Encapsulation of Lead Ions in Sand-Cement-Clay Mixture

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ABSTRACT

This study was carried out to test the feasibility of a mixture of sand, cement and clay for immobilizing lead ions from retention into water resources. Various samples with different mass ratios of this mixture were tested to determine their efficiency for holding lead. The compressive test, cation exchange capacity, adsorption equilibrium, and the leaching test were applied to each sample. The sample that proved the high cation exchange capacity with 53.1 meq/100g and compressive test with 11.05 kN/m^2 is 25% sand, 50% cement and 25% clay. The equilibrium data for Pb^{2+} removal using this sample showed a monolayer of adsorption, which can be fitted using Redlich-Peterson adsorption isotherm model with a regression coefficient of 0.995. The maximum lead uptake obtained from the experimental data was 192 mg/g solid. Introducing clay into this sample proved its sorption capacity while the presence of sand and cement enhanced the resistant of this sample to compressive test.

KEYWORDS: Encapsulation, Solidification, Stabilization, Sand, Cement, Clay, Lead, Adsorption, Cation Exchange Capacity.

INTRODUCTION

Heavy metals contamination to water resources is of a major concern. The geochemical mobility of these metals accompanied with their toxicity to human and animal paid the attention toward finding suitable remediation technologies for these metals. One of the powerful techniques is the precipitation of these toxicants as metal hydroxides [1,2]. However, this technique produces large

amount of sludge with high concentration of metals. Treatment of sludge can be achieved using different technologies. These include stabilization [3,4], thickening [5], dewatering [6], drying and incineration [7,8], and physical solidification or stabilization using either cementations or pozzolanic materials [9]. One dominant method of metal and sludge disposal is the cement-based solidification/stabilization process. This method offer a combined benefit of reducing the volume of the sludge to be disposed and trapping the metal ions from leaching out to water resources. Several researchers adopted this encapsulation technique toward radioactive isotopes [10,11], organic matters [12,13] and heavy metal [14,15]. This treatment involves mixing the metals of interest with binding reagent. The effectiveness of this technique depends on the amount of these mixtures to uptake metals as well as their resistance to permeability, leachability and hardness. Several additives such as cement, limestone, fly ash, gypsum or phosphate mixture can bind heavy metals [10,16-18]. These additives were added either to enhance the hardness of the grout mixture or increase the resistibility to leaching. The effective binding agent, however, is the one that combine the decrease in leachability of these metals in the solid matrix as well as enhance the strength of this solid matrix to compressive load. In this paper, a mixture of three components (sand, cement and clay) is used with different weight percentages as matrix for holding of lead ions from solution.

EXPERIMENTAL METHODS

Materials

Clay and sand were brought from Al-Tafela area in the southern part of Jordan while cement was manufactured by Jordan Cement Factories Company, Jordan. These materials were combined, crushed, and sieved to a particles sizes less than 45 μm. All chemical were analytical grade reagents supplied by Sigma Chemical Company. The glassware was Pyrex washed with diluted nitric acid, soap, and deionized water to minimize surface adsorption of metals of interest.

Methods

Compressive strength test

Fifteen samples of sand, cement and clay with different mass ratios were mixed thoroughly with sufficient amount of water. These samples were brought into polyvinyl chloride (PVC) cylindrical molds to test their compressive strength. According to ASTM C 109M-02 the specimens were allowed to cure for different period of times. Then these specimens were caped with molten sulfur to smooth their faces and a constant rate of loading was allowed until failure occurs. The compressive strength for the specimens was determined by dividing the maximum load attained during the test by the cross sectional area of the tested specimen.

Cation exchange capacity test

Cation exchange capacity (CEC) was determined using sodium acetate procedure proposed by Environmental Protection Agency (EPA) according to SW-846 Method 9080. The technique involved treating 4 g of the sample under investigation with excess amount of sodium acetate solution (1.0 N). Subsequently, the sample was rinsed several times with isopropyl alcohol. Then ammonium acetate solution (1.0 N) was added to replace the adsorbed sodium with ammonium ions. The concentration of displaced sodium was then determined using SOLAAR S4 Atomic Absorption Spectrophotometer.

Adsorption isotherm

Equilibrium experiments were conducted by mixing different concentrations of lead solutions (25–2000 mg/L) with 0.1 g of the composite material that having the highest CEC and compressive strength. These solid-solution mixtures were placed in 250-ml Erlenmeyer flasks and agitated in an isothermal shaker at constant temperature of ($22\pm1^{o}C$) for 24 hr. After the solutions get equilibrated, the concentration of lead was analyzed using SOLAAR S4 atomic absorption spectrophotometer.

