



Physicochemical characteristics of Sepiolite and Vermiculite clay soils as landfill clay liners

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ABSTRACT: The liners are the principal components of solid waste landfills which have the main role in controlling the spread of pollution through the landfills. The high cost of artificial materials and their un-usability in large projects for preventing leaks is a major concern that has led to more attention to natural liner materials with low permeability and effective adsorption and stabilization condition. Clay minerals have a high capacity to adsorb heavy metals due to their high specific adsorption levels and bonding sites with numerous negative charges. Along with absorption properties, clay soils should have suitable hydraulic and geotechnical properties as landfill liners. Therefore, this study aimed to evaluate the efficiency of 5 types of soil (vermiculite clay, sepiolite clay, silty soil, silt+clay mixtures as 90% silt and 10% clay) as clay liner. The chemical, physical and mechanical properties of the study soils were evaluated to address the quality of soils as a landfill liner. The results showed that in terms of environmental quality (pollutant adsorption), soils containing sepiolite clay had a better adsorption capacity to adsorb cations rather than vermiculite clay soils. From a physical and mechanical point of view, soils containing sepiolite clay compared to vermiculite clay soil revealed a variety of landfill liner characteristics in terms of strength, permeability, and plasticity properties, respectively. Based on the technical and economic perspective, the silt and sepiolite mixtures supply good features which may justify their potential use as a liner material in solid waste landfills.

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1- Introduction

Sustainable landfilling of residual waste (after recycling, reuse, and other manners of volume reduction) is defined as a concept of the safe disposal and subsequent degradation of waste within a landfill, with limited pressure on the environment and by the most financially efficient method [1].

The most commonly reported health hazards in the vicinity of landfills are groundwater contaminated by waste leachate [2]. Landfills are designed and constructed with liners to avoid contaminants transverse into the ground. Liner is a compacted clay layer (CCL) and geosynthetic materials of various designed thicknesses preferred to the specified landfills [3].

Landfill leachate contains a large variety of pollutants at very different concentrations, and there will be competitive adsorption as these pollutants are transported through the landfill's compacted clay liner (CCL) [4]. Compacted clay liners (CCLs) are the simplest and most widely used impermeable layers for use in landfills to prevent the infiltration and flow of waste leachate [5]. Natural clay minerals are widely used in various environmental protection technologies as cheap, accessible, and effective sorbents [6, 7].

Research on a variety of clay materials such as meerschaum [8], meerschaum-treated olivine [9], shale [10], chlorite, vermiculite [11], montmorillonite [12], zeolite [13], sepiolite [14] has been done as a landfill liner; each of them has its advantages and disadvantages according to the geo-environmental conditions. The performance of clay liners is usually measured in terms of hydraulic conductivity, flexibility, and strength. These factors are controlled by the soil structure and can be altered during the life of the clay liner. Many clay soils including bentonite soils were used as liners at the landfill sites, which high compaction and plasticity resulted in that are not being used directly as liner materials and are not suitable [15].

The sustainability of landfilling may be studied in most circles of sustainability but the environmental impacts of landfills (limiting or preventing the direct and indirect emissions) may be considered as crucial [14, 16]. Using low permeability soils in landfill liners is a guaranteed leachate control and prevents leakage which causes environmental pollution. In this matter, the application of natural materials provides more capable filters that are used for reducing leachate pollutants and modifying the geotechnical properties of liners [17].

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The results of the current studies indicated that sepiolite is the dominant material that affects both the geomechanical and geo-environmental properties of liners. An increase in sepiolite content increased the strength, swelling potential, and metal adsorption capacities of the soil mixtures. Moreover, the hydraulic conductivity of the mixtures decreased significantly with the addition of sepiolite [14]. Vermiculite, as a natural hydrate mineral, is one of the most competitive candidates for materials in various areas including wastewater treatment, energy-saving building, green agriculture, etc. [18, 19].

The low cost, ease of implementation, natural presence in most regions, and attenuation capacity of clay liners makes them more attractive than geosynthetic liners on their own in landfill liner systems, particularly in low-income countries. However, clays are very diverse in their physicochemical properties and the suitability of the clayey substratum as a potential liner must be properly evaluated [16]

In this study, the feasibility of two natural clayey substrates along with mixing with silty soils fractions as landfill liners was evaluated. Their physicochemical, mineralogical, and geotechnical characteristics were studied and the results were discussed in terms of strengths and weaknesses as candidate materials for landfill liners. Finally, the potential for attenuation of pollutants in leachate by clay soil materials was evaluated for sustainable landfill applications. The aim was to characterize the relevant properties of the different clays to identify those which are geotechnical stable and effective in pollutant attenuation for liner design. This is essential to prevent pollution of the environment and protect human health from leachate spreading over groundwater aquifers or adjacent rivers and lands. The mixing with silt fraction was investigated to assess the effect of it on a better clay implementation in the field in regard to shrink/ swell and compaction properties.

2- Materials and Methods

2- 1- Study soil samples

Soils were collected from native Iranian natural resources; so that sepiolite clay from northeast Iran (Fariman, Khorasan Razavi), vermiculite clay from southeast Iran (Jiroft, Kerman), and silty soil were sampled from the Sirjan University of Technology campus.

Characteristics of soil samples include sepiolite clay (S), vermiculite clay (V), silty soil (Si), a mixture of silt and sepiolite clay soil (10% silty soil and 90% sepiolite clay) (SS), and a mixture of silty soil and vermiculite clay (10% silt and 90% vermiculite clay) (VS); were measured and analyzed as natural landfill liner. The experiments are based on the portion of soil passing a 2 mm sieve and oven-dried at 105 to 115°C

2- 2- Soil samples characterization

Hydrometer test to determine the soil particle size distribution and soil classification (ASTM D422 [20]), Atterberg limits or consistency limits of remolded states (plastic, and liquid limits) (ASTM D4318 [21]), the particle size of the soil solids density (specific gravity of soil solids)

using water picnometry (ASTM D 854 [22]), Unconfined Compressive Strength (UCS) for unconfined cylindrical specimen of soil the axial compression test (ASTM D 2166 [23]), different dynamic-compaction energies were applied to the sepiolite mixture specimen: 596 kJ/m³ for the Standard Proctor SP; 2680 kJ/m³ for the Modified Proctor MP; 5360 kJ/m³ for double energy of Modified Proctor MP (ASTM D698 [24]). The objective of these tests was to define the optimum water contents, which lead to the highest dry densities for given energy input, and permeability coefficient by the falling head permeability test (ASTM D 2434 [25]). The pH of soils in the saturated extract was measured by a pH meter [26]. The cation exchange capacity of soil samples was measured [27]. Gypsum was determined by acetone method [28], and equivalent calcium carbonate by reverse titration with sodium hydroxide [29]. Elemental analysis of the clay soils was performed by X-ray fluorescence spectroscopy made in the Netherlands by the PHILIPS Company (PW1410 model). The most common method of identifying clay minerals is to use X-ray diffraction [30, 31]. X-ray diffraction (XRD) analysis was performed using the PHILIPS PW1730 model with a K-Cu beam on air-dried powder samples.

