



Batch and Column Studies on Nickle and Cadmium Removal Using Iranian Clay-based Geopolymer

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ABSTRACT

The production rate of industrial and agricultural waste is increasing due to population growth. Soil is the most important receiver of industrial and agricultural waste. Contaminants such as heavy metals in various waste after reception by the soil, immediately become part of the cycle that has different impacts on the environment. Geopolymer, as a chemical stabilizer has the potential to stabilize heavy metals in the soil. In this research, several geopolymers for the stabilization of heavy metals in soil were synthesized. Silicon dioxide (SiO_2) and aluminosilicate (Al_2SiO_4) must be used to produce the geopolymers. Rice husk ash was used as the SiO_2 source. Also, Iranian zeolite and sepiolite, and red clay soil were utilized as the source of Al_2SiO_4 . The synthesized geopolymers were investigated for the adsorption of nickel and cadmium. Also, batch and column studies of using geopolymers for the chemical stabilization of heavy metals in soil were conducted. The results revealed a high adsorption capacity of the geopolymers. The zeolite, sepiolite, and red clay geopolymer-soil samples adsorbed 100% of the heavy metals (i.e., Ni and Cd) at a concentration of 100 ppm. The zeolite geopolymer adsorbent adsorbed 57% and 96% of Ni and Cd at a concentration of 1000 ppm, respectively. In general, it was concluded that the use of geopolymer compounds in soils with high heavy metal adsorption capacity could be an efficient approach to prevent groundwater resource pollution.

KEYWORDS: heavy metals; leaching; adsorption; zeolite; sepiolite.

INTRODUCTION

The soil is an essential ancient building material (Cristelo et al., 2012). It has been subjected to numerous environmental issues due to industrial and mineral advancements in recent decades. The stabilization of pollutants in the soil is a technique for coping with such problems (Zhang et al., 2010). Heavy metals are components of municipal and industrial waste and bedrock (Zwolak et al., 2019), and it is crucial to control them from entering the ecosystem. The soils of many regions across the world are contaminated with heavy metals. It is essential to stabilize heavy metals in soil to prevent them from moving towards groundwater (Liang et al., 2014). Stabilization is a process in which a contaminant combines with a binding agent, and its leaching is reduced. Also, in the stabilization process, hazardous wastes transform into an eco-friendly form that can be disposed of in the ground or utilized in construction (El-Eswed et al., 2017).

Stabilization methods include physical and chemical approaches. Physical approaches involve physical procedures to improve the soil's properties, while chemical soil stabilizers convert the contaminant into a less leachable form (Park, 2000). Soil stabilization through polymers offers some advantages, such as high affordability and effectiveness (Maghchiche et

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al., 2010). Also, polymer stabilizers impose fewer hazards on the environment (Swain, 2015). The geopolymer technology has been recently considered as a suitable solution to reuse and recycle solid industrial waste. It is a sustainable and cost-effective development (He et al., 2013). Geopolymerization is a relatively new method based on an old principle, which has been employed to solve environmental problems in recent years (Verdolotti et al., 2008). A geopolymer is an inorganic polymer gel (Sun et al., 2018) fabricated by the reaction of an aluminosilicate substance with an alkaline activator (Ding et al., 2017). Depending on the raw substances and initial processing, geopolymers can exhibit a wide range of properties, including high compressive strength, low shrinkage, acid resistance, fire resistance, low thermal conductivity (Duxson et al., 2007), porosity, excellent mechanical properties, and thermal and chemical durability and stability (Bai & Colombo, 2018). Environmentally, low energy is required to synthesize geopolymers (Lirer et al., 2017). By forming a coherent structure, geopolymers not only improve the strength of the soil but can also adsorb the industrial waste releasing heavy metals in an aquatic environment (Vu & Gowripalan, 2018). Several studies investigated the effects of geopolymers on the removal of heavy metals. El-Eswed et al., (2017) studied the heavy metals stabilization capability of geopolymer synthesized using metakaolin and alkaline activator. The results indicated that the heavy metals were effectively stabilized in the metakaolin geopolymer, and an increase in the ionic size of heavy metals enhanced the stabilization efficiency. Sun et al., (2018) explored the compressive strength and immobilization efficiency of heavy metals using sludge-synthesized geopolymers and reported the Cu and Zn immobilization of 72.2% and 68.6%, respectively. Li & Poon (2017) innovatively stabilized a Pb-contaminated soil using wastewater sludge ash. Nguyen et al., (2018) investigated the leachability of Fe, Cu, Zn, Cd, Pb, and Cr heavy metals from geopolymer synthesized using red mud and rice husk ash, and their results demonstrated that the leaching of these metal ions is low for a solution with pH at 7. Andrejkovičová et al., (2016) evaluated the effects of clinoptilolite (a natural zeolite) geopolymer as a filling soil on the mechanical performance of the soil and heavy metal adsorption capacity. The results showed incorporation of zeolite filler to metakaolin resulted in the production of eco-friendly materials with suitable mechanical properties and high stabilization capacity of heavy metals. Due to the importance of pollutants stabilization in soil, the capability of several geopolymers synthesized from sepiolite, zeolite and red clay (red soil) for the stabilization of heavy metals in sandy soil was investigated.

