

Functionalization of L-Cystein On Magnetite As Magnetic Adsorbent Metals for SDG 14

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ABSTRACT

Objective: The increasing consumption of gold (Au) in the electronics, catalysis, and medical sectors has led to the depletion of primary ore resources while increasing the accumulation of electronic waste (e-waste) which reaches 62 million tons per year globally. Therefore, the development of selective, efficient, and environmentally friendly Au(III) recovery technology from secondary sources is very urgent. This study aims to synthesize and characterize magnetic adsorbents based on magnetite (Fe₃O₄@Cys) functionalized with L-Cysteine (Fe₃O₄@Cys) and evaluate its performance in the recovery of Au(III) ions from aqueous solutions. **Method:** L-Cysteine was chosen because it contains a thiol group (-SH) which has a high affinity for Au(III) based on the hard-soft acid-base (HSAB) theory. The synthesis was conducted through silica coating followed by L-cysteine immobilization using GPTMS as a coupling agent. **Results:** FTIR analysis confirmed the presence of Fe-O, Si-O-Si, and Si-OH groups, indicating successful functionalization. XRD results showed that the magnetite crystal structure was retained after modification, with a crystallite size of 16.43 nm and the presence of amorphous silica. **Novelty:** The synthesized Fe₃O₄@Cys exhibited good acid stability, demonstrating its potential as a selective magnetic adsorbent for Au(III) recovery from secondary resources.

INTRODUCTION

The demand for gold (Au) has increased significantly in recent decades, driven by its widespread use in the electronics industry, catalysis, dentistry, and as a financial investment (Lu et al., 2020; Shukla et al., 2023; Zhou et al., 2021). However, the scarcity of natural resources and the depletion of high-grade gold ore reserves have prompted the need to explore alternative sources, such as mining tailings and electronic waste (e-waste) (Hut et al., 2023; Lahtinen et al., 2017; Neag et al., 2020; Rao et al., 2020; UNITAR, 2024). It is estimated that one ton of used mobile phones contains approximately 340 grams of gold, which is a much higher grade compared to primary ores (Gómez et al., 2023; Kubota et al., 2019). Therefore, the development of efficient and environmentally friendly technologies for the recovery of Au(III) from these secondary sources is crucial.

Various methods have been developed for gold recovery, including chemical precipitation, solvent extraction, ion exchange, and adsorption (Kim et al., 2024; Perez et al., 2019; Yang et al., 2024). Among these methods, adsorption is considered the most promising approach due to its relatively low operational costs, simple process design, and effectiveness at low metal concentrations (Chen et al., 2022; Chillè et al., 2022; Liu et al., 2022). A number of adsorbent materials have been explored, such as activated carbon, resins, biomass, and metal organic frameworks (MOFs) (Chen et al., 2023; Sheraz et al., 2024; Wang et al., 2023). However, the main challenges often encountered are the low selectivity toward Au (III) in the presence of other interfering metal ions (such as Cu (II), Zn (II), and Ni (II)), as well as the difficulty in separating the adsorbent

from the solution after the adsorption process (Aghei et al., 2017; Hastuti et al., 2024; Huang et al., 2020).

To overcome these separation challenges, the development of magnetic adsorbents has emerged as a highly efficient solution. Magnetic materials, such as magnetite (Fe_3O_4), allow for the rapid and easy separation of the adsorbent from the solution simply by applying an external magnetic field, eliminating the need for time- and energy-consuming centrifugation or filtration (Donga et al., 2024; Moosavi et al., 2020; Tatarchuck et al., 2023; Wai et al., 2020). Furthermore, to increase the adsorption capacity and selectivity towards Au(III) , functionalization of magnetite surface with sulfur (S) or nitrogen (N) containing groups becomes a very effective strategy (Razak et al., 2018; Wang et al., 2020; Wu et al., 2024; Zhao et al., 2019). This is based on the hard-soft acid-base (HSAB) theory, where Au(III) as a soft ion has a high affinity towards soft bases such as sulfur atoms (Fang et al., 2024; Fusaro et al., 2023; Khatiyar et al., 2024; Qomariyah et al., 2021).

