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Photocatalytic reduction of iodine in radioactive waste water using maghemite and titania nanoparticles in PVA-alginate beads

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ABSTRACT

The presence of iodine ions in nuclear waste water is a major concern due to its high level of toxicity. In this study three different types of beads were prepared; i) maghemite (γ-Fe_2O_3) PVA-alginate beads, ii) titania (TiO_2) PVA-alginate and iii) combined γ-Fe_2O_3 and TiO_2 nanoparticles embedded in PVA-alginate defined as maghemite and titania PVA-alginate beads respectively. These beads were used in batch sorption experiments for iodine ions removal from radioactive waste water under sunlight. The combined γ-Fe_2O_3 and TiO_2 nanoparticles embedded in PVA-alginate was able to remove the I(1) rapidly with maximum efficiency. Results revealed that I(1) removal was enhanced under sunlight irradiation and XPS findings proved that I(1) was reduced to I(0) indicating that photocatalytic process has occurred. Maximum removal of I(1) was achieved at maximum pH of 8. The maghemite and titania PVA-alginate beads were robust; losing only 13% of its photocatalytic properties after recycling for seven times. Kinetic studies illustrated that I(1) removal followed the pseudo-second-order model with the $R^2 > 0.99$.

1. Introduction

Radioactive iodine is known as potentially hazardous fission product because of its high yield and/or relatively long half-life, and the radioactivity released to the atmosphere by this incident is estimated to be 1.6×10^{17} Bq (Ministry of Economy, Trade and Industry, 2011) [1]. Iodine excess may lead to thyroid diseases. Previous 5-year prospective survey showed that the prevalence and incidence of hypothyroidism or autoimmune thyroiditis increased with iodine intake [2]. It was found that iodine shows low affinity towards subsurface sediment [3], and iodine is weakly adsorbed on sediment materials [4]. The weak adsorption capabilities of clays for iodine can be enhanced by exchanging the cations in the natural inorganic interlayer with certain organic cations [5]. Activated aerogels impregnated with silver ion can enhance the iodine adsorption due to an increase in electrostatic attraction [6].

The presence of iodine in environmental samples is relatively low. The main source of contamination of the environment by iodine is thin film transistor liquid crystal displays (TFT-LCD) [7]. In the TFT-LCD, wastewater is detrimental to the proper operation of the wastewater treatment facility due to its potential biocidal effect toward microorganisms [8]. Several reports have been published on the removal of iodine from water samples. Madrakian et al. [9] reported that adsorption of iodine on Mg–Al layered double hydroxide (LDH) is an anion-exchange process. Kentjono et al. used synthesized Mg–Al (NO_3) LDH and used it to remove boron and iodine from polarizer manufacturing wastewater [9].

Recently, the correlation between titania (TiO_2) and wide band gap semiconductors has attracted many researchers attention due to its big pores and surface area that are essential in luminescence, photocatalysis, self-cleaning surfaces, highly specific chemical sensors, solar cells and carbon nanotubes [10-14]. Remarkably, one of the most popular photocatalysts is TiO_2 because of its great thermo stability and photocatalytic effectiveness. Recently, considerable research has been conducted on the TiO_2 powders use in photodegrading different organic pollutants in the water. Additionally, the studies on how to enhance the catalytic attributes of TiO_2 have also considerably increased. A number of researchers have begun to couple semiconductor materials, such as TiO_2/CdS [15], ZnO/CdS [16] and SnO_2/Fe_2O_3 [17] so as to expand its general application [18,19].

On the other hand, Fe_2O_3 nanoparticle with band-gap of 2.2 eV is an appropriate candidate and a remarkable n-type semiconducting material to be utilized as a photocatalyst in sunlight irradiation [20]. The Fe_2O_3 nanoparticle's photocatalytic nature is studied in water splitting [21], semiconductor electrode functions and photo degradation of organic contaminants [22]. Furthermore, Fe_2O_3 can be applied as a sensitizer to TiO_2 photocatalyst because of its narrow band-gap. As Fe_2O_3–TiO_2 is exposed with sunlight; the electrons in the Fe_2O_3 valence group are eager to attack the conduction group and make holes. Employing the construction of the built-in field in Fe_2O_3–TiO_2

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heterojunction causes the electrons in the valence bands of TiO_2 to transmit into Fe_2O_3 since the photo created holes transmit the TiO_2 valence band in the opposite direction. An efficient procedure in improving the photocatalytic movement of the composition is the control transmission between the valance bands of TiO_2 and Fe_2O_3, since it leads to a growth of the electron–hole recombination time [23].

Some studies used alginate to encapsulate magnetic nanoparticles to produce it in the form of beads. Polyvinyl alcohol (PVA) is another biopolymer that is commonly used to remove heavy metals of waste water because it is non-toxic, safe and cheap. But PVA has the tendency to agglomerate, therefore PVA is usually combined with alginate to reduce the agglomeration [24].

Previous studies [25-28] have showed that γ-Fe_2O_3 nanoparticles in PVA-alginate beads and TiO_2 nanoparticles in PVA-alginate beads have been used as adsorbents to remove Pb(II) and Cd(II). Majority of the prior researches utilized TiO_2 and γ-Fe_2O_3 PVA-alginate beads separately, which were formed by embedding only γ-Fe_2O_3 nanoparticles in PVA-alginate beads and TiO_2 nanoparticles in PVA-alginate beads when treating Pb(II) and Cd(II) in aqueous solutions. The removal of iodine ions using the aforementioned beads has not been extensively explored. In this research an effort is made to improve the performance of I(I) removal by using photo catalyst beads containing both TiO_2 and γ-Fe_2O_3 nanoparticles that are combined together and embedded in the PVA-alginate beads. In addition the optimum experimental conditions, kinetics of I(I) removal and reusability of maghemite and titania PVA-alginate beads were determined. It is hoped that these combinations will enable the possibility of enhancing I(I) removal *via* photocatalytic reduction.

