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ADVANCED MAGNETIC FERRITE NANO ADSORBENT FOR COPPER (II) REMOVAL: ROLE OF LANTHANUM DOPING

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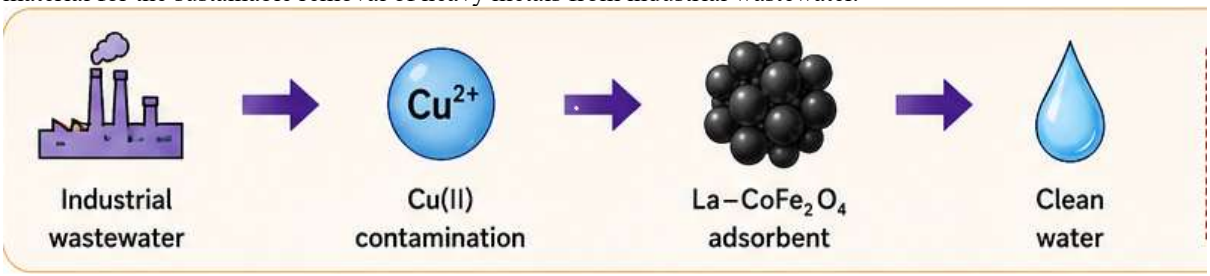
ABSTRACT

The adsorption behaviour of copper(II) ions on lanthanum-doped cobalt ferrite (La–$CoFe_2O_4$) nanoparticles in acidic and basic aqueous media. The adsorbent was synthesized using an appropriate chemical method and characterized by techniques such as X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDS), and Brunauer–Emmett–Teller (BET) surface area analysis to confirm its crystal structure, morphology, elemental composition, and surface characteristics. Batch adsorption experiments were carried out to evaluate the effects of solution pH, contact time, initial copper ion concentration, adsorbent dosage, and temperature on the adsorption efficiency. The adsorption experiments were conducted to evaluate the influence of solution pH, contact time, adsorbent dosage, initial copper ion concentration, and temperature on the adsorption process. The adsorption efficiency was strongly dependent on the pH of the solution. Under acidic conditions, the adsorption of Cu(II) ions was suppressed due to protonation of the adsorbent surface and competition from hydrogen ions for active adsorption sites. In contrast, adsorption was significantly enhanced in basic medium because of increased surface deprotonation and stronger electrostatic interactions between Cu(II) ions and the negatively charged adsorbent surface. Equilibrium data were found to fit the Langmuir adsorption isotherm, indicating monolayer adsorption, while the kinetic results were consistent with the pseudo-second-order model, suggesting that chemical interactions play a significant role in the adsorption mechanism. The magnetic nature of the adsorbent enabled rapid separation from the treated solution without secondary pollution. The findings demonstrate that lanthanum doping effectively improves the adsorption performance of cobalt ferrite toward copper ions, particularly under alkaline conditions. Owing to its high adsorption efficiency, reusability, and ease of magnetic recovery, lanthanum-doped cobalt ferrite is a promising material for the sustainable removal of heavy metals from industrial wastewater.



INTRODUCTION

Water pollution caused by heavy metals has become one of the most serious environmental concerns worldwide due to rapid industrialization and urbanization. Heavy metals are non-biodegradable, persistent, and tend to accumulate in living organisms through the food chain, resulting in severe ecological and health hazards. Among these pollutants, copper (Cu^{2+}) is widely released into the environment from electroplating, mining, metal finishing, battery manufacturing, fertilizer production, pesticides, pigments, and printed circuit board industries. Although copper is an essential micronutrient required for various biological functions, excessive exposure can lead to liver and kidney damage, gastrointestinal disorders, neurological abnormalities, and adverse effects on aquatic ecosystems (Fu and Wang, 2011). The World Health Organization (WHO) has established a guideline value of **2.0 mg L^{-1}** for copper in drinking water to minimize health risks [1]. Numerous technologies have been employed for the removal of heavy metals from wastewater, including chemical precipitation, ion exchange, membrane filtration, electrochemical treatment, solvent extraction, coagulation-flocculation, and adsorption. Among these techniques, adsorption is considered one of the most efficient and economical methods because of its simplicity, high removal efficiency, low operating cost, and ability to remove metal ions even at low concentrations. Furthermore, adsorption produces minimal secondary pollutants and allows regeneration and reuse of the adsorbent [2]. In recent years, magnetic nanomaterials have attracted considerable attention as advanced adsorbents owing to their high specific surface area, abundant active adsorption sites, excellent chemical stability, and ease of magnetic separation from aqueous media. Among these materials, spinel ferrites (MFe_2O_4,

