__Original Research Article__

Removal of Heavy Metals from Waste Water by using Bi-Mg Bimetallic Nanoparticles Incorporated with Orange peels

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ABSTRACT

Plant-mediated synthesis of the nanoparticles has attracted significant interest because of their biocompatible properties. Bimetallic nanoparticles comprise two different types of metals that play a significant role in wastewater. Bimetallic nanoparticles possess a greater surface area, increasing their adsorption than monometallic nanoparticles. In this, synthesis and the adsorption behavior of Bi-Mg bimetallic nanoparticles and their removal efficiency toward heavy metals (cadmium, lead, zinc) from wastewater is observed. Synthesis of bimetallic nanoparticles by natural resources (plant extract) is more significant than conventional methods because these are environment friendly, reliable, nontoxic and least expensive. Plant extract obtained from the biomass wastes like roots, flowers, leaves and fruit peels comprised of novel secondary metabolites like terpenoids, flavonoids and alkaloids that act as stabilizing and reducing agents. Different techniques like SEM, EDX and XRD are used to analyze the morphology, composition and size of synthesized nanoparticles.The removal of heavy metals depends upon the pH, dosage of adsorbent and initial concentration of metal. The results showed that the plant-mediated synthesized nanoparticles could act as an efficient adsorbent to remove heavy metals from wastewater.

Keywords: Bimetallic nanoparticles, Plant-mediated synthesis, reducing agent, adsorption, heavy metals.

1. INTRODUCTION

Water is the basic need of living things. However, due to industrialization, water becomes contaminated with many hazardous substances such as heavy metals Pb, Zn, Cu and Hg. Heavy metals are those metals that have higher density and toxicity even in lower quantity. Heavy metal term is for the group of metalloids and metals having atomic density more than 4.00 grams per cubic centimeter or 5 times or greater than the density of water [1]. Due to their toxicity, removing heavy metals from water is essential. Conventional treatment methods to remove heavy metals from wastewater are not economically beneficial and produce large quantities of chemicals [2]. Green synthesis of metallic nanoparticles has recently attracted much attention [3,4,5,6]. Nanoparticles are used to remove heavy metals from wastewater [7]. Nanoparticles are the smallest particles that have size ranges between 1 to 100nm. Nanoparticles can be defined in various ways depending on types of materials and fields [8]. Bimetallic nanoparticles are more significant than monometallic nanoparticles and consist of metals of two different types, e.g.for example Cu-Niand, Ag-Ni etc, while monometallic nanoparticles are comprised of only single metal e.g. for example Cu or Ni etc [9,10]. Nanoparticles can be synthesized by two approaches. In a top-down approach, the bulky substances broke into nano-sized particles. Examples are chemical vapor deposition, physical vapor deposition and milling. The bottom-up approach is the reverse of a top-down approach. In this, nano-sized particles could combine for the formation of bulky material. It is also known as building-up method (Figure 1). Example of this method includes reduction and sedimentation (Figure 2). A bottom-up approach could be preferable because there is more contamination risk in top down-approach [11]. Synthesis of bimetallic nanoparticles by natural resources is more significant because of toxic chemicals, which are harmful for the environment, so the biological methods are used because these are environment-friendly, reliable and nontoxic (Figure 3) [12,13,14]. Plant-mediated green synthesis of BNPs depends upon the extract of plants [15]. It is also cost-effective to synthesize the bimetallic nanoparticles because plant extract obtained from biomass wastes like roots, flowers, leaves and fruit peels [16].]. Plants' Crude extract comprises novel secondary metabolites like terpenoids, flavonoids, and alkaloids with hydroxyl and carbonyl groups that act as stabilizing and reducing agents [17,18]. The formation of bimetallic nanoparticles takes place by these compounds, which are helpful in the reduction of metal ions into the metallic nanoparticles [19]. Plant-mediated synthesis in forming these particles depends upon the plants' capacity to uptake, accumulate, utilize and recycle many mineral species. The plant-mediated synthesis method is very rapid and economically beneficial upon capacity of the plants to uptake, accumulation, utilization and recycling of many mineral species. The plant mediated synthesis method is very rapid and economically beneficial. [20]. Plant mediated synthesis involves single step; therefore, it is preferable over conventional methods [21]. Bimetallic nanoparticles are synthesized by combining salt solution of two metals and plant extract, which behave as stabilizing and reducing agents. It gives unique properties to the two different metals required to form nanoparticles due to the synergy (Figure 4) [22,23].

