



Original Research Article

Enhancing Ciprofloxacin Removal: Unveiling the Potential of Graphene Oxide Synthesized from Cassava Peels through Box-Behnken Design Optimization

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ABSTRACT

The adsorption of ciprofloxacin from an aqueous solution using graphene oxide as an adsorbent derived from cassava peel waste using a modified Hummers method was described. The properties of the adsorbent were characterized using Fourier-Transform Infrared Spectroscopy, X-ray diffraction, Raman Spectroscopy and Scanning Electron Microscopy-Energy Dispersive X-ray techniques. The influence of the operational variables including potential of hydrogen, adsorbent mass, and contact time in the adsorption of ciprofloxacin was evaluated by response surface methodology. In particular, the interactions between the operational variables were evaluated using the Box-Behnken Design to determine the optimum conditions. The results indicated that the optimum conditions were achieved at pH 3, contact time of 20 minutes, using 35 mg of graphene oxide adsorbent, resulting in an adsorption efficiency of 91.71%. The results demonstrated that the graphene oxide material derived from cassava peel waste can be effectively used as an adsorbent for ciprofloxacin from aqueous solutions.

KEYWORDS

Ciprofloxacin, Adsorption, Graphene Oxide, Cassava Peel Waste, "Box Behnken Design"

INTRODUCTION

The contamination of water sources by pharmaceutical residues, particularly antibiotics, has become a growing concern due to its potential adverse effects on ecosystems and human health [1]. Antibiotic residues are introduced into the environment through diverse pathways, including the discharge of waste materials from healthcare facilities [2], pharmaceutical

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manufacturing processes [3], agricultural practices such as livestock farming, as well as the direct excretion of antibiotics by both human and animal populations [4]. The continuous utilization of antibiotics in both human medical care and veterinary medicine has been linked to the growing demand for antibiotics and the consequent increase in antibiotic production, which in turn raises the likelihood of increasing levels of antibiotic residues in the environment. It's worth emphasizing that an estimated 75% to 95% of administered antibiotics undergo incomplete metabolic breakdown or remain unmetabolized within the organisms [5]. This incomplete breakdown and the persistence of antibiotics within organisms contribute significantly to the release of antibiotic residues into the environment, thereby intensifying the problem of antibiotic contamination across various ecosystems. Thus, it is imperative to address the issue of antibiotic residues in aquatic ecosystems to ensure the continued availability of uncontaminated water, which is fundamental for sustaining all forms of life on Earth.

Among these antibiotics, ciprofloxacin (CIP) has garnered attention as a widely used antibiotic, known for its efficacy against a range of bacterial infections. Ciprofloxacin (CIP) is a well-known fluoroquinolone-class antibiotic recognized for its efficacy against a broad spectrum of Gram-negative bacterial infections such as *Escherichia coli* and *Salmonella* spp, which are linked with a range of diseases, including gastroenteritis, urinary tract infections, and abdominal infections [6]. Additionally, CIP demonstrates notable efficacy against specific Gram-positive bacteria, particularly *Staphylococcus aureus* [7]. Notably, CIP exhibits high stability and water solubility across a wide range of pH conditions [8], leading to the anticipated presence of CIP residues in surface waters across diverse regions of Asia, Europe, and the Americas is a predictable occurrence. Typically, the global average concentration of CIP in freshwater surfaces falls within the range of 10-100 ng/L, with the highest recorded concentrations in lakes reaching levels between 2.5-6.5 mg/L [9]. The persistence of such antibiotic residues in the environment poses substantial risks, including the development of bacterial resistance, ecotoxicological implications, chondrotoxic effects on wildlife, and the emergence of various diseases, such as intestinal and cutaneous infections in humans [10]. Therefore, despite the manifold advantages associated with CIP, it becomes imperative to develop methodologies for the removal of antibiotic residues, particularly from aquatic ecosystems, to safeguard human health and preserve existing ecological systems [11].

Numerous technologies have been proposed to address the removal of antibiotics. These include membrane-based approaches, such as the use of hybrid membranes composed of activated carbon and magnetic activated carbon for the removal of azithromycin [12], and the combination of membrane processes with advanced oxidation processes, adsorption, and biological treatments for the removal of active pharmaceutical ingredients [13]. In addition, electrochemical methodologies have also been employed for the removal of fluoroquinolone, ampicillin and chloramphenicol, as well as tetracycline [14]. This technique usually employs electrical energy to drive chemical reactions that degrade, transform, or remove antibiotic contaminants [15]. This technique, relying on the use of electrodes to facilitate oxidation-reduction reactions and generate reactive species, has been proven highly effective for eliminating numerous persistent antibiotic pollutants [16].

