Digest Journal of Nanomaterials and Biostructures Vol. 17, No. 2, April - June 2022, p. 443 - 455

Application of visible light activated thiolated cobalt doped ZnO nanoparticles towards arsenic removal from aqueous systems

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Populations at large are exposed towards Arsenic (As) contamination in water worldwide making it unfit for drinking and human consumption. This study was designed to assess As removal efficiency of newly developed thiolated chitosan cobalt-doped zinc oxide (Co-ZnO) nanoparticles (NP) under visible light spectrum. In this study the Co-ZnO NP of various sizes (40–60 nm) were prepared through the co-precipitation method. Removal of As with Co-ZnO NP was investigated in batch tests experiments alongside determining the optimal dose of NP, kinetic rates, effect of light, pH and ultra-sonication. This was followed by a continuous flow test with Co-ZnO layered on Whatman® grade 42 filter paper. Overall, the Co-ZnO NP effectively treated As i.e. in sunlight (100%), neutral pH (100%), ultra-sonication (100%) and in continuous-flow system (100%). The removal of As was maximum (88%) at NP:As ratio of < 1:5 and minimum (25%) at 1:100. Similarly, darkness (21.4%) and (11.1%) uptake at low and high pH respectively. It was found that Co-ZnO NP can efficiently reduce As to non-toxic state i.e. below the WHO permissible limit of (10 µg/L) in drinking water.

(Received December 2, 2021; Accepted April 3, 2022)

Keywords: Arsenic, Drinking water, Co-ZnO, Nanoparticles, Visible light, Removal

1. Introduction

Arsenic ($^{75}_{33}As$) exist in various forms and oxidation states across soils and rocks, atmosphere, natural waters and organisms [1]. Arsenic generally exists in four different oxidation states such as arsenic (As^{0}), arsine (As^{-III}), arsenite (As^{III}), and arsenate (As^{V}). The solubility is directly influenced by ions environments and pH. Among these forms arsenite (As^{III}) and arsenate (As^{V}) are more common [2, 3]. In mineralic form, around 60% of As exist as arsenates, 20% being sulfides and sulpho-salts, and the remaining 20% in the form of silicates, oxides, arsenide, arsenite, and elemental As [4, 5]. Various oxidation states of As is attributed to the existence of different

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https://doi.org/10.15251/DJNB.2022.172.443

redox conditions and pH [6, 7, 8]. Being so far its abundance is concerned, and it is graded 20th in the earth crust, 14th in the hydrosphere, and 12th in the human body [9, 10]. The presence of a higher concentration of As is mainly caused by weathering reactions, products of volcanic eruptions, biological activities, and a series of anthropogenic activities [11, 12]. Major environmental problems related to As are due its mobilization under natural condition. Human activities such as burning of fossil fuels, gold mining, use of As crop desiccants, herbicides, and insecticides [13, 14], arsenic additives to livestock feed [15] etc. causes the addition of As into the environment. Although the use of As related agricultural chemicals is reduced in the past few years; it is still used for wood preservation which leads to environmental pollution [16, 17]. Arsenic and its derivatives are still used in electronics, medicine and material sciences [18]. The waste of these industries increases As level in the environment especially water bodies [19, 20]. Other sources of As comprise of by-products from burning practices (e.g. cement and coal plants, incinerations mills), the release of wastewater from in-situ mining practices (e.g., oil, natural gas and uranium), and use of As based insecticides [21].

As enters into human bodies during water consumption i.e. in the form of drinking water and other ingestion pathways [22, 23]. Other forms of As and its versatile behavior are of great concern to know about its potential toxicity. In the groundwater As is normally present as an oxyanion of the inorganic type [24]. A major concern regarding As is its prevalence in water bodies due to associated toxicity. As in water can come from natural sources, e.g. mainly from the dissolution of bedrock and weathering of As-containing minerals [25]. Very high concentration of As has been found in groundwater of many countries like USA, China, Pakistan, Japan, Korea, Mexico, Bangladesh, Vietnam, Argentina, Nepal, Hungary, Canada, Chile, Cambodia, and Myanmar [26, 27]. Most of the research areas in these countries revealed that the As level in drinking water sources surpassed the WHO standard limit i.e. 10 µg/L [28, 29]. Consumption in the form of ingestion and inhalation of As has been shown to cause cancer in both cases [30, 31]. Some of the most common human health impacts of As include organ damage e.g. skin infections, kidney and bladder cancer, hyperkeratosis, endocrine disruption, appetite loss, and physical weakness etc. [32, 33]. The growing risk of As carcinogenicity in developing countries has attracted the attention of scientists towards water treatment i.e. As decontamination and removal [34, 35]. Various techniques for the removal of As from water are reported in the literature e.g. oxidation, adsorption, ion exchange, co-precipitation, bio-strategies, transitional metal and graphene and carbon nanotubes to name a few [36, 37]. Some of these techniques are preferred over the others due to the associated advantages such as faster reaction rates and lesser release of by-products into water sources followed by additional removal of organic substances. However, the already established techniques have their own limitations such as comparatively higher capital and operational costs, various chemistry and complex designs [38, 39].

