Removal of pesticides from water by anionic clays

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RÉSUMÉ

L'bchange des ions chlorure par les ions d'une molécule appartenant à la famille des pesticides 2,4-dichlorophénoxyacétate (2,4D) dans l'argile anionique [Zn-Al-Cl] a été étudiée par diffraction des rayons X et spectroscopie infrarouge. Les influences de la concentration en 2,4D de la solution d'échange et de la température ont été étudiées afin d'optimiser les conditions de l'échange..La meilleure cristallinité a été obtenue à 100°C dans une solution 0.004 M en 2,4D. Une phase préparée dans ces conditions a été caractérisée par analyse chimique et microscopie électronique à balayage. L'échange a été réalisée sans degradation de l'anion pesticide.

Mots clés : Argile anionique, hydroxyde double lamellaire, phénoxyacétate, échange ionique, intercalation.

ABSTRACT

The exchange of chloride ions by ions from the pesticide family 2.4-dichlorophe-noxyacetate (2.4D) in [Zn-Al-Cl] anionic clay was investigated by X-ray diffraction and infrared spectroscopy. The effects of 2.4D concentration in solution and temperature on the ion exchange were studied. The best sample in terms of crystallinity, was obtained at 100°C with a 2.4D concentration corresponding to the solubility limit of the ion in water. This sample was further characterised by chemical analyses and scanning electron microscopy. The anion intercalation was effected without degradation of the pesticide anion.

Keywords : Anionic clay, layered double hydroxide, phenoxyacetate, ion exchange, intercalation.

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INTRODUCTION

Anionic clays, also called layered double hydroxides or hydrotalcite-like compounds [1], are layered solids which have a stacking of positively charged octahedral sheets. The net positive charge, which is due to substitution of trivalent by divalent metal ions in the brucite-like metal hydroxide $M(OH)_2$, is balanced by an equal negative charge of the interlayer solvated anions. The anionic clays 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 $[M^{II}\text{-}M^{III}\text{-}X]$,

where, $M^{II} = Mg^{2+}, Zn^{2+}, Mn^{2+}, ..., M^{III} = Al^{3+}, Cr^{3+}, Fe^{3+},...;$ and $X^{m-} = Cl^-, NO_3^-,$ $CO_3^{2-}, PO_4^{3-}, ...$

These materials have received substantial attention in recent years owing to their potential technological applications in various domains such as catalysis, electrochemistry, separation technology, and medicine [4-10]. This attention results from their layered structure and their high anion exchange capacity [11,12].

This study forms part of a wider investigation undertaken on the study of the anion exchange ability of anionic clays [13,14] and their use as sorbents for undesirable organic and inorganic anions [8,15]. We report here on the results obtained in the case of pesticides which are present in many agricultural and industrial water streams [16-18]. It concerns the intercalation of ions from a molecule belonging to the pesticide family 2.4-dichlorophenoxyacetic acid, abbreviated as 2.4D, in [Zn-Al-Cl] by ion exchange. The effects of the anion concentration in solution and temperature were studied in order to determine the optimum conditions under which an intercalated clay is obtained with good crystallinity and high exchange extent. Both the [Zn-Al-Cl] precursor and the exchanged phases were characterised by powder X-ray diffraction (XRD) and Fourier transform infrared spectroscopy (IR). The best sample, in terms of crystallinity, obtained in the series was subjected to further characterisation by

chemical analyses and scanning electron microscopy (SEM).

EXPERIMENTAL

The anionic clay [Zn-Al-Cl], with the [Zn]/[Al] ratio equal to 2, was synthesised by coprecipitation at a constant pH of 9.0 [8].

The anion exchange reactions were achieved at a pH near 7 with 24 h of ageing time on 200 mg of the [Zn-Al-Cl] suspended in 500 mL of solution containing 2.4D. The solids were separated from the solution by centrifugation and then washed three times with water. They were then dried on air at ambient temperature for 24 h.

All experiments were carried out under a stream of N_2 in order to avoid, or at least minimise, the contamination by atmospheric CO_2.

