The Removal of 4-Chlorophenol and Dichloroacetic Acid in Water Using Ti-, Zr- and Ti/Zr-Pillared Bentonites as Photocatalyst

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Abstract: Heterogeneous photocatalysis could be alternative remediation technology for water since it does not need the addition of any chemicals and it is suitable for treating low concentrations of pollutant. Although the TiO_2 Degussa P 25 is most used photocatalyst its photonic efficiency still low and its recovery from water is considered as an awkward process. In this study the effect of zirconium addition to titanium was investigated. Ti/Zr-pillared montmorillonites 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 and dichloroacetic acid in water. The influence of preparation conditions and the calculation method, on these activities has been investigated. It was found that the photocatalytic activities increase by the addition of zirconium in pillorying process and the calculation by Microwaves (MW) improves the photocatalytic activities.

Key words: Photocatalytic Activities, Zirconium, Calcinations, Microwaves, Photonic Efficiency

INTRODUCTION

The need for water reuse on the large scale, particularly in the countries with limited hydric resources, becomes increasingly a reliable option. This is due to the non availability of water at low prices. The halocarbons in particularly Chlorophenols (CP) and Dichloroacetic (DCAA) are abundant industrial toxic component as it has been recognized from different polluting sources, like herbicides, pesticides, chemical and solvent manufacturing and the paint industry. The presence of recalcitrant pollutants in aqueous environment is the principal obstacle, which up to date prevents the water recycle. The 4-chlorophenol, characterized by its acute toxicity and low biodegradability and dichloroacetic acid is considered as animal carcinogens with a qualitative target level of 50 µg L^-1 in drinking water. They are not degradable by conventional water treatment, enabling them to go through the wastewater treatment station without being abated.

One of very promising technology, based on the total mineralization of hazardous organic compounds that are hard to degrade is the heterogeneous photocatalytic oxidation. This technology can be an alternative remediation technology and much attention has been paid to its application in the aqueous environment since (i) it does not need the addition of any chemical; (ii) it is suitable for treating water with low concentrations of organic pollutants, (iii) it is not specific and (iv) it can lead to total mineralization of organic compounds.

Indeed in the natural aqueous system a larger part of the purification is caused by sunlight initiating the decomposition of recalcitrant compounds into simpler molecules. The use of semiconductor catalysts promotes the oxidation processes, which occurs on semiconductor surfaces.

This technology combines heterogeneous catalysis with solar energy, which can be of particular interest for sunny countries.

Some TiO_2 semiconductors are by far the most active photocatalyst applied for degrading organic pollutants dissolved in gaseous or aqueous phases.

As it is well known, when TiO_2 is illuminated with UV irradiation an electron is promoted from the valence band to the conduction band to give an electron-hole pair.

The photocatalytic oxidation reactions often described for irradiated titanium dioxide are summarized as follows:

\[
\text{TiO}_2 + \text{hv} \rightarrow e^- + h^+ \quad (1)
\]

\[
e^- + h^+ \rightarrow \text{heat} \quad (2)
\]

\[
e^- + \text{O}_2(\text{ads}) \rightarrow \text{O}_2^* \quad (3)
\]

\[
h^+ + \text{H}_2\text{O} \rightarrow \cdot \text{OH} + \text{H}^+ \quad (4)
\]

\[
h^+ + \text{OH}_{\text{ads}} \rightarrow \cdot \text{OH} \quad (5)
\]

Equation 1 represents the rate of electron-hole Generation in the titanium dioxide. Equation 2
represents the rate of electron-hole recombination, which occurs within the surface and the volume of the particle. The produced hydroxyl radical, which is known as a very strong oxidant attack the aromatic ring of 4-chlorophenol and the reaction, can lead to total mineralization in the form of CO$_2$ and H$_2$O.

Presently the most of TiO$_2$ powders have photonic efficiencies for most degradation processes less than 10%. Therefore it becomes evident why novel materials have to be developed and investigated\cite{6}.

The improvement of photocatalytic activities can be achieved principally by:

* Decreasing the particle size of photocatalysts down to nanoparticles
* Development and optimization of binary semiconductors nanostructured materials
* Reducing the overall process cost requires avoiding microfiltration by immobilizing the semiconductor catalyst on support.

