# الامتصاص التنافسي لبعض أيونات المعادن ثنائية وثلاثية التكافؤ بواسطة الكاولين الليبي وأطواره المعدلة

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## مقدمة

**تستند** هذه الدراسة على المنافسة في الامتصاص على الأسطح المعدنية (طين ليبي – كاولين) بين أيونات الفلزات ثنائية وثلاثية التكافؤ. هذه الأيونات الفلزية هي: $Eu^{3+}$, $La^{3+}$, $Cr^{3+}$, $Ni^{2+}$, $Cd^{2+}$& $Co^{2+}$ . تم دراسة أربعة أطوار من معدن الطين بحجم حبيبي أقل من 250mm وهي: (i) K-N وتمثل المعدن الطبيعي دون إجراء أي معالجة. (ii) KT-5 وتمثل المعدن الطبيعي المعالج حراريا عند500°C لمدة ساعتين. (iii) KT-10 وتمثل المعدن الطبيعي المعالج حراريا عند1000°C لمدة ساعتين. (iv) KT-Mn وتمثل العينة المعدلة بالمنجنيز. أخذ في الاعتبار أربعة عوامل مختلفة هي: زمن التلامس، الأس الهيدروجيني، تركيز أيون الفلز، وأخيرا تم دراسة خط التحاور للامتصاص (sorption isotherm). أظهرت الدراسة أنه لا تأثير لزمن التلامس على الامتصاص بعد عشرين دقيقة لجميع الأيونات. ومع ذلك كان امتصاص أيونات الفلزات ثلاثية التكافؤ عند الحد الأقصى تقريبا بالنسبة للعينات K-N و KT-10 و KT-Mn حيث كان الترتيب على النحو:$Cr^{3+}>Eu^{3+}>La^{3+}$ واتبع امتصاص الفلزات ثنائية التكافؤ الإتجاه$Ni^{2+}>Co^{2+}>Cd^{2+}$ لجميع العينات. زادت قوة الامتصاص مع زيادة الأس الهيدروجيني، وكانت باستمرار أقوى للأيونات ثلاثية التكافؤ وكان الترتيب على النحو: $Cr^{3+}>Eu^{3+}>La^{3+}>Ni^{2+}\geq Co^{2+}>Cd^{2+}$ . في حين وجد أن قوة امتصاص جميع الأيونات عدا أيون الـ $Cr^{3+}$ عند أعلى قيمة مع الطين المعدلة بالمنجنيز. انخفضت قيمة الـ Kd لأيون $Cr^{3+}$ مع زيادة تركيزه عند ملامسته للعينة KT-Mn . وانطبق ذلك على الأيونات $Ni^{2+}$ و $Co^{2+}$

و $Cd^{2+}$ لكن بمعدل انخفاض أقل. انخفضت قيم الـ Kd للأيونات $Eu^{3+}$ و $La^{3+}$ بزيادة تركيز الأيون في حالة العينة K-N ، بينما أظهر أيون $Cr^{3+}$ زيادة في الامتصاص مع KT-Mn و K-N كلما زاد تركيز أيونه. لا تأثير يذكر لتركيز الأيون على امتصاص الأيونات ثنائية التكافؤ مع العينات K-N و KT-5 و KT-10 . أظهرت العينة KT-Mn أعلى قيمة للامتصاص مع جميع الأيونات عدا أيون $Cr^{3+}$ الذي أظهر امتصاصا أكبر على العينة K-N .

# Competitive sorption of some di- and tri-valentmetal ions by Libyan kaoliniteand its modified phases

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## Abstract :

This study is based on the investigation of sorption competition on mineral surfaces (Libyan clay, kaolinite) between di and tri-valent metal ions. These metal ions are $Eu^{3+}$, $La^{3+}$, $Cr^{3+}$, $Ni^{2+}$, $Cd^{2+}$ and $Co^{2+}$. Four different mineral phases were investigated with a particle size less than 250 mm (i) K-N is the natural sample without treatment; (ii) KT-5 is K-N heated for 2 hrs at 500 °C; (iii) KT-10 is K-N heated for 2 hrs at 1000 °C and (iv) KT-Mn is the Mn-modified sample taking into consideration four different factors:- time of contact, pH, metal ion concentration, and finally the isotherm sorption. There is no significant effect of time on the metal ion sorption beyond 20 minutes. However, the sorption of the trivalent metal ions was almost at its maximum for the samples: K-N, KT-10 and KT-Mn in the order $Cr^{3+}>Eu^{3+}>La^{3+}$. The sorption of divalent metal ions follows the trend $Ni^{2+}>Co^{2+}>Cd^{2+}$ for all kaolinite samples.

The sorption strength increased with increase in pH, and was consistently stronger for trivalent ions in the order

$Cr^{3+}$> $Eu^{3+}$> $La^{3+}$> $Ni^{2+}$ ≥ $Co^{2+}$> $Cd^{2+}$. While the sorption for all metal ions except for $Cr^{3+}$was found higher in the Mn-modified clays. The Kd value decreasedas the $Cr^{3+}$ metal ion concentration increasedin the presence of KT-Mn. This is also true for $Ni^{2+}$, $Co^{2+}$ and $Cd^{2+}$ but at a lower rate of decrease. The Kd value for $Eu^{3+}$ and $La^{3+}$decreasedslightly as metal ion concentration increasedin the case of K-N, whereas chromium showed an increase when contacted with K-N and KT-Mn (as the metal ion concentration increased). Whereas divalent metal ions are not affected by the metal concentration in the case of K-N, KT-5 and KT-10 samples. The Mn-hydrothermal (KT-Mn) sample showedthe best sorption strength for all the metal ions except $Cr^{3+}$, which showed stronger sorption on K-N.