where M = Co, Ni, Zn, Mn, etc.) have emerged as promising candidates for wastewater treatment because of their remarkable magnetic properties and environmental stability. Cobalt ferrite ($CoFe_2O_4$), in particular, exhibits high coercivity, excellent mechanical hardness, chemical resistance, thermal stability, and moderate saturation magnetization, making it an attractive magnetic adsorbent for environmental remediation. After adsorption, cobalt ferrite nanoparticles can be rapidly separated using an external magnetic field, thereby eliminating the need for filtration or centrifugation and reducing operational costs [3]. The adsorption performance of cobalt ferrite can be significantly improved through rare-earth metal doping. Lanthanum (La^{3+}), owing to its larger ionic radius and unique electronic configuration, modifies the crystal lattice, particle size, magnetic behavior, surface defects, and porosity of cobalt ferrite nanoparticles. Incorporation of lanthanum into the spinel structure increases the specific surface area and generates additional active adsorption sites, thereby enhancing the adsorption capacity toward heavy metal ions. Lanthanum substitution also induces lattice distortion and changes the cation distribution within the spinel structure, which can improve both adsorption performance and magnetic recoverability. Studies have shown that the BET surface area of lanthanum-doped cobalt ferrite increases significantly with increasing lanthanum content, thereby providing more accessible adsorption sites for contaminant removal [4]. The adsorption of Cu^{2+} ions onto lanthanum-doped cobalt ferrite nanoparticles generally involves multiple mechanisms, including electrostatic attraction, surface complexation, ion exchange, and chemisorption. The adsorption efficiency depends on several experimental parameters such as solution pH, contact time, initial copper concentration, adsorbent dosage, temperature, and ionic strength. The equilibrium behavior is commonly described using Langmuir and Freundlich adsorption isotherms, while adsorption kinetics are analyzed using pseudo-first-order, pseudo-second-order, and intraparticle diffusion models. Thermodynamic investigations further provide insight into the spontaneity, feasibility, and nature of the adsorption process. Recent studies on ferrite-based magnetic adsorbents have demonstrated that copper adsorption is frequently well described by the Langmuir isotherm and pseudo-second-order kinetic model, indicating predominantly monolayer adsorption controlled by chemisorption[5]. Compared with conventional adsorbents such as activated carbon, natural clays, and polymeric resins, lanthanum-doped cobalt ferrite nanoparticles offer several advantages, including high adsorption capacity, excellent structural stability, rapid magnetic separation, easy regeneration, and multiple reuse cycles. These characteristics make them promising materials for sustainable wastewater treatment and environmental remediation. In addition, lanthanum-based materials have demonstrated excellent affinity toward various inorganic contaminants because of their high surface reactivity and strong interaction with metal ions [6]. The present study focuses on the synthesis and characterization of lanthanum-doped cobalt ferrite nanoparticles and evaluates their adsorption performance for the removal of Cu^{2+} ions from aqueous solution. The influence of adsorption parameters including pH, contact time, adsorbent dosage, and initial copper concentration is systematically investigated. Adsorption equilibrium, kinetics, and thermodynamic models are employed to elucidate the adsorption mechanism and evaluate the applicability of lanthanum-doped cobalt ferrite as an efficient, magnetically recoverable adsorbent for copper removal from contaminated water.

