

## Removal of heavy metals from aqueous solutions using Tunisian smectite clay intercalated by functionalized crown ethers

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(Received: 18 April 2017, accepted: 01 November 2017)

**Abstract:** Solid-liquid extraction is one of the most used methods for the environment protection and especially for removal of heavy metals. The solid phase used in this work was a Tunisian smectite clay saturated by  $\text{Na}^+$ , and intercalated by functionalized crown ethers: Dibenzo-14-Crown-4 ( $\text{NO}_2$ )<sub>2</sub> (**1**), Dibenzo-14-Crown-4( $\text{NO}_2$ )<sub>2</sub>(Br)<sub>2</sub> (**2**), Dibenzo-14-Crown-4(Br)<sub>4</sub> (**3**) and Dibenzo-14-Crown-4( $\text{COOH}$ )<sub>2</sub> (**4**). These new obtained hybrid materials were firstly characterized by X-ray diffraction (XRD), IR spectroscopy and thermal analysis (DSC and DTA-TGA). After that they were used to extract heavy metals (Fe, Cu, Cd, Zn, Pb, Mn and Co). Extraction percentages by modified clays varied in the following decreasing order  $\text{Fe}^{3+} \geq \text{Cu}^{2+} \geq \text{Pb}^{2+} > \text{Co}^{2+} \geq \text{Mn}^{2+} > \text{Cd}^{2+} \approx \text{Zn}^{2+}$ .

**Keywords:** Functionalized crown ethers, Intercalation, Removal of heavy metals, Tunisian Smectite.

### INTRODUCTION

Modification of clay minerals have received a considerable interest according to their use in many applications areas such as catalysis [1-7], adsorption of organic pollutants [8-10] and protection of environment from heavy metals [11-23]. Generally the intercalation of organic molecules in the interlayer space of mineral clay presents the most significant modification of these materials. Shipeng et al. [24] studied the intercalation behavior of polyethylene glycol (PEG) in organically modified montmorillonite. A series of hybrids with different PEG content were prepared and characterized by X-ray diffraction and differential scanning calorimetry.

Casal et al. [25] were interested in the intercalation of some macrocyclic compounds (crown ethers: 18-crown-6 and 15-crown-5), in the interlayer space of the phyllo-silicate (2:1).

We describe in this paper the purification of the smectite taken from the area of Gafsa (Tunisia) by a solution of sodium chloride (1M) then the intercalation of some functionalized Dibenzo-14-Crown-4 in the interlayer space of the obtained sodium exchanged smectite clay (Figure 1).

The new obtained materials (ST- $\text{Na}^+$  & Clay [ $\text{Na}^+$ ]-Crown ether) were subsequently used to remove heavy metals such as Fe, Cu, Pb, Cd, Zn, Mn and Co from aqueous solutions.

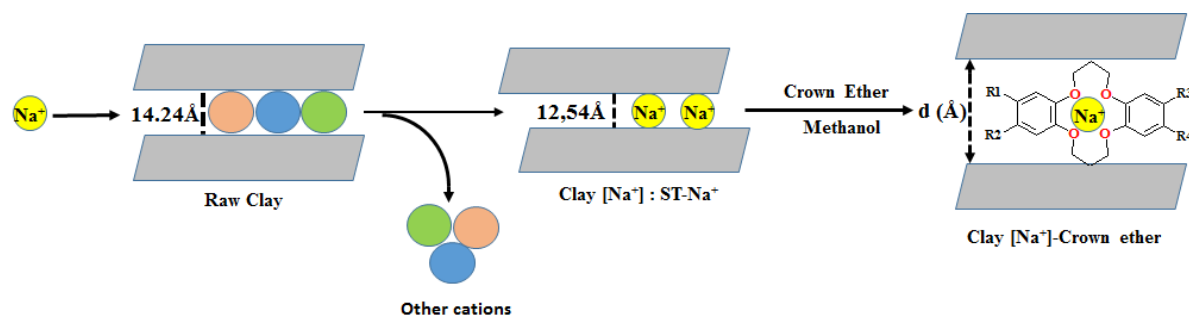
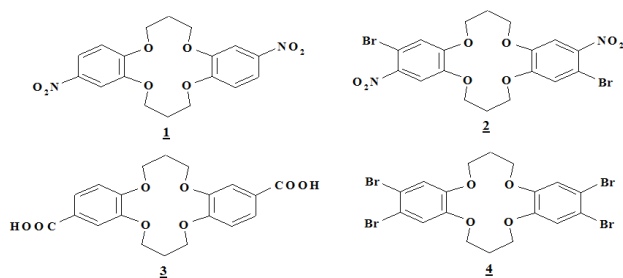


