

Removal of Pb(II) from wastewater by biosorption using powdered waste sludge

Hana Jang¹, Nohback Park² and Hyokwan Bae^{*3}

¹Graduate School of Environmental Engineering, Pusan National University, 63 Busandeahak-ro, Geumjeong-gu, Busan 46241, Republic of Korea

²Aquaculture Management Division, National Institute of Fisheries Science, 216 Giganghaean-ro, Gijang-eup, Gijang-gun, Busan, 46083, Republic of Korea

³Department of Civil and Environmental Engineering, Pusan National University, 63 Busandeahak-ro, Geumjeong-gu, Busan 46241, Republic of Korea

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Abstract. Lead is a highly toxic heavy metal that causes serious health problems. Nonetheless, it is increasingly being used for industrial applications and is often discharged into the environment without adequate purification. In this study, Pb(II) was removed by powdered waste sludge (PWS) based on the biosorption mechanism. Different PWSs were collected from a submerged moving media intermittent aeration reactor (SMMIAR) and modified Ludzack-Ettinger (MLE) processes. The contents of extracellular polymeric substances were similar, but the surface area of MLE-PWS (2.07 m²/g) was higher than that of SMMIAR-PWS (0.82 m²/g); this is expected to be the main parameter determining Pb(II) biosorption capacity. The Bacillaceae family was dominant in both PWSs and may serve as the major responsible bacterial group for Pb(II) biosorption. Pb(II) biosorption using PWS was evaluated for reaction time, salinity effect, and isotherm equilibrium. For all experiments, MLE-PWS showed higher removal efficiency. At a fixed initial Pb(II) concentration of 20 mg/L and a reaction time of 180 minutes, the biosorption capacities (q_e) for SMMIAR- and MLE-PWSs were 2.86 and 3.07 mg/g, respectively. Pb(II) biosorption using PWS was rapid; over 80% of the maximum biosorption capacity was achieved within 10 minutes. Interestingly, MLE-PWS showed enhanced Pb(II) biosorption with salinity values of up to 30 g NaCl/L. Linear regression of the Freundlich isotherm revealed high regression coefficients ($R^2 > 0.968$). The fundamental Pb(II) biosorption capacity, represented by the K_F value, was consistently higher for MLE-PWS than SMMIAR-PWS.

Keywords: lead; biosorption; activated sludge; Freundlich isotherm; bacterial community structure

1. Introduction

Lead is one of the most useful heavy metals due to its highly malleable and ductile properties. It is increasingly used in the production of lead-acid batteries, bullet, weights, solder, pewter, and fusible alloys (Cheng and Hu 2010). In some cases, industries discharge wastewater containing lead ions, Pb(II), into the environment without adequate purification after uses in the petrochemical, painting and coating, newsprint, smelting, metal electroplating, mining, plumbing, and battery-related processes (Zhan and Zhao 2003). Also, high Pb(II) concentration has been observed in acidic mine drainage (Cui *et al.* 2012). Numerous cases of lead poisoning have been reported (Wani *et al.* 2015), resulting in renal, cardiovascular, reproductive, and central nervous system dysfunction. Especially, lead is particularly hazardous to children (Bellinger 2011).

Pb(II) is conventionally removed from wastewater by chemical precipitation, ion exchange, evaporative recovery, or reverse osmosis. Adsorption using synthetic materials has also been utilized for specific heavy metals (Khan *et al.*

2013). However, the application of synthetic materials is restricted due to high costs and the inadequate disposal of used adsorbents (Dubey *et al.* 2009). Thus, the adsorption capacities of more cost-effective materials such as fly ash, agricultural wastes, clay materials, and seafood processing wastes were recently investigated (Rafatullah *et al.* 2010). Cheap biomass is an abundant source of low-cost adsorption materials and has the potential to be utilized on a large scale (Malik *et al.* 2017).

