

# Nghiên cứu tổng hợp $\text{CoFe}_2\text{O}_4/\text{rGO}$ và ứng dụng làm vật liệu điện cực phân tích dư lượng kháng sinh ciprofloxacin trong nước thải nuôi trồng thủy sản

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## TÓM TẮT

Trong nghiên cứu này,  $\text{CoFe}_2\text{O}_4/\text{rGO}$  đã được tổng hợp. Hình thái và cấu trúc của  $\text{CoFe}_2\text{O}_4/\text{rGO}$  được đặc trưng bởi gián đồ nhiễu xạ tia X (XRD), phổ tán xạ năng lượng tia X (EDX), hiển vi điện tử quét (SEM) và quang phổ hồng ngoại biến đổi Fourier (FT-IR). Điện cực dán than chì biến tính bởi  $\text{CoFe}_2\text{O}_4/\text{rGO}$  (GPE- $\text{CoFe}_2\text{O}_4/\text{rGO}$ ) đã được chuẩn bị và sử dụng để phát hiện dư lượng kháng sinh ciprofloxacin (Cip). Một phương pháp phân tích Cip đã được xây dựng trong các điều kiện tối ưu với khoảng tuyến tính là  $0,5 - 100 \mu\text{M}$  ( $R^2 = 0,991$ ). Giới hạn phát hiện và giới hạn định lượng của phương pháp phân tích được xác định lần lượt là  $0,094 \mu\text{M}$  và  $0,314 \mu\text{M}$ . Nồng độ Cip trong các mẫu nước thải nuôi trồng thủy sản ở Bình Định được xác định bằng phương pháp đề xuất với độ thu hồi đạt từ 93,7–101,0%.

**Từ khóa:**  $\text{CoFe}_2\text{O}_4$ , graphene oxide bị khử, graphite paste electrode, Von – Ampe hòa tan anot sóng vuông, ciprofloxacin.

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# Research on the synthesis of $\text{CoFe}_2\text{O}_4/\text{rGO}$ and its application as electrode materials to analyze ciprofloxacin antibiotic residues in aquaculture wastewater

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## ABSTRACT

In the present study,  $\text{CoFe}_2\text{O}_4/\text{reduced graphene oxide}$  ( $\text{CoFe}_2\text{O}_4/\text{rGO}$ ) has been synthesized. The morphology and structure of nanocomposites  $\text{CoFe}_2\text{O}_4/\text{rGO}$  were characterized by X-ray diffraction (XRD), Energy Dispersive X-Ray spectrometer (EDX), scanning electron microscopy (SEM), and Fourier Transform infrared spectroscopy (FTIR). The  $\text{CoFe}_2\text{O}_4/\text{rGO}$  modified graphite paste electrode (GPE- $\text{CoFe}_2\text{O}_4/\text{rGO}$ ) was prepared and used for the electrochemical detection of ciprofloxacin (Cip) antibiotic residues. A Cip analytical method formed under the optimal conditions had a good linear relationship between the Cip signal with its concentration range from 0.5 to 100  $\mu\text{M}$  ( $R^2 = 0.991$ ). The limit of detection and quantity was observed as 0.094  $\mu\text{M}$  and 0.314  $\mu\text{M}$ , respectively. Finally, Cip concentration in aquaculture wastewater samples was determined by the proposed method with recovery = 93.7–101.0%.

**Keywords:**  $\text{CoFe}_2\text{O}_4$ , reduced graphene oxide, graphite paste electrode, square wave anodic stripping voltammetry, ciprofloxacin.

## 1. INTRODUCTION

Reduced graphene oxide (rGO) has electrical conductivity, high surface area, and electrochemical stability that can be used to manufacture electrodes. Recently, rGO-supported composites have indicated fascinating advantages as a sensing platform in electrochemical sensors.<sup>1</sup> Among them are composites of rGO and spinel ferrites nanoparticles with the chemical formula  $\text{CoFe}_2\text{O}_4$  which is a very important magnetic material,<sup>2</sup> and can appreciate the optical, magnetic, and electrochemical properties of rGO.<sup>3</sup>  $\text{CoFe}_2\text{O}_4$  nanoparticles have attracted increasing interest in the construction of sensors because of

their low toxicity, strong superparamagnetic properties, easy preparation, and high adsorption ability. Its composite with rGO can improve rGO characteristics. Accordingly, a combination of  $\text{CoFe}_2\text{O}_4$  with rGO is hoped to result in a composite with electrical conductivity, high surface area, and a possibility of application in electrochemistry.

