Research Article

Arsenate Removal from Water by Simultaneous Green Tea Nano-Zerovalent Iron and Ultrasonic Wave

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Nano-zerovalent iron (NZVI) was synthesized using green tea (GT) extract and it was used as an adsorbent in arsenate removal from water. FESEM, PSD, and XRD employed in the examination of particles and their characterizations. Results showed that the particles were spherical lumped together in a texture structure with sizes ranging from 20 to 70 nanometers. All experiments were accomplished in a batch mode. Adsorption isotherm, adsorption kinetics, and the effects of pH, GT-NZVI dosage, and ultrasonic wave power on arsenate separation capabilities were explored. The results suggested that the arsenate removal efficiency enhanced with increasing GT-NZVI dosage. Increase in pH from 3 to approximately 6 leads to increase in the removal efficiency; however, increasing the pH further decreased the removal efficiency. The effect of ultrasonic power on As(V) removal was dependent on pH and NZVI dosages. The positive effect was more pronounced at low adsorbent dosages and acidic solution in which the As(V) removal efficiency improved with increasing ultrasonic power. However, in highly alkali solutions As(V) removal efficiency reduced with increasing ultrasonic power. The adsorption kinetics followed second order, while the adsorption isotherm was fitted best with Langmuir equation at a maximum capacity of 34.2 mg g⁻¹.

1. Introduction

The expression of heavy metals in environmental field refers to a category of metals and metalloids that have a rather high density and are poisonous or toxic even at small concentrations. They consist of arsenic, mercury, cadmium, chromium, lead, barium, and so forth [1]. Arsenic found in surface and ground water turned out to be a main danger for the human being and helpful microorganisms [2–7]. Arsenic amount in water can increase because of some emission sources such as mineral dissolution, pesticide usage, fly ash release and disposal, mine drainage, and geothermal discharge [8].

Inorganic species of arsenate ions such as H₃AsO₄, H₂AsO₄⁻, HAsO₄²⁻, AsO₄³⁻, and arsenite ions, for example, H₃AsO₃, H₂AsO₃⁻, and HAsO₃²⁻ are the main types of arsenic found in groundwater and surface water [9]. As(V) exists as H₂AsO₄⁻ and HAsO₄²⁻ near pH 7, while the As(III) type is found as H₃AsO₄ at pH less than 9.2. Furthermore, As(III) species exist in soil and groundwater at anaerobic conditions (small redox potential) but As(V) is favored at a redox potential more than 100 mV and in oxygenated water [9]. The amount of arsenic species found in water is primarily dependent on redox potentials [10]. Arsenic is considered as a carcinogen for human being by the International Agency for Research on Cancer and the National Research Council [11]. To protect people from poisonous arsenic, the World Health Organization (WHO) and several worldwide legislator organizations recommended a maximum permissible concentration of 10 μg/L in water [12]. As the present amount of arsenic in drinking water at small concentrations brings about critical health outcomes, separation of arsenic has emerged increasingly vital [12].

There are numerous processes for arsenic removal including coagulation, precipitation, reverse osmosis,
separation, microfiltration, ion-exchange, ozone oxidation, bioremediation, and adsorption techniques [11, 13]. Most of the used arsenic separation processes have great maintenance cost and need comparatively costly sorbents adsorbents. Consequently, arsenic adsorption by metals from water has gained extra consideration because of its excessive application performance and low cost [11].

Removal of As(III) and As(V) from groundwater by zerovalent iron has become one of the most widespread practice in recent years [14]. The reaction velocity of zerovalent iron has been enhanced greatly by the introduction of nano-zerovalent iron [9]. Many authors have reported the capability of NZVI in the removal of arsenic ions from water [9, 10, 15].

Many chemical and physical procedures are used to synthesize NZVI of certain sizes and characteristics [16]. The aggregation of NZVI particles to form chain-similar arrangement is responsible for decreasing interfacial area [15]. Aggregation prevention of NZVI particles to stabilize them can be performed by conveying electrostatic repulsion, using organic surfactants, utilizing coating, or synthesizing them by means of support of inorganic material [16].

In synthesizing NZVI, sodium borohydride is widely used; however, it is very toxic [17]. Saving the environment requires that sodium borohydride is replaced with a more friendly substance. Green tea is recognized to include polyphenols acting as both reducing and coating agents for Fe [17]. In addition to it being biodegradable, green tea has a high water solubility and low toxicity [17]. These favorable properties of green tea make it a good candidate for replacing sodium borohydride in synthesizing NZVI.

There are limited data on capability of GT-NZVI to uptake arsenate from polluted water. Furthermore, the effect of ultrasonic power on this removal requires more research. An effort has been made in this paper to fill the mentioned gap and provide more data. In this study, NZVI particles were synthesized using extract of green tea leaves at ambient temperature and pressure. The major objective of the present work is to examine the capability of synthesized GT-NZVI in the elimination of As(V) from water. Another goal of this study is to find the adsorption isotherm of As(V). Furthermore, the effects of GT-NZVI dosage, pH, and ultrasonic wave power on As(V) uptake from water are examined.

