

## Solidification and stabilization of cadmium ions in sand–cement–clay mixture

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### Abstract

This study was carried out to test the ability of a mixture of sand, cement and clay for immobilizing cadmium ions from leaching out into water resources. Various samples with different mass ratios for this mixture were tested to determine their efficiency for adsorbing cadmium. The compressive test, cation exchange capacity (CEC), adsorption equilibrium and leaching test were applied to each sample. The sample that showed the highest cation exchange capacity with 53.1 meq/100 g and compressive strength with 11.05 N/mm<sup>2</sup> consists of 25% sand, 50% cement and 25% clay. The equilibrium data for Cd<sup>2+</sup> removal using this sample showed a multilayer adsorption, which could be fitted using Brunauer–Emmett–Teller adsorption isotherm model with a regression coefficient of 0.999. The maximum cadmium uptake obtained from this model was 82.618 mg/g solid. The mobility of Cd<sup>2+</sup> in acidic solution drawn-off after 18 h of initial mixing was 66.06 mg when the solid sample initially contains 6.0 g Cd<sup>2+</sup>. This value decreased to 14.33 mg when only 1.0 g Cd<sup>2+</sup> was initially spiked in the sample. Introducing clay into this sample enhanced its sorption capacity while the presence of sand and cement enhanced its compressive strength.

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**Keywords:** Encapsulation; Cation exchange capacity; TCLP; Adsorption; Heavy metals; Composite material; Sand–cement–clay mixture

### 1. Introduction

Heavy metals contamination in water resources is a major concern. The geochemical mobility of these metals accompanied with their toxicity to human and animal draws attention towards 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 amounts 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 cement or pozzolanic materials [9]. One dominant method of metal and sludge disposal is the cement-based solidification/stabilization process. This method has a capability of trapping the metal ions from leaching out to water

resources. Several researchers adopted this encapsulation technique towards radioactive isotopes [10,11], organic matters [12,13] and heavy metal [14,15]. This treatment involves mixing the metals of interest with binding reagents. The effect of this technique depends on the affinity of these mixtures to uptake metals as well as their resistance to permeability, leachability and compressibility. Several additives such as cement, limestone, fly ash, gypsum or phosphate mixtures can bind heavy metals [10,16–18]. These additives were added either to enhance the compressive strength of the grout mixture or increase its resistibility to leaching out the encapsulated solute of interest. The effective binding agent, however, is the one that combines the decrease in leachability of these metals in the solid matrix as well as enhances the strength of this solid matrix to compressive load. While cadmium can be retained in cement, it could be leached out at relatively high level when the final pH of the leachant drops around 7. Jordan reserves large amounts of natural resources, such as clay, oil shale, gypsum and white sand that can be mined by open pit. Therefore, utilizing of these naturally occurring material as

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adsorbent for remediation of heavy metal is of great national interest. In this paper, a mixture of three components (sand, cement and clay) is used with different weight percentages as matrix for preventing of cadmium ions from leaching out into solution. This matrix is then tested for its applicability as filler in construction material.

## 2. Experimental methods

### 2.1. Materials

Clay and sand were brought from Al-Tafela area in the southern part of Jordan while cement was type I Ordinary Portland Cement (OPC) manufactured by Jordan Cement Factories Company, Jordan. 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. These clay materials were combined, crushed and sieved to a particle size less than 45  $\mu\text{m}$ . All chemical were analytical grade reagents supplied by Scharlau Chemical Company. The glassware was Pyrex washed with diluted nitric acid, soap and deionized water to minimize surface adsorption of cadmium ions.

### 2.2. Methods

Fifteen samples of sand, cement and clay with different mass ratios (Table 2) were mixed thoroughly with sufficient amount of water in 500 ml beaker until the mixture becomes paste. The water to cement ratio (w/c) for these samples ranges from 0.64 to 0.71 where the total water required to past the mixture ranges from 10 to 380 ml depending on the amount of each constituent in the mixture. These samples were brought into polyvinyl chloride (PVC) cylindrical molds (2 in. i.d. and 4 in. length) and allowed to solidify at room temperature ( $22 \pm 1$  °C) in a closed container. According to ASTM C 109M-02 the specimen were allowed to cure for different periods of times. The container was kept at saturated humidity by spraying reasonable amount of water in a fixed period of 4 h.

