Available online at www.sciencedirect.com

ScienceDirect

Solar Energy 129 (2016) 45–53

SOLAR ENERGY

www.elsevier.com/locate/solener

Photodecolorization of rhodamine under sunlight irradiation driven by chabazite

J. Ramírez-Aparicio, A. Sánchez-Martínez, R. Ramírez-Bon *

Centro de Investigación y de Estudios Avanzados del I.P.N. Unidad Querétaro, Apdo. Postal 1-798, 76001 Querétaro, Qro, Mexico

Received 17 December 2015; received in revised form 20 January 2016; accepted 25 January 2016

Communicated by: Associate Editor Gion Calzaferri

Abstract

Natural zeolite chabazite was studied for the discoloration of rhodamine 6G solutions in dark and under sunlight irradiation. The discoloration of rhodamine aqueous solutions containing chabazite was monitored by UV–vis absorption and photoluminescence spectroscopies and high-performance liquid chromatography measurements on aliquots of the rhodamine solutions. After the discoloration experiments the chabazite powders were collected, dried and analyzed by Fourier-Transform Infrared spectroscopy to obtain additional information about the discoloration process. The results show that chabazite produces the discoloration of the rhodamine solutions in both conditions, dark and under sunlight, with different discoloration mechanisms and rates. In dark, chabazite removes the rhodamine molecules from the solution by adsorption and cation exchange mechanisms. Under sunlight irradiation, additional photo induced mechanisms produce the degradation of the rhodamine molecules and a faster discoloration of the solution. The discoloration process followed a first order kinetics with rate constants of 4.9×10^{-3} and $1.2 \times 10^{-2}\,\mathrm{min}^{-1}$ in dark and under sunlight conditions, respectively. It is proposed a mechanism for the photodegradation of rhodamine molecules under sunlight irradiation, where the role of chabazite is fundamental.

Keywords: Natural zeolites; Rhodamine; Chabazite; Photodegradation; Adsorption; Cation exchange

1. Introduction

Nowadays the lack of drinking water in many regions of the world is becoming a serious social problem. This is because the rapid growth of the world population and, by the other hand, because the technological and industrial development has contributed to the generation of large amounts of polluting wastes affecting the clean water resources. Many of the effluents generated by industries contain a variety of contaminants such as heavy metals, organic and inorganic compounds, which in general are toxic to people and fauna. Among the toxic organic compounds, dyes are a common waste of textile industry. The removal of these dyes in industrial wastewater has become a major concern in the treatment of sewage. One of the most toxic and dangerous dyes is rhodamine (Bokhale et al., 2014; Edgar French, 1989; Das et al., 2008) because it is a carcinogenic organic compound that damages the health of living beings, especially humans (Bokhale et al., 2014; Edgar French, 1989; Biparva et al., 2010). Furthermore, it is also harmful to the ambient because it blocks the sunlight inhibiting the photosynthesis (Bokhale et al., 2014; Gan and Li, 2013; Xia et al., 2013).

Semiconductor photo catalysis is one of the most important methods to remove contaminants from water (Houas et al., 2001) and absorption is an alternative one, which

---

* Corresponding author.

http://dx.doi.org/10.1016/j.solener.2016.01.050
0038-092X/

has been the focus of great research interest in the last decades. Unlike photo catalysis, this method does not employ semiconductor materials, being the most important absorbent materials activated carbon, clays, bio absorbents and natural and synthetic zeolites. Most of these materials have the capability to absorb contaminants, not only from water but also from soil and air, such as heavy metals, and organic molecules. There are several studies about the removal of dyes in water using different materials and techniques (Xu et al., 2010; Sharma et al., 2012; Lu et al., 2011; Muruganandham and Swaminathan, 2004; Muthuvel and Swaminathan, 2008). Some of these include: oxidative degradation of rhodamine 6G using ZSM-5 zeolite doped with Cu and Fe (Bokhale et al., 2014), removal of rhodamine B using rice crack supported on silica and iron catalyst (Gan and Li, 2013), degradation of rhodamine 6G by sonocathalysis and sonophotocatalysis using CuO and TiO_2 as catalysts (Bokhale et al., 2014), degradation of rhodamine B by ZnO nanoparticles (Rahman et al., 2013) and photocatalytic degradation of rhodamine B using multiwall carbon nanotubes doped with silver nanoparticles (Yan et al., 2011).