2. Materials and Methods

2.1. Materials Used. Na$_2$HAsO$_4$·7H$_2$O, FeSO$_4$·7H$_2$O, HCl, and NaOH were reagent grade obtained from Sigma Aldrich Chemical Co. Green tea obtained from Refaah brand, Iran, and Qudix particle size analyzer (Republic of Korea) were used in this study.

2.3. Experimental Preparation. All glass vessels and tubes used in test scrubbed and acid cleaned using 10% aqueous nitric acid and then triple-rinsed with deionized water. Arsenate aqueous solution of concentration 5 mg/L was prepared on the day of experimentation by diluting the stock solution with deionized water. Hydrochloric acid (1 M) and sodium hydroxide (1 M) used for adjusting the pH using a calibrated pH meter. All experiments were conducted at laboratory temperature ($25 ± 1\textdegree$C).

2.4. Synthesis of GT-NZVI. The preparation of NZVI was performed using green tea extracts [16]. Green tea extract was made by heating green tea until boiling; one liter of deionized water was boiled in a beaker and then a quantity of 20 g green tea was added to it. The beaker was covered with an aluminum foil and the tea was heated for further 5 minutes. After that, the beaker was removed from the heater and the tea leaves left to settle for one hour and cooled to reach the room temperature ($25\textdegree$C). Finally, the green tea extract was vacuum-filtered. Independently, in a one-liter balloon, a solution of 0.10 M FeSO$_4$·7H$_2$O was made by dissolving 28.7 g of solid FeSO$_4$·7H$_2$O in sufficient deionized water (to get one liter solution). Afterward, the solution of 0.10 M FeSO$_4$·7H$_2$O was added in a dropwise manner to the green tea extract in 2:3 volume ratio in the beaker under magnetic stirring (600 rpm) at room temperature for 5 minutes. Next, 1.0 M NaOH or HCl aqueous solution was added dropwise until the pH was 6.0. Evidence of intense black precipitate manifested as the appearance of GT-NZVI particles. The GT-NZVI particles were then separated first by evaporating most of water from the solution using a hot plate and afterward by drying them overnight in a fume hood [1, 17–19].

2.5. Adsorption Isotherm. The adsorption experiments conducted using a batch system. One hundred mL of As(V) solution with an initial concentration of 5 mg L$^{-1}$ was poured in a 250 mL Erlenmeyer flask. Then a specific amount of GT-NZVI was added to the flask. The pH of the resulting solution was adjusted to 6 by adding 1 M HCl or NaOH using a calibrated pH meter. The content of Erlenmeyer flask was mixed next by means of magnetic stirrer at speed of 350 rpm at laboratory temperature ($25 ± 1\textdegree$C). After reaction completion, the flask removed from magnetic stirrer and allowed to settle for 5 min at laboratory temperature. Subsequently the adsorbent separated by centrifuging the solution at speed of 3000 rpm for 15 min. Finally, 50 mL of treated sample filtered through a 0.45 µm Millipore membrane. A PerkinElmer (USA) atomic absorption spectrophotometer equipped with a graphite furnace HGA, a cathode-ray (EDL lamp), a palladium matrix modifier, and WinLab32 software was used to measure of As(V) in treated samples [20]. The detection limit of the instrument was 0.3 µg/L.

2.6. Ultrasonic Effect on Adsorption. The adsorption runs were performed in a batch system as stated in the previous
section except for mixing method; ultrasonic device was used instead of the magnetic stirrer. Two sets of experiments were conducted with ultrasonic powers of 150 and 300 W, while the dosage of adsorbent was set at 0.1, 0.55, and 1 g L\(^{-1}\) and pH was adjusted at 3, 7, and 11. In each experiment, the solution mixed for 15 minutes using ultrasonic power. At the end of each experiment, 50 mL of treated sample was filtered through a 0.45 μ Millipore membrane. GF-AAS technique was employed for measuring the concentration of As(V) in treated samples.

2.7. Adsorption Kinetics. Seven experiments were carried out to determine the kinetics rate constants of arsenate adsorption by GT-NZVI at seven time intervals (including 5, 30, 60, 90, 120, 180, and 210 min). In each run, 0.1 g of GT-NZVI was added to a beaker containing 100 mL of solution of 5 ppm arsenate at pH 6. The content of beaker was mixed using a magnetic stirrer at laboratory temperature (25 ± 1°C) for the required time. At the end of each run, the remaining As(V) in the filtered sample was measured by HGAAS method. Each experiment was done in duplicate and the mean value was reported.