Table 1. Chemical Analysis of clay and cement used in this study

Component (wt%)	Clay	Cement
SiO_2	58.86	21.2
Al_2O_3	17.11	5.5
Fe_2O_3	4.20	3.1
CaO	10.85	64.18
MgO	1.66	2.5
SO_3	-	2.63
Na_2O	2.83	0.18
K_2O	2.30	0.71
TiO_2	0.57	-

RESULTS AND DISCUSSIONS

The chemical composition of clay and cement is shown in Table 1. The analysis to these materials revealed that they contain mainly silica, alumina and calcium oxide, which they account for 89.57% of the total weight. Fifteen samples of concrete were prepared by mixing sand, cement and clay at different compositions. Table 2 shows these percentages were the particle size of each constituent was less than 45 (m. The cementation process for these samples was conducted in a 500-ml beaker by perfect mixing 200 g of each solid sample with distilled water until the mixture becomes paste. The water to solid ratio was varied according to the percentage of cement and clay substitution in order to have a fixed fluidity of all samples. Then, these samples were placed in cylinders (1 in. ID and 2 in. length) and allowed to solidify at room temperature ($22\pm1^{o}C$) in a closed container for two weeks. The container was kept at saturate humidity by spraying reasonable amount of water in a fixed period of 4 h.

Table 2. Percentage of sand, cement and clay in the composite samples

Sample number	Sand %	Clay %	Cement %	Water (ml)
1	25	50	25	285
2	25	25	50	488
3	25	0	75	383
4	25	75	0	315

5	0	75	25	543
6	0	50	50	393
7	0	25	75	578
8	50	50	0	298
9	50	25	25	186
10	50	0	50	185
11	75	25	0	246
12	75	0	25	51
13	100	0	0	15
14	0	0	100	230
15	0	100	0	533

Compressive strength for different cured batches was tested at the end of each week during the curing time. Figure 1 illustrates the values of compressive strength with the sample number. The maximum compressive strength was for the sample that contains 25% sand, and 75% cement with a value of 12.83 kN/m^2 obtained after two weeks of curing. Moreover, the samples that containing pure cement or 25% sand, 25% clay and 50% cement showed also quite good compressive strength with values of 11.84 and 11.05 kN/m^2, respectively, while the samples that containing no cement did not show any resistant to compression. In all samples the increase in curing time proved a better resistant to compression. This is due to the slow formation of cementation agent that is produced as a result of reaction of lime with fine samples particles. This agent crystallizes slowly into an interlocking matrix and increases the samples strength. Longer curing period allows longer time for lime to react and form a strong skeleton structure throughout the material binding the grains together [19].
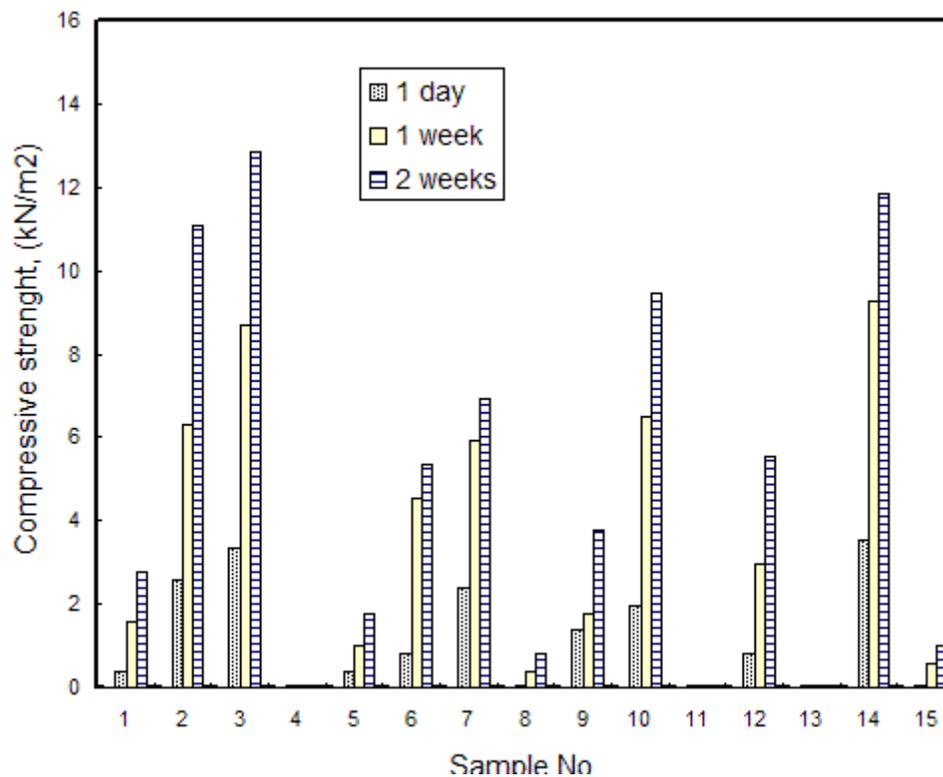