Several advanced treatments such as cavitation based technologies, advanced oxidation processes, constructed wetlands, microalgae treatment, and microbial electrochemical systems have also been explored for the removal of numerous antibiotics [17]. Cavitation-based technologies, relying on the use of bubble collapse in a liquid to create intense conditions that degrade contaminants, has been successfully employed to remove sulfadiazine, enrofloxacin and amoxicillin [18]. The above-techniques have also been thoroughly summarized for their application in the removal of tetracycline, involving the biodegradable and non-biodegradable routes [19]. Finally, adsorption techniques based on the use of numerous carbon-based absorptive materials like biochar, carbon nanotubes, activated carbon, and graphene have been proven effectively to remove contaminants, although challenges in process integration,

production, and modification necessitate further research [20]. Adsorption-based methods, in particular, exhibit significant efficacy as they can eliminate both soluble such as 4-nonylphenol [21] and insoluble biological contaminants and pollutants such as estriol [22]. Moreover, adsorption processes offer the advantage of being straightforward to implement and cost-effective. Nevertheless, there remains a pressing need to develop methodologies that combine the use of low-cost natural adsorbents but with high efficiency to tackle the removal of these pollutants.

Recent study has highlighted the successful use of mesoporous or nanomaterials, such as Graphene Oxide (GO), in the removal antibiotic pollutants [23]. In particular, numerous studies have explored the effectiveness of GO in adsorbing various antibiotics. Lebron *et al.* utilized statistical physics modelling to optimize the condition for the adsorption of norfloxacin onto GO and found that norfloxacin adsorption occurs by a multi-molecule process with a 99% removal [24]. Gupta *et al.* optimized the removal of methadone using magnetic GO using response surface methodology and revealed that the optimum removal efficiency of methadone was 87.30 mg g⁻¹ [25]. Salihi *et al.* employed GO for the adsorption of trimethoprim and isoniazid and obtained that the adsorption capacities for both compounds were 204.08 mg g⁻¹ and 13.89 mg g⁻¹, respectively [26]. GO is a chemical compound known for its relatively polar and hydrophilic properties, primarily due to its abundant oxygen-containing groups, such as hydroxyl, epoxy, and carboxyl groups [27]. Typically, commercial production of GO involves the synthesis of pure graphite. However, achieving high purity GO from natural based sources can be challenging. Therefore, there is a need for alternative sources that are cost-effective, and readily available, aligning with environmental considerations.

Agricultural waste represents one such environmentally friendly resource that can be harnessed as a raw material for producing GO. Adsorbents derived from agricultural waste not only contribute to the removal of antibiotic pollutants but also help in minimizing agricultural waste. Several studies have stated that agricultural waste can be utilized as the source of adsorbents such as wheat bran, banana peel, avocado peel, peanut shell, and sugarcane bagasse to remove lead (II) and chromium (VI) ions [28], cotton industry waste to remove methylene blue [29], marigold flowers waste to remove cadmium (II) and chromium (VI) ions [30]. Cassava peel waste, for example, contains a substantial carbohydrates, cyanide acid, protein, minerals, and sulphur group making it a suitable candidate for GO production [31]. Based on data from the Indonesian Central Statistics Agency in 2018, Lampung Province is one of the largest cassava producers in the country, with an impressive cassava production volume of approximately 6.68 million tons and an average yield of 25 tons per hectare each harvest season. This abundance underscores the potential of cassava peel waste as a valuable raw material for generating GO, which can serve as an efficient adsorbent for antibiotic pollutants, aligning with the region's high cassava production figures and the associated increase in cassava peel waste production. This research focuses on the use of cassava peel waste as a source for producing highly efficient GO-based adsorbent aimed at tackling antibiotic residues in aquatic environments. Specifically, this research centres on examining the adsorption of CIP on GO-based adsorbents synthesized via the modified Hummers method, while also exploring the influence of different operational conditions.

