Contents lists available at ScienceDirect

Environmental Nanotechnology, Monitoring & Management

Degradation of methyl orange using iron boride nanoparticles supported in a natural zeolite

E. Xingu-Contreras [a,b], G. García-Rosales [b], A. Cabral-Prieto [a,*], I. García-Sosa [a]

[a] *Instituto Tecnológico de Toluca, Av. Instituto Tecnológico s/n, Ex-Rancho la Virgen, Metepec, Edo. de México, C. P. 52140, Mexico*
[b] *Instituto Nacional de Investigaciones Nucleares, Carretera México-Toluca s/n, La Marquesa, Ocoyoacac, Edo. de México, C. P. 52750, Mexico*

ARTICLE INFO

ABSTRACT

The degradation of methyl orange (MO) in presence of a natural zeolite from San Luis Potosí, México, previously homo-ionized with Na cations (HNaZ) and impregnated with iron boride nanoparticles (HNaZ-Fe) is presented. Iron boride nanoparticles (FeB-NPs) synthesized by chemical reduction, as well as HNaZ and HNaZ-Fe materials were characterized by using Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM), Energy Dispersive X-ray (EDX), Mössbauer and UV–vis spectroscopies. SEM and TEM measurements showed characteristic spherical shapes associated with FeB-NPs with mean diameter of 120 nm and located on the zeolite's surface. Whereas the homo-ionized zeolitic material, HNaZ, did not present any type of interactions with MO, the HNaZ-Fe material, with a mass ratio 1:0.06 of HNaZ:Fe, respectively, mostly degraded this dye. The kinetic study showed that the degradation process of MO followed the second order kinetic reaction with a degradation rate constant of 0.0012 g/(mg h) and an 80% dye degradation was always obtained for all used concentrations of MO, which ranged from 50 up to 500 mg/L. The degradation of MO was confirmed by the presence of sulfanilic acid, as detected by UV–vis spectroscopy through the band at 248 nm.

1. Introduction

The azo dyes represent more than half of dyes nowadays used in various industries such as in the manufacturing of textiles, paper, cosmetics and plastics (Akgül, 2014), and usually their wastewaters contain a significant amount of color. One of the main effects of these azo dyes in wastewaters is their reduction of light penetration, which can in turn modify the photosynthetic activity (Ch. Leodopoulos et al., 2012), as well as the production of amines as a consequence of the cleavage of the azo bond by chemical processes, causing several diseases if they persist in drinking water. In human beings these dyes affect several organs such as the brain, liver, kidneys and nervous and reproductive systems (Sánchez et al., 2010). A good example of an azo dye is methyl orange (MO) with the molecular formula of $C_{14}H_{14}N_3SO_3Na$. Generally, the removal of azo dyes is difficult because of their high solubility in water, complex structure and synthetic origin (Alver and Metin, 2012). Some of the traditional methods used to remove dyes from wastewaters

are: biological methods (Hou et al., 2007), inorganic and organic oxidation or reduction methods (Hou et al., 2007; Hao et al., 2015; Hu et al., 2016), ozonation (Koch et al., 2002), membrane filtration (Ciardelli et al., 2001), sorption (Ch. Leodopoulos et al., 2012) and degradation using Co nanoparticles (Sha et al., 2016), all these methods present certain limitations and disadvantages, although the degradation by using nanoparticles (NPs) has become a relatively fast and low cost method (Sha et al., 2016).

Currently, nanomaterials (NMs) are being used as a versatile tool for environmental studies of pollution, including the degradation of azo dyes as MO (Shih et al., 2010; Fan et al., 2009). Particularly iron nanoparticles (Fe-NPs) have been widely used because iron sources are economic, not toxic and environmentally friendly (Sánchez et al., 2010). For instance, Nairat et al. (2014) obtained a degradation of almost 100% with an initial concentration (C_i) of 100 mg/L of MO while using doses of 0.5 g/L of Fe-NPs at 30 °C in few minutes time. Great care must be taken into account while preparing the Fe-NPs since they tend to agglomerate and oxidize if not properly protected. The magnetic and surface properties of these NPs change with agglomeration and generally decrease the sorption or degradation effectiveness in decontamination of wastewaters (Nairat et al., 2014). In this sense, the use of supporting materials during the synthesis of NPs, such as clays (Chen et al., 2011), carbon (Gutiérrez Muñiz et al., 2013) and synthetic (Wang et al.,

2010) and natural (Nairat et al., 2014) zeolites have been tried as a means of limiting the aggregation of NPs. The use of the zeolites could give advantages over others supporting materials (Wang et al., 2010). Particularly, natural zeolites present a great potential in the wastewater treatment because of their large surface area, high metal selectivity, large ion exchange capacity, chemical and thermal stability and more importantly, their relatively low cost (Bosch et al., 2012). Thus, the main goal of this work was to use FeB-NPs supported on natural zeolite clinoptilolite for the degradation of the dye MO while varying the concentration of MO and contact time.

2. Experimental methodology

2.1. Materials

The natural zeolite clinoptilolite (NZC) was a gift from YEMAZA del Potosí S. A. de C V, a Mexican Company from San Luis Potosí. The $FeCl_3 \cdot 6H_2O$, NaCl and NaOH were from Merck, and MO, CH_3COONH_4, HCl, $NaClO_4$, $HClO_4$, $NaBH_4$ and $AgNO_3$ were from SIGMA-ALDRICH. All these reagents were reagent grade and were used without any further treatment.