Figure 1. Compressive strength for different compositions of sand-clay-cement mixture obtained at different curing times

Figure 2 shows the variation of compressive strength with the percentage of clay added to the samples free of sand. It is also seen as the curing time decrease the resistant to compression is decreased. This trend is severely accentuated by the addition of clay to these samples. This decrease in compression test with the addition of clay is attributed to the fact that clay contains individual layers of colloidal particles. When these particles are suspended in water, some of these interlayers absorb the positive ions that exist in the specimen leading to expanding these layers. As a result this specimen becomes more elastic as the ratio of clay to cement increase. This leads to less resistance to compression with a value of $0.98kN/m^2$ when the sample contains pure clay.

On the other hand, when the specimen contains sand and cement only (Figure 3), the increase in sand percentage from 0 to 100% yields a gradual decrease in the compression test to reach 0 kN/m^2 at 100% sand. It is worth to notice that a sluggish decrease in compression test with the addition of the sand while a severe decrease with the addition of clay to a sample contains only cement. This could be attributed to that fact that sand contains hard spherical particles, which resist the compression more than that of clay.
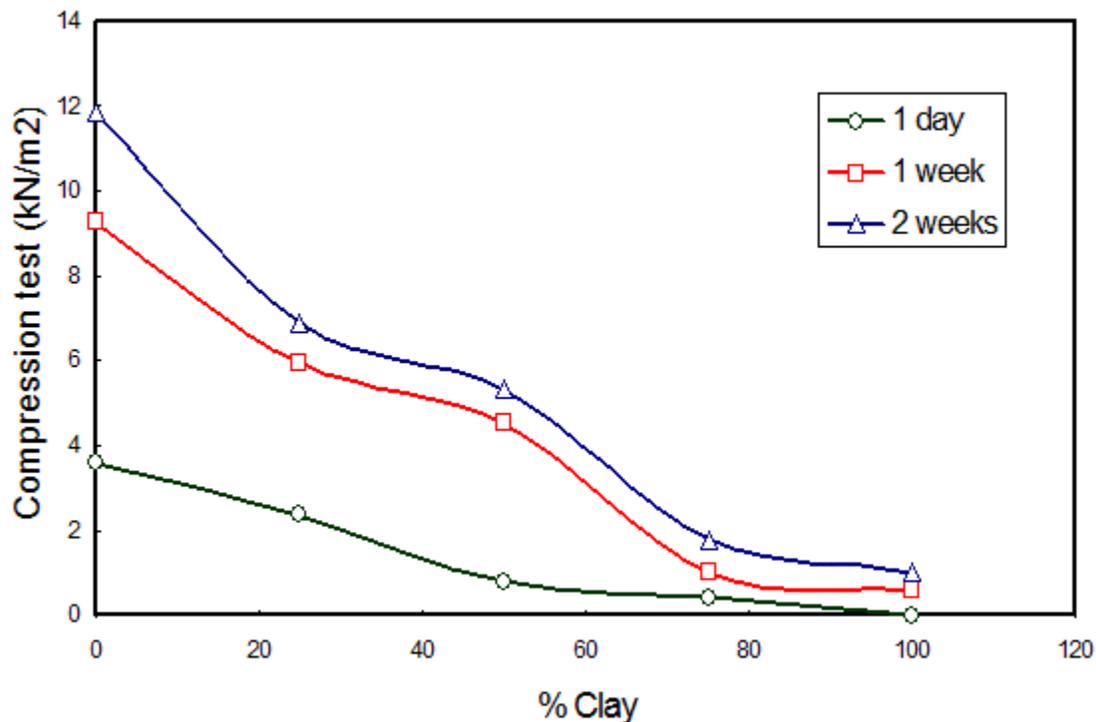