2- 3- Adsorption experiments

The adsorption of the metals in the soils was assessed using the standard batch equilibration method [32, 33] with different concentrations (10, 20, 40, 60, 80, and 100 mg/l). The concentrations of nickel and cadmium in the filtered solutions were measured by atomic absorption spectrometer apparatus with 3 replications. The difference between the initial and the residue concentration of the element indicated the amount of element adsorbed by the study soils. The obtained data were then fitted using adsorption isotherms.

Adsorption isotherms are equations that show the distribution of the adsorbed material between the dissolved phase and the adsorbed in an equilibrium state and are characteristic of the system at a given temperature. Among isothermal models, Freundlich and Langmuir's isotherms are the most widely used. Therefore, Freundlich and Langmuir's isotherms were used to plot the adsorption data. Two parameters q_e and C_e are used to describe the equilibrium status.

2- 3- 1- Freundlich model

Equation (1) shows the nonlinear equation of the Freundlich isotherm.

$$qe = KC_e^{1/n} \quad (1)$$

q_e : Adsorption capacity at equilibrium time in mg/g.

C_e : Equilibrium concentration in mg/L.

K: Freundlich constant obtained by plotting C_e/q_e versus C_e .

n: Freundlich constant obtained by plotting log versus $\log C_e$ and showing the adsorption capacity.

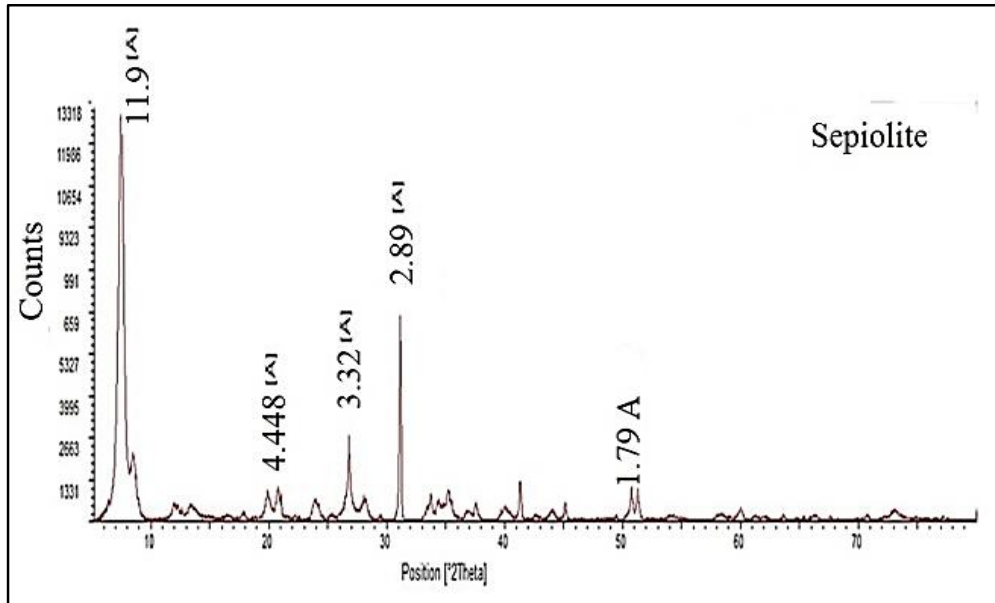


Fig. 1. X-ray diffraction analysis of Sepiolite soil (S)

2- 3- 2- Langmuir model

Equation (2) shows the principal equation of the Langmuir isotherm [33].

$$qe = \frac{Q_M K_L C_e}{1 + K_L C_e} \quad (2)$$

C_e : Equilibrium concentration in mg/L.

Q_M : The amount of monolayer adsorption capacity in the Langmuir model.

K_L : Langmuir constant in mg/L.

In general, the process of adsorption of ions from the solution by an adsorbent is a multi-step process and includes:

I: Dispersion of ions from the dissolved phase on the adsorbent surface;

II: Scattering of metal ions from the boundary layer on the adsorbent surfaces;

III: Transfer of ions from the surface to the interior spaces of the adsorbent (dispersion within the mass);

IV: Adsorption of ions on active sites of adsorption through chemical reactions such as ion exchange, complex formation, etc. [34].

3- Results and Discussion

3- 1- Characteristics of the study soils

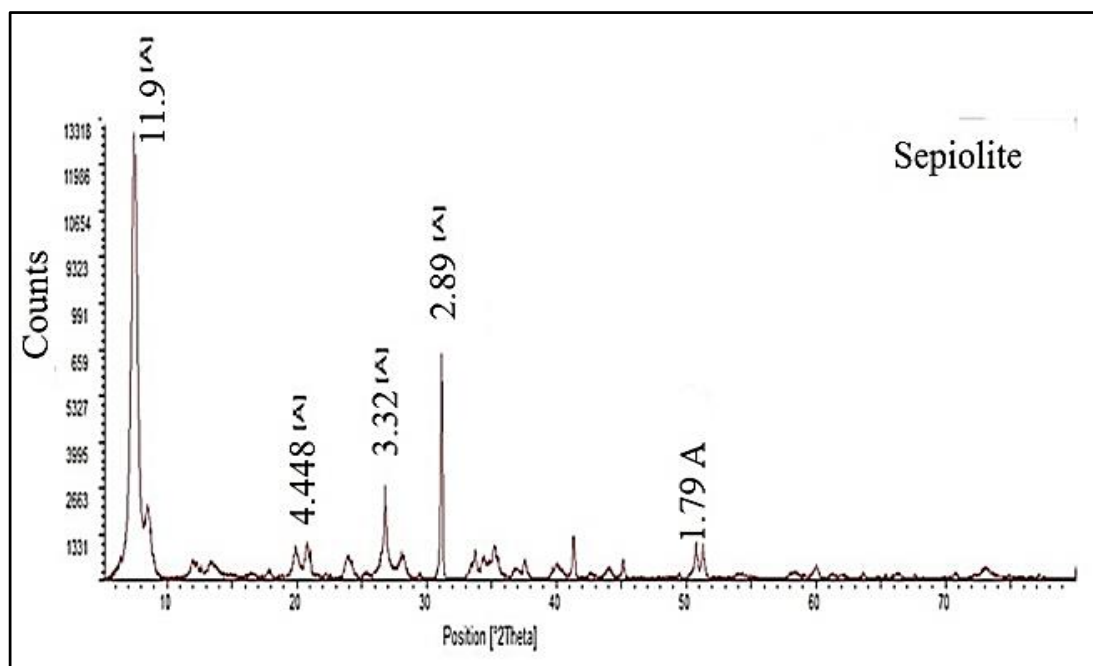
Sepiolite is a fibrous phyllosilicate, whose chemical formula is $Si_{12}O_{30}Mg_8(OH)_4(OH_2)_4 \cdot nH_2O$. Sepiolite structure is formed by sheets similar to 2:1 mineral groups, but the tetrahedra undergo a periodic inversion (every 6 tetrahedra) along the b- axis, leading to channels with dimensions of 3.6 Å × 10.6 Å, which contains both physisorbed and zeolitic water. The structure of sepiolite gives rise to materials with a high adsorption capacity both on the fiber surfaces as well as into the nanochannels [35]. Sepiolite mineral, due to its structural properties, has unique properties including high porosity and specific surface area, strong adsorbent, and special rheological properties.

