Preparation of green synthesized copper oxide nanoparticles for efficient removal of lead from wastewaters

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ABSTRACT
Green synthesis is a clean and eco-friendly process in which metal nanoparticles can be produced by the reaction between a metal salt solution and plant organ extract. In the present study, three copper oxide nanoparticles were green synthesized from the leaf extracts of astragalus (Astragalus membranaceus), rosemary (Salvia rosmarinus), and mallow (Malva sylvestris) as predominant plant cover in the study area was characterized. The effectiveness of three green synthesized nanoparticles in the adsorption of lead ions from polluted water was studied. According to the results, the removal efficiencies of the copper oxide nanoparticles synthesized from astragalus (A-CuO-NPs), rosemary (R-CuO-NPs), and mallow leaf extract (M-CuO-NPs) especially at the highest initial concentration of lead (1.5 mM), were 88.4%, 84.9%, and 69.6%, respectively. Probably due to the smooth morphology and more uniform configuration of the M-CuO-NPs, the changes between equilibrium adsorption ($q_e$) and equilibrium concentration ($C_e$) were more regular than those of the A-CuO-NPs and R-CuO-NPs. Therefore, the best fit of the data to the Langmuir and Freundlich isotherms belonged to the adsorption of lead onto the M-CuO-NPs. According to the results reported herein, the copper oxide nanoparticles synthesized from different plant covers are efficient adsorption agents for lead from wastewaters solution.

Novelty statement
1. Comparison of the efficiency of copper oxide nanoparticles prepared by green synthesis method using the leaf extracts of astragalus (Astragalus membranaceus), rosemary (Salvia rosmarinus) and mallow (Malva sylvestris) plants in removing lead ions from wastewater.
2. Astragalus, as an abundant plant cover in the study area, has a capable leaf extract for green synthesis of copper nanoparticles, which its efficiency for the removal of toxic metal ions from aqueous solutions has not been already studied in previous researches.

KEYWORDS
Adsorption; copper oxide; green synthesis; lead; nanoparticles; removal efficiency

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Introduction

Water pollution by heavy metals is considered one of the most serious consequences of industrialization in the world. Accumulation of these metals in living organisms can cause diseases or even death (Zare-Dorabei et al. 2016). According to the World Health Organization (WHO), Zn$^{2+}$, Cu$^{2+}$, Ni$^{2+}$, Cd$^{2+}$, Pb$^{2+}$, and Cr$^{6+}$ are toxic ions that must be removed from the environment (Gupta et al. 2021). The bioavailability of lead (Pb) in aquatic ecosystems is very high and therefore can easily enter the food chain (Yari et al. 2016). Thus due to the high toxicity of Pb, its concentration must be kept at very low levels (Nekouei et al. 2016). Pb cations are commonly present in wastewaters issuing from agricultural activities (insecticides), vehicles factories producing brake pads, tires and lubricants, ceramic producers, paints, batteries and etcetera (Deniz and Ersanli 2016). Low concentrations of Pb have negative effects on the kidney, liver, brain, and reproductive system (Zafar et al. 2016). Industrial effluents affect all physical, chemical, and biological properties of the environment over time (Shayesteh et al. 2021). Several approaches have been carried out for wastewater treatment such as reduction, ion exchange, precipitation, membrane separation (Shayesteh et al. 2016a,b). The microfluidic technique is a method in which flowculants including cationic and anionic polymers can separate contaminated droplets such as crude oil from water (Dudek et al. 2020). Another method is sorption, which is the most common due to its low cost, availability of materials, having no environmental effects and etcetera (Lin et al. 2020).