Figure 1. Intercalated crown ethers in smectite clay

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**Figure 2.** Crown ethers structures

## MATERIALS AND METHODS

### 1. Materials

As we have already mentioned, the mineral clay used in this study comes from Gafsa (south west Tunisia, around 34° 23' N / 8° 31' E). This clay is a di-octahedral phyllosilicate (2:1) with the following structural formula:  $\text{Ca}_{0,537} \text{K}_{0,263} \text{Na}_{0,038} (\text{Si}_{7,418} \text{Al}_{0,582}) (\text{Al}_{2,442} \text{Fe}_{0,954} \text{Mg}_{0,468}) \text{O}_{22}$  [26]. This smectite clay has a high cation exchange capacity (84 meq /100g). Crown ethers intercalated in the studied clay were synthesized according to protocols mentioned in [27, 28]. The crown structures are represented in the Figure 2.

Metallic salts like  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ,  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ ,  $\text{Pb}(\text{NO}_3)_2$ ,  $\text{CdCl}_2 \cdot \text{H}_2\text{O}$  and  $\text{ZnCl}_2 \cdot 6\text{H}_2\text{O}$  were purchased from Fluka.  $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$  and  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  were produced by Riedel-de Haen AG.

### 2. Characterization

The characterization of the purified clay was done using an X-Ray Fluorescence (XRF) coupled with X-Ray Diffraction (XRD); on a Thermo Scientific ARL 9900 XRF series workstation. Infrared analysis using the attenuated total reflectance technique (ATR/FTIR) was recorded on a Nicolet IR 200 FTIR spectrometer. Differential Scanning Calorimetry (DSC) was performed on a DSC SETARAM DSC 131. The samples (2.8 mg) were placed in 40  $\mu\text{L}$  aluminum pans, and the DSC thermograms were recorded under argon between 25 and 400°C at a heating speed of 10°C min<sup>-1</sup>. Differential thermal analysis (DTA) and thermo gravimetric analysis (TGA) were performed on a SETARAM TGA92. The samples (23 mg) were placed in 40  $\mu\text{L}$  aluminum pans and analyzed under argon between 30 and 800°C at a heating speed of 10°C min<sup>-1</sup>. The amount of remaining metal ions in solution was evaluated by atomic absorption spectroscopy Analytic Jenna NovAA 400.

## 3. Preparation protocols

### 3.1. Studied clay

The natural clays were taken at 40 cm under the surface. The raw clay was powdered, sieved (100  $\mu\text{m}$ ) and used for the purification procedure (sodium exchange). The purified clay was obtained by placing 20g of the sieved raw clay in suspension in 400mL of aqueous solution of sodium chloride (1M). The suspension was stirred (100rpm) for 12h before being centrifuged (4.000 rpm, 10 min). The supernatant was removed and the clay was retreated in the same way five other times using fresh molar NaCl aqueous solution.

The excess of NaCl was removed by stirring in water (400mL, 100rpm, 5min) and centrifugation (4.000 rpm, 10 min), followed by dialysis. The dialysis was performed on 2g samples suspended in 200mL of distilled water placed in a dialysis membrane (cellulose, 20 cm long, 20.4mm diameter, MWCO 6-8 kD) against 1L of distilled water. Distilled water was changed from time to time until complete disappearance of chloride ions using silver nitrate test ( $\text{AgNO}_3$ :1M). After overnight standing, the suspension was decanted, evaporated and dried at 50°C in order to obtain the purified and sodium exchanged clay [12].

### 3.2. Intercalated crown ethers within Smectite

In the first time, we prepared the oriented films by placing a drop of the solution of sodium exchanged clay directly on a glass lame (2 cm<sup>2</sup>) was dried at room temperature. In the second step, these films were directly immersed in methanolic solutions of crown ethers ( $C = 10^{-4} \text{ mol.L}^{-1}$ ). After 72h of crown ethers intercalation in the interlayer space of saturated clay with Na<sup>+</sup> cations, the oriented films were washed slowly three times with methanol (3 x 20 mL) and then dried at room temperature during 24h.

