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Green synthesis of copper oxide nanoparticles using *Gundelia tournefortii* and *Aloe vera* extract and removal of lead ions from wastewater

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ABSTRACT

Since the industrial revolution, water pollution, including wastewater, has attracted researchers' attention. An effective and environmentally friendly method for the green synthesis of copper oxide nanoparticles (CuO NPs) with aqueous extracts of *Aloe vera* and *Gundelia tournefortii* as an adsorbent for heavy metals has been developed. The formulated NPs were analyzed by X-ray diffraction, Fourier-transform infrared spectroscopy, field-emission scanning electron microscopy, and energy-dispersive X-ray spectroscopy techniques. Absorption experiments were performed on aqueous solutions at various concentrations and pH. The elimination rate of Pb^{2+} was investigated by an atomic absorption system. Different conditions for the removal of lead ions were considered, and the green-produced CuO NPs presented high photocatalytic activity for removing lead ions from wastewater. According to the results, the optimum condition for eliminating heavy cation Pb^{2+} with more than 99% efficiency was achieved at a concentration of 200 mg/L, pH = 7.5, and 0.008 g of CuO NPs. According to experiments, by increasing the amount of NPs, the percentage of lead ions has increased owing to the high available absorption sites against the fixed amount of metal ions.

Keywords: *Aloe vera* extract; *Gundelia tournefortii*; Copper oxide nanoparticles; Wastewater; Green synthesis

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1. Introduction

The unchecked and excessive evacuation of heavy metal ions is now a significant issue. Human life is dependent on the environment, while environmental pollution, especially water, has long been considered in public health [1]. The development of the industry has made life easier and more convenient. Meanwhile, contamination's harmful consequences also have a negative impact on the ecosystem [2]. Heavy and toxic metals enter the environment through natural processes as well as anthropogenic activities such as metallurgical, galvanizing, electroplating, electronic device manufacturing, mining, and power regeneration [2–6]. The World Health Organization regularly monitors the impacts of heavy metals on human health [4]. Increasing the concentration of heavy metals beyond the permissible limit causes serious risks and disorders in the health and normal functioning of humans and animals [2,7–9]. Toxic heavy metals include, nickel, chromium, lead, cadmium, mercury, and copper [10], which are not simply removed without specialized or advanced treatment. Pb^{2+} is one of the most toxic heavy metals with long stability and is an environmental pollutant [5,11]. Several industries, such as battery manufacturing, glass production, electroplating, metal finishing, printing, and tanning, produce large amounts of lead-containing waste [12]. The acceptable levels of Pb^{2+} in drinkable water and wastewater are 0.05 and 0.005 mg/L, respectively [13,14]. Lead may impact almost every organ and body system of a living organism. Lead exposure could severely hurt the nervous and reproductive systems (e.g., infertility), kidneys, liver, especially for pregnant women [15], the brain, and kidneys in adults and children, and finally cause death [2]. There are various techniques, including chemical sedimentation [16], adsorption [17], electrochemical decrease [18], ultrafiltration [19], solvent extraction [20], and ion exchange [21], used to remove toxic metal ions. These technologies have disadvantages: it is expensive to treat and dispose of secondary toxic metal sludge (2) Ineffective when lead levels in wastewater are low [22]. On the other hand, the absorption technique is one of the most appropriate and effective techniques owing to its easiness and a variety of adsorbents are readily available [23]. An effective adsorption procedure depends on the efficiency of the adsorbents and the continuing supply of ingredients for the procedure [24]. The cost of using adsorption technology can be reduced if the adsorbent is cheap. Therefore, there is a continuous search for inexpensive alternative adsorbents [25]. New developments in technology, particularly nanotechnology, have led to the development of a novel concept of NP synthesis [1]. Processes that play a significant role in preventing pollution and identifying and treating pollutants. To decontaminate and change pollutants into harmless or less harmful materials owing to their small size, large cross-section, crystalline shape, unique lattice order, and great reactivity [26]. Nanoparticles have recently been reported as adsorbents in various studies. For example, using iron oxide to remove chromium from water [24], removal of nickel ions using iron(III) oxide nanoparticles from aqueous solutions [27], removal of xylene from water by zinc nano oxide as an oil adsorbent [28], manganese dioxide nanoparticles and evaluation of their performance in copper removal from aqueous solutions [29]. CuO is a semiconductor material with a thin bandgap of 1.7 eV [30]. Because of their simple synthesis method, environmental friendliness, and photocatalytic properties, copper oxide nanoparticles (CuO NPs) synthesized from plant extract may be used to eliminate contaminations [31]. In this study, the production of green copper oxide NPs was designed to eliminate heavy metal contaminants from water and wastewater.

2. Experimental

2.1. Material and method

Aloe vera leaves were purchased from a Tehran Pharmacy in Iran. *Gundelia tournefortii* were prepared at the local market in Iran. Copper(II) acetate and other chemical agents were obtained from Sigma-Aldrich (St. Lo., USA) and Merck companies and applied without any purification.