L-Cysteine ($\text{C}_3\text{H}_7\text{NO}_2\text{S}$), a natural amino acid containing a thiol group ($-\text{SH}$), an amino group ($-\text{NH}_2$), and a carboxyl group ($-\text{COOH}$), is a highly potent chelating agent (Lu et al., 2020; Ooi et al., 2021; Shukla et al., 2022; Wang et al., 2022). The thiol group of L-Cysteine exhibits a strong affinity for noble metal ions such as Au(III) through the formation of stable coordinate bonds (Fischer et al., 2012; Ramek et al., 2021; Witkowski et al., 2023; Yoshinari et al., 2023). In addition, its amino and carboxyl groups can also contribute to metal binding through electrostatic interactions or complex formation (Boles et al., 2020; Chillè et al., 2022; Wang et al., 2024). Previous research by Karamipour et al. (2015) has demonstrated the use of L-Cysteine as a linker on the surface of $\text{Fe}_3\text{O}_4@\text{Au}$ for targeted drug delivery applications, indicating the ease of L-Cysteine binding to metal surfaces through its thiol group (Karamipour et al., 2015; Kalantarian et al., 2025; Torres et al., 2024). In a similar context, L-Cysteine functionalization on carbon-coated magnetite significantly enhanced the adsorption capacity towards Hg(II) , which is also a soft metal ion, with a capacity value reaching 94.33 mg/g (Dai et al., 2025; Srihaow et al., 2020; Wan et al., 2021; Zhao et al., 2019). This finding reinforces the great potential of L-Cysteine ligands when immobilized on magnetite surfaces for noble metal recovery applications.

Based on the above description, the synthesis of magnetic adsorbents functionalized with L-Cysteine offers a synergistic approach: ease of separation due to the magnetic properties of Fe_3O_4 and high selectivity towards Au(III) due to the chemical affinity of the thiol group. Therefore, this study is focused on the synthesis and characterization of magnetite-modified L-Cysteine material ($\text{Fe}_3\text{O}_4@\text{Cys}$).

RESEARCH METHOD

Materials

The materials utilized in this work consisted of Magnetic (Fe_3O_4), SiO_2 , 3-Glycidoxypentyltrimethoxysilane (GPTMS), L-Cysteine (Cys), HCl, and Deionized water.

Instruments

The functional groups were monitored using Fourier Transform Infrared (FTIR) spectroscopy. The crystalline phase, framework structure, and average crystallite size were determined through X-Ray Diffraction (XRD) analysis. Quantitative determined of dissolved iron (Fe) ions in the acidity stability test was performed using an Atomic Absorption Spectrophotometer (AAS).

Experimental procedures

Functionalization of L-cysteine on magnetite

0.5 g of magnetite is suspended in 5 mL of deionized water, then sonicated for 5 minutes and decanted. Magnetite was added with 6 mL of sodium silicate (1:1) and sonicated again for 15 minutes, followed by mechanical stirring for 30 minutes. The magnetite mixture was added with GPTMS according to the molar ratio and stirred mechanically for 30 minutes. L-Cysteine (Cys) was added according to the molar ratio, stirred for 1 hour, and ethanol was added gradually in 3 mL during stirring. 2 M HCl was added dropwise while stirring until a gel was formed and the pH reached 7. The gel was left overnight, then washed with deionized water and ethanol until the pH stabilized at 7 and dried in an oven at 65°C. The sample obtained was labeled as MSGC.

Acid stability evaluation (Fe leaching test)

To evaluate the chemical stability of the MSGC in corrosive environments, Fe leaching test were systematically conducted. A series of adsorbent samples were exposed to aqueous solutions adjusted to distinct pH level ranging from 1.0 to 6.0. The mixtures were continuously agitated using a shaker for 3 hours to promote potential dissolution. Afterward, the solid MSGC particles were efficiently isolated from the liquid phase using an external permanent magnet. The residual concentration of dissolved Fe ions present in the collected filtrate was quantitatively measured via AAS, where the magnitude of released Fe served as a direct indicator of the material's structural instability.

RESULTS AND DISCUSSION

Results

Fourier Transform Infrared (FTIR) spectroscopy

The successful synthesis of L-cysteine-functionalized magnetite was confirmed through the identification of functional groups using FTIR spectroscopy. As shown in Figure 1, the characteristic Fe-O stretching vibration of magnetite appears at 582 cm^{-1} . In the spectra of L-cysteine-functionalized magnetite, this absorption band shifts to lower wavenumbers to 557 cm^{-1} (Figure 1), appearing at 3331, 1628, 1059, 794, and 446 cm^{-1} .

The characteristic absorption bands of GPTMS are not observed in the spectra of the MSGC samples. However, a weak absorption band appears in 959 cm^{-1} . The MSGC 1:4 samples exhibit only a very small peak.

