Influence of pH on Adsorption of Manganese, Cadmium and Cobalt by Activated Clay

Y Asfers[1*], H Taouil[1,2], K Arouya[1] and S Ibn Ahmed[1]

[1]Laboratory of Materials, Electrochemistry and Environment, Faculty of Sciences University Ibn TofailKénitra, Morocco
[2]Laboratory of Analytical Chemistry and Physical Chemistry of Materials, Hassan II University of Casablanca, Morocco

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Abstract

The influence of pH on the adsorption of heavy metals cadmium, manganese and cobalt was studied on a chemically modified clay. The isotherms were realized at pH 2; 3; 4 and 6.5. The heavy metals were applied as nitrates with initial concentrations ranging from 10 to 50 ppm. The adsorption was quantified according to the Freundlich model and the results show that there is a linear relationship between ln Kf and the pH whose slopes are respectively 0.55; 0.33 and 0.10 for cobalt, manganese and cadmium. The retention power decreases in the following direction: Cd >Co >Mn

Keywords: Heavy metals; Clay; Adsorption; pH; kf;
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INTRODUCTION

Before going into the study of the influence of the adsorption pH, it seems useful to study the precipitation of each metal element as a function of the pH under the working conditions chosen. However a study was realized using a basic solution allows to have an idea on the range of the pH in which we will study the effect of this parameter on the process of adsorption. The results obtained give indications on the reaction of the metal salt with the complexing agent NaOH and give us information on the pH of the beginning of the precipitation of heavy metals. It appears obviously for a concentration of 100 mg/l in Pb, Ni, Cu and Zn, the beginning of precipitation occurs between pH=6.2 and pH=7. However, this pH increases when the concentration of the metal decreases [30]. Although, an approximate calculation allowed us to define the precipitation domain, this calculation can be done from the value of the solubility product, which makes it possible to predict for which value of the pH, the precipitation of a given hydroxide begins and end. Let us make this calculation for the case of metal hydroxides, whose solubility product Ps (M (OH) 2) is given at 20 ° C, with the exception of that of cobalt hydroxide which is at 25 ° C. The precipitation start pH is formulated by the following equation:

$$pH=14+1/2*\log (Ps/[M])$$

The following Table 1 illustrates the theoretical pH of the onset of hydroxide precipitation for metal salt concentrations ranging from 10 to 50 mg/l. According to this table, it can be seen that the pH of the precipitation start has reached a value greater than the chosen limit value which is 6.5. In order to study the influence of the pH parameter on the adsorption of metal ions Co, Mn and Cd by activated clay, the same experimental protocol was used (C (metal)=10 mg/l, Vagi=400 rpm, T (medium)=20 ° C, φ (Clay): φ ≤ 63 um, C Adsorbent=0.2 mg/l), varying only the pH of the mixture. The pH values chosen are: 2, 3, 4 and 6.5. PH adjustment was performed by the addition of a solution of HCl (0.1 N) or NaOH (0.1 N). The choice of pH values was taken to optimize the maximum fixation without precipitation of the metal.

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Table 1: Theoretical values of the pH of beginning ofprecipitation

Metalhydroxides	Concentration mg/l	Solubility product	pH of begining of precipitation
Co(OH)$_2$	10	13*10^{-15}	8.05
	20		7.9
	30		7.81
	40		7.75
	50		7.7
Mn(OH)$_2$	10	2*10^{-13}	8.65
	20		8.5
	30		8.41
	40		8.35
	50		8.3
Cd(OH)$_2$	10	4.5*10^{-9}	10.82
	20		10.67
	30		10.58
	40		10.52
	50		10.97

MATERIAL AND METHODS

The experiments were realizedat pH 2, 3, 4 and 6.5. The heavy metals were applied as nitrates with initial concentrations ranging from 10 to 50 ppm with a 10 ppm step. A precise mass of clay sieved at 63 μm, successive drops of N/5 chloridicacid are added. 100 ml solutions were prepared, the pH of the suspensions was adjusted and maintained at the desired value (by addition of HCl or NaOH). After mechanical stirring in a thermostatic chamber stabilized at 20 C, the suspensions are filtered using a syringe with a porosity of 45 μm. Preliminary experiments had shown that equilibrium was reached in less than 20 minutes. After which, the heavy metal content, by atomic absorption, and the pH of the supernatant are determined. The amount adsorbed by the clay matrix is obtained by difference between the initial and equilibrium concentrations.

