

ZEOLITE AND ACTIVATED CARBON COMBINED WITH BIOLOGICAL TREATMENT FOR METALS REMOVAL FROM MIXTURES OF LANDFILL LEACHATE AND DOMESTIC WASTEWATER

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ABSTRACT

Current study was carried out to investigate the heavy metals removal from landfill leachate and urban wastewater by powdered activated carbon and powdered zeolite augmented SBR technique. The research was carried out in six 2000 mL breakers (working size was 1200 ml). The reactors were parted into 2 groups covering 3 for activated carbon augmented SBRs (PAC-SBR), and 3 for powdered zeolite augmented SBRs (PZE-SBR). The response surface methodology (RSM) and the central composite design (CCD) were employed to explain the most advantageous settings of the independent variables (aeration rate (I min⁻¹), reaction time (h), and leachate-to-wastewater mixing ration (%; v/v) and their resopnses (dependent variables including Fe, Mn, Ni and Cd). The results indicated that the PZE-SBR showed higher performance in removal efficiencies while compared to PAC-SBR. At the optimum conditions of contact time (13.83 h), aeration rate (2.81 I min⁻¹) and leachate to domestic wastewater proportion (20.00%) for the PZE-SBR, the removal efficiencies for Fe, Mn, Ni, and Cd were 65.65%, 61.56, 63.41%, and 60.44%, respectively.

Keywords: Activated carbon, Heavy Metals, Landfill Leachate, Sequencing Batch Reactor, Zeolite

1. Introduction

Sanitary landfills are the most prevalent way of solid waste treatment in most countries. Although this type of solid waste treatment provides some benefits, it has a disadvantage, including, the production of leachate. At present, approximately 230 landfills are located in Malaysia, most of which are old dumping grounds and do not have systems for environmental treatment. The leachate is released directly into water resources without any treatment and threatens neighboring ecosystem, particularly in places where landfills are situated upstream of the water intake (Aziz *et al.*, 2011a). Landfill leachate is a type of wastewater that has significant environmental impacts because of its high-contaminant concentrations. Urban landfill leachates have contaminants that may be divided into four vital groups: dissolved organic

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matters; inorganic compounds such as calcium, potassium, sodium, ammonium, magnesium, sulphates, and chlorides; heavy metals such as lead, nickel, copper, cadmium, chromium and zinc; xenobiotic organic materials (Aziz *et al.*, 2011b). Leachate is created when water carrying some forms of pollutants penetrates through the waste in a landfill (Foul *et al.*, 2009). Heavy-metal pollution is a global problem, although the severity and levels of contamination differ from place to place. Common heavy metals include cadmium, lead, nickel, cobalt, zinc, and chromium (Mojiri, 2011). Heavy metals are the unique class of toxicants because they cannot be fragmented down to non-toxic forms (Waoo *et al.*, 2014). Literature states that not more than 10% of the metals in dumpsite leachate are free metal ions (Chaari *et al.*, 2011).

Methods for removing metals in wastewater include biological treatments, ion exchange, solvent extraction, chemical precipitation, and reverse osmosis or adsorption (Mohan and Gandhimathi, 2009). Zeolites are the most common and generally available natural ion exchangers, which has an aluminosilicate molecular structure with weak cationic bonding sites (Guisnet and Gilson, 2002). Mojiri (2011) stated that zeolite has displayed a reasonable ability to adsorb metals (copper, cadmium, lead, and zinc), and this property can be suitable for removing toxicants. Activated carbon (AC) is considered one of the best effective adsorbents, particularly for substances containing refractory organic compounds that resist biodegradation and persist in the environment. Generally, the using of AC adsorption is helpful for the removal of non-biodegradable compounds in landfill leachate (Blaney *et al.*, 2007). Recently, many studies have focused on metal removal in wastewater and landfill leachate by using different methods (Guisnet and Gilson, 2002; Blaney *et al.*, 2007; Mohan and Gandhimathi, 2009; Chaari *et al.*, 2011).

Also in literature, researchers have suggested the co-treatment of landfill leachates and wastewater because of some reasons: (1) Landfill leachate treatment using biological methods is difficult because of the high COD/BOD ratio, high ammonium content, and the presence of heavy metal ions (Nesaj *et al.,* 2007).; (2) The co-treatment process has been preferred because of low maintenance and low operating costs (Abbas *et al.,* 2009).

