Bimetallic ZnO/CuO and MnO/CuO Nanoparticles as Sustainable Adsorbents for Heavy Metal Removal

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Introduction

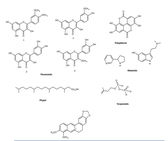
Water pollution, driven by industrial and human activities, has become a pressing global issue especially in developing nations where waste management systems are often inadequate. The discharge of pollutants into water bodies not only threatens human health but also disrupts ecological balance. Conventional treatment methods are often ineffective against persistent contaminants, thus highlighting the need for innovative approaches in nanotechnology as a cutting-edge solution for water purification.

Nanoscience focuses on the manipulation of matter at the nanoscale (1–100 nm), producing materials with novel and enhanced properties (Bayda *et al.*, 2020). Green synthesis of nanoparticles using plant or microorganism-based extracts has gained popularity as an eco-friendly alternative to traditional chemical methods.

This approach leverages phytochemicals like flavonoids, alkaloids, and phenolic acids found in plants to reduce metal ions into nanoparticles (Patil *et al.*, 2022; Ejidike *et al.*, 2023).

Although, monometallic nanoparticles have been extensively studied for their ability to remove both organic and inorganic contaminants however, bimetallic nanoparticles have demonstrated an improved catalytic activity for pollutant reduction as a result of their synergistic effect.

In order to contribute to sustainable wastewater treatment and expand the application of green nanotechnology, we report the synthesis of ZnO/CuO and MnO/CuO bimetallic nanoparticles using *Anacardium occidentale* leaves extract evaluating their structural, morphological, and adsorptive characteristics in removing Cd^{2+}, Fe^{3+}, and Cr^{3+} ions from aqueous solutions under varying physicochemical conditions and analyzing their adsorptive mechanisms through isotherm and kinetic models and also determining the thermodynamic feasibility of the adsorption process.



Phytochemicals in *Anacacardium occidentale* leaves extract

Preparation *of Anacardium occidentale* leaves extract

10g of properly washed, dried and grounded *Anacardium occidentale* leaves powder was boiled in 200 mL of distilled water at 80 °C for one hour, cooled, and filtered. The filtrate served as a natural reducing and stabilizing agent.

Synthesis of ZnO/CuO and MnO/CuO Nanoparticles

ZnO/CuO nanoparticles were synthesized by adding 20 mL of the leaves extract to 80 mL of mixed metal salt solution containing zinc nitrate and copper sulfate (2:8 molar ratio). The mixture was heated at 80 °C under continuous stirring for one hour, and NaOH (0.1 M) was added dropwise until precipitation occurred. The mixture was aged for 24 hours, washed with distilled water, and oven-dried at 80°C to obtain nanopowder. MnO/CuO nanoparticles were synthesized similarly, substituting manganese sulfate for zinc nitrate(Farjana *et al.* (2022)

Characterization of the synthesized ZnO/CuO and MnO/CuO Nanoparticles

UV–vis analysis of extract and synthesized ZnO/CuO and MnO/CuO NPs

The UV-Visible spectrophometric analysis was used to determine the optical property of the extract and the synthesized adsorbents. The UV-Visible spectrophometric analysis of *Anacardium occidentale* leave extract showed in fig.1 recorded highest absorbance at peak 300nm. This is considered to be due to the surface Plasmon vibration and excitation of the bio reduction and capping agent (phytochemicals) present in the leaf extract.

ZnO/CuO nanoparticles were synthesized by adding 20 mL of the leaf extract to 80 mL of mixed meta l salt solution containing zinc nitrate and copper sulfate (2:8 molar ratio). The mixture was heated at 80 °C under continuous stirring for one hour, and NaOH (0.1 M) was added dropwise until precipitation occurred. The mixture was aged for 24 hours, washed with distilled water, and oven-dried at 80°C to obtain nanopowder. MnO/CuO nanoparticles were synthesized similarly, substituting manganese sulfate for zinc nitrate(Farjana *et al*. 2022) .

FTIR Spectroscopy extract and synthesized ZnO/CuO and MnO/CuO NPs

The FTIR results for the prepared extract show several peaks at 3330 cm^{-1}, 1636 cm^{-1}, and 1222 cm^{-1}. The peak at 3330 cm^{-1} represents an OH stretching vibration due to alcohol, 1636 cm^{-1} indicates C=C weak vibration alkenes due to the secondary metabolites' aromatic ring, and 1222 cm^{-1} is for the C-N aliphatic amines and C-O-C strong stretching vibration (Titus *et al.*, 2021). Futhermore, FTIR results for synthesized ZnO/CuO and MnO/CuO NPs displayed several peaks at 3893 cm^{-1}, 3424 cm^{-1}, 2726 cm^{-1}, 2326 cm^{-1}, 1871 cm^{-1}, 1560 cm^{-1}, 1364, 1110 cm^{-1}, and 872 cm^{-1}. The peaks at 3893 cm^{-1} and 3424 cm^{-1} represent O-H stretches due to free hydroxyl alcohol and phenols; 2726 cm^{-1} and 2326 cm^{-1} are due to H-C=O aldehydes; 1871 cm^{-1} is due to C=C triple bond alkynes in the secondary metabolites; 1560 cm^{-1} and 1364 cm^{-1} indicate C-H bends and C-H rocks in aliphatic alkanes; 1110 cm^{-1} is due to C-H alkanes; and 872 cm^{-1} is due to C-Br alkyl halides (Ali et al., 2020).