3. Results and Discussion

3.1. Characterization of GT-NZVI Particles. The synthesized GT-NZVI particles were characterized via FESEM, XRD, and PSD techniques. The GT-NZVI particles were distributed over adhesive carbon tapes held on metallic disks, and their images were taken at several magnifications using FESEM. The FESEM image illustrated in Figure 1 shows the GT-NZVI particle sizes and structures. As indicated in Figure 1(d), GT-NZVI particles consisted of spherical particles assembled in texture structure. Figures 1(a), 1(b), and 1(c) also indicate that the GT-NZVI particles have diameters around 30 nm.

The structure of GT-NZVI particles was found using XRD type apparatus and the results are demonstrated in Figure 2. The samples of GT-NZVI were washed three or four times with pure ethanol before XRD analysis to decrease the NaCl amount that crystallized out during the production stage and scanned within the 2θ limit of 0–118°. The scanning rate set at 2.0°/min considered all most important varieties of iron and iron oxides. The XRD pattern of unused GT-NZVI particles indicates a major characteristic peak at 2θ degrees of 44.71 showing the existence of zerovalent iron (Fe\(^0\)). In addition,
the figure demonstrates two other peaks that are relatively smaller at 2θ degrees of 27.2 and 35 that are related to the presence of iron hydroxide (FeOOH) and Fe$_3$O$_4$, respectively.

3.2. Effect of GT-NZVI Dosage. Adsorption of arsenate by GT-NZVI was investigated using 5 mg/L As(V) solution at three different GT-NZVI concentrations of 0.1, 0.55, and 1 g/L at constant ultrasonic power and pH as shown in Figures 3(a), 3(b), and 3(c). The contact time between the adsorbent and adsorbate was 20 minutes for all experiments. As these figures indicate, the efficiency of arsenate removal increases with increasing in the concentration of GT-NZVI.

The increase in the efficiency of arsenate removal with increasing in the concentration of GT-NZVI is in accord with the results of other researcher [15, 21]. It can be attributed to the increase in surface area of adsorbent at higher dosages that increased the sites for arsenate adsorption. Increase in the active surface sites increases the possibility of collision between nanoparticles and arsenate ions [22]. Also, more available surface area is provided for oxidation and deduction reactions [23].

3.3. Effect of pH on As(V) Removal. The pH effect on As(V) removal by GT-NZVI was studied and the results are indicated in Figures 4(a), 4(b), and 4(c). During the examination, the amount of adsorbent (0.1, 0.55, and 1 g/L) and ultrasonic power (0, 150, and 300 W) were kept constant. Increase in pH from 3 to approximately 5.5–7 leads to increase in the efficiency of removal; however, increasing the pH further decreases the removal efficiency. In other words, at highly acidic or highly alkaline conditions, the efficiency of NZVI toward arsenate adsorption was depleted.

Results of other studies confirm this finding [10, 24]. The removal mechanism of arsenic ions by NZVI in aqueous medium is primarily a result of adsorption and coprecipitation of arsenic ions with oxides of iron(II) and iron(III) and ferric hydroxide that developed during NZVI oxidation [10]. In the pH range of 5.5 to 7, the amorphous hydroxide solid of ferric ion is stable; therefore, the arsenate adsorption on NZVI is excessive. On the contrary, outside this range the efficiency decreased because of instability of iron hydroxide [24]. At high pH, H$_2$AsO$_3^-$ is the predominant form of arsenic species, while the NZVI corrosion product surfaces are also negative (Fe(III)–O$^-$) causing electrostatic repulsion [10].

3.4. Effects of Ultrasonic Wave Power on As(V) Removal. The effect of ultrasonic power on As(V) removal at constant adsorbent amount (0.1, 0.55, and 1 g/L) and constant pH (3, 7, and 11) is shown in Figures 5(a), 5(b), and 5(c). The positive effect is more pronounce at 0.1 and 0.55 g/L adsorbent dosages and pH 3 (acidic solution) in which the As(V) removal efficiency improves with increasing ultrasonic power. On the other hand, at pH 11 (alkali solution) the As(V)
Figure 4: As(V) removal efficiency versus pH at different ultrasonic powers.

Figure 5: As(V) Removal efficiency versus ultrasonic wave power.
removal efficiency reduces with increasing ultrasonic power. In neutral aqueous solutions (pH 7) and adsorbent dosages of 0.1 and 0.55 g/L, the As(V) removal efficiency increases with increasing ultrasonic power to a maximum at ultrasonic power of 150 W and then decreases afterward as the ultrasonic power increase from 150 W to 300 W.

Improvement of As(V) removal efficiency with increasing ultrasonic power is probably due to more dispersion of GT-NZVI particles in acidic solution at low dosage of NZVI (0.1 and 0.55 g/L). However, at the higher NZVI concentration (1 g/L) more collisions lead to increase in agglomeration rate that result in As(V) removal efficiency reduction.