## Introduction:

Clay minerals such as kaolinite, bentonite and montmorillonite are very fine natural particles and accordingly have high specific surface area. Due to their very fine particle size, clays can easily form a colloidal dispersion in aqueous solution (Kim 2003). Clay mineral structure always contains the silicon-oxygen linkage with the shared oxygen linked usually to Al, Mg or Fe. This kind of inter-linkage is called a tetrahedral-octahedral structure, TO or 1:1 structure regarding the ratio of tetrahedral and octahedral coordinated cations (Grim, et al., 1968; Velde and Barre, 2010). The octahedrally and tetrahedrally coordinated ions can be in the sequence tetrahedral-octahedral-tetrahedral, or TOT structure (2:1). Kaolinite is a clay mineral with the molecular formula $Al_2Si_2O_5(OH)_4$ and has a 1:1 layer structure with the basic unit consisting of a tetrahedral sheet of silicates connected through oxygen ions to one octahedral sheet of alumina, as the octahedral cation (Moayedi et al., 2011, Bhattacharyya and Gupta, 2008). The sorption of metal ions onto minerals was reported to follow the general sequence for ion-exchange equilibria, for example, the sorption of caesium, strontium and europium on kaolinite and montmorillonite increases in the order $Cs^+ < Sr^{2+} < Eu^{3+}$ (Adeleye et al., 1994). The sorption of metal ions by clay minerals is a complex process controlled by a variety of environmental parameters.

Sorption of $Mn^{2+}$, $Pd^{2+}$, $Cd^{2+}$, $Zn^{2+}$, $Ni^{2+}$, $Cu^{2+}$ and $Cr^{3+}$ onto Na-montmorillonite has been studied as a function of pH and found to decrease with decreasing pH (Abollino et al,. 2003). The immobilization of $Pb^{2+}$, $Cd^{2+}$ and $Ni^{2+}$ on kaolinite and montmorillonite has been studied under different conditions such: time, ion concentration, pH, adsorbate concentration and temperature (Gupta and Bhattachayya 2008). The uptake was found to be rapid with maximum adsorption within 180 min for $Pb^{2+}$ and $Ni^{2+}$, while it was 240 min for $Cd^{2+}$. Increasing pH resulted in increasing the removal of metal ions from the aqueous solution, as they started to precipitate out in the form of hydroxides (Gupta and Bhattachayya2008). In some other studies it was found that adsorption of $Cu^{2+}$ on kaolinite increased with pH till $Cu^{2+}$ ions became insoluble in alkaline medium (Bhattacharyya and Gupta, 2006).

## **Experimental**:

All reagents used in these experiments were purchased as analytical reagents and used as received without any further treatment or purification.

The $K_d$ was determined from the equation:

$$K_d = \frac{(Co - C)}{C} . \frac{V}{m}$$

Where: Co and C are the metal ion concentration (ppm) of the initial solution

andfinal solution after the sorption takes place respectively.

m = mass of the kaolinite (g).

V = volume of the electrolyte solution (ml)

## **Modification of Kaolinite:**

The Kaolinite sample from the Industrial Research Centre (IRC) Libya was ground to a particle size less than 250 mm, treated in four different ways as follows: (i) K-N is a natural sample left as it is;(ii) KT-5is a natural sample heated at 500 $^{o}$C for 2 hours;(iii) KT-10 is a natural sample heated at 1000 $^{o}$C for 2 hours and (iv) KT-Mn is a modified sample by the

Mn-hydrothermal method: Typically 15 g sample was immersed in 100 ml of 1 M $MnCl_2.4H_2O$ solution (19.7844 g of $MnCl_2.4H_2O$ were dissolved in 100 ml deionisedwater). The pH was adjusted to 7.0 with 3 M NaOH solution. The reaction was maintained at 100 $^oC$ for 2 hours inside a paraffin oil bath under stirring, the beaker containing paraffin oil was surrounded by aluminium foil and then a piece of cardboard. It was also raised ~1 cm from the top surface of the hot plate to make the heat homogenously distributed around the beaker. See Figure1.After the treatment, the sample was filtered and dried at 100 $^oC$ for 24 hours. All these samples were stored in tightly sealed glass bottles until use.

More recent work (e.g. Lima et al., 1998 for the modification of bentonite;Fusova, 2009 for the modification of Ca-montmorillonite;Li et al 2009 for the manganese oxide and micro-emulsion modification of diatomite; Chaisena and Rangsriwatananon 2004 for thermal and acid treatment on diatomite) have focused upon the modification of mineral surfaces in order to improve the sorption capacity and the characteristics of the solid phases. The treatments in this work were carried out to investigate the effect of heat or thermochemical treatment on the enhancement of the adsorption property of clays.

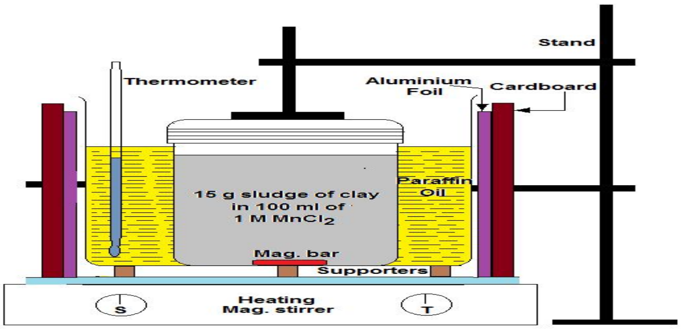

**Figure 1 A diagram of Mn-hydrothermal modification of clay**

### Preparation of 1000 ppm stock solutions of the metal ions

1000 ppm solutions of the metal ions ($Co^{2+}$, $Zn^{2+}$, $Cd^{2+}$, $Ni^{2+}$, $Eu^{3+}$, & $Cr^{3+}$) were prepared individually using nitrate salts, in 0.1 M $HNO_3$ and the solutions were kept in 500 ml plastic containers for use.

### Preparation of 10 ppm mixture solution:

20 ml of each of the above solutions were transferred to 2 litre volumetric flasks to make 10 ppm of the elements: Co, Zn, Cd, Ni, Cr and Eu in deionized water.

