



## **Cu (II) Extraction from Sulfate Media by Functionalized Algerian Bentonites**

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### **ABSTRACT**

The solid-liquid extraction of Cu(II) from sulfate media at 25°C by sodium homoionic montmorillonites impregnated either with di-2,4,4-trimethylpentyl phosphinic acid (DTMPPA) whose commercial name is Cyanex 272, or with 1-tolyl-3-methyl-4-dodecanoylpyrazol-5-one (HTMDDP) has been studied. The extracting agent impregnated solids were characterized by infrared spectroscopy (IR) and X-ray diffraction. The total amounts of loaded extractants were determined by UV spectrometry on washings and/or parent solutions. The ability of each impregnated clay to remove copper from aqueous media was studied in terms of shaking time, equilibrium pH and solid/liquid ratio. The different experimental results have shown that the clay containing HTMDDP leads to better performances for the extraction of copper with respect to capacity as well as pH values. The capacities for HTMDDP and DTMPPA impregnated solids are found to be 320 mmol/kg and 200 mmol/kg and extraction is total at equilibrium pH above 2.2 and 4.7, respectively. The HTMDD-impregnated clay has been found to have high metal ion extractability and hence good potential as an alternative to established solvent extraction systems

**Key words:** Bentonite; clay – impregnation; Solid-liquid extraction; Copper; Separation.

### **INTRODUCTION**

Over the last few years, the pollution due to heavy metals has reached critical levels. It may often end up in ground and surface water short-term poisoning because of its occurrence in aqueous waste streams and soils surrounding many industrial areas. Consequently, the

development of advanced methods that can combine high efficiency to remove heavy metal pollutants from waste streams and low cost is needed. In this context, abundant and inexpensive materials such as clays and clay minerals are often implicated. Several substances such as kaolin, montmorillonite and illite are commonly used in order to remove lead, copper, zinc and cadmium

from acid aqueous solutions<sup>1-10</sup>. However, if all these materials show a certain activity, the results obtained remain below expectations. Several studies dealing with the sorption of heavy metals on extractant-loaded solid supports have been performed during the last decade with the aim to improve the sorption capacity<sup>11-15</sup>. Surface modification of the latter was shown to be an important feature for developing their practical applications such as fillers and adsorbents. This was obtained by means of intercalation reactions through interlamellar grafting of organic molecules<sup>16-26</sup>. Although organophosphorous and pyrazolone chelating extractants are often used in the liquid-solid extraction process of metals<sup>11, 17-18, 27-38</sup>, any investigation concerning clays functionalized by pyrazolones is not described in the literature. In this work, the solvent extraction reagents DTMPPA and HTMDDP are introduced by the dry impregnation method into a montmorillonite clay previously treated. The obtained sorbents are characterized by infrared spectroscopy, chemical analysis and X-ray diffraction and their behaviors with respect to the extraction of copper from dilute sulfate solutions are compared.

## EXPERIMENTAL

### Materials and Reagents

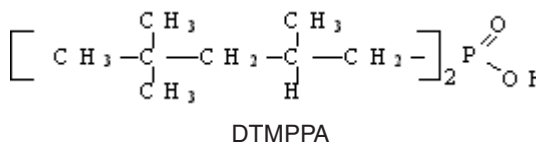
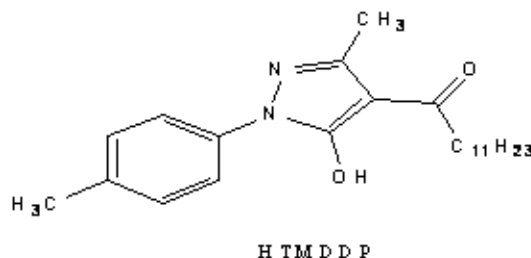
Natural montmorillonite clay (natural clay) was supplied by ENOF Corp., Algeria. DTMPPA was provided by CYTEC as Cyanex 272 and used after purification [39]. HTMDDP was supplied by the SNPE Corp., France. Stock solutions of Cu (II) (1 g/L) were prepared by dissolving the corresponding salt (CuSO<sub>4</sub>, Merck a.r. grade) in deionised water. Products used for the preparation of the different solutions such as Na<sub>2</sub>SO<sub>4</sub>, NaCl, HCl, H<sub>2</sub>SO<sub>4</sub>, ethanol and toluene were all Merck a. r. grade.