Development in nanotechnology has been provided nanoparticles including nanotubes, nanowires, and metal nanoparticles (Mondal 2020). Remarkable properties such as high specific area and strong metal sorption capacity are the main reasons for the application of metal oxide nanoparticles to remove heavy metal ions from polluted waters (Farghali et al. 2013). Human beings have used copper and its compounds extensively as water purifiers. The use of copper nanoparticles has advantages such as low cost and easy production and small size (Ghaedi et al. 2016). Due to the high need for the use of copper oxide nanoparticles in various fields of science and technology, there are several procedures to synthesize these compounds including a thermal or chemical reduction (Chemical reduction of an element by heating in a very high-temperature furnace and then slowly lowering the temperature), wire explosion (Production of plasma by sending a very strong electrical pulse through a thin wire and production of metal vapor due to this heat, which eventually cools the metal vapor due to cooling of the surrounding environment and turns into metal nanoparticles), and laser ablation in which nanoparticles are produced by a laser beam hitting solid dots in a liquid and during the condensation of the plasma plume followed by nucleation and agglomeration of the solids (Din and Rehan 2017; Sportelli et al. 2018; Ghosh et al. 2019; Kanishka et al. 2020). The size and purity of the produced copper oxide nanoparticles vary depending on the technique used. Some of the mentioned techniques, for example, thermal processes require reducing agents such as hydrazine, which has a devastating effect on the environment (Gawande et al. 2016). The hydrothermal method is another approach for producing metal nanoparticles. For example, Riaz et al. (2020) used cetyl trimethyl ammonium bromide (CTAB), NiCl$\cdot$6H$_2$O, HCl, NaOH and urea that reacted in a Teflon lined stainless steel autoclave for the preparation of NiO nanoparticles.

The green synthesis method is an eco-friendly and low-cost approach for the synthesis of metal oxide nanoparticles using organisms such as bacteria, algae, fungi, and phytoc hemicals present in plant extracts (Sharma et al. 2021). Among the organisms, plants are the best selection because they are more suitable for large-scale and fast rate production of metal nanoparticles. In this method, active functional groups in leaf extract of a selected plant act as reducing agents of metal ions (Irvani 2011). Many researchers have studied the biosynthesis of metal oxide nanoparticles: Kamath et al. (2020) used the extracts of black tea, oak, green tea, pomegranate, and eucalyptus leaves to produce iron nanoparticles to remove arsenic from water. Copper oxide nanoparticles were synthesized by Siddiqui et al. (2021) using pomegranate (Punica granatum) peel extract to control the antibacterial activity of Escherichia coli (E. coli). Velsankar et al. (2020) prepared CuO nanoparticles using Allium sativum extract and cupric nitrate (Cu(NO$_3$)$_2$) to investigate their antimicrobial and antioxidant activities.

It is hypothesized that copper oxide nanoparticles synthesized from different plant extracts have different adsorption capacities. Astragalus (Astragalus membranaceus), rosemary (Salvia rosmarinus), and mallow (Malva sylvestris) are three abundant plant covers in the study area, which contain important phytoc hemicals such as saponin, tannins, flavonoids, rosmarinic acid, and carnosol (Darie-Ni et al. 2018; Zheng et al. 2020; Mrváčková et al. 2020). These compounds have a large number of active functional groups that act as metal ions reducing agents and cause the production of metal oxide nanoparticles. Also, the concentration of Pb is much higher than other toxic elements in the effluents of our study area. Therefore the main objectives of the present study were (i) green synthesis of copper oxide nanoparticles from the leaf extracts of the three plants mentioned and (ii) to characterize the synthesized nanoparticles and investigate their effectiveness for the removal of Pb ions from polluted water.

Materials and methods

Green synthesis of CuO nanoparticles

The green synthesis process was performed according to the method proposed by Sankar et al. (2014). Three plants (Figure 1): mallow and astragalus as self-growing and predominant plant covers and rosemary as a vastly cultivated plant in Iran, Fars, Shiraz, Bajigah, were collected.
Plants leaves were separated and washed thoroughly with deionized water then dried in an oven at 50°C until complete drying. The dried plant leaves were powdered and 10 g of each sample were added to 100 mL deionized water and heated at 60°C for an hour to obtain the plant leaf extracts. The extracts were filtered using Whatman No. 42 then stored in the refrigerator for the next steps. 10 mL of each filtered extract was mixed with 90 mL of cupric sulfate (CuSO₄·5H₂O) solution (20 mM) and kept for 24 hours to complete change in the color of the solution in comparison with the initial solution as an indicator for forming the suspensions of copper oxide nanoparticles. Copper oxide nanoparticles were prepared as dry matter following the evaporation of suspensions' liquid at 50°C. The dry weight obtained (g per 100 mL) from each leaf extract was reported as dry matter yield.