Nanoparticles (NP) have been defined as particles having a size <100 nm [40]. The NP possess unique characteristics making them highly suitable for removing a variety of contaminants from aqueous systems, such as As and other heavy metals. These properties include increased surface area, compact size, easy separation, high reactivity and availability of active sites to name a few [41, 42]. The NP can change the toxic heavy metals into a non-toxic form following ion-exchange, ion-precipitation, adsorption and reduction pathways [43]. Numerous studies have reported the application of NP targeting As removal from water establishing 5-10% removal-efficiency as compare to micron-sized particles [44, 45], such as with iron oxides (Fe_3O_4), Alumina combined with chitosan-graft-polyacrylamide (CTSg-PA) and Cupric oxide (CuO) [46, 47, 48]. On the other hand, metal oxides NP like ZnO, TiO_2, CeO_2, have been found more preferable due to their photochemical stability, low-cost, and non-toxicity to human health and the environment [49, 50]. Among metal oxide NP, ZnO NP are more commonly used because of their non-toxicity, higher stability and sensitivity to visible light [51, 52].

A key issue with metal oxide NP is their activation in the visible and ultraviolet spectrum of light. To prevent this problem and improve the NP ability to perform in visible light, researchers are investigating the effect of various doping materials upon NP. Doping is a commonly used technique for enhancing NP to augment their capacity to produce large surface area, work actively in sunlight, and improve electrical and optical activities of NP [53, 54]. This study set out to investigate the application of Co-ZnO NP developed for the removal of As from water thereby optimizing the performance and removal efficiency of the Co-ZnO NP. In doing so, the required optimum dose of Co-ZnO NP, the effect of pH, light and agitation, kinetics rate of removal, and removal in continuous flow have been explored and reported in this study. The results of this study are useful towards the development of novel materials for in-situ decontamination of As from an aqueous solutions. The remaining part of the paper proceeds as Materials and Methods (section 2), Results and Discussion (section 3), Conclusions and way forward (section 4)

2. Materials and methods

2.1. Experimental Material and Reagents

Analytical grade reagents i.e. arsenic trioxide (As_2O_3), nitric acid (HNO_3), hydrochloric acid (HCl), sodium borohydride ($NaBH_4$, 98%), acetone (C_3H_6O) and sodium arsenate dibasic heptahydrate ($Na_2HAsO_4.7H_2O$) were used in this study obtained from Perkin Elmer. We used deionized water (Milli-Q grade) for all types of solutions preparations and analysis. A stock solution of As (1000 mg/L) was made by dissolving 4.2g of ($Na_2HAsO_4.7H_2O$) in one liter of deionized water and preserving it with 0.5% (HNO_3). The standard stock solution was utilized to calibrate the atomic absorption spectrophotometer (AAS) instrument after adequate dilution [55]. Standard solutions of 25, 50, and 100 mg/L were used for AAS calibration. Various volume and sizes of pipettes and volumetric flasks were used obtained from Borosil glass manufacturers. Necessary solutions preparations and analysis of As by AAS photometer were performed at National Centre of Excellence in Geology (NCEG), University of Peshawar, Pakistan.

2.2. Synthesis of Co-ZnO Nanoparticles

The co-precipitation technique was used to synthesize the Co-ZnO NP for the removal of As [48]. In doing so, zinc, cobalt, and hydroxide (O.H-) were used to make the Co-ZnO NP in methanol. To make the Co-ZnO NP, KOH (140 mmol) was mixed with 100 mL methanol and kept for about two h at 52 ^{o}C while constantly stirring it. The mixture was allowed to cool at room temperature before being stored for 48 h. The precipitates were then separated by filtering and rinsing the solution with deionized water and ethanol several times. The Co-ZnO NP were then dried at 127 °C temperature yielding nanocrystalline powder.

