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Selective Removal of Zinc, Cadmium, and Lead from Industrial Effluents using Bimetallic Nanoparticles Synthesized via Green Route

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ABSTRACT

The biocompatible qualities of nanoparticles, synthesized by plant medium, have garnered a considerable attention. Nanoparticles made of two different metals (thus the name "bimetallic") are crucial in the process of purifying wastewater. Adsorption is enhanced for bimetallic nanoparticles due to their larger surface area as compared to the monometallic nanoparticles. The current study examined the adsorption characteristics of Mg-Bi bimetallic nanoparticles and their efficacy in removing cadmium, lead, and zinc from wastewater. The synthesis of bimetallic nanoparticles from natural resources (plant extract) is more significant than conventional methods due to its low cost, dependability, non-toxicity, and environmental friendliness. Plant extract made from biomass wastes including roots, flowers, leaves, and fruit peels contains terpenoids, flavonoids, and alkaloids which are new secondary metabolites and work as stabilizing and reducing agents. SEM, UV- Visible, EDX, and XRD are some of the methods used to examine synthesized nanoparticles for shape, content, and size. Heavy metal removal is sensitive to changes in pH, adsorbent dose, and metal concentration at the outset. The results confirmed that the plant-mediated synthesized nanoparticles can be used as a systematic adsorbent for the elimination of heavy metals in wastewater.

Keywords: absorption, green synthesis, heavy metals, nanoparticles, reducing age

1. INTRODUCTION

Living organisms need water to survive. However, as a result of industrialization, water is contaminated with numerous hazardous compounds including heavy metals, such as Pb, Zn, Cu, and Hg. Heavy metals exhibit increased toxicity and density even at lower concentrations. Heavy metals are a class of metalloids and metals having an atomic density

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greater than 4.00 grams per cubic centimeter which is five times greater than the density of water [1] It is crucial to remove heavy metals from water due to their toxicity. Traditional techniques to treat waste water in order to remove heavy metals are not cost-effective and generate a considerable amount of chemicals [2]. Nanoparticles are utilized to extract these heavy metals from wastewater [3]. Nanoparticles are the smallest particles that have size ranging between 1-100nm. Nanoparticles can be defined in various ways depending upon types of materials and fields [4].

Bimetallic nanoparticles are more significant than the monometallic nanoparticles and consist of metals of two different types, for instance Cu-Ni and Ag-Ni. While, monometallic nanoparticles are comprised of only single metal, for instance Cu or Ni. Nanoparticles can be synthesized by following two approaches. The heavy substance breaks up into nanoparticles in a top-down manner. Milling, chemical vapor deposition, and physical vapor deposition are a few examples. The top-down technique is reversed in a bottom-up manner. In this case, the combination of nanoparticles could result in the production of bulky material. It also goes by the name "building up method". Figure 1 illustrates this technique through reduction and sedimentation. Since there is a greater chance of contamination with a top-down strategy, a bottom-up approach might be better [5].

Synthesis of bimetallic nanoparticles by natural resources is more significant. This is because in conventional methods toxic chemicals are used which are harmful for the environment, so the biological methods are used as these are environment-friendly, reliable, and nontoxic (Figure 2) [6].. Plant-mediated green synthesis of bimetallic nanoparticles is dependent upon the extract of plants [7].. It is also a cost-effective method to synthesize the bimetallic nanoparticles since plant extract is obtained from the biomass wastes, such as roots, flowers, leaves, and fruit peels. Crude extract of plants is comprised of novel secondary metabolites, such as terpenoids, flavonoids, and alkaloids having hydroxyl and carbonyl groups which act as stabilizing and reducing agents. The formation of bimetallic nanoparticles takes place by these compounds which are helpful in the reduction of metal ions into the metallic nanoparticles [8]. Plant-mediated synthesis in the formation of these particles depends upon the capacity of the plants to uptake, accumulate, utilize, and recycle many mineral species. The plant-mediated synthesis method is quite rapid and economically beneficial [9]. This method involves a single step therefore, it is preferable over conventional methods [10].

