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Removal of PAHs and heavy metals in composting leachate using the anaerobic migrating blanket reactor (AMBR) process

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ABSTRACT

In this study, the occurrence and removal of polycyclic aromatic hydrocarbons (PAHs) and heavy metals (HMs) in an anaerobic migrating blanket reactor (AMBR) were investigated. The chemical analyses were performed on leachate samples from different treatment processes, using solid-phase extraction and gas chromatography (GC), and inductively coupled plasma–optical emission spectrometry (ICP–OES). The organic loading rate (OLR) applied to the system gradually increased from 1 to 19.65 g COD/l d in 11 runs during a 280-d study period. The concentration of Σ8PAHs in the raw composting leachate was 50.13 μg/l. The main component of PAHs in the raw composting leachate was pyrene, when the average removal efficiency of Σ8PAHs in AMBR was 73%. The optimum OLR for removal of heavy metal was 10.1 g COD/l d. In this OLR, maximum and minimum removal efficiency for Pb and Cd were 55 and 42%, respectively. The order of heavy metal concentration in AMBR sludge was: Ni < Zn < Cr < Cd < Pb < Cu. The AMBR process presented high removal efficiency in treatment of COD organic loading rate, especially when OLR was lower than 4 g COD/l d. The AMBR could be an appealing option for treatment of PAHs and heavy metals in composting leachate and changing it into non-hazardous products and also a suitable option for the pre-treatment method.

Keywords: Composting leachate; Anaerobic migrating blanket reactor; Polycyclic aromatic hydrocarbons; Heavy metals

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1. Introduction

The windrow composting approach was used for processing organic waste in the large cities in Iran. In these processes, leachate forms a major environmental affection [1–3]. Composting leachate constitutes a very complex composition which may contain a large number of xenobiotic organic compounds in the solid waste disposal site formed as a result of biological and chemical processes [4,5].

Recently, one of the most important problems facing the nature is the chemical pollution of inorganic and organic origin catalysed by the presence of heavy metals and organochloride products, compromising the water quality for human consumption [6]. Among

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the various contaminants, heavy metals have received special notice, since some of them are extremely toxic for a large variety of organisms [7,8]. The durability of some heavy metals on plants or animals is investigated, while others are toxic at low concentrations [9]. The treatment of heavy metals is a special concern due to their recalcitrance and persistence in the environment [10]. The biosorption phenomenon is crucial in biological wastewater treatment [11]. The metal ion can only be changed to the base metal [12], volatilized [12–14], precipitated [15–18] or complexed with an organic ligand [19,20] to remove heavy metals [11]. One way for heavy metal remediation involves the formation of stable complexes between nuclides of microbial biomass and heavy metals [11,21]. These complexes are commonly the result of electrostatic charge between the negatively charged cellular biopolymers and metal ligands [16,20].

Some of the identified organic compounds such as polycyclic aromatic hydrocarbons (PAHs) are carcinogenic, highly toxic or even mutagenic; while they might be found in trace levels [4,22,23]. These organic pollutants may create a risk for the quality of receiving water and becoming a new pollution cause of water sources [24,25]. Therefore, many studies have reported growing concerns on occurrence, identification and toxicity of PAHs in leachates. Baun et al. identified that the concentration of PAHs in raw landfill leachate was from “not detected” (ND) to 305 μg/l and the measurements of Herbert et al. showed that PAHs concentration was from “not detected” (ND) to 60.52 μg/l [4,25–27].

The treatment of leachate is very complicated, expensive and generally requires various and combined process applications [28]. Therefore, physicochemical processes such as membrane and advanced oxidation processes have been extensively used as final treatment of biological pre-treated leachate [28–30]. Biological treatment of composting leachate is a suitable process for the recalcitrant substances of composting leachate are less than landfill leachate when they have a relatively high BOD_5/COD ratio [31]. Hence, these processes are hardly efficient for removing bioresistant organics [32]. As a result of high organic load, it is better to treat leachate by the anaerobic methods [24,33,34]. The anaerobic treatment is a suitable pre-treatment for stabilization of young leachate [35]. Although it has been shown that amonical nitrogen is not removed by the anaerobic digestion of leachate, it is in fact more likely to increase its concentration [36].

