Toxic effects of arsenic and its adsorption through thiolated cobalt doped silver nanomaterials from water resources

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Recently, the rapid increase in population and industrialization has been created a lot of problems to water resources around the world. Most of the world population are exposed directly or indirectly towards heavy metals (HMs) such as Arsenic (As) contamination and thus making the water resources unfit for drinking and other human purposes. The current study was planned to find the As adsorption potential of novel thiolated cobalt-doped silver nanoparticles (Co-Ag NPs) under various environmental setups. In present work the Co-Ag NPs of sizes (20–22 nm) were synthesized through co-precipitation process. Adsorption of As with Co-Ag NPs was tested in batch experiments with respect light, pH and competing anions. Overall, the Co-Ag NPs effectively adsorbed the As in presence of sunlight (100%) and neutral pH (>99%). The removal of As was maximum (>99%) at Co-Ag NPs:As ratio of < 0.5:1. Similarly, the synthesized Co-Ag NPs did not showed the goodadsorption efficiency in dark condition about (21.4%) and only (11.1%) uptake at low and high pH respectively. Results of the current study showed that Co-Ag NPs can efficiently adsorb the As and reduce to non-toxic form i.e. below the WHO standard limit (10 μg/L)in drinking water.

1. Introduction

Nowadays human activities and their basic needs are growing rapidly due to increased population in all countries and as a result our water resources have been contaminated with a greater quantity of harmful pollutants especially heavy metals (HMs) from different sectors [1, 2]. Certain adverse effects of urbanization such as depletion of resources, increasing carbon emissions and water pollution are reported regionally and globally that are disturbing human health and environment [3]. Industrialization also has effects on social and economic change of people and also needs innovations for improvement [4]. Due to industrial processes, large amount of pollutants is releasing into local water bodies and as a result causing water pollution especially surface and groundwater pollution. Industrialization not only produces HMs but also producing different types of wastes that effects environment [5].

Because of industrial revolutions, there is great discharge of chemical substances to the environment [6].Water pollution is a serious problem around the world that will disturb human health and environment [7]. Water pollution with HMs such as arsenic (As) is a growing concern for public health and environmental sustainability [8]. Water is an important source of drinking water for many communities, and contamination with As can pose a serious threat to public health [9]. As is a highly toxic metalloid that poses a significant threat to human health and the environment [10]. Itis found in soil, groundwater, and air, and exposure to As can cause a range of health problems [11].

The presence of As in water can also have a negative impact on agriculture and food security. As is difficult to remove, and can change to a variety of forms or interact with other substances to produce insoluble compounds [12]. The two oxidation states of As ions that are most prevalent are As(III) and As(V) which are primarily in their oxyanions forms, both are extremely hazardous to living things [13]. As-contaminated water is a problem that affects the entire world and now a major obstacle for scientists, engineers, and most decision-makers. Therefore, effective remediation technologies are needed to remove As from contaminated water.

However, various approaches had been used to control this problem but still it is a concern for humans. As with a great density is reported to be more toxic even in fewer amounts [14, 15]. As greatly affects the function of lungs, kidney and brain and also reduced energy level in humans [16, 17, 18, 19, 20] As is a carcinogenic because of their frequently exposure [21, 22]. Therefore, it is essential to offer suitable method for As treatment from water systems [23, 24, 25].

Several methods such as ion-exchange, coagulation, adsorption, oxidation or reduction, and phytoremediation have been used to treat As from aqueous solutions [26, 27]. All these methods have their own advantages and disadvantages but almost these methods are expensive and time consuming [28]. A new approach must be planned to safeguard human health and environment from the consequences of water pollution, and nanotechnology is reported one of promising and efficient technique for HMs treatment [29, 30]. Nanotechnology method has developed as a relatively cost-effective and showed good efficiency for the removal of As from water and soil and make it toxic-free compounds [31]. NPs adsorb As and other pollutants in eco-friendly way as compared to other methods [32]. NPs can be applied on both sites such as in-situ and ex-situ [33].

