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Copper, Cadmium and Ferrous Removal by Membrane Bioreactor

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Abstract

One of the important concerns in Tehran municipal landfill is the production of leachate and its potential for water resources pollution. This paper investigates the removal of heavy metals from landfill leachate by using a membrane Bioreactor (MBR). The leachate was collected from a landfill in the vicinity of Tehran nearly 1 year old. The results of this study indicated that the system provided high removals of Fe, Cu and Cd equal to 96%, 23% and 84% respectively and heavy metal concentration in MBR effluent is a function of aeration ratio and bioaccumulation. Among the metals investigated in the present study it can be concluded that the extracellular adsorption, is the principal removal process of the metals, compared to other removal mechanisms such as bioaccumulation or intracellular accumulation.

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1. Introduction

The method of anaerobic sanitary landfill for the disposal of municipal solid wastes continues to be widely used in most countries throughout the world [1-3]. One of the most important issues of concern in landfill management is the production of landfill leachate and its potential for degrading water resources [4].

Heavy metals constitute one of the pollutant groups that are kept under surveillance in leachate from

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landfills for municipal solid waste (MSW) [5]. Since 1970s heavy metals have been causing a growing concern over their toxic effects on humans and aquatic ecosystems. A significant part of anthropogenic emissions containing heavy metals ends up in wastewaters treated by activated sludge processes, affecting microbial biomass growth and thus the depurative efficiency of the treatment. In fact biological wastewater systems are mainly designed for organic matter removal and only side-benefit can be observed in the treatment of heavy-metal-bearing streams. Microorganisms of activated sludge can remove heavy metals by different mechanisms, which can be classified according to their dependence or less on the metabolism activity as bioaccumulation and biosorption, respectively [6]. The chemical forms of heavy metals are rather complex in leachates, and usually consist of organic complexes, inorganic complexes, and free ions. Of these three forms, organic and inorganic complexes are usually the major components, which mean that a portion (often the major portion) of the heavy metals is colloid-bound [7]. The technologies available for the removal of heavy metals include chemical precipitation, adsorption, ion exchange and Reverse Osmosis. Metal removal in biological treatment processes is mainly by adsorption and complexation of the metals with the microorganisms, Microorganisms combine with metals and adsorb them to cell surfaces because of interactions between the metal ions and the negatively charged microbial surface. Metals may also be complexed by carboxyl groups found in microbial polysaccharides and other polymers, or absorbed by protein materials in the biological cell. A significant amount of soluble metal removal has been observed in biological processes, with removal ranging from 50 to 98 percent depending on the initial metal concentration, the biological reactor solids concentrations and systems SRT [8]. This finding indicated that main mechanisms operating in metal removal by active sludge are metabolism-independent biosorption mechanisms. The prominence of biosorption phenomena in metal removal by activated sludge has been already reported in the literature [6]. The removal of metals in biological processes has been found to fit adsorption characteristics displayed by the Freundlich isotherm model. The Freundlich isotherm is used most commonly to describe the adsorption characteristics [8]. In this study, Using these values Fe, Cu, and Cd Removal (QMe, mg/g VSS) can be calculated by the metal material balances in the reactor by equation number 1 [6]:

$$F \cdot (C_0 - C) = F_w \cdot X \cdot Q_{Me} \quad (1)$$

Where F (L/d) and F_w (L/d) are the influent and the sludge withdrawal flow-rates, respectively. C_0 (mg/l) and C (mg/l) are influent and residual metal concentrations at steady rate, and X (g/l) is the biomass concentration at the end of the aerobic phase in the sludge withdrawal stream [6].

Regarding the above facts, the present study set one of its goals to investigate the efficiency of municipal landfill leachate metals removal in a combined adsorption and biological treatment system. In the experimental phase of the study, a MBR system used in the pilot scale to assess the treatability of metals removal and defining the absorption rate of metals (Fe, Cu and Cd) by absorbent (MLSS).

