

ORIGINAL RESEARCH PAPER

Development of a Platform for Removal of Iron (III) Ions from Aqueous Solution Using CuO Nanoparticles

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Received: 2020-09-10

Accepted: 2020-10-26

Published: 2021-02-01

ABSTRACT

The present study aimed to synthesize copper oxide (CuO) nanoparticles (NPs), which were used as an adsorbent for the sequestration of Iron (Fe) (III) ions from an aqueous solution. The synthesized NPs have been characterized with the help of X-ray diffraction (XRD) spectroscopy, Field Emission scanning electron microscopy (FESEM), and Energy-dispersive X-ray spectroscopy (EDS). The SEM and XRD analyses indicated the average size of CuO NPs was ~25 nm with a rod-like shape. Based on the batch experiments the maximum adsorption was observed at pH 9 with a removal efficiency of 98.38%, initial metal ion concentration of 10 ppm, and contact time 60 min. This study also revealed that adsorption capacity increases when the concentration of adsorbents decreases. To specify the adsorption characteristics of CuO NPs, the adsorption equilibrium data were treated with Langmuir and Freundlich models, which demonstrated that the removal of Fe (III) ions was mostly favored by the physical process followed by the multilayer adsorption on the heterogeneous surface of the adsorbents. Finally, this study concludes that CuO NPs could be used as a promising material for the removal of Fe(III) ion from aqueous solution.

Keywords: Heavy metals, wastewater, adsorption, nanoparticles.

How to cite this article

Chakrabarty S., Mahmud M.A., Ara M.H., and Bhattacharjee S. Development of a Platform for Removal of Iron (III) Ions from Aqueous Solution Using CuO Nanoparticles. J. Water Environ. Nanotechnol., 2021; 6(1): 41-48.

DOI: 10.22090/jwent.2021.01.004

INTRODUCTION

Every year a large number of industries are being established to accelerate the economic growth of developing countries. Due to the rapid industrialization and improper waste management systems, different types of harmful substances are drastically entering the food chain and causing ecological imbalance [1-4]. For several decades, water pollution has become a major environmental issue worldwide, and it is increasing day by day. Clean and fresh water is safe for drinking and other household activities. On the other hand, impure water is the prominent carrier of many types of pollutants. As a developing country, Bangladesh is facing a great threat to public health due to groundwater contamination. Among the several types of water contaminants, heavy metals are

responsible for causing environmental problems. Sometimes, only a small amount of heavy metals (especially Fe, Mn, Ni, Cu, Zn, etc.) is responsible for initiating several physiological functions. Contrarily, the intake of elevated levels of these metals may cause serious health implications [3, 5, 6].

Iron (Fe) is recognized as a well-known groundwater pollutant, which imposes Alzheimer's disease, Parkinson's disease, type (II) diabetes, and injuries to vital organs like the heart, liver, pancreas, thyroid, and the nervous system [7-10]. Generally, groundwater contains lower levels of iron and is safe for drinking. When it exceeds the recommended level, it creates an unshrinking damaging impact on human physiology and different biological systems [11, 12]. Long-term or excessive uptake of iron may increase the probability of developing cancer, which is a matter of concern [7, 13, 14]. For a long time, many

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Table 1. Entire test performed in this study

Objectives	Methods, instruments and test performed
Synthesis of CuO NPs	Precipitation method
Characterization	XRD, FESEM, EDS
Batch experiment studies	Effect of pH, Contact time, Concentration of Fe(III) and CuO NPs
Isotherm studies	Langmuir and Freundlich isotherm
Removal efficiency	UV-Visible spectrophotometer

scientists are trying to develop new methods for the sequestration of toxic substances from wastewater in a convenient way. Still now, membrane filtration, chemical precipitation, and adsorption methods are widely used for the complete eradication of heavy metals [15-19]. Among these methods, the adsorption process is considered very suitable due to its cost-viability and adaptability in structure and activity [1, 20-22]. In this method, activated carbon, biomass, polymeric materials, zeolite, and clay minerals are used as adsorbents, which adsorb toxic metals from wastewater and generate clean water [23-25].