Figure 2. Effect of variation of clay to cement ratio on the compressive strength for samples free of sand
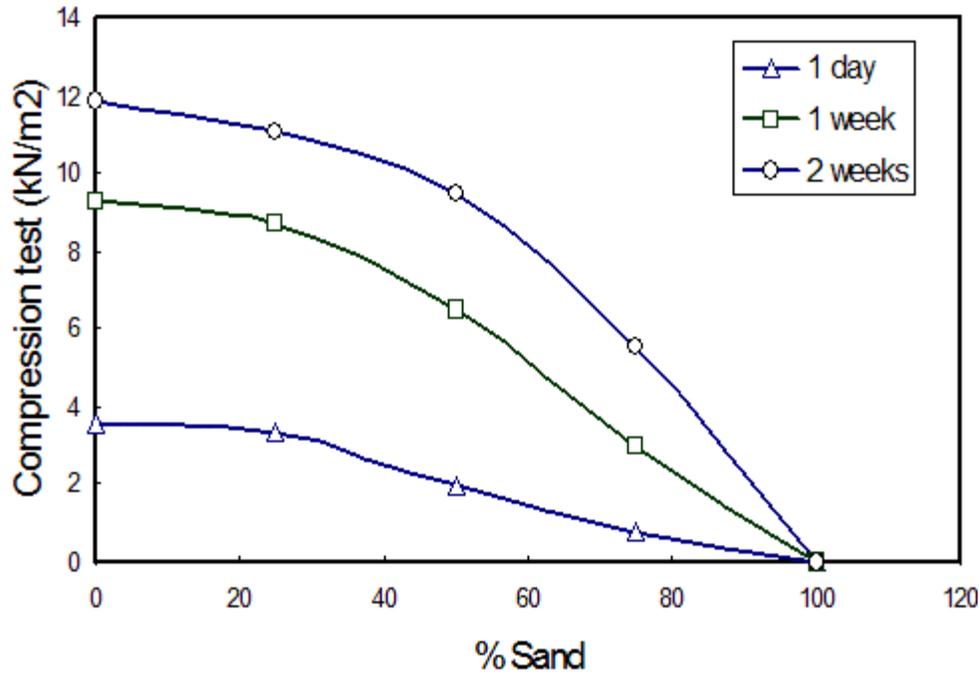
Figure 3. Effect of variation of sand to cement ratio on the compressive strength for samples free of clay

The CEC was determined using the ammonium acetate method after washing several times with alcohol. This CEC governs the extent of migration of lead from the clay-sand-cement matrix. The higher CEC value of the mixture is the better one for retaining the pollutants from leaching out into water resources. The maximum CEC was achieved for the sample that contains 25% clay and 75% cement with a value of 62.8 meq/100g solid (Figure 4).
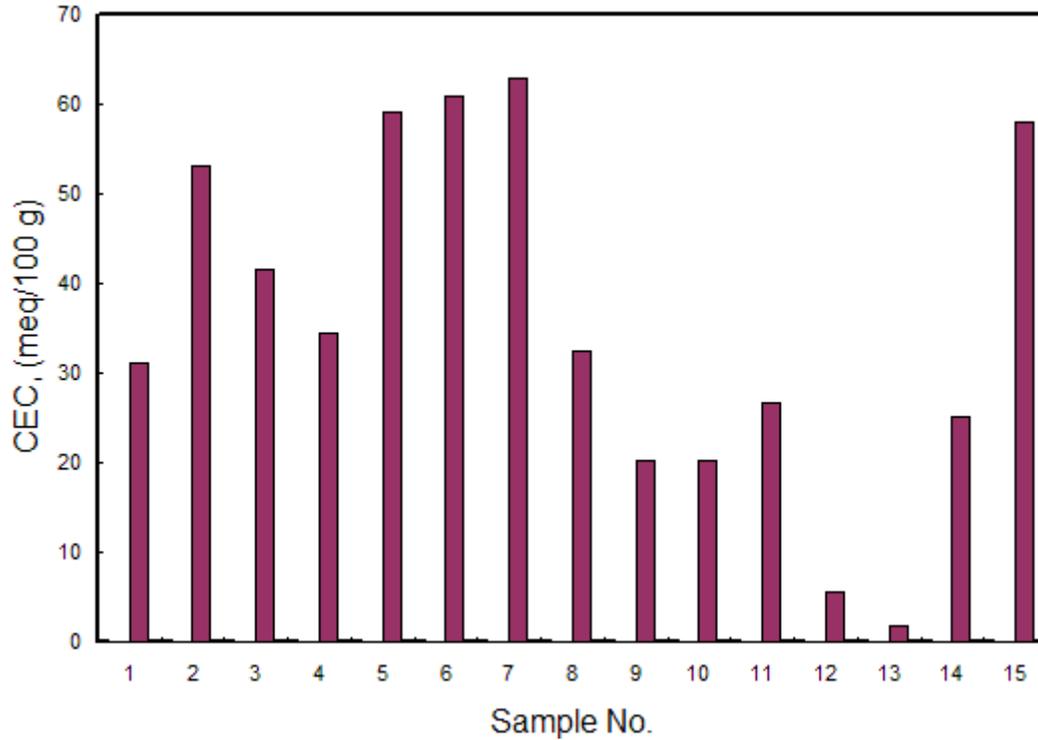
Figure 4. Cation exchange capacity of samples containing different clay-sand-cement ratios.