2.2. Characterization

Fourier-transform infrared spectroscopy (FTIR) measurements were carried out with a spectrometer (Tensor 27, Bruker Co., Ettlingen, Germany), using a KBr-pellet method. To analyze the sample of NPs (synthesized CuO NPs by *G. tournefortii* extract and synthesized CuO NPs by *Aloe vera*, leaves extract), the X-ray diffraction (XRD) of them was scanned with a Holland Philips X-Pert X-ray Powder Diffractometer through a Cu source by a peak Kα of 0.1540 nm from an angle of 1°–70° with the rate of 1°/min. To investigate the surface, structure morphology of produced NPs, and images of the catalyst's surface, field-emission scanning electron microscopy (FESEM; FESEM-TESCAN MIRA3 model) was utilized.

2.3. Green Synthesis of CuO NPs by G. tournefortii extract

2.3.1. G. tournefortii extract preparation

The aerial organs of the *G. tournefortii* plant were washed three times in a row with deionized water and dried at room temperature for one week. Next, they were milled and screened via a laboratory screen through mesh 20 until a uniform powder was obtained. In a reflux balloon, 14.53 g of meshed powder was mixed with 145.3 mL of deionized water, which was then thoroughly stirred and refluxed at 80°C for 120 min. After the reaction was completed, it was filtered.

To synthesize copper oxide nanoparticles, the first 50 mL of artichoke extract were mixed with 50 mL of 0.003 M $CuCl_2$ solution and stirred at 60°C for 120 min. After a few minutes, the color of the mix was altered from light brown to dark brown. To adjust the pH, 2 mL of NaOH 0.2 M was added. The resulting solution was sited in an oven at 24°C for 1 d. The synthesized NPs were filtered, washed with deionized water three times, and then dried for 12 h at room temperature [30].

2.4. Green Synthesis of copper(II) oxide nanoparticles by the extract of Aloe vera, leaves

2.4.1. Preparation of Aloe vera leaves extract

The synthesis was performed in accordance with the methods described in the published literature (REF). In summary, the *Aloe vera* fresh leaves were collected from the trees, washed with deionized water, and dried at 25°C. The cleaned *Aloe vera* leaves were cut into small pieces. The chopped leaves were added to 1,000 mL of deionized water and boiled at 120°C for 50 min. The achieved extract was filtered with Whatman Filter Paper. Next, 20 mL of a 2 M solution of potassium chloride was added to the obtained extract until the pH increased to 8.5 and the mixture cooled down to room temperature.

To green synthesis of CuO NPs, 500 mL of a 100 mm aqueous solution of copper nitrate was added to 50 mL of *Aloe vera* extract under continuous stirring at 100°C–120°C. The solution's color changed from blue to colorless and then to brick and dark red during the 24 h stirring. The solution was centrifuged at 10,000 rpm at room temperature for 10 min, and the deposition was collected in a glass [31].

2.4.2. Study of absorption

To investigate the photocatalytic effect of synthesized NPs, they were separately placed in beakers containing 75 mL of Pb^{2+} solution (200 mg/L) at room temperature and pH = 7.5, and the amount of heavy metal removal was studied using an atomic absorption device (Unicam 939). Then the impact of NPs doses on the elimination of heavy metal ions (0.002–0.1 g), the effect of pH in different pH (2.5, 4, 6, 7.5, and 8.5), and the effect of the concentration of primary metals (100, 200, 300, and 400 mg/L) were investigated. The content of absorbed metal per unit mass of NPs (q) and the percentage removal of heavy metals (R) were measured following Eqs. (1) and (2).

$$q = \frac{\left(C_0 - C_e\right) \times V}{M} \tag{1}$$

$$R = \frac{C_0 - C}{C_0} \times 100 \tag{2}$$

where C_0 is the primary concentration, C_e is the equilibrium concentration of metal ions in solution (mg/L), V is the volume of the solution (L), C indicates the concentration of metal ions and M is the absorbing mass [32].

3. Results and discussion

3.1. XRD analysis

The XRD curves of synthesized CuO NPs by *G. tournefortii* extract and produced CuO NPs by the extract of *Aloe vera* leaves are revealed in Figs. 1 and 2, respectively. The green synthesis of CuO NPs studied by XRD indicates

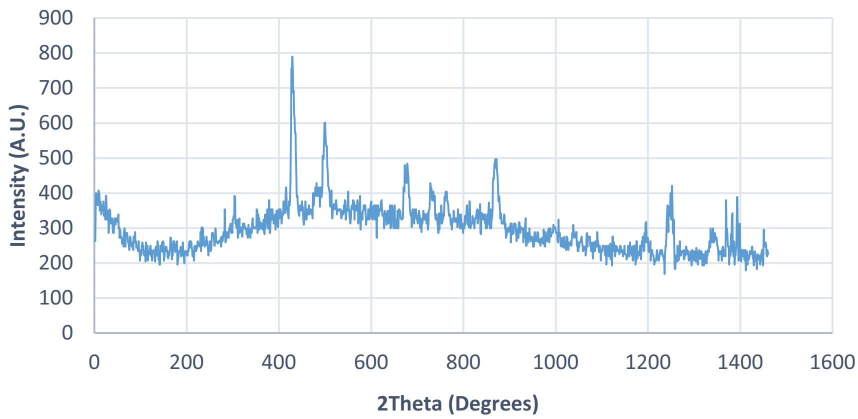

Fig. 1. XRD pattern of produced CuO NPs by *Gundelia tournefortii* extract.