Although the mentioned technologies are applicable for the removal of heavy metals, they have some limitations such as secondary waste formation and low adsorption capacities. Therefore, there is an urgency to fabricate novel adsorbents, which are associated with their high adsorption capacity, simplicity of operation, and advanced separation rate. In recent years, nanomaterials, including nanotubes (carbon nanotubes, titanium nanotubes), metal oxide, and nanomaterials have gained much attention as efficient adsorbents [26-31]. Due to their unique adsorption capacity, surface effect, small size effect, and binding capabilities, these nanomaterials could be effectively used in wastewater treatment [2]. Numerous literature reported that CuO NPs act as an excellent adsorbent for the removal of heavy metals from aqueous solutions with high removal efficiency [32-34]. To the best of our knowledge, sequestration of Fe (III) from aqueous solutions has not been carried out using CuO NPs. In this study we selected CuO NPs due to the following special features:

- The starting materials (CuCl_2) were used to synthesize CuO NPs, which are comparatively cheaper and easily available.
- CuO NPs could easily be synthesized using a simple and eco-friendly method
- In comparison to other adsorbents, CuO exhibits higher efficiency and accuracy towards the

removal of iron ions at lower concentrations [35-40].

Therefore, the specific objectives of this study were to synthesize CuO NPs based on the precipitation method; to assess their feasibility and suitability as adsorptive material for the removal of Iron (III) ions from an aqueous solution. Besides, the effect of pH, contact time, and concentration of Fe (III) and adsorbents have also been extensively investigated.

MATERIALS AND METHODS

Reagent and Materials

Ammonium iron (II) sulfate, copper chloride (CuCl_2), Sulphuric acid (H_2SO_4), and Ethanol (CH_3OH) were purchased from Merck, Mumbai. Hydrochloric acid (HCl) was obtained from Sigma-Aldrich. Sodium Hydroxide (NaOH) pellets were purchased from Loba Chemie Pvt Ltd. The chemicals used in this experiment were of analytical grade and did not undergo any further treatment.

Equipment

The surface morphology and size of CuO NPs were investigated with the help of FESEM (model: JSM 7600F, JEOL-Japan) attached with EDS. Moreover, the crystal structure of the NPs was analyzed using X-ray diffraction (XRD) (model: Empyrean, PANalytical-Netherlands). The concentration of the Iron (III) solution was determined using a UV-Visible Spectrophotometer (model UVD-3200, Labomed, USA). The pH of the solution was determined using a pH meter (model HI96107, Hanna Instruments, USA). The entire test performed in this study has been summarized in Table 1.

Synthesis of CuO NPs

CuO nanostructures were synthesized based on the precipitation method [41]. To prepare a 0.1 M solution of CuO NPs, CuCl_2 (1.524g) was taken into a 250 mL round bottom (RB) flask containing 100 mL deionized water. Separately, 0.5 g NaOH was dissolved into 100 mL deionized water and added drop-wise into the freshly prepared CuCl_2 solution.

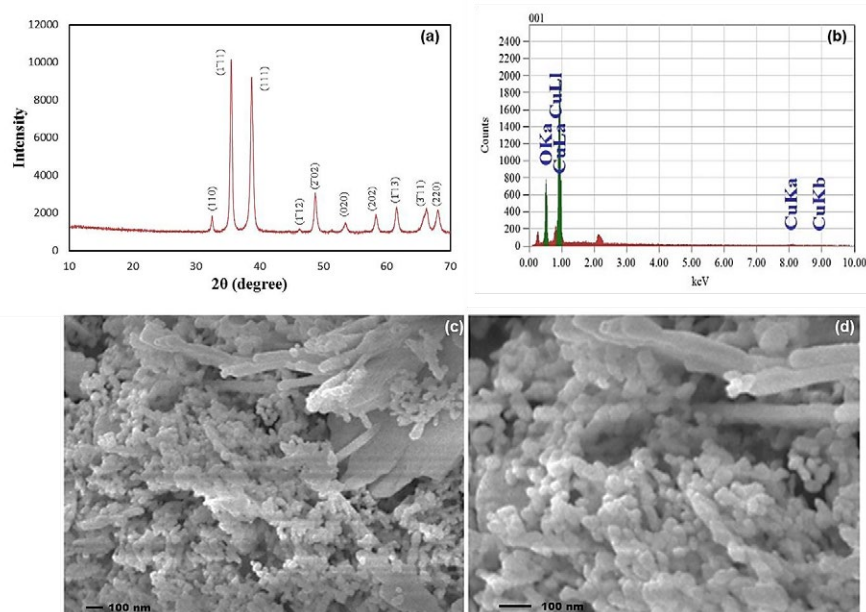


Fig. 1. (a) XRD pattern (b) EDS mapping (c)&(d) FESEM image of CuO NPs.

