Influence of Impregnation Ratio on Chemically Modified Silica Sand for Heavy Metals Removal from Stabilized Landfill Leachate

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Abstract—Landfill leachate generated from landfill normally contains high concentrations of organic and inorganic constituents. Consequently, the disposal of untreated leachate could be hazardous to both surrounding ecosystems and human beings. In the present study, the ability of chemically modified silica sand in reducing heavy metal concentrations for ferrous and zinc ions from stabilized landfill leachate were investigated. The effects of impregnation ratio (IR) on adsorption performance were studied in terms of adsorbent dosage, contact time, and pH. Equilibrium isotherms were analyzed by using Langmuir and Freundlich isotherms to describe the adsorption characteristics of the adsorbent. From the laboratory experiments, IR of 1.5 was found to be optimum for heavy metal adsorption, at the dosage of 20 g and pH 7. The adsorption isotherm data were fitted well to Freundlich isotherm with \( R^2 \) value of 0.9862.

Keywords—Stabilized Landfill Leachate; Heavy Metals; Silica Sand; Adsorption

I. INTRODUCTION

Landfilling has emerged as one of the prominent options for solid waste disposal. This simple economical technology has received significant attention over the last decades [1]. Leachate is produced from the interaction between decomposed solid wastes and liquid percolating through the landfill body. Leachate composition depends on a variety of parameters, namely the type of waste, climatic conditions, operation mode and landfill age [2, 3]. Although landfill leachate is a complex mixture of chemicals, there are some broad underlying pollutants which are common to all landfill effluents. Various findings have reported the risk of leachate contaminants posing multiple, synergistic, carcinogenic, acute toxicity and genotoxicity [4]. For instance, leachate with a high concentration of ammoniacal nitrogen (NH\(_{3}\)-N) may contain suspended solids, being turbid and toxic to many organisms [3]. In most cases, landfill leachate is highly contaminated with calcium (Ca\(^{2+}\)), magnesium (Mg\(^{2+}\)), sodium (Na\(^{+}\)), potassium (K\(^{+}\)), ammonium (NH\(_{3}\)), ferrous (Fe\(^{2+}\)), manganese (Mn\(^{2+}\)), chloride (Cl\(^{-}\)), sulphates (SO\(_{4}\)\(^{2-}\)) and bicarbonates (HCO\(_{3}\)) coupled with heavy metals (arsenic, cadmium, chromium, cobalt, copper, lead, mercury, nickel and zinc) that are readily soluble at fixed concentrations during the degradation processes. Leachate could migrate away from the landfill and cause severe pollution to groundwater aquifer and nearby surface water. Discharging untreated leachate to water bodies could endanger both surrounding ecosystems and human populations [5-8].

Treatments of leachate are very expensive, difficult and usually require a combination of several treatments, due to its high loading, complex chemical composition and seasonal variable volume [7, 10]. Adsorption process is considered as one of the suitable methods for the removal of contaminants from water. It is defined as a surface phenomenon, by which a multi-components fluid (gas or liquid) mixture is attracted to the surface of a solid adsorbent and form attachments via physical or chemical bonds [4].

Until now, few studies have focused on leachate adsorption by natural adsorbents i.e. limestone [15], zeolite [9] and clinoptilolite [16]. Not many attempts have been carried out to obtain a comprehensive understanding of leachate treatment using natural adsorbents. Adsorption based processes offer more reliable and more efficient removal of complex inorganic and organic metals than many conventional treatment methods [12, 13, 17]. Thus, there is a need to investigate the use of low cost adsorbent as an alternative for landfill leachate treatment.

II. MATERIALS AND METHODS

A. Leachate Sampling

Leachate samples were collected using Teflon containers from an oxidation pond of Pulau Burung Stabilized Landfill located in Penang, Malaysia and stored at 4 °C until analyses were carried out to ensure leachate remained unchanged. Portable pH meter (Hach, sens ion 1, USA) was employed to determine the pH values of the leachate onsite. COD was measured with Calorimetric Method (5220-D) while the heavy metal concentrations of ferrous and zinc were measured using a UV spectrophotometer (HACH DR 2500). The methods used to measure ferrous and zinc concentrations were FerroVer 265 and Zinc 786 respectively. Readings were taken after filtering agitated leachate samples using 0.45µm GC-50 glass micro fibre filters (Advantec, Japan). The percentage removal of ferrous or zinc was calculated as follows:

\[
\text{Removal (\%) } = \frac{C_i - C_f}{C_i} \times 100
\]

(1)

Where, \( C_i \) and \( C_f \) are the initial and final concentrations of heavy metal (mg/L) respectively. Prior to experiments, leachate sample was immediately characterized according to [18]. Table 1 illustrates the characteristics of the raw leachate sample based on 6 samples collected for 3 months, from September to November 2010. All the experimental readings were taken on the triplicate procedure basis.