The XRD equipment used was a Siemens D 501 diffractometer using copper K_α radiation. Absorbance IR spectra were recorded on a Perkin Elmer 16 PC spectrophotometer from samples in form of pressed KBr disks. SEM examination of gold-coated samples was carried out on a Cambridge Stereoscan 360 microscope operated at an accelerating voltage of 20 kV. Chemical analyses were effected by atomic absorption at the "Service Central d'Analyses" of the CNRS at Vemaison (France).

RESULTS AND DISCUSSION

Characterisation of the [Zn-Al-Cl] precursor

The XRD pattern for [Zn-Cr-Cl] (Fig. 1) indicates that the solid consists of a well crystallised single phase with large constituting crystallites. The pattern is 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: R3m) are: a = 0.306 nm, c = 2.33 nm (d = c/3 = 0.778 nm).

The IR spectrum of the sample (Fig. 2) presents 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 [13,8]. It is noteworthy that, despite the precautions taken during the materials syntheses, the IR spectrum shows some contamination by CO_3^{2-} ($1478\ cm^{-1}$) for the solid. However, CO_3^{2-}, which is known to form stable anionic clays [21], is only present as traces since no carbonate-clay phase is seen on the XRD pattern.
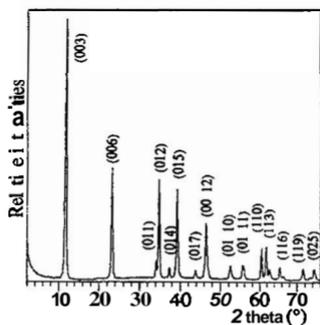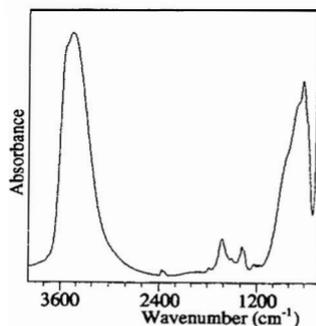

Fig. 1: XRD pattern of [Zn-Al-Cl].   Fig. 2 IR spectrum of [Zn-Al-Cl].

Influence of the 2.40 concentration

The phases obtained with various concentrations are of hydrotalcite type (Fig. 3). The displacement of the (001) lines towards the low values of 2θ indicates the possibility of exchange [22,23]. The widening of XRD lines indicates a crystallinity reduction upon exchange, and the observed disymmetry of these lines can be due to the turbostratic character of the new phases. The significant background noise observed between $20°$ and $30°$ in 2θ, can be attributed to the presence of an amorphous phase of $Al(OH)_3$ [24]. The highest exchange extent is observed for the concentration which corresponds to the limit of solubility of 2.4D in water (0.004 M). The existence of peaks corresponding to the chloride phase, for lower

concentrations, shows that the exchange is not total.

The IR spectra (Fig. 4) show clearly the existence of the 2.4D anion between the layers. The broad and intense band around 3430 cm^{-1} corresponds to the valence vibrations of hydroxyl groups. The band around 1620 cm^{-1} is that of the carboxylate ion vibrations, it masks the band which corresponds to the deformation vibrations of water molecules. The bands at 1490 and 1420 cm^{-1} correspond to C=C vibrations of the aromatic nucleus. The two bands located at 1280 and 1060 cm^{-1} correspond to the asymmetric and symmetric vibrations of (C-O-C), respectively. The band at 860 cm^{-1} can be allotted to the C-CI vibration and the bands at 770 and 800 cm^{-1} correspond to the (CH) vibrations of benzenic deformation out of the plane of the ring. The vibrations of the network appear in the low frequency areas. The bands located near 600 cm^{-1} correspond to the valence vibrations of MO, A_{2u} and E_u. That located at 430 cm^{-1} corresponds to the deformation vibrations of O-M-O [25,26].
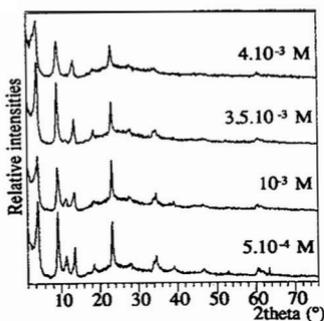

