Improved Separation and Adsorption of Ciprofloxacin Using Magnetic Graphene Oxide

Rinawati[1], Agung Abadi Kiswandono[2], Widiarti[3], Amelia Rizky Az-zahra[4], Herlian Eriska Putra[5], Dian Septiani Pratama[6]

{rinawati@fmipa.unila.ac.id[1], agung.abadi@fmipa.unila.ac.id[2], widiarti08@gmail.com[3], 2117011058@student.unila.ac.id[4], herl004@brin.go.id[5], dian.septiani@fmipa.unila.ac.id[6]}

Department of Chemistry, Universitas Lampung, Bandar Lampung[1,2,4,6], Department of Mathematics, Universitas Lampung, Bandar Lampung [3], Research Center for Chemistry, National Research and Innovation Agency (BRIN), Bandung[5]

Corresponding author: rinawati@fmipa.unila.ac.id

Abstract. Water pollution caused by antibiotic residues, particularly ciprofloxacin (CIP), has become a serious global issue as it threatens aquatic ecosystem. This study aims to modify Graphene Oxide (GO) into Magnetic Graphene Oxide (MGO) to be used as an adsorbent in the Dispersive Solid Phase Extraction (DSPE) technique for the preparation and monitoring of CIP residues in aquatic environments. MGO was synthesized via the coprecipitation method by combining GO with magnetic Fe_3O_4 particles, which impart magnetic properties and facilitate the separation process in DSPE. The characterization of MGO was carried out using Fourier Transform Infrared Spectroscopy (FTIR), X-Ray Diffraction (XRD), Scanning Electron Microscopy-Energy Dispersive X-Ray (SEM-EDX), and UV-Vis spectrophotometry. The results showed that MGO possesses functional groups that support CIP adsorption, with optimal adsorption conditions at pH 5, an MGO mass of 20 mg, and a contact time of 40 minutes. The adsorption efficiency of MGO reached 75.28%, which is higher than that of GO at only 65.53%. This study demonstrates that MGO can be used as an adsorbent for CIP antibiotics and offers an easy separation process in the DSPE technique for monitoring CIP antibiotic residues in aquatic environments.

Keywords: Graphene oxide, magnetic graphene oxide, ciprofloxacin, dispersive solid phase extraction.

1 Introduction

The presence of antibiotic residues in aquatic environments has become a global concern due to their potential ecologic al and health impacts. Ciprofloxacin (CIP), a broad-spectrum fluoroquinolone antibiotic, is frequently detected in surface waters and wastewater because of its extensive medical and veterinary use [1,2]. Continuous exposure to CIP in aquatic environments not only disrupts ecological balance in aquatic

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organisms but also accelerates the development of antimicrobial resistance and toxicity in the environment due to its low biodegradability and persistence., ultimately posing a serious threat to human health [3–5]. Therefore, effective monitoring and removal strategies for CIP residues are urgently required.

Sample preparation techniques play an important role in detecting and measuring antibiotic residues because they can increase sensitivity, selectivity, and prevent instrument damage [6,7]. Conventional methods such as liquid–liquid extraction and solid-phase extraction (SPE) have limitations, including high solvent consumption, lengthy extraction times, and potential analyte loss [8,9]. Dispersive Solid Phase Extraction (DSPE) has emerged as a promising alternative due to its simplicity, shorter extraction times, and reduced solvent usage. In DSPE, the adsorbent is directly dispersed into the sample, enabling efficient interaction with the target analyte [10,11]. The performance of DSPE largely depends on the properties of the adsorbent material.

Graphene oxide (GO), a carbon-based nanomaterial with high surface area and abundant oxygen-containing functional groups, has attracted significant attention as an adsorbent in DSPE [12,13]. However, GO as an adsorbent has the disadvantage of being difficult to separate from the solution, requiring a relatively long time [14]. This results in low adsorption values and GO residue, which has the potential to become a secondary pollutant if not properly separated [15]. Incorporating magnetic nanoparticles such as Fe_3O_4 into GO produces magnetic graphene oxide (MGO), which exhibits superparamagnetic properties that facilitate rapid and efficient separation, while maintaining or even enhancing adsorption capacity [16,17].

