Desalination and Water Treatment
www.deswater.com

doi:10.5004/dwt.2017.21076

83 (2017) 253–260
July

Removal of LPS endotoxin from reclaimed wastewater through adsorption using soil

Guizani Mokhtar[a,*], Kato Hideyaki[b], Funamizu Naoyuki[a]

[a]*Faculty of Engineering, Hokkaido University, Kita 13-jo, Nishi 8-chome, Kita-ku, Sapporo, 060-8628, Japan, Tel. +81-11-706-6273, email: g_mokh@yahoo.fr, mguizani@eng.hokudai.ac.jp (G. Mokhtar)*
[b]*Graduate School of Engineering, Hokkaido University, Kita 13-jo, Nishi 8-chome, Kita-ku, Sapporo, 060-8628, Japan*

Received 28 December 2015; Accepted 26 December 2016

ABSTRACT

The removal of LPS endotoxin from reclaimed wastewater using four different types of soils was studied at ambient temperature. An efficient removal of LPS endotoxin by adsorption to soils was possible and the best performance was achieved by silt and fine sand. At a dose of 5.8 g/L, more than 90% of the adsorption of LPS endotoxin occurred in less than 3 h of contact time, and further contact time did not improve the adsorption. The removal efficiency depends on the dose of adsorbents. Moreover, LPS endotoxin adsorption is found to depend heavily on the initial LPS endotoxin concentration. A comparison between fresh soils and one-year-old soils (used as wastewater filtration media) showed better performance for fresh soils. In addition, adsorption experiments showed that the adsorption data fit with both Freundlich and Langmuir isotherms. Moreover, the LPS endotoxin concentration to fine sand is highly favourable, i.e., its fixation capacity grows rapidly with concentration in equilibrium in the liquid phase. This explains why, in an earlier study, LPS endotoxin removal using soil columns showed good efficiency in the early stage and then degraded. It can be concluded that soil can be an affordable alternative for LPS endotoxin removal form reclaimed wastewater if properly maintained.

Keywords: LPS endotoxin; Adsorption; Isotherm; Potable reuse

---

1. Introduction

Water demand is currently one of the major challenges facing the world. Colossal efforts are being implemented around the globe to ensure access to potable water and sanitation. With the ever-increasing stresses on water resources, wastewater recycling for potable purposes is becoming inevitable [1]. This is supported by the fact that potable reuse appears to be more economical and environmentally friendly than desalination. In recent decades, potable reuse has become increasingly common. Indeed, several wastewater treatment plants across the globe treat their wastewater to the potable level. For example, the Goreangab plant in Windhoek, Namibia, blends the reclaimed wastewater with dam water to provide water to consumers; this plant represents the only case for direct potable reuse to date [2]. Several other potable reuse plants exemplified by the three luggage points in Australia and the potable reuse plant operated by the public utility board (PUB) of Singapore have been commissioned in the last few years [3]. Even in the Gulf countries, where potable water is mainly supplied from desalination plants, there is a paradigm shift occurring towards potable reuse. In 2005, the most advanced potable reuse plants in the water reuse sector emerged in Sulaibiya, Kuwait [4]. These successful projects prove that high-grade reclaimed water can be produced from sewage. Note that the term "used water" has therefore emerged as a substitution for the word "wastewater", as a new source of water can be produce from it. PUB has developed the NEWater brand, which is a high-grade reclaimed water produced from used water. Similarly, in Australia, 100% puri-

---

*Corresponding author.

Presented at the 5th Maghreb Conference on Desalination and Water Treatment — CMTDE 2015, December 21–24, 2015, Hammamet, Tunisia

fied recycled water is bottled [5]. Although their reclaimed wastewater is treated to a potable level, the product is only used for industrial activity requiring high-quality water [4]. To overcome the lack of public acceptance of potable reuse for consumption, several planned indirect potable reuse projects are in operation, as exemplified by water factory 21 in the USA and the Koksijde groundwater replenishment plant in Belgium, among others. Numerous planned potable reuse plants will be constructed in the future.

Even though potable reuse has been successfully implemented in recent decades without drawbacks and disease outbreaks, there are several micro-pollutants in water that are still poorly understood. Among these emerging micro-contaminants is the lipo-polysaccharide endotoxin known as LPS endotoxin (LPS endotoxin). This chemical is an essential component of the outer membrane of gram-negative bacteria and some cyanobacteria [6–8]. The presence of LPS endotoxin in potable water is of great concern due to the potential harmful effects it may induce. Indeed, two researches, exemplified by the studies of Narita et al. [9,10] and Eckenfelder [11] have revealed that the toxicity found in secondary treated wastewater is caused by the release of organic matter during treatment. Guizani et al. [12] reported that effluents of activated sludge operated plants and effluent from rapid sand filtration induced stress response to Chinese hamster ovary cells. In other works, Guizani et al. [13,14] reported a high LPS endotoxin concentration in the secondary effluent of wastewater treatment plants. Although there is a lack of data to quantify potential health risks associated with the presence of LPS endotoxin in water, it is well known that LPS endotoxin has adverse health effects in some circumstances [15–17]. Therefore, the removal of LPS endotoxin from reclaimed wastewater is crucial to ensure safe potable reuse [12]. Removal of LPS endotoxin from biological preparations has attracted the attention of many researchers [18]. However, few works are reported in the literature regarding the presence of LPS endotoxin in reclaimed wastewater. The removal techniques employed in biological preparations are not well suited for the potable water reuse sector as a result of their high cost and large difference between the endotoxin levels in biological preparations and in reclaimed wastewater. Therefore, the main question is how LPS endotoxin removal from reclaimed wastewater can be performed in an economical manner. One of the removal alternatives of concern is the soil aquifer treatment. Indeed, LPS endotoxins are composed of a hydrophilic polysaccharide moiety that is covalently linked to a hydrophobic lipid moiety (Lipid A). The hydrophobic character of Lipid A is believed to play a significant role in the adherence of LPS endotoxins to soil.

