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ADSORPTION OF SOME HEAVY METAL IONS FROM AQUEOUS SOLUTIONS BY USING KAOLINITE CLAY

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ABSTRACT :

Adsorption of some heavy metal ions such as lead, Pb(II), Copper, Cu(II), Iron, Fe(III), Manganese, Mn(II) and Zinc, Zn(II) by sorption on kaolinite clay was investigated. Kaolinite clay is considered as a good ion exchanger since it is easily available at low cost and high capacity. The effects of contact time, pH, volume of an aqueous to mass of kaolinite clay and concentration of metal ions were studied. Data show that kaolinite clay favorably adsorbs the current heavy metal ions and their adsorption are belong to Freundlich isotherm model.

INTRODUCTION:

Heavy metal ions such as Pb^{2+}, Cu^{2+}, Fe^{3+}, Mn^{2+} and Zn^{2+} are present in drinking water due to development of industrial process for different reasons and as a result of metal pipes corrosion, where metal pipes have been used for the transportation of drinking water [1].
However, originally the problem is mostly related to bad tasting colored or discolored water but in recent time, the water quality has become the focal issue towards preventing adverse medical effects. Safe drinking water has always been a concern to both those who consume it and to those who provide it. Ion exchange and adsorption methods can be used for elimination of these pollutants. Obviously, the economical cost of adsorption process should be reduced using an available cheaper adsorbents, having high adsorptive capacity and no effect on physical and chemical characteristics of the solution. Clay is a natural material that can statisfy the previous conditions. The ion exchange properties of clays have been intensively studied[2,3]. Ion exchangers have a varying degree of preference for each metal ion depending on exchange type, operating conditions and the metal being removed. Usually the only pretreatment required a head of the ion exchange is pH adjustment. A pH of about 4 to 7 is usually optimum because a lower pH will prevent the metal from loading onto the exchanger and higher pH could cause precipitation of the heavy metal hydroxides[3]. Once the capacity of the ion exchange is exhausted, the exchanger is regenerated to remove the heavy metal ions and return the exchanger to its usable form. Regeneration process is accomplished by passing strong acids and some inorganic salt solutions. The mechanism by which the adsorption process that takes place by clay is concerned mainly with the nature of forces

acting between the adsorbed trace element and the adsorbent. According to the forces involved, three basic kinds of adsorption can be distinguished as; physical adsorption, chemisorption[4],and electrostatic adsorption[5,6]. The aim of this study is using kaolinite clay as a natural adsorbent and ion exchanger for removal of some heavy metals.

EXPERIMENT:

1-Clay Sampling:

The kaolinite clay sample was collected from Upper Egypt area. Quartering technique was used to get a representative sample[7].

2-Chemical procedure for the analyses of investigated water and clay samples:

The chemical analysis of the metal ions Pb^{2+}, Cu^{2+}, Fe^{3+}, Mn^{2+} and Zn^{2+} were carried out using atomic absorption type of AA-Scan 4, Thermo Jarrell Ash, USA. X-ray fluorescence of clay sample was performed using X-Ray Fluorescence, Model 2400, Philips, USA. Table1 presents the obtained results of two kaolinite samples.

Table (1) : X-Ray Analysis Data of Clay sample expressed as parts per million of oxide.

Sample No.	Fe	Ti	Mg	Ca	Al	Na	K	V	Si
1	4.10	2.10	0.50	11.60	6.90	0.70	1.10	<.01	23.7
2	4.20	2.20	0.47	12.00	6.87	0.75	1.16	<.01	24.8

3-Batch Equilibrium Sorption Technique :

This technique is applied for investigation of the effect of different variables on sorption of metal ions by kaolinite clay. The concerned variables are; contact time, pH, metal ion concentration, and volume of aqueous phase to mass of clay. The practical technique consists of the following different steps :

1-The required amount of kaolinite clay (m) is weighed (in dry condition) in a 50 ml dry polyethylene bottle, followed by 10 ml of the solution containing the respective heavy metal ion.