Recent studies indicate that MGO can effectively adsorb various organic pollutants, including antibiotics, heavy metals, and dyes, from wastewater [18,19]. In this research, focuses on the utilization of MGO not only as an adsorbent. But as an integrated DSPE material for monitoring ciprofloxacin residues in aquatic environments, which enhances adsorption efficiency while simultaneously simplifying the separation process through its magnetic properties. This study emphasizes the role of MGO in improving the practicality and efficiency of analytical preparation environmental analysis.

2 Materials and method

The instruments used included beakers, thermometers, graduated cylinders, volumetric flasks, glass funnels, rubber bulbs, wash bottles, centrifuge tubes, spatulas, stirring rods, dropper pipettes, a pH meter (XS pH 60 Vio Lab), centrifuge (Fischer Scientific 1827001027164), hot plate magnetic stirrer (Stuart Biocote R200000 685), analytical balance (AND HR-150A 152 g/0.1 mg), ultrasonic bath (1510 Branson), oven (Heareus), XRD (XPERT PRO PANalytical PW3040/60), FTIR (Shimadzu QATR-S), SEM–EDX (EVO® MA 10), and UV–Vis spectrophotometer (Shimadzu UV-1780).

Materials used were graphite (Supelco SigmaAldrich), standard CIP antibiotic (Hexpharm Jaya), H_2SO_4 97% (Supelco SigmaAldrich), $KMnO_4$ (Merck™), H_2O_2 30% (Supelco SigmaAldrich), HCl 37% (Merck™), $BaCl_2$ (Merck™), NaOH (Merck™), filter paper, $FeSO_4 \cdot 7H_2O$, $FeCl_3 \cdot 6H_2O$ (Supelco SigmaAldrich), and distilled water.

2.1 The preparation of graphene oxide by modified Hummers method

An amount of 1 g of graphite was weighed and mixed with 23 mL of 96% H_2SO_4 in a 500 mL beaker, followed by stirring for 30 min in an ice bath. Subsequently, 3 g of $KMnO_4$ were slowly added while keeping the temperature below 10 °C. The mixture was stirred at 35 °C for 30 min, then 46 mL of distilled water was added until the temperature reached 98 °C and left for 15 min. Next, 140 mL distilled water was added, followed by 10 mL of 30% H_2O_2 while stirring for 10 min. The suspension was washed with 5% HCl to remove sulfate ions, tested with $BaCl_2$ until no white precipitate appeared, then washed with distilled water to pH 5 and centrifuged for 10 min. The solid was dispersed in 450 mL distilled water, sonicated for 2 h, filtered, and dried at 60 °C for 5 h [20].

2.2 The preparation of magnetic graphene oxide by coprecipitation method

One hundred milliliters of distilled water were mixed with 0.556 g $FeSO_4 \cdot 7H_2O$ and 1.081 g $FeCl_3 \cdot 6H_2O$ and stirred for 30 min at 40 °C. In another beaker, 0.025 g GO was dissolved in 50 mL distilled water and stirred for 15 min. The GO solution was then added to the magnetic solution, and 1 M NaOH was gradually added until pH 10 while stirring for 1–2 h. The precipitate was washed with distilled water to neutral pH and dried in an oven at 60–80 °C [21].

2.3 The characterization of magnetic graphene oxide

The MGO was characterized by SEM–EDX to determine morphology, elements, and quantitative composition; FTIR to identify functional groups; XRD to determine crystalline phases; and UV–Vis spectroscopy to examine electronic transitions.

2.4 Standard preparation

A 500 ppm CIP stock solution was prepared by dissolving 50 mg of CIP in distilled water to the mark in a 100 mL volumetric flask and homogenizing. Standard solutions of 100 ppm and 50 ppm were obtained by dilution. Standard solutions 2; 4; 6; 8 and 10 ppm were obtained by serial dilution of the 50 ppm stock solution. Then, the solutions were analyzed using a UV-Vis spectrophotometer at a maximum wavelength [22].