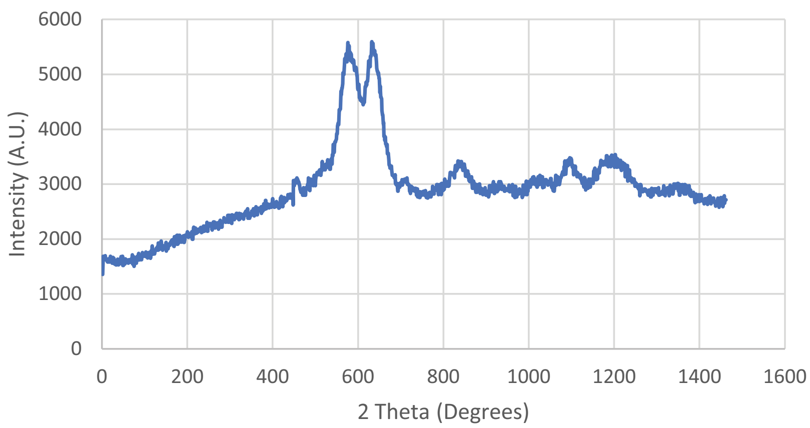

Fig. 2. XRD curves of synthesized CuO NPs by *Aloe vera*, leaves extract.

more crystallinity. The diffraction peaks at (110), (111), (220), (202), (020), (113), (311) and (440) show CuO NPs [33].

Slight flattening of the peak in the sample prepared from *G. tournefortii* extract indicates less crystallinity in this sample.

The crystallite size of the samples was measured by the Scherrer equation:

$$D = \frac{k\lambda}{\beta \cos\theta} \quad (3)$$

where D is the average of crystallite size, k is the crystal constant that is equal to 0.89, θ is the Bragg angle, λ is X-ray wavelength, and β is the full width at half maximum (FWHM) of the strongest peak [34].

The crystallite size of synthesized CuO NPs by *G. tournefortii* extract and produced CuO NPs by the extract of *Aloe vera* leaves were assessed based on the Scherrer model at around 13.7–33.29 and 5.76–26.95 nm, respectively; the mean of the particles' crystallinity was identical at 21.37 and 12.22 nm, respectively.

3.2. FTIR analysis

The FTIR transmission spectra in Fig. 3 show the formation of the CuO phase. The presence of OH^- and carbonyl (C=O) is indicated by the available peak in 2,800–4,000 cm^{-1} in Fig. 3a and b. The presence of peaks in 500–700 cm^{-1} (618, 622) corresponds to specific stretching vibrations of the Cu–O bond in the CuO NPs [33,35]. The strong width observed around 2,900 cm^{-1} is associated with the symmetric tension of water molecules [34].

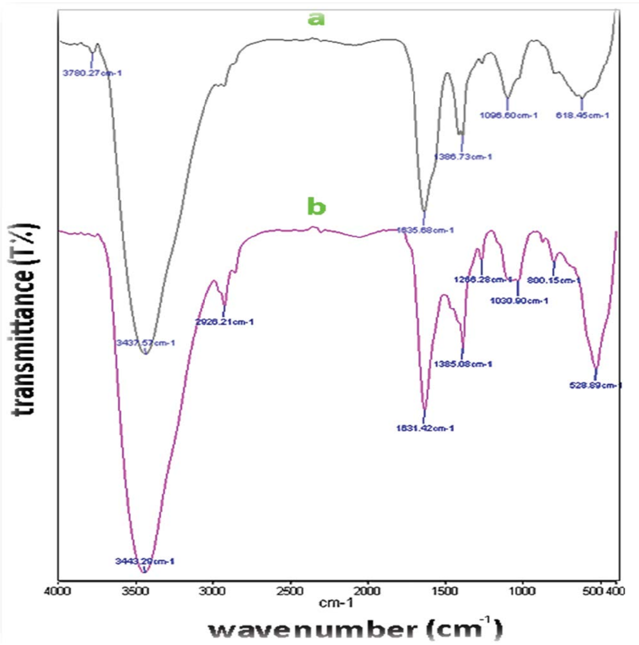

Fig. 3. FTIR spectra of NPs (a) by the *Aloe vera* leaves extract and (b) by the *Gundelia tournefortii* extract.

3.3. FESEM analysis

The obtained results of morphology investigation of produced CuO NPs by the *G. tournefortii* extract with polygon morphology is shown in Fig. 4. The FESEM images show the good dispersion of CuO.

The FESEM images of synthesized CuO NPs by the extract of *Aloe vera* leaf extract with approximately the same morphology as cauliflower as shown in Fig. 5. The FESEM images indicate the good dispersion of CuO.

3.4. Removal process

3.4.1. Effect of the amount of adsorption

By increasing the amount of NPs, the elimination percentage of heavy metals has increased owing to the high available absorption sites with the fixed metal ion content. Also, increasing the amount of NPs reduced the maximum heavy metal ion absorption capacity, which could be related to the number of unsaturated absorption sites throughout the procedure in Figs. 6 and 7 [35]. For example, the adsorption capacity of Pb^{2+} under the synthesized CuO NPs by the *G. tournefortii* extract (Fig. 6) decreases from 2,077.5 to 1,456.5 mg/g when the NPs amount increases from 0.002 to 0.01 g. According to Figs. 6 and 7, there is an insignificant variance between the elimination ratios when the nanoparticles are 0.008 and 0.01 g, respectively. Therefore, 0.008 g of nanoparticles was chosen as the optimal.