1.1. Novel Bimetallic NP's

1.1.1. Pt-based Bimetallic NP's. Since Platinum NPs have a larger surface area than other materials, they function as catalytic converters and are also being used presently. The effect of platinum-based electrodes could be increased by synthesizing Pt-based nanoparticle catalyst [11]. Pt-X is a Pt-based nanoparticle with a better catalytic efficiency (X could be Ag, Au, and Cu). In addition to lowering the need for noble metal, the incorporation of additional metal may help to boost its catalytic activity. As an illustration, Pt-Au catalyst exhibits superior catalytic activity as compared to single metal [12].

1.1.2. Ni-based Bimetallic NP's. Magnetic properties as well as the catalytic ability of Ni-based nanoparticles play a very useful role. It shows versatile properties when combined with another metal [13]. 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 the efficacy of chemical reactions[14].

1.1.3. Fe-based Bimetallic NP's. Bimetallic Fe-Cu catalysts system has become more significant nowadays [15]. High catalytic efficiency is demonstrated by Fe-Cu-based bimetallic catalysts when supported by MCM-41, as opposed to iron or copper alone [16]. To remediate chlorinated pollutants, various bimetallic nanoparticles are created including Pd-Fe, Pd-Zn, and Ni-Fe [17].

1.1.4. Pd-based Bimetallic NP's. Nanoparticles are beneficial since they are readily available and inexpensive. In alkaline media, the Pd-based bimetallic nanoparticles aid in the oxidation of alcohol and exhibit increased stability in acidic media [18]. The Suzuki coupled reaction may benefit from the increased catalytic efficiency of Pd-Au bimetallic nanoparticles [19]. Bimetallic nanoparticles of Pd and Ag may serve as a sensor to aid in the electrochemical detection of L-cysteine [20].

1.1.5. Au-based Bimetallic NP's. These nanoparticles exhibit a better catalytic activity and act as biosensors. Gold-based nanoparticles are helpful to enhance the catalytic efficiency and selectivity. 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 [21]

1.2. Utility of Bimetallic Nanoparticles vs. Monometallic Nanoparticles

Bimetallic nanoparticles exhibit greater scientific significance than monometallic ones. These properties are determined by the size and type of metal. As compared to monometallic nanoparticles, bimetallic nanoparticles have a larger surface area which increases their adsorption capacity, allowing them to function as effective catalysts[10, 22].

2. EXPERIMENT

In this experiment, bimetallic nanoparticles were synthesized via a green route using plant extracts. The nanoparticles were characterized using SEM, XRD, and FTIR, and then applied to industrial effluents for the selective removal of zinc, cadmium, and lead. Batch adsorption experiments were conducted, and the metal concentrations were analyzed using UV-Visible spectroscopy to determine removal efficiency.

2.1. Materials

All chemicals which were used must be analytical reagent grade that are Bi $(No_3)_3$, ($MgCl_2$), and Sodium thiosulphate. The analysis of heavy metals was conducted using AAS. To prepare the solutions, deionized water was used in the experiment.

2.2. Extract Preparation

Oranges were picked up from a neighborhood market situated in Lahore. To get rid of chemicals and dust from the surface of orange peels, oranges were washed with distilled water. After washing them, it was ensured that the oranges were completely dry. To eliminate moisture, oranges were peeled and stored in a shaded area for fifteen days. Using an analytical weight balance, thirty grams of dried peels were weighed. In a flask, 30g of weighted peels were submerged in 100ml of double-distilled water. Afterwards, this flask was placed on the heating mantle and was wrapped with aluminum foil. In order to prevent the evaporation of the extract's volatile components, the heating mantle's temperature was adjusted to 70°C. The color changed from being colorless to yellowish after two hours and the extract was ready. Whatman filter paper No. 1 was used to filter the mixture. The utilized extract was filtrated. The extract was now refrigerated to be used later.

2.3. Synthesis Method of Bimetallic Nanoparticles

To create fine-sized particles, orange peel extract was continuously stirred into solutions containing bismuth nitrate and magnesium chloride to create a nano solution. The following was the experimental setup: 50 milliliters of leaf extract was placed in a flask and 50 milliliters of $MgCl_2$ and Bi $(NO3)_3$ solutions were placed in burettes. Drop by drop, salt solutions were added to the extract while stirring constantly. Sodium thiosulphate was added to the solution as a catalyst. The solution was stirred continuously while the mixture was heated to 70^0C for six hours. Thiosulphate of sodium was added as a catalyst. The discernible color shifts from yellowish to brownish provided visual proof of the formation of nanoparticles. The mixture was placed in the oven for three hours at 80.7°C. Samples should be kept in sample vials once they have dried.