B. Preparation of Adsorbent

Natural raw silica sand was procured from bed sediments of a former tin mining site in Serdang, Kedah, Malaysia. It is considered as abundant in nature as tin mining industry in Malaysia has past its successful era during 1970s. The samples were washed several times with distilled water to
remove physical earthen impurities [19]. Prior to experiment, the silica sand was oven-dried using UNP-200 convection oven (Memmert, Germany) at 105 °C prior to activation process. Subsequently, it was sieved to 0.6-1.18 mm particle size using laboratory sieve. The silica sand was impregnated with a weighted amount of NaOH aqueous solution. The impregnation ratio is defined as the weight (g) of NaOH to the weight (g) of precursor (dried silica sand) as in Eq. (2). The modified silica sand was prepared with different impregnation ratios (IR) i.e. 0.5, 1.5 and 2.5.

\[
\text{Impregnation ratio} = \frac{\text{Weight of NaOH}}{\text{Weight of the silica sand}}
\]

50 g of dried silica sand were poured into three conical flasks which filled with 600 ml aqueous NaOH. The concentration of alkali used was 96% by weight. The mixtures were stirred thoroughly in the conical flasks and kept for 72 hours to allow homogenous substrate reaction. Laboratory film (Parafilm M, USA) was wrapped on the lid of each conical flask to prevent air intrusion into the mixture throughout the activation process. After the activation process, the modified silica sand was washed with boiled and distilled water to eliminate the residual organic and mineral matter attached on the sample surface. A vacuum pressure pump (Barnant Co., USA) connected to 500 ml filter flask (Pyrex, USA) was set up to retain the substrate from the residual during the entire washing and cleaning process. The solutions were separated from the samples using 0.45 µm glass micro fiber filter papers (Advantec, Japan) on the filter funnel retainer. The samples prepared were oven-dried at 105 °C and stored in air tight containers prior to use.

C. Batch Experiment

In the experimental works, a series of batch experiments were carried out in order to obtain the removal patterns of ferrous and zinc from leachate samples. To determine the optimum impregnation ratio of modified silica sand, factors such as adsorbent dosage, contact time and pH were chosen as the indicators of the modified silica sand capacity to remove heavy metals from leachate sample. Thereafter, the adequacies of these experimental works were based on the ranges stated as follows:

D. Adsorbent Dosage

Batch adsorption experiments were conducted by adding various amounts of solvent (5, 10, 15, 20 and 25 g) into five 250 ml conical flasks containing 100 ml locate. To ensure satisfactory agitating process, each flask was wrapped with laboratory film. The agitating speed was maintained at 300 rpm. In this case, 150 minutes of agitating period were allocated as the equilibrium time for each impregnation ratio and 10 g of sorbents of each flask was selected. Finally, the isotherm adsorption was measured for both ferrous and zinc using a UV spectrophotometer. The experiments were repeated using modified silica sand with different impregnation ratios.

E. Contact Time

Batch adsorption experiments were conducted by carefully adding three different impregnation ratios impregnated modified silica sand into three 250 mL conical flasks containing 100 mL leachate sample. For each conical flask, 10 g of modified silica sand was added. Each flask was covered with laboratory film (Parafilm M, USA) on top of its lid to avoid spillage during agitating process. The prepared flasks were then placed on orbital shaker model 720 (Protech, Malaysia) and agitated at 300 rpm. Subsequently, the heavy metal concentrations of leachate samples were measured at preset time intervals of 30, 60, 90, 120, 210, 240 and 270 minutes.

