Journal of Alloys and Compounds 741 (2018) 240–245

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: http://www.elsevier.com/locate/jalcom

Application of mechanically alloyed MnAl particles to de-colorization of azo dyes

Mitra AboliGhasemabadi [a], [*], Wael Ben Mbarek [b], Oriol Casabella [c], Helena Roca-Bisbe [c], Eloi Pineda [a], Lluïsa Escoda [d], Joan J. Suñol [d]

[a] *Departament de Física, Universitat Politècnica Catalunya - BarcelonaTech, Catalonia, Spain*
[b] *Laboratoire de Chimie Inorganique, Faculté des Sciences, Universitéde Sfax, Ur-11-Es-73, Tunisia*
[c] *Escola Superior d'Agricultura de Barcelona, Universitat Politècnica Catalunya - BarcelonaTech, Catalonia, Spain*
[d] *Departament de Física, Universitat de Girona, Catalonia, Spain*

ARTICLE INFO

Article history:
Received 1 August 2017
Received in revised form
11 December 2017
Accepted 9 January 2018
Available online 10 January 2018

Keywords:
Mechanical alloying
Melt spinning
Decolorization
Orange II
Metallic particles
Zero valent metals

ABSTRACT

The use of metallic particles has been shown to be an effective, low-cost method for degradation of many contaminating compounds. In this work, we analyze the efficiency of MnAl metallic powders for degrading azo dyes, which are the class of colorant compounds most utilized by the textile industry. We used different routes to produce the metallic particles obtaining different internal structures as characterized by X-ray diffraction and electronic microscopy. The ability to act as discoloration materials was assessed by decolorization experiments of Reactive Black 5 and Orange II azo dyes aqueous solutions. The degradation reaction of the dye molecules was monitored by ultraviolet−visible (UV) spectrophotometry showing fast kinetics, with reaction times among the shortest found in literature. The effect of the different production methods on their performance as decolorizing materials was studied as function as various parameters such as initial pH, dye concentration and temperature. The electrochemical and corrosion properties of the MnAl compounds seem to be the key factors explaining the high decolorization efficiency of these materials.

1. Introduction

During recent decades, chemical processing industries involved in wet preparing, resizing, scouring, blanching, dyeing, or printing processes have grown considerably in size, resulting in an increased amount of variously colored industrial wastewater being released into the environment. These industrial water effluents, sullied with textile colors, have caused great concern because of their impact on health and their resistance to biodegradation [1]. While textile colorants do differ in substance composition they often exhibit a common component: they are exceptionally stable under normal aerobic conditions. Modern dyes are often designed to resist long exposure to daylight, water, and different conditions, which accordingly makes wastewater containing such dyes more troublesome to treat [2]. This makes it difficult to remove color from wastewater and low concentrations of dying compounds are very visible [3]. Most synthetic industrial dyes possess one or more azo bonds acting as chromophores and connected to various aromatic structures, these azo compounds standout amongst the better known groups of colorants utilized by the textile and leather treatment industries. A critical step during the treatment of water contaminated by these groups is the degradation of the compounds via the decay of the −N=N- bonds resulting in the decolorization of the water [4,5].

Different kinds of physical, chemical, and biological methodologies are applied to the treatment of effluents polluted with azo colorants. Adsorption, biodegradation, coagulation, ozonation, and hypochlorite treatment methodologies have all been broadly used [6,7]. Among these methodologies, color removal using zero-valent metals (ZVM) has been considered as an environmentally friendly solution. This is due to its benefits of easy and quick application, low cost, efficient degradation of azo compounds, its ability to cleave dye molecules into products that are more agreeable to mineralization in biological treatment processes and a simple operation [8,9]. The application method is very simple, the ZVM is put in contact with the dyed solution, acting as a donor of electrons

---

[*] Corresponding author.
E-mail addresses: mitra.aboligh asemabadi@upc.edu (M. AboliGhasemabadi), eloi.pineda@upc.edu (E. Pineda).

https://doi.org/10.1016/j.jallcom.2018.01.131
0925-8388/© 2018 Elsevier B.V. All rights reserved.

and promoting a reaction leading to the cleavage of the azo bound. The application can be in form of particles or other configurations [10], the kinetics of the decolorization reaction being proportional to the total surface of ZVM in contact with the solution [11].

Recently, the use of metastable nanocrystalline and amorphous metals as advanced materials acting as ZVM in water treatment processes has received a lot of attention [8–10,12–15]. The aim behind this research effort is to improve the reaction efficiency not by simply increasing the specific surface area but by increasing the reactivity of ZVM material. For example, particles of the same composition but with different internal structure, amorphous or nanocrystalline, showed important differences in their behavior as decolorization materials [10]. Different production routes used in materials science and physical metallurgy to produce metastable compounds, such as mechanical alloying or rapid solidification techniques like melt spinning and gas atomization, have been used to produce advanced decolorizing materials, the production method leading to important changes in the degradation efficiency shown by the materials [8]. Ball milling is a well-known method to synthesize new materials and compounds for a wide range of applications [16,17]. In metallic systems, the high energy introduced during the process is able to produce solid solutions of the metallic elements as well as new metastable phases [18]. Recently, some advanced biocompatible alloys containing Mn have been produced by this method [19].

