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Lead (II) adsorption from aqueous systems using visible light activated cobalt doped zinc oxide nanoparticles

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In this study, co-precipitation method was used to produce cobalt doped zinc oxide (Co-ZnO) nanoparticles (NPs) by reacting zinc, cobalt and hydroxide (OH^-) in methanol at 60 °C and used as an adsorbent for the removal of lead (Pb) from aqueous systems. Co-ZnO NPs were characterized by X-ray diffraction (XRD) via X-ray Diffractometer (JDX-3532, JEOL, Japan), while Transmission electron microscopy (TEM) was carried out for the shape and size of the NPs. Results shows that Co-ZnO NPs was oval in shape within the size range between 40 to 60 nm. Moreover, the Pb(II) adsorption on Co-ZnO NPs surface was carried out with respect to time, optimum dose, different pH, light effects, filtration and sonication process. The result shows that Co-ZnO NPs can remove Pb(II) efficiently from aqueous systems in the presence of sunlight, optimum dose, neutral pH, and sonication process, while the same NPs could not show effective removal of Pb(II) with respect to darkness, tube light, low and high pH respectively. Using Co-ZnO NPs, Pb(II) can be reduced up to the permissible limit set by World health organization (WHO). Co-ZnO NPs work effectively in pH range of 5.8–7.2 so therefore, no need to adjust the pH of test solution for the activation of these NPs. The synthesized Co-ZnO NPs are eco-friendly and a capable adsorbent for the removal of Pb(II) from aqueous systems.

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1. Introduction

Water contamination actually poses a significant problem globally due to growing human population and rapidly increasing industrial development, household and agricultural operations [1].Therefore, pollution of water bodies with heavy metals (HMs) pollutants has drawn considerable attention due to severe poisoning and carcinogenetic at even low amounts [2]. Even so, HMs like lead ions are non-degradable contaminant and can persist longer in biological systems [3]. This further contributes to diseases that mostly cause serious injuries and deaths [4].

These HMs are generally released to the environment as industrial waste water such as exfoliating in leather, excavating of minerals, smelting, electronic, paper and wood, metal working, steel and battery production [5]. HMs pollution in the past several years had been a serious ecological concern and health issues to humans [6]. HMs are known chronic pollutants that won't be degrade quickly to harmless materials. The effective elimination of HMs from water ecosystems may be a good way to control waste water treatment [7]. Lead is among the most prevalent and hazardous HMs, found in waste water as well as in drinking water that originates from domestic pipes and natural corrosion implosion [8]. Which ultimately cause severe harm to liver, kidneys and nervous system of all living organisms [9]. In developing countries, the rapid risk of lead carcinogenicity has gained a huge research interest on its treatment. Several methods have been applied such as adsorption, oxidation, ion exchange and co-precipitation for the treatment of lead [10].

All these procedures have their particular merits and demerits. In recent times, NPs in environmental restoration have obtained much consideration to treat contaminants from aqueous systems [11]. NPs have distinctive features like small size, high reactivity, larger surface area, can be easily separated and have more adsorption sites that made it a good method to eliminate lead ions and other HMs from aqueous systems [12]. Usage of NPs is a new technique to treat contaminants especially HMs from aqueous systems [10]. NPs have been described to have a size less than 100 nm [13].

NPs can rapidly alter the harmful HMs to harmless through ion-exchange, ion-precipitation and adsorption method. NPs can be made from the materials such as polymeric media or ceramics [14]. NPs having toxic HMs on its surface goes up to the ecosystems and thus create problems therefore, using of NPs for lead ions or other HMs treatment may be carefully studied [15].

To remove Pb(II) from aqueous systems, several kinds of NPs have been used such as Titanium Dioxide (TiO_2), zinc oxide (ZnO), cupric oxide (CuO), iron oxide (Fe_2O_3) and other numerous NPs [16]. Nowadays the use of ZnO NPs gaining the attention of researchers across the world. ZnO NPs are harmless, efficient and effectively work in neutral pH, hence receiving greater attention recently [17].

In the removal of HMs using NPs, major drawback of NPs is the activation in the visible and UV spectrum. To overcome this challenge and to improve the capability of NPs to work efficiently in visible light, doping was done.

In this study, for improved and effective removal of Pb(II), the ZnO NPs were modified to cobalt doped ZnO NPs with the use of potassium hydroxide (KOH) and subjection to thermal decomposition. Co-ZnO NPs have more economic and technological importance such as steadiness, harmless, cost-effective, photosensitivity and synergistic effects that make Co-ZnO NPs a best and promising adsorbent for HMs removal from aqueous systems [18].

