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Green synthesis of silver nanoparticles and its application towards As(V) removal from aqueous systems

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Arsenic (As) contamination in one of the most serious water quality concern due to its toxic effects and worldwide availability. To avoid its poisoning effects, especially in the form of As(V), it is important to develop new techniques for its treatment. The current study was conducted to investigate the As(V) removal from aqueous systems using silver (Ag) nanoparticles (NPs). The Ag NPs were synthesized through a simple method by using *Vernonia Anthelmintica* (L.) plant extract and characterized by using UV-visible spectroscopy, Fourier transform infrared (FT-IR) spectroscopy, X-ray diffraction (XRD), Energy dispersive X-ray (EDX) spectroscopy and Scanning electron microscopy (SEM). The removal of As(V) was tested with respect to time, optimum dose, effect of light and pH, treatment with ultra-sonication and continuous flow process. The results showed that Ag NPs can effectively remove As(V) from aqueous systems in the presence of sunlight (100%), ultra-sonication process (100%), neutral pH (100%), and continuous flow (71.6%). While the same NPs could not show effective removal of As(V) with respect to low dose (15%), darkness (38.9%), low pH of 3.4 (21.4%) and high pH of 11 (11.1%). Using Ag NPs can reduce As(V) to the permissible limits set by World health organization (WHO). Moreover, the Ag NPs work efficiently in sunlight and in the neutral pH range, therefore adjustment of pH is not required to activate these NPs.

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Keywords: Green synthesis, Silver nanoparticles, As(V), Removal, Water treatment, WHO

1. Introduction

Water pollution is a major environmental concern because of rapid population and industrial activities and has potential to cause many problems to human health and environment [1,

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2]. In the last few decades, heavy metals (HMs) have been appeared as the most problematic water pollutants. The occurrence of these HMs and their impacts on human health and environment have been largely studied and scrutinized [3, 4, 5].

Among these HMs, the arsenic (As) is found to cause toxic health effects due to its occurrence in fresh water sources. Some of the major anthropogenic sources of As are mining wastes, agricultural wastes, refineries, sewage sludge, ceramic manufacturing factories, and fly ash due to burning of coal that increases As amount in both underground as well as surface running water [6, 7, 8]. The natural sources of As contains the weathering of rocks, erosion from soil and rocks and volcanic eruptions also increases As concentration [9, 10].

As exists in nature in more than 200 minerals forms. Among these, approximately 60% are present in the form of arsenates, 20% as sulpho-salts and sulphides, and 20% as arsenite, silicates, arsenide, oxides, and elemental As [11, 12, 13]. The presence of As in fresh water also occur because of its natural presence in bedrock beneath the earth [14, 15, 16]. In fresh water, As is present as inorganic arsenate and arsenite and dimethyl and methyl compounds of arsenic [17, 18, 19]. In water As(V) may pose a major threats to human health especially in countries like Afghanistan, Bangladesh, Pakistan, China and India. As(V) has the capability to cause health problems to human like, organ damage, skin alteration and cause lung, kidney and bladder cancer as well as hyperkeratosis, endocrine disruptors, appetite loss, muscular weakness, etc [20, 21]. For As, the WHO has set a limit of 10 μg/L [1, 22].

In developing countries, the rapid risk of As(V) carcinogenicity has caught the research attention on its removal. Numerous methods have been used to treat As(V) such as oxidation, adsorption, ion-exchange and co-precipitation [23, 24, 25].

All these methods have their own advantages and shortcomings. Recently, NPs in environmental remediation have gained increased attention to treat pollutants from water resources. NPs have unique properties such as large surface area, small size, can be easily separated, have more active sites and high reactivity that makes this technology attractive to remove As(V) from aqueous systems [26, 27]. Using NPs is a new method to remove HMs from water resources [28, 29, 30].

To remove As(V), different types of NPs have been used like iron oxide (Fe_2O_3), cupric oxide (CuO), zinc oxide (ZnO) and so many others NPs [31, 32]. Currently, the applications of Ag NPs are attracting the attention of researchers around the world. Ag NPs are nonhazardous and show much stability. Ag NPs efficiently remove the HMs in the pH range from 5.8 to 7.8 and thus gaining increased attention recently [33, 34 ,35].

