

## Removal of chromate ions from water by anionic clays

B. Hourri<sup>1,\*</sup>, A. Legrouri<sup>2,\*</sup>, A. Barroug<sup>1</sup>, C. Forano<sup>3</sup> and J.-P. Besse<sup>3</sup>

<sup>1</sup> School of Science & Engineering, Al Akhawayn University,  
P.O. Box 1871, 53000 Ifrane, Morocco

<sup>2</sup> Laboratoire de Chimie Physique, Faculté des Sciences Semlalia,  
Université Cadi Ayyad, B.P. 2390, 40001 Marrakech, Morocco

<sup>3</sup> Laboratoire des Matériaux Inorganiques, UPRES-A 6002,  
Université Blaise Pascal Clermont-Ferrand II, 63177 Aubière cedex, France

---

Correspondence and reprints.

### RÉSUMÉ

L'élimination des ions chromate de solutions aqueuses par les argiles anioniques [Mg-Al-Cl], [Zn-Al-Cl] et [Zn-Cr-Cl] a été étudiée. Les solides, préparés par coprecipitation à pH constant, ont été caractérisés par diffraction des rayons X et spectroscopie infrarouge à transformée de Fourier. L'interaction de ces matériaux avec les ions  $\text{CrO}_4^{2-}$  a été suivie par spectroscopie UV-visible. Le traitement de solutions contenant de 15 à 300 ppm de  $\text{CrO}_4^{2-}$  a donné de bons résultats. La capacité d'élimination de ces argiles anioniques pour les ions  $\text{CrO}_4^{2-}$  est d'environ 1 mmol/g.

Mots clés : Argile anionique, hydroxyde double lamellaire, échange ionique, chromate, traitement de l'eau.

### ABSTRACT

The removal of chromate ions from aqueous solutions by [Mg-Al-Cl], [Zn-Al-Cl] and [Zn-Cr-Cl] anionic clays was investigated. The solids, prepared by coprecipitation at constant pH, were found to be pure upon characterisation by X-ray diffraction and Fourier-transform infrared spectroscopy. The interaction of the solid materials with  $\text{CrO}_4^{2-}$  ions has been studied by UV-visible spectroscopy. The treatment of solutions containing 15 to 300 ppm of  $\text{CrO}_4^{2-}$  was successful. The sorption capacities of the anionic clays for the  $\text{CrO}_4^{2-}$  ions are close to 1 mmol/g.

Keywords : Anionic clay, layered double hydroxide, ion exchange, chromate, water treatment.

---

\* Permanent Address: Département de Chimie & d'Environnement, Faculté des Sciences & Techniques, Université Cadi Ayyad, B.P. 523, Béni Mellal 23000, Morocco.

## INTRODUCTION

Anionic clays, also called layered double hydroxides or hydrotalcite-like compounds [1], are layered materials in which **divalent** and trivalent metal cations occupy randomly the centres of coplanar edge-sharing  $M(OH)_6$  octahedra, forming thus sheets similar to those in the brucite,  $Mg(OH)_2$ . These sheets alternate with charge compensating anions and water. They can be represented by the general formula [2,3]:

$[M^{II}_{1-x}M^{III}_x(OH)_2]^{x+}[X^{m-}_{x/m}.nH_2O]^{x-}$ , abbreviated as  $[M^{II}-M^{III}-X]$ ,  
 where,  $M^{II} = Mg^{2+}, Zn^{2+}, Mn^{2+}, \dots$ ,  $M^{III} = Al^{3+}, Cr^{3+}, Fe^{3+}, \dots$ ; and  $X^{m-} = Cl^-, NO_3^-, CO_3^{2-}, PO_4^{3-}, \dots$

The ion exchange ability of these solids, added to their oxidation-reduction and acid-base behaviours, makes them potential materials for extremely varied practical applications as anion exchangers, adsorbents, catalysts, electrolytes, ionic conductors, and for medical uses [4-8]. Their high ion exchange capacity (3.3 meq/g for natural hydrotalcite [4-9]), as compared to that of **cationic** clays (about 1 meq/g [4]), opens the perspective for their use in the removal of ecologically undesirable anions from dilute aqueous waste streams. Another advantage of these materials is the simplicity of their synthesis and its relative low cost.

