CR(VI) REMOVAL FROM WASHING WA-TER USING LAMINAR DOUBLE HYDROXI-DES. OBTAINMENT OF CERAMIC PIGMENT ECO-PRECURSORS

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RESUMEN

Chromium is widely used in the ceramic industry in formulating various ceramic pigment compositions. Owing to the oxidising atmosphere during the firing process, most of the chromium oxidises to form Cr(VI), which is very soluble in aqueous media. This is a disadvantage because solutions rich in Cr(VI) are highly polluting and harmful to the environment and human health, so that all such waste must be treated as highly toxic. This study shows the removal capability of compounds of the hydrotalcite type, also known as laminar double hydroxides, owing to their great adsorption capacity of Cr(VI) in aqueous media. These compounds have a multi-layer structure, consisting of divalent and trivalent hydroxide layers, whose excess charge is compensated by the anions located between the layers. An extensive variety of metals can be used, thus changing the type of inter-laminar anion. Three different systems have studied, varying the divalent cation (Mg, Co and Ni), the systems being placed in contact with a solution that contained Cr(VI) in order to verify the adsorption process as such. The study showed the ability of this compound to adsorb Cr(VI) in aqueous solution, which allows recovery of such waste by introducing it as a source of chromium in different industrial processes.

1. INTRODUCTION

Chromium is widely used in the ceramic industry as a colouring oxide in formulating many ceramic pigment compositions. Owing to the oxidising atmospheres during the sample calcination processes, much of this chromium oxidises to Cr(VI), which is very soluble in aqueous medium. This is a major disadvantage because solutions rich in Cr(VI) are highly polluting and harmful to the environment and human health, so that all such waste must be treated as highly toxic.

 Cr_2O_3 is isostructural with Al_2O_3 , i.e. it has a compact hexagonal packing, the Cr occupying two thirds of the available octahedral holes [1-3].

One of the relatively more simple systems is that made up of the Cr oxide and the Al oxide, consisting of one region with a liquid phase and another with a solid phase separated by a two-phase (solid-liquid) region. The Al_2O_3 - Cr_2O_3 solid solution is substitutional and, in this, Al(III) substitutes Cr(III) and vice versa. This solution exists for any composition below the melting point of Al_2O_3 , as the chromium and aluminium cations have the same charge and similar radii.

The ease with which this type of solid solution forms, together with the wide range of oxidation states that Cr (II to VI) can exhibit, makes it a very versatile element when it comes to designing ceramic pigments, thanks to the enormous range of colours that can be obtained. Thus, green, red, pink, black, brown, and orange pigments can be found, obtained by varying the Cr contents and oxidation state in the corresponding crystal structures.

The industrial preparation of ceramic pigments takes place by means of the traditional solid-state reaction procedure, as this provides the best results at present: the reagents are cheaper and not very complicated reaction facilities are required. However, one of the problems involved is the high energy input needed to produce interdiffusion between the reagents and formation of the corresponding crystal structure. Another problem is the presence of raw materials that have not been incorporated into the synthesised crystalline phase and need to be removed to avoid colorimetric distortions in the final ceramic pigment [4].

The removal of these unreacted reagents is performed by a pigment washing process. Owing to the high temperature needed for synthesis, as well as the use of oxidising atmospheres and mineralisers, the Cr that is not incorporated into the crystal structure of the pigment oxidises to Cr(VI), which is soluble in water. When the relevant washings are performed, this solubilises, making the resulting wastewater a liquid that cannot be cleaned by the traditional route and that requires handling as toxic, hazardous waste.

Chromium is of great importance, as it is used in different industrial activities.