In higher pH (alkali conditions), the dissolved ferrous ions collided with hydroxyl ions to give ferrous hydroxide precipitation on the iron outer surface. The sedimentation fills the outside active sites of nanoparticles and prevents it from adsorbing arsenate [15]. On the other hand, ultrasonication is associated with cavitation that produces very reactive hydroxyl radicals [25]. The produced OH+ radicals also that are deposited on active sites of nanoparticles lead to decrease in the removal efficiency of arsenate from water. Also as explained in the previous section, at high pH, H3AsO4+ is the principal form of arsenic species, while the NZVI corrosion product surfaces are also negative (Fe(III)–O−) producing electrostatic repulsion [10]. This explanation may justify the decreases in As(V) removal efficiency with increasing the ultrasonic wave power at high pH solutions.

3.5. As(V) Adsorption Kinetics. There are a number of kinetic models to identify the performance of the adsorbent and to inspect the dominating mechanism of the adsorption process [26–29]. To study the mechanism of adsorption process the experimental kinetic data for the uptake of As(V) by NZVI particles were modeled using the following equations of pseudo-first-order (1) and pseudo-second-order (2):

\[
q_t = q_e \left[1 - e^{-K_1 t}\right],
\]

\[
q_t = \frac{tK_2q_e^2}{1 + tK_2q_e}. \tag{2}
\]

Linearization of the above equation gives (3) and (4), respectively, as follows:

\[
\log(q_e - q_t) = \log(q_e) - \frac{K_1}{2.303}t, \tag{3}
\]

\[
\frac{t}{q_t} = \frac{1}{K_2q_e^2} + \frac{1}{q_e}t. \tag{4}
\]

In above equations, \(q_t\) is the amount of As(V) adsorbed per unit of adsorbent (mg g\(^{-1}\)) at time \(t\), \(K_1\) the pseudo-first-order rate constant (min\(^{-1}\)), \(t\) the contact time (min), \(K_2\) the pseudo-second-order rate constant (g mg\(^{-1}\) min\(^{-1}\)), and \(q_e\) the equilibrium adsorption capacity (mg g\(^{-1}\)).

Figure 6 illustrates plots of linearized form of pseudo-first-order and pseudo-second-order equations for the experimental data. The value of regression coefficient \(R^2\) for pseudo-first-order model is less than that for pseudo-second-order as indicated in Figure 6. Therefore, the pseudo-second-order kinetic model matches better the experimental data than the pseudo-first-order model does and the studied sorption of As(V) by GT-NZVI follows a pseudo-second-order model. The results are in agreement with the literature [30].
3.6. Adsorption Isotherms. The adsorption isotherm points out how the adsorbate is distributed between the liquid phase and the solid adsorbent when an equilibrium state was accomplished at constant temperature. The two familiar equilibrium models of Freundlich [31] and Langmuir [32] were used in the analysis of experimental data. In Langmuir model (5), a monolayer adsorption on homogeneous surface is presumed; however, the Freundlich model (6) is empirical and it can be used for multilayer adsorption on a heterogeneous surface. The linearized forms of the equations are provided as follows:

\[
\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m}, \quad (5)
\]

\[
\log q_e = \log K_F + \frac{1}{n} \log C_e. \quad (6)
\]

Figure 7 shows the adsorption isotherms of arsenate adsorption at pH 6 and room temperature. The capability of the two isotherm models is evaluated by calculating the correlation coefficients $R^2$, and the results are illustrated in Table 1. The correlation coefficient of Langmuir model (0.9963) is more than that of Freundlich model (0.9670) which reveals the more suitability of Langmuir model to fit the experimental equilibrium data.

The reported adsorption capacity of NZVI in the literature is shown in Table 2. The synthesized NZVI has a capacity of 34.2 mg/g toward arsenate, which is higher than the adsorption capacity of many of reported adsorbents in Table 2.

4. Conclusions

GT-NZVI adsorbent was synthesized using aqueous solution of FeSO$_4$·7H$_2$O and green tea extract as a reducing agent. Analysis of FESEM and XRD images indicated that the GT-NZVI particles had spherical shapes collected in texture structure with diameter sizes approximately 30 nm. Batch adsorption investigation showed that the synthesized adsorbent was successful for the elimination of arsenate with comparatively rapid kinetics. The adsorbent revealed high elimination efficiency of arsenate from water at approximately pH 6. The As(V) adsorption capacity at pH 6 was 34.2 mg/g, which is greater than many of reported data on arsenic capacity in the literature. At small adsorbent dosages and acidic solution the As(V) removal efficiency improved with increasing ultrasonic power. However, in strong alkali solutions, arsenic removal efficiency decreased with increasing ultrasonic wave power.
Conflict of Interests
The authors declare that they have no conflict of interests regarding the publication of this paper.

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