Figure 1 shows the X-ray diffraction analysis of the sepiolite clay soil; X-ray diffraction shows the presence of sepiolite (86%) as the main phase, dolomite (11%), and muscovite (less than 3%) as impurities. The presence of sepiolite was ascertained by the peak intensity of the 11.9, 3.32, and 1.79 Å reflections.

The results of the elemental composition of sepiolite clay as oxide (percent) by X-ray fluorescence are given in Table 1. The results show that sepiolite clay is a magnesium- silicate mineral that has a high content of silicon and magnesium. The most constituent element of this clay is SiO_2 with a 52.9% value.

Table 1. elemental analysis of sepiolite soil by X-ray fluorescence

Elements	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	Na ₂ O	MgO	K ₂ O	TiO ₂	MnO	P ₂ O ₅	LOI
Soil Type	%										
Sepiolite (S)	52.9	2.56	1.23	0.10	0.01	23.6	0.05	0.001	0.09	0.01	2.08
Vermiculite (V)	48.96	3.50	5.78	4.76	0.82	28.11	0.212	0.027	0.128	.014	7.50

**Fig. 2. X-ray diffraction analysis of Vermiculite soil (V)**

Vermiculite clays are produced when their crystals are exposed to high temperatures. The general chemical formula of vermiculite is $(Mg^{2+}, Fe^{2+}, Fe^{3+}) 3[(SiAl)_4O_{10}] OH_2.4H_2O$ [36]. Its density is in the range of 2.2-2.5 g/cm³. Vermiculite has a remarkable ion exchange capacity that can be used to prepare materials for the extraction of heavy metals, salts from water, as well as the adsorption of various contaminants. The laminar structure of the vermiculite makes it highly lubricating over a wide range of temperatures; therefore, it can be used as a fire-resistant material, a filler of lightweight porous materials for thermal insulation, as a thin inorganic membrane for coatings, as well as mineral fillers for composite clay polymers [37].

The results of vermiculite elemental composition in Table 1 show that vermiculite clay is an aluminosilicate mineral and the most constituent of this soil is SiO₂ with an amount of 48.9% and also the results of semi-quantitative X-ray diffraction analysis (Figure 2) demonstrate the presence of vermiculite mineral (61%), as the main phase and the minerals

of muscovite (13%), talc (5%), dolomite (5%), calcite (8%) and gypsum (1%) as impurities. The presence of vermiculite was ascertained by the peak intensity of the 7.2, 3.59, and 1.69 Å reflections.

XRD of silty soil is shown in Figure 3, whose semi-quantitative analysis indicates about 25% quartz (Qz), 20% mica (Mi), 17% 2: 1 phyllosilicate (chlorite) (2:1), 25% feldspar (Fd), 13% calcite (Ca)/dolomite (Do) minerals.

3- 2- Physical and mechanical properties of soils

3- 2- 1- Atterberg limits and soil activity

The Atterberg limits of the study soils are shown in Table 2. In general, the plasticity index of a soil depends on two factors:

I: Weight percentage of clay particles less than 2 microns; the higher the clay, the more plasticity Index,

II: The type of clay minerals in such a way that at the same weight percentage,

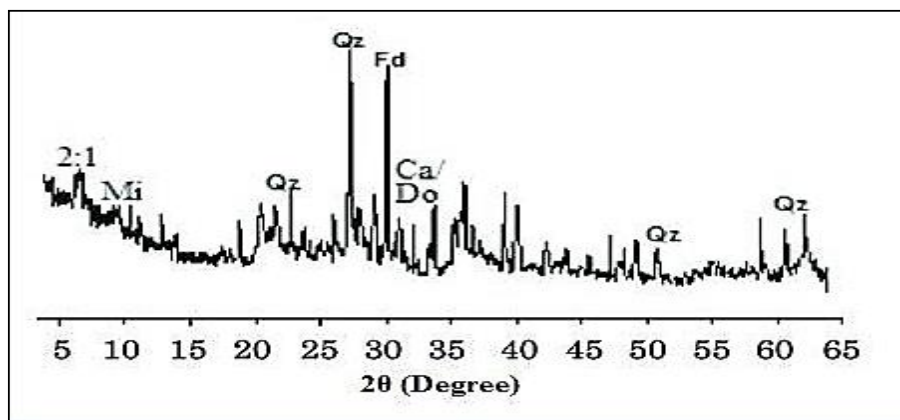


Fig. 3. X-ray diffraction analysis of silty soil (Si)

Table 2. Atterberg limits and activity of study soils

Soil type properties	Sepiolite (S)	Vermiculite (V)	Silt (Si)	Sepiolite+Silt (SS)	Vermiculite+Silt (VS)
Shrinkage Limit (SL)	57.2	31.1	15.3	19.8	18.0
Plastic Limit (PL)	87.2	38.3	22.0	21.5	19.1
Liquid Limit (LL)	101	48.6	21.1	31.6	25.7
Plastic Index (PI)	14.0	10.3	2.10	10.1	6.67
Activity	1.60	2.01	0.70	1.20	1.12

According to the results given in Table 2, the liquid limit of the mixtures (SS and VS) is higher than the pure silt; However, its plasticity limit has decreased, and the reason for this is that if the percentage of clay particles in the soil increases, the amount of water adsorbed by these particles increases and the soil mass must adsorb more moisture as free water to reach the liquid limit. Therefore, with increasing the percentage of clay, the liquid limit of soils increases, and also the presence of clay particles and surface adsorption of water is the cause of plasticity behavior and non-cracking of soil mass. Thus, the more clay particles there are, the slower the soil cracks and the lower the moisture content, resulting in a decrease in the plasticity limit [38].

The soil activity parameter is used to compare the ability of clays to produce a plastic property. The amount of activity can be shown according to Equation (3):

$$A = \frac{PI}{2\% \mu m} \quad (3)$$

Where PI is the plastic index of clay soil and % 2µm represents the mass percentage of particles smaller than 2 microns.

Activity is a criterion for identifying the swelling potential of clay soils [39]. According to the specified range for soil activity, if the activity number is less than 0.75, the soil is in the inactive clay group. If the activity number is ranging from 0.75 to 1.25, the soil is classified in the semi-active clay group. And if the activity number is more than 1.25, the soils are classified in the active clay group. According to equation 3, the activity values of vermiculite and sepiolite clays are equal to 2.01 and 1.60, respectively. Therefore, these clay soils are in the range of active soils and have a more plastic index than other soils that are in the kaolinite and illite clay minerals group. The silt with clay activity of 0.7 is in the inactive soil range and the mixture of clays with silt is considered semi-active according to the defined range of soil activity.

