.2
Ni	0.2
As	0.2
Zn	0.2

2.3 Sampling and analytical methods

Samples were collected 4 times per week from the membrane effluent. Influent and effluent heavy metal (Ni, Pb, As and Zn) concentration was continuously measured. Heavy metal analysis was carried out by inductively coupled plasma mass spectrometry (ICP-MS). The samples were measured for their chemical oxygen demand (COD), ammonium (NH_4-N), nitrate (NO_3-N) and phosphate (PO_4-P) content. MLSS, mixed liquor volatile suspended solids (MLVSS), total suspended solids (TSS), COD and NH_4-N were analyzed according to standard methods of analysis. The TSS were determined according to the 2540B Standard Method and the COD analysis was accomplished according to the 5220C Standard Method. Samples were filtered through Whatman membranes (0.45 μm) and the filtrate was measured photometrically for its NH_4-N, NO_3-N and PO_4-P content using a Merck Pharo 300 spectrometer. NH_4-N, NO_3-N and PO_4-P analysis was succeeded by Merck kits (NH_4-N with no: 14752; NO_3-N with no: 09713 and PO_4-P with no: 14842).

3. Results

The HRT decrease from 12.8 to 10.4 h caused a 25% increase in the membrane flux (from 16 to 20 L m^{-2} h^{-1}). Removal of Ni, Zn, Pb, As and COD decreased from 96.9% to 92.6%, from 98 to 95%, from 98.3 to 96.4%, from 8.5 to 5.8%, and from 96% to 85.2%, respectively. The NH_4-N measured in the effluent increased from 0.87 to 18.9 mg L^{-1} while the NH_4-N removal decreased from 98.9 to 76.5%. PO_4-P concentration in the effluent was observed to rise from 11.7 to 20.4 mg L^{-1} translated into a decrease in the removal from 46 to 7%. When the membrane flux was further increased to 24 L m^{-2} h^{-1}, the removal of Ni, Zn, Pb and As further decreased to 92.2, 86.5, 95.8 and 1.4%, respectively. COD removal dropped at 84.4% as microorganisms were exposed to heavy metal toxicity. NH_4-N and PO_4-P concentrations in the effluent were 31.7 and 24.5 mg L^{-1}, respectively. NH_4-N removal was 60.3% and PO_4-P was found to be below 5%. After GAC adsorption, all heavy metals' concentration was under the limit of detection.

4. Conclusion

During the study, the efficiency of a MBR (pre-treatment) combined with GAC (post-treatment) in removing selected heavy metals (Ni, Pb, As and Zn) from synthetic wastewater was investigated at lab-scale for different flux values (16, 20 and 24 L m^{-2} h^{-1}). The highest heavy metal removal after the 1st treatment stage (i.e. MBR effluent) was obtained at the lowest flux value (i.e. 16 L m^{-2} h^{-1}). Ni, Pb, Zn and As removals were measured as equal to 96.9, 98.3, 98 and 8.5%, respectively. Under the lowest flux value, COD, NH_4^+-N and PO_4^{-3}-P removals were also found to be the highest (96.8, 98.9 and 46%, respectively) for the MBR effluent due to minimized heavy metal toxicity. After the GAC post-treatment, over 99% removal was achieved for all heavy metals.

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