It is generally known that the adsorptive properties of any adsorbents are highly dependent upon active surface sites including functional groups, particle size, and specific surface area [32]. The rich functional groups present in the active surface sites are important in the adsorption process as they facilitate specific interactions between the adsorbent and the target contaminants [33]. Moreover, the particle size and specific surface area of the adsorbent material significantly influence its adsorption capacity and efficiency, emphasizing the importance in designing the adsorbent material with suitable size and surface area [34]. In the present research, the GO material derived from cassava peel waste was analysed using advanced analytical techniques, including Fourier Transform Infrared (FTIR) spectroscopy, Scanning Electron Microscopy-Energy Dispersive X-Ray (SEM-EDX), and X-ray Diffraction

(XRD), to determine its properties and characteristics. Moreover, it is known that the optimum adsorption is highly dependent on the adsorption conditions such as pH, adsorbent mass, and contact time in the adsorption [35]. The impact of these operational variables on CIP adsorption using GO material was evaluated using response surface methodology (RSM), which establishes mathematical models correlating variables with responses to determine optimal process conditions [36]. In particular, the interactions between the operational variables were evaluated using the Box Behnken Design (BBD) to determine the optimum conditions for CIP adsorption on GO, as this technique has been proven successful in optimizing diverse adsorption processes, including the removal of methadone from environmental samples [25], the treatment of textile waste contaminated with methylene blue [37], and the sequestration of heavy metals from aquatic environments [38].

MATERIALS AND METHODS

All chemicals used in this research were of analytical grade and were used as received without any further purification. The standard CIP was obtained from Hexpharm Jaya and was used for the preparation of CIP standard solution. Other chemicals, such as iron (III) chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$), concentrated sulfuric acid (H_2SO_4), 30% hydrogen peroxide (H_2O_2), ethanol ($\text{C}_2\text{H}_5\text{OH}$), methanol (CH_3OH), were obtained from Supelco Sigma Aldrich and were used as received. Some other chemical used in this research were potassium permanganate (KMnO_4) (MerckTM), barium chloride (BaCl_2) (MerckTM), sodium hydroxide (NaOH) (MerckTM), 37% hydrochloric acid (HCl) (Smart-Lab), glacial acetic acid (Smart-Lab), and distilled water. The materials used in this study were cassava peel waste obtained from local farmers in Lampung Province.

In this study, various equipment were employed, including an analytical balance (AND HR-150A, 152 g capacity, 0.1 mg precision), a hot plate magnetic stirrer (Stuart Biocote R200000 685), a centrifuge (Fischer Scientific 1827001027164), an oven (Memmert 55), a pH meter (Water Tester EZ-9901), and an ultrasonic device (1510 Branson). Several advanced analytical instruments such as Fourier Transform Infrared Spectroscopy (FTIR) instrument (Agilent Cary 630), Scanning Electron Microscope with Energy Dispersive X-ray (SEM-EDX) capability (EVO® MA 10), X-ray Diffraction (XRD) apparatus (XPRT PRO PANalytical PW3040/60), were employed in the characterization of the resulting GO material. A UV-Vis Spectrophotometer (Agilent Cary 100) was used in the determination of CIP concentration in various samples.

The preparation of graphite from cassava peel waste

Cassava peel waste was washed thoroughly with water to remove impurities. Subsequently, the clean cassava peel waste was cut into small pieces and was left to air-dry under the sunlight for a period of 2 to 3 days. Following the initial drying phase, the cassava peels were further dried in an oven at 100°C for 1.5 hours. Once completely dried, the cassava peels were crushed into smaller particles and then placed into a crucible cup, with a total mass of approximately 6 g. The crushed material was subjected to high-temperature treatment, with the temperature reaching a maximum of 350°C and maintained at this level for 2 hours. The resulting charcoal was allowed to cool for 15 minutes within a desiccator, and subsequently, it was finely ground using a mortar and sifted through a 100-mesh sieve.

A total of 5 g of the resulting carbon material obtained from the previous step were weighed and placed into a 1000 mL glass beaker. Subsequently, 500 mL of distilled water was added to the beaker, and the mixture was stirred at 600 rpm using a magnetic stirrer. To this suspension, 4 mL of 1 M $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ solution was introduced. The addition of 4 mL of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ leads the colour change into solid black. Transition metals, like iron, possess the capability to break the intra- and intermolecular hydrogen bonds in the cellulose of cassava peels at low temperatures. This produces simpler molecules as well as a significant amount of

long chain alkanes. This capability allows the process to operate at lower temperatures. Additionally, the interaction between iron and amorphous carbon resulted in the formation of graphite structures. Such catalytic prowess underscores the exceptional performance of iron in the catalytic pyrolysis of solid waste, leading to the production of structured carbon nanomaterials [39]. However, the specific effects of iron in this procedure have not been thoroughly elaborated, presenting a challenge for future research aimed at improving the graphitization process.