3.4.2. Effect of initial metal ion concentration

The impact of the primary concentration of heavy metals on the removal efficacy is exposed in Figs. 8 and 9. Enhancing the primary concentration of metal ions decreased the removal percentage that is associated to the attendance of a constant number of adsorption positions against increasing the number of metal ions. Though, enhancing the initial concentration of heavy metal ions caused an increase in absorption. For instance, when the primary concentration of Pb^{2+} enhances from 100 to 400 mg/L, the removal percentage reduces from 97.77% to 53.82%, although the adsorption enhances from 916.593 to 2,018.25 mg/L, respectively. These obtained results show that the content of ions adsorbed on the surface of nanoparticles increases with the initial enhance in the concentration of metal ions, which indicates an enhance in the concentration gradient's moving force. According to Figs. 8 and 9, metal ion adsorption happens quite quickly in the first few minutes. The uncoated surface and active positions on the surface of the adsorbent may be the cause of the ions' fast adsorption at this phase [30].

3.4.3. pH effect

Figs. 10 and 11 illustrate the impact of pH on the elimination of heavy metal ions. The findings show which the absorption percentage increased by raising the pH. The least amount of absorption in the acidic pH was due to the higher content of H^+ in comparison to the metal ions throughout the absorption procedure [36,37]. At alkaline pH, metal ion hydrolysis can result in lower adsorption

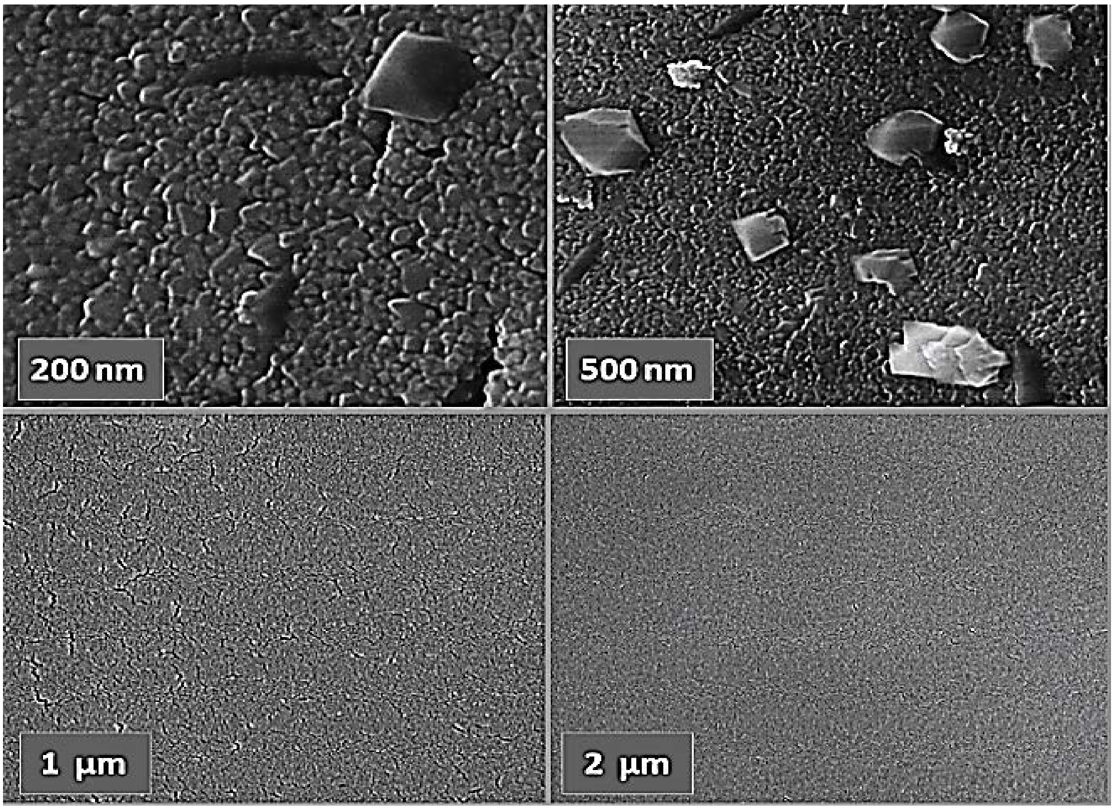

Fig. 4. FESEM image of synthesized CuO NPs by the *Aloe vera* leaves extract.

