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Fast zero-order hydro-cracking reaction of X-3B over crystal Al-Fe alloys: Effect of electrochemical corrosion behaviors

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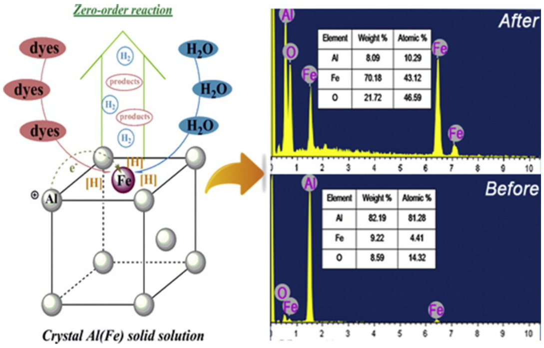
HIGHLIGHTS

- Mechanical alloying process led to the formation of crystal Al(Fe) solid solution.
- A degradation efficiency of 99% for X-3B was achieved within only a few min under Al-Fe alloys treatment process.
- The electrochemical corrosion processes of the Al-Fe alloys significantly promote the degradation reaction.
- The degradation of the X-3B solution was fit to the zero-order kinetic model.

GRAPHICAL ABSTRACT



Element	Weight %	Atomic %
Al	8.09	10.29
Fe	70.18	43.12
O	21.72	46.59

Element	Weight %	Atomic %
Al	82.19	81.28
Fe	9.22	4.41
O	8.59	14.32

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ABSTRACT

The present study described the excellent degrading ability of as-synthesized Al-Fe alloys for degradation of high-concentration X-3B in high salinity, alkaline aqueous solutions and its degradation mechanism. Al-Fe alloys were prepared by high-energy ball-milling of pure Fe and Al powders and further characterized by XRD, SEM, and BET. The results showed that the mechanical alloying process led to the formation of crystal Al(Fe) solid solution. Batch experimental results confirmed that a high concentration of X-3B could be completely removed from an aqueous solution with 2 g/L Al-Fe alloy particles within 3 min. The degradation of X-3B followed zero-order kinetics, for initial dye concentrations value from 100 to 2000 mg/L. The major factors that affect the degradation of X-3B were also investigated. Furthermore, the intermediate products were identified via UV–vis, FTIR, and GC–MS analysis, and the potential mechanism was discussed. It was also found that the biodegradability, as expressed by the BOD_5/COD ratio, was significantly increased following the degradation reaction. Therefore, the Al-Fe alloys system was confirmed as an effective and simple strategy for the pre-treatment of azo dye wastewater.

1. Introduction

Dyestuff loss in the textile industry has become one of the major environmental threats due to its toxic and carcinogenic characteristics [1–4]. Azo dyes (with N═N bonds) constitute the majority of dyes that are produced and consumed around the world, and it is difficult to treat them since they have vivid color, high COD, and low biodegradability [5–8]. In recent years, various physical and chemical approaches have been used to treat azo dye wastewater, such as adsorption, flocculation, reduction, chemical oxidation, photodegradation and biological methods. [9–11] However, all these methods have drawbacks. For

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example, oxidation methods, such as Fenton and photo-catalysts, are costly, biological methods are time-consuming, and flocculation and adsorption are ineffective as they only transfer the phase of pollutants instead of destroying them [12,13]. For these reasons, the methods for the proper treatment of azo dye wastewater should be based on the combination of quick pre-treatment and advanced biological treatment.

In recent years, nanoporous metals have attracted a lot of attention as novel, functional materials that can be applied in various fields, such as catalysis, sensors, actuators, and fuel cells [8,14–19]. Among the active nanoporous materials, Fe-based alloys have received an increasing interest in this field due to their excellent performance in removing dyes from aqueous solutions. As a modification of ZVI (Zero Valent Iron), the incorporation of a second, catalytic metal, such as Pd, Zn, Ni or Pt, may alter the structure and local chemical composition of the alloys, resulting to a significant enhancement of the degradation ability of the catalyst. [20–22] Tee et al. reported quick degradation of trichloroethylene with the formation of ethane by using Ni/Fe nanoparticles [23]. Zhu et al. reported that monochlorobenzene, dichlorobenzene, and 1,2,4-trichloro-benzene could be completely degraded into benzene through the reduction of the number of Pd/Fe nanoparticles [24]. Xu et al. developed subcolloidal Ag/Fe (1% Ag) particles to dechlorinate chlorinated benzenes [25]. However, most Fe-based alloys were studied under acidic or neutral pH conditions, and do not comply with the high pH value of actual azo dyes wastewater.

Additionally, porous metals can be fabricated by dealloying solid solution alloy systems [26–28]. Dealloying (also called selective alloy corrosion) is an electrochemical process referring to the electron transfer process and the dissolution of one or more components of the alloy [14,16,18]. In fact, the degradation mechanism is also known as the reductive cleavage of the azo group, as azo dye molecules will accept electrons from metals and degrade to smaller molecules when combined with H^+. However, little attention has been paid to the relation between the corrosion behavior of alloys and the degradation mechanism.

