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Ti/Cr-pillared clay as photocatalysts for 4-chlorophenol removal in water

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ABSTRACT

Ti-pillared and Ti/Cr-pillared montmorillonite have been prepared from natural bentonite and characterized by UV-Vis DRS and X-ray diffraction. The photocatalytic activities have been tested for the removal of 4-chlorophenol in water. The influence of the Ti/Cr ratio and the calcinations method on these activities has been investigated. It was found that the photocatalytic activities increase with increasing the Cr/Ti ratio up to 0.1 after which it becomes almost constant.

Keywords: Photocatalysis; Pillared clays; Chlorophenols; Water reuse

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1. Introduction

Many regions in the world are confronting constraints of water supply shortage and the imbalance between natural water availability and demands. This imbalance is continuously exacerbating with time, mainly because of insufficient sanitation services, increased industrial activities with inadequate means for treatment of liquid disposal and increasing use of fertilisers and pesticides. At the same time, these wastewaters could represent an important resource of water. In this regard, technologies of wastewater treatment are essential not only in terms of environmental impact, but also for provision of economically sound and sanitarily safe water which could be used for agriculture, industrial cooling, etc.

One technology, which is expected to develop in the future, is heterogeneous photocatalysis, since: (i) it does not need any chemicals addition; (ii) it is suitable for treating water with low concentrations of organic pollutants, (iii) it is non-specific, and (iv) it can lead to the total mineralization of organic compounds. This technology can use solar energy, which can be of particular interest for Southern countries.

Some TiO_2 samples are by far the most active photocatalysts for degrading organic pollutants in gaseous or aqueous phases [1].

4-Chlorophenol is considered as a priority pollutant in water stream. It is used as an intermediate in organic synthesis and furthermore it can be generated as a by-product during chlorine disinfection of water containing phenolic compounds. Because of its toxic and carcinogenic properties and its resistance to biological treatment, this compound has been taken as a model molecule in this investigation.

Currently many research projects are designed to improve the performance of TiO_2 photocatalyst. That can be achieved by decreasing the particle size of the photocatalyst down to nanoparticles, by coupling semiconductors or adding another adsorbent to the

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semiconductor [1-3]. On the other hand, reducing the overall process cost requires to avoid microfiltration by immobilising the semiconductor catalyst on a support. However, this immobilisation should be carried out to limit a decline in the photocatalytic activity.

The progress realised in the clay pillaring process by various metallic species opens the route for the application of pillared clays as photocatalysts. These solids should, in principle, add to the photocatalytic properties of the semiconductor intercalated in the interlayer space owing to the physico-chemical properties of clays, such as the adsorption capacity due to the large surface area, and the flocculation facility [4]. Furthermore, the pillared clays are characterized by their nanosized metal oxide pillars which can increase the photocatalytic activities of these interlamellar semiconductor oxides [5-6]. Whilst the role of the adsorption step in the photocatalytic process has been studied, and several studies have shown that the reaction rate depends on the ability to concentrate the target compounds on the TiO_2 surface or in its vicinity [7]. In another hand doping of the semiconductor crystals with various transition metal ions also results in rather high quantum efficiency of photocatalytic systems [8–9].

This work aimed to explore the photocatalytic activity of nanosized mixed TiO_2/Cr_2O_3-pillared montmorillonite and the influence of varying the Ti/Cr ratio and the calcination method.

2. Experimental part

Bentonite from Maghnia in Western Algeria has been used as starting material for preparing the photocatalytic materials. It is composed essentially of montmorillonite with minor impurities (quartz, feldspar, calcite, etc.). It has a cation exchange capacity (CEC) of 90 meq 100 g^{-1} of bentonite. Its chemical composition (wt %) is: SiO_2 69.4; Al_2O_3 14.7; Fe_2O_3 1.2; MgO 1.1; CaO 0.3; Na_2O 0.5; K_2O 0.8; TiO_2 0.2. Its mass loss by ignition at 1173K is 11%. It was firstly purified and homogenized as described in a previous work [4]. The fraction with a particle size smaller than 2 μm was recovered and employed in the pillaring process.