The new obtained hybrid materials (sodium exchanged clay intercalated by crown ethers) were presented in the Figure 1.

### 3.3. Removal of heavy metals

In this work, we performed the removal of the following metal cations ( $\text{Fe}^{3+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Cd}^{2+}$  and  $\text{Zn}^{2+}$ ) by the modified smectite clay. Aqueous solutions of  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ,  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ ,  $\text{CdCl}_2 \cdot \text{H}_2\text{O}$ ,  $\text{ZnCl}_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{Pb}(\text{NO}_3)_2$ ,  $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$  and  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  were prepared at a concentration of 50mg.L<sup>-1</sup>. For the modified clay, a thin film was prepared prior to incubation directly in a petri dish (D=10cm) by placing 0.2g of the clay in 10mL of distilled water and leaving it to

**Table I.** pH values of aqueous solutions.

Metal	Fe <sup>3+</sup>	Cu <sup>2+</sup>	Mn <sup>2+</sup>	Co <sup>2+</sup>	Cd <sup>2+</sup>	Zn <sup>2+</sup>	Pb <sup>2+</sup>
pHi	5,3	5,0	5,4	5,1	5,4	5,2	5,0
pHf	7,2	6,9	6,0	6,2	6,0	6,1	6,7

evaporate slowly at 50°C. 100mg of the obtained clay film was incubated in 20mL of the metal ion solution at 25°C for 48h. The suspension was then filtrated and water solution analyzed.

We give in Table I pH values before and after metal extraction.

The amount of remaining metal ions in solution was evaluated by atomic absorption spectroscopy. The extraction percentage (%) was calculated using the following formula:

$$\% \text{ Extraction} = ((C_i - C_f) / C_i) \times 100 \quad (1)$$

Where  $C_i$  and  $C_f$  are the concentrations of the metal ion in initial and final solutions, respectively.

## RESULTS AND DISCUSSION

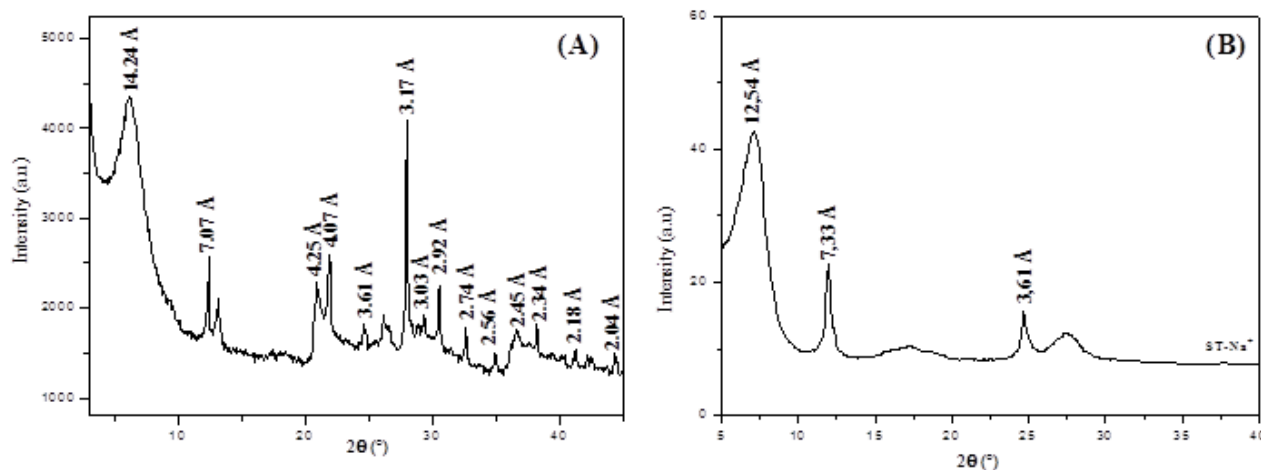
### 1. XRD pattern

The X-ray diffraction of studied raw clay shows that this material contains the smectite (14.24Å, 4.25Å, 4.07Å, 2.74Å), kaolinite (7.07Å, 3.61Å, 2.56Å, 2.45Å), Calcite (3.03Å, 2.34Å, 2.18Å) and the quartz (3.17Å, 2.04Å). After purification of this clay by the solution of sodium chloride (1M), several metal cations (Mg<sup>2+</sup>, Ca<sup>2+</sup>...) are changed by the sodium cation, The interlayer space of this clay was reduced from 14.24 to 12.54Å. These

results were coherent with those found by Bouguerra *et al.* [29].