Several attempts at attaching titanium oxides to a variety of supports, such as a glass tube, fiberglass, etc., have been made, as the recovery of micron sized particles from water decontaminated by a TiO$_2$ slurry may be an awkward process. Generally the efficiency of the overall process decreases as the catalysts are immobilized because the illluminated surface area is smaller by several orders of magnitude\cite{5}.

The progress realized in the clay pillaring process by various metallic species points to the application of semiconductor-pillared clays as photocatalysts. The intercalated semiconductors in the interlayer spaces of clays, in the form of nanosize pillars could improve its photocatalytic activity. In addition, the high adsorption capacity of clay and its high surface area could to facilitate the retention of the pollutants and their intermediate products of photocatalytic degradation. Finally, pillared clays easily flocculate\cite{6-9}. Mixed pillaring by coupling the semiconductors allows enhancing the photonic efficiencies of the final solids and the same time produce large micropores, improving the thermal stability and increasing the surface acidity. Although the mixed pillared smectites has been investigated in catalysis, to our knowledge this the first time where an attempt is made to explore the photocatalytic activity of coupled semiconductor in mixed pillared bentonite as photocatalysts.

The aim of this study was to study, the influence of the addition of another semiconductor (zirconium oxide) and the synthesis conditions on photocatalytic activity of these based bentonite obtained catalysts.

**MATERIALS AND METHODS**

Bentonite from Maghnia in Western Algeria has been used as starting material for preparing the photocatalysts. It was firstly purified and harmonized as described in our previous study\cite{6}, which we sum up briefly here. The raw bentonite is dispersed in 1 M NaCl solution in order to have harmonized Na-montmorillonite, then it is separated from the solution and washed several times with distilled water. For separating the fraction of size <2 µm, a suspension of 2 wt % is placed in gradual cylinders for allowing particles >2 µm to settle down. The suspension at the depth of 10 cm containing only the particles of size <2 µm is collected with an Andreason pipette. This operation is repeated several times until the suspension becomes almost transparent at the depth of 10 cm. The particles of a size smaller than 2 µm are recovered by centrifugation, washed with distilled water and finally dialyzed to eliminate chloride ions in excess. This fraction was used in the pillaring process. Titanium tetraisopropoxide [Ti (C$_3$H$_7$O)$_4$] was used as the precursor of TiO$_2$. Hydrochloric acid was added to it, under vigorous stirring, in order to obtain a H$^+$/Ti molar ratio of 4. To this mixture, distilled water was added and the resulting white sole was peptized further for several hours until a clear solution was obtained. Zirconyl chloride (ZrOCl$_2$) was used for preparation of the zirconium pillaring solution.

The intercalation was performed by adding, drop by drop, the pillaring solution to the clay suspension with vigorous stirring. The stirring was then continued for three hours. The solid was separated by centrifugation, rinsed several times with distilled water, dried and finally 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 characterized by UV-Vis. Spectroscopy using a Perkin-Elmer spectrophotometer lambda 45 equipped with a Labsphere Diffuse Reflectance (DR) accessory.

Tests have been performed in a cylindrical 125 cm$^3$-batch reactor made of borosilicate glass open to 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 (cutoff at 340 NM) and a 2 cm thick glass cell in which cold water was circulated (to prevent warming of the suspension by infrared irradiation) were interposed between the lamp and the photoreactor (Fig. 1). The radiant power entering the reactor was 445 mW; it was calculated to correspond to $ca. 1.4 \times 10^{18}$ photons per second potentially absorbable by TiO$_2$.