2-The bottles are closed with polyethylene stopper and shaken at room temperature using mechanical shaker of the type (Jain Heng HY 3024 USA) with adjustable speed of 700 oscillations per minute.

3-After the desired time of shaking each bottle is centrifuged at 3500 rpm for 10 minutes and 1

ml of clear supernatant is pipetted into a glass vial for analysis using atomic absorption technique.

4-In each series of experiments, two bottles are prepared under the same conditions of experiment without the kaolinite clay.

5- A pH meter of type Cole palmer series 5986 is used to measure the pH of solutions before and after the experiment. Preliminary sorption experiments showed that 0.1g kaolinite clay in a volume of 10 ml of the respective solution is suitable to obtain a reasonable measurable volume per mass values for the investigated heavy metal ions. The temperature during the experiments is kept at 25°C, using a thermostatic shaker. In all experiments, the solution containing the inorganic compound is contacted with the kaolinite clay until equilibrium was attained. The obtained data are presented in the form

of percentage uptake (U%) using the following formula :

$$U\% = [(C_0–C_e)\ /C_0]× 100$$

where:

C_0: is the initial concentration in the aqueous phase, expressed as mg/l

C_e: is the final concentration in the aqueous phase at equilibrium, expressed as mg/l

4-Materials:

The entire chemicals used are of A.R. Grade , and the bi-distilled water is used for the analytical purposes. The heavy metal ions are Pb^{2+}, Cu^{2+}, Fe^{3+}, Mn^{2+} and Zn^{2+}. These elements were chosen based on the specification for waste water that can be discharged into the surface water. Chlorides of Cu^{2+}, Fe^{3+}, Mn^{2+}, Zn^{2+} and lead acetate are used in this study.

RESULTS AND DISSCUSION:

1-Effect of contact time of Pb^{2+}, Cu^{2+}, Fe^{3+}, Mn^{2+} and Zn^{2+} on kaolinite Clay:

To study the capacity of the Kaolinite clay for the sorption of the heavy metal ions, samples of synthetically polluted water are prepared by adding the specific quantity of pollutants such as Pb^{2+}, Cu^{2+}, Fe^{3+}, Mn^{2+} and Zn^{2+}. The variation of percent uptake of the selected ions as a function of contact time is given in Table (2). From this table, it is clear that the sorption of Pb^{2+}, Cu^{2+}, Fe^{3+}, Mn^{2+} and Zn^{2+} increases with contact time to reach a nearly saturation level of the metal ion species. However, the time of saturation totally varies with metal ions. It is obvious, that the 30min., is the specific time of saturation for Pb^{2+}, and Zn^{2+} but for Fe^{3+} and Mn^{2+}, the sorption shows saturation time equal to 60 min. Moreover, 10min.dipping time, Cu^{2+} exhibits the larger value of sorption rather than others. Also, the maximum uptake of Cu^{2+} is attained in 60 minutes and reached about 96%. Results show also that copper is the more

sorbed metal ion on the kaolinite clay. This conclusion is analogous to the previously publication concerning the strong sorption of copper by hydrous iron, manganese oxides, clay minerals (e.g. kaolinite) and organic matter[8]. Hence, the affinity of the Kaolinite clay for sorption of the investigated metal ions runs in the order :

$$Cu^{2+} > Fe^{3+} > Pb^{2+} = Mn^{2+} > Zn^{2+}$$
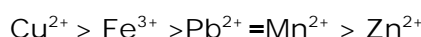
2-Effect of pH on the sorption of Pb^{2+}, Cu^{2+}, Fe^{3+}, Mn^{2+} and Zn^{2+} by kaolinite clay:

Figure (1) shows the effect of varying the pH on the uptake (%U) of Pb^{2+}, Cu^{2+}, Fe^{3+}, Mn^{2+} and Zn^{2+}. From these data, it is clear that the percentage uptake of heavy metal ions gradually increases by increasing the pH until to reach maximum value at the pH 7. The uptake percent of the investigated ions shows the same previous rank. Meanwhile, the sorption of zinc slightly increases at lower pH values until to reach through the critical range of 5 to 7, which increases greatly. This result is well match to that previously cited[8]. In case of copper, results are consistent to Huang[9] study. The sorption of copper is very low below pH 4 and increases rapidly at pH 6 coming to maximum at pH 7. It is well known that the process of sorption depends largely on the concentration of the hydrogen ion in solution. Increasing pH of solution results in decrease in H^+ ion leading to less competition for the vacant exchange sites of the clay, and hence more uptake% of metal ions is occurring. At higher pH values (alkalinieside), the dissociation of counter ions in the clay matrix may increase resulting in a lower percent absorption of the given metal ion[10]. At higher pH>7, the precipitation of the metal ion hydroxides is expected to take place[3]. In contrast, at lower pH values hydrogen ion

strongly competes for the vacant sites in the **percentage of uptake.**
crystal lattice giving rise to a decrease in the

Table (2): Variation sorption uptake percent of Pb^{2+}, Cu^{2+}, Fe^{3+}, Mn^{2+} and Zn^{2+}
at different contact times.

Time/min.	Cation	C_0 mg/L	C_e mg/L	X mg/g	Uptake%
10		5.2	4.16	1.04	20
20		5.2	3.64	1.56	30
30	Fe^{3+}	5.2	1.04	4.16	80
45		5.2	0.78	4.42	85
60		5.2	0.52	4.68	90
90		5.2	0.52	4.68	90
10		3.4	2.04	1.36	40
20		3.4	1.36	2.04	60
30	Pb^{2+}	3.4	0.51	2.89	85
45		3.4	0.51	2.89	85
60		3.4	0.51	2.89	85
90		3.4	0.51	2.89	85
10		6.8	4.76	2.04	30
20		6.8	2.04	4.76	70
30	Mn^{2+}	6.8	1.7	5.1	75
45		6.8	1.36	5.44	80
60		6.8	1.02	5.78	85
90		6.8	1.02	5.78	85
10		1.9	0.95	0.95	50
20		1.9	0.57	1.33	70
30	Zn^{2+}	1.9	0.475	1.425	75
45		1.9	0.456	1.444	76
60		1.9	0.437	1.463	77
90		1.9	0.418	1.482	78
10		3.8	1.52	2.28	60
20		3.8	0.76	3.04	80
30	Cu^{2+}	3.8	0.57	3.23	85
45		3.8	0.532	3.268	86
60		3.8	0.418	3.382	96
90		3.8	0.152	3.648	96

C_o = Initial concentration of pollutants. Mass of clay = 0.1g.
C_e = Finial concentration of pollutants. Volume of water = 10 mL.
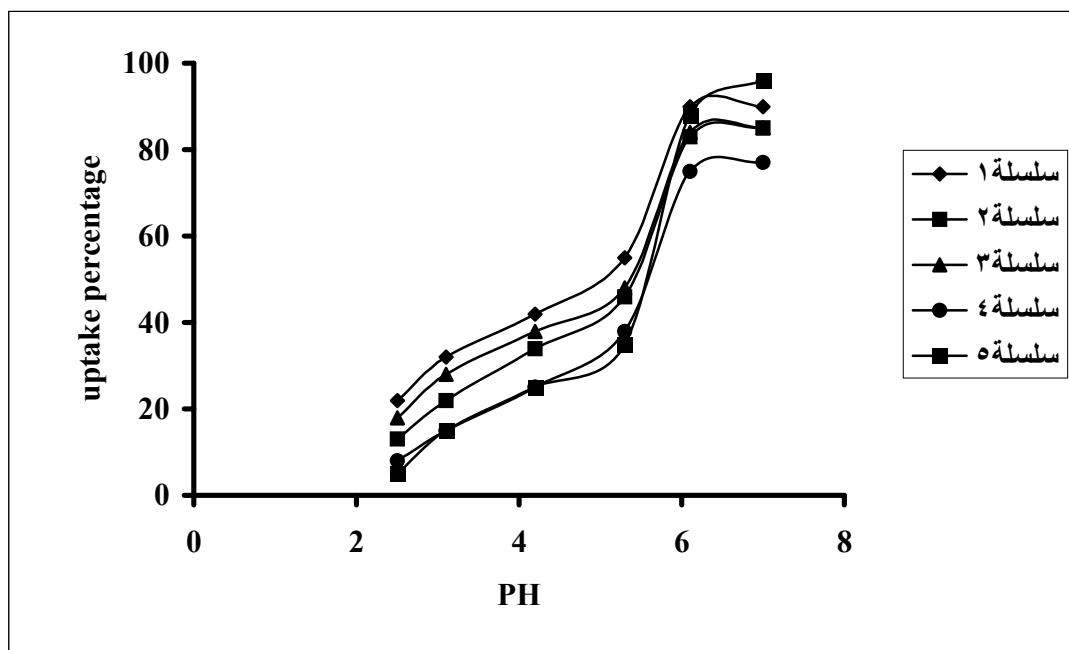X = The amount of ions sorbed on clay.