SEM ANALYSIS.

Samples	Morphology
ZnO/CuO	Irregular granular -shape morphology that are partially spherical with well compacted arrangement.
MnO/ZnO	Partially spherical mono dispersed morphology with closed compact arrangement at higher magnification.

X-RAY DIFFRACTION (XRD) ANALYSIS .

Samples	Bragg's angle	Plane of symmetry	Structure	Parti(cle size
ZnO/CuO	23.79-50.40°	111 ,211,321,310	FCC	39.60nm
MnO/ZnO	14.52-48.59°	301	FCC	55.14nm

X-RAY FLUORESCENCE (XRF) ANALYSIS

	Composition	ZnO	SiO_2	Nb_2O_5	SO_3	Al_2O_3	ZrO_2	Fe_2O_3	CuO
ZnO/CuO	Weight percentage	18.04	2.54	1.68	1.15	0.82	1.36	0.07	36.98
	Composition	MnO	SiO_2	Nb_2O_5	SO_3	Al_2O_3	ZrO_2	Fe_2O_3	CuO
MnO/CuO	Weight percentage	52.72	1.18	0.55	1.23	0.49	0.19	0.25	13.14

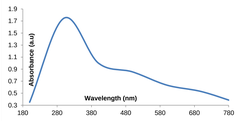


Fig.1 UV-Visible spectra for Extract

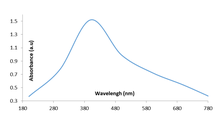


Fig.2. UV-Visible spectra for ZnO/CuO NPs

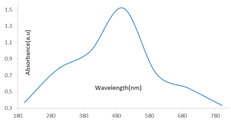


Fig.3 UV-Visible spectra for MnO/CuO NPs

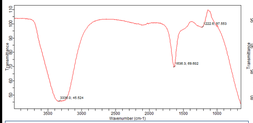


Fig.4 FTIR spectra spectra for Extract

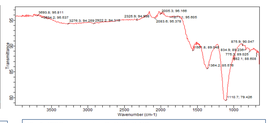


Fig 5. FTIR spectra for ZnO/CuO NPs

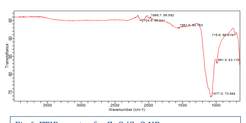


Fig 6. FTIR spectra for ZnO/CuO NPs

Summary of Adsorption Studies

Batch adsorption experiments were conducted using 100 mL of metal ion solutions (Cd^{2+}, Fe^{3+}, and Cr^{3+}) with concentrations of 10–30 mg/L. Variables such as pH (2–10), contact time (10–50 min), adsorbent dose (0.1–0.5 g), and temperature (25–60°C) were optimized. Metal ion concentrations were determined using Atomic Absorption Spectrophotometry (AAS).

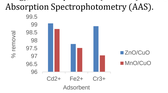


Fig.7. Effects of initial Conc.

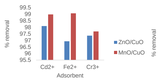


Fig.8. Effects of dosage

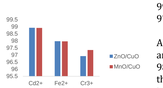


Fig.9. Effects of contact time

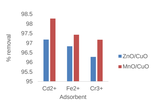


Fig.10. Effects of Temperature.

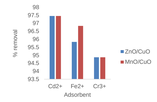


Fig.11. Effects of pH

The percentage removal for Cd^{2+}, Fe^{3+}, and Cr^{3+} decreases with an increase in concentration of the adsorbate from 10ppm to 30ppm with the highest percentage removal at 99.08%, 97.77% and 98.90% by ZnO/CuO NPs and 98.72%, 97.52% and 97.05% at 10ppm for the metal ions respectively.

At 0.4g dosage, the optimum percentage removal of Cd^{2+}, Fe^{3+} and Cr^{3+} by ZnO /CuONPs; 98.09%, 96.93%, 97.33% and 98.98%, 99.06%, 97.68% by MnO/CuONPs for the removal of the metal ions indicating an increase in removal as the dosage increases.

Similarly, there is an increase in percentage removal with increase in contact time. At optimum time of 40min,, highest removal efficiency was attained at 98.92% , 97.97% , 96.92% by ZnO/CuO NPs and 98.91%, 97.96% and 97.35% by MnO/CuO. for the removal Cd^{2+}, Fe^{3+} and Cr^{3+}

The percentage removal increases with an increase in temperature. At optimum temperature of 55°C, 97.18%, 96.83%, 96.28% and 98.27%, , 97.43%, 97.17% was obtained for the removal of Cd^{2+}, Fe^{3+} and Cr^{3+} by ZnO/CuO NPs and by MnO/CuONPs respectively.