The mixture was stirred at room temperature until the pH reached 14 and a black precipitate was obtained. It is noted that when the pH increases, the concentration of OH⁻ ions also increases. An excess amount of OH⁻ ion forces the Cu(OH)₂ molecules to be converted into more stable CuO NPs through the dehydration process [42]. The precipitate was filtered and washed with ethanol and distilled water. After that, the precipitate was subjected to oven-dry at 80 °C for 16 hours, and finally, the obtained solid mass was calcined at 500 °C for 4 hours to get black colored CuO NPs

Batch Adsorption Experiment

For batch adsorption studies, 0.01 g synthesized CuO NPs were added to 50 mL of experimental iron (III) solution. The mixture was shaken at 25 °C and a rotation speed of 220 rpm. At that point, the solution was pulled back at a standard time interval, and the nano-adsorbents were separated through a centrifuge machine. Finally, the concentration of the iron ions was determined by using a UV-Visible spectrophotometer. The removal percentage of iron (III) ion in spent was calculated using the following equation (1).

$$\% R = \frac{C_i - C_f}{C_i} \times 100 \quad (1)$$

Here, C_i and C_f are initial and final concentrations of iron respectively in the solution. The adsorption capacity of CuO NPs (mg/g) was calculated by using the following equation (2).

$$W_e = \frac{C_i - C_f}{M} \times V \quad (2)$$

Here, W_e are the metal adsorbed capacity (mg/g), V is the volume of the metal solution (L) and M is the amount of adsorbent (g).

Isotherm Studies

To assess the adsorption characteristics of CuO NPs, the Langmuir (equation 3), Freundlich (equation. 4) isotherm was adopted [43, 44].

$$\frac{C_e}{Q_e} = \frac{C_e}{Q_m} + \frac{1}{bQ_m} \quad (3)$$

$$\log Q_e = \log K_f + \frac{1}{n} \log C_e \quad (4)$$

Where Q_m = Langmuir constant, which denotes the adsorption capability, and b = adsorption energy. C_e = the equilibrium concentration of Fe (III) in mgL⁻¹, Q_e = the amount of metal adsorbed per unit weight of adsorbent in mg/g. K_f expresses the relative adsorption capacity of adsorbent and n represents a deviation for the adsorption system under study.

RESULTS AND DISCUSSION

Characterization of Nanoparticles

The CuO NPs were prepared by using the precipitation method. Fig. 1(a) shows the XRD patterns of CuO NPs. The obtained diffraction peaks with 2θ of 32.49, 35.45, 38.71, 46.09, 48.68, 53.36, 58.22, 61.44, 66.15, and 67.94° which are

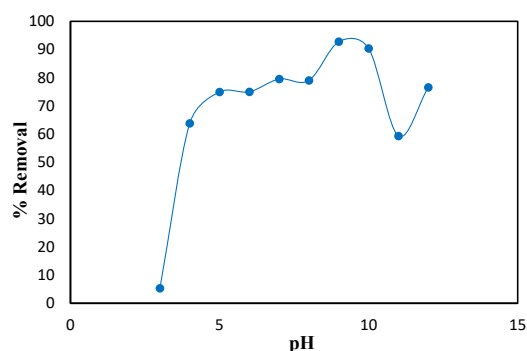


Fig. 2. Effect of pH for the percentage removal of iron (III) ions by CuO NPs.

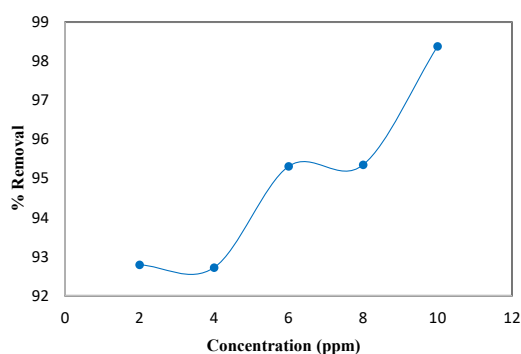


Fig. 3. Effect of initial metal ion concentration for the percentage removal of iron (III) by CuO NPs.

ascribed to crystal planes of CuO NPs (110), ($\bar{1}11$), (111), ($\bar{1}12$), ($\bar{2}02$), (020), (202), ($\bar{1}13$), ($\bar{3}11$) and (220), respectively. The obtained result confirmed the formation of CuO nanoparticles and showed great regularity with the same former pattern of CuO nanoparticles (JCPDS card no. 80-0076) [45]. Also, no other peaks were detected in this spectrum, which indicated the synthesized NPs were highly pure. The size of the CuO NPs was determined by using the Debye-Scherrer equation [1, 46] based on the line-broadening of the magnetite ($\bar{1}11$) reflection and the calculated average crystallite size was found to be ~ 18 nm.