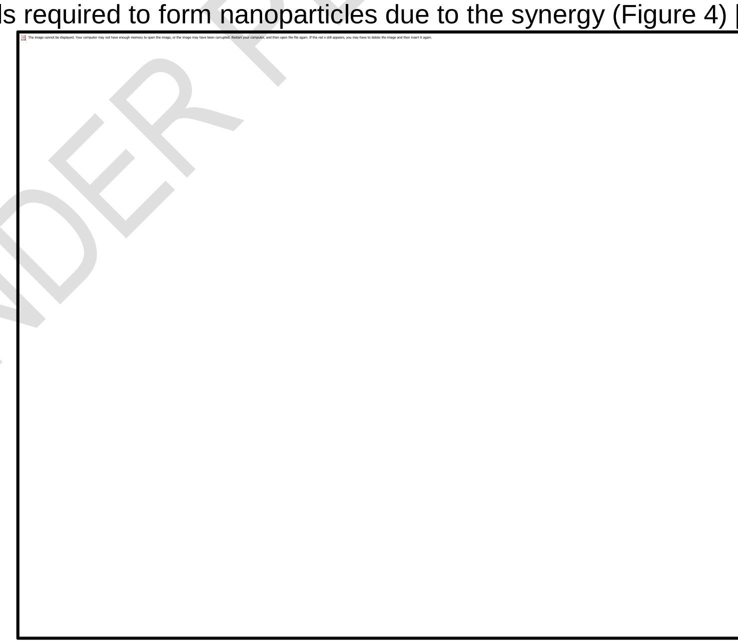


Fig. 1 Schematic representation of the building up of nanoparticles

1.1 Novel bimetallic NPs

Novel bimetallic NPs are synthesized to get more benefits. They may be Pt-based bimetallic NPs, Ni-based bimetallic NPs, Au-based bimetallic NPs, Fe -based bimetallic NPs, Pd -based bimetallic NPs.

1.2 Pt-based bimetallic NPs

Pt NPs are used nowadays because they act as catalytic converters because of their ability to have a higher surface area. Pt base nanoparticles catalyst could be synthesized to increase platinum base Electrodes' effect [24]. The catalytic efficiency of pt-based NPs (Pt-X X may be Ag, Au or Cu, etc) is higher. Pt-based bimetallic nanoparticles are helpful in catalytic hydrogenation and act as catalysts. The combination of additional metal with noble metal can reduce the requirement of noble metal and is also useful to increase its catalytic activity. For instance, the Pt-Au catalyst shows better catalytic activity than the single metal [25, 26].

1.3 Ni-based bimetallic NPs

Magnetic properties and catalytic ability of Ni-based nanoparticles are very useful. It shows versatile properties when combined with another metal [27]. Ni-based catalysts are useful because they are less expensive and highly stable. Nickel and tin-based nanoparticles can be synthesized in the required composition and size. Bimetallic nanoparticles of various compositions are synthesized by changing the stoichiometric ratio of tin and nickel. Cu-Ni bimetallic nanoparticles can be used to improve chemical reaction efficacy [28].

1.4 Fe-based bimetallic NPs

The bimetallic Fe-Cu catalysts system has become more significant nowadays. Fe-Cu based bimetallic catalysts, when supported with MCM-41 exhibit higher catalytic efficiency than iron or copper both would be supported with MCM-41 [29]. Different bimetallic nanoparticles such as Pd-Fe, Pd-Zn and Ni-Fe are prepared to treat chlorinated pollutants [30].

Fig. 2 Synthesis approaches to prepare bimetallic nanoparticles

1.5 Pd-based bimetallic NPs

Nanoparticles are useful because it is cheap and easily available. The Pd-based bimetallic NPs show greater stability in the acidic media and help to oxidize alcohol in the alkaline media [31]. Pd-Au bimetallic nanoparticles have greater efficiency to act as catalysts that are useful in Suzuki coupled reactions [32]. Pd-Fe-based bimetallic nanoparticles are economically important because they have the ability to transform chlorinated compounds. Pd-Ag bimetallic nanoparticles can act as sensors that would be helpful for the detection of L-Cysteine electrochemically [24].

1.6Au-based bimetallic NPs

These nanoparticles exhibit better catalytic activity and act as biosensors. Gold-based nanoparticles help to enhance the catalytic efficiency and selectivity. Au-Pd nanoparticles are synthesized recently and exhibited the electrochemical, catalytic and structural properties. Au-Ag bimetallic nanoparticles can act as medical sensors. Au-Ni can be synthesized in various forms and shapes. Au-Ag bimetallic nanoparticles are used to detect glucose and show the properties of chemiluminescence [33].