MATERIALS AND METHODS

The sandy soil was taken from 20 km northwest of Sirjan, Kerman Province, Iran, as problematic soil. Table 1 provides the mechanical and chemical properties of this soil. The grading curve of the studied soil is shown in Fig. 1.

Commercial NaOH (Merck company) and Rice Husk Ash (RHA) were employed as the alkaline agent and SiO₂ source, respectively. Also, Iranian zeolite, Iranian sepiolite, and red clay soil were utilized as the aluminosilicate source. Table 2 shows X-Ray Fluorescence (XRF) analysis results of initial materials used for geopolymer synthesis.

Table 1. Mechanical and chemical properties of the studied soil

pH	UCS(MPa)	ω (%)	SE(%)	K (cm/s)	G _s	d ₁₀	C _c	C _u
7.7	0	13.5	79	0.001	2.65	0.1	1.3	2.5

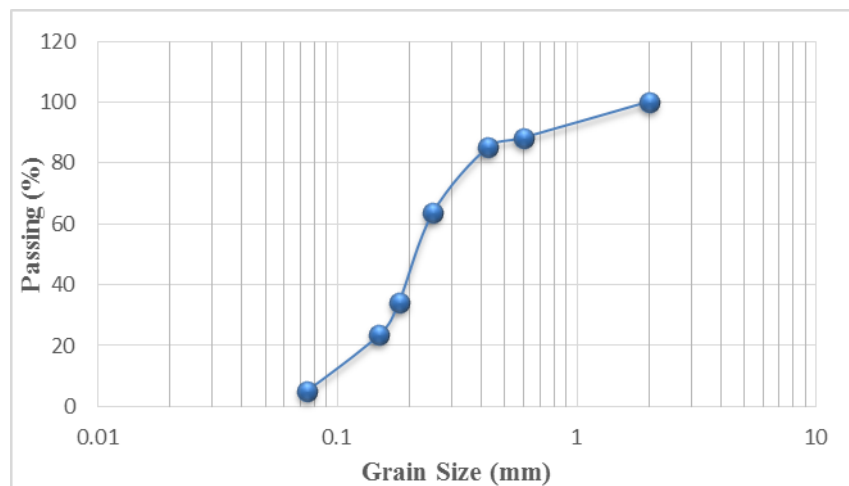


Figure 1. Grading curve of the studied soil

Table 2. X-Ray Fluorescence (XRF) analysis for the raw materials used for geopolymer synthesis

(%) Chemical Compounds	Zeolite	Sepiolite	RHA	Red clay soil
SiO ₂	61.91	52.9	89.5	49.482
Al ₂ O ₃	11.02	2.56	0.287	12.377
Fe ₂ O ₃	0.99	1.23	0.651	7.592
CaO	0.32	0.1	1.364	9.099
Na ₂ O	6.75	0.01	0.744	0.493
MgO	0.79	23.6	1.64	4.588
K ₂ O	2.47	0.05	3.559	2.856
TiO ₂	0.176	0.09	0.034	0.643
MnO	0.001	0.09	0.097	0.098
P ₂ O ₅	0.014	0.01	1.152	0.093
LOI	14.34	19.8	0.8	12.5

Ground RHA, NaOH, and distilled water were mixed at the ratios of $\frac{SiO_2}{Na_2O} = 1.5$ and $\frac{H_2O}{Na_2O} = 10$ to synthesis the alkaline activator solution. Based on the ratios, 3.33 gr of RHA, 6.95 gr of NaOH, and 20 ml of distilled water were mixed at 100°C for 2 hours. The resulting mixture was then passed through filter paper to separate the alkaline activator solution (Tchakoute et al., 2016).

Soil-geopolymer samples were synthesized by blending the sandy soil, main bed (zeolite, sepiolite, and red clay), and alkaline activator solution. 30% of the sandy soil was replaced with zeolite, sepiolite, and red clay, separately. Then 30 ml of the alkaline activator solution was employed to substitute for the optimal moisture in the samples. Table 3 shows the name of the experimental samples.

Table 3. The name of Soil-geopolymer samples

Specimen Code	Sandy Soil (%)	Main Bed (%)	Alkaline Activator (cc)
Zeo ^a ₃₀ S ^b ₇₀ A ^c ₃₀	70	30	30
Sep ^d ₃₀ S ^b ₇₀ A ^c ₃₀	70	30	30
Red ^e ₃₀ S ^b ₇₀ A ^c ₃₀	70	30	30

a = Zeolite

b = Sand

c = Alkaline Activator

d = Sepiolite

e = Red Clay Soil

Several soil-geopolymers and sandy soil samples were used as the adsorbents for Ni and Cd using batch and column experiments. A 0.01 M CaCl_2 solution was used as the electrolyte solution. CdCl_2 and NiCl_2 from Merck Company were utilized to production synthetic metal ions solution.

The sandy soil, zeolite soil-geopolymer, sepiolite soil-geopolymer, red clay soil-geopolymer, and zeolite geopolymer were applied to stabilize Ni and Cd. 0.1 g of each adsorbent and 10 ml of a heavy metal solution were mixed for 24 hours.