Fig. (1) Effect of pH values on the adsorption of cations by kaolinite clay at (1 hr.),
Series: 1) Fe^{3+}; 2) Pb^{2+}; 3) Mn^{2+}; 4) Zn^{2+}; 5) Cu^{2+}

3-Effect of Volume of The Aqueous Phase to Mass of Clay Ratio on Sorption of Pb^{2+}, Cu^{2+}, Fe^{3+}, Mn^{2+} and Zn^2 by the Kaolinite Clay:

The study of the sorption of the selected metal ions (Pb^{2+}, Cu^{2+}, Fe^{3+}, Mn^{2+} and Zn^{2+}) by batch techniques is carried out through determination of the ratio of the volume of aqueous phase to the mass of the Kaolinite clay (V/m). In sorption studies, the uptake percent of the respective ion is found to vary with V/m ratio. In practice, it is necessary to determine an appropriate V/m value that can result in reasonably high uptake percent.   In our case the variation of uptake percent with the V/m ratios is studied for the cases of Pb^{2+}, Cu^{2+}, Fe^{3+}, Mn^{2+} and Zn^{2+} on the Kaolinite clay sample. Data are presented in Table (3). From these data, it is clear that the uptake percent, increases as V/M decreases, or increasing the mass of clay.

4-Effect of the metal ion concentration on Sorption of Pb^{2+}, Cu^{2+}, Fe^{3+}, Mn^{2+} and Zn^{2+} on Kaolinite clay:

The relationship between the sorbed amount of metal ion per gram,(X/m) against the equilibrium concentration [C] on a log-log scale shows a straight lines as illustrated in Figure (2). This linear relationship indicates that the sorption process can be described by a Freundlich type isotherm. Based on these data it can be concluded that the sorption of the investigated elements of Pb^{2+}, Cu^{2+}, Fe^{3+}, Mn^{2+} and Zn^{2+} by the kaolinite clay takes place mainly through the formation of a single monolayer (Piccinini and Ferrero, 1975)[11]of sorbed species. The following general equation is applied to describe the data in a quantitative way:

The amount of ion sorbed per gram clay

$$(X/m) = (C_0 - C_e).V/m$$

where:

C_0 : is the initial concentration in the aqueous phase (mg/L).

C_e : is the final concentration in the aqueous phase at equilibrium (mg/L).

V : is the volume of the aqueous phase (ml),

m : is the weight of the clay sample (g).

Hence, $X/m = K C^{1/n}$

$\log (X/m) = \log K + 1/n \log [C]$

Where K and 1/n are empirical constants depending on the nature of the aqueous and the solid phase used at constant temperature. Similar relations have been proposed[12] for the sorption of zinc.