Guizani et al. [19] investigated the removal of Endotoxin from reclaimed wastewater using soil aquifer treatment (SAT). Four different columns were used, and each was packed with a specific soil. Column 1 contained large sand with a specific diameter ranging from 0.85 to 1.4 mm. Column 2 was packed with 0.45–0.85 mm sand (medium sand). Columns 3 and 4 were packed with fine sand (0.25–0.45) and silt (0.125–0.25 mm), respectively. The different columns showed different efficiencies. Unfortunately, the LPS endotoxin removal efficiencies of the four columns decreased a few weeks after their operation and further became instable. To understand the observed trends, one need to understand the mechanisms that control the fate of LPS endotoxin during its movement through the columns. Indeed, during SAT treatment, several mechanisms coexist and these include, but not limited to, filtration of endotoxin aggregates, endotoxin generation during decay of bacteria from biofilm, biodegradation, and adsorption and desorption. Adsorption is assumed to be of a major effect. Indeed, LPS endotoxin has amphiphilic character and is composed of a hydrophobic lipid A and a hydrophilic [20,21]. The hydrophobic Lipid A of LPS endotoxin favors its adsorption to soil. Uncharged hydrophobic membranes and hydrophobic adsorbents were frequently used to remove endotoxin from proteins and biological preparations [22,23]. Moreover, LPS endotoxin has a net negative charge. Therefore, LPS endotoxin adsorption can be achieved also by ionic interaction. However, desorption was also reported by Sagar et al. [24]. Hence in this paper, batch adsorption tests was conducted to elucidate the adsorption process and to understand the adsorption behavior of LPS endotoxin on the different soils used in SAT column experiment. The study will focus on the adsorption efficiency (LPS endotoxin removal percentage), the effect of soil dose, and the effect of contact time. The tests were performed of LPS endotoxin and to predict its behavior. The adsorption data will be correlated with a suitable isotherm. The findings would help us understand the results reported from SAT experiments.

2. Materials and methods

2.1. Water samples

Endotoxin-containing water samples were collected from the secondary effluent of an activated-sludge-operated wastewater treatment plant in Sapporo, Japan. The LPS endotoxin concentration in the samples was measured using a chromogenic endpoint test before and after the adsorption experiments. All samples were pre-filtered through a 0.45 μm filter prior to the LPS endotoxin measurements.

2.2. Preparation and characterization of adsorbents

The tests of endotoxin adsorption were performed using 4 different filter materials: silt, fine sand, medium sand and coarse sand. The properties of the studied soils are shown in Table 1.

All of the adsorbents were taken from the upper layer (first 50 cm) of pre-operated soil columns used to assess the LPS endotoxin removal from wastewater. Samples were

Table 1
Properties of studied soils

Soil ID	Soil type	Grain size (mm)	Particle density (g/cm^3)
Soil 1	Coarse sand	0.125–0.25	2.65
Soil 2	Medium sand	0.25–0.45	2.65
Soil 3	Fine sand	0.45–0.85	2.65
Soil 4	Silt	0.85–1.4	2.8

taken after 12 months of operation. Indeed, after one year of operation, the soil column efficiency decreased significantly, as reported in an earlier study [19]. This work is aimed to understand the endotoxin adsorption efficiency of different soils after one year of soil column operation. All soils were washed several times with deionized water to remove the organic matter and dirt found in the soil. The samples were then dried at 110°C. The dried and cleaned sand was then used for the adsorption test.

2.3. Measurements

An LAL reagent kit was used to measure LPS endotoxin concentrations in water samples. We used the chromogenic end point test for the measurements [25]. The pH of the solutions was measured using a pH meter with a glass electrode. The water samples were filtered through a 0.45 µm filter, and measurements were reported for the supernatant. An analytical balance model AHAUS PA series was used for weighing the soil for the batch adsorption tests [26].

2.4. Experimental procedure

A ZR4-6 jar tester was used to conduct all endotoxin adsorption tests at ambient temperature. Sand was mixed at rates of 1.8 g/L, 3.8 g/L, and 5.8 g/L with the corresponding water samples. Suitable amounts of soil sample were placed in different 1 L beakers containing 500 mL of wastewater solution of a known LPS endotoxin concentration. The one-litre solutions were stirred at 520 rpm for 48 h. The stirring allows the soil particles to come in contact with the lipo-polysaccharide, enabling the polysaccharide to be adsorbed. Samples were collected at 2,4,6,8,10,12,18, 24 and 48 h. Each sample was filtered through a 0.45 µm filter, and then the endotoxin concentration was measured. The experiments were performed at the original pH of the solution. All experiments were performed in triplicate at ambient temperature.