Table 1  
Chemical analysis of clay and cement used in this study

Component (wt.%)	Clay	Cement
SiO <sub>2</sub>	58.86	21.2
Al <sub>2</sub> O <sub>3</sub>	17.11	5.5
Fe <sub>2</sub> O <sub>3</sub>	4.20	3.1
CaO	10.85	64.18
MgO	1.66	2.5
SO <sub>3</sub>	–	2.63
Na <sub>2</sub> O	2.83	0.18
K <sub>2</sub> O	2.30	0.71
TiO <sub>2</sub>	0.57	–

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

Sample number	Sand (%)	Clay (%)	Cement (%)	Total water (ml)
1	25	50	25	210
2	25	25	50	130
3	25	0	75	50
4	25	75	0	288
5	0	75	25	301
6	0	50	50	225
7	0	25	75	144
8	50	50	0	195
9	50	25	25	116
10	50	0	50	38
11	75	25	0	103
12	75	0	25	25
13	100	0	0	10
14	0	0	100	71
15	0	100	0	380

#### 2.2.1. Compressive strength test

In order to perform the compressive strength test to the studied samples the specimens were capped with molten sulfur to smooth their faces and a constant rate of loading (0.2 MPa/s) was allowed until failure occurred. 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.

#### 2.2.2. Cation exchange capacity test

Cation exchange capacity (CEC) was determined using sodium acetate procedure that is 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 (1.0N). Subsequently, the sample was rinsed several times with isopropyl alcohol. Then ammonium acetate solution (1.0N) was added to replace the adsorbed sodium with ammonium ions. The concentration of displaced sodium was then determined using SOLAAR S4 Atomic Absorption Spectrophotometer.

#### 2.2.3. Toxicity characteristic leaching procedure (TCLP)

The TCLP test was conducted using EPA procedure of SW-846 Method 1311 in order to determine the mobility of cadmium ions in solution. The composite that showed the high value for both CEC and compressive strength was used in this test, which was mixed thoroughly with fixed amounts of cadmium nitrate (1.0–6.0 g Cd<sup>2+</sup>) for 10 min and allowed to solidify for 2 weeks. These samples were then crushed and sieved to particle sizes pass a 9.5 mm standard sieve. Fifty grams of each sample of interest were agitated with 1.01 of dilute acetic acid (pH 2.88  $\pm$  0.05) in a closed polyethylene containers. After 18 h, the leachant concentration for cadmium was determined using SOLAAR S4 atomic absorption spectrophotometer.

### 2.2.4. Adsorption isotherm

Equilibrium experiments were conducted by mixing 100 ml of different initial concentrations of cadmium nitrate solutions ( $25\text{--}2000\text{ mg Cd}^{2+}\text{ l}^{-1}$ ) with 0.1 g of the composite material that has 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 ( $22 \pm 1^\circ\text{C}$ ) for 24 h. After the solutions get equilibrated, the concentration of cadmium was analyzed using SOLAAR S4 atomic absorption spectrophotometer. Similar procedure was used for blank samples where 0.1 g of composite material was mixed with deionized water and analyzed for cadmium ions.

## 3. Results and discussions

### 3.1. Compressive strength

Compressive strength for different cured batches was tested at the end of each week during the curing time. Fig. 1 shows 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  $12.83\text{ N/mm}^2$  obtained after 2 weeks of curing. Moreover, the samples that contained pure cement or 25% sand, 25% clay and 50% cement showed also quite good compressive strength with values of 11.84 and  $11.05\text{ N/mm}^2$ , respectively, while the samples that contained no cement did not show any resistant to compression. These values are low compared to that of common cement mortar (about  $20\text{ N/mm}^2$ ). This could be attributed to the increase in the total amount of water used in the paste, which increases the water to cement ratio. This increase in w/c will reduce the ultimate strength achieved in the final product. Hence, the excess water used in the mix migrates to the surface of the concrete and evaporates leaving a network of flow channels that decrease the concrete density by increasing its porosity.

