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Metals removal from municipal landfill leachate and wastewater using adsorbents combined with biological method

Amin Mojiri[a], Hamidi Abdul Aziz[a,*,1], Nastaein Q. Zaman[a], Shuokr Qarani Aziz[b], Mohammad Ali Zahed[c]

[a]*School of Civil Engineering, Engineering Campus, University Sains Malaysia, 14300 Nibong Tebal, Penang, Malaysia, Tel. +60175120024; email: amin.mojiri@gmail.com (A. Mojiri), Tel. +60 45996215; Fax: +60 45941009; email: cehamidi@usm.my (H.A. Aziz), Tel. +60 45996287; email: cenastaein@usm.my (N.Q. Zaman)*
[b]*Department of Civil Engineering, College of Engineering, University of Salahaddin–Erbil, Iraq, Tel. +964 750 462 5426; email: shoker71@yahoo.com*
[c]*Department of Civil Engineering, Auburn University, Auburn, AL 36849, USA, email: zahed51@yahoo.com*

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ABSTRACT

Different physical, chemical, and biological treatment methods are used to eliminate heavy metals and pollutants from wastewater and landfill leachate. Sequencing batch reactor (SBR) is a type of biological treatment. This study was conducted to study heavy metals elimination from urban wastewater and landfill leachate using an adsorbent, namely powdered ZELIAC (PZ) that improved SBR. PZ consists of portland cement, limestone, rice husk ash, activated carbon, and zeolite. Response surface methodology and central composite design were used to elucidate the nature of the response surface in the experimental plan and determine the optimum settings of the independent variables [aeration rate (L/min), contact time (h), and leachate to wastewater ratio (%; v/v)] and their reactions. To study the aerobic process, four dependent factors (Fe, Mn, Ni, and Cd) were evaluated as reactions. The results indicated that compared with SBR, PZ-SBR removed heavy metals more efficiently. At the optimum contact time (11.70 h), aeration rate (2.87 L/min), and leachate to wastewater ratio (20.13%) in PZ-SBR, removal efficiencies for Fe, Mn, Ni, and Cd were 79.57, 73.38, 79.29, and 76.96%, respectively.

Keywords: Iron; Landfill Leachate; Nickel; Sequencing batch reactor; Wastewater; Adsorbent

1. Introduction

A sanitary landfill is a common solid waste management method in most countries. While sanitary landfills have a number of advantages, their primary disadvantage is that they generate leachate [1]. Urban dumping site leachate is wastewater that has a major negative environmental impact. The characteristics of landfill leachate vary depending on the degradation process and the age of the landfill. Ecological contamination and health problems are frequently linked to insufficient landfill leachate treatment [2,3].

The main sources of heavy metals in landfills are fluorescent tubes, pharmaceuticals, photographic chemicals, detergents, individual care goods, garden

*Corresponding author.
[1]Solid Waste Management Cluster, Engineering Campus, Universiti Sains Malaysia, 14300 Nibong Tebal, Seberang Perai Selatan, Pulau Pinang, Malaysia.

pesticides, waste oil, batteries, paint, electronic waste, electrical tools, and wood treated with dangerous substances, among other household wastes [4].

When water sources are polluted by leachate containing heavy metals, the mechanism leading to health hazards is bioaccumulation [5]. Heavy metal toxicity can result in damaged or reduced mental, central nervous function, etc. [6]. Heavy metals are unique class of toxicants, since they cannot be broken down to non-toxic forms [7].

Recent studies have focused on heavy metals elimination from aqueous solutions. Heavy metals are eliminated using different methods such as biological methods, ion exchange, solvent extraction, chemical precipitation, reverse osmosis, or adsorption [8]. Biological treatments contain different processes, and sequencing batch reactor (SBR) is a model. SBR with five normal phases is used for the treatment of municipal, domestic, diary, synthetic, slaughterhouse, industrial and toxic wastewaters, and landfill leachates [1,8]. Due to low biodegradability ratio, high concentration of heavy metals, COD, NH_3-N, and other compounds in landfill leachate the capability of SBR in leachate treatment is lower than that for municipal and industrial wastes [1,3]. In the reported works, adsorption method was supplemented SBR process for increasing removal efficiencies of organic matter, heavy metals, NH_3-N, and other pollutants. Researchers have also suggested co-treatments of landfill leachate and wastewater [9,10]. Some of the reasons include:

(1) Landfill leachate treatment using biological methods is difficult due to high COD/BOD ratio, high ammonium content, and the presence of heavy metal ions [9].
(2) To date, landfill leachates are frequently treated with urban sewage in urban wastewater treatment plants. However, with stricter regulation of nitrogen discharge and problems with the potential effect of recalcitrant leachate constituents on the biological treatment phase, demand for separate treatment and disposal of landfill leachate has increased [10,11].
(3) The co-treatment process has been preferred for its easy maintenance and low operating costs [12].

To increase biodegradability ratio of landfill leachate and improving the proficiency of SBR process, landfill leachate was mixed with wastewater and treated by ZELIAC augmented SBR technique in the current study. Furthermore, ZELIAC is characterized as an adsorbent and ion exchanger at the same time which improves the performance of SBR process. In literature, a number of studies [2,4,8,13–16] have verified that using sorbents can remove a large amount of metals from wastewater and landfill leachate. In the extant literature, a gap of knowledge can be noticed in the SBR field, particularly, augmenting adsorption and ion exchange processes for the treatment of mixed landfill leachate with wastewater.

The aims of the current research were: (1) to evaluate the performance of sequencing batch reactor (SBR) with and without powdered ZELIAC (PZ) in removing iron, cadmium, nickel, and manganese from Semeling landfill (Sungai Petani) leachate and household wastewater from Bayan Baru wastewater treatment plant in Malaysia. (2) To introduce a novel process, i.e. powdered ZELIAC augmented SBR process.

2. Materials and methods

2.1. Landfill leachate sampling

Leachate samples were gathered from the Sungai Petani dumping site from June 2012 to March 2013. The dumping site (geographical coordinates, 05˚43´N and 100˚29´E) is located in Kedah, Malaysia and has been actively used since 1990. The total landfill region of Sungai Petani is 11.24 ha. Leachates remain in the compilation pond until maintenance is conducted and are then discarded directly in the environment without being treated. The samples were instantly brought to the laboratory after they were gathered and were kept in a cold room at 4˚C before reducing chemical and biological responses [17]. The traits of the samples are shown in Table 1. To identify the leachate's ecological risks, the obtained factor values were compared with those given in the 2009 Regulations of the 1974 Environmental Quality Act of Malaysia [18].

2.2. Domestic wastewater and activated sludge samplings

Activated sludge and domestic wastewater were obtained from the Bayan Baru wastewater treatment site in Penang, Malaysia. The features of the activated sludge and wastewater are shown in Table 1.