In this study, Ag NPs were investigated for the As(V) removal. The study was mainly based on studying the optimum dose of NPs required, kinetic rate and pH and light effect on As(V) removal. The main objectives of this study were to develop an ecofriendly and cost-effective method for the removal of As(V) from aqueous systems. The outcomes of the current study are useful towards the development of new materials for in-situ decontamination of As(V) 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. Chemicals and reagents

The silver nitrate ($AgNO_3$) was purchased from (E. Merck. D-6100 Darmstadt, F.R. Germany). Nutrient agar for bacterial culture and Mueller–Hinton broth were obtained from (Merck, Pakistan). Plant extracts, fungal strains, petri plates, agar medium, silver NPs, incubator, micropipettes, screw cap test tubes, autoclave, magnetic stirrer, standard antifungal drugs, dimethyl sulfoxide (DMSO), potato dextrose agar (SDA) and 2,2-diphenyl-1-picrylhydrazyl (DPPH) were used in this study.

2.2. Collection and preservation

Fresh specimen of aerial parts of *V. Anthelmentica* (L.) at their leafy stage were collected from Surkh-Rod hills, (34.4064° N, 70.3599° E), Surkh-Rod district, Nangarhar, Afghanistan. The identification of plant sample was done by a Taxonomist and plant voucher sample (MM 2022) were prepared and stored in Herbarium Department of Botany, University of Peshawar, Pakistan.

2.3. Preparation of plant extract

For the preparation of extract aerial parts of *V. Anthelmintica* (L.) were grinded by using an electric grinder to 60 mesh diameter powders. Powders sample of 500 g was soaked in 250 ml methanol (70%) for almost fifteen 48 hours. Then, *V. Anthelmintica* (L.) extract was passed over Whatman filter paper grade No. 42 for two times and evaporated at 50 °C in a rotatory evaporator to dilute the plant extracts. The obtained plant extracts were then kept at 3-4 °C before its usage. The standard drug and *V. Anthelmintica* (L.) plant extracts were dissolved in DMSO at the amount of 15 mg/ml and 1mg/ml for antimicrobial, Antifungal and Antioxidant activities respectively. The dissolved *V. Anthelmintica* (L.) plant extract was diluted with deionized water [36, 37].

2.4. Preparation of $AgNO_3$ solution

[38] was followed to prepare the $AgNO_3$ solution. In initial stage the glass wares were cleaned by aqua regia and then washed thoroughly by deionized water. $AgNO_3$ (1mM) solution was synthesized by mixing 0.0169 g of $AgNO_3$ in deionized water and diluted up to 100 ml in a volumetric flask (150 ml).

2.5. Preparation of plant extract solution

The extract solution was prepared by dissolving 0.5 g of *V. Anthelmintica* (L.) extract in distilled water and then diluting up to 100 ml in a volumetric flask [39].

2.6. Synthesis of Ag NPs

The *V. Anthelmintica* (L.) plant extracts solution was mixed with a 1mM diluted solution of $AgNO_3$ in various proportions by volume such as 1:2, 1:4, 1:6 and 1:8. Then the reaction mixture was reserved under continuous magnetic stirring for a period of 4 hours, until the color of solution was altered from pale black to dark brown. This change in the color of aqueous solution confirms the first indication of synthesis of Ag NPs [40].

2.7. Surface characterization of Ag NPs

The prepared biosynthetic Ag NPs were analyzed via using UV-visible spectrophotometer. The optical property of these NPs was studied ranged within 200–600 nm through UV-Vis spectroscopy (UV-1800, Shimadzu). The crystalline structure of Ag NPs was examined using XRD analysis (Shimadzu-6000) and scanning of Ag NPs was carried out for 1.5h (10°-70°) while the functional voltage was 50 kv with power of 40 mA Cu-Ka radiation. The FT-IR spectrum was analyzed and recorded with KBr pellet technique with consistent scanning and ranged within 400-3000 cm^{-1} (IRAffinity-1, Shimadzu). SEM combined with EDX were used to scan the morphology, size as well as the elemental composition of biosynthesized Ag NPs (Hitachi's-4500).

2.8. Analysis

As(V) 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. The variation in concentrations was shown using standard deviation. GraphPad Prism (GraphPad Software, Inc., San Diego, CA, USA) and Origin Pro 2018 (Origin-Lab) were used for data analysis and preparation of graphs.

3. Results and discussion

3.1. Biosynthesis and optimization of Ag NPs

This study mainly focused on the biosynthesis of Ag NPs by using a biosynthetic process and to find its removal efficiency for As(V) from aqueous solutions. The biosynthesis of Ag NPs was achieved using *V. Anthalmentica* (L.) aerial part extracts as reducing and capping agent. The aerial extract of *V. Anthalmentica* (L.) and $AgNO_3$ solution was mixed with different ratios such as 1:2, 1:4, 1:6 and 1:8 and placed on a magnetic stirr until color changed from pale black to dark brown color that shows the initialization of Ag NPs formation see in (Fig. 1(a)). This change in the color of aqueous solution is due to the SPR. The electromagnetic rays (EMR) falling on the surface of the metal ion get penetrated deep more than the 60 nm. The electron on the surface of the metal are the most significant and their oscillation are called SPR. The biomolecules present in aerial extract of *V. Anthalmentica* (L.) covered over the surface of silver cation (Ag^+) and reduce its size to convert it into bioactive metal (Ag0).