The biosorption is based on a diverse range of mechanisms including adsorption and absorption (Fomina and Gadd 2014). In general, biosorption is categorized as a subdivision of adsorption, where the sorbent is a biological matrix (Michalak *et al.* 2013). Biosorption is carried out by various mechanisms of ion exchange, chelating, and diffusion through cell walls and membranes (Gavrilescu 2004). Heavy metals are adsorbed onto functional groups such as carboxyls, amino, phosphates, sulfates and hydroxyls on polysaccharides, proteins, and lipids of the microbial surface (Liu *et al.* 2018). In addition to the passive formation of metal-organic complexes in biosorption, heavy metals can also be removed through various microbial processes of energy-requiring active uptake via bioaccumulation (Gavrilescu 2004). In general, biosorption is effective when removing heavy metals present at a low concentration (100 mg/L or less). For

*Corresponding author, Professor
E-mail: hyokwan.bae@pusan.ac.kr

example, lead biosorption was saturated at the equilibrium concentration of ~50 mg/L when using chaff (Han *et al.* 2005). Lead adsorption was most effective at an acidity level of pH 5, whereas the optimal pH for nickel and zinc by mycelial by-products was 7 (Fourest and Roux 1992). For waste sludge, acidic conditions of pH 4 or 5 were optimum to remove lead, copper, cadmium, nickel, and zinc (Hammaini *et al.* 2007). These studies show that an optimum pH is important to remove the lead ion from the acidic wastewaters, as commonly found in mining effluents and waste electroplating solution (He *et al.* 2015).

Activated sludge is an excellent source of biosorbents. In conventional biological wastewater treatment, biodegradable organic and inorganic substances are consumed by the suspended microbial culture. Activated sludge settles from suspension in a sedimentation tank, but excess activated sludge is wasted. This is a serious problem because sludge treatment and disposal processes constitute more than 40% of the wastewater treatment costs (Ruiz-Hernando *et al.* 2010). Whereas primary sludge is mostly biodegradable, waste sludge is mainly composed of microbial cells, which have an excellent capacity for heavy metal biosorption due to their negative surface charge and membrane compositions (Trzcinski 2018, Araujo *et al.* 1998, Kargi and Cikla 2006). Thus, waste sludge has been utilized as an economically viable adsorbent, and numerous studies have reported the removal of heavy metals using waste sludge (Hammaini *et al.* 2007).

There are various studies on the removal of Pb(II) using powdered waste sludge (PWS), but none have compared the PWS from different biological wastewater treatment processes. Control factors such as hydraulic retention time, sludge retention time, and the dissolved oxygen concentration differentiate the bacterial community structure of differentially sourced waste sludge samples, all of which could influence Pb(II) biosorption. In this study, it was hypothesized that Pb(II) biosorption capacity depends on the bacterial community structure and the material properties of PWSs. Following the suggested hypothesis, this study aimed at assessing the Pb(II) biosorption capacity according to the different PWS sources with a consideration of operational parameters such as biosorption time, salinity, and equilibrium Pb(II) concentration. Total organic carbon (TOC), structural properties, and the bacterial community structure were analyzed as potential reasons for differences in the biosorption capacities of the PWS samples.

2. Materials and methods

2.1 Origin of biomass

The sludge was obtained from a submerged moving media intermittent aeration reactor (SMMIAR) and the modified Ludzack-Ettinger (MLE) process. The SMMIAR performs organic matter removal and phosphorus release in the anaerobic tank, and it introduces BLOWHEEL® as an immobilization bed for the biofilm into the main aerobic tank. Concentrated waste sludge was taken from the wasting line of the SMMIAR in the Hwajeon sewage treatment plant, Republic of Korea (HRT of 7.4 hr, reactor

Table 1 Wastewater characteristics (mg/L)

		BOD	COD	SS	T-N	T-P
SMMIA	In	111.7	125.5	113.3	34.3	13.2
	R Out	4.0	14.1	3.1	9.8	1.2
MLE	In	336.0	222.2	201.8	47.1	5.4
	out	0.9	9.6	1.8	6.0	0.04

volume of 6,833 m³, flow rate of 57.2 m³/d, pH 7.0, and DO of 4 mg/L). MLE is an advanced method of standard activated sludge process; it improves the denitrification reaction by circulating the mixed liquor suspended solids with effluent from the aerobic tank into the anoxic tank. The organic matter is continuously supplied to the anoxic tank as an electron donor to reduce the nitric acid produced from the aerobic tank. The waste sludge of the MLE process was obtained from the Yangsan wastewater treatment plant, Republic of Korea (HRT of 23.6 hr, reactor volume of 8,568 m³, flow rate of 7,214 m³/d, SRT 21.6 hr, pH 6.9, MLSS of 3,044 mg/L, and DO of 2.0~2.5 mg/L). The characteristics of wastewater are shown in Table 1.