Several kinds of NPs have been used to treat As from wastewater [34, 35] NPs are frequently available and can be easily synthesized in laboratory [36, 37]. Various studies have proved that various kinds of NPs remove As, thus enhanced water quality [38, 39, 40, 41]. In current research work, thiolated cobalt doped silver NPs were used to adsorb toxic As from water at various As amount to find a more competent and eco-friendly technique for As polluted water. The outcomes of the current study are useful towards the development of novel materials for the decontamination of As from an aqueous solutions.

2. Materials and methods

2.1. Chemicals and reagents

The silver nitrate ($AgNO_3$) and cobalt chloride ($CoCl_2$) was purchased from (E. Merck. D-6100 Darmstadt, F.R. Germany). The stock solutions of As were prepared from the dissolution of arsenic trioxide (As_2O_3) (>99.98 %, Shanghai Macklin Biochemical Co., Ltd). 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. All chemicals and dilutions were made using deionized water (18.2 M). All of the remaining reagents in present work were of analytical grade and used as required.

2.2. Synthesis of Co-Ag NPs

Co-cores were prepared by dissolving the desired amount of cobalt precursor (cobalt acetate) about (50 mM) in a solvent (ethylene glycol) about 25 ml to create a cobalt precursor

solution. The concentration of the cobalt precursor depended on the desired doping level. Similarly, dissolved the appropriate amount of silver precursor (silver nitrate) about (50 mM) in a separate solvent (ethylene glycol) about 25 ml to create a silver precursor solution. Later, the cobalt precursor solution and the silver precursor solution were mixed in a reaction vessel and stir the mixture gently to ensure proper mixing. By adding a reducing agent (hydrazine hydrate) about 0.5 ml to the mixture and thus reducing agent reduced both cobalt and silver ions to their respective metal NPs in the presence of stabilizing agent (PVP) about (0.25 mM). As the reduction proceeds, cobalt ions incorporated into the silver crystal lattice, leading to the formation of Co-Ag NPs. The overall reaction was carried out under refluxing conditions with constant stirring of 100 RPM at 195 °C (stage 1) and 120 °C (stage 2).
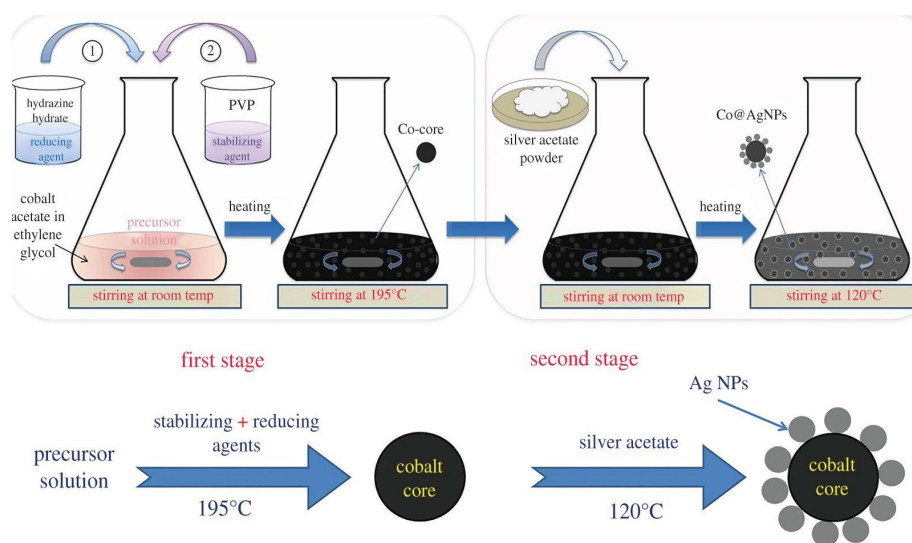

Fig. 1. Synthesis of Co-Ag NPs.

2.3. Experimental setup

All experiments were carried out in volumetric flasks (250 ml) containing As contaminated water. These volumetric flasks were washed with HNO_3 (10%) to avoid As contamination and then washed with distilled water. Co-Ag NPs were added to all volumetric flasks to find the removal efficiency for As. The whole experiments were carried out for one month at room temperature of 25 °C. For more precision and accuracy each experiment was performed in triplicate.