### (i) Effect of contact time:

30 ml of each of the mixture solution were added to 50 ml graduated centrifuge tubes. The pHof these solutions were adjusted to the required value (pH = 6.0 ± 0.1), using 0.01 or 0.001 N HCl or NaOH solutions as required. The final volume was adjusted to 40 ml, and then 0.08 g (2 g/l) kaolinite was added. Following this, the pH was readjusted

again to 6.0 ± 0.1. These experiments were triplicated. The solutions were kept shaking at different timeintervals: 20, 60, 90, 120, 150, 240, 300, 360, 1440 & 2880 minutes, and centrifuged at 3500 rpm for 20 min. 5 ml aliquots of the samples were diluted to 10 ml using 1.0 M $HNO_3$ solution. The same procedures were carried on a solution without mineral; this was considered as a sample to define the initial concentrations. The diluted solutions were analysed using ICP-AES (Perkin-Elmer Optima 5300 dual view).

### (ii) Effect of pH:

30 ml of each of the mixture solutions were added to 50 ml graduated centrifuge tubes. The pH values were adjusted from 2.0 to 7.0 ± 0.1 at 1 pH unit intervals. The maximumpH 7 was set to prevent any metal ion precipitation. Triplet samples were takenfor each solution. 0.08 g kaolinite was added to each tube. The samples were kept shaking for 24 hours and then centrifuged at 3500 rpm,decanted, and then 5 ml of each was diluted to 10 ml total volume using 1.0 M $HNO_3$ solution. The same procedures were carried out for solutions without mineral, which served as control experiments. The diluted solutions were analysed using ICP-AES.

### (iii) Effect of metal ion concentration

Different amounts of the 10 ppm mixture solution ( i.e 6, 12, 18, 24 & 30 ml) were transferred to 50 ml graduated centrifuge tubes to represent different concentrations (2, 4, 6, 8 & 10 mg/l) of the selected metal ions. All solutions were adjusted to 30 ml total volume, and then the pH was adjusted to 6.0 ± 0.1, using 0.01 or 0.001 N HCl or NaOH solutions as required. After that 0.08 g of kaolinite was added to each tube, the pH was readjusted again. The same procedures were carried out for another series without mineral, which were considered as initial concentrations.

## Results and discussion

### Mineral characterization

Figure 2 shows the X-Ray pattern of the original kaolinite sample,showing the main two peaks of kaolinite at 2-theta = 12.4$^{o}$ (d=7.08Å) and 25$^{o}$ (d=3.56Å) and a large peak of quartz at 2-thata = 26.2$^{o}$ (d=3.40Å). In addition toalunite at 2-theta = 15$^{o}$ (d=5.90Å), 18$^{o}$ (d=4.92Å) and 30$^{o}$ (d=2.98Å) and Halite at 2-theta = 31.5$^{o}$ (d=2.84Å) and 45.5$^{o}$ (d=1.99Å).

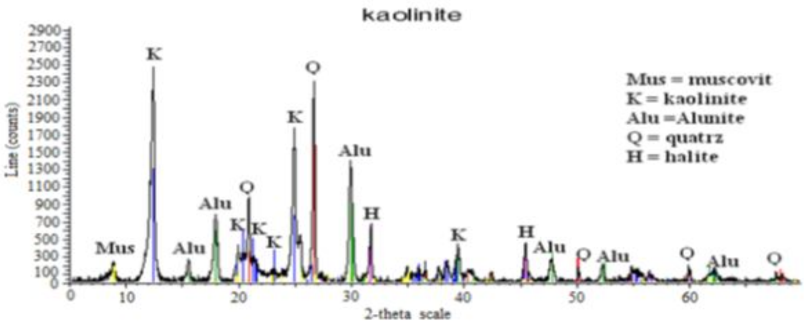

**Figure 2 XRD patterns of natural kaolinite.**

## XRD for the thermally treated kaolinite

The treated kaolinite sampleswere characterised with the XRD technique to investigate any changes in their mineralogy: the four different samples were: (i) Natural kaolinite (K-N); (ii) 500 °C treated sample (KT-5); (iii) 1000 °C treated sample (KT-10); and (iv) Manganese thermal modified sample (K-Mn). Figure 3 shows comparison patterns of the K-N and KT-5 samples.

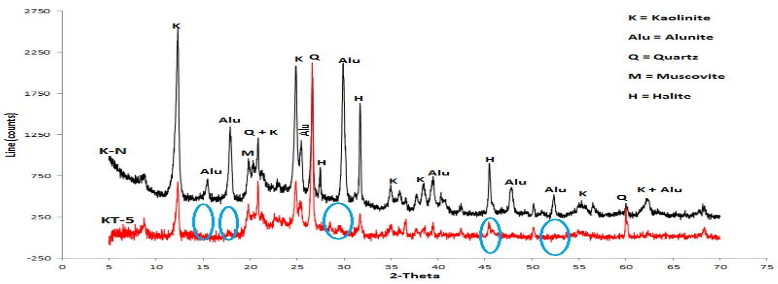

**Figure 3 XRD patterns of natural kaolinite together with 500 °C treated kaolinite**

It can be seen that the Alunite, $KAl_3(SO_4)_2(OH)_6$, peaks at 2-theta equal to 15° (d=5.90 Å), 18° (d=4.92 Å), 28° (d=3.18 Å) and 52.5° (d=1.74 Å) have almostly or completely disappeared. Such behaviour could be due to the heat induced transformation of the mineral phase. Alunite mineral can be associated with Kaolinite mineral ore as a minor and trace constituent (Al-Momani 2006). There is no evidence to suggest that alunite starts decomposing at <500 $^{o}$C, but associated water is liberated at these temperatures (Ogburnet al., 1932; Fink et al., 1931). Arazi and Krenkel (1970) also claimed that the dehydroxylation of Alunite can be achieved in the temperature range 430-590 $^{o}$C,whilst Becker et al (2008) showed that the liquid-vapour homogenization temperature could be in the range from 150 to 500 $^{o}$C.