Some studies (Nayono; Toprak; Angenent; Katal et al.) discovered that anaerobic digestion for a highly polluted liquid was obtained from the pressing facility for the organic fraction of municipal solid waste in a composting plant which gave a high biogas yield even at very high loading rates. The chemical oxygen demand (COD) removal efficiency correlated inversely with the organic loading rate when AMBR achieved the maximum organic loading rate and the maximum COD removal was 94.8% [37–40].

In this study, an AMBR was applied to treat a composting leachate. The AMBR process is an appropriate process for treatment of high organic compounds owing to its resistance to hydraulic shock loads [41,42]. The leachate samples were taken from a composting factory in Isfahan, Iran, which is located in 8 km Isfahan west and has an average altitude of about 1,550 m above mean sea level. The facility covers an area of approximately 100 ha and receives 1,200 tons/d of generated waste from the Isfahan area and its surroundings. The organic waste constitutes about 70% of the waste stream resulting in relatively high moisture (60–70%).

The aim of this study is to investigate the removal of PAHs and heavy metals in the composting leachate using the AMBR system. The study also focuses on the removal of organic constituents (COD, SCOD, rbCOD, BOD_5) and the effect of HRT on reactor performance.

2. Materials and methods

2.1. Experimental set-up, sampling and operation

The AMBR consisted of a rectangular, Plexiglas reactor (inside dimensions: length = 43 cm, height = 23.5 cm, width = 10 cm) with an active volume of 10 L (Fig. 1). The AMBR reactor (10 L) contained vertical mixers and standing baffles which divided the reactor into four

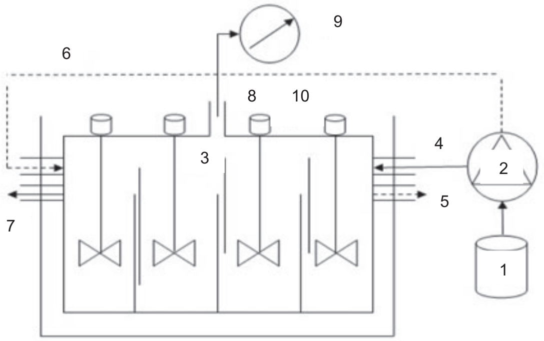

Fig. 1. Schematic diagram of the AMBR.
Notes: (1) Feed Tank; (2) Injection Pump Diaphragm; (3) AMBR Reactor; (4) and (6) Influents; (5) and (7) Effluents; (8) Biogas Output; (9) Gas Meter; (10) Mixers.

identical compartments (2.5 L). All pumps were injection diaphragm pumps made by Etatron Co, Italy. Biomass sampling valves were installed at a height of approximately 8 cm from the top of each chamber. A programmable logic controller (PLC) system was used to control the reactor operation (Omron, Japan). The system was properly sealed to ensure anaerobic condition and prevent gas leakage.

Influent was injected into top of the AMBR using a peristaltic pump. The AMBR reactor was inoculated with 5 L of sludge from an anaerobic digester (north Isfahan, IR) that operated at 35°C. TSS, VSS, VSS/TSS and pH of the sludge used in the AMBR were 35,500 mg/l, 26,650 mg/l, 0.75 and 7.55, respectively. The distilled water was used for washing the sludge and removing coarse particles and then sludge was sieved with a pore diameter of 2 mm. The composting leachate samples were taken from the Isfahan composting factory (Fig. 2). Samples were taken from an influent evaporative lagoon and under standard conditions transferred to the laboratory of Environmental Health Engineering group of the University of Medical Science, Isfahan, Iran. The composting leachate was diluted by tap water to a final concentration. It was made fresh every seven days and stored in a refrigerator at 4°C and then 1 L was directly and continuously delivered into a Plexiglas reactor.

The reactor was maintained at 35°C in a water bath. The start of hydraulic retention time (HRT) was 10 d and then decreased to 5 d; initially, the AMBR reactor was operated at an OLR of 1 g COD/l d and OLR was gradually increased to 19.65 g COD/l d. The OLR is calculated according to the following equation:

$$\mathrm{OLR} = \frac{Q \times C}{V}$$

where OLR is the acceptable organic loading rate (kg COD/m^3 d), V is the volume of the reactor (m^3), Q is the influent flow rate, (m^3/d), C is the influent COD (kg COD/m^3).