The X-ray diffractogram of sodium exchanged clay (Figure 3) shows typical rays of a sodium-rich smectite clay (12.54 Å), probably a Montmorillonite [Ca<sub>0,537</sub> K<sub>0,263</sub> Na<sub>0,038</sub> (Si<sub>7,418</sub> Al<sub>0,582</sub>) (Al<sub>2,442</sub> Fe<sub>0,954</sub> Mg<sub>0,468</sub>) O<sub>22</sub>], which structure involves colloidal particle size (<2 μm) These results were consistent with those found in literature [19].

The XRD of intercalated clay by crown ethers (Figure 4) shows an increase in the interlayer distance (Table II). The macrocyclic compounds intercalation in the interlayer space of clay exhibit relatively good crystalline organization along the c-axis, as deduced from the (001) rational orders on the XRD patterns. A representative example of that is illustrated in the Figure 4 which shows XRD patterns intercalated by crown ethers (1, 2, 3 and 4). The basal spacing increases ( $\Delta d$ ), caused by the use of different intercalated crown ethers in the clay interlayer space. The observed changes in the basal spacing ( $\Delta d$ ), was varying from 3.63 to 5.40Å. As shown in Table III. Most of the macrocyclic compounds are intercalated, forming 1:1 (ligand / cation) intracrystalline complex. The obtained results in the present study were in agreement with

**Figure 3.** XR diffractograms of raw clay (A) and purified clay (B) .

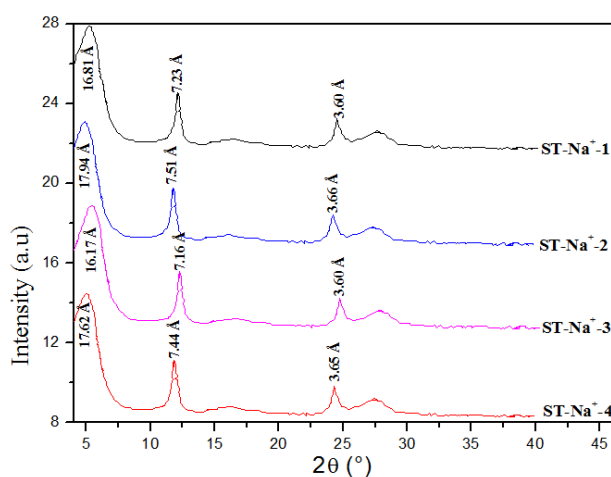
**Table II.** Interlayer distances of clay before and after intercalation by crown ethers.

	$d_{001}$ (Å) (smectite)
ST-Na <sup>+</sup>	12.54
ST-Na <sup>+</sup> -1	16.81
ST-Na <sup>+</sup> -2	17.94
ST-Na <sup>+</sup> -3	16.17
ST-Na <sup>+</sup> -4	17.62

those found in the literature [25, 30, 31]. The increase of basal layer distance  $\Delta d$  after intercalation of substituted crown ethers can be explained by the nature of substituents fixed on the benzenic rings of different crown ethers. Thus  $\Delta d$  is bigger with crown ethers bearing big bromo atoms. This fact gives  $\Delta d = 5,40$  Å with crown ether substituted by two bromo atoms and two nitro groups. We found also  $\Delta d = 5,08$  Å in the case of crown ether substituted by four bromo groups. The other groups, nitro and carboxylic group are flat groups and they lead to lower  $\Delta d$  values (3,63 and 4,27 Å). The (002) reflection was not evident in the XR diffraction because this study was realized at short time [32].