2.5. Adsorption isotherms

When adsorption equilibrium was reached, the amount of LPS endotoxin adsorbed per endotoxin equivalent unit is calculated as follows:

$$Q_e = \frac{(C_i - C_e)V}{m} \quad (1)$$

where C_i and C_e are the initial and equilibrium concentrations (EU/ml), respectively, m is the mass of the adsorbent soil (g) and V is the volume of the solution (ml). The LPS endotoxin removal percentage is calculated as follows:

$$R(\%) = 100 \times \frac{(C_i - C_e)}{C_i} \quad (2)$$

The residual LPS endotoxin concentration was determined from the filtered supernatant solution using a chromogenic end test point, and then the amount of LPS endotoxin adsorbed was calculated. The distribution of adsorbate (LPS endotoxin molecules) between the liquid phase and the solids (sorbents) can be approximated by several isotherm models, which connect the amount of adsorbate to the amount of adsorbent [27]. Langmuir and Freundlich isotherm models were fitted to the adsorption data, and then their constants were determined and evaluated. The conformity of the model with the experimental data was expressed by the correlation coefficient (R^2). In this section, we focused only on fine sand, as soil aquifer treatment columns showed better removal efficiency for fine sand and silt, but with less clogging potential in the case of fine sand [19].

3. Results and discussions

3.1. LPS endotoxin adsorption into soils

In this section we report the average LPS endotoxin concentration remaining in the solution after 48 h of batch adsorption tests conducted using the four different soils. The removal percentages are deducted. The average LPS endotoxin concentration in the water samples collected from the wastewater treatment plant and used for adsorption tests is 1337 ± 57 EU/ml, which is equivalent to 13.4 ng/L of standard endotoxin EC-5. As shown in Table 2, after 48 h of adsorption batch tests, the treated samples showed average concentrations of 1306.3 ± 28, 1309 ± 30, 1313 ± 11 and 1313.5 ± 12 for silt, fine sand, medium and coarse sand, respectively. It corresponds to removal percentages of 1.76%, 1.79%, 2.09% and 2.32%, respectively for coarse sand, medium sand, fine sand and silt respectively (Table 2). These low percentages should not hide the effectiveness of the system. Indeed, what matters most is the amount of endotoxin removed per gram of soil, and to increase removal percentage we need to adjust the amount of soil needed. For these batch adsorption tests, 5535EU/g (5.5 µg/g), 5283 EU/g (5.35µg/g), 4528 EU/g (4.5 µg/g) and 4528 EU/g (4.5 µg/g), respectively were removed using silt, fine sand, medium sand and coarse sand , respectively. It should be noticed that a similar adsorption study was conducted by Rezaee A. et al. [28] to study the adsorption of LPS endotoxin from an aqueous solution to bone char. Although they claim 98% removal, the adsorbed amount is as low as 627.2 EU/g. This suggests that soil achieves a good removal potential as compared to bone char. However, for an efficient removal of endotoxin from treated wastewater, one must consider increasing the dose of adsorbent. Effect of the dose of the adsorbent on endotoxin removal will be discussed in Section 3.3.

Table 2
Average LPS endotoxin concentration (EU/ml) and removal percentage in the samples

	Average value ± St. dev.	Removal %
Raw sample	1337 ± 57	–
Silt treated	1306.3 ± 28	2.32
Fine sand treated	1309 ± 30	2.09
Medium sand tread	1313 ± 11	1.79
Coarse sand treated	1313.5	1.76

We should remind here that soils used in this study for adsorption tests were taken from SAT columns after one year of operation. A comparison between the adsorption efficiency using virgin soils and soils previously used in SAT columns will be discussed in Section 3.5.

3.2. Effect of the soil type

From results presented in 3.1, it is clear that each soil perform differently from other soils. So, in this paragraph we will investigate closely the effect of soil type on LPS endotoxin removal. The LPS endotoxin removal percentages using four different soils at an influent concentration of 1337EU/ml are shown in Fig. 1. At a given soil amount used, the removal percentages were similar in shape but the quantities are different. Equilibrium was reached at different times depending on soil properties. Indeed, for silt and fine sand it took shorter time to reach the equilibrium, while slightly longer time was required for medium sand and coarse sand, respectively, to reach the equilibrium. At a dose of 5.8 g/L, the equilibrium was reached at nearly 3 h for silt and fine sand, while approximately 5 h were required to reach equilibrium in case of coarse and medium sand as illustrated in Fig. 1.

For the same amount of soil, the removal percentage of LPS endotoxin from water samples was the highest in the case of silt, followed by fine sand, medium sand and coarse sand. At a dose of 5.8 g/L, the silt achieved nearly 2.3% removal (Fig. 1). This removal percentage decreased in the case of other soils and reached to lower than 2% in the case of coarse sand. The difference in the adsorption performance of the soils is expected because of the difference in their properties. Thibodeaux J.L summarizes typical specific surface area of various soils [29]. Values of 22 cm^2/g, 45 cm^2/g, 90 cm^2/g and 450 cm^2/g, respectively for coarse sand, medium sand, fine sand and silt, respectively, were reported. Silt and fine sand have larger surface areas than medium and coarse sands and therefore offer larger areas for adsorption.