2.3. Reactor characteristics

Six 2000-mL beakers that have an effective capacity of 1,200 mL, an internal width of 113 mm, and a height of 200 mm were employed. A magnetic mixer at the bottom of the reactors was used for blending. Experiments were performed at room temperature, and an air pump provided air to the reactors (Yasunaga Air Pump Inc., voltage: 240 V, frequency: 50 Hz, input power 61 W, model: LP-60A, pressure: 0.012 MPa, air volume:

Table 1
Characteristics of landfill leachate, domestic wastewater, and sludge

No.	Parameter	Leachate average value	Wastewater average value	Activated sludge average value	Standard discharge limit[a]
1	Temperature (°C)	28.7	28.6	28.6	40
2	pH	8.25	6.87	6.60	6–9
3	EC (ms/cm)	3.94	1.00	1.09	–
4	Salinity (g/L)	2.10	0.02	0.03	–
5	Total solids (mg/L)	5,723	–	10,711	–
6	Suspended solids (mg/L)	710	–	9,234	50
7	Total hardness (mg/L $CaCO_3$)	1912	–	–	–
8	Colour (Pt. Co)	1,690	6.00	–	100
9	BOD_5 (mg/L)	269.0	64.2	87.5	20
10	COD (mg/L)	1,301	156	218	400
11	BOD_5/COD	0.20	0.41	0.40	0.05
12	TDS (%)	5.72	1.03	1.44	–
13	ORP (mV)	11.6	–	−126.0	–
14	MLVSS/MLSS	–	–	0.82	
16	Nitrite (mg/L NO_2-N–HR)	54.10	10.1	–	–
17	Total phosphorus (mg/L PO_4^{3-})	17.8	81.13	–	–
18	NH_3-N (mg/L)	532.0	149.0	160.0	5.0
19	Total organic carbon (mg/L TOC)	44.2	29.0	36.0	–
20	Sulfide (mg/L)	0.300	0.600	0.654	0.5
21	Total iron (mg/L)	6.03	1.21	1.95	5.0
22	Total manganese (mg/L)	1.98	0.67	0.91	0.20
23	Total zinc (mg/L)	1.89	1.71	1.89	2.0
24	Total copper (mg/L)	1.17	1.11	1.82	0.20
25	Total aluminum (mg/L)	0.034	0.031	0.047	–
26	Total nickel (mg/L)	4.94	0.51	0.78	0.20
27	Total chromium (mg/L)	0.21	0.12	0.12	0.20
28	Total cobalt (mg/L)	0.81	0.02	0.27	–
29	Total lithium (mg/L)	0.64	0.51	0.52	–
30	Total molybdenum (mg/L)	0.78	0.30	0.33	-
31	Total cadmium (mg/L)	2.71	0.39	0.39	0.01
32	Total calcium (mg/L)	121.45	25.11	102.0	–
33	Total magnesium (mg/L)	25.34	8.404	34.0	–
34	Phenols (mg/L)	1.69	0.04	0.07	0.001

[a]Environmental quality (Control of pollution from solid waste transfer station and landfill) Regulations 2009, under the Laws of Malaysia–Malaysia Environmental Quality Act 1974 [10].

60 L/min, serial no. 08110014, made in China). An air flow meter was used to adjust the air flow rate manually (Dwyer Flow Meter, model: RMA-26-SSV).

2.4. Sludge acclimatization

In accordance with Aziz et al. [17], approximately 1,080 mL of the activated sludge (90%) was combined with 120 mL (10%) of the gathered landfill leachate. After the reaction and settling phases, 120 mL of the supernatant was removed. In a new cycle, an additional 120 mL of unprocessed leachate was placed in the reactor. The procedure was continued for at least 10 d to allow the system to adjust to empirical conditions. Afterwards, the acclimated sludge was employed as seed in SBRs.

2.5. ZELIAC preparation

To create ZELIAC, zeolite, limestone, portland cement, activated carbon, and rice husk ash were pulverized and passed through a 300 μm mesh sieve. The components were then blended and combined with water. After mixing evenly, the mixture was emptied into a mold. The materials were eliminated from the mold after 24 h. Then, the mixture was saturated in water for 3 d in preparation for treatment. The materials were dehydrated within 2 d and were then compressed and passed through a sieve. Table 2 shows the features of ZELIAC with autosorb (Quantachrome AS1win™, version 2.02) testing. Table 3 and Fig. 1 show the XRF and XRD results of ZELIAC, respectively. Zeolite and activated carbon are present in the ZELIAC; thus, ZELIAC can act as both adsorbent and ion exchanger.

In this research, powdered ZELIAC (PZ) with a size of 75–150 μm (passed through sieve No. 100 and retained on sieve no. 200) was used as adsorbent in powdered ZELIAC augmented SBR technique (PZ-SBR) [1]. ZELIAC can act as both adsorbent and ion exchanger due to the presence of zeolite, activated carbon, and limestone. Also, it has the specifications of rice husk ash and cement. The rice husk ash and cement were used in the some studies [19], as adsorbents. Table 4 shows the values of raw materials required to prepare 50-kg of ZELIAC [20].

2.6. Operation of reactors

SBR consists of five steps, namely, load, react, settle, idle, and draw. In all experiments, the loading (20 min), blending (20 min), settling (90 min), idle (10 min), and drawing (10 min) periods were present. Different contact times of 2, 12, and 22 h, aeration rates of 0.5, 4, and 7.5 L/min, and leachate to wastewater ratios (20–80%; v/v) were used in both SBR and PZ-SBR. The beakers were loaded with 120 mL (10%) of acclimated sludge and 1,080 mL (90%) of household wastewater and Semeling landfill leachate (in diverse proportion) at a blending proportion of 25–75% (v/v). The primary features of activated sludge, wastewater, and leachate are shown in Table 1.

The reactors were separated into two groups. Three reactors were used for SBR (normal SBR), and three reactors were used for PZ-SBR (PZ-supplemented SBR). Based on the pre-SBR experiments, 3.24 g of PZ (specifically, PZ dosage = 3 g/L) was added to each PZ-SBR prior to aeration. The PZ that was used as adsorption contaminant in PZ-SBR was pre-dehydrated at 103–105°C and measured 75–150 μm

