

Removal of Congo Red from Aqueous Solutions by Cationic-Starch/Clay Bionanocomposites

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INTRODUCTION

Adsorption has been turned to as one of the most effective and low-cost wastewater treatment methods. Activated carbon is one of the most available adsorbents. However, the relatively high production and regeneration cost of activated carbon and approximately 10-25% loss during regeneration by chemical or thermal treatment makes this adsorbent economically less applicable. Therefore much research concerning adsorbents made from natural sources such as clays, zeolites, sawdust and/or other low-cost and available solid materials to remove dyes from wastewater has been undertaken (Özdemir et al, 2004).

Clay minerals and specially organoclays are commonly used for environmental applications of including water treatment, removal of pollutants as well as controlled release and stabilization of pesticides (Ruiz-Hitzky et al., 2010a). In this context, conventional organoclay materials based on alkylammonium cations have proved to be useful for the removal of organic pollutants from water and effluents (Ruiz-Hitzky et al., 2010a).

The organophilic properties of these organoclays enhance the capability to efficiently adsorb organic compounds, especially aromatic molecules pollutants such as frequently used dyes. Hydrophilic biopolymers can be also used as organomodifiers in order to better match the polarity of the matrix. This is the case of organoclays prepared by association of clays with polysaccharides such as chitosan (Darder et al., 2012).

Starch, a polysaccharide derived from corn, wheat, rice or potato, is one of the main neutral polysaccharides specially used in the preparation of green

nano-composites (Ruiz-Hitzky et al., 2010b).

Most of the bionanocomposites are prepared by incorporation of natural or synthetic clay minerals, with and without organic modifications, as inorganic nanofillers, which results in intercalation or exfoliation compounds (Xie et al., 2011).

The preparation of charged starch-derivatives attracts increasing interest as it could be more easily assembled to charged nanofillers as it is the case of charged nanofillers for other applications beside bioplastics. In this context, it has been reported the use of cationic starches as effective adsorbents for removal of dyes present in wastewater (Ju, 2000). More recently, Xing et al. (2012) have reported the association of cationic starch with clays for removal of brilliant blue X-BR dye.

In the present study, we have prepared bionanocomposites based on the assembly of a cationic starch to smectites with the aim to develop new adsorbents for organic dye pollutants. In this way, a cationic potato starch (CST) was intercalated in two types of smectites, a commercial Cloisite®Na (CL) and a natural purified bentonite (Bnt) from Algeria (Khalaf et al., 1997), and the resulting materials were tested in the adsorption of Congo Red (CR) in aqueous solution.

MATERIAL AND METHODS

Potato starch and glycidyltrimethylammonium chloride ((2,3-epoxypropyl) trimethyl ammonium chloride) were supplied by Aldrich, sodium hydroxide was obtained from Fluka and absolute ethanol from J.T. Baker. Commercial Cloisite®Na was obtained from Southern Clay Products and the natural bentonite from Maghnia (Algeria) was kindly supplied by the Société des

Bentonites d'Algérie (BENTAL) company. CR dye was purchased from Aldrich, and was used without purification. The structure of this dye is shown in Fig. 1.

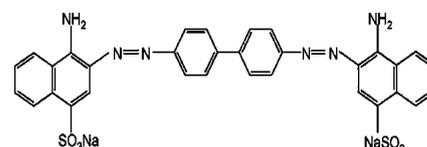


fig 1. Molecular structure of Congo red dyestuff.

Starch has been cationised by treatment with (2,3-epoxypropyl) trimethyl ammonium chloride in the presence of sodium hydroxide at 80 °C for 24 h. Then, absolute ethanol was added to the mixture, and the precipitated starch was filtered. The raw product was washed several times with ethanol and dried at 40 °C for 24 h. The sodium bentonite (Na-Bnt) was prepared by ion-exchange reaction of the raw bentonite with sodium chloride. Both sodium exchanged smectites (Na-Bnt and CL) suspended in water were assembled to the cationic starch (CST) by direct adsorption, using a clay:CST=1:2 ratio. The resulting hybrid materials were recovered by centrifugation, washing with ethanol (50 %) and bidistilled water, and finally dried by freeze-drying. The starting compounds and the resulting bionanocomposites were characterized by: CHN elemental analysis (Perkin-Elmer 2400 series II), XRD (Bruker D8 T2T Advance), ATR (Shimadzu, GLADIATOR10), ¹³C solid state NMR (NMR Spectrometer AVANCE II (BRUKER), DSC (SEIKO SSC/5200) and FE-SEM (FEI NanoSEM230).