For each adsorbent, tests were repeated three times at the concentrations of 10, 20, 40, 60, 80, and 100 ppm of Ni and Cd. Also, for zeolite based geopolymer adsorbent, initial concentrations of Ni and Cd between 100-1000 ppm was investigated. The samples after equilibrium were filtered and diluted. Then, the metal concentrations were measured by an 800 Analyst Atomic Absorption Spectroscopy (AAS)- Perkin Elmer. Isothermal modeling was carried out to explain the adsorbate-adsorbent interaction and adsorption equilibrium (Kara et al., 2018). The adsorption data were fitted using Langmuir and Freundlich isotherm models. Also, adsorption curves and model's constant were obtained using GraphPad Prism v.7.04.

In the column test, the sandy soil, zeolite soil-geopolymer, and zeolite geopolymer adsorbents were employed at the Ni and Cd concentrations of 1000 ppm. Polyethylene tubes with an inner diameter of 2 cm and a height of 30 cm were utilized to produce adsorption columns (Majeed, 2017). To prevent the bed grains from exiting, the exit parts of the columns were blocked by a wire fabric. Grained soil with a mean diameter of 2 mm and a height of 5 cm was applied to the soil bed's underlying layer. Then, a paper filter was placed to prevent adsorbent washing. The adsorbent was applied onto the column at the height of 10 cm and became somewhat dense. In the next layer, grained soil was placed with a height of 5 cm. A total of six adsorption columns were fabricated and tested. Then, the columns were saturated with distilled water. The contaminated solutions were poured onto the column with a fixed flow rate. Leachate was collected at the time of 10, 30, 60, 60, 120, 150, and 180 min, and then concentrations of the heavy metals in leachate were measured.

RESULTS AND DISCUSSION

Removal percentages of Ni using the various adsorbents were studied, and the results were presented in Fig. 2. The sandy soil showed very small adsorption capacity. It exhibited an adsorption capacity of 2% at a 100 ppm concentration of Ni. However, all geopolymer samples exhibited an adsorption capacity of 100% in all Ni concentrations up to 100 ppm. Fig. 2b illustrates the adsorption results of the zeolite-based geopolymer adsorbent at high concentrations up to 1000 ppm. The geopolymer sample had significantly great adsorption capacity at high concentrations, yielding adsorption values of greater than 57%.

Isothermal models were utilized to describe the adsorption process. An adsorption isotherm signifies the specific relation between the equilibrium concentration of the adsorbate and its quantity on the adsorbent surface at a fixed temperature (Araujo et al., 2018). Fig. 3 and Table 4 provide the results of fitting experimental Ni adsorption data to the Langmuir and Freundlich models.

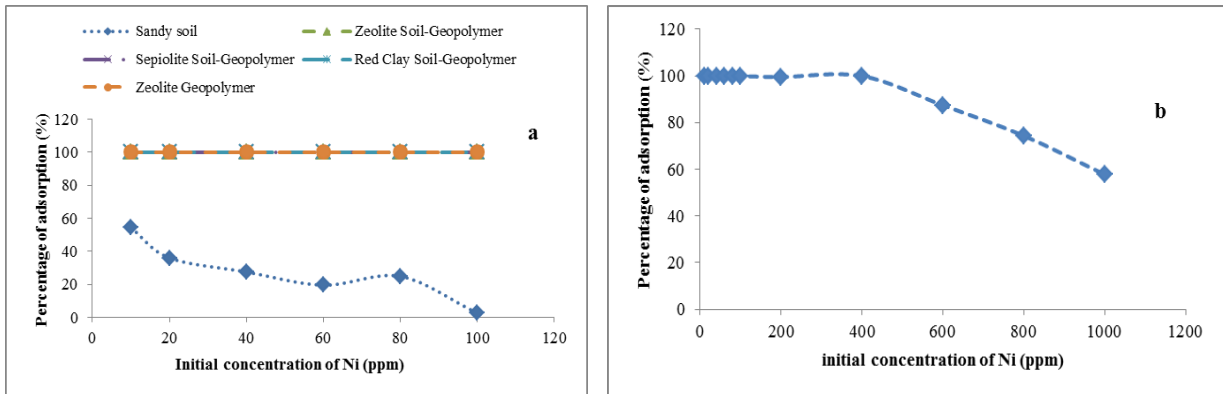


Figure 2. Percentage of Ni adsorption at different concentrations using (a) different adsorbents, (b) zeolite based geopolymer adsorbent

