



Research article

Simultaneous photooxidation and sorptive removal of As(III) by TiO₂ supported layered double hydroxideSang-Ho Lee ^a, Kyoung-Woong Kim ^{a,*}, Heechul Choi ^a, Yoshio Takahashi ^b^a School of Environmental Science and Engineering, Gwangju Institute of Science and Technology, Gwangju, Republic of Korea^b Department of Earth and Planetary Science, Graduate School of Science, The University of Tokyo, Tokyo, Japan

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ABSTRACT

The present study focused on the enhanced removal of As(III) by the simultaneous photooxidation and removal process using TiO₂ nanoparticles supported layered double hydroxide (TiO₂/LDH). The TiO₂/LDH nanocomposites were synthesized using a flocculation method, and nanosized (30–50 nm) TiO₂ particles were well-distributed on the LDH surface. The XPS and DLS data revealed that the TiO₂/LDH nanocomposites were both chemically and physically stable in the aquatic system. The optimum ratio of TiO₂ was 20 wt.% and the calcination process of LDH enhanced the removal capacity of As(III) by the reconstruction process. In the kinetic removal experiment, UV irradiation improved the removal rate of As(III), based on the continuous conversion of As(III) to As(V), and that the removal rate was faster under alkaline conditions than acidic and neutral conditions due to the abundance of oxidants and negative charged As(III) species (pKa: 9.2). The main mechanism of As(III) photooxidation is the direct oxidation by h_{νb}⁺, which is generated by supported TiO₂ nanoparticles. X-ray near edge structure results also confirmed that the As(III) was completely oxidized to As(V). Consequently, the simultaneous photooxidation and removal process of As(III) by TiO₂/LDH nanocomposites may be the effective removal option in As(III) contaminated water.

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1. Introduction

Arsenic (As) is a toxic element that has also been classified as a strong carcinogen (Bissen and Frimmel, 2003). In general, arsenic exists in four oxidation states i.e., +5, +3, 0, and –3, with trivalent arsenic [arsenite; As(III)] and pentavalent arsenic [arsenate; As(V)] being the dominant arsenic species in an aquatic environment (Smedley and Kinniburgh, 2002). Arsenic in the environment can be originated from both natural and anthropogenic sources; nevertheless, naturally occurring sources negatively impact the aquatic ecosystem such as in the contamination of ground and surface water (Chapagain et al., 2009; de Figueiredo et al., 2007; Yang et al., 2009). Recently, severe arsenic contamination in drinking water has been observed around the world, making the chronic exposure of arsenic a global issue due to increases in kidney, lung, bladder, and skin cancer (Anawar et al., 2001; Kurttio et al., 1999; Smith et al., 2000, 1992). In fact, previous studies have reported that the people who drink the arsenic contaminated

water display considerable arsenic accumulation in their body, such as in their hair, nails, toenails, and urine showing the positive correlation with the contamination level of their groundwater (Phan et al., 2010, 2013). From the risk of arsenic contamination in drinking water, the US Environmental Protection Agency (USEPA), World Health Organization (WHO), and European Commission have set to the maximum level of arsenic in drinking water to be 10 µg/L (10 ppb) (Environmental Protection Agency, 2001; WHO, 2011).

Representative arsenic removal techniques in drinking water include the precipitation/coagulation, adsorption, ion exchange processes and membrane treatments such as reverse osmosis and nanopore filtration systems. In particular, adsorption and ion exchange processes have been widely applied to the contaminated areas due to their cost-effectiveness and installation convenience (Mohan and Pittman, 2007). A common problem in arsenic removal systems is that the removal efficiency of As(III) is lower than that of As(V), that is because As(III) exists in a non-ionic form as H₃AsO₃ in neutral conditions, and therefore has a higher mobility than As(V) species, which exist in negative charged forms such as H₂AsO₄[–], HAsO₄^{2–}, and AsO₄^{3–} (Lin and Wu, 2001). For this reason, oxidation