**Characterization of the synthesized copper oxide nanoparticles**

Functional groups of the synthesized copper oxide nanoparticles were characterized using Fourier-transform infrared spectroscopy (FTIR) (Bruker Tensor II, Germany). The morphology of the produced copper oxide nanoparticles was recognized by scanning electron microscope (SEM), TESCAN-Vega 3. The chemical composition of the synthesized nanoparticles was determined by energy-dispersive X-ray spectroscopy (EDX). X-ray diffraction analysis was performed using XRD, Philips model: PW1130, Cu Kα radiation, 2θ = 20–70°.

**Sorption experiments**

Equilibrium experiments were performed as follows: the initial concentrations of 0.15, 0.3, 0.6, 1, and 1.5 mM of Pb as an aqueous solution of Pb nitrate were prepared. 30 mL from each concentration was added to 0.2 g of the synthesized copper oxide nanoparticles each in duplicates in separate polyethylene containers and the experiments were carried out at a pH of 7. The solutions were agitated for 24 h at 25°C at 200 rpm then filtered by Whatman No. 42 (Contreras et al. 2017). To evaluate the effect of pH, the amount of adsorption was measured at pHs of 3, 5, 7, 9, and 11 at a concentration of 1 mM of Pb nitrate. The concentrations of Pb in the filtrates were measured using an atomic absorption spectrophotometer. The amounts of Pb adsorbed by copper oxide nanoparticles and removal efficiency (RE) of metal (%) were determined by Equations (1) and (2) (Azarang et al. 2019):

\[ q_e = \frac{[(C_0 - C_e)V]}{W} \]  

(1)

\[ \text{RE} = \left( \frac{(C_0 - C_e)}{C_0} \right) \times 100 \]  

(2)

The distribution coefficient, \( K_d \) (L g⁻¹) was calculated using Equation (3):

\[ K_d = \frac{\text{mass of adsorbate sorbed}}{\text{mass of adsorbate in solution}} \]  

(3)

Sorption of Pb cations onto nanoparticles was modeled using linear sorption isotherms of Langmuir, type II (4) and Freundlich (5) according to Al-Ghouti and Da’ana (2020):

\[ 1/q_e = 1/C_e \times k_1 b + 1/b \]  

(4)
ln \( q_e = 1/(n(ln \ C_e) + ln \ k_F) \) (5)

Gibb’s free energy \( (\Delta G \text{ kJmol}^{-1}) \) was evaluated using Equation (6) and (7) (Zafar et al. 2018).

\[
q_e = q_e/C_e \tag{6}
\]

The van’t Hoff equation:

\[
\Delta G = -RT\ln k_e \tag{7}
\]

where \( q_e \) is the metal adsorbed onto copper oxide nanoparticles at equilibrium \((\text{mg g}^{-1})\), \( C_0 \) and \( C_e \) are initial and equilibrium concentrations of Pb in solution \((\text{mg L}^{-1})\), respectively. \( V \) is the volume of solution \((\text{mL})\), and \( W \) is the mass of nanoparticles \((\text{g})\). \( k_b \) is the Langmuir constant \((\text{L mg}^{-1})\), \( b \) is monolayer sorption capacity with metal ions \((\text{mg g}^{-1})\), \( n \) is sorption intensity, \( k_F \) \((\text{mg g}^{-1} \text{L mg}^{-1}n)\) is the sorption capacity of the adsorbent, \( k_e \) is the thermodynamic equilibrium constant, \( R \) is the gas constant \((8.314 \text{Cmol}^{-1} \text{K}^{-1})\), \( k_F \) and \( C_e \) in Equation (7) are in ppm.

**Results and discussion**

**Synthesis mechanism**

In the green synthesis of copper oxide nanoparticles, the extract of plant organs especially leaves are used as sources of the active functional groups such as carboxylic and phenolic acids. These functional groups act as reducing agents. Following the transfer of a proton from a functional group to \( \text{Cu}^{2+} \), \( \text{Cu}^+ \) is formed, and subsequently, the transfer of the second proton from other functional groups to \( \text{Cu}^+ \), the nanoparticle of \( \text{CuO} \) is produced (Nasrollahzadeh et al. 2016).

