

## HIGHLY EFFECTIVE REMOVAL OF CIPROFLOXACIN FROM AQUEOUS SOLUTION USING GRAPHENE OXIDE FUNCTIONALIZED ZEOLITE

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### ABSTRACT

Graphene oxide (GO) functionalized zeolites (ZGO) was synthesized as an adsorbent for swift and successful removal of the ciprofloxacin (CIP) antibiotic. The as-prepared nanocomposite was characterized by field emission scanning electron microscopy (FESEM), Fourier transform infrared spectroscopy (FTIR), and RAMAN spectroscopy. The adsorption ability of ZGO for CIP was investigated at different pH (2-11), contact time (5-120 min), and adsorbent dosage (0.1-0.75 g L<sup>-1</sup>) to obtain the optimum condition for maximum removal percentage of target adsorbate. The results provided very fast (15 min only) highly effective removal of CIP (97.67%) for 0.25 g L<sup>-1</sup> ZGO, while the pH of the aqueous solution was 7.0. Kinetic and isotherm analysis of this study indicated that the adsorption process happened on the multilayer and heterogeneous surface of ZGO and was carried out by a chemical reaction between CIP and ZGO. The highest adsorption capacity ( $q_m$ ) was calculated as 61.35 mg g<sup>-1</sup> at 40°C, while 8.28 and 12.45 mg g<sup>-1</sup> were at 20, and 30°C, respectively, which suggested the stimulation of greater sites of ZGO surface with the increment of temperatures during the adsorption process. Furthermore, strong stability and superior reusability of ZGO revealed that it could be a potential adsorbent for easy removal of CIP antibiotics from the aqueous solution.

**Keywords:** Functionalized GO, Ciprofloxacin antibiotic, Adsorbent, Adsorbate, Zeolites

### 1. INTRODUCTION

Currently, safe water availability is a great challenge due to its necessity for all existing creatures of the universe. Regular surveillance of ground and surface water is very essential since all living animals, plants, and human beings are directly dependent on them (Mohiuddin *et al.*, 2021; Samal *et al.*, 2022). We should take appropriate steps to secure germ-free, immaculate surface water for significant human health and environmental sustainability (Igwegbe *et al.*, 2021). However, the surface water is sometimes polluted by various chemicals, especially widely used antibiotics, pesticides, and heavy metals (Walker *et al.*, 2019). Pharmaceutical contaminants (PCs) are a unique group of emerging contaminants of global concern due to their persistent nature in the natural ecosystem, genotoxic and mutagenic effects on human and aquatic lives, and difficulties in degradation through conventional techniques (Akpotu *et al.*, 2019; Magesh *et al.*, 2022).

Recently, the manufacturing and consumption of antibiotics have expanded significantly due to their wide uses in agriculture, animal husbandry, and pathogens' resistance to antibiotics (Al-Musawi *et al.*, 2021; Tang *et al.*, 2017). Ciprofloxacin (CIP) is a synthetic antibiotic and broadly used to treat chest, skin, and bone bacterial infections (Zhu *et al.*, 2015; Pham *et al.*, 2020). CIP is extremely soluble in water ( $\approx 1.35$  mg mL<sup>-1</sup>) (Kümmerer *et al.*, 2009), and it is arduous to degrade in nature due to the presence of fluorine atoms (Mohammed *et al.*, 2019). Recently, the existence of CIP residue has been reported in the range of 100 ng L<sup>-1</sup> to 10  $\mu$ g L<sup>-1</sup> in the wastewater, one hundred ng L<sup>-1</sup> to  $\mu$ g L<sup>-1</sup> in surface water, 25  $\mu$ g L<sup>-1</sup> in the environment, and from 100 to 500 mg L<sup>-1</sup> in industrial and hospital effluents (Jara-Cobos *et al.*, 2023; Ghosh *et al.*, 2023; Antonelli *et al.*, 2020; Tran *et al.*, 2022). These remarkable CIP concentrations in the wastewater and soil could cause antibiotic-resistance bacteria as well as be responsible for serious health threats such as salmonella typhimurium, which leads to genotoxic effects on aquatic organisms (Diwan *et al.*, 2010; Espinosa *et al.*, 2015; Cox *et al.*, 2002; Kümmerer *et al.*, 2000; Bui *et al.*, 2013; Van Wieren *et al.*, 2012). It is highly necessary to remove CIP from wastewater due to the concern for human health, the environment, and the ecosystem. There are numerous techniques such as photocatalytic degradation (Dao *et al.*, 2018), advanced oxidation (Karthikeyan *et al.*, 2012; Biancullo *et al.*, 2019), membrane process (Radjenović *et al.*, 2008; Tran *et al.*, 2016; Tran *et al.*, 2017), ozonation (Moreira *et al.*, 2016), bioremediation (Polesel *et al.*, 2016; Sarangapani *et al.*, 2019), and adsorption (Grimes *et al.*, 2019; Le *et al.*, 2018; Tran *et al.*, 2019) for antibiotic removal that have been introduced. Out of them, the adsorption process offers superior advantages because of its simple procedure, easy maintenance, low cost, and low eco-friendliness (Ahmed *et al.*, 2015; Homem *et al.*, 2011).