2.3. Photocatalytic Reduction of Arsenic

The removal of As via reduction using the Co-ZnO NP was investigated using both batch and continuous flow systems. First batch tests were carried out to examine the effect of different parameters such as the Co-ZnO NP dose, pH, irradiation source and ultra-sonication. The experimental conditions for these tests have been summarized in Table 1.

Table 1. Experimental conditions during photocatalytic reduction of arsenic.

S. No.	Tested conditions	Co-ZnO NPs dose (mg/L)	Arsenic Concentration (mg/L)	Co-ZnO:As ratio
1.	Effect of time	1	100	1:100
		1	50	1:50
		10	100	1:10
		10	50	1:5
2.	Effect of pH	10	10	1:1
3.	Effect of light	15	15	1:1
4.	Effect of ultra-sonication	15	10	1.5:1
		15	15	1:1
5.	Removal in continuous flow	10	10	1:1
		10	10	1:1

All the tests were performed in duplicate. For all experiments, the total volume of As was taken as 50 mL. For the continuous flow experiment, the NP were adsorbed onto Whatman® grade 42 filter paper. During the first run of the investigation, 50 mL of As solution with a concentration of 10 mg/L was filtered over filter paper. While during the second run, the solution was repeatedly filtered over the filter paper five times. Later, the filtrate was examined for As removal from aqueous systems.

As was analyzed using AAS-HH (Perkin Elmer, Germany), taking 50 mL volume at 193.7 nm (wavelength) with argon as carrier gas. Each analysis was performed in duplicates [56]. The variation in concentrations was shown using standard deviation. GraphPad Prism (GraphPad Software, Inc., San Diego, CA, USA) and OriginPro 2018 (Origin-Lab) were used for data analysis and preparation of graphs.

3. Results and discussion

3.1. Characterization of Co-ZnO Nanoparticles

X-Ray diffraction (XRD) analysis of poly-crystalline Co-Zno NP reveals strong and sharp points i.e. major deflection points of ZnO (hexagonal) at 2θ=28.76°, 32.94°, 44.38°,47.86°, 56.54°, 59.08° and 71.04°. The points 455, 379, 373, 396, 378 and 374 of XRD spectra shows crystalline structure of Co-Zno NP (Figure 1a). Due to little dissolution of Co in ZnO medium, the fixing improved the crystallite size of NP and then there was no chance of secondary phase impurities. In order to analyze the shape and size of the particles, transmission electron microscopy (TEM) was carried out (Figure 1b). TEM images of Co-ZnO NP, revealed that, shape of the particles are oval ranging in size from 40 to 60 nm.

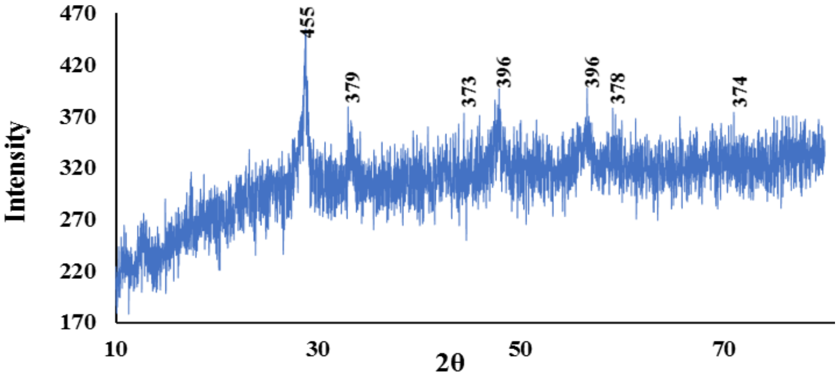

Fig. 1a. XRD spectra for crystalline structure of Co-ZnO nanoparticles.