2.6. Analytical methods

After the completion of different reactions at different environmental setups, samples were collected from each volumetric flask to check the removal percent of As using Co-Ag NPs. Samples were analysed using Atomic Absorption Spectrometer (AAS) (Perken Elmer, USA) using 50 mL volume at 195.2 nm (wavelength) while argon (Ar) gas was used as a carrier at Shanghai Key Laboratory of New Drug Design, East China University of Science and Technology, Shanghai, China.

2.7. Surface characterization of Co-Ag NPs

The prepared Co-Ag NPs were analyzed using UV-visible spectrophotometer. The optical property of Co-Ag NPs was studied ranged within 200–600 nm through UV-Vis spectroscopy (UV-1800, Shimadzu). The crystalline structure of Co-Ag NPs was examined using XRD analysis (Shimadzu-6000) and scanning of Co-Ag NPs was carried out for 1.5 h (10°-70°) while the functional voltage was 50 kv with power of 40 mA Cu-K*a* radiation. The FT-IR spectrum was analyzed and recorded with KBr pellet technique with consistent scanning and ranged within 400-

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3000 cm^{-1}(IRAffinity-1, Shimadzu). SEM were used to scan the morphology and size of Co-Ag NPs (Hitachi's-4500).

2.8. Statistical analysis

In this current study the data was analyzed using two-way analysis of variance (ANOVA). All graphs were made using GraphPad Prism (GraphPad Software, Inc., San Diego, CA, USA) and OriginPro 2018 (Origin-Lab), using individual medium to present the mean values.

3. Results and discussion

3.1. XRD analysis

During this study the XRD was mainly done to analyze the crystalline structure and size of the synthesized Co-Ag NPs. The XRD patterns of Co-Ag NPs synthesized by the plant extract as shown in (Fig. 2), 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 (Ag0). Thus, the XRD patterns confirmed the crystalline nature of Co-Ag NPs. The Co-Ag NPs of plant extract 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. The results of XRD of Co-Ag NPs in this study are reported similar to the previous studies.
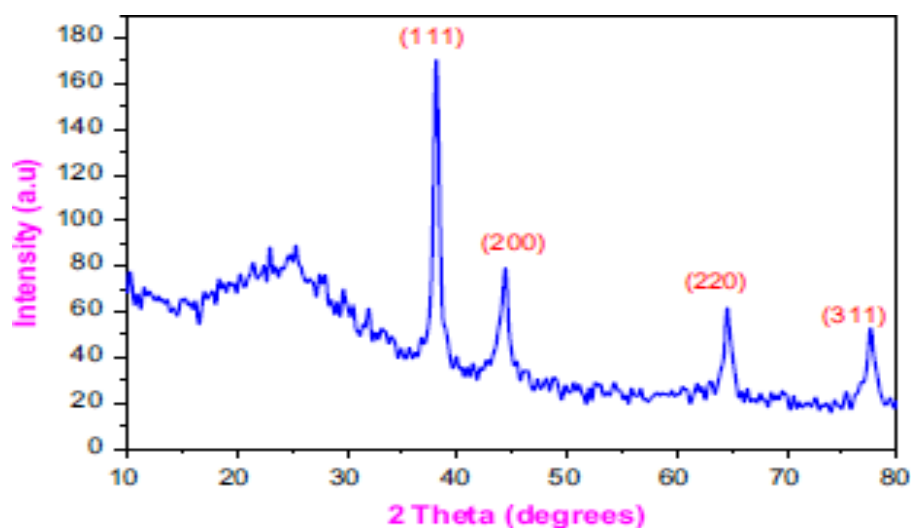

Fig. 2. XRD analysis of Co-Ag NPs with 1mM AgNO$_3$ [42].