3- 2- 2- Soil Compaction

Maximum dry density and optimum moisture contents are among the most important mechanical properties of the soil used as liners. The soils with the higher maximum dry density

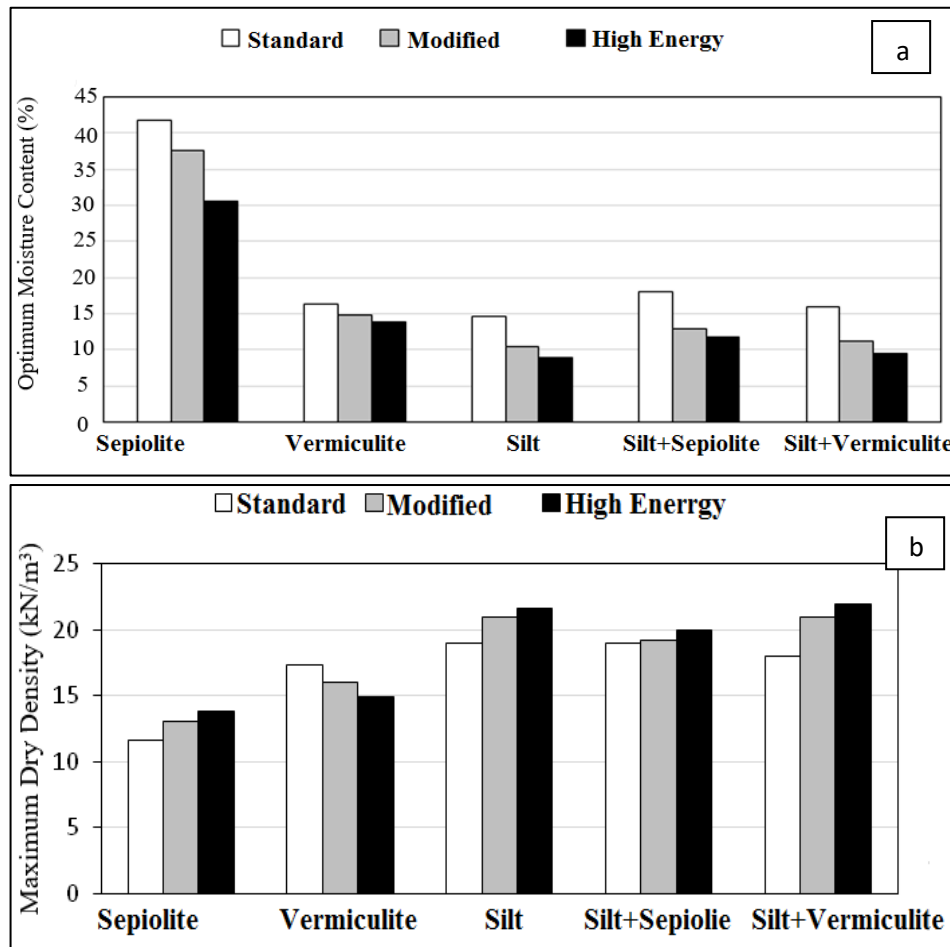


Fig. 4. Changes in soil moisture in the compaction with different energies, a) Optimum moisture content, b) maximum dry density

at the lowest moisture content are the more cost-effective material to assess as a liner. The results of compaction tests at different energies for different soil samples are presented in Figure 4. According to these diagrams, the highest dry densities belonged to the lowest moisture content. By adding silt to the clay soils and consequently increasing the average particle size, the amount of dry density of the soil mixture increases more than clay soil samples with compaction. The reason for the increase in density is the higher volumetric mass of the silt particles and the filling of the soil pores among particles with clay materials and water due to the appropriate density. Another noteworthy point is that with increasing the weight percentage of silt and decreasing the available clay particles, the amount of water adsorption and moisture content of the soil mixture decreases; therefore, mixed materials are better materials in terms of compressibility [40] to the extent that it does not have a negative effect on soil pollutant adsorption.

As can be seen, with increasing compaction energy, the percentage of moisture decreases, and the maximum dry density increases; during the compaction process, the soil particles come closer together and air between them escapes. The compaction in cohesive soils is the breaking

of electrochemical connections and sometimes clay plates and displacement and the collapse of these plates in each other, while, the reason for compaction in the other soils is the displacement of grains and the rolling of grains in and towards each other. With the higher soil plastic property, the soils will be more sticky and its compaction is more difficult [41]. As shown in the figure, sepiolite (ML), vermiculite (ML), and then a mixture of them have a more difficult density, respectively.

3- 2- 3- Unconfined Compressive Strength (UCS)

As the compressive strength increases, the bearing capacity of the soil increases, as well. The UCS of the studied soils at different compaction energies is shown in Figure 5. The amount of UCS increases with increasing density; with increasing density, the contact and friction surface between the particles increases, then the soil will be more resistant to the stresses [42].

The highest UCS is related to SS (Figure 5e), S (Figure 5b), VS (Figure 65d), Si (Figure 5a), and V samples (Figure 5c), respectively. Ternan et al. (1996) identified clay as a mortar among soil particles and found that as the amount of