Titanium tetraisopropoxide [Ti $(C_3H_4O_2)_4$] was used as the precursor of TiO_2. Hydrochloric acid (1 mol L^{-1}) was added under vigorous stirring, in order to obtain an H^+/Ti molar ratio of 4. To this mixture, distilled water was added and the resulting white sol was peptized further for several hours until a clear solution was obtained. The intercalation was performed by adding, drop by drop, the pillaring solution to the 1% Na-montmorillonite suspension with vigorous stirring. The stirring was then continued for three hours. The solid was separated by centrifugation, rinsed several times with distilled water and dispersed again in water. For intercalating chromium clusters, the pillaring agent containing hydroxychromium polycations was prepared by adding NaOH (0.2 mol L^{-1}) to Cr $(NO_3)_3$ (0.1 mol L^{-1}) drop by drop under vigorous stirring up to OH/Cr molar ratio value of 2. The resulting solution was aged for one week at room temperature. The Cr-intercalation was performed by adding the pillaring on week aged solution, drop by drop, to the dispersed clay suspension with vigorous stirring in such proportions as to achieve a required Cr/Ti ratio.

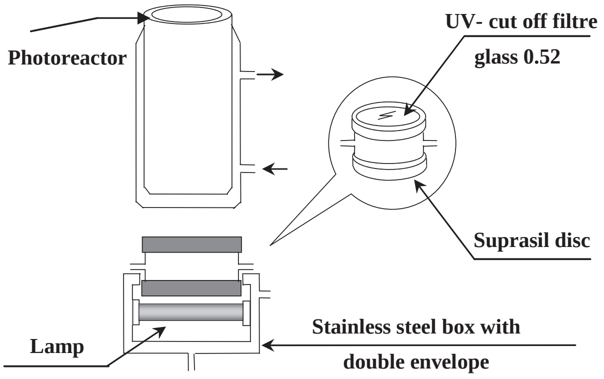

Fig. 1. Scheme of photoreactor.

The solids thus obtained were calcined at various temperatures or by microwave (MW) in a commercial MW oven operating at 2.45 GHz and at a power level up to 300 W for 15 min. The calcined solids have been characterised by UV-Vis. spectroscopy using a Perkin-Elmer spectrophotometer lambda 45 equipped with a Labsphere diffuse reflectance accessory. The mass of TiO_2 intercalated corresponded to 22% of the clay mass, whilst the chromium content has been varied between 0.19 to 0.42%.

Photocatalytic tests have been performed in a cylindrical 125 cm^3-batch reactor made of borosilicate glass on air and comprising at its basis an optical Pyrex glass window. The suspension was continuously stirred using a magnetic bar, and irradiated by a high-pressure mercury lamp (Philips HPK 125 W). An optical filter (cut-off at 340 nm) and a 2-cm thick glass cell in which cold water circulating (to prevent warming of the suspension by infrared irradiation) were interposed between the lamp and the photoreactor (Fig. 1).

The experiments were carried out with 20 cm^3 of solution containing 1.55×10^{-4} mol L^{-1} (20 ppm) of 4-chlorophenol. The powder (with and without Ti and

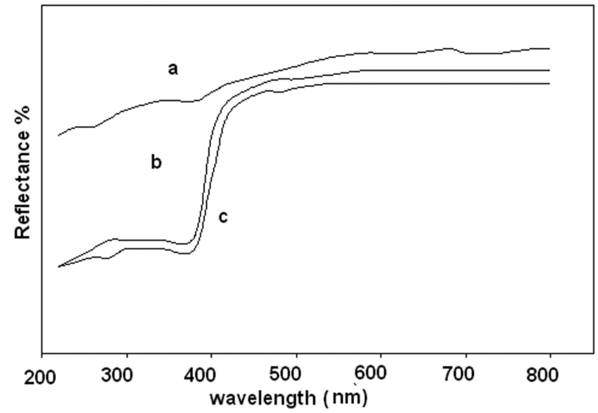

Fig. 2. The UV-Vis Diffuse reflectance spectra of: (a) Na-Montmorillonite; (b) Ti-Pillared Montmorillonite; (c) Ti/Cr-pillared Montmorillonite (Cr/Ti molar ratio = 0.1).