In the period of adaptation phase, pH value was relatively constant with NaOH in the range of 7–8. The operating time of the AMBR reactor for all OLRs was 280 d. Initially, in order to prevent the washout of biomass floc, the final compartment was not mixed. After two months of operation, all four compartments were mixed equally for 10 s every 15 min at 80 rpm to ensure gentle mixing (Mixers: Model Landa). During the stabilization period, several parameters (EC, pH, BOD_5 and COD) were measured routinely in the feed and the effluent of the reactor. Organic pollutant samples were collected in brown glass bottles with glass seals and kept at 4°C until extraction. The period of storage did not exceed 7 d [43]. Temperature and pH were controlled. Reduction of COD, SCOD, rbCOD and BOD_5 were also monitored. Steady-state condition was identified when the value of the effluent was measured to be the same for two or three consecutive steps.

2.2. Analyses

pH and EC were measured with a calibrated pH & EC meter (Schott). COD measurement was conducted based on the dichromate method (closed reflux, 5220 C, colorimetric method, Spectrophotometer Milton Roy Company 2OD), and BOD_5 in accordance with the Winkler's method (5210 B) (APHA, 2005) [44]. The floc/filtration method was used for measurement of rbCOD concentration [45]. rbCOD is a part of the carbon compounds that is rapidly absorbed by the biomass. rbCOD as a part of the COD directly effects the kinetics of the active sludge [45]. Series Optima Perkin Elmer 4000 ICP–OES was used to detect the concentration of Cr, Cd, Cu, Pb, Ni and Zn. The total content of each HMs determined by a 0.5-g sample was digested in a 20 mL of mixture of nitric, hydrochloric and hydrofluoric acid (in the ratio 1:1:2) [46,47]. GC–MS

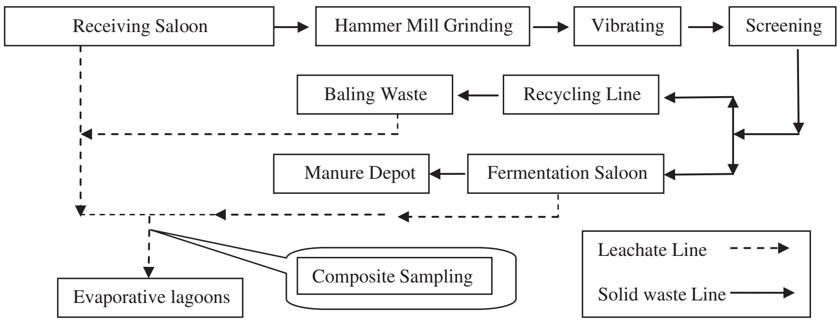

Fig. 2. Processing municipal solid waste in Isfahan composting factory.

model of GC 6,890 N Agilent & MS 5975 C, Mode EI was operated in the electron impact mode (70 eV). A 30 m HP-5 column (0.25 mm I.D, 0.25 μm treated film thickness) was used to separate the conventional PAHs, while high-grade helium gas was used as the carrier gas. Injection was made in splitless mode. The oven temperature increased from 80 to 255°C at 15°C min^{-1}, then increased to 265°C at a rate of 1°C min^{-1}, then increased to 295°C at a rate of 2.5°C min^{-1} and finally was kept at 295°C for 1 min [48].

3. Results

3.1. Removal efficiency of the basic parameters

Influent and effluent concentrations of COD, SCOD, rbCOD and BOD_5 were within the ranges of 10.43–100.77, 3.34–40.31, 1.56–29.22, 4.90–69.53 and 1.85–25, 0.42–7.25, 0.07–2.3, 0.52–8.56 g/L, respectively. Furthermore, the influent and effluent ranges of BOD_5/COD ratio were 0.47–0.69 and 0.28–0.38, respectively (Table 1). The average removal efficiencies of COD, SCOD, rbCOD and BOD_5 in HRT = 10 d were 80.88, 85.70, 94.43 and 89%, respectively, while the best removal efficiency was found at an OLR of 3.8 g COD/l d. The removal efficiency of COD, SCOD, rbCOD and BOD_5 in HRT = 5 d were reduced to 74.6, 79.3, 87.7 and 83.8%, respectively (Fig. 3).