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processes have been applied as a pretreatment in arsenic removal systems in attempts to enhance the overall removal efficiency. To oxidize As(III) in the pretreatment system, advanced oxidation processes such as O_3 and H_2O_2 and TiO_2 -mediated photooxidation process have been applied (Neppolian et al., 2009; Pettine et al., 1999; Ryu and Choi, 2006). The application of nanosized TiO_2 suspension in conjunction with UV irradiation has been a promising remediation technique to oxidize As(III) to As(V) in treatment systems. However, the direct application of nanosized TiO_2 particles can be still challenging problem due to the difficulty of separation. To date, several researchers have focused on the immobilization of nanosized TiO_2 particles on substrates such as adsorbents (Li et al., 2014), electrodes (Pifferi et al., 2013) and membranes (Zhang et al., 2015). In recent, TiO_2 immobilization techniques have been applied to arsenic adsorbents such as iron oxide and aluminum oxide in order to synthesize bi-functional nanocomposites to induce the simultaneous photocatalytic oxidation and adsorption process (Yu et al., 2013; Zhou et al., 2008).

The layered double hydroxide (LDH) is the anionic clay that is based on the staking of positively charged brucite-like layers with interlayers of anion and water molecules. The LDHs can be denoted by the general formula $[M^{II}_{1-x}M^{III}_x(OH)_2]^{x+}(A^{n-})_{x/n} \cdot nH_2O$, where M^{II} and M^{III} are divalent and trivalent cations, respectively, x is equal to the molar ratio of $M^{II}(M^{II} + M^{III})$, A is an interlayer anion having charge m , and n is the number of water molecules (Goh et al., 2008). The LDH has the large surface area and high anion exchange capacity, and has been applied to remove the anionic contaminants such as arsenic (Türk et al., 2009), phosphate (Cheng et al., 2009), chromium (Das et al., 2004) and antimony (Kameda et al., 2012) based on the mechanisms of adsorption, anion exchange in the interlayer region, and the reconstruction of a calcined LDH structure. Furthermore, LDHs have been combined with materials such as graphene (Li et al., 2010), polymers (Cho et al., 2013), and inorganic metals (Jiao et al., 2009) to enhance their reactivities by maximizing their inherent properties (e.g., large surface area and layered structure). Previous research reported that LDHs have been applied as substrates to the synthesize TiO_2 /LDH nanocomposites for the photodegradation of organic pollutants (Paušová et al., 2012; Shao et al., 2014), and TiO_2 /LDH nanocomposites increased the photodegradation of organic pollutants by activating hydroxyl groups on the LDH surface (Mendoza-Damián et al., 2013).

This study presents the results obtained by combining LDH and TiO_2 to remove As(III) using a simultaneous photooxidation and removal process in drinking water. The TiO_2 /LDH nanocomposites are the effective bi-functional material that has both the higher oxidation and removal efficiency of arsenic in comparison with other commercial adsorbents. Therefore, this TiO_2 /LDH nanocomposites could be an effective nanocomposites for environmental applications in targeting for the As(III) contaminated areas.

2. Materials and methods

Carbonate type LDH was synthesized by the modified method with previous study (Paredes et al., 2011). In brief, Soln. 1 (1 M $NaHCO_3$ with 3.5 M $NaOH$) was slowly added into Soln. 2 (1 M $Mg(NO_3)_2 \cdot 6 \cdot H_2O$ and $Al(NO_3)_3 \cdot 9H_2O$) using drop-wise method until the pH of the mixed solution reached 9.5. After mixing, the solution was aged for 24 h at 60 °C to increase its crystallinity. The precipitate was then centrifuged at 6000 rpm and washed using deionized water. The samples were dried at 80 °C in a dry oven for 24 h and finally stored in a desiccator.

