USE OF THE ION-EXCHANGE PROPERTIES OF LAYERED DOUBLE HYDROXIDES FOR WATER PURIFICATION

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The sorption of chromate and dichromate ions by a [Zn–Al–Cl] layered double hydroxide was investigated. The anionic clay, prepared by coprecipitation at pH 8, was found to be pure upon characterization by X-ray diffraction, Fourier-transform infrared spectroscopy, and thermogravimetry and to have low BET surface area and small pore volume. The interaction of the clay with both chromate and dichromate ions has been studied by UV-VIS spectroscopy. The treatment of water containing 15–300 ppm of CrO_4^{2-} or $Cr_2O_7^{2-}$ was successful. The sorption capacities of the clay for CrO_4^{2-} and $Cr_2O_7^{2-}$ are close to 1 and 0.6 mmol/g, respectively.
Key words: Waste water treatment; Ion exchange; Intercalation; Hydrotalcite phase; Chromates; Dichromates.

Lamellar double hydroxides (LDH)s are layered materials which contain two types of metal cations in the sheets. They are also called anionic clays, with respect to the presence of anionic species in the interlamellar domains, and also compounds of hydrotalcite type, with reference to the natural mineral hydrotalcite $Mg_6Al_2(OH)_{16}(CO_3)\cdot4\,H_2O$. They can be represented by the general formula[1]:

$$[M_{1-x}^{II}M_x^{III}(OH)_2]^{x+}[X_{x/m}^{m-}\cdot n\,H_2O]^{x-}$$ symbolized by [M^{II}–M^{III}–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-},..., with x varying between 0.20 and 0.33 (refs[2,3]).

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A detailed study of their structure was performed using single-crystal X-ray diffraction of sjögrenite and pyroaurite isotypes[4–6] and later hydrotalcite[7]. The divalent and trivalent metal cations occupy randomly the centers of coplanar edge-sharing $M(OH)_6$ octahedra, forming thus the hydroxylated sheets $M(OH)_2$ which are similar to those in the brucite, $Mg(OH)_2$. These sheets alternate with charge-compensating layers of anions and water (Fig. 1).

The lamellar structure of LDHs is accountable for by their important anion exchange ability as well as by their oxidation-reduction and acid-base behaviours which make them potential materials for extremely variable practical applications as anion exchangers[8,9], adsorbents[10], catalysts[11,12], electrolytes[13], ionic conductors[14,15], and for medical uses[8,16]. The high anion-exchange capacity of these materials, which is of 3.3 meq/g for the natural hydrotalcite[8,17], as compared to that of cationic clays, which is of about 1 meq/g (ref.[8]), makes them promising materials for the sorption of ecologically undesirable anions, both inorganic and organic, 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 use of LDH as anion exchangers and sorbents for organic and inorganic anions. We report here on the results obtained with chromate and dichromate ions, which are present in many industrial water streams. In fact, chromium, which is known for its hazardous effects[18], has found widespread use in electroplating, leather tanning, and metal finishing[19–21]. The sorption kinetics of CrO_4^{2-} and $Cr_2O_7^{2-}$ ions, from aqueous solutions, by a [Zn–Al–Cl] LDH phase was investigated by UV-VIS spectroscopy. The sorbent synthesized was characterized by X-ray diffraction (XRD), Fourier-transform infrared spectroscopy (IR), thermogravimetry (TG), and surface area measurement (BET).
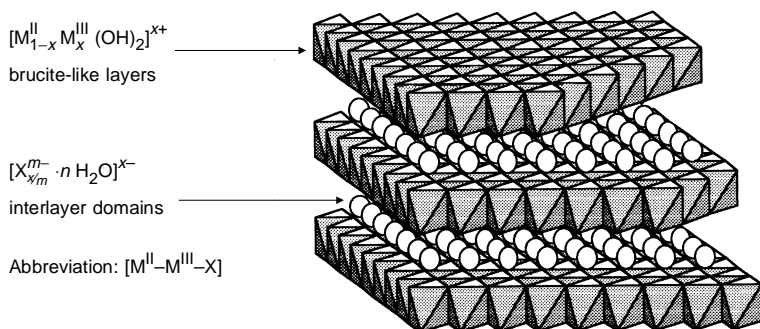