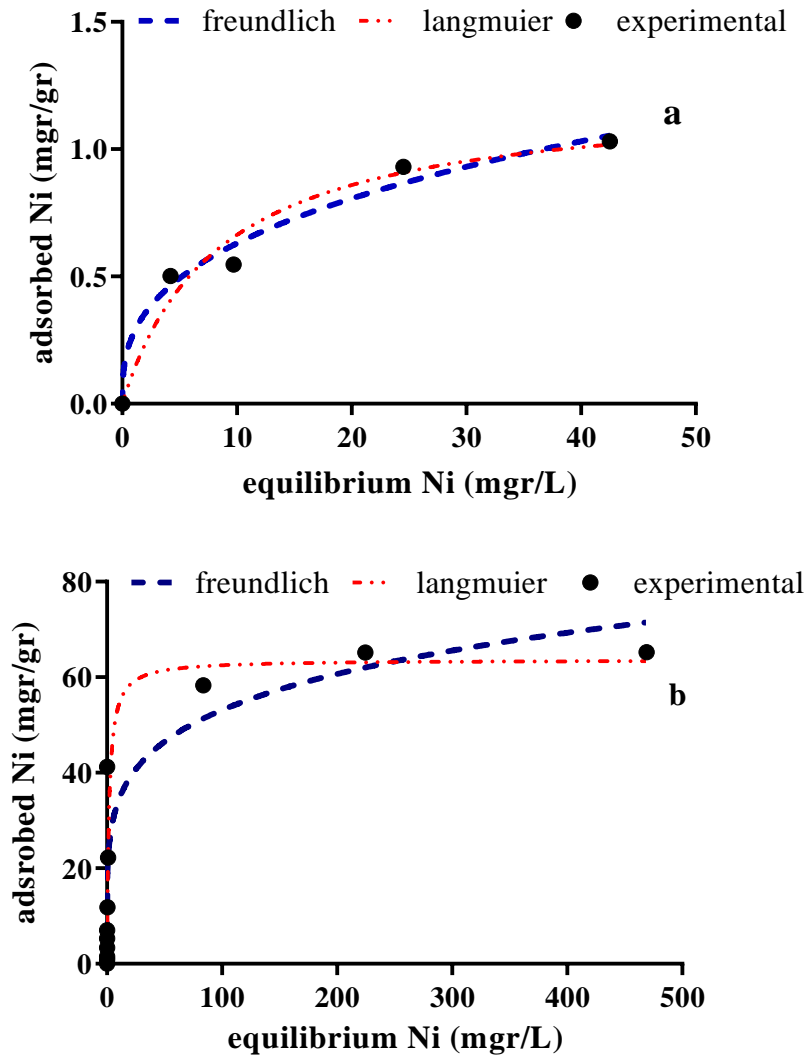


Figure 3. Results of fitting Ni adsorption data with Langmuir and Freundlich models for (a) sandy soil, (b) zeolite geopolymer

Table 4. Langmuir and Freundlich isotherms constants for adsorption of Ni using sandy soil and zeolite geopolymer

Langmuir Model	q_{\max} (mg/g)	K_L (L/mg)	R^2	$S_{v,x}$
Sandy soil	5.504 ± 2.759	0.0078 ± 0.005	0.9297	0.2329
Zeolite Geopolymer	63.62 ± 8.001	0.5605 ± 0.4594	0.7642	13.47
Freundlich	K_F	N	R^2	$S_{v,x}$
Sandy soil	0.1113 ± 0.4807	0.6687 ± 0.1049	0.951	0.1944
Zeolite Geopolymer	21.95 ± 9.159	0.1919 ± 0.07765	0.7497	13.88

The Langmuir model represents the single-layer adsorption process (Kalavathy et al. 2005). It is based on the assumes that the entire adsorption sites are at the same activity level, and have homogenous-energy surfaces and there is no interaction between the adsorbed molecules (Araujo et al., 2018). Thus, the better fitting results of the Langmuir model show monolayer sorption on identical homogenous sites on the active adsorbent surfaces (Aljeboreea et al., 2017). However, the Freundlich isotherm model is employed for heterogeneous adsorbent surfaces. The Freundlich model assumes the adsorbent surface has adsorption centers with different energies (Araujo et al., 2018). Thus, the better fitting results of the Freundlich model suggest that the adsorbent surface is heterogeneous and shows the exponential distribution of active sites and their energies (Ayawei et al., 2017).

The correlation coefficient R^2 was investigated in the adsorption analysis. A higher correlation coefficient represents a higher correlation between the experimental and modeling adsorption data and the suitability of the model for adsorption prediction. The correlation coefficient of the Ni adsorption on sandy soil was higher in the Freundlich model. Thus, the Freundlich isotherm model was selected to predict the Ni adsorption using sandy soil. Both R^2 -values for Ni adsorption using zeolite -based geopolymer showed in Table 4 were the same for Langmuir and Freundlich model, but Langmuir isotherm gave the best fit with the higher R^2 -value.

According to the results, the adsorption of the geopolymer adsorbent was obtained to 100% at a concentration of up to 100 ppm. It was also found to be very high at a concentration of up to 1000 ppm. According to the parameters of the Langmuir model, the maximum adsorption capacity (q_{\max}) for geopolymer adsorbent was higher than sandy soil. The affinity of the binding sites and energy of adsorption, K_L was obtained 0.007 and 0.56 L/mg for sandy soil and zeolite geopolymer, respectively.

The dimensionless constant separation factor, $R_L (= \frac{1}{1+K_L C_i})$ can be used to predict the affinity between the adsorbate and adsorbent. K_L is the Langmuir constant, and C_i is the adsorbate initial concentration. An R_L of 1 stands for the irreversibility isotherm, while An R_L of 0 represents the isotherm's linearity. Furthermore, An R_L of below 1 represents satisfactory metal ion adsorption, while An R_L of above 1 stands for unsatisfactory adsorption. In general, R_L between 0 and 1 represents satisfactory adsorption (Desta, 2013). Since the Langmuir constant was obtained to be a positive value for the sandy soil and zeolite geopolymer adsorbents, it is concluded that data fitting using the Langmuir model is favorable for both adsorbents.