2. Materials and Methods

2.1. Chemicals and Reagents

All chemicals and reagents used were of good grade (Perkin Elmer) and were used as received. Cobalt nitrate hexahydrate ($Co(NO_3)_2.6H_2O$) (Scharlau), zinc nitrate hexahydrate ($(Zn(NO_3)_2.6H_2O)$) (Scharlau), potassium hydroxide (KOH) (Scharlau) resorcinol, formaldehyde, sulphuric acid, ethanol (AnalaR), methanol (AnalaR), iron sodium nitrate, nutrient agar (Oxoid), phosphate buffer saline (BPS), potassium permanganate ($KMnO_4$), ethidium bromide (Scharlau), hydrogen chloride (HCl) and hydrogen peroxide were used for the synthesis and determination of lead (purchased from Merck, Germany). Deionized (DI) water (Milli-Q grade) was used to prepare all kinds of samples and solutions. Nitrogen (N2) gas with purity 99.99% was bought from Sigma Gases (India).

Instruments used in this study are; Incubator (Panasonic, Japan), sonicator (Elmasonic, China), oven (Memmert, Germany), spectroscopy (Thermo Scientific Multiscan Go, USA), agitator (Velp scientific, Italy), pH meter, shaking incubator (Heidolph, Germany), micro centrifuge (Thermoscientific, USA), vortex mixer (Thermoscientific, USA), furnace (Nabertherm, Germany), autoclave (Hirayama, Japan), beakers (250 ml, 100 ml), chemical reagent bottles (100 ml), volumetric flasks (250 ml), burette (50 ml), test tubes (Borosil), funnel, cuvette, pipettes, aluminum foil, spirit lamp, tweezers, parafilm, plates, Eppendorf tubes and Falcon tubes (20 ml, 50 ml) from Thermo Fisher Scientific.

2.2. Preparation of Standard Solutions of Pb(II)

Stock Solution of lead (0.1 percent Pb) can be prepared by dissolving 0.4 g of lead nitrate in deionized water containing 2 ml of nitric acid and then increase enough water to make 250.0 ml solution. After proper dilution, the standard lead solution was utilized for standardization of (AAS) [19]. For standardization of AAS, stock solutions of different concentrations like 50 mg/L, 100 mg/L and 150 mg/L were calibrated.

2.3. Preparation of Co-ZnO NPs

To prepare Co-ZnO NPs, co-precipitation method was used [13]. These proposed NPs were synthesized by reacting Co, Zn and OH^- in methanol solution. In preparation of 10% cobalt doped zinc oxide NPs, zinc and cobalt salts were taken with the ratio of 9:1 respectively. 0.09 M of Zinc nitrate hexahydrate ($Zn\ (NO_3)_2.6H_2O$) and 0.01 M of Cobalt nitrate hexahydrate ($Co\ (NO_3)_2.6H_2O$) salts were mixed in 100 ml of methanol (CH_3OH) with constant stirring for 30 minutes at 60 °C. Similarly, 0.5 M of KOH was mixed in 100 ml of methanol (CH_3OH) and stirred for 30 minutes keeping the temperature at 60 °C. Then KOH solution was added dropwise to zinc nitrate and cobalt nitrate solution while it was continually stirred at 150 rpm for 2 hours at 60 °C in the absence of light. Later an hour the particles were settled. The solution of these NPs was then taken in 50 ml falcon tubes and centrifuged for 10 minutes on 7000 rpm. Supernatant was removed and washed the NPs two times with double distilled water and 70% ethanol by centrifugation for 15 minutes respectively to remove all the impurities. NPs were then dried in oven for 48 hours at 70 °C and finally were calcinated for 3 hours in furnace at 400 °C to get nano-crystalline powder [20].

2.4. Co-ZnO NPs characterization

X-Ray Diffractometer (JDX-3532, JEOL, Japan) was used to record X-Ray diffraction (XRD) of Co-ZnO NPs and Cu-K α radiation was used with a tube voltage of 2.5 to 30 mA and 20 to 40 KV with 0-160° of 2θ ranges. While for shape and size of these NPs, Transmission electron microscopy (TEM JEOL-2100, China) was used and operated at 100 to 200 keV. TEM used an electron beam of high energy, which passed through a very thin sample. On TEM grid, only a small drop of NPs solution was tipped and it was dried at normal temperature. Digital camera was used to record the image.