Although chromium can exist in different oxidation states, in nature the only stable states are (III and VI). The environmental behaviour of chromium depends on its oxidation state; the compounds with hexavalent chromium (mainly chromates (CrO_4^{-2-}) and dichromates $(Cr_2O_7^{-2-})$) are highly toxic for aquatic and land organisms, in which they can lead to genetic alterations [5]. This is because of the different chemical properties of these ions: Cr(VI) compounds are highly soluble, strong oxidisers that can easily cross

biological membranes, whereas Cr(III) compounds tend to form relatively inert precipitates at a pH close to 7. Chromium (VI) compounds are toxic if ingested, the lethal dose being a few grams. At non-lethal levels, Cr(VI) is a carcinogen. Most chromium (VI) compounds irritate the eyes, the skin, and the mucous membranes. Chronic exposure to chromium (VI) compounds can cause permanent damage to eyes.

Since 1958, the World Health Organisation (WHO) has recommended a maximum concentration of 0.05 mg/litre of chromium (VI) in water for consumption. Though this value has been reviewed and new studies have been conducted on chromium (VI) effects on health, it has remained constant.

Owing to the importance of chromium pollution in the last decade, the scientific community has conducted numerous studies aimed at finding a method for adsorbing and recovering the Cr(VI) present in liquid effluents [6-15].

The performance of this process by laminar double hydroxides affords a series of very important advantages. These include low cost, possible reusability, appropriate for a pH close to 7, and ease of hydrotalcite synthesis [16].

Hydrotalcite belongs to a class of compounds known as anionic clays or, when they are synthetic, known as laminar double hydroxides. Hydrotalcite structure is similar to that of brucite, $Mg(OH)_2$, in which magnesium is octahedrally coordinated with six hydroxyl groups. As these octahedrons share their vertices, they form bidimensional sheets [17].

When some Mg(II) cations are replaced with Al(III), hydrotalcite forms and it acquires a positive residual charge. To compensate this positive charge, an anion is required, generally located in the interlaminar area, together with water molecules. The interlaminar anion can be exchanged with many other anions in an aqueous or organic medium. Hydrotalcites or similar materials can be readily synthesised in the laboratory. The variety of families of materials of the hydrotalcite type that can be prepared is enormous.

$[M^{2+}_{1-x}M^{3}+_{x}(OH)_{2}]^{x+}[A^{n-}]_{x/n} \cdot mH_{2}O$

Where M(II) can be divalent cations of the Mg(II), Zn(II), Ni(II) type, etc. and M(I-II) cations of the Al(III), Fe(III), Ga(III) type, etc. The A anion can be $(CO_3)^{2-}$, Cl^- , $(NO_3)^{-}$, $(SO_4)^{2-}$, iso and heteropolyanions, and carboxylates, among others.

Hydrotalcite-type compounds can only be obtained when $0.2 \le x \le 0.33$: for values of x outside this range, hydroxides or oxides without an excess cation form, mixed with hydrotalcite.

The calcination temperature significantly affects hydrotalcites and produces various changes in their physico-chemical properties.

Hydrotalcite calcination products have the ability to reconstruct the initial laminar structure when they come into contact with aqueous solutions that contain the initial anion or another, different ion [18-22].

2. EXPERIMENTAL PROCEDURE

The experimental procedure for preparing hydrotalcite is described by I.Nebot-Díaz [17]. The systems studied were MgAI, CoAI, and NiAI. In each system, the stoichiometric ratio between the divalent and trivalent cations was varied, the nomenclature indicating the stoichiometric ratio between them (e.g. MgAl41, is the system Mg-AI, with a ratio of 4:1 Mg:AI).

The method of radiation absorption at a certain wavelength was used to determine a curve calibration by the Lambert-Beer Law. The wavelength used was 360nm, as this was the experimentally determined wavelength at which radiation absorption by the chromate anion maximised.

2.1. CHARACTERISATION METHODS

• **X-ray diffraction (XRD):** The X-ray diffraction technique was used to determine the crystalline phases in the sample, after the synthesis process.

A BRUKER-AXS, Mod D4 Endeavor, instrument with Cu cathode, in a range 2°q from 5 to 75°, with a measurement parameter of 0.05° 20 every 1.5sec was used. Samples were prepared by milling and subsequent deposition on a plastic mount 4mm in diameter.

