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In-situ deposition of silver–iron oxide nanoparticles on the surface of fly ash for water purification

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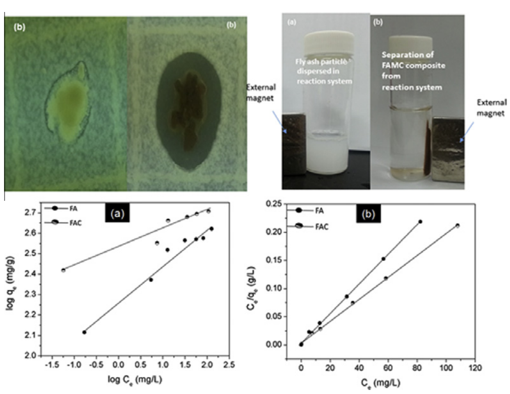
GRAPHICAL ABSTRACT



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ABSTRACT

In this study, a fly ash based composite, Ag–iron oxide/fly ash, was synthesized via a facile one-pot hydrothermal process using fly ash, ferrous chloride, and silver nitrate as precursors. Field emission scanning electron microscopy (FE-SEM), EDX, transmission electron microscopy (TEM), X-ray diffraction (XRD), Fourier transform infra-red spectroscopy (FTIR), Photoluminescence (PL) and Brunauer–Emmet t–Teller (BET) surface area measurement confirmed the formation of composite particle. FA provided a suitable surface for the in-situ deposition of Fe_3O_4 and Ag NPs during hydrothermal treatment. As a result, the particle size of Fe_3O_4 and Ag NPs was sufficiently decreased, and the surface area of the NPs as well as, a whole matrix was increased. The antimicrobial activity of the composite was accessed by *Escherichia coli* inhibition assay. Lead(II) ion adsorption efficiency of the composite was analyzed from a series of batch adsorption experiments (the effects of concentration, contact time, pH and adsorbent dose on the adsorption of Pb(II) ion from aqueous solution). Results indicated that as-synthesized composite has high antibacterial capacity, and the metal ions uptake efficiency compared to fly ash particle. Furthermore, incorporation Fe_3O_4 NPs onto the fly ash make it easily separable from a reaction system

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using an external magnet. The composite synthesis protocol is a simple method that utilizes a readily available industrial byproduct to produce a unique composite for environmental remediation.

1. Introduction

In recent years, environmental contamination caused by toxic metal ions has become a worldwide environmental problem due to the bioaccumulation tendency of these toxic materials [1–3]. Removal of heavy metal from aqueous solution have been a focus area of research over recent years [4]. Various methods have been used to remove heavy metal ions from aqueous environments such as chemical precipitation [5,6], solvent extraction [7], ion exchange [8], reverse osmosis and adsorption [4]. Among these processes, adsorption with a selection of suitable adsorbent can be an effective technique for the removal of heavy metal ions from wastewater. Activated carbon, alumina, silica, fly ash, and ferric oxide are commonly used adsorbents that have high metal adsorption capacity. However, most of them are expensive and difficult to separate from wastewater after water treatment. Therefore, a low cost fly ash based magnetic composite could be an alternative material that could be mechanically removed by magnetic separation.

Fly ash (FA) is a waste byproduct generated from coal-industrial plants and consists of fine, powdery particles with a spherical shape, lower density and substantial granular components of silicon dioxide (SiO_2), alumina (Al_2O_3), calcium oxide (CaO), and magnesium oxide (MgO) as explained in our previous report [9]. Every year large quantity of FA is produced as a byproduct from thermal plant, worldwide. However, only a small amount (10–20%) of this waste fly ash is reused [10]. In recent years, many studies have investigated effective ways to modify FA for valuable applications [11]. It has been shown that FA can be used as an additive in the cement industry, in the building industry for brick making, for glass, lightweight materials, ceramic tableware and art ware, composite materials production, materials recovery, as an adsorbent for waste management and, waste stabilization, as well as other uses [12]. Furthermore, FA is a potential substrate to incorporate metal and metal oxide NPs, such as Ag, TiO_2, ZnO for various applications [13–15].