Figure 4 shows the XRD patterns of natural kaolinite together with kaolinite treated at 1000 $^{o}$C (KT-10). Again, the Alunite peaks at 2-theta equal to: 15$^{o}$ (d=5.90 Å), 17.5$^{o}$ (d=5.71 Å), 30o (d=2.98 Å) and 48$^{o}$ (d=1.89 Å) and the halite peaks at 27.5$^{o}$ (d=3.24 Å), 32$^{o}$ (d=2.78 Å) and 46$^{o}$ (d=1.97 Å) diminished on 1000 $^{\square}$C treatment. The significant result here is that the main Kaolinite peaks at 12$^{o}$ (d=7.37 Å) and 25$^{o}$ (d=3.56 Å) are also affected by the high temperature and disappeared. At the same time, small peaks appeared at 16.5$^{o}$ (d=5.37 Å) due to the formation of MulliteAl($Al_{1.272}Si_{0.728}O_{4.864}$). Two small peaks representing quartz can be seen at 31$^{o}$ (d=2.88 Å) and 34$^{o}$ (d=2.64 Å).

Further, the intensity of the main quartz peak at 26.5$^{o}$ (d=3.36 Å) increases on treatment at 1000 $^{o}$C.

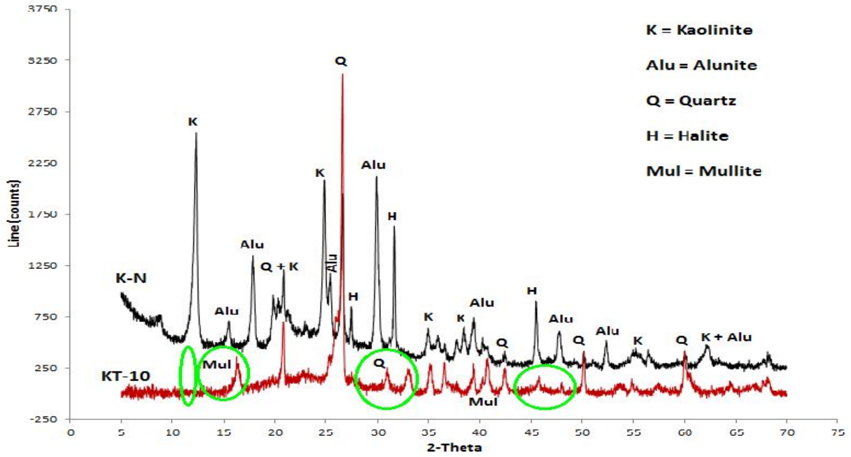

Figure 4 XRD patterns of natural kaolinite together with 1000 $^{o}$C treated kaolinite

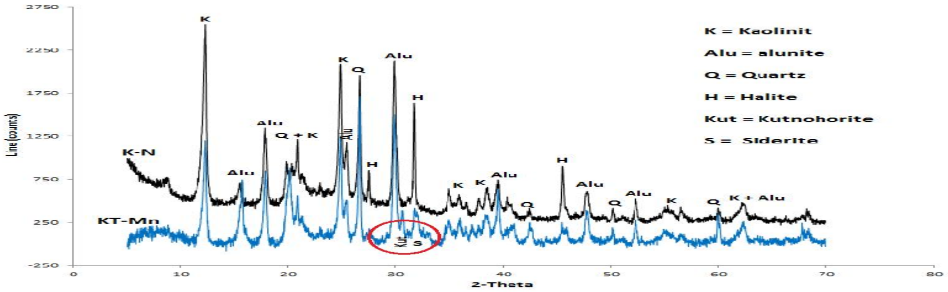

Figure5 XRD patterns of natural kaolinite together with Mn-modified kaolinite

Figure 5 shows the XRD patterns of natural kaolinite together with the Mn-modified sample. Although, there is no significant effect of the Mn-modification on the kaolinite structure, a slight decrease in the intensity of the main peaks was observed. The diffractogram also shows a small peak at 2-theta equal to 31$^o$ (d=2.88 Å) due to the formation of Kutnohorite, a magnesian phase Ca(Mn, Mg)$(CO_3)_2$ and a small peak representing the formation of Siderite ($FeCO_3$) at 32$^o$ (d=2.80 Å).

**Table 1 Chemical composition of kaolinite samples**

| **Samples type □** | **K-N** | **KT-5** | **KT-10** | **KT-Mn** |
|---|---|---|---|---|
| **Contents □** | | | | |
| **$SiO_2$** | 40.6 | 41.2 | 46.1 | 37.8 |
| **$Al_2O_3$** | 34.2 | 35.9 | 38.9 | 32.6 |
| **$Fe_2O_3$** | 2.1 | 2.03 | 2.6 | 1.8 |
| **MgO** | 0.32 | 0.40 | 0.42 | 0.20 |
| **$K_2O$** | 3.2 | 3.2 | 3.7 | 2.7 |
| **$Na_2O$** | 2.2 | 2.8 | 4.02 | 1.3 |
| **CaO** | 0.67 | 0.68 | 0.9 | 0.13 |
| **Ti** | 0.67 | 0.67 | 0.85 | 0.59 |
| **Mn** | 0.02 | 0.02 | 0.03 | 6.1 |
| **Zn** | 0.01 | 0.01 | 0.01 | 0.01 |
| **F** | 0.23 | 0.26 | — | 0.19 |
| **$SO_3$** | 13.0 | 12.1 | 1.9 | 11.3 |
| **$P_2O_5$** | 0.25 | 0.24 | 0.31 | 0.23 |
| **Cl** | 2.6 | 0.34 | — | 5.0 |
| **Others *** | 0.12 | 0.12 | 0.16 | 0.12 |
| **Total** | 100.0 | 99.99 | 100.0 | 99.9 |
| * = Cr, Ni, Cu, Ga, Rb, Sr, Y, Zr, Nb, Ba, Ce, Pb, Br, Co, Nd&Th | | | | |