1.7 Utility of bimetallic nanoparticles than monometallic nanoparticles

Scientifically bimetallic nanoparticles are more significant than that of monometallic nanoparticles [34]. The properties of nanoparticles depend upon the metal types and size [35]. It has great importance in technological and industrial aspects. Bimetallic nanoparticles are comprised of an extra degree of freedom than that of monometallic nanoparticles [36]. The surface area of bimetallic nanoparticles is greater, enhancing the adsorption power and can behave as a better catalyst than monometallic nanoparticles [37,38,39]. With the help of a bimetallic catalyst, catalytic properties can be enhanced than that of monometallic [26].

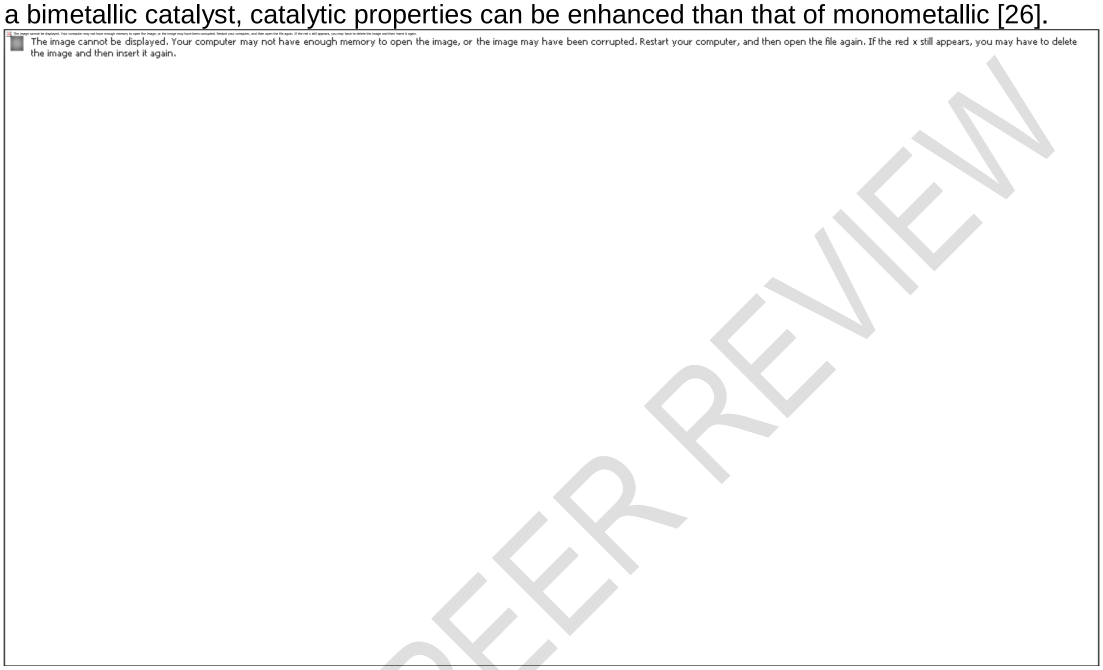


Fig. 3 Key merits of plant-mediated synthesis of bimetallic nanoparticles

Fig. 4 Mechanism of green synthesis of NPs

2. EXPERIMENTAL DETAILS
2.1 Material Synthesis

All chemicals used must be analytical reagent grade: Bismuth nitrate Bi $(No_3)_3$, Magnesium chloride ($MgCl_2$) and Sodium thiosulphate. The analysis of heavy metals has been conducted by the use of AAS. To prepare the solutions, distilled water was used in the experiment.

2.1.1 Preparation of extract

Oranges were collected from the local market of Lahore. To remove chemicals and dust on the orange peels, wash the oranges in distilled water. Dry these washed oranges so that they have no more water. Peel off the oranges and keep these in a shady place for 15 days to remove moisture. Weight 30g of dried peels with the help of analytical weight balance. In a flask, these weighted peels (30g) were dipped into 100ml double distilled water. This flask is then covered with aluminum foil and placed on the heating mantle. The temperature of the heating mantle was set at 70°C so that volatile extract components were not evaporated. After 2 hours, the color of the solution was changed from colorless to yellowish. The extract is prepared. The mixture was filtered using Whatman filter paper No. 1. Filtrate was used as an extract. Now, extract was stored in the refrigerator for further use.