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Zeolites are microporous aluminosilicate crystalline minerals with 3-dimensional frameworks of SiO<sub>4</sub> and AlO<sub>4</sub> tetrahedra that are linked through oxygen atoms to give orderly interconnected cages and tunnels (Chen *et al.*, 2015; Yu *et al.*, 2013). Recently, zeolites have been used frequently in the adsorption process due to their microporosity, large surface area, low cost, thermal stability, and high cation-exchange capacity (Cheng *et al.*, 2017). But the smaller pore size of zeolites compared to the molecular size of the antibiotics restrains their broad application for wastewater treatment (Farghali *et al.*, 2021). Surface modification and/or functionalization could be a simple technique to overcome this problem as well as enhance the adsorption performances of zeolites (Mohiuddin *et al.*, 2022). GO, one of the most remarkable inventions of the twentieth century, could modify the surface area and porosity of zeolites to improve their adsorption capacity towards adsorbents. The adsorption capacity of GO for CIP and Cs (I) from water was reported as 18.6 and 32.53 mg g<sup>-1</sup>, respectively (Yadav *et al.*, 2018; Tan *et al.*, 2016). The adsorption capacities of reduced GO-modified magnetite composites and GO-modified zeolite for CIP and rhodamine B were determined as 18.2 and 55.56 mg g<sup>-1</sup>, respectively (Tang *et al.*, 2013). But GO is highly dispersible in water, and it is hard to distinguish the dispersed GO after completing the adsorption process from the wastewater (Farghali *et al.*, 2021). In order to solve the separation problem of GO and overcome the pore size trouble of zeolites, GO functionalized zeolite was proposed for the effective removal of CIP from the aqueous solution.

In this study, GO functionalized zeolite (ZGO) was synthesized through a simple hydrothermal process. The successful formation of ZGO was confirmed by FESEM, FTIR, and RAMAN. The adsorption ability of ZGO for CIP was examined by different parameters such as pH of the aqueous solution, contact time of the adsorption process, dosages of ZGO, initial CIP concentration, and temperature. Kinetic and isotherm analysis were obtained as a function of the variable of contact time and the initial concentration of CIP, respectively. For adsorption kinetics, the experimental data were fitted to pseudo-first-order, pseudo-second-order, Elovich, and intra-particle diffusion models, whereas analyzed Langmuir, Freundlich, and Temkin models for adsorption isotherms.

## 2. EXPERIMENTAL

### 2.1 Synthesis of Zgo

Following a modified version of the Hummer's method, GO was obtained from graphite powder (Mohiuddin *et al.*, 2021). Firstly, 2.0 g zeolite was added to the mixture of 1.0 mL concentrated H<sub>2</sub>SO<sub>4</sub> and 25.0 mL distilled water (DW) in a 100 mL round-bottomed flask. After sonication for 30 min, 1 mg mL<sup>-1</sup> GO dispersion dropwise was added into the flask. After completing the reaction, the reaction composition was refluxed for 24 h under magnetic stirring at 100 °C. After that, the mixture was kept overnight to settle down. Then, the homogeneous mixture was centrifuged at 4000 rpm and washed with DW and absolute ethanol (EtOH). The obtained black powder was finally dried (50°C, 12 h) in a vacuum oven, and 1.9139 g of ZGO was collected.

### 2.2 Adsorption Studies

100 mg L<sup>-1</sup> stock aqueous solution of CIP was prepared in methanol from standard 1000 mg L<sup>-1</sup> CIP adsorbate and reserved in the refrigerator. The pH of the aqueous solution was prepared and controlled by using 0.1 M H<sub>3</sub>PO<sub>4</sub> and 0.1 M NaOH. For adsorption studies, the initial concentration of CIP solution was 0.4 mg mL<sup>-1</sup>. Following that, a certain amount of ZGO was put in the CIP solution and shaken at 200 rpm at room temperature (RT) using an orbital shaker. After a definite shaking time, the solution of ZGO and CIP was centrifuged at 4000 rpm and separated the residue with a 0.45 µm CHROMAFIL® Xtra syringe filter. The blank concentration (without adsorption) and different concentrations of adsorption of CIP by different dosages of ZGO were measured by a LC-MS/MS (Agilent 1290 TQ 6420) in positive electron spray ionization mode (ESI+). The adsorption ability of ZGO for CIP was determined by Equation (1).

$$\text{Removal percentage} = \frac{C_o - C_t}{C_o} \times 100 \quad (1)$$

where  $C_o$  is the initial, and  $C_t$  is the concentration at time  $t$  (mg L<sup>-1</sup>) of CIP solution. Adsorbed amount of CIP by ZGO at time  $t$  ( $q_t$ ), and at equilibrium ( $q_e$ ) were determined by Equations (2) and (3), respectively.