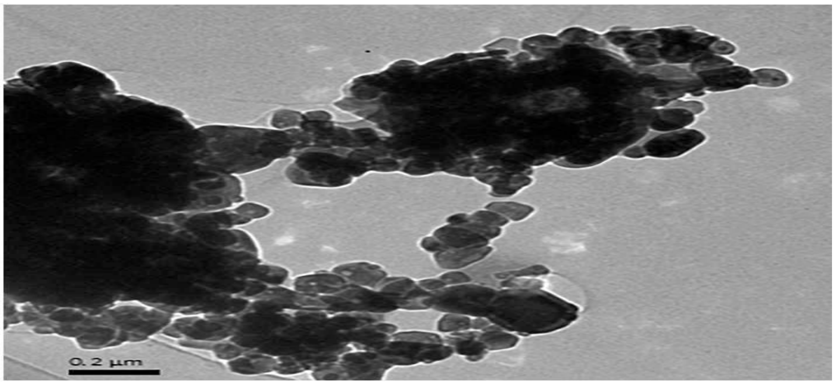

Fig. 1b. TEM image of Co-ZnO nanoparticles showing oval shape [57].

3.2. Fourier-transform infrared spectroscopy (FTIR) analysis

Fourier-transform infrared spectroscopy (FTIR) was used to study the quality and composition of the Co-ZnO NP. The FTIR spectra of Co-ZnO NP are shown in (Figure 2). The spectra show the zinc-oxygen (Zn-O) bond seem at about 440–500 cm^{-1}. This band may be due to oxygen deficiency or oxygen vacancy in zinc oxide. The deficiency of oxygen might be translating into an improved green emission in ultraviolet absorption spectra. The peaks at 1047 and 1112 cm^{-1} due to C-O absorption on the surface of ZnO. The absorption band at 1539 cm^{-1} stands for carbonate due to carbon dioxide that possibly comes from atmosphere during the synthesis of these NP. The wide-ranging peaks about 3410 cm^{-1} is because of the O-H stretching mode of (-OH) group. In Co-ZnO NP, the whole peak transmittance % got quenched. Although the results discovered the impurities that were occur near the surface of ZnO. However, no other peaks were observed in the spectra.

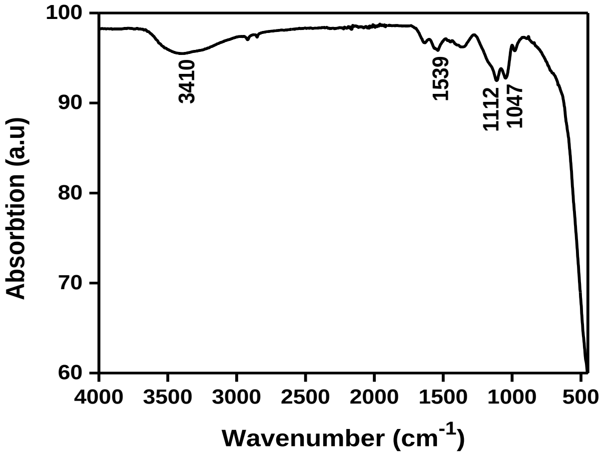

Fig. 2. FTIR spectra of Co-ZnO nanoparticles.

3.3. UV-Vis absorption characteristics of Co-ZnO nanoparticles

Co-ZnO NP were examined for the optical properties using UV-Vis absorption (400–900 nm) as shown in (Figure 3). Co-related peaks between 250 and 400 nm increase due to increasing cobalt amount in Co-ZnO NP. The observed transitions of these NP in the absorption spectra propose that Co^{2+} ions effectively replaced Zn^{2+} within the hexagonal ZnO wurtzite structure.

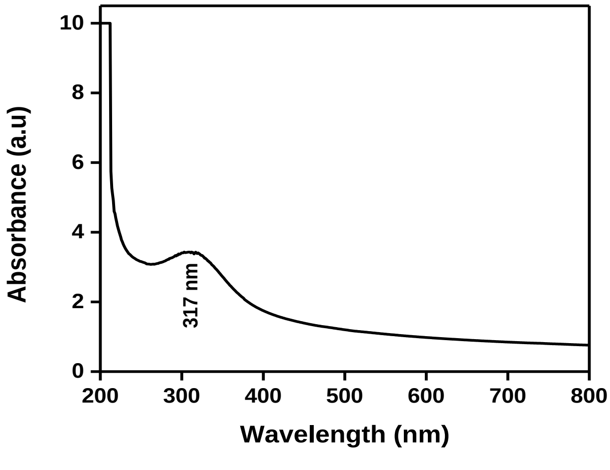

Fig. 3. UV-Vis absorption graph of Co-ZnO nanoparticles.

