



Effect of adsorption parameters on the Removal of heavy metal cations from water by two Algerian clays

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Abstract : Heavy metal pollution has become one of the most serious environmental problems nowadays. The treatment of heavy metals is of particular concern due to their recalcitrance and persistence in the environment. In recent years, various techniques for heavy metal removal from wastewater have been extensively studied. These technologies include chemical precipitation, ion-exchange, adsorption, membrane filtration, coagulation–flocculation, flotation and electrochemical methods. This paper deals with the factors affecting the use of the Algerian bentonite and kaolinite in the removal of heavy metal cations namely: Equilibration Time, Solid/Liquid ratio and pH.

Keywords : adsorption, metal cations, bentonite, kaolinite.

Introduction

Pollution by heavy metals is one of the most serious environmental problems facing life and earth. They are stable and persistent environmental pollutants since they cannot be degraded or destroyed. Therefore the concentration of these heavy metals must be reduced to the maximum permissible concentration [17-34]. Heavy metals are introduced into the environment through natural phenomena and human activities such as agricultural practices, transport, industrial activities and waste disposal. When heavy metals present in waste streams, they can be absorbed by marine animals and enter the human food chain [1]

The accumulation of these heavy metals in wastewater depends on the type of industries in the region, and the awareness of the people of the impacts of careless disposal of waste. On the other hand, the toxicity of these heavy metals cations depends on metal species and concentration, pH and sludge level [2].

Some previous studies reported the feasibility of using natural bentonite for the removal of Cu(II) and Zn(II) from aqueous solutions [3,4]. Nassem and Tahir reported the effect of different parameters such as pH of the solution, equilibration time and temperature on the removal of Pb(II) from acidic aqueous solutions by natural bentonite [5].

Other studies focused on using modified clays with grafting coupling agents to remove these toxic cations where the surface modification of naturally pyrophyllite minerals by grafting 3-(2-aminoethylamino) propylmethyldimethoxysilane exhibits a higher removal capacity for Pb(II), than that of natural pyrophyllite [6]. It was found that 93 % of lead (II) was removed by modified pyrophyllite mineral, while natural pyrophyllite did only uptake 35 % of this cation under the same experimental conditions.

It was reported as well that a modified bentonite with quaternary amines is able to remove oil and grease from water and the montmorillonite modified with sodium dodecylsulfate is an efficient extractant of Cu^{2+} and Zn^{2+} from aqueous solutions [7,8].

Other researchers found that the adsorption of lead on the kaolinite and montmorillonite samples had a maximum capacity equal to the cation exchange capacity of the clays. They also found that the adsorption was dependent on pH and ionic strength of the solution. They concluded that the effect of pH was due to precipitation of metal salts at high pH values and that high ionic strength affected adsorption by competing ions [9-15].

Harter [16] conducted a similar study on the effect of pH on the adsorption of lead, copper, zinc and nickel onto soils. He noted that the adsorption of all ions is increased dramatically at a solution pH above about 7.0. This was attributed to the precipitation. There was no apparent correlation in his data between the cation exchange capacity of the soils and the maximum adsorption capacity for metal cations. Instead, he suggested that the variations in metal retention could be explained by the organic content of the soils. Dissolved organic matter can interact with cations by providing ligands for complexation. Depending on the nature and concentration, organic matter can have a significant effect on the mobility of metal cations.

Materials and methods

Spectrometer of atomic absorption

The quantitative analysis of the heavy metal cations in aqueous solutions, is performed using a flame atomic absorption spectrometer (FAAS) (AA-250 Varian) with air and acetylene gas as a flame. The apparatus is calibrated using standard solutions of the studied metal cations. Table 1 illustrates the FAAS conditions of use. The calibration curves are obtained for Cr^{3+} , Cu^{2+} , Ni^{2+} , Zn^{2+} et Pb^{2+} using a standard series samples in the range of 0.9 ppm to 300 ppm for each metal ion. The concentrations of the standard samples are plotted against the analytical signal expressed as emission intensity (I).