**Characterization of the synthesized copper oxide nanoparticles**

FTIR analysis before and after Pb adsorption is shown in Figure 2. Before adsorption, strong absorbance (100 %Transmission) in the wavenumbers of 435.4, 436.4, and 601.44 cm\(^{-1}\) in the synthesized copper oxide nanoparticles from the leaf extracts of astragalus (A-CuO-NPs), rosemary (R-CuO-NPs), and mallow (M-CuO-NPs), respectively, confirmed the vibrations of Cu-O bonds (Thekkai Padil and Černík 2013). Strong absorbances between the wavenumbers of 1,000–1,300 cm\(^{-1}\) indicated the presence of C-O groups (alcohols, ethers, esters, carboxylic acids, anhydrides) and broad peaks in the range of 2,400–3,400 cm\(^{-1}\) were the indicatives of carboxylic acids (O-H) probably on the surfaces of all three synthesized nanoparticles (Pavia et al. 2013). After-adsorption FTIR analysis showed that the peaks observed after Pb adsorption were similar to the before-adsorption peaks. The difference was that the after-adsorption peaks were observed in absorbances less than those of the before-adsorption. A decrease in absorbances indicated a decrease in the amount of the functional groups. Because Pb ions reacted with the oxygen of CuO during the adsorption process as well as with the other observed functional groups such as C-O and (O-H).

Figure 3 shows the FTIR analysis of three plant leaf extracts before using for the synthesis of nanoparticles. This figure shows a very high variety of observed peaks from the wavenumbers of 500–4,000 cm\(^{-1}\). The observed functional groups included alkanes (C-H: 2,850–3,000 cm\(^{-1}\)), alkynes (C=C: 2,100–2,250 cm\(^{-1}\)), ketones (C=O: 1,705–1,725 cm\(^{-1}\)), primary and secondary amines, and amides (N-H: 3,500–3,100 and 1,640–1,550 cm\(^{-1}\)), amines (C-N: 1,000–1,350 cm\(^{-1}\)), alkenes, ketenes, isocyanates, iso-thiocyanates \((X=C=Y: 2,270–1,940 \text{ cm}^{-1})\), fluoride, chloride, bromide, and iodide \((1,400–1,000, 785–540 \text{ and } < 667 \text{ cm}^{-1})\), (C-O) and (O-H) groups. The highest absorbances were C-N, C-O and C-H observed for astragalus and rosemary. Mallow leaf extract contained mainly C-N, C-O, and C-X (bromide and iodide). Due to the reaction of the functional groups as reducing agents with copper ions, this diversity was not observed in FTIR analysis after the synthesis of CuO nanoparticles from these plant leaf extracts.

SEM micrographs of three nanoparticles before Pb adsorption were shown in Figure 4. These photos display the agglomerative shapes of the nanoparticles, which probably their surfaces and intermediates are filled with other organic compounds that varies depending on plant origin as explained in FTIR analysis. A-CuO-NPs, R-CuO-NPs, and M-CuO-NPs represented almost cubic, prismatic, and lineolate shapes, respectively. The A-CuO-NPs and R-CuO-NPs had course configurations whereas the appearance of M-CuO-NPs was relatively smooth.

Figure 5 shows the SEM micrograph of nanoparticles after Pb adsorption. Similar to what is shown in the before-adsorption image, after adsorption, the morphology was smoother in the M-CuO-NPs than the other two nanoparticles. The highly coarse and dense structure in this image indicates the Pb-loaded nanoparticles. In addition, the surfaces of nanoparticles are almost white, which can indicate the presence of oxides as reported by Ahmad and Mirza (2018).

The chemical composition and EDX spectra of the synthesized nanoparticles are shown in Figure 6. The before-adsorption spectra confirm the presence of copper and oxygen and the after-adsorption spectra show that Pb adsorption was successfully achieved by the synthesized nanoparticles. This analysis showed that the composition of the produced nanoparticles contained a higher weight percentage of oxygen than copper. The chemical composition after Pb adsorption showed that the weight percentages of Pb in the A-CuO-NPs, R-CuO-NPs, and M-CuO-NPs were 30.21, 31.76, and 26.15, respectively, which confirmed the lower adsorption of Pb by the M-CuO-NPs.