The chemical compositions of the natural raw kaolinite (K-N), 500 $^{o}$C treated kaolinite (KT-5),1000$^{o}$C treated kaolinite (KT-10) and Mn-thermal modified kaolinite (KT-Mn) are shown in Table 1. The raw kaolinite and the 500 $^{o}$C treated kaolinite (KT-5) showed no significant difference in the chemical composition and the mineral ratios. whilst, the 1000 $^{o}$C treated sample showed some increase in the percentages of $SiO_2$, $Al_2O_3$ and $Na_2O$, which may be due to the loss of $SO_3$, which showed a decrease from 13 % to 2 %. The Mn-modified sample shows an increase in the Mn and Cl compositions, which affected the $SiO_2$ and $Al_2O_3$ concentrations. The $Al_2O_3$ : $SiO_2$ ratios remain almost the same for all samples: 1 : 1.19 for K-N, 1 : 1.15 for KT-5, 1 : 1.18 for KT-10 and 1 : 1.16 for KT-Mn. Thus the Al : Si ratios are 1 : 1.5, 1 : 1.01, 1 : 1.05 and 1 : 1.03 for K-N, KT-5, KT-10 and KT-Mn, respectively.

## Sorption study

Solutions of three trivalent metal ions ($Cr^{3+}$, $Eu^{3+}$ and $La^{3+}$) and three divalent metal ions ($Cd^{2+}$, $Co^{2+}$ and $Ni^{2+}$) were contacted with natural kaolinite clay mineral in four different protocols. (i) Natural kaolinite without any treatment (K-N); (ii) Kaolinite heated at 500 $^{o}$C (KT-5); (iii) Kaolinite heated at 1000 $^{o}$C (KT-10) and finally the Mn-hydrothermaly treated sample (KT-Mn). The main task of this experiment is to investigate the sorption competition between di– and trivalent metal ions within the mineral, the effect of the modifications on the metal ion binding properties at the mineral surface. The parameters taken into account were contact time, pH and metal ion concentration. Each experiment was repeated three times and the error bars are plotted in the figures as 2□ values.

## Effect of contact time

Figure 6 shows the sorbed amount of selected metal ions $Ni^{2+}$, $Co^{2+}$, $Cd^{2+}$, $Eu^{3+}$, $La^{3+}$ and $Cr^{3+}$ by the kaolinite samples K-N, KT-5, KT-10 and KT-Mn as a function of time. There is no significant effect of the time beyond 20 minutes on the sorbed amount of the metal ions. The sorption of $Eu^{3+}$, $La^{3+}$ and $Cr^{3+}$ was at a maximum (□ 100 %) for the samples: K-N, KT-10 and KT-Mn, whilst for the KT-5 the sorption of these trivalent metal ions was 95 %, 70 % and 55 % respectively and decreases in the order $Cr^{3+}>Eu^{3+}>La^{3+}$. The sorption of trivalent metal ions was always higher than that for divalent metal ions for all the kaolinite samples

Although the sorption of divalent metal ions follows the trend ($Ni^{2+}>Co^{2+}>Cd^{2+}$), for all kaolinite samples, the sorption affinity was different from sample to sample. KT-5 showedthe smallest sorbed amounts for divalent metal ions: □ 40 %, □ 35 % and □ 18 % for $Ni^{2+}$, $Co^{2+}$ and $Cd^{2+}$ respectively. The other three samples show almost similar values: □ 60 %, □ 50 % and □ 30 % for $Ni^{2+}$, $Co^{2+}$ and $Cd^{2+}$, respectively.

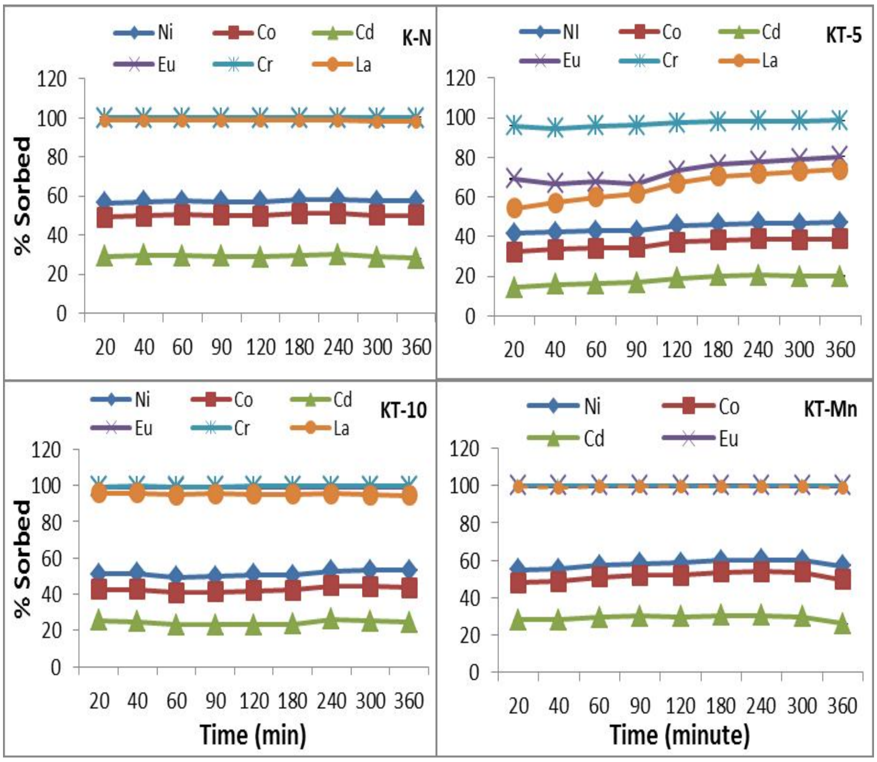

**Figure 6 the sorption behaviour for metal ions ($Ni^{2+}$, $Co^{2+}$, $Cd^{2+}$, $Cr^{3+}$, $Eu^{3+}$& $La^{3+}$) onto each mineral samples, K-N, KT-5, KT-10 and KT-Mn as a function of time, pH = 6.0 ± 0.**

## Effect of pH

The sorption of the metal ionswas studied as a function of pH for the different kaolinite samples in the range of pH 2 – 7 at1 pH unit intervals.