The objectives of this research are as follows: (1) study the performance of SBR with powdered zeolite (PZE-SBR) and powdered AC (PAC-SBR) on the removal of cadmium, iron, manganese, and nickel from Sungai Petani Landfill leachates and household wastewater from the Bayan Baru Wastewater Treatment Plant in Malaysia; (2) compare the performance of PZE-SBR and PAC-SBR in removing heavy metals from landfill leachate and domestic wastewater.

2. Materials and methods

2.1. Landfill Leachate Sampling

Leachate samples were collected from the Sungai Petani landfill site from June 2012 to March 2013. The landfill site (geographical coordinates, 05° 43' N and 100° 29' E) is located in Kedah, Malaysia. The landfill received nearly 350-400 tons of solid waste daily; it was measured by using Weight Bridge. This open dumping site has been actively applied since 1990. The total landfill area of Sungai Petani is 11.24 ha. The leachates remain in the collection pond depending on retention time, and then they are discharged directly into the environment with no treatment. After collecting the samples, they were directly carried to the laboratory and kept in a cold room at 4 °C so as to minimize biological and chemical reactions (Aziz *et al.*, 2011b). The characteristics of the samples are given in Table 1. To determine the risks of the leachates to the environment, the obtained parameter values were compared against the 2009 Regulations of the Malaysia Environmental Quality Act of 1974 (2009).

2.2. Domestic Wastewater and Activated Sludge Sampling

The activated sludge and municipal wastewater were gathered from the Bayan Baru wastewater treatment plant in Penang, Malaysia. Table 1 shows the characteristics of the activated sludge and wastewater.

2.3. Reactors characteristics

Six 2000 ml beakers were used throughout the study; each of them had a working volume of 1200 ml, with an inner diameter of 113 mm, and a height of 200 mm. A magnetic stirrer was employed for mixing in the bottom of reactors. The experiments were carried out at room temperature, and an air pump (YASUNAGA, Air pump INC. voltage: 240 V, Frequency: 50 Hz, Input power 61 W, Model: LP-60A, Pressure: 0.012 MPa, Air volume: 60 l min⁻¹, Serial No.: 08110014, Made in China) was providing the reactors with air. The air flow speed was manually regulated, using an air flow meter (Dwyer Flow meter, Model: RMA-26-SSV).

| 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 | рН | 8.25 | 6.87 | 6.60 | 6-9 |
| 3 | EC (ms cm ⁻¹) | 3.94 | 1.00 | 1.09 | - |
| 4 | Salinity (g l ⁻¹) | 2.10 | 0.02 | 0.03 | - |
| 5 | Total solids (mg l ⁻¹) | 5723 | - | 10711 | - |
| 6 | Suspended solids (mg l ⁻¹) | 710 | - | 9234 | 50 |
| 7 | Total Hardness (mg l⁻¹ CaCO₃) | 1912 | - | - | - |
| 8 | Colour (Pt. Co) | 1690 | 6.00 | - | 100 |
| 9 | BOD₅ (mg l ⁻¹) | 269.0 | 64.2 | 87.5 | 20 |
| 10 | COD (mg l ⁻¹) | 1301 | 156 | 218 | 400 |
| 11 | TDS (%) | 5.72 | 1.03 | 1.44 | - |
| 12 | ORP (mV) | 11.6 | - | -126.0 | - |
| 13 | MLVSS/MLSS | - | - | 0.82 | |
| 14 | Total iron (mg l ⁻¹) | 6.03 | 1.21 | 1.95 | 5.0 |
| 15 | Total manganese (mg l ⁻¹) | 1.98 | 0.67 | 0.91 | 0.20 |
| 16 | Total nickel (mg l ⁻¹) | 4.94 | 0.51 | 0.78 | 0.20 |
| 17 | Total cadmium (mg l ⁻¹) | 2.71 | 0.39 | 0.39 | 0.01 |

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

^aEnvironmental Quality (Control of Pollution from Solid Waste Transfer Station and Landfill) Regulations 2009, under the Laws of Malaysia–Malaysia Environmental Quality Act 1974

2.4. Sludge Acclimatization

Based on Aziz *et al.*, (2011b) studies, 120 mL (10%) of the collected landfill leachate was mixed with about 1080 mL of the activated sludge (90%). When the reaction was terminated and after settling phases, 120 ml of the supernatant was withdrawn. In another cycle, an additional 120 ml of the raw leachate was added to the reactor. This procedure was sustained for at least 10 d so as for the system to adapt to the experimental situation. This adjusted sludge was later employed as seed in the SBRs.