### Preparation of impregnated sorbents

First, the natural clay was purified with a hydrochloric acid solution according to the following protocol: a mixture of clay (10 g) with an aqueous chlorhydric acid solution (500 ml, 2M) was prepared and stirred up for 24h at 25°C; the solid was then separated by centrifugation and washed with distilled water in order to eliminate the cationic impurities present in the natural clay. The clay structure constancy was checked by DRX. Second,

the substrate was added to an aqueous sodium chloride solution (500 ml, 0.5 M) and the obtained suspension was stirred up for 4 h at 70 °C. The solid obtained was subsequently separated by centrifugation. This treatment was repeated four times. Consequently, the homoionic clay obtained was washed thoroughly with distilled water to remove excess NaCl, dried at 80 °C for 24 h and ground to pass 63 µm mesh sieve. DTMPPA and HTMDDP were introduced into the solid clay supports by means of the dry impregnation method already successfully used<sup>20</sup>. An appropriate amount of homoionic clay (1g) was mixed with 10 mL of an ethanolic solution containing 1 mmol (0.29 g) of DTMPPA, or with 10 mL of a toluene solution containing 1mmol (0,358 g) of HTMDDP. In both cases, the mixture was continuously stirred up under atmospheric pressure until total solvent evaporation. The obtained solid was washed with HNO<sub>3</sub> 0.5 M, to avoid the ligand dissolution in the aqueous phase in the form of its anion A<sup>-</sup>, then dried under atmospheric pressure at 80°C for 24 h and finally ground to pass 63µm mesh sieve.

The two impregnated materials obtained are named HTMDDP@clay and DTMPPA@clay.



### Methods of characterization

The chemical compositions of the starting materials (natural and homoionic clays) were determined following their dissolution in aqua regia solution, removal of the insoluble silica by filtration and analysis with atomic emission spectrometry (ICP-AES Varian Liberty 220). Silica content was determined by gravimetric analysis of the insoluble

residue using hydrofluoric acid to form volatile silicon tetrafluoride. FTIR Attenuated Total Reflectance spectra (4000–400  $\text{cm}^{-1}$ ) of the solids were recorded with a Spectrum One Perkin Elmer instrument. The XRD powder patterns were performed with  $\text{CuK}\alpha_1$  radiation (1.5406  $\text{\AA}$ ) on a Siemens D5000 diffractometer. The mass of loaded HTMDDP or DTMPPA was quantitatively determined by UV spectrometry (HP 8453 Hewlett Packard) on the washing solutions and the mass-balance of the extractant.

#### Metal extraction procedure

The extraction of Cu (II) (100 mg/L, 1.57 mM) was carried out in polypropylene tubes. 0.1 g of impregnated solid was mixed mechanically for 150 min with 10 mL of Cu (II) 100 mg/L at (25  $\pm$  0.2) $^\circ\text{C}$ . The ionic strength of the solution was maintained constant by addition of 0.33 M ( $\text{H}^+$ ,  $\text{Na}^+$ ) $\text{SO}_4^{2-}$  solution. The phases were then separated by high speed centrifugation (12000 rpm for 10 min) and the liquid phase pH (equilibrium

pH:  $\text{pH}_e$ ) was measured. Copper contents in the aqueous phases were determined by atomic absorption spectroscopy on a Perkin–Elmer 2380 spectrophotometer using an air acetylene flame.

## RESULTS AND DISCUSSION

### Characterization of the solids

The chemical compositions of natural and homoionic clays are reported in Table 1. The acid treatment followed by the sodium exchange allowed the partial elimination of Fe, Mg and Ca elements which degrade the extraction yields by complexation of the loaded ligands in the impregnated solids as shown in figure 4.

The DTMPPA and HTMDDP contents of the impregnated solid supports are quite similar: we found 720  $\text{mmol}\cdot\text{kg}^{-1}$  and 730  $\text{mmol}\cdot\text{kg}^{-1}$ , respectively. This result allows a direct comparison of the two solids efficiencies.