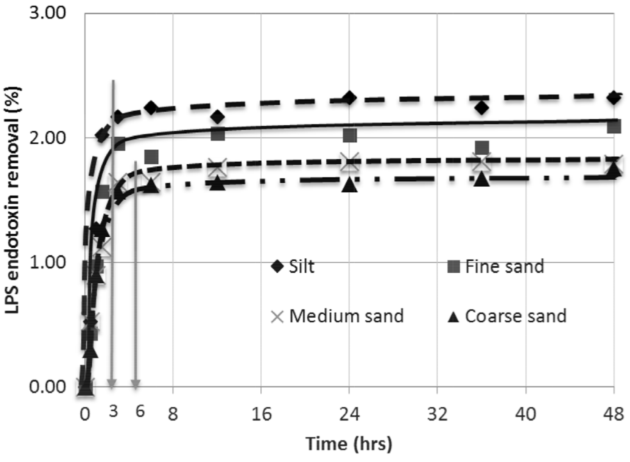

Fig. 1. Effect of soil type on the LPS endotoxin removal efficiency (soil dose 5.8 g/L).

3.3. Effect of the dose of the adsorbent

The effect of the amount of soil on the removal of LPS endotoxin from reclaimed wastewater was investigated as well. Fig. 2 illustrates a series of contact time curves with three different doses of fine sand 1.9 g/L, 3.8 g/L and 5.8 g/L. The results showed that the LPS endotoxin removal percentage increases as the dose of the soil increases. This increasing trend is expected due to the increase of the number of adsorption sites (specific surface area).

As shown in Fig. 3, the increase in percentage removal of LPS endotoxin following the increase of soil amount (adsorbent) is more significant at lower amounts of soil than at higher soil doses. The increase in removal percentage becomes insignificant. When the dose doubled from 1.9 g/L to 3.8 g/L the removal percentage increased in the case of silt from 1.28% to 1.92% (0.64% increase). However, the silt dose increase from 3.8 g/L to 5.8 g/L (an increment of 1.9 g/L), the removal percentage increased from 1.92% to 2.3% (0.4% increase). Same trend for other adsorbent is observed as illustrated in Fig. 3. Therefore it is clear that at a higher dose of adsorbent (5.8 g/L), the LPS endotoxin removal percentage does not increase at the same rate of adsorbent dose. Indeed, at higher doses, we are approach-

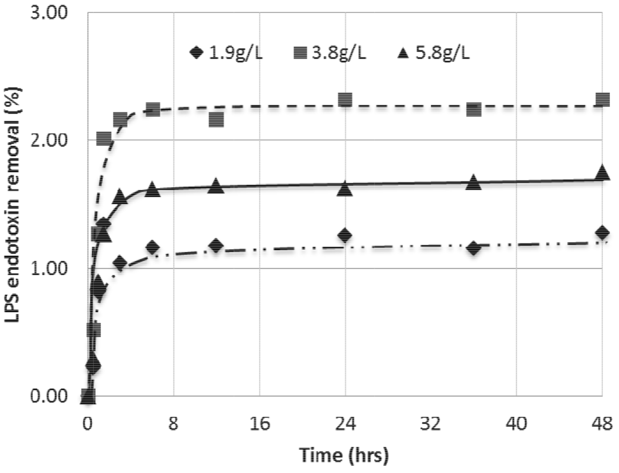

Fig. 2. Effect of soil dose on the adsorption efficiency.

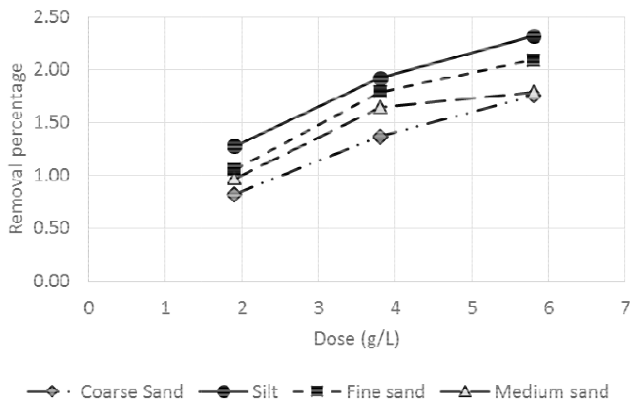

Fig. 3. Removal percentage versus soil dose.

ing the maximum adsorption where the removal percentage remains constant independently of the dose. The dose above which the removal percentage remains constant independently of the dose increase is called optimum dose. Unfortunately, the data obtained during this study is not sufficient to know the optimum dose.

3.4. Effect of the contact time

The contact time is an important parameter in the adsorption tests. To understand the effect of the contact time, the LPS endotoxin adsorption in the different soils was investigated at different times. The adsorption experiments were run for 48 h. Fig. 4 illustrates the remaining LPS endotoxin with respect to the contact time. It was observed that the LPS endotoxin concentration in the solution decreases rapidly during the first three hours of operation for all soil samples. After three hours, the LPS endotoxin concentration declines slowly until it reaches equilibrium between 3 and 12 h. A further increase in the contact time did not improve the removal efficiency. The rapid decrease in the LPS endotoxin concentration in the early stage occurs as a result of the abundance of active sites on the soil surface where LPS endotoxin is adsorbed. Once these sites are saturated with LPS endotoxin, soils cannot further adsorb LPS endotoxin, resulting in an equilibrium state. The equilibrium for all soil types (silt, fine sand, medium sand and large sand) occurred within 3 to 12 h. Similar trends for adsorption onto soils have been reported by several researchers [30–32].

