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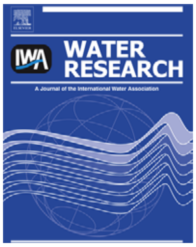

Phenol degradation in water through a heterogeneous photo-Fenton process catalyzed by Fe-treated laponite

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ABSTRACT

New photo-Fenton catalysts have been prepared from synthetic layered clay laponite (laponite RD). Two series of Fe-laponite catalysts were synthesised, with or without thermal treatment of the mixture Fe polycations-laponite in the intercalation procedure. In each series, the intercalated solids underwent calcination at four temperatures, 250, 350, 450, and 550 °C. The catalysts were used for photo-assisted Fenton conversion of phenol, analyzing the influence of five operating factors: the wavelength of the light source (254 nm UV-C and 360 UV-A radiation), the amount of the catalyst (between 0 and 2 g/L), the initial phenol concentration (between 0.5 and 1.5 mmol/L), the initial concentration of hydrogen peroxide (between 20 and 100 mmol/L), and the initial pH of the solution (between 2.5 and 3.5). In all experiments, the temperature was kept constant at 30 °C. The results have shown that the almost complete conversion of phenol was possible, after only 5 min, under the following operating conditions: UV-C radiation; a pH of the aqueous solution of 3; a dose of 1 $g_{catalyst}$/L, and a hydrogen peroxide concentration of 50 mmol/L for a solution containing 1 mmol/L of phenol. The catalyst prepared under thermal treatment and calcined at 350 °C showed the best catalytic performance. A kinetic model was proposed for the process, testing its validity and estimating the rate constants.

1. Introduction

Phenols have become the most abundant pollutants in industrial wastewater, due to their wide utilization in several industries. The world production of phenol is over three million tons per year, being used in the synthesis of resins, dyes, pharmaceuticals, perfumes, pesticides, tanning agents, solvents or lubricating oils. Long-term exposure to phenol paralyzes the human central nervous system and damages kidneys and lungs. It is also classified as a teratogenic and carcinogenic agent. Thus, phenol is listed in water hazard class 2 in several countries. Biodegradability is only 90% in surface waters after seven days, and the aquatic toxicity of phenol (LC_{50}) is 12 mg/L (*Daphnia magna*, 48 h). In EU countries, the maximum concentration of phenol allowed in drinking water is 0.5 μg/L (Weber et al., 2008).

Commercial wastewater treatment methods utilize the combination of biological, physical and chemical treatments (Droste, 1997). Biological treatment units tend to become very large due to the slowness of biological reactions. The physical methods only transfer waste components from one phase to another. Chemical treatment of phenols, such as chlorination,

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can result in the formation of chlorinated phenols and other by-products that have been reported as toxic and non biodegradable. An attractive alternative for the removal of organic contaminants from wastewater is the so-called Advanced Oxidation Processes (AOPs). They operate at near-ambient temperature and atmospheric pressure, with generation of reactive radicals, mainly $HO^{\bullet}$, in sufficient amount to oxidize the majority of the organics present in the effluent water (Kavitha and Palanivelu, 2004; Poulopoulos et al., 2006). In particular, the oxidation using Fenton's reagent, a powerful source of oxidative $HO^{\bullet}$ radicals generated from H_2O_2 in the presence of added Fe^{2+} ions (Walling, 1975), has proved to be a promising and attractive treatment method for the effective destruction of a large number of hazardous and organic pollutants (Kavitha and Palanivelu, 2005; Oliveira et al., 2006). The $HO^{\bullet}$ radicals are powerful, non-selective oxidants with the ability of decomposing many organic compounds, including dyes (Swaminathan et al., 2003). AOP laboratory methods for phenol degradation have recently been reviewed and compared (Gimeno et al., 2005), and photo-Fenton has been found as the most effective. Its effectiveness is attributed to the formation of Fe(II) ions upon photolysis of Fe(III) in step (1), followed by reaction between Fe(II) and H_2O_2 to yield the hydroxyl radicals ($HO^{\bullet}$, step (2)):

$$Fe(OH)^{2+} + h\nu \rightarrow Fe^{2+} + HO^{\bullet} \tag{1}$$

$$Fe^{2+} + H_2O_2 \rightarrow Fe(OH)^{2+} + HO^{\bullet} \tag{2}$$

However, the homogeneous Fenton process has a significant disadvantage because it needs up to 50–80 ppm Fe in solution. This is well above the EU directives, which allow a maximum of 2 ppm Fe in treated water to be discharged directly into the environment (Walling, 1975). In addition, the application of the homogeneous photo-Fenton treatment to large water flow rates may produce large amounts of sludge in the final neutralization step (Sabhi and Kiwi, 2001).