Table 2
Powdered ZELIAC characteristics

Parameter	Unit	Value
Surface area data		
Multipoint BET	m^2/g	6.760e + 01
Langmuir surface area	m^2/g	1.328e + 02
BJH method cumulative adsorption surface area	m^2/g	9.638e + 00
DH method cumulative adsorption surface area	m^2/g	1.019e + 01
t-method external surface area	m^2/g	3.421e + 01
t-method micropore surface area	m^2/g	3.338e + 01
DR method micropore area	m^2/g	1.153e + 02
Pore volume data		
Total pore volume for pores with diameter less than 4.06 nm at $P/P0 = -0.501894$	cc/g	4.029e − 02
BJH method cumulative adsorption pore volume	cc/g	9.930e − 03
DH method cumulative adsorption pore volume	cc/g	1.011e − 02
t-method micropore volume	cc/g	1.803e − 02
DR method micropore volume	cc/g	4.098e − 02
HK method cumulative pore volume	cc/g	3.172e − 02
SF method cumulative pore volume	cc/g	3.222e − 02
Pore size data		
Average pore diameter	nm	2.384e + 00
BJH method adsorption pore diameter (Mode DV(d))	nm	3.652e + 00
DH method adsorption pore diameter (Mode Dv9d))	nm	3652e + 00
DA method pore diameter (Mode)	nm	1.760e + 00
HK method pore diameter (Mode)	nm	3.675e − 01
SF method pore diameter (Mode)	nm	4.532e − 01

Table 3
XRF results for ZELIAC

Compounds/elements	Composition (%)	Compounds/elements	Composition (%)
C	14.350	MgO	1.000
CaO	32.401	Na_2O	0.100
SiO_2	42.002	P_2O_5	0.030
Al_2O_3	7.300	SO_3	0.030
Fe_2O_3	1.502	Others	0.280
K_2O	1.005	MgO	1.000

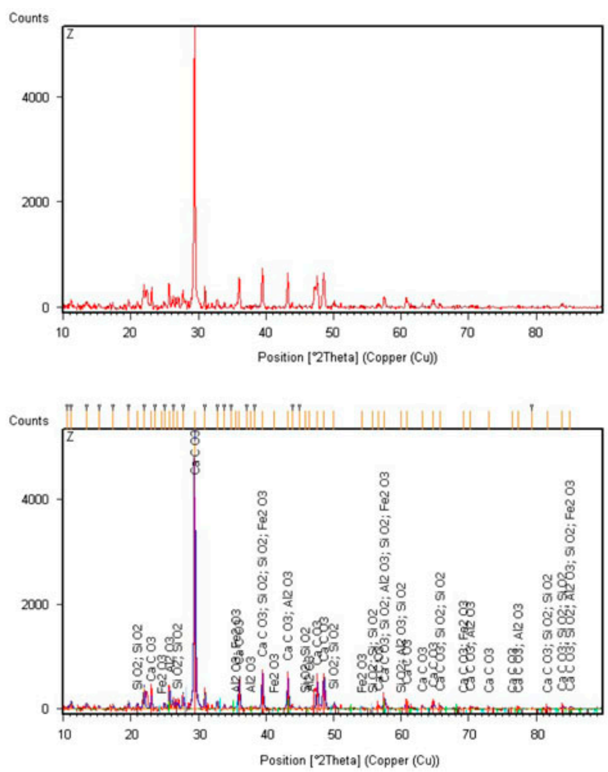

Fig. 1. The XRD results for ZELIAC.

(passed through sieve no. 100 and retained on sieve no. 200).

The removal effectiveness of Fe, Mn, Cd, and Ni were experimentally verified by evaluating objective factors before and after treatment. The following equation [Eq. (1)] was used to measure removal effectiveness:

$$\text{Removal (\%)} = \frac{(C_i - C_f) \times 100}{Ci} \tag{1}$$

where C_i and C_f are the first and last concentrations of the factors, respectively.

2.7. Analytical methods

All experiments were performed in compliance with the Standard Methods for the Examination of Water and Wastewater [21]. YSI 556 MPS (YSI incorporated, USA) was used to record the rates of pH, temperature (°), electrical conductivity (ms/cm), total dissolved solids (TDS) (%), salinity (g/L), and oxidation–reduction potential (ORP; mV). A spectrophotometer (DR/2500 HACH) was used to evaluate phenols (mg/L), total organic carbon (mg/L TOC), ammonia NH_3-N (mg/L), total phosphorus (PO_4^{3-} mg/L), sulfide (mg/L S^{2-}), nitrite (mg/L), color (Pt. Co), chemical oxygen demand (COD) (mg/L), total nitrogen (mg/L), total iron (mg/L Fe), manganese (mg/L Mn), chromium (mg/L Cr), zinc (mg/L Zn), aluminum (mg/L Al), copper (mg/L Cu), and nickel (mg/L Ni). ICP (ICP Varian, OES 715) was used to evaluate calcium (mg/L $CaCO_3$), lithium (mg/L Li), molybdenum (mg/L Mo), cobalt (mg/L Co), magnesium (mg/L), and cadmium (mg/L Cd).

Table 4
The values of raw materials to prepare 50 kg of ZELIAC

Raw materials	Value (kg)	Raw materials	Value (kg)
Zeolite	22.97	Rice husk ash	2.19
Limestone	7.66	Portland cement	15.00
Activated carbon	2.19	Water	30.00

2.8. Experimental plan and data analysis

In the present work, the central composite design (CCD) and response surface methodology (RSM) were applied for designing the experiments and data analysis. CCD was recognized through Design Expert Software Version 6.0.7. RSM was used to control the optimum process parameter levels. RSM collects mathematical and statistical methods that are suitable for the modeling and analysis of problems, in which responses of interest are affected by some variables; additionally, the goal was to optimize these responses [22,23]. The total number of experiments for the three factors (aeration rate (L/min), contact time (hr), and leachate to wastewater mixing ratios (%) were obtained as 20 (=$2^k + 2k + 6$), where k is the number of factors (k = three), Tables 5 and 6. The experiments were enhanced with six replications to assess the pure error. As there are only three levels for each factor, the appropriate model is the quadratic model Eq. (2).

$$Y = \beta_0 + \sum_{i=1}^{k} \beta_i X_i + \sum_{i=1}^{k} \beta_{ii} X_i^2 + \sum_{i_i<j}^{k} \sum_{j}^{k} \beta_{ij} X_i X_j + \cdots + e, \tag{2}$$

where Y is the response; X_i and X_j are the variables; β_0 is the stable coefficient; β_j, β_{jj}, and β_{ij} represent the interaction coefficients of linear, quadratic, and second-order terms, respectively; k is the number of analyzed parameters; and e is the error. The results were investigated using ANOVA in the Design Expert Software Version 6.0.7.

In the current study, each of the three operating variables was considered at three levels, low (−1), central (0), and high (+1). CCD and RSM were applied to evaluate the relationship between the most significant operating variables i.e. aeration rate (L/min), contact time (h), and leachate to wastewater mixing ratios (%) [1,24] and their responses (dependent variables), in addition to optimize the appropriate situations of operating variables in order to expect the best value of responses. Different contact times (2, 12, and 22 h), aeration rates (0.5, 4, and 7.5 L/min), and leachate to wastewater blending proportions (80, 50, and 20 v/v %) were used in SBR and PZ-SBR. To carry out an adequate analysis of the aerobic process, removals of four dependent parameters (Fe, Cd, Ni, and Mn) were measured as responses (Tables 5 and 6). Three-dimensional plots with the respective contour plots were obtained from the results of the experiments. From these, the effects of the interaction between the three factors on the responses were studied. The mentioned software was used to determine the value of the responses at optimum operational parameters (Table 7).