Cr) was added to this aqueous solution in an amount equal to 2.5 g L^{-1}. The suspension was stirred in the dark. The concentration of 4-chlorophenol (C) decreased slightly and became stable beyond 30 min. Although the Ti and Ti/Cr-pillared clay are more hydrophobic than the Na-clay, but at these experimental conditions no significant reduction in 4-chlorophenol content was observed due to adsorption phenomenon by these solids. This is explained probably, because the mass of catalyst added was not high enough for engendering a significant adsorption. C was measured by high performance liquid chromatography using an isocratic pump, a detector adjusted at 266 nm and a reverse phase C_{18} column (25 cm long; 4.5 mm diameter; 5 μm film thickness).

3. Results and discussion

The UV-Vis diffuse reflectance spectra (Fig. 2) of Ti-pillared montmorillonite Ti/Cr-pillared montmorillonite show an increased absorption toward longer wavelengths with respect to Na-montmorillonite. The most pronounced shift in the absorption onset was observed for Ti/Cr-pillared montmorillonite.

The XRD patterns (Fig. 3) allow one to determine the increase in montmorillonite basal spacing d_{001} because of the insertion of polycationic metallic species in the interlamellar space. The registered d_{001} values varied from 2.1 up to 2.4 nm, which represented an increase of 0.9–1.2 nm relative to the Na-montmorillonite precursor. The specific surface areas of samples were determined by N_2 adsorption measurements. Prior to measurements the samples were pre-treated in vacuum at 523 K for 1 h. The isotherms were analysed by the BET method. The specific surface area of the Na-montmorillonite used as support is 46 m^2/g, which increase to 140 m^2/g for Ti-montmorillonite and 171 m^2/g for Ti/Cr-montmorillonite.

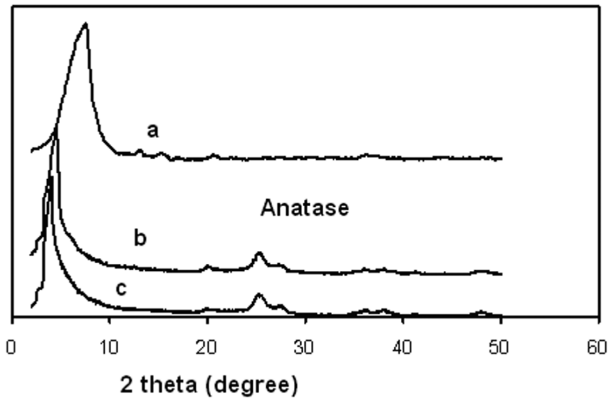

Fig. 3. XRD patterns of (a) Na-Montmorillonite; (b) Ti-pillared Montmorillonite; (c) Ti/Cr-pillared Montmorillonite (Cr/Ti molar ratio = 0.1).

3.1. Control experiments

In preliminary experience the potential leaching of Cr ions from the solid was checked by analyzing the used aqueous solution, after the solid separation, by complexation of chromium and analysed by UV spectrophotometer [10]. It was not found Cr ions in the solution.