RESULTS AND DISCUSSION

The curves of the adsorption isotherms of Co; Mn and Cd on clay obtained at different pH are illustrated in the Figure 1, Figure 2, Figure 3.
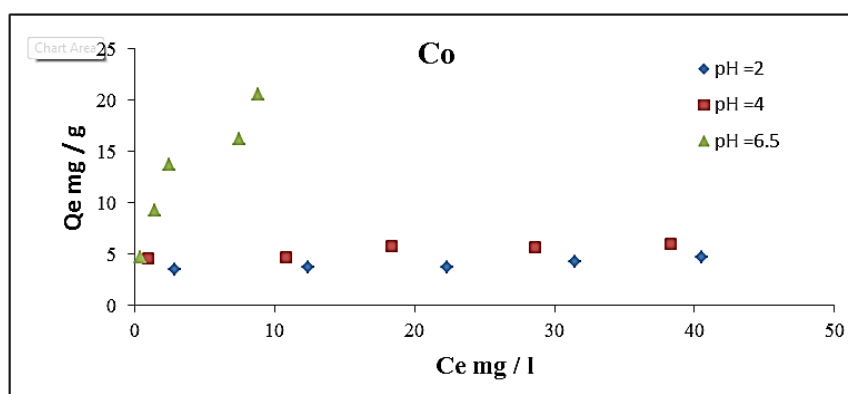

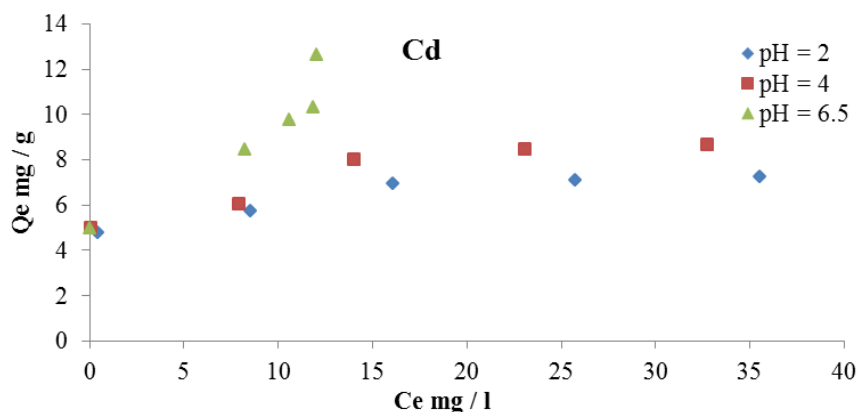**Figure 1: Co adsorption isotherm on clay at different pH values**

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Figure 2: Cd adsorption isotherm on clay at different pH values
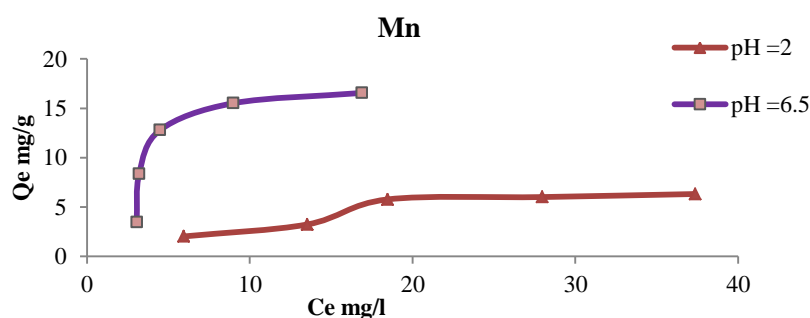

Figure 3: Mn adsorption isotherm on clay at different pH values

It is noted that the amount adsorbed for each metal increases markedly with the pH.