Figure 1. Steps for the Synthesis of Bi-Mg Bimetallic Nanoparticles

3. RESULTS AND DISCUSSION

This section evaluates the efficiency of green-synthesized bimetallic nanoparticles in removing zinc, cadmium, and lead from industrial effluents. Key findings on removal efficiency and the impact of experimental conditions are discussed in this section, along with insights into the adsorption mechanisms involved.

3.1. Scanning Electron Microscopy (SEM)

Bimetallic nanoparticle-distributed materials have drawn interest due to their special characteristics. The size and surface shape of these materials determine their properties. SEM examination was utilized to assess the surface morphology of the Bi-Mg bimetallic nanoparticles. The synthesized Bi-Mg bimetallic nanoparticles were homogeneous in size and spherical in shape, as shown by SEM images (Figure 2).

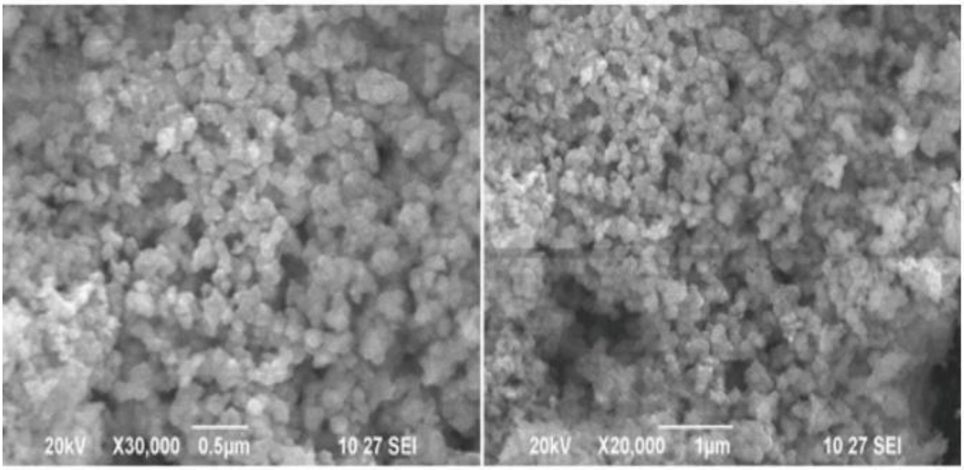

Figure 2. SEM Images of Bimetallic (Bi-Mg) NPs

3.2. EDX Analysis

EDX is involved in elemental analysis research. Bi-Mg bimetallic nanoparticles' EDX profile shows two prominent signal peaks at 1.3 and 2.6 keV. The peak at 1.3 keV might be explained by metallic magnesium, whereas the peak at 2.6 keV could be explained by metallic bismuth. The different components' weight % fractions in Bi-Mg bimetallic nanoparticles were as follows: 31.15% Bi, 14.2% C, 36.33% Mg, and 28.32% O (Figure 3). All the previously described observations indicate that the sample has a minimum number of organic components (components derived from plants) and a maximum quantity of inorganic components (Bi, Mg).