The stirring speed was then increased to 900 rpm while maintaining the mixture at room temperature. The pH of the combined solution was gradually adjusted to approximately pH 2 by the slow addition of 1 M HCl. The pH was adjusted to the targeted value, with measurements taken both initially and before each subsequent measurement. However, for the larger scale production, it is crucial to maintain the pH of the solution using buffer solution. The stirring continued at 900 rpm for a duration of 5 hours at a temperature of 60°C. Following this, the solution was subjected to centrifugation at 5000 rpm (2795 g) to separate the supernatant from the graphite precipitate. The precipitate was rinsed until it reached a neutral pH of 7, using distilled water, and was subsequently filtered using filter paper. The resulting precipitate was then dried in an oven, initially at 50°C for 8 hours and subsequently at 110°C for 5 hours. Finally, the dried material was allowed to cool within a desiccator for a period of 15 minutes [40].

The preparation of graphene oxide using the modified hummers method

The synthesis of GO was performed by mixing 1 g of graphite with 23 mL of concentrated H₂SO₄ in a 500 mL beaker. This mixture was continuously stirred at 500 rpm using a magnetic stirrer and maintained at a cold temperature in an ice bath for a duration of 30 minutes. Subsequently, 3 g of KMnO₄ were slowly added into the mixture while the temperature was maintained below 10°C. The stirring was then continued for an additional 30 minutes at 35°C. The temperature of the mixture was increased by a slow addition of 46 mL of distilled water until the temperature reached 98°C, after which the mixture was maintained at room temperature for about 15 minutes [41].

To further enhance the optimization of the oxidation reaction, 140 mL of distilled water was added to the mixture. While being stirred at 500 rpm with a magnetic stirrer for 10 minutes, 10 mL of a 30% H₂O₂ solution was slowly added. The resulting suspension was then washed multiple times using a 5% HCl solution to remove sulphate ions. This was confirmed by testing the suspension with BaCl₂ solution to ensure the absence of sulphate ions, which was indicated by the absence of a white precipitate. Subsequently, the material was thoroughly rinsed with distilled water until it reached a pH of 5. The solution was then subjected to centrifugation at 5000 rpm for 10 minutes to separate the precipitate. The resulting precipitate was dispersed in 450 mL of distilled water, subjected to sonication for 30 minutes, and then filtered using filter paper. The separated precipitate was subsequently dried in an oven at 60°C for 5 hours [42].

The characterization of graphene oxide

The resulting GO material was further analyzed using several advanced analytical instruments to determine its properties and characteristics. The analysis functional group of the GO material was determined using the FTIR instrument. The morphological characteristics, elemental content, and quantitative composition of the GO were assessed using SEM-EDX. This enables a comprehensive examination of the material's surface and its elemental components. An XRD technique was employed to examine the material's structural arrangement and crystalline properties of the GO material to assess the extent of its crystallinity.

Experimental design of Box Behnken Design

The experimental design employed the Box Behnken Design (BBD) method, which involves varying variables at three levels: high (+1), medium (0), and low (-1), with five additional central repetition points, as outlined in **Table 1**. The design generated a total of 17 experiments based on the specified values derived from the BBD design. These experiments were carefully and precisely planned using the Design-Expert software (DX7).

Table 1. Selected levels of independent variables in BBD Design

Influencing factors	-1	0	1
Adsorbent dose (mg)	20	27,5	35
pH (-)	2	3	4
Contact time (minute)	20	30	40

In this study, the experiments were performed sequentially, following the prescribed values outlined in **Table 1** of the BBD design. For each sample, a specific concentration of the antibiotic CIP solution was mixed with a designated quantity of the GO adsorbent under controlled pH conditions and for a specified contact time. The solutions with pH values of 2, 3, and 4 were prepared by the addition of dropwise of HCl until reaching the desired solution's pH. Subsequently, the GO was separated through a combination of centrifugation and filtration methods, allowing for the measurement of the remaining antibiotic concentration in the solution using a UV-Vis spectrophotometer set at a wavelength of 277 nm. A fit analysis was conducted to assess the accuracy and validity of the obtained results. To achieve this, the percentage of antibiotic adsorption was established as the response variable, following Equation (1).

$$\text{Adsorption (\%)} = \frac{C_0 - C_x}{C_0} \times 100 \quad (1)$$

C_0 and C_x representing the initial and final concentrations of CIP in solution (ppm).