2.5. Powdered Zeolite and Powdered Activated Carbone

In this research, powdered zeolite and powdered activated carbon of size 75-150 μ m were employed as adsorbent (Aziz *et al.*, 2011a) in the PZE-SBR and PAC-SBR. Table 2 shows the features of the zeolite and activated carbon with the autosorb (Quantachrome AS1wintm, version 2.02) testing. In the current study, zeolite was from Indonesia.

Zeolite consist has an aluminosilicate molecular structure with weak cationic bonding sites (Mojiri, 2011) so the most elements in the zeolite are Al and Si. This structure is useful for ion exchange. Activated carbon is generally applied for adsorbtion of natural organic complexes, taste and odor, and synthetic organic chemicals in drinking water treatment (Lin *et al.*, 2010).

| Parameter | | Powdered AC | Powdered Zeolite | | | | |
|--|--------------------|-------------|------------------|--|--|--|--|
| | | Value | | | | | |
| Surface Area Data | | | | | | | |
| MultiPoint BET | m² g-1 | 5.857e + 02 | 4.936e + 01 | | | | |
| Langmuir surface area | m² g-1 | 9.607e + 02 | 9.480e + 01 | | | | |
| BJH method cumulative adsorption surface area | m² g-1 | 1.832e + 01 | 6.404e + 00 | | | | |
| DH method cumulative adsorption surface area | m² g-1 | 1.938e + 01 | 6.770e + 00 | | | | |
| t-method external surface area | m² g-1 | 8.681e + 01 | 2.420e + 01 | | | | |
| t-method micropore surface area | m² g⁻¹ | 4.989e + 02 | 2.517e + 01 | | | | |
| DR method micropore area | m² g⁻¹ | 9.303e + 02 | 8.305e + 01 | | | | |
| Pore Volume Data | | | | | | | |
| Total pore volume for pores with Diameter less than 4.06 nm at P/P0= 0.501894 | cc g ⁻¹ | 3.283e - 01 | 2.897e – 02 | | | | |
| BJH method cumulative adsorption pore volume | cc g ⁻¹ | 1.887e - 02 | 6.639e – 02 | | | | |
| DH method cumulative adsorption pore volume | cc g ⁻¹ | 1.921e – 02 | 6.756e – 02 | | | | |
| t-method micropore volume | cc g ⁻¹ | 2.714e – 01 | 1.323e – 02 | | | | |
| DR method micropore volume | cc g ⁻¹ | 3.306e - 01 | 2.952e – 02 | | | | |
| HK method cumulative pore volume | сс g ⁻¹ | 3.051e – 01 | 2.285e – 02 | | | | |
| SF method cumulative pore volume | cc g ⁻¹ | 3.071e – 01 | 2.328e – 02 | | | | |
| Pore Size Data | | | | | | | |
| Average pore Diameter | nm | 2.242e + 00 | 2.348 + 00 | | | | |
| BJH method adsorption pore Diameter (Mode DV(d)) | nm | 3.374e + 00 | 3.666 + 00 | | | | |
| DH method adsorption pore Diameter (Mode Dv(d)) | nm | 3.374e + 00 | 3.666e + 00 | | | | |
| DA method pore Diameter (Mode) | | 1.180e + 00 | 1.740e + 00 | | | | |
| HK method pore Diameter (Mode) | nm | 3.675e + 01 | 3.675e – 01 | | | | |
| SF method pore Diameter (Mode) | nm | 4.532e + 01 | 4.523e – 01 | | | | |

Table 2. Powdered Activated Carbone and Powdered Zeolite Characteristics

2.6. Operation of Reactors

The SBR phases include filling, reacting, settling, drawing and idling. In all the experiments, the duration for filling and mixing (20 min), settling (90 min), drawing, and idling (10 min) were fixed. Different aeration rates of 0.5, 4, and 7.5 I min⁻¹, contact times of 2, 12, and 22 h, and different ratio of leachate to wastewater (20 to 80%; v/v) were applied in both methods, the PZE-SBR and PAC-SBR. The beakers were filled with 120 ml (10%) of adjusted sludge and 1080 mL (90%) of domestic wastewater and Sungai Petani landfill leachate (in different ratio), with the mixing ratio of 20% to 80% (v/v). Table 1 shows the main features of wastewater, leachate, and activated sludge.

