Removal of Heavy Metals via Adsorption using Natural Clay Material

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Abstract
Removal of heavy metals from its solution has been investigated by using adsorption clay material from El-Hammam district (Alexandria), with high silica content ~ 53 wt % was selected to verify this purpose. The clay material has been characterized by applying different techniques; x-ray analyses to investigate the crystalline structure (x-ray diffraction), the constitutes of the clay material (x-ray florescence) and thermal analysis to trace the structure changes that accompanying the thermal treatment.$FeCl_2$, $Ni(NO_3)_2.6H_2O$, and $ZnCl_2$ solutions have been used as metal model compounds to evaluate the adsorption efficiency of the clay material. Results indicated that the adsorption of heavy metals from its single metal solutions followed the order Fe> Zn > Ni.
Key words: Adsorption, Adsorbent, Bentonite, Montmorillonite, Heavy metals

1. Introduction

The problem of removing pollutants from water is an important process and is becoming more important with the increasing of industrial activities (Yakun et al., 2014). Therefore, removal of heavy metals such as cadmium, lead, nickel, chromium, iron, zinc and copper from aqueous solution is necessary because of the frequent appearance of these metals in waste streams from many industries (Missana and Garcı, 2007).

The heavy metals in the waste streams can be readily adsorbed by marine animals and directly enter the human food chains, thus presenting a high health risk to consumers (Lin et al., 2000 and Ulmanu et al., 2003).

Different techniques for the removal of metal ions from aqueous solutions have been developed as chemical precipitation, filtration, ion-exchange, reverse osmosis, membrane systems and ………etc. However, all these techniques have their inherent advantages and limitations in application. In the last few years, adsorption has been shown to be an alternative technique for removing dissolved metal ions from liquid wastes (Bayat, 2002).

In solution, heavy metals can be present either as free-ions or complexes with organic and inorganic ligands (Alleoni et al., 2003). In order to minimize processing costs, several investigations have focused on the use of low cost adsorbents, e.g. agricultural by-products (Samantaroy et al., 1997), biosorbents (lku¨ and Haluk, 2001; Pino et al., 2005), slag (urkovic´ et al., 2001) and clay materials (Mikhail et al 1971, Harvey and Chantawong, 2001).

Adsorbents, mainly clay minerals, are readily available, inexpensive materials and offer a cost-effective alternative to conventional treatment (Mikhail et al 2002 and Sanchez et al., 2002). Clay porous structure and high surface area provide benefits in the absorption of liquids and the adsorption of heavy metals (G&W Product Information, 2001).

The present study deals with the use of clay material as an adsorbent for the removal of Fe(II), Ni(II), and Zn(II) from solutions, as an alternative to existing commercial adsorbents. The effect of various parameters affecting adsorption behavior as contact time, initial metal ion concentration, amount of adsorbent and pH of solution have been investigated and data on adsorption isotherms have been presented.

2. Experimental

2.1 Preparation of the adsorbent material

Clay material from El-Hammam district (Alexandria) was selected to be used as an adsorbent. The clay material was grounded, sieved to mesh size ‹ 100 mesh and then dried at 120 ^{0}C for 4 hours.

2.2 Characterization of the adsorbent material

The clay material was fully characterized physically and chemically through different techniques such as; chemical analysis, differential thermal analysis (DTA) and thermo gravimetric analysis to trace the structural changes accompanying the thermal treatment. X-ray analyses were carried out to study the crystalline structure (x-ray diffraction) and the constituents of the clay material (x-ray fluorescence).

2.3 Preparation of the adsorptive compounds

Analytical grade metal salts $FeCl_2$, $Ni(NO_3)_2.6H_2O$, and $ZnCl_2$ were used without further purification. All experiments employed distilled water. Stock solutions (1000 mg/l) of Fe(II), Ni(II), and Zn(II) were prepared in distilled water. The stock solutions were diluted as required to obtain standard solutions containing 10–50 mg/l

of Fe(II), Ni(II), and Zn(II).