According to the EDS results [Fig. 1(b)], the average content of Copper (Cu) and Oxygen (O) in the CuO sample was 73.82% (atomic percentage) and 26.18%, respectively, which confirmed the stoichiometry of Cu (II) oxide (Cu:O = 3:1) phase. Furthermore, the structure and morphology of the NPs were inspected by FESEM (Fig. 1c-d) which suggested that the average particle size of CuO nanoparticles was ~ 25 nm, having a rod-like shape.

Influence of pH

The initial pH of the metallic solution is

considered as one of the fundamental controlling parameters that affect the degree of ionization, the surface charge of adsorbents, and the specification of adsorbate during the adsorption process [47]. In this study, the influence of pH on the sequestration capacity of Fe (III) was studied at a wide range of pH (3 to 12). During this study, the following conditions were maintained: concentration of Fe (III) ions = 2 mg/L; contact time = 30 min, concentration of CuO NPs = 0.01 g.

According to Fig. 2, the irregular removal efficiency of CuO NPs was noticed. The maximum removal efficiency (98.38%) was attained at pH 9. This phenomenon could be explained by the fact that at higher pH levels, only fewer protons are available to compete with the Fe (III) ions in solution at the active sites of CuO NPs [3]. On the other hand, the removal efficiency of NPs was decreased from pH (10 to 12) because the iron (III) ions started to precipitate at these pH levels [7].

Influence of Initial Metal Ion concentration

Fig. 3 represents the effect of metal ions on the percentage of the removal capacity. In this study, the effect of metal ion was investigated by varying

Table 2. Comparison of Iron removal capacity of CuO NPs with other adsorbents.

Adsorbent	Concentration range (mg/L)	Maximum Iron Removal Efficiency (%)	References
Palm fruit bunch and maize cob	1-10	57-80	[35]
Activated carbon prepared from Chemical activation of sawdust	1-6	95	[36]
Coir fibers	73-444	36.71	[37]
Pine bark waste	55-111	54.68	[38]
Activated carbon derived from wooden Parts of <i>Mangifera Indica</i> by chemical activation with $ZnCl_2$	2-40	82±2.21	[39]
Alkali Treated Coir Fibers	50-300	59.16	[40]
CuO	2-10	98.38	This work

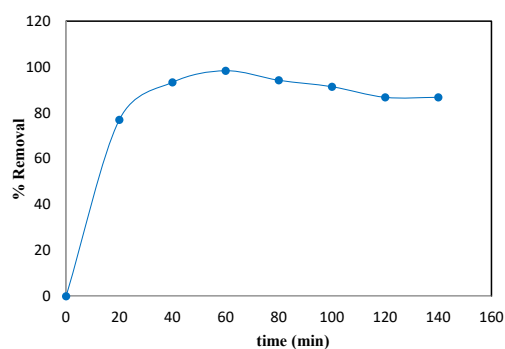


Fig. 4. Effect of contact time for the percentage removal of iron (III) ions by CuO NPs.

the concentration of Fe (III) (2, 4, 6, 8, and 10 ppm).

Increasing the initial concentration of metal ions leads to an increase in the percentage of Fe removal. This phenomenon arises due to the noncompetitive diffusion of heavy metals through the structure of the NPs [48]. Moreover, it is assumed that the concentration gradient acts as a driving force, which enables mass transfer between the adsorbate and adsorbent species by overcoming the resistance [49]. The findings of the present study have been compared with other similar studies, where different types of sportive materials were used for the sequestration of heavy metals by varying doses (Table 2). From this table, it could be seen that the maximum removal efficiency (98.38%) of CuO NPs was comparatively better than the previously reported adsorbents.