Table 5
Experimental variables and results for the SBR

Run	Aeration rate (L/min)	Contact time (h)	Leachate to wastewater ratio (%)	Fe rem. (%)	Mn rem. (%)	Ni rem. (%)	Cd rem. (%)
1	4.0	12	80	19.71	18.64	19.44	18.42
2	7.5	22	20	43.14	35.11	42.81	41.69
3	0.5	22	80	18.22	17.02	17.93	17.71
4	0.5	22	20	42.61	36.80	43.77	42.31
5	0.5	12	50	36.97	30.25	32.22	31.97
6	0.5	2	20	40.83	36.62	42.43	42.73
7	4.0	12	50	38.91	32.59	32.91	32.41
8	7.5	12	50	35.51	28.53	31.92	30.72
9	4.0	2	50	38.03	29.19	32.68	30.77
10	4.0	22	50	36.04	29.69	32.89	31.63
11	7.5	22	80	16.70	15.93	15.62	15.22
12	4.0	12	50	37.78	32.93	32.43	31.92
13	7.5	2	80	16.82	15.68	14.94	14.77
14	4.0	12	50	38.91	31.78	32.98	32.22
15	0.5	2	80	16.97	16.83	17.22	17.71
16	7.5	2	20	40.71	35.91	42.01	41.83
17	4.0	12	50	37.99	32.61	32.87	32.11
18	4.0	12	50	37.88	32.24	31.99	32.41
19	4.0	12	20	45.59	37.96	44.62	43.48
20	4.0	12	50	36.58	31.72	32.78	32.62

Table 6
Experimental variables and results for the PZ-SBR

Run	Aeration rate (L/min)	Contact time (h)	Leachate to wastewater ratio (%)	Fe rem. (%)	Mn rem. (%)	Ni rem. (%)	Cd rem. (%)
1	4.0	12	80	43.59	43.51	41.31	39.59
2	7.5	22	20	76.48	70.39	76.74	72.10
3	0.5	22	80	44.27	44.56	38.55	38.11
4	0.5	22	20	78.21	71.58	77.30	74.31
5	0.5	12	50	72.33	59.77	56.78	56.24
6	0.5	2	20	78.88	73.21	79.09	76.57
7	4.0	12	50	72.53	61.85	60.83	59.38
8	7.5	12	50	71.49	60.58	58.79	56.24
9	4.0	2	50	71.77	60.92	58.79	57.20
10	4.0	22	50	71.77	61.06	58.89	57.89
11	7.5	22	80	37.76	39.31	36.58	36.06
12	4.0	12	50	71.58	63.69	61.24	57.57
13	7.5	2	80	43.51	42.29	37.02	36.17
14	4.0	12	50	71.94	62.60	57.78	57.71
15	0.5	2	80	45.69	45.67	38.88	39.57
16	7.5	2	20	76.48	71.63	75.19	74.74
17	4.0	12	50	74.51	59.81	58.81	59.99
18	4.0	12	50	73.66	62.89	60.58	60.48
19	4.0	12	20	80.06	73.38	78.11	76.37
20	4.0	12	50	72.32	62.86	60.41	59.60

2.9. Adsorption isotherms

Adhesion of atoms, ions, bimolecules or molecules of gas, liquid, or dissolved solids to a surface is called adsorption. The quantity of adsorbate accumulated on the adsorbent was calculated by the variation between the quantity in the initial adsorbate concentration and the residue inside the solution after equilibrium with the adsorbent. The following equation explains this phenomenon [25].

$$q_e = \frac{(C_0 C_e)V}{M} \tag{3}$$

where q_e is the quantity of solute adsorbed per unit weight of adsorbent (mg/g), C_0 is the initial adsorbate concentration, C_e is the equilibrium adsorbate concentration (mg/L), V is the volume of solution (L), and M is the mass of the adsorbent (g). Langmuir and Freundlich isotherms were used to show powdered ZELIAC adsorption characteristics in this study.

3. Results and discussions

Table 1 shows that Sungai Petani leachate contains high levels of iron (6.03 mg/L), manganese (1.98 mg/L), cadmium (2.71 mg/L), and nickel (4.94 mg/L). These values exceed the standards established by the 1974 Environmental Quality Act of Malaysia [18]. Metals were eliminated from unprocessed leachate of Semeling landfill during co-treatment with household sewerage using PZ-improved SBR to reduce ecological risks from Sungai Petani landfill leachate. ZELIAC can be an ion exchanger, because of zeolite, rice husk ash, activated carbon, and limestone make ZELIAC a suitable adsorbent. The 3D surface plots for the pollutant removal (Fe, Mn, Ni, and Cd) in normal SBR and PZ-SBR are shown in Figs. 2 and 3, respectively.

3.1. Reactor performance

3.1.1. Iron removal

Iron is a typical component of the Earth's surface, and its concentration in the ecosystem varies. Iron is a constant pollutant, because it cannot be destroyed or eliminated. Human activities have considerably altered biogeochemical cycles and equilibrium of many metals. Primary anthropogenic resources of iron are different industrial sources, such as current and past mining activities, steel manufacturing, smelters and foundries, and various resources such as piping, components of goods, and combustion side effects.

The removal effectiveness of SBR varied from 16.70% (aeration rate = 7.5 L/min, contact time = 22 h,