$$q_t = \frac{C_o - C_t}{M} \times V \quad (2)$$

$$q_e = \frac{C_o - C_e}{M} \times V \quad (3)$$

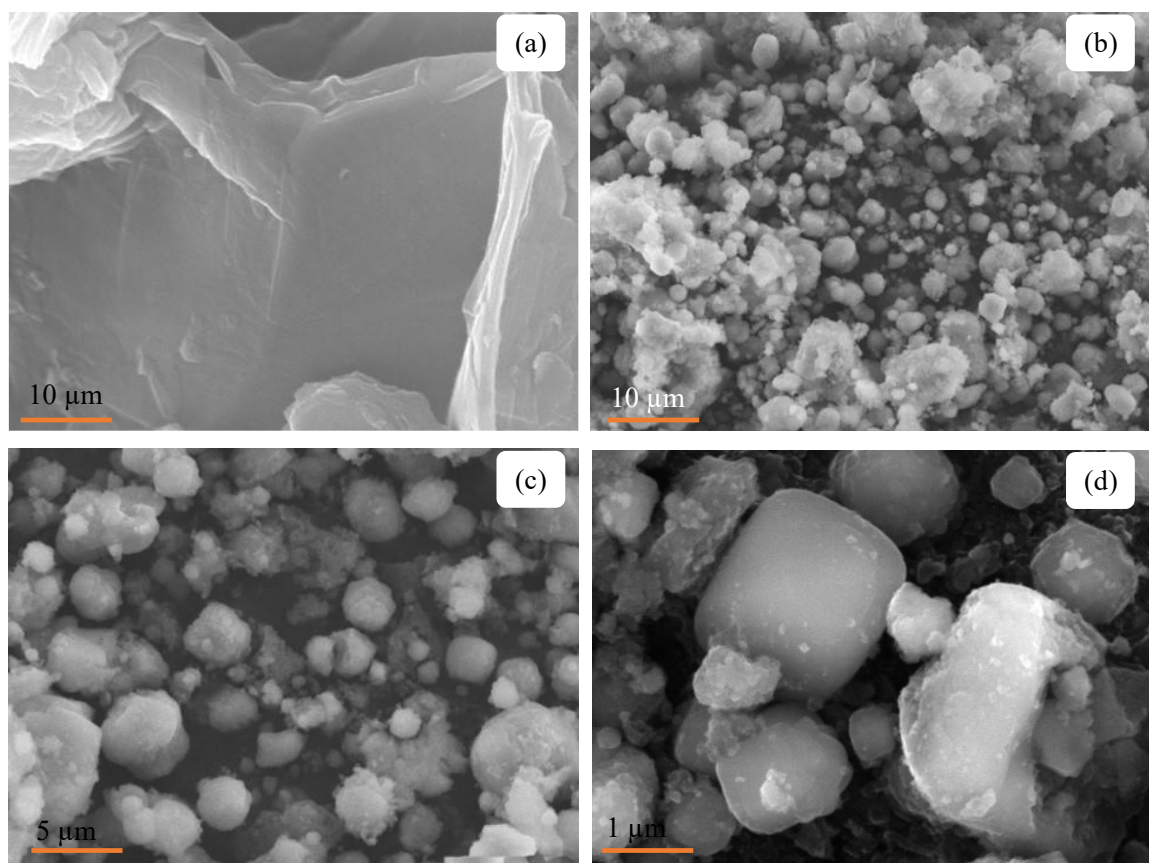
where  $C_e$  is the equilibrium concentration of CIP solution ( $\text{mg L}^{-1}$ ).  $M$  and  $V$  represent the dosage of ZGO (g), and the volume (L) of CIP solution.

### 3. RESULTS AND DISCUSSION

#### 3.1 Characterization

##### 3.1.1 Morphology Analysis

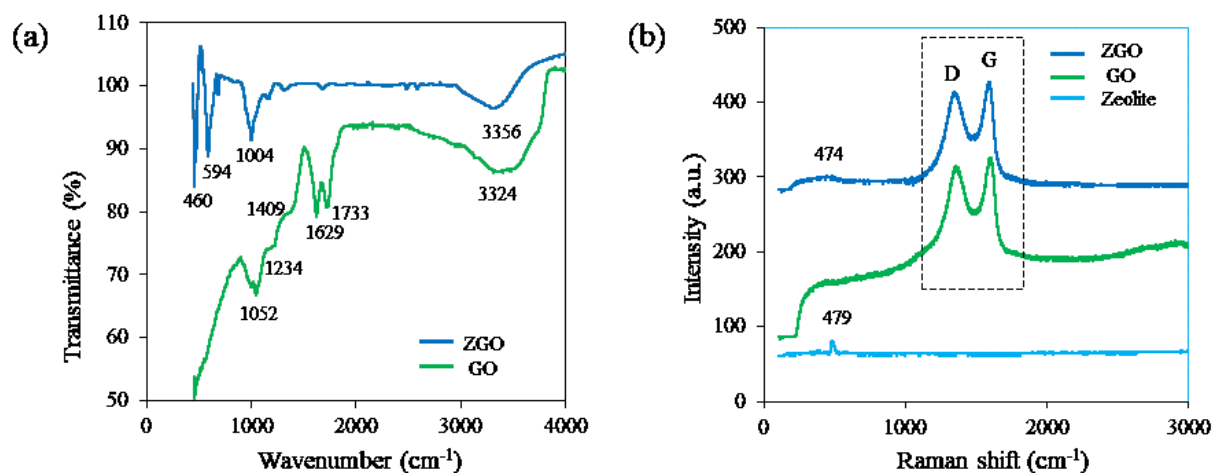
FESEM was conducted to study the surface morphologies of GO and ZGO. Figure 1a exhibited a well-packed layered structure of GO with wave-like cloud morphology (Gurunathan *et al.*, 2016). Figures 1b to 1d revealed the FESEM images of ZGO at different magnifications. Figure 1b showed the scatter distribution of numerous numbers of zeolites nanoparticles (NPs) on the GO surface, whereas Figure 1c illustrated that the GO surface was decorated with different diameters of zeolites nanoparticles. Figure 1d demonstrated that the crystal shape of zeolite nanoparticles was cubic (Li *et al.*, 2020).