The use of antibiotics and other chemicals is common in aquaculture. More than 20 antibiotics have been used to prevent and treat diseases in shrimp and fish farming, including banned antibiotics. Interestingly, the most used antibiotic in shrimp farming is Ciprofloxacin (CIP), which has been banned

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for a long time. The antibiotic Ciprofloxacin has the IUPAC name: 1-cyclopropyl-6-fluoro-4-oxo-7-(piperazin-1-yl) quinoline-3-carboxylic acid. Ciprofloxacin belongs to the quinolone antibiotic class. A wide range of techniques have been used for the determination of CIP, such as spectrophotometry,<sup>4,5</sup> capillary electrophoresis,<sup>6</sup> spectrofluorometry,<sup>7,8</sup> high-performance liquid chromatography (HPLC),<sup>9,10</sup> and electrochemical analysis.<sup>11,12,13</sup> Among all the above, the electrochemical technique may be the most widely applied owing to its advantages of low cost, relatively short analysis time compared to other analytical techniques, simple instruction, high sensitivity, and facile miniaturization.

The use of  $\text{CoFe}_2\text{O}_4/\text{rGO}$  composite materials as electrode materials in analyzing Cip antibiotics by electrochemical method has not been of interest in the country and the world. The electrodes modified by  $\text{CoFe}_2\text{O}_4/\text{rGO}$  nanocomposite materials have the advantage of increasing selectivity and increasing the sensitivity of the analysis, and the limit of detecting antibiotics on these electrodes is reduced. This research reported the synthesis of  $\text{CoFe}_2\text{O}_4/\text{rGO}$  and its application as electrode materials to analyze ciprofloxacin antibiotic residues in aquaculture wastewater.

## 2. MATERIALS AND METHODS

### 2.1. Reagents and apparatus

*Chemicals:* Ciprofloxacin hydrochloride ( $\text{C}_{17}\text{H}_{18}\text{FN}_3\text{O}_3 \cdot \text{HCl} \cdot \text{H}_2\text{O}$  (Cip), 98.0%) was purchased from TCI company Japan. Graphite powder and paraffin oil were received from Sigma-Aldrich.  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ;  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  were purchased from Macklin (China), absolute ethanol ( $\text{C}_2\text{H}_5\text{OH}$ ), ammonia ( $\text{NH}_4\text{OH}$ ),  $\text{KH}_2\text{PO}_4$ ,  $\text{K}_2\text{HPO}_4$  were purchased from Guangdong – Guanghua Sci-Techn Co. Ltd (China).

### 2.2. Preparation of $\text{CoFe}_2\text{O}_4/\text{rGO}$ material

At first, prepare a mixture containing 50 mL of distilled water, 30 mL of ethanol, and 0.10 g rGO and stir for 10 minutes. Ultrasonic vibration for 1 hour is mixed 1. Subsequently, add 3.232 g

$\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  and 0.952 g  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  to the above mixture, and stir for 60 minutes. Afterwards, add another 15 mL solution  $\text{NH}_3$  and stir for another 120 minutes. Then transfer the entire solution to the Teflon flask, and conduct hydrothermal at 180 °C for 12 hours (in the drying oven). Finally, filter and wash the precipitate several times with distilled water and ethanol (until  $\text{pH} = 7$ ). Dried under at 60 °C for 24 hours. Heating the solid at 500 °C for 5 hours.<sup>14,15</sup>  $\text{CoFe}_2\text{O}_4/\text{rGO}$  was obtained.

### 2.3. Preparation of $\text{CoFe}_2\text{O}_4/\text{rGO}$ -GPE modified electrode

The  $\text{CoFe}_2\text{O}_4/\text{rGO}$ -GPE modified electrode was prepared by thoroughly mixing 40 mg of graphite powder and 10 mg  $\text{CoFe}_2\text{O}_4/\text{rGO}$  powder with 15  $\mu\text{L}$  of paraffin oil. The obtained paste was put into the cavity of a Teflon holder. The obtained electrode surface was smoothed using paper. Next, using an in pin, stuff the resulting paste into an inlet tube 52 mm long, inner diameter ( $3.0 \pm 0.1$  mm), the upper part has a metal pin that can be connected to the electrochemical machine as an electric current.

