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 TiO₂ 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 calcination method, on these activities has been investigated. It was found that the photocatalytic activities increase by addition of zirconium in pillaring process and the calcination 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, in particularly in the countries with limited hydric resources, become increasingly a reliable option. This is due to the no 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 [1] and dichloroacetic acid is considered as animal carcinogens with qualitative target level of 50 μg L⁻¹ in drinking water [2]. They are not degradable by conventional water treatment, enabling them to go through 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 purification is caused by sunlight initiating the decomposition of recalcitrant compounds into simpler molecules. The use of semiconductors 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 TiO₂ semiconductors are by far the most active photocatalyst applied for degrading organic pollutants dissolved in gaseous or aqueous phases [3].

As it is good known , when TiO₂ is illumined 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 follow:

\[ TiO_2 + h^+ \rightarrow e^- + h^+ \] (1)
\[ e^- + h^+ \rightarrow \text{heat} \] (2)
\[ e^- + O_2(ads) \rightarrow O_2^* \] (3)
\[ h^+ + H_2O \rightarrow \cdotOH + H^+ \] (4)
\[ h^+ + OH_{ads} \rightarrow \cdotOH \] (5)

Equation 1 represents the rate of electron-hole recombination.