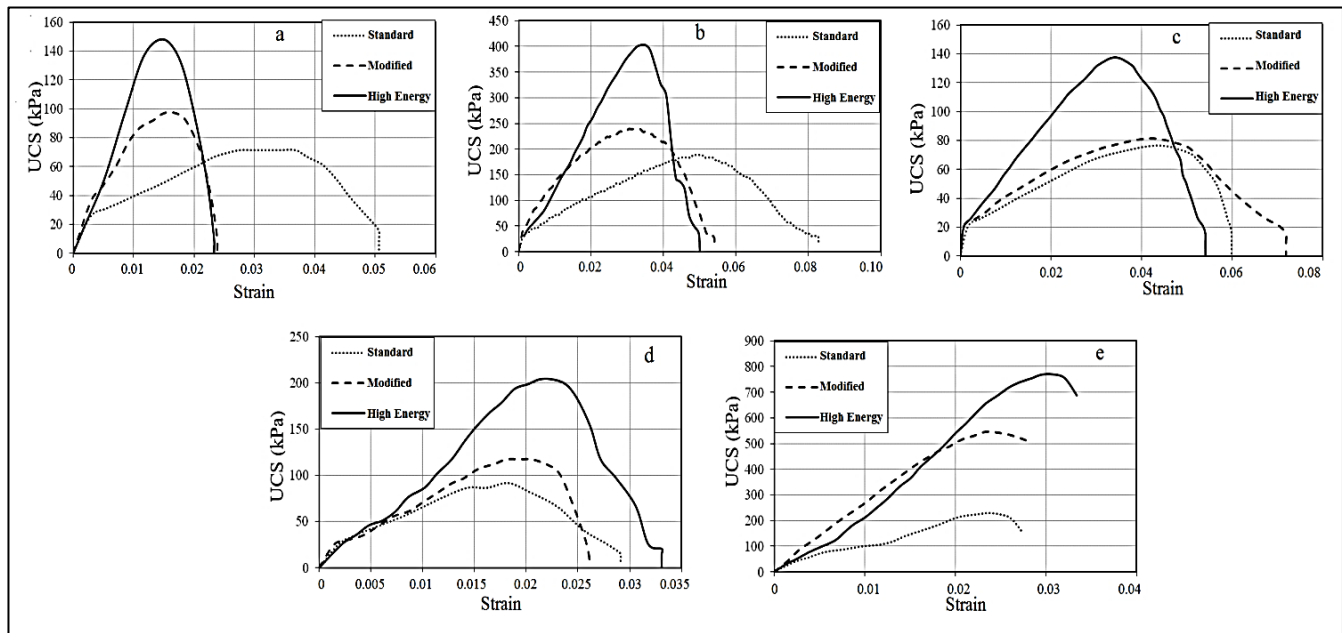


Fig. 5. UCS of soil samples: Si (a), S (b), V (c), VS (d), and SS (e)

Table 3. Hydraulic conductivity coefficient of study soil samples (cm/s)

Si	S	V	SS	VS
1.8×10^{-6}	7.0×10^{-8}	5.6×10^{-8}	3.1×10^{-7}	2.6×10^{-7}

clay increased, the stability of the soil structure increased [43]. For this reason, the strength of the silt-clay mixture is higher than that of the silt alone. However, the difference in the strength of the SS sample with the VS sample is due to the variety of clay structures (sepiolite and vermiculite). The composition of the clay minerals affects the soil structure and affects the mechanical strength of the soil. On the other hand, the structural stability of soils with predominant 2:1 clay values may increase their resistance to erosion [44].

Daniel and Wu (1993) suggested that the UCS of 200kPa or greater is required for a liner; it can be inferred that the SS sample at all three compression energies and the Sepiolite at modified and high energy compaction and the VS sample at only high energy energies compactions met required values [45].

3- 2- 4- Permeability characteristics

The permeability of compacted clay soils is affected by several factors such as sample moisture content, degree of saturation, compaction method, compaction energy, hydraulic gradient, clay aggregate size, pore size distribution, chemical properties of the fluid passing through pores, age and size of testing samples, type of instrument, flow direction, etc. [46].

Bayram and Bahmani (2015) stated that in general, as the plasticity of the soil increases, saturated hydraulic conductivity decreases due to the fineness of soil particles [47].

Permeability testing was performed on all 5 soil types (table 3); the sepiolite and vermiculite clay soils met the permeability values for landfill liners, which have been reported to be 1×10^{-7} cm/s [48].

3- 3- Elemental adsorption characteristics

Figures 6 to 10 show the fitting of the data obtained from the adsorption of nickel and cadmium on the studied soils by Freundlich and Langmuir models which are classified as L type following the classification proposed by Giles et al. (1960) [49], indicating a high tendency for soils to adsorb nickel and cadmium at low concentrations. With increasing concentrations of nickel and cadmium in solution, the slope of the graphs has decreased, which indicates a decrease in adsorption with the increasing concentration due to the occupation of adsorption sites by two heavy metals. Also, the pattern of nonlinear changes in nickel indicates limited adsorption of nickel and high adsorption tendency at low concentrations.

The two parameters that can be mentioned in the Freundlich equation are the constants K_F , and $1/n$, which indicate the adsorption energy [50]. According to the results in Table 4, the highest values of K_F in the soils of S, SS, and VS are related to cadmium elements, and in the soil of vermiculite and silty soils are related to nickel elements. The deviation of $1/n$ coefficient from the number one also indicates nonlinear adsorption of adsorbed heavy metal on the adsorbent.

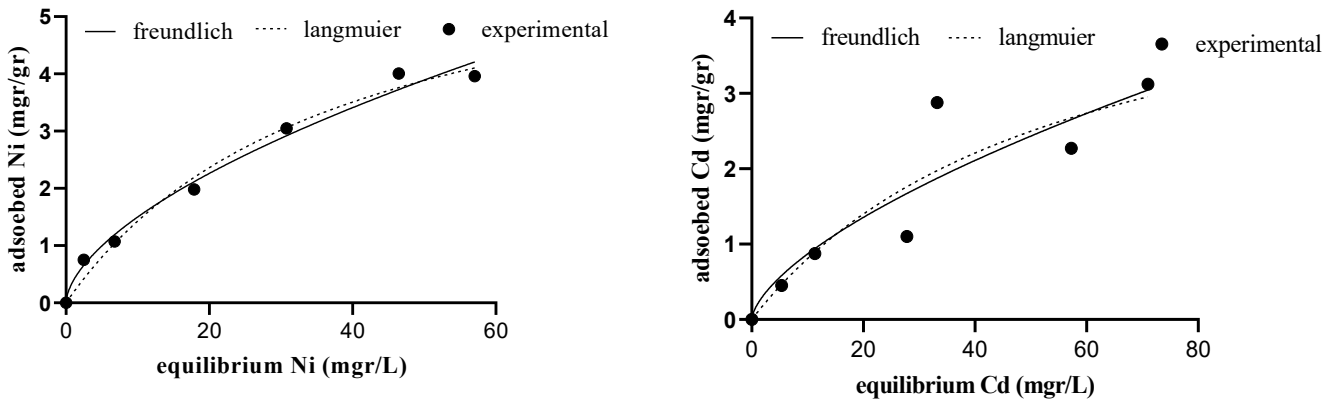


Fig. 6. Fitting of Langmuir and Freundlich models to adsorption data by vermiculite, a) Nickel, b) cadmium

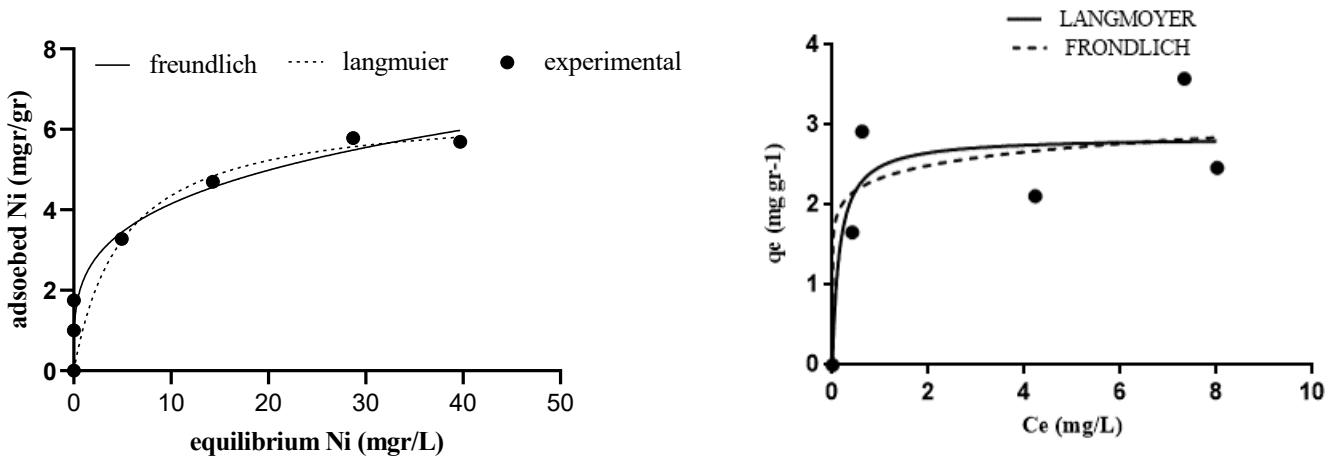


Fig. 7. Fitting of Langmuir and Freundlich models to adsorption data by sepiolite, a) Nickel, b) cadmium