This study forms part of a wider investigation undertaken on the study of the anion exchange ability of anionic clays [10,11] and their use as sorbents for undesirable organic and inorganic anions [12,13]. We report here on the results obtained in the case of chromate ions, which are present in many industrial water **streams**. In fact, chromium, which is known for its hazardous effects even at low concentrations [14], has found widespread use in electroplating, leather tanning, and metal finishing [15-17]. The sorption kinetics of  $CrO_4^{2-}$  ions, from aqueous solutions, by the three clays [Mg-Al-Cl], [Zn-Al-Cl] and [Zn-Cr-Cl] which were synthesised by coprecipitation at constant pH and **characterised** by powder X-ray diffraction

(PXRD) and Fourier-transform infrared spectroscopy (FT-IR), was investigated by UV-visible spectroscopy (UV-VIS).

## EXPERIMENTAL

The anionic clays were synthesised by coprecipitation at constant pH according to the procedure which was described previously [12]. The pH was adjusted to 11.0, 8.0 and 4.9 for [Mg-Al-Cl], [Zn-Al-Cl] and [Zn-Cr-Cl], respectively. The solids were prepared with the following ratios: [Mg]/[Al] = 3, [Zn]/[Al] = 3 and [Zn]/[Cr] = 2.

The PXRD equipment used was a Siemens D 501 diffractometer using copper  $K_{\alpha}$  radiation ( $\lambda = 1.5405 \text{ \AA}$ ).

Absorbance FT-IR spectra were recorded on a Perkin Elmer 16 PC spectrophotometer from samples in form of pressed KBr disks.

Experiments for the chromate removal were effected by suspending the clays in the ion-containing solutions whose pH was between 4 and 5. The mixtures were stirred (300 rpm) at room temperature and the solids were then separated from solution by centrifugation. The liquid was analysed by UV-VIS using a Perkin Elmer Lambda 2S spectrometer. The absorbance was recorded at 370 nm, at pH 9.5-10.

## RESULTS AND DISCUSSION

The PXRD patterns for the three samples (Fig. 1) indicate that each solid consists of a well crystallised single phase with large constituting crystallites. The patterns are in good agreement with those found for the hydrotalcite-like compounds [2,19]. The lattice parameters, refined on the hexagonal setting with a rhombohedral symmetry (space group:  $R\bar{3}m$ ), are given in Table 1.

Table 1: Lattice parameters of the three anionic clays.

Sample	a (nm)	c (nm)
[Mg-Al-Cl]	0.307	2.39
[Zn-Al-Cl]	0.307	2.32
[Zn-Cr-Cl]	0.312	2.32

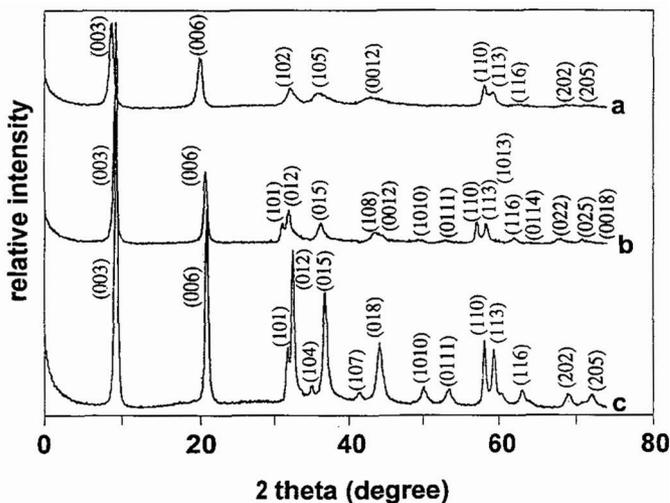


Fig. 1: PXRD patterns of (a) [Mg-Al-Cl], (b) [Zn-Cr-Cl] and (c) [Zn-Al-Cl].

The FT-IR spectra of the samples (Fig. 2) present profiles which resemble those exhibited by all hydrotalcite-like phases [19,20]. The attributions of the typical bands have already been discussed in previous papers [10,12]. It is noteworthy that, despite

the precautions taken during the materials syntheses, the FT-IR spectra show some contamination by  $\text{CO}_3^{2-}$  ( $1478 \text{ cm}^{-1}$ ) for the solids prepared in basic solution. However,  $\text{CO}_3^{2-}$ , which is known to form stable anionic clays [18], is only present as traces since no carbonate-clay phase is seen on the PXRD pattern.

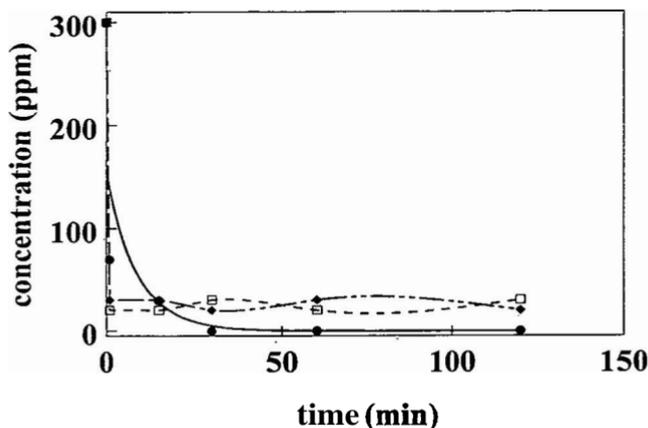


Fig. 2: FT-ZR spectra of (a) [Mg-Al-Cl], (b) [Zn-Cr-Cl] and (c) [Zn-Al-Cl].