3.2. Heavy metals

The contents of HMs in the influent and effluent of the AMBR system are presented in Table 2. Pb, Cr, Cd, Ni, Zn and Cu are the selected HMs. The influent concentrations of Pb, Cr, Cd, Ni, Zn and Cu are within the ranges of 0.12–1.45, 0.15–2.6, 0.05–0.85, 0.16–2.8, 0.43–5 and 0.1–2.3 mg/L and their effluent concentrations are within the ranges of 0.07–0.75, 0.11–1.38, 0.04–0.54, 0.09–1.43, 0.31–3.2 and 0.06–1.08 mg/l, respectively.

In addition, the removal efficiencies of Pb, Cr, Cd, Ni, Zn and Cu at OLRs of 1.8, 4.3, 10.1 and 19.65 g COD/l d are presented in (Fig. 4). The minimum and maximum removal efficiencies are at OLRs of 1.8 and 10.1 g COD/l d, respectively, except for Cu. The maximum removal efficiency (55%) at an OLR of 10.1 g COD/l d is for Pb and the minimum removal efficiency (42%) is for Cd.

Fig. 5 shows the contents of heavy metals in AMBR sludge. The concentrations of Pb, Cr, Cd, Ni, Zn and Cu are within the ranges of 0.07–1.34, 0.05–1.5, 0.02–1.25, 0.06–1.37, 0.12–1.35 and 0.06–2.07 g/kg dry weight, respectively. A maximum concentration of 2.07 g/kg is for Cu and the most heavy metal contents in the AMBR sludge are at OLRs of 10.1 and 19.7 g COD/l d.

3.3. Polycyclic aromatic hydrocarbons

The composting leachate was monitored for Σ8PAHs during the treatment processes as shown in Table 3. The total concentrations of Σ8PAHs in the influent, effluent and sludge were 50.13, 13.5 and 25.8 μg/kg, respectively. The main component of PAHs in the raw composting leachate was 15.8 μg/l pyrene. Furthermore, the concentrations of Σ8PAHs in

Table 1
Average concentration of COD, SCOD, rbCOD, BOD_5, EC and BOD_5/COD ratio in influent and effluent of AMBR reactor

				COD (g/l)		SCOD (g/l)		rbCOD (g/l)		BOD_5 (g/l)		BOD_5/COD		EC (ms/cm)	
Time (d)	Run	HRT (d)	OLR (gCOD/l d)	In	Out	In	Out	In	Out	In	Out	In	Out	In	Out
1–37	1	10	1.04	10.43	1.85	3.34	0.42	1.56	0.07	4.90	0.52	0.47	0.28	3.50	2.88
38–46	2	10	1.34	13.38	2.30	4.55	0.73	2.21	0.14	6.76	0.75	0.51	0.33	4.38	3.52
47–59	3	10	1.79	17.89	3.52	6.26	0.99	3.22	0.24	9.48	1.28	0.53	0.36	5.95	4.81
60–74	4	10	2.02	20.19	3.82	7.27	0.98	3.94	0.22	11.20	1.12	0.56	0.29	7.00	5.34
75–98	5	10	3.79	37.87	6.63	14.01	2.00	7.39	0.26	21.40	2.00	0.57	0.30	14.00	10.37
99–128	6	10	4.34	43.43	8.50	16.50	2.53	9.77	0.41	26.28	3.25	0.61	0.38	17.50	12.64
129–159	7	10	5.84	58.38	12.56	22.77	3.10	14.01	0.85	36.78	4.32	0.63	0.34	24.50	17.23
160–189	8	10	7.71	77.09	15.23	30.84	4.20	20.43	1.00	51.26	4.85	0.67	0.32	31.50	22.96
190–248	9	10	10.08	100.77	20.33	40.31	5.65	29.22	2.21	69.53	7.54	0.69	0.37	35.00	25.10
249–263	10	5	18.52	92.61	23.33	38.90	7.25	17.60	1.90	56.49	8.56	0.61	0.37	35.70	27.54
264–279	11	5	19.65	98.26	25.00	31.44	6.52	18.67	2.30	50.11	8.15	0.51	0.33	36.75	28.85
Minimum			1.04	10.43	1.85	3.34	0.42	1.56	0.07	4.90	0.52	0.47	0.28	3.50	2.88
Maximum			19.65	100.77	25.00	40.31	7.25	29.22	2.30	69.53	8.56	0.69	0.38	36.75	28.85