**Table 1: Chemical composition of the starting clay materials**

	Content (weight %)								
	$\text{SiO}_2$	$\text{Al}_2\text{O}_3$	$\text{Fe}_2\text{O}_3$	MgO	CaO	$\text{Na}_2\text{O}$	$\text{K}_2\text{O}$	$\text{TiO}_2$	LOI*
Natural clay	64	13	2,1	3,1	1,2	2,15	0,6	0,2	13
Homoionic clay	62,5	12,8	1,15	1,6	0,3	2,27	0,5	0,022	18,8

\*: Loss on Ignition at 1000 $^\circ\text{C}$

### IR analysis

FTIR spectra of the homoionic clay and impregnated solids are illustrated in figure 1. The IR spectrum of homoionic clay shows the presence of absorption bands of the clay phase and the characteristic absorption bands of impurities such as quartz and calcite. The bands observed between 3200 and 3600  $\text{cm}^{-1}$  correspond to both the OH stretching vibration of adsorbed water and the silicated skeleton; the peak at 1650  $\text{cm}^{-1}$  is also attributed to adsorbed water. Other impurities such as quartz are difficult to identify since the main Si-O vibration band of montmorillonite appearing at 1050  $\text{cm}^{-1}$  is wide enough to mask the corresponding band of free silica in quartz which ranges from 900  $\text{cm}^{-1}$  to 1200  $\text{cm}^{-1}$ . Another band located at 1394  $\text{cm}^{-1}$  characterizes calcite.

Besides the absorption bands characterizing montmorillonite, the IR spectrum of DTMPPA@clay shows the characteristic vibration bands of DTMPPA between 2970  $\text{cm}^{-1}$  and 2890  $\text{cm}^{-1}$  assigned to the stretching modes of the methyl groups and aliphatic C—H groups<sup>11</sup> and near 1380  $\text{cm}^{-1}$  assigned to the phosphoryle stretching<sup>40</sup>. In the case of HTMDDP@clay, the IR spectrum shows the presence of the main vibration bands characteristic of HTMDDP between 2960  $\text{cm}^{-1}$  and 2870  $\text{cm}^{-1}$  assigned to the stretching modes of aliphatic groups<sup>41</sup>. These results confirm the presence of DTMPPA and HTMDDP in the corresponding solids.

X-ray diffraction

Figure 2 presents the XRD powder pattern of natural and homoionic clays. The former is characteristic of montmorillonite and is in good agreement with earlier works <sup>42</sup>. This mineral contains also an impurity identified as quartz characterized by a strong reflection at  $2\theta = 26.6^\circ$  in agreement with the IR results.

The XRD pattern of homoionic clay shows a decrease in the basal spacing from 14.53 to 12.03. This behavior is probably due to the cation exchange of interlayer hydrated metallic ions by sodium cations.

Figure 2 also shows the XRD powder patterns of DTMPPA@clay and HTMDDP@clay. The noticeable modification with respect to the ligand free clay pattern is observed on the (001) reflection. It is moved toward lower angles for both impregnated solids due to an enlargement of the interlayer space from 12.30 Å to about 14.30 Å. In both cases, the increase in the interfoliar distance is probably due to the intercalation of the organic ligand between the sheets. Some reflections from the HTMDDP crystallized ligand are clearly visible at  $2\theta = 5.9^\circ$  ( $15\omega$ ) and  $8.4^\circ$  ( $10.5\omega$ ). Surprisingly, new reflections may be observed on the XRD pattern of the DTMPPA@clay sample in particular at  $2\theta = 5.6^\circ$  and  $6.15^\circ$ . It is possible that the confinement of the

DTMPPA ligand in the interlayers induces its crystallization.

### Metal extraction

The ability of impregnated-clays to adsorb copper metal ions from aqueous solutions was studied by varying different parameters namely the contact time, the pH and the amount of solids.

The solid-liquid extraction of a metal ion may be described by the following equilibrium:



where the highlighted species are in the solid phase. The extraction percentage of a metal may be expressed as:

$$E(\%) = 100 \times \frac{n_{Mt,s}}{n_{Mt,aq}} \dots(1)$$

where  $n_{Mt,s}$  and  $n_{Mt,aq}$  denote the total mole number of metal in the solid phase at equilibrium and the initial total mole number of metal in the aqueous phase, respectively; "total" means "under any chemical form". This percentage may also be determined from the analytical concentrations of the metal in the aqueous phase.