Influence of contact time

Fig. 4 indicates the effect of contact time on the removal capacity of iron (III) ions using 0.1 g of the Cu NPs at room temperature and 20 min

of interval. The result revealed that the removal capacity of CuO NPs was remarkably increased with the increasing of time. This is due to the elongated interaction between the Fe(III) ions and the surface of CuO NPs [50, 51]. However, the maximum removal efficiency (98.37%) was observed at 60 min and the percentage removal of metal ions reached equilibrium within 120 minutes. This is principally due to the large surface area of the adsorbent, after which further increase in time resulted in desorption until 120 min. As time is passed, the exhaustion of the adsorbent's active sites will be achieved, thus achieving equilibrium. Furthermore, the rate at which the adsorbate is shipped from the outside to the inside places of the adsorbent particles is responsible for controlling the uptake rate [52].

Influence of dose

The effect of the adsorbent concentration on the removal of iron (III) ions is shown in Fig. 5. When the amount of nano-adsorbent was increased (0.01

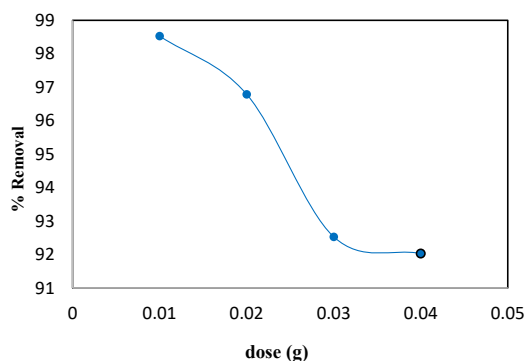


Fig. 5. Effect of adsorbent dose for the percentage removal of iron (III) ions by CuO NPs.

Table 3. mathematical parameters obtained from the isotherm models.

Heavy metal	Adsorbent	Langmuir constant			Freundlich constant		
		B	Q _m	R ²	k	n	R ²
Fe ³⁺	CuO NPs	0.19	3.43	.009	.001	1.70	0.14

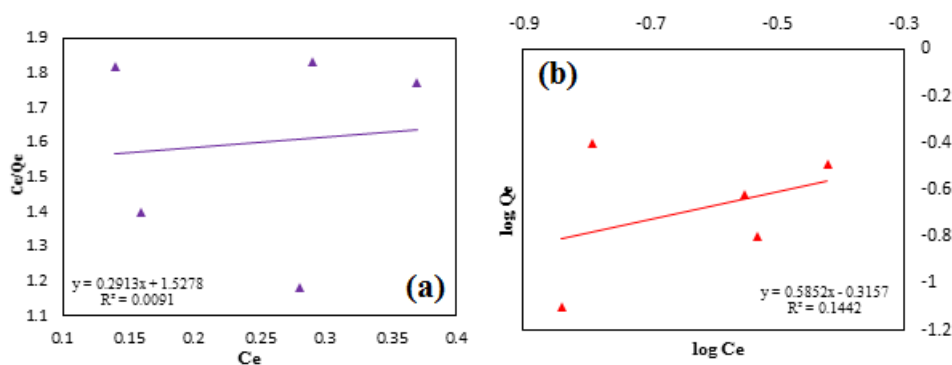


Fig. 6. (a) Langmuir and (b) Freundlich isotherm for adsorption of Iron (III) ions onto CuO NPs.

to 0.04g), the removal capacity started to decrease. This is due to fact that a reduction in the total surface area of the adsorbent available for the metal ion to bind because of aggregation or overlapping of adsorption places [53]. Therefore, the increase of the nano-adsorbent weight is responsible for decreasing the metal removal capacity.

Isotherm Studies

The adsorption equilibrium data of this study were treated with the Langmuir and Freundlich models, which are shown in Table 3 and Fig. 6 (a-b).

The linear regression correlation coefficient ($R^2=0.14$) for all the adsorbents revealed that the adsorption data were partially fitted in the Freundlich model. On the other hand, the linear

regression correlation coefficient ($R^2=0.09$) suggested that the Langmuir model is not supported for this adsorption mechanism. However, the isotherms fit here very little because the adsorption capacity may have been slightly inhibited at the low concentrations range. The value of "n" for the adsorbents was greater than unity (1.0), which revealed that the adsorption of Fe(III) ion onto the surface of CuO NPs was mostly favored by the physical process [42]. This result also suggested that the uptake of metal ions was taken place by the multilayer adsorption on the heterogeneous surface of the adsorbents [54].