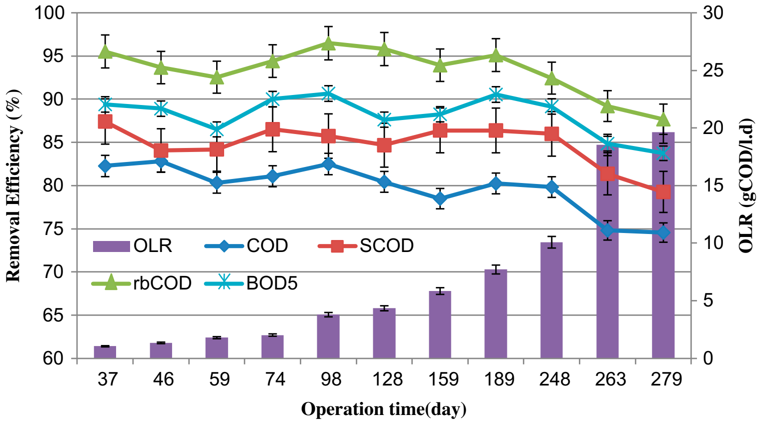

Fig. 3. Removal efficiency of COD, SCOD, rbCOD and BOD_5 in AMBR reactor at different OLRs during the periods of operation.

Table 2
Average concentration of heavy metals in influent and effluent of AMBR reactor

		Concentration (mg/l)	
Heavy metals	OLR(g COD/l d)	In	Out
Cr	*A*	0.15	0.11
	B	0.80	0.54
	C	2.60	1.38
	D	2.00	1.24
Zn	*A*	0.43	0.31
	B	1.50	0.93
	C	4.20	2.35
	D	5.00	3.20
Ni	*A*	0.16	0.09
	B	0.78	0.44
	C	2.80	1.43
	D	1.98	1.07
Cu	*A*	0.10	0.06
	B	0.48	0.27
	C	1.52	0.79
	D	2.30	1.08
Cd	*A*	0.05	0.04
	B	0.23	0.15
	C	0.60	0.35
	D	0.85	0.54
Pb	*A*	0.12	0.07
	B	0.45	0.24
	C	1.30	0.59
	D	1.45	0.75

Notes: *A* = 1.8; *B* = 4.3; *C* = 10.1; *D* = 19.7.

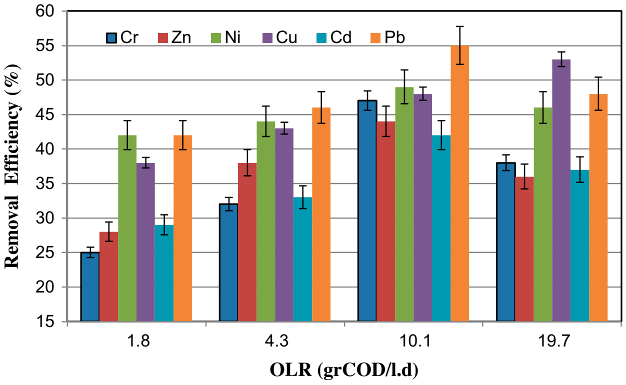

Fig. 4. Removal efficiency of heavy metals in AMBR reactor at different OLRs.