The experiments were carried out with 20 cm$^3$ of solution containing 1.55x10$^{-5}$ mol L$^{-1}$ (20 ppm) of 4-chlorophenol or 1.54 x 10$^{-6}$ mol L$^{-1}$ (20 ppm) of dichloroacetic acid. The powder photocatalyst 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, C, of 4-chlorophenol or dichloroacetic acid decreased slightly and become stable beyond 30 min.
C of 4-CP was measured by high performance liquid chromatography using an isocratic pump, a detector adjusted at 226 nm and a reverse phase C$_{18}$ column (25 cm long; 4.5 mm diameter; 5 µm film thickness). The mobile phase consisted of a mixture of water/methanol (40/60), the analysis of dichloroacetic acid was accomplished with HPLC Waters 600 pump equipped with degasser on line, Column SARASEP CAR-H (30 cm long, 4.6 mm diameter and 10 µm thickness) was used. The detector adjusted at 210 µm. Aqueous solution of H$_2$SO$_4$ 5 x 10$^{-3}$ Mol L$^{-1}$ was used as eluent and the flow rate was kept at 0.7 ml min$^{-1}$.

RESULTS AND DISCUSSION

Solid Characterization: Figure 2 shows the UV-Vis diffuse reflectance spectra of Na-montmorillonite, titanium pillared montmorillonite and titanium-zirconium pillared montmorillonite calcined in conventional oven at 673 K or by MW.

Compared with the Na-bentonite spectrum, the spectra of pillared clays show an absorption edge at about 400 nm shifted toward higher wavelength for the mixed pillared solid. The shift of the absorption edge is more pronounced in the case of the Ti/Zr-pillared montmorillonite calcined by MW. This might be due to a change in the size of the TiO$_2$ and ZrO$_2$ particles.

The X-ray diffraction patterns (XRD) of untreated and pillared clay were performed using a Philips model PW 1710 diffractometer and Ni-filtered Co Kα radiation. Oriented specimens were prepared by spreading the sample on a glass slide, then exposing it to thermal treatment at 673 K for 3 hours or irradiated by MW for 15 min.

**Fig. 1: Schema of the Photoreactor**

**Fig. 2: UV-Vis Diffuse Reflectance Spectra a) Na-bentonite; b) Ti-pillared montmorillonite; c) Ti/Zr-pillared Montmorillonite Calcined at 400°C; d) Ti/Zr-pillared montmorillonite Calcined by MW**

Figure 3 shows XRD patterns in the 2θ = 20° range. The orientation of the specimens allows the (001) diffraction peak to be more intense. The pattern of untreated Na-montmorillonite shows the (001) peak at 2θ = 10.2° (d = 1.0 nm) typical for montmorillonite, while the pattern of Ti/Zr-pillared montmorillonites shows a very sharp (001) peak at 2θ = 4.2° (d= 2.4 nm) due to intercalation of polycationic species of titanium and zirconium. This change indicates an important increase in the basal spacing d (001). These results reveal that the pillared clay samples have good ordered layers structure with insertion of titanium and zircon pillars, which causes an increase in the clay basal spacing.

**Photocatalytic Tests:** In Fig. 4 are plotted the abatements of 4-chlorophenol concentration as a function of time using Ti-, Zr-pillared or mixed Ti/Zr-pillared samples dried and calcined by various methods, viz.
Calcined at 673 K in an ordinary oven or calcined by MW. To evaluate the photocatalytic activities of these solids with respect to powder TiO$_2$, the results of one test performed under the same operating conditions, but using TiO$_2$ Degussa P-25, are also plotted. From these curves it can be concluded that the Ti/Zr-pillared clays is more efficient when calcined by MW than the sample calcined first by titanium and then by zirconium. This may be explained by a lower content of Zr$^{4+}$ cation intercalated in the former case, because the Zr$^{4+}$ cations cannot replace Ti$^{4+}$ cations in the interlayer space. The presence of ZrO$_2$ in the nano environment of montmorillonite can affect the acidic properties of the solid. Further research is needed on the basis of these working hypotheses.

CONCLUSION

On investigating the effect of coupling semiconductors on the photocatalytic activity for the removal of 4-chlorophenol and dichloroacetic acid in the water it was found that mixed pillaring enhance the photocatalytic activity. This enhancement has been shown to depend on the preparation method of these new types of supported photocatalysts. It was more pronounced in the case of DCAA elimination. Further work is needed in particular on the effect of the ratio of the semiconductor on the interaction of Zr-Ti in the nano environment of the clay and accordingly on their photocatalitic efficiency.

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REFERENCES


