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ZnS Nanoparticles for Efficient Removal of Lead(II) Ions from Aqueous Solutions

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Abstract

Currently, nanoparticles with properties like large surface area, good volumetric potential, stability under different operational conditions with exceptional sorption behavior, and being easy to recover and reprocess are showing promising approaches for removing heavy metals from wastewater. Here, we planned to investigate the applicability of zinc sulfide nanoparticles (ZnS NPs) for the selective elimination of toxic heavy metals from mixed aqueous solutions. ZnS NPs were successfully synthesized using the chemical sol-gel technique with zinc sulphate and sodium sulphide. Prepared NPs were characterized using XRD (X-ray diffraction), UV-Vis (Ultraviolet-Visible), FE-SEM (Field emission-scanning electron microscope), and EDX (Energy dispersive X-ray spectroscopy) techniques. XRD revealed the cubic phase of ZnS NPs. The optical band gap was estimated using UV-Vis absorption spectra. The EDX microanalysis confirmed the presence of zinc and sulfur in the sample. The performance of the ZnS NPs for the removal of lead (Pb^{2+}) ions from aqueous solutions was inspected. Prepared ZnS NPs exhibited very high metal removal efficiency after 72 h of experimental observation. The results show that the NPs may serve as a promising adsorbent for the removal of Pb^{2+} ions from contaminated aqueous solutions.

Keywords

Zinc sulfide, Nanoparticles, Band gap, Toxic metal removal

Introduction

The accumulation of toxic heavy metals in water bodies is a regular issue that affects our society in many ways. Waste materials from the manufacturing or mining industry, tannery, textile, and dye industries are the leading sources of such heavy metals that are introducing extremely toxic and non-biodegradable elements into our ecosystem and polluting it excessively. Once they move into the food chain, they have the capability to accumulate regularly at very low concentrations in our living organisms, with the potential to initiate adverse effects on others in the ecosystem. Several well-known physico-chemical methods, such as chemical precipitation, solvent extraction, ion exchange, and membrane separation, can be successfully applied for the elimination of metals from groundwater and wastewater.

Environmental pollution has grown significantly in recent years, becoming one of the most severe problems that contemporary society is currently confronting. Pollutants, which may be a naturally occurring compound or foreign element, have a contrary effect on our ecosystem when they come into contact with the environment [1-3]. Industrialization, which is a part of modern civilization, has several negative effects on the ecosystem, though it improves our quality of life in many ways. Industrial effluents are the foremost factor in polluting our environment when they are exposed directly to water or air without any purification. A notable accumulation of toxic metals like Ni, Cd, Pb, As, Se, Cu, Cr, etc. in aquatic bodies is a very common fact in recent days. It is increasing due to the contaminated exposure of public or private sector company wastes from such factories like power plants or metallurgical firms, mining, coal, tannery, textile, and dye industry effluents, or the irresponsible dumping of sewage sludge and pharmaceutical residues from medical laboratories openly into nearby waterbodies. Heavy metal pollutants must be physically removed because they do not degrade naturally over time. If not, consuming excessive amounts of the polluted water over an extended period of time may harm human organ systems like the kidney, liver, brain, immune, or nervous systems and even result in death [1-6]. According to reported literature a variety of methods, such as chemical precipitation, filtration, ion exchange, electrochemical treatment, membrane technology, and absorption, have been developed to remove heavy metals from water [4-8]. Increasing the efficacy and acceptability of such methods to purify contaminated water from heavy metals has become a real challenge for researchers over the years. Though adsorption is preferred as one of the most effective and promising techniques for removing heavy metals from contaminated water due to its advantages of high effectiveness, low cost, easily available materials, low energy consumption, adaptability of use and no possible secondary pollution [4, 9]. In adsorption technique, ion-exchange systems and complexation with a high sorption efficiency are the most efficient part for effortless metal recovery. Reusability of the adsorbents is also an added advantage of the process, which altogether makes adsorption one of the most convenient, effective, and appropriate options to extract heavy metals from aqueous solutions [10]. Nanomaterials, or nanoparticles, are identified as materials with a varying dimension of a few nanometers, and they often possess unique size-dependent properties that are quite improved from their bulk counterparts. Due to their unique qualities, including a high adsorption capacity, unsaturated surfaces, a large surface-to-volume ratio, and ease of operation and production, nanoparticles are also receiving a lot of attention for the purpose of removing heavy toxic metals from industrial wastewater [11-16].