Table 7
ANOVA results for response parameters

SBR type	Response	Final equation in terms of actual factor	Prob.	R^2	Adj. R^2	Adec. P.	SD	CV	PRESS	Prob. LOF
SBR	Fe	$37.91 + 1.328A + 0.377B + 0.222C - 0.156A^2 - 0.011B^2 - 0.006C^2 - 0.002AB - 0.002AC - 0.001BC$	0.0001	0.9947	0.9899	40.70	0.99	2.94	60.17	0.2994
	Mn	$37.38 + 0.870A + 0.357B - 0.038C - 0.012A^2 - 0.015B^2 - 0.002C^2 - 0.003AB + 0.0001AC + 0.0004BC$	0.0001	0.9930	0.9867	37.69	0.88	3.04	32.50	0.0424
	Ni	$47.60 + 0.890A + 0.203B - 0.266C - 0.106A^2 - 0.005B^2 - 0.001C^2 - 0.002AB - 0.002AC - 0.0003BC$	0.0001	0.9979	0.9960	67.66	0.61	1.95	18.70	0.0722
	Cd	$48.04 + 0.504A + 0.208B - 0.278C - 0.067A^2 - 0.009B^2 - 0.001C^2 + 0.002AB - 0.004AC + 0.0004BC$	0.0001	0.9994	0.9989	131.15	0.31	1.02	5.49	0.2108
PZ-SBR	Fe	$68.55 + 0.550A + 0.331B + 0.677C - 0.064A^2 - 0.009B^2 - 0.012C^2 - 0.013AB - 0.005AC - 0.002BC$	0.0001	0.9963	0.9929	48.13	1.20	1.80	120.03	0.3834
	Mn	$75.48 + 0.943A + 0.089B - 0.144C - 0.104A^2 - 0.004B^2 - 0.003C^2 - 0.005AB - 0.006AC - 0.005BC$	0.0001	0.9913	0.9836	34.13	1.39	2.33	92.63	0.4511
	Ni	$90.44 + 0.823A + 0.135B - 0.660C - 0.147A^2 - 0.007B^2 + 0.001C^2 + 0.011AB + 0.007AC - 0.0002BC$	0.0001	0.9947	0.9899	41.94	1.42	2.43	120.03	0.4122
	Cd	$87.65 + 1.075A + 0.025B - 0.596C - 0.163A^2 - 0.006B^2 - 0.0002C^2 + 0.003AB - 0.001AC + 0.001BC$	0.0001	0.9958	0.9920	47.65	1.21	2.11	63.01	0.4969

Notes: Prob: Probability of error; R^2: Coefficient of determination; Adj. R^2: Adjusted R^2; Adec. *P*: Adequate precision; SD: Standard deviation; CV: Coefficient of variance; PRESS: Predicted residual error sum of square; Prob. LOF: Probability of lack of fit. In final equations, where A is the aeration rate (L/min), B is contact time (h), and *C* is the leachate to wastewater mixing ration (%; v/v).

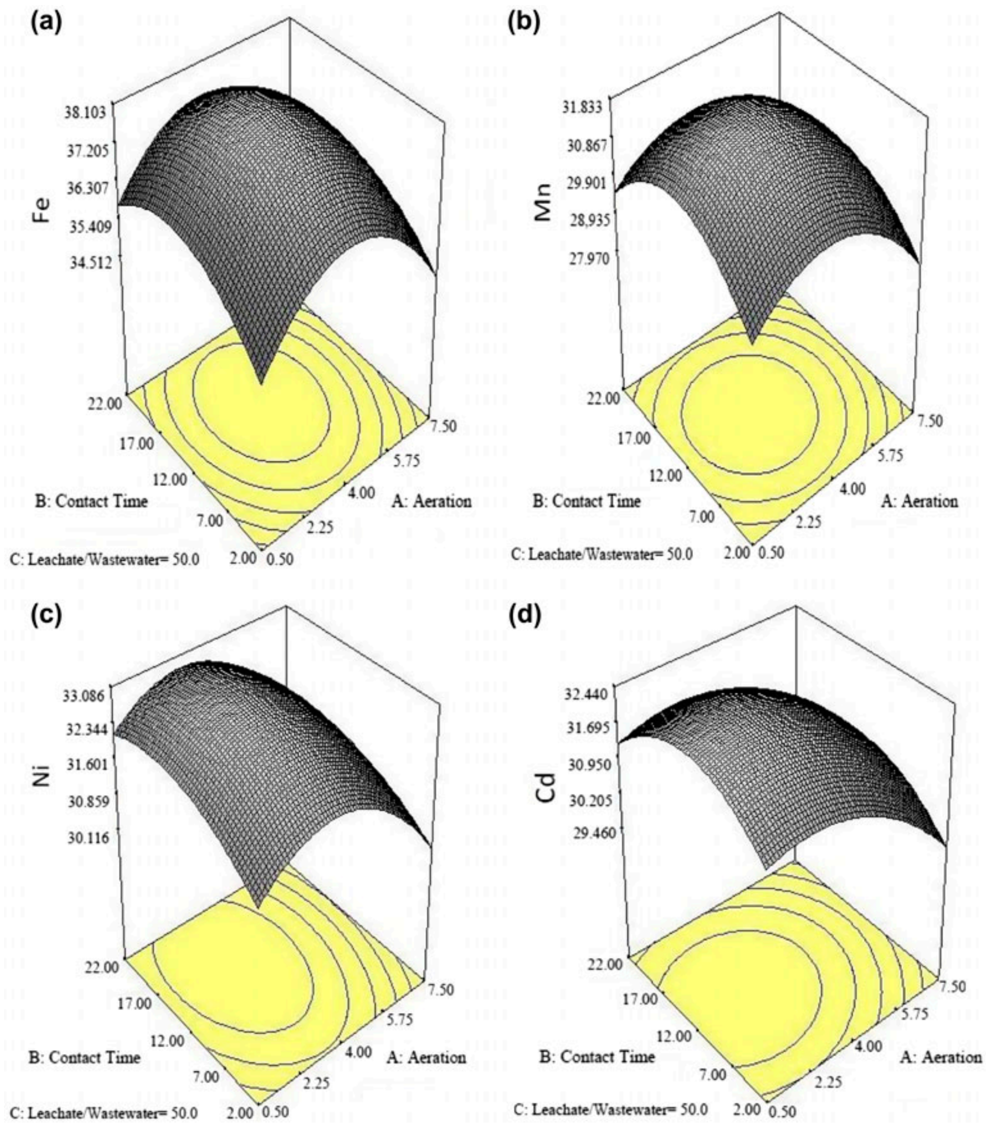

Fig. 2. The 3-D surface plots of (a) Fe, and (b) Mn, (c) Ni, and (d) Cd removal in normal-SBR.

and leachate to wastewater ratio = 80%) to 45.59% (aeration rate = 4.0 L/min, contact time = 12 h, and leachate to sewerage ratio = 20%) (Table 5). The optimum Fe removal of SBR (45.12%) was attained at an aeration rate of 3.97 L/min, contact time of 15.24 h, and leachate to sewerage ratio of 20%.

The removal effectiveness of PZ-SBR varied from 37.76 (aeration rate = 7.5 L/min, contact time = 22 h, and leachate to wastewater ratio = 80%) to 80.06% (aeration rate = 4.0 L/min, contact time = 12 h, and leachate to wastewater ratio = 20%) (Table 6). The optimum Fe removal of PZ-SBR (80.06%) was attained at an aeration rate of 1.71 L/min, contact time of 12.87 h, and leachate to sewerage ratio of 25.73%.

3.1.2. Manganese removal

Manganese (Mn) ions are released in wastewaters by numerous industries, such as pyrolusite (MnO_2) treatment, ink and dyes, glass and ceramics, paint and varnish, steel alloy dry cell batteries, fireworks and match manufacturing, and galvanized metal waste processing plants [26].

Taffarel and Rubio [26] investigated Mn^{2+} ion removal through adsorption onto natural and activated Chilean zeolites. This procedure was able to remove Mn efficiently.