For a concentration of 10 mg/l in the solution and an increase in the initial pH of 2 to 6.5, the adsorbed amount increases from 3.54 to 4.793 mg/g, 2.03 to 3.47 mg/g and 4.78 to 4.975 mg/g respectively for Co, Mn and Cd. In this range of pH, it is noted that the fixation rate of metal ions varies from 1.293, 1.44 and 0.195 mg/g respectively for Co, Mn and Cd. This difference of the adsorbed quantity gradient is probably due to the nature and physicochemical properties of the adsorbed metal. Many authors have also observed a similar effect of pH on the adsorption of heavy metals by soil [1-3] or by its main constituents such as organic matter [34], iron oxides, aluminum oxides, manganese [5-7] as well as clay minerals [8-9]. The increase in adsorption is explained by the increase in the number of pH-dependent adsorption sites (carboxyl groups of organic matter, hydroxyl groups of oxides and clay minerals) and the decrease in ion competition. H^+, as well as the preferential adsorption of the hydrolysed species (Co $(OH)^+$, Mn $(OH)^+$, Cd $(OH)+$). Each of the isotherms is correctly represented by the Freundlich relation. The various constants deduced from the equations of the lines obtained are gathered in the following Table 2.

The results show that the adsorption capacity increases with the pH: for Cobalt, it goes from 0.645 mg/g to pH=2 to reach 7.58 mg/g at pH=6.5. Indeed, at this value of pH=6.5, the adsorption capacity of Mn ions has a maximum value of 6.35 mg/g, whereas Cd has an adsorption capacity which can be reached at high values of the order of 8.11 mg/g. Kamal and all (2001) [10] studied the adsorption of metal ions such as copper, lead and cadmium by a rasoulite clay. His results showed that the adsorption capacity of cuprous ions goes from 0.75 mg/g to pH=3 to reach 8.89 mg/g at pH=6. Similar results were observed by Halen and all [11] in the study of the adsorption of heavy metals by clay minerals. Many authors have also observed a similar effect of pH on the adsorption of heavy metals by clays [12-13].

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Table 2: Freundlich parameter values deduced from adsorption isotherms Co, Mn and Cd ions on clay for different pH

	pH	Kf (mg/g)	1/n	R
Co	2	0.645	0.664	0.903
	3	0.849	0.599	0.897
	4	0.95	0.610	0.853
	6.5	7.58	0.434	0.961
Mn	2	0.645	0.664	0.903
	3	0.939	0.599	0.898
	4	0.9502	0.610	0.853
	6.5	6.35	0.367	0.781
Cd	2	5.15	0.092	0.910
	3	5.71	0.090	0.859
	4	6.41	0.077	0.484
	6.5	8.11	0.096	0.944

In this study, it was also noted that a low pH value favors relatively low capacitance values, such a remark probably results in competition between H+ions and metal ions [14-15]. The evolution of the percentage of adsorption of Co and Cd ions on the clay as a function of the pH is illustrated in the following Figures 2 and Figure 3.
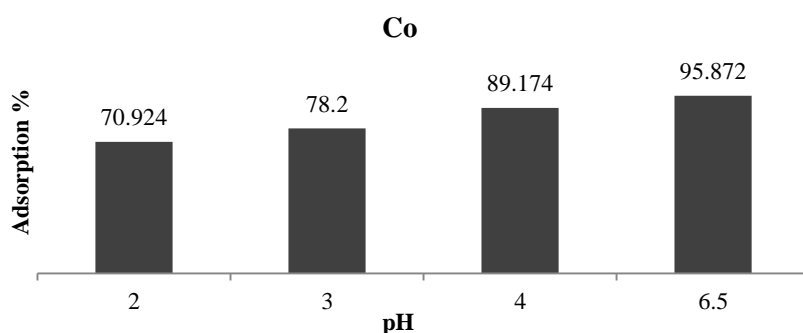