The objective of this study is to provide an effective method for the pre-treatment of azo dyes in high salinity, alkaline aqueous solutions, and also to investigate the effect of corrosion on the degradation mechanism. Herein, Al-Fe alloys were prepared by high energy mechanical ball-milling process. Aluminum was selected as the source material due to its easy access, nontoxic properties, and its extensive applications in engineering practice [29]. Reactive Brilliant Red X-3B was selected as a target reactive azo dye to be degraded in batch experiments. The effect of initial pH value and initial dyes concentration on the removal ability of X-3B dyes was investigated. The morphological characteristics and corrosion behavior of the Al-Fe alloy particles were studied via SEM and TEM. The post-treatment product was identified in details by UV–vis absorption spectrum, FTIR and GCMS techniques. A possible degradation pathway and mechanism were also proposed.

2. Experimental

2.1. Materials and reagents

Reactive Brilliant Red X-3B is of industrial grade and used without further purification. Iron powders (200 mesh, 98.0% purity), aluminum powders (200 mesh, 99.0% purity) and all other chemical reagents are of analytical grade. All solutions were prepared with deionized water.

2.2. Synthesis and characterization of Al-Fe alloy

Mechanical alloying (MA) was performed under nitrogen atmosphere using a GN-2 high-energy ball-milling machine (Shanghai Hua Yan Equipment Co., Ltd.). The molar ratio of the Al to Fe was selected to be 19:1 according to the earlier experiments. (Fig. S1 and Fig. S2) The stainless steel balls of 6, 10 and 12 mm diameters were used as milling medium, with a mass ratio of 4:1:1, and the value of ball-to-powder weight ratio was 15:1. Absolute alcohol (8 wt% of powders) was used as process control agent to prevent excessive welding of powders. The rotation speed was selected as 600 rpm. After 9 h ball milling, the powders were collected and labeled as Al—Fe alloy. Physical mixtures of aluminum and iron was prepared for the contrast experiment and labeled as Al—Fe mixture. The X-ray diffraction patterns (XRD) of alloy were recorded by a Rigaku D/Max-RA 3400 (Rigaku Corporation, Japan) powder diffraction system with Cu Kα radiation (40 kV, 50 mA, $\lambda = 0.15418$ nm). Scanning electron microscopy (SEM) analysis was performed in a S-520 (HITACHI, Japan). The specific surface area of alloy was measured using the BET N_2 adsorption method with a Quadrasorb SI (Quantachrome, USA).

2.3. Batch experiment

The degradation experiments were carried out in a glass beaker at room temperature, the stock solution was prepared with appropriate amount of X-3B in 100 mL deionized water. 5 g sodium chloride was dissolved to achieve a high-salinity condition, which was similar to the sanity of actual azo dyes wastewater. The pH values were adjusted to a given value by anhydrous sodium carbonate. Degradation experiments were performed with 0.2 g Al-Fe alloy particles dispersed in the solution under vigorous stirring. At given time intervals, 5 mL aliquot of the aqueous solution was filtered through a Millipore filter (pore size 0.45 μm) to remove particles. The filtrates were then diluted to a suitable concentration range and analyzed by recording the UV–vis spectra of X-3B using a UV-2550 UV–vis spectrophotometer (Shimadzu Corporation, Japan) and calculating its concentration based on a standard curve.

Corrosion experiment was carried out in 100 mL sodium hydroxide solution with 5 g of NaCl, 0.2 g of Al-Fe alloy particles and a pH value of 14. After 30 min treatment, alloy particles were washed and then dried at 80 °C for further characteristic analysis.

2.4. Analytical methods

The degradation intermediates followed the degradation of X-3B dye was detected by using UV–vis absorption spectra in the range of 200 to 800 nm which were recorded by a UV-2550 UV–vis spectrophotometer (Shimadzu Corporation, Japan). The FT-IR spectra were recorded by a Avatar 370 (Thermo Nicolet, USA) to assess the differences in the general functional groups of the samples. Each sample was ground with KBr as tablet and scanned between the wavelengths of 4000 and 400 cm^{-1}. GC–MS analysis of degradation products was carried out using a QP2010S mass spectrophotometer (Shimadzu corporation, Japan). The initial column temperature was 60 °C, then increased linearly at 15 °C/min to 200 °C. The temperature of injection port was 230 °C and the helium was used as carrier gas. In addition, the following parameters were determined according to standard methods for examination of wastewater [30,31]: Chemical Oxygen Demand (COD), Biochemical Oxygen Demand (BOD), ammonia and sulfate.

3. Results and discussion

3.1. Characterization of synthesized Al-Fe alloys

The XRD patterns of the samples are presented in Fig. 1. Fig. 1(a) and Fig. 1(d) showed the phases of pure Al and Fe, respectively. Compared to the Al + Fe mixture (Fig. 1(b)), Al-Fe alloys (Fig. 1(c)) showed broader peaks of higher intensity after the MA process. This indicates that lattice structure of Al was maintained and the formation of the crystal Al(Fe) solid solution, due to the dissolution of Fe atoms into the Al lattice [32]. Furthermore, there are no peaks related to any of the remaining metal oxide detected after the MA process, which also suggests the high crystallinity of the Al alloys. On the other hand, the relative intensity of the peak [Al (200), Fe (110)] was further increased from 57.6% to 72.4%, which indicates incomplete alloying of the Fe.