Study of the adsorption of Pb(II), Cu(II), Fe(II) and Cd(II) by using modified natural clay

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Abstract: The removal of heavy metals (Cu^{+2}, Pb^{+2}, Fe^{+2}, and Cd^{+2}) onto modified clay using batch-adsorption technique has been studied. The influence of concentration, on the adsorption process has also been studied. The natural clay obtained from New Valley in Egypt was crushed into powder and passed through 200 mesh sieve and then modified with sodium acetate. It rinsed and dried up. Results show that removal efficiency reached within about 120 minutes. The increase in contact time did not show significant change in equilibrium concentration. The adsorption isotherm fitted well by the Langmuir and Freundlich models, and adsorption increase by increasing temperature, and decrease by decreasing pH.

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1. Introduction:

Environmental pollution is currently one of the most important issues facing humanity. It increased exponentially in the past few years and reached alarming levels in terms of its effects on living creatures [1,14,15]. Although many heavy metals are necessary in small amounts for the normal development of the biological cycles, most of them become toxic at high concentrations [2].

Heavy metals are dangerous because they tend to bioaccumulation. Bioaccumulation means an increase in the concentration of a chemical in a biological organism over time compared to the chemical concentration in the environment. Heavy metals can enter a water supply by industrial and consumer waste [3, 18, 19]..

Heavy metals in water are removed by many separation methods such as precipitation, chemical reduction, ion exchange, membrane separation, solvent extraction, adsorption and biological treatment [4, 16,17]. Development of low cost adsorbents and the ease of application and reuse have made adsorption from liquid phase an attractive process for use treatment of contaminated water [5].

Clay is such an effective low cost adsorbent which can be found in large amount in New Valley and contains montmorillonite. Montmorillonite detected, in clay materials were collected from Fayoum area and Alamine area. It is classified into calcium montmorillonite and sodium montmorillonite. Calcium montmorillonite is observed in Fayoum type while sodium montmorillonite is detected in both samples of Alamin type [6].

In order to enhance the adsorption capacity of the clay, its usage should be preceded by some modification. The acidic treatment of clay materials has been well known for many years. Modification of clay materials by alkaline solutions leads usually to zeolitization, and significantly increases their uptake capacity for heavy metal and ammonium ions [7].

In this study, the premodified natural clay obtained from New Valley have been applied for for adsorbtion of metals (Pb^{2+}, Cd^{2+}, Fe^{2+} and Cu^{2+}). The behaviors from equilibrium aspect by variation at contact time, concentration, pH, and temperature have been also studied. The adsorption isotherm fitted well by different models (Langmuir and Freundlich).

2. Materials and methods

2.1. Clay adsorbents

Natural clay used in this study obtained from New Valley in Egypt. We used it for first time in water treatment.

2.2. Adsorbate solution

The adsorption experiment was conducted by using synthetic effluent containing Pb (II), Cu(II), Cd(II), Fe(II). The stock solution containing 1000 mg of Pb (II) and Cu(II) Cd(II), Fe(II) was prepared by dissolving $Pb(NO_3)_2$ in 1 L, $CuSO_4$ in 1L, $FeSO_4$ in 1L and $3CdSO_4.8H_2O$ in 1L was used to prepare the adsorbate solution by appropriate dilution.

2.3. Natural clay characterization

The structure of the clay have been obtained through XRD analysis using X-ray diffraction (XRD) on a brukur advanced X-ray diffractometer model D8 kristalloflex (Ni-filtered Cu Kα radiation; λ= 1.544 A). The SEM results by using a QUANTA FE250- EDAX Genesis field emission scanning electron microscope

(Holland) equipped with an energy dispersive X-ray microanalyzer (EDS).

2.4. Modifying solution

The chemical material CH3COONa.3H2O was weighted in the amount of a half of each molecular weight and dissolved in 500 ml of aquadest to make 1 M of modifying solutions.

2.5. Modification of clay

Twenty five grams of clay was put into 1000 ml of round-bottom flask. Then the modifying solutions were poured into the glass. Afterwards, the mixtures-contained flask was equilibrated and stirred with magnetic stirrer at room temperature for 5 h. then the mixture was filtered by vacuum filtration. Finally, the raw sample was dried at 100^{o}C in an oven until constant weight attained.