2.4 Adsorption method

Adsorption measurements were made by a batch technique at room temperature (25 ± 1^0C). The batch mode was selected because of its simplicity and reliability. In all experiments known amount of clay material were weighed in a bottle flask (50 ml capacity) and heated for 4 hours at 120 ^{0}C. After cooling, the required volume (10 ml) of the adsorptive compound solution was added at room temperature (25 ± 1^0C). The solutions were then shaken vigorously for a given time period to reach equilibrium. The agitation speed was kept constant for each run to ensure equal mixing. After completion of a pre-selected shaking time, the suspensions were then filtered. The amount adsorbed was determined by analyzing the metal content before and after each experiment using A Varian GTA model 100 Atomic Absorption Spectrometer (AAS) operating with an air–acetylene flame.

Experimental operating conditions:

- *Contact time, min*   *30-240*
- *Amount of adsorbent, gm*   *0.1-0.7*
- *Concentration of adsorptive solutions, mg/l*   *10-50*
- *PH of solution*   *1.5-9*
- *Adsorptive compounds*   *$FeCl_2$, $Ni(NO_3)_2.6H_2O$, and $ZnCl_2$*

Langmuir and Freundlich isotherm models were fitted to the adsorption data and their constants were evaluated. Satisfactory conformity between experimental data and the model-predicted values was expressed by the correlation coefficient (R^2).

3. Results and discussion

3.1 Physical characteristics of the adsorbent material

3.1.1 Chemical analysis

Chemical analysis was carried out to evaluate total silica, alumina, iron and alkali metals by x-ray fluorescence. The results are presented in Table1.

Table 1. Chemical analysis of raw-clay material

compound	wt %
SiO_2	53.25
Al_2O_3	18.15
Fe_2O_3	6.65
Na_2O	4.97
MgO	1.42
K_2O	1.05
Cl-	0.62
*I.L	13.85
SiO_2/Al_2O_3 molar ratio	~ 5

* *Ignition Loss (I.L)* is determined by burning one gram sample at 1000 ^{0}C till constant weight.

Chemical analysis of raw material indicates that, it is composed of sodium-bentonite and kaolinite as signified from the low alumina content, high percentage of iron (Fe_2O_3), sodium (Na_2O), relatively low percentage of potassium (K_2O) and high silica/alumina molar ratio.

3.1.2 X-ray diffraction

The information concerning the crystalline phases was determined by comparing the characteristics d-spacing (^{0}A) and the relative intensity I/I_0 with the data given in the ASTM cards (1978). The x-ray diffraction pattern for the clay material in fig. 1 reveals the presence of the following minerals:
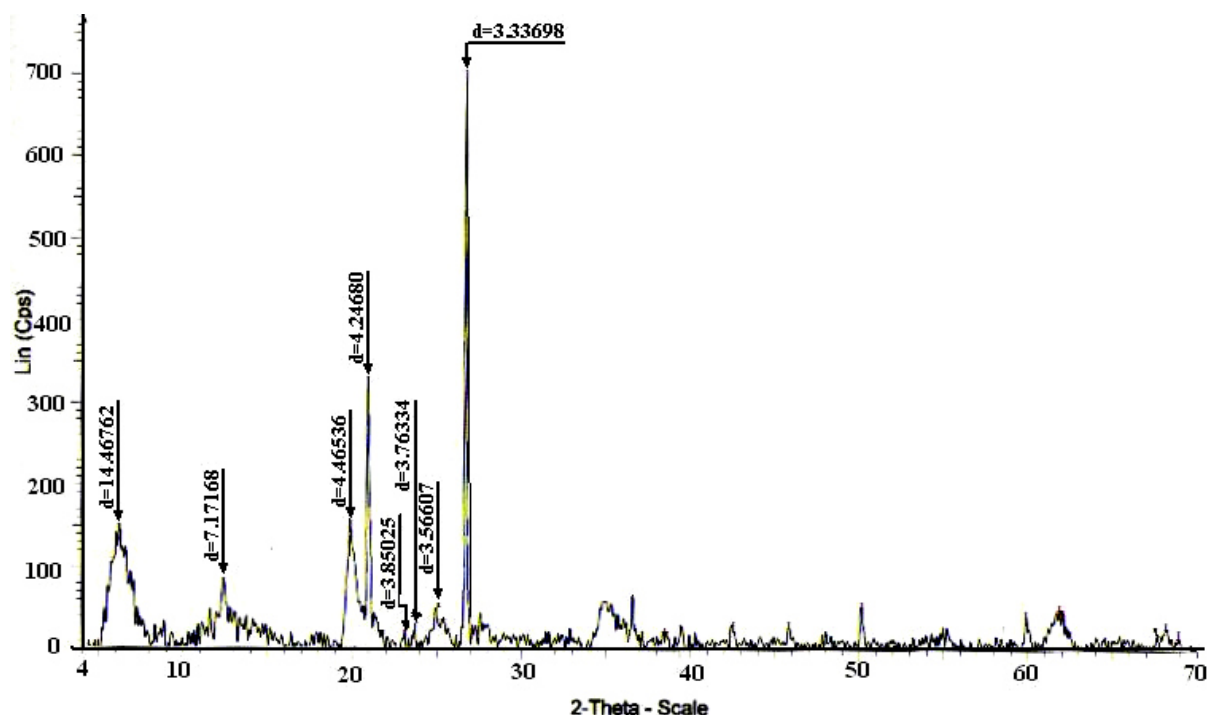
Figure 1. X-ray diffraction pattern for raw-clay.