3.4. Bandgap Analysis of Co-ZnO Nanoparticles

Bandgap analysis of the developed Co-ZnO NP was performed as shown in (Figure 4). In the figure, F(R) denotes the Kubelka-Munk function, hv denotes the energy and R denotes the absolute value of reflectance. The energy was derived by plotting the energy in electron volts (eV) vs square root of the Kubelka-Munk function F(R) 1/2. The bandgap of ZnO NP was reduced to 2.2 eV from 3.3 eV by doping with Co, thus caused a modification in the photosensitivity of the NP. This may cause the reduction in the bandgap energy by adding Co atoms, thus resulting in the structural interruption of the ZnO by Co, thus resulting in a lesser energy gap between the valence band and conduction band.

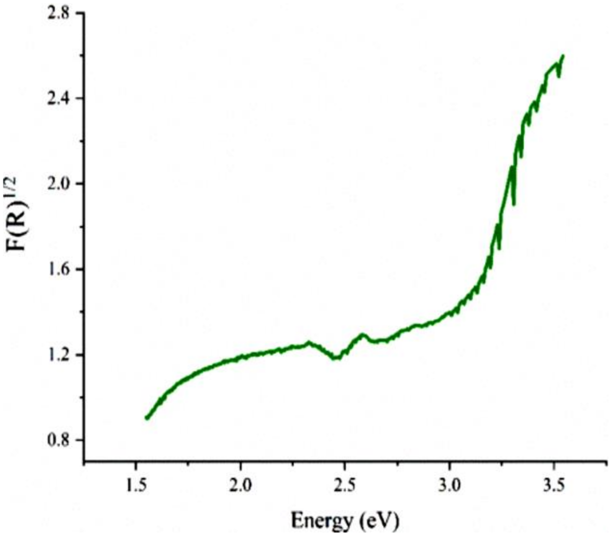

Fig. 4. Bandgap analysis of Co-ZnO nanoparticles [57].

3.5. Optimum Co-ZnO dose for As removal

As removal and reduction efficiency of the Co-ZnO NP were revealed and optimized by taking various doses of Co-ZnO NP in different combinations. The results show that, As removal was significant at (Co-ZnO: NP) ratio of 1:5 i.e. with a total removal efficiency of 100% after 7.5 h of the NP addition (Figure 5). A study was conducted by [58] aimed at determining optimum doses of NP doses of 10, 50 and 100 mg/L on the elimination of (As^{III}) & (As^{V}) from waste water at three different As amounts of (100, 500 and 1000µg/L) were tested. According to the study the elimination of As was improved when the NP dose was increased to 100 mg/L. Gutierrez-Muñiz et al [59] examined the removal of As at different time intervals, with acetate functionalized ZnO-NP, and it was discovered that As removal was rapid in the beginning, with >99.9%. According to the current study, findings NP can remove As efficiently by increasing the dose up to possible limits.

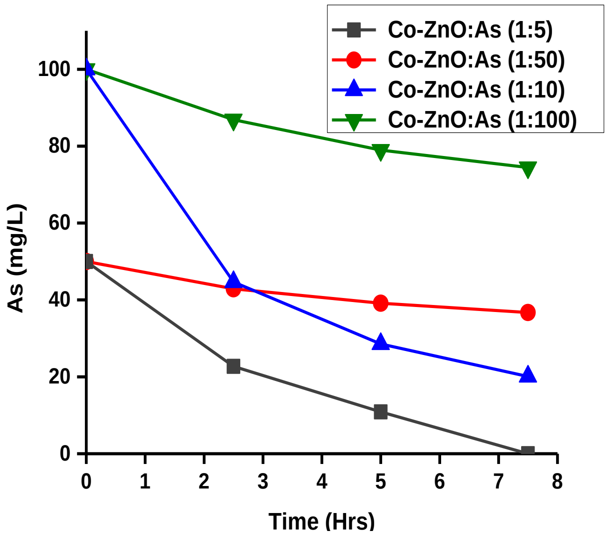

Fig. 5. Removal of As with optimum dose (1 and 10 mg/L) nanoparticles.