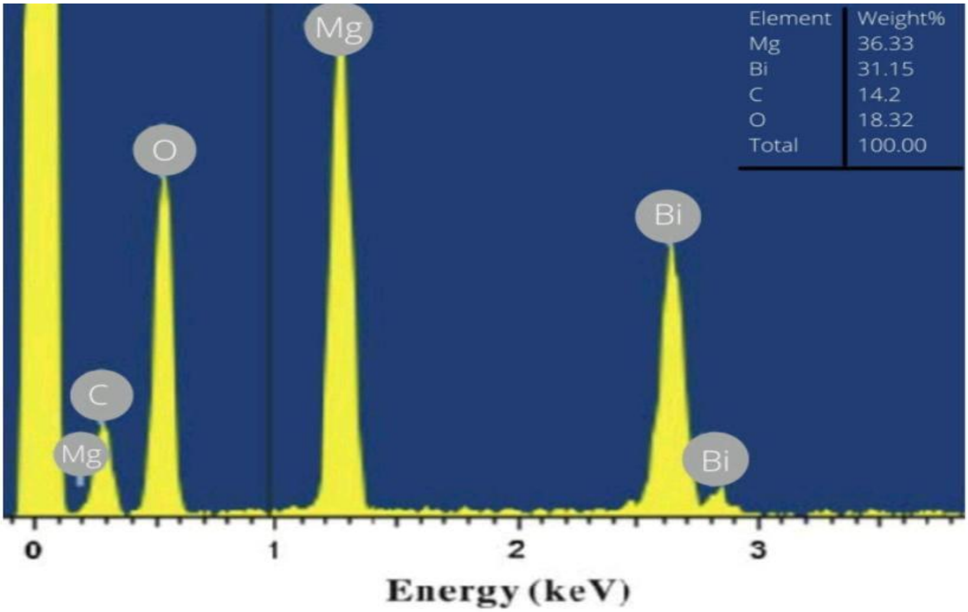

Figure 3. EDX of Bimetallic (Bi-Mg) NPs

3.3. Spectrophotometric Analysis

3.3.1. UV-visible Spectroscopy. Spectra of absorption are used in UV-visible spectroscopy. It is used to determine how well a sample absorbs light in the visible and ultraviolet spectrums. The lambda max value of a sample can be ascertained by examining the entire spectrum which provides details on the absorption of light at various wavelengths. The wavelength at which a sample exhibits its maximum absorption is known as lambda max. In this analysis, an absorption peak is obtained at 285 nm for green synthesized Bi-Mg bimetallic nanoparticles. The peaks of Bi and Mg NPs are found in literature to be between 270 and 300 nm.

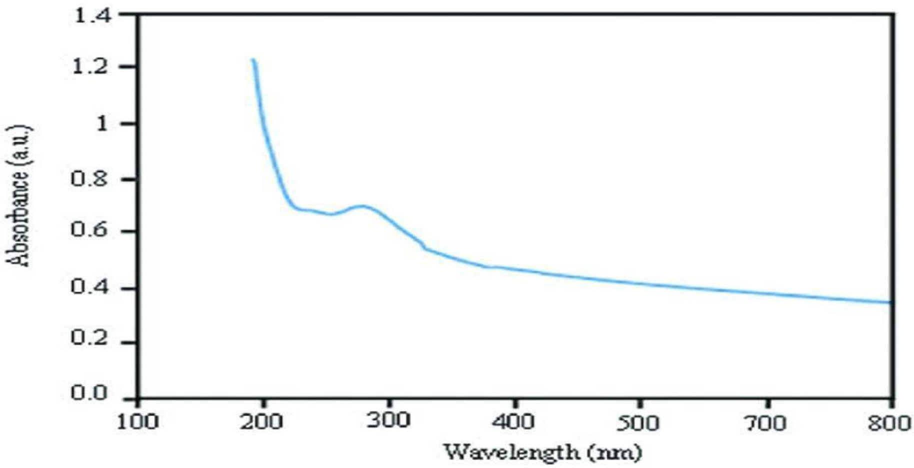

Figure 4. UV-Visible Adsorption Spectra of Bimetallic (Bi-Mg) NPs

3.3.2. X-Ray Diffraction Analysis. Bi-Mg bimetallic nanoparticles' crystalline structure was examined using XRD. Figure 5 displays the four major diffraction peaks found in the XRD pattern of Bi-Mg bimetallic nanoparticles which are located at 2θ = 280 (120), 33.050 (122), 34.5(200), and 47.340 (041). By comparing the results with the standard XRD spectrum, it is depicted that the synthesized bimetallic nanoparticles are highly crystalline in nature and have fcc morphology (face centered cubic structure).