### 2.4. Electrochemical measurements

Electrochemical measurements (cyclic voltammetric (CV) and square wave voltammetry (SWV) were performed on a system Autolab Electrochemical CPA-HH5 (Hanoi, Vietnam), with a three-electrode configuration (GPE- $\text{CoFe}_2\text{O}_4/\text{rGO}$  modified electrode or GPE unmodified electrode as a working electrode,  $\text{Ag}/\text{AgCl}$  reference electrode, and platinum wire as an auxiliary electrode.

All experiments described in this section were performed at room temperature ( $25 \pm 1$  °C).

## 3. RESULTS AND DISCUSSION

### 3.1. Morpho-structural characterization of $\text{CoFe}_2\text{O}_4/\text{rGO}$ material

#### 3.1.1. XRD and TEM study

Figure 1 shows the XRD patterns of the  $\text{CoFe}_2\text{O}_4/\text{rGO}$  composite. The peaks at 2θ values

of 30.5; 35.7; 43.3; 57.1, and 62.9 correspond to respective (220), (311), (400), (511), and (440) are consistent with the spinel ferrite structure of  $\text{CoFe}_2\text{O}_4$  (JCPDS 75 – 0033).<sup>16</sup> Apart from the characteristic lines for the spinel cubic crystal structure of the oxide compound, no other peaks can be observed indicating the high purity of  $\text{CoFe}_2\text{O}_4$ /rGO. This result is completely consistent with previous publications.<sup>16,17</sup>

The TEM image of the  $\text{CoFe}_2\text{O}_4$ /rGO shows the appearance of sharp  $\text{CoFe}_2\text{O}_4$  particles with size about 50 nm on the surface of rGO thin sheets (Figure 2).

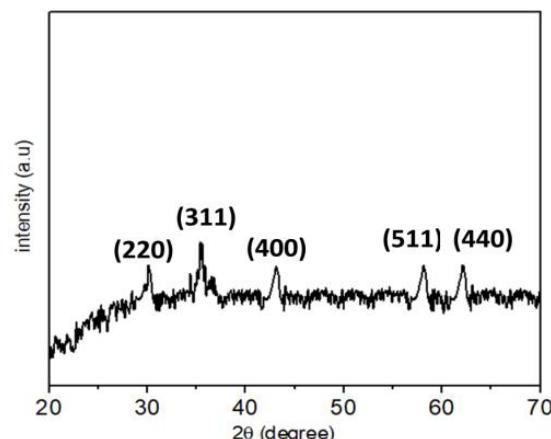


Figure 1. XRD pattern of  $\text{CoFe}_2\text{O}_4$ /rGO.

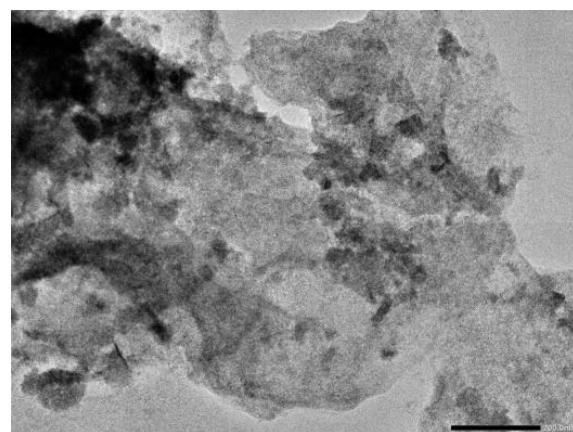


Figure 2. TEM images of  $\text{CoFe}_2\text{O}_4$ /rGO.

### 3.1.2. FTIR study

The FTIR spectrum of the  $\text{CoFe}_2\text{O}_4$ /rGO nanocomposites is shown in Figure 3. The O–H stretching vibration of absorbed water molecules and structural O–H groups is shown as a typical peak at  $3448\text{ cm}^{-1}$  with an observed peak at

$1720\text{ cm}^{-1}$  assigned for the carboxylic (C=O) functional groups. The O–H bending vibration can be observed as a peak at  $1536\text{ cm}^{-1}$ . The presence of an absorption peak at wave number  $592\text{ cm}^{-1}$  is believed to be the strain oscillation of the Fe (Co)- O bond in cobalt ferrite shown in the FTIR spectrum of  $\text{CoFe}_2\text{O}_4$ /rGO. Fe (Co)- O bonds are formed due to electrostatic attraction between functional groups (COOH, COH) on the rGO surface with  $\text{Co}^{2+}$  and  $\text{Fe}^{3+}$ .<sup>18</sup> This evidence confirms the cobalt ferrite precursor in the obtained rGO.