ZnS is a nature amending metallic chalcogenide with astonishing characteristics, such as a wide band gap (Eg ~3.6 eV) in cubic phase, high electrical mobility, thermal stability, being economical during laboratory synthesis, being non-toxic in nature, and being insoluble in water [11, 17]. Such amicable characteristics increase its wide industrial appeal and potential applications in opto-electronic factories in various shapes like thin film, NPs, nano-flakes, etc. [2]. Again, according to Pala and Brock [3] sulfide-based ion exchange materials may be an ideal candidate for heavy metal elimination applications from contaminated water due to their soft basic frameworks and the affinity towards softer Lewis acids (heavy metal like Pb^{2+}, Cd^{2+}, and Hg^{2+} ions) shoots up rapidly. Zhao et al. [4] and Almomani et al. [5] reported successful use of ZnS NPs in the sequential elimination of multi-component heavy metals from polluted aqueous solutions. The stimulus for the work stemmed from the above discussion, and in this study, we planned to synthesize ZnS NPs to utilize them to eliminate heavy metal ions like Pb^{2+} from the aqueous solution. Though, lead is a substance that has been utilised by humans since the dawn of time and has substantial industrial significance. All forms of lead are regarded as cumulative toxins [6]. The neurological system and gastrointestinal tract can both be impacted by acute lead poisoning due to uncontrolled exposure of it for a long time [7]. It was reported that the selectivity of different heavy toxic metals during adsorption on the sorbent is directly associated to the solubility product of heavy metal sulphides. Here we have focussed on the adsorption technique, which is a widely accepted low-cost method to remove Pb^{2+} ions from contaminated water. Initially, we prepared ZnS NPs using a chemical sol-gel process, and then the prepared NPs were characterized using XRD, UV-Vis, FE-SEM, and EDX techniques. The results show that the NPs serve as a promising adsorbent for the removal of Pb^{2+} ions from contaminated aqueous solutions.

Materials and Methods

Chemicals for synthesis

The chemicals used in the synthesis procedure are zinc sulfate [$ZnSO_4.7H_2O$] (Loba Chem, India) and sodium sulfide flakes [$Na_2S.H_2O$] (Himedia, India). Deionized water was used as a solvent during sample preparation. The reagents were used as they were, without any further purification. The purity of the reagents can also be confirmed by the outcomes of the experiment. Acetone and deionized water were used to clean all the glassware before and during the experiment.

Preparation of ZnS NPs

A detailed synthesis procedure is available in our previous report [11]. During the synthesis, after introducing sodium sulfide, we kept the solution on a magnetic stirrer with a high rpm for a long time to increase the possible NPs yield and reduce the probability of particle agglomeration. A flow chart is given below (Figure 1) to understand the steps quickly.

Methodology for removal of Pb^{2+} ions

An atomic absorption spectrophotometer (AAS) (with an acetylene flame, Shimadzu) was used to determine the heavy metal content of the water samples [8]. Pb^{2+} ions containing water sample was analyzed using a specific hollow cathode lamp and wavelength. They were then compared to standard metal solutions in an AAS. 100 ml of the synthetic wastewater sample was measured and placed into 250 ml beakers to determine the amount of adsorption. 100 ml of synthetic wastewater was placed in a beaker along with 100 mg of the synthesized ZnS NPs. The containers holding the synthetic

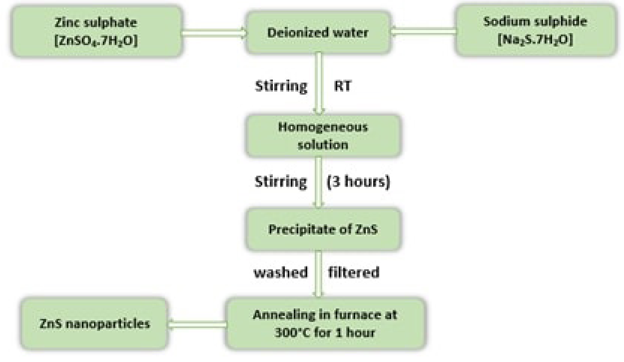

Figure 1: Schematic synthesis diagram of ZnS NPs.