2.2 Powdered waste sludge

The obtained waste sludge was settled for 1 hour by gravity and the supernatant was removed. The rapid mixing was briefly applied to the sludge with a mixer (HT-120DX, Daihan Scientific Inc. Republic of Korea) at 500 rpm for 5 min. Then, the waste sludge was sieved with a mesh of 0.45 mm to remove the colloidal particles. To remove the water content, the sludge was dried at 50°C for 7 days using a drying oven (C-DHD, Changsin Science, Republic of Korea), and then ground to a powder using a homogenizer (SFM-555SP, Shinil Electronics, Republic of Korea). The powder was sieved for particles less than 500 µm. The PWS was stored in a desiccator until use. The storage of the dried PWSs in the desiccator showed the insignificant additional dehydration.

2.3 Biosorption

Pb(NO₃)₂ (99.0%, Duksan, Republic of Korea) and HNO₃ (60%, Junsei, Japan) were used to prepare the standard solution of Pb(II). NaCl (99.0%, Daejung, Republic of Korea) was used to control the salinity level (0–40 g NaCl/L). Batch experiments of biosorption were carried out in flasks with a working volume of 50 mL. For each experiment, 0.5 g of PWS was immersed in distilled water for 60 minutes to allow swelling before the biosorption reaction. Then, various initial Pb(II) concentrations (25–80 mg/L) were created by using the appropriate dilution of the Pb(II) standard solution. To apply various adsorption time, the mixture of Pb(II) and PWS was stirred for 10 to 180 minutes using a magnetic bar. The reaction time was intentionally extended to 180 min to identify the maximum Pb(II) biosorption capacity (Zhan *et al.* 2003). The effluent samples were filtered with a 0.45-µm syringe filter (SC25P045S, Hyundai, Republic of Korea) as

soon as possible after the sample was taken from the flasks to prevent further reaction. All the experiments were performed at a pH of approximately 2 to simulate the condition of acidic mine drainage by using HNO₃ (Feng *et al.* 2004).

2.4 Analysis

2.4.1 Pb(II)

The samples were pretreated with nitric acid-perchloric acid-hydrofluoric acid digestion (APHA, AWWA, WEF, 2017). If necessary, the samples were filtered with filter paper (5A, Advantec, Republic of Korea). Inductively coupled plasma atomic emission spectroscopy (ICP-AES) (ICPE-9820, Shimadzu, Japan) was used to quantify Pb(II). The samples were injected into argon plasma formed by a high-frequency induction coil, and the emission intensity was measured at 220.353 nm for Pb(II). A calibration curve was prepared in the range of 0–20 mg/L of Pb(II), and the sample was diluted within the range of the calibration curve for the analysis. All the ICP-AES analyses were performed in triplicate.

2.4.2 Extracellular polymeric substances

The concentration of extracellular polymeric substances (EPS) was measured using a cation exchange resin (CER) (Dowex Marathon C, Na⁺-form, Sigma-Aldrich, PA, USA) extraction method (Jeong *et al.* 2017). The exchange resin (70 g of CER/g VSS) was added to 50 mL of mixed liquor sample and mixed at 600 rpm for 2 h at 4°C. The mixture (50 mL) was then centrifuged for 15 min at 12,000 g to remove suspended solids, and the supernatant was filtered through a 4.5- μ m syringe filter (SC25P045S, Hyundai, Republic of Korea). For the analysis of TOC, a suitable amount of the sample was put into a high-temperature combustor filled with an oxidizing catalyst, and the carbon dioxide produced from the organic carbon was quantitatively analyzed. A calibration curve was prepared in the range of 0–40 mg/L of the standard sample of C₆H₄COOH (99.5–100.2%, Daejung, Republic of Korea). All measurements were performed in triplicate, and the average of the three runs was used.

2.4.3 BET analysis

Nitrogen gas was adsorbed on the surface of the PWS sample, and the adsorbed amount of nitrogen per partial pressure was measured using a Brunauer, Emmett and Teller (BET) machine (ASAP2020, Micromeritics Instruments, USA). The surface area, pore size, and porosity were calculated for each PWS.

2.4.4 Bacterial community structure

To identify the bacterial community structure, DNA was extracted with a FastDNA SPIN Kit for Soil (MP Biomedicals, USA). The extracted genomic DNA was sent to Macrogen Inc. (Republic of Korea) to generate paired-end reads of the 16S rRNA gene on the Illumina MiSeq platform (Illumina, USA). The polymerase chain reaction was carried out with primers of 341F and 805R. After sequencing, low-quality reads such as potential chimeric sequences or ambiguous bases were screened. The number

of valid reads is 266,302 and 265,522 for SMMIAR- and MLE-PWSs, respectively. The refined sequences were clustered into operational taxonomic units (OTUs) based on < 3% divergence using CD-HIT-OTU. The bacterial 16S rRNA gene sequences were matched with the National Center for Biotechnology Information (NCBI) database.