The Freundlich isotherm parameters are K_F representing the adsorption capacity, and N is a function of the strength of adsorption in the adsorption process. N is dependent on the heterogeneity of the adsorbent surface. The deviation of N from unity indicates nonlinear sorption on heterogeneous surfaces. The value of N was lower than 1 for both adsorbents, suggesting this model is nonlinear.

Fig. 4 represents the percentage of Cd adsorption at the concentrations of 10-100 ppm. According to Fig. 4a, Cd was properly adsorbed at the concentrations of 10-100 ppm into the adsorbent surfaces. The sandy soil exhibited a very small adsorption capacity; while, geopolymer samples showed excellent Cd adsorption capacity. Hence, the capability of zeolite geopolymer adsorbent to remove the high concentration of Cd up to 1000 ppm was studied, as shown in Fig. 4b.

According to Fig. 4b, significantly high adsorption of Cd occurred for the zeolite geopolymer adsorbent. As can be seen, the adsorption capacity of approximately 96% happened at a concentration of 1000 ppm. The Cd adsorption of the geopolymer adsorbent was obtained to be 100% at a concentration of up to 100 ppm, while it was considerably high at a concentration of up to 1000 ppm, even higher than the Ni adsorption. El-Eswed et al. (2015) studied the stabilization process of Pb, Cu, Cd, and Cr in kaolin and zeolite-based geopolymers and showed efficient removal capacity of kaolin/zeolite -based geopolymer toward these heavy metals.

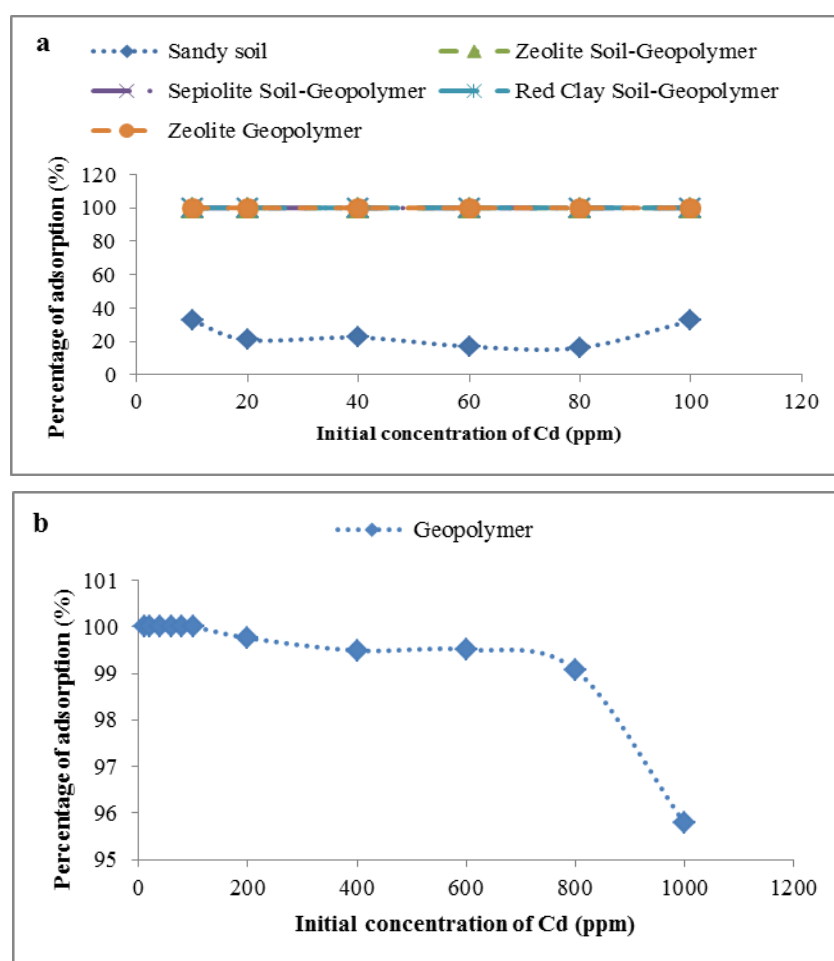


Figure 4. Percentage of Cd adsorption at different concentrations using (a) different adsorbents, (b) zeolite geopolymer adsorbent

Fig. 5 fits the experimental Cd adsorption data of the sandy soil and zeolite geopolymer to the Langmuir and Freundlich models. Table 5 shows the adsorption parameters of fitting the isotherm models to the experimental data obtained for Cd adsorption by the adsorbents.