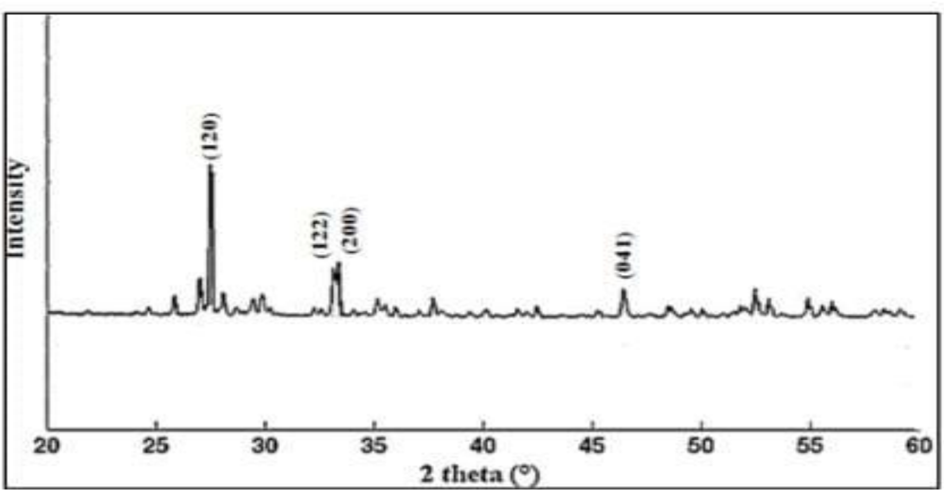

Figure 5. XRD Scan of Bimetallic (Bi-Mg) NPs

3.4. Adsorptive Removal of Zn, Cd, and Pb

The study focused on evaluating the ability of bimetallic nanoparticles to adsorb and remove zinc (Zn), cadmium (Cd), and lead (Pb) from industrial effluents. Various factors such as pH, contact time, and nanoparticle dosage were optimized to enhance removal efficiency. The results demonstrated by the nanoparticles in adsorbing these heavy metals are discussed in this portion, This is offering a promising approach for treating contaminated water.

3.5. Effect of pH

The adsorption of heavy metals, accomplished by nanoparticles, was significantly impacted by pH. Figure 6 illustrates how the elimination of heavy metals increases in tandem with pH. The greatest amount of lead is eliminated at pH 6. The highest elimination of zinc and cadmium was recorded at pH 7 and pH 9, respectively.

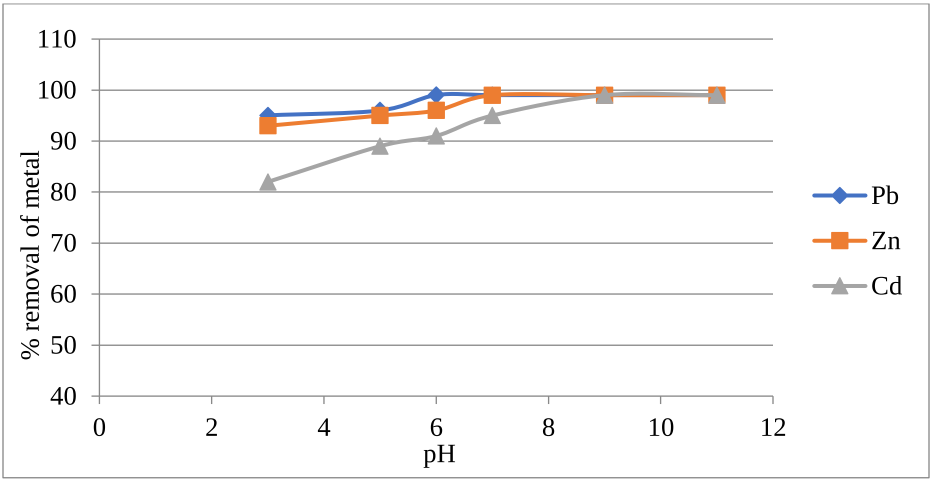

Figure 6. pH Effect on Adsorption

3.6. Effect of Adsorbent dose

Different concentrations (0.1g, 0.2g, 0.3g, 0.4, and 0.5g in 200 milliliters of solution) were used in this with a contact period of 100 minutes and a starting concentration of 1ppm of heavy metal-containing waste water at pH 7. Lead, cadmium, and zinc removal outcomes are shown in Figure 7 as a function of adsorbent dosage. Results showed that, as bimetallic nanoparticle concentration grew, so did the effectiveness of heavy metal removal. Th reason for this is the bimetallic nanoparticles' increased active site availability. Adsorbent dosages of 0.5g for cadmium and 0.4g for lead and zinc were found to be the most effective for their removal.