Montmorillonite: as indicated by its basal reflections near 14.46, 4.24 and 3.85 ^{0}A and it is the main constituent of this clay material.

Kaolinite: as indicated by its two basal reflections near 7.17 and 3.56 ^{0}A.

Quartz: considerable amounts of quartz were detected at 3.33 ^{0}A.

Traces of feldspars: were also identified.

Thus, it can be concluded that the clay material from El-Hammam district is composed of sodium-montmorillonite, kaolinite together with non-clay minerals of quartz and feldspars, which is in accordance with the chemical analysis.

3.1.3 Thermal analysis

The differential thermal analysis (DTA) and thermal gravimetric analysis (TGA) are important techniques used to distinctly show the effect of heating in the performance and thermal stability of the solid material. Differential thermal profile for the raw clay (Fig.2) exhibits a large endothermic peak that occurs between 100-200 ^{0}C accompanied by a loss in weight that ranges between 9 and 11 wt. % (TGA line).

The absence of the "shoulder" which normally appears near to the 200 ^{0}C endothermic peak in the DTA curve in case of Ca- Montmorillonite proved that this raw martial is the sodic-type (Barashad 1950). This is in line with the x-ray diffraction data as well as the chemical analysis.

The large symmetric endothermic peak that takes place at 510 ^{0}C (DTA) and the other at ~ 720 ^{0}C are caused mainly by the loss of the structural OH similar to which is observed with Montmorillonite and kaolinite which accompanied also by a loss in weight (Grim and Bradley 1940).

According to Zulfugarov, et al (1962) the adsorption capacity of clay is directly proportional to the amount of water adsorbed on the clay surface, represented by the first endothermic peak at 100-200 ^{0}C. The exothermic peak that appears at 930 ^{0}C is structural one. Its exothermic component may be attributed to the destruction of the bentonite structure similar to that occurs with Montmorillonite and kaolinite structures and formation of new phases. This reaction is not accompanied by any loss in weight.

Thus, the DTA picture of the raw material indicates that the clay material from El-Hammam district is bentonitic- kaolinitic clay. Consequently, it can be concluded that the bentonite clay material from El-Hammam district have lamella structure (x-ray diffraction and thermal analysis) which is the essential prop to bring the structure easily accessible for adsorption.
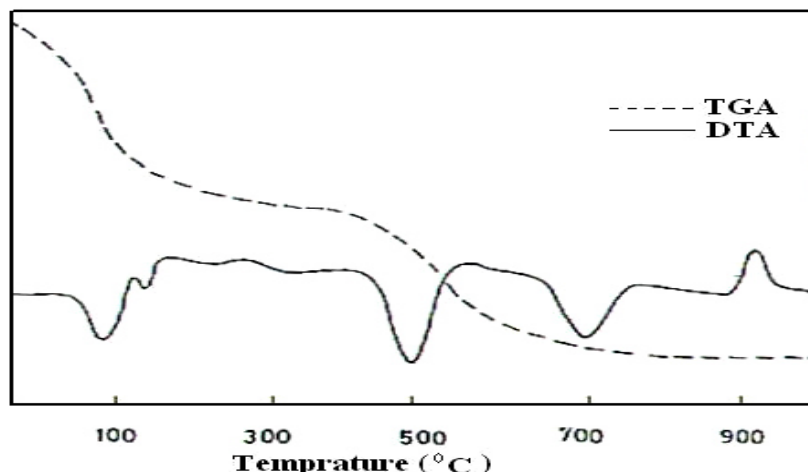
Figure 2. Thermal analysis curves for raw-clay.