2.6. Adsorption experiment

The batch adsorption experiment was carried out in a 100 ml Erlenmeyer flask by mixing 1 gm of clay and 50 ml aqueous solution of metal ion and shaking the mixture at constant rate shaker for 2 hours. The mixtures were centrifuged (2500 rpm) and the metal ion remaining unadsorbed in the supernatant liquid was determined with (I.C.P), Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES) with Ultra Sonic Nebulizer (USN). The experiments carried out with different concentrations, time, temperatures and pH.

2.7. Kinetic studies

1 gram of adsorbents was left in contact with 50 ml of the metal solutions at the initial pH of (5.4),(4.4), (2.5), (5.5) for Cu(II), Pb (II), Fe (II) and Cd (II) respectively at room temperature. Kinetic of adsorption was determined by analyzing the adsorptive uptake of metal from aqueous solution at different time intervals (5, 15, 30, 60, 90, 120, 150 min).

The amount of metal adsorbed on the adsorbents q_e (mg.g-1) was calculated using the following expression:

$$q_e = (C_o - C_e) / M \quad (1)$$

Where, C_o and C_e are the initial and equilibrium metal concentrations of the test solution (mg. L-1), respectively, M is the amount of adsorbents per liter (g. L-1).

3. Results and Discussion

3.1. XRD Analysis:

As shown from the XRD analysis fig (1) the Clay contains montmorillonite, quartz, Sidrite and Muscovite.

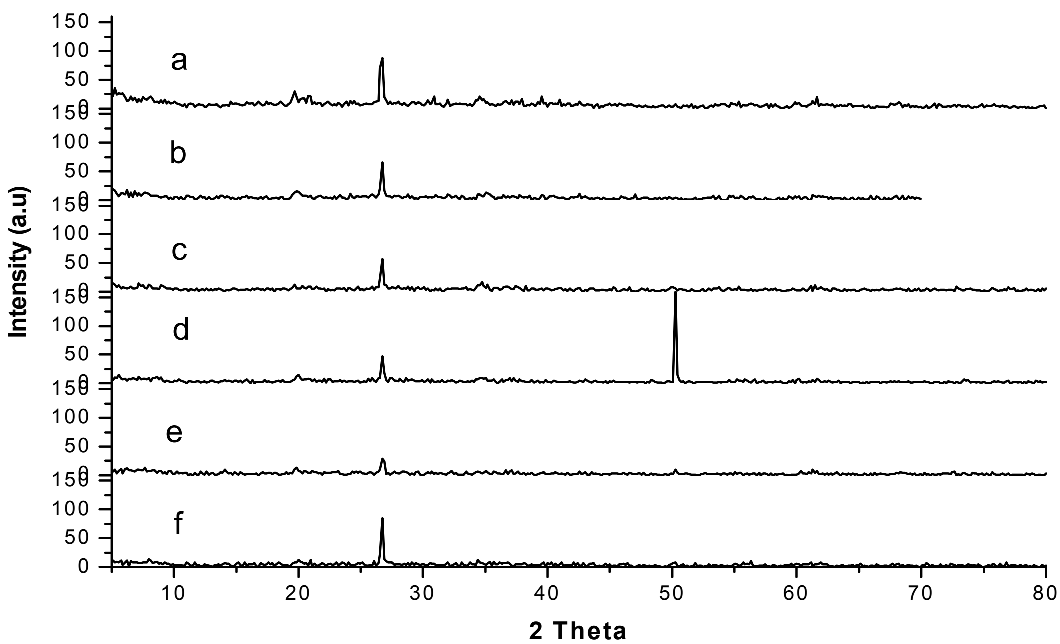
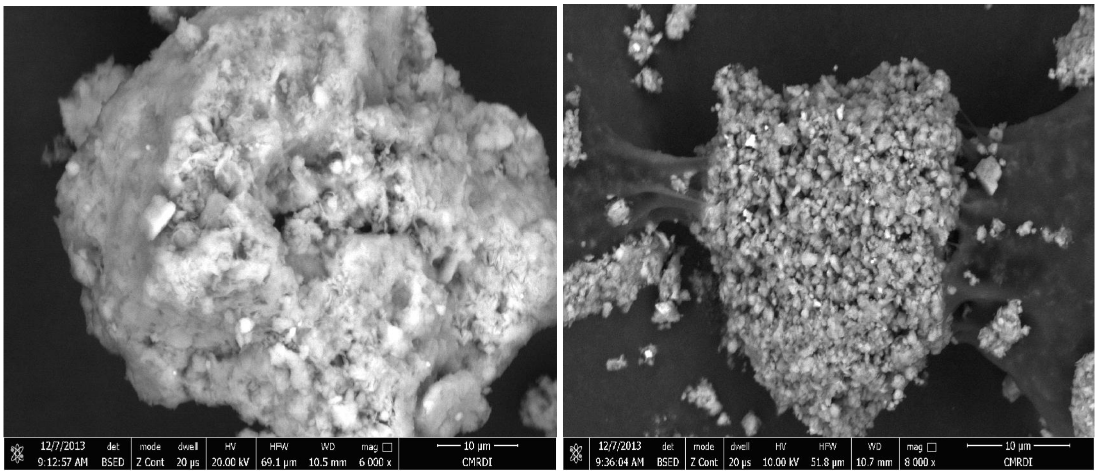