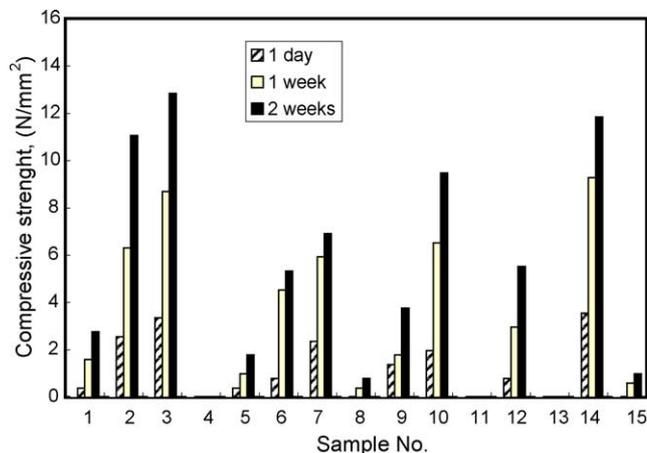


Fig. 1. Compressive strength for different compositions of sand–clay–cement mixture obtained at different curing times.

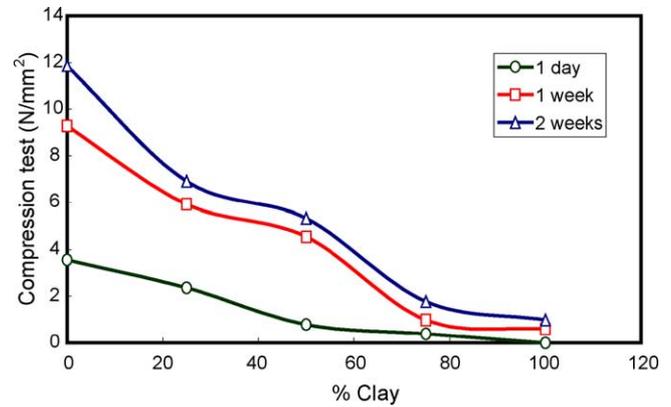


Fig. 2. Effect of variation of clay to cement ratio on the compressive strength for samples free of sand.

On the other hand, the increase in curing time for all samples will lead a better resistance to compression. This is due to the slow formation of hydrated calcium silicates that is produced as a result of reaction of anhydrous silicate constituents of cement with water. This agent crystallizes slowly into an interlocking matrix and increases the samples strength. Longer curing period allows longer time for anhydrous silicate to react and form a strong skeleton structure throughout the material that binding the grains together [19].

Fig. 2 shows the variation of compressive strength with the percentage of clay added to the sample. It is seen that as the curing time decreases the resistance to compression is decreased. This trend was severely accentuated by the addition of clay to the sample.

The 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 increases.

On the other hand, when the specimen contains sand and cement only (Fig. 3), the increase in sand percentage

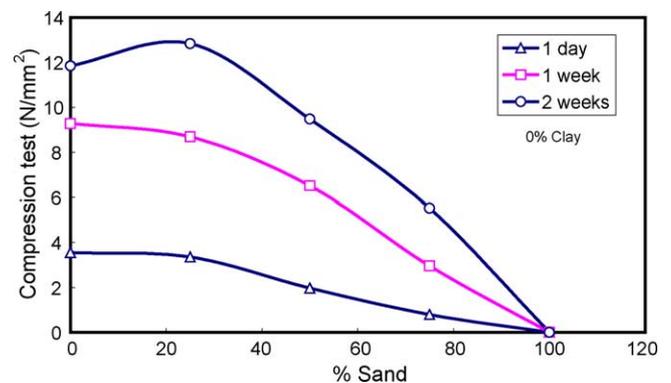


Fig. 3. Effect of variation of sand to cement ratio on the compressive strength for samples free of clay.