## 2. ATR/ FTIR analysis

In ATR/FTIR spectra of studied clays (Figure 5), characteristic bands of OH groups can be seen


**Figure 4.** X-ray diffractograms of modified studied clays.

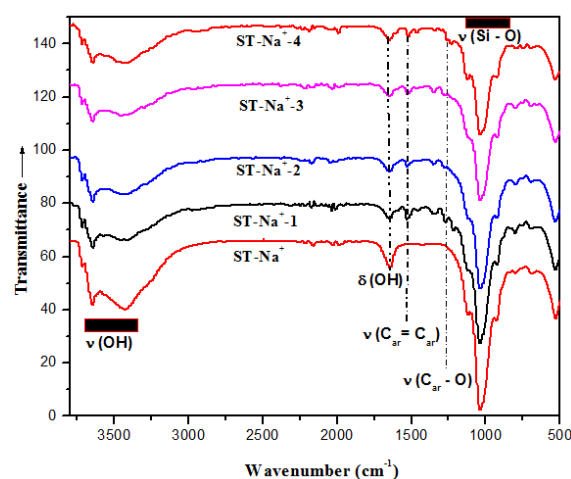
**Table III.** Basal spacing increases ( $\Delta d$ ), intercalation of crowns ethers (1, 2, 3 and 4), and proposed models for the interlayer complex arrangements [25].

Complex arrangement $\Delta d$ (Å)	Complex arrangement $\Delta d$ (Å)
ST-Na <sup>+</sup> -1 4.27	ST-Na <sup>+</sup> -3 3.63
ST-Na <sup>+</sup> -2 5.4	ST-Na <sup>+</sup> -4 5.08

at 3645 and 1630 $\text{cm}^{-1}$ , as well as those of SiO at 1033 and 918 $\text{cm}^{-1}$ . These results, confirmed the purification and sodium-exchange of the studied clay.[9] The ATR/FTIR results of intercalated clay by crown ethers, show the presence of characteristic bands ( $\nu_{\text{C-O-C}}$ ) of crown ethers at 1124-1046 $\text{cm}^{-1}$  and ( $\nu_{\text{Ar-O}}$ ) at 1260-1250 $\text{cm}^{-1}$ , These results are in agreement with those obtained by Ayari *et al.* [33].

## 3. DSC and TGA-DTA analyses

The DSC curve of ST-Na in the Figure 6 shows an endothermic peak situated at 121°C which is probably due to water evaporation this result is confirmed by Ayari *et al* [17]. After functionalized crowns intercalation the DSC curves present new exothermic peaks situated at 337, 341, 327 and 308°C for the compounds 1, 2, 3, and 4, respectively, which are due to the decomposition

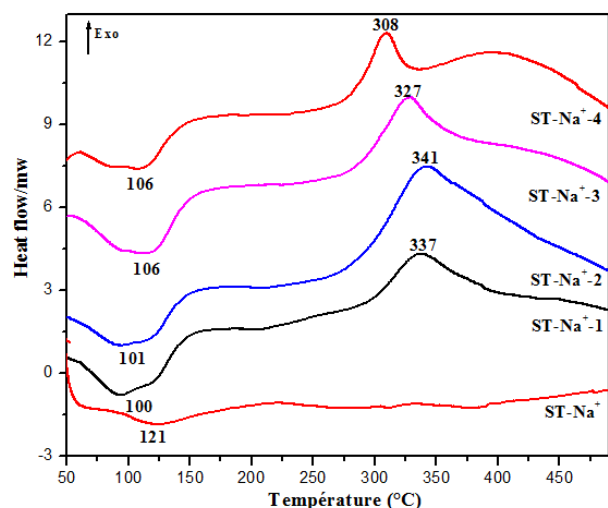

**Figure 5.** ATR/FTIR curves of modified studied clay

**Table IV.** DSC Results of modified clays.

	Observed peak	Interpretation
ST-Na	121°C (Endo)	- Water evaporation.
ST-Na <sup>+</sup> -1	92°C (Endo) 337°C (Exo)	- Water evaporation. - Decomposition of crown ether in interlayer space of clay.
ST-Na <sup>+</sup> -2	101°C (Endo) 341°C (Exo)	- Water evaporation. - Decomposition of crown ether in interlayer space of clay.
ST-Na <sup>+</sup> -3	106°C (Endo) 327°C (Exo)	- Water evaporation. - Decomposition of crown ether in interlayer space of clay.
ST-Na <sup>+</sup> -4	97°C (Endo) 308°C (Exo)	- Water evaporation. - Decomposition of the crown ether in interlayer space of clay.

of those crown ethers intercalated in the smectite clay.