2.5 Optimization of adsorption parameters

The optimization of ciprofloxacin adsorption conditions was carried out by varying solution pH, adsorbent mass, and contact time. In determining the optimum pH, ten milliliters of 4 ppm ciprofloxacin solution were added into the vial, and the pH was adjusted to 3, 5, 7, 9, and 11 using 0.1 M HCl or 0.1 M NaOH. Then, 0.01 g of MGO was added, and the mixture was sonicated for 10 minutes. The suspension was centrifuged at 5000 rpm for 10 minutes, and the supernatant was analyzed using a UV-Vis spectrophotometer at the maximum absorption wavelength of ciprofloxacin. In determining the optimum adsorbent mass, ten milliliters of 4 ppm ciprofloxacin solution at the optimum pH were placed in a vial, and different amounts of MGO (5 mg, 10 mg, 20 mg, and 30 mg) were added. The mixtures were sonicated for 10 min, centrifuged at 5000 rpm for 10 min, and the filtrates were analyzed by UV–Vis spectrophotometry. In determining the optimum contact time, ten milliliters of 4 ppm ciprofloxacin solution at optimum pH and optimum adsorbent mass were added to a vial. The mixtures were sonicated for 5, 10, 20, 30, and 40 min. Each suspension was centrifuged at 5000 rpm for 10 min, and the supernatants were analyzed by UV–Vis spectrophotometry [13].

The adsorption percentage is calculated based on the difference between the initial concentration (C_0) and the equilibrium concentration (Ce) of ciprofloxacin using equation (1).

$$Adsorption\ (\%) = \frac{Co-Cx}{Co} \times 100. \tag{1}$$

3 Result and discussion

3.1 Magnetic graphene oxide characterization

The FTIR spectrum of the synthesized Magnetic Graphene Oxide (MGO) (**Figure 1**) exhibited characteristic absorption bands corresponding to carboxyl (–COOH), epoxy (C–O–C), hydroxyl (–OH), aromatic C=C, and Fe–O groups. These functional groups confirm the successful oxidation of graphite to graphene oxide and the subsequent anchoring of Fe_3O_4 nanoparticles on the GO surface. Similar bands were also reported by Souhuat et al (2024) for GO-based magnetic composites, supporting the successful functionalization of GO in this study. The presence of Fe–O bands indicates the magnetic property of MGO, which is advantageous for rapid separation during DSPE [23].

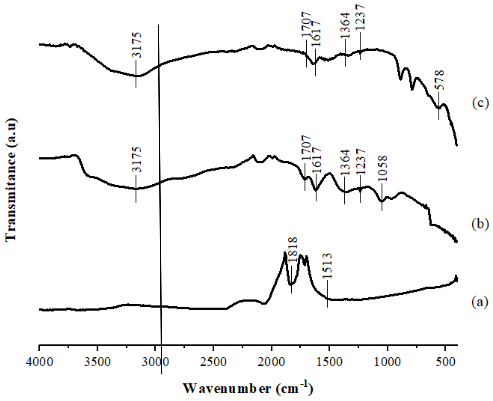
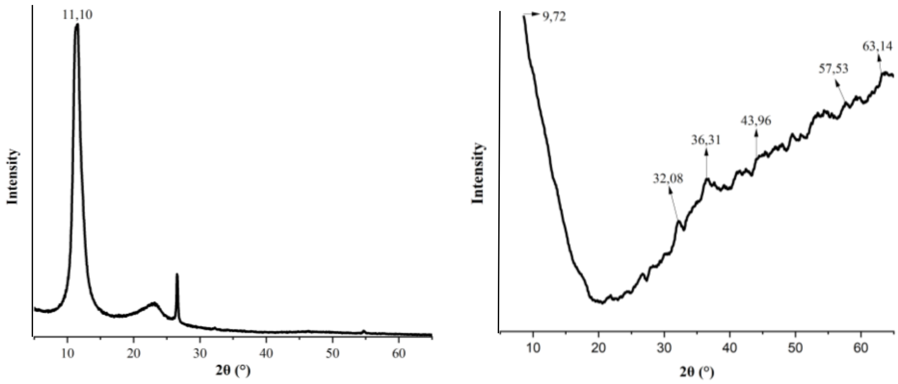


Fig. 1. FTIR spectrum results of (a) graphite, (b) GO, and (c) MGO.