The reactors were divided into 2 groups consisting of 3 reactors for PZE-SBR (powdered zeolite augmented SBR) and 3 for PAC-SBR (powdered activated carbon augmented SBR). Based on preliminary experiments, 3.24 g of PZE and PAC (i.e. PZE and PAC dosage = 3 g l^{-1}) were added to each reactor, the PZE-SBR and PAC-SBR, before aeration. The PZE and PAC which were used for adsorption pollutants in the PZE-SBR and PAC-SBR were pre-dried at 103–105 °C and sized 75–150µm.

The removal effectiveness of manganese (Mn), iron (Fe), nickel (Ni), and cadmium (Cd) were closely observed during the experiments. Removal effectiveness was determined by measuring the target parameters before and after the treatment process. Calculation of the removal efficiency was done based on the following equation (Eq. 1):

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

where Ci stands for the initial and Cf for final concentrations of the parameters.

2.7. Analytical Methods

Experiments were completed consistent with the Standard Methods for the Examination of Water and Wastewater (APHA, 2005). YSI 556 MPS (YSI incorporated, USA) was applied for documenting the rates of pH, electrical conductivity (ms cm⁻¹), temperature (°C), salinity (g l⁻¹), TDS (%), and oxidation decrease potential, explicitly, ORP (mV). The average of pH was around 6-6.5 which was close to the normal pH. A spectrophotometer (DR/2800 HACH) and ICP (ICP Varian, OES 715) were applied for evaluating metals (Bashir *et al.*, 2010; Aziz *et al.*, 2011a; Amr, 2013; Mojiri *et al.*, 2014).

2.8. Experimental plan and data analysis

The central composite design (CCD) and the response surface methodology (RSM) were applied in order to explain the nature of the response surface in the experimental design and elucidate the optimal conditions of the independent variables. CCD was launched through Design Expert Software (6.0.7). The performance of the system is labelled through equation 2an empirical second-order polynomial model (Eq. 2.):

$$Y = \beta_0 + \sum_{i=1}^k \beta_i X_i + \sum_{i=1}^k \beta_i X_i^2 + \sum_{i < j}^k \sum_j^k \beta_i X_i X_j + ... + e$$
(2)

where Y is the response; Xi and Xj are the variables; $\beta 0$ is a constant coefficient; βj , $\beta j j$, and $\beta i j$ are the interaction coefficients of linear, quadratic and second-order terms, respectively; k is the number of study factors; and e is the error (Mojiri *et al.*, 2013b).

| Aeration | | Contact | Leachate to | | | | |
|----------|-----------|-----------|-------------|-------------|-------------|-------------|-------------|
| Run | Rate | Time (b) | Wastewater | Fe rem. (%) | Mn rem. (%) | Ni rem. (%) | Cd rem. (%) |
| | (l min⁻¹) | Time (II) | Ratio (%) | | | | |
| 1 | 4.0 | 12 | 80 | 31.49 | 26.11 | 23.96 | 26.00 |
| 2 | 7.5 | 22 | 20 | 51.13 | 49.06 | 47.21 | 48.74 |
| 3 | 0.5 | 22 | 80 | 31.06 | 23.98 | 23.00 | 24.13 |
| 4 | 0.5 | 22 | 20 | 52.11 | 49.27 | 47.61 | 49.94 |
| 5 | 0.5 | 12 | 50 | 37.04 | 32.70 | 32.10 | 32.16 |
| 6 | 0.5 | 2 | 20 | 57.91 | 51.19 | 51.09 | 51.73 |
| 7 | 4.0 | 12 | 50 | 43.75 | 40.49 | 40.91 | 40.15 |
| 8 | 7.5 | 12 | 50 | 39.17 | 34.94 | 36.15 | 35.17 |
| 9 | 4.0 | 2 | 50 | 34.04 | 31.70 | 30.10 | 31.16 |
| 10 | 4.0 | 22 | 50 | 42.42 | 37.22 | 39.16 | 39.19 |
| 11 | 7.5 | 22 | 80 | 29.04 | 21.31 | 20.74 | 22.02 |
| 12 | 4.0 | 12 | 50 | 43.43 | 40.13 | 39.96 | 40.14 |
| 13 | 7.5 | 2 | 80 | 29.97 | 22.24 | 21.21 | 23.43 |
| 14 | 4.0 | 12 | 50 | 43.06 | 39.71 | 40.93 | 40.02 |
| 15 | 0.5 | 2 | 80 | 30.39 | 23.13 | 21.76 | 23.00 |
| 16 | 7.5 | 2 | 20 | 46.86 | 43.24 | 41.51 | 43.63 |
| 17 | 4.0 | 12 | 50 | 43.99 | 39.89 | 40.91 | 41.02 |
| 18 | 4.0 | 12 | 50 | 43.75 | 39.98 | 39.88 | 40.41 |
| 19 | 4.0 | 12 | 20 | 60.06 | 52.55 | 55.40 | 56.53 |
| 20 | 4.0 | 12 | 50 | 43.91 | 41.82 | 40.44 | 42.00 |
| | | | | | | | |