Thermal analysis was performed using DTA coupled with TGA; the curves contain three mass loss domains. In the region 100-150°C, the endothermic peak appeared and was probably due to water evaporation coming from the surface and the intercalated water in the main structure of the clay [34]. The endothermic peak observed at 500°C accompanied by a slight loss of mass revealing the presence of a deshydroxylation of minerals present in the clay, these results were consistent with those found in the literature [34, 35]. The third exothermic peak appears at 340°C accompanied by a small weight loss observed only with the clays with the intercalated crown ethers,

**Figure 6.** DSC curves of modified clays.

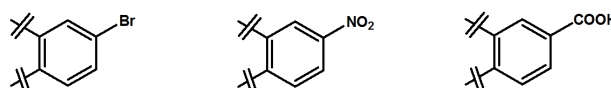
corresponding to crown ethers degradation. The studied crown ethers in this paper are bearing different substituents: nitro, bromo or carboxylic acids (Figure 7) on benzenic rings.

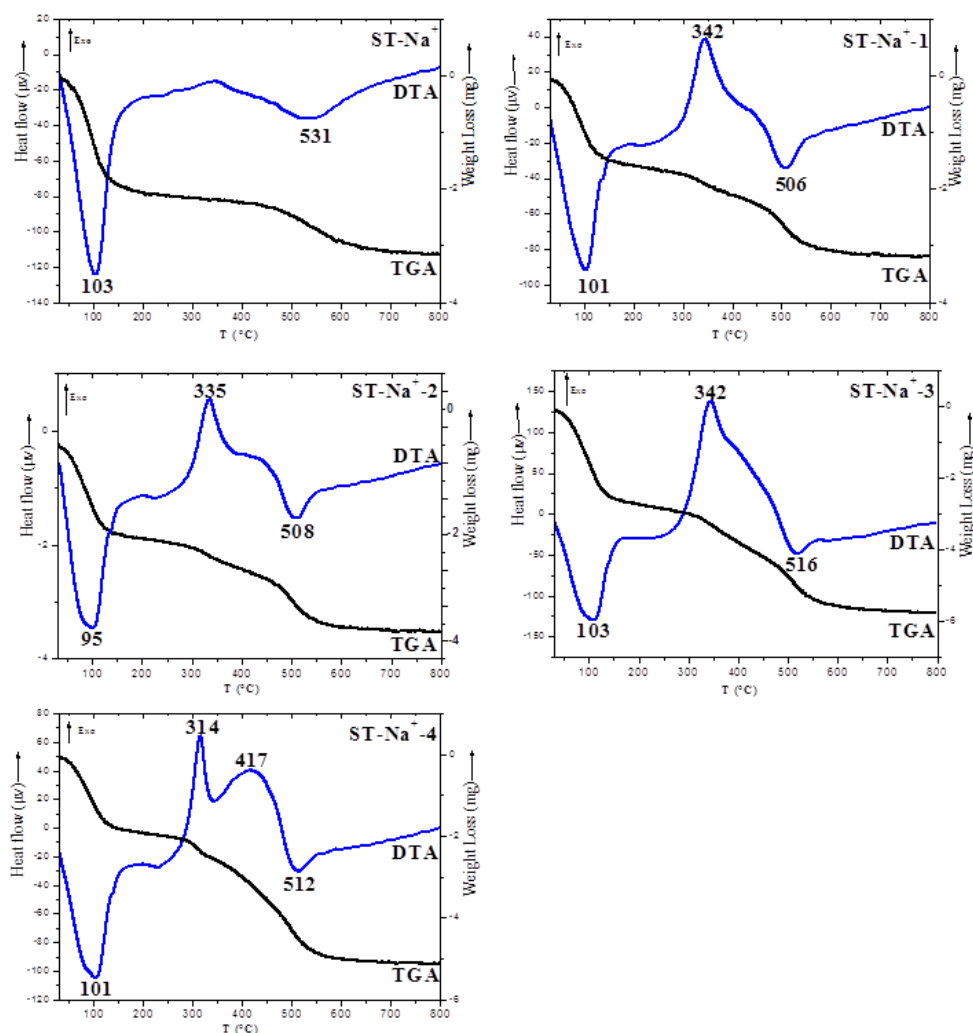
The DTA-TGA curves of intercalated clay by crown ethers studied in this work are summarized in the Figure 8 and Table V. (according to water evaporation [25]).