2.5. Experimental plan for removal of Pb(II) with Co-ZnO NPs

To find out the elimination of Pb(II) via Co-ZnO NPs from aqueous systems, different experiments were done with various aspects as shown in **Table 1**. For adsorption tests with NPs, same Pb(II) stock solution was taken for making Pb(II) media solutions of various concentrations for every test listed as follows. All the tests were done in triplicate.

2.6. Analysis

The Pb(II) concentration in water was examined by AAS-HH, 50 mL volume was taken at 193.7 nm (wavelength) using argon as carrier gas. All the tests for Pb(II) amount were performed in triplicates [21]. Data analysis was performed using OriginPro 9.0 (Origin-Lab) and Microsoft Excel.

Table 1. Experiment types and conditions.

S. No.	Experiments	Volume of Pb(II) solution (mL)	Co-ZnO Dose	Pb(II) amount (mg/L)	Ratio of Co-ZnO: Pb(II)
1.	Dose and time effect	100	0.5 mg/L	50	1:100
		100	0.5 mg/L	25	1:50
		100	05 mg/L	50	1:10
		100	05 mg/L	25	1:5
2.	Light effect	100	20 mg/L	20	1:1
3.	pH effect	100	15 mg/L	15	1:1
4.	Sonication effect	100	20 mg/L	20	1:1
		100	20 mg/L	15	2:1.5
5.	Filtration experiment	100	15 mg/L	15	1:1

3. Results and Discussion

3.1. Characterization of synthesized Co-ZnO NPs

Portrayed poly-crystalline structure of Co-ZnO NPs was showed by the strong and sharp points. The major deflection points were noted to zinc oxide (Hexagonal) at 2θ=28.76°, 32.94°, 44.38°, 47.86°, 56.54°, 59.08° and 71.04°. The points 454, 379, 373, 396, 378 and 374 of XRD spectra shows crystalline structure of Co-ZnO Figure 1a. Due to less dissolution of Co in ZnO medium, the fixing improved the crystallite size of NPs and then there was no chance of secondary phase impurities.

To analyze the shape and size of the particles TEM was carried out. Figure 1b display the TEM images of Co-ZnO NPs, which presented that shape of the particles are oval with 40 to 60 nm size r ranges [20].

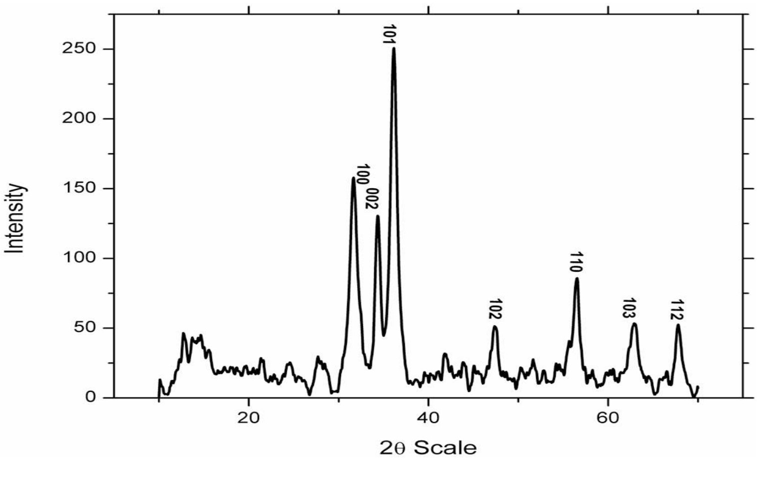

Fig. 1a. XRD pattern of Co-ZnO NPs [20].

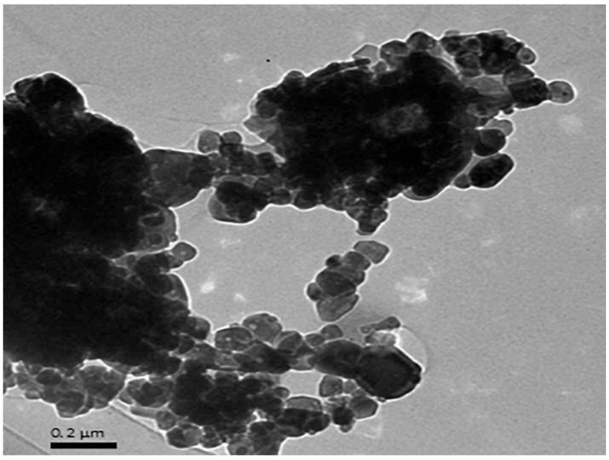

Fig. 1b. TEM image of Co-ZnO NPs showing oval shape [20]