In addition, the samples that containing 50% clay and 50% cement, 100% clay, and 25% clay, 25% sand and 50% cement show pretty good CEC values of 60.86, 57.98, 53.1 meq/100g, respectively. In the absence of cement, the increase in the ratio of sand to clay, Figure 5, is associated with a decrease in the value of CEC till it reaches 1.6 meq/100g for pure sand one. This is as a result of decreasing of the density of surface charge with increasing the sand to clay ratio. On the other hand, when the ratio of sand to cement increases from 0 to 25% in the absence of clay (Figure 6, region 1), the trend for CEC value increase noticeably from 25 to 41.6 meq/100g and then decrease exponentially to a value of 1.68 meq/100g when the specimen is pure sand (region 2).
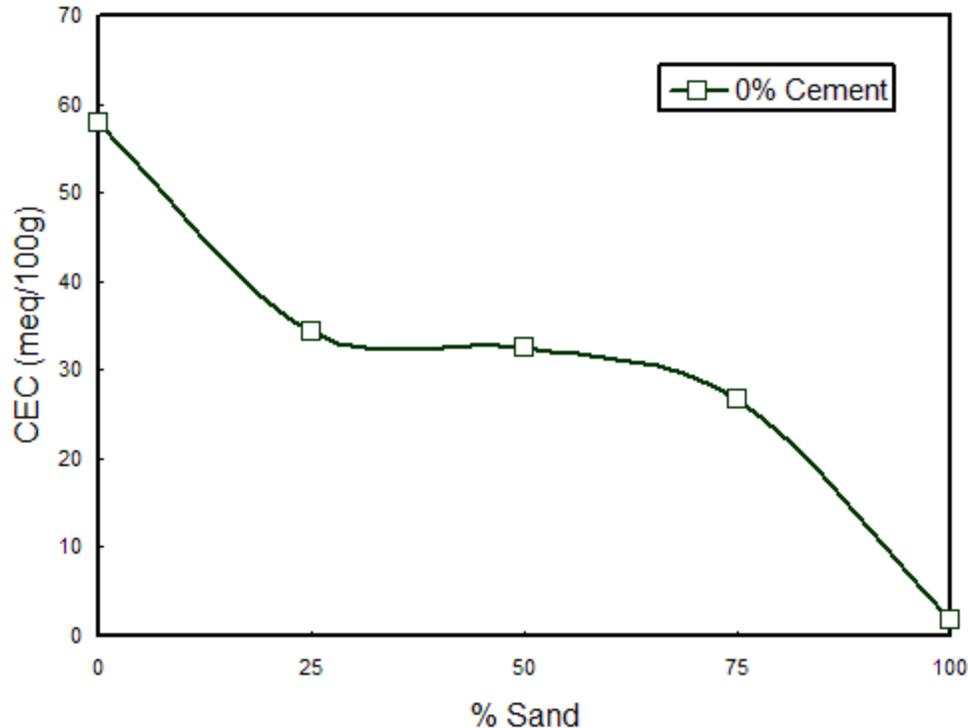
Figure 5. Effect of variation of sand to clay ratio on the cation exchange capacity of the mixture