#### 4. Metal ions extraction by the modified clay

The extraction results of heavy metals by modified clay were presented in the Figure 9.

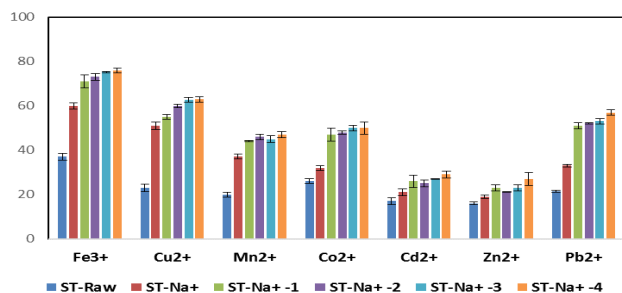
Figure 9 shows that the extractions percentage of the studied metals with purified clay is better than with raw washed clay [12]. The histogram shows also that the extraction of Fe<sup>3+</sup>, Cu<sup>2+</sup> and Pb<sup>2+</sup> using intercalated clay with crown ethers is better than that obtained using the sodium exchanged clay. The extraction percentages of Fe<sup>3+</sup>, Cu<sup>2+</sup> and Pb<sup>2+</sup> by intercalated clays with crown ethers is in the order of 76% ± 1.4, 63% ± 1.7 and 57% ± 2.1 by sodium exchanged clay. The extraction efficiency of cations such as Fe<sup>3+</sup> and Cu<sup>2+</sup> is from 60% ± 1.3 to 51% ± 2. The extraction of (Co<sup>2+</sup>) is from 50% ± 1.7 with studied clays. Exceptionally for Pb<sup>2+</sup> the yield is 33% ± 1.4 with ST-Na. When looking in the Figure 8, we find that the extraction of (Cd<sup>2+</sup> and Zn<sup>2+</sup>) is low using modified clays, the

**Figure 7.** Substituents on studied crown ethers.


**Figure 8.** DTA and TGA curves of modified clays.

**Table V.** DTA-TGA results of intercalated clay by crown ethers.

	DTA	TGA	Interpretation
ST-Na <sup>+</sup>	103°C (Endo) 531°C (Endo)	9.1 (%) 4.5(%)	- Water evaporation [17]. - Elimination of (OH) groups from the clay [17].
ST-Na <sup>+</sup> -1	101°C (Endo) 342°C (Exo) 506°C (Endo)	8.5 (%) 3.7 % 5.0 (%)	- Water evaporation. - Combustion of crown ether in interlayer space of clay [33]. - Elimination of (OH) groups from the clay.
ST-Na <sup>+</sup> -2	95°C (Endo) 335°C (Exo) 508°C (Endo)	10 (%) 3.9 (%) 5.7 (%)	- Water evaporation. - Combustion of crown ether in interlayer space of clay. - Elimination of (OH) groups from the clay.
ST-Na <sup>+</sup> -3	103°C (Endo) 342°C (Exo) 516°C (Endo)	10 (%) 6.0 (%) 5.1 (%)	- Water evaporation. - Combustion of crown ether in interlayer space of clay. - Elimination of (OH) groups from the clay.
ST-Na <sup>+</sup> -4	101°C (Endo) 314°C (Exo) 417°C (Exo) 512°C (Endo)	9.8 (%) 3.0 (%) 1.2 (%) 13 (%)	- Water evaporation. Double Combustion of the crown ether of interlayer. Clay space: The first one is mentioned at 314°C and the second one is revealed at 417 °C. - Elimination of (OH) groups from the clay.