CONCLUSIONS

In the present work, CuO NPs were synthesized by the precipitation method, and the obtained

NPs were used to remove iron (III) ions from the aqueous solution. Overall examination of the structure of CuO NPs, it was found that the average particle size was about ~25 nm with a rod-like shape. The optimum conditions for removing iron (III) ions were attained at pH 9, contact time 60 min, and initial metal ion concentration 10 ppm. Also, the maximum removal efficiency (98.38%) was observed at a very low concentration of adsorbents and when the concentration was increased the percentage removal was decreased. Analysis of Langmuir and Freundlich isotherms suggested that the adsorption of Fe (III) ions was partially supported by the Freundlich isotherm. In summary, this study introduces a novel platform for removing iron (III) ions using CuO NPs.

CONFLICT OF INTEREST

The authors affirm that there is no conflict of interest regarding the publication of this manuscript.

REFERENCES

- Fato FP, Li D-W, Zhao L-J, Qiu K, Long Y-T. Simultaneous Removal of Multiple Heavy Metal Ions from River Water Using Ultrafine Mesoporous Magnetite Nanoparticles. *ACS Omega*. 2019;4(4):7543-9.
- Subramaniam MN, Goh PS, Lau WJ, Ismail AF. The Roles of Nanomaterials in Conventional and Emerging Technologies for Heavy Metal Removal: A State-of-the-Art Review. *Nanomaterials*. 2019;9(4).
- Dawodu FA, Akpomie KG. Simultaneous adsorption of Ni(II) and Mn(II) ions from aqueous solution onto a Nigerian kaolinite clay. *J Mater Res Technol*. 2014;3(2):129-41.
- Ahluwalia SS, Goyal D. Microbial and plant derived biomass for removal of heavy metals from wastewater. *Bioresour Technol*. 2007;98(12):2243-57.
- Carolin CF, Kumar PS, Saravanan A, Joshiba GJ, Naushad M. Efficient techniques for the removal of toxic heavy metals from aquatic environment: A review. *J Environ Chem Eng*. 2017;5(3):2782-99.
- Wang S, Shi X. Molecular mechanisms of metal toxicity and carcinogenesis. *Mol Cell Biochem*. 2001;222(1):3-9.
- Mamun KR, Saha NK, Chakrabarty S. A Comparative Study of the Adsorption Capacity of Tea Leaves and Orange Peel for the Removal of Fe (III) Ion from Wastewater. *Journal of Chemical Health Risks*. 2019;9(2):107-15.
- Abdel-Rahman LH, El-Khatib RM, Nassr LAE, Abu-Dief AM. Synthesis, physicochemical studies, embryos toxicity and DNA interaction of some new Iron(II) Schiff base amino acid complexes. *J Mol Struct*. 2013;1040:9-18.
- Simpson SL, Batley GE. Disturbances to metal partitioning during toxicity testing of iron(II)-rich estuarine pore waters and whole sediments. *Environ Toxicol Chem*. 2003;22(2):424-32.
- Halliwell B. Antioxidants in Human Health and Disease. *Annu Rev Nutr*. 1996;16(1):33-50.
- Fu F, Wang Q. Removal of heavy metal ions from wastewater: A review. *J Environ Manage*. 2011;92(3):407-18.
- Lee XJ, Hiew BYZ, Lai KC, Lee LY, Gan S, Thangalazhy-Gopakumar S, et al. Review on graphene and its derivatives: Synthesis methods and potential industrial implementation. *J Taiwan Inst Chem Eng*. 2019;98:163-80.