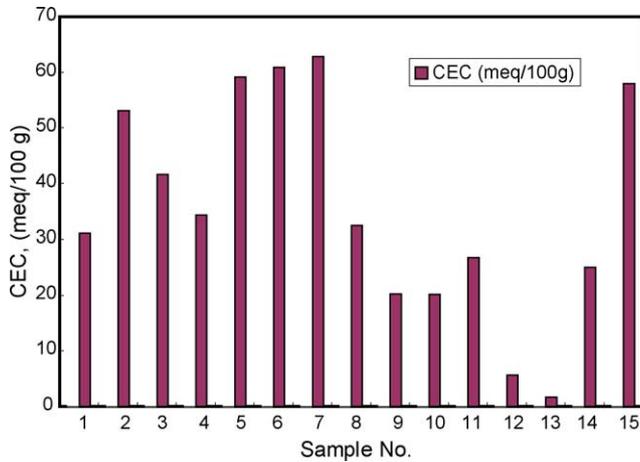


Fig. 4. Cation exchange capacity of samples containing different clay-sand-cement ratios.

from 0 to 100% provided a gradual decrease in the compression strength to attain  $0\text{N/mm}^2$  at 100% sand. It is worth noticing that a sluggish decrease in compression with the addition of the sand, while a severe decrease will be obtained by the addition of clay to a sample contains only cement. This could be attributed to the reduction of adhesion capability of the cement hydrates to the surface of clay particles.

### 3.2. Cation exchange capacity

The CEC was determined using the ammonium acetate method after washing several times with alcohol. This CEC governs the extent of migration of cadmium 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. The maximum CEC was achieved for the sample that contains 25% clay and 75% cement with a value of 62.8 meq/100 g solid (Fig. 4). In addition, the samples that contains 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 and 53.1 meq/100 g, respectively. In the absence of cement, the increase in the ratio of sand to clay, Fig. 5, is associated with a decrease in the value of CEC till it reaches 1.6 meq/100 g for pure sand one. This is due to the decreased in 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 (Fig. 6, region 1), the trend for CEC values increases noticeably from 25 to 41.6 meq/100 g and then decreases exponentially to a value of 1.68 meq/100 g when the specimen is pure sand (region 2). This could be attributed to the increase in the void volume of the sample in the first region, which enhances the diffusivity 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

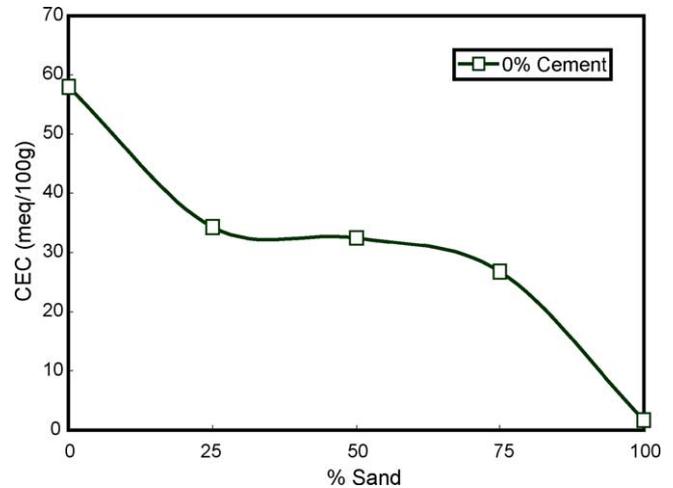


Fig. 5. Effect of variation of sand to clay ratio on the cation exchange capacity of the mixture.

oxides in its content, this potential decreases as a result of decreasing the net surface charge of the whole sand-cement samples in the second region. In the third case, when the ratio of clay to cement increases in the sample that has no sand (Fig. 7) the potential to ion exchange increases to a maximum value of 62.86 meq/100 g, then a slow decrease to a value of 57.98 meq/100 g 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 uptake capacity is increased [20]. Pure cement sample contains major portions of basic metal oxides (mainly  $\text{Na}_2\text{O}$  and  $\text{K}_2\text{O}$ ), which they incorporate of having high solution pH upon hydration. The addition of 25% clay to the specimen, however, 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