• **Differential thermal analysis and thermogravimetric analysis:** The thermal analyses used in characterising the samples were thermogravimetric (TG) analysis (variation of mass as a function of temperature) and differential thermal analysis (DTA) (heat absorption or release as a function of temperature). DTA/TG allows the different processes (crystallisation, sintering, decomposition, etc.) that take place when a sample is subjected to thermal treatment at high temperatures to be studied.

A BAHR, Mod. STA503, instrument was used, using alumina crucibles and calcined alumina as reference material. A heating cycle at 1200°C with constant-rate heating of 10°C/min was used.

• **Infrared spectrometry:** The use of infrared radiation allows the type of atomic bond in the sample to be characterised, thanks to the characteristic energy absorption of the different types of vibration from the different bonds.

A JASCO Mod. FT/IRFT-6200, instrument in a range of 4000-400cm⁻¹ with a resolution of 1cm⁻¹ was used. The samples were prepared in pellets using KBr as a base transparent to the radiation.

• Scanning electron microscopy (SEM): The SEM technique is of major importance for the microstructural characterisation of the elements. In this technique, electrons are accelerated in an electric field in order to use their wave behaviour; this takes place in the column of the microscope, where they are accelerated by a voltage difference of 1000 to 30000 volts. The accelerated electrons leave the gun and are focused by the condenser lenses and objectives, which reduce the image of the filament, so that the smallest possible electron beam impinges on the sample. When this beam impinges on the sample, many interactions take place between the electrons in the beam and the atoms in the sample. On the other hand, the energy that the electrons lose when they hit the sample can cause other electrons to be ejected and produce X-rays.

The instrument used was a LEICA Leo 440i unit with microanalysis by OXFORD Instruments. The samples were coated with carbon. The microscope operating conditions were as follows: acceleration voltage 10–20kV, focal distance 10–25mm, and secondary and backscattered electron detectors were used. The filament used was made of W and of LaB₆.

 UV-Vis spectrophotometer: The UV-Vis radiation absorption technique by diluted solutions allows, by means of the Lambert-Beer equation, the determination of the target concentration as a function of the absorption of a certain wavelength, using calibration straight lines.

A JENWAYS, Mod.6405, instrument at a fixed wavelength of 360nm was used.

3. RESULTS AND DISCUSSION

3.1. Mg-Al SYSTEM

The XRD analyses (Figure 1) showed that a hydrotalcite phase was obtained in every case, though in the MgAl12 sample, the excess aluminium that did not become part of the hydrotalcite precipitated as bayerite $(Al(OH)_3)$, as was to be expected. It may also be observed that, as the molar ratio between Mg and Al decreased, the crystallinity of the hydrotalcite phase decreased, the worst being in the ratio MgAl12.



Figure 1a. XRD MgAl41 system.

Figure 1b. XRD MgAl12 system.

The thermal tests show what was to be expected in view of the diffraction results (Figure 2). Two endothermic signals were detected in the differential thermal analysis, accompanied by mass losses at about 200 and 400°C. These signals corresponded at 200°C to hydrotalcite hydration water loss, while the (stronger) signal at 400°C corresponded to interlayer carbonate and water loss. In the case of sample MgAl12, this signal was weaker than in the others, owing to the poor formation of the hydrotalcite structure, as was observed in the corresponding X-ray diffraction diagram (Figure 2b).



Figure 2a. DTA/TG MgAl41 system.

Figure 2b. DTA/TG MgAl12 system.

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The infrared absorption spectra (Figure 3) show two clearly differentiated regions. In the first to about 1200cm⁻¹, three well-defined signals can be observed: 3500cm⁻¹, corresponding to the stretching vibration of the –OH group; at 1650cm-1, corresponding to the u₃ mode of the CO₃ group; and at 1400cm⁻¹, corresponding to the bending vibration of H₂O [23].

In the second region, at wavelengths below 1200cm⁻¹, a multitude of signals may be observed, which corresponded to the translation vibrations of the Mg-OH and Al-OH bonds. Owing to the multitude of possible vibrations, the signals in this region were very difficult to assign.



Figure 3a. IR MgAl41 system.