Fig (1) XRD analysis of clay (a) clay before modification (b) clay after modification (c) sample b after adsorption of lead (d) sample b after adsorption of copper (e) sample b after adsorption of cadmium (f) sample b after adsorption of iron.

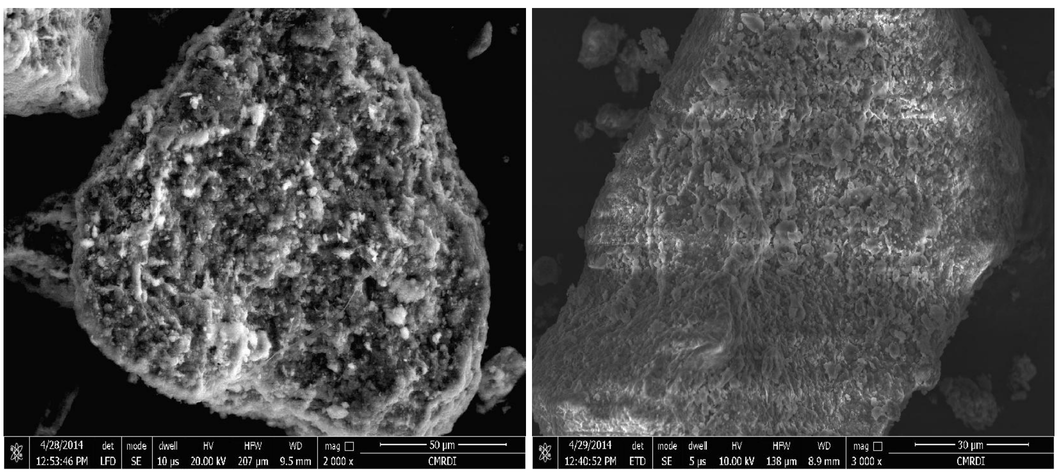
3.2. The SEM Analysis:

The SEM analysis showed clay before modification appears sponge shape and contains some pores, It noticed that the pores increases after modification and decreases after adsorption of Pb^{+2}, Cu^{+2}, Cd^{+2} and Fe^{+2} fig (2) and fig (3).