Figure 2: Evolution of the percentages of adsorption of Co as a function of the pH for an initial concentration Co=10 mg/l
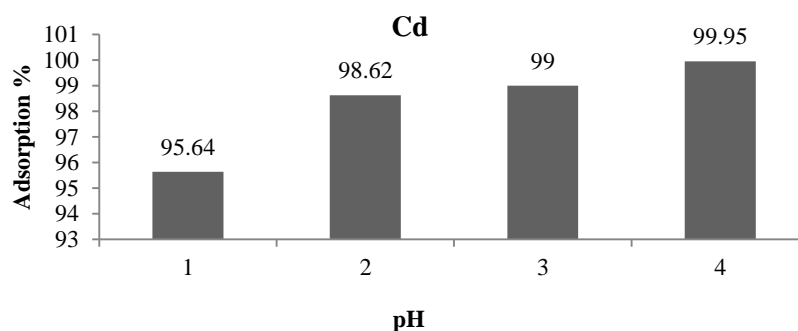

Figure 3: Evolution of Cd adsorption percentages as a function of pH for an initial concentration Co=10 mg/l

The results illustrated from the figures above, confirm the same observations recorded in the isothermal study. The percentage increases with pH, this behavior is also manifested on other surfaces [15]. In addition, and to accentuate and expand the field of study, another axis has been chosen to give more arguments. This is the study of the effect of pH on the percentage of adsorption with different initial concentrations (Figure 4 and Figure 5).
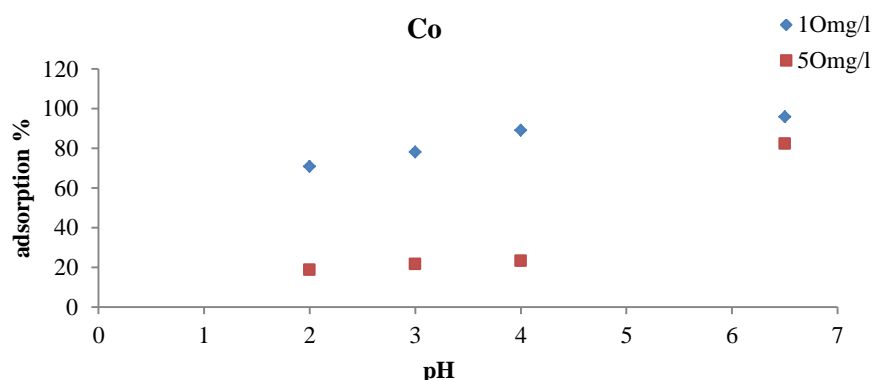
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Figure 4: Variation of adsorption percentages of Co ions on clay as a function of pH for different initial concentrations
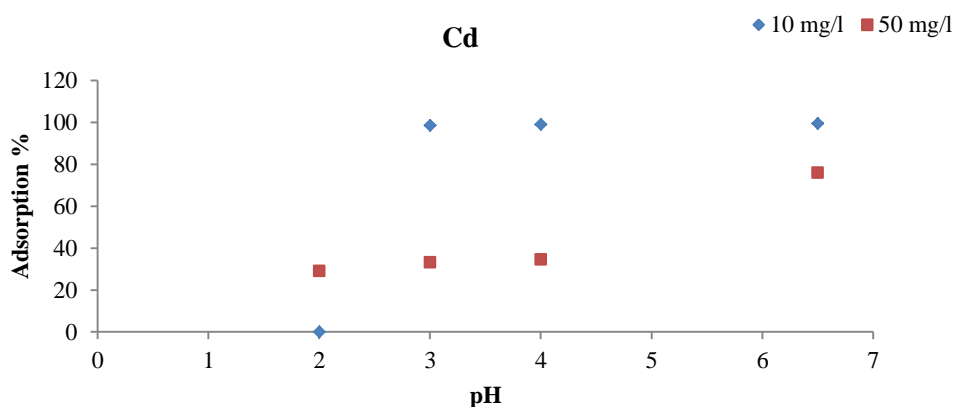

Figure 5: Variation of adsorption percentages of Co ions on clay as a function of pH for different initial concentrations