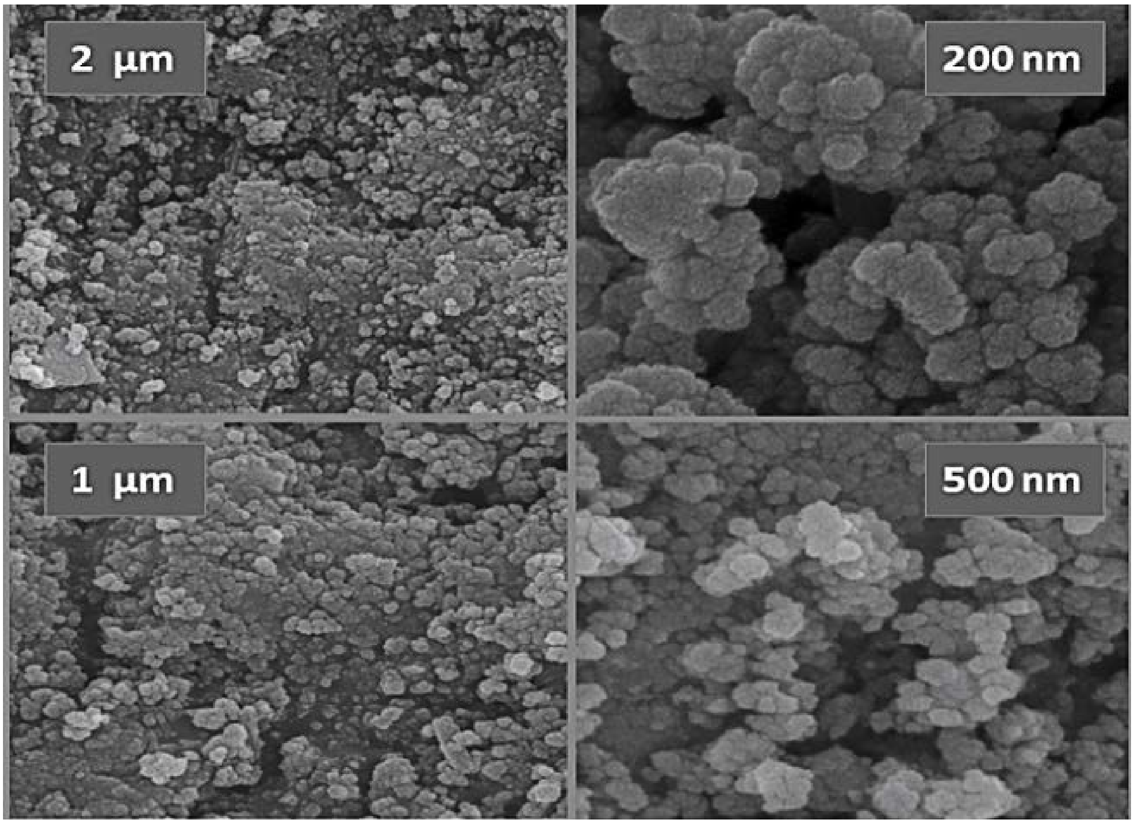

Fig. 5. FESEM images of synthesized CuO NPs by the *Gundelia tournefortii* extract.

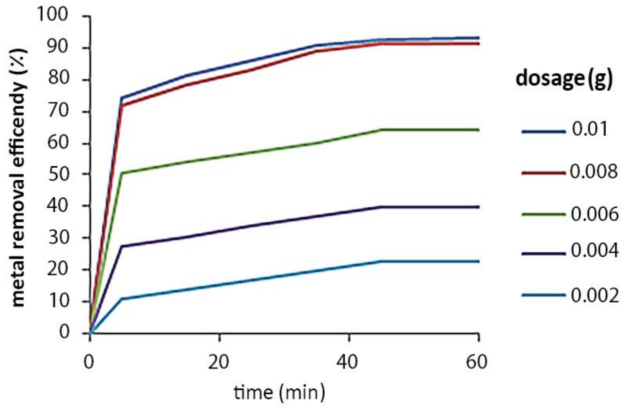

Fig. 6. Effect of adsorbent on the removal of heavy metal ions under the synthesized CuO NPs by the *Gundelia tournefortii* extract.

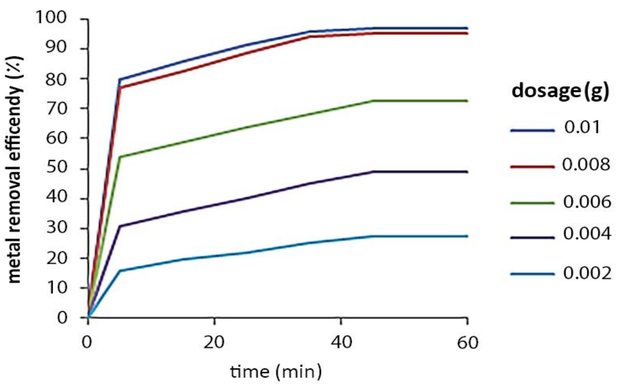

Fig. 7. Effect of adsorbent on the removal of heavy metal ions under the synthesized CuO NPs by the *Aloe vera* leaves extract.