The synthesized Ag NPs gave the peak in the range of 400-500 nm as given in (Fig. 1(b)). Optimization of Ag NPs were carried out to check the particular amount of NPs synthesis that gives maximum absorbance peak. Hence the different ratios such as 1:2, 1:4, 1:6 and 1:8. All of these ratios give absorbance band ranged from 400-500 nm for Ag NPs, however, 1:2 give sharp peak with maximum absorbance see in **(**Fig. 1(b)).

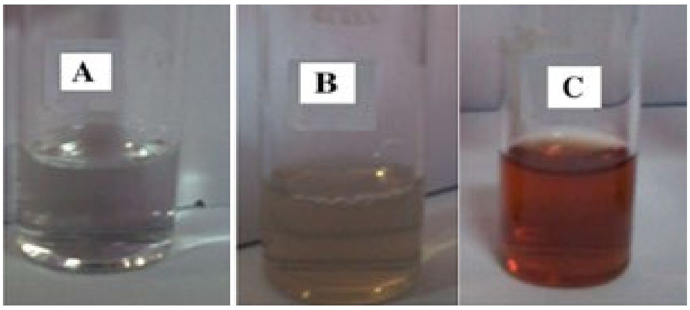

Fig. 1. (a). Flasks containing samples of (a) silver nitrate, (b) V. Anthalmentica, (c) Ag NPs.

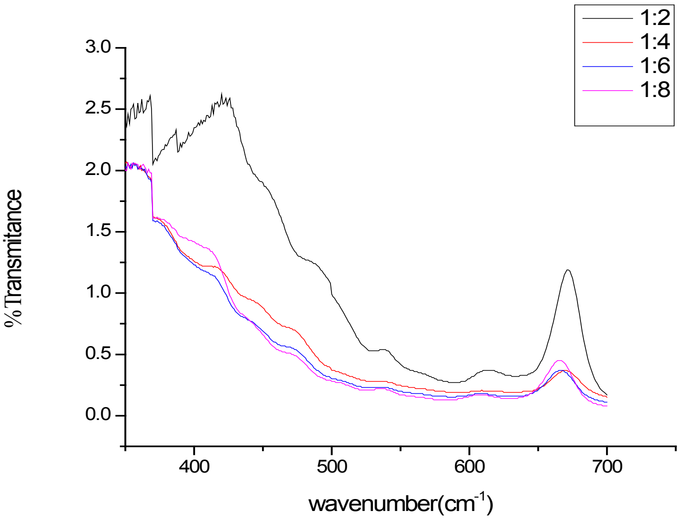

Fig. 1(b). Absorbance at different ratio of silver and extract solution

3.2. UV-visible analysis

The primary color of aqueous extract was observed light black and altered to dark brown color which confirms the initial biosynthesis of Ag NPs by mixing *V. anthelmintica* (L.) aerial part extract with $AgNO_3$ solution. The change in color occurred due to SPR phenomena of biosynthesized Ag NPs [41]. During the experimental phase the change in color slowly increased, thus Ag+ ions totally reduced to steady dark brown color. The biosynthesis of Ag NPs by using *V. anthelmintica* (L.) plant extract was confirmed due to SPR which presented UV-visible absorbance peak at 420 nm as shown in the (Fig. 2). Likewise, [42] stated that *Seripheidium quettense* extract showed Ag NPs attained UV-Visible absorbance peak at 428 nm by adding 4 mM of $AgNO_3$. [43]

reported the biosynthesis of Ag NPs with *Couroupita guianensis* flower petal extracts showed UV-visible absorbance peak at 418-424 nm which was the initial confirmation of Ag ion in solution. [44] also reported the biological synthesis of Ag NPs by using *Azadirachta indica* leaf extract and UV-visible absorbance peak was observed at 420 nm. From the above-mentioned studies, we have confirmed that UV-visible spectroscopy of Ag NPs of *V. Anthelmintica* (L.) plant extract is similar to the reported studies showing SPR peak at 420 nm as given in (Fig. 2).