- Jaishankar M, Tseten T, Anbalagan N, Mathew BB, Beeregowda KN. Toxicity, mechanism and health effects of some heavy metals. *Interdisciplinary Toxicology*. 2014;7(2):60-72.
- Coup MR, Campbell AG. The effect of excessive iron intake upon the health and production of dairy cows. *N Z J Agric Res*. 1964;7(4):624-38.
- Rajput S, Pittman CU, Mohan D. Magnetic magnetite (Fe₃O₄) nanoparticle synthesis and applications for lead (Pb²⁺) and chromium (Cr⁶⁺) removal from water. *J Colloid Interface Sci*. 2016;468:334-46.
- Afkhami A, Conway BE. Investigation of Removal of Cr(VI), Mo(VI), W(VI), V(IV), and V(V) Oxy-ions from Industrial Waste-Waters by Adsorption and Electrosorption at High-Area Carbon Cloth. *J Colloid Interface Sci*. 2002;251(2):248-55.
- Afkhami A, Madrakian T, Amini A, Karimi Z. Effect of the impregnation of carbon cloth with ethylenediaminetetraacetic acid on its adsorption capacity for the adsorption of several metal ions. *J Hazard Mater*. 2008;150(2):408-12.
- Hota G, Kumar BR, Ng WJ, Ramakrishna S. Fabrication and characterization of a boehmite nanoparticle impregnated electrospun fiber membrane for removal of metal ions. *J Mater Sci*. 2008;43(1):212-7.
- Wang J, Chen C. Biosorbents for heavy metals removal and their future. *Biotechnol Adv*. 2009;27(2):195-226.
- Dave PN, Chopda LV. Application of Iron Oxide Nanomaterials for the Removal of Heavy Metals. *Journal of Nanotechnology*. 2014;2014:398569.
- Dil EA, Ghaedi M, Ghaedi AM, Asfaram A, Goudarzi A, Hajati S, et al. Modeling of quaternary dyes adsorption onto ZnO-NR-AC artificial neural network: Analysis by derivative spectrophotometry. *J Ind Eng Chem*. 2016;34:186-97.
- Nekouei F, Nekouei S, Tyagi I, Gupta VK. Kinetic, thermodynamic and isotherm studies for acid blue 129 removal from liquids using copper oxide nanoparticle-modified activated carbon as a novel adsorbent. *J Mol Liq*. 2015;201:124-33.
- Jiang M-q, Wang Q-p, Jin X-y, Chen Z-l. Removal of Pb(II) from aqueous solution using modified and unmodified kaolinite clay. *J Hazard Mater*. 2009;170(1):332-9.
- Munagapati VS, Yarramuthi V, Nadavala SK, Alla SR, Abburi K. Biosorption of Cu(II), Cd(II) and Pb(II) by *Acacia leucocephala* bark powder: Kinetics, equilibrium and thermodynamics. *CHEM ENG J*. 2010;157(2):357-65.
- Kantarli IC, Yanik J. Activated carbon from leather shaving wastes and its application in removal of toxic materials. *J Hazard Mater*. 2010;179(1):348-56.
- Anjum H, Johari K, Gnanasundaram N, Ganesapillai M, Arunagiri A, Regupathi I, et al. A review on adsorptive removal of oil pollutants (BTEX) from wastewater using carbon nanotubes. *J Mol Liq*. 2019;277:1005-25.
- Suhas, Gupta VK, Carrott PJM, Singh R, Chaudhary M, Kushwaha S. Cellulose: A review as natural, modified and activated carbon adsorbent. *Bioresour Technol*. 2016;216:1066-76.
- Burakov AE, Galunin EV, Burakova IV, Kucherova AE, Agarwal S, Tkachev AG, et al. Adsorption of heavy metals on conventional and nanostructured materials for waste-