**Figure 1:** FESEM images of (a) GO, and (b-d) ZGO at different magnifications.

##### 3.1.2 Structural Analysis

FTIR was investigated to analyze the bonding configuration of GO and ZGO. Figure 2a exhibited the FTIR spectra of GO and ZGO. GO showed characteristic peaks at  $1052\text{ cm}^{-1}$ ,  $1234\text{ cm}^{-1}$ ,  $1629\text{ cm}^{-1}$ , and  $1733\text{ cm}^{-1}$ , which were due to stretching vibration of alkoxy C-O, stretching vibration of epoxy C-O, stretching vibration of C=C, and stretching vibration of C=O, respectively. Furthermore, a weak peak at  $1409\text{ cm}^{-1}$  and a wide peak at  $3324\text{ cm}^{-1}$  were due to O-H deformation and stretching and vibration of O-H, respectively (Mohiuddin *et al.*, 2023). On the other hand, ZGO showed characteristic peaks at  $460\text{ cm}^{-1}$ ,  $594\text{ cm}^{-1}$ , and  $1004\text{ cm}^{-1}$ , which were due to internal vibrations of  $\text{MO}_4$  ( $M = \text{Al/Si}$ ). Moreover, the disappearance of stretching vibration of C=O peaks ( $1733\text{ cm}^{-1}$ ) and shifting of the stretching and vibration O-H peaks to  $\sim 3356\text{ cm}^{-1}$  indicated that the -C=O groups might have been converted to Al/Si-O-C bonds, resulting in the formation of the ZGO nanocomposite (Choudhury *et al.*, 2021; Huang *et al.*, 2012).



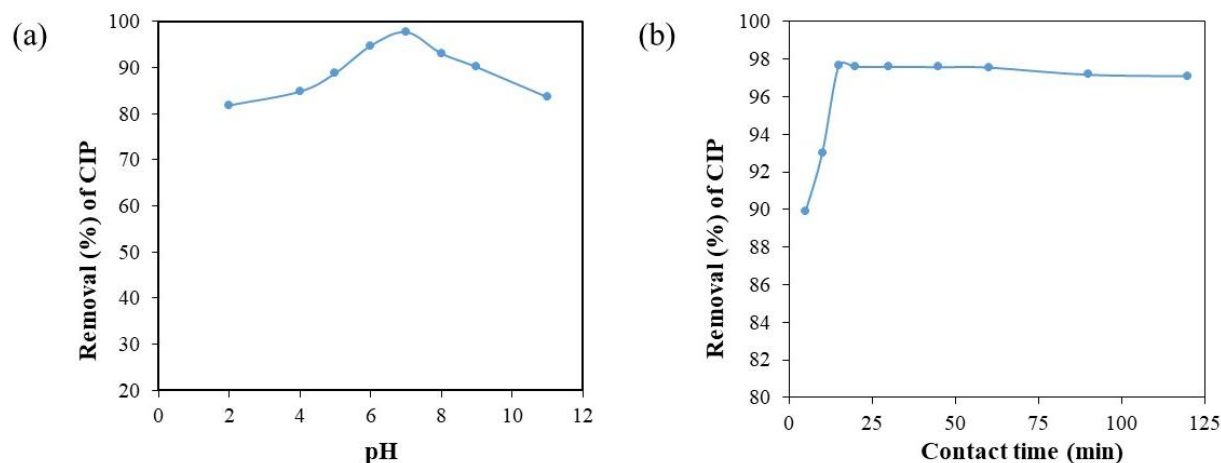
**Figure 2:** (a) FTIR spectra of GO, and ZGO, and (b) Raman spectra of GO, and ZGO with zeolite as reference.

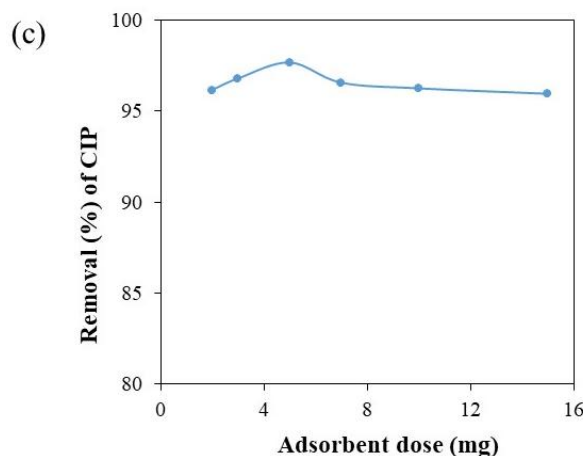
Raman spectroscopy was examined to study the chemical structure and molecular interactions of the prepared samples. Figure 2b exhibited the Raman spectra of zeolites, GO, and ZGO. A sharp peak at  $\sim 479$   $\text{cm}^{-1}$  in the zeolites sample corresponds to M-O in the zeolite structure (Yu *et al.*, 2013). The D and G bands of GO materialized at  $\sim 1353$   $\text{cm}^{-1}$  and  $\sim 1596$   $\text{cm}^{-1}$ , respectively, which slightly shifted to  $\sim 1348$   $\text{cm}^{-1}$  (5  $\text{cm}^{-1}$ ) and  $\sim 1594$   $\text{cm}^{-1}$  (2  $\text{cm}^{-1}$ ) for ZGO. This red shift indicated the remarkable bond configuration between the M-O bond of zeolites and the carbon atom of the GO plane (Banu *et al.*, 2020). Furthermore, ZGO also showed a slight change in peak position (at  $\sim 474$   $\text{cm}^{-1}$ ), which suggested the existence of zeolites on the GO surface.