In order to avoid these disadvantages and to synthesize reusable catalysts, several Fe-containing heterogeneous catalysts have been tested for this reaction. The first one has been prepared by immobilization of Fe(III) on a Nafion membrane, but it is not practical because of the high cost of the membrane (Dhananjeyan et al., 2001). Then, Fe cations have been supported on resins, zeolites, silica, alumina or carbons, among other supports, and bulk Fe-oxides, such as hematite, have also been used. The resulting catalysts have been used in a large variety of reactions, mainly for the degradation of dyes (Liou et al., 2005; Noorjahan et al., 2005; Ramirez et al., 2007a).

Clays, both natural and physico-chemically modified, are attractive materials for the preparation of supported catalysts (Gil et al., 2000, 2008). Fe has usually been incorporated by pillaring of smectites, yet polymerization of Fe(III) produces polyoxocations that can intercalate swellable clays by substitution of their exchangeable cations. For example, Sum et al. prepared a Fe-laponite catalyst, using it for the photo-Fenton degradation of Orange II and Acid Black 1 azo-dyes (Sum et al., 2005). Similar preparation procedures have been employed by other authors; Timofeeva et al. (2005) have pillared montmorillonite by co-intercalation with Al and Fe species, using the catalysts in the removal of phenol, while Carriazo et al. have pillared bentonite with mixed Al–Fe, Al–Cu and Al–Ce–Fe species, also using the catalysts in the removal of phenol (Carriazo et al., 2008). Sanabria et al. (2008) have recently pillared a Colombian bentonite with Al–Fe polymeric species, using the material in the oxidation of phenol with hydrogen peroxide. They have found 100% conversion of phenol after two hours, although the elimination of total organic carbon was between 49 and 53% after 4 h of reaction.

However, intercalation pillaring with Fe has a main disadvantage because it is not easily reproducible (Belver et al., 2004). Differently from the Al_{13} polycation, well known and easy to prepare, Fe forms various polycations depending on the preparation conditions (such as pH, temperature, ageing). Thus, Ramirez et al. have used a new strategy for the preparation of Fe–clay catalysts, which involves the impregnation with Fe-salts of previously prepared Al-pillared saponite. In this way the textural properties of the support are well maintained, because of the high stability of Al-pillared saponite, and the amount of the Fe-active phase can easily be controlled. The described materials have been used for the degradation of azo-dye Orange II, with excellent results (Ramirez et al., 2007b, 2008).

In the present paper, we report the preparation of Fe-catalysts by treating laponite with Fe polycations by two procedures. The prepared solids have been used for the photo-Fenton degradation and mineralization of phenol, proposing a kinetic model for the process and testing its validity.

2. Experimental

2.1. *Preparation of the catalysts*

The synthetic laponite clay (laponite RD) was supplied by Kremer Pigmente GmbH (Aichstetten/Allgäu, Germany), and used as starting material to prepare a series of Fe-laponite catalysts. Treatment with Fe polycations was carried out by adapting the method reported by Feng et al. (2003, 2005). Sodium carbonate (Sigma–Aldrich, 99.5%) was added slowly in powder form into a vigorously stirred 0.2 mol/L solution of $Fe(NO_3)_3 \cdot 9H_2O$ (Fluka, 98%), up to a molar ratio of 1:1 for $[OH^-]/[Fe^{3+}]$. The obtained solution was added very slowly into a suspension of laponite in water, previously prepared by adding, under vigorous stirring, 2 g of the clay to 100 mL of H_2O (Milli-Q quality). The ratio Fe/clay was 11 mmol/g; after addition of the polycations, the resulting suspension was stirred for 2 h. At this point, the suspension was divided into two portions. One portion was kept in an oven at 100 °C for two days, while the other portion was maintained at room temperature for the same two days. The first portion will be referred to as "thermally treated" or "thermally aged". Once finished the ageing time, all the suspensions were centrifuged and the resulting solids were washed several times with deionized water to ensure that all the Na^+ ions were removed. It followed air-drying in oven for 24 h at 120 °C, and finally calcination at four temperatures within each series (thermally ages or not): 250, 350, 450, and 550 °C for 24 h. The original clay