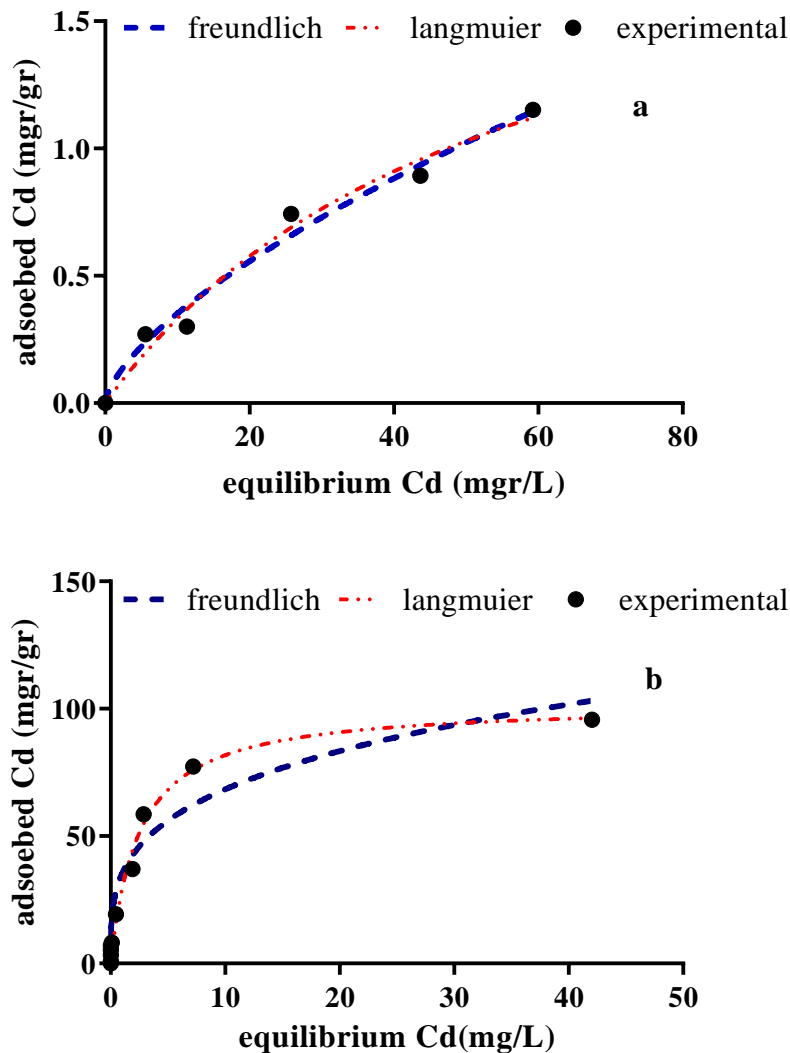


Figure 5. Results of fitting Cd adsorption data with Langmuir and Freundlich models for (a) sandy soil, (b) zeolite geopolymer

Table 5. Langmuir and Freundlich isotherm constants for adsorption of Cd using sandy soil and zeolite geopolymer

Langmuir Model	q_{\max} (mg/g)	K_L (L/mg)	R^2	$S_{v,x}$
Sandy soil	2.162 ± 0.4775	0.01817 ± 0.0007	0.9817	0.06625
Zeolite Geopolymer	102 ± 4.804	0.4030 ± 0.6236	0.9848	4.311
Freundlich Model	K_F	N	R^2	$S_{v,x}$
Sandy soil	0.07638 ± 0.0214	0.66330.07454	0.9828	0.06430
Zeolite Geopolymer	35.35 ± 4.113	0.28640.03974	0.9422	8.410

Both Langmuir and Freundlich models were suitable for describing the Cd adsorption using sandy soil and zeolite geopolymer adsorbents (Table 5). According to the parameters of the Langmuir model, the maximum adsorption capacity of the zeolite geopolymer adsorbent was higher ($q_{\max}=102$ mg/g) than sandy soil ($q_{\max}=2.16$ mg/g). The RL values of two adsorbents were obtained between 0, and 1 indicated Favorable adsorption. The K_f of the Freundlich model for Cd adsorption data using sandy soil and zeolite geopolymer was

obtained at 0.07 and 35.35, respectively indicated higher adsorption capability of zeolite geopolymer compared to sandy soil. The results of the N value revealed the heterogeneous surface of both adsorbents.

Fig. 6 depicts the leaching results of Ni and Cd at a concentration of 1000 ppm. According to Fig. 6, the sandy soil showed high leaching of Ni and Cd due to its low adhesion property and a weak reaction with the contaminants. In coarse-grained soils such as sandy soil, the mass transfer rate is high, and there is no interaction between pollutants and soil media. Thus, leaching in these soil types is high, and their adsorption capability is localized and small. In fact, coarse-grained soils have high pore speeds and large local variations.

zeolite-geopolymer and zeolite soil- geopolymer showed much less leaching of Ni and Cd than sandy soil. Since the texture of the soil directly influences the transfer rate of contaminants, the flow rate was very low in the soil-geopolymer and zeolite geopolymer, whose structures were strengthened by the formation of silica gels. Thus, the adsorbate had sufficient time to be trapped in the adsorbent structure, leading to a considerable leaching decline. The flow rate considerably affects adsorption and leaching (Ciosek & Luk, 2017). The flow rate was obtained to be 0.025, 0.006, and 0.0008 mL/s for the columns containing sandy soil, zeolite soil-geopolymer, and zeolite geopolymer, respectively. The flow rate is an important parameter for the estimation of using adsorbent for future continuous adsorption. It is associated with the contact between the adsorbent and the adsorbate. Higher adsorption occurs at a lower flow rate since it provides for the adsorbent a longer time to effectively bond with the metal (Podder & Majumder 2016). Hence, sand had high leaching and low adsorption as its flow rate was high, while the geopolymer showed minimal leaching since its flow rate was the lowest. Also, Podder and Majumder (2016) obtained a higher As adsorption at a lower flow rate.