Table 3. Experimental variables and results for the PAC-SBR

*Three replications were done during this experiment

The outcomes were finally analyzed by analysis of variance (ANOVA) in the Design Expert Software. Each of the 4 functional variables was regarded at 3 levels, low (-1), central (0), and high (+1). In the current study, CCD and RSM were used to assess the relationship between the most significant functional variables (Mojiri *et al.*, 2013a), explicitly, aeration rate (I min⁻¹), reaction time (contact time, h), and

leachate-to-wastewater mixing portion (%; v/v) and their reactions (dependent variables) as well as improving the proper condition of functional variables to foresee the paramount value of reactions. Contact times (2, 12, and 22 h), aeration rates (0.5, 4, and 7.5 l min⁻¹), and leachate to wastewater blending proportion (80, 50, and 20 v/v %) were employed with PZE-SBR and PAC-SBR. With the purpose of performing a sufficient study of the aerobic procedure, 4 dependent factors (Fe, Cd, Mn and Ni) were considered as responses (Tables 3 and 4).

| | Aeration | Contact | Leachate to | | | | |
|-----|-----------|----------|-------------|-------------|-------------|-------------|-------------|
| Run | Rate | Time (h) | Wastewater | Fe rem. (%) | Mn rem. (%) | Ni rem. (%) | Cd rem. (%) |
| | (l min⁻¹) | e (, | Ratio (%) | | | | |
| 1 | 4.0 | 12 | 80 | 31.96 | 32.13 | 32.17 | 30.91 |
| 2 | 7.5 | 22 | 20 | 59.11 | 54.76 | 58.38 | 56.11 |
| 3 | 0.5 | 22 | 80 | 31.01 | 30.72 | 30.43 | 28.89 |
| 4 | 0.5 | 22 | 20 | 63.03 | 57.09 | 61.27 | 57.24 |
| 5 | 0.5 | 12 | 50 | 47.18 | 41.19 | 47.83 | 44.73 |
| 6 | 0.5 | 2 | 20 | 61.70 | 55.76 | 60.00 | 56.26 |
| 7 | 4.0 | 12 | 50 | 52.96 | 49.13 | 50.14 | 46.81 |
| 8 | 7.5 | 12 | 50 | 45.00 | 39.00 | 46.40 | 41.97 |
| 9 | 4.0 | 2 | 50 | 49.19 | 42.99 | 47.13 | 44.12 |
| 10 | 4.0 | 22 | 50 | 49.13 | 42.09 | 46.11 | 44.64 |
| 11 | 7.5 | 22 | 80 | 29.90 | 28.74 | 25.14 | 28.04 |
| 12 | 4.0 | 12 | 50 | 52.84 | 47.79 | 48.09 | 46.74 |
| 13 | 7.5 | 2 | 80 | 30.02 | 27.31 | 26.19 | 27.17 |
| 14 | 4.0 | 12 | 50 | 53.11 | 49.00 | 47.11 | 46.99 |
| 15 | 0.5 | 2 | 80 | 31.90 | 28.94 | 27.77 | 27.99 |
| 16 | 7.5 | 2 | 20 | 56.18 | 51.56 | 47.97 | 52.93 |
| 17 | 4.0 | 12 | 50 | 53.44 | 48.06 | 49.01 | 47.13 |
| 18 | 4.0 | 12 | 50 | 53.11 | 47.91 | 49.92 | 47.27 |
| 19 | 4.0 | 12 | 20 | 65.08 | 59.93 | 63.18 | 60.41 |
| 20 | 4.0 | 12 | 50 | 53.04 | 47.91 | 48.71 | 48.00 |