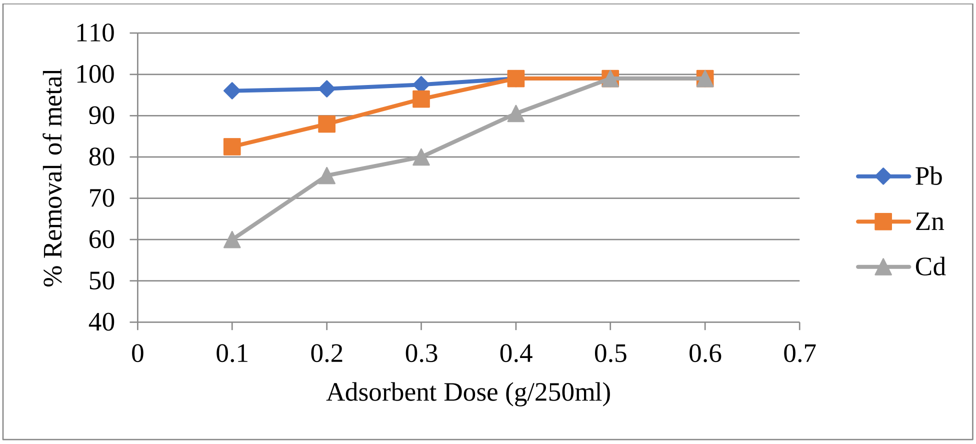

Figure 7. Effect of Adsorbent Dose on Removal of Metals

3.7. Effect of Metal Concentration

Figure 8 shows that as lead, cadmium, and zinc concentrations increased, a declining trend in metal concentrations was seen. Higher metal concentrations lead to reductions in binding sites on the adsorbent which, in turn, resulted in lower adsorption effectiveness at higher concentrations. The lead and zinc were entirely eliminated from the waste water in 100 minutes, according to the results.

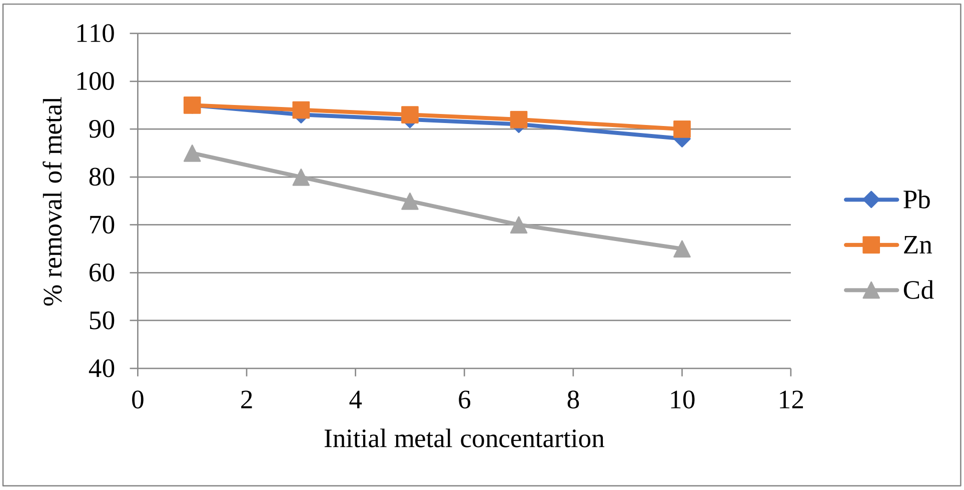

Figure 8. Effect of Metal Concentrations

4. CONCLUSION

Although, water is a necessity for our daily living, industrialization has led to the contamination of water with various dangerous compounds including heavy metals (Pb, Zn, and Cd). Thus, it has become quite difficult to get rid of these harmful substances. Bi-Mg NPs work well as an adsorbent to remove heavy metals for this reason. Orange peel extract is used in the synthesis of these BNPs, serving as a stabilizing and lowering agent. Spherical shape of the synthesized bimetallic nanoparticles was revealed by SEM images. At increasing pH values, heavy metal adsorption increases, whereas at lower pH values, it decreases significantly. Best amount of adsorbent to remove cadmium was 0.5g, while the best amount to remove lead and zinc was 0.4g. Bi-Mg BNPs have good adsorption qualities, making them suitable for water treatment. Due to their inexpensive and environmentally favorable support, they may be synthesized in huge amounts.

CONFLICT OF INTEREST

The authors of the manuscript have no financial or non-financial conflict of interest in the subject matter or materials discussed in this manuscript.

DATA AVALIABILITY STATEMENT

Data availability is not applicable as no new data was created.

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No funding has been received for this research.

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