Silver nanoparticle based nanocomposites have attracted research interest due to a variety of applications including as antimicrobial, catalysts, optoelectronics, sensing, biomedicine, and as an adsorbent. Many studies have established the chemisorption of heavy metal ions on nanoparticles [16], and the interaction of silver nanoparticles (NPs) with mercuric and lead ions have been reported [16–19]. However, the use of such composites is limited due to difficulties associated with separation after their use. Such a drawback could be solved by doping magnetic NPs onto the surface of FA particles that could be separated using the magnetic field. This would be beneficial in a situation where filtration is not a simple option. This process would alleviate difficulties associated with separating nanoparticles dispersed in media directly for purification purposes [20]. Furthermore, fly ash is a potential support for deposition of different inorganic NPs on its surface [13,14,21,22]. Therefore, the simultaneous growth of silver and magnetic iron oxide NPs on the surface of fly ash could provide an effectively bonded composite. The fixed attachment of iron oxide and Ag NPs on the surface of high aspect ratio FA, could be useful not only for separation but also act as an antibacterial agent, and assists in the adsorption of aqueous pollutants during water treatment. Therefore, the deposition of Ag and Fe_3O_4 NPs on fly ash could be an efficient way to construct a composite with improved properties required for water treatment. Iron oxide nanoparticles deposited on the fly ash surface not only improves the separation performance but also effective for heavy metal ion adsorption. Kumari et al. [23] synthesized the magnetically separable magnetite nanospheres using template free solvothermal method for the effective removal of chromium and lead from aqueous solution. Recently, Abdullah and coworkers [24] reported that the Ag and Fe NPs have excellent efficiency for the adsorption/removal of Cr(II) and Pb(II) ions from the aqueous solutions. The removal/uptake mechanism involves the interaction between the metal ions and the oxide/hydroxyl layer around the spherical metallic core of nanoparticle in water medium [24].

The aim of the present work is to investigate an efficient, low-cost and easily separable composite for the simultaneous removal of the Pb(II) ions and microbial bodies from aqueous solution. This simple approach highlights the possibility of using a composite for waste-water purification, where one byproduct material, fly ash, was used to control other pollutants in a scalable and inexpensive process.

2. Experimental

2.1. Materials

Fly ash obtained from Won Engineering Company Ltd. (Gunsan, Korea) was ball-milled for 12 h before use. Ferrous chloride tetrahydrate ($FeCl_2{\cdot}4H_2O$) from Samchun Chemicals, ammonium hydroxide (NH_4OH, 28% NH_3 in water) and silver nitrate ($AgNO_3$) from Showa chemicals, poly (vinylpyrrolidone) (PVP, MW-5800) from Alfa Aesar, and lead(II) nitrate ($Pb(NO_3)_2$) from Sigma Aldrich were used as received.

2.2. Preparation of the Ag–iron oxide/Fly ash composite

Ag–iron oxide/fly ash, a fly ash based composite (FAC) particles were synthesized using a one-step hydrothermal approach based on our previous reports [25]. In brief, 400 mg of ball-milled FAPs (using 3 mm zirconia balls for 12 h and sieved) was washed and sonicated for 30 min in 20 ml distilled water. 40 mg of PVP was added to a 20 ml aqueous solution containing 200 mg of $FeCl_2{\cdot}4H_2O$, 1 ml of ammonium hydroxide (28%) and sonicated fly ash suspension was added to this mixture followed by shaking at a rate of 200 rpm for 45 min. After shaking, 10 ml of 4.07×10^{-2} M $AgNO_3$ was added, and the mixture was transferred to an autoclave for hydrothermal treatment at 120 °C for 3 h. The obtained composite was washed several times with distilled water and ethanol, and was dried at 80 °C for 12 h.

2.3. Characterization

The surface morphologies of fly ash and the as-synthesized particles were studied by field-emission scanning electron microscopy (FE-SEM, S-7400, Hitachi, Japan) and transmission electron microscopy (TEM-2010, Orius SC10002). EDX was also performed using FE-SEM. Information about the phase and crystallinity of the material was obtained using Rigaku X ray diffractometer (XRD, Rigaku, Japan) with Cu Kα (λ = 1.540 Å) radiation over Bragg angles ranging from 10° to 80°. Nitrogen adsorption/desorption isotherms were obtained at the liquid nitrogen temperature of 77 K using a Quantachrome Nova 2200e automated gas adsorption system.