3.2. Fourier-transform infrared spectroscopy (FTIR) analysis

FTIR spectroscopy was used to investigate the quality and composition of the Co-ZnO NPs. The FTIR spectra of Co-ZnO NPs are shown in Figure 2. The spectra show the zinc-oxygen (Zn-O) bond seem at about 440–500 cm^{-1}. This band may be due to oxygen deficiency or oxygen vacancy in zinc oxide. The deficiency of oxygen might be translating into an improved green emission in UV absorption spectra. The peaks at 1047and 1112 cm^{-1} due to C-O absorption of ZnO surface. The absorption band at 1539 cm^{-1} stands for carbonate due to carbon dioxide that possibly comes from atmosphere during the synthesis of these NPs. The wide-ranging peaks about 3410 cm^{-1} is due to the O-H stretching mode of hydroxyl group. In Co-ZnO NPs, the whole peak transmittance % got quenched. Although the results discovered the impurities that were occur near the surface of ZnO. However, no other peaks were observed in the spectra [22].

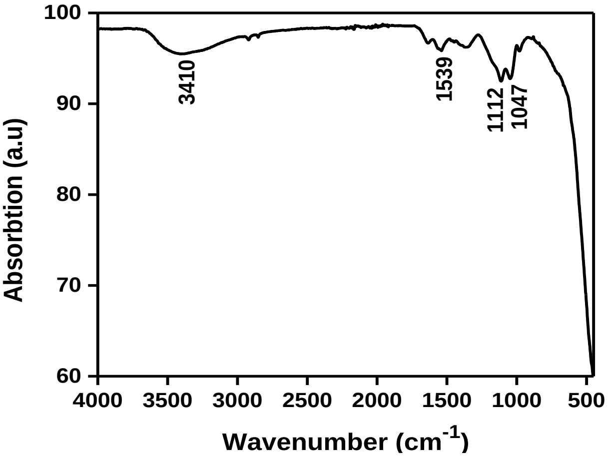

Fig. 2. FTIR spectra of Co-ZnO NPs.

3.3. UV-Vis absorption characteristics of Co-ZnO NPs

Co-ZnO NPs were examined for the optical properties using UV-Vis absorption (400–900 nm) as shown in Figure 3. Co-related peaks between 250 and 400 nm increase due to increasing cobalt amount in Co-ZnO NPs. The observed transitions of these NPs in the absorption spectra propose that Co^{2+} ions effectively replaced Zn^{2+} within the hexagonal ZnO wurtzite structure [23].

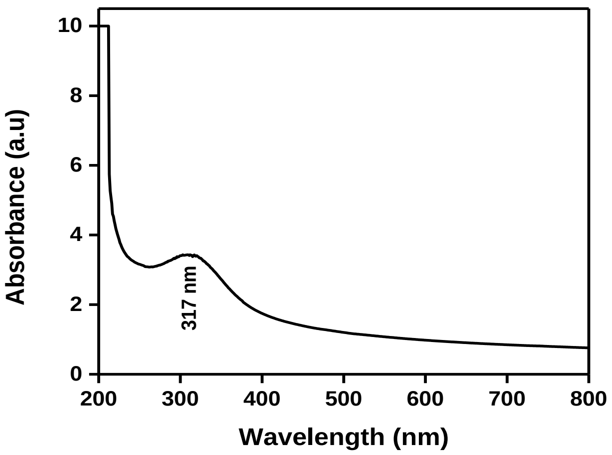

Fig. 3. UV-Vis absorption graph of Co-ZnO NPs.

3.4. Lead removal with respect to optimum dose and time

This experiment was carried out to find the optimum dose of Co-ZnO NPs essential to eliminate Pb(II) and to regulate the kinetics of Pb(II) removal. Co-ZnO NPs was added in 4 separate doses that associated with NP:Pb(II) ratios of 1:5, 1:10, 1:50 and 1:100 see Figure 4. The time interval was kept as 2 hours for reactors and the total time for this experiment was 6 hours. After adding 5 mg/L of NPs, Pb(II) amount of 25 mg/L was decreased to 14.39 mg/L and 50 mg/L decreased to 33.82 mg/L in the first 2 hours reaction. After 4 hours reaction, Pb(II) amounts were decreased below half of the first amount. Afterward 6 hours reaction, the concentrations were more decreased and very little concentration of Pb(II) remains at ratios of 1:5 and 1:10. Pb(II) removal was efficient at NPs:Pb(II) ratios of 1:5 and 1:10 with elimination efficiency of 90% and 78% respectively in overall 6 hours experiment.