In general for all the mineral samples, the sorption affinity of the metal ions decreased in the order: $Cr^{3+}$> $Eu^{3+}$> $La^{3+}$> $Ni^{2+}$ ≥ $Co^{2+}$> $Cd^{2+}$. Trivalent metal ions were more influenced by the pH than the divalent metals above pH 5, andthe Kd values increase with increasing pH. The K-N and KT-Mn samples show greater uncertainties for chromium, as shown in Figure 7. Similar behaviour was reported by Yanai and Itami (2006), who investigated the sorption of $Cd^{2+}$ and $Cu^{2+}$ ions onto a variety of soil clay minerals, including montmorillonite and kaolinite. They found that the sorption was highly pH-dependent in the range between 5 and 7, where 50 % sorption was achieved. $Eu^{3+}$ and $La^{3+}$ show the sorption strength in the order of KT-Mn≈K-N>KT-10>KT-5 at pH from 3 to 7. Generally, the sorption strength increases with increasing pH at pH above 5, for all the elements with all the mineral samples.

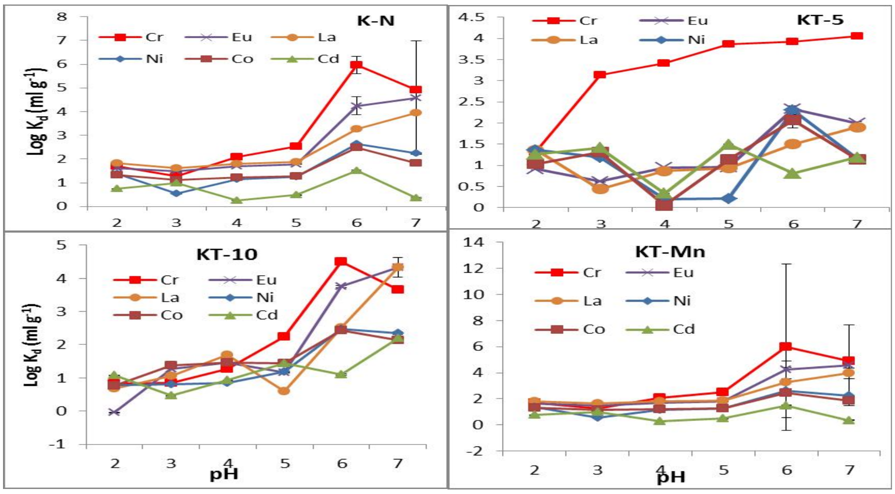

**Figure 7 the effect of pH on the sorption of (Ni$^{2+}$, Co$^{2+}$, Cd$^{2+}$, Cr$^{3+}$, Eu$^{3+}$& La$^{3+}$) onto each mineral sample, K-N, KT-5, KT-10 and KT-Mn**

## Effect of metal ion concentration

The effect of concentration on the sorption of the metal ions is shown in Figure 8. The distribution coefficients for the trivalent metal ions were higher than those for the divalent metals.

The order of log Kd is Cr$^{3+}$> Eu$^{3+}$> La$^{3+}$> Ni$^{2+}$ ≈ Co$^{2+}$> Cd$^{2+}$ for K-N; Cr$^{3+}$> Eu$^{3+}$> (La$^{3+}$, Ni$^{2+}$, Co$^{2+}$& Cd$^{2+}$) for KT-5. Whilst, that for KT-5 and KT-Mn samples is Cr$^{3+}$> Eu$^{3+}$> La$^{3+}$> Ni$^{2+}$ ≈ Cd$^{2+}$> Co$^{2+}$ and Cr$^{3+}$> Eu$^{3+}$> La$^{3+}$> Ni$^{2+}$ ≈ Co$^{2+}$> Cd$^{2+}$ respectively.

There are significant differences in sorption for Eu$^{3+}$ and La$^{3+}$ for all of the mineral samples. The Kd decreases as the metal ion concentration increases in the caseof KT-Mn. This is also true for $Ni^{2+}$, $Co^{2+}$ and $Cd^{2+}$ but the rate of decrease is lower. $Eu^{3+}$ and $La^{3+}$ Kd decreases slightly as metal ion concentration increases in the case of K-N, whereas chromium shows an increase when contacted with K-N and KT-Mn (as a metal ion concentration increases). Divalent metal ions are not affected by the metal concentration in the case of K-N, KT-5 and KT-10 samples. In general, the highest sorption was for K-N and KT-Mn.