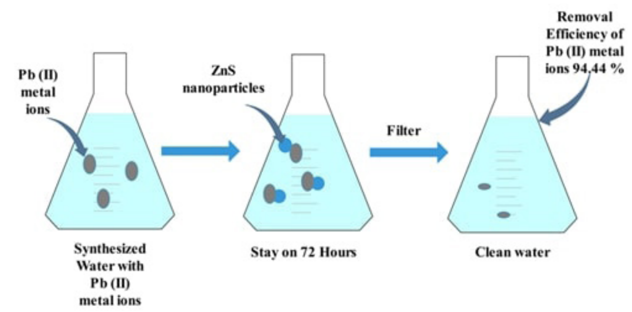

Figure 2: Pictorial representation of steps to understand the Pb^{2+} ion elimination process adopted during the experiment.

wastewater and adsorbent were left at room temperature for 72 h to establish equilibrium. The suspension was filtered using filter papers (Figure 2).

Characterization

The structural properties of the ZnS NPs were investigated at room temperature under normal ambience with a XRD machine (Rigaku Smart Lab) maintaining 2θ scanning range between 20° - 80°. The morphological studies of the as-prepared sample were carried out with FE-SEM (JOEL JSM-7610F-Plus) equipped with an EDX (EDAX, USA) analyser. The UV-Vis absorption of the samples was recorded using UV-Vis spectrometer (Shimadzu UV2600, Japan) in the wavelength range 200 - 800 nm.

Results and Discussion

XRD analysis

XRD technique was used to investigate the structural properties of the ZnS NPs. The scanning range of 2θ was 20° to 80°. There were three major peaks observed in the spectrum aligned to the (111), (220) and (311) planes. On the basis of these major peaks, it can be concluded that the synthesized ZnS NPs are in cubic phase. We have reported the XRD pattern for ZnS NPs in our previous work [11, 17]. The crystallite size for the observed XRD pattern was within the nano range as was calculated with the help of the Debye-Scherrer expression (Equation 1) [2].

$$DS = k\lambda/\beta\cos\theta \quad (1)$$

Where k is the shape factor with a constant value of 0.9, wavelength of incident copper K-alpha radiation is taken as 1.5406 Å and it is denoted as λ in the above expression. β is considered as full width half maxima of the XRD diffraction peak [9].

Morphological study using FE-SEM

The morphological properties of the samples investigated using FE-SEM technique. The results are mentioned in the figure 3. Both the micrographs are showing low and high magnified results of the sample. The results show flakes like agglomerated structures which are common for such kinds of materials [11]. Agglomeration is a primary issue with these types of NPs. Hence, to prevent it and keep the size of the particle in the nano range, we continue the stirring process with high rpm for a longer time during synthesis, as mentioned above. The purity of the sample was determined by EDX spectrum.

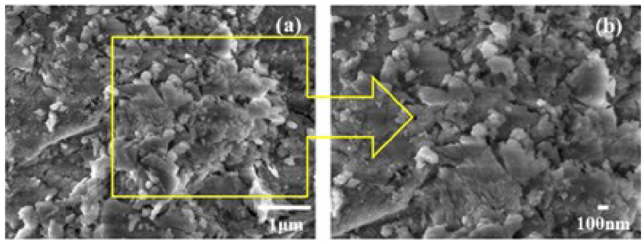

Figure 3: FE-SEM micrographs of synthesized ZnS NPs. Showing **(a)** lower and **(b)** higher magnification of the sample.

EDX analysis

The EDX spectra of the synthesized ZnS NPs is shown in figure 4. The spectrum supports the successful synthesis of pure ZnS sample. In figure 4 we can see elemental zinc and sulfur signals without any peaks from contaminants. In addition, on the basis of XRD and EDX measurements, we can say that the sol-gel chemical method is effective in producing pure ZnS NPs.