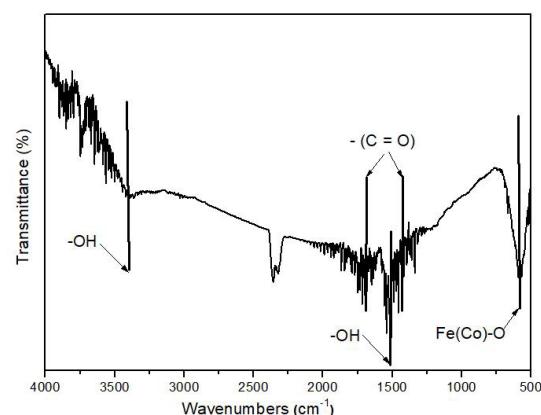


Figure 3. FTIR pattern of  $\text{CoFe}_2\text{O}_4$ /rGO.

### 3.1.3. SEM Analysis

The surface morphology of the  $\text{CoFe}_2\text{O}_4$ /rGO is investigated by SEM with different scales.

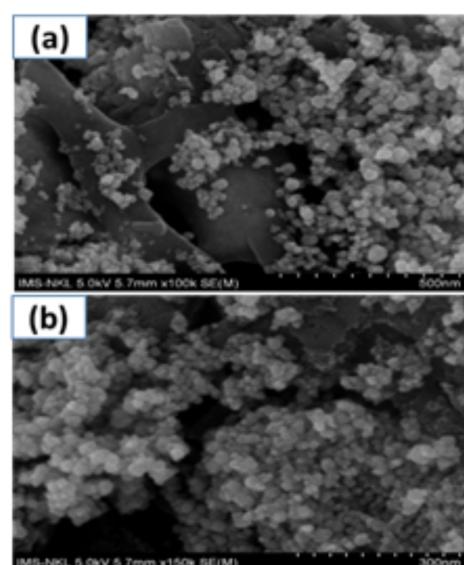


Figure 4. SEM images of  $\text{CoFe}_2\text{O}_4$ /rGO with different scales.

The surface morphology of  $\text{CoFe}_2\text{O}_4/\text{rGO}$  with different scales shown in Figure 4a-b is the  $\text{CoFe}_2\text{O}_4$  particles with a particle size of about 30-50 nm dispersed on rGO sheets according to an ordered structure conducive to the diffusion process and analyte adsorption.

### 3.1.4. EDX study

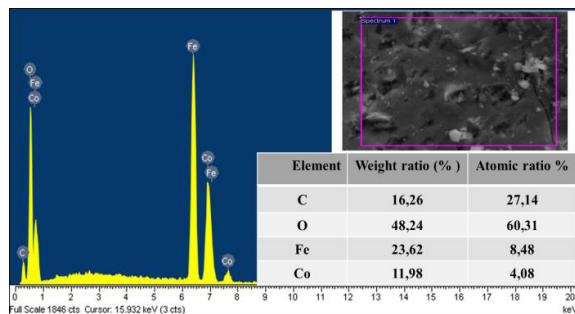


Figure 5. EDX spectra of  $\text{CoFe}_2\text{O}_4/\text{rGO}$ .

The analysis of the Energy Dispersive X-Ray spectrometer pattern in Figure 5 confirms the existence of C, O, Fe, and Co elements in the composites. The results show the presence of 4 elements C, O, Fe, and Co with the respective mass ratios of 12.53%; 39.02%; 32.13%, and 16.32%. The ratio of Fe/Co atoms was found to be 2:1, confirming the successful formation of the  $\text{CoFe}_2\text{O}_4/\text{rGO}$  structure. This result is completely consistent with the results of the previous studies.