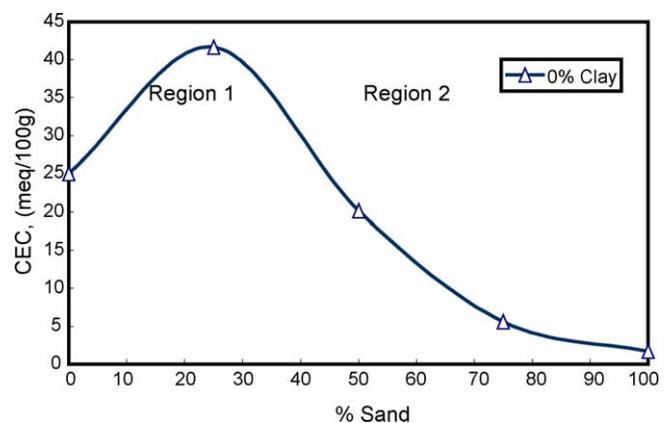


Fig. 6. Effect of variation of sand to cement ratio on the cation exchange capacity of the mixture.

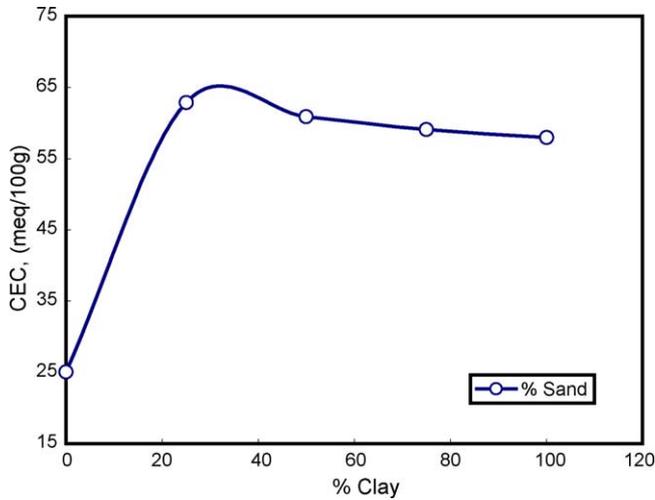


Fig. 7. Effect of variation of clay to cement ratio on the cation exchange capacity of the mixture.

silica and alumina in the whole sample becomes 30.6 and 8.4%, respectively. This also increases the active exchangeable site with increasing the silica and alumina content in the sample. Nevertheless, the additional increase of clay to cement ratio will decrease the total sodium and potassium oxides and reduces the pH to the zero point of charge (ZPC), which leads to a sluggish reduction in the value of CEC.

To identify the best sand–cement–clay ratio that proved high CEC and compressive strength, a comparison was carried out for all samples as shown in Fig. 8. It is seen that some samples with high CEC, unfortunately, having lower compressive strength and vice versa. In contrast the sample that contains 25% clay, 25% sand and 50% cement proved satisfactory high value of CEC and compressive strength, as well. As a result this sample was used further for the adsorption capacity and TCLP tests.

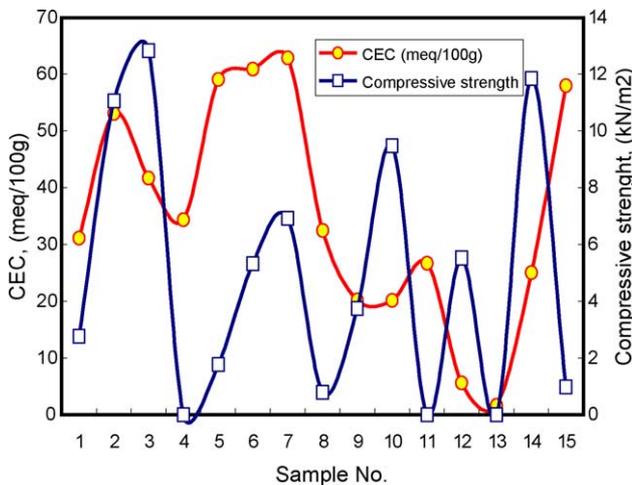


Fig. 8. Values of cation exchange capacity and compressive strength for different sand–cement–clay mixtures.