We have found that the adsorption of metal ions depends simultaneously on pH and initial concentration. For example, for the Co and Cd ions, the adsorption is more favorable at pH=6.5 and for an initial dose of 10 mg/l of adsorbate. The yields calculated in these media for the Co and Cd ions are respectively: 95.87% and 99.55%. However, for a dose of 50 mg/l of each metal ion Co and Cd, the adsorption density is respectively 18.8 and 28.98%. Such remarks are made by a study on kaolinite [16]. At pH=2, adsorption is less important at high concentrations. Research by Assameur H and all (2009) [17] found similar results in the study of the mechanism of adsorption of Co ions by activated clay from an aqueous system. The authors found that the percentage of elimination increases gradually in the pH range: 1-5 to reach 95% at pH=5. Indeed, for low pH values, the presence of positive charges (proton) on the surface of the clay causes the electrostatic repulsion between the metal ion and this positively charged surface [18]. In a less acid medium (pH>5), the surface of the clay becomes less charged, and the electrostatic repulsions decrease.

Benhebal H and all noted that better metal adsorption is achieved with lead at pH 5.5 [19]. This leads us to note that the decrease of the pH disadvantage the adsorption of the cations because the H^+ions having a high mobility, are easily exchanged with the compensating cation at the expense of metal cation.

Previous studies [20-24] have shown that pH plays an important role. Moreover, it is the main parameter that considerably influences the adsorption of metals on clays [11-13]. Kaolinite binds H+ions between pH=3 and pH=6, and illite binds H+ions between pH=3 and pH=6.8 [25]. The analysis of results by Bendaho and all 2014. [26] Shows that the amount of Cu (II) adsorbed on activated clay increases with increasing pH. Elimination of Cu (II) is very low at pH less than 3 because there is competition between copper ions and H+protons from acid. When the pH exceeds 6, the amount of Cu (II) removed from the solution increases rapidly, and reaches a maximum corresponding to a percentage of elimination of the order of 78% for activated clay and 72% for the activated clay. raw clay. This can be explained by the decrease in the H+ion concentration, which favors the adsorption of Cu (II) on the negative surface of the two adsorbents used.

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The elimination of Zn^{2+} was tested by Velis and All 2007. [27] usingCankiri bentonite (Turky). They have shown that pH is a significant factor in the adsorption process because it produces electrostatic changes in solutions. They also showed that the balance was reached after a very short period of 5 minutes. The results of adsorption experiments of heavy metals by superficial sediments [28] realized at different pH values (pH=5, 6, 7 and 8), show that the elimination of Zn leads to a systematic increase in the rate of adsorption from 75% to 95% when the pH increases. Various studies carried out on heavy metals such as copper, zinc, mercury or cadmium confirm the rapidity of the retention reactions of these elements by the clays. The results obtained showed that bentonite is an effective adsorbent for heavy metals and that the adsorption is relatively influenced by pH [29-31]. The results of the experiments realized by Achour and all 2003, [30] show a systematic increase of the adsorption rate when the pH increases. For the Maghnia bentonite, the best yields are obtained in basic medium, the best of which is obtained at pH=9, with an elimination rate equal to 98.44 %. The same result was obtained by goethite in a basic medium where the elimination rate reached 92.26%.

The work of Sen and All 2011, and Larakeb and All, and Mohammed and All 2013, [33-35] confirmed that there is an increase in zinc removal efficiency on bentonite with increasing pH. According to the authors [32-36], adsorption of metal ions on sodium bentonite decreases with decreasing pH. At low pH, hydrogen ions compete with heavy metals for surface sites. In addition, the Si-O- and Al-O- groups are less deprotonated and hardly formed complexes with the bivalent and trivalent ions. Researchers [37] have shown that the elimination of zinc by the use of bentonite as an adsorbent is highly pH dependent. The percentage of elimination increases with increasing pH from 1 to 7. The low yields at pH<2 may be due to the increase in competition for the adsorption sites between H+ and Zn^{2+}. By increasing the pH, the number of sites with negative charges increases which facilitates the adsorption of more Zn^{2+} ions. At pH>7, the precipitation of Zn (OH) 2 plays a major role in the elimination of Zn^{2+}. Studies by several authors [38] demonstrate the effect of pH on the adsorption of copper, lead and zinc on goethite. These found that the yield is close to 80% for copper and lead at pH=7 and pH=8 respectively. But for zinc, the yield is 70% at pH=7 and between 50% and 60% at the basic medium (pH=8 and pH=9). In the adsorption study of copper, zinc and cadmium on goethite, the researchers found that there is an increase in zinc adsorption efficiency from 15 to over 90% with increasing pH between 6 to 7 and for a dose of goethite of 2.12 g/l [39].