UV-Vis absorbance analysis

The UV-Vis absorbance spectrum of ZnS NPs given in figure 5. The spectrum was recorded in the wavelength range of 200 to 800 nm. It is predicted that semiconductor materials will undergo quantum confinement if their dimensions decrease below the exciton's Bohr radius. In this case, the absorption edge will be moved to a higher energy in response to the quantum confinement effect [10]. In the graph, an absorption peak at 328 nm can be seen which is shifted to lower wavelength, showing blue shift compared to bulk ZnS (340 nm). Similar kinds of results were also observed and reported, where confinement effects were considered one of the major causes behind such a wavelength shift [11]. The blue shift of the sample is also in agreement with the XRD results and supports the claim that the size of the particles lies within the nano range. Using the absorption results band gap of the sample was estimated using energy equation (Equation 2).

$$E_g = hc/\lambda \quad (2)$$

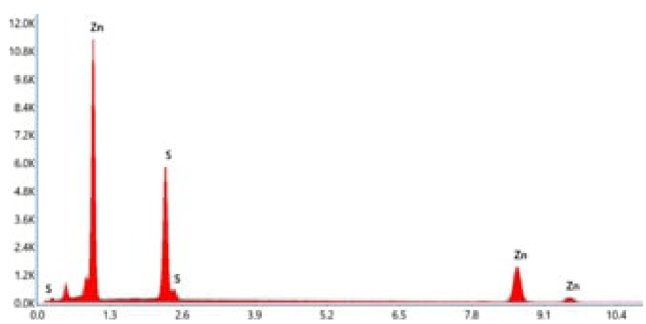

Figure 4: EDX spectra showing the elemental composition of the ZnS NPs.

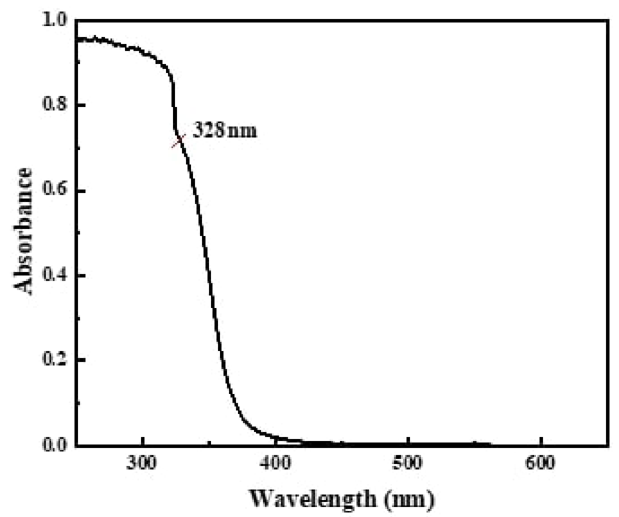

Figure 5: Absorption spectra of the ZnS NPs.

Here, h is Planck's constant and λ is the wavelength of the incident radiation. E_g is the estimated energy band gap of the sample.

Application in heavy metal (Pb^{2+}) removal

For a quantitative measurement to understand the amount of Pb^{2+} ions absorbed by the adsorbent (i.e., ZnS NPs), we used an AAS, and the % removal efficiency was calculated based on the equation 3 [12].

$$\%removal = (C_o - C_t)/C_o \times 100 \quad (3)$$

Where C_o is taken as initial concentration and C_t as final concertation of the metal in the formula.

To analyze the efficiency of Pb^{2+} ions removal we allow ZnS NPs to disperse inside the prepared lead solution for next 72 h in room temperature under ordinary environment. In this situation ZnS NPs show a maximum removal efficiency of 94.44% for Pb^{2+} ions. A similar experimental report was given by Pak and Yoo [13], showing 79%, 89%, and 87%, removal of Pb(II), Cr(II), and Cd(II) ions, respectively using nickel ferrite NPs.

Conclusion

In conclusion, we can say that there is no doubt that heavy metal ions are one of the major environmental concerns, and lead (Pb) is one of them. The toxicity of such heavy metal ions has been found to lead to many health complications in living creatures, and in this study, we investigated the possibility of using ZnS NPs to remove Pb^{2+} ions from contaminated aqueous solutions. It can be said from the observed results that ZnS NPs, which shows excellent adsorption capacity (~94%) for Pb^{2+} ions, may be synthesized very cost-effective way in the laboratory. Overall, the whole study shows a feasible and novel approach to prepare a low-cost nano-adsorbent (ZnS NPs), which has great application potential in wastewater management and treatment.

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Conflict of Interest

None.

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