



Photocatalytic reduction of Cr(VI) on nanosized Fe₂O₃ supported on natural Algerian clay: Characteristics, kinetic and thermodynamic study

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HIGHLIGHTS

- The work deals with the Cr(VI) reduction on Fe₂O₃ loaded clay under visible light.
- The conduction band of Fe₂O₃ (−1.08 V) is more negative than the HCrO₄[−]/Cr³⁺ level.
- The Fe₂O₃/clay hetero-system is synthesized by impregnation.
- The Cr(VI) reduction follows a pseudo first order kinetic with of oxalic acid.

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ABSTRACT

Nanosized α-Fe₂O₃ (hematite) supported on Algerian clay (Fe₂O₃/clay), by impregnation is successfully used for the chromate reduction under visible light. The hetero-system is investigated by X-ray diffraction, FT-IR, scanning electron microscopy and energy dispersive spectroscopy (EDS) analysis. The microscopic observation shows that the supported hematite α-Fe₂O₃ is uniformly spread on the clay which consists mainly of ~80% illite. The BET measurement gives a specific surface area of 140 m² g^{−1}. The photo-electrochemical characterization is undertaken to assess the photoactivity. The sensitizer Fe₂O₃ has a conduction band (−0.76 V_{SCE}) more cathodic than the chromate level (−0.1 V_{SCE}). As application, the reduction is optimized with respect to catalyst dosage, Cr(VI) concentration, pH and temperature. A remarkable performance is obtained in less than 3 h for a concentration of 50 ppm at pH ~ 2 with a dosage of 1 mg/mL. The chromate removal obeys to a pseudo first order kinetic with an apparent constant of 0.013 min^{−1}. The negative enthalpy and free energy indicate a spontaneous and exothermic process. Upon solar irradiation, the reduction of 100 ppm Cr(VI) solution is completed after only 50 min.

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1. Introduction

The discharge of toxic metals in the aquatic environment is considerably increased over the last decades and is of major issue, because of the increasing industrial activities [1]. Since the metals are not biodegradable unlike organic pollutants, their concentrations must be reduced below the levels setup by the guidelines of the water standard. In this line, chromium is an active metal that has several oxidation states whose most stable are Cr(VI) and Cr(III). The hexavalent state is reported to be carcinogenic owing to its strong oxidant irritating plant [2]. It is released improperly in water without any restriction, resulting mainly from various industries like leather tanning, chemical manufacturing (e.g. dyes, rubber and plastic products), and electroplating [3–6]. The admissible concentration of chromium is fixed at 0.05 mg L^{−1} by the

World Health Organization. Accordingly, many techniques for its removal have been reported such as the ion exchange, electrochemical reduction, solvent extraction, reverse osmosis, chemical precipitation and adsorption [7–9]. However, such methods are high cost and often do not comply with the standard of the water pollution. Therefore, the development of effective treatment processes that can convert pollutants into non-toxic forms would be desirable. At this level, the photocatalysis has proved to be quite attractive in the reduction of heavy metals into less harmful oxidation states and semiconductors are privilege materials for playing a part of photo electrodes [10–12]. Cr(VI) is photoelectrochemically reduced to trivalent state. Cr(III) is readily precipitated because of the low solubility of Cr(OH)₃, less toxicity (about 300 times smaller) and can be either chelated by organic molecules or adsorbed by various substrates [13].

On the other hand, many adsorbents are currently used to remove chromium from aqueous solutions, such as clays, zeolites, silica and activated carbons [14–19]. Clays are gaining tremendous

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