Table 4. Experimental variables and results for the PZE-SBR

*Three replications were done during this experiment

3. Results and discussions

As Table 1 shows, Sungai Petani leachate contained high-intensity Mn (1.98 mg l⁻¹), and high concentration of Ni (4.94 mg l⁻¹). Also, Cd had a high concentration (2.71 mg l⁻¹). In addition, the concentration of pollutants exceeded the permissible limits issued by the 1974 Environmental Quality Act of Malaysia (2009). In the present study, the heavy metals removal from raw leachate of the Sungai Petani landfill and domestic wastewater was performed through PZE and PAC augmented SBR process to decrease the environmental risks caused by the SG Petani landfill leachate. The 3D surface plots of pollutants removal "Fe, Mn, Ni, and Cd" in PAC-SBR and PZE-SBR are shown in the Figures 1 and 2.

3.1. Reactor performance

3.1.1. Iron removal

Iron is present in varying concentrations in all ecosystems that they are stable and persistent environmental contaminants since they cannot be degraded or destroyed.

In PAC-SBR, 58.57% was reached as the optimum removal of Fe at the aeration rate of 2.94 l min⁻¹, 10.93 h contact time, and 20.00% leachate-to-wastewater proportion. In PZE-SBR, 65.11% was achieved as the optimum removal of Fe at the aeration proportion of 3.63 l min⁻¹, 13.63 h reaction time, and 21.14% leachate-to-wastewater ratio.

3.1.2. Manganese removal

It is well known that leachates produced by water percolation through solid waste often contain high concentrations of dissolved Fe and Mn (Lebrun *et al.,* 2007; Siegel and Siegel, 2007).

In PAC-SBR, 52.60% was attained as the optimum removal of Mn effectiveness of at the aeration rate of 4.21 I min⁻¹, 20.84 h reaction time, and 20.05% leachate-to-wastewater ratio. In PZE-SBR, 60.77% was attained as the optimum Mn removal effectiveness of at the aeration proportion of 2.57 I min⁻¹, 8.77 h reaction time, and 20.14% leachate to wastewater proportion.



Figure 1. The 3D surface plot of (a) Fe and (b) Mn, (c) Ni and (d) Cd removal in the PAC-SBR

3.1.3. Nickel removal

Leachate and wastewater may enclose a huge amount of heavy metals, such as nickel, which is a nonbiodegradable toxic heavy-metal ion present in wastewater (Al-Qodah, 2006). Several materials have been applied as adsorbents to remove Ni (II), including AC, ion-exchange resins, silica, rock materials, agricultural wastes, microbial and plant derived biomass, and chitin. However, developing a low-cost, easily available, and high-adsorption material for wastewater treatment remains necessary (Varma *et al.*, 2013). In PAC-SBR, the best possible Ni removal effectiveness of 54.69% was attained at the aeration proportion of 3.28 l min⁻¹, contact time of 13.77 h, and leachate-to-wastewater proportion of 20.00%. In PZE-SBR, the optimum Ni removal effectiveness of 63.19% was attained at the aeration proportion of 1.61 l min⁻¹, contact time of 13.40 h, and leachate-to-wastewater proportion of 21.13%.



Figure 2. The 3D surface plot of (a) Fe, (b) Mn, (c) Ni and (d) Cd removal in the PZE-SBR

3.1.4. Cadmium removal

Cadmium is a soft, malleable, white metal that is generally used in batteries, alloys, electroplating, solar cells, plastic stabilizers, and pigments. Cadmium is a highly toxic metal and exposure to it is known to cause cancer. Cadmium is also a hazard to the environment mainly because of fossil fuel combustion (Baker *et al.*, 2012).

In PAC-SBR, the best possible Cd removal effectiveness of 56.33% was attained at an aeration rate of 3.36 l min⁻¹, reaction time of 14.50 h, and leachate-to-wastewater proportion of 20.00 %. In PZE-SBR, 60.41% was achieved as the optimum removal of Cd at an aeration proportion of 2.76 l min⁻¹, reaction time of 15.39 h, and leachate-to-wastewater proportion of 20.03%.

3.2. Statistical analysis and Experimental condition optimization

A fundamental composite plan and a reaction surface method were employed to display the nature of the reaction surface in the empirical plan and clarify the best possible setting of the independent variables. CCD was launched via Design-Expert 6.0.7. Aeration rate (I min⁻¹), reaction time (h), and leachate–to-wastewater combining ratio (%; v/v) were the independent factors. Four dependent factors (Fe, Mn, Ni, and Cd) were evaluated as responses (Tables 3 and 4).