$[M_{1-x}^{II} M_x^{III} (OH)_2]^{x+}$
brucite-like layers

$[X_{x/m}^{m-} \cdot n\,H_2O]^{x-}$
interlayer domains

Abbreviation: $[M^{II}–M^{III}–X]$

FIG. 1
Structural model for the hydrotalcite-like compounds

EXPERIMENTAL

Materials

The syntheses[1] were carried out under a stream of N_2 in order to avoid, or at least minimize, the contamination by CO_3^{2-} from atmospheric CO_2. An aqueous solution (250 ml) containing $ZnCl_2$ (25.55 g, 0.1875 mol) and $AlCl_3$ (15.08 g $AlCl_3 \cdot 6\ H_2O$, 0.0625 mol), $[Zn^{2+}]/[Al^{3}] = 3$, was added dropwise into 250 ml of distilled and decarbonated water, which pH was previously set at the desired value (pH 8) by addition of 1 M NaOH solution, over a period of about 24 h with vigorous stirring at room temperature. The pH of the solution was maintained constant by a simultaneous addition of the sodium hydroxide solution. The resulting slurry was then left under stirring for 24 h at 38 °C. The precipitate was separated by centrifugation and washed several times with water. The final product was dried at 38 °C on air. The chemical composition of the material corresponds[1] approximately to: $Zn_3Al(OH)_8Cl \cdot 2\ H_2O$ with traces of CO_3^{2-}, as detected by IR.

Methods

The XRD equipment used was a Siemens D 501 diffractometer. Samples of unoriented powder were exposed to CoKα radiation (λ = 0.15415 nm). Measurement conditions were: 2θ range 2–76°, step size 0.08° 2θ, step counting time 4 s. Data acquisition was effected on a DACO-MP microcomputer. Unit cell constants were calculated using a least-squares refinement.

IR absorption spectra in the range 400–4 000 cm^{-1} were recorded on a Perkin–Elmer 16 PC FTIR spectrometer, at a resolution of 2 cm^{-1} and averaging over 100 scans. Samples were pressed into KBr disks.

TG experiments were performed in air on a Setaram TG-DTA 92 instrument. The curves were recorded over a range of temperatures up to 1 000 °C at a rate of 5 °C/min using 14.5 mg of test samples.

BET surface area and pore volume measurements were carried out on a Fisons Instruments Sorptomatic 1900 by adsorption of nitrogen at liquid air temperature. LDH samples were pretreated at 100 °C for 24 h in air atmosphere and at 80 °C for 4 h under vacuum (1.3 Pa).

Sorption Measurements

The anionic clay was suspended in solutions containing chromate or dichromate ions (200 ml). The pH of the solutions, which was measured to be between 4 and 5, was adjusted to a value between 7 and 8 in order to preserve the structure of the clay, prepared at pH 8. The mixtures were stirred (300 rpm) at room temperature for different contact times and the solid was then separated from the solution by centrifugation. The liquid phase was analyzed by UV-VIS spectroscopy using a Perkin–Elmer Lambda 2S spectrometer. The absorbance was recorded at 370 nm at pH 9–10 for CrO_4^{2-} and at 350 nm at pH 2–3 for $Cr_2O_7^{2-}$. The uncertainty on the measured values was estimated to 0.2%.

RESULTS AND DISCUSSION

Characterization of the Solid

The XRD pattern for a [Zn–Al–Cl] sample (Fig. 2) is well resolved with narrow peaks. It indicates that the sample, consisting of a single phase, is very well crystallized and that the size of its constituting crystallites is very large. This pattern is in agreement

with those found for the hydrotalcite-like minerals[22]. The angular position of the first peak (003) gives an approximate value for the interlamellar distance ($c = 3\ d_{003}$). The (110) peak, situated around 60° in 2θ, allows to determine an approximate value for the cell parameter a, which is related to the metal–metal interatomic distance within the sheet ($a = 2\ d_{110}$). The XRD powder data, refined on the hexagonal setting with a rhombohedral symmetry (space group: $R\bar{3}m$, No. 166), provided the lattice parameters for the sample: $a = 0.3072(2)$ nm and $c = 2.323(2)$ nm.