In the current study, the lowest and highest Mn removal effectiveness attained by SBR reactors were

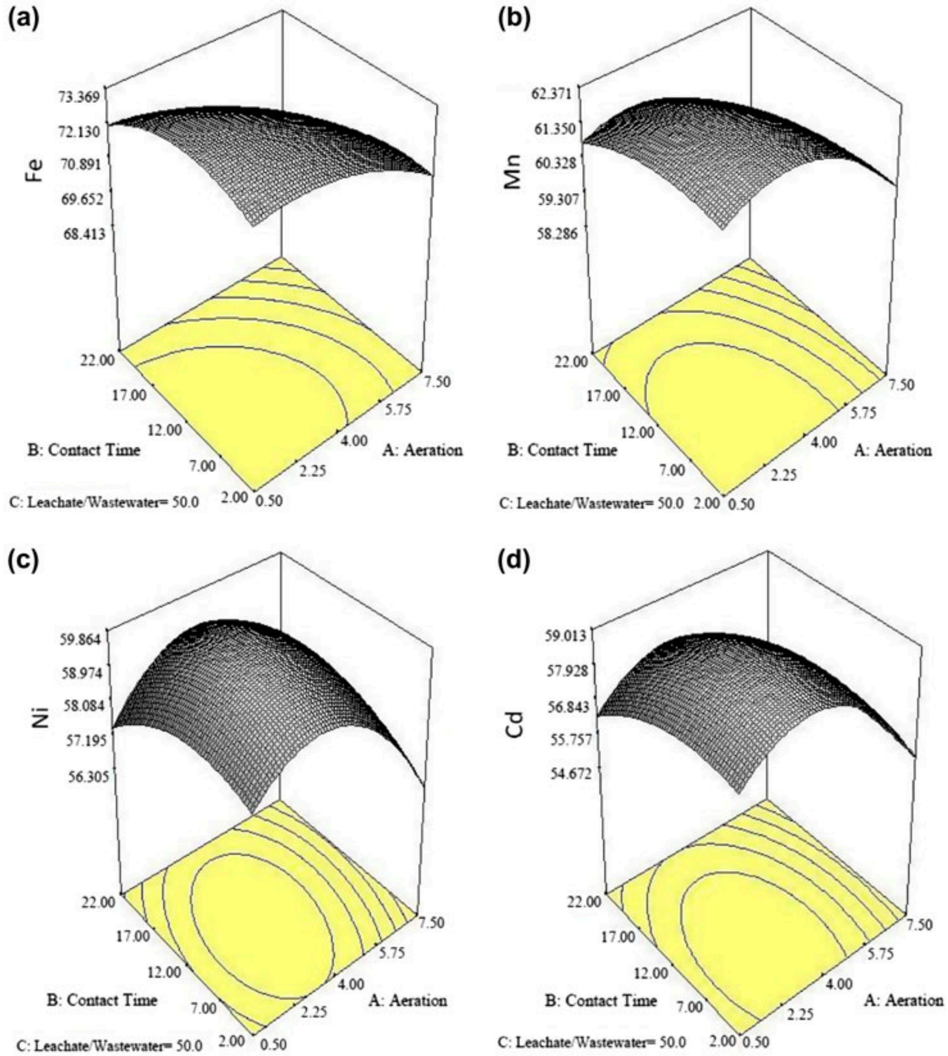

Fig. 3. The 3-D surface plots of (a) Fe, and (b) Mn, (c) Ni, and (d) Cd removal in PZ-SBR.

15.68% (contact time = 2 h, aeration rate = 7.50 L/min, and leachate to wastewater ratio = 80%) and 37.96% (contact time = 12 h, aeration rate = 4.0 L/min, and leachate to wastewater ratio = 20%), respectively (Table 5). The optimum Mn removal of SBR (38.17%) was attained at an aeration rate of 5.47 L/min, contact time of 12.87 h, and leachate to wastewater ratio of 21.25%.

The lowest and highest Mn removal effectiveness attained by PZ-SBR reactors was 39.31% (aeration rate = 7.50 L/min, contact time = 22 h, and leachate to wastewater ratio = 80%) and 73.38% (aeration rate = 4.00 L/min, contact time = 12 h, and leachate to wastewater ratio = 20%), respectively (Table 6). The optimum Mn removal of PZ-SBR (73.38%) was attained at an aeration rate of 3.92 L/min, contact time of 7.71 h, and leachate to wastewater ratio of 20.69%.

3.1.3. Nickel removal

Nickel is a toxic heavy metal that occurs naturally and is used in many industrial applications. In addition, nickel is an embryotoxin and teratogen. High Ni levels affect human health and cause headache, dry cough, nausea, tightness of the chest, dizziness, vomiting, rapid respiration, shortness of breath, chest pain, extreme weakness, and cyanosis [27]. Al-Dwairi and Al-Rawajfeh [28] investigated the elimination of cobalt and nickel from wastewater using inexpensive Jordan bentonite and zeolite. Their findings indicate that zeolite can be used to remove cobalt and nickel from wastewater.

The removal effectiveness of SBR varied from 14.94% (aeration rate = 7.5 L/min, contact time = 2 h, and leachate to wastewater ratio = 80%) to 44.62% (aeration rate = 4.0 L/min, contact time = 12 h, leachate to wastewater ratio = 20%) are shown in (Table 5). The optimum nickel removal of SBR (44.62%) was attained at an aeration rate of 3.21 L/min, contact time of 12.26 h, and leachate to wastewater ratio of 20.05%.

The removal effectiveness of PZ-SBR varied from 36.58 (aeration rate = 7.5 L/min, contact time = 2 h, and leachate to wastewater ratio = 80%) to 78.09% (aeration rate = 0.50 L/min, contact time = 2.0 h, leachate to wastewater ratio = 20%) are shown in (Table 6). PZ-SBR attained its optimum nickel removal (79.10%) at an aeration rate of 3.22 L/min, contact time of 9.15 h, and leachate to wastewater ratio of 20.22%.

3.1.4. Cadmium removal

Cadmium has recently been identified as a major environmental threat, because it is released to natural water sources. Cadmium pollution is mainly caused by the following: (i) Ni/Cd battery manufacturing that might release Cd^{++} and Ni^{++} into groundwater through unprocessed aqueous wastes or unmanaged disposal of consumed batteries; (ii) cadmium plating, which releases cyanide; and (iii) cadmium that is released directly to the ground and then to groundwater sources in a cultivated region in which cadmium-rich phosphate-based fertilizers are used. Non-ferrous metal mines are another major contributor of cadmium to the marine ecosystem. Pollution can result from mine drainage water, ore processing wastewater, tailing pond overflow, and flow of rainfall from a mining area [29].