Anatase type titanium dioxide was synthesized using the hydrolysis method described by Yun et al. (2012). In brief, 50 mL of

0.5 M $TiCl_4$ (99.9%; Sigma Aldrich, USA) was prepared and the titanium solution was mixed with ammonium sulfate $((NH_4)_2SO_4$; Sigma Aldrich, USA) to prepare the anatase TiO_2 . The mixed solution was constantly stirred at 110 °C for 24 h in the reflux system. Subsequently, the produced precipitate was separated from the solution and washed with deionized water to remove excess ions such as chloride and sulfate. Finally, the precipitate was dried at 80 °C and stored in a desiccator.

The process for synthesizing TiO_2 /LDH nanocomposites was previously described by Seftel et al. (2010). Here, 0.8 g of LDH and 0.2 g of well-dispersed TiO_2 nanoparticles were mixed into a 1 L bottle containing deionized water. The mixed solution was vigorously stirred for 48 h at room temperature. Prior to stirring the mixed solution, N_2 gas was purged to prevent carbonate contamination. The final slurry was centrifuged and calcined at 400 °C in a furnace, and finally filtered using a 100 mesh sieve.

For the characterization, powder XRD patterns were measured using a high resolution X-ray diffractometer (HR-XRD) with $Cu K\alpha$ radiation (40 KV, 24 mA) over a 2θ range of 5°–85°. The BET surface area was analyzed using an ASAP2010 (Micromeritics, USA), and the morphological characteristics and elemental composition of the samples were obtained using scanning electron microscope (FE-SEM; Hitachi S-4700, Japan). The TiO_2 /LDH surface was analyzed using the X-ray photoelectron spectrometer (XPS; ESCA VG Multi-lab 2000, UK) to determine the differences in elemental characteristics on the surface of TiO_2 /LDH nanocomposites. The IR spectra were obtained using FT-IR (Jasco-4600 plus; USA), and arsenic K-edge X-ray absorption near-edge structure (XANES) spectra were obtained from the BL6A of a photon factory (High-Energy Accelerator Research Organization, KEK, Japan).

The six UV lamps (NEC CFL3UV37, Japan; output: 5.2 mW/cm²; wavelength: 368 nm) were mounted in a shaking incubator (HB-201SS, Hanbaek Science, Korea) equipped with a constant temperature circulator. The 30 mL of As(III) solution (10–50 mg/L) was mixed with TiO_2 /LDH nanocomposites and vigorously stirred at 180 rpm under UV irradiation. The solution was filtered using a 0.45 μ m-sized membrane filter and the filtered solution was then passed through an anion exchange cartridge (Supelco LC-SAX SPE 57071, USA) to separate the As(III) species in the solution. The arsenic concentration in the stored solution was subsequently analyzed by inductively coupled plasma mass spectrometry (ICP-MS; Agilent 7500 ce, USA).

3. Results and discussion

3.1. Characterization of TiO_2 /LDH nanocomposites

Fig. 1 shows the XRD patterns for LDH, TiO_2 , and TiO_2 /LDH nanocomposites synthesized by spontaneous flocculation after mixing LDH with TiO_2 nanoparticles. The XRD data revealed that uncalcined LDH shows typical structures of LDH (Fig. 1a), with basal reflection (003) and (006) at low 2θ corresponding to the layered structure. Generally, the calculated thickness of the LDH interlayer is 7.65 Å (carbonate \approx 2.85 Å; layer thickness \approx 4.80 Å), which almost corresponds to the d-spacing value of the uncalcined LDH (7.80 Å) (Lu et al., 2012; Seftel et al., 2013). After the calcination process at 400 °C, the typical LDH peaks disappeared due to the structural collapse caused by the loss of interlayer anions and water molecules incurred during the thermal treatment. Characteristics of the anatase phase (101) of TiO_2 were generally observed at approximately 25°, with both uncalcined and calcined TiO_2 displaying the typical anatase crystalline phase. The XRD pattern of uncalcined TiO_2 /LDH (Fig. 1c) includes both properties of LDH and TiO_2 in basal planes (003), (006) and (101) planes. Interestingly, the calcined TiO_2 /LDH (Fig. 1d) shows that the (003) reflection

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