The IR spectrum of the sample (Fig. 3) resembles those exhibited by all hydrotalcite-like phases[22]. Typical of this spectrum are the large band at 3 490 cm^{-1}, the band at 1 620 cm^{-1}, and the small shoulder at 830 cm^{-1}, which correspond to the valence vibration of hydroxy groups, the bending vibration of water $\delta(H_2O)$, and the planar lattice vibration of hydroxy groups $\delta(OH)$, respectively. The bands observed in the low-frequency region

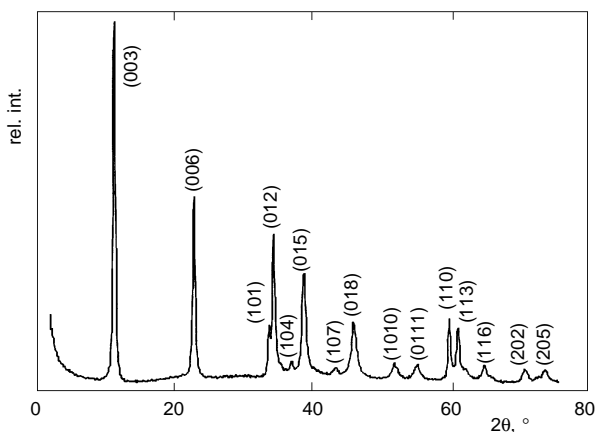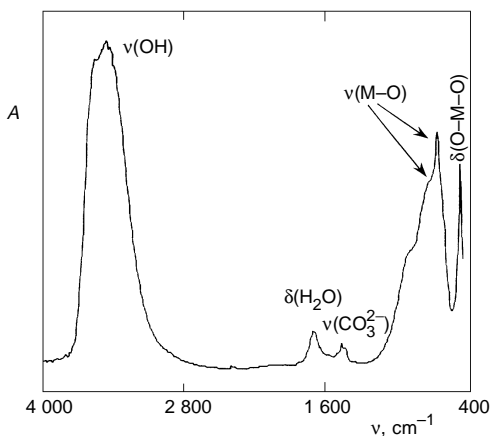FIG. 2
XRD pattern of the [Zn–Al–Cl] phase

FIG. 3
IR spectrum of the [Zn–Al–Cl] phase

of the spectrum correspond to the lattice vibration modes and can be attributed to M–O (841 and 647 cm^{-1}) and O–M–O (435 cm^{-1}) vibrations. It is noteworthy that despite the precautions taken during the preparation of the sample, the IR spectrum shows the valence vibrations for the carbonate ion at 1 478 cm^{-1}. This contamination by atmospheric CO_2 may be explained by the stability of CO_3^{2-} in basic solution and the high selectivity of LDH for this anion[23]. However, CO_3^{2-} is only present as traces since no carbonate–LDH phase is seen on the XRD pattern.

According to the TG curve obtained for the [Zn–Al–Cl] phase (Fig. 4), the thermal decomposition takes place in three consecutive stages. First, the adsorbed and the interlayer water molecules are lost between room temperature and 200 °C. Subsequently, the octahedral layers are dehydroxylated in the range 200–380 °C. At temperatures higher that 380 °C, the third stage corresponds to the elimination of the interlayer anion in the form of HCl (refs[24,25]) and Cl_2 (ref.[26]), followed by the transformation of the solid into a mixture of zinc oxide (ZnO) and a spinel-type phase ($ZnAl_2O_4$), as confirmed by XRD measurement (Fig. 5). All the losses of water, HCl and Cl_2 molecules were recently identified by mass spectrometry analysis coupled to the TG apparatus[26].

The BET surface area measurements indicate that the sample exhibits low surface area (29.4 m^2/g) and pore volume (0.322 ml/g). Similar results were encountered for synthetic anionic clays. Higher surface area and pore volume were obtained upon thermal treatment of the starting materials[27–29].

