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Arsenic removal by photo-catalysis hybrid system

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Abstract

Arsenic is a toxic semi-metallic element that can be fatal to human health. Arsenic pollution in water is found in many parts of the world, especially in developing countries such as Bangladesh, India, Nepal, and Vietnam. Photo-oxidation experiments with titanium dioxide (TiO_2) as photo-catalyst showed that photo-oxidation of As(III) to As(V) is possible within minutes. Further, TiO_2 can also adsorb both As(III) and As(V) on its surface. Photo-catalysis reaction with TiO_2 reduced about 98% of arsenite from water containing 500 μg/L of arsenite. By adding nano-scale zero valent iron (nZVI) of 0.05 g/L in the photo-reactor, arsenic removal can be significantly enhanced. Further the TiO_2 requirement is five times less in this photo-catalysis nZVI hybrid system. The photo-catalytic degradation processes was modeled using the first-order, second-order and Langmuir–Hinshelwood kinetics equations and removal rates were simulated.

Keywords: Arsenic; Photo-catalyst; Nano-scale zero valent iron

1. Introduction

Arsenic is a toxic element that can be fatal to humans. Arsenic exists in several oxidation states (−III, 0, +III and +V) in the environment. However, in natural water, arsenic is mostly found in an inorganic form as oxyanions of trivalent arsenite (As(III)) or pentavalent arsenate (As(V)). Arsenic enters the human body either from respiration or through the mouth. The toxicity of arsenic is highly dependant on its speciation. The toxicity of arsenite is 25–60 higher than that of arsenate. The toxicity decreases in the order of arsine > inorganic As(III) > organic As(III) > inorganic As(V) > organic As(V) > arsonium compounds and elemental As [1]. Ingestion of inorganic arsenic can result in both cancer (skin, lung and urinary bladder) and non-cancer type effects. In addition, inorganic arsenic in drinking water may affect the central and peripheral nervous systems, dermal, cardiovascular, gastrointestinal and respiratory systems. Keratoses and hyperpigmentation are the most common ailments and occur after 5–15 years of arsenic exposure equivalent to 700 μg/day for a 70 kg adult. Further it was found that people who drink water with arsenic levels of 3 μg/L have a one in 1000 risk of developing cancer [2]. At 10 μg/L, the risk increases to three in 1000. Non-cancer health effects include gangrene, limb loss, cardiovascular and pulmonary disease, endocrine and hematological disorders, and reproductive/developmental problems. In addition, arsenic is an “accumulative enabler”, meaning people who are predisposed to various cancers, diabetes, high blood pressure and other ailments are more likely to fall ill.

There are a number of different treatment technologies such as coagulation, ion exchange, adsorption, and membrane processes that can be used to remove arsenic from drinking water to produce safe potable water.

As arsenite [As(III)] is present in uncharged form at pH values typical of drinking water, this form of arsenic is more difficult to be removed from water than arsenate [As(V)]. As(III) is typically removed by first oxidizing it to As(V) and then arsenate is removed using adsorption, precipitation, or ion exchange processes. Khoe et al. [3] claimed that photo-assisted oxidation using UV light effectively oxidizes As(III) to As(V). However, a pilot study conducted with a 200 nm UV light indicated that UV oxidation was only effective at extremely high UV intensities (7000 times the UV dose required than for *E. coli* inactivation). Researchers from Australian Nuclear Science and Technology Organisation [4] evaluated both UV lamp reactors

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and sunlight-assisted-photo-oxidation. Tests demonstrated that almost complete oxidation of As(III) is possible using the photo-chemical process, preferably in the presence of excess of dissolved Fe(II) (iron to arsenic mole ratio: 22:1). Hug et al. [5] investigated thermal and photo-chemical As(III) oxidation, and found that dissolved oxygen and micromolar hydrogenperoxide did not oxidize As(III) within a time scale of hours. In solutions containing 0.06–5 mg/L Fe(II, III), over 90% of As(III) could be oxidized photo-chemically within a 2–3 h period by illumination with 90 W/m^2 UV-A light. Kocar and Inskeep [6] investigated the photo-chemical oxidation of As(III) in irradiated ferrioxalate solutions and found that the rate of this oxidation decreased with higher pH (from 255 ± 16 μM/h at pH of 3 to 14 μM/h at pH of 7.0). The results also suggested that OH* is the important free radical responsible for As(III) oxidation.