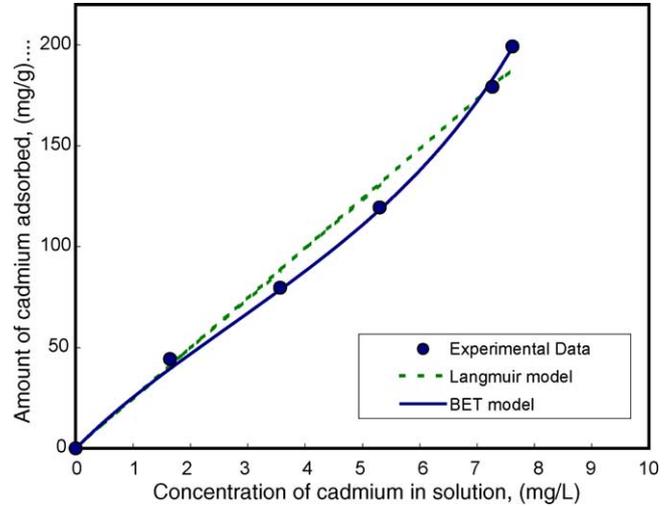


Fig. 9. Fitting equilibrium adsorption of cadmium on 25% sand, 50% cement and 25% clay mixture.

### 3.3. Cadmium adsorption

This sample was mixed with cadmium solution at different concentrations and allowed to equilibrate over time. Fig. 9 shows the adsorption isotherm curve for this sample. This curve shows a maximum uptake of 160.6 mg Cd<sup>2+</sup>/g solid leaving 9.4 mg/l in the solution when the initial solution concentration of Cd<sup>2+</sup> is 170 mg/l at pH 11.8. It is shown that multilayer of adsorption takes place due to the presence of chemical reaction (precipitation) besides adsorption of Cd<sup>2+</sup> on the active sites of the solid matrix. To model these data, Langmuir and Brunauer–Emmett–Teller (BET) models were used. Langmuir model describes the monolayer coverage of Cd<sup>2+</sup> ions on the surface of the solid mixture as:

$$q_e = \frac{QbC_e}{1 + bC_e} \tag{1}$$

where  $Q$  (mmol/g) is the maximum amount of Cd<sup>2+</sup> that can be adsorbed per unit mass of solid mixture to form a complete monolayer and  $b$  (l/mmol) is the Langmuir constant related to the affinity of binding sites. The experimental data were fitted to this model with correlation coefficient,  $r^2 = 0.987$  and  $(error)^2 = 342$ . The values  $Q$  and  $b$  are  $6.968 \times 10^4$  mg/g and  $3.551 \times 10^{-4}$  l/mg, respectively.

On the other hand, BET model assumes that a number of layers of adsorbed molecules form at the surface of adsorbent and that the Langmuir equation is applied to each layer of adsorption, thus:

$$q_e = \frac{Qk_1C_e}{(1 - K_mC_e)[1 + (k_1 - k_m)C_e]} \tag{2}$$

where  $k_1$  and  $k_m$  are the equilibrium constants for the first and subsequent layers, respectively. This BET model gave a closer fit to the trend of experimental data as is expected to fol-

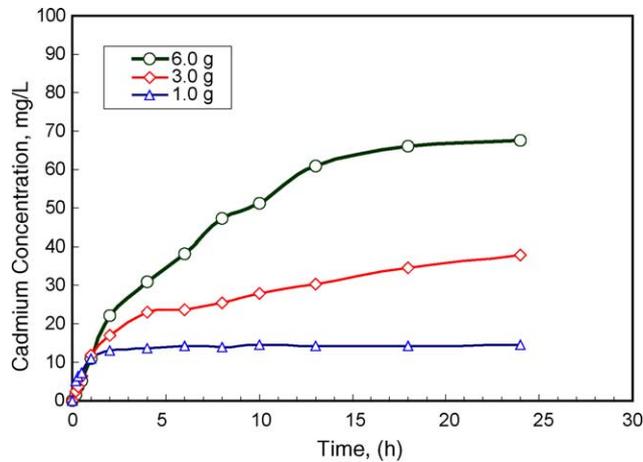


Fig. 10. Leaching of cadmium from the sample that containing 25% sand, 50% cement and 25% clay during TCLP test.

low a multilayer trend. The correlation coefficient,  $r^2 = 0.999$  and  $\Sigma(\text{error})^2 = 10.596$ . The values of  $Q$ ,  $k_1$  and  $k_2$  were 82.618 mg/g, 0.448 and 0.082 l/mg, respectively.