Figure 3b. IR MgAl12 system.

In all images obtained by the SEM technique (Figure 4), it may be observed that the synthesised material had a nanometric particle size. Particles sized below 200nm were involved in every case, which provided the material with a high specific surface area, as well as many future possibilities in applications where a nanostructured material would be required.

In sample MgAl41 (Figure 4a), the plate-like structure of the hydrotalcite phase can be clearly observed. As the Mg/Al ratio decreased, this definition was lost, it again being the MgAl12 sample where the plate-like structure could hardly be seen (Figure 4b).



Figure 4a. MEB sistema MgAl41.

Figure 4b. MEB sistema MgAl12.

The results obtained after the adsorption process and reconstruction of the hydrotalcite in the Cr(VI)solution are detailed in Table1.

SAMPLE	End abs	Start ppm	End ppm	% reduction
MgAl41Cr	0.11	100	2.66	97.34
MgAl21Cr	0.13	100	3.37	96.625
MgAl12Cr	0.17	100	5.21	94.792

Table 1. Reduction of Cr(VI) concentration in the water using the MgAl system.

The degree of reduction of the Cr(VI) concentration was always above 90%, indicating the high Cr(VI) removal capability from aqueous media. A detail to be taken into account was the high reduction obtained with the MgAl12 sample, which suggests that Cr(VI) removal occurred mainly by a surface adsorption process, while the smallest part entered the interlayer, reconstructing the hydrotalcite-type compound.

A possible explanation for this fact could be the high affinity of the calcined compound for the CO_3^{2-} anion in order to proceed with the reconstruction. This CO_3^{2-} would come from environmental CO_2 that dissolves in the reaction medium.

3.2. Co-Al SYSTEM

In the CoAl system, the hydrotalcite phase formed in the two studied ratios (2:1 in red and 1:2 in blue). When the CoAl ratio was greater, the degree of hydrotalcite development improved (Figure 7).

The halite (NaCl) phase was detected in both samples, owing to lack of thorough washing (2:1 in blue and 1:2 in red).





Figure 5a. XRD CoAl21 system.

Thermal analysis (Figure 6) showed no clear separation between the signals for hydration water and carbonate loss, as had been noted in the MgAl system. Carbonate loss took place at temperatures close to 300°C, the signal overlapping with that of hydration water loss.

The presence of a pronounced endothermic signal at about 820°C, without a related mass loss, was attributed to the melting process of the NaCl present in the samples. Above 850°C, a continuous mass loss began, associated with a sintering process of the sample, owing to the presence of the molten NaCl.



Figure 6a. DTA/TG CoAl21 system.



Using the SEM technique, the plate-like structure of the hydrotalcite in sample CoAl21 could be observed in detail (Figure 7a). A hydrotalcite particle was involved, which is viewed from above. As this particle slopes slightly, the different superimposed sheets can be observed.

The crystals with cubic symmetry correspond to the NaCl that precipitated during sample drying.

In the CoAl12 sample (Figure 7 b), the laminar structure of hydrotalcite was not observed, as had been verified in the case of the CoAl21 sample. Cubic crystals corresponding to NaCl could be observed, as is the case in the image shown in detail.

Figure 5b. SEM CoAl12 system.





Figure 7a. SEM CoAl21 system.



Figure 7b. SEM CoAl12 system.

The degree of reduction of the Cr(VI) concentration differed greatly with respect to that of the MgAl system (Table 2). A possible explanation is that the presence of chlorides in the sample, owing to lack of washing, inhibited the hydrotalcite adsorption capacity.

SAMPLE	End abs	Start ppm	End ppm	% reduction
CoAl21Cr	1.22	100	48.87	51.125
CoAl12Cr	1.43	100	57.62	42.375

Table 2. Reduction of Cr(VI) concentration in the water using the CoAl system.

Once again it may be observed that with better hydrotalcite formation, in the case of sample CoAl21, there was a greater reduction in the Cr(VI) concentration in the solution. In this case, the difference was much more noticeable than in the MgAl system.