Indeed, a reverse behavior has been observed in the case of the retention of Mn ions on the adsorbent matrix. We see that for a high pH=6.5, an increase in the initial concentration of metal ions Mn promotes good retention. As an example for an initial concentration Co=10 mg/l, the adsorption density is 65.5%. While for an initial dose of 30 mg/l, the adsorption of Mn ions is optimal, and the adsorption density reaches 85.06% (Figure 6).
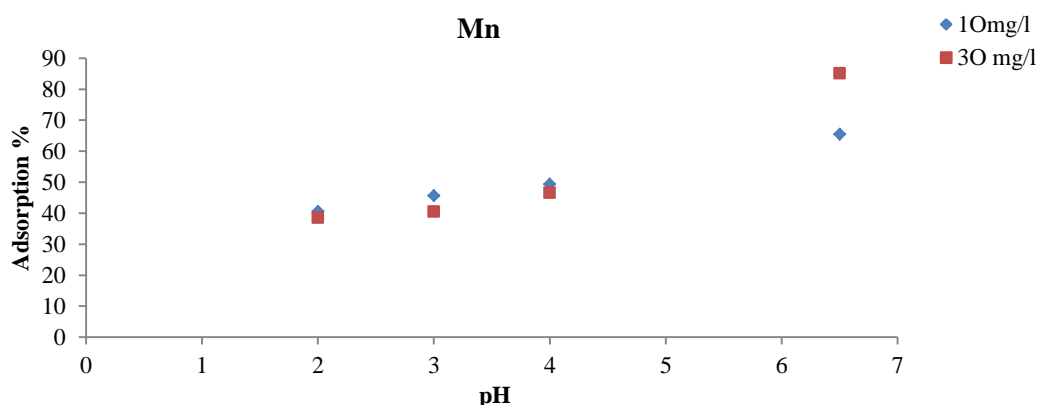

Figure 6: Variation of adsorption percentages of Mn ions on clay as a function of pH for different initial concentrations

In the same subject, the authors [40] have shown that the adsorption of Mn ions is affected by pH, however they have found that the adsorption is optimized at pH=4 for an initial dose of adsorbate which is 30 mg/l.

Moreover, in the range of pH [2-4], there is a slight variation of the adsorption rate at pH=3 and vanishes at pH=2 and 4. This occurs when the initial concentration of Mn ions increases. . This situation reflects the absence of the effect of the initial concentrations on the retention of Mn ions in this pH range. Apparently, the effect of

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pH on the evolution of the adsorption percentage as a function of the initial concentration of the metal considered is clearly evident in this study.
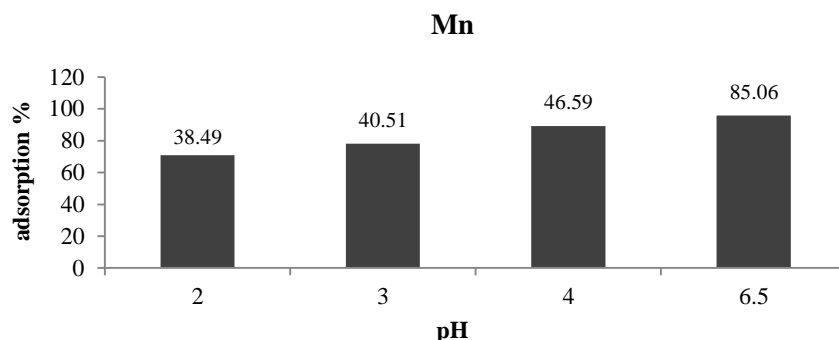
Mn