This could be attributed to the increase in the void volume of the sample in the first region, which enhances the permeability of the exchangeable ions on its surface. However, this potential to ion exchange decreases with increasing the sand content. Bearing in mind the fact that cement has better potential for ion exchange than that of sand, as a result of the distribution of different metal oxides in its content, this potential decreases as a result of decreasing the net surface charge of the whole sand-cement sample in the second region. In the third case, when the ratio of clay to cement increases in the sample that having no sand, Figure 7, the potential to ion exchange increases to a maximum value of 62.86 meq/100g, then a slow decrease to a value of 57.98 meq/100g when the sample contains pure clay. This could be ascribed to the change of pH value of the clay-cement mixture after the successive addition of clay. As the pH of this mixture increases to a value higher than that of the isoelectric point, the exchangeable capacity is increased [20]. Pure cement sample contains 64.18% CaO which can be converted to CaOH upon reaction with water.
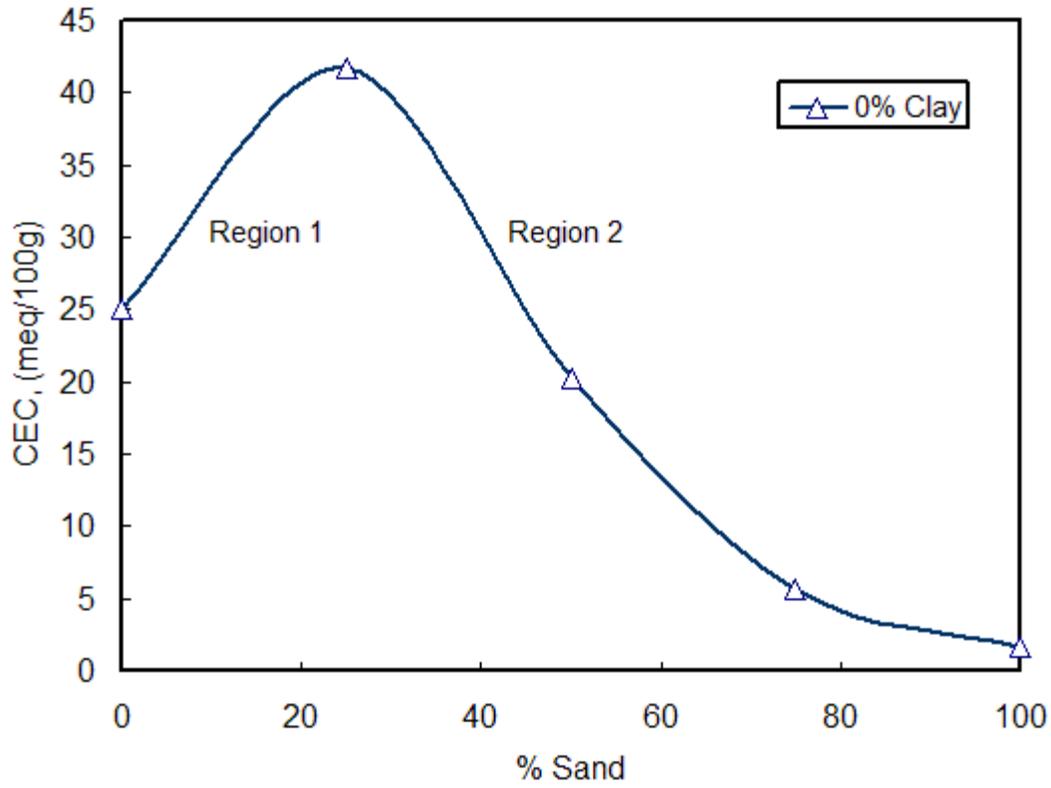
Figure 6. Effect of variation of sand to cement ratio on the cation exchange capacity of the mixture
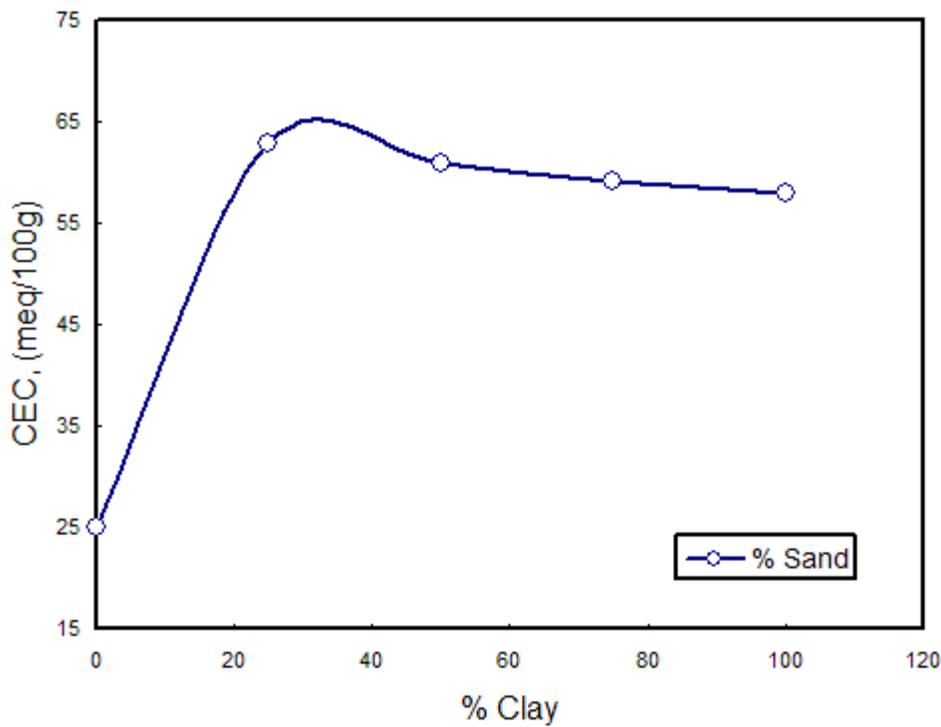