3.5. Effect of the initial LPS endotoxin concentration

The initial concentration of adsorbate is an important factor to be considered because it may influence the rate of adsorption. The effect of different initial LPS endotoxin concentrations on the adsorption efficiency is shown in Fig. 5. Initial concentrations of 65, 220, 650 and 1337 EU/ml were investigated. The findings indicate that the amount of LPS endotoxin adsorbed per unit mass of soil increased with an increase in the initial LPS endotoxin concentration for all tested soils. Indeed, a higher driving force of the concentration gradient occurs at a higher initial LPS endotoxin concentration. The LPS endotoxin concentration adsorbed by silt increased from 431.03 EU/g (for an initial LPS endotoxin concentration of 65 EU/ml) to 2672.41 EU/g (for an initial LPS endotoxin concentration of 1337 EU/ml); it increased from 172.41 EU/g (for an initial LPS endotoxin concentration of 65 EU/ml) to 2025.86 EU/g (for an initial LPS endotoxin concentration of 1337 EU/ml) in the case of large sand.

3.6. Effect of the soil freshness

Guizani et al. [19] reported that LPS endotoxin removal using soil aquifer treatment columns was not stable and decreased over time. Several factors might affect the removal efficiency and the adsorption is one of factors. Indeed, when maximum adsorption capacity is reached, endotoxin removal using via adsorption will not be an option. Knowing that biofilm formation in the upper layers of soil might lead to endotoxin generation, in addition to the low degradability of LPS endotoxin as reported by Guizani et al. [14], it becomes crucial to know if we could regenerate the adsorption of soil for its sustainable use as an option for endotoxin removal. Therefore, in this section we evaluate the adsorption of LPS endotoxin using virgin soil (not used) and soil collected from an average depth of 50 cm from soil columns operated for 1 y for sewage treatment. Both soil samples were washed with de-ionized water to remove impurities and to desorb all chemicals previously adsorbed. Fig. 6 illustrates LPS endotoxin removal by adsorption to fresh and used fine sand. Fresh sand is more efficient than used sand: the fresh sand removal efficiency reaches 3.75%, whereas it is approximately 2.09% in the case of used fine sand. Equilibrium is reached by both types of sand at nearly the same time. The difference in adsorption efficiency between fresh and used sand could be attributed to the fact that during soil washing with de-ionized water,limited amount of previously adsorbed endotoxin has been desorbed. Goyal et al. [24] report that rainfall can elute adsorbed endotoxin from soil columns. However, the desorbed endotoxin is by far less than the applied endotoxin. This finding suggests that the adsorption potential cannot be fully regenerated.

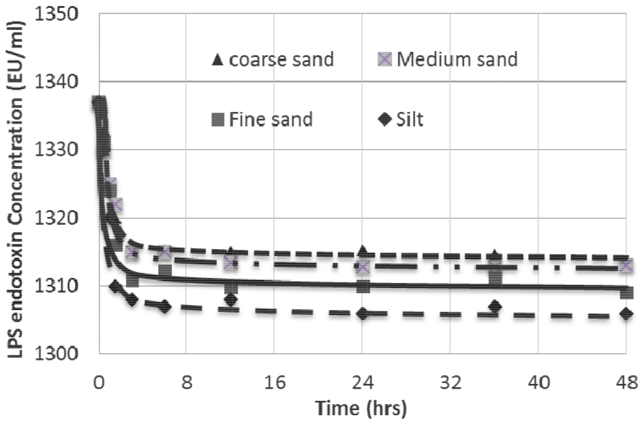

Fig. 4. Effect of the contact time on the LPS endotoxin adsorption into soil.

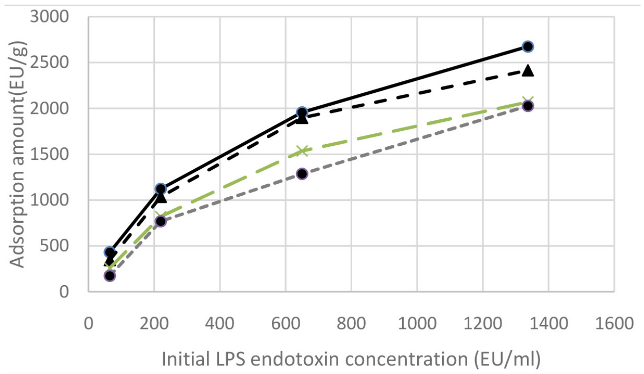

Fig. 5. Effect of the initial LPS endotoxin concentration on adsorption.

