

Characterization of ZrO_2 Nano Particles Prepared by Glycothermal Method and their Efficiency as Adsorbent of As(III) and As(V) from Waste Water

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Abstract

In this studied ZrO_2 nano particles are prepared by glycothermal method. Characterization of the prepared nano particle was done using XRD, TEM and SEM. According to the obtained results, ZrO_2 nano particles prepared by glycothermal method are mainly t- ZrO_2 phase with tetragonal shape with an average size in the range of 30-50 nm. The formation of t- ZrO_2 as the main phase of zirconium nano particles could be related to the presence of sodium hydroxide in the generation step. The removal efficiency of ZrO_2 nano particles for adsorbing As(III) and As(V) from waste water is studied. The efficiency of removal is significantly increased with increasing the dose of zirconia nano particles till 0.5 g/L. This related to increasing in the active site which are available for the removal of arsenic species by increasing the dose of the nano particles. For both As(III) and As(V), the removal efficiency increased by decreasing pH value of the solution and increasing the contact time.

Keywords: ZrO_2 nano particles; Glycothermal; As(III); As(V)

Introduction

Zirconium oxide is a widely used multifunctional material. It has high chemical resistance, thermal stability and high mechanical properties. For these unique properties ZrO_2 has been used in many applications in various fields such as optics, electronics, and magnetism, and others. In recent years, usage of Zirconium dioxide nanoparticles (nano- ZrO_2) is rapidly growing in biological fields [1,2]. They are widely used as drug delivery carriers for some medicines like itraconazole, penicillin, alendronate and zoledronate as gene delivery vehicles with target specificity for some tissues for improving the properties of traditional bone cements in orthopedics and some other purposes such as production of poisons like parathion or nerve agents. Although ZrO_2 is a neutral bioceramic material [3]. The usefulness of Zirconium oxide nanoparticles depend on their size and physical properties which highly depend on the method of preparation [4,5]. Arsenic is an element that naturally occurring in the environment of high mobility. Its mobility depends on various factors such as the oxidation state, the parent mineral form and mobilization mechanisms [6]. Arsenic can exist in four oxidation forms, these are arsenite (As(III)), arsenate (As(V)), arsenic (As(0)), and arsine (As(III)). Among these four-arsenic species, the most prevalent forms, which are commonly found in water, are the inorganic arsenite and arsenate [7]. Because of slow transformations, arsenite and arsenate are present in both reduced and oxidized environments. However, under anoxic reducing conditions (e.g., subsurface waters, reduced sediments), arsenic primarily exists as arsenite, whereas arsenate is prevalent in aerobic oxidizing environments, such as surface waters [8]. The pH also plays an important role in determining the state of arsenic [9]. Arsenic is known to be highly toxic to all living organisms [10]. This element has been classified by the World Health Organization as a group 1 human carcinogenic substance [11]. As(III) is more harmful for human health than As(V) as it is more cytotoxic, genotoxic, mobile, and soluble [7,10]. With the accumulation of trivalent intermediates in the human body, there is a higher possibility of developing arsenic-induced diseases [12]. Many approaches have been developed to remove As from contaminated water [13]. The arsenic disposal technologies can be specifically classified into three major categories: membrane separation, coagulation-precipitation, and adsorption [14,15]. The interactions of arsenic species with metal oxides and hydroxides are

important in order to control the mobility of arsenic in the natural environment, which can be used for removing arsenic with metal-based coagulants and adsorbents. Adsorption has been reported as the most widely used technique for arsenic removal due to its several advantages including relatively high arsenic removal efficiencies [16,17], easy operation, and handling [18], cost-effectiveness [19].

The aim of the present work to prepare ZrO_2 nanoparticles by glycothermal method. The prepared zirconium dioxide nanoparticles are characterized using X-ray diffraction (XRD) Scanning electron microscope (SEM) and transmission electron microscope (TEM). The efficiency of the prepared nanoparticles for removing of Arsenate ions from waste water are studied.

Experimental

Chemicals

The chemicals used in this study were $ZrOCl_2 \cdot 8H_2O$, ethanol, ethylene glycol and NaOH supplied from Merck. The solutions were prepared by dissolving the adequate quantities of the compounds in deionized water. Arsenic solutions were arranged by dissolving the $NaAsO_2$ in deionized water and determined in 520 nm by UV/VIS spectrophotometer (Shimadzu-1700, Japan).