The results revealed that the ratio of NPs:Pb(II) lesser than 1:5 was optimal for efficient removal of Pb(II). Another study on optimal dose of NPs by [24] examined NPs dosages of 100 mg/L, 50 mg/L and 10 mg/L for the removal of Pb(II) at 3 separate Pb(II) amounts (1000 µg/L, 500 µg/L and 100µg/L). Results show that the treatment of Pb(II) improved with rising NPs dose up to 100mg/L.

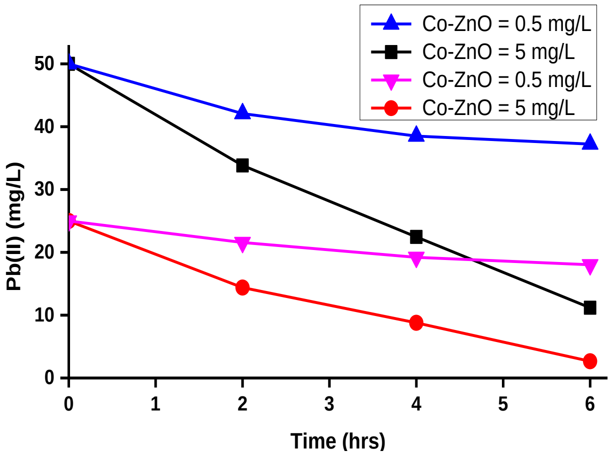

Fig. 4. Pb(II) removal regarding optimum dose and time.

3.5. Light effect on the removal of Pb(II)

This experiment was conducted to check the light effect on Pb(II) removal from water systems in the presence of tube light, sunlight and darkness. For this purpose, 20 mg/L of Pb(II) amount were taken in 3 separate volumetric flasks of 100 mL volume and 20 mg/L of Co-ZnO NPs were added to it and put these volumetric flasks in sunlight, tube light and in darkness for 2 hours. The 20 mg/L of Pb(II) amounts were decreased to 4.10 mg/L, 9.84 mg/L and 15.60 mg/L by adding 20 mg/L of Co-ZnO NPs in the presence of sunlight, tube light and dark conditions respectively. After 4 hours reaction, the Pb(II) quantity was reduced to 4.05 mg/L and 13.17 mg/L in tube light and dark condition, while Pb(II) totally removed in the presence of sunlight see Figure 5. Result shows that 100% adsorption of Pb(II) was attained in the presence of sunlight, 80% in tube light and 35% in dark conditions.

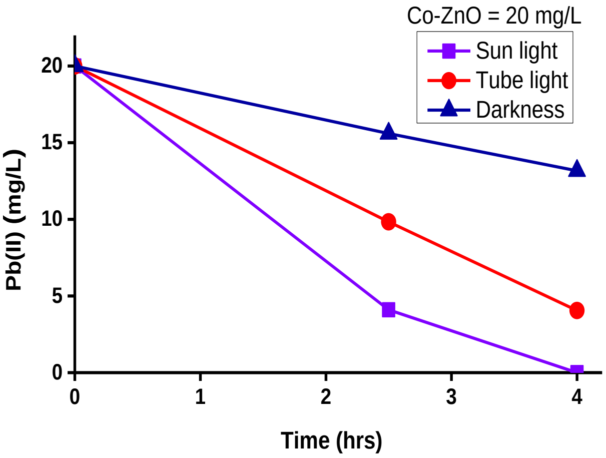

Fig. 5. Effect Light effect on Pb(II) removal using Co-ZnO NPs.