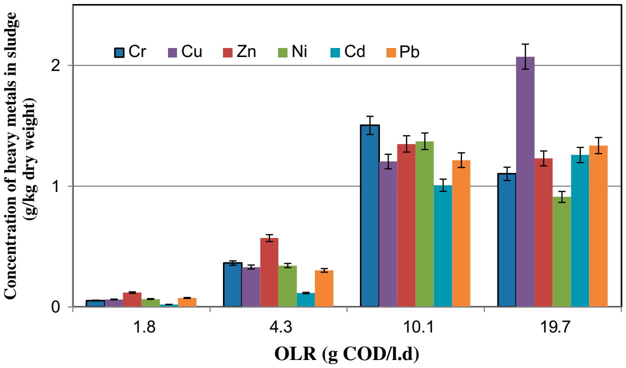

Fig. 5. The concentration of heavy metals in sludge of AMBR reactor.

Table 3
Concentration of Σ8PAHs detected in the leachate and sludge of AMBR reactor

	PAH (μg/l)		
Analyte	In	Out	Sludge
Naphthalene	ND	3.20	2.00
Acenaphthylen	6.80	1.50	3.30
Acenaphthene	ND	ND	ND
Flurene	2.00	ND	ND
Phenanthrene	13.90	4.40	7.70
Antheracene	5.50	ND	2.00
Fluoranthene	6.13	ND	2.50
Pyrene	15.80	4.40	8.30
Total	50.13	13.50	25.80

Note: ND: Not detected.

the sludge (25.8 μg/kg) were more than the AMBR effluent (13.5 μg/l). The average removal efficiency of PAHs in AMBR was 73%.

4. Discussion

4.1. Removal efficiency of basic parameters

In this study, the maximum removal efficiency of COD, SCOD, rbCOD and BOD_5 were 82.8, 87.42, 96.48 and 90.65% at OLRs of 4 g COD/l d and lower. The removal efficiencies of rbCOD and BOD_5 were higher than COD and SCOD. High-removal efficiencies were achieved for COD, SCOD, rbCOD and BOD_5 by AMBR reactor due to leachate's high biodegradability.

Hashemi et al. showed that the COD removal efficiency was in the range of 76–81%, depending on organic loading rates [49]. Amin et al. studied a complementary treatment of leachate using sequencing batch reactor (SBR). The results showed that the COD removal efficiency increased up to 70% in bioreactor with time increase in all experiments. The removal efficiency was 40–80% depending on the feeding values [35].

Hashemi et al. studied in macropollutant removal from compost leachate using membrane separation process, total COD values ranging from 50 to 2,200 mg/l in the feed decreased to 32.5 and 4 mg/l in the HFM and FSM permeate, respectively [50].

Hence et al. identified that the maximum specific organic removal rate for anaerobic treatment of sucrose waste is in the range of 0.7–1.2 g COD/g VSS d [51]. Ndon and Dague studied the effect of HRT on an anaerobic sequencing batch reactor and achieved 80–90% SCOD removal efficiency at different dilute substrate concentrations [52]. Angenent et al. showed that AMBR was very efficient in 94.9% SCOD removal for loading rates up to 25 g COD/l d at an HRT of 12 h [39].

The raw composting leachate has an average BOD_5/COD ratio of 0.58 which suggests that the leachate is biodegradable by a biological treatment process. Xu et al. showed that landfill leachate had a BOD_5/COD ratio of 0.71 [43].

When increasing the OLR to 19.65 g COD/l d and HRT = 5 d (Fig. 3), removal efficiency of COD, SCOD, rbCOD and BOD_5 decreased. The slope of the curve decreases because the COD removal rate efficiency cannot be maintained while the loading rate increases and HRT decreases. Chang also treated municipal leachate at a concentration of 58,400 mg COD/l using a continuous UASB-type reactor. COD removal efficiencies were 81.7–92.8% for OLR below 13 kg COD/m^3 d; nonetheless, they decreased to 67.9% when the OLR increased to 22 kg COD/m^3 d [53]. Toprak discovered that the COD removal efficiency correlates inversely with the organic loading [38]. The results of Agdag et al. study showed that when the OLR increased from 4.3 to 16 kg/m^3 per day, the COD removal efficiency decreased [54]. Increasing of flow rate was affecting poor substrate with biomass contact and least degradation of the incoming COD. Channelling in parts of the reactor can happen over short-time periods. Although enough biomass was present in the reactor to degrade the organic load, the high flow rate made it infeasible for the biomass inside the reactor to decay the substrate completely [41,55]. Additionally, when AMBR is treating leachate at a 5 d HRT, signs of stress were visible characterized by a marked decrease in both the soluble COD removal efficiency and accumulation of VFA in the reactor [56].

