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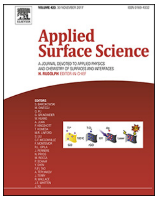

Full Length Article

Synthesis of a novel magnetic $Fe_3O_4/\gamma\text{-}Al_2O_3$ hybrid composite using electrode-alternation technique for the removal of an azo dye

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ABSTRACT

A novel magnetic adsorbent of $Fe_3O_4/\gamma\text{-}Al_2O_3$ hybrid composite (denoted as M-Fe/Al-H) was developed electrochemically via a sequential application of iron and aluminum electrodes in a one-pot fashion, which called here as electrode-alternation technique, followed by pyrolysis. Physical and chemical properties of the prepared adsorbents were characterized and their feasibility towards the removal of di-anionic azo dye Acid Black 1 (AB1) was assessed. Textural and structural characterization revealed that the prepared M-Fe/Al-H possesses superior properties than those of M-Fe (sole usage of iron electrode), which may improve the adsorption capacity. Kinetics revealed that the adsorption equilibrium was reached within 12 h with approximately 90% of the equilibrium adsorption capacity within the first 3 h. Comprehensive analysis using the pseudo-second order and intraparticle diffusion models indicated that the dominant mechanism of the reaction is film diffusion with intraparticle diffusion being the rate determining step. The adsorption equilibrium isotherm data were best represented by the Sips isotherm model, which found to be approximately 1501, 1786, and 1959 mg/g at 283, 293, and 303 K, respectively. The exceptional performance as well as its ease of separation allows M-Fe/Al-H to be a promising candidate as an effective for azo dye removal from various aqueous medium.

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1. Introduction

With increasing industrialization, huge quantity of dye-containing wastewater is produced from various manufacturing industries such as food, rubbers, cosmetics, textile, paper, printing and others. Due to the ease of dissolution in water and resistance towards biodegradation, synthetic dyes have become one of the significant contributors to water pollution [1]. In particular, azo dyes and their metabolites have been recognized as toxic, mutagenic, as well as carcinogenic to the aquatic ecosystem and humans [2]. Consequently, a substantial increase in effort to develop sustainable means of dye containing wastewater treatment and improve the efficiency of the process is ongoing.

Numerous approaches have been unearthed and developed to treat dye-containing wastewater such as coagulation/flocculation, chemical oxidation, ultrasonication, adsorption, and so on. Among such techniques, adsorption process has evolved into one of the most promising methods due to its flexibility, simplicity of design, no release of harmful byproducts, and economical technique [3,4]. In particular, metallic nano-sized materials, especially metallic nanoparticles, have recently gained widespread attention in the adsorption of dye molecules from solution phase due to its outstanding stability and adsorption capacity at low adsorbent dosage, as well as high productivity and cost efficiency [5,6]. Out of the heavily investigated metallic nanoparticles, gamma alumina ($\gamma\text{-}Al_2O_3$) has been renowned as one of the promising candidates as an adsorbent because of its unique surface property (i.e., spinel structure), allowing favorable interaction with adsorbates, and thereby possessing a high potential to exhibit highly effective adsorption performance for various contaminants [7–12]. Nonetheless, it is still considered to be an undesirable process with restricted applicability in industrial application due to its difficulty in separation without any post-treatment processes such as filtration or centrifugation, which may lead to the potential generation of secondary pollutants.

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In this regard, use of nanoparticles in magnetic materials (e.g. Fe_3O_4, magnetite) offer tremendous potential as promising adsorbents for wastewater treatment than conventional (non-magnetic) adsorbents because of its synergistically improved properties and comfortable re-collectability and separability from aqueous solution by applying external magnetic field at the post-adsorption stage, which leads to improving the system's attractiveness with respect to the simplicity and cost-effectiveness of the process [13]. Various methodologies have been utilized for synthesizing Fe/Al-based magnetic nanocomposites, which are mostly based on chemical synthetic method such as incipient-wetness impregnation [3], modified wet impregnation method [14], hydrothermal method [15], sol-gel method [16], and chemical precipitation method [17]. However, owing to its complexity, the physicochemical properties of final products would be unstable and un-reproducible, which ultimately may lead to inconsistent adsorption capacity.

Given the interest in developing an alternative route to synthesize magnetic nanoparticles, electrochemical synthesis using Fe electrodes has emerged as an alternative option for the fabrication of magnetite, specifically based on anode dissolution and electro-precipitation processes [18]. In this method, released iron from the anode is oxidized to ferrous ion (Fe^{2+}), which is then further oxidized into ferric ion (Fe^{3+}) in the presence of electrolytes. Subsequently, the generated hydroxyl ion (OH^-) at the cathode via reduction of water molecules bind to the Fe^{3+} to yield $Fe(OH)_3$. Finally, $Fe(OH)_3$ is reduced to Fe_3O_4 under alkaline condition ($7.0 < pH < 9.0$). If OH^- is not enough presented in the solution, it may dehydrate to generate a non-magnetic ferric oxide [19]. The overall reactions are as the following [20,21]:

$$Fe \rightarrow Fe^{2+} + 2e^- \quad (1)$$

$$Fe^{2+} \rightarrow Fe^{3+} + e^- \quad (2)$$

$$H_2O \rightarrow 2H^+ + 2e^- + 1/2O_2 \quad (3)$$

$$2H_2O + 2e^- \rightarrow H_2\uparrow + 2OH^- \quad (4)$$

$$Fe^{3+} + OH^- \rightarrow Fe(OH)_3 \quad (5)$$

$$3Fe(OH)_3 + H^+ + e^- \rightarrow Fe_3O_4 + 5H_2O \quad (6)$$

Similarly, when an aluminum electrode is applied, Al^{3+} and OH^- ions can be generated by electrochemical reactions at the anode and cathode, respectively. According to complex precipitate reactions, Al^{3+} is finally transformed into $Al(OH)_3$, an important precursor for the thermal synthesis of γ-Al_2O_3. The reaction scheme of the process is as the following [22].