3.2. SEM analysis

The surface morphology and size of Co-Ag NPs was observed through scanning electron microscopy. SEM images of the Co-Ag NPs using plant extract were observed as spherical in shape and their average size was calculated to be 21 nm as shown in (Fig. 3). Same shape and structure of Co-Ag NPs using *Cassia Auriculatasem* were reported by [41]. 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).
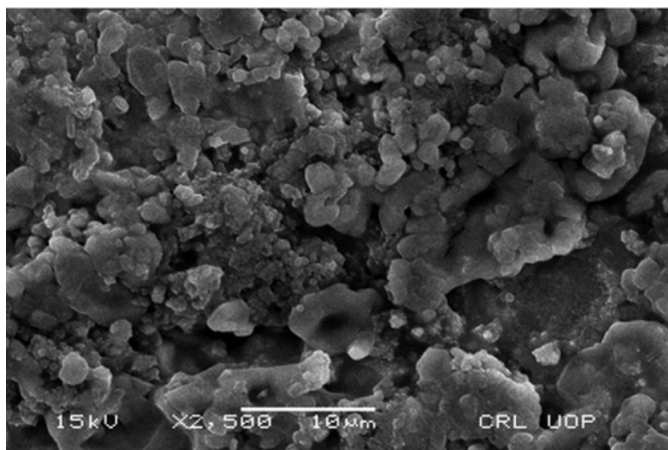
Fig. 3. SEM analysis of synthesized Co-Ag NPs [42].

3.3. FT-IR analysis

To find the functional group responsible for the synthesis of Co-Ag NPs, the FT-IR analysis was carried out. The mediated spectra of Co-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. 4). 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.

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 Co-Ag NPs synthesis. Biosynthesis of Co-Ag NPs by utilizing plant extracts, performed individually the role of stabilizing and capping agent.
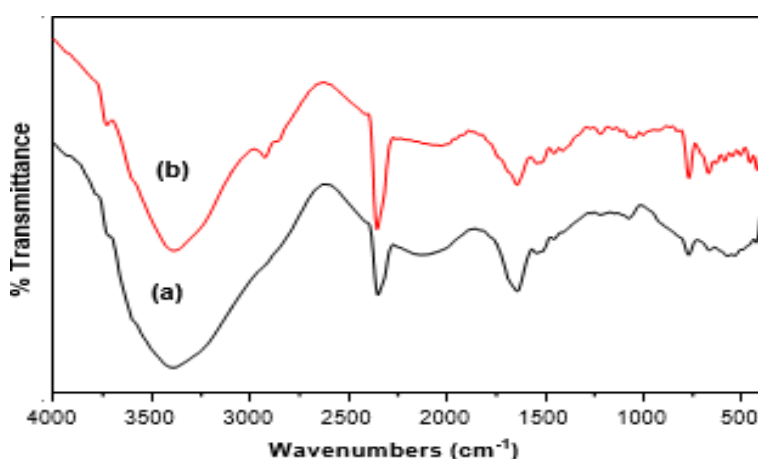

Fig. 4. (a) FT-IR spectra of extract solution and (b) FT-IR spectra of Co-Ag NPs [42].

3.4. UV-visible analysis

The primary color of aqueous extract was observed light black and altered to dark brown color which confirms the initial synthesis of Co-Ag NPs by mixing plant extract with AgNO$_3$

solution. The change in color occurred due to SPR phenomena of synthesized Co-Ag NPs. During the experimental phase the change in color slowly increased, thus Ag^+ ions totally reduced to steady dark brown color. The synthesis of Co-Ag NPs by using plant extract was confirmed due to SPR which presented UV-visible absorbance peak at 420 nm. Other studies also reported the biosynthesis of Co-Ag NPs by using leaf extract and UV-visible absorbance peak was observed at 420 nm. We have confirmed that UV-visible spectroscopy of Co-Ag NPs of plant extract is similar to the reported studies showing SPR peak at 420 nm as given in (Fig. 5).
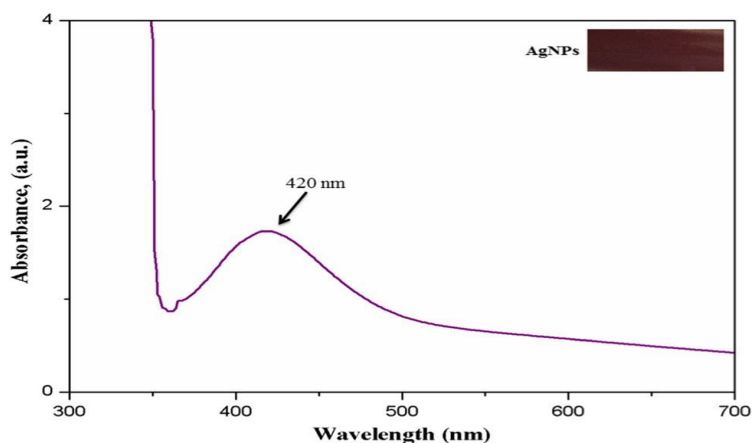

Fig. 5. UV-visible spectra of synthesized Co-Ag NPs.