3.2 Evaluation of the adsorptive power of the bentonite clay material

To evaluate the adsorption capacity of the clay material toward the removal of the different cations; Fe(II), Ni(II), and Zn(II). The effects of; contact time, amount of clay, concentration of adsorptive solutions and PH of the solutions were studied. Data are illustrated graphically in figures (3-6)

3.2.1 Effect of contact time

The time-dependent behavior of iron, nickel and zinc was measured by varying the equilibrium time between the adsorbate and adsorbent in the range of 30–240 min. The initial concentration of metal ions was 50 ppm. The pH was kept as 1.5 and the amount of clay added was 0.1 g.

Figure (3) represents the relation between the specific adsorption (initial volume of adsorbate x amount adsorbed / gm adsorbent) and contact time. Results show that the equilibrium is reached quickly (~30 min), indicating that, the adsorption sites are well exposed. It is clear that with the increase in contact time from 30 to 60 min the amount adsorbed slightly increased [Fe(II) and Zn(II)] or decreased [Ni(II)] followed by a constant adsorption upon further increasing in contact time. Consequently, the shaking time was fixed at 60 min for the rest of the batch experiments to ensure that adsorption equilibrium was reached in each case. This finding is in agreement with the results of Ulmanu et al. (2003), who investigated heavy metals removal from aqueous solution using peat.
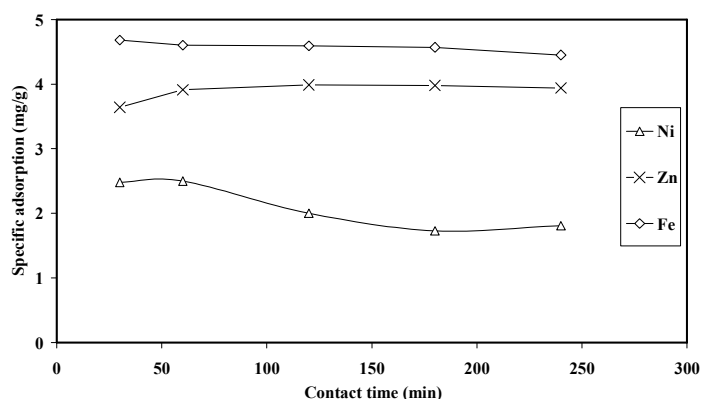

Figure 3. The relation between the specific adsorption and contact time.

3.2.2 Effect of amount of adsorbent

The amount of clay adsorbent was varied from 0.1 to 0.7 gm with using initial metals concentration of 50 mg/l and agitation time of 60 min. For Ni solution the extent of adsorption (%) increased rapidly as more and more of the adsorbent was added until reach 100 %, whereas for Zn and Fe the extent of adsorption % is smoothly increased with the gradual increase in the amount of adsorbent clay material as represented histogrammatically (Fig 4-a) and also in fig 4-b. Availability of increasing number of exchangeable sites ensured enhanced uptake. This is a common observation whenever either the number of adsorption sites or the active surface area is