3.7. Adsorption isotherms

Fig. 7 illustrates the amount of adsorbed LPS endotoxin per mass unit of soil versus the equilibrium concentration. LPS endotoxin is clearly observed to not adsorb in the same manner on the surface of different soils. Indeed, LPS endotoxin adsorption to large and medium sands is weaker than its adsorption to fine sand and silt. In addition, all isotherms reach a saturation level. Moreover, the equilibrium adsorption data were first fitted to the Freundlich isotherm model, and the model parameters were estimated. The Freundlich isotherm model assumes that the adsorption isotherm formula can be written as $Q_e = k·C_e 1/n$, where k is the Freundlich equilibrium constant and $1/n$ is an arbitrary coefficient obtained by linearizing the Freundlich adsorption isotherm equation. The plots of log Q_e vs. log C_e are shown in Fig. 8, which shows a straight line for the four adsorbents. This observation suggests that there is no change in the rate and extent of adsorption. Table 3 indicates the adsorption parameters of endotoxin (k and $1/n$). The found results show that the endotoxin adsorption of soil fitted to the Freundlich adsorption isotherm. Note that the value of n is greater than one for all soils, which indicates that the adsorption of LPS endotoxin to soil is a physical process. Indeed, the literature reports that if n is larger than one, then the adsorption is physical, whereas it is considered a chemical process if n is smaller than one.

The same data were fitted better to the Langmuir isotherm model, and model parameters were also estimated. The Langmuir isotherm model is described by the following formula: $C_e/Q_e = 1/(Q_{max}·k)·C_e/Q_{max}$.

The model assumes a monolayer adsorption with no transmigration of adsorbates in the plane surface. Fig. 8 illustrates that the LPS endotoxin adsorption to soil fits to the Langmuir isotherm model. Table 3 shows the Langmuir isotherm parameters. The constants Q_{max} and k represent the maximum adsorption and the energy required for adsorption, and k is the Langmuir constant and C_e is the equilibrium concentration.

The Freundlich and Langmuir adsorption constants and correlation coefficients reveal that LPS endotoxin adsorption onto soil fits better to the Langmuir isotherm with an $R^2 = 0.99$ (all soils) instead of 0.98, 0.96, 0.97 and 0.94 for large sand, medium sand, fine sand and silt, respectively.

The value of K (Langmuir constant) is equal to 0.0025. 0.0019, 0.00135 and 0.00017 for silt, fine sand, medium sand and large sand, respectively. Being larger than zero (but very close to zero) and smaller than one, these values of R indicate that the adsorption of LPS endotoxin to these soils is highly favourable, as described by Bhole et al. and Raji et al. [33,34]. An isotherm is favourable if its fixation capac-

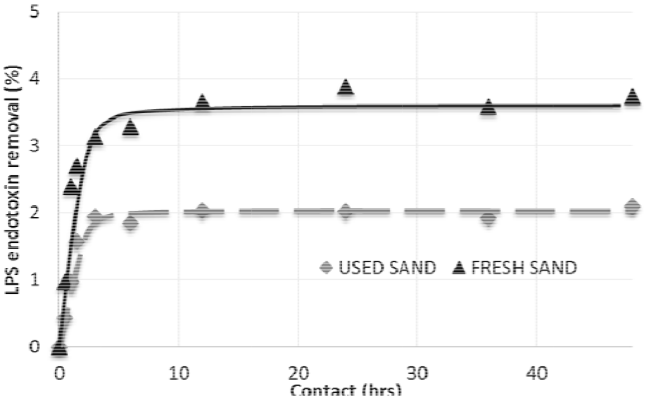

Fig. 6. LPS endotoxin adsorption: used sand vs. fresh sand.

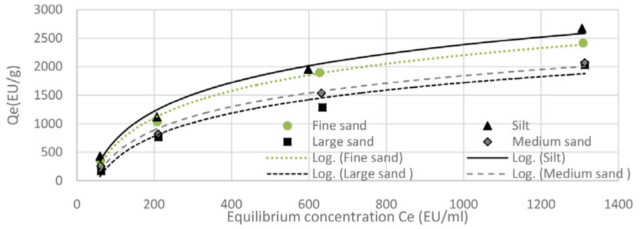

Fig. 7. LPS endotoxin adsorption amount per mass unit of soil versus equilibrium concentration.

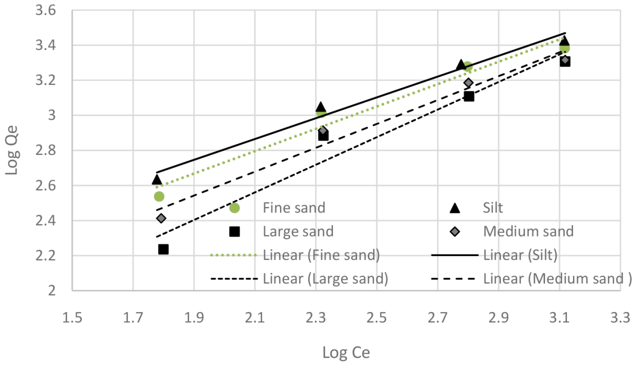

Fig. 8. Freundlich adsorption isotherm for LPS endotoxin log Q_e vs. log C_e.