3.6. Effect of light

Light is an important factor for determining the quality of the material developed for As removal. Therefore, the effect of light was investigated to understand the performance and efficiency of Co-ZnO NP under various intensities of light. In doing so, 15 mg/L of As and NP (1:1) were added to three distinct volumetric flasks of 100 mL volumes and kept in sunlight, tube light, and darkness for two h each. With the addition of 15 mg/L of NP in the presence of sunlight, tube light, and dark, the 15 mg/L of As level was decreased to 2.45, 5.63, and 10.22 mg/L, respectively see (Figure 6). Under the tube light and darkness, the As level was reduced to almost 2.29 and 9.16 mg/L after three h, respectively, and was fully removed under sunlight. The results showed that in a sunlight, 100% removal of As was obtained, 85% removal under the tube light, and 39% elimination in the darkness. It is because, ZnO NP gets activated which generates ROS (H_2O_2) upon exposure to ultraviolet-vis sunlight [52] and cause Co-ZnO NP to effectively remove As in the presence of sunlight.

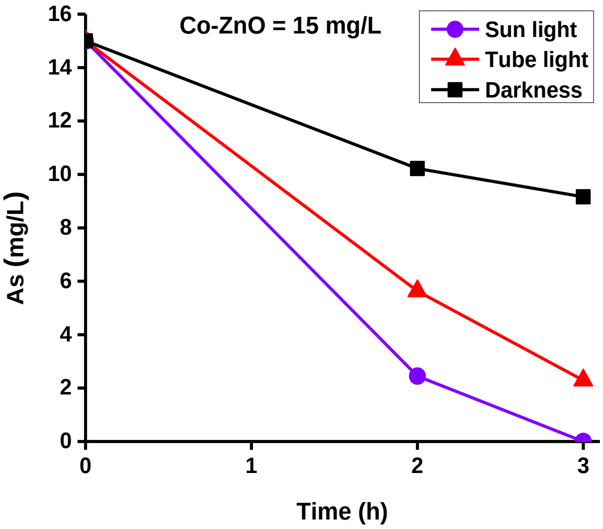

Fig. 6. Effect of light on removal efficiency of arsenic using 15 mg/L of Co-ZnO-NPs.

3.7. Effect of pH

We treated As with Co-ZnO NP at three different pH levels i.e. normal, low, and high. Two solutions were used to adjust pH of the medium i.e. 0.001 N HCl for lowering the pH, whereas 0.001 N NaOH to raise the pH. A 1:1 solution of As-NP i.e. 10 mg/L was taken in 5 different volumetric flasks.

The pH of solution 1 was kept neutral, ranging from 7.0 to 7.2. After two h of reaction, the solutions were tested, and As reduction from 10 mg/L to 0 mg/L was achieved, as shown in (Figure 7).

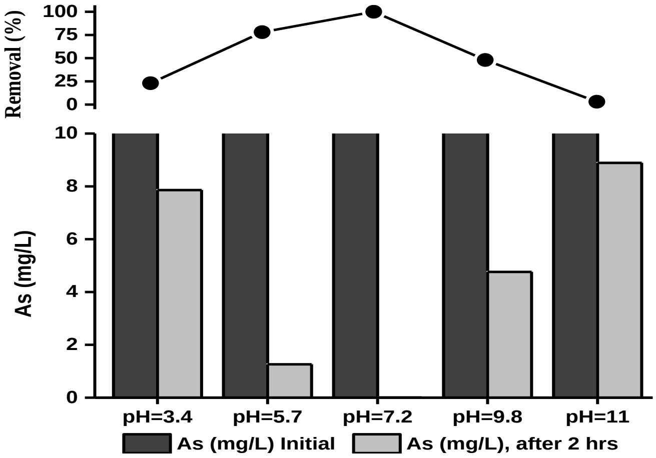

Fig. 7. Effect of pH on As removal using Co-ZnO-NPs.