The removal of  $\text{CrO}_4^{2-}$  by the three solid samples from aqueous solutions, whose initial concentrations vary from 15 to 300 ppm, increases when either contact time or anionic clay mass is increased. Saturation is reached very rapidly (less than 30 min in all cases) after contact between the anionic clay and the anion in solution (Fig. 3). The eliminated amount is important and [Zn-Al-Cl] seems to eliminate more of the anion than [Mg-Al-Cl] or [Zn-Cr-Cl].

The yellow solids obtained after removal of  $\text{CrO}_4^{2-}$  leached some of the anion on washing them with water. In all cases, the amount of leached anions decreases

with the number of washings and the solids preserve their yellow colour after several washings. The **PXRD** spectra of these solids, dried at room temperature, are nearly identical to those of fresh anionic clays; only a little decrease in the intensity of the PXRD lines was observed. This indicates a little **amorphotisation** of the phases, more particularly for **[Mg-Al-Cl]** and **[Zn-Cr-Cl]**, which might be due to exfoliation of the anionic clays following long stirring time in the solution. No sensitive variation of the *c* parameter was noted indicating that the  $\text{Cl}/\text{CrO}_4^{2-}$  ion exchange did not take place to a noticeable extent. This implies that the anion is probably simply adsorbed on the positive sheets of the anionic clays, even if the solids do not leach the entire quantity of the anion removed from water after several washings.

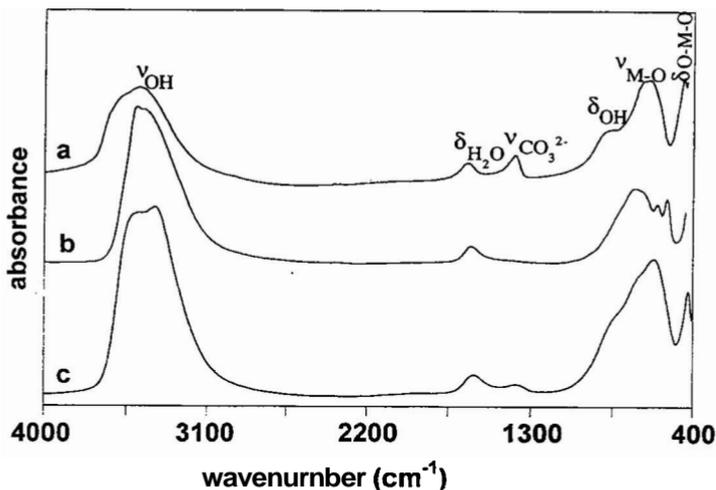


Fig. 3: Variation of  $\text{CrO}_4^{2-}$  concentration in the solution with stirring time using 900 mg of the clay. (◆) [Mg-Al-Cl], (□) [Zn-Cr-Cl] and (●) [Zn-Al-Cl].

200 mg of each anionic clay were suspended in solutions containing  $\text{CrO}_4^{2-}$  with different initial concentrations, varying between 500 and 2500 ppm, for 30 min. Fig.

4 indicates that the **absorption** capacity of the anionic clays varies between 0.1 and 0.3 mmol. The capacity being lower for high concentrations. It can be concluded from these experiments that 200 mg of the anionic clay can in average absorb about 0.2 mmol of the ion in 30 min of stirring time at 300 rpm. The absorption capacity of the clay for the ion studied is about 1 mmol  $\text{CrO}_4^{2-}/\text{g}$  [ $\text{M}^{\text{II}}-\text{M}^{\text{III}}-\text{Cl}$ ].