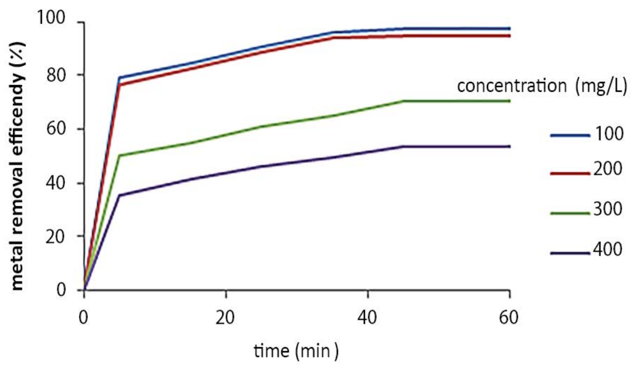

Fig. 8. Impact of primary heavy metal ion concentration on removal efficiency ions under the synthesized CuO NPs by the *Aloe vera* leaves extract.

efficiencies. Also, in strongly alkaline conditions, metal ions are precipitated in solution owing to the more content of OH^- ions. In an alkaline solution, oxygen atoms have a negative charge that is suitable for absorbing heavy metal ions. In this regard, electrostatic absorption could occur among metal ions and oxygen atoms by various loads.

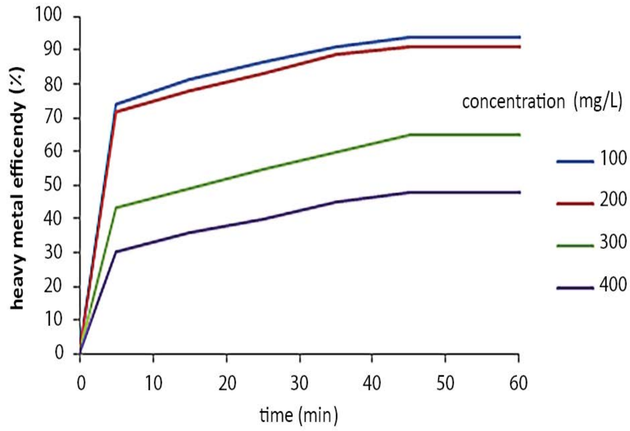

Fig. 9. Impact of primary heavy metal ion concentration on removal efficiency ions under the synthesized CuO NPs by the *Gundelia tournefortii* extract.

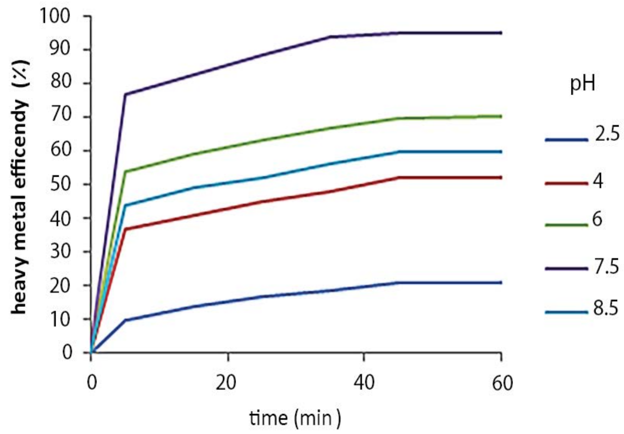

Fig. 10. Effect of pH on elimination efficacy under the synthesized CuO NPs by the *Gundelia tournefortii* extract.

Extreme metal absorption at pH 7.5 has occurred. At this pH, the metal ion can bond by the oxygen electron pair.

4. Conclusion

In conclusion, CuO NPs with high scale-up were synthesized at 25°C. The green synthesis of CuO NPs was performed with *G. tournefortii* and *Aloe vera* extract. The CuO NPs presented photocatalytic activity as a heavy metal (Pb^{2+}) remover. According to experiments, by increasing the amount of NPs, the percentage of lead ions has increased owing to the high available absorption sites against the fixed amount of metal ions. Furthermore, owing to the attendance of a continuous number of absorption positions by raising the number of Pb^{2+} ions, the primary concentration of lead ions was reduced by a certain percentage. However, the absorption capacity increases with the increasing concentration of heavy metal ions.

Conflicts of interest

The authors declare no competing interests.

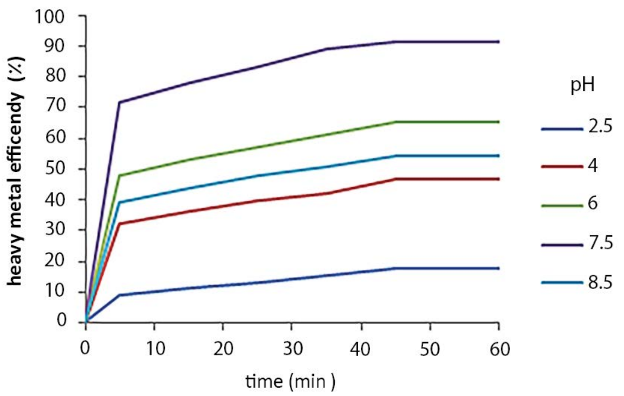

Fig. 11. Effect of pH on removal efficiency under the synthesized CuO NPs by the *Aloe vera* extract.

References

[1] M. Eisapour Chanani, N. Bahramifar, H. Younesi, Synthesis of Fe_3O_4@silica core–shell particles and their application for removal of copper ions from water, J. Appl. Res. Water Wastewater, 2 (2015) 176–182.

[2] M. Naushad, Surfactant assisted nano-composite cation exchanger: development, characterization and applications for the removal of toxic Pb^{2+} from aqueous medium, Chem. Eng. J., 235 (2014) 100–108.