Figure 7: Evolution of the Mn adsorption percentages as a function of the pH for an initial concentration Co=30 mg/l

According to the Figure 7, we find that the adsorption of Mn ions depends on pH. So at pH=2 the adsorption rate is 38.49%. While at pH=6.5, there is a rather large increase in the percentage removal of Mn ions and the elimination rate reaches 85.05%. This situation has already been observed by Kamal (2001) [40].

• pH-adsorption relationship of metal ions on clay

Among the factors that control the phenomenon of adsorption of heavy metals, pH appears as a parameter of primary importance. However, few authors have been able, so far, to establish a relationship between this parameter and the adsorption of heavy metals. by clays. This is the reason why we studied more particularly the behavior of Co, Mn and Cd at different pH on our clay, which must make it possible to evaluate the variation of the adsorption, following a modification of the pH. The FreundlichKf parameter, as an evaluative index of the adsorption of metal ions, can be expressed as a function of pH as illustrated in Figure 8. The shape of the curves for the three metal ions is exponential, which indicates that the adsorption appears more sensitive to a change in pH. In the pH range [2-4], however, the Co and Mn ions show a more similar behavior to each other. However, this behavior is absent from the high pH where it is shown that the Co retention capacity is larger than that of Mn. Moreover, the adsorption of Cd ions always appears significantly higher than those of the other ions. For all metals, a linear relationship has been established between Ln (Kf) and pH, this is illustrated in Figure 9.
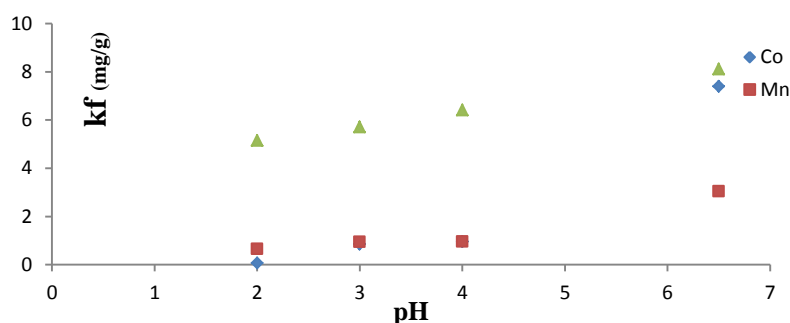