### 3.2 Optimization of the Experimental Conditions

#### 3.2.1 pH Effect

The pH significantly controls the removal percentage of CIP in the aqueous solution. Figure 3a showed the influence of different pH (2-11) in the removal percentages of CIP for the 0.25  $\text{g L}^{-1}$  ZGO at 15 min. The figure demonstrated that the removal percentages of CIP improved step by step from pH 2.0 to 7.0, then declined from pH 7.0 to 11.0. CIP is mostly anionic ( $\text{CIP}^-$ , deprotonated due to COOH) at  $\text{pH} > 8.7$ , zwitterionic (neutral CIP) in the range of pH 6.1 to pH 8.7 and cationic ( $\text{CIP}^+$ , deprotonated due to  $\text{NH}_2$ ) at  $< 6.1$  (Wang *et al.*, 2016). On the other hand, the COOH group of ZGO has a pKa of 4.5 (Chen *et al.*, 2015). At pH 2.0, the removal percentage of CIP was lowest due to all neutral COOH species of ZGO and the largest amount of CIP in the aqueous solution. With the increasing of pH, the COOH group of ZGO started to deprotonate and turned into negatively charged  $\text{COO}^-$ . At pH 4.5, around 85% of the  $\text{CIP}^+$  is adsorbed by negatively charged ZGO. In the range of pH 4.5 to 6.1, electrostatic repulsion occurs due to positively charged ZGO and  $\text{CIP}^+$ . At pH 5.0, about 80% of the -COOH group deprotonated ( $\text{COO}^-$ ), while at pH 9.0, all -COOH groups deprotonated (Chen *et al.*, 2015). At pH 6.1, around 95% of the CIP adsorbed by ZGO and adsorption process still increased instead of positively charged ZGO and neutral CIP. It may be due to the H-bonding or electron acceptor mechanism between ZGO and CIP (Alameri *et al.*, 2022). At pH 7.0, the maximum removal of CIP was 96.77%.





**Figure 3:** (a) Effect of pH on the adsorption of CIP from the aqueous solution by ZGO ( $C_o = 100 \text{ mg L}^{-1}$ , ZGO =  $0.25 \text{ g L}^{-1}$ ,  $t = 15 \text{ min}$ , shaking = 200 rpm,  $T = 32 \text{ }^\circ\text{C}$ ), (b) effect of contact time on the adsorption of CIP by ZGO ( $C_o = 100 \text{ mg L}^{-1}$ , ZGO =  $0.25 \text{ g L}^{-1}$ , pH = 7, shaking = 200 rpm,  $T = 32 \text{ }^\circ\text{C}$ ), and (c) effect of adsorbent dose on the adsorption of AZM from the aqueous solution onto ZGO ( $C_o = 100 \text{ mg L}^{-1}$ , pH = 7,  $t = 15 \text{ min}$ , shaking = 200 rpm,  $T = 32 \text{ }^\circ\text{C}$ ).

### 3.2.2 Effect of Contact Time

Contact time is the foremost consideration for economical and effective removal of selective pollutants in the wastewater treatment process. Figure 3b showed the influence of different contact times (5–120 min) in the removal percentages of CIP for the  $0.25 \text{ g L}^{-1}$  ZGO at pH 7.0. The figure illustrated that the removal percentages of CIP sharply increased from 1 to 15 min, then remained almost constant up to 120 min. Initially, the adsorption of CIP by ZGO was very low due to the lack of enough time for physical contact for the chemical reaction (Alameri *et al.*, 2022). At 5 minutes, it was almost 90% due to the large amount of CIP and lot of free active sites of ZGO [54]. At 15 minutes, saturation occurs and the chemical reaction reaches equilibrium. The maximum removal of CIP was 97.67% at 15 min.

### 3.2.3 Effect of Adsorbent Dosage

Figure 3c showed the influence of different amounts of ZGO (2–15 mg) in the removal percentages of CIP for 15 min at pH 7.0. The figure exhibited that the removal percentages of CIP improved gradually from 96.15 to 97.67% for 2 to 5 mg of ZGO, which reflects the identical concurrence with previously reported zeolites adsorbent (Samarghandi *et al.*, 2015). Then the removal percentages of CIP decreased and remained almost constant up to 15 mg due to aggregation of the adsorbent. 5 mg ( $0.25 \text{ g L}^{-1}$ ) was selected as the optimum dosage of ZGO for this study.

### 3.2.4 Adsorption Kinetics

To get information about the physical and/or chemical interaction between CIP and ZGO, the adsorption kinetics were investigated. The mathematical linear forms of pseudo-first-order (equation 4: where,  $k_1$  is the pseudo-first-order rate constant,  $\text{g mg}^{-1} \text{ min}^{-1}$ ), pseudo-second-order (equation 5: where,  $k_2$  is the pseudo-second-order rate constant,  $\text{g mg}^{-1} \text{ min}^{-1}$ ), Elovich (equation 6: where,  $a_e$  and  $b_e$  is the initial adsorption rate,  $\text{mg g}^{-1} \text{ min}^{-1}$ ; and magnitude of surface coverage and activation energy for chemisorption,  $\text{g mg}^{-1}$ , respectively), and intra-particle diffusion (equation 7: where,  $k_i$  and  $C_i$  is the rate constant associated with the intra-particle diffusion model,  $\text{mg g}^{-1} \text{ min}^{-0.5}$ ; and the constant and proportional to boundary layer thickness,  $\text{mg g}^{-1}$ , respectively), were calculated for  $0.5 \text{ mg L}^{-1}$  initial concentration of CIP and  $0.25 \text{ g L}^{-1}$  adsorbent dose of ZGO at pH 7.0 for 5-120 min at RT (Wahab *et al.*, 2021; Azam *et al.*, 2022; Upoma *et al.*, 2022).