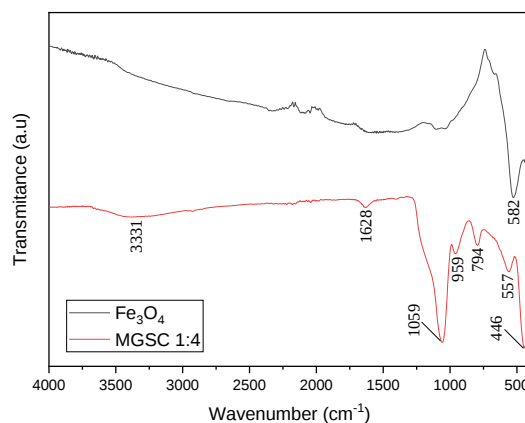


Figure 1. FTIR spectra of: Fe_3O_4 and MSGC 1:4

X-Ray Diffraction (XRD)

The X-Ray Diffraction (XRD) patterns of magnetite before and after silica coating and L-cysteine functionalization are presented in Figure 2. Based on the XRD diffractograms, all diffraction peaks observed for both unmodified magnetite and silica-coated, L-cysteine-functionalized magnetite can be indexed to the crystallographic planes (111), (220), (311), (400), (511), and (440). In the 2θ range of 20° – 26° , the synthesized samples exhibit a broad and diffuse diffraction peak.

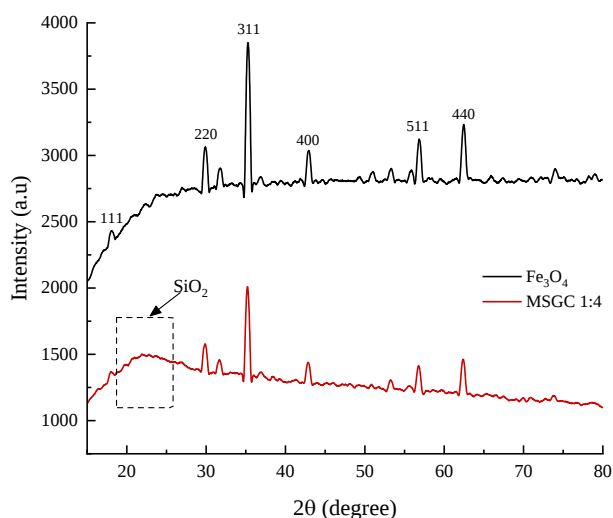


Figure 2. XRD patterns of Fe_3O_4 and MSGC 1:4 samples

The diffraction intensity of the principal (311) reflection was highest for the uncoated magnetite sample and decreased after silica coating and L-cysteine functionalization, indicating a reduction in crystallinity following surface modification. The crystallite size was estimated using the Scherrer equation:

$$D = \frac{K \lambda}{\beta \cos \theta}$$

where K is the Scherrer constant (0.89), λ is the X-ray wavelength ($1.54 \text{ \AA}$), β is the full width at half maximum (FWHM) of the diffraction peak, and θ is the Bragg diffraction angle. The calculated crystallite sizes are summarized in Table 1.

Table 1. Comparison of XRD parameters for magnetite and silica-coated magnetite samples

Adsorben	2θ ($^\circ$)	d_{311}	D (nm)
Fe_3O_4	35.24	2.54	16.30
MSGC 1:4	35.18	2.55	16.43

As shown in Table 1, the silica-coated and L-cysteine-functionalized magnetite samples exhibited slightly larger crystallite sizes than the uncoated magnetite.

Discussion

FTIR analysis discussion

The shift of the Fe–O absorption band to a lower wavenumber (557 cm^{-1}) indicates that the magnetite surface was successfully coated with silica and subsequently functionalized with L-cysteine. The presence of these characteristic silica bands (3331 , 1628 , 1059 , 794 , and 446 cm^{-1}) in the MSGC sample confirms that the synthesized magnetite particles were successfully coated with silica. Silica can be synthesized from rice husk waste, which is often discarded and polluting the environment. Utilization of waste will increase the economic value of rice husk waste into adsorbent material. The FTIR spectrum shows that silica adsorbent can be produced using an energy-efficient sol-gel method. This innovation enables a more sustainable water treatment infrastructure compared to energy-intensive commercial adsorbents (e.g., activated carbon).

The absence of the characteristic absorption band of GPTMS, combined with the appearance of a weak absorption band at 959 cm^{-1} , indicates that an additional reaction occurs between the epoxy ring of GPTMS and the nitrogen atom of the amino group in L-cysteine. The reduced intensity of the characteristic absorption band of L-cysteine in the 1:4 MSGC indicates a lower degree of L-cysteine functionalization on the magnetite surface. This phenomenon may be due to the insufficient number of amino groups compared to the available epoxy groups, resulting in incomplete epoxy ring opening and limited covalent bond formation. Consequently, functionalization of magnetite with L-cysteine in the 1:4 MSGC sample likely improves its effectiveness compared to other synthetic materials. This opens up the possibility of enhancing its ability to adsorb heavy metal waste. In addition, the production of silica magnetite adsorbents can naturally absorb carbon. FTIR is used in climate research to monitor the adsorbent's ability to capture CO_2 (when modified with amine groups, a band of $\sim 3300\text{ cm}^{-1}$ for N–H is seen). This is a low-cost solution for reducing greenhouse gas emissions.