Figure 7. Effect of variation of clay to cement ratio on the cation exchange capacity of the mixture

The latter will raise the pH to a value greater than 12, which shift the condition of exchanging sodium ions fare away from the zero point of charge (ZPC) for this mixture. Unfortunately, the presence of calcium ions with sulfate ions in the pure cement sample leads to formation of gypsum upon hydration, which blocks the microspores channels inside this sample and consequently lowers the CEC value. The addition of 25% clay to the specimen, however, will decrease the percentage of gypsum and plays a role of enhancing the liquid limit and plasticity index. Thus more micro and macrospores will be opened to improve more ion exchange on the active sites of the sample. Moreover, the cement contains iron, magnesium and aluminum oxides besides the silica. When mixing 25% clay to 75% cement, the percentage of silica and alumina in the whole sample becomes 30.6 and 8.4%, respectively. This is also increases the active exchangeable site with increasing the silica and alumina content in the sample. Nevertheless, the more increase of clay to cement ratio will decrease the total calcium oxide content and reduces the pH to a closer value to the ZPC which leads to a sluggish reduction in the value of CEC.
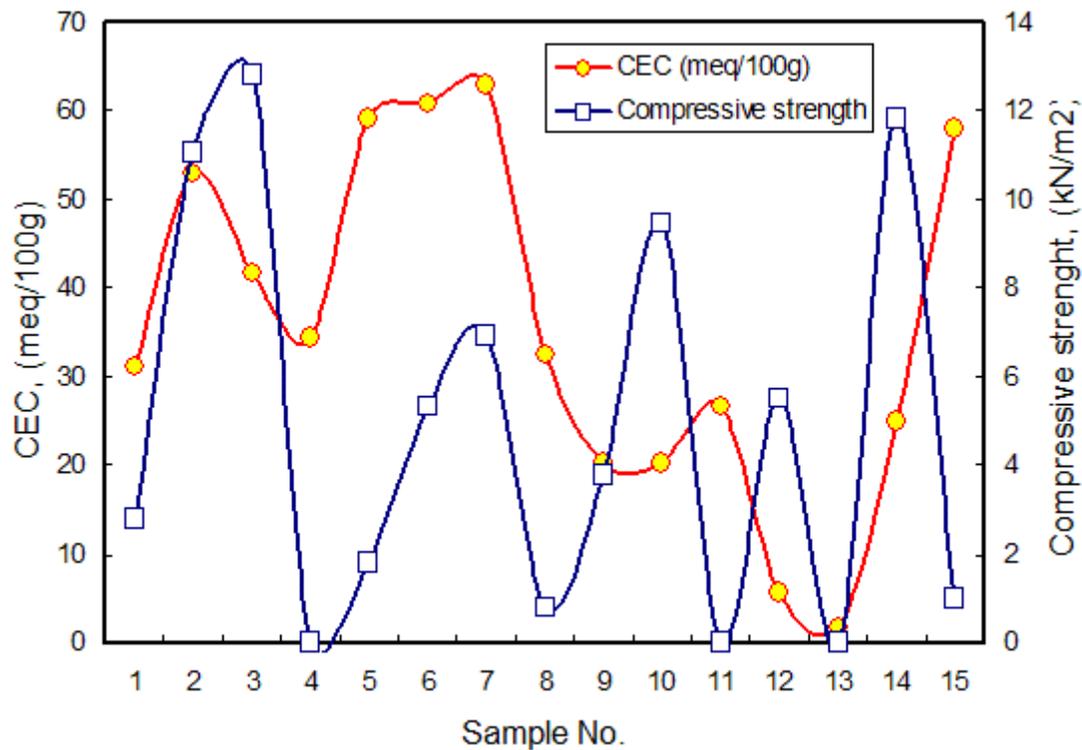

Figure 8. Values of cation exchange capacity and compressive strength for different sand-cement-clay mixtures