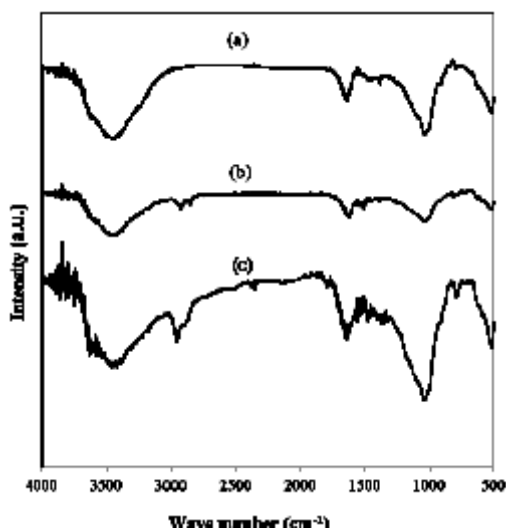


Fig. 1: FTIR spectra of the homoionic clay (a), DTMPPA@clay (b) and HTMDDP@clay (c)

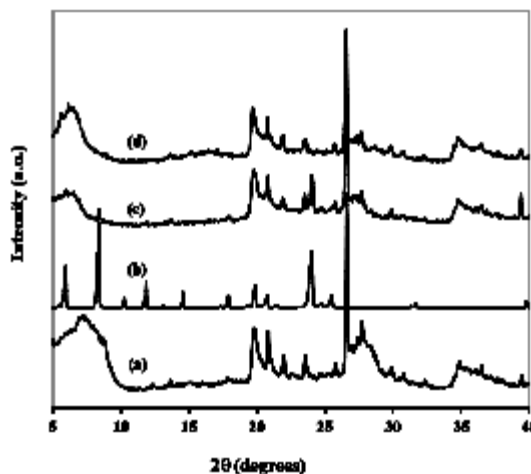


Fig. 2: Powder XRD pattern (Cu Kα1) homoionic clay (a), HTMDDP ligand (b), HTMDDP@clay (c) and DTMPPA@clay (d)

$$E (\%) = 100 \times \frac{[M]_{aq,i} - [M]_{aq,e}}{[M]_{aq,i}} \quad \dots(2)$$

where  $[M]_{aq,i}$  and  $[M]_{aq,e}$  are the concentrations in the aqueous phase before and after extraction, respectively.

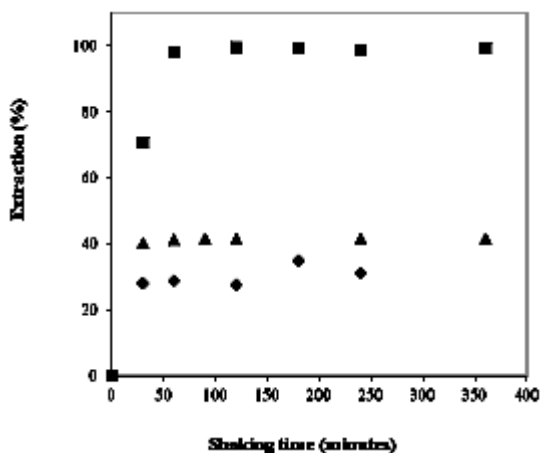
### Effect of contact time

The effect of the shaking contact time was studied for an initial pH ( $pH_i$ ) fixed at 4.3 for HTMDDP@clay and 4.8 for DTMPPA@clay solids. Figure 3 shows the evolution of extraction versus shaking time. The extraction reaches a plateau within 30 minutes for homoionic clay and DTMPPA@clay whereas HTMDDP@clay extracts 100% of the available copper after 60 minutes of contact. To check that the observed plateau is not due to the absence of free ions in solution, an experiment with a higher copper content (1000 mg/L) was realized. This experiment confirmed that 60 minutes were sufficient to reach the adsorption equilibrium. For the remainder of the study, the shaking time was set up to 150 minutes

### Effect of equilibrium pH

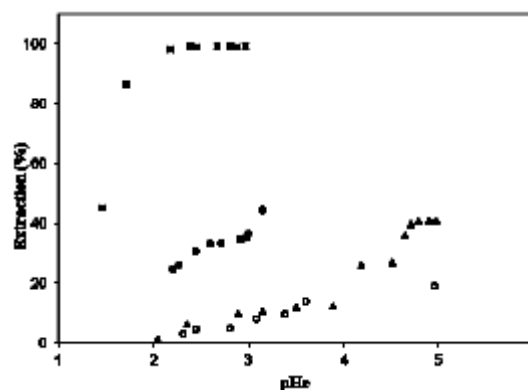
The pH of the aqueous solutions is an important variable for the extraction of metals on the adsorbents, especially with these  $H^+$  exchanger