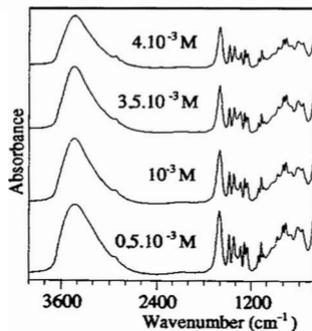Fig. 3: XRD patterns of [Zn-Al-2.4D] phases obtained in solutions with different 2.4D concentrations.

Fig. 4: IR spectra [Zn-Al-2.4D] phases obtained in solutions with different 2.4D concentrations.

Influence of the temperature

XRD (Fig. 5) shows that the layered aspect is preserved in the exchanged phases with a slight crystallinity improvement with increasing temperature. This is perfectly observable for the (001) lines which become less broad and more intense.

The IR spectra (Fig. 6) show that the exchange is possible at 25, 60 or 100°C with a clear reduction in the intensity of the CO_3^{2-} band (1360 cm^{-1}).
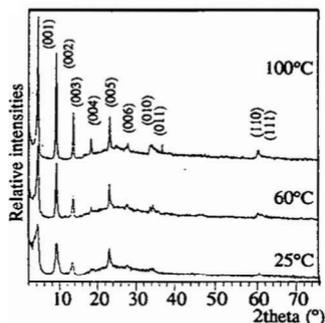

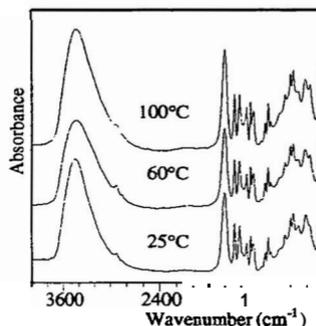*Fig. 5: XRD patterns of [Zn-Al-2.4D] phases obtained at different temperatures.*

Fig. 6: IR spectra [Zn-Al-2.4D] phases obtained at different temperatures.

It can be concluded from these investigations that the best exchanged phase with high extent of ion exchange can be obtained at 100°C in a 0.004 M 2.4D solution with 24 h of stirring time. The XRD powder data, obtained for a phase prepared under these conditions, were refined on the hexagonal setting (space group: P6₃/mmc). The cell parameters were: $a = 0.306$ nm, $c = 1.91$ nm and $d = 1.91$ nm.

Chemical analyses of the [Zn-Al-2.4 D] phase confirm the chloride–2.4D ion exchange and show that the exchange is almost total. The average composition of the phase corresponds to the formula: $[Zn_{1.9}Al(OH)_{5.8}][Cl_2C_6H_3OCH_2CO_2.2.83H_2O]$.

The examination of the parent and the 2.4D-intercalated material by SEM (Fig. 7) revealed that the crystals present almost the same morphological features. They look to result from the superposition of several leaflets with the dimensions of the particles being of about 2 mm. The small morphological alteration of the layers, upon exchange, can be due to the decrease in crystallinity observed by XRD in the sample.
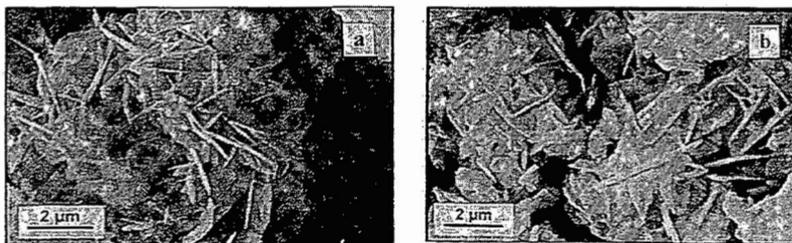
Fig. 7 : SEM photographs of (a) [Zn–Al–Cl] and (b) 2.4D-exchanged phase.