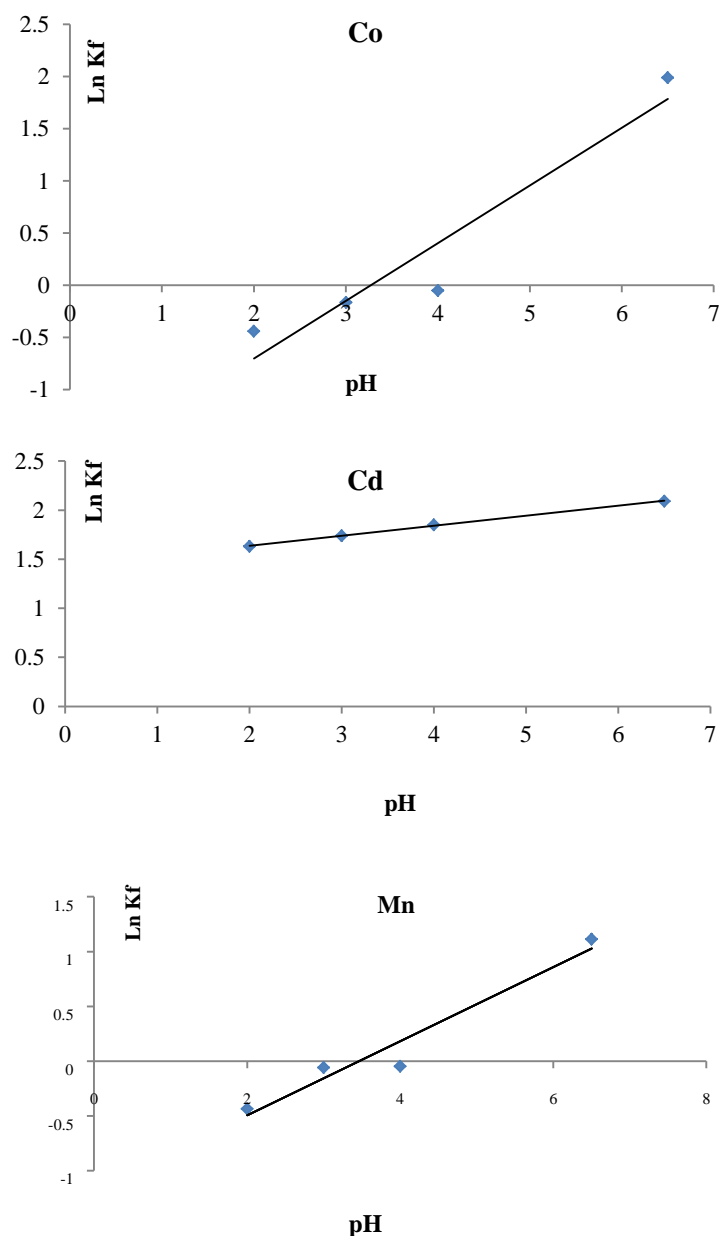**Figure 8: Evolution of the adsorption capacity kf as a function of the pH**

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Figure 9: pH-adsorption relationship of Co, Mn and Cd ions

The adsorption can be described by an equation of the type: Ln (Kf)=a. (pH)+b Where a and b are empirical constants. The relationships Ln Kf=f (pH) for the adsorption of Co, Mn and Cd ions on clay are similar to those reported by other authors [11-12].

Examination of these results firstly shows that the adsorption of metal ions is influenced by the pH variation. However, a strong correlation is established between the Kf parameter and the pH in the case of cadmium (R=0.99). indicates the high affinity of the Cd ions for the adsorbent matrix. This is explained by the possibility of formation of cadmium hydroxides and the increase of the numbers of the absorbing sites. The values of the regression parameters: Ln Kf=a. pH+b are collated in Table 3.

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Table 3: Parameters of regressions Ln Kf=a. pH+b

	a	B	R
Co	0.55	-1.806	0.915
Mn	0.33	-1.17	0.946
Cd	0.101	1.43	0.99

Such results are to be compared to the work of Barrow N et al [41], who also reported minimal sensitivity to adsorption pH of metal ions on clay minerals and soils.

CONCLUSION

According to this study, the pH is a factor determining the adsorption phenomena of heavy metals on the adsorbent supports. It has been reported that a pH rise close to 6.5 greatly affects the adsorption process. Indeed, this influence is generally interpreted in various ways in the literature of which we quote some:

At low pH (less than 6), there is competition between the H+ions in solution and the metal ions. These are the H+which are preferentially fixed. There is also competition between the Al^{3+}, Mg^{2+}, Fe^{3+}ions released by the octahedral sites of clay in acid solution (Cousin, 1980) [42]

- At high pH (above 6), there would be an increase in the number of sites such as the hydroxides of clay minerals (Serpaud et al. 1994) [43]. According to Cousin (1980), hydroxyl groups in water could also attach to incomplete tetrahedral silicas. These groups will be even more ionized as the pH increases. This will increase the number of negative charges.

The parameter Kf as a characteristic index of adsorption, evolves exponentially with pH. The empirical equation: Ln Kf=a pH+b makes it possible to evaluate the adsorption capacity of each metal with a view to pH [2 – 6.5]. The calculated values of the slopes are variable according to the metal considered. In general, the retention power decreases in the following direction:

Cd>Co>Mn

The isothermal study of the effect of pH on the processes of removal of heavy metals by activated clays has shown that the adsorption of Cd ions is more affected by a variation in pH than that of Co and Mn ions.

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