increased. However, the amount of adsorbed per unit mass (qe) of the adsorbent (specific adsorption) at equilibrium decreased with an increase in the amount of the clay adsorbent (Fig. 4-c). Although the number of adsorption sites per unit mass of an adsorbent should remain constant, independent of the total adsorbent mass, increasing the adsorbent amount in a fixed volume reduces the number of available sites as the effective surface area is likely to decrease.
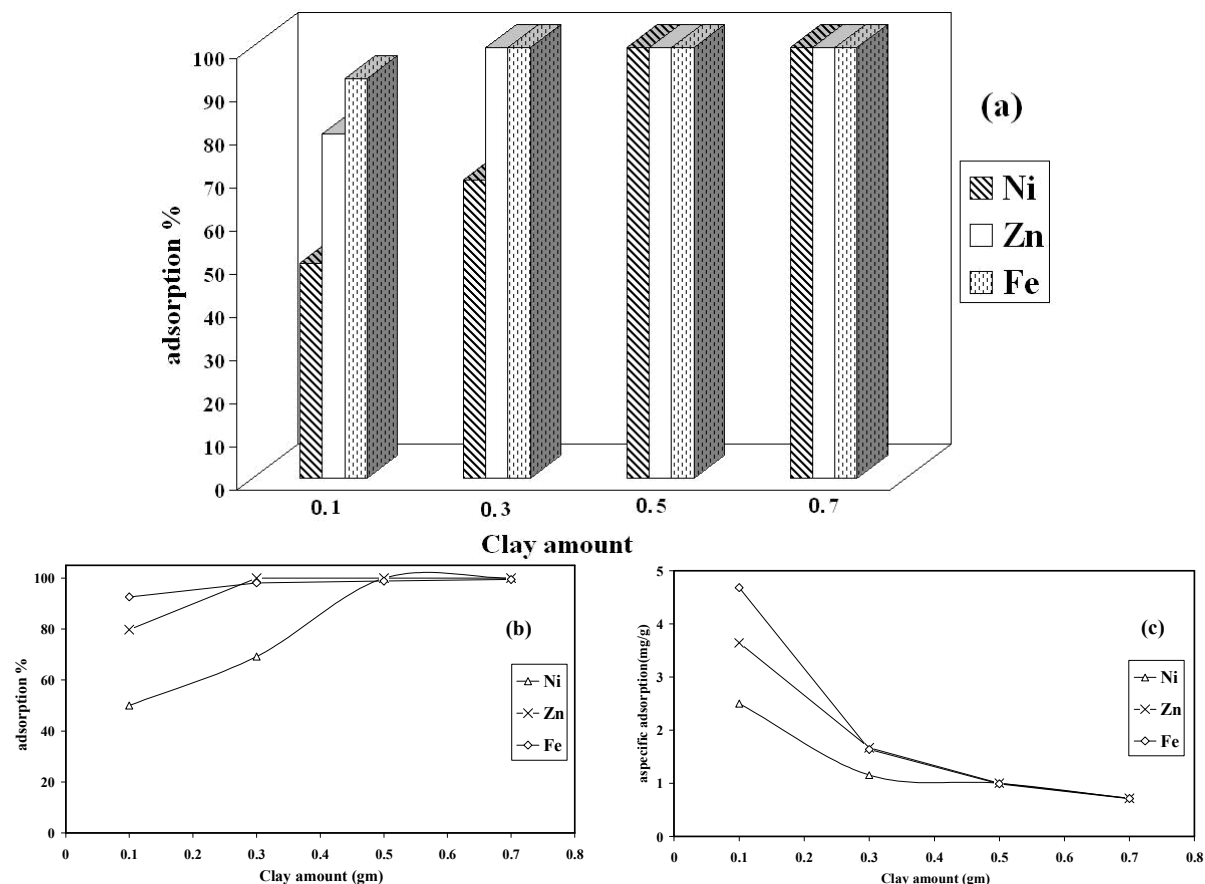

Figure 4. Relation between clay amount and; (a) histogram of adsorption %;
(b) adsorption %; (c) specific adsorption.

3.2.3 Effect of pH of the adsorptive solution

The pH of the aqueous solution is an important variable which controls the adsorption of the metal at the clay–water interfaces. Hence, the influence of pH on the adsorption was investigated in the pH range of 1.5–9 using clay amount of 0.1 gm and metals concentration of 50 mg/l. As the acidity of the medium decreased from 1.5 to 3, the extent of adsorption (%) as well as the amount adsorbed (qe) showed a positive variation (Fig. 5). With further increase in the PH of solution, the adsorption % is constant.