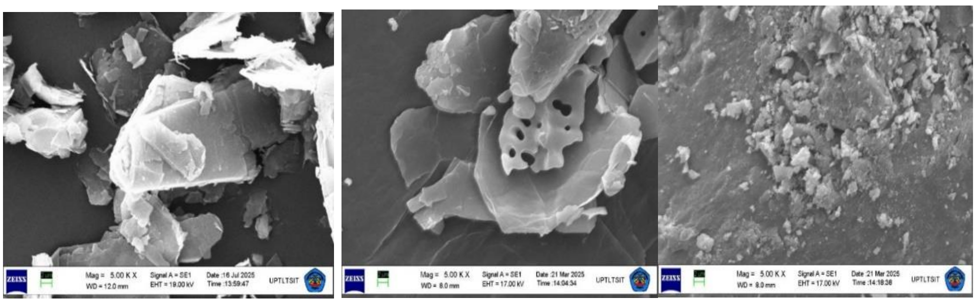
The XRD diffractogram of MGO (**Figure 2**) shows a peak at 2θ = 9.72° corresponding to the crystalline nature of GO, and additional peaks at 32.12°, 36.54°, 43.96°, 57.53°, and 63.14° attributed to Fe_3O_4 crystalline phases. These diffraction patterns indicate the successful incorporation of Fe_3O_4 into the GO structure [24,25]. Such peaks are characteristic of spinel ferrite Fe_3O_4, confirming the magnetic nature of the synthesized composite [26].



(a) (b)

Fig. 2. XRD results (a) GO, (b) MGO.

The morphological structure of graphite shows a dense stack of thick layers with a layered structure (**Figure 3a**) [27], while SEM images of GO (**Figure 3b**) display thin layered sheets with smooth surfaces and some wrinkled regions. In contrast, MGO (**Figure 3c**) exhibits bright dots corresponding to Fe_3O_4 particles distributed on the wrinkled GO surface, confirming successful deposition [28]. The wrinkled morphology of GO facilitates Fe_3O_4 attachment but also leads to some agglomeration [18].



(a) (b) (c)

Fig. 3. SEM results of (a) graphite, (b) GO, and (c) MGO.

EDX analysis (**Figure 4**) further supports the elemental composition. GO contained mainly carbon (59.85%) and oxygen (40.1%), whereas MGO exhibited C (4.25%), O (44.93%), and Fe (50.82%), confirming the presence of Fe_3O_4 in MGO [15,29].