Fig. 4 shows the influence of the Cr/Ti molar ratio on the photocatalytic activity by following the reduction of 4-chlorophenol concentration in aqueous media. The experimental results indicated that the activity increased from Cr/Ti = 0 to Cr/Ti = 0.1 and then slightly decreased for Cr/Ti = 0.2. This increase might be explained by the reduction of the electron-hole pair recombination rate. The Cr ions can play the role of

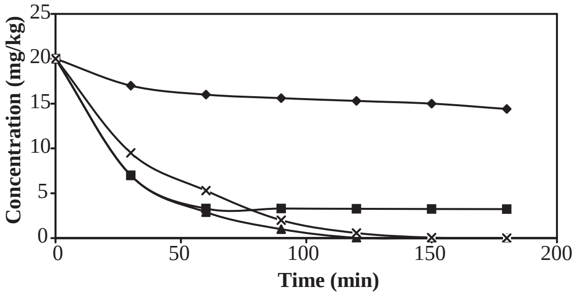

Fig. 4. The influence of Cr/Ti ratio on photocatalytic activities by measuring the reduction of 4-chlorophenol concentration: ◆-Cr/Ti = 0; ■-Cr/Ti = 0.2; ×-Cr/Ti = 0.1; ▲-uncalcined TiO_2 Degussa P-25 (the mass of TiO_2 corresponded to the mass intercalated in the clay).

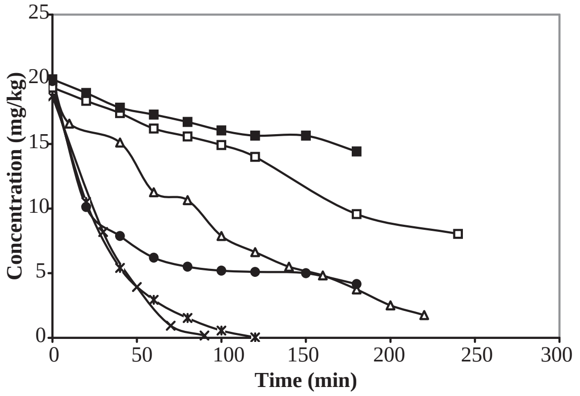

Fig. 5. The influence of calcination methods on the photocatalytic degradation of chlorophenol: (■-Ti-pillared Montmorillonite; □ -Ti/Cr-pillared Montmorillonite calcined at 600 C (Cr/Ti molar ratio = 0.1); Δ-Ti-pillared Montmorillonite calcined by MW; ● - Ti/Cr-pillared Montmorillonite calcined by MW (Cr/Ti molar ratio = 0.1); ∗ -Ti/Cr-pillared Montmorillonite calcined at 400 C (Cr/Ti = 0.1 molar ratio); ×-uncalcined TiO_2 Degussa P-25 (the mass of TiO_2 corresponded to the mass intercalated in the clay).

electron acceptors. Hence, photogenerated electrons and holes would be more efficiently separated. When the Cr ions content increases too much, holes may recombine with electrons trapped at the Cr ions, which might explained an optimum in Cr content. The same phenomenon was observed by other authors [11-13] in the case of powder TiO_2. Alternatively, chromium oxide might decrease the accessibility of 4-chlorophenol to TiO_2.

In Fig. 5 the abatement of 4-chlorophenol concentration is plotted as a function of time for Ti and Cr/Ti samples dried and calcined at 400 or 600 °C in an ordinary oven, or calcined by MW. The Cr/Ti-pillared clay calcined at 400 °C was found to be the most active, because beyond this temperature(at 600 °C) the clay structure might be start deteriorated. At equal mass of TiO_2, it was as active as TiO_2 Degussa P-25, a sample often used as a reference. The use of MW heating improved the activity of Ti-pillared clay, but not that of Cr/Ti-pillared clay.

4. Conclusion

On investigating the effect of addition of other cations to titanium during the pillaring process of montmorillonite upon the photocatalytic activity of these new class of solid photocatalysts, it has been found that adding chromium to titanium improves to a great extent the photocatalytic activity for the removal of 4-chlorophenol in water. This appears of interest for a novel use of clays—that are largely available, in particular in Algeria—for environmental purposes.

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