Fadil et al. [30] investigated cadmium and lead eliminations from urban dumping site leachate using a carbon adsorbent produced from palm oil shell. Batch test showed that more than 60% of Pb and Cd were eliminated from leachate samples. Bai and Bartkiewicz [31] studied elimination of cadmium from sewerage using ion exchange resin Amberjet 1200H columns. Sorption capacity was 3.0 meq Cd/g and resin can be produced by HCl.

In this study, the lowest and highest Cd removal effectiveness attained by SBR reactors were 14.77% (aeration rate = 7.50 L/min, contact time = 2 h, and leachate to wastewater ratio = 80%) and 43.48% (aeration rate = 4.0 L/min, contact time = 12 h, and leachate to wastewater ratio = 20%), respectively (Table 5). The optimum Cd removal of SBR (43.52%) was attained at an aeration rate of 1.57 L/min, contact time of 7.99 h, and leachate to wastewater ratio of 20.12%.

The lower and highest Cd removal effectiveness attained by PZ-SBR reactors was 36.06% (aeration rate = 7.50 L/min, contact time = 2 h, and leachate to wastewater ratio = 80%) and 76.57% (aeration rate = 0.50 L/min, contact time = 2.0 h, and leachate to wastewater ratio = 20%), respectively (Table 6). The optimum Cd removal of PZ-SBR (76.59%) was attained at an aeration rate of 3.68 L/min, contact time of 15.31 h, and leachate to wastewater ratio of 20.03%.

Also the activated sludge micro-organisms can remove heavy metals via different mechanisms, which can be categorized according to their dependence or less on the metabolism activity as bioaccumulation and biosorption, respectively. Bioaccumulation is a metabolism dependent process, and biosorption is a passive uptake process, which is commonly fast, frequently reversibl,e and independent from cell viability [32].

3.2. Adsorption isotherms

3.2.1. Langmuir isotherm

Langmuir's isotherm describing the adsorption of adsorbate (A) onto the surface of the adsorbant (S) requires three assumptions: (1) The surface of the adsorbant is in contact with a solution containing an adsorbate which is strongly attracted to the surface. (2) The surface has a specific number of sites where the solute molecules can be adsorbed. (3) The adsorption involves the attachment of only one layer of molecules to the surface, i.e. monolayer adsorption. The chemical reaction for monolayer adsorption can be represented as follows:

$$A + S \Leftrightarrow AS$$

where AS represents a solute molecule bound to a surface site on S [33].

$$\frac{x}{m} = \frac{abC_e}{(1 + bC_e)} \tag{4}$$

where x/m is the mass of the adsorbate adsorbed per unit mass of adsorbent (mg adsorbate per g activated carbon), a and b are the empirical constants, and C_e is the equilibrium concentration of adsorbate in the solution after adsorption (mg/L).

Fig. 4 shows Langmuir isotherm regression for (a) Fe, (b) Mn, (c) Ni, and (d) Cd. Table 8 shows all the constants and correlation coefficients, R^2 values

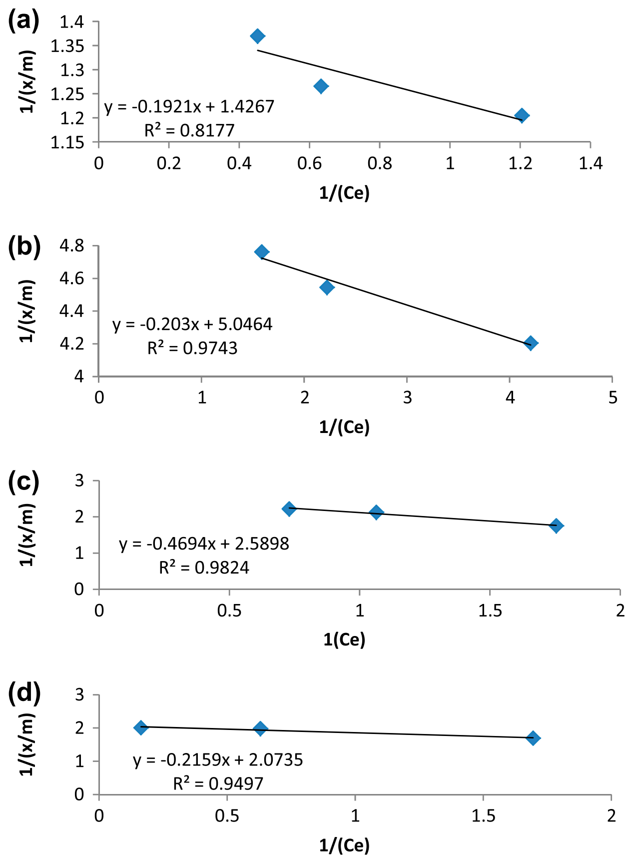

Fig. 4. Langmuir isotherm regression for (a) Fe, (b) Mn, (c) Ni, and (d) Cd.

attained from Langmuir isotherm for Fe, Mn, Ni, and Cd. The dimensionless equilibrium parameters R_L could be used to express the characteristics of Langmuir isotherm [34]. R_L has been shown in Table 8. Based on R^2, the adsorption of metals by ZELIAC can follow Langmuir adsorption isotherm.

The R^2, b, and Q were 0.8177, −8.15, and 0.700 for Fe, respectively. Abdulrasaq and Basiru [35] reported $R^2 = 0.882$, $Q = 0.09$ for Fe removal by coconut husk. The R^2, b, and Q were 0.9743, 3.18, and 0.198 for Mn, respectively. The R^2, b, and Q were 0.9824, −5.52, and 0.386 for Ni, respectively. Desta [36] reported $R^2 = 0.998$ and $b = 0.189$ for Ni removal from wastewater by activated carbon. The R^2, b, and Q were 0.9497, −5.86, and 0.482 for Cd, respectively.

3.2.2. Fruendlich isotherm

The Freundlich equation or Freundlich adsorption isotherm, an adsorption isotherm, is a curve relating the concentration of a solute on the surface of an adsorbent to the concentration of the solute in the liquid with which it is in contact [25].

The Freundlich equation can be written as [37]:

$$\frac{x}{m} = K_f C_e^{1/n} \tag{5}$$

where K_F is the constant indicative of the relative adsorption capacity of the adsorbent (mg$^{1-(1/n)}$ L$^{1/n}$ g^{-1}) and n is the constant indicative of the intensity of the adsorption.

Constants in the Freundlich isotherm can be found by plotting log(x/m) against log(C_e) and using following equation [25].

$$\log\left(\frac{x}{m}\right) = \log K_f + \left(\frac{1}{n}\right)\log C_e \tag{6}$$

where x/m is the mass of the adsorbate per unit mass of adsorbent (mg/g), K_f is the Freundlich capacity factor, C_e is the equilibrium concentration of the adsorbate in the solution after adsorption (mg/L), and $1/n$ is the Freundlich intensity parameter. Fig. 5 shows Freundlich isotherm regression for (a) Fe, (b) Mn, (c) Ni and, (d) Cd. Table 9 shows all the constants and correlation coefficients, R^2 values attained from Freundlich isotherm for Fe, Mn, Ni, and Cd.