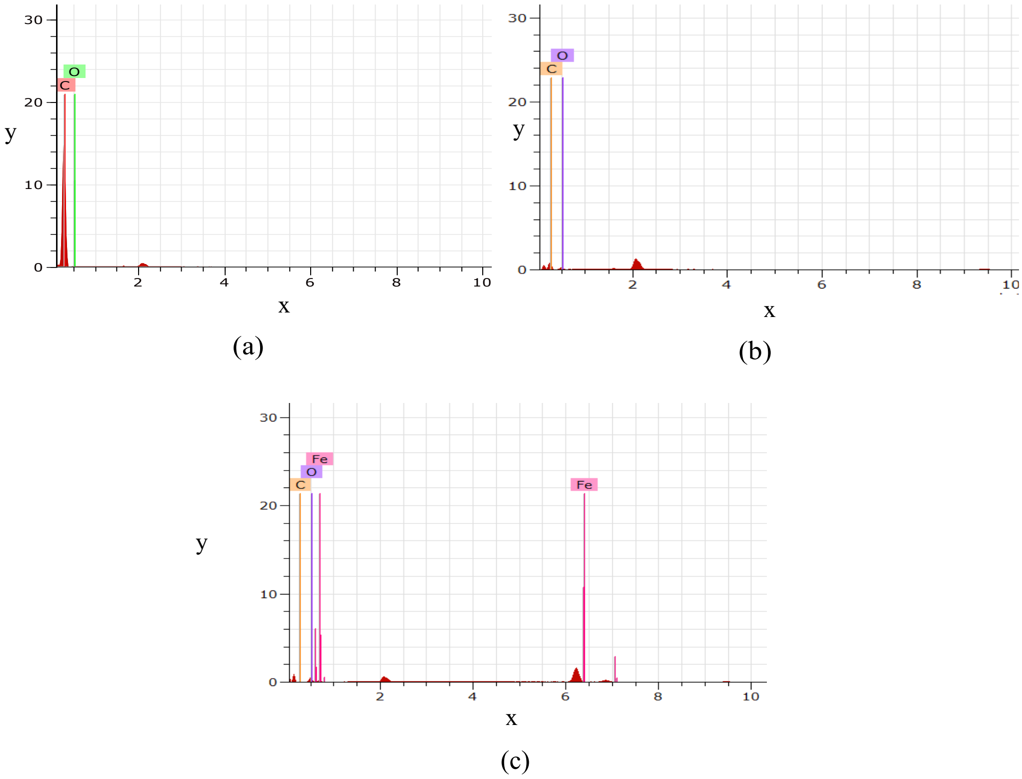


Fig. 4. EDX results of (a) graphite, (b) GO, and (c) MGO.

3.2 Optimization of ciprofloxacin adsorption parameters

The adsorption of ciprofloxacin (CIP) onto MGO reached its optimum at pH 5 (**Figure 5**). At lower pH, proton competition decreased adsorption, while at higher pH, electrostatic repulsion reduced interaction. This behaviour occurs due to reported stronger electrostatic attraction between protonated MGO and ionized CIP at mildly acidic conditions [30].

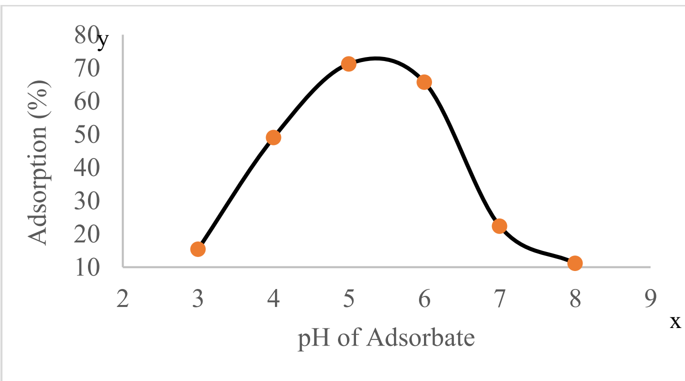


Fig. 5. Adsorption test result of adsorbate pH variation.

The maximum adsorption (57.82%) was achieved at 20 mg MGO (Figure 6). Increasing mass beyond 20 mg decreased efficiency due to particle aggregation and reduced accessibility of active sites [28]. Beyond 20 mg, the adsorption efficiency plateaued, indicating that the maximum adsorption capacity was reached and further addition of adsorbent did not significantly increase removal efficiency [17].

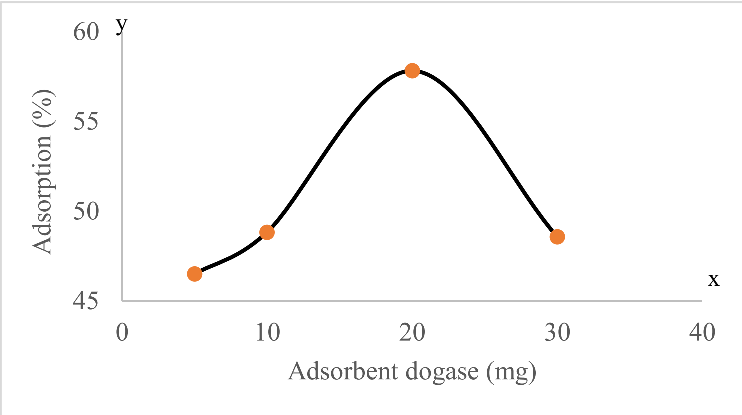


Fig. 6. Adsorption test results of adsorbent mass variation.

The adsorption of CIP on MGO peaked at 75.28% after 40 minutes (**Figure 7**). Longer times cause a decrease in adsorption, because all active sites have been filled and equilibrium has been reached. Thus, the adsorption process experiences a saturation condition which causes the adsorbate to be desorbed back into the solution [13].