Time is another parameter that considerably affects column adsorption. The ideal contact time between the adsorbent surface and adsorbate is important (Ciosek & Luk 2017). When the retention time is not long enough to obtain adsorption equilibrium, the adsorbent easily becomes saturated at the high flow rate, and consequently, adsorption is not completed (Podder & Majumder, 2016). Kara et al., 2017 investigated the column adsorption of heavy metals, including Ni and Zn using metakaolin- based geopolymer and it showed higher removal capacity for both metal ions in the earlier stage of the adsorption process. Afterward, ion concentrations in the leaching solution increased with a further increase in process time.

The column bed height is directly associated with adsorption. An increase in bed height enhances adsorption (Davood, 2018). As the flow moves along the column, the mass that enters the column is adsorbed into the active layers, and its concentration gradually decreases. The decreased mass at each point raises adsorption at the next point. Therefore, a higher bed height leads to a higher mass reduction and adsorption increase (Davood, 2018). Ciosek & Luk (2017) calculated a suitable ratio of the column bed height to the particle diameter to be larger than 20. This ratio was considerably larger than 20 in all the columns in the present study. Thus, it can be concluded that a suitable bed height was selected.

The shape and volume of the leaching curve versus time is an essential parameter in determining the dynamic and operating conditions of an adsorption column (Borna et al. 2016). In the sandy soil leaching diagram, the curve slope is initially high but reduced over time and became almost zero (a horizontal line) at the end. An explanation for the high slope in short times is the insufficient retention time and incompleteness of adsorption equilibrium, which enhances leaching (Podder & Majumder, 2016).