To identify the best sand-cement-clay ratio that proves high CEC and compressive strength, a comparison was carried out for all samples as shown in Figure 8. It is seen that some samples with high CEC, unfortunately, having lower compressive strength and vice versus. Fortunately the sample that contains 25% clay, 25% sand and 50% cement only proved satisfactory high value of CEC and compressive strength, as well. As a result this sample was used further for measuring the adsorption capacity of this target mixture.
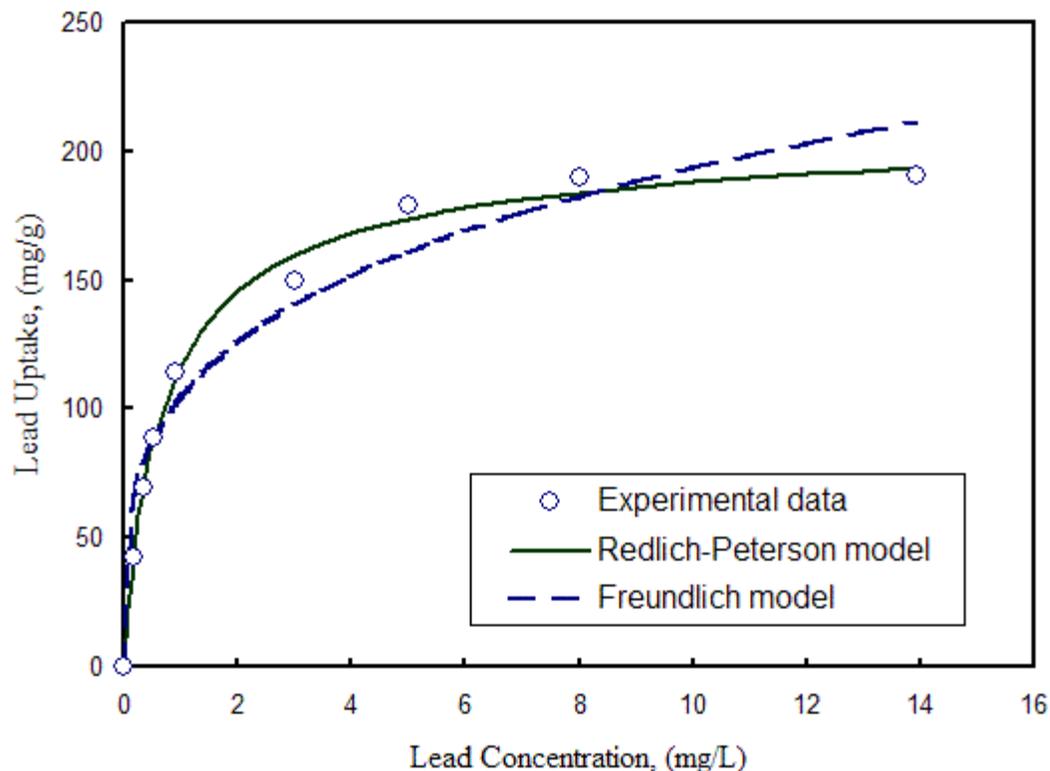
Figure 9. Fitting equilibrium adsorption of lead on 25% sand, 50% cement and 25% clay mixture

This sample was mixed with lead solution at different concentrations and allowed to equilibrate over time. Figure 9 shows the adsorption isotherm curve for this sample. This curve shows a maximum uptake of 192 mg Pb^{2+}/g solid and retains 8 mg/L in the solution when the initial solution concentration of Pb^{2+} is 200 mg/L at pH value of 11.8. In this trend it is expected that monolayer of adsorption is taken place between Pb^{2+} and the actives sites on the solid matrix. To model these data, Freundlich and Redlich-Peterson models were used. Freundlich model describes the coverage adsorbate on heterogeneous surfaces of the solid mixture in which the heat of adsorption varies with surface coverage as

$$q_e = K_f C_e^n$$

Where K_f and n are constants and K_f is proportional to the enthalpy of the adsorption according to:

$$K_f \propto RTne^{\Delta H / RT}$$

The experimental data were fitted this model with correlation coefficient, r^2=0.952 and $\Sigma(error)^2$=810. The values K_f and n are 104.608 mg/g and 0.2672, respectively.

On the other hand, Redlich-Peterson model describes the monolayer coverage combined with the features of Fruendlich adsorption isotherms as

$$q_e = \frac{QC_e}{1 + \alpha Ce^\beta}$$

Where Q, α and β are constants. This model gave a closer fit to the trend of experimental data. The correlation coefficient, r^2=0.952 and $\Sigma(error)^2$=810. The values of Q, α and β are 324.614, 1.772 and 0.963, respectively.

CONCLUSIONS

An effort was made to utilize a low cost adsorbent for retaining metal ions from leaching out into water resources. This study analyzes the ability of a mixture of sand-cement-clay mixture with mass percentages of 25% sand, 50% cement and 25% clay to encapsulate metal ions from solution. This mass ratio proved a maximum adsorption capacity toward lead with a high compressive strength. Clay played a role in increasing the adsorption capacity toward lead, sand used to enhance the compressive strength while cement was beneficial as a solidification agent to both clay and sand mixture. The advantage of utilizing this solidification/stabilization mixture is the low cost of its raw material and a relatively the safe treatment of this process.

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