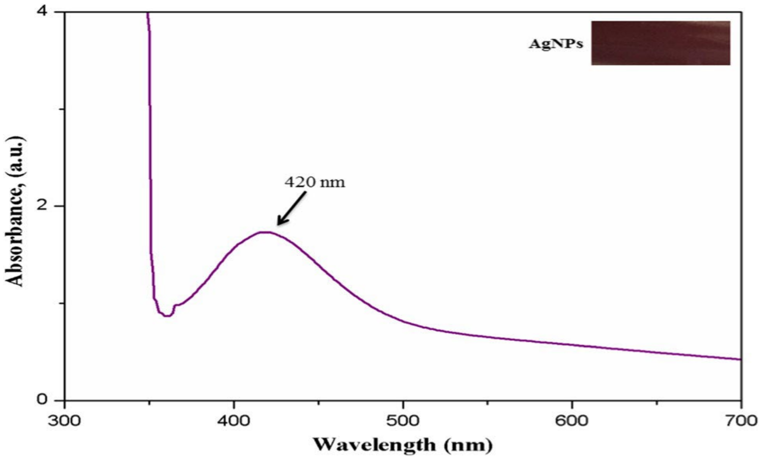

Fig. 2. UV-visible spectra of biosynthesized Ag NPs.

3.3. XRD analysis

During this study the XRD was mainly done to analyze the crystalline structure and size of the biosynthesized Ag NPs. The XRD patterns of Ag NPs synthesized by the aerial part of *V. Anthelmintica* (L.) as shown in (Fig. 3), after the complete reduction of Ag^+ to Ag^0. A number of Bragg reflections are present, which can be indexed on the basis of crystalline structure of synthesized Ag^0. The diffraction peaks at 2θ = 37.95 (111), 41.12 (200), 64.30 (220), 76.85 (311) obtained are identical with those reported for standards silver metal (Ag^0) (Jancy et al., 2012). Thus, the XRD patterns confirmed the crystalline nature of Ag NPs. The Ag NPs of aerial part extract of *V. Anthelmintica* (L.) show high intensity at 37.95 (111). The average particles size of these NPs was also measured through Debye-Scherrer equation by checking the width of the (111) Bragg reflection which was about 20 nm in size given in (Table 1).

Table 1. Debye-Scherrer equation done to sum the crystalline size of Ag NPs.

S.No	2θ (degree)	FWHM	β =Y(radians)×2× π/360	Crystalline size (nm)
1	37.95	1.6560	0.00912	21
2	41.12	0.9155	0.00722	19
3	64.30	1.8121	0.00804	20
4	76.85	1.6547	0.00845	21

The biological activities mostly depend on the size and concentration of Ag NPs [45]. Similar results were reported earlier for synthesized AgNPs by using leave extract of *Ocimum tenuiflorum* (AgNP1) and *Catharanthus roseus* (AgNP2). AgNP1 showed three distinct diffraction peaks at 27.1°, 32.2° and 46.2°, which may be assigned to the (226), (264) and (200) reflection planes of the cubic face-centered silver. While AgNP2 four peaks are observed at 2θ values of

27.1°, 32°, 39.2°, 44.8°, which may be indexed to the reflection planes of silver (226), (264), (111) and (200) respectively [46]. The results of XRD of Ag NPs of *V. Anthelmintica* (L.) in this study are reported similar to the previous studies.

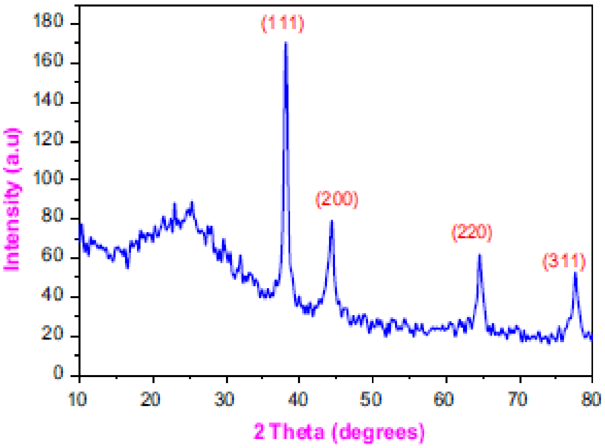

Fig. 3. XRD analysis of Ag NPs with 1mM $AgNO_3$.

3.4. SEM analysis

The surface morphology and size of these biosynthesized Ag NPs was observed through scanning electron microscopy. SEM images of the biosynthesized Ag NPs using *V. anthelmintica* (L.) plant extract were observed as spherical in shape and their average size was calculated to be 21 nm as shown in (Fig. 4). Same shape and structure of these biosynthesized Ag NPs using *Cassia Auriculatasem* possessed strong antimicrobial activates against the drug resistant *S. aureus* and *Citrobacter* [47]. The EDX analysis shows the presence of Ag and several organic compounds that comprise the Ag sums like chlorine (Cl), fluorine (F), carbon (C) oxygen (O) and silicon (Si) see in (Fig. 5).