### 3.4. Cadmium leaching

The TCLP was performed on the sample that contains 25% clay, 25% sand and 50% cement. Fig. 10 illustrates the rate of dissolution of  $\text{Cd}^{2+}$  from the solid matrix with time. As the initial concentration of  $\text{Cd}^{2+}$  ions in solid sample increases, the leaching rate is increased. In the case of the sample that mixed with 6.0 g  $\text{Cd}^{2+}$  the total weight of the studied composite sample was 343.6 g obtained. Dissolving 50 g from this sample ( $\sim 873$  mg  $\text{Cd}^{2+}$ ) into 1.01 solution shows that the rate of leaching was initially high and then decreased with time until it becomes constant. The amount of leachate was 66 mg obtained after 18 h of mixing with acetic acid solution. This value increased only by 1.5 mg in the next 7 h thereafter. On the other hand, when the initial cadmium concentration in the solid sample was 1.0 g ( $\sim 149$  mg  $\text{Cd}^{2+}$  in 50 g sample), the solution reached the saturated value of 13.1 mg  $\text{Cd}^{2+}$  after 2 h and kept constant after that. These values were greatly affected by the composition of cement and clay. During the cementation process the presence of metal oxides shows a maximum inhibition of cadmium leaching besides the adsorption of this cadmium by clay [21].

A mathematical correlation was proposed to fit these experimental data as [22]:

$$C(t) = \frac{t}{A + Bt} \quad (3)$$

where  $C(t)$  is the concentration of  $\text{Cd}^{2+}$  in solution at any time,  $t$ , and  $A$ ,  $B$  are constants.

A plot of the ratio of time to concentration versus time, Fig. 11, revealed a linear relation for the three samples that containing initially 1.0, 3.0 and 6.0 g  $\text{Cd}^{2+}$ . The maximum concentration of the leached cadmium will be obtained at infinite leaching time, i.e.  $C_{\text{max}} = 1/B$  at  $t \rightarrow \infty$ . The intercepts

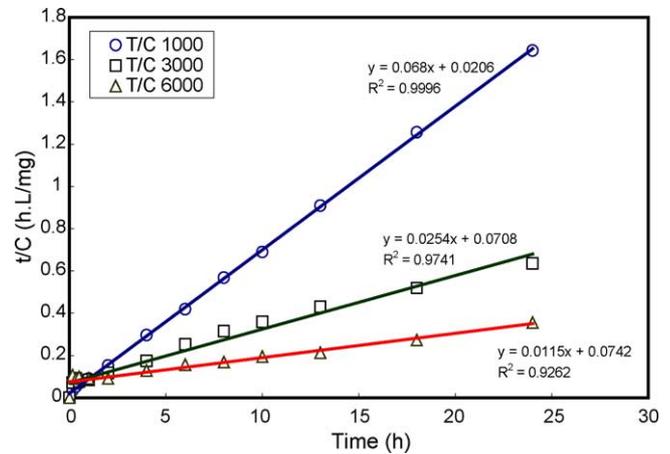


Fig. 11. Linear from of the leaching model for different initial cadmium concentrations.

for these lines were 0.0206, 0.0708 and 0.0742, respectively, while the slopes were 0.068, 0.0254 and 0.0115 in that order. It is noticeable that the slope of this equation is decreasing with increasing the initial concentration of cadmium while the intercept is relatively constant. The maximum  $\text{Cd}^{2+}$  concentrations leached out into the solution are 14.7, 39.4 and 86.9 mg  $\text{Cd}^{2+}$ , respectively.

## 4. Conclusions

An effort was made to utilize a low-cost adsorbent for holding metal ions from leaching out into water resources. A sand–cement–clay mixture with mass percentages of 25% sand, 50% cement and 25% clay was eligible for obtaining a maximum adsorption capacity toward cadmium, the metal of interest, and having a good compressive strength. Clay played a role in increasing the adsorption capacity toward cadmium, 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 the raw material and the relatively safe treatment process.

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