Table (3): Variation of the uptake percent, of different heavy metal ions with different V/m values

V/m	Cation	Co mg/L	C_e mg/L	X mg/g	Uptake%
1000		3.4	2.376	1.024	30.1
333.3		3.4	1.989	1.411	41.5
200	Pb^{2+}	3.4	1.343	2.057	60.5
142.8		3.4	0.826	2.574	75.5
100		3.4	0.51	2.89	85
1000		5.2	4.132	1.068	20.5
333.3		5.2	3.608	1.592	30.6
200	Fe^{3+}	5.2	2.08	3.12	60
142.8		5.2	1.206	3.994	76.8
100		5.2	0.577	4.623	88.9
1000		6.8	5.419	1.381	20.3
333.3		6.8	4.039	2.761	40.6
200	Mn^{2+}	6.8	2.72	4.08	60
142.8		6.8	1.428	5.372	79
100		6.8	1.02	5.78	85
1000		1.9	1.472	0.428	22.5
333.3		1.9	0.906	0.994	52.3
200	Zn^{2+}	1.9	0.661	1.239	65.2
142.8		1.9	0.57	1.33	70
100		1.9	0.418	1.482	77
1000		3.8	3.404	0.396	10.4
333.3		3.8	2.648	1.152	30.3
200	Cu^{2+}	3.8	1.493	2.307	60.7
142.8		3.8	0.752	3.048	80.2
100		3.8	0.152	3.648	96

C_o = Initial concentration of pollutants.

C_e = Finial concentration of pollutants. Time = 1hr.

X = The amount of ions sorbed on clay. Volume of water = 10 mL

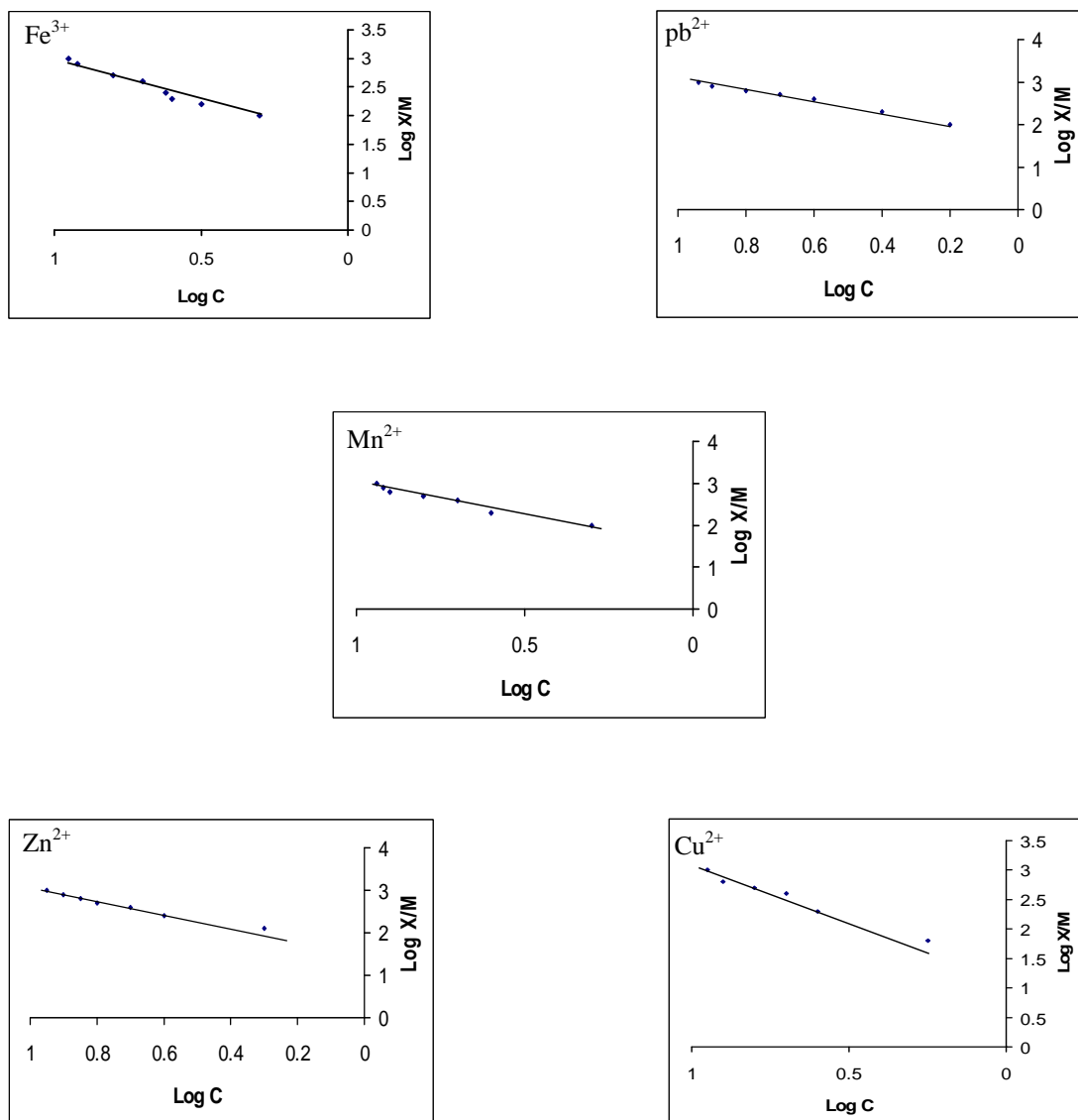Mass of clay = (0.01,0.03,0.05,0.07 and 0.1g)