Using performance data from Table 1 and BOD_5: COD ratio, the AMBR is treating 100% leachate produced effluent that would exceed regulations. For this particular case, it would seem that anaerobic treatment is better suited as a pre-treatment method. The factors resulting in the COD removal stabilization could be the high chloride concentration along with low nitrate and phosphate concentrations. However, further research is required to quantify the effect of inhibiting factors such as ammonical nitrogen, chloride and low concentrations of phosphate and nitrate.

4.2. Heavy metals

The enlargement of heavy metal concentration variations in influent is greater than in effluent, while the greatest variations in influent was for Zn and the lowest was for Cd (Table 2). Similar observations were reported by Oliver and Cosgrove [57]. The maximum removal efficiency of HMs was at OLR of 10 g COD/l d (Fig. 4). The study of Hammaini et al. explored the biosorption process with activated sludge, which showed the amount of protons released from biomass increased with biomass concentration. This would verify the hypothesis of ion exchange between protons and metal cations during the process [58]. Removal efficiency decreased at an OLR 19.7 g COD/l d except for Zn and Cu. Sorption capacity was steady or decreased with biomass concentration due to the screen effect between cells. This produced a block of the cell active sites by an increase of biomass in the system [58].

Generally, there was a removal of heavy metals by the AMBR treatment system; nevertheless, the removal efficiency was low, when the maximum removal efficiencies were 55, 42, 53, 49, 45 and 47%, for Pb, Cd, Cu, Ni, Zn and Cr, respectively. The lowest efficiency was for Cd and Zn. Stoveland et al. study showed that heavy metals can be removed in the biological wastewater treatment processes [59]. Metcalf et al. indicated that the anaerobic digester treatment was quite effective in removing all metals except Zn removed about 50% [60]. Maleki et al. results showed that 90% HMs removal can be achieved at pH 6.5 (optimum for alum) with the addition of 1.4 g/l alum, while 86% removal efficiency can be attained at pH 10 (optimum for ferric chloride) with the amount of 2 g/l by a coagulation–flocculation process [61].

Due to the complexity of the anaerobic process, heavy metal removal mechanisms may be a result of many physicochemical processes including (1) adsorption to the solid fraction, either biomass or inert particulate matter, (2) precipitation as carbonate, sulphide and hydroxides, (3) uptake by the micro-organisms of sludge and (4) the formation of complexes in solutions with intermediates and product compounds produced during digestion. Among these metal forms, only free forms of soluble metals are toxic to the micro-organisms [62].

Jong et al. indicated that adsorption processes are perhaps responsible for the slight loss in metal concentration in the AMBR system [63]. The optimum pH was 4 for Cd, Cu and Pb sorption and 5 for Ni and Zn [58]. In this study, this pH occurred in the first compartment of the AMBR reactor. At high pH levels, more ligands with negative charge would be exposed with the subsequent increase in attraction sites to positively charged metal ions; nonetheless, cell wall ligands would be closely associated to H_3O^+ in very low pH value (1–2) and the access of metal ions to ligands would be limited as a result of repulsive forces [64].

Another study showed that the biosorption phenomenon is decisive with regard to microbial removal of heavy metals. Biosorption is a metabolism-independent binding of heavy metals for living cells, non-living biomass or microbial extracellular polymers [11]. Macaskie et al. showed specific metabolic pathways resulting in bioprecipitation of heavy metals. Heavy metal binding by biopolymers happens haphazardly, while the comparative removal efficiency depends upon the metal concentration and species, the composition of other wastewater components and the reactivity of the available biopolymers or biomass. In addition, surface exposure of metal binding biopolymers to the better metal binding properties of micro-organisms is based not only on biosorption, but also on microbial metabolic activities. Furthermore, it is evident that biological wastewater treatment is a complex process depending not only on many physicochemical and biological situations, but also the process operating conditions and design [17,65].