The EDX peak of Ag NPs showed almost 60% yield of Ag. Relatively strong and sharp signals were observed at 2-3 keV which show the crystalline structure of the synthesized Ag NPs. However, some weak peaks are observed at 3-4 keV with Ag due to the emission of X-ray from phenolic and alcohol compounds [48]. The bioactive particles contain some inorganic composition bands shows the impurities in Ag NPs [49].

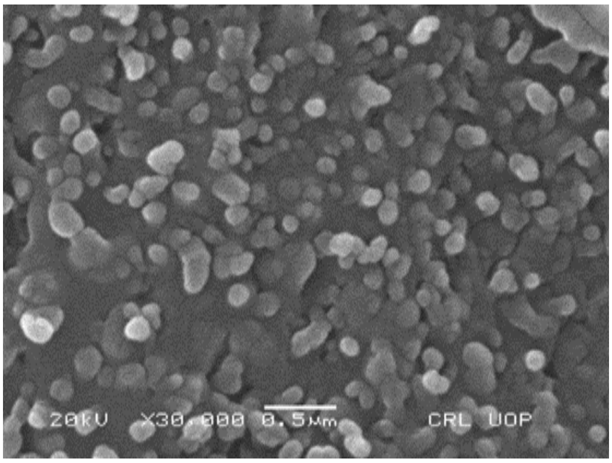

Fig. 4. SEM analysis of biosynthesized Ag NPs

3.5. EDX analysis

The result obtained from the EDX analysis give an indication regarding the elements of the NPs. The EDX sample of Ag NPs shows a strong signal of Ag atoms confirmed that Ag NPs contain pure Ag at the 2.5 KeV due to SPR as shown in (Fig. 5). The presence of Cl and Si elements in EDX spectrum due to plant extracts. The presence of C, O and F along with Ag signal suggest that the surface of Ag NPs was covered with biomolecules see in (Fig. 5). The EDX analysis result demonstrated that the Ag NPs are successfully synthesized using aerial part extract of *V. Anthelmintica* (L.) in this study. Same results were reported earlier for Ag NPs like [50] Ag NPs were synthesized using *Azadirachta indica* leaves and *triphala* extract and EDX spectrum presented a strong signal of Ag at 2.8 KeV. [51] used aqueous *Abutilon indicum* leaf extract for biosynthesis of Ag NPs and EDX analysis presented strong signal of Ag at 2.7 KeV. [52] used *Canna indica* for green synthesis of Ag NPs and EDX spectrum displayed a strong signal of Ag at 3 KeV.

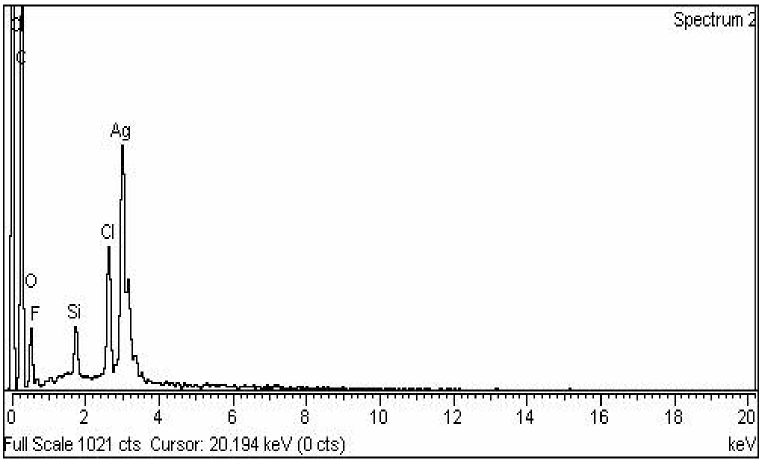

Fig. 5. EDX analysis of biosynthesized Ag NPs

3.6. FT-IR analysis

To find the functional group responsible for the biosynthesis of Ag NPs the FT-IR analysis was carried out. The mediated spectra of *V. anthelmintica* (L.) extract Ag NPs presented absorption peak at 3295.50, 3275.12, 2894.14, 2898.08, 2351.12, 2355.11, 1640.22, 1643.32, 768.56 and 424.35 cm^{-1} see in (Fig. 6). The peak at 3295.50 cm^{-1} was occurred due to C–H stretching in alkanes, however, the peak observed at 2894.14 cm^{-1} due to C-C stretching of aromatics, the peak observed at 3275.12, cm^{-1} due to stretching of (O=) PO–H in phosphonic acid. Bands at 2898.08 cm^{-1} shows C-F stretching of carboxylic acids and thus steady the NPs whenever proteins act as capping agents [53, 54, 55].