Ytterbium (Yb), which absorbs at 371.03 nm, is added to the samples as internal standard, because it is the most used and most suitable to standard conditions. Because it is not the target sample, it does not cause any spectral interference with the analyte, and has sufficient emission intensity in relation to the added amount. A fixed amount of internal standard element (1 ppm) was added to all samples.

X-ray Diffraction (XRD)

The X-ray diffraction is performed using the diffractometer (XRD-6000, Shimadzu) with x-ray copper radiation filtered by nickel ($\text{CuK}\alpha$, $\lambda = 1.5406 \text{ \AA}$), wherein Cu is the material target which produces primary X-rays with voltage of 30 kV and a current of 30 mA. Scanning is done by the following steps: scanning range 2-80 2θ without interruption with speeds of $2^\circ / \text{min}$ and a receiving slit width of 0.3 mm.

X-ray fluorescence (XRF)

The chemical composition of the bentonite, kaolinite and their modified samples is determined using the X-ray fluorescence spectrometer (XRF-1800, Shimadzu). The microscope of type 3400T Wraymer 40-200 with an optical magnification ratio is used to determine the form of bentonite. The shape and surface morphology of the samples are also made with Shimadzu SSX-Sem Super Scan Series. The concentrations of metal ions were determined using ICP (ICPS-7510, Shimadzu) under the conditions: RF Power = 1.2 kilowatts, the refrigerant gas flow = 14.0 l / min gas flow rate plasma = 1.20 L/min and carrier gas flow rate = 0.70 L/min.

Standard extraction process

Series of experiments were carried out by introducing an appropriate amount of the clay mineral in a test tube. A preselected volume of the aqueous solution of the adsorbate with a known initial metal concentration is added. The tube is closed tightly and sealed with para-film and covered with a polythene bag. The tube is then placed on the support of the stirring device in a thermostatically controlled water bath. The tube must be placed vertically on a support and retained in the thermostatic bath throughout the night after two hours of stirring. The supernatant aqueous phase was removed by pipette and centrifuged at 3000 rev / min for fifteen minutes. A portion of the clear solution was sampled for proper quantitative analysis

Adsorption Isotherms

The isotherms of the systems adsorbent-adsorbate are obtained to 25 and 45 °C, by balancing a preselected quantity of mineral clay with 10 ml of the aqueous solution containing a known concentration of metal cation. This mixture is agitated during two hours in a thermostated bath then let rest during a whole night.

Calculation of the percentage of adsorbate extraction:

The percentage of extraction of the adsorbate is calculated by using the following equation:

$$\% \text{ Removal} = \frac{(C_i - C_{eq})}{C_i} \times 100$$

Where C_i is the initial concentration (mg/L) et C_{eq} is the concentration at equilibrium (mg/L).

Results and discussion

Equilibration Time

To ascertain the time required for the bentonite and kaolinite to reach saturation in the removal of metal cations from aqueous solution; initial concentration of the metal cations were chosen 100 ppm for (Cr^{3+} , Cu^{2+} , Ni^{2+} , Pb^{2+} and Zn^{2+}).

Figures 1 and 2, show the curves of the adsorbed quantity versus the contact time for all metals.

Table 1 gives the shortest time to reach saturation for all sixteen systems. Such periods are in the range of 25-200 min.

For all systems and in all subsequent investigations, a shaking time of 240 minute was conveniently adopted followed by the standing overnight in the thermostated bath.