- water treatment purposes: A review. ECOTOX ENVIRON SAFE. 2018;148:702-12.
29. Ou H-H, Lo S-L. Review of titania nanotubes synthesized via the hydrothermal treatment: Fabrication, modification, and application. *Sep Purif Technol.* 2007;58(1):179-91.
 30. Sheet I, Kabbani A, Holail H. Removal of Heavy Metals Using Nanostructured Graphite Oxide, Silica Nanoparticles and Silica/ Graphite Oxide Composite. *Energy Procedia.* 2014;50:130-8.
 31. Masteri-Farahani M, Ghahremani M. Surface functionalization of graphene oxide and graphene oxide-magnetite nanocomposite with molybdenum-bidentate Schiff base complex. *J Phys Chem Solids.* 2019;130:6-12.
 32. Mahdavi S, Jalali M, Afkhami A, editors. Removal of heavy metals from aqueous solutions using Fe₃O₄, ZnO, and CuO nanoparticles. *Nanotechnology for Sustainable Development*; 2014 2014//; Cham: Springer International Publishing.
 33. Taman R, Ossman M, Mansour M, Farag H. Metal oxide nanoparticles as an adsorbent for removal of heavy metals. *J Adv Chem Eng.* 2015;5(3):1-8.
 34. Hassan KH, Mahdi ER. Synthesis and characterization of copper, iron oxide nanoparticles used to remove lead from aqueous solution. *Asian journal of applied sciences.* 2016;4(3).
 35. Nassar MM, Ewida KT, Ebrahiem EE, Magdy YH, Mheaedi MH. Adsorption of Iron and Manganese Using Low Cost Materials as Adsorbents. *Journal of Environmental Science and Health, Part A.* 2004;39(2):421-34.
 36. El-Sherif I, Fathy N, Hanna AA. Removal of Mn (II) and Fe (II) ions from aqueous solution using precipitation and adsorption methods. *Journal of Applied Sciences Research.* 2013;9(1):233-9.
 37. Shukla SR, Pai RS, Shendarkar AD. Adsorption of Ni(II), Zn(II) and Fe(II) on modified coir fibres. *Sep Purif Technol.* 2006;47(3):141-7.
 38. Acemioğlu B. Removal of Fe(II) ions from aqueous solution by Calabrian pine bark wastes. *Bioresour Technol.* 2004;93(1):99-102.
 39. Duru CE, Duru IA. Studies of sorbent efficiencies of maize parts in Fe (II) removal from aqueous solutions. *ILCPA.* 2017;72:1-8.
 40. Shukla PM, Shukla SR. Biosorption of Cu(II), Pb(II), Ni(II), and Fe(II) on Alkali Treated Coir Fibers. *Sep Sci Technol.* 2013;48(3):421-8.
 41. Phiw dang K, Suphankij S, Mekprasart W, Pecharapa W. Synthesis of CuO Nanoparticles by Precipitation Method Using Different Precursors. *Energy Procedia.* 2013;34:740-5.
 42. Zayyoun N, Bahmad L, Laánab L, Jaber B. The effect of pH on the synthesis of stable Cu₂O/CuO nanoparticles by sol-gel method in a glycolic medium. *Appl Phys A.* 2016;122(5):488.
 43. Langmuir I. THE CONSTITUTION AND FUNDAMENTAL PROPERTIES OF SOLIDS AND LIQUIDS. PART I. SOLIDS. *J Am Chem Soc.* 1916;38(11):2221-95.
 44. Freundlich H. Über die adsorption in losungen, zeitschrift für physikalische chemie. *Z Phys Chem.* 1906;62(5):121-5.
 45. Manyasree D, Peddi KM, Ravikumar R. CuO nanoparticles: synthesis, characterization and their bactericidal efficacy. *Int J Appl Pharmaceut.* 2017;9(6):71-4.
 46. Yang L, Chen Z, Cui D, Luo X, Liang B, Yang L, et al. Ultrafine palladium nanoparticles supported on 3D self-supported Ni foam for cathodic dechlorination of florfenicol. *CHEM ENG J.* 2019;359:894-901.
 47. Imamoglu M, Tekir O. Removal of copper (II) and lead (II) ions from aqueous solutions by adsorption on activated carbon from a new precursor hazelnut husks. *DESALINATION.* 2008;228(1):108-13.
 48. Almomani F, Bhosale R, Khraisheh M, kumar A, Almomani T. Heavy metal ions removal from industrial wastewater using magnetic nanoparticles (MNP). *Appl Surf Sci.* 2020;506:144924.
 49. Das B, Mondal N. Calcareous Soil as a New Adsorbent to Remove Lead from Aqueous Solution: Equilibrium, Kinetic and Thermodynamic Study. *Universal Journal of Environmental Research & Technology.* 2011;1(4).
 50. Bernard E, Jimoh A. Adsorption of Pb, Fe, Cu and Zn from industrial electroplating wastewater by orange peel activated carbon. *International Journal of Engineering and Applied Sciences.* 2013;4(2):95-103.
 51. Bernard E, Jimoh A, Odigire J. Heavy metals removal from industrial wastewater by activated carbon prepared from coconut shell. *Research Journal of Chemical Sciences ISSN.* 2013;2231:606X.
 52. Verma A, Chakraborty S, Basu JK. Adsorption study of hexavalent chromium using tamarind hull-based adsorbents. *Sep Purif Technol.* 2006;50(3):336-41.
 53. Barka N, Abdennouri M, El Makhfouk M, Qourzal S. Biosorption characteristics of cadmium and lead onto eco-friendly dried cactus (*Opuntia ficus indica*) cladodes. *J Environ Chem Eng.* 2013;1(3):144-9.
 54. El-Hendawy A-NA. Surface and adsorptive properties of carbons prepared from biomass. *Appl Surf Sci.* 2005;252(2):287-95.