Peak at 2355.11cm^{-1} occurred due to C-N stretching of amine, band at 1640.22 cm^{-1} shows C-H stretching of alkanes, band at 1643.32 cm^{-1} represent C-H stretching of aromatics or due to alkanes, band at 424.35 cm^{-1} due to C-Br stretching of alkyl halides, the functional groups reported here are responsible for the capping agent for bio-reduction of Ag NPs synthesis [56]. Biosynthesis of Ag NPs by utilizing plant extracts, performed individually the role of stabilizing and capping agent [57].

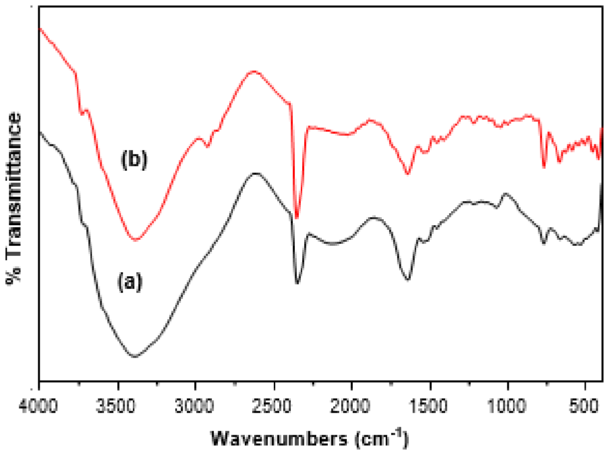

Fig. 6. (a) FT-IR spectra of plant extract and (b) FT-IR spectra of Ag NPs.

3.7. Optimum Ag NPs dose for As(V) removal

As(V) removal efficiency of the Ag NPs were revealed and improved by taking many doses of Ag NPs in different combinations. The outcomes show that, As(V) removal was significant at (Ag:NPs) ratio of 1:5 i.e. with a total removal efficiency of 100% after 7.5 h of the Ag NPs addition see in (Figure 7). With regards to kinetics, linear fit of the trends showed the rate of reduction was highest at the ratio of 1:5 as 5.8 mg/L/h while that with 1:10 was 10.2 mg/L/h. This showed that the removal followed a pseudo first-order reaction rate with the decrease of reactants concentration reliant on As(V) concentration in the system.

A relevant study was carried out by [58] aimed at determining the optimum doses of NPs of 10, 50 and 100 mg/L on the removal of (AsIII) & (AsV) from wastewater at three different amounts of (100, 500 and 1000µg/L) were tested. According to that study the removal of As was enhanced when the NPs dose was increased from 10 to 100 mg/L. Another study conducted by [59] showed the elimination of As at different time intervals, with acetate functionalized ZnO NPs, and it was revealed that As elimination was fast in the start, with almost >99.9%. According to this study, Ag NPs can remove As(V) efficiently by increasing the dose up to possible limits.

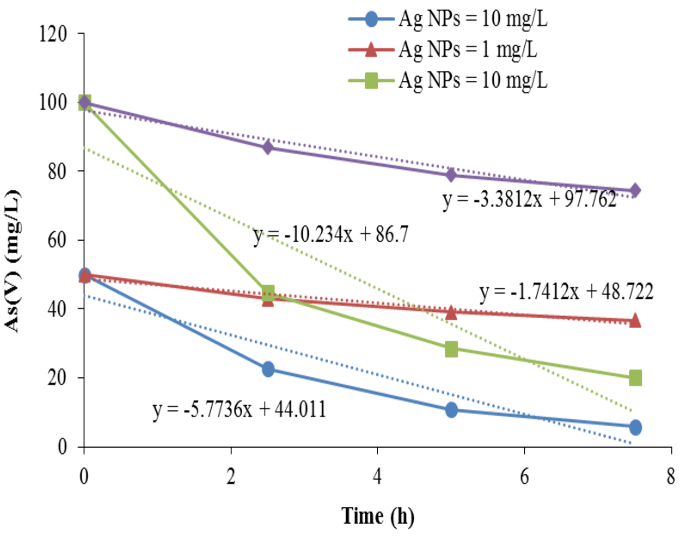

Fig. 7. Removal of As(V) with optimum dose (1 and 10 mg/L) of Ag NPs.