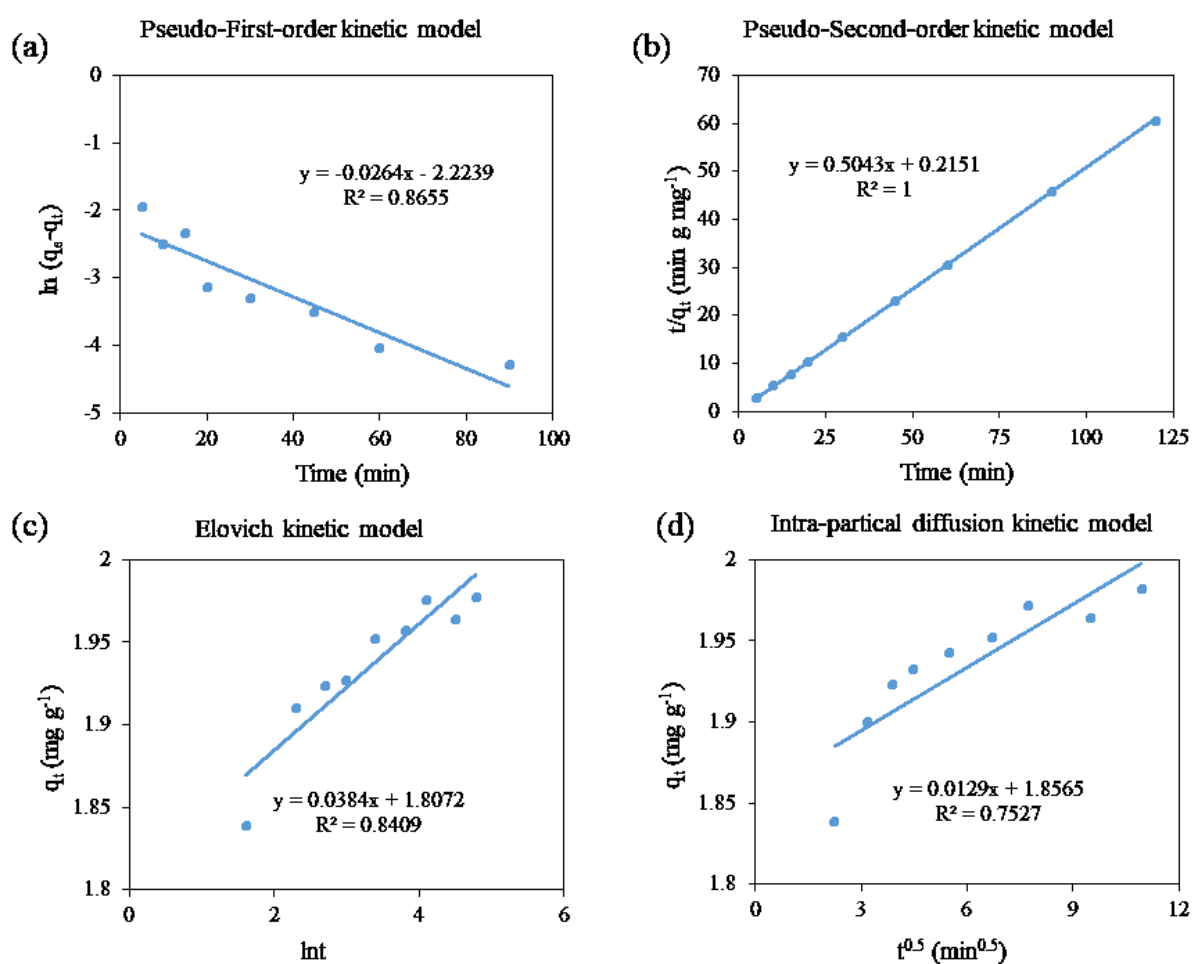
$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (4)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (5)$$

$$q_t = \frac{\ln a_e b_e}{b_e} + \frac{1}{b_e} \ln t \quad (6)$$

$$q_t = k_i t^{0.5} + C_i \quad (7)$$

Figure 4 shows the calibration curves for four kinetic models according to their expressed equations. The plot of  $\ln(q_e - q_t)$  versus time for pseudo-first-order kinetics exhibited linear regression:  $\ln(q_e - q_t) = -0.0264t \text{ (min)} - 2.2239$ ,  $R^2 = 0.8655$ , where  $R^2$  is the correlation coefficient [Figure 4a]. The plot of  $t/q_t$  versus time for pseudo-second-order kinetics demonstrated a linear regression equation:  $t/q_t \text{ (min g mg}^{-1}\text{)} = 0.5043t \text{ (min)} + 0.2151$ ,  $R^2 = 1$  [Figure 4b]. The plot of  $q_t$  versus  $\ln t$  for Elovich kinetics illustrated a linear regression equation:  $q_t \text{ (mg g}^{-1}\text{)} = 0.0384 \ln t + 1.8072$ ,  $R^2 = 0.8409$  [Figure 4c]. The plot of  $q_t$  versus  $t^{0.5}$  for intra-particle diffusion kinetics provided a linear regression equation:  $q_t \text{ (mg g}^{-1}\text{)} = 0.0129t^{0.5} \text{ (min}^{0.5}\text{)} + 1.8565$ ,  $R^2 = 0.7527$  [Figure 4d]. The variable parameters were determined by the respective equation and summarized in Table S1. The experimental data were best fitted with the pseudo-second-order kinetic model considering  $R^2$  values, which confirmed that the adsorption process was carried out by a chemical reaction between CIP and ZGO (Ciopec *et al.*, 2012; Li *et al.*, 2017).