3.6. Effect of pH on Pb(II) removal

In this experiment, the pH effect on Pb(II) adsorption in water systems by Co-ZnO NPs was founded. Pb(II) was tested at different pH values i.e. neutral, acidic and basic as shown in Figure 6. To make acidic medium, a solution of 0.002 N hydrochloric acid (HCl) pH values were added to the Pb(II) solution, whereas to make a basic medium, higher pH values of 0.002 N sodium hydroxide (NaOH) were added. Later, for testing, 100 mL of reactors with 15 mg/L of Pb(II) amounts were taken in all five reactors in 250 mL volumetric flasks, and 15 mg/L of Co-ZnO NPs were added to all these reactors. The value of sample 1 was retained at normal pH 7, and the Co-ZnO NPs showed effectiveness in Pb(II) removal. After 3 hours reaction, the samples were examined and Pb(II) was decreased from 15 mg/L to 1.05 mg/L.

Results also show that Co-ZnO NPs also remove efficiently in pH 5.8, and Pb(II) has reduced from 15 mg/L to 2.13 mg/L after 3 hours reaction. Sample of pH 3.5 revealed that Co-ZnO NPs eliminate less amount of Pb(II) at low pH, with a total decrease to 9.45 mg/L after 3 hours reaction. Pb(II) reduction efficiency of Co-ZnO NPs was much lower in acidic pH, because ZnO changed to $ZnCl_2$ in the occurrence of HCl. Pb(II) solution of 9.7 pH value was decreased to 6.10 mg/L after 3 hours completion. In this pH range, Co-ZnO NPs presented acceptable results but not too much efficient.

At 12 pH value, Pb(II) removal was very low once again. Hence, 15 mg/L of Pb(II) amount was reduced to 9.75 mg/L after 3 hours reaction. The results of pH testing revealed that Co-ZnO NPs reduced the Pb(II) amount at neutral pH, thus the addition of any base or acid is not essential for the removal purpose. [16] have examined the effect of pH on Pb(II) elimination and reported 99.93% elimination at pH 5.8 and 99.25% at pH 7.2. At pH 12, the removal of Pb(II) suddenly falls, because of the alteration of ZnO to $Na_2Zn(OH)_4$ with the addition of dilute sodium hydroxide (NaOH), hence Pb(II) removal was less at higher pH values. [24] also reported an important effect of pH on Pb(II) removal with NPs.

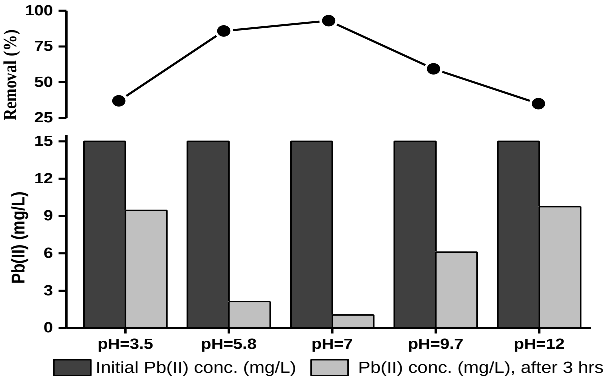

Fig. 6. pH effect on Pb(II) removal using Co-ZnO NPs.

3.7. Sonication effect on Pb(II) removal

This experiment was carried out in batch reactors with sonication process. For this purpose, 2 different volumetric flasks of 250 mL were used. Two different concentrations (20 mg/L and 15 mg/L) of Pb(II) were taken in flasks and 20 mg/L of NPs were added to both of the reactors. After 1-hour reaction, the solutions were tested with AAS-HH. The results show that the sonication process reduced the Pb(II) concentration from 20 mg/L to 3.87 mg/L and 15 mg/L of Pb(II) was reduced to 0.65 mg/L as shown in Figure **7a**. Results revealed that, sonication process greatly affect the Pb(II) removal efficiency. The overall experiment was completed in 1.5 hour.

3.8. Removal of Pb(II) in continuous flow with Co-ZnO NPs

To check the efficiency of Co-ZnO NPs for the removal of Pb(II) from water systems, filtration method was used. Filter paper Whatman 42 was used for this experiment and the 2 same solutions of 15 mg/L of Pb(II) were taken in 2 separate volumetric flasks. In first run, with one-time filtration from Co-ZnO NPs adsorbed filter paper, the Pb(II) amount was reduced from 15 mg/L to 11.38 mg/L, whereas in second run, with six-times filtration through Co-ZnO NPs absorbed filter paper, the amount of Pb(II) effectively reduced to 3.75 mg/L from 15 mg/L with a total reduction of 75% as shown in Figure 7b. The overall experiment was done in 1-hour, and results revealed that Co-ZnO NPs were also active in continuous flow setup and can be enhanced with more experiments/ filtrations.