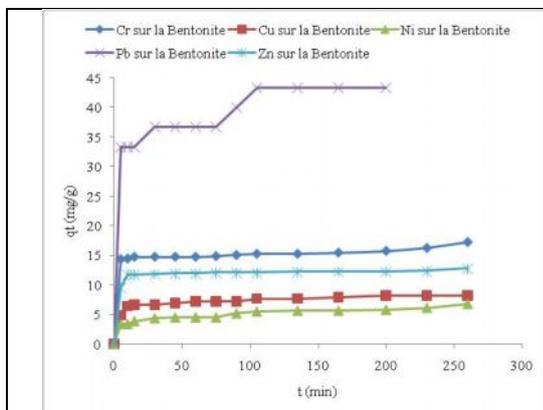


Figure 1: Equilibrium time of B-Cr, B-Cu, B-Ni, B-Pb and B-Zn

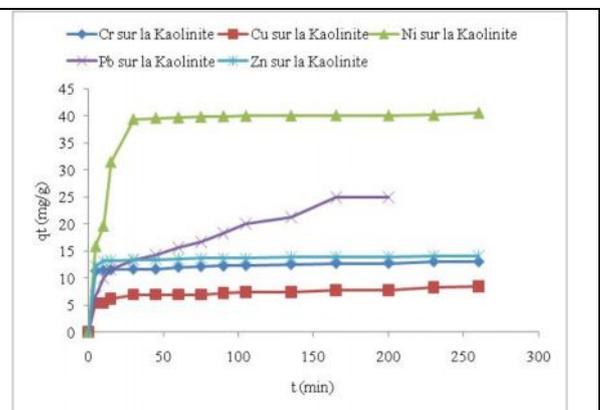


Figure 2: Equilibrium time of K-Cr, K-Cu, K-Ni, K-Pb and K-Zn

Table 1: Equilibration time of metal cations

Adsorbent		Time (min)
Bentonite	Cr	260
	Cu	200
	Ni	260
	Pb	105
	Zn	260
Kaolinite	Cr	230
	Cu	260
	Ni	260
	Pb	165
	Zn	230

1. Effect of Solid/Liquid ratio

To determine in each system the optimum working ratio of (weight of adsorbent/ volume of adsorbate solution (S/L g/L), experiments were performed as described before.

The increase of %R with the increase of S/L for each system can be explained on the basis of an increase in the number of active sites of the solid adsorbent for a fixed initial solute concentration.

The results are plotted as %R vs. S/L ratio for all systems and typical curves are shown in Figure 3. From these results, the working ratios were chosen for all the systems and as given in Table 2.

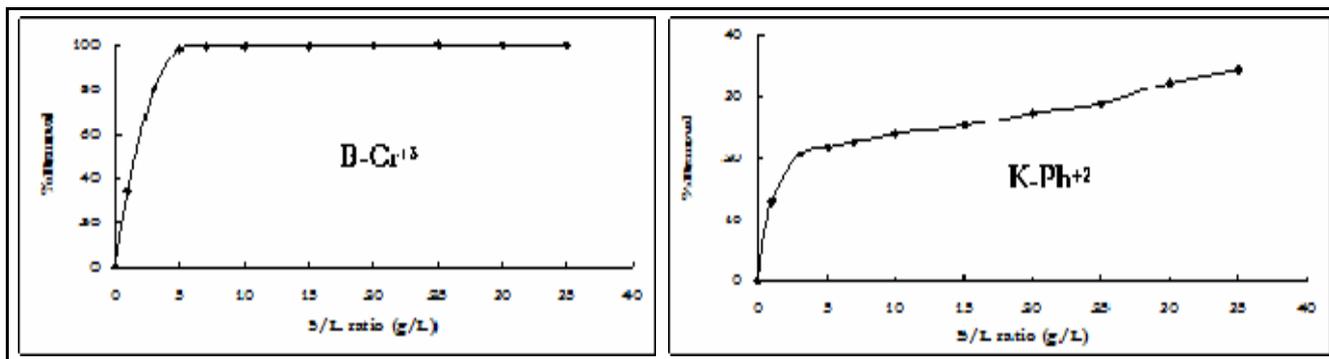


Figure 3: Effect of solid/liquid /ratio of the adsorption of the metal cations by Bentonite and Kaolinite

Table 2: working ratios of adsorbent weight /volume of aqueous solution for the metal cation extraction

adsorbent	Adsorbate	ratio S/L (g/L)
Bentonite	Cr ⁺³	3
	Cu ⁺²	5
	Ni ⁺²	5
	Pb ⁺²	10
	Zn ²⁺	5
Kaolinite	Cr ⁺³	10
	Cu ⁺²	10
	Ni ⁺²	10
	Pb ⁺²	10
	Zn ²⁺	10

2. Effect of pH

To determine the optimum pH of the aqueous solution to be adopted for each system, a study was conducted as described before. The experimental data for all twelfth systems are given in Table 3 for the preselected values of S/L.