In principle, the results of this study indicated that AMBR reactor reached to the compliance limits (Cd, 0.1; Cr, 0.5; Cu, 1; Ni, 2; Pb, 1; Zn, 2 mg/l) for treated wastewater except for Cd, Cr and Zn in accordance with the decree issued by the Ministry of Environmental Protection of Iran regarding the characteristics of wastewater to be disposed to surface water.

Fig. 5 shows the concentration of heavy metals in sludge of AMBR reactor. It was found the order to be: Ni < Zn < Cr < Cd < Pb < Cu, as well as an increase in heavy metal concentrations; whereas sludge is not proportionally dependent on their initial influent concentrations as observed in their removal efficiencies from influent wastewater. Brown and Lester paper (1979) indicated that the solubilities of heavy metals in sewage would be: Pb < Cu < Cd, and volatilization of metals to the atmosphere from activated sludge systems was found [66], whereas Jenkins et al. found the solubility order would be: Cu < Pb < Cd < Zn, in the order of increasing solubilities [67]. The maximum sorption uptake of the studied metals by the activated sludge showed the following decreasing order: Pb > Cu > Cd > Zn > Ni [58]. Another study (Rincon et al.) showed the maximum sorption capacities for the activated sludge by the following sorption order: Pb > Cu > Cd > Zn > Ni [68]. Moreover, it showed that increases in heavy metal contents in digested sludge during anaerobic digestion results in biodegradable organic and inorganic matter decomposing into the end products including CH_4, CO_2, N_2, H_2S and many other gases [60]. Precipitated heavy metals in sludge are investigated to: aggregate of soluble metal and biopolymers; metal precipitates in the sludge flocs; accumulated soluble metal in the microbial cells and soluble metal ions [66]. However, it is not known which inorganic and organic sludge components are anaerobically degraded and how such degradation processes affect the concentrations of heavy metals in sludge [69].

The content of heavy metals in AMBR sludge was in accordance with the compliance limits (Cd, 10; Cr, 150; Cu, 650; Ni, 120; Pb, 200; Zn, 1,300 g/kg), in accordance with the decree issued by the Institute of Standards and Industrial Research of Iran about the characteristics of compost—physical and chemical specifications for agricultural land application.

4.3. PAHs

Contamination of Σ8PAHs in raw composting leachate was medium (50.13 μg/l), as the total amounts of Σ8PAHs have been reported in landfill leachates at low concentrations of 485.2–1,188 ng/l (XU et al.) [43], whereas Herbert et al. reported the total amounts of PAHs in landfill leachates at concentrations up to 114 μg/l [27]. Additionally, Baun et al. identified that the concentration of PAHs in raw landfill leachate was high (305 μg/l) [25,26].

In this study, the average removal efficiency of PAHs in AMBR was 73%, which is considered to be suitable. XU et al., achieved 58% removal efficiencies of PAHs in the treatment of landfill leachate [43].

The anaerobic processes removed the most PAHs in leachate due to the unsubstituted low-molecular polycyclic aromatic compounds being able to degrade in anaerobic conditions, under nitrate-reducing, iron-reducing, sulphate-reducing and methanogenic conditions [70–72]. Therefore, in this study, decreasing low molecular weight PAHs in the composting leachate was attributed to anaerobic biodegradation, which reflected the electron acceptor conditions in the stimulated biodegradation of PAHs.

5. Conclusion

In general, suitable removals of both total organic constituents and trace organic contaminants could be achieved by the AMBR reactor, while the COD removal efficiency correlates inversely with the organic loading. The enlargement of HMs concentration variations is greater in influent than effluent of reactor and the greatest variations in influent is for Zn and the lowest for Cd. The content of HMs in AMBR sludge was in accordance with the decree issued by the Institute of Standards and Industrial Research of Iran regarding the characteristics of compost—physical and chemical specifications for agricultural land application. The main component of PAHs in the raw composting leachate was pyrene. In principle, this study indicated that the AMBR reactor meets the compliance limits for treated wastewater except for Cd, Cr and Zn in accordance with the decree issued by the Ministry of Environmental Protection of Iran regarding the characteristics of wastewater to be disposed to surface water.

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