Table 3
Parameters of the Freundlich and Langmuir isotherms for fresh and used medium sand

	Freundlich Isotherm parameters			Langmuir isotherm parameters		
	k	$1/n$	R^2	Q_{max}	K (L/mg)	R^2
Silt	8.111478	0.78	0.9498	8.230453	0.0025	0.9998
Fine sand	17.76233	0.6806	0.9706	6.242197	0.0019	0.9987
Medium sand	28.64178	0.6373	0.9652	4.514673	0.0014	0.9981
Large sand	41.66775	0.5931	0.9887	2.815315	0.0002	0.9863

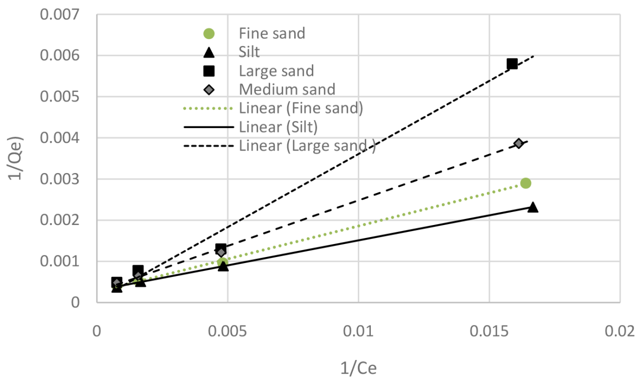

Fig. 9. Langmuir adsorption isotherm for LPS endotoxin.

ity increases rapidly with concentration in equilibrium in the liquid phase, resulting in a convex form. The maximum for a highly favourable isotherm is irreversible adsorption, where the amount adsorbed does not depend on the decrease in concentration, down to very low values. In other words, when a high endotoxin concentration is supplied in the reclaimed wastewater, the soils adsorb endotoxin very quickly until the maximum adsorption capacity is reached. This explains why the soil columns showed very good removal of endotoxin in the early stage of operation, whereas later, the efficiency dropped significantly as reported by Guizani et al. [19].

4. Conclusion

This study showed that different soils (silt, fine sand, medium sand and coarse sand) could be used as effective adsorbents for the removal of LPS endotoxin from reclaimed wastewater. These natural materials are relatively abundant worldwide, particularly in low-income countries, and can be advantageous for indirect potable reuse. The different soils performed well with an endotoxin removal of few thousands Endotoxin equivalent units per gram of soil with the best adsorption results for the silt and fine sand. It should be noticed that the soils performed differently and equilibrium was reached at different times depending on soil properties. Shortest time (nearly 3 h) was observed in the case of silt and fine sand, while approximately 5 h were required to reach equilibrium in case of coarse and medium sand. Longer contact times do not improve the removal. Moreover, endotoxin removal increases with soil dose. However, the increase in percentage removal of LPS endotoxin following the increase of soil amount (adsorbent) is more significant at lower amounts of soil than at higher soil doses. It was also found that LPS endotoxin removal rate depends on initial endotoxin concentration. Comparison between fresh and used sand indicated that not all adsorbed endotoxin can be desorbed, which induces a lower efficiency of used sand. Furthermore, the study showed that the adsorption of LPS endotoxin into the four different soils can be represented by both Freundlich and Langmuir isotherms. The findings from these isotherms suggest that the adsorption is favourable and almost irreversible.

Acknowledgments

The authors gratefully acknowledge the financial support from the Japan Society for the Promotion of Sciences (JSPS) for the first author, who conducted this research when he was a visiting scholar as an International Research Fellow.

References

[1] H.L. Leverenz, G. Tchobanoglous, T. Asano, Direct potable reuse: a future imperative, J. Water Reuse Desal., 1(1) (2011) 2–10.

[2] B. Van der Merwe, P. Pisani, J. Menge, E. Konig, Water reuse in Windhoek, Namebia: 40 years and still the only case of direct water reuse for human consumption. In Jimenez B. and Asano T. (Ed.), Water reuse: An international survey of current practice, issues and needs). London, UK: IWA Publishing, 2008, pp. 142–160.

[3] N. Funamizu, X. Huang, G.H. Chen, H. Jiangyong, C. Visvanathan, Water reuse in Asia. In B. Jimenez, T. Asano, eds,, Water reuse: An international survey of current practice, issues and needs pp. 142–160. London, UK: IWA Publishing 2008.

[4] J.M. Alhumoud, Public perceptions on water reuse options: the case of Sulaibiya Wastewater Treatment Plant, In Kuwait. International Business & Economics Research Journal, 2010, 9(1).

[5] N. Apostolidis, C. Hertle, R. Young, Water recycling in Australia, Water, 3 (2011) 869–881.

[6] W.B. Anderson, R.M. Slawson, C.I. Mayfield, A review of drinking-water-associated endotoxin, including potential routes of human exposure, Canad. J. Microbiol., 48 (2002) 567–587.

[7] K.L. William, Endotoxins: Pyrogens, LAL Testing and Depyrogenation (Drugs and the Pharmaceutical Sciences), 3rd ed., Indiana, USA,2007.

[8] D.J. Barker, D.C. Stukey, A review of soluble microbial products (SMP) in wastewater treatment system, Water Res., 33(14) (1999) 3063–3082

[9] H. Narita, I. Isshiki, N. Funamizu, T. Takakuwa, H. Nakagawa, S.I. Nishimura, Organic matter released from activated sludge bacteria cells during their decay process, Env. Technol., (2005) 433–440.

[10] H. Narita, N. Funamizu, T. Takakuwa, M. Kunimoto, Toxicity assessment of treated wastewater using cultured human cell lines, Environ. Monit. Assess., 129 (2007) 71–77.