The XRD patterns of the synthesized copper oxide nanoparticles are shown in Figure 7. The most strong peaks were observed at \( 2\Theta = 31.37^{\circ} \) for the A-CuO-NPs, \( 2\Theta = 28.29^{\circ} \) and 25.78\(^{\circ} \) for the R-CuO-NPs and \( 2\Theta = 28.61^{\circ} \) for the M-CuO-NPs, which indicated the presence of CuO. In other research, Kuppusamy et al. (2017) found an obvious peak at \( 2\Theta = 24^{\circ} \) for their green synthesized copper oxide nanoparticles. Singh et al. (2017) reported that the most intense
peak at $2\theta = 31.6^\circ$, showed the presence of crystalline CuO in their biosynthesized copper oxide nanoparticles.

Due to the interaction of the synthesized nanoparticles and Pb ions during the agitation for 24 hours, the structure of the adsorbents was probably disturbed and no obvious peaks were observed in the XRD analysis after adsorption. However, the after-adsorption XRD analysis showed that the peaks indicating CuO observed in the before-adsorption analysis were re-observed only for the M-CuO-NPs. The most regular morphology and lowest adsorption of Pb by the M-CuO-NPs during contact time maybe because the structure of these nanoparticles was less degraded.

Figure 2. Infrared spectra of the studied copper oxide nanoparticles before and after Pb adsorption. A-CuO-NPs, R-CuO-NPs, and M-CuO-NPs show copper oxide nanoparticles synthesized from astragalus, rosemary, and mallow leaf extracts, respectively.
Figure 3. Infrared spectra of the used plant leaf extracts. A, R and M represent astragalus, rosemary, and mallow, respectively.

![Infrared spectra](image)

Figure 4. SEM micrographs of three studied copper oxide nanoparticles before the adsorption of Pb$^{2+}$. A-CuO-NPs, R-CuO-NPs, and M-CuO-NPs show copper oxide nanoparticles synthesized from astragalus, rosemary, and mallow leaf extracts, respectively.

![SEM micrographs](image)

Figure 5. SEM micrographs of three studied copper oxide nanoparticles after the adsorption of Pb$^{2+}$. A-CuO-NPs, R-CuO-NPs, and M-CuO-NPs show copper oxide nanoparticles synthesized from astragalus, rosemary, and mallow leaf extracts, respectively.

![SEM micrographs](image)
Following the reactions between the leaf extracts and CuSO₄·5H₂O solution after the adequate time (24 hours), the formation of copper oxide nanoparticles became complete and the suspensions of the nanoparticles were observed in the containers. As is shown in Figure 8, the densest suspension was formed in the mallow leaf extract. The nanoparticles synthesized by rosemary leaf extract were finer than that of mallow and the suspended nanoparticles in astragalus leaf extract were the smallest. The dry matter yield of the synthesized copper oxide nanoparticles per 100 mL of each plant leaf extract were 4.3, 3.05, and 1.81 g for the M-CuO-NPs, R-CuO-NPs, and A-CuO-NPs, respectively. In general, with the same volume of each leaf extract and equal concentrations of CuSO₄·5H₂O solution, the highest dry mass was obtained for the M-CuO-NPs. Larger particles formed in mallow leaf extract can be related to the smooth and broad morphology of the M-CuO-NPs. However, finer particles in rosemary and astragalus leaf extracts may be due to the rough configurations in the A-CuO-NPs and R-CuO-NPs (Figure 4).

**Sorption of Pb onto the synthesized copper oxide nanoparticles**

Maximum values of \( q_e \) were 41.19, 39.88, and 32.44 (mg g⁻¹) for the A-CuO-NPs, R-CuO-NPs, and M-CuO-NPs, respectively. Higher \( q_e \) values for the A-CuO-NPs and R-CuO-NPs, probably were due to more course configuration in these two nanoparticles in comparison with the M-CuO-NPs. Larger particles formed in mallow leaf extract can be related to the smooth and broad morphology of the M-CuO-NPs. However, finer particles in rosemary and astragalus leaf extracts may be due to the rough configurations in the A-CuO-NPs and R-CuO-NPs (Figure 4).