3.8. Effect of light on As(V) removal

Light is a significant factor to determine the quality of the synthesized material developed for the removal of As(V) from aqueous systems. Thus, the effect of light was examined to realize the performance and effectiveness of Ag NPs under several intensities of light. The effect of light on As(V) removal was conducted in sunlight, tungsten light and dark conditions. For this purpose, we have used 20 mg/L of As(V) concentration into three different volumetric flasks with 50 mL volume and added 10 mg/L of Ag NPs and kept these volumetric flasks in sunlight, tungsten light and in dark conditions for 2 h each.

The 20 mg/L of As(V) amount was reduced to 2.45, 5.63 and 10.22 mg/L respectively with addition of 10 mg/L of Ag NPs in the presence of sunlight, tungsten light and dark respectively. After 3 h reaction, the As(V) amount was reported 2.29 and 9.16 mg/L under tungsten light and dark conditions respectively and completely removed under the sunlight. Results of the current study revealed that 100% removal of As(V) was achieved in the presence of sunlight, 85% removal in tungsten light and 39% removal in dark condition.

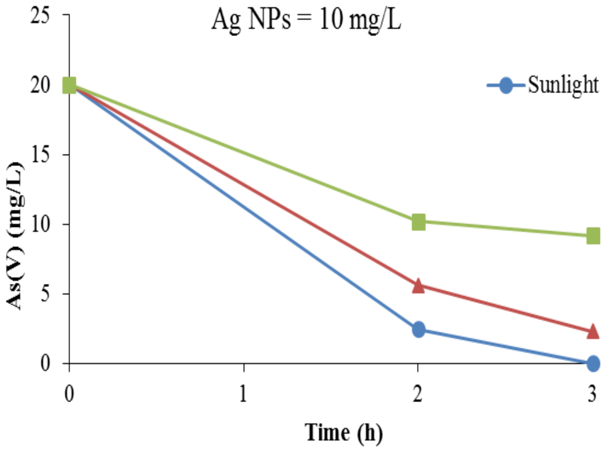

Fig. 8. Effect of light on removal efficiency of As(V) with 10 mg/L of Ag NPs

3.9. Effect of pH on As(V) removal

The effect of pH on As(V) removal from aqueous systems using Ag NPs were studied. For this purpose, As(V) was treated at different pH values i.e. neutral pH, lower and higher pH. To lower the pH value of solution 0.001 N HCl was added to the solution, while to higher the pH value 0.001 N NaOH was added. For this experiment five different volumetric flasks of 250 mL were taken and 10 mg/L As(V) concentration was taken in all five flasks while the Ag NPs amount of 10 mg/L was added to all these flasks. Solution 1 pH value was kept neutral i.e. 7.0-7.2, and thus Ag NPs showed good efficiency for As(V) removal. After 2 h reaction, the solutions were analyzed and As(V) was reduced from 10 mg/L to 0 mg/L.

Study reveals that these NPs works properly in this range and As(V) amount has been reduced from 10 mg/L to 1.26 mg/L after 2 h reaction. Solution with pH 3.4 showed that Ag NPs remove lesser amount of As(V) and almost reduced to 7.86 mg/L after 2 h. This is due to Ag conversion into $AgCl_2$ in presence of HCL. As(V) solution with pH 9.8 was reduced to 4.76 mg/L after 2 h reaction. In this range of Ag NPs showed satisfactory performance but not efficient. At pH 11.2 the As(V) was again very low and 10 mg/L of As(V) was decreased to 8.89 mg/L after 2 h. The effect of pH showed that that these NPs removed the As(V) at neutral pH, therefore no addition of acid or base is required for the removal purpose.

[60] investigated that As removal enhanced with the increase of pH and showed 99.92% removal at pH 5.8 and 99.26% at pH 7.8 respectively. At pH 12, the removal of As suddenly dropped to 10% due to the conversion of Ag to $Na_2Ag(OH)_4$ with the addition of diluted NaOH, hence As(V) removal was low in basic medium.

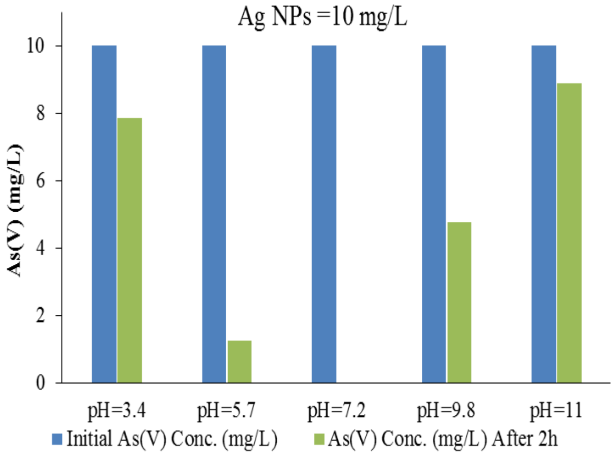

Fig. 9. Effect of pH on As(V) removal using Ag NPs.