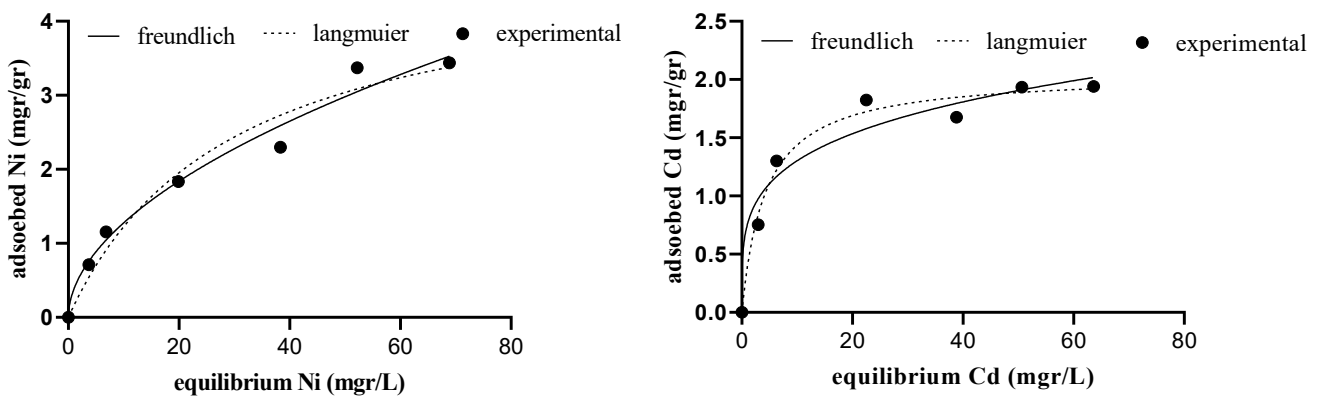


Fig. 8. Fitting of Langmuir and Freundlich models to adsorption data by VS, a) Nickel, b) cadmium

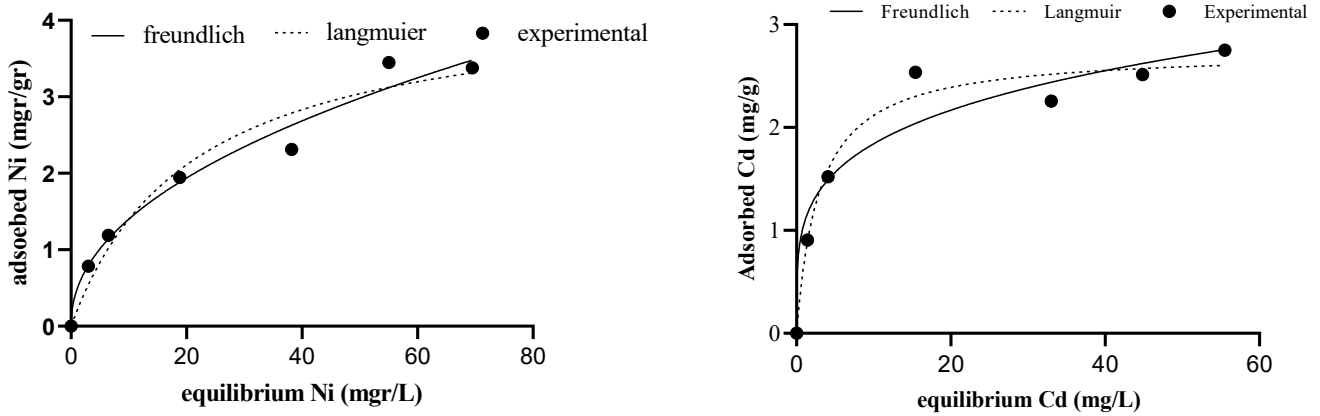


Fig. 9. Fitting of Langmuir and Freundlich models to adsorption data by SS, a) Nickel, b) cadmium

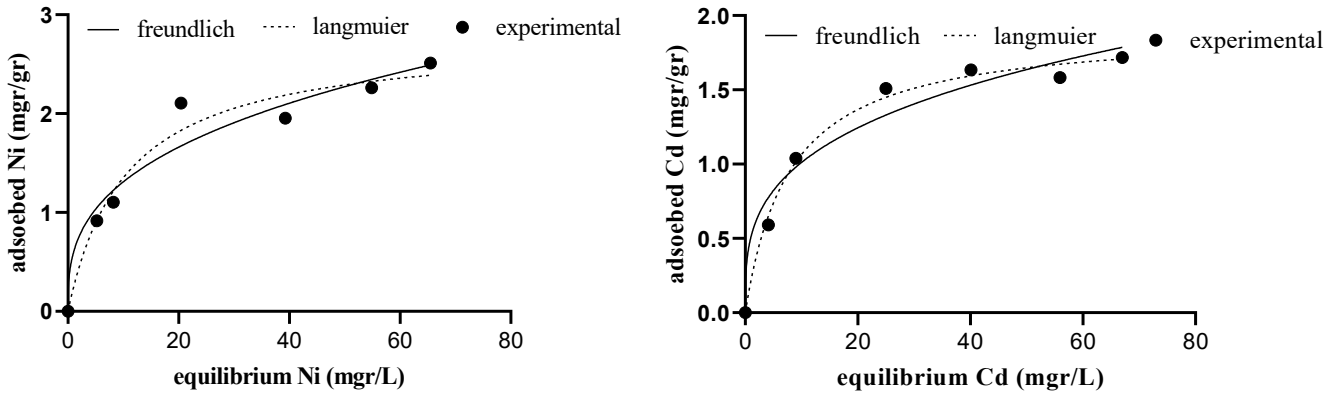


Fig. 10. Fitting of Langmuir and Freundlich models to adsorption data by silt, a) Nickel, b) cadmium

Table 4. Parameters and correlation coefficients obtained from the fit of the Freundlich model of nickel and cadmium adsorption data by the study soils