Tables 5 illustrates the reaction values for each factor. These boundaries were selected fairly near to the attained utmost removal and viability principles of treatment sites. The improvement of the empirical settings was recognized by regarding whether the rates of Fe, Mn, Cd, and Ni removal were higher than the randomly selected restraint values. The best possible settings were envisaged by the Design-Expert software. Further, Table 5 displays the reduced quadratic models in terms of actual factors. All models were significant at the 5% confidence level because probability values were less than 0.05. The coefficient of determination (R²) offered the proportion of total variation in the response predicted by the model, indicating the ratio of sum of squares due to regression to total sum of squares. R² values close to 1 were wanted, and a high R² coefficient guaranteed suitable modification of the quadratic model to the experimental data. In the present study, all obtained R2 were greater than 0.95, Table 5.

Adsorption is now identified as an effective and economic way for heavy-metal wastewater treatment. The adsorption procedure proposals flexibility in design and operation and will produce high-quality treated water many cases. Furthermore, given that adsorption is sometimes reversible, adsorbents can be regenerated by the suitable deception process. AC adsorbents are widely employed in removing of contaminants (Aghamohammadi *et al.,* 2007; Aziz *et al.,* 2011a; 2011b; 2011c; Aziz *et al.,* 2012; Mojiri *et al.,* 2014). A large number of researchers are investigating the usage of AC to remove heavy metals (Fu and Wang, 2011; Aziz *et al.,* 2011c; Mojiri *et al.,* 2014).

Ion-exchange processes have been generally applied to remove heavy metals from wastewater because of their benefits, such as high treatment capacity, high removal effectiveness, and fast kinetics. Many researches have confirmed that zeolites display a good ion-exchange abilities for removing heavy-metal under different experimental environments (Motsi *et al.*, 2009; Ostroski *et al.*, 2009; Taffarel *et al.*, 2009).

In current study, the PZE-SBR performance was more than PAC-SBR performance because zeolite could do ion exchange and also the metals can fix in the pores of it. But activated carbon cannot do ion exchange and just heavy metals can fix in the pores. In addition, based on some business websites, the zeolite price is less than activated carbon price so using zeolite is more affordable than activated carbon (http://www.alibaba.com/showroom/zeolite-price.html, http://www.alibaba.com/showroom/activated-carbon-price.html).

| SBR Type | Responses | Final equation in terms of actual factors | Prob. | R ² |
|----------|-----------|---|---------|----------------|
| | Fe | $69.544 - 0.786C - 0.371A^2 + 0.004C^2$ | <0.0001 | 0.9652 |
| | Mn | 58.895- 0.661C – 0.280A ² | <0.0001 | 0.9647 |
| PAC-3DN | Ni | 58.380 – 0.652C | <0.0001 | 0.9508 |
| | Cd | 61.699-0.811C-0.361A ² | <0.0001 | 0.9594 |
| PZE-SBR | Fe | 67.032 + 1.823A - 0.312C - 0.341A ² | <0.0001 | 0.9869 |
| | Mn | 64.516 - 0.622C - 0.390A ² | <0.0001 | 0.9755 |
| | Ni | 63.568 – 0.296C –0.028B ² | <0.0001 | 0.9830 |
| | Cd | 63.162 + 1.320A + 0.510B - 0.413C - 0.229A ² - 0.018B ² | <0.0001 | 0.9965 |

Table 5. ANOVA results for response parameters

*Prob.: Probability of error; and R²: Coefficient of determination.

**In final equations, where A is Aeration rate (I min⁻¹), B is contact time (h), and C is leachate to wastewater mixing ration (%; v/v)

4. Conclusions

Elimination of heavy metals from Sungai Petani landfill leachate and domestic wastewater was performed via powdered zeolite and powdered activated carbon supplemented SBR procedure. A number of pollutants in Sungai Petani landfill leachate went beyond the allowable discharge restrictions comprising Fe, Mn, Ni and Cd. In the PAC-SBR treatment case, the obtained optimum removal levels of Fe, Mn, Ni, and Cd were 58.47%, 54.32%, 54.68 and 56.30%, respectively. On the other hand, using the PZE-SBR treatment led to 65.65%, 61.56, 63.41%, and 60.44% removals, respectively. Thus, it can be concluded that, for heavy metals removal from landfill leachate and domestic wastewater, employing the PZE-SBR method was more effective than the application of the traditional PAC-SBR.

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