[11] W.W. Eckemfelder, Alternative strategies for meeting stringent effluent guidelines, Wat. Sci. Technol., 29(8) (1994) 1–7.

[12] M. Guizani, Y. Nogoshi, F.B. Fredj, J. Han, H. Isoda, N. Funamizu, Heat shock protein 47 stress responses in Chinese hamster ovary cells exposed to raw and reclaimed wastewater. J Environ Monit., 14(2) (2012) 492–498.

[13] M. Guizani, M. Dhahbi, N. Funamizu, Assessment of endotoxin activity in wastewater treatment plants, J. Environ. Monit., 11(7) (2009) 1421–1427.

[14] M. Guizani, M. Dhahbi, N. Funamizu, Survey on LPS endotoxin in rejected water from sludge treatment facility, J. Environ. Monit., 11(11) (2009) 1935–1941.

[15] S.H. Hindman, M.S. Favero, L.A. Carson, N.J. Peterson, L.B. Schonberger, J.T. Solano, Pyrogenic reactions during haemodialysis caused by external endotoxins, Lancet, (1975) 732–734.

[16] P. Bhattacherjee, R.N. Williams, K.E. Eakins, An evaluation of ocular inflammation following the injection of bacterial endotoxin into the rate foot pad, Association for research in vision and ophthalmology, 24 (1983) 196–202.

[17] J. Thorn, The inflammatory response in Humans after inhalation of bacterial endotoxin, J. Inflam. Res., 50(5) (2001) 254–261.

[18] P.O. Magalhães, A.M. Lopes, P.G. Mazzola, C. Rangel-Yagui, T.C. Penna, A.J. Pessoa, Methods of endotoxin removal from biological preparations: a review, J. Pharm. Pharm. Sci., 10(3) (2007) 388–404.

[19] M. Guizani, M. Dhahbi, N. Funamizu, Assessing the removal potential of soil aquifer treatment system (soil column) for endotoxin, J. Environ. Monit., 13 (2011) 1716–1722.

[20] M. Guizani, N. Yusuke, M. Dhahbi, N. Funamizu, Characterization of endotoxic indicative organic matter (2-keto-3deoxyoctulosonic acid) in raw and biologically treated domestic wastewater, Water Res., 45(1) (2011) 155–162.

[21] C. Raetz, C. Whitfield, Lipopolysaccharide endotoxins, Annu. Rev. Biochem., 71(1) (2002) 635–700.

[22] C.M. Ongkudon, J.H. Chew, B. Liu, M.K. Danquah, Chromatographic removal of endotoxins: A bioprocess engineer's perspective, ISRN Chromatography, (2012) pp. 649746-1–649746-9.

[23] I. Bononi, V. Balatti, S. Gaeta, M. Tognon, Gram-negative bacterial lipopolysaccharide retention by a positively charged new-generation filter, Appl. Environ. Microbiol., 74(20) (2008) 6470–6472.

[24] M.G. Sagar, P.G. Charles, L. Clearence, Movement of endotoxin through soil columns, Appl. Environ. Microbiol., 39(3) (1980) 544–547.

[25] L.K. Williams, Endotoxins: Pyrogens, LAL Testing and Depyrogenation (Chap. 4: Endotoxin Structure, Function and Activity). 3rd ed., 2007, CRC, Indiana.

[26] C.A. Black, Methods of Soil Analysis: Part I Physical and mineralogical properties". American Society of Agronomy, Madison, Wisconsin, USA. 1965.

[27] A.Z. Aroguz, J. Gulen, R.H. Evers, Adsorption of methylene blue from aqueous solution on pyrolyzed petrified sediment, Bioresour. Technol., 99 (2008) 1503.

[28] A. Rezaee, Gh. Ghanezadeh, Gh. Behzadiannejad, Ar. Yazdanbakhsh, SD. Siyadat, E. Hajizedeh, Adsorption of endotoxin from aqueous solution using bone char, Bull. Environ. contam. Toxicol., 82 (2009) 732–737.

[29] J.L. Thibodeaux, Environmental Chemodynamics: Movement of Chemicals in Air, Water, and Soil, 2nd ed., 1996.

[30] S.B. Olugbenga, Adsorptive removal of malachite green with activated carbon prepared from oil palm fruit fibre by KOH activation and CO_2 gasification, S. Afr. J. Chem., 66 (2013) 32–41.

[31] O. Hamdaoui, F. Saoudi, M. Chiha, E. Naffrechoux, Sorption of malachite green by a novel sorbent, dead leaves of plane tree: equilibrium and kinetic modeling, Chem. Eng. J., 143 (2008) 73–84.

[32] R. Ahmad, R. Kumar, Adsorption studies of hazardous malachite green onto treated ginger waste, J. Environ. Manage., 91 (2010) 1032–1038.

[33] A.G. Bhole, P.N. Shastri, S. Thakre, Treatment of dairy waste using kaolin as an adsorbent, J. IPHE, India, 1 (2002) 22–25.

[34] C. Raji, T.S. Anirudhan, Chromium (VI) adsorption by sawdust: Kinetics and equilibrium, Ind. J. Chem. Technol., 4 (1997) 228–236.