**Fig (2) Different concentrations of heavy metal ions adsorbed at constant amount of Kaolinite clay.**

5-Desorption of Fe^{3+}, Pb^{2+}, Mn^{2+}, Zn^{2+} and Cu^{2+} from the loaded kaolinite clay:

Basically, the sorption of the respective metal ion is supposed to take place mainly by an ion exchange mechanism and/or specific adsorption. Some desorption experiments are carried out by batch technique to release the adsorbed metal ions from the loaded Kaolinite clay. The desorption percent for Fe^{3+}, Pb^{2+}, Mn^{2+}, Zn^{2+} and Cu^{2+} from Kaolinite clay by distilled water is very low and almost equal to zero. This may be explained by the fact that these metal ions are fixed in the clay lattice which do not desorb under the given experimental conditions. Therefore, regeneration of the loaded Kaolinite clay is carried out using solutions of magnesium chloride or sodium chloride (to form Na or Mg-Kaolinite) or hydrochloric acid solution (6N) [13]. In the regeneration process using saturated solutions of $MgCl_2$, NaCl and (6N) of HCl, the

heavy metal ions (Fe^{3+}, Pb^{2+}, Mn^{2+}, Zn^{2+} and Cu^{2+}) loaded on the clay can be replaced by Mg^{2+}, Na^+ or H^+ ions to form the Kaolinite salts (Mg- Kaolinite, Na- Kaolinite) and H- Kaolinite which can be used for further sorption investigations. Figure (3) illustrates the data for using these methods. It appears that hydrochloric acid is one of the most suitable
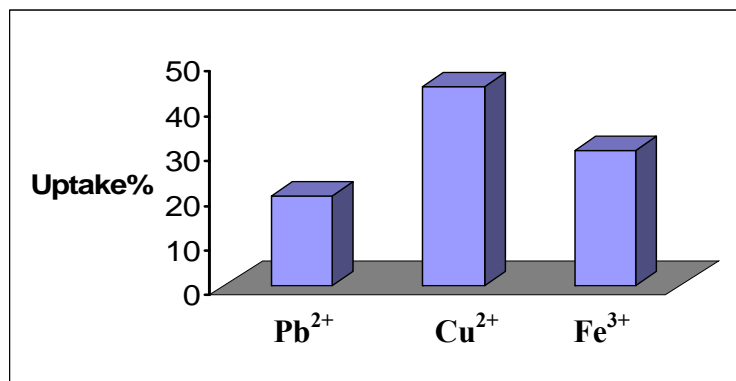