Fig. 5 Preparation of extract

2.1.2 Synthesis method of bimetallic nanoparticles

Nano solutions were prepared by adding orange peel extract in bismuth nitrate and magnesium chloride solutions in a continuous stirring manner so that fine-sized particles were obtained. Take 50 ml of leaf extract in a flask while 50 ml of MgCl2 and Bi (NO3)3 were filled in burettes. Salt solutions were added dropwise in the extract with continuous stirring. Add sodium thiosulphate as a catalyst in the solution and keep it on the 78-1 magnetic hot plate at 70oC for 6 hours with continuous stirring. Add sodium thiosulphate as a catalyst. The visual evidence for nanoparticles synthesis was the color change from yellowish to brown. Place the solution in an oven at 80.7 o C for 3 hours. When it was dried, store the sample in the sample vial.

Fig. 6 Steps for the Synthesis of Bi-Mg bimetallic nanoparticles

2.2 Adsorption of heavy metals over Bi-Mg bimetallic nanoparticles

Adsorption experiment was performed for the determination of adsorption phenomenon of the heavy metals (Pb, Cd, Zn) at different conditions (pH, dosage of adsorbent and initial concentration of metal). The experiment was performed in the 500 mL bottles having stoppers that contain 250 mL solution of metals having desired concentrations. These bottles are shaken in the electric shaker and stirred continuously at 200 rpm at room temperature (that may be 25 ± 0.5°C). When the reaction time is completed, filter the solution with the help of syringe filters of 0.2 micrometers and analyze it. To check the effect of adsorbent dose, take solutions of heavy metals having concentration 2ppm and add it in different concentrations of synthesized nanoparticles (0.1 grams, 0.2 grams 0.3 grams, 0.4 grams, 0.5 grams and 0.6 grams). Keep these in a shaker for about 3 hours. 3 mL of metal solution could be withdrawn at the interval of 5 minutes and analyzed. The effect of the solution pH upon heavy metals removal could be determined by varying the pH (initial) of the solution from pH 3-11 by using the 1M HCl and 0.1M NaOH. For the elucidation of the effects of initial metal concentrations, different concentrations of heavy metals solutions (ranges from the 1-10ppm) were used. All solutions that are prepared could be treated for about 3 hours at room temperature.

3. RESULTS AND DISCUSSION

3.1 CHARACTERIZATION OF NANOPARTICLES

3.1.1 SEM

Materials with distributed bimetallic nanoparticle structures got attention because of their unique properties. The properties of these materials depend upon their size and surface morphology. For the evaluation of surface morphology of Bi-Mg bimetallic nanoparticles SEM analysis was used. SEM images exhibited that the shape of synthesized Bi-Mg bimetallic nanoparticles is hexagonal and homogenous in size (Figure 7).

Enlarge Figure 7

Fig. 7 SEM images of Bi-Mg bimetallic nanoparticles

3.1.2EDX Analysis

EDX investigates elemental analysis. In the EDX profile of Bi-Mg bimetallic nanoparticles, strong signal peaks are observed at 1.3 and 2.6 keV. The peak at 1.3 keV may be because metallic magnesium and metallic bismuth gives the peak at 2.6Kev. The fraction of weight percentages of numerous elements in Bi-Mg bimetallic nanoparticles was 36.33% Mg, 31.15% Bi, 14.2% C and 28.32% O) (Figure 8). All the above observations stated that the sample has minimum organic components (plant based components) and a maximum amount of inorganic components (Bi, Mg).

Fig. 8 EDX of Bi-Mg bimetallic nanoparticles

3.1.3XRD

The crystalline structure of Bi-Mg bimetallic nanoparticles can be investigated by using XRD. The XRD pattern of Bi-Mg bimetallic nanoparticles showed four sharp and prominent diffraction peaks at 2θ = 28^o(120), 33.05^o (122), 34.5^o (200), 47.34^o (041). By comparing the results with the standard XRD spectrum, it is depicted that the synthesized bimetallic nanoparticles has high crystalline nature. As seen in Figure 9, Bi nanoparticles (28^o, 34.5^o) exhibit more distinct diffraction and have greater peak intensities than Mg NPs (33.05^o, 47.34^o). This shows that the Bi-Mg bimetallic nanoparticles contain a greater percentage of Bi nanoparticles.