Clays are known to possess a negative surface charge in solution as pH changes, surface charge also changes, and the sorption of charged species is affected (attraction between the positively charged metal ion and the negatively charged clay surface). It is conceivable that at low pH values, where there is an excess of H_3O^+ ions in solution, a competition exists between the positively charged hydrogen ions and metal ions for the available adsorption sites on the negatively charged clay surface. As the pH increases and the balance between H_3O^+ and OH^- are more equal, more of the positively charged metal ions in solution are adsorbed to extent limit on the negative clay surface and thus the percentage removal of the metal ions increases.

On the other hand, (i.e. directed to basicity) precipitation of metal hydroxides may also occur as the pH in solution increases, which will lead to a corresponding decrease in the amount of metal ions adsorbed onto the clay. Thus it can be concluded that the change of PH of solution from weak acid to neutral then to basic (from 3 to 7 then to 9 respectively) there is no effect on the extent of adsorption.
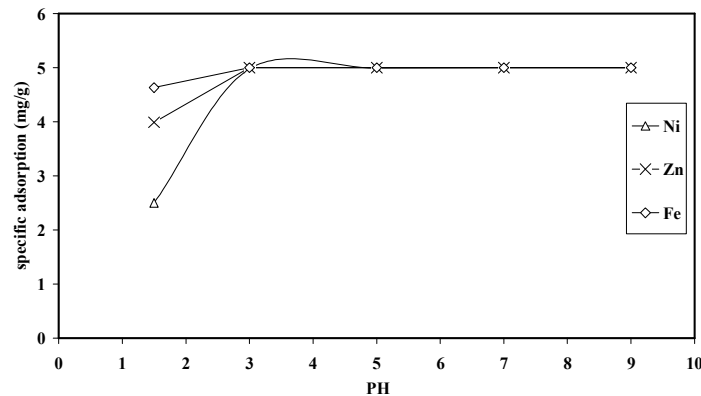
Figure 5. Effect of PH of the adsorptive solution on specific adsorption.

3.2.4 Effects of initial metals concentration

When the initial concentration of metals was changed from 10, 20, 30, 40 to 50 ppm using clay amount of 0.1 gm, agitation time 60 min and pH 1.5, the extent of adsorption (%) slightly decreased with the gradual increase in initial metals concentration for Zn and Fe, but for Ni a remarkable decrement was noticed (Fig. 6-a). Such observation is quite common. The amount adsorbed per unit mass (qe) however showed an increase with gradual increase in concentration of metals (Fig. 6-b).

At low initial concentration, the ratio of the number of ions to the number of available adsorption sites is small and consequently the adsorption is independent of the initial concentration, but as the concentration increases, the situation changes and the competition for adsorption sites becomes fierce. As a result, the extent of adsorption comes down considerably, but the amount adsorbed per unit mass of the adsorbent increases.
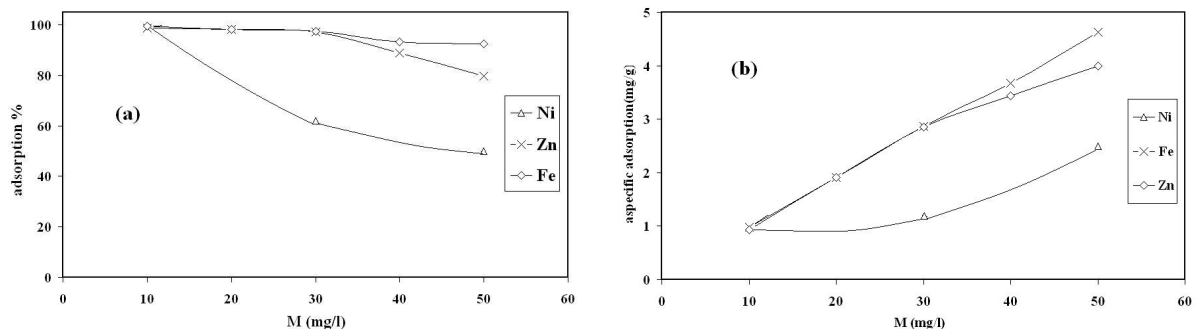

Figure 6. Effect of initial metals concentration on; (a) adsorption %; (b) specific adsorption.