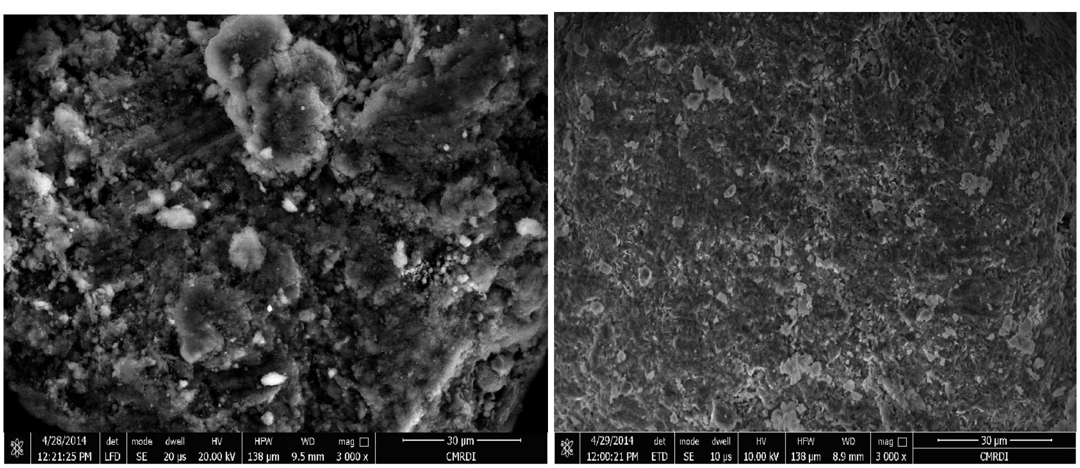


(a) (b)

Fig (2) SEM (a) Clay before modification and (b) Clay after modification



(a) (b)



(c) (d)

Fig (3) SEM (a) Clay after adsorption of Cu(II) and (b) Clay after adsorption of Pb(II), (c) clay after adsorption of Cd(II) and (d) clay after adsorption of Fe(II).

3.3. Adsorption isotherm

For the solid-liquid system, the studies of adsorption isotherms are very important to realize information about adsorption capacity of adsorbents

[8].

The most important models for evaluating the adsorption equilibrium is Langmuir and Freundlich isotherms. The Langmuir isotherm is obtained under an assumption that the adsorption occurs at a specific homogeneous surface of the adsorbent [9]. The linearly transformed Langmuir isotherm is used to fit the adsorption data in this study and is expressed as:

$$C_e/q_e = C_e/q_m + 1/q_m b \qquad (2)$$

Where, Ce is the equilibrium concentration of the metal ion in solution ($mg \cdot L^{-1}$), qe is the amount of metal ion adsorbed on adsorbents ($mg \cdot g^{-1}$), and qm and b are the monolayer adsorption capacity (mg·g-1) and the binding constant, respectively.

The Freundlich isotherm is an empirical equation which is used for the heterogeneous systems[10, 11] hs represented as:

$$lg\ q_e = lg\ K_f + 1/n\ lg\ C_e \qquad (3)$$

where K_f and n are indicative of the extent of the adsorption and the adsorption intensity, respectively.

The amount of the adsorbed metals at different initial concentrations per 1 gram modified clay were calculated, see Figures (4), (5).

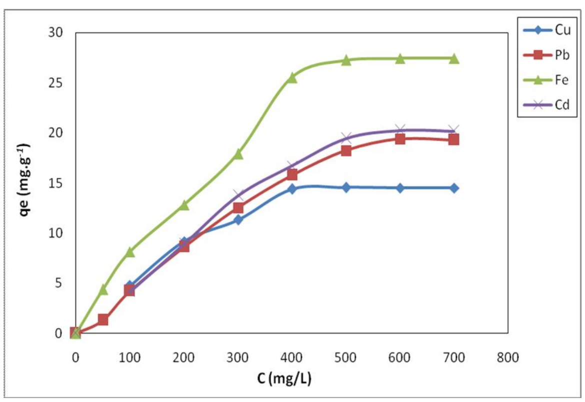


Fig (4) Adsorption of Cu(II), Pb(II), Fe (II), and Cd(II) at different initial concentrations