The %R at 25°C was determined at the prechosen conditions as a function of pH (2--10) ranging from the highly acidic to the neutral and alkaline environment. The pH value was measured before and after equilibrium. The two measurements in each system were in agreement to within ± 0.1 . Figure 3.13 shows the plots of %R vs. pH value for the typical systems (B-Cu²⁺ and K-Pb²⁺).

As an indication, in the two systems (B-Cu²⁺ and K-Pb²⁺); the R % increases with the pH. For B-Cu²⁺ one notes at pH approximately 5, a stability of output; in the same way for K-Pb²⁺ for which the output is stabilized at pH approximately 7.

It was thus decided to carry out the detailed study concerning the actual value of the pH of the aqueous solution of the metal cation and at its selected initial concentration. These values of pH are chosen for all the systems and are given in Table 3.

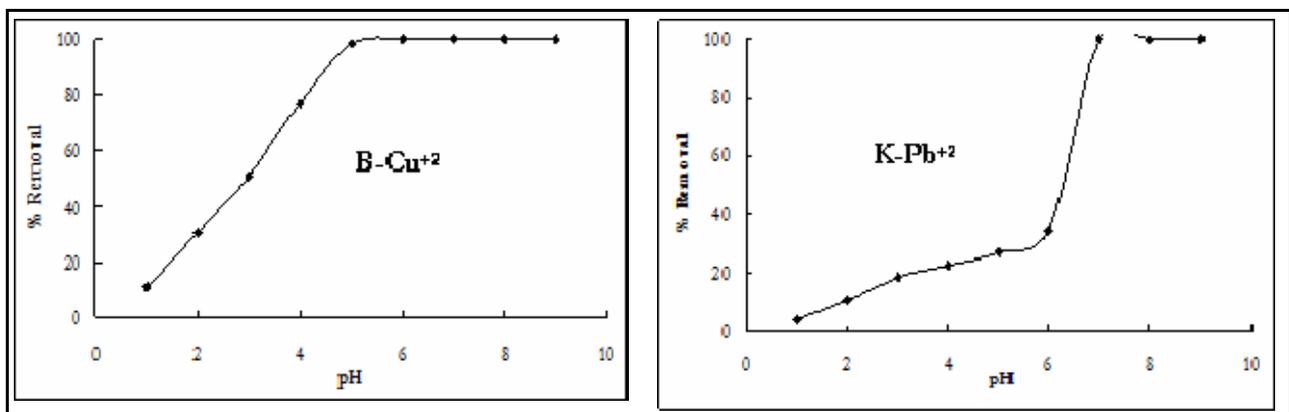


Figure 4: Effect of pH for metal cations removal by the bentonite and kaolinite

Table 3: Adopted working pH value of metal cations

Adsorbate	Working C_i (mg/L)	pH
Cr ³⁺	100	5.3
Cu ²⁺	100	6.2
Ni ²⁺	100	5.8
Pb ²⁺	100	5.7
Zn ²⁺	100	6.3

Adsorption Isotherms

The adsorption isotherms of the metal cations on each of two clays were studied using the isothermal models of Langmuir, Freundlich and Dubinin-Radushkevich. Tables 4 and 5, show the data of the calculated isotherms for bentonite and kaolinite. In each system a certain degree of compatibility between the experimental values and the best adjustment was obtained. Such a degree is given by calculating the coefficient of correlation, R^2 . From the slopes and interceptions of these linear curves; values of K_L and q_{max} (Langmuir model), those of K_F and n (Freundlich model) and those of q_{max} and E^2 (Dubinin-Radushkevich model) are obtained. See Tables 4 and 5

Table 4 : The parameters of the isotherms of Langmuir. Freundlich and Dubinin-Radushkevich for bentonite