Preparation of ZrO_2 nano particles

Zirconium dioxide nano particles were prepared by glycothermal method as follow [20]: 15.3 g of $ZrOCl_2 \cdot 8H_2O$ was dissolved in one liter of water then slowly NaOH (0.05 Molar) was added with rapid stirring,

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Received November 16, 2017; **Accepted** November 20, 2017; **Published** November 27, 2017

Citation: Al-Farhan BS (2017) Characterization of ZrO_2 Nano Particles Prepared by Glycothermal Method and their Efficiency as Adsorbent of As(III) and As(V) from Waste Water. J Environ Anal Toxicol 7: 533. doi: [10.4172/2161-0525.1000532](https://doi.org/10.4172/2161-0525.1000532)

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till the pH of solutions became 9. The precipitated ZrO₂ was decanted and washed by using ethanol for five times. Excess solution was decanted after the final washing and the wet precursor was re-dispersed in 200 mL ethylene glycol under vigorous stirring. The resulting suspension was placed in a 1 L stainless steel pressure vessel. The vessel was then heated to 270°C at a rate of 10°C min for 6 h. The characterization of the synthesized particles was observed using transmission electron microscope (TEM, JEM 2100F), X-ray diffract meter.

Removal studies

Batch experiments were used for studying the removal of arsenic ions using the prepared ZrO₂ nano particles. Batch experiments were performed with 100 ml beaker covered with aluminum foil. The beaker was mixed by magnetic stirrer (150 rpm) at room temperature. After given period of time the sample centrifuged at 3000 rpm for 15 min. Then the solution filtered through 0.45 µm membrane filter and analyzed for arsenic by Silver Diethyl dithiocarbamate method (SDDC) [21]. The effect of various parameters such as contact time (2, 5, 10, 15 and 30 min), pH (2.5, 9 and 11) and ZrO₂ nanoparticles mass (0.1, 0.25, 0.5 and 1 g/L) were studied in term of their effect on reaction process.

The amount of the pollutant removed was calculated using equation 1;

$$R\% = \frac{C_i - C_f}{C_i} \times 100 \quad (1)$$

Where q is the amount of the pollutant removed (mg/g), C₀ is the initial concentration of As(III) or As(V), C is the concentration after the removal process, V volume of the solution and m is the mass of ZrO₂ nanoparticles used in the removal process.

The removal efficiency was calculated using equation 2;

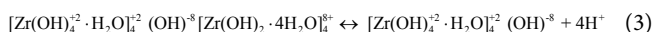
$$R\% = \frac{C_i - C_f}{C_i} \times 100 \quad (2)$$

where C_i and C_f are the initial and final concentrations of As species. For each experiment, the average of three replicates was recorded.

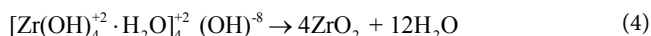
Results and Discussion

Mechanism of preparation of ZrO₂ nanoparticles

When (ZrOC₁₂·8H₂O) is dissolved in water, [Zr(OH)₄·4H₂O]⁸⁺ is formed [22]. Gradual addition of NaOH (basic medium) leads to increase in pH value of the solution forcing the hydrolysis of the zirconium cations according to equation 3:



Subsequent poly condensation takes place by oxolation (Zr-OH+HO-Zr → Zr-O-Zr+H₂O) process leading to the formation of hydroxyl- and oxo-bridges between tetramer units, respectively. The product at such step is less ordered amorphous gel. The gel was re dispersed in ethylene glycol and transformation of an amorphous gel to a metastable tetragonal ZrO₂ is formed by heating and subsequent loss of the hydration water.



Characterization of ZrO₂ nano particles

Figure 1 shows the TEM images of the synthesized ZrO₂ nano particles. According to Figure 2; the ZrO₂ particles are mainly appeared

as a tetragonal particles and do not appeared a discrete particles but form a small aggregation with an average size in the range of 30-50 nm. These size range indicates that the nano ZrO₂ particles are obtained which reflects the high surface areas of the nano particles that increases the efficiency of their removal capacities.