Maximum As removal efficiency was achieved under neutral pH using Co-ZnO NP developed in this study. Under acidic pH conditions i.e. 5.7, the As amount reduced from 10 mg/L to 1.26 mg/L. Similarly, a total decrease from 10 mg/L to 7.86 mg/L was achieved with 3.4 pH solution. This is perhaps due to conversion of ZnO to $ZnCl_2$ in the presence of HCL [37]. On the other hand, the concentration of As reduced to about 4.76 mg/L in a pH 9.8 solution. Increasing pH further, i.e. up to pH 11 caused reduction in As removal i.e. from, 10 mg/L to only 8.89 mg/L. Again the reason for this little removal is the conversion of ZnO to $Na_2\ Zn(OH)_4$ i.e. due to the addition of diluted NaOH. [59] found that, a total removal efficiency of 99.92% and 99.26% for As at pH 5.8 and pH 7.8 respectively. According to [56] pH has considerable impact on As removal using NP. The Co-ZnO NP show optimal performance in neutral pH, because it is not required to activate the Co-ZnO NP in a neutral pH range.

3.8. Effect of Ultra-Sonication

In order to assess the impact of irradiation on dispersal of NP, ultra-sonication of the medium developed for As removal was performed for over two h using the batch reactors of As and Co-ZnO NP. The media were shaken continuously with a sonicator at a speed of 200 rounds per minute (RPM). The samples were analyzed by AAS-HH after a two h reaction to check the effect of sonication. Our results show that, the sonication procedure lowers the concentration of As from 15 mg/L to 2.67 mg/L which is within acceptable limits of WHO, whereas an amount of 10 mg/L of As was reduced to almost zero (Figure 8). This experiment confirmed that sonication has a significant impact on the removal efficiency of As from aqueous systems. A similar study was conducted by [56] aimed at assessing the effect of ultra-sonication over the As with ZnO for 5 to 6 min, followed by centrifuge at 7000 to 8000 RPM for quick operation. Co-ZnO NP removed As from polluted water effectively within the prescribed limits for drinking water.

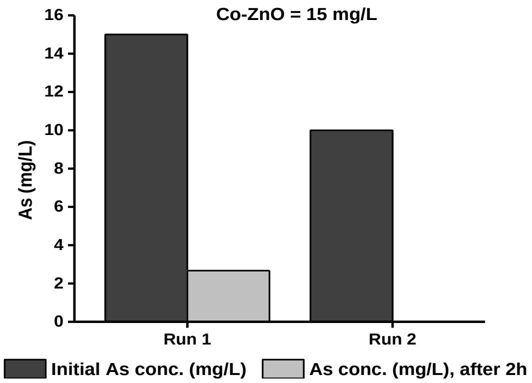

Fig. 8. Ultra-sonication effects on removal of As using Co-ZnO-NPs.

3.9. Removal in continuous-flow

The removal efficiency of Co-ZnO NP was also tested using a filtration procedure. Two identical solutions of As concentration (10 mg/L) were placed into two distinct reactors using Whatman filter paper 42. The amount of As was successfully reduced from 10 mg/L to 6.72 mg/L with a one-time passage from NP adsorbed on Whatman filter paper 42. In comparison, the amount of As was reduced from 10 mg/L to 2.84 mg/L with an overall efficiency of 72% in the second reactor with a five-times passage from NP adsorbed medium. The current testing revealed that the NP was also effective in a continuous flow environment, and further testing can improve their effectiveness.

3.10. Decontamination Mechanism

The removal of As upon the addition of NP with Co-ZnO showed that As ions reacted with Co-ZnO NPs and its electronic structure was altered by the doping process [60]. This mechanism can be clarified by band theory easily, stating that; whenever a high-energy photon strikes a N.P, the electron of its atoms stimulates and transfer from lowest filled valence band to highest unfilled conduction band and which is responsible for conductivity while the electron take off gaps within the valance band, which continue to carry on as positive charge carriers additionally moves through the valance band. Charge carriers in semi-conductors have a capacity of 1021 m^{-3}, but there is a space between the valance and conduction bands that cannot be filled by electrons, known as the band gap. Most electrons in an atom can fill several separate energy states which are known as permissible energy levels.

In ZnO NP, the band gap is 3.3 eV, which causes the change more possible [61], this change happened by doping of cobalt (Co) and thus results in the decontamination of arsenic. Presently, the Co doping decreased the band gap of ZnO NP from 3.3 eV to 2.2 eV hence making it further prone to the sun's visible light. This doping also improved the photocatalytic action of the NP, which assisted in the additional generation of reactive oxygen species (ROS) [62].