Adsorbent	T °C	Constants of Langmuir isotherm				Constants of Freundlich isotherm			Constants of Dubinin-Radushkevich isotherm		
		Q _{max} (mg/g)	K _L	R _L	R ²	K _F	n	R ²	Q _{max} (mg/g)	E (KJ.mol ⁻¹)	R ²
Cr	25	37.037	0.035	0.221	0.9340	1.683	1.406	0.973	15.410	0.448	0.7880
	45	22.222	0.054	0.157	0.9830	2.193	1.919	0.943	14.820	0.259	0.9120
Cu	25	34.483	0.036	0.219	0.9760	8.770	1.445	0.903	8.077	0.407	0.5130
	45	12.500	0.051	0.165	0.9160	6.622	0.754	0.971	19.279	0.305	0.8530
Ni	25	9.901	0.072	0.122	0.9700	1.130	1.961	0.85	7.114	0.383	0.9430
	45	7.692	0.033	0.231	0.9680	0.505	1.751	0.981	3.995	0.352	0.7060
Pb	25	1.437	0.975	0.010	0.9990	5.508	1.437	0.999	42.991	0.514	0.7500
	45	1.706	0.492	0.020	0.9890	15.560	1.706	0.989	67.830	0.786	0.8310
Zn	25	18.182	0.149	0.063	0.9990	3.319	2.326	0.919	12.949	0.792	0.7720
	45	16.129	0.046	0.179	0.9220	1.282	1.783	0.898	9.291	0.396	0.6840

Table 5: The parameters of the isotherms of Langmuir. Freundlich and Dubinin-Radushkevich for kaolinite

Adsorbent	T °C	Constants of Langmuir isotherm				Constants of Freundlich isotherm			Constants of Dubinin-Radushkevich isotherm		
		Q _{max} (mg/g)	K _L	R _L	R ²	K _F	n	R ²	Q _{max} (mg/g)	E (KJ.mol ⁻¹)	R ²
Cr	25	22.222	0.056	0.151	0.9650	2.477	2.096	0.91	14.910	0.312	0.8470
	45	25.000	0.240	0.040	0.9920	10.00	4.630	0.788	22.897	0.468	0.9750
Cu	25	500.000	0.002	0.816	0.2760	1.459	1.120	0.979	8.215	0.156	0.7250
	45	125.000	0.023	0.304	0.9770	5.370	1.567	0.995	56.430	0.269	0.7980
Ni	25	142.857	0.030	0.252	0.9790	5.117	1.304	0.997	45.196	0.535	0.8030
	45	142.857	0.159	0.059	0.9810	21.33	1.626	0.993	73.921	1.225	0.8350
Pb	25	50.000	0.035	0.222	0.9200	3.228	1.718	0.994	21.955	0.485	0.6240
	45	90.909	0.103	0.089	0.9850	11.11	1.706	0.989	48.473	0.786	0.8300
Zn	25	28.571	0.043	0.187	0.9900	2.382	1.828	0.996	16.346	0.272	0.8950
	45	33.333	0.040	0.200	0.9790	2.399	1.721	0.996	17.637	0.318	0.8490

According to values of R², for the various systems, we can deduce that the model of Langmuir is better adapted for the first system: B-Cr⁺³, B-Cu⁺², B-Ni⁺², B-Pb⁺² and B-Zn⁺² while the model of Freundlich is more convenient for the second system: K-Cr⁺³, K-Cu⁺², K-Ni⁺², K-Pb⁺² and K-Zn⁺².

From the values of the capacity of saturation, q_{max}, it can be deduced that the order of the adsorption capacity of studied metal cations for two clays is as follows:

Bentonite Pb⁺² > Cr⁺³ > Cu⁺² > Ni⁺² > Zn⁺²
 Kaolinite Pb⁺² > Cr⁺³ > Cu⁺² > Ni⁺² > Zn⁺²

For each adsorption of the metal cation on the two clays, the order is:

Cr⁺³ bentonite > kaolinite;
 Cu⁺² kaolinite > bentonite;
 Ni⁺² bentonite > kaolinite;
 Pb⁺² kaolinite > bentonite;

Zn⁺² kaolinite > bentonite;

Consequently, the bentonite is the better for the adsorption of Cr³⁺ and Cu²⁺ starting from water, while kaolinite is better for the Pb²⁺ removal.

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