## 3.2. Electrochemical results analysis

### 3.2.1. Electrochemical behavior of GPE and GPE modified $\text{CoFe}_2\text{O}_4/\text{rGO}$

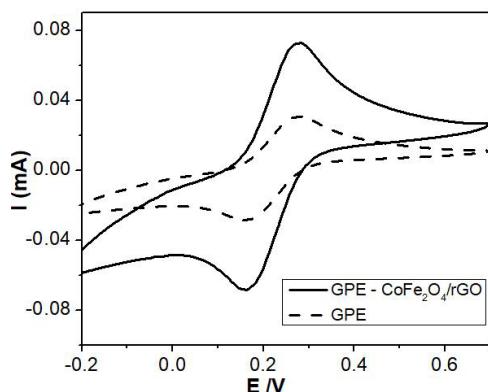


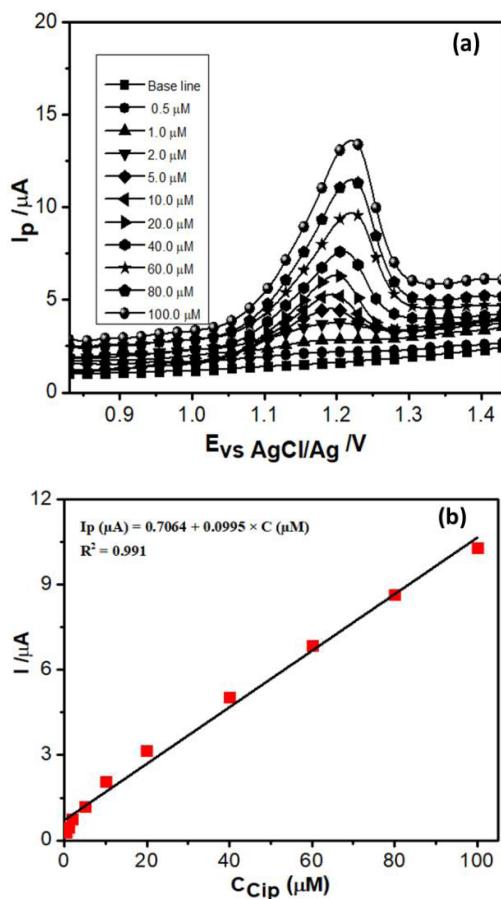
Figure 6. Cyclic voltammograms were obtained at a bare GPE and GPE- $\text{CoFe}_2\text{O}_4/\text{rGO}$  in 0.2 M phosphate buffer solution (PBS), pH, 7.0 containing 5 mM  $\text{K}_3\text{Fe}(\text{CN})_6$  at a scan rate of 0.1 V.s<sup>-1</sup>.

The cyclic voltammograms of a GPE and GPE modified  $\text{CoFe}_2\text{O}_4/\text{rGO}$  (GPE- $\text{CoFe}_2\text{O}_4/\text{rGO}$ ) in 5 mM  $\text{K}_3\text{Fe}(\text{CN})_6$  dissolved in 0.2 M phosphate buffer solution (PBS), pH, 7.0 showed the electrochemical behavior of the electrode. The electrochemical peaks of the bare GPE in the PBS are low. Their electrochemical peaks could also be observed at the GPE- $\text{CoFe}_2\text{O}_4/\text{rGO}$ , with the intensity increased significantly. Based on the Randles-Sevcik equation, the electrochemically active surface areas of the GPE- $\text{CoFe}_2\text{O}_4/\text{rGO}$  modified electrode were calculated as 0.2182 cm<sup>2</sup> larger than the bare GPE (0.0501 cm<sup>2</sup>). The surface area calculated according to the BET model of the GPE- $\text{CoFe}_2\text{O}_4/\text{rGO}$  modified electrode is 54.903 m<sup>2</sup>/g, which is nearly 4 times higher than that of the bare GPE. This result is completely consistent with the calculation results based on the Randles-Sevcik equation.

### 3.2.2. Analytical performance of the $\text{CoFe}_2\text{O}_4/\text{rGO}$ modified graphite paste electrode (GPE- $\text{CoFe}_2\text{O}_4/\text{rGO}$ )

**Linear range:** To investigate the ciprofloxacin analytical performance on the proposed electrode, SWV was carried out in Cip solutions with concentrations ranging from 0.5 – 150  $\mu\text{M}$  under optimal conditions (0.2 M phosphate buffer solution (pH = 2.0) with 240 s accumulation time, 50 mV pulse amplitude, and 0.25 V.s<sup>-1</sup> scan rate). The wide linearity range was good in the range of 0.5 – 100.0  $\mu\text{M}$ . The corresponding calibration plot is  $I(\mu\text{A}) = 0.7064 + 0.0995 \times C (\mu\text{M})$ . The SWASVs and linear regression lines/ equations for the Cip are shown in Figure 7a and 7b, respectively.

**Limit of detection (LOD):** The limit of detection (LOD) was calculated as  $3\sigma$ . The LOD was found as 0.094  $\mu\text{M}$  and  $\text{LOQ} = 3 \times \text{LOD} = 0.314 \mu\text{M}$ . Table 1 presents the performance of various modified sensors in Cip analysis for comparison.