2.2. Ion exchange capacity of NZC

The NZC was ground in an agate mortar and sieved with a 100-mesh (0.15 mm). The cation exchange capacity (*CEC*) was determined by the ammonium distillation method (Wang et al., 2010), which was carried out in three stages. The first stage consisted on the cation exchange of Na^+, Ca^{2+}, K^+ and Mg^{2+} ions contained in the NZC by NH_4^+ cations. For this purpose, 50 g of NZC were treated with a 0.5 M solution of CH_3COONH_4 for 48 h under agitation in a mechanical rotor. At the end of this process the solid phase was by centrifugation separated and washed five times with 20 mL of ethanol to eliminate the ammonium excess. In the second stage, the previously NH_4^+-exchanged zeolite was put in contact with 20 mL of a 0.5 M solution of NaCl under agitation for 15 min at room temperature to totally exchange the NH_4^+ cations by Na^+ cations. At the end of this process the decanted solid was separated by centrifugation and the remaining solution was kept safely in a closed flask to prevent the out take of the dissolved ammonium. This second stage was repeated four times in order to complete five exchanging steps; as already mentioned, the remaining solutions after centrifugation were safely recovered and put together into a single flask. In the third stage, a 40% NaOH solution was added to the NH_4^+ solution previously separated to from NH_4OH which was distilled by the Kjeldahl method. In this way the content of NH_4^+ was measured by titration with a 0.01 N solution of HCl. The *CEC* was calculated by using Eq. (1) (Pulido et al., 1992).

$$CEC = N * V_{HCl} \frac{V_T * 100}{a * p} \qquad (1)$$

where the *CEC* of the zeolite is given in m_{eq}/g, *N* being the normality of the titrate HCl solution, V_{HCl} the spent volume of HCl in the titration process (mL), V_T is the total volume (mL) recovered after the five exchange steps of the second stage, *a* is the distilled volume (mL) in the third stage and *p* is the zeolite sample mass (g).

2.3. Homo-ionized process of the NZC

The homo-ionized material was prepared as follows: 50 g of NZC were put in contact with a 5N solution of NaCl during eight days at room temperature. After this process, the solid phase was washed several times until chlorine was completely eliminated by using the $AgNO_3$ test (Bosch et al., 2012). The resulting homo-ionized material was called HNaZ.

2.4. Preparation of FeB-NPs supported zeolite

The synthesis of FeB-NPs supported on the HNaZ was carried out by chemical reduction as follows: the mass proportion used of Fe to zeolite was 0.06–1, respectively. The HNaZ material was put in contact with a 0.03 M solution of $FeCl_3 \cdot 6H_2O$. The reducing agent consisted of a 0.1 M solution of $NaBH_4$ which was added drop wise to the previous mixture by keeping mechanical stirring (Xingu-Contreras et al., 2015) and without controlling the pH solution. The fast reduction of Fe^{3+} can be represented as indicated next (2):

$$4FeCl_3 + 12NaBH_4 + 30H_2O \rightarrow 2Fe_2B + 10B(OH)_3$$
$$+ 39H_2 + 12NaCl \qquad (2)$$
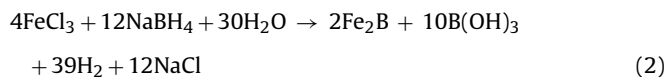
To prevent oxidation of the produced FeB-NPs a volume ratio of water to ethanol of 1–4, respectively, was used in the solution reaction. The obtained black powder was filtered off from the mother liquid phase by using two Whatman filter sheet papers and under vacuum (10^{-3} Torr). This black powder was washed three times using 25 mL of absolute ethanol to remove all the water content. This washing process is a key step of the synthesis to prevent oxidation of the produced FeB-NPs. All solutions, including the absolute ethanol were previously degassed and saturated with Ar before any use. Finally, the black solid was dried at 50 °C and identified as HNaZ-Fe. This black powder was easily attracted by an external magnetic field.

2.5. Samples characterization

2.5.1. SEM and EDS
The morphologic analysis of the zeolitic materials (NZC, HNaZ, HNaZ-Fe) was carried out by *SEM* using the JEOL® model JSM-5900LV. The solid sample was first sprinkled on metallic disks and covered with gold during 100 s, using the cation sputtering model AJA ATC 1500. Images of samples were recorded at different magnifications. This procedure was performed for each of the studied samples.

The chemical composition of the materials was determined using the *EDS* system (model Oxford® 7279) coupled to the scanning electron microscope. The samples were mounted directly on adhesive copper tapes and a series of five analyses were performed for each sample with a 100X magnification in different zones.

2.5.2. TEM
The morphology and size of the FeB-NPs supported on the HNaZ-Fe material was observed by using TEM, the model JEOL®-2010. The sample was prepared by dispersing a tiny amount of HNaZ-Fe material in ethanol by means of an ultrasonic bath, and subsequently few drops of the suspension were placed on a holey carbon film supported on copper substrate. TEM images were recorded at different magnifications.

2.5.3. Mössbauer spectroscopy (MS)
Mössbauer spectra of the FeB-NPs supported on the zeolitic material were obtained by placing about 100 mg of HNaZ-Fe in a sample holder, made of Lucite. A WISEEL® Mössbauer spectrometer, operating in the constant acceleration mode was employed. A radioactive source of $^{57}Co/Rh$ was attached to the transducer and the resulting isomer shifts of the recorded Mössbauer spectra are referred to that of metallic iron.