Sorption of Chromate and Dichromate Ions

The sorption of chromate and dichromate ions by the HDL was performed for initial concentrations varying between 15 and 300 ppm, at which the same observations can be made for both ions. The sorption by the anionic clay increases when either time of stirring or mass of [Zn–Al–Cl] is increased, except for the dichromate, in concentra-
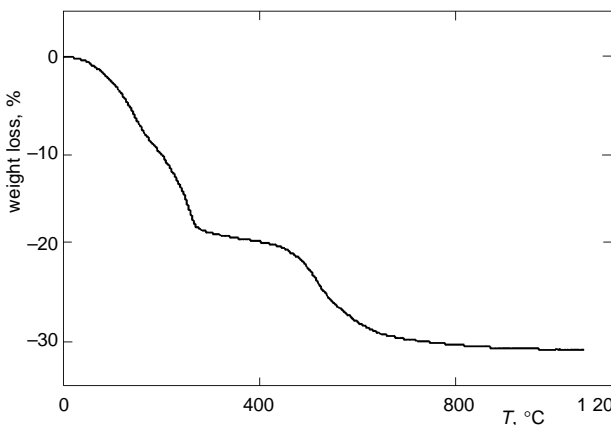

Fig. 4
TG curve of the [Zn–Al–Cl] phase

tions 100 to 300 ppm, which was released from the clay after a long-time stirring. This phenomenon can be attributed to a slow dissolution of the LDH, favored by the vigorous stirring, and/or a gradual dissolution of atmospheric CO_2, forming CO_3^{2-} which displaces the large $Cr_2O_7^{2-}$. This ion release is enhanced when low masses of the clay are used.

The variations of the chromate and dichromate concentration as a function of stirring time for an initial concentration of 300 ppm are reported in Figs 6 and 7. Figure 6 shows that the chromate concentration decreases with the time of stirring or mass of [Zn–Al–Cl]. The removal of the chromate is almost total after 30 min stirring for 900 mg of the clay. Figure 7 reveals that the dichromate concentration decreases rapidly with time of stirring for the three masses of [Zn–Al–Cl]. The removal of the dichromate is almost complete after 15 min stirring. However, if the stirring is continued, the clay starts to release some of the dichromate into the solution after 30 min. This phenomenon is more significant for the low mass (600 mg).

Fig. 5
XRD pattern of the [Zn–Al–Cl] phase after TG indicating the presence of [Zn–Al–Cl] (Δ), ZnO ($\bigcirc$), and $ZnAl_2O_4$ ($\square$)
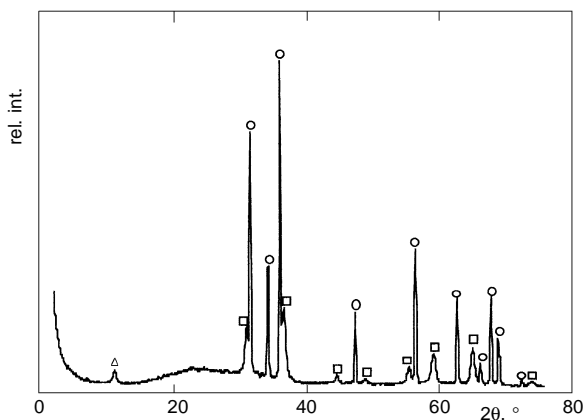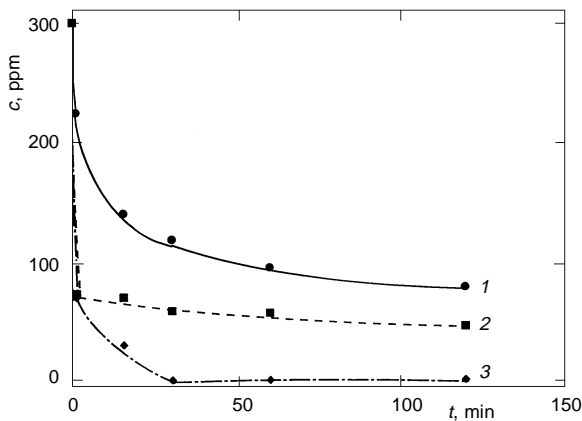