2.5 Freundlich isotherm

The surface of the sorbent is assumed to have a non-uniform distribution of sorption heat. This equation was originally proposed on an empirical basis for the adsorption phenomena occurring on gas–solid interfaces, but it can be theoretically applied to an adsorption model for biosorption (Çolaka *et al.* 2009).

The Pb(II) adsorption capacity (q_e) for PWS was calculated based on the initial concentration (C_0) and the equilibrium concentration (C_e), with the added mass of the PWS (m) using the following equation:

$$q_e = \frac{(C_0 - C_e) \cdot V}{m}$$

The relationship between the amount of Pb(II) adsorbed and the concentration of Pb(II) at equilibrium is summarized by:

$$q_e = K_F C_e^{1/n} \quad (1)$$

The logarithmic equation can be transformed into a linear equation as:

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \quad (2)$$

where q_e is the adsorption capacity (mg/g), K_F is the Freundlich constant ($\text{mg}^{1-(1/n)} \text{L}^{1/n} \text{g}^{-1}$, mg: amount of adsorbed adsorbate, g: weight of adsorbent), $1/n$ is the adsorption intensity, and C_e is the equilibrium concentration in solution (mg/L).

3. Results and discussion

3.1 Properties of PWS

3.1.1 EPS concentration

It was well-known that the EPS has a critical role in metal biosorption (Li and Yu, 2014). It was expected that the EPS content is largely different between the two PWSs because the SMMIAR process utilizes the attached growth system. Actually, biofilms are composed of cells enclosed in a hydrated EPS matrix and EPS is aggregated with the cells (Sutherland, 2001). Thus, EPS concentration was measured as a candidate parameter for the Pb(II) biosorption. The average measured TOC concentrations of EPS did not significantly differ: 0.144 and 0.158 g/g for SMMIAR- and MLE-PWSs, respectively. The EPS contents of this study were two times higher than those of the anaerobic digestion sludge, ranging from 0.02–0.08 g/g (Jeong *et al.* 2017). As a result, the PWS from the aerobic wastewater treatment process can be an appropriate source for the Pb(II)

Table 2 Surface area and pore volume of SMMIAR- and MLE-PWSs

	Pore volume (cm ³ /g)	Pore diameter (Å)	Surface area (m ² /g)	Pb(II) per area (mg/m ²)*
SMMIAR-PWS	0.007	36.0	0.82	4.76
MLE-PWS	0.007	14.3	2.07	2.18

*The Pb(II) biosorption was calculated per area at the equilibrated status applying the maximum Pb(II) concentration of 80 mg/L.

biosorption rather than the anaerobic sludge due to the high EPS content. Liu *et al.* (2000) also showed that EPS extracted from an aerobic granular sludge largely exhibited superior Pb(II) removal than Cd(II) and Zn(II). However, the calculated TOC contents per PWS were significantly similar for the SMMIAR and MLE processes. As a result, the significant difference of Pb(II) biosorption capacity will not be caused by the EPS content in this study.

3.1.2 Structural properties

The BET analysis showed that the pore volume of the two PWSs is the same (0.007 cm³/g; Table 2). However, the surface area of the SMMIAR- and MLE-PWSs are 0.82 and 2.07 m²/g, respectively. The surface area of the MLE-PWS is much larger than that of the SMMIAR-PWS because the pore size of the MLE-PWS (14.3 Å) is smaller than that of the SMMIAR-PWS (36.0 Å). It was expected that the surface area of the PWS is the main operational factor for the biosorption efficiency, rather than the EPS concentration.

3.2 Bacterial community structure

The dominant bacteria with a relative abundance of more than 1.0% in SMMIAR- and MLE-PWSs are shown in Table 3. The putative active bacteria for Pb(II) biosorption were found in this study; both the SMMIAR- and MLE-PWSs were predominantly occupied by Firmicutes and Proteobacteria. In the SMMIAR-PWS, the Firmicutes phylum had high relative abundance, consisting of the genera *Bacillus*, *Massilibacterium*, and *Fervidicella* in the class Bacilli, with relative abundances of 19.4, 23.2, and 9.5%, respectively. The MLE-PWS bacterial community structure consisted of *Lysinibacillus* (5.4%) and *Massilibacterium* (25.2%) in Firmicutes and *Azovibrio* (19.6%), *Comamonas* (12.9%), *Tepidimonas* (6.2%), and *Thauera* (9.7%) in Proteobacteria.