[3] S. Sharifi, R. Nabizadeh, B. Akbarpour, A. Azari, H.R. Ghaffari, S. Nazmara, B. Mahmoudi, L. Shiri, M. Yousefi, Modeling and optimizing parameters affecting hexavalent chromium adsorption from aqueous solutions using Ti-XAD7 nanocomposite: RSM-CCD approach, kinetic, and isotherm studies, J. Environ. Health Sci. Eng., 17 (2019) 873–888.

[4] Mu. Naushad, Z.A. Al-Othman, M. Islam, Adsorption of cadmium ion using a new composite cation-exchanger polyaniline Sn(IV) silicate: kinetics, thermodynamic and isotherm studies, Int. J. Environ. Sci. Technol., 10 (2013) 567–578.

[5] M.H. Falsafi, M. Moghaddas, J. Moghaddas, Removal of heavy metals from synthetic wastewater using silica aerogel-activated carbon composite by adsorption method, J. Appl. Res. Water Wastewater, 7 (2020) 90–96.

[6] M. Heidarzadeh, N. Abdi, J. Varvani Farahani, A. Ahmadi, H. Toranjzar, The effect of *Typha latifolia* L. on heavy metals phytoremediation at the urban and industrial wastewater entrance to the Meighan wetland, Iran, J. Appl. Res. Water Wastewater, 7 (2020) 167–171.

[7] S. Afshin, Y. Rashtbari, M. Vosough, A. Dargahi, M. Fazlzadeh, A. Behzad, M. Yousefi, Application of Box–Behnken design for optimizing parameters of hexavalent chromium removal from aqueous solutions using Fe_3O_4 loaded on activated carbon prepared from alga: kinetics and equilibrium study, J. Water Process Eng., 42 (2021) 102113, doi: 10.1016/j.jwpe.2021.102113.

[8] B. Kiani, F. Hashemi Amin, N. Bagheri, R. Bergquist, A.A. Mohammadi, M. Yousefi, H. Faraji, G. Roshandel, S. Beirami, H. Rahimzadeh, Association between heavy metals and colon cancer: an ecological study based on geographical information systems in North-Eastern Iran, BMC Cancer, 21 (2021) 414, doi: 10.1186/s12885-021-08148-1.

[9] A. Esmaeili, S. Shamaei, E. Molaee Aghaee, Z. Nosrati Akhtar, S.F. Hosseini, S. Shokri, Health risk assessment of heavy metals in edible mushrooms and their effect on anemia: a review study, J. Chem. Health Risks, 12 (2021) 597–607.

[10] A. Manouchehri, M. Pirhadi, S. Shokri, G.J. Khaniki, The possible effects of heavy metals in honey as toxic and carcinogenic substances on human health: a systematic review, Uludağ Arıcılık Dergisi, 21 (2021) 237–246.

[11] Q. Feng, Q. Lin, F. Gong, S. Sugita, M. Shoya, Adsorption of lead and mercury by rice husk ash, J. Colloid Interface Sci., 278 (2004) 1–8.

[12] N. Rouniasi, S.M. Monavari, M.A. Abdoli, M. Baghdadi, A. Karbasi, Removal of heavy metals of cadmium and lead from aqueous solutions using graphene oxide nanosheets process optimization by response surface methodology, Iran. J. Health Environ., 11 (2018) 197–214.

[13] Z.A. Al-Othman, Mu. Naushad, A. Nilchi, Development, characterization and ion exchange thermodynamics for a new crystalline composite cation exchange material: application for the removal of Pb^{2+} ion from a standard sample (Rompin Hematite), J. Inorg. Organomet. Polym. Mater., 21 (2011) 547–559.

[14] S. Sam, S.P. Malinga, N. Mabuba, Carbon nanodots embedded on a polyethersulfone membrane for cadmium(II) removal from water, Membranes (Basel), 11 (2021) 114, doi: 10.3390/membranes11020114.

[15] T.G. Ambaye, M. Vaccari, E.D. van Hullebusch, A. Amrane, S. Rtimi, Mechanisms and adsorption capacities of biochar for the removal of organic and inorganic pollutants from industrial wastewater, Int. J. Environ. Sci. Technol., 18 (2021) 3273–3294.

[16] M.M. Brbooti, B.A. Abid, N.M. Al-Shuwaiki, Removal of heavy metals using chemicals precipitation, Eng. Technol. J., 29 (2011) 595–612.

[17] K.C. Khulbe, T. Matsuura, Removal of heavy metals and pollutants by membrane adsorption techniques, Appl. Water Sci., 8 (2018) 19, doi: 10.1007/s13201-018-0661-6.

[18] X. Yang, L. Liu, M. Zhang, W. Tan, G. Qiu, L. Zheng, Improved removal capacity of magnetite for Cr(VI) by electrochemical reduction, J. Hazard. Mater., 374 (2019) 26–34.

[19] J. Huang, F. Yuan, G. Zeng, X. Li, Y. Gu, L. Shi, W. Liu, Y. Shi, Influence of pH on heavy metal speciation and removal from wastewater using micellar-enhanced ultrafiltration, Chemosphere, 173 (2017) 199–206.