3.3 Adsorption isotherms

The adsorption isotherms for Fe(II), Ni(II) and Zn(II) removal were studied using initial concentration of metal ions between 10 and 50 mg/l, room temperature ($25 \pm 1 \,^{0}C$) an using adsorbent mass of 0.1 g. The data obtained were fitted to the Langmuir isotherm.

$C_e/q_e = 1/(bq_m)+(1/q_m)C_e$ …………………………(1)

where C_e and q_e are the initial concentration of the adsorbate and the amount adsorbed at equilibrium respectively. Where b and q_m are Langmuir coefficients representing the equilibrium constant for the adsorbate–adsorbent equilibrium and the monolayer capacity.

The data obtained from the various plots (Figs 7-9) as summarized in Table 4 show that adsorption of Ni(II), Zn(II) and Fe(II) follow the Langmuir isotherm model fairly well. The adsorption data for all metal ions also fit the Freundlich isotherm reasonably well, but not as well as the Langmuir equation.
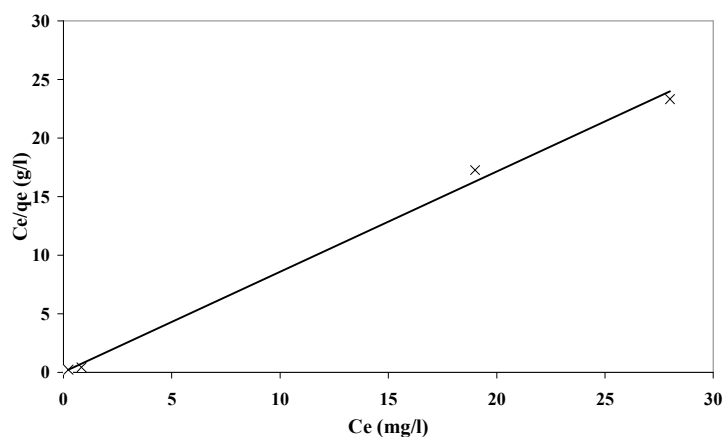
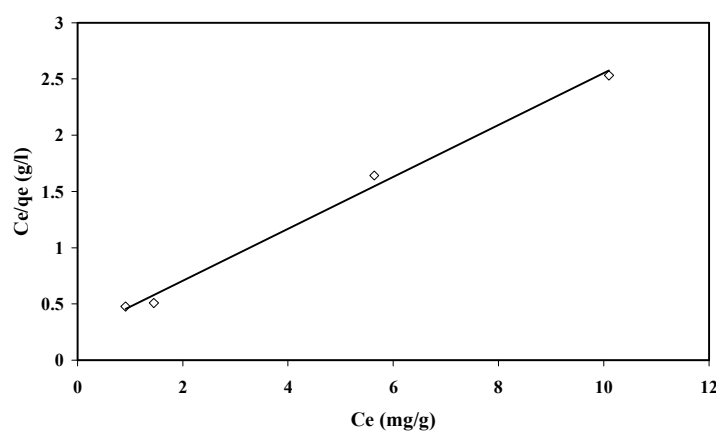Figure 7. Langmuir Isotherm for Ni(II) adsorption on clay.

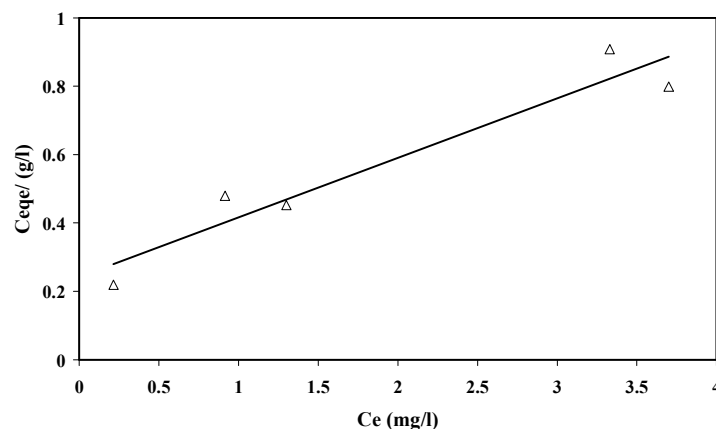Figure 8. Langmuir Isotherm for Zn(II) adsorption on clay.

