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Sorption study of an anionic dye – benzopurpurine 4B – on calcined and uncalcined Mg–Al layered double hydroxides

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ABSTRACT

In this paper, the elimination from aqueous solution of the pollutant benzopurpurine 4B by Mg–Al–CO_3 hydrotalcite and its modified form Mg–Al–500 has been studied. Mg–Al–CO_3^{2-} layered double hydroxide with an Mg/Al molar ratio of 2.0 was synthesized by the co-precipitation method, and its modification was carried out by calcination. The affinity of these materials with a mixture of benzopurpurine 4B was studied as a function of dye–adsorbent contact time, initial pH of the solution, initial dye concentration and temperature. The results indicate that HDLs were effective in removing benzopurpurine 4B anionic dye. Their saturated adsorption capacities are very high, particularly for the calcined material Mg–Al–500 compared to the standard one Mg–Al–CO_3^{2-}.

The characterisation of the solid Mg–Al–500, both fresh and after removal of the dye by X-ray diffraction and infrared spectroscopy, shows that the benzopurpurine 4B adsorption on this calcined phase is enhanced by reconstruction of a matrix hydrotalcite intercalated by the dye, with basal spacing of 23.77 Å, which is larger than that of Mg–Al–CO_3^{2-} LDHs (7.57 Å).

1. Introduction

Removal of textile dyes from wastewater is one of the several major environmental concerns because they are difficult to be removed by conventional treatment systems (such as chemical coagulation, oxidation, filtration, carbon adsorption and photodegradation techniques) [1,2].

However many dyes are designed to be resistant to biological degradation and conventional chemical treatments because of their complex structure and xenobiotic properties [3,4].

Recently the possibility of an adsorption process to remove dyes from textile industries has been considered, especially when they are non-biodegradable [5].

In this way the application of layered double hydroxides (LDHs) and their calcined products (CLDHs) as adsorbents to remove anionic dyes from wastewater have received considerable attention in the recent decade because of their unique layered structures and high anion exchange capacities [6–9]. Layered double hydroxides (LDHs), also known as anionic clays, consist of positively charged brucite-like hydroxide sheets with anions intercalated in between the layers. Their general formula may be represented as $[M^{II}_{1-x}M^{III}_x(OH)_2]A^{n-}_{x/n}\cdot mH_2O$, where M^{II} and M^{III} are metal cations that occupy octahedral sites in the hydroxide layers. A^{n-} is an exchangeable interlayered anion and x is defined as the $M^{III}/M^{II}+M^{III}$ ratio [10].

By heating at a temperature of 500 °C, LDHs are converted into mixed oxides [11]. An important property of calcined LDHs (CLDHs) is the so-called "memory effect", that is the calcined anionic clays can reconstruct their original layered structure after adsorption of various anions.

In the present study, the adsorptive capabilities of benzopurpurine 4B (Fig. 1) were investigated as a model for the toxic anionic and organic contaminant, which may be useful in treating effluents from textile industry.

The removal of this dye onto calcined and uncalcined Mg–Al–CO_3^{2-} LDHs was evaluated by studying the effect of various factors such as dye–adsorbent contact time, pH, initial concentration of dye and temperature.

2. Materials and methods

Mg–Al–CO_3^{2-} LDH has been prepared by the co-precipitation method from magnesium chloride, aluminium chloride and sodium carbonate at moderate conditions following Reichle's procedures [12]. The material obtained is called Mg–Al–CO_3^{2-}.

Part of Mg–Al–CO_3^{2-} LDH with Mg/Al=2 was calcined in air at 500 °C during 4 h to prepare the mixed oxide. The material obtained is called Mg–Al–500.

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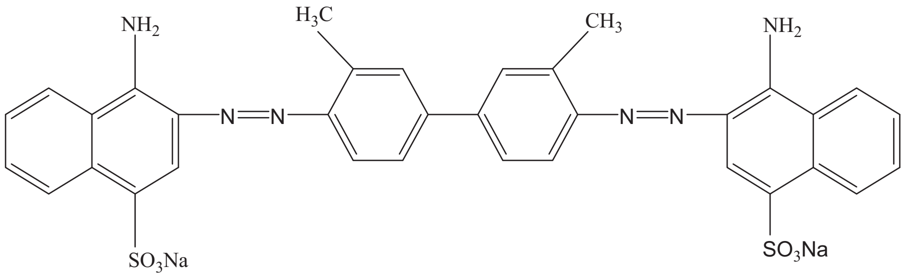

Fig. 1. Chemical structure of benzopurpurine 4B dye.

3. Sorption experiments

All experiments of the dye removal were performed using a batch method by shaking a predetermined amount of adsorbent into 100 ml conical beakers containing 50 ml dye solutions of varying concentrations.

After a given contact time for adsorption (16 h) at room temperature, the solid material was separated by centrifugation.