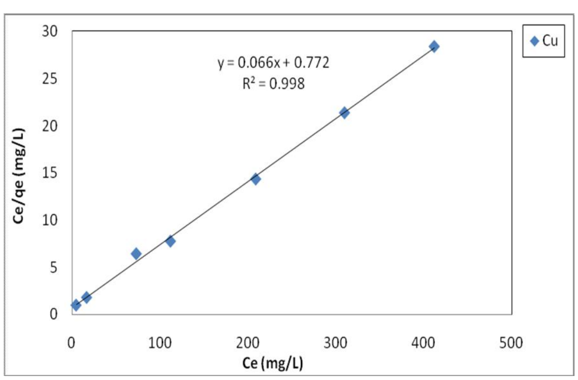


Fig (5) Langmuir isotherm for adsorption of Cu (II) on modified clay

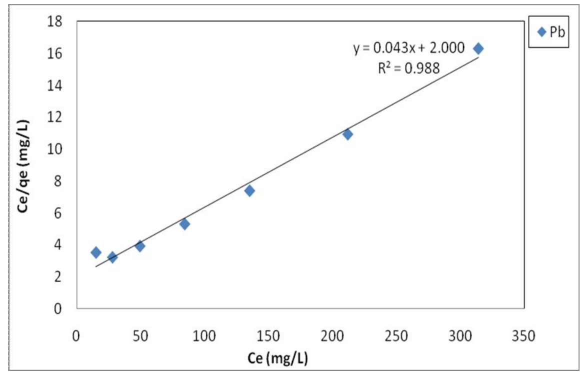


Fig (6) Langmuir isotherm for adsorption of Pb (II) on modified clay

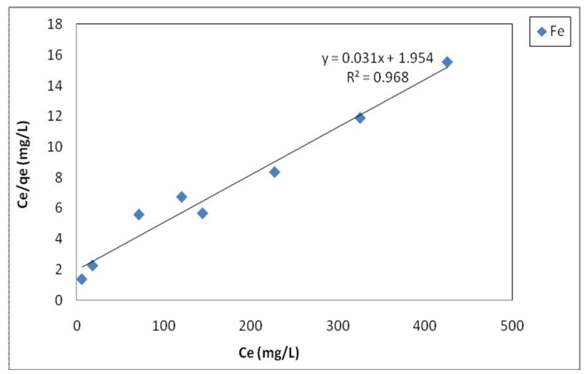


Fig (7) Langmuir isotherm for adsorption of Fe (II) on modified clay

As shown in fig (4) the amounts of Pb (II), Cu (II), Fe (II), and Cd(II) are increased as the initial concentration increases. It means that the adsorption is highly dependent on Pb (II), Cu (II), Fe (II), and Cd (II) initial concentration and the active sites are still available in a large number for the Pb (II), Cu (II), Fe (II), and Cd (II) ions to reside.

3.4. Langmuir isotherm

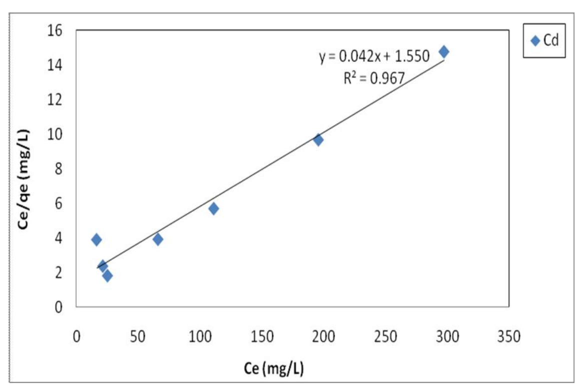


Fig (8) Langmuir isotherm for adsorption of Cd (II) on modified clay

Table (1) Langmuir constants *b* and q_{max}

Element	q_m (mg.g^{-1})	B (L.mg^{-1})	R
Cu	1.515	0.855	0.998
Pb	23.256	0.0215	0.988
Fe	32.258	0.0159	0.968
Cd	1.954	0.0271	0.967

Adsorption is usually described by isotherm, which is a function that, connect the amount of adsorbate on the adsorbent. The Langmuir isotherm describes the distribution of metal ions between the liquid phase and the solid phase. Langmuir isotherm assumes monolayer adsorption onto a surface containing a finite number of adsorption sites of uniform strategies with no transmigration of adsorbate in the plane surface [12]. Once a site is filled, no further sorption can take place at that site. This indicates that the surface reaches a saturation point where the maximum adsorption of the surface will be achieved.

Langmuir adsorption isotherm is showing the variation between specific adsorption (C_e/q_e) against the equilibrium concentration (C_e) for adsorption of metal ions onto modified clay Figs (5, 6, 7, 8). The linear plot shows that the adsorption obeys the Langmuir model. The constants *b* and q_{max} relate to the energy of adsorption and maximum adsorption capacity, and their values are obtained from the slope and intercept represented in Table (1).