[20] J. Kończyk, J. Dlugosz, Selective solvent extraction of some heavy metal ions from aqueous solutions by octafunctionalized resorcin arenes, Physicochem. Probl. Miner. Process., 56 (2020) 271–285.

[21] A. Bashir, L.A. Malik, S. Ahad, T. Manzoor, M.A. Bhat, G. Dar, A.H. Pandith, Removal of heavy metal ions from aqueous system by ion-exchange and biosorption methods, Environ. Chem. Lett., 17 (2019) 729–754.

[22] Z.A. AlOthman, M.M. Alam, M. Naushad, Heavy toxic metal ion exchange kinetics: validation of ion exchange process on composite cation exchanger nylon 6,6 Zr(IV) phosphate, J. Ind. Eng. Chem., 19 (2013) 956–960.

[23] D.W. O'Connell, C. Birkinshaw, T.F. O'Dwyer, Heavy metal adsorbents prepared from the modification of cellulose: a review, Bioresour. Technol., 99 (2008) 6709–6724.

[24] Y. Li, Q. Du, X. Wang, P. Zhang, D. Wang, Z. Wang, Y. Xia, Removal of lead from aqueous solution by activated carbon prepared from *Enteromorpha prolifera* by zinc chloride activation, J. Hazard. Mater., 183 (2010) 583–589.

[25] Z. Djedidi, M. Bouda, M.A. Souissi, R.B. Cheikh, G. Mercier, R.D. Tyagi, J.-F. Blais, Metals removal from soil, fly ash and sewage sludge leachates by precipitation and dewatering properties of the generated sludge, J. Hazard. Mater., 172 (2009) 1372–1382.

[26] M. Samadi, M. Saghi, K. Ghadiri, M. Hadi, M. Beikmohammadi, Performance of simple nano zeolite Y and modified nano zeolite Y in phosphor removal from aqueous solutions, Iran. J. Health Environ., 3 (2010) 27–36.

[27] M. Ghaedi, M.N. Biyareh, S.N. Kokhdan, S. Shamsaldini, R. Sahraei, A. Daneshfar, S. Shahriyar, Comparison of the efficiency of palladium and silver nanoparticles loaded on activated carbon and zinc oxide nanorods loaded on activated carbon as new adsorbents for removal of Congo red from aqueous solution: kinetic and isotherm study, Mater. Sci. Eng., C, 32 (2012) 725–734.

[28] L. Wang, J. Zhang, R. Zhao, Y. Li, C. Li, C. Zhang, Adsorption of Pb(II) on activated carbon prepared from *Polygonum orientale Linn.*: kinetics, isotherms, pH, and ionic strength studies, Bioresour. Technol., 101 (2010) 5808–5814.

[29] E. Pehlivan, T. Altun, S. Parlayıcı, Utilization of barley straws as biosorbents for Cu^{2+} and Pb^{2+} ions, J. Hazard. Mater., 164 (2009) 982–986.

[30] M. Ghasemi, M. Naushad, N. Ghasemi, Y. Khosravi-Fard, Adsorption of Pb(II) from aqueous solution using new adsorbents prepared from agricultural waste: adsorption isotherm and kinetic studies, J. Ind. Eng. Chem., 20 (2014) 2193–2199.

[31] M. Nasrollahzadeh, M. Maham, S.M. Sajadi, Green synthesis of CuO nanoparticles by aqueous extract of *Gundelia tournefortii* and evaluation of their catalytic activity for the synthesis of *N*-monosubstituted ureas and reduction of 4-nitrophenol, J. Colloid Interface Sci., 455 (2015) 245–253.

[32] F.A. Tapouk, R. Nabizadeh, S. Nasseri, A. Mesdaghinia, H. Khorsandi, M. Yousefi, M. Alimohammadi, M. Khoobi, Embedding of L–Arginine into graphene oxide (GO) for endotoxin removal from water: modeling and optimization approach, Colloids Surf., A, 607 (2020) 125491, doi: 10.1016/j.colsurfa.2020.125491.

[33] K. Phiwdang, S. Suphankij, W. Mekprasart, W. Pecharapa, Synthesis of CuO nanoparticles by precipitation method using different precursors, Energy Procedia, 34 (2013) 740–745.

[34] M.S. Rahmati, R. Fazaeli, M.G. Saravani, R. Ghiasi, Cu–curcumin/MCM-41 as an efficient catalyst for in situ conversion of carbazole to fuel oxygenates: a DOE approach, J. Nanostruct. Chem., 12 (2022) 307–327.

[35] A. Almasian, N.M. Mahmoodi, M.E. Olya, Tectomer grafted nanofiber: synthesis, characterization and dye removal ability from multicomponent system, J. Ind. Eng. Chem., 32 (2015) 85–98.

[36] P.K. Neghlani, M. Rafizadeh, F.A. Taromi, Preparation of aminated-polyacrylonitrile nanofiber membranes for the adsorption of metal ions: comparison with microfibers, J. Hazard. Mater., 186 (2011) 182–189.

[37] K. Krishnamoorthy, S.-J. Kim, Growth, characterization and electrochemical properties of hierarchical CuO nanostructures for supercapacitor applications, Mater. Res. Bull., 48 (2013) 3136–3139.