**Figure 7.** SWVs of Cip samples ranging in concentration from 0.5 to 100.0  $\mu\text{M}$  (a) and the relationship between Cip concentrations with corresponding peak current (b).

**Table 1.** Comparison of the data obtained using various electrodes for the determination of Cip.

Electrode	Method	LOD ( $\mu\text{M}$ )	Range ( $\mu\text{M}$ )	Ref.
Graphene SPCE	SWV	0.1	0.1-100	[19]
Ch-AuMIP/GCE	DPV	0.21	1-100	[20]
PANI – $\beta$ -CD/fMWCNT		0.05	10-80	[21]
MgFe <sub>2</sub> O <sub>4</sub> -MWCNTs/GCE	CV	0.01	0.1-1000	[13]
MWCNT/GCE	CV	6	40-1000	[22]
<b>GPE-CoFe<sub>2</sub>O<sub>4</sub>/rGO</b>	<b>SWV</b>	<b>0.094</b>	<b>0.5-100</b>	<b>This work</b>

SWV: Square Wave Voltammetry, DPV: Differential Pulse Voltammetry, CV: Cyclic Voltammetry, SPCE: Screen printed carbon electrode, MIP: Molecularly Imprinted Polymer, GCE: glassy carbon electrode, PANI: PolyAniline,  $\beta$ -CD:  $\beta$ -cyclodextrin, MWCNT: Multi-Walled Carbon Nanotube, GPE: graphite paste electrode.

### 3.3. Real sample analysis

A real sample tested by the proposed method is four samples of shrimp farming wastewater in Binh Dinh province, Vietnam.

Measurement results are in Table 2. The trueness is evaluated through the recovery of the experimental results measured in the real sample with three individual measurements. Table 2 exhibits the obtained analytical results in four samples of shrimp farming wastewater in Binh Dinh with recovery values in the range of 93.7% to 101.0%, proving that the measurement has good precision.

The results of the analysis of farmed shrimp samples showed that the Cip antibiotic index exceeded the allowable threshold from 1.8 to 3.0 times. Thus, it can be concluded that wastewater from shrimp ponds is a source of pollution. If this water source is discharged directly into the environment, the risk of environmental pollution and disease spread is very high. It also facilitates the growth of antibiotic-resistant bacteria.

**Table 2.** Analytical results for the Cip determination using GPE-CoFe<sub>2</sub>O<sub>4</sub>/rGO in aquaculture wastewater samples in Binh Dinh province, Vietnam.

Sample	Sample location	Cip (μM)		
		Added	Found	Recovery(%)
Samples of wastewater 1	Tuy Phuoc, Binh Dinh	13°50'03.3"N 109°11'40.8"E	0 10	0.53 ± 0.26 10.54 ± 0.22
		13°49'47.0"N 109°11'18.7"E	0 10	0.92 ± 0.25 10.86 ± 0.28
Samples of wastewater 2	Tuy Phuoc, Binh Dinh	14°22'10.7"N 109°07'17.3"E	0 10	0.66 ± 0.33 10.76 ± 0.27
		14°22'10.8"N 109°07'17.0"E	0 10	0.85 ± 0.19 10.22 ± 0.26
Samples of wastewater 3	Phu My, Binh Dinh	14°22'10.7"N 109°07'17.3"E	0 10	0.66 ± 0.33 10.76 ± 0.27
		14°22'10.8"N 109°07'17.0"E	0 10	0.85 ± 0.19 10.22 ± 0.26
Samples of wastewater 4	Phu My, Binh Dinh	14°22'10.7"N 109°07'17.3"E	0 10	0.66 ± 0.33 10.76 ± 0.27
		14°22'10.8"N 109°07'17.0"E	0 10	0.85 ± 0.19 10.22 ± 0.26

#### 4. CONCLUSIONS

CoFe<sub>2</sub>O<sub>4</sub>/reduced graphene oxide nanocomposite material was successfully synthesized by a simple easy hydrothermal method. Successful application of modified graphite paste CoFe<sub>2</sub>O<sub>4</sub>/rGO to determine ciprofloxacin in aquaculture wastewater. The signal of Cip on the modified electrode is 4.41 times higher than on the graphite paste electrode. The sensor provided satisfied LOD (0.094 μM) and LOQ (0.314 μM). The Cip concentration in aquaculture wastewater in Binh Dinh province, Vietnam was determined with good recovery (93.7–101.0%).

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