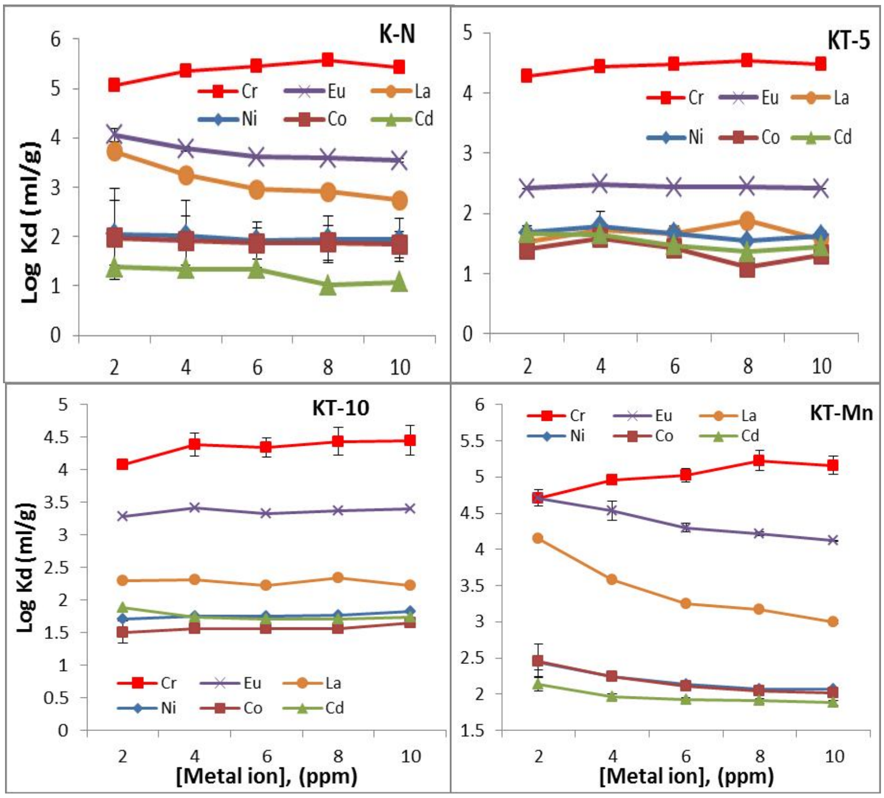

Figure8 the effect of metal ion concentration on the sorption of ($Ni^{2+}$, $Co^{2+}$, $Cd^{2+}$, $Cr^{3+}$, $Eu^{3+}$& $La^{3+}$) onto each mineral sample, K-N, KT-5, KT-10 and KT-Mn

## Sorption isotherm

The sorption isotherm data for each element on the different kaolinite samples are shown in Figures 9 – 14.

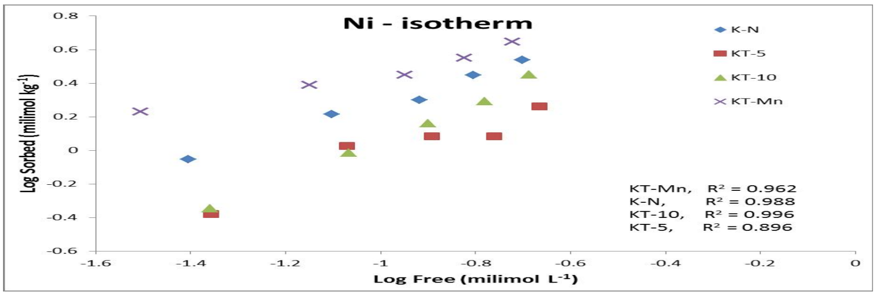

**Figure 9 sorption isotherm for the $Ni^{2+}$metal ion on the different kaolinite samples (K-N, KT-5, KT-10 and KT-Mn), pH = 6 ± 0.1**

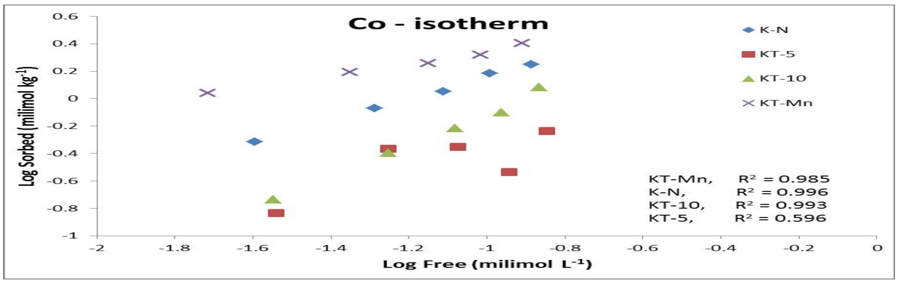

**Figure 10 sorption isotherm for the $Co^{2+}$metal ion on the different kaolinite samples (K-N, KT-5, KT-10 and KT-Mn), pH = 6 ± 0.1**

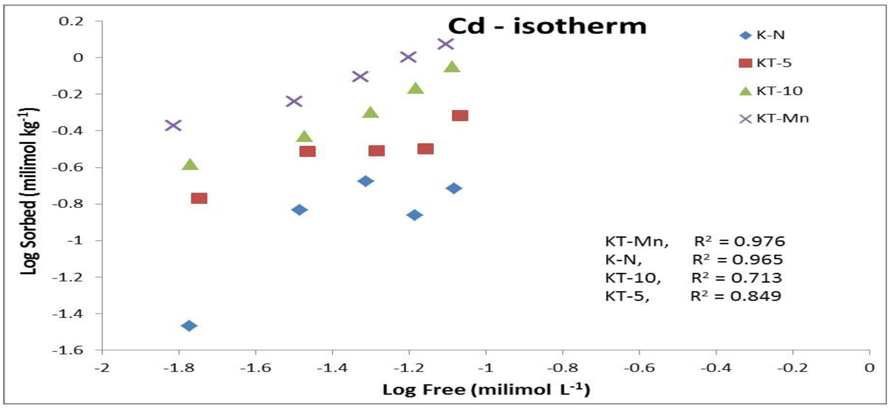

**Figure 11 sorption isotherm for the metal ions $Cd^{2+}$, on the different kaolinite samples (K-N, KT-5, KT-10 and KT-Mn), pH = 6 ± 0.1**