3.3. Ni-Al SYSTEM

The same trend was repeated as in the previous cases: that is, with a 2:1 Ni:Al ratio, hydrotalcite was formed and detected, whereas in the lower Ni:Al ratio, hydrotalcite did not form, though the bayerite phase, $AI(OH)_3$, appeared.

Once again, lack of washing generated NaCl, halite, and as $Ni(NO_3)_2$ was used as Ni precursor salt, NaNO₃ also formed in both samples.





Figure 8b. XRD CoAl12 system.

The thermal behaviour was analogous to that of the previous cases (Figure 10). In the case of the NiAl21 sample, the signal corresponding to carbonate loss could be slightly differentiated, whereas that in the NiAl12 sample overlapped with the hydration water loss signal.

The signal corresponding to NaCl fusion and $NaNO_3$ decomposition, by mass loss at about 700°C, was also observed.



Figure 9a. DTA/TG NiAl21 system.

Figure 9b. DTA/TG CoAl12 system.

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The micrograph obtained by SEM of the NiAl21 sample displays a detail of the plate-like structure of hydrotalcite (Figure 10a).

In sample NiAl12, this laminar structure was not observed, though the particle morphology seemed to resemble the structure of NaCl and $NaNO_3$ (Figure 10b).



Figure 10a. SEM NiAl21 system.



Figure 10b. SEM CoAl12 system.

The values obtained for Cr(VI) reduction (Table 3) were similar to those obtained in the CoAl system. In addition to the explanation suggested for that system, Goswamee et al. [24] showed that Cr(VI) adsorption by laminar double hydroxides based on the system Ni-Al and Zn-Al decreased notably in comparison with adsorption by Mg-Al systems.

SAMPLE	End abs	Start ppm	End ppm	% reduction
NiAl21Cr	1.15	100	45.96	54.04
NiAl12Cr	1.38	100	55.54	44.46

Table 3. Reduction of Cr(VI) concentration in the water using the NiAl system.

4. CONCLUSIONS

When the molar ratio between M(II)/M(III) was reduced, hydrotalcite formation decreased, the hydrotalcite exhibiting a very low degree of crystallinity.

Calcined hydrotalcite had a greater Cr(VI) adsorption capacity owing to the elimination of the CO_3^{2-} anion and H₂O from the interlayer and increased specific surface area.

The MgAl hydrotalcite was saturated in the first 5 minutes of contact with the Cr(VI) solution, but the CoAl and NiAl hydrotalcites displayed a slower adsorption process of about 30 minutes. This is because the MgAl hydrotalcite exhibits better formation and is therefore the standard hydrotalcite.

When the molar ratio between the divalent cation and aluminium was 1:2, as the work was not performed in the stoichiometry corresponding to hydrotalcite, an aluminium segregation took place and bayerite $(AI(OH)_3)$ formed.

When the molar ratio in the same system was decreased, the hydrotalcite adsorption capacity decreased, as hydrotalcite formation was also impaired.

The NaCl found in hydrotalcite owing to lack of washing of the hydrotalcite reduced the hydrotalcite adsorption capacity.

The use of precursors of the hydrotalcite type for obtaining compounds of the spinel type could be applied to the ceramic pigment industry. This would reduce energy costs in the synthesis process, as well as completely eliminate all mineralisers, with the ensuing environmental benefit. This could all be done without the synthesis process entailing any modification of current industry infrastructures.

The use of hydrotalcite as a Cr(VI) adsorbing medium can be considered a valorisation system for toxic waste, as it can be used as a source of Cr in different reaction media.