In this work, Manganese—-Aluminum (MnAl) metallic powders were fabricated by different routes, obtaining particles with different inner structure. The study of this compositional system was motivated because of the good performance shown by Mn compounds [20] and Al-based alloys as decolorizing materials [21]. The aim is to compare the influence of the production route and the corresponding inner structure on the decolorization process. The obtained metallic particles were characterized by XRD, EDX and SEM. Afterwards they were applied to decolorization of Reactive Black 5 and Orange II aqueous solutions and the degradation of the dye molecules was monitored by UV–vis spectrophotometry. The degradation and removal of Orange II was studied under many different conditions, thus allowing us to compare the efficiency of the MnAl particles with that of other materials found in literature. Finally, the effect of initial pH, dye concentration, and dosage were investigated. The results show that the inner crystalline phase of the MnAl particles has not a determinant influence in the reaction kinetics. On the other hand, they reveal the prominent role of Mn as the main reactive element in the dye degradation reaction as well as that the presence of Al widens the range of conditions in which these materials show high decolorizing efficiency.

2. Materials and methods

Two different production routes of MnAl particles were used, in all cases pure metals of Mn and Al with a purity over 99.8% were utilized as the initial materials. A batch of powder was fabricated by melt-spinning of a master alloy with nominal composition of $Mn_{70}Al_{30}$ at.%, the ribbons obtained by this rapid solidification method were subsequently ball-milled during 15 h. Other batches were fabricated by direct mechanical alloying of elemental Mn and Al powders by milling during 20 h, 30 h, 60 h and 200 h. The ball milling process was performed under a highly purified argon atmosphere with a high-intensity shaker ball milling device (SPEX 8000). The milling protocol consisted always in 10 min of processing followed by rest periods of 5 min, these were applied to prevent the powder from overheating, self-agglomerating or adhering to the container's interior walls or to the milling balls. The microstructure and morphology of the milled powder were characterized by scanning electron microscopy (SEM) and energy dispersive X-ray (EDX) microanalysis using a Hitachi TM3030Plus SEM. The milled powder was verified by X-ray diffraction (XRD) on a Bruker D8 Advance equipment using Cu-K radiation to check out the structural changes of the milled powders. Specific surface measurements were performed by means of the Brunauer–Emmett–Teller (BET) model in a Micrometrics ASAP 2020 apparatus using nitrogen as adsorbate and helium as non-adsorbing gas for the dead volume calibration.

The decolorization study was performed on two azo dyes: Reactive Black 5 (RB5) and Orange II sodium salt (both purchased from Sigma-Aldrich). Each experiment was designed to evaluate the effectiveness of $Mn_{70}Al_{30}$ particles with regards to the decolorization of the dyed aqueous solutions. The dye solutions were prepared with 40 mg of RB5 or Orange II per liter of water ($40\ mg\ l^{-1}$). From the prepared dyed solution, 100 ml was extracted and moved to a 250 ml Erlenmeyer glass. Following this, different quantities of powder (from 50 to 250 mg depending on the test) were added and agitated by using magnetic stirring at a speed of 500 rpm. To investigate the effect of pH, the original dye solutions with $pH = 6.8$ were altered to $pH = 4$ by adding diluted HCl at 1.0 M and $pH = 10$ by adding diluted NaOH at 1.0 M. The initial pH changed always towards more basic conditions during the treatments ($pH_{final} = 7.6–7.8$ for initial $pH = 4$ and 7, and $pH_{final} = 10.6$ for initial $pH = 10$). During the decolorization experiments, 2.5 ml of solution were extracted at regular time intervals and analyzed in a UV/VIS spectrophotometer (2600 Shimadzu). The UV–vis spectra were recorded from 200 to 800 nm using a quartz cell of 1.0 cm path length. The concentration of dye was quantified by measuring the absorbance at $\lambda_{max} = 597$ nm (RB5) and $\lambda_{max} = 483$ nm (Orange II), corresponding to the maximum of the absorbance peaks of the colorants. The concentration and absorbance linear relation was assessed by measuring the absorbance spectrum of aqueous solutions of various initial concentrations.

3. Results and discussion

The efficiency as dye degradation materials of the MnAl powders was evaluated by decolorizing RB5 and Orange II aqueous solutions. Both Mn and Al have a high value of reduction potential, making them good candidates to act as reducing agents. Mn and Al compounds have been used as azo dye degradation materials before [20,21] but the high efficiency of MnAl compounds was discovered recently [22]. As specified in the materials and methods section, MnAl powders were obtained by different production routes; namely, melt spinning and subsequent ball milling (MS+BM particles) and direct mechanical alloying of elemental Mn and Al powders with different milling times (BM-20 h, 30 h, 60 h and 200 h particles). All the particles were produced with the same nominal composition of $Mn_{70}Al_{30}$. Pure Mn and Al powders were also used to test the efficiency of these elements as decolorizing materials. In the case pure Mn the decolorization efficiency was tested for both as-purchased powders (Mn-AP) and 30 h ball milled Mn (Mn-30 h).

Fig. 1 shows the degradation kinetics of RB5 aqueous solutions obtained by MnAl MS+BM, BM-30 h and BM-200 h particles, as well as pure Mn-AP and Mn-30 h. In this work the degradation process is assumed to be described by first-order reaction kinetics following $C(t) = C_{sat} + (C_0 - C_{sat})e^{-t/\tau}$, with $C(t)$ the dye concentration, C_0 the initial concentration, C_{sat} the final concentration and τ the rate constant characterizing the speed of the reaction. The reactions obtained in this work show $C_{sat} \sim 0$ indicating a complete decolorization in all cases. The deviations from the exponential decay observed in the initial stays could be attributed to a double step process, as seen in some decolorizing materials [23]. This double step is only observed in the slowest reactions studied in this work