Fig. 6
Dependence of the residual chromate concentration, c, in solution on stirring time with masses of [Zn–Al–Cl] equal to 200 mg (*1*), 650 mg (*2*), and 900 mg (*3*)

Sorption Limit of Chromate and Dichromate Ions by the Clay

An amount of 200 mg of the clay was suspended within 30 min in solutions of chromate or dichromate ions with initial concentrations varying between 500 and 2 500 ppm. Figure 8 indicates that the sorption capacity of the clay for the chromate varies between 170 and 270 ppm, the capacity being lower for high concentrations. The same observations were made with the dichromate, the clay absorbing less (150 to 200 ppm). It can be concluded from these experiments that for chromate and dichromate initial concentrations varying between 500 and 2 500 ppm, 200 mg of [Zn–Al–Cl] can absorb on average about 200 ppm of the ion in 30 min of stirring at 300 rpm. The sorption capacities of the clay for CrO_4^{2-} and $Cr_2O_7^{2-}$ are 1.1 and 0.56 mmol/g, respectively.
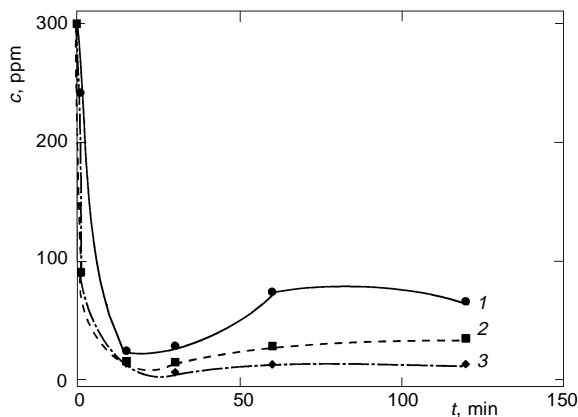

Fig. 7

Dependence of the residual dichromate concentration, c, in solution on stirring time with masses of [Zn–Al–Cl] equal to 600 mg (*1*), 900 mg (*2*), and 1 100 mg (*3*)
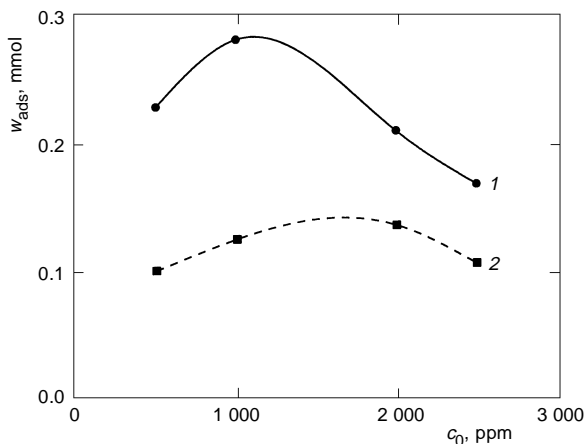

Fig. 8

Dependence of the amount, w_{ads}, of chromate (*1*) and dichromate (*2*) sorbed by 200 mg of [Zn–Al–Cl] on their initial concentrations, c_0, in solution

CONCLUSIONS

A layered double hydroxide [Zn–Al–Cl] phase was prepared from chloride precursors by the coprecipitation method at constant pH. Physicochemical characterization by XRD and IR showed that the clay is a hydrotalcite-like compound with a good crystallinity. TG revealed the different stages which the clay undergoes upon thermal treatment. BET surface area showed that the material possesses a small surface area and low pore volume. The interaction of the clay with both chromate and dichromate ions, which are known for their polluting effect, has been studied by UV-VIS spectroscopy. Concentrations of the ppm order were used in order to approach the concentrations found in industrial or urban water streams. The treatment with the clay of water containing between 15 and 300 ppm of each ion was successful. The sorption capacities of the clay for CrO_4^{2-} and $Cr_2O_7^{2-}$ are close to 1 and 0.6 mmol/g, respectively, for 30 min of stirring time.

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