The existence of NP encourages As to receive two electrons thus changing it to non-toxic As which has two valence electrons. The current mechanism can be clarified by ROS's action, which is produced from the outer surface of Co-ZnO NP when visible to sun-light [63]. Later, Co-ZnO NP reacted with As in the existence of visible light (15 lm/W); however, the unpaired electrons from ROS reacted with As and thus decreased it to its lower oxidation state i.e. from converting it from (As^{V}) to (As^{III}) and later on from (As^{III}) to (As^{0}).

3.11. Activity Regeneration

In testing gas-phase photocatalytic oxidation of Sulphur dioxide (SO_2), the photocatalytic action of used (deactivated) Co-ZnO NP can almost be restored as before by rinsing with deionized water and then drying at 75 °C for almost 20 to 24 h after centrifugation process. Furthermore, it also proved that the inactivation of these NPs must be mainly assigned to the adsorption of the oxidation products like Water (H_2O), Carbon dioxide (CO_2) and Sulphur trioxide (SO_3).

3.12. Comparisons of Decontamination Capacity of Arsenic with other Nanoparticles

From the literature it has been reported that different types of nanoparticles such as Fe-TiO_2, α-Fe_2O_3, Mt-nZVI, δ-FeOOH, CuO, CFe, γ-Al_2O_3, ZrO_2, nZVI-RGO and CaO_2 have been investigated for the decontamination of As in aqueous systems with almost same pH values. All of the reported nanoparticles presented the best efficiency for removing As with a pH value of 7 (Table 2). Co-ZnO NP showed the optimal As reduction at a pH value of 7.2 and almost 100% reduction occurred. The same NP also showed 100% removal efficiency in the presence of sunlight (visible light), ultra-sonication and in continuous flow. From this comparison we have concluded that the Co-ZnO NP are most promising, cost-effective and readily available for treating As and other toxic heavy metals.

Table 2. Decontamination capacity of As following various nanoparticles.

Nanoparticle	**Nanoparticle size (nm)**	**Specific pH value**	**Arsenic species**	**Removal efficiency (mg g^{-1})**	**References**
Fe-TiO_2	65	7	As(V)	19.9	[44]
α-Fe_2O_3	5	7	As (III)	95	[45]
Mt-nZVI	1.19	7	As (III)	59.9	[46]
δ-FeOOH	20	7	As(V)	37.7	[47]
CuO	40	8	As(tot)	1.09	[48]
CFe	80	10	As(V)	-	[49]
γ-Al_2O_3	3-6	7.2	As(tot)	25	[50]
ZrO_2	7-15	7	As(V)	32.5	[51]
nZVI-RGO	2-4	6.8	As(V)	35.83	[52]
CaO_2	15-25	7.5	As(III)	25	[53]

4. Conclusions and way forward

Co-ZnO NP of different sizes ranging from 40–60 nm has been effectively prepared using the co-precipitation method. Various tests were carried out to determine the best dose, kinetics rate, effect of pH, sonication, light, and continuous flow performances. The developed ZnO NP were doped with Co on its surface. Co-ZnO NP can successfully remove As from aqueous systems at ZnO:As a ratio of less than 1:10. Furthermore, the removal was effective in the sunlight and at neutral pH. The innovative application of Co-ZnO NP to eliminate the As from the aqueous systems and to make it potable. Using Co-ZnO NP 100 mg/L of As can be decreased to the permissible limit set by WHO and EPA. The doping of Co onto ZnO NP responsible for the better treatment of As from aqueous systems.

The Co-ZnO NP effectively remove As in the pH range of 5.7– 7.2, so there is no need to set the pH value of a testing solution. Several other NP include Fe-TiO_2, α-Fe_2O_3, Mt-nZVI, δ-FeOOH, CuO, CFe, γ-Al_2O_3, ZrO_2, nZVI-RGO, CaO_2 stated in the literature for the treatment of As were also compared with the results in this study. These reported NP remove As in lesser amounts mostly in µg/L and take much time compared to Co-ZnO NP. The method used to synthesize Co-ZnO NP is simple, economical and time-saving and can be used for bulk production of Co- ZnO NP. The treated water with Co- ZnO NP can be utilized for drinking and other domestic purposes. The results are repeated several times and the standard deviation in the finding of As in two duplicates is found to be lesser than 2.5%.

Acknowledgements

This work was not supported financially by any organization.

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