MATERIAL AND METHODS

Cobalt nitrate hexahydrate ($Co(NO_3)_2 \cdot 6H_2O$), ferric nitrate nonahydrate ($Fe(NO_3)_3 \cdot 9H_2O$), lanthanum nitrate hexahydrate ($La(NO_3)_3 \cdot 6H_2O$), sodium hydroxide (NaOH), copper sulfate pentahydrate ($CuSO_4 \cdot 5H_2O$), hydrochloric acid (HCl), and sodium hydroxide (NaOH) were of analytical grade and used without further purification. Deionized water was used throughout the experiments.

1.Preperation: Cobalt ferrite and lanthanum doped cobalt ferrite are prepared by sol-gel method. The characterization is done XRD, SEM, FTIR, SEM-EDX were done to confirm the structure. The crystal structure of the synthesized nanoparticles was characterized by X-ray diffraction (XRD) using Cu-Kα radiation ($\lambda = 1.5406$ Å) over a 2θ range of 20–80°. Functional groups and metal–oxygen vibrations were identified using Fourier Transform Infrared Spectroscopy (FTIR) in the range 400–4000 cm^{-1}. The morphology and particle size were examined using Scanning Electron Microscopy (SEM), while Energy Dispersive X-ray Spectroscopy (EDS) was employed to determine the elemental composition.

2. Adsorption of metal: Standard copper sulphate was prepared and adsorption were taken firstly by charcoal. Then the prepared ferrites were added 0.1 gram and adsorption were recorded on SHIMADZU UV Spectrophotometer, UV-1800 at different time interval. The medium that is acidic and basic is maintain by HCl and KOH.

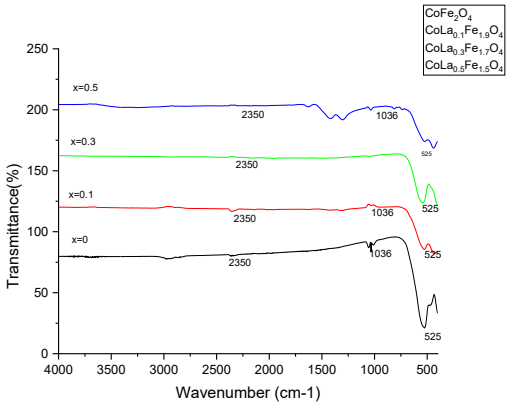
DISCUSSION

The FTIR spectra of $CoFe_2O_4$ and La-doped $CoFe_2O_4$ nanoparticles exhibit the characteristic absorption band at approximately 525 cm^{-1}, corresponding to the stretching vibration of metal–oxygen bonds in the tetrahedral sites of the spinel ferrite lattice. The persistence of this band in all La-substituted samples confirms that the spinel structure remains intact after lanthanum incorporation. A slight shift and broadening of the absorption band with increasing La concentration indicate lattice distortion caused by the larger ionic radius of La^{3+} compared to Fe^{3+}. Weak absorption bands around 1035–1085 cm^{-1}, 2350 cm^{-1}, and 3400–3600 cm^{-1} are assigned to residual carbonate/nitrate species, atmospheric CO_2, and surface hydroxyl groups, respectively. Overall, the FTIR results confirm the successful formation of phase-pure La-doped cobalt ferrite nanoparticles with preserved spinel structure. Fig. 1

The XRD patterns of pure $CoFe_2O_4$ and La-doped $CoFe_2O_4$ nanoparticles exhibit well-defined diffraction peaks corresponding to the (220), (311), (400), (422), (511), and (440) crystallographic planes of the cubic spinel ferrite structure. The dominant (311) reflection confirms the formation of highly crystalline cobalt ferrite. No additional diffraction peaks associated with secondary phases such as La_2O_3, Fe_2O_3, or CoO are evident, indicating successful incorporation of La^{3+} ions into the spinel lattice. A slight shift of the diffraction peaks toward lower diffraction angles and modest peak broadening with increasing La content indicate lattice expansion and enhanced micro strain resulting from the larger ionic radius of La^{3+} relative to Fe^{3+}. These observations confirm that lanthanum substitution modifies the crystal lattice without disrupting the spinel framework. fig 2