The most abundant genus of the SMMIAR- and MLE-PWSs was *Massilibacterium* sp. (relative abundances were more than 20 %). Gram-negative facultative *Massilibacterium* sp. was newly found in 2016 (Alou *et al.* 2016). The high relative abundance *Massilibacterium* sp. could be attributed its heterotrophic functions of ethanol degradation and carbon source storage in the form of poly-β-hydroxybutyrate during wastewater treatment (Leng *et al.* 2019). The biosorption capacity of *Massilibacterium* sp. has never been reported, but biosorption by *Massilibacterium* sp. is feasible since the family *Bacillaceae*, which comprises the genera *Massilibacterium*, *Lysinibacillus*, *Bacillus*, and *Oceanobacillus*, has a high metal biosorption capacity due

to surface layer proteins (Mathew *et al.* 2015). Previous research has documented efficient metal biosorption capacity for the second most abundant genus in the SMMIAR-PWS, *Bacillus* sp. (Velásquez and Dussan 2009, Nourbakhsh *et al.* 2002). The metal biosorption capacity of the second most abundant genus in MLE-PWS, *Azovibrio* sp., has not been investigated. However, *Comamonas* sp., the third most abundant genus in MLE-PWS, showed efficient metal biosorption activity and tolerance to toxic heavy metals (Rudakiya and Pawar 2013, Black *et al.* 2014). Based on these results, the competitiveness of metal biosorption for the different bacterial species cannot be judged, but the bacterial taxonomic evidence of biosorption function for SMMIAR- and MLE-PWSs was found from the 16S rRNA gene information.

3.3 Pb(II) adsorption

3.3.1 Biosorption speed

The contact time between the pollutant and adsorbent is critically important for wastewater treatment, and the biosorption speed depends on the biosorption mechanism (Mall *et al.* 2006, Bellinger 2011). The uptake of heavy metals into microbial cells is rather slow, as this metabolic process is energy-dependent and is influenced by the toxicity to basic microbial metabolisms (Raja *et al.* 2006). Therefore, chemically active dead cells and metabolically inactive cells would be appropriate to adsorb large amounts of toxic metal compounds (Volesky 1994). Passive biosorption seems to occur rapidly based on an ion-exchange process using negatively charged binding sites on the cell wall (Pardo *et al.* 2003).

The Pb(II) biosorption capacity of the SMMIAR- and MLE-PWSs per increasing reaction time is shown in Fig. 1. The MLE-PWS had higher biosorption capacity than the SMMIAR-PWS, by 5.5 ± 2.0% on average. The reaction time was tested from 0 to 180 minutes at a fixed initial Pb(II) concentration of 20 mg/L. At the reaction time of 180 minutes, the maximum Pb(II) adsorption capacities for the SMMIAR- and MLE-PWSs were 2.86 and 3.07 mg/g, respectively. Pb(II) biosorption was nearly complete within 60 minutes, and further adsorption exhibited no significant increase in Pb(II) biosorption capacity. After 10 minutes reaction time, the SMMIAR- and MLE-PWSs achieved Pb(II) biosorption capacities of 2.46 and 2.54 mg/g, respectively. Therefore, the Pb(II) adsorption of the SMMIAR- and MLE-PWSs was almost saturated at 86 and 83%, respectively. Thus, PWS showed rapid biosorption within the first 10 minutes because PWS relies on a metabolically inactive passive adsorption mechanism.

3.3.2 Salinity effect

Previous work has shown that salinity negatively influenced the biosorption capacities of Cu(II) and Cd(II) (Li *et al.* 2017), possibly due to high ionic strength that inhibited the ion exchange mechanisms (Aksu and Balibek 2010). In this study, the effect of salinity was tested in the range of 1-40 g NaCl/L for 60 minutes. Similar to Fig. 1, the biosorption capacity of MLE-PWS was higher than SMMIAR-PWS by 9.3 ± 11.1%. The large standard deviation weakens the significance of the effect of salinity on the two PWSs. The significant difference in the

