

Adsorption of crystal violet on montmorillonite (or iron modified montmorillonite) followed by degradation through Fenton or photo-Fenton type reactions

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ABSTRACT

In this work we demonstrate the feasibility to couple adsorption with Fenton and photo-Fenton process to separate and mineralize crystal violet (CV) dissolved in water. Montmorillonite (MMT) and iron modified montmorillonite (MMT-Fe) were studied as adsorbents and heterogeneous catalysts for Fenton and photo-Fenton like oxidation of cationic dye CV. The clays were characterized by XRD, SEM, EDX, BET surface area and electrophoretic mobility. MMT-Fe presents iron in the interlayer space and oxhydroxide particles on its surface. Both clays present a high CV adsorption capacity that can be modeled by a two-site Langmuir equation. MMT-Fe oxidizes faster and have a higher mineralization rate of adsorbed CV than MMT with Fe(II) or Fe(III) added externally. The oxidation of the adsorbed dye release organics to the solution which are further mineralized in solution. The Fenton oxidation can be modeled by a double exponential decay and photo-Fenton oxidation by a pseudo-first order kinetic model. Photo-Fenton oxidation leads to higher mineralization rates than Fenton.

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Introduction

Waste water treatment is one of the environmental problems that concern the modern industrial society. In particular, the disposition of colored effluents produced by textile, paper pulp, plastic and other industries represent a technological problem that affects several countries all around the world. It is difficult to calculate the annual amount of waste produced by these industries but some estimates indicate that there are over 100,000 types of synthetic dyes available in the market with an output of 7×10^5 tons per year, and approximately 5–10% is discarded during their production and utilization [1–3]. There are several types of commercial dyes [1,4], and some of these dyes possess a high resistance to biodegradation and persist a long time in the environment [5–7]. These compounds and their degradation byproducts are generally believed to be carcinogenic or toxic and become harmful to humans or to the environment where they

are discarded [8–13] and are easily detectable with the naked eye at very low concentrations. Triarylmethane dyes (TAM) are recalcitrant dyes that have been used as antimicrobial and antifungal agents [14–16]. These compounds typically display a net positive charge, being crystal violet (one of the best known members of this family of compounds) a good model to represent cationic dyes.

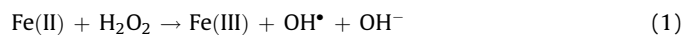
Adsorption processes have been proposed as a fast alternative to remove contaminants from water. Several natural low cost adsorbents have been tested to remove synthetic dyes [3,17]. In particular, montmorillonite (a clay belonging to the family of smectites) have been broadly studied as adsorbents of synthetic dyes [18–20]. Smectite clays have a layered structure where each layer is composed by tetrahedral silicate units fused into an edge-shared octahedral plane of aluminum. The isomorphous substitution of Al(III) for Fe(II) or Mg(II) and Si(IV) for Al(III) generates charge deficiencies on the surface and interlayer space. When Al(III) is replaced by Mg(II) the structure corresponds to montmorillonite (MMT). The intrinsic negative charge is compensated with inorganic cations (as Na(I) or Ca(II) in MMT) in the interlayer that can be exchanged by other inorganic or organic cations, being suitable for adsorption of cationic synthetic dyes. However, after adsorption and separation from the aqueous effluent a new solid

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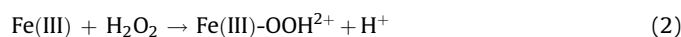
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residue containing the dye is generated. This waste, rich in poorly biodegradable dye, should be adequately disposed as a dangerous solid.

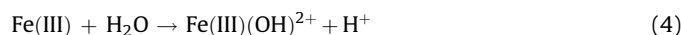
Another alternative to decontaminate dye containing waters are advanced oxidation treatments (AOTs). AOTs are highly efficient treatments to remove recalcitrant dyes based on the oxidative power of the radical species formed. In particular, Fenton and photo-Fenton like processes have proved to be efficient in the oxidation of organic compounds [21,22] using homogeneous iron [23,24], heterogeneous insoluble iron oxides [25,26] or supporting the catalyst in matrixes like clays [27,28]. The Fenton reaction is based in the capacity of Fe(II) to generate hydroxyl radicals from H₂O₂.



These hydroxyl radicals are highly oxidative and can generate chain reactions with organic matter that leads to the mineralization of contaminants. Fe(II) acts as a catalyst and is regenerated from Fe(III), generating even more radicals.



In water, Fe(III) undergoes several hydrolysis reactions. At pH 3 almost all Fe(III) is in the form of Fe(OH)²⁺ [29]. This iron complex can absorb light in a broad irradiance spectrum, leading to the photoreduction of Fe(III) [30].



This reaction accelerates the regeneration of Fe(II) from Fe(III), increasing the efficiency of hydroxyl radical production and the reaction velocity. The complex between Fe(III) and H₂O₂ also absorbs polychromatic light leading to the formation of an excited state that accelerates the reduction of Fe(III) [30].



This light assisted Fenton reaction is commonly known as photo-Fenton reaction.