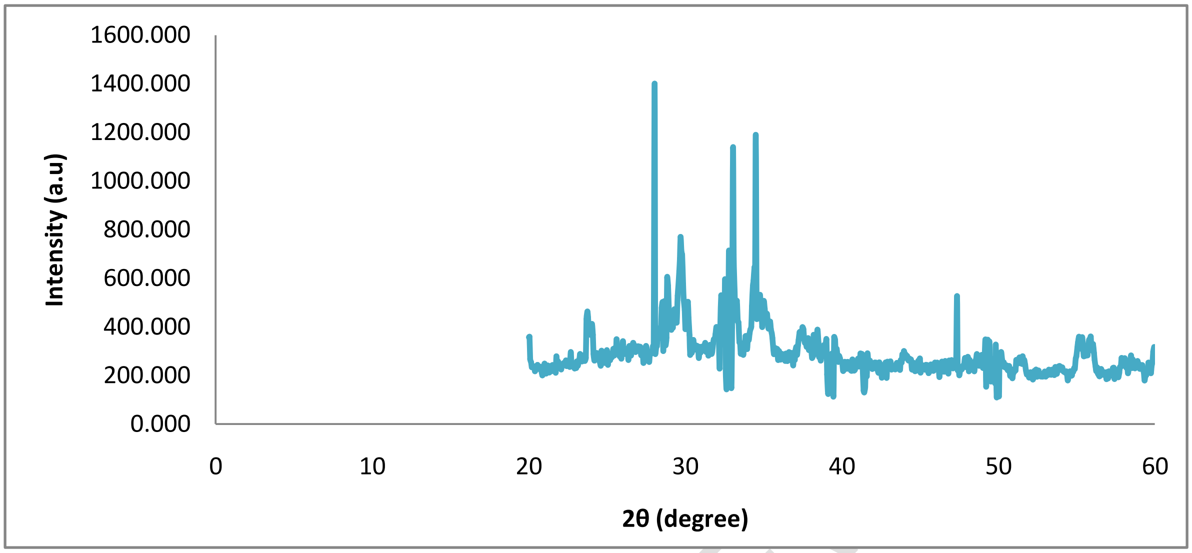


Fig. 9 XRD image of Bi-Mg bimetallic NP's

3.2 Adsorption Studies

Adsorption studies of heavy metals depend upon pH, metals concentration and adsorbent dose.

3.2.1 Effect of pH

pH exhibited a significant effect on the adsorption of heavy metals, which is done by Bi-Mg bimetallic nanoparticles. Figure 10 demonstrates that with the increase of pH, the removal of heavy metals is also increased. At pH 6, maximum removal of lead is occurred. In the case of cadmium and zinc, the maximum removal was found at pH 9 and 7.

3.2.2 Effect of adsorbent dose

In this, varied amounts of adsorbents (0.1 grams, 0.2 grams, 0.3 grams, 0.4 grams, 0.5 and 0.6 grams in the 200 milliliters of the solution) have been utilized, having initial concentration of 1ppm of wastewater containing heavy metals at pH 7 and contact time is 100 minutes. Figure 11 exhibited the effects of the adsorbent dose to remove lead, cadmium and zinc. The outcomes demonstrated that with the increase of bimetallic nanoparticles, heavy metal removal efficiency is also increased. This is because of the extra availability of active sites on the bimetallic nanoparticles. The optimum adsorbent dose of Bi-Mg bimetallic nanoparticles for the removal of cadmium was 0.5g and 0.4g for lead and zinc.

3.2.3 Effect of metal concentration

Figure 12 demonstrated that the decreasing trend of metals removal was seen as the initial concentration of lead, cadmium and zinc has been increased. Reductions of binding sites on the Bi-Mg bimetallic nanoparticles (adsorbent) occur because of increasing concentrations of heavy metals; consequently, it causes the reduction of adsorption efficiency in higher concentrations.