TiO_2-catalysed photo-oxidation of As(III) to As(V) has been studied by Bissen et al. [7] and Lee and Choi [8]. UV oxidation occurs when the energy from the UV light source is transferred directly to the reaction. TiO_2 photo-oxidation utilises a semi-conducting photo-catalyst in which TiO_2 absorbs light that has energy greater than the band gap energy of the TiO_2 (about 3.2 eV or 380 nm light), producing electrons and holes on the surface of the oxide. The strongly oxidising holes can convert As(III) to As(V). Lee and Choi [8] observed that photo-oxidation with suspensions of TiO_2 effectively oxidises As(III) to As(V). Bissen et al. [7] demonstrated that nano-particulate suspensions of TiO_2 illuminated with UV light could oxidise As(III) to As(V) in less than 3 min. Here, no reverse reaction takes place as the photo-catalytic reduction of As(V) is much slower than the photo-catalytic oxidation of As(III). A disadvantage of this method is that it can be difficult to separate the treated solution from the particulate TiO_2 photo-catalyst [8]. This technology requires further development before it can be recommended for use in practice.

Nano-scale zero valent iron (nZVI) alone or together with other processes can be used to treat arsenic. It is extremely small in particle size, has large surface area, and high in situ reactivity. In addition, due to its capacity to remain in suspension, nZVI can be transported effectively by groundwater and can be injected as sub-colloidal metal particles into contaminated soils, sediments, and aquifers [9,10]. Kanel et al. [11] found that the particle sizes of nZVI ranged from 10 to 100 nm. Arsenic(III) adsorption kinetics were rapid and occurred within minutes. This follows a pseudo first-order rate expression with observed reaction rate constants of 0.07–1.3 min^{-1}, about 1000 higher than that of micron size ZVI. The combination of this material with advanced technologies, such as membrane or photo-catalysis can lead to very high treatment efficiency. However, no studies have reported the efficiency of hybrid systems of photo-catalysis with in-line addition of nZVI on arsenic removal. In this study, the experiments were performed using photo-catalysis alone and in combination with in-line addition of nZVI.

The main objectives of this study were to: (i) evaluate the effect of TiO_2 concentration (photo-catalyst) on oxidation of As(III) into As(V) and (ii) determine the effect of addition of nZVI on the effectiveness of photo-oxidation reaction of arsenic.

2. Experiments

2.1. Experimental materials

Synthetic water was prepared by adding arsenic stock solution (1 g/L) in deionized water to obtain a predetermined concentration of arsenic. Arsenic concentration of this synthetic water used in experiments was in a range of 100–1000 μg/L. These concentrations are representative of the concentration of arsenic contaminated water found in the field.

All chemicals used in the studies were reagent grade, and used without any purification. The required standard solutions were prepared daily from the corresponding stock solution for the studies. All glassware and sample bottles were washed with a detergent solution, rinsed with tap water, soaked in 10% nitric acid for at least 12 h, and finally rinsed with distilled water three times. Distilled (double) deionized water and Milli Q water were used in the preparation of standard solutions and for dilution purposes.

nZVI was prepared as per the method outlined by Sherman et al. [12]. Ten grams of $FeSO_4 \cdot 7H_2O$ was dissolved in 100 mL of 30% technical grade ethanol, and 70% deionized water (v/v) in a non-oxygen environment. The pH was adjusted to about 6.8 with 3.8 M NaOH. $NaBH_4$ powder (1.8 g) was added incrementally to the mixture, allowing the foaming to subside between increments. After addition of all of the $NaBH_4$, the mixture was stirred for 20 min. The solid was washed twice with technical grade ethanol, effectively substituting ethanol for the water in the mixture. This step helps to prevent immediate rusting as the filtration process is completed.

The characteristics of titanium dioxide TiO_2 (P25 Degussa) powder used as catalyst in the photo-catalytic experiments are shown in Table 1. The distribution of TiO_2 particle sizes investigated with a laser particle size analyzer (LS-230, Beckman Coulter, USA) is presented in Fig. 1.

2.2. Experimental studies

Photo-catalysis experiments were conducted with TiO_2 under UV light to study the efficiency of oxidation of As(III) to As(V). Photo-catalysis experiments were conducted with powdered P25

Table 1
Characteristics of P25 Degussa photo-catalytic TiO_2

Specification	P25 Degussa TiO_2
Structure	Non-porous
Components	65% anatase, 25% rutile, 0.2% SiO_2, 0.3% Al_2O_3, 0.3% HCl, 0.01% Fe_2O_3
Average aggregate particle diameter	Non-porous
Mean particle size	1.8 μm
Mean pore diameter	6.9 nm
Band gap	3.03 (from 500 to 300 nm) with UV–vis
Apparent density	130 kg/m^3
Surface area	42.32 ± 0.18 m^2/g
Type	Powdered
Product code	Degussa P25, Frankfurt am Main, Germany