ligands. The metal extraction by homoionic and impregnated montmorillonite clays was studied as a function of pH in the limited range from 1 to 5 in order to avoid hydroxide precipitation occurring at higher pH values. Figure 4 shows the measured copper extraction percentage as a function of  $pH_e$ . The lowest  $Cu^{2+}$  sorption percentage is obtained in the case of the homoionic clay. The  $Na^+$  cations are merely exchanged with  $Cu^{2+}$  cations contained in the aqueous solutions. The highest adsorption rates are observed with the impregnated clay samples because of the presence of the organic ligands. However, HTMDDP@clay displays noticeably higher capacity than DTMPPA@clay: 100% adsorption against only 40%. This fact may be explained by the thorough availability of each HTMDDP molecule in the solid to the contrary of the partial use in the case of DTMPPA ligand. It should be noticed that neither XRD nor FTIR spectroscopy is suited to reveal any differences in the ligand setting in the clay. It could be assumed that the interaction between the ligand and the clay let the complexing head more accessible to metal ions in the case of HTMDDP than DTMPPA. With the latter ligand, we could also suspect the formation of aggregates in the solid. This was generally observed in organic solvents for organo phosphinic acids. The species extracted are generally assumed



HTMDDP@clay ( $[Cu]_i = 100 \text{ mg/L}$ ) ■, HTMDDP@clay ( $[Cu]_i = 1000 \text{ mg/L}$ ) ◆ and DTMPPA@clay ( $[Cu]_i = 100 \text{ mg/L}$ ) △.  $pH_i = 4.82$ ;  $[Na^+, H^+ - SO_4^{2-}] = 0.33 \text{ M}$ ;  $T = 25^\circ \text{C}$ ;  $m = 0.1 \text{ g}$

**Fig. 3: Evolution of copper's extraction percentage as function of shaking time**



HTMDDP@clay ■, DTMPPA@clay △ and HTMDDP@clay without acidic treatment ◆  $[Na^+, H^+ - SO_4^{2-}] = 0.33 \text{ M}$ ;  $T = 25^\circ \text{C}$ ;  $t = 150 \text{ min}$ ;  $m = 0.1 \text{ g}$ ;  $[Cu]_i = 100 \text{ mg/L}$ .

**Fig. 4: Evolution of copper's extraction percentage as function of the equilibrium pH ( $pH_e$ ) and the nature of solid support used: homoionic clay**

to be  $ML_2(HL)_x$  with  $x = 2$  or  $3$ <sup>40</sup>. With this assumption, 4 or 5 ligand molecules are necessary to achieve the complexation. On the contrary, the formation of more simple species ( $ML_2$ ) is generally observed with the b-dicetone ligand family to which HTMDDP belongs.

Figure 4 shows that the extraction of copper by HTMDDP impregnated solid is total when the  $pH_0$  value is equal to 2.2. On the other hand, the maximum amount of copper extracted by the solid impregnated with DTMPPA is only 41% and this at a  $pH_0$  above 4.7. In liquid-liquid extraction, copper ions in sulfate medium are extracted by DTMPPA in the same pH range<sup>43</sup>. It appears that if the acylpyrazolones such as HTMDDP are efficient to extract copper in the clay, the organophosphorus acids such as DTMPPA are not. However, previous studies showed that immobilized DTMPPA is efficient for zinc extraction whatever the nature of the solid (Levextrel or Amberlite XAD-2 resins<sup>[44-46]</sup>, sol-gel<sup>47</sup> or mesoporous silica<sup>48</sup>, clays<sup>20</sup>, and the extraction method<sup>49</sup>). Thus, the present DTMPPA impregnated solid may be envisaged for continuous separation of zinc and copper from their dilute sulfate solutions. As observed in liquid-liquid extraction for a similar

ligand, 1-phenyl-3-methyl-4-stearoyl-5-hydroxypyrazole, noted HPMSP, the b-dicetone ligand HTMDDP allows the copper extraction at lower pH than DTMPPA. Furthermore, for HPMSP, the extraction pH is lowered to 2 when the extraction occurs with a solid support like mesostructured silica, but only to 4 when the extraction is performed with an organic solvent<sup>37</sup>. With this ligand, the confinement imposed might lead to a decrease in the distance between the two complexing heads required for the formation of the stable  $CuL_2$  complex, enhancing the extraction. We have observed the same phenomenon with HTMDDP immobilized in clay.

#### Effect of the mass of the solid

The effect of the solid mass was studied by varying the amount of the impregnated solids from 0.05 to 0.5 g. The initial pH,  $pH_i$ , was fixed at 2.6 and 4.54 for the HTMDDP and DTMPPA impregnated solids, respectively. Figure 5 shows that the variation of the adsorption percentage of metal ions as a function of the impregnated solid mass is linear. An extraction maximum (~100%) was obtained with a mass of HTMDDP@clay equal to 0.1 g. When using the DTMPPA@clay, 0.3 g is needed for a 100% extraction yield.