F. pH

Batch adsorption experiments were carried out by adding 10 g of modified silica sand into each of the five 250 mL conical flasks filled with 100 mL leachate. Prior to the experiment, the pH of leachate samples was adjusted to 2, 5, 7, 11 and 13 by using either 0.1 M H 2SO4 or NaOH solution. The lids of the flasks were wrapped with laboratory film to avoid spillage during agitating process. The flasks were placed in an orbital shaker and agitation was provided at 300 rpm for 150 minutes. After 150 minutes, the concentrations of ferrous and zinc were measured using UV spectrophotometer. This set of experiments was repeated using modified silica sand with different impregnation ratios.

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III. RESULTS AND DISCUSSIONS

Table 1 illustrates some of the leachate’s characteristics at PBLs. Even though the samples were collected on different days or at different times, the leachate’s characteristics demonstrate similar fashion and are broadly comparable for most of the parameters. The pH of the leachate samples was in the range of 7.34 to 7.81. According to Umar et al. [20] the pH of young leachate is less than 6.5 while old landfill leachate has a pH higher than 7.5. Initial low pH is due to high concentration of volatile fatty acids (VFAs). Similarly, stabilized leachate shows a fairly constant pH with little variations and it may range between 7.5 and 9. The presence of significant amount of ammoniacal nitrogen (2696 mg/L) in the leachate indicates degradation of soluble nitrogen due to
the decomposed waste. As a result, the concentration of ammoniacal nitrogen increases with the increase in the age of the landfill which is due to hydrolysis and fermentation of nitrogenous fractions of biodegradable refuse substrate [21]. Higher concentration of ammonical nitrogen enhances algae growth and promotes eutrophication due to decreased dissolved oxygen content. The high value of pH and low concentrations of COD, BOD5 and heavy metals indicate that the leachate was in the phase of methane fermentation and classified as anaerobic phase [3]. The low BOD/COD ratio (0.17) indicates that the leachate was stable and difficult to be further degraded biologically [11]. The presence of heavy metals, ferrous and zinc (5.3 and 2.9 mg/L) were due to metal solubility in organic acids from the solid waste degradation. Furthermore, a decrease of metal concentration was expected as the pH of leachate decreased at a later stage of the landfill and produced organic acids. Nevertheless, the solubility and mobility of metal may present in the form of natural and synthetic complexing ligands such as EDTA and humic substance [22].

A. Effect of Adsorbent Dosage

The removal of ferrous and zinc as a function of adsorbent dosage at different IRs namely 0.5, 1.5 and 2.5 were determined. By varying the adsorbent dosage, removal pattern of the heavy metals could be investigated. From a preliminary analysis of leachate sample, initial concentration of total ferrous was 5.30 mg/L while 2.9 mg/L for zinc. Fig. 1 (a) shows the variations of ferrous adsorption at different dosages of modified silica sand while Fig.1 (b) shows the variations of zinc adsorption at different modified silica sand dosages. These results indicate that the percentage of removal of ferrous increased with an increase in adsorbent dosage from 5 to 25 g as shown in Fig.1 (a). A similar trend was observed for zinc removal as shown in Fig. 1 (b). These trends were predicted because when the adsorbent dosage increased, more sorption surface and adsorption sites available which results in attachment of more adsorbates to the surfaces [23]. Most likely, the available surface of modified silica sand preferably captured ferrous and zinc charges and precipitated them on it. This was in agreement with the result found by Ghaly et al. [14] which concluded negative surface charge of quartz was responsible to attraction of Fe$^{2+}$ and Zn$^{2+}$. In addition, sand served as a scavenger for precipitation reaction and as a result, buildups of precipitate on ionic charges were minimized [24]. Even though adsorption increased with respect to an increase in dosage, the tendency of amount adsorbed per unit mass reduced by increasing dosage as shown in Figs. 1 (a, b). The percentage of removal of ferrous increased as the IR increased from 0.5 to 2.5 as shown in Fig. 2 (a). The optimum removal of ferrous enhanced by 27.55, 41.70 and 47.55 % for IR 0.5, IR 1.5 and IR 2.5 respectively, when the adsorbent dosages were increased from 5 to 25 g. A significant increment of removal was observed in IR 2.5 compared to other impregnation ratios. Optimum zinc removal of 48.62% was achieved for IR 2.5 by using 25 g of adsorbent. Zinc removal was slightly higher compared to ferrous removal when similar dosage and IR were used. A uniform increment for IR 0.5 was observed when the adsorbent dosage was increased from 5 to 25 g. Meanwhile, the percentage of removal for IR 1.5 increased slightly from 23.79 to 24.48% when the dosage was increased from 10 to 15 g. For IR 1.5 and 2.5, zinc removal percentage increased slightly from 30.69 to 31.72% and 47.59 to 48.62% respectively when the adsorbent dosage increased from 20 to 25 g. It can be concluded that higher removal could be achieved when the adsorbent dosage and IR increased. In other words, the IR is directly proportional to the percentage of removal. The difference in removal of metal ions at various initial adsorbent dosages may be due to the differences in chemical resemblance and ion exchange capacity, with respect to the chemical functional groups on the surface of the silica sand. The decrease in adsorption capacity with an increase in adsorbent dose is mainly due to the strong attractive forces between the metal ions and the silica sand surfaces which initiated fast diffusion of the mixtures. It was followed by fast pore diffusion into the intra-particle matrix to reach quick equilibrium at the later stage of adsorption. Further, higher impregnation ratios prevent the formation of silicate salt which deters the adsorption capacity of silica sand. As such, the formation of sodium silicate was abrupt due to proton depletion, and it is generally considered to be unfavorable for contaminant reduction as passivating layers develop on the surface of metal ions [24]. That any further addition of the adsorbent beyond this did not cause any significant change in the adsorption may be due to the decreased surface area resulting from the formation of adsorbent particle clusters [23].