Figure 2 show the XRD pattern of the prepared ZrO₂ nano particles. There are a broad peak corresponding to 100% reflection of t-ZrO₂ besides there are narrow peaks corresponding to m-ZrO₂ were also identified. The formation of t-ZrO₂ as the main phase of zirconium nano particles could be related to the presence of sodium hydroxide in the generation stage of the [Zr(OH)₄]²⁺·H₂O]4+2(OH)⁻⁸ hydroxo -complex, its role in the formation of zirconia nano particles with one or another crystallite structure was previously noted [23]. Sodium ions are kept in a zirconia nano particle structure, thus stabilizing the tetragonal phase [24]. Use of NaOH as a hydrothermal solution provides pH value, which is enough to activate dilution of t-ZrO₂ nano particles, stabilized by impurity ions. SEM images of ZrO₂ nano particles are shown in Figure 3 before and after adsorption of As(III) ions. According to Figure 3a, ZrO₂ nano particles formed by glycothermal method have a tetragonal to monoclinic crystal shape. After loading with As(III), ZrO₂ nanoparticles show a change in the morphology and structure, see Figure 3b. The crystals are embedded in the surface after adsorption with As(III) with a noticeable surface heterogeneity.

Removal experiments

Effect of ZrO₂ nano particles dosage on removal efficiency: Mass of the substrate used in the removal of pollutant species is an important parameter because this determines the capacity of the substrate for a given initial concentration of the pollutant at the operating conditions. The effect of mass of ZrO₂ nano particles on the removal of As(III) or As(V) is shown in Figure 4. This was performed by treating 20 mg/L of As(III) or As(V) with different dose of ZrO₂ nano particles (0.1, 0.25, 0.5 and 1 g/L) for 10 minutes contact times at pH 5.

Figure 4 shows that for both As(III) and As(V), the removal capacity significantly increases with increasing the dose of zirconia nano particles till 0.5 g/L. This related to increasing in the active site which are available for the removal of arsenic species by increasing the dose of the nano particles [25]. Availability of specific surface area and micro pore volumes plays a vital role for surface adsorption process. At 1 g/L, the effect of increasing the dose of zirconia nano particle was very little on the removal process of both As(III) and As(V). This may be due to the saturation of the available active sites by the arsenate ions beside decreasing the driving force for removal which is a fraction between the numbers of the removing ions to the numbers of the available active site. This leads to decreasing the rate of diffusion of the pollutants ions towards the surface of the nano particles leading to decrease the net percentage of the removal efficiency and a state of equilibrium are achieved.

According to Figure 4, the removal of As(III) species was higher than those of As(V) species [26]. About 93 and 70% are removed using 1 g/L of zirconia nano particles for As(III) and As(V) respectively. Such results indicates the high removal efficiency of ZrO₂ nano particles for removal of both As(III) and As(V) relative to other zirconium salts [27]. This could be related to the high surface areas of the nano materials which reflected on availability of higher numbers of active sites.

Effect of solution pH: The pH is one of the important factors in the As(III) removal using nano particle zirconium dioxide. For investigation effect of pH, 10 mg/L As (III) was adsorbed on 1 g/L ZrO₂ nano particles

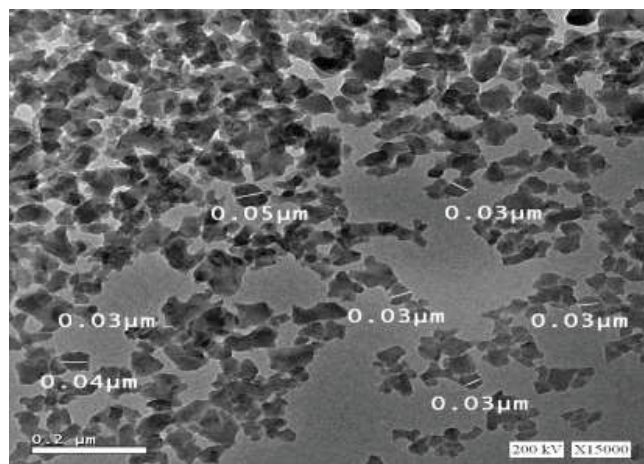


Figure 1: TEM of ZrO₂ nanoparticle.