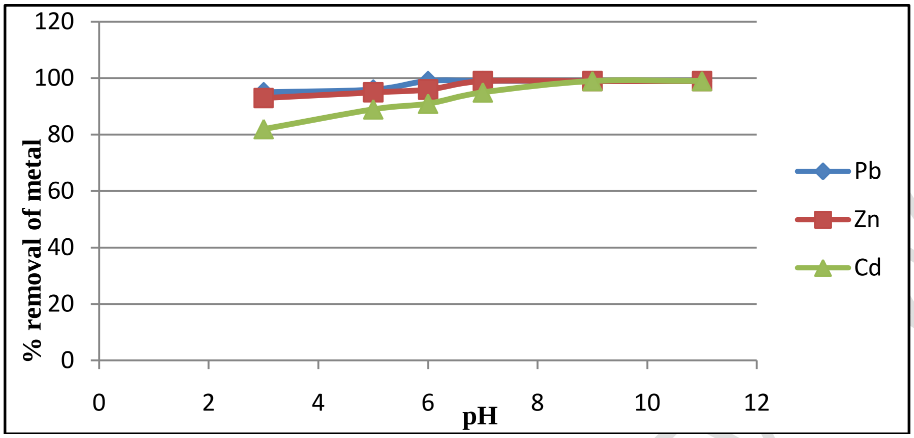
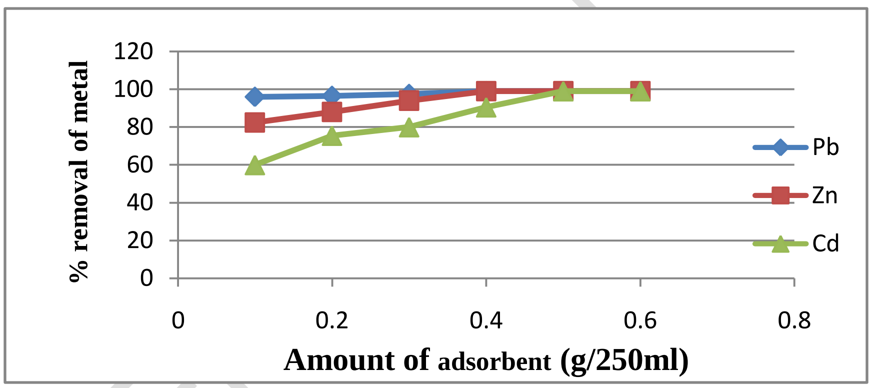


Fig. 10 Effect of pH on adsorption



. Fig. 11 Effect of adsorbent dose on the removal of heavy metals

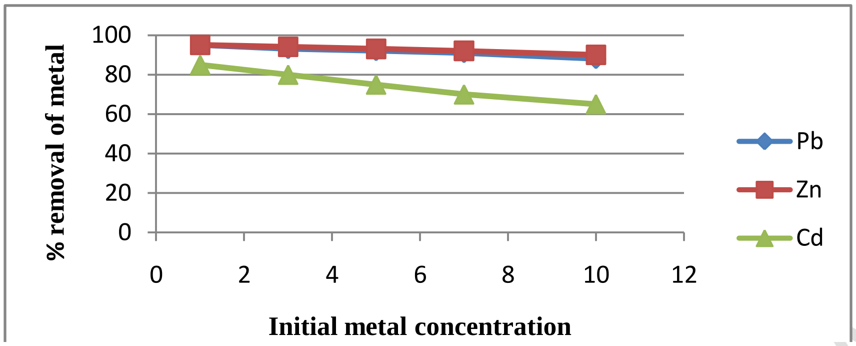


Fig. 12 Effect of initial metal concentrations

4. CONCLUSION

Water is a basic need of daily life, but due to industrialization, water becomes contaminated with many hazardous substances like heavy metals (Pb, Zn, Cd). So, the removal of these toxic chemicals become challenging. For this purpose, Bi-Mg BNPs behave as a good adsorbent to remove heavy metals. These BNPs are synthesized with the help of orange peel extract, which behave as a stabilizing and reducing agent. SEM images showed that the shape of synthesized bimetallic nanoparticles is hexagonal. The XRD pattern of Bi-Mg bimetallic nanoparticles showed four prominent diffraction peaks at $2\theta = 28^o$ (120), 33.05^o (122), 34.5^o (200), 47.34^o (041). In EDX, strong signal peaks at 1.3 and 2.6 keV are observed in Bi-Mg bimetallic nanoparticles. Fraction of weight percentages of numerous elements in Bi-Mg bimetallic nanoparticles was 36.33% Mg, 31.15% Bi, 14.2% C and 28.32% O). Adsorption of heavy metal is increased at the higher pH and decreasing drastically at lower pH. Adsorption efficiency was reduced with the increase of initial concentration of metals. The optimum adsorbent dose for removing cadmium was 0.5g and 0.4g for lead and zinc. Considering the excellent adsorption properties of Bi-Mg BNPs, these can be synthesized in large quantities because of their eco-friendly and least expensive support and can be useful in water treatment.

6. Declarations

Ethical Approval: Not applicable (NA)

Availability of data and materials: Not applicable (NA)

Consent to participate. NA

Consent for publication. NA

Availability of data and material/ Data availability. NA

Code availability (software application or custom code). NA

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KEY/LEGEND

YELLOW: Delete and write the abbreviated letters or acronyms in full

BRIGHT GREEN: Suggestion