CONCLUSION

2.4D-intercalated [Zn–Al] anionic clay phases were prepared from a chloride precursor, which was obtained by coprecipitation method at constant pH, by exchange reaction in a 2.4D-containing solution. The effects of the anion concentration and temperature on the exchange were studied in order to determine the optimum conditions under which the intercalated clay is obtained with a good crystallinity and high exchange extent.

XRD and IR revealed that, in all cases, the crystallinity of intercalated phases is lower than that of the precursor. Intercalation was also observed to cause certain disorder in the layers without destruction of the layered structure of the material. The best crystalline material, with high exchange extent, was obtained by carrying out the exchange at 100°C in a 0.004 M 2.4D solution. The anion intercalation was effected without degradation of the pesticide anion.

SEM observation of the parent material and the sample obtained upon intercalation showed that the morphology of the crystals did not undergo a large modification following the ion exchange.

Chemical analyses of the intercalated phase, obtained under the optimum

conditions, confirmed the anion exchange and provided the average composition of the sample which corresponds to the formula:

$$[Zn_{1.9}Al(OH)_{5.8}][Cl_2C_6H_3OCH_2CO_2.2.83H_2O]$$

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REFERENCES

1. Allmann R. (1970) *Chimia* **24,** 99-108.
2. De Roy A., Forano C., El Malki K., Besse J.P. (1992) In *"Synthesis of Microporous Materials" (Occelli 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, Cavani F., Trifiro F., Vaccari A. (1991) *Catal. Today* 11,173-301.
5. Kwon T., Tsigdinos G.A., Pinnavaia T.J. (1988) J. *Am. Chem. Soc.* **110,** 3653-3654.
6. Suzuki E., Okamoto M., Ono Y. (1989) *Chem. Lett.* 1485-1486.
7. Clause O., Rebours B., Merlen E., Trifiro F., Vaccari A. (1991) J. *Catal.* 133, 231-242.
8. Houri B., Legrouri A., Barroug A., Forano C., Besse J.P. (1998) *Collect. Czech. Chem. Commun.* 63,732-740.
9. Playle A.C., Gunning S.R., Llewellyn A.F. (1974) *Pharm. Acta Helv.* **49,** 298-302.
10. Takagishi Y., Iwamoto K., Mackawa H. (1978) *Yakuzaigaku* 38, 166-171.
11. Bohem H.P., Steinle J., Vieweger C. (1977) *Angew. Chem., Int. Ed. Eng. 16,* 265-266.
12. De Roy A., Besse J.P., Bondot P. (1985) *Mater. Res. Bull.* 20,1091-1098.
13. Badreddine M., Khaldi M., Legrouri A., Barroug A., Chaouch M., De Roy A., Besse J.P. (1998) *Mater. Chem. Phys.* 52,235-239.
14. Badreddine M., Legrouri A., Barroug A., De Roy A., Besse J.P. (1998) *Collect. Czech. Chem. Commun.* 63,741-748.
15. 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.

16. Wettasinghe A. (1992) *MSc Thesis,* Oregon State University,USA.
17. Tortensson N.T.L.,Stark J., Goransson B. (1975) *Research* 15,159-164.
18. Wilson R.G., Cheng H.H. (1978) *J. Environ. Qual.* 7, 281-286.
19. Miyata S. (1975) *Clays Clay Miner.* 23,369-375.
20. Hernandez-Moreno M.J., Ulibarri M.A., Rendon J.L., Serna J.S. (1985) *Phys. Chem Miner.* 12, 34-38.
21. Miyata S. (1980) *Clays Clay Miner.* 28, 50-56.
22. Sato T., Wakabayashi T., Shimada M. (1986) *Ind. Eng. Chem Prod. Res. Dev.* 25, 89-97.
23. Reichle W.T. (1986) *Solid State Zonics* 22,135-139.
24. Bonnet S. (1997) *Blaise Pascal University Thesis,* Clermont-Ferrand,France.
25. Van Oosterwyck-Gastuche M.C., Brown G., Mortland M.M. (1967) *Clay Miner. 7,* 177-192.
26. Bish D.L.,Brindley G.W. (1977) Am *Mineral.* 62,458-464.