REFERENCES

- [1] J.L.Amorós, A.Barba, V.Beltrán. ESTRUCTURAS CRISTALINAS DE LOS SILICATOS Y ÓXIDOS DE LAS MATERIAS PRIMAS CERÁMICAS. Ed. ITC (1994)
- [2] G.Buxbaum. INDUSTRIAL INORGANIC PIGMENTS, Ed. Wiley-VCH (1991)
- [3] J.W.Mullin. CRYSTALLIZATION, Ed BH (2000)
- [4] P.Escribano, J.B.Carda, E.Cordoncillo. ENCICLOPEDIA CERÁMICA, Vol1. ESMALTES Y PIGMENTOS CERÁMICOS: Ed. Faenza Editrice Ibérica, SL (2001)
- [5] Katz, S A, Salem, H , Journal of applied toxicology 13 (3), p.217-224, (1993)
- [6] Boddu, Veera M. / Smith, Edgar Dean, UNITED STATES PATENT AND TRADEMARK OFFICE PRE-GRANT PUBLI-CATION, Apr 2002 patno:US20020043496
- [7] Li, Zhaohui / Bowman, Robert S. , Water Research, 35 (16), p.3771-3776, Nov 2001
- [8] Wei, Linsen / Yang, Gang / Wang, Ren / Ma, Wei, Journal of hazardous materials, 164 (2-3), p.1159-1163, May 2009
- [9] Zachara, J.M. / Heald, S.M. / Jeon, B.H. / Kukkadapu, R.K. / Liu, C. / McKinley, J.P. / Dohnalkova, A.C. / Moore, D.A., Geochimica et Cosmochimica Acta, 71 (9), p.2137-2157, May 2007
- [10] C. Unnithan Harikuttan / I. Dhanya / P. Predeep , AIP Conference Proceedings, Apr 2008
- [11] Li, Xiaohong / Birnbaum, Jerome C / Williford, Rick E / Fryxell, Glen E / Coyle, Chris A / Dunham, Glen C / Baskaran, Suresh, Chemical communications (Cambridge, England), (16), p.2054-2055, Aug 2003
- [12] Kaball, Z. / Hemidouche, S. / Allalou, O. , Desalination, 249 (2), p.768-773, Dec 2009



- [13] Namasivayam, C / Sureshkumar, M V , Bioresource technology, 99 (7), p.2218-2225, May 2008
- [14] Han, Xu / Wong, Yuk Shan / Wong, Ming Hung / Tam, Nora Fung Yee, Water environment research: a research publication of the Water Environment Federation, 80 (7), p.647-653, Jul 2008
- [15] Bai, Yu / Zhang, Jie / Li, Yi-Fan / Gao, Yu-Nan / Li, Yong , Journal of Zhejiang University. Science. B, 6 (5), p.427-432, May 2005
- [16] Lazaridis, N K / Asouhidou, D D , Water research, 37 (12), p.2875-2882, Jul 2003
- [17] I.Nebot-Díaz, ESTUDIO Y CARACTERIZACIÓN DE COMPUESTOS TIPO ESPINELA MEDIANTE RUTAS DE SÍNTESIS NO CONVENCIONALES. APLICACIÓN A LA INDUSTRIA CERÁMICA. Tesis Doctoral. Universitat Jaume I, (2001)
- [18] F.Cavani, A.Trifiro, A.Vaccari, Catalysis Today 11 (2) pp 177-301 (1991)
- [19] F.M.Labajos, V.Rives, Inorganic Chemistry 35 pp 5313-5318 (1996)
- [20] S. Martinez-Gallegos, H. Pfieffer, E. Lima, M.Espinosa, P. Bosh, S. Bulbilian, Microporus and Masoporous Materials 94 (2006) 234.242.
- [21] E. Kanezaki, Solid State Ionics 106 pp. 279-284 (1998).
- [22] S. Martinez-Gallegos, S. Bulbulian, Clays and Minerals, Vol. 52, No. 5, 650-656 (2004).
- [23] Kloprogge, J. Theo and Frost, Ray L. and Hickey, Laisel (2004) FT- Roman and FT-IR spectroscopic study of the local structure of synthetic Mg/Zn/Al-hydrotalcites, Journal of Roman Spectroscopy, 35pp. 967-974.
- [24] Rajib Lochan Goswamee, Pinaki Sengupta, Krishna Gopal Bhattacharyya, Dipak Kumar Dutta, Applied Clay Sience, 13, 21-34 (1998).