Figure 9. Langmuir Isotherm for Fe(II) adsorption on clay.

Table 4: Langmuir and second order constants and correlation coefficients associated with adsorption isotherms and kinetic of Ni(II), Zn(II) and Fe(II) onto clay.

	Langmuir equation			second order equation		
	qm (mg g/l)	b (l/mg)	R^2	qe (mg/g)	K_2 (g/mg)	R^2
Ni(II)	1.17	19.75	0.99	1.70	-0.04	0.99
Zn (II)	4.33	0.93	0.99	3.99	0.17	0.99
Fe (II)	5.74	0.72	0.92	4.44	-0.09	0.99

3.4 Kinetic of adsorption

Kinetic modeling results using the Lagergren's first-order equation wasn't appropriate for the description of this type of adsorption and removal.

Fig. 10 shows the kinetic curves of adsorption of Ni(II), Zn(II) and Fe(II) obtained from evaluation of kinetic data using the following equation.

$$t/q_t = 1/k_2 q^2_e + (1/q_e)t \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(2)$$

In such cases, pseudo second order kinetics represented by the linear equation where k_2 is the second order rate constant and $k_2 q^2_e$ known as the initial sorption rate, could be tested. The linear plots of t/q_t vs t allow computation of q_e, k_2 and the initial rate (Table 4).
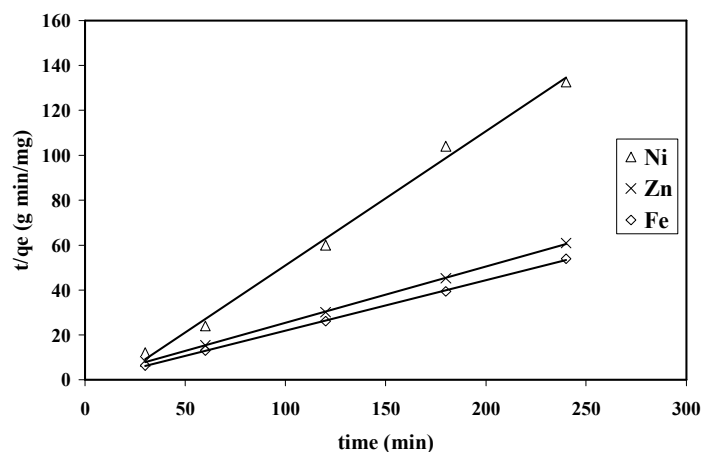

Figure 10. Second order plot for Ni(II), Zn(II) and Fe(II) adsorption on clay.

4. Conclusion

From the previous results, it can be concluded that:

- This study clarified that heavy metals like Ni(II), Zn(II) and Fe(II) can be adsorbed and thus removed in significant amounts using cheapest clay material (adsorbent) from aqueous solutions.
- Clay material from El-Hammam district have lamella structure characterized by well-ordered arrangement of large platelets stacked face to face with large amount of micro- porosity and accordingly that pocessess Brônsted acid sites, which is the essential prop to brind the clay structure accessible for adsorption.
- In batch mode adsorption studies, removal of metal ion increased with the increase of amount of adsorbent.
- The increase in initial metal ion concentration increased the amount of metal uptake per unit weight of the adsorbent (mg/g). Whereas the extent of adsorption % decreased.
- The Langmuir model better represented the adsorption process than the Freundlich model.
- Kinetic modeling results showed that the pseudo second order kinetics equation was appropriate for the description of this type of adsorption and removal.
- Adsorption of heavy metals from the single-metal solutions followed the order of:
  Fe> Zn > Ni.
- For industrial applications, one will have to compliment the batch results with those from columns to derive the necessary design data.

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