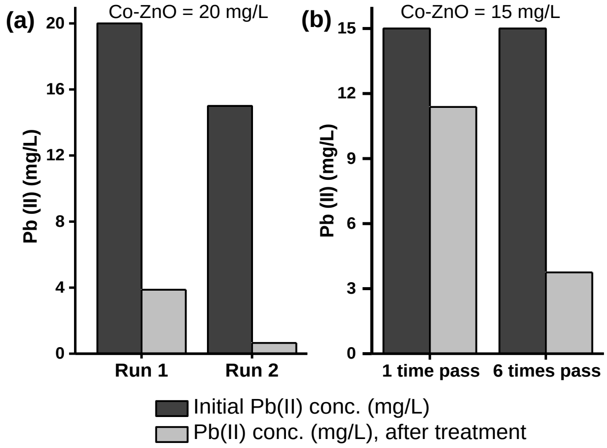

Fig. 7a. Sonication effect on (Pb) removal using Co-ZnO NPs; 7b. Pb(II) removal in constant flow using Co-ZnO NPs.

3.9. Adsorption Mechanism of Pb(II) onto Co-ZnO NPs

The mechanism of adsorption of Pb(II) on the surface of Co-ZnO NPs can be described by the electrostatic attraction between the positive charge of Pb(II) and the negative charge sites on the surface of Co-ZnO NPs. The Pb(II) can be attracted easily by the negative sites onto the surface of Co-ZnO NPs. The electrons that are present on the surface of NPs can increase the generation of hydroxyl ions which ultimately enhances the rate of adsorption of different HMs from aqueous systems because of more interactions.

3.10. Activity Regeneration of used Co-ZnO NPs

In testing gas-phase photocatalytic oxidation of Sulphur dioxide (SO_2), the photocatalytic action of used (deactivated) Co-ZnO-NP can almost be restored as before by rinsing with deionized water and then drying at 75 °C for almost 20 to 24 h after centrifugation process. Furthermore, it also proved that the inactivation of these NPs must be mainly assigned to the adsorption of the oxidation products like Water (H_2O), Carbon dioxide (CO_2) and Sulphur trioxide (SO_3).

3.11. Comparison of Adsorption capacities of Pb(II) using adsorbents

Till date researchers have been used various kinds of adsorbents for the removal of Pb(II) from water and wastewater such as Carbon aerogel, Modified palygorskite clay, Zeolite/CuO nanocomposites, Nanomaterials of carbon nanotubes/silica, Carbon derived from waste rubber, Zeolite/Fe_3O_4 nanocomposites and ZnO/talc see Table 2. All these adsorbents have their own advantages and disadvantages for the treatment of Pb(II) from aqueous solutions. Most of the reported adsorbents have showed good removal efficiency for Pb(II). However, the adsorbent used in the current study has showed the promising removal of Pb(II) from aqueous systems in short time with low-cost with maximum removal as compared to the reported adsorbents see Table. 2.

Table 2. Adsorption capacity of lead using various adsorbents.

Types of adsorbents	**Removal efficiency (mg. g^{-1})**	**References**
Modified palygorskite clay	62.10	[25]
Nanotubes/silica	13	[26]
ZnO/talc	48.3	[27]
Zeolite/CuO NCs	45	[28]
Zeolite/Fe3O4 NCs	50	[28]
Carbon derived from waste rubber	26	[29]
Carbon aerogel	0.75	[30]

4. Conclusions

The removal efficiency of Co-ZnO NPs were checked for the removal of Pb(II) through adsorption method from aqueous systems. Different experiments were carried out for optimum dose, kinetics, sonication, pH and light effect. Co-ZnO NPs were found to efficiently remove the Pb(II) from aqueous systems at the ratio of Co-ZnO:Pb(II) less than 1:5. However, the removal was effective in the presence of sunlight (100%), neutral pH (100%) and continues flow (75%). The results showed that using of Co-ZnO NPs can reduce the Pb(II) up to the permissible limit set by WHO. Many other adsorbents such as Carbon aerogel, Modified palygorskite clay, Zeolite/CuO nanocomposites, Nanomaterials of carbon nanotubes/silica, Carbon derived from waste rubber, Zeolite/Fe_3O_4 nanocomposites and ZnO/talc were reported for the removal of Pb(II) were also compared with the results of Co-ZnO NPs. Co-ZnO NPs can remove the Pb(II) in short time with low-cost as compared to other reported adsorbents.

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