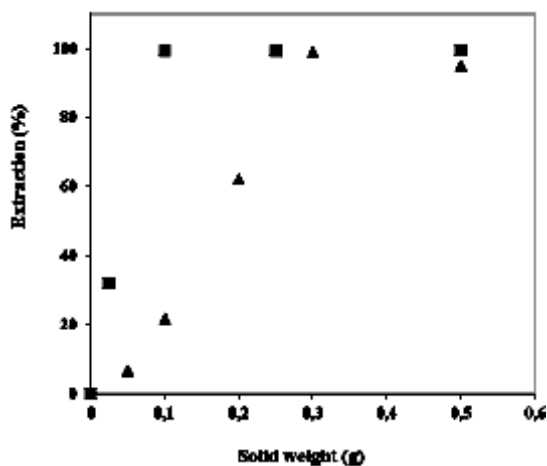


Fig. 5. Evolution of copper's extraction percentage as function of the mass of solid: , HTMDDP@clay ( $pH_i = 2.56$ ), , DTMPPA@clay ( $pH_i = 4.54$ );  $[Na^+, H^+ - SO_4^{2-}] = 0.33M$ ;  $T = 25^\circ C$ ;  $t = 150$  min.

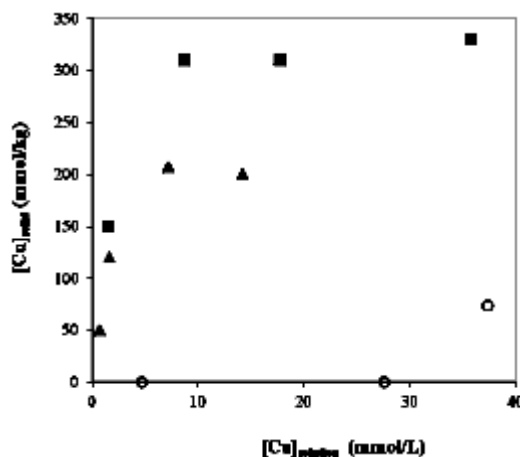


Fig. 6. Copper extraction capacity: , HTMDDP@clay;  $pH_i = 3.9$ , , DTMPPA@clay ( $pH_i = 4.54$ );  $[Na^+, H^+ - SO_4^{2-}] = 0.33M$ ;  $T = 25^\circ C$ ;  $t = 150$  min.



### Copper loading capacities

Copper extraction capacities of the impregnated montmorillonite clays were studied. The results are given in figure 6. A capacity of 320 mmol/kg is obtained for HTMDDP@clay. This capacity is higher than the DTMPPA@clay one whose value is 200 mmol/kg. The ligand/metal ratio  $L_s/M_s$  is calculated with  $L_s$  the total number of free or coordinated "HTMDDP" or "DTMPPA" sites and  $M_s$  the total number of copper ions in the solid.  $L_s/M_s$  ratio is equal to 2 for HTMDDP and corresponds to the formation of  $CuL_2$  complex. For DTMPPA, this ratio is equal to 3.5. This is probably due to the formation of a mixture of species such as  $ML_2(HL)_x$  with  $x = 1$  or 2. The immobilization of the phosphorous ligand in the clay can limit its movement to form the higher level aggregates with  $x = 2$  or 3 as observed in liquid-liquid extraction.

### CONCLUSION

In this paper, montmorillonite homoionic clay is successfully loaded with either DTMPPA or

HTMDDP by the dry impregnation method. It is shown that the two impregnated solids can be profitably used for the extraction of copper from dilute aqueous solutions. However, HTMDDP loaded clay displays a better performance than the phosphorous ligand loaded clay for the adsorption of copper. Indeed, the extraction of copper by the former is complete even at a pHe value as low as to 2.2. This fact may be advantageously exploited for the treatment of acidic effluents. This study also demonstrates a full accessibility of the HTMDDP molecules impregnated in the homoionic clay to the metal ions. The dependence of the extraction on pH implies that the extraction mechanism of the metal ions proceeds by exchange of the acylpyrazolone protons. The formation of  $CuL_2$  complex is observed in the case of HTMDDP but more complex stoichiometries are obtained with DTMPPA.

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