The mass ratio of Pb sorbed onto nanoparticles (mg g⁻¹) to Pb in solution (mg L⁻¹) is defined as distribution coefficient \( (K_d) \). The highest values of \( K_d \) were observed in the lowest \( C_0 \) for all three nanoparticles (1.42, 1.21, and 1 L g⁻¹ for the A-CuO-NPs, R-CuO-NPs, and M-CuO-NPs, respectively). In the highest initial concentration of Pb (1.5 mM), the \( K_d \) values were in the following order: A-CuO-NPs (1.13 L g⁻¹) > R-CuO-NPs (0.88 L g⁻¹) > M-CuO-NPs.

![Figure 6. Chemical composition and the EDX spectra of the synthesized copper oxide nanoparticles before and after Pb²⁺ adsorption.](image)

In general, the differences in the change of \( C_c \) vs. \( C_0 \) can be attributed to the different morphology and removal capacities of the three studied nanoparticles.
Therefore the notable result was the highest RE and $K_d$ values for the A-CuO-NPs, which implies the considerable capacity of this synthesized nanoparticle for Pb adsorption in comparison with the other two. Nozohour Yazdi et al. (2018) reported that $K_d$ value in Pb adsorption ($200 \mu g \ L^{-1}$) by fabricated polysulfides as a novel adsorbent was $2.42 \ L \ g^{-1}$.

The effect of solution pH on the adsorption rate is shown in Figure 10. According to this figure, the amount of Pb adsorption by all three synthesized nanoparticles increased by increasing pH of the solution. Increasing pH causes the decrease of hydrogen ions in the solution. The reduction of hydrogen ions produces negative charges due to the creation of lone electron pair in the oxygen of CuO and absorbs divalent positive Pb ions (Azizi et al. 2017). This effect was stronger at higher pHs and resulted in the highest removal efficiencies at pH 11. Figure 10 also confirms that the highest and lowest REs belonged to the A-CuO-NPs and M-CuO-NPs, respectively. In addition, the increase in RE with the increase in pH in the M-CuO-NPs is more regular than that of the other two nanoparticles.

**Sorption isotherms**

Parameters derived from Langmuir and Freundlich isotherms in the sorption of Pb ions by three synthesized copper oxide nanoparticles are given in Table 3. The best fit of the data to the Langmuir and Freundlich isotherms belonged to the adsorption of Pb onto the M-CuO-NPs (with $R^2$ values of 0.99 and 0.98 for Langmuir and Freundlich, respectively). For the M-CuO-NPs, Langmuir constant ($K_L$) was $0.061 \ L \ mg^{-1}$. Monolayer surface adsorption ($b$) in Langmuir isotherm for the M-CuO-NPs was $50 \ mg \ g^{-1}$. The values of $K_F$ and $n$ in Freundlich isotherm show that the adsorption capacity and sorption intensity in the M-CuO-NPs were $4.7 \ (mg \ g^{-1} \ (L \ mg^{-1})^{1/n})$ and $1.15,$
respectively. The values of standard errors in Table 3 showed that Langmuir was a better model in comparison with Freundlich for the adsorption of Pb by the synthesized nanoparticles. The overall morphology of the three synthesized copper oxide nanoparticles was an important factor in determining the adsorption properties of Pb ions. The smooth configuration of the M-CuO-NPs in comparison with coarse shapes in the A-CuO-NPs and R-CuO-NPs (Figure 4) probably caused more uniform adsorption in the M-CuO-NPs as compared to the other studied copper oxide nanoparticles. Sorption characteristics of Pb by other adsorbents have also been reported in other studies. Akram et al. (2019) showed that parameter b in Langmuir isotherm in the removal of Pb by 0.5 g of cotton shells powder was 2.87 mg g⁻¹. Verma et al. (2017) reported that the maximum adsorption of Pb by copper nanoparticles synthesized by the sputtering method was 37 mg g⁻¹ and fitted with the Langmuir model.

The negative values of Gibb's free energy, presented in Table 4, show that the sorption processes of Pb by all three

![Figure 8](image)

**Figure 8.** The close photos of the suspensions represent the density of the synthesized copper oxide nanoparticles. A-CuO-NPs, R-CuO-NPs, and M-CuO-NPs show copper oxide nanoparticles synthesized from astragalus, rosemary, and mallow leaf extracts, respectively.

![Figure 9](image)

**Figure 9.** Relationships between equilibrium adsorption (q_e) and equilibrium concentrations (C_e). A-CuO-NPs, R-CuO-NPs and M-CuO-NPs show copper oxide nanoparticles synthesized from astragalus, rosemary and mallow leaf extracts, respectively.