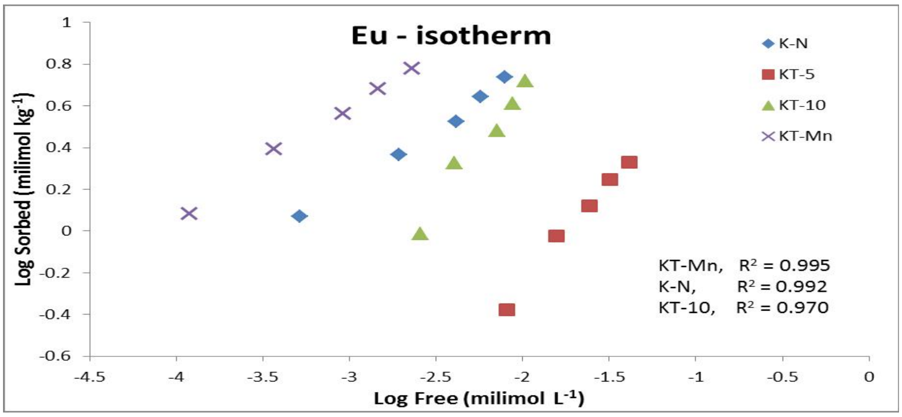

**Figure 12 sorption isotherm for the metal ions $Eu^{3+}$, on the different kaolinite samples (K-N, KT-5, KT-10 and KT-Mn), pH = 6 ± 0.1**

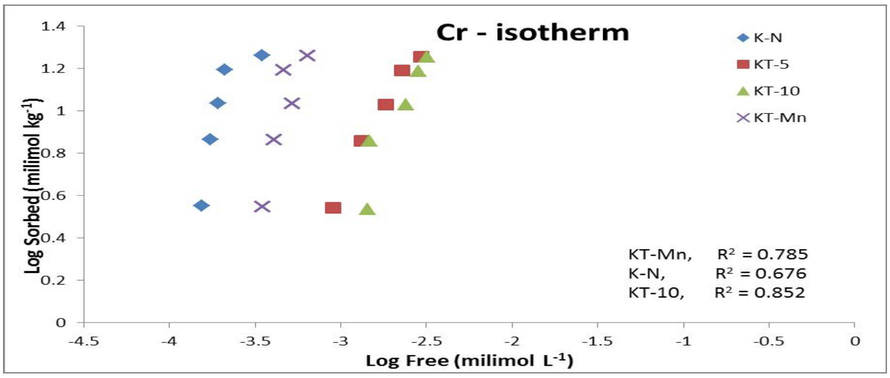

Figure 13 sorption isotherm for the metal ions $Cr^{3+}$, on the different kaolinite samples (K-N, KT-5, KT-10 and KT-Mn), pH = 6 ± 0.1

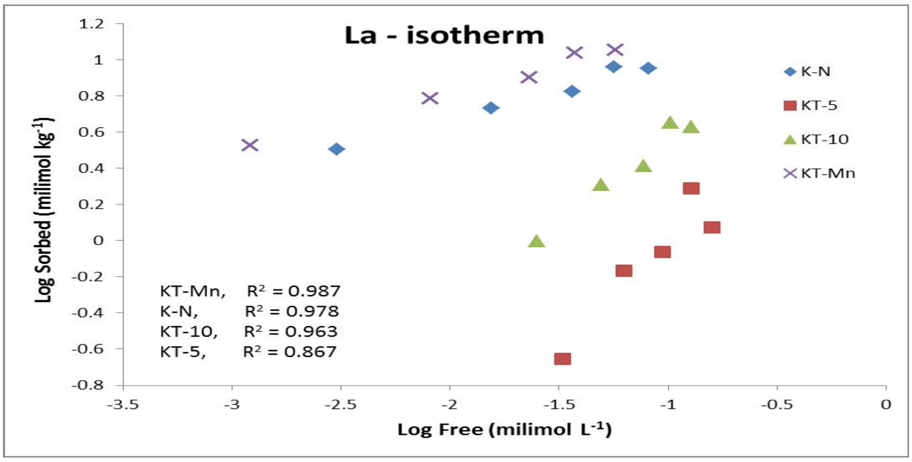

Figure 14 sorption isotherm for the metal ions $La^{3+}$, on the different kaolinite samples (K-N, KT-5, KT-10 and KT-Mn), pH = 6 ± 0.1

From the isotherm data shown in Figures 9 – 14, the binding strength follows the following orders:

(i) $Co^{2+}$, $Ni^{2+}$, $Eu^{3+}$& $La^{3+}$: KT-Mn>K-N>KT-10>KT-5
(ii) $Cd^{2+}$: KT-Mn>KT-10>KT-5>K-N
(iii) $Cr^{3+}$: K-N>KT-Mn>KT-5>KT-10

Therefore, the Mn-hydrothermal (KT-Mn) sample shows the best sorption strength for all the metal ions except $Cr^{3+}$, which chooses to sorb on K-N more strongly.

The linearity was good with R2 in the range between 0.85 and 0.99, except for $Cr^{3+}$ with KT-Mn (R2 = 0.79) and K-N (0.68) and Co with KT-5 (0.59) and Cd with KT-10 (0.71).

The binding strengths for the kaolinite samples follow the following orders:

(i) For K-N and KT-Mn: $Cr^{3+}> Eu^{3+}> La^{3+}> Ni^{2+}> Co^{2+}> Cd^{2+}$
(ii) For KT-10: $Cr^{3+}> Eu^{3+}> La^{3+}> Ni^{2+} \geq Cd^{2+}> Co^{2+}$
(iii) For KT-5: $Cr^{3+}> Eu^{3+}> Ni^{2+} \geq La^{3+}> Cd^{2+} \geq Co^{2+}$

## 6.3. Conclusion

On conclusion, there was no significant effect of time on the sorption of the studied metal ions onto the kaolinite mineral. Trivalent metal ions showed higher sorption strength than the divalent metal ions. The sorption increasedwith pH and the rate of increase of Kd with pH becomes greater at pH>5. For metal ion concentrations in the range 2-10 mg $L^{-1}$ the sorption strength of the divalent metal ions decreases with increasing the metal ion concentration, whilst there is no real change for the trivalent metal ions. The KT-Mn sample shows best sorption strength for all metal ions, while the K-N samples gave highest sorption strength for $Cr^{3+}$, andKT-5 was the weakest.

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