The CR adsorption studies were conducted in a thermostated water bath by shaking for 24 h 50 mg of sample (pristine clay or the CST/clay bionanocomposite) in 20 ml of solution containing 20 ppm of CR. The solids were recovered by centrifugation and the residual concentrations of the dye in

palabras clave: Minerales de la arcilla, Almidón catiónico, Rojo Congo

key words: Clay minerals, Cationic starch, Congo red.

the supernatants were determined with a UV-vis spectrophotometer (Shimadzu UV-2401) at 497 nm (Lambert-Beer law).

RESULTS AND DISCUSSION

ATR spectra (not shown) and the elemental chemical analysis confirm that the cationic ammonium group was introduced in the starch by the appearance of the characteristic band at 1477 cm⁻¹ (Wang et al., 2009) and by the amount of nitrogen present in the cationic starch (Table 1)

Material	%C	%H	%N
ST	39.57	6.26	0
CST	40.83	7.92	4.1
CST/Na-Bnt	12.16	2.74	1.11
CST/CL	13.50	2.78	1.18

Table 1. Elemental chemical analysis.

Assembly of CST to the clays was deduced from ATR spectra in the 4000-400 cm⁻¹ range (not shown). In the spectra of both CST/Na-Bnt and CST/CL bionanocomposites are observed characteristic absorption bands of both, the cationic starch and the pristine clay.

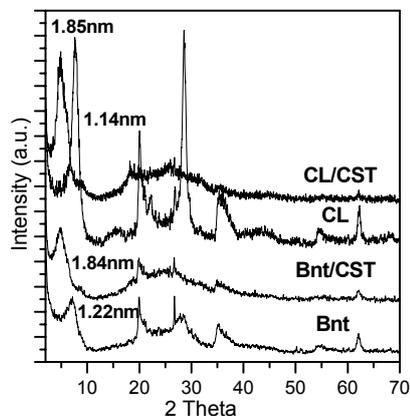


fig 2. XRD patterns of clays and Clays/CS bionanocomposites, with 1/2 ratio.

Intercalation was studied by XRD (Fig. 2). The basal spacing values of starting clays were 1.23 nm for Na-Bnt and 1.14 nm for CL. After the treatment with the cationic starch, the typical diffraction peaks of both clays shift to lower 2theta angles and the deduced values of the basal spacing increase in both cases to values around 1.85 nm. These results confirm that the cationic starch has been successfully intercalated into the interlayer region of both smectites. It is difficult to conclude whether the CST is arranged in monolayer or bilayer in these bionanocomposites because the

conformation of the polymer is still unknown.

In view to explore the properties of these bionanocomposites in remediation of polluted water we have evaluated their capacity of adsorbing aromatic dyes. Sodium pristine clays and CST/clay bionanocomposites were kept in contact with 20 ppm CR water solutions for 24h. Fig. 3 shows the retention capacity of each material.

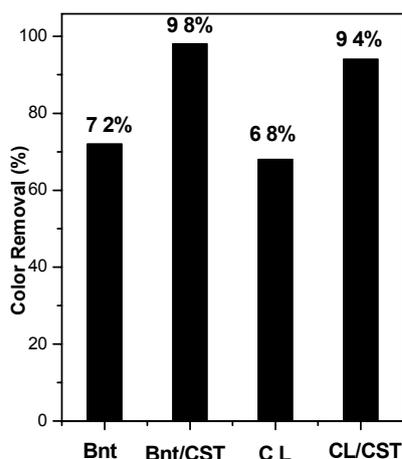


fig 3. Congo red removal by clays and clays/cationic starch bionanocomposites

In both systems, the presence of intercalated cationic starch results in a greater adsorption capacity for this anionic dye in comparison to the sodium smectites. This behavior may be related with two relevant features in the bionanocomposites:

- 1) their higher interlayer distances compared to pristine clays and
- 2) the presence of cationic sites coming from the protonated organic groups present in the intercalated cationic starch.

CONCLUSION

In this work, we have introduced some preliminary results concerning the preparation of bionanocomposites based on intercalation of a cationic starch into two types of smectites, a commercial one and a bentonite from Algeria, for potential uses in environmental applications. The bionanocomposites here prepared show interlayer distances larger than those reported in the literature. Moreover, we have shown their adsorption properties for removal of anionic dyes, such as CR,

which could be of interest for applications in the environmental remediation area.

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