Heavy metals Adsorbents	Nickel			Cadmium		
	K_F	$1/n$	R^2	K_F	$1/n$	R^2
S	2.256	0.26	0.87	2.655	0.45	0.91
V	0.38	0.6	0.99	0.2	0.64	0.83
SS	0.47	0.47	0.98	1.072	0.24	0.94
VS	0.38	0.53	0.98	0.75	0.24	0.95
Si	0.6	0.34	0.95	0.51	0.3	0.96

Table 5. Parameters and correlation coefficients obtained from the fit of the Langmuir model of nickel and cadmium adsorption data by the studied soils

Heavy metals Adsorbents	Nickel			Cadmium		
	K_L	q_m	R^2	K_L	q_m	R^2
S	0.198	6.544	0.87	0.645	7.732	0.9
V	0.026	6.817	0.98	0.018	5.24	0.84
SS	0.048	4.306	0.96	0.34	2.743	0.98
VS	0.034	4.824	0.96	0.24	2.049	0.98
Si	0.095	2.77	0.97	0.13	1.9	0.99

Another parameter that was examined in the adsorption analysis was the R^2 parameter. This parameter shows the correlation coefficient in both models and the higher R^2 value indicates the greater correlation of the adsorption data with that model and also the fit of the model for the adsorption of metal ions by adsorbent [50]. The coefficient of variation (R^2) in the Freundlich model for cadmium element is in the range of 0.83-0.96 and nickel (R^2) is between 0.87-0.99. According to the high R^2 value (more than 0.83), both Freundlich and Langmuir models can describe the adsorption data.

Table 5 shows the parameters and correlation coefficients obtained from the fit of the Langmuir model on nickel and cadmium adsorption data. The values of q_m obtained from Langmuir models indicate the amount of adsorption of metal ions required to form a monolayer, which is higher in the adsorption of nickel element rather than cadmium element for all soils except sepiolite clay soils. This indicates that more amounts of nickel are needed to form a monolayer on soil particles [50]. For this reason, the adsorption capacity of nickel element is higher than that of cadmium element. Another parameter that can be mentioned in the Langmuir equation is K_L , which is the bond energy constant. The higher values of the K_L parameter indicate the higher adsorption energy at surfaces. Cadmium element is adsorbed with more energy rather than nickel element in soils containing sepiolite clay (SS and S samples).

The coefficient of variation (R^2) in the Langmuir model for the cadmium ranged from 0.84 to 0.99 and for the nickel ranged between 0.87-0.97. Freundlich and Langmuir's models had a similar performance in nickel removal.

3- 4- Heavy metal adsorption percentage

Figures 11 and 12 show the adsorption of nickel and cadmium elements on the studied soils. The results of the present study indicate a decrease in removal efficiency with increasing concentrations of nickel and cadmium. At lower initial concentrations of pollutants, there are sufficient active sites for adsorption. However, at high concentrations, each adsorbent has a limited number of active adsorption sites and these active sites are located on the adsorbent surface that they are saturated with contaminants and the removal

efficiency decreases [51].

Adsorption of metals depends on various factors such as organic matter content, cation exchange capacity, clay minerals, calcium carbonate, iron-manganese oxides, ionic strength, soil material, specific surface adsorption, soil particle size distribution, and etc. [52].

Nickel element was more adsorbed in sepiolite and vermiculite clay soils and then their mixtures, respectively. Cadmium element adsorption was more done by sepiolite clay soils and its mixture and then vermiculite and its mixture.

Sepiolite mineral has unique properties due to its structural properties that can be noted for its high porosity and specific surface area, strong adsorption, and special rheological properties. It was also observed that the heavy metal adsorption of silty soil after mixing with vermiculite and sepiolite clay has increased. The reason for this increase can be attributed to the increase in the percentage of clay as well as the increase in cation exchange capacity and specific surface area due to the presence of vermiculite and sepiolite clay in the soil mixture. Achiba et al. (2009) stated that the presence of high clay and silt in the soil increases the adsorption sites for metals [53].

Sepiolite is classified as a fibrous mineral and has been effective in removing heavy metals such as nickel, cadmium, zinc, and copper from aqueous solutions [54]. Hojjati and Khademi (2014) reported that Iranian sepiolite has a high potential for cadmium uptake and this potential increased with increasing cadmium concentration, contact time, and increasing adsorbent dose [55]. Mohammadinejad et al. (2016) stated that zeolite and sepiolite minerals can effectively adsorb nickel elements [56].

Wang et al. (2007) also found that by fitting the Langmuir and Freundlich models on cadmium uptake data on Palygorskite, both models well describe the cadmium uptake process through Palygorskite mineral [57].

Adsorption experiments were also performed on chromium. The studied soils were not successful in adsorbing chromium. Because clays in their natural state often have anion-repellent properties and are not able to adsorb water-insoluble, non-polar molecules and non-ionic organic molecules [58].

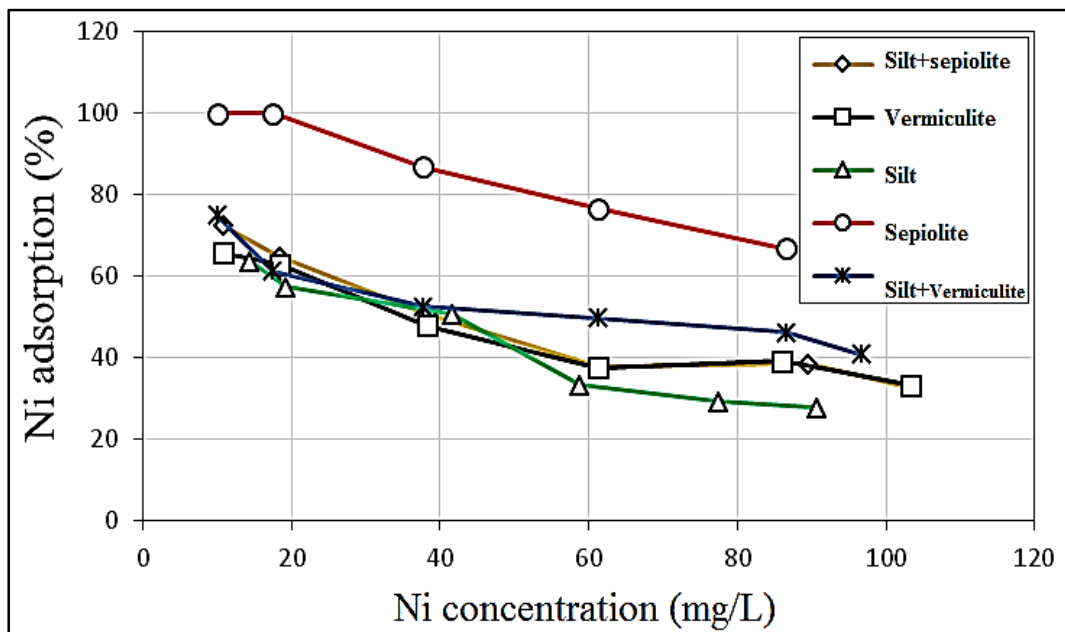


Fig. 11. Percentages of nickel adsorption in different concentrations using different soils