![Fig. 1 Effect of different adsorbent dosage on the amount adsorbed of (a) ferrous, and (b) zinc using modified silica sand](image-url)
The adsorption process took approximately 270 mins to reach the equilibrium condition. In the case of IR 2.5, the removal of ferrous increased uniformly after contact time 30 mins and the percentage of removal kept increasing until it reached equilibrium period of 90 mins contact time, albeit steady increment was observed at the early stage of adsorption. The percentage of removal was the highest compared to IR 0.5 and 1.5 where 50.94% of ferrous was successfully removed. A similar trend was observed in the case of zinc adsorption curve as shown in Fig. 3 (b). A slight decrease in the percentage of removal was observed during 120 and 120 mins time interval for IR 0.5. In order to explain this behavior, the dependency of the removal capacity of the Sorbent chemical structure was considered. Formation of modified silica sand was particularly due to the reaction of SiO₂ and NaOH. The preference of sodium silicate for ferrous adsorption may be explained on the basis of metal ion electro-negativity and ionic radius. Better adsorption of ferrous was justified with its higher electro-negativity and smaller ionic radius. Incomplete reaction between ferrous metal and sodium silicate reduced electro-negativity, eventually reduced its attractive forces onto the surface of modified silica sand during adsorption process. This was further justified by the limited formation of silicate structural units which deterred chemisorptions transition to the zinc element and thus preventing adsorption on the surface of modified silica sand [25]. Overall, higher IR of silica sand contributes larger adsorption capacity for heavy metals removal which mainly be attributed by stabilizing surface affinity and functional groups available, subsequently enhanced the adsorption process providing that the contact time was longer.

C. Effect of pH

The ferrous and zinc percentage of removal as a function of pH at different impregnation ratios of 0.5, 1.5 and 2.5 was investigated. The results are presented in Fig. 4 (a, b). Adsorption capacity for total ferrous at various pH values is presented in Fig. 4 (a). The relationship between the adsorbent and the adsorbate was established by varying the pH of leachate sample from acidic to alkaline state. Solution pH would affect both aqueous chemistry and surface binding sites of the adsorbents. Generally, at acidic pHs, positively charged species start dominating and the surface tends to acquire positive charge while the adsorbate species are still negatively charged. As the adsorbent surface is positively charged the increasing electrostatic attraction between negatively charged adsorbate species and positively charged adsorbent particles would lead to increasing adsorption of the metal complex anions [26]. Adsorption of metals is strongly dependent on the pH, increases when the pH of the solution increases. Therefore, the role of hydrogen ion concentration in the removal of total ferrous was examined. The maximum removal for ferrous adsorption achieved by IR 0.5, IR 1.5 and IR 2.5 were 34.02, 45.08 and 51.12% respectively, at alkaline pH range 7-13. The removal efficiency increased significantly with increasing pH for all adsorbents. At the pH of 2 to 5, low percentage of removal was observed for all IRs. A constant increment observed as the pH of leachate sample was further increased. This phenomenon could be explained by the surface complexion of silica sand. The greater enhancement of reaction rate may be attributed to its higher surface area, greater affinity for reaction products and pH buffering effect [24]. A similar trend was observed in the case of zinc absorption. As the pH of leachate sample increased from 2 to 7, the zinc removal percentage of zinc increased uniformly for IR 0.5, 1.5 and 2.5, respectively. However, IR 0.5 and 1.5 showed a little increment when the
pH of the solution was in the range of 2 to 5 with 20.69 and 35.86%, respectively. The maximum sorption was obtained at pH 13 with 55.77% removal for IR 2.5. The adsorption of dissolved silica is likely to be manifested at high pH as the solubility of silica increases with pH. The difference in removal efficiency was due to the solution pH that is largely attributed to the precipitation of sodium silicate (Na₂SiO₃) at a higher pH. Increasing the pH implied a promotional increase of OH ions concentrations in solution disturbing equilibrium which could be achieved again through formations of greater amount of hydroxide out of the solution. In view of that, the sorption of metal ions can take place by the cation exchange reaction through the substitution of protons from silanol groups on the surface of the metal ions from the solution, as follows [23]:

\[ \text{M (SiOH)} \leftrightarrow \text{M(SiO}^{-}\text{)} + \text{mH}^{+} \]  
\[ \text{Mn}^{+} + \text{m(SiO}^{-}\text{)} \leftrightarrow \text{M(OSi)m}^{(n-m)+} \]  

The overall reaction can thus be represented as:

\[ \text{Mn}^{+} + \text{m (SiOH)} \leftrightarrow \text{M (OSi)m}^{(n-m)+} + \text{mH}^{+} \]  

Where Mn⁺ is metal ion with n⁺ charge, SiOH is the silanol group on SiO₂ surface, mH⁺ is the number of hydrogen released. In ferrous and zinc system, oxidation of these metals consumes proton. At high pH, the silanol groups dissociate to compensate the depletion of protons. In this case, the optimum pH for both ferrous and zinc adsorption was found optimum at pH 7, respectively. Maximum removal of chromium around this pH may be associated with the presence of significantly high electrostatic attraction between adsorbate and adsorbent resulting in fixation of surface compounds (19).

\[ M \text{ (SiOH)} \leftrightarrow m \text{ (SiO}^{-}\text{)} + \text{mH}^{+} \]  
\[ \text{Mn}^{+} + m \text{ (SiO}^{-}\text{)} \leftrightarrow \text{M (OSi)m}^{(n-m)+} \]  
\[ \frac{x}{m} = \frac{QdC}{1 + bC} \]  
\[ \frac{1}{(x/m)} = \frac{1}{QbC} + \frac{1}{Q} \]  

Where x is the amount of material adsorbed (mg), m is the weight of adsorbent (g), C is the equilibrium concentration of adsorbate in solution after adsorption is complete (mg/L), Q (mg/g) and b are the Langmuir adsorption constant related to the maximum adsorption capacity and the energy adsorption. The Freundlich isotherm is an empirical equation, assuming that the adsorption process takes place on heterogeneous surfaces. The linear form of Langmuir isotherm equations is given as (1):

\[ q_e = K_f C_e^{1/n} \]  

Where \( q_e \) is the amount of adsorbate adsorbed at equilibrium, (mg/g), \( C_e \) is the equilibrium concentration of adsorbate, (mg/L), \( K_f \) and \( n \) are Freundlich constants with \( n \) as a measure of the deviation of the model from linearity of the adsorption and \( K_f \) (mg/g (L/mg) 1/n) indicates the adsorption capacity of the adsorbent. The equation is conveniently used in the linear form by taking the logarithms of both sides as:

\[ \log q_e = \log K_f + \frac{1}{n} \log C_e \]  

The results of the ferrous adsorption obtained by each isotherm are shown in Fig. 5 (a, b). Based on the results shown in Fig. 5 (a) for Langmuir isotherm and Fig. 5 (b) for Freundlich isotherm, both isotherms showed very good fitness for adsorbate with corresponding coefficient (R²) values above 0.9 except for IR 0.5. Although the R² values obtained for both Langmuir and Freundlich isotherms were relatively high for all IRs, Freundlich isotherm yielded the best fit with the highest R² value of 0.9862 represented by IR 1.5 compared to others. It indicates that the surface heterogeneity of the adsorbent and thus was responsible for multilayer adsorption due to the presence of energetically heterogeneous adsorption sites.