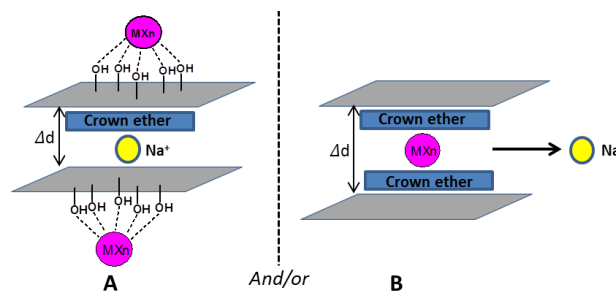


**Figure 9.** Percentages of metal cations extraction by the modified clays.

extraction yield is in the order of  $19\% \pm 1.8$ . Metals extraction by modified clays taken from Gafsa area (Jebel Es Sath) varied in the following decreasing order  $Fe^{3+} \geq Cu^{2+} \geq Pb^{2+} > Co^{2+} \geq Mn^{2+} > Cd^{2+} \approx Zn^{2+}$ . In addition, clay is highly selective for iron in a ternary mixture Fe / Cd / Zn, which allows us to obtain a rich mixture in Cd and Zn. Generally, clays intercalated with crown ethers extract slightly better than the sodium saturated clay (Figure 9). The extraction of metal cations is significant for metals ( $Fe^{3+}$ ,  $Pb^{2+}$ ,  $Co^{2+}$ ,  $Cd^{2+}$  and  $Cu^{2+}$ ) and low for the others. We can explain these results by the adsorption of metals on the external surfaces of clay in a first time and followed by its desorption in aqueous solution in the second time (Figure 10-A) [37]. On the other hand, we can explain these obtained results of extraction by the intercalation of metal with sodium in the interlayer space of smectite clay (Figure 10-B); the interlayer space of the clay is saturated with metal cation. For this reason the extraction efficiency cannot be elevated. For the other reason, the metal can take the place of sodium in the interlayer space of clay, and the sodium cation can be discharged in the aqueous solution, The formed complex in the interlayer space of the clay is 1:2 (cation / ligand),

**Table VI.** Analysis results of discharged  $Na^+$ .

Sample	$Na^+$ (mg / L)
Water (Fe : 12.56 mg/L)	0
ST- $Na^+$ -1	50.450
ST- $Na^+$ -2	50.125
ST- $Na^+$ -3	37.325
ST- $Na^+$ -4	40.325



**Figure 10.** General Patterns of extraction of heavy metals by exchanged sodium smectite clay

the interlayer space will be saturated and the extraction efficiency decreases (Figure 10-C) [37]. For the purpose of showing that when iron ions are taken by modified clays, sodium ions are discharged in water solutions, we have done the next described experiments. In these experiments 1g of modified clay was put under stirring in contact with 20 ml of aqueous solutions containing iron at the concentration of 12.56 mg/L. Stirring was maintained for 48 hours.

After standing and filtration aqueous solution was analyzed by atomic absorption for determining sodium release. The results are given in table VI. These experiments show that when iron is extracted by the modified clays, sodium ions are released in aqueous solutions.

The copper and cadmium extracted by the bentonite [13] and Kaolinite [14] present higher percentage compared with the extraction level done by the smectite in our case.

It may be noted that the extraction of Zinc by smectite clay taken from the same region by Mhamdi and al. [12] gives very close results to our clay, with a percentage extraction within 20%.

The aim of this work was to improve the extraction of cations by the studied clay, as can be seen in Figure 9. The extraction percentages of all the cations have been improved by the intercalation of the crown ethers.

In all cases of the studied cations, the percentages of extraction by the intercalated clays did not vary much with the various substituents. For example for  $Co^{2+}$  the following percentages were obtained, 47% with ST- $Na^+$ -1, 48% with ST- $Na^+$ -2, 50% with ST- $Na^+$ -3 and 50% with ST- $Na^+$ -4. This seems to show that the substituents have little influence on the extraction percentages, which shows also that the extraction of the cations takes place by their complexation in the crown cavity.

## CONCLUSION

The present work has been focused on the intercalation of some crown ethers in the interlayer space of the smectitic sodium exchanged clay deposits from Jebel Es stah in the Gafsa region (south Tunisia). The new obtained materials are then used for removal of heavy metals (Fe, Pb, Cu, Mn, Cd, Zn and Co) found in an aqueous solution. This intercalation of crown ethers was confirmed by XRD, ATR/FTIR spectroscopy and thermal analysis (DSC, and DTA-TGA). The extraction of metal cations ( $\text{Fe}^{3+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Cd}^{2+}$  and  $\text{Cu}^{2+}$ ) by modified clay varied in the following decreasing order  $\text{Fe}^{3+} \geq \text{Cu}^{2+} \geq \text{Pb}^{2+} > \text{Co}^{2+} \geq \text{Mn}^{2+} > \text{Cd}^{2+} \approx \text{Zn}^{2+}$ .

**Acknowledgments:** The authors would like to thank the Tunisian research project 05/UR/12-05.

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