The Percentage removal increases with an increase in pH up to the optimum at pH 6 highest percentage removal was attained at 97.45% , 95.83%, for the removal of Cd^{2+}, Fe^{3+} , 94.87% for the removal of Cr^{3+} at pH 8 by ZnO/CuO NPs and 98.91% , 96.83% , 97.35% by MnO/CuO. For the removal of Cd^{2+}, Fe^{3+} and Cr^{3+} respectively.

THE ISOTHERM PARAMETERS OF NANOPARTICLES

Table1. ISOTHERM PARAMETERS (ZnO/CuO)

THE ISOTHERM PARAMETERS (ZnO/CuO)		Cd^{2+}	Fe^{3+}	Cr^{3+}
Langmuir	R^2	0.9479	0.9775	0.9456
	Q_m	3.4566	4.6382	3.3738
	K_L	5.8209	1.5646	5.0667
Freundlich	R^2	0.9925	0.9889	0.9968
	1/n	0.4206	0.5713	0.4047
	K_f	3.2908	2.8563	2.9587

Table2. ISOTHERM PARAMETERS (MnO/CuO)

THE ISOTHERM PARAMETERS (MnO/CuO)		Cd^{2+}	Fe^{3+}	Cr^{3+}
Langmuir	R^2	0.9973	0.9926	0.9944
	Q_m	6.8306	3.6590	5.0226
	K_L	0.6259	2.8768	0.5694
Freundlich	R^2	0.9912	0.9923	0.9975
	1/n	0.5165	0.5743	0.6471
	K_f	2.1130	0.6471	0.9975

The Freundlich isotherm showed a good fit for the adsorption of Cd^{2+}, Fe^{3+} and Cr^{3+} by ZnO/CuO NPs and the adsorption Cr^{3+} by MnO/CuO NPs while the Langmuir isotherm showed a good for for the adsorption Cd^{2+}, Fe^{3+} due to higher correlation value.

PSEUDO-FIRST AND SECOND ORDER KINETICS

KINETIC PARAMETER OF VARIOUS ADSORBATES (ZnO/CuO)		Cd^{2+}	Fe^{3+}	Cr^{3+}
Pseudo-first order	K_1	0.0209	0.0287	0.0240
	q_e	0.0044	0.0016	0.0038
	R^2	0.8390	0.8578	0.7964
Pseudo-second order	K_2	1.9212	2.6261	1.8508
	q_e	1.2511	1.2352	1.2252
	R^2	1	1	0.9999

Table3. KINETIC PARAMETER OF VARIOUS ADSORBATES (ZnO/CuO)

KINETIC PARAMETER OF VARIOUS ADSORBATES (MnO/CuO)		Cd^{2+}	Fe^{3+}	Cr^{3+}
Pseudo-first order	K_1	0.0159	0.0210	0.0058
	q_e	0.0017	0.0022	0.0039
	R^2	0.8197	0.8549	0.6907
Pseudo-second order	K_2	4.1580	2.5233	5.0531
	q_e	1.2441	1.1148	1.2214
	R^2	0.9999	0.9994	1

Table4. KINETIC PARAMETER OF VARIOUS ADSORBATES (MnO/CuO)

The kinetics studies indicate that the adsorption process of the synthesized metal oxide NPs followed the pseudo-second-order model due to higher correlation coefficient (R^2) value for the adsorption of all metal ions indicating that the adsorption was majorly dominated by chemisorption behavior and their rapid uptake unto the adsorbents.

THERMODYNAMIC STUDIES

		$\Delta G°$ at 25° C (kJ.mol^{-1})	$\Delta H°$ (kJ.mol^{-1})	$\Delta S°$ (kJ.mol^{-1}.K^{-1})
ZnO/CuO	Cd^{2+}	-2.4345	20.3485	0.0765
	Fe^{3+}	-2.1252	14.8563	0.0570
	Cr^{3+}	-1.9056	12.5691	0.0486
MnO/CuO	Cd^{2+}	-3.7092	11.8940	0.0524
	Fe^{3+}	-2.8482	11.5797	0.0484
	Cr^{3+}	-2.2356	16.7419	0.0637

Negative -ΔG (KJ/mol) obtained implies that the process is feasible and spontaneous while the positive value of ΔS indicates an increase in the degree of randomness at the solid solution interface during the adsorption of ΔH suggests the endothermic nature of the adsorption anof the metals (Cd^{2+}, Fe^{3+}, and Cr^{3+}) using ZnO/CuO and MnO/CuO. The positive value d a possible bond that occurs between the adsorbates and the adsorbents.

Conclusions

The removal efficiency for all synthesized adsorbent was determined and found to be effective for the removal of the studied metals in aqueous medium as enhanced by their surface reactivity and redox properties.

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