Table 1. Average quality of landfill leachate used as fed

Parameter	Values	Parameter	Values
COD, mg/L	68250±8000	Cl, mg/L	14800±1000
BOD, mg/L	44500±3000	SO ₄ , mg/L	5500±300
NH ₃ +NH ₄ -N, mg/L	1470±90	Conductivity, μmhos/cm	44150±4500
NO ₃ + NO ₂ -N, mg/L	150±50	Turbidity, Ntu	190±8.4
pH	6.9±0.2	Fe, mg/L	35.85
PO ₄ -P, mg/L	130±40	Cu, mg/L	2.149
BOD/COD	0.65	Cd, mg/L	0.489

2. Material and Methods

2.1. Leachate feed

The leachate used in this study was collected from a municipal landfill located in a suburban area of Tehran city, Kahrizak. The landfill has been in operation since 1985. The age of the landfill for sampling is 0.5-1 year. The characteristics of the landfill leachate investigated are shown in Table 1; the leachate used for this study was young because it contained readily biodegradable organic matter [9].

2.2. Process configuration and system design

The investigations were carried out at a laboratory scale in a MBR. The MBR with a working volume of 175 L was made of Plexiglas. Dissolved oxygen was supplied using 2 fine bubble disc diffusers (Ecoflex 250 Cv), made by USA Diffuser Tech Co., placed at the bottom of the reactor, producing bubbles of pour size. A blower pump with the capacity of 190 m³/h and pressure of 320 mbar, supplied system air requirement. The pump also had an adjustable air-control valve. Fig. 1 presents the schematic diagram of the system in which the membrane module was directly submerged. The dissolved oxygen concentration (DO) was maintained at 3.2 and 2.3 mg/L by adjusting the air flow to 4 m³/h (1.03 kg O₂/kg COD) and 2 m³/h (0.58 kg O₂/kg COD) respectively. The level of the water in the bioreactor was controlled by a level-controller and a level-sensor. The concentration of the mixed liquor suspended solids (MLSS) at solid retention time of 55 days, were 6300 and 3800 mg/L, at high aeration ratio (4 m³/h) and low aeration ratio (2 m³/h), respectively. The sludge was withdrawn continuously with a pump set at different solid retention times (SRTs). Hydraulic retention time (HRT) was controlled for 15 days by a rotary flow meter under the operational condition of invariable membrane flux; the effluent of the bioreactor was connected to an automatic vacuum effluent system directly by a rotary flow meter.

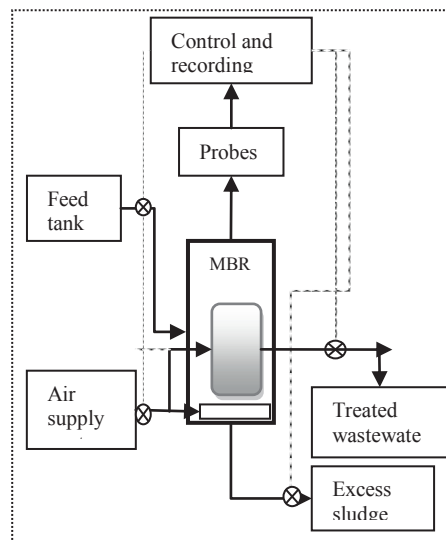


Fig. 1. Schematic diagram for MBR process

In this pilot-plant test, a hollow-fiber polypropylene microfiltration (MF) membrane system was used with pore size of 0.1 μm, the effective surface area of the MF membrane module at 4 m². Membrane flux was between 0.5 and 0.8 m³/d.

Influent characteristics were measured once a week. Chemical oxidation demand was analyzed

colorimetrically using tests and photometer of the HACH firm (DR 2010). The heavy metals in the leachate were determined according to the standard methods, 20th ed. [10] and the concentrations of Fe, Cu and Cd were measured by using Direct Air-Acetylene Flame Atomic Absorption Spectrometric method.

3. Results and discussion

3.1. Aeration rate effects on heavy metal removal in MBR

MBR was run for approximately six months. In this work the attention was specifically focused on the mechanisms of metals removal on MBR with tow aeration rates. The concentration of the mixed liquor suspended solids (MLSS) at high aeration ratio (4 m³/h) and low aeration ratio (2 m³/h) were 6300 and 3800 mg/L, respectively.