### Table 1. RE and equilibrium concentrations (C_e) of Pb after 24 hours at different initial concentrations (C_0).

| C_0 (mM) | A-CuO-NPs | R-CuO-NPs | M-CuO-NPs |
|----------|------------|------------|------------|
| 0.15     | 0.013 (91.3%) | 0.016 (89.3%) | 0.019 (87.3%) |
| 0.3      | 0.106 (64.6%)  | 0.108 (64%)  | 0.103 (65.6%)  |
| 0.6      | 0.221 (63.1%)  | 0.241 (59.8%) | 0.217 (63.8%)  |
| 1        | 0.217 (78.3%)  | 0.278 (72.2%) | 0.311 (68.9%)  |
| 1.5      | 0.174 (88.4%)  | 0.226 (84.9%) | 0.455 (69.6%)  |

A-CuO-NPs, R-CuO-NPs and M-CuO-NPs show copper oxide nanoparticles synthesized from astragalus, rosemary, and mallow leaf extracts, respectively. The percentages in parentheses indicate removal efficiency (RE). Each figure is a mean of two replications.

### Table 2. Pb RE using various absorbents in previous studies.

| Absorbent used | Time | RE |
|----------------|------|----|
| Trichoderma harzianum | 24 h | 75% for 100 mg L⁻¹ of Pb |
| Azadirachta indica (Neem) leaves | 24 h | 82.7% with 0.1 g biosorbent in 100 mL solution of Pb |
| Moringa oleifera leaves powder | 180 min | 50% of Pb from 100 mL of an aqueous solution |
| ZnO/Carbon nanofibers | 80 min | 80% removal of Pb in a 20 mL of 10 ppm Pb solution |

RE: Removal efficiency.
studied nanoparticles were spontaneous reactions. The highest and lowest spontaneity were observed for the adsorption of Pb onto the A-CuO-NPs ($\Delta H_{f}^{\text{r}} = 15.74 \text{kJmol}^{-1}$) and M-CuO-NPs ($\Delta H_{f}^{\text{r}} = 14.77 \text{kJmol}^{-1}$), respectively. Therefore the quantities of Gibb’s free energy also confirm that the highest and lowest tendency for Pb adsorption in solution belonged to the A-CuO-NPs and M-CuO-NPs, respectively. Accordingly, Gibb’s free energy quantities for Pb and Ni adsorption at 318°K were $-8.27$ and $-4.71 \text{kJmol}^{-1}$, respectively. It can result that the negative quantities of Gibb’s free energy and spontaneity in a sorption reaction increase with increasing the sorption strength of an adsorbent.

### Conclusion

The results of the present study showed that all three green synthesized copper oxide nanoparticles were efficient in the removal of Pb from aqueous solution but their adsorption properties and morphologies were different. Comparison between the adsorption capacity of the three synthesized nanoparticles showed that the nanoparticles synthesized from astragalus leaf extract had the highest efficiency for the removal of Pb from aqueous solution. The sorption properties and morphology of the nanoparticles synthesized from rosemary were almost similar to those synthesized from astragalus. The sorption strength in nanoparticles synthesized from rosemary was relatively lower than that of synthesized from astragalus. In comparison with rough morphology in copper oxide nanoparticles synthesized from astragalus and rosemary, the smooth configuration in the nanoparticles synthesized from mallow leaf extract caused lower removal efficiency in these nanoparticles as compared to those synthesized from astragalus and rosemary. Sorption of Pb onto the nanoparticles synthesized from mallow leaf extract caused lower removal efficiency in these nanoparticles as compared to those synthesized from astragalus and rosemary. The patterns that emerge from the present study were the preparation of environmentally friendly nanoparticles efficient in Pb removal using abundant plant covers.
and low-cost and easy preparation processes. Also, the native plants of each region are valuable sources for the synthesis of green metal nanoparticles.

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**Author contributions**

The manuscript was based on a draft written through the contributions of AZ and RGH. Both authors read and approved the final manuscript.

**Disclosure statement**

The authors declare that they have no competing interests.

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**Data availability statement**

The datasets used and/or analyzed during the current study are available from the corresponding author on reasonable request.

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