The R^2, $1/n$, and K_f were 0.9219, −0.116, and 0.23 for Fe, respectively. $K_f = 0.28$ and $R^2 = 0.99$ for Fe adsorption by activated carbon has been reported by [38]. The R^2, $1/n$, and K_f were 0.9599, −0.0868, and 0.49 for Mn, respectively. $K_f = 0.35$ and $R^2 = 0.95$ for

Table 8
Langmuir equation for Fe, Mn, Ni, and Cd

Parameters	Q (mg/g)	b	R^2	$R_L = \frac{1}{(1+bC_o)}$	Isotherm type
Fe	0.700	−8.15	0.8177	−0.19	Unfavorable
Mn	0.198	3.18	0.9743	0.13	Favorable
Ni	0.386	−5.52	0.9824	−0.04	Unfavorable
Cd	0.482	−5.86	0.9497	−0.57	Unfavorable

Note: $0 < R_L < 1$ = favorable; $R < 1$ = unfavorable [23].

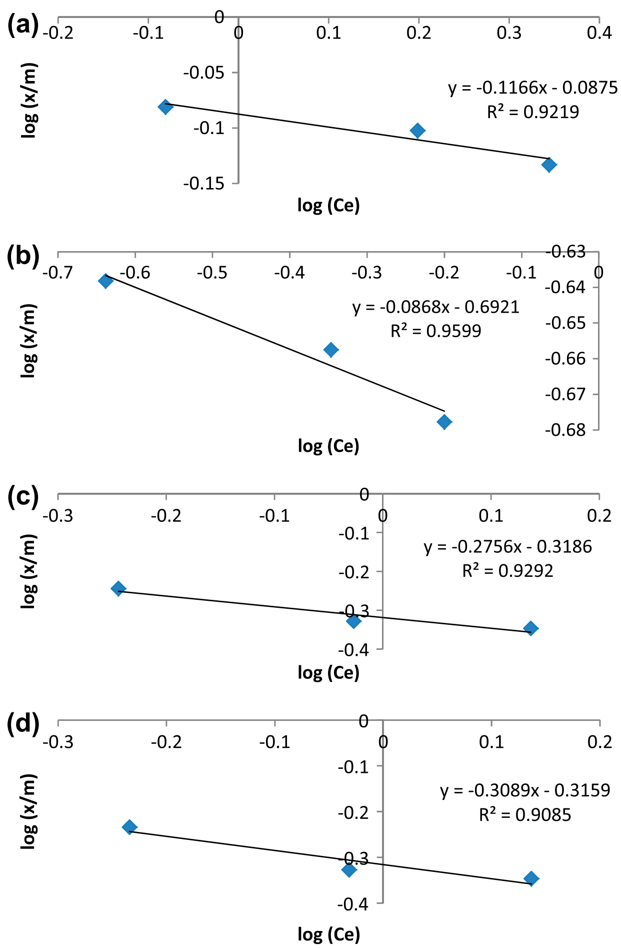

Fig. 5. Freundlich isotherm regression for (a) Fe, (b) Mn, (c) Ni, and (d) Cd.

Mn adsorption by activated carbon has been reported by Akl et al. [38].

The R^2, $1/n$, and K_f were 0.9292, −0.2756, and 0.48 for Ni, respectively. Kaur et al. [39] reported the K_f = 0.66, $R^2 = 0.91$ for nickel adsorption by some activated carbon which were produced by agriculture residues. $K_f = 0.54$ and $R^2 = 0.967$ for nickel adsorption by zeolite was reported by [28]. The R^2, $1/n$, and K_f were 0.9085, −0.3089, and 0.39 for Cd, respectively

Table 9
Freundlich equation for Fe, Mn, Ni and Cd

Parameters	K_f (mg/g (L/mg)$^{1/n}$)	$1/n$	n	R^2
Fe	0.23	−0.116	−8.57	0.9219
Mn	0.49	−0.0868	−11.52	0.9599
Ni	0.48	−0.2756	−3.62	0.9292
Cd	0.39	−0.3089	−3.23	0.9085

3.3. Statistical analysis and experimental condition optimization

CCD and RSM were used to show the nature of the reaction surface in the empirical plan and determine the optimum setting of the independent variables. CCD was developed by using Design Expert Software (6.0.7). Aeration rate (L/min), contact time (h), and leachate to wastewater ratio (%; v/v) were independent factors. Four dependent factors (Fe, Mn, Cd, and Ni) were evaluated as reactions to investigate the aerobic process (Tables 5 and 6).

These selected settings were somewhat close to the highest removal and viability standards of treatment sites. The empirical settings improved if the Fe, Mn, Cd, and Ni removal rates were higher than the randomly selected restraint values. The optimum settings were determined using Design Expert Software. Compared with the model, the improved settings were observed in the SBR reactor at an aeration rate of 3.98 L/min, contact time of 15.23 h, and leachate to wastewater ratio of 20%, which resulted in 45.12, 38.75, 44.73, and 43.72% removal rates for Fe, Mn, Ni, and Cd, respectively. The second highest settings for the PZ-SBR reactor were observed at an aeration rate of 2.87 L/min, contact time of 11.70 h, and leachate to wastewater ratio of 20.13%, which resulted in 79.57, 73.38, 79.29, and 76.96% removal rates for Fe, Mn, Ni, and Cd, respectively.

ZELIAC can serve as an ion exchanger because of zeolite, and it can be an adsorbent because of activated carbon, limestone, and rice husk ash. Therefore, PZ-SBR can efficiently remove heavy metals from leachate.

4. Conclusion

Several pollutants in Sungai Petani landfill leachate exceeded the allowable discharge restrictions for Fe, Mn, Ni, and Cd. Heavy metals from Sungai Petani landfill leachate and domestic wastewater were eliminated by performing PZ-supplemented SBR. The reactors were separated into two groups. Three reactors were used for SBR (normal SBR), and three reactors were used for PZ-SBR (powdered ZELIAC-supplemented SBR). Central composite design and response surface methodology were employed in order to illustrate the nature of the response surface in the experimental design, and explain the optimal conditions of the independent variables. The main conclusions of this study are presented below.

(1) SBR was able to remove 45.12, 38.75, 44.73, and 43.72% of Fe, Mn, Ni, and Cd, respectively,

(2) PZ-SBR removed 79.57, 73.38, 79.29, and 76.96% of Fe, Mn, Ni, and Cd, respectively.
(3) This result indicates that PZ-SBR can treat non-biodegradable dumping site leachate more efficiently than conventional SBR.

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