**Figure 4:** (a) Pseudo-first-order kinetic model, (b) pseudo-second-order kinetic model, (c) Elovich kinetic model, and (d) Weber–Morris intraparticle diffusion model [conditions:  $C_0 = 500 \text{ mg L}^{-1}$ ,  $\text{pH} = 7$ ,  $\text{ZGO} = 0.25 \text{ g L}^{-1}$ ,  $t = (5\text{--}120) \text{ mins}$ , shaking = 200 rpm,  $T = 32 \text{ }^\circ\text{C}$ ].

### 3.2.5 Adsorption Isotherms

To study the adsorption behavior of CIP on ZGO and determine the capacity of the ZGO, the Langmuir, Freundlich, and Temkin isotherm models were considered and analyzed by different concentrations of CIP from 0.05 to 0.5  $\text{mg L}^{-1}$  at constant temperature and constant pH (7.0). The simple form of the Langmuir isotherm (equation 8; where  $q_m$  is the maximum adsorption capacity of ZGO,  $\text{mg g}^{-1}$ ; and  $K_L$  is the Langmuir adsorption constant,  $\text{L mg}^{-1}$ ), the Freundlich isotherm (equation 9; where,  $K_F$  is the Freundlich adsorption constant,  $\text{mg}^{1-1/n}$



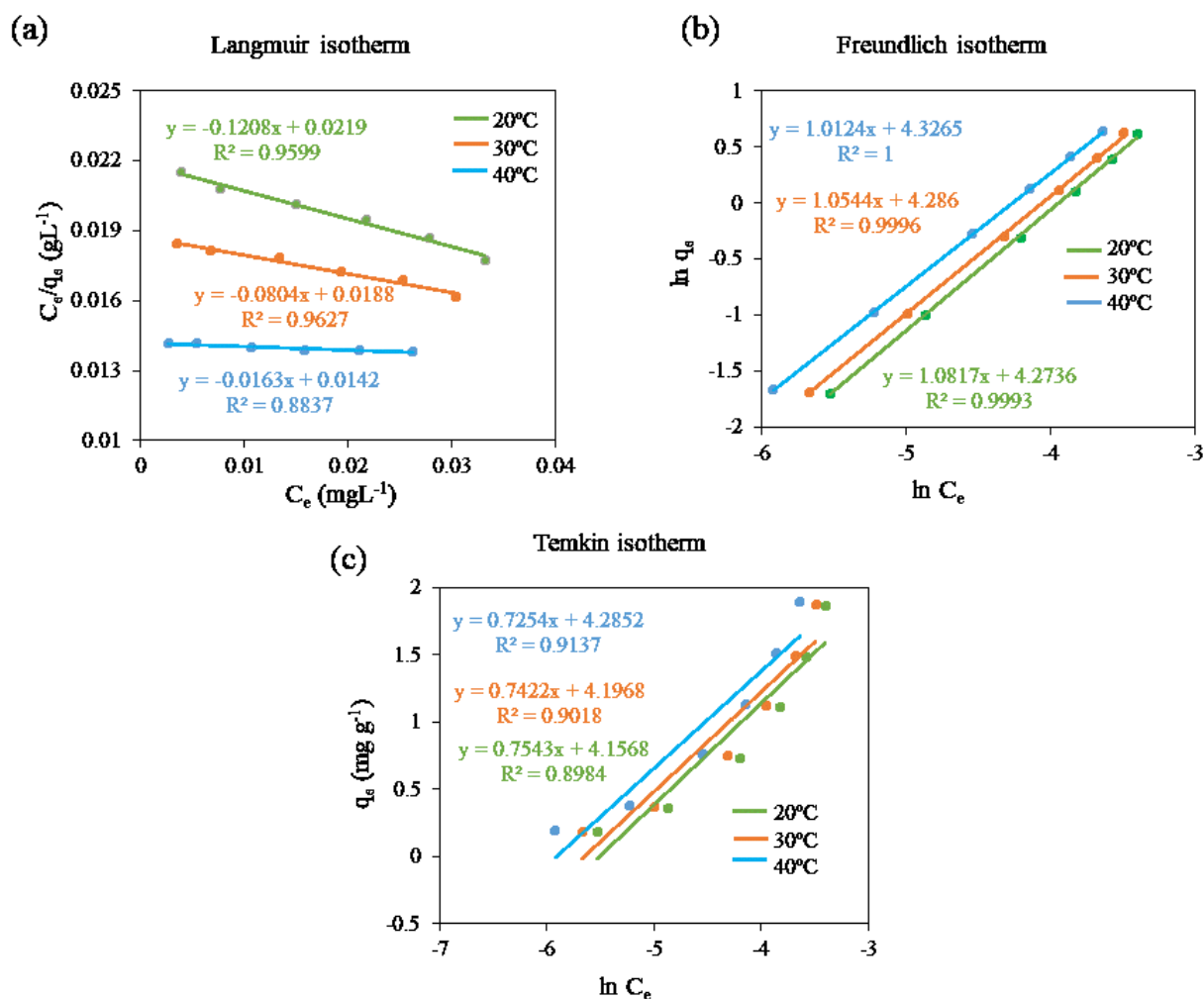
$L^{-1/n} g^{-1}$ ; and  $n$  is a constant related to adsorption intensity), and the Temkin isotherm (equation 10; where,  $R$  is the real gas constant,  $J K^{-1} mol^{-1}$ ;  $T$  is the temperature,  $K$ ;  $K_T$  refers the equilibrium binding constant,  $L g^{-1}$ ; and  $b$  is the heat of adsorption constant,  $J mol^{-1}$ ) are expressed as following equations (Kwak *et al.*, 2016).