Table 3 Bacterial community structure of PWS

Phylum	Class	Genus	SMMIAR	MLE
Actinobacteria	Actinobacteria	<i>Nonomuraea</i>	1.2 %	< 0.1 %
		<i>Rhodococcus</i>	2.8 %	< 0.1 %
		<i>Streptomyces</i>	1.0 %	< 0.1 %
		Sum	5.1 %	-
Firmicutes	Bacilli	<i>Aneurinibacillus</i>	2.5 %	0.3 %
		<i>Bacillus</i>	19.4 %*	1.7 %
		<i>Brevibacillus</i>	2.6 %	0.1 %
		<i>Lysinibacillus</i>	3.6 %	5.4 %
		<i>Massilibacterium</i>	23.2 %	25.2 %
		<i>Oceanobacillus</i>	2.9 %	0.1 %
		<i>Ureibacillus</i>	< 0.1 %	2.3 %
		<i>Caloramator</i>	4.3 %	1.3 %
		<i>Clostridium</i>	1.8 %	< 0.1 %
		<i>Fervidicella</i>	9.5 %	0.8 %
		<i>Lutispora</i>	1.6 %	1.5 %
		<i>Romboutsia</i>	1.2 %	0.1 %
		<i>Tissierella</i>	1.9 %	< 0.1 %
		Sum	74.5 %	38.8 %
		Proteobacteria	Alphaproteobacteria	<i>Chelatococcus</i>
<i>Microvirga</i>	1.8 %			< 0.1 %
<i>Azovibrio</i>	< 0.1 %			19.6 %
<i>Castellaniella</i>	2.7 %			< 0.1 %
Betaproteobacteria	<i>Comamonas</i>		0.8 %	12.9 %
	<i>Tepidimonas</i>		< 0.1 %	6.2 %
	<i>Thauera</i>		2.2 %	9.7 %
Gammaproteobacteria	<i>Pseudomonas</i>		0.6 %	1.8 %
	<i>Pseudoxanthomonas</i>		1.2 %	0.8 %
	Sum		9.3 %	52.4 %

*The relative abundances of more than 5% are highlighted.

adsorption capacity is valid only for 10, 20 and 30 g/L of NaCl addition. The biosorption capacity of Pb (II) per increasing concentrations of NaCl, at an initial Pb(II) concentration of 20 mg/L, is shown in Fig. 2. The biosorption capacity of the SMMIAR-PWS was increased by 13% when 1 g NaCl/L was added. Then, the SMMIAR-PWS biosorption capacity did not significantly change between 1 and 40 g NaCl/L. Interestingly, the biosorption capacity for the MLE-PWS increased continuously up to 30 g-NaCl/L. Finally, in comparison to 0 g NaCl/L, the Pb(II) biosorption capacity increased from 2.57 to 3.64 mg/g at 30 g NaCl/L. These results imply that during the Pb(II) biosorption, the PWS does not compete with Na⁺ for the negatively charged surfaces of SMMIAR- and MLE-PWSs. However, the mechanism underlying the increase in Pb(II) biosorption capacity with higher salinity is still unclear. The MLE-PWS would be applied to Pb(II) wastewaters with high salinity, such as those from textile-manufacturing or dye-producing industries (Maurya *et al.* 2006).