RESULTS AND DISCUSSION

In this section, the results of the research were provided, and comprehensive analysis of the results was conducted to reveal significant insights into the underlying trends and implications of the findings. These include the characteristics of the synthesized GO material based on the results of the measurements using several analytical instruments, including FTIR, SEM, and XRD. After that, a detailed discussion was conducted on the optimization of the adsorption condition of CIP using GO, with a comprehensive comparison with the experimental data.

Graphene oxide characterization

The GO obtained was then further characterized using FTIR, SEM, and XRD instruments. The results of GO characterization using FTIR, XRD, and SEM are shown in **Figure 1**. **Figure 1(a)** shows the FTIR characterization result of commercial graphite, biomass graphite and GO. Both FTIR of graphite biomass and GO spectra exhibit characteristics absorption of the stretching vibration of the -OH (hydroxyl) group, as evident by the peaks at 3198 cm^{-1} and 3205 cm^{-1} . The presence of the -OH group in GO spectra can be attributed to the presence of water (H_2O) within the GO structure [41]. Furthermore, there is absorption at 1699 cm^{-1} , indicating the absorption of C=O (carbonyl) groups in GO spectra. The observed absorptions at 1595 cm^{-1} and 1028 cm^{-1} in GO's spectra demonstrate the presence of C=C (alkene) and C-O-C (epoxy) groups in the generated GO. As was previously mentioned, the functional groups in modified GO Hummers have oxygen groups, namely carbonyl (-C=O), carboxyl (-COOH),

and hydroxyl (-OH). This FTIR spectrum shows that the manufacture of GO was successful since it has a functional group that is suitable for pure GO [43]. In accordance with the results reported by Sujiono *et al.* [41] and Surekha *et al.* [44], it is established that GO contains oxygen-based functional groups, encompassing carbonyl (-C=O), carboxyl (-COOH), hydroxyl (-OH), and epoxy (C-O-C) groups. The similarity observed in the FTIR spectra of graphite and the produced GO can be attributed to several factors including minor impurities, surface functional groups, or structural defects present in graphite samples, which can result in weak peaks or absorption bands in the FTIR spectrum. These features, though often subtle, may be observable and have been evident in graphite derived from biomass in various studies reported by Kanta *et al.* [45], Kim *et al.* [46], and Hedge *et al.* [47]. This starkly contrasts with commercial graphite, sourced independently of biomass, which lacks peaks associated with functional groups (refer to **Figure 1**). The differentiation between the spectra of graphite and GO becomes apparent with the appearance of epoxy peaks absent in the graphite spectrum. While not distinctly visible in the FTIR spectrum, the augmentation of functional groups in the resultant GO is discernible through the outcomes EDX analysis.

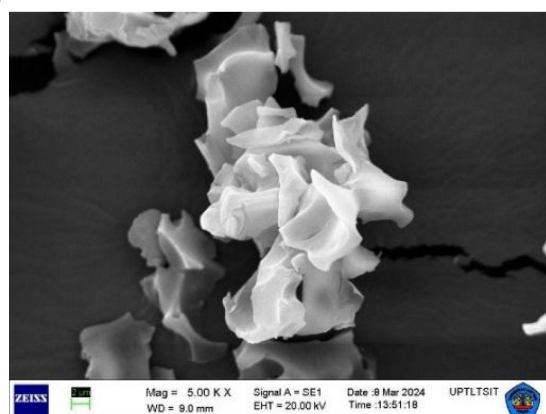
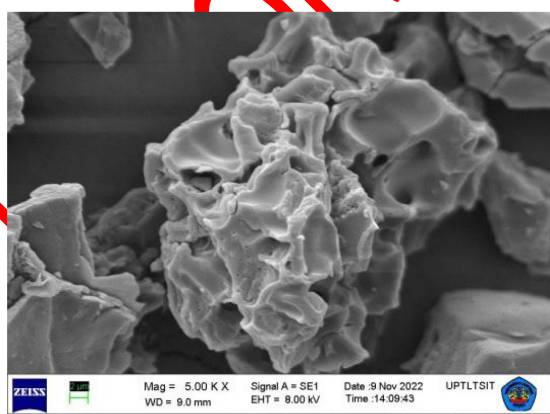