$$Al \rightarrow Al^{3+} + 3e^- \quad (6)$$

$$2H_2O + 2e^- \rightarrow H_2\uparrow + 2OH^- \quad (7)$$

$$Al^{3+} + H_2O \rightarrow Al(OH)^{2+} + H^+ \quad (8)$$

$$Al(OH)^{2+} + 2H_2O \rightarrow Al(OH)_3 + 2H^+ \quad (9)$$

In general, a rapid increase of pH of the system occurs during the intercourse of electrochemical synthesis due to the generation of OH^- at the cathode such that the final pH may reach above 10.0 even when the initial pH is acidic. On the other hand, Al electrode acts neutralization neutralizer when the initial pH is alkaline [23]. This phenomenon serves as a potent tool in the synthesis of magnetic nanocomposites via electrochemical process because the consecutive usage of Fe electrode followed by Al counterpart can prevent the possible formation of unwanted ionized byproducts such as $Fe(OH)_4{}^-$. Taking these phenomena into account, the development of a novel approach to synthesize magnetic hybrid composite by the application of Fe electrode followed by Al electrode, or simply electrode-alteration technique, is investigated in this study. The specific objectives of the this work were to (i) synthesize magnetic Fe_3O_4/γ-Al_2O_3 hybrid composite (denoted as M-Fe/Al-H) by applying a novel electrode-alternation method and (ii) characterize its physicochemical properties as well as its potential application as an adsorbent for removing azo dye from aqueous media. To elucidate the adsorption mechanisms and behaviors of M-Fe/Al-H, kinetic and equilibrium isotherm studies were conducted under different temperatures. To our knowledge, no study has been reported on the application of electrochemically prepared M-Fe/Al-H as an adsorbent for the removal of AB1 from aqueous solutions up to date.

2. Materials and methods

2.1. Chemicals and materials

To investigate the M-Fe/Al-H for dye adsorption, an amino acid staining di-azo dye acid black 1 (AB1, purity > 96.0%), which has a chemical formula of $C_{22}H_{14}N_6Na_2O_9S_2$ with a molecular weight of 616.49 g/mol was used as a model adsorbate, was purchased from Samchun Pure Chemical Co., Ltd. (South Korea). The chemical structure of AB1 is illustrated in Fig. S1 (see supplementary material). The stock dye solution was prepared by dissolving 1.0 g of AB1 in 1.0 L of deionized distilled water (Milli Q plus, Merck Millipore Co., Germany) and stored at 277 K before use. The solution pH was adjusted with 0.1 M HCl and NaOH using a LabQuest2 portable meter (LQ2-LE, Vernier, USA). All chemicals used for this study were of analytical reagent grade. The final concentrations of AB1 after adsorption tests were analyzed using a UV–vis Spectrophotometer (DR5000, HACH Company, Netherlands) at a maximum wavelength (λ_{max}) of 619 nm. The respective concentrations were calculated using the calibration curves in the range of 0–10 mg/L (Abs_{619} at 10 mg/L = 1.465). For the electrochemical synthesis of magnetic adsorbents, an appropriate current density was applied using a power supply (0–100 V and 0–12 A, Programmable DC Power Supply, ODA, South Korea) and equivalent size of sacrificial Fe and Al electrodes with a dimension of $\Phi 10 \times 400$ were employed. In order to remove impurities, the electrodes were soaked in an acetone solution (purity > 99.5%, Samchun Pure Chemical Co., Ltd., South Korea) for 30 min prior to their use. 1.0 g/L of NaCl (purity > 99.0%, Samchun Pure Chemical Co., Ltd., South Korea) was employed as a source of electrolyte.

2.2. Preparation of magnetic nanoparticles: selection of the best adsorbent

Prior to this study, in order to select the most suitable magnetic nanoparticles as an adsorbent, comparative study on the adsorption performance was conducted using different types of the electrochemically prepared adsorbents. In this test, four types of adsorbents were prepared at room temperature under the following conditions: (1) monopolar mode: anode-cathode = Fe–Fe (denoted as M–Fe); (2) bipolar mode: anode-cathode + anode-cathode = Fe–Fe + Al–Al (denoted as M–Fe + Al); (3) electrode-alternation mode I: anode-cathode = Fe–Fe → Al–Al (M–Fe/Al–H); (4) electrode-alternation mode II: anode-cathode = Al–Al → Fe–Fe (denoted as M-Al/Fe-H). For the preparation of the adsorbents, the initial pH was adjusted to 5.0 using 0.1 M HCl and 0.1 M NaOH and the operation period was fixed at 30 min. For electrode-alternation mode I and II, each duration of Fe–Fe and Al–Al was 15 min, respectively. The electrodes were placed perpendicularly in 500 mL of a NaCl solution (1.0 g/L) and the distance between the anode and cathode was fixed at 3 cm. Subsequently, current density of 24.87 mA/cm^2 was applied under a constant stirring at 150 rpm. Then, the products were separated from the mixture via centrifu-

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