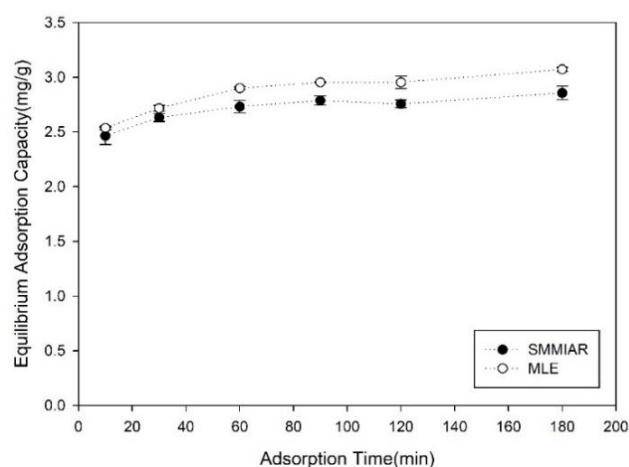


Fig. 1 Equilibrium biosorption capacity of Pb(II) per increasing reaction time

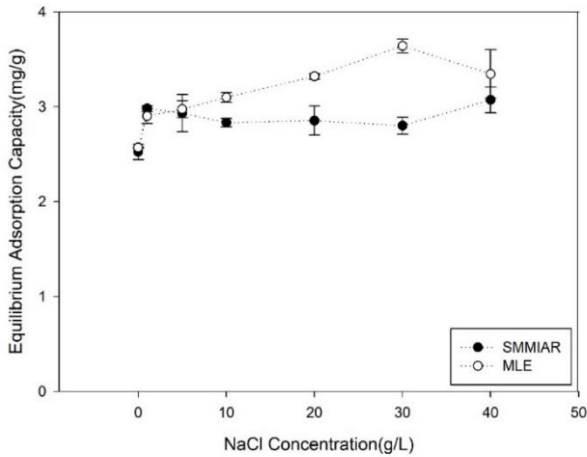


Fig. 2 Equilibrium biosorption capacity of Pb(II) per increasing NaCl concentrations

3.3.3 Freundlich isotherm

For 60 minutes reaction time, the initial Pb(II) concentrations (C_0) of 25–80 mg/L led to equilibrium concentration (C_e) in the range of 8–40 mg/L (Fig. 3). The biosorption capacity of the MLE-PWS was higher than that of the SMMIAR sludge by $47.5 \pm 16.2\%$, on average. Thus, it seems that the large surface area of the MLE-PWS affects Pb(II) biosorption (Table 2).

In this study, the affinity is defined as the amount of adsorbed Pb(II) per unit area of the PWS. The affinity seems to be affected by the initial Pb(II) concentration and the dose of biosorbent. Thus, the affinity values are not comparable to the other values in the literatures. However, the affinity is still usable for the evaluation of the characteristics of biosorbents. In previous study, the Pb(II) affinity of an oak bark char was 0.5157 mg/m^2 which is much larger than 0.031 mg/m^2 for commercial activated carbon (Mohan *et al.* 2007). For this study, at the equilibrium concentration (C_e) of 35 ~ 40 mg/L, the biosorption capacities (q_e , mg/g) divided by the surface area (m^2/g) yields higher Pb(II) affinity for SMMIAR-PWS (73.0 mg/m^2) than for MLE-PWS (43.5 mg/m^2). The Pb(II) affinity of MLE-PWS was $45.3 \pm 6.9 \%$ lower than that of SMMIAR-PWS for overall C_0 of 25–80 mg/L. These results imply that the Pb(II) affinity contributes lesser to the Pb(II) biosorption than the surface area of the PWS.

The results of q_e in relation to C_e were fitted with the Freundlich isotherm and the results of the linear regression following Eq. (2) are shown in Fig. 4 and Table 4. The quality of the regression was excellent, with high R^2 values more than 0.968 for both SMMIAR- and MLE-PWSs. The SMMIAR-PWS exhibited a K_F value of 0.14 and an n value of 0.95. The MLE-PWS, on the other hand, had a relatively large K_F constant (0.85). The K_F constant determines the fundamental adsorption capacity when an adsorbate presents in extremely low concentration. Thus, the adsorption capacity for low Pb(II) concentrations is higher for the MLE-PWS. However, the $1/n$ constant which determines the increase of adsorbed Pb(II) according to C_e . The $1/n$ for the MLE-PWS was smaller than that of the SMMIAR-PWS. Therefore, the Pb(II) adsorption for MLE-PWS shows a gentle slope with increasing C_e . Based on the

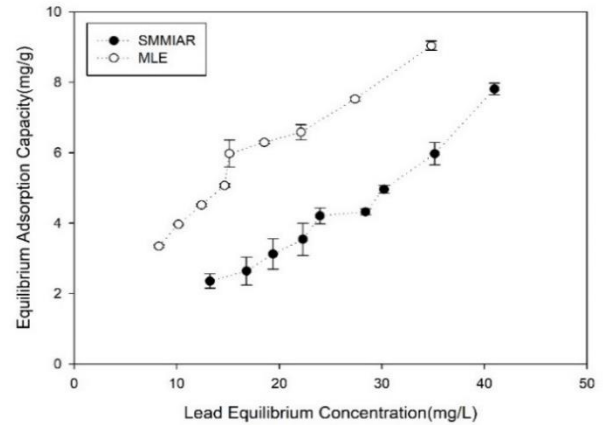


Fig. 3 Biosorption capacity of Pb(II) per increasing equilibrium concentrations

Table 4 Parameters of Freundlich isotherm models for the biosorption of Pb(II)