Fig. 6 (a) and (b) illustrate the Langmuir and Freundlich isotherms for zinc adsorption. It can be seen that the corresponding coefficient (R²) values for IR 0.5, 1.5 and 2.5 were above 0.8 except for IR 0.5 for the Freundlich isotherm. From the Figs, it shows that IR 1.5 yielded the highest R² value (0.8566) that fits better for Freundlich compared to Langmuir isotherm. It shows that the adsorption of zinc is a favorable physical process. Nevertheless, Freundlich isotherm
for IR 0.5 produced lower $R^2 (0.7593)$ indicating that the data were not described by the isotherm.

![Figure 5: Langmuir (a), and Freundlich (b) isotherm of ferrous](image)

![Figure 6: Langmuir (a), and Freundlich (b) isotherm of zinc](image)

**E. Adsorbent Characterizations**

In this work, the optimum performance of modified silica sand was characterized based on the performance of isotherm model. In view of this, it was found that the modified silica sand with an impregnation ratio of 1.5 exhibits satisfactory condition. The characteristic of the adsorbent was analyzed using Autosorb A1 (Quantachrome, USA) and referring to the Brunauer, Emmett and Teller (BET) surface area. Generally, the main property of an adsorbent is its adsorptive capacity which is related to the specific area. The BET surface area of the prepared modified silica sand was found to be 0.45 m$^2$/g. The BET surface area in this study was comparable to the other findings reported by Oh et al. and Sharma et al. [20] whereas it was much lower compared to the result reported by Vaishya and Gupta [17]. The high BET surface area of the modified silica sand was due to the chemical process which utilized NaOH as activating agent. The SEM and EDX analysis were carried out by means of scanning electron microscope (Leo Supra 55 VP, Germany). The SEM and EDX of original sand particles are shown in Figs. 7 and 8. Different shapes, sizes, contrast, and porosity for the silica sand grain are shown in Fig. 7 (a). At the optimum condition, it can be seen from Fig. 7 (b) that the silica sand surface was coated with sodium silicate compound. The surface of the modified silica sand was rough with heterogeneous structures in scattered arrangement. It was assumed that the impregnation process chemically modified the structure component of the silica sand. From Fig. 8 (a), it shows that the SiO$_2$ compound was the main composition of the silica sand grain. The inclusions of NaOH solution as chemical agent impregnating silica sand grain has emerged Na element remarkably as shown in Fig. 8 (b). It can be inferred that sodium silicate (Na$_2$SiO$_3$) compound formed from the reaction between the SiO$_2$ and NaOH is responsible to the removal of heavy metal content from leachate sample. This was due to the hydrolysis process occurred after the inclusions of sodium silicate (Na$_2$SiO$_3$) compound. A surface functional group in silicates plays significant role in the adsorption process. It is a plane of oxygen atom bound to the silica tetrahedral layer and hydroxyl groups which are associated with the edges of silicate structural units. It was found that the functional groups provide surface sites for the chemisorptions of transition and heavy metals [25].

![Figure 7: SEM images of (a) silica sand grain, and (b) modified silica sand](image)
In this study, the efficiency of modified silica sand under varied impregnation ratios to remove heavy metal concentrations namely ferrous and zinc from stabilized landfill leachate was investigated. Based on the batch adsorption and isotherm model, it was found that impregnation ratios strongly affected the absorption ability of modified silica sand. In addition, the physical characteristics of modified silica sand were influenced by the chemical agent (NaOH) presence during the activation process. From adsorption isotherm, IR 1.5 was found to be the optimum condition of modified silica sand with the BET surface area of 0.45 m²/g. From the SEM image procedure, it shows that the optimum surface of modified silica sand was coated with sodium silicate compound. That the surface of the modified silica sand was a rough and scattered arrangement of heterogeneous structures was observed. The inclusion of NaOH solution as chemical agent for impregnation indicates that the structure of modified silica sand was largely influenced by the reaction between the SiO₂ and NaOH compound. In view of that, modified silica sand is a promising adsorbent for stabilized landfill leachate treatment, particularly during physiochemical process in the early stage of leachate treatment.

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REFERENCES

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