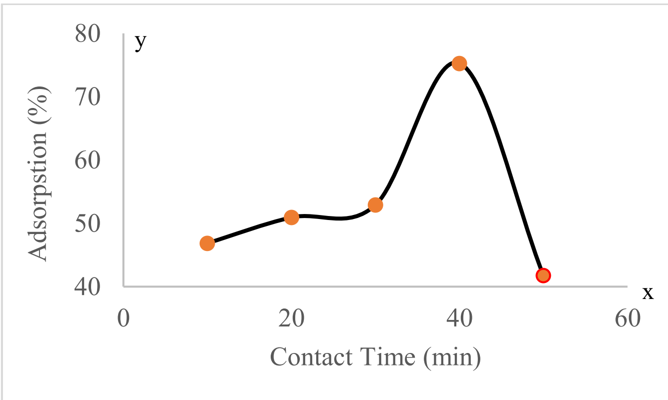


Fig. 7. Adsorption test of contact time variation.

3.3 Comparison between GO and MGO in DSPE

Under identical optimum conditions (pH 5, 20 mg adsorbent, 40 min), GO achieved 65.53% adsorption of CIP, whereas MGO reached 75.28% (**Figure 8**). This 9.75% increase is attiributed to the higher adsorption capacities of MGO for antibiotics and dyes compared to GO [27]. The enhancement is attributed to the magnetic Fe_3O_4 particles increasing surface area and active sites. In addition, MGO can form hydrogen bonds between its –OH groups and CIP's carbonyl and fluorine groups, and also attract CIP via Van der Waals forces [30]. Its magnetism enables rapid separation without centrifugation or filtration, further improving DSPE efficiency.

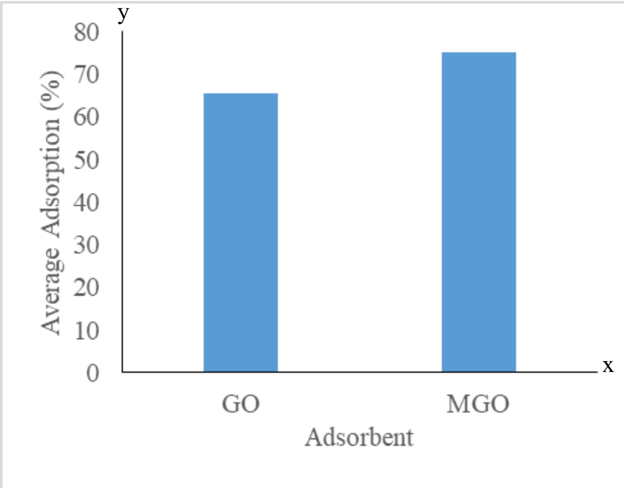


Fig. 8. Comparison of adsorption test using GO and MGO

4 Conclusion

Magnetic graphene oxide (MGO) was successfully synthesized from graphene oxide (GO) using a modified Hummers method followed by coprecipitation with Fe^{3+}/Fe^{2+}. FTIR, XRD, SEM–EDX, and UV–Vis analyses confirmed the successful oxidation of graphite, the retention of oxygen functional groups, and the incorporation of Fe_3O_4 nanoparticles into the GO structure.

Under optimized conditions (pH 5, 20 mg adsorbent, 40 minutes contact time), MGO achieved a ciprofloxacin adsorption efficiency of 75.28%, higher than that of pristine GO (65.53%). The enhanced adsorption performance is attributed to the increased active sites, electrostatic interactions, and hydrogen bonding provided by the Fe_3O_4–GO composite. The superparamagnetic property of MGO also enables rapid and easy separation from aqueous solutions, overcoming one of the main limitations of GO in DSPE applications.

These findings demonstrate that MGO is a promising adsorbent for dispersive solid-phase extraction of fluoroquinolone antibiotics from environmental water samples. The combination of high adsorption efficiency, magnetic separability, and simple synthesis makes MGO a viable candidate for practical monitoring and removal of pharmaceutical residues in aquatic environments.

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