Arsenic removal in groundwater by UV based photocatalysis with immobilized ZnO-nanoparticle on ceramic plate

A Adnan¹, S Notodarmodjo¹², Q Helmy¹²³,*
¹Environmental Engineering Department, Faculty of Civil and Environmental Engineering, Institute of Technology Bandung, Bandung, Indonesia
²Water and Wastewater Engineering Research Group, Environmental Engineering Department, Institute of Technology Bandung, Bandung, Indonesia
³Bioscience and Biotechnology Research Center, Institute of Technology Bandung, Bandung, Indonesia

*Corresponding Author: helmy@tl.itb.ac.id

Abstract. Arsenic (As) is naturally present in the lithosphere (earth crusts, soil, rock and sediment) and hydrosphere (surface water, aquifers, deep wells, and oceans). It can exist in the groundwater from the weathering process of rocks which caused a high concentration of As in groundwater and increased risk of health when consuming the contaminated water. To reduce this risk, As standard in drinking water was set by WHO and Indonesia's drinking water standard of 0.01 mg/L. In this study, arsenic contaminated water treatment is carried out using advanced oxidation process ZnO/UV photocatalytic. The immobilize ZnO nanoparticle catalyst coated onto a ceramic plate by dip coating method. Kinetic study was performed in a batch reactor with artificial ground water using sodium arsenite (NaAsO₂) at pH 4, 7, and 10 with initial concentration of arsenic set aside at 1 mg/L, 3 mg/L, and 5 mg/L. ZnO was irradiated by UV-C light (λ = 265 nm) for photocatalysis of arsenite As(III) oxidation into arsenate As(V) for 2 hours. Removal efficiency using ZnO/UV photocatalysis for arsenic total (99.99% of 1 mg/L, 83.25% of 3 mg/L, and 51.82% of 5 mg/L) and for As(III) (99.99% of 1 mg/L, 96.34% of 3 mg/L, and 77.73% of 5 mg/L) in acidic condition. Data analysis in the study used the AAS method to calculate the value of the total arsenic concentration tested and the colorimetric spectrophotometer method to calculate the value of As(III) and to determine the absorb of ceramic plate coated ZnO. The characteristics of ceramic plate immobilized ZnO nanoparticles is analyzed by SEM-EDS. ZnO nanoparticles coated onto ceramic plate surfaces is 80.65% (5.5 mg/cm²). This study was conducted to determine the optimum dose of catalyst used to oxidize As (III) to As (V) and the capacity of the immobilized ceramic plate catalyst in adsorbing arsenic compounds in solution which was then presented in the final research report.

1. Introduction
Arsenic compounds (As) can be formed from the weathering process of rocks which caused high concentrations of As in ground water and increased health risk while consuming water contained As. Arsenic in groundwater is divided into two forms, namely reduced forms, occurring under anaerobic conditions, referred to as arsenite. Another form is the oxidized form, occurring in aerobic conditions, referred to as arsenate. In the aquatic environment, under oxidation conditions, arsenic forms pentavalent arsenate As(V), whereas under reduced conditions, arsenic forms trivalent arsenite As(III). Mobility
and absorption by sediment, clay soils, and soil minerals depend on the arsenic form. In anoxic conditions, microbial activity forms arsenic in methylene, which is in solid form and able to enter the atmosphere. Compared to As (V), As(III) is more difficult to set aside from solution. Deposition of arsenic is usually carried out with As (V) compounds in solution [1].

Arsenic distributed in groundwater is found in inorganic form as oxyanions of trivalent arsenite As (III), or pentavalent arsenate As (V) [2] which depend on pH and redox potential [3][4]. In pH 7 (neutral), groundwater with typical anoxic will be found more As (III), more danger, and easier to move than As (V), while groundwater with typical anoxic will be found more As (V) [5]. Arsenite has low affinity to mineral surfaces, while arsenate adsorbs easily to solid surfaces [6]. Photocatalysis quickly oxidizes arsenite (As (III)) to arsenate (As (V)) which is unstable and non-toxic, then be removed by adsorption onto the photocatalyst surface [6].

In previous studies, the photocatalytic process used to oxidize As (III) to As (V) was carried out by UV/TiO\textsubscript{2}. The arsenic compounds in the solution is completely removed through oxidation of As (III) to As (V) which is then followed by the adsorption of As(V) onto the TiO\textsubscript{2} surface in acidic media [6][7]. The results of this study indicated that arsenic removal according to the World Health Organization's drinking water quality standard of 10 μg/L can be achieved [6][8]. Furthermore, this study will investigate the photocatalytic oxidation of As (III) to As (V) as a function of arsenic total and As(III) concentration, pH, catalyst loading, light intensity, type of ZnO surface, and ceramic plate which used to determine kinetics and mechanism of As (III) oxidation in the UV/ZnO system. Photocatalytic to oxidize As (III) to As (V) lasts for several minutes and follows the first and second order kinetics so that it can meet drinking water quality standards according to WHO standards and Indonesian drinking water standards of 10 μg/L.