2. Materials and methods

2.1. Materials

Iron (II) chloride, iron (III) chloride, trisodium citrate, sodium alginate, acetone, boric acid, nitric acid, ammonia solution, acetylacetone, hydrochloric acid, polyvinyl alcohol (PVA), calcium chloride, titanium isopropoxide, urea and NaI powder were bought from Sigma–Aldrich.

2.2. Methods

2.2.1. TiO_2 powder synthesis

Initially a combination of 2 ml titanium and 2 ml acetyl acetone was added to 40 ml ethanol solution and stirred at room temperature (beaker 1). In another beaker, 0.5 g of soluble urea was dissolved in 10 ml of deionized water. Both of these solution (beaker 1 and 2) were then added in drops to 40 ml of deionized (DI) water with continuous stirring until reaching a pale yellow solution in pH 5.6. The above solution was kept under vigorous stirring for 1 hour and transferred into a teflonlined stainless steel autoclave which was then placed in an oven and heated at 150 °C for 18 h. Finally, the content was cooled to room temperature. The sample was centrifuged after washing with ethanol and deionized and was then dried at 80 °C for 3 h and stored in a clean and dry bottle for further use [27,29].

2.2.2. Preparation of γ-Fe_2O_3 nanoparticles

The maghemite (γ-Fe_2O_3) nanoparticles were synthesized by co precipitation method in a stoichiometric combination of ferric and ferrous chlorides with ammonium hydroxide solution. The initially magnetite (Fe_3O_4) precipitate was acidified by nitric acid and oxidized into maghemite (γ-Fe_2O_3) at 90 °C with iron (III) nitrate. Then, the γ-Fe_2O_3 particles were coated by citrate anions to achieve an unchanging maghemite distribution, and is well matched with an alginate gel as a neutral medium. Subsequently, the coated nanoparticles were distributed in water after precipitation with acetone to get a constant ferro fluid with pH 8. The maghemite nanoparticles characteristics were reported in our previous paper [26].

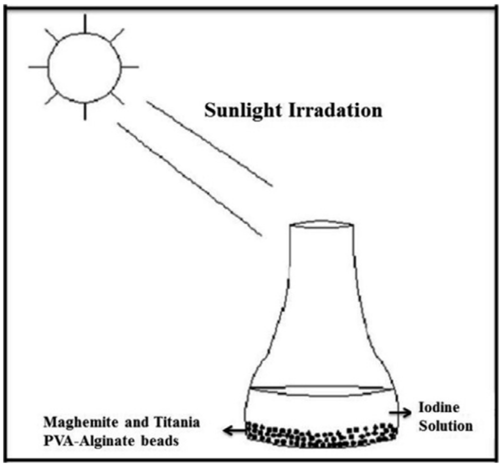

Fig. 1. Schematic diagram of photo catalytic activity under sunlight irradiation.

2.2.3. Preparation of maghemite, titania and maghemite and titania PVA-alginate beads

100 mL of precursor solution was prepared using 12 g of PVA and 1 g of alginate in presence of deionized water. After which 12 g of PVA was dissolved using 72 mL of distilled water and heated at 80 °C for 5 hours. The PVA was also heated in a microwave for 4 min as to attain dissolution. Meanwhile, alginate was dissolved in 20 mL of deionized water in another beaker and now the PVA and alginate solution were mixed together. For the preparation of maghemite PVA-alginate beads, 0.1 g of γ-Fe_2O_3 nanoparticles was added to the prepared solution and for the titania PVA-alginate beads, 0.1 g of TiO_2 nanoparticles was added to the prepared solution. In the case of maghemite and titania PVA-alginate, γ-Fe_2O_3 nanoparticles were mixed with TiO_2 nanoparticles in different TiO_2/Fe_2O_3 ratios (1:1, 1:10 and 1:60) and then mixed to above solution. This solution was then passed through a peristaltic pump into a solution containing 2% calcium chloride ($CaCl_2$) and 6% boric acid and left in the solution for 24 h. The beads were then washed with distilled water and kept in deionized water until further use [30].

2.3. Characterization

The morphological and structural of maghemite and titania PVA-alginate beads were analysed with the aid of field emission scanning electron microscope (FESEM, Hitachi S4800). A complimentary test was performed to determine the Brunauer–Emmett–Teller (BET) surface area, pore diameter and volume of maghemite and titania PVA-alginate beads by utilizing N_2 isotherms at 80 °C and the Quantachrome NovaWin 2 analyzer. X-ray ($2\theta = 20$–90) diffractometer (XRD, Bruker D-8 Advance) employing Cu Kα radiation of wavelength $\lambda = 1.5406$ Å was utilized to determine the phase [29] and the functional groups in the adsorbent using Fourier Transform Infrared Spectroscopy as FTIR spectrum [31] within the range of 400–4000 cm^{-1} [32]. X-ray photoelectron spectroscopy (XPS) was used to characterize the iodine ions treatment.

2.4. Photocatalytic activity under sunlight

2.4.1. Iodine removal using maghemite–titania beads (TiO_2:Fe_2O_3 = 1)

The batch photocatalytic experiment was performed in a 500 ml flask filled with 200 ml of I(I) solution and 10 g of maghemite and titania PVA-alginate beads were added. The whole set up as shown in Fig. 1 was placed under direct sunlight and another similar set up was placed away from sunlight. 5 ml of samples were collected every 20 min and analyzed for I(I)concentration. Another beaker without