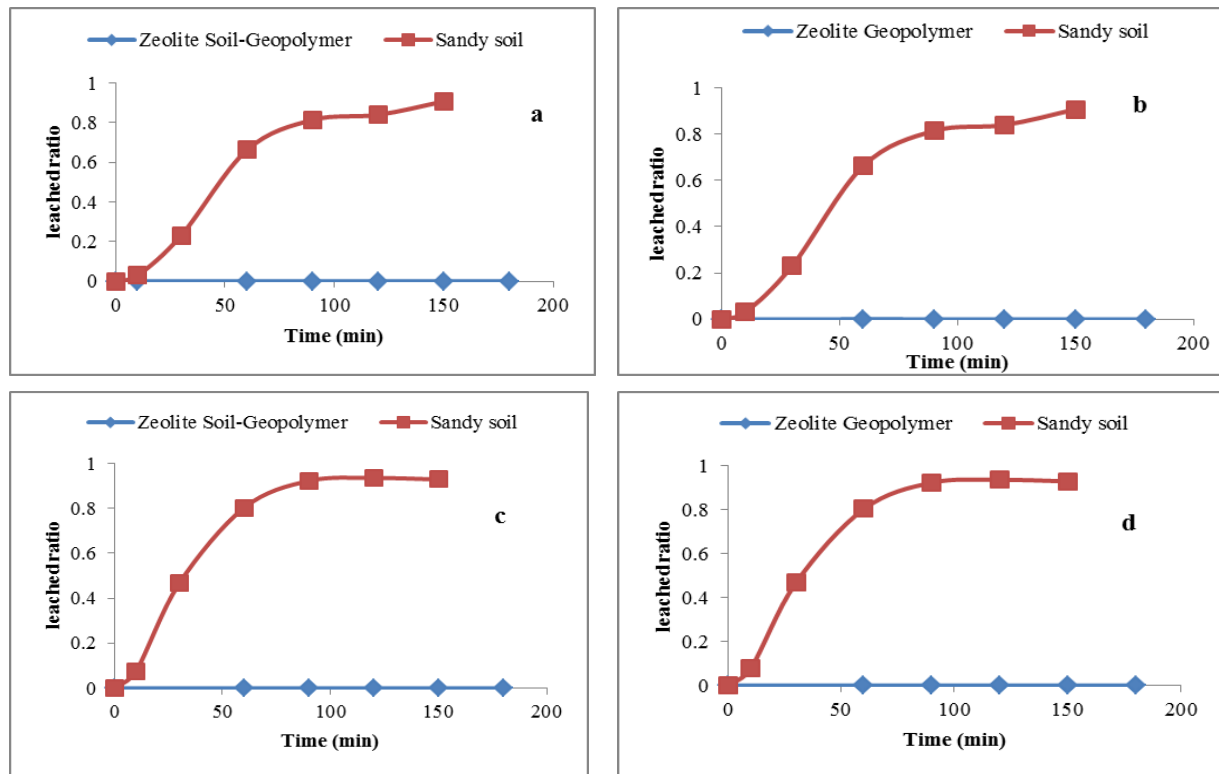


Figure 6. Results of column adsorption data of (a,b) Ni and (c,d) Cd

Adsorption percentage of Ni and Cd at concentrations of 10-1000 ppm using different adsorbents is shown in Table 6. As can be seen, adsorbents had higher Cd adsorption capacity than Ni. The stabilization of heavy metals in a geopolymer matrix is affected by different parameters that influence the metals solubility, including the heavy metal nature, the raw material properties of the geopolymer, pH, and alkaline activator (Vu & Gowripalan, 2018). Hence, there is no exact mechanism for metal stabilization in geopolymer matrixes. El-Eswed et al., (2017) showed the atomic radius of heavy metals is the important reason for the stabilization of heavy metals using geopolymeric materials. The atomic radius of an element is the distance from the center of the nucleus to the boundary of the surrounding shells of electrons. In the stabilization comparison of metals with the same type of electric charge, the atomic radius is an important factor in the description of the adsorption results. Adsorption of metals having a large ionic radius is stronger than that of metals with smaller ionic radius (Bohli et al., 2013). Phair & Van-Deventer (2001) studied the stabilization of Cu and Pb using ash geopolymer adsorbents. They reported that Cu exhibited lower stabilization in the geopolymer structure due to its smaller atomic radius. Thus, to describe the Ni and Cd adsorption results in this study, it can be said that Cd has a higher adsorption than Ni due to its larger ionic radius. Therefore, it is revealed that the adsorbents had higher Cd adsorption capacity than Ni.

Table 6. Percentages of Ni and Cd adsorption with different studied adsorbents

Initial concentration (mg/L)	Adsorbent	Ni adsorption (%)	Cd adsorption (%)
10-100	Zeolite Geopolymer	100	100
	Zeolite Soil-Geopolymer	100	100
	Sepiolite Soil-Geopolymer	100	100
	Red Clay Soil-Geopolymer	100	100
100-1000	Zeolite Geopolymer	57.78	95.79

Fig. 7a demonstrates the Scanning Electron Microscopy (SEM) image of the sandy soil. As can be seen, the sand structure was composed of fine crystalline grains. The fine crystalline grains arose from the crystalline albite phase (Ulloa et al., 2018). Stabnikov et al., (2013) evaluated the SEM images of untreated sandy soil and described the structure of the sandy soil to be composed of closely-bonded fine grains. According to Fig. 7b, the zeolite geopolymer specimen had a coherent structure since the geopolymer gel functioned as an adhesive and bonded the soil particles, enhancing the strength and hardness (Zhang et al., 2015). Lier et al., (2017) studied the SEM images of a synthesized geopolymer of fly ash and sandy soil. They observed that the geopolymer generated a strong structure in the final product.

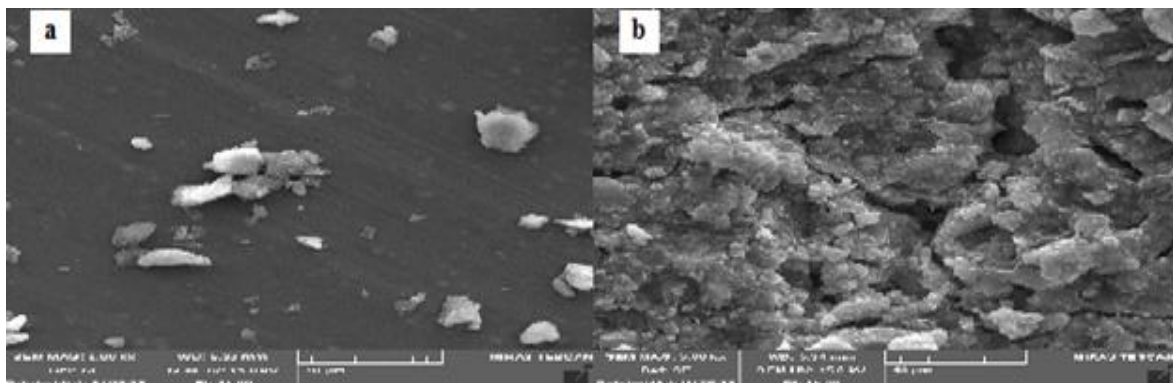


Figure 7. SEM analysis for (a) sandy soil and (b) zeolite geopolymer

CONCLUSION

The sandy soil is problematic and loose soil. Thus, it lacks adhesion and is readily leached, transmitting heavy metal contaminants. It is very weak in terms of stabilization, strength, and heavy metal adsorption. The ability of sandy soil compared to sandy soil stabilized with geopolymer in adsorption and release of nickel and cadmium was investigated. Results showed zeolite, sepiolite, and red clay soil-geopolymer adsorbents were able to remove 100% of contaminants at a concentration of up to 100 ppm. Furthermore, the zeolite geopolymer adsorbent adsorbed up to 60% of Ni ions at a concentration of 1000 ppm, and up to 96% of Cd ions at a concentration of 1000 ppm.

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CONFLICT OF INTEREST

The authors declare that there is not any conflict of interests regarding the publication of this manuscript. In addition, the ethical issues, including plagiarism, informed consent, misconduct, data fabrication and/ or falsification, double publication and/or submission, and redundancy has been completely observed by the authors.

LIFE SCIENCE REPORTING

No life science threat was practiced in this research.

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