3.10. Removal of As(V) in continuous flow with adsorbed Ag NPs

The removal efficiency of As(V) from aqueous systems using Ag NPs with filtration process was also carried out. Whatman filter paper 42 was used for this purpose and the two same identical solutions of As(V) concentration (10 mg/L) were taken in to two different reactors. With one time passage through NPs adsorbed on Whatman filter paper 42, As(V) amount was reduced from 10 mg/L to 6.72 mg/L 33% efficiency, while in the second reactor with five times passage through same NPs adsorbed medium the amount of As(V) successfully decreased from 10 mg/L to 2.84 mg/L with overall efficiency of 72%. The overall experiment continued for 30 minutes. The experiment showed that the Ag NPs were also effective in continuous flow setup and can be optimized with further tests.

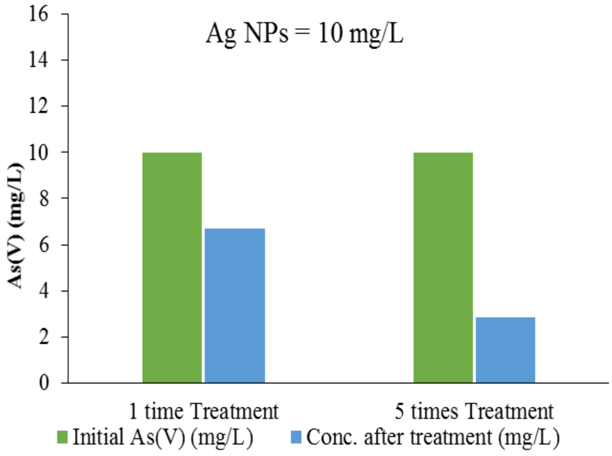

Fig. 10. Removal of As(V) in continuous-flow with adsorbed Ag NPs

3.11. Effect of ultrasonication on As(V) removal

This test was conducted under constant shaking of the batch reactors with sonication. The media were shaken continuously with a sonicator at a speed of 200 rounds per minute (RPM) for two h, and later the samples were analyzed through AAS-HH. The results show that the sonication process reduced the As(V) concentration to 2.67 mg/L i.e. within the permissible limit of WHO, while 10 mg/L of As(V) amount was reduced to zero see in (Figure 11). Results showed that sonication process highly effected the As(V) removal.

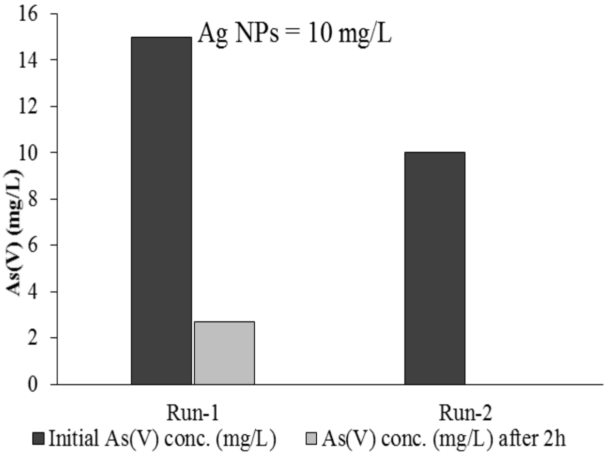

Fig. 11. Ultra-sonication effects on removal of As(V) using Ag NPs.

4. Conclusions

The effectiveness of Ag NPs was investigated for the removal of As(V) via adsorption from aqueous medium. Different experiments were carried out such as optimum dose, kinetics, effects of pH, ultra-sonication and light and performance in continuous flow. Ag NPs was found to effectively remove the As(V) from aqueous systems at Ag:As(V) ratio of less than 1:10. Moreover, the removal was efficient in sunlight and also at neutral pH. The removal was also effective in continuous flow with overall removal up to 72%. The results showed that using Ag NPs can reduce the As(V) up to the permissible limits set by WHO. Many other NPs such as cerium oxide, titanium oxide, magnetic ferric oxide and manganese oxide were reported in the literature for removal of HMs were also compared with the results of this study. The Ag NPs removed the As(V) in fewer amounts in less time as compared to the reported NPs.

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