Adsorbent	K_F ($\text{mg}^{1-(1/n)}\text{L}^{1/n}\text{g}^{-1}$)	R^2	n	Source
Untreated				
aerobically digested sludge	3.86	0.983	1.65	Soltani <i>et al.</i> 2010
H ₂ O ₂ treated aerobically digested sludge	8.48	0.990	1.90	
Activated sludge	0.73	0.995	1.35	Sulaymon <i>et al.</i> 2013
Chitin nanofiber	15.35	0.999	2.49	Siahkamari <i>et al.</i> 2017
Chitosan nanoparticle	24.06	0.732	2.87	
SMMIAR-PWS	0.14	0.968	0.95	This study
MLE-PWS	0.85	0.970	1.49	

extension of the Freundlich isotherm to the high C_e , the Pb(II) adsorption of SMMIAR-PWS is more efficient when C_e exceeds 110.1 mg/L (Fig. 4).

The K_F values of this study are much lower than those of the other biosorbents. Note that the K_F constant is the fundamental adsorption capacity for extremely low concentration of adsorbate. This implies biosorbents such as chitin nanofiber and chitosan nanoparticle would be more feasible for low strength Pb(II) due to the large K_F values (Table 4). The low K_F values of PWS can be enhanced by modifying the surface of the PWS. For example, acid and base treatment of distillery sludge using NaOH, HCHO, and sodium dodecyl sulfate resulted in higher K_F for Pb(II), but autoclave and treatments with HCl did not change the value of K_F in a previous study (Nadeem *et al.* 2008). Besides, the n constant reflects the intensity of adsorption of the Pb(II) onto the adsorbent surface. A larger value of n (smaller value of $1/n$) implies a stronger interaction between the adsorbent and the adsorbate (Anah and Astrini 2018). Considering Eq. (2), the high intensity of adsorption result in a gentle slope, i.e., small $1/n$, which is insensitive to C_e . For the MLE-PWS, Pb(II) biosorption is favorable because n of 1.49 is larger than 1 (Saruchi and Kummar 2019). However, the n need to be improved in comparison to the untreated aerobically digested sludge, H₂O₂ treated aerobic digested sludge chitin nanofiber and chitosan nanoparticle in Table 4.

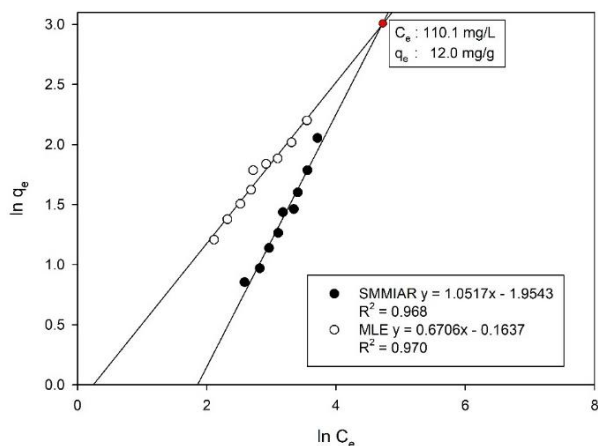


Fig. 4 Freundlich isotherm plots for Pb(II) biosorption

4. Conclusions

The higher surface area of the MLE-PWS (2.07 m²/g), compared to that of the SMMIAR-PWS (0.82 m²/g), was expected to be the main parameter determining Pb(II) biosorption capacity. However, the TOC concentration as EPS content of the SMMIAR- and MLE-PWSs were similar. The major bacterial groups responsible for Pb(II) biosorption were the Firmicutes and Proteobacteria phyla. The biosorption of Pb(II) was tested using PWSs from wastewater treatment processes of SMMIAR and MLE. Pb(II) biosorption was achieved with biosorption capacities (q_e) of 2.46 and 2.54 mg/g for SMMIAR- and MLE-PWSs, respectively, within 10 minutes. The q_e values for the SMMIAR- and MLE-PWSs were saturated with 2.86 and 3.07 mg/g, respectively, at the reaction time of 180 minutes. MLE-PWS showed positive effects of salinity on Pb(II) biosorption, with 3.64 mg/g at 30 g NaCl/L. For the initial Pb(II) concentrations of 25–80 mg/L, the biosorption capacity of the MLE-PWS was higher than SMMIAR sludge by $47.5 \pm 16.2\%$, on average. The biosorption results were fitted to the Freundlich isotherm, with a high quality of regression. Compared to the other biosorbents (e.g., chemically modified biosorbents,) the K_F and n values of the PWSs needs to be enhanced for a practical application to Pb(II) wastewater.

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