The other investigated fact was related to the capability of heavy metals removal from the leachate through MBR with tow aeration rate. Fig. 2 shows the efficiencies of these two reactors in this regard. The behavior of the Cu was slightly different from other heavy metals. The average percentage removal of Cu in MBR was 23.88%. This was the lowest removal observed of all heavy metals. The presence of Cu in the outlet of the MBR system indicated that copper was in soluble ionic or complex form.

The data also shows that the system provided high removals in terms of Fe, Cu and Cd equal to 96%, 23% and 84% respectively. However, effluent concentrations of Fe, Cu and Cd were 1.383, 1.633 and 0.075 mg/L respectively. MBR effluent samples are below the regulation limits in all periods of degradation. And Heavy metal concentration in the MBR effluent is a function of aeration ratio. Increasing the aeration ratio in membrane bioreactor has a partly positive effect on leachate treatment and heavy metal removal. In this regard as the presented data indicate, with increasing the aeration ratio, the Fe, Cd and Cu removal percentage increase to 84.55 from 78.14, to 84.55 from 78.14 and to 23.88 from 19.25, respectively.

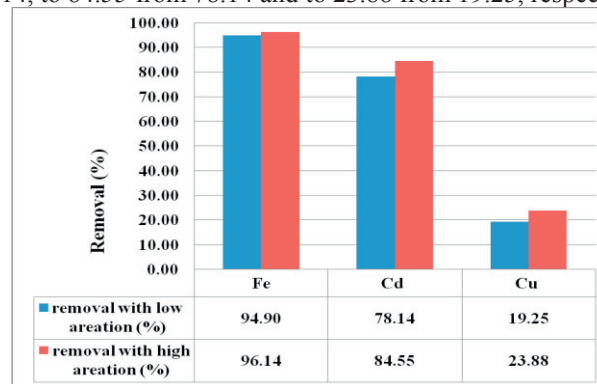


Fig. 2. Heavy metals removal in the MBR outlet with tow aeration ratio

3.2. Removal of Fe, Cu and Cd in MBR

The results of the metals adsorption summarized in table 2, the results obtained from Equation 1 and Table 2 indicates that the rate of the Cu, Fe and Cd absorbance with high aeration and with 6300 mg/L of MLSS, is equal to 0.26, 21.6 and 0.242 mg/g MLSS and with low aeration and with 3.8 g/L of MLSS is equal to 0.533, 36.2 and 0.435 mg/g MLSS, respectively. This means that the rate of absorbance at low aeration with less adsorbent substance is almost two times more. The average outlet concentration at higher MLSSs is rather less. This results show that the main metals surface-removal mechanism is based on a combination of physical

and chemical mechanisms such as ionic exchange and surface micro precipitation reaction involving a large variety of binding sites of extracellular polymeric substances and bacterial cell surfaces. The same results also indicate that the removal of heavy metals has little connection with intracellular accumulation mechanism.

Table 2: Metals adsorption rate and concentrations in the MBR inlet and outlet

metals		Fe	Cd	Cu
Influent	average (mg/L)	35.858	0.489	2.146
	standard deviation	6.854	0.498	1.796
Effluent with high aeration	average (mg/L)	1.383	0.075	1.633
	standard deviation	0.115	0.022	0.426
Effluent with low aeration	average (mg/L)	1.828	0.107	1.733
	standard deviation	0.152	0.015	1.460
Q_{Me} (mg/gMLSS)	High aeration	21.606	0.242	0.260
	low aeration	36.284	0.435	0.533

4. Conclusions

The conclusions from this study are as follows: The capability of heavy metals removal through MLSS and micro-organisms at low aeration with low MLSS, is high and is equal to almost 1.5 to 2 times the removal at high aeration. Based on the above results and the fix temperature, pH, SRT and HRT, at two different aerations, it can be concluded that the extracellular adsorption, is the principal removal process of the metals, compared to other removal mechanisms such as bioaccumulation or intracellular accumulation. Among the metals investigated in the present study.

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