In this work we propose to use the high adsorption capacity of pure montmorillonite (MMT) and iron modified montmorillonite (MMT-Fe) to remove crystal violet, a model TAM dye, from water and then use homogeneous and heterogeneous Fenton and photo-Fenton like processes to oxidize the adsorbed dye. In this way the dye can be quickly removed from water and concentrated in a smaller volume of water-clay suspensions to be treated.

Materials and methods

Synthesis and characterization of MMT-Fe

MMT-Fe was prepared from Argentinean natural bentonites (MMT), containing 96% of sodium montmorillonite (MMT-Na) (more details in Ref. [31]). MMT-Fe was prepared following the procedures indicated elsewhere [32,33]. Briefly, 300 g/L of MMT were dispersed in acetone containing 1.11 mol/L FeCl₃. The dispersion was stirred for 2 h and centrifuge at 10,000 G to separate the solid phase. The solid was rinse with acetone, ethanol and water in this order, followed by centrifugation after each step. Finally, the solid was lyophilized.

The morphology of MMT and MMT-Fe was determined by scanning electron microscopy (SEM) with a FEG-SEM Zeiss Supra 40. The crystalline structure of the samples was determined by X-ray diffraction (XRD) with a Siemens D5000, CuK α radiation,

operated at 30 mA and 40 kV. Electrophoretic mobility of MMT and MMT-Fe dispersed in 1 mM KCl solution was determined with a Brookhaven 90 Plus/Bi-MAS. Iron content in MMT and MMT-Fe was determined by dispersing 1 g/L of the sample in exactly 100.0 mL of 5 M nitric acid during 24 h. The concentration of iron in the acid solution was determined by atomic absorption spectroscopy (SensAA dual, GBC Sci. Equipment). Surface area and porosity was determined by adsorption of N₂ at 77 K using a Micromeritics ASAP 2020 V3.05 G. The samples were out-gassed by heating at 200 °C under a flow of helium for 12 h. The data were recorded with P/P_0 between 0.0005 and 0.99.

Adsorption isotherms

1.5 g/L of MMT or MMT-Fe were dispersed in water solutions containing crystal violet (CV) concentrations in the range 0.245–2.45 mM. The dispersion was stirred during 24 h to equilibrate the system and then centrifuge at 10,000 G during 15 min. The concentration of the dye remaining in solution was measured by UV–vis spectroscopy (PG Instruments T70+).

Determination of the adsorbed dye

To determine the amount of CV adsorbed on MMT or MMT-Fe, the dye was desorbed by treatment with an aqueous solution of sodium dodecyl sulfate (SDS). The desorbed dye was quantified by UV–vis spectroscopy in the extractive solution. To optimize the extraction of CV from MMT, the following procedure was realized: 0.15 g/L of MMT or MMT-Fe were dispersed in 100 mL of 0.060 mM CV solution and stirred during 3 h; the solid was separate by centrifugation at 10,000 G during 15 min and resuspended in 100 mL of water solutions containing different concentration of SDS. The optimum concentration of SDS to remove all the dye from the adsorbent was 0.17 M (see supplementary Fig. 1).

Supplementary material related to this article can be found, in the online version, at [doi:10.1016/j.jece.2014.02.007](https://doi.org/10.1016/j.jece.2014.02.007).

Fenton and photo-Fenton reaction set-up

To simulate the removal of pollutants in water by adsorption followed by advanced oxidation, CV was first adsorbed on MMT (or MMT-Fe), separated from the water and re-dispersed in a lower amount of water, were it was oxidized by Fenton or photo-Fenton process. The experimental procedure can be summarized as follows: 100 mL 0.060 mM CV were stirred during 24 h with 1.5 g/L MMT (or MMT-Fe) to reach adsorption equilibrium condition. The sorbent/sorbate system was separated from solution by centrifugation at 10,000 G. The solid was re suspended in 50 mL of water at pH 3.0 (acidify with H₂SO₄). The suspension was placed in a 100 mL double jacket borosilicate glass batch reactor, thermostated at 25 °C and magnetically stirred. Enough 30% H₂O₂ to reach a final concentration of 50 mM was added as oxidant and, for the system with MMT, 0.5 mM FeCl₃ or Fe(NH₄)₂(SO₄)₂ was added as catalyst [24]. For photo-Fenton experiments, the reactor was illuminated from above with a 300 W solar lamp (OSRAM, Ultravitalux). 5 mL samples were taken from the reactor at fixed times, quenched with sodium sulfite or acetonitrile, and centrifuged at 10,000 G to remove the adsorbent. Total Organic Carbon (TOC) and iron concentration were measured in the supernatant solution using a Shimadzu TOC-5000 and an atomic absorption spectrophotometer SensAA dual, GBC Sci equipment, respectively. The dye was desorbed from the adsorbent with a 0.17 M sodium dodecyl sulfate water solution. The concentration of the extracted dye was measured by UV–vis spectrophotometry. Details about the extraction procedure are given as supplementary material.

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