3.5. Freundlich Isotherm

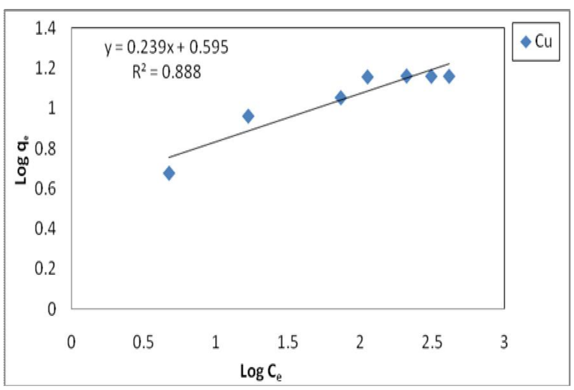


Fig (9) Freundlich isotherm for adsorption of Cu (II) on modified clay

Freundlich equilibrium constants were determined from the plot of Log C_e versus Log q_e. From Figures (9, 10, 11, 12) on the basis of the linear of Freundlich (equation 3), the n value indicates the degree of nonlinearity between solution concentration and adsorption as follows: if n=1, then adsorption is linear; if n<1, then adsorption is a chemical process; if n>1, then adsorption is a physical process [13].

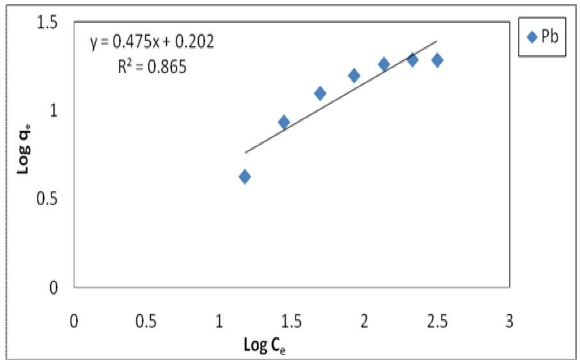


Fig (10) Freundlich isotherm for adsorption of Pb (II) on modified clay

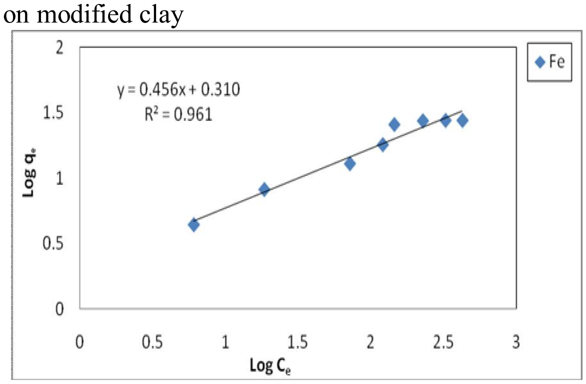


Fig (11) Freundlich isotherm for adsorption of Fe (II) on modified clay

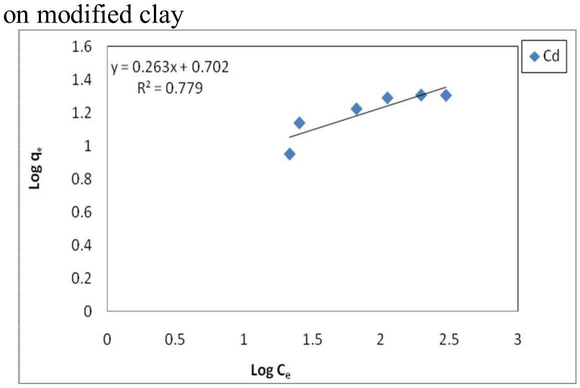


Fig (12) Freundlich isotherm for adsorption of Cd (II) on modified clay

The obtained results indicate n values were ranged from 2.105 – 4.184, Table (2). In the present study, since *n* lies between 1 and 10 indicates the adsorption of metal ions onto the modified clay surface is physical adsorption.

Table (2) Freundlich equilibrium constants

Element	N	K_f	R
Cu	4.184	3.935	0.888
Pb	2.105	1.592	0.865
Fe	2.193	2.042	0.961
Cd	3.802	5.035	0.779

Conclusion

At several modifying materials were used in this research that sodium acetate could improve the capacity of adsorption of New Valley clay on the adsorption Pb (II), Cu (II), Fe (II), and Cd(II) from aqueous solution especially at low concentration. Adsorption of these metal ions with the sodium acetate modified clay by applying Langmuir and Freundlich isotherms obeys the Langmuir model and physical adsorption.

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