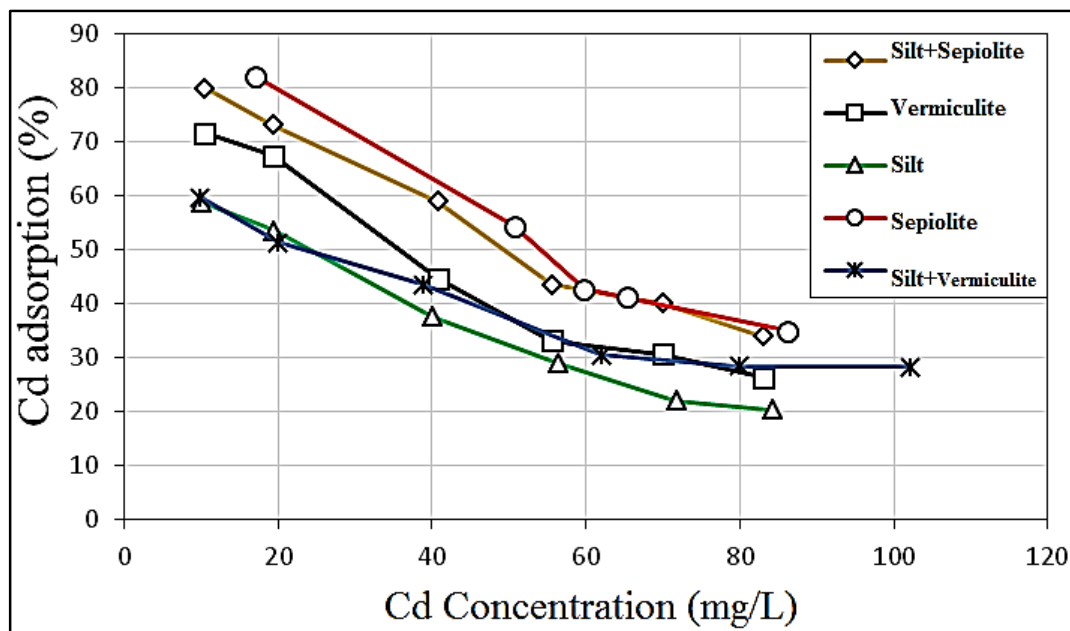


Fig. 12. Percentages of cadmium uptake in different concentrations using different soils

Table 6. Physical and hydraulic properties required of the soil of a clay liner

Properties		Soil type				
		S	V	SS	VS	Si
K (Cm/s)		7×10^{-8}	5.6×10^{-8}	3.05×10^{-7}	2.6×10^{-7}	1.8×10^{-6}
LL (%)		101.2	45.6	31.6	25.72	1.24
PI (%)		14.02	12.27	10.12	6.67	0.50
finer than 0.002 mm		39	33	35	30	3
coarser than 0.063 mm		14	16	17	20	21
soil classification		CH	CL	CL	CL-ML	ML
activity		1.6	2.05	1.2	1.12	0.7
UCS (kPa)	Modified	242	80	540	120	98
	High energy	400	138	766	204	147
MDD* ¹ (kN/m ³)	Modified	13.2	16.2	18.8	21	21.1
	High energy	13.8	15	19	22.2	21.9
OMC* ² (%)	Modified	37.5	15	12.9	11.6	10.7
	High energy	30.7	14.2	12	9.6	9.1
Density		2.24	2.47	2.48	2.7	2.9

*¹MDD: maximum Dry Density, *²OMC: Optical Moisture Content

Table 6 shows the physical and hydraulic properties of the soil required for a clay liner following the literature review recommendations to evaluate the performance of soils as a clay liner (Table 7).

The selection of suitable clay in the first stage is based on the permeability coefficient and Atterberg limits regarding soil geotechnical properties. Clay with a permeability coefficient of 1×10^{-7} cm/s or less can be used as a liner. A liquid limit of more than 20% and a plastic index of more than 7 are recommended for liners (table 7). Clay is more susceptible to cracking when drying, and less used with a low plastic limit or plastic index amount. Also, soils that have higher amounts of clay, due to water adsorption and creating a barrier around the particles, show more resistance to the applied forces and show better performance in the construction of engineering-sanitary liners. According to the data in tables 6 and 7, in terms of particle size distribution, soil classification, Atterberg limits, density, compaction, strength, and permeability soils follow the suitability of using as natural landfill liners as SS, S, VS, V, and Si soils, respectively.

4- Conclusion

The performance of two natural clayey soils (Sepiolite and Vermiculite) and their mixtures with silty soils as potential landfill liners was assessed by measuring their physicochemical properties and pollutant adsorption capacity upon contact with heavy metals.

In terms of permeability parameters, sepiolite, and vermiculite clay soils may be classified as suitable natural clay liners in landfills ($K \leq 1 \times 10^{-7}$).

Vermiculite soils and the mixture of silt + sepiolite soils represented suitable plasticity limit properties as liners. The liquid limit and plastic index of sepiolite soils are in the range of the expansive soils which varied and ranged between 35 and 170%; the plasticity index ranged from 14 to 120%. The vermiculite and sepiolite soils were classified as clay of low to very high plasticity (CL–CH) based on the Unified Soil Classification System (USCS), respectively.

Sepiolite clay is not suitable due to its high liquid limit; but after adding it to the soil, its liquid limit decreases and it is in the appropriate range. In general, the high liquid limit of the clays can be improved by mixing with silty soils.

Table 7. Requirements for soil liner material

Parameters	Standard requirement	references
Particle size analysis	Clay fraction $\geq 30\%$	[59]
	Largest grain size $\leq 63\text{mm}$	[60]
	Silt size content $\geq 15\%$	[61]
	%gravel $\leq 30\%$	[62]
Atterberg limit	LL $\geq 20\%$, PI $\geq 7\%$	[63]
	Activity ≥ 0.3	[64]
Classification	CL	[65]
Density	≥ 2.2	[61]
Compaction	Maximum dry density $\geq 1.7\text{Mg/m}^3$	[66]
Thickness	300-600 mm	[67]
	$\geq 50\text{cm}$	[68]
	$\geq 1\text{m}$	[69]
UCS	$\geq 200\text{kPa}$	[45]
Coefficient of permeability	$\leq 1 \times 10^{-7}$	[65]

In general, in terms of environmental quality (pollutant adsorption), sepiolite soil specimens have better adsorption capacity than vermiculite soils and have been more effective in adsorbing cations. From a physical and mechanical point of view, sepiolite soils compared to vermiculite soils demonstrated completely different properties for designing as landfill liners in terms of strength, permeability, and plasticity characteristics

The suitability of soils for using clay liners from both environmental and geotechnical aspects, soils in terms of suitability for natural landfill liners include sepiolite+silt, Sepiolite, vermiculite+silt, vermiculite, and silty soils, respectively.

The low cost, ease of implementation, natural presence in most regions, and attenuation capacity of clay liners make them more attractive than geosynthetic liners on their own in landfill liner systems.

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