recommended methods for the regeneration process. Moreover , washing with $MgCl_2$ solution shows results better than NaCl. This may be attributed to the absolute mobility of radical cations, which decreases in the order: $H^+>Mg^+>Na^+$ (H^+=0.003620, Mg^+=0.000550, and Na^+=0.00025 Cm^2/volt.s)[14].
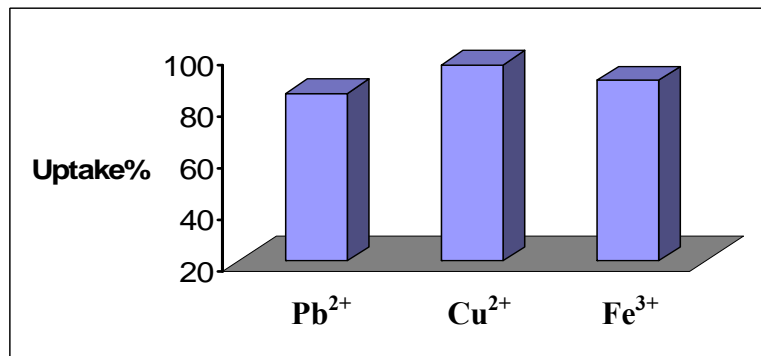
a-(6N) of HCl solution
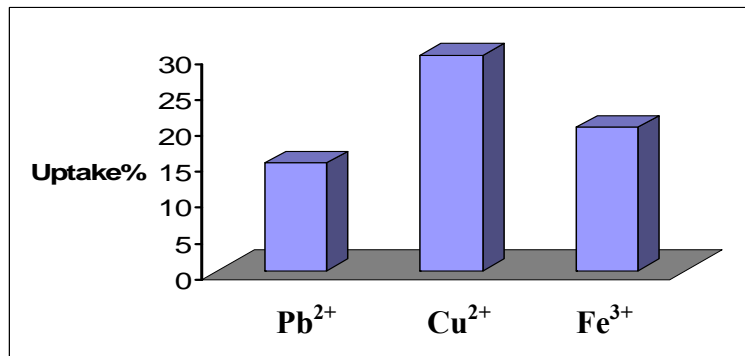
b- Saturated solution of NaCl

c- saturated solution of $MgCl_2$

Fig. (3): Effect of washing solutions for regeneration of kaolinite clay on sorption process

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امتزاز بعض أيونات المعادن الثقيلة باستخدام طفلة الكاولينيت

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أظهر استخدام طفلة الكاولينيت فى إزالة بعض أيونات المعادن الثقيلة مثل (الرصاص– النحاس– الحديد – المنجنيز – الزنك) نتائج طيبة. وتعد الطفلة من المواد الطبيعية ذات التكلفة الرخيصة والتى لها القدرة على الاستبدال الأيونى والامتزاز. ولقد أظهرت دراسة العوامل المختلفة المؤثرة على عملية الإزالة أن زمن تشبع عينات الطفلة يختلف من عنصر إلى أخر. كما أوضحت الدراسة أن عملية الإزالة اعتمدت على الأس الهيدروجينى pH وتركيز هذه العناصر وكذلك نسبة الوسط المائى إلى وزن الطفلة. ومن خلال هذه الدراسة وجد أن ملائمة طفلة الكاولينيت لإزالة هذه العناصر يتبع الترتيب الآتى :

$Cu^{2+} > Fe^{3+} > Pb^{2+} = Mn^{2+} > Zn^{2+}$
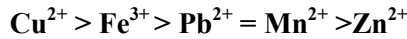
وأثبتت النتائج أن امتزاز هذه العناصر على سطح طفلة الكاولينيت يتم من خلال تكوين طبقة واحدة مفردة أى يتبع نظام Freundlich isotherm.