SEM micrographs of pure and La-doped $CoFe_2O_4$ nanoparticles reveal irregular, nearly spherical particles with pronounced agglomeration. The observed agglomeration is attributed to the magnetic nature and high surface energy of cobalt ferrite nanoparticles. The pure $CoFe_2O_4$ sample consists of loosely packed nanoparticle clusters with rough surfaces. Upon La substitution, the morphology remains largely unchanged; however, particle aggregation and cluster size increase gradually with increasing La concentration. The $CoLa_{0.3}Fe_{1.7}O_4$ sample exhibits relatively uniform particle distribution and an interconnected porous structure, while $CoLa_{0.5}Fe_{1.5}O_4$ forms denser aggregates with visible interparticle voids. The rough and porous morphology of all samples is advantageous for adsorption applications because it provides a high density of accessible surface-active sites and facilitates the diffusion of Cu^{2+} ions to the adsorbent surface. Fig 3

The EDS spectra confirm the successful synthesis of pure and La-doped cobalt ferrite nanoparticles. Pure $CoFe_2O_4$ contains only Co, Fe, and O, while the La-doped samples additionally exhibit characteristic La peaks whose intensity increases with increasing La concentration. The absence of impurity elements demonstrates the high purity of the synthesized materials. The progressive increase in La signal and corresponding decrease in Fe signal support the substitution of Fe^{3+} by La^{3+} ions in the spinel ferrite lattice. Fig 4



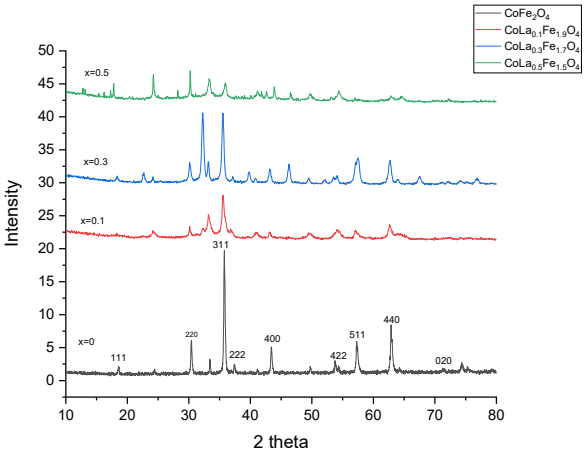


Fig. 1: FTIR Spectrum of $CoLa_xFe_{2-X}O_4$ (x=0,0.1,0.3,0.5)

Fig-2: XRD Pattern obtained for CoLaxFe2-Xo4 (x=0.1,0.3,0.5)

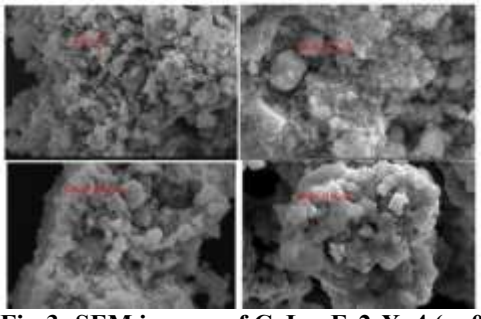


Fig-3: SEM images of CoLaxFe2-Xo4 (x=0,0.1,0.3,0.5)

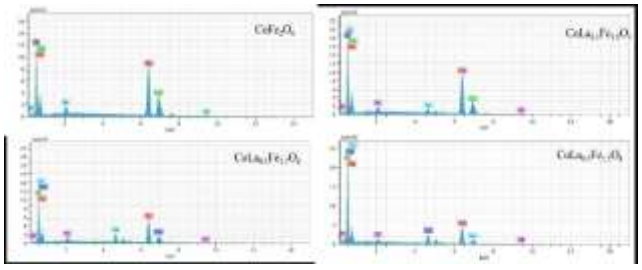


Fig.-4: EDX of CoLaxFe2-Xo4 (x=0,0.1,0.3,0.5)