2. Research Method

2.1. Materials

Sodium arsenite (NaAsO\textsubscript{2}) was used as a source of As (III). The colorimetric method used (1:1) H\textsubscript{2}SO\textsubscript{4}, chloroform (CHCl\textsubscript{3}), and potassium iodate (KI) to test As (III) by spectrophotometer UV-VIS. Ceramic plate (obtained from Bandung Ceramic Research Center, Indonesia) with 10 cm in diameter and 1 cm in thickness used as coat media of ZnO nanoparticle. ZnO adhesive material used is gelatine food grade which can be found in the Indonesian market. ZnO pro analysis grade was obtained from Merck, Germany with the particle size is 276-762 nm [9]. All reagents were used pro-analysis grade without further purification and all solutions were used deionized water.

2.2. Preparations

2.2.1. Arsenic solution. The arsenic solution is made by diluting sodium arsenite (NaAsO\textsubscript{2}) solution using deionized water with varying concentrations of 1 mg/L, 3 mg/L, and 5 mg/L. The arsenic solution is then set to pH 4 (acid), pH 7 (neutral), and pH 10 (base) by adding a solution of (1:1) H\textsubscript{2}SO\textsubscript{4} and 1N NaOH.

2.2.2. Preparation of ceramic plate. Ceramic as a medium for immobilizing ZnO nanoparticles for research was obtained from Bandung Ceramic Research Center, Indonesia. Ceramic made contains 50% w/w of fine clay, 30% w/w of Bangka Kaolin fine clay, 10% w/w of sodium feldspar from PT Sibeico, and 10% w/w of Refractory Chamotte. All of these materials are mixed with a slow stirring speed for 15 minutes and a high speed for 10 minutes using special liquid containing 35% of tap water and 65% of water glass with a ratio of 1:4 (dry mixture: special liquid by w/w). The mixture in the slurry form is then poured into a ceramic plate mould and left for 5 minutes. The ceramic plate formed was taken out from the ceramic mould and left at room temperature for 5 days, then heated gradually using a furnace at 100°C for 1 hour, 300°C for 1 hour, and 900°C for 3 hours. After heating for 5 hours, the ceramic plate is cooled at room temperature and then can be used for ZnO nanoparticle immobilization media.
2.2.3. **Preparation of ZnO solutions.** ZnO solution for immobilized is made by mixing 5% w/v of gelatine food grade and 5% w/v of ZnO pro analysis in deionized water gradually at a certain temperature. Deionized water is heated at 60°C for 3 hours. Food grade gelatine is gradually poured into deionized water while stirring using a stirrer at 60°C for 30 minutes. After the gelatine solution is thoroughly mixed, pour the ZnO powder slowly until a milky white solution is formed. Set the lower temperature of ZnO/gelatine solution which has been mixed at room temperature and keep stirring for 4 hours.

2.2.4. **Dip-coating of gelatine/ZnO solutions on the ceramic plate.** Ceramic plates are dipped in ZnO/gelatine solution for 2 minutes, then left at room temperature for 5 minutes. Repeatedly 5 times. The ceramic plate that has been coated by ZnO/gelatine is then heated at 550°C for 3 hours. After that, the ceramic is cooled at room temperature. This process is considered as a single coating. Then the same process was carried out again up to 3 times.

2.2.5. **Reactor condition.** The arsenic solution will be treated in a batch reactor 2.3 liters. 4 ceramic plates are used. The reactor speed used is 100 rpm. The reactor uses 2 antibacterial UV-C lamps 15 watts with a wavelength in 265 nm. UV lamp is placed 10 cm from arsenic solution. The contact area of ceramic/ZnO with the arsenic solution is 95%. Reactor batch scheme can be seen in figure 1.

![Figure 1. Photocatalytic rotating disc reactor](image)

2.2.6. **Colorimetric methods.** Colorimetric method is used to calculate the value of arsenite (As(III)) in solution. Samples are directly tested maximum 3 hours after sampling [10]. H₂SO₄ 8.34 ml was added with an arsenic sample to reach a volume of 50 ml. The mixture is put into a separating flask and added with chloroform 10 ml and potassium iodate 0.2 grams. The mixture in the separating flask is then shaken for 2 minutes until the mixture dissolves and let stand for 15 minutes and pink colour of the solution is taken for testing As(III) using spectrophotometer UV-VIS with wavelength 510 nm.