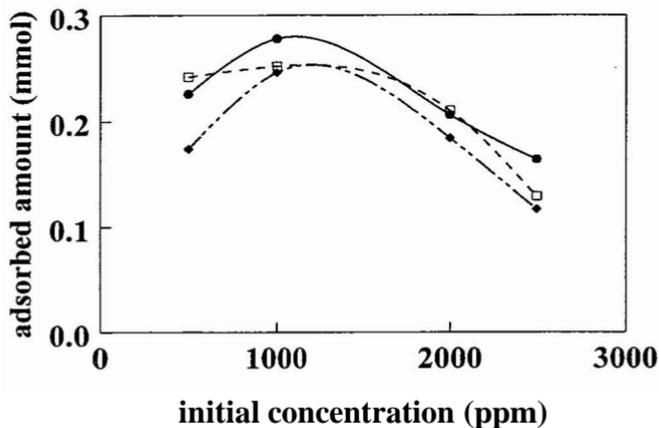


Fig. 4: Variation of the amount of  $\text{CrO}_4^{2-}$  removed by 200 mg of clay with the initial concentration of the solution. (●) [Mg-Al-Cl], (□) [Zn-Cr-Cl] and (●) [Zn-Al-Cl].

## CONCLUSION

The anionic clays [Mg-Al-Cl], [Zn-Al-Cl] and [Zn-Cr-Cl] were prepared by coprecipitation at constant pH. Physicochemical characterisation by PXRD and IR showed that the clays correspond to hydrotalcite-like compounds with good crystallinity and large crystallites.

The interaction of the clay with  $\text{CrO}_4^{2-}$ , which is known for its polluting effect, has been studied by UV-visible spectroscopy. Concentrations of the ppm order were

used in order to approach the concentrations found in industrial water streams. The treatment by the anionic clays for concentrations between 15 and 300 ppm was successful. The absorption capacity of the clay for the two ions draws near 1 ppm  $\text{CrO}_4^{2-}/\text{mg}$  [ $\text{M}^{\text{II}}-\text{M}^{\text{III}}-\text{Cl}$ ], with 30 min of stirring time.

## ACKNOWLEDGEMENT

The authors wish to thank the "Comité Mixte Interuniversitaire Franco-Marocain" for the financial support (Integrated Action No. 951856).

## REFERENCES

1. Allmann R., Jepsen H.P. (1966) *Neues Jahrb. Mineral. Monatsh.* **12**, 544-551.
2. De Roy A., Forano C., El Malki K., Besse J.P. (1992) In "*Synthesis of Microporous Materials*" (*Ocelli M.L., Robson H.E., Eds*). Van Nostrand Reinhold, New-York, pp. 108-169.
3. Ulibarri M.A., Hernandez M.J., Cornejo J. (1986) *Mater. Chem. Phys.* **14**, 209-217.
4. Reichle W.T. (1986) *Chemtech* **16**, 58-63.
5. Cavani F., Trifiro F., Vaccari A. (1991) *Catal. Today* **11**, 173-301.
6. Mousty C., Therias S., Forano C., Besse J.P. (1994) *J. Electroanal. Chem.* **374**, 63-69.
7. Playle A.C., Gunning S.R., Llewellyn A.F. (1974) *Pharm. Acta Helv.* **49**, 298-302.
8. Trifiro F., Vaccari A. (1996) *Compr. Supramol. Chem* **7**, 251-291.
9. Bish D.L. (1980) *Bull. Mineral.* **103**, 170-175.
10. Badreddine M., Khaldi M., Legrouri A., Barroug A., Chaouch M., De Roy A., Besse J.P. (1998) *Mater. Chem Phys.* **52**, 235-239.
11. Badreddine M., Legrouri A., Barroug A., De Roy A., Besse J.P. (1998) *Collect. Czech. Chem Commun.* **63**, 741-748.
12. Hourî B., Legrouri A., Barroug A., Forano C., Besse J.P. (1998) *Collect. Czech. Chem. Commun.* **63**, 732-740.
13. Lakraimi M., Legrouri A., Barroug A., de Roy A., Besse J.P. (1998) *Actes de la Rencontre du Groupe Français d'Etude des Composés d'Insertion, GFECI'98, Egat - Font Romeu*, pp. 120-121.
14. Mearns A.J., Oshida P.S., Sherwood M.J., Young D.R., Reish D.J. (1976) *J. Water Pollut. Control Fed* **48**, 1929-1939.

15. Sharma D.C., Forster C.F. (1993) *Water Res.* 27, 1201-1208.
16. Alves M.M., Gonzalez Beca C.G., Guedes de Carvalho R., Castanheira J.M., Sol Pereira M.C., Vasconcelos L.A.T. (1993) *Water Res.* 27, 1333-1338.
17. Ajmal M., Rao R.A.K. Siddiqui B.A. (1996) *Water Res.* 30, 1478-1482.
18. Miyata S. (1980) *Clays Clay Miner.* 28, 50-56.
19. Miyata S. (1975) *Clays Clay Miner.* 23, 369-375.
20. Hernandez-Moreno M.J., Ulibam M.A., Rendon J.L., Sema J.S. (1985) *Phys. Chem. Miner.* 12, 34-38.