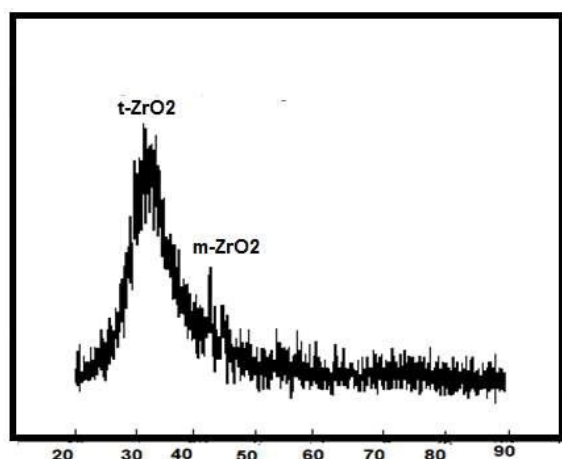
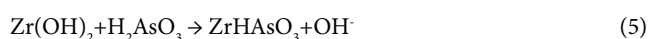


Figure 2: XRD of ZrO₂ nanoparticles.

at various pH ranges (2, 5, 9 and 11) for a contact time 15 minutes. It was determined that the removal of both and As (III) can be performed by zirconium nano particles at different pH values. As shown in Figure 5, the As (III) removal efficiency increased significantly with decreasing pH value of the removing solution. The removal efficiency in detention time of 15 min and pH range 2-11 was 96-79%. These values indicates in all pH ranges, the removal of As(III) species using ZrO₂ nano particles reduces the level of these toxic species to the world regulatory level permit for ground water.

The pH dependent behavior can be explained by ionization of both the adsorbate and the adsorbent causing repulsion at the surface and decreasing the net As (III) adsorption. Below 9, H₃AsO₃ is the predominant species which easily interact with zirconia nano particles via hydrogen bonding and the major species being adsorbed [28]. When the pH is above 9, H₂AsO₃ is the predominant As species and the zirconia nano particles become highly negatively charged causing electrostatic repulsion. However some arsenic exchange can be occurred on the charged surfaces of nano particles according to equation 5:



For As(V), the removal process was also pH dependent. The removal % increased from 55% at pH 2 to be 72% at pH 5. However

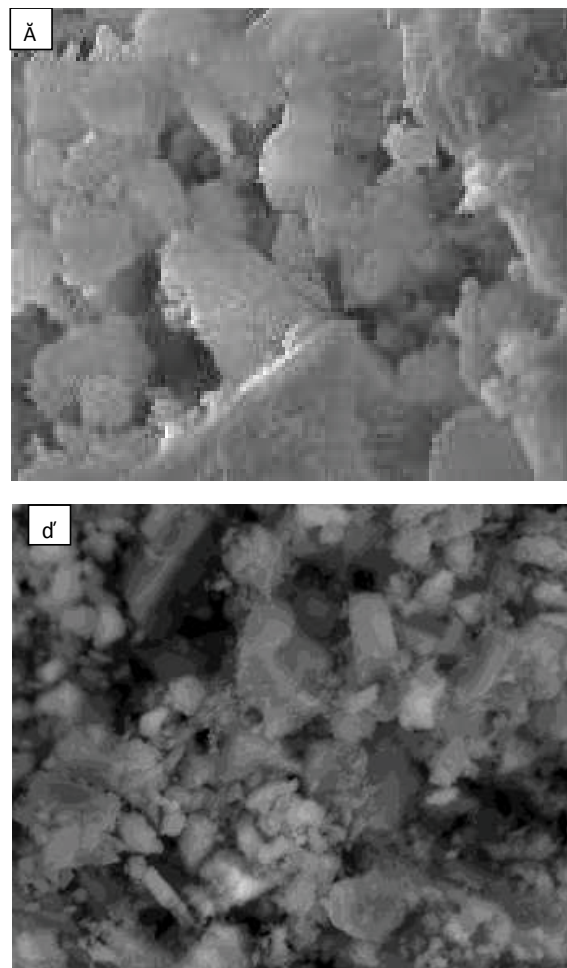


Figure 3: SEM of ZrO₂ nano particles a) before removal process b) after removal process.

increasing pH of the removal process above pH 5 leads to decrease the percentage of removal to 50 and 43% at pH 9 and 11 respectively.