Adsorption study

The incorporation of La^{3+} ions into cobalt ferrite appears to enhance the stability of adsorption performance. The larger ionic radius of La^{3+} introduces lattice distortion and may increase the number of surface defects and active adsorption sites, resulting in more consistent adsorption over varying experimental conditions. In contrast, pure $CoFe_2O_4$ exhibits lower adsorption capacity under most conditions, while charcoal demonstrates high adsorption only under specific conditions and shows large fluctuations. The relatively stable behavior of $LaCoFe_2O_4$ suggests that it is a more reliable adsorbent for Cu^{2+} removal from aqueous solutions. Figure 5

The adsorption efficiency of Cu^{2+} ions under basic conditions is strongly influenced by contact time and the nature of the adsorbent. Although charcoal exhibits rapid initial adsorption, its efficiency decreases significantly with time. Pure $CoFe_2O_4$ shows moderate adsorption with gradual improvement. In contrast, La-doped $CoFe_2O_4$ exhibits a continuous increase in adsorption efficiency and achieves the highest adsorption (≈18%) after 30 min,

demonstrating that lanthanum incorporation enhances the adsorption capacity and stability of cobalt ferrite. These results suggest that $LaCoFe_2O_4$ is a more effective and promising magnetic adsorbent for the removal of Cu(II) ions from alkaline wastewater due to its improved adsorption performance, chemical stability, and ease of magnetic separation. Figure 6

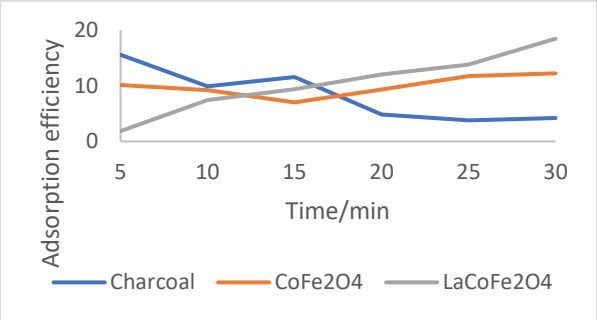


Fig.5 Adsorption Copper in Acidic medium medium

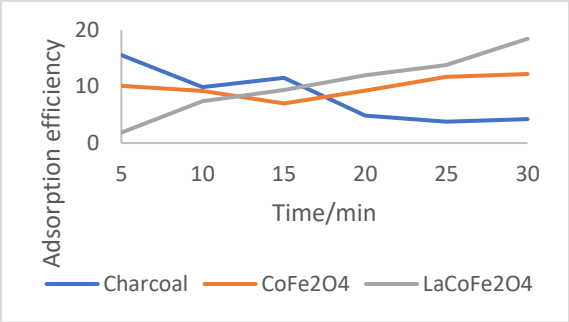


Fig.6 Adsorption of copper in basic

CONCLUSION

The comparative adsorption study clearly demonstrates that solution pH, contact time, and adsorbent composition play significant roles in the removal of Cu^{2+} ions from aqueous solutions. Adsorption was considerably higher in the basic medium than in the acidic medium because deprotonation of the adsorbent surface enhanced the electrostatic attraction between Cu^{2+} ions and the negatively charged adsorption sites. Increasing the contact time improved adsorption until equilibrium was reached, with 30 min providing the highest adsorption efficiency. Lanthanum (La^{3+}) doping modifies the crystal lattice of cobalt ferrite by introducing lattice defects and increasing the number of surface-active sites. These structural modifications enhance the adsorption of Cu^{2+} ions by improving electrostatic attraction and surface complexation. In addition, the magnetic nature of $LaCoFe_2O_4$ allows rapid and simple separation of the adsorbent from the treated solution using an external magnetic field, making it suitable for practical wastewater treatment.

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