The dye concentrations were measured at a wavelength $\lambda_{\max}=500$ nm, which corresponds to maximum absorbance of the benzopurpurine 4B, using double-beam SAFAS spectrophotometers.

The adsorption capacity q_e (mg/g), which represents the amount of adsorbed dye per amount of dry adsorbent, was calculated using the following equation:

$$q_e=(c_i-c_e)\frac{V}{M} \tag{1}$$

where c_i and c_e are the initial and final concentrations (mg/l) of dye, respectively, and M is the mass of adsorbent (g) and V is the solution volume.

4. Results and discussion

Representative XRD pattern (Fig. 2a) of Mg–Al–CO_3^{2-} shows a structural feature characteristic of hydrotalcite-like compounds with relatively good crystallinity [13].

The lattice parameters are a=3.02 Å and c=22.71 Å, with d_{003}=7.57 Å.

The turbostratic feature is confirmed by TEM. Indeed, Mg–Al–CO_3^{2-} LDH appears as aggregates of thin crumpled sheets with any definite form (Fig. 3).

For Mg–Al–500, Fig. 2c shows that the layered structure of Mg–Al–CO_3^{2-} was destroyed by heating at 500 °C and indicates only MgO peaks, suggesting an almost total decomposition of the LDH and elimination of most interlayer carbonate anions and water [14].

The IR spectrum of Mg–Al–CO_3^{2-} resembles those of other hydrotalcite-like phases. Fig. 4a shows a broad peak at 3385 cm^{-1} due to OH stretching and adsorbed molecules of water. Carbonate and metal hydroxide stretching appeared at 1362–1462 and 763 cm^{-1}, respectively.

The Mg–Al–CO_3^{2-} LDH and Mg–Al–500 exhibit significant different behaviour. On the one hand, the Mg–Al–CO_3^{2-} LDH after uptake of benzopurpurine 4B gives a basal spacing of 7.7 Å (Fig. 2b), which is almost the same as that of LDH precursor. Because the affinity of dye ion towards LDH is much lower than that of carbonate, the ion-exchange of benzopurpurine 4B for carbonate in the LDHs interlayer is difficult [15,16]. As a result, the uptake of benzopurpurine 4B by Mg–Al–CO_3^{2-} mainly occurs by physisorption on the surface of LDH [17].

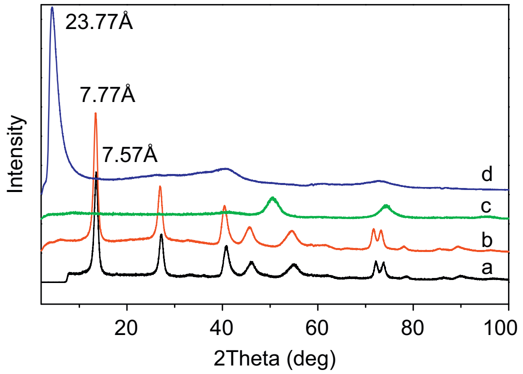

Fig. 2. X-ray diffractogram of (a) Mg–Al–CO_3^{2-}, (b) Mg–Al–CO_3^{2-}dye, (c) Mg–Al–500, (d) Mg–Al–500 (dye).

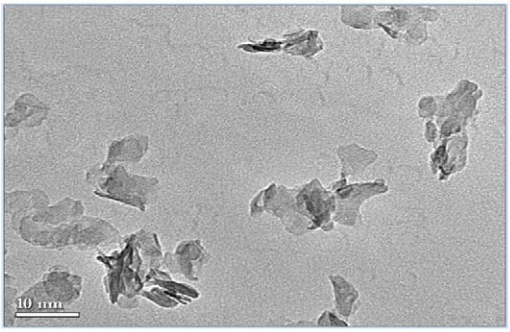

Fig. 3. TEM micrograph of Mg–Al–CO_3^{2-}.

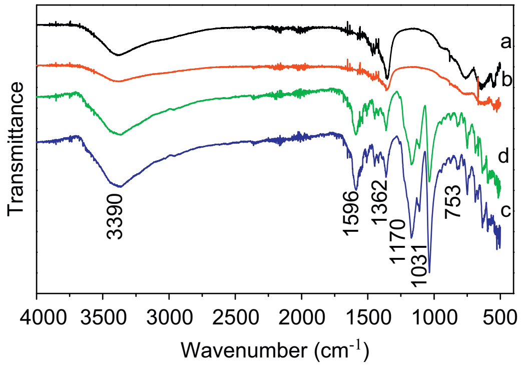

Fig. 4. FT–IR spectra for (a) Mg–Al–CO_3^{2-}, (b) Mg–Al–500, (c) Mg–Al–500 (dye), (d) benzopurpurine 4B.

On the other hand, reconstruction of Mg–Al–500 has been observed to take place after dye sorption, giving a basal spacing of 23.77 Å (Fig. 2d); this clearly shows that the dye anion has been intercalated in between the layers. We can explain that the high