XRD Analysis Discussion

From the XRD analysis, the feature of a broad and diffuse diffraction peak in the the 2θ range of 20° – 26° is indicative of the presence of amorphous SiO_2 , consistent with JCPDS No. 46-1045. The decrease in the diffraction intensity of the principal (311) reflection after silica coating and L-cysteine functionalization indicates a reduction in crystallinity following surface modification.

The amount of GPTMS used during the synthesis of magnetite may influence the crystal structure and crystallinity of the resulting magnetite-based adsorbent. Among the modified samples, an increase in GPTMS concentration was associated with a slight decrease in crystallite size. The presence of amino-containing groups from L-cysteine may promote the hydrolysis of iron ions on the magnetite surface due to their basic nature, leading to a reduction in crystallite size and a corresponding decrease in the intensity of the characteristic magnetite diffraction peaks. These results suggest that increasing the GPTMS content enhances surface modification while simultaneously reducing the crystallinity of the magnetite core. The XRD diffractogram pattern confirms the successful synthesis of magnetite adsorbent consisting of magnetite crystal phase (Fe_3O_4) dispersed in amorphous silica matrix. No significant impurity peaks were found, indicating good material purity. The successful synthesis of this material contributes directly to the implementation of this material to purify industrial

wastewater from heavy metals, through the utilization of waste as a silica precursor and its reusability, in the development of environmentally friendly technologies.

CONCLUSION

Fundamental finding: L-cysteine-functionalized magnetite ($\text{Fe}_3\text{O}_4@\text{Cys}$) was successfully synthesized through silica coating and subsequent surface modification using GPTMS as a coupling agent. FTIR characterization confirmed the presence of silica and L-cysteine functional groups on the magnetite surface, indicating successful functionalization. XRD analysis showed that the crystalline structure of magnetite was retained after modification, while the appearance of an amorphous silica phase verified the formation of a silica coating layer. The crystallite size of the modified material remained within the nanometer range, demonstrating that the surface modification process did not significantly alter the magnetite core structure. **Implication:** Overall, the synthesized $\text{Fe}_3\text{O}_4@\text{Cys}$ exhibited good structural integrity and chemical stability, making it a promising magnetic adsorbent for the selective recovery of Au(III) ions from secondary resources such as mining waste and electronic waste. **Limitation:** The limitation of this study is that it focuses primarily on the synthesis and structural characterization of the $\text{Fe}_3\text{O}_4@\text{Cys}$ material. The practical evaluation of its actual adsorption capacity, selectivity, and regeneration performance has not yet been conducted within the scope of this paper. **Future research:** Further adsorption studies are required to evaluate its adsorption capacity, selectivity, and regeneration performance under practical operating conditions.

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AUTHOR CONTRIBUTIONS

Amaria led the study by developing the research concept and design, supervising the research process, interpreting the findings, and reviewing and refining the manuscript. **Dina Kartika Maharani** contributed to the methodological design, data analysis, interpretation of the findings, and critical revision of the manuscript. **Amalia Putri Purnamasari** supported data collection, laboratory procedures, data validation, and manuscript preparation. **Sari Edi Cahyaningrum** provided academic supervision, validated the research process and findings, and critically reviewed the manuscript. **Aisha Setiyanti** conducted data collection and analysis and prepared the original draft of the manuscript. All authors contributed to the development of the study, reviewed the final manuscript, and approved its publication.

CONFLICT OF INTEREST STATEMENT

The authors confirm that there are no conflicts of interest, either financial or personal, that may have influenced the content or outcome of this study.

ETHICAL COMPLIANCE STATEMENT

This manuscript complies with research and publication ethics. The authors affirm that the work is original, conducted with academic integrity, and free from any unethical practices, including plagiarism.

STATEMENT ON THE USE OF AI OR DIGITAL TOOLS IN WRITING

The authors acknowledge the use of ChatGPT (OpenAI) as a language-support tool during the preparation of this manuscript. The tool was utilized solely to assist with language refinement, grammar checking, and improving the clarity and readability of the text. ChatGPT was not involved in the research design, data collection, data analysis, interpretation of findings, or the generation of research results. All AI-assisted outputs were carefully reviewed, verified, and revised by the authors to ensure accuracy, academic integrity, and compliance with ethical standards. The authors take full responsibility for the content of this manuscript and all conclusions presented herein.

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