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{K_L q_m} \quad (8)$$

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \quad (9)$$

$$q_e = \frac{RT}{b} \ln K_T + \frac{RT}{b} \ln C_e \quad (10)$$

Figure 5 showed the calibration curves for 0.25 g L<sup>-1</sup> adsorbent dose of ZGO while shaking at 20, 30, and 40 °C for three isotherm models according to their expressed equations. The plot of  $C_e/q_e$  versus  $C_e$  for the Langmuir isotherm demonstrated three linear regression equations with correlation coefficients of 0.9599, 0.9627, and 0.8837 for 20, 30, and 40 °C, respectively [Figure 5a]. The plot of  $\ln q_e$  versus  $\ln C_e$  for the Freundlich isotherm provided three linear regression equations with correlation coefficients of 0.9993, 0.9996, and 1.0000 for 20, 30, and 40 °C, respectively [Figure 5b]. The plot of  $q_e$  versus  $\ln C_e$  for the Temkin isotherm illustrated three linear regression equations with correlation coefficients of 0.8984, 0.9018, and 0.9137 for 20, 30, and 40 °C, respectively [Figure 5c]. The variable parameters were determined by the respective equation and summarized in Table S2. From the  $R^2$  values of all isotherm models, experimental data best fitted to the Freundlich isotherm, which indicated that the adsorption of CIP happened on the multilayer and heterogeneous surface of ZGO (Yadav *et al.*, 2018).



**Figure 5:** (a) Langmuir isotherms, (b) Freundlich isotherms, and (c) Temkin isotherm model (conditions:  $C_o = 50\text{--}500 \text{ mg L}^{-1}$ ,  $pH = 7$ ,  $ZGO = 0.25 \text{ g L}^{-1}$ ,  $t = 15 \text{ min}$ , shaking = 200 rpm,  $T = 20, 30, \text{ and } 40 \text{ } ^\circ\text{C}$ ).

The  $q_m$  was determined as 8.28, 12.45, and 61.35 mg g<sup>-1</sup> for 20, 30, and 40 °C, respectively (as shown in Table S2), which confirmed the stimulation of greater sites of ZGO surface with the increment of temperatures during the adsorption process (Tang *et al.*, 2013). Table 1 represents the comparison in the different parameters of ZGO with other previously reported adsorbents for CIP removal.

**Table 1:** Comparison in the different parameters of ZGO with other previously reported adsorbents for CIP removal.

Adsorbent	Fitted model		Optimum pH	Adsorption capacity (mg g <sup>-1</sup> )	References
	Kinetics	Isotherms			
Graphene oxide	Pseudo-2nd order	Langmuir	7	18.6	Yadav <i>et al.</i> , 2018)
Reduced graphene oxide/magnetite composites	Pseudo-2nd order	Langmuir and Temkin	6.5	18.2	(Tang <i>et al.</i> , 2013)
Chitosan/kaolin/ Fe <sub>3</sub> O <sub>4</sub> magnetic microspheres	Pseudo-2nd order	Langmuir	6	47.8	(Ma <i>et al.</i> , 2014)
Carbon nanofibers	Pseudo-2nd order	Langmuir	6	10.3	(Li <i>et al.</i> , 2016)
Titanate nanotubes	Pseudo-2nd order	Langmuir	4	18.9	(Xu <i>et al.</i> , 2019)
Clinoptilolite	Pseudo-2nd order	Langmuir	6	5.4	(Ngeno <i>et al.</i> , 2019)
Carbon nanosheets supported TiO <sub>2</sub>	Pseudo-2nd order	Freundlich	7	40.5	(Li <i>et al.</i> , 2019)
MgO nanoparticles	Pseudo-2nd order	Langmuir	6	3.46	(Khoshnamvand <i>et al.</i> , 2017)
ZGO nanoparticles	Pseudo-2nd order	Freundlich	7	61.35	This study

### 3.2.6 Stability and Reusability

Effects of stability and reusability of ZGO were examined several times regenerated after adsorption of CIP, and the decline of the removal percentage of CIP was shown in Figure S1. ZGO adsorbent demonstrated excellent removal percentage of CIP (~90%) for eleven consecutive sequences after washing by acetone every time. After first three cycles, the removal percentage of CIP moderately reduced 97.67% to 96.88%, then almost constant from forth to seven cycles (96.24-95.11%), but significantly decreased last five cycles. Because of strong stability and superior reusability, ZGO adsorbent could be considered as a potential candidate for real-time applications.

## 4. CONCLUSIONS

GO-functionalized zeolites (ZGO) were synthesized through a simple hydrothermal process for the adsorption of CIP from the aqueous solution. FESEM images revealed the scatter cubic-shaped zeolite NPs on the GO surface. FTIR and RAMAN demonstrated the successful formation of ZGO nanocomposites. The covalent bond between Al and/or Si with the different functional groups of GO (such as -COOH, -OH, and -C-O-C-) provided excellent results in 97.67% removal of CIP within only 15 min. Adsorption kinetics between ZGO and CIP followed the pseudo-second-order model, whereas experimental data best fitted to the Freundlich adsorption isotherm with a maximum  $q_m$  of 61.35 mg g<sup>-1</sup> at the highest temperature (40 °C) of this study. In addition, ZGO adsorbent could be considered as a potential candidate for real-time applications owing to its remarkable stability and reusability.

## ACKNOWLEDGEMENT

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