Effect of contact time: Studying the effect of contact time on the removal process gives an important information on the removal rate. The percentage of removal efficiency of both of As(III) and As (V) by ZrO₂ nano particles was studied a function of time (0-30 minutes) at pH 5, using 1 g/L of the nano particles, is shown in Figure 6. As shown in this figure the removal efficiency increased with elapse of contact time and the removal efficiency was fast during the first 10 minutes. About 75% of As(III) are removed during the first 15 minutes. While about 59% of As(V) species are removed during that period. Therefore, it could be concluded that the rate of element binding with the nano particles was high in the initial stages. This can be related to the high diffusion rate of the adsorbate ions from the bulk of the solution to the adsorbent surface. In the time period 15-30 minutes, the rate of removal become constant and state of equilibrium are achieved. About 83 and 70% of both As(III) and As(V) are removed after 15 minutes.

However, there was not 100% removal for these toxic species from the tested solutions, the high speed of the removal of both As(III) and As(V) species gives the advantage of using ZrO₂ nano particles as a removing materials for treating arsenate ions. Other arsenate adsorbent could perform higher removal efficiency like nano sized zerovalent iron [29].

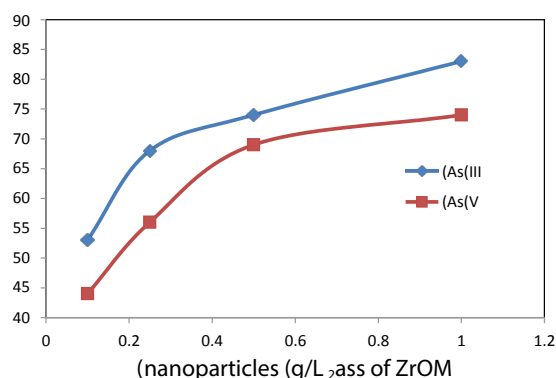


Figure 4: Effect of dose of ZrO_2 nano particles on the removal efficiency of arsenate ions.

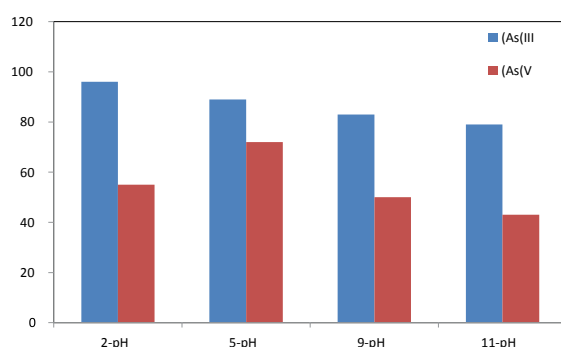


Figure 5: Effect of pH of the solution on the removal efficiency of arsenate ions.

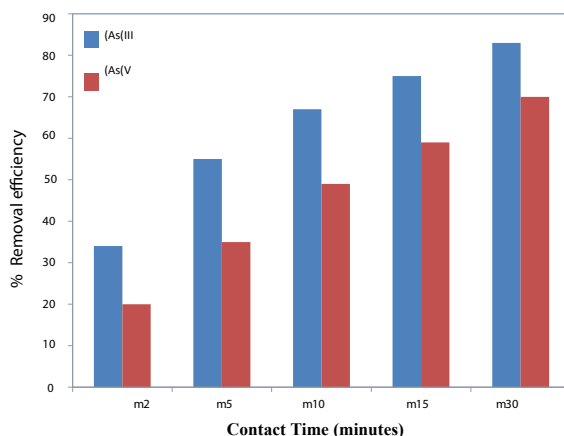


Figure 6: Effect of Contact Time of the solution on the removal efficiency of arsenate ions.

Conclusions

- ZrO_2 nano particles appeared by glycothermal method are mainly t- ZrO_2 phase with tetragonal shape with an average size in the range of 30-50 nm.
- The formation of t- ZrO_2 as the main phase of zirconium nano particles could be related to the presence of sodium hydroxide in the generation step. Use of NaOH as a hydrothermal solution provides pH value, which is enough to activate dilution of t- ZrO_2 nano particles, stabilized by impurity ions.

- The removal efficiency of ZrO_2 nano particles for adsorbing As(III) and As(V) significantly increases with increasing the dose of zirconia nano particles till 0.5 g/L. This related to increasing in the active site which are available for the removal of arsenic species by increasing the dose of the nano particles.
- For both As(III) and As(V), the removal efficiency increased by decreasing pH value of the solution and increasing the contact time.

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