Natural zeolites are low cost aluminosilicate materials because of their abundance and widespread availability in the world, and have been extensively studied for removing organic and inorganic contaminants from water (Chatti et al., 2007), among a number of others applications. Zeolites have great capability for ion exchange, adsorption, and catalysis, which are intimately related with their nanometric porous crystalline structure (Liu et al., 1995; Jänchen et al., 2004). Chabazite, along with clinoptilolite and heulandite, is one of the most abundant natural zeolites in the world and particularly in Mexico. Chabazite has a crystalline structure consisting of six rings stacked in well-ordered sequences. Each chabazite cage is linked to six others through eight ring windows yielding to a highly porous three-dimensional structure. The variation in the stacking sequence of the six rings produces a structure with cages and channels of different sizes, which are commonly occupied by monovalent cations such as Na^+, Ca^+, K^+, Mg^+ and water. These cations are easily interchangeable and their migration is responsible for the ionic conductivity of the zeolite. The structural characteristics of the ordered three-dimensional array of cages and channels of chabazite play an important role in the reaction kinetics and provide effective electrostatic stabilization of organic and inorganic species. Chabazite is generally considered a small pore zeolite with a Si/Al ratio of 2–4, characteristics, which make it rather deficient in the exchange process of cations. However, the ionic exchange capability of chabazite, and in general of natural zeolites, can be improved by adequate activation processes for better absorption of organic and inorganic species (Corma and Zones, 2010; Flores-López et al., 2012; Ruiz-Serrano et al., 2010). Some of the reported applications of chabazite include the removal of ammonia in aqueous solutions (Leyva-Ramos et al., 2010), support for the synthesis of silver nanoparticles used as bactericide (Flores-López et al., 2012) and absorption of heavy metals in water treatments (Egashira et al., 2012), among others.

In this work, we have applied chabazite to the removal of rhodamine 6G from aqueous solutions. For this, the natural zeolite from Sonora, México was previously conditioned with ammonium chloride solutions to improve the cation exchange capabilities and then added to rhodamine 6G aqueous solutions. The discoloration of the rhodamine solutions, in dark and under sunlight illumination conditions, was monitored by means of ultraviolet–visible (UV–vis) and photoluminescence (PL) spectroscopies and high-performance liquid chromatography (HPLC) measurement as a function of time. The results show that in both conditions, chabazite produces an effective discoloration of the rhodamine aqueous solutions with a faster rate under sunlight conditions. These results suggest that sunlight irradiation produces photo-induced mechanisms, which decompose the rhodamine 6G molecules in the solutions containing chabazite.

2. Experimental details

Chabazite was obtained from a deposit in the state of Sonora, Mexico. The chabazite tuff was ground and sieved at 200 mesh for use in this work. Then the natural cations of chabazite were partially exchanged by NH_4^+ ions from an aqueous solution. This conditioning process of the chabazite was done by refluxing the chabazite powder (1 g/10 ml) in a 0.5 M solution of NH_4Cl for 30 min. After the exchange process, the mixture was separated by filtration, rinsed successively in deionised water and finally, the product was vacuum dried at room temperature.

Rhodamine 6G (Sigma–Aldrich), with chemical formula $C_{28}H_{30}N_2O_3 \cdot HCl$, was used as the dye to degrade. Rhodamine aqueous solutions were prepared at 0.03 mM concentration. Two sets of degradation experiments were performed by adding 0.1 g of chabazite into 100 ml beakers with rhodamine solution in each case; one of the beakers was placed in dark and the other under sunlight illumination (20°43′20″N, 100°28′10″W, 1820 m above sea level). It was not used stirring of any kind during these experiments. To follow the reaction kinetics, aliquots of rhodamine solutions were taken from both beakers at times of 15, 30, 60, 180 and 360 min, and analyzed by UV–vis absorption spectroscopy (Ocean optics spectrometer), photoluminescence (PL) (JobinYvonHoriba Spectrofluorimeter Model Fluoro Max-3) and high performance liquid chromatography (HPLC) (LC-20AT pump and UV–Vis SPD-20A detector, equipped with a ODS Hypersil (5 μm 250 × 4.6 mm) column). At the end of experiments, the precipitated chabazite powders were collected, dried and analyzed by Fourier transform infrared (FTIR) spectroscopy (Perkin Elmer, Spectrum GX).