2.2.7. **Atomic Adsorption Spectrophotometric (AAS).** AAS method is used to calculate the total value of arsenic in solution. Measuring of total arsenic follows APHA 3114-As method [11]. The total arsenic value obtained by the AAS method is then used to calculate the value of As (V) by comparing the value of As(III) obtained from the colorimetric method before.

3. **Results and Discussion**

3.1. **Arsenic removal**
Arsenic removal can be identified by determining the decrease of the value of As (III) concentration in solution. Removal is carried out by oxidizing hazardous As (III) to non-hazardous As (V). The effect of UV intensity on decreasing the value of As (III) concentration by testing samples at a concentration of 3 mg/L can be seen in figure 2.a. Samples tested that are affected by UV will be better than non-UV, and application of ZnO/UV gives the best removal results. So that the photocatalytic process due to
ZnO/UV effects on compound removal can be achieved. Arsenic removal concentrations of 1 ppm, 3 ppm, and 5 ppm can be seen in figure 2.b.

![Figure 2](image)

**Figure 2.** (a) UV effect on arsenic removal at concentration of 3 mg/L; (b) % arsenic total removal at concentration of 1 mg/L, 3 mg/L, and 5 mg/L.

### 3.2. Kinetics

#### 3.2.1. The rate of reaction

The rate of reaction is influenced by the amount of catalyst and UV intensity used to remove arsenic. The kinetics of the rate of arsenic removal reaction with UV/ZnO photocatalytic can be seen in figure 3. Based on the graph in figure 3, it can be seen the value of the reaction rate constant for each reaction order. The photocatalytic process for each concentration can be determined based on the $R^2$ value of each reaction order. Photocatalytic processes occur in orders that have a greater $R^2$ value. At a concentration of 1 mg/L, the photocatalytic process takes place in the second order with the reaction rate constant $(k)$ is 18.822/minute. Whereas at a concentration of 3 mg/L and 5 mg/L, the photocatalytic process takes place in first order with the reaction rate constants is 0.0267/minute and 0.0122/minute respectively. The constant rate of the reaction is directly proportional to the rate of the removal reaction. The greater the reaction rate constant, the faster the reaction rate, and the faster the removal [12].

### 3.3. Ceramic/ZnO nanoparticles analysis

After coating ZnO nanoparticles with the dip-coating method, immobilized ZnO nanoparticles were made by coating them to a ceramic plate and heated to temperature 550°C. Then ceramic plates which was coated by ZnO were taken 5x5 mm for scanning electron microscopy (SEM) test. SEM test is to determine the particle size of the ZnO nanoparticles. The test results show the particle size is 1-100 nm. This is in accordance with the size of the particles can be called nanoparticles when they are at a size of 1-100 nm [13]. So that the dip-coating method done can be said to be successful to reach nanoparticles size. Based on figure 4.a, it can be seen that ZnO is evenly distributed to all parts of the ceramic surface (right). The results of SEM analysis were tested on ceramic plates from ceramic/ZnO and ceramic/non-ZnO (blank) samples. It aims to see the comparison before and after being coated to ZnO on the ceramic surface. SEM test for samples before coating ZnO with 8.000 X magnification and after coating ZnO with 10.000 X magnification can be seen in Figure 4.
Figure 3. (a) Reaction rate kinetics first-order, (b) Reaction rate kinetics second-order

Figure 4. (a) Comparison of before (left) and after (right) coated by ZnO; (b) SEM test result before coated by ZnO; and (c) SEM test result after coated by ZnO

In addition to SEM, an energy dispersive x-ray spectrophotometer (EDS) was also conducted to find out the elements contained in the ceramic plates. Based on the results of the EDS analysis, it is known that the composition of the compounds contained in ceramic plates consists of elements of Carbon (6.75%), Al₂O₃ (3.87%), SiO₂ (8.73%), and ZnO (80.65%).
Figure 5. Element composition contained on the ceramic plate surface.

In this study, 5.5 mg/cm² of ZnO nanoparticles coated to the ceramic surfaces reached the maximum dose after 3 cycles. Based on the EDS data, it can be assumed that there are 19.35% of ZnO which do not coat to the ceramic surface or even enter the ceramic pore. This composition can be seen in figure 5 above.

4. Conclusion
Arsenic removal in groundwater using a new type of synthesis of Ceramic/ZnO was successfully synthesized using gelatine food grade as a dispersive agent for ZnO powder nanoparticles in Gelatine/ZnO solution. Photocatalytic conditions with variations in pH can affect the ability of photocatalytic activity using ceramic/ZnO/UV in absorbing arsenic compounds in solution. In this study, the optimum pH occurs under acidic conditions (pH 4) and can achieve a removal efficiency of 100% arsenic compounds within 60 minutes with an initial concentration of 1 mg/L.

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