3.5. Effect of pH$_{PZC}$ on As adsorption

The pH of the wastewater had no effect on the amount of adsorbed As, except at pH 3, as seen in Fig. 6. The quantity of adsorbed As was marginally smaller in an alkaline environment because acidic circumstances are more favorable for As removal by Co-Ag NPs. However, even in an alkaline environment (pH 10), the Co-Ag NPs sample still had an amount of As adsorption of roughly 18 mg/g. This demonstrates that a wide pH range can be used with Co-Ag NPs.

The surface of Co-Ag NPs was therefore positively (or negatively) charged when the pH of the wastewater was less than (or more than) 7.5 [43, 44]. The surface of Co-Ag NPs was protonated and positively charged in neutral and acidic environments. This makes it easier for As to adhere strongly to the surface of Co-Ag NPs, which results in a significant amount of As adsorption. Over a broad pH range (3–7), Co-Ag NPs can maintain an excellent As adsorption capacity thanks to a high pH$_{PZC}$ value. The surface of Co-Ag NPs was deprotonated and negatively charged in an alkaline environment, indicating that electrostatic adsorption was compromised and the phosphate adsorption capacity was decreased. Additionally, in alkaline circumstances, As ions and OH ions competed for the binding sites. It is noteworthy that the final pH rose within the original pH range of 3–8.
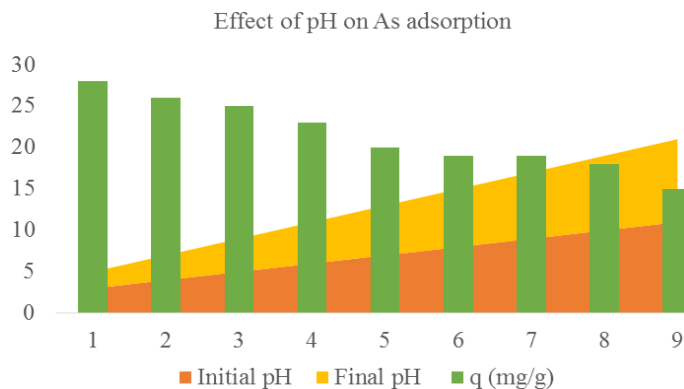

Fig. 6. Effect of pH on As removal from water using Co-Ag NPs.

This alteration happened as a result of ligand exchange between the hydroxyl groups on the Co-Ag NPs surface and the As ions in the wastewater, which released a lot of hydroxide ions and raised the pH and OH concentration of the wastewater [44]. In conclusion, the methods by which As is removed by Co-Ag NPs are ligand exchange and electrostatic adsorption.

3.6. Effects of light on As adsorption

The quality of the material created for As removal depends on light, which is a crucial aspect. In order to comprehend how Co-Ag NPs, behave and function under a range of light intensities, the impact of light was examined. Thus, three separate volumetric flasks of 250 mL each were filled with 30 mg/L of As and Co-Ag NPs (1:0.5) and maintained for two hours each under sunshine, tungsten light, and darkness. The 30 mg/L As level was reduced to 5.50, 10.80, and 15.25 mg/L, respectively, with the addition of 15 mg/L of Co-Ag NPs in the presence of sunlight, tungsten light, and darkness (Fig. 7). The As level decreased to almost 7.90 and 12.30 mg/L after three hours, in tungsten light and dark condition respectively, and was fully removed under sunlight. The results showed that in a sunlight, 100% removal of As was obtained. It is because, Co-Ag NPs gets activated which generates ROS (H_2O_2) upon exposure to ultraviolet-vis sunlight [52] and cause Co-Ag NPs to effectively remove As in the presence of sunlight.
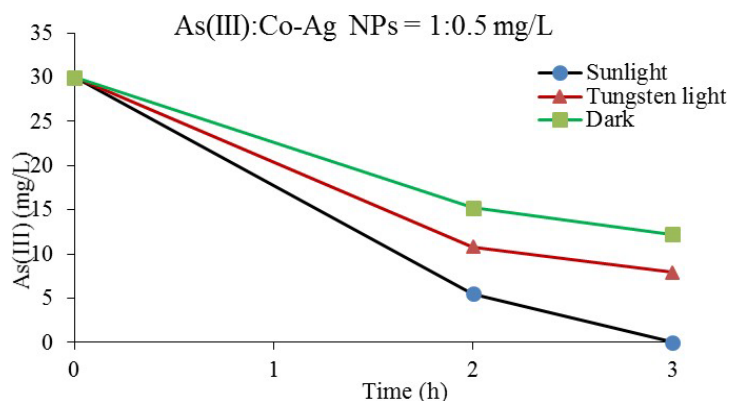

Fig. 7. Effect of light on adsorption of As using Co-Ag NPs.

3.7. Effects of competitive anions and humic acid

Competing anions, such as Cl^-, HCO_3^-, NO_3^-, and SO_{42}^-, and organic compounds, such as HA, are ubiquitous in water and usually interfere with the adsorption of As by adsorbents. Hence, the effects of these substances on the As adsorption capacity of Co-Ag NPs were investigated. Except for a slight negative effect of HCO_3^- and HA, the other competing anions had almost no negative effect on the amount of adsorbed As. This shows that Co-Ag NPs has good selective adsorption of As. This phenomenon may be related to the inner-sphere complexes formed between the Co-Ag NPs particles and As. The outer-sphere associations formed by electrostatic interactions are highly sensitive to the concentration of anions, whereas the inner-sphere complexes formed by ligand exchange tend to be insensitive to the concentrations of coexisting anions [45]. The negative effect of HCO_3^- on As adsorption may be because HCO_3^- has a similar structure to As(III) and can form inner-sphere complexes to compete with As for the binding sites on Co-Ag NPs [46].

3.8. Decontamination mechanism

Co-Ag NPs have been shown to effectively remove of As from water due to their unique physical and chemical properties given in (Fig. 8). The mechanism behind the removal of As by Co-Ag NPs involves inner-sphere complexes, electrostatic interactions and adsorption mechanism in this study. When Co-Ag NPs come into contact with As in a solution, the As ions can be

attracted to the surface of the Co-Ag NPs due to electrostatic forces, van der Waals forces, and chemical bonds. The Co-Ag NPs act as a sort of magnet, attracting the As ions to their surface [1].

Once the As ions are adsorbed onto the surface of the Co-Ag NPs, they can be effectively removed from the solution. The adsorption capacity of Co-Ag NPs for As is determined by several factors, including the size and shape of the NPs, the concentration and nature of the As ions, competing ions and the pH of the solution. Overall, the adsorption mechanism of Co-Ag NPs for As is a promising approach for the removal of As from polluted water sources, as it is a simple and effective method that does not require complex equipment or chemicals.
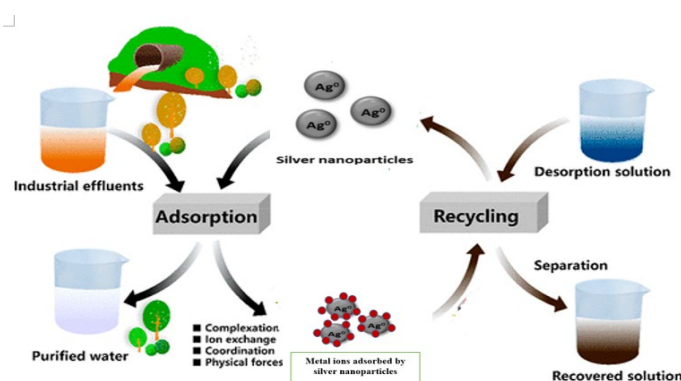

Fig. 8. Proposed mechanism of As removal by using Co-Ag NPs.

3.9. Reusability of Co-Ag NPs

Regenerating of Co-Ag NPs after use can be challenging and depends on the specific application and conditions under which they were used. In some cases, Co-Ag NPs may lose their efficacy after use due to agglomeration, oxidation, or contamination. One common method for regenerating Co-Ag NPs is by using a reducing agent such as sodium borohydride or hydrogen gas. The reducing agent can help to reduce silver ions back to their nanoparticle form. The method involves adding the reducing agent to the solution containing the used silver Co-Ag NPs and allowing the reaction to occur. The resulting mixture is then filtered and washed to remove any residual reducing agent or by-products.

3.10. Comparison of Co-Ag NPs with other NPs for As removal

Co-Ag NPs are one of the most widely studied NPs for HMs such as As removal due to their unique physicochemical properties such as high surface area, large number of surface active sites, and ability to form strong chemical bonds with As ions. However, there are several other NPs that have also been investigated for As removal, including iron oxide nanoparticles (Fe NPs), titanium dioxide nanoparticles (TiO_2 NPs), zinc oxide nanoparticles (ZnO NPs), Copper oxide nanoparticles (CuO NPs), carbon nanotubes (CNTs), magnesium oxide nanoparticles (MgO NPs) and gold nanoparticles (Au NPs). All of the stated nanoparticles showed the best efficacy for eliminating HMs with a neutral pH value (Tab 1).

Table 1. Removal efficiency of As using various NPs.

Nanoparticles type	Arsenic removed	Removal efficiency (%)	Specific pH values	Reference
Iron oxide NPs	As(III) and As(V)	>80%	7.0	[47]
Titanium dioxide NPs	As(III)	>82%	6.5	[48]
Zinc oxide NPs	As(III)	>85%	7.2	[49]
Copper oxide NPs	As(V)	>75%	7.5	[50]
Gold NPs	As(III) and As(V)	>78%	6.8	[51]
Carbon nanotubes	As(III) and As(V)	>80%	8.0	[52]
Magnesium oxide NPs	As(V)	>82%	7.7	[53]
Zirconium oxide NPs	As(III)	>81%	6.5	[54]
Cerium dioxide NPs	As(III) and As(V)	>75%	6.0	[55]
Cobalt doped silver NPs	As(III)	>90%	7.0	This study

4. Conclusions

Current study was carried out for the removal efficiency of As from water systems by using Co-Ag NPs. The removal efficiency of these Co-Ag NPs were affected by initial As concentration in the water samples. High adsorption of As were reported in the initial time of the experiment in water solutions. Co-Ag NPs removed the As efficiently and the removal efficiency was almost >95%. The co-precipitation approach has been successfully used to synthesize Co-Ag NPs in a variety of sizes between 20 and 22 nm. Using Co-Ag NPs, several tests were conducted to ascertain the effect of pH, light, competing anions, and the adsorption process of As. The surface of the synthesized Ag NPs was doped with Co. At a ratio of less than 0.5:1, Co-Ag NPs may successfully remove As from aqueous systems. Additionally, the removal was good in presence of sunlight and with a neutral pH. 30 mg/L of As can be reduced to the standard limits set by USEPA and WHO by using Co-Ag NPs. The improved adsorption of As from aqueous systems is due to the doping of Co onto Ag NPs.

Several other NPs such as iron oxide NPs, titanium dioxide NPs, zinc oxide NPs, copper oxide NPs, gold NPs, carbon nanotubes, magnesium oxide NPs, zirconium oxide NPs and cerium dioxide NPs were reported in the literature for the adsorption of As were compared with the results of current study. These stated NPs adsorb As in lesser amounts almost in µg/L and need more time as compared to Co-Ag NPs. The technique used to prepare Co-Ag NPs is simple, low-cost, time-saving, eco-friendly and can be applied for bulk production of Co-Ag NPs. The results of current study were repeated for two times and the standard deviation in the finding of As in duplicates is found to be lesser than 2.5%. However, further research should be conducted on optimizing As removal with Co-Ag NPs in continuous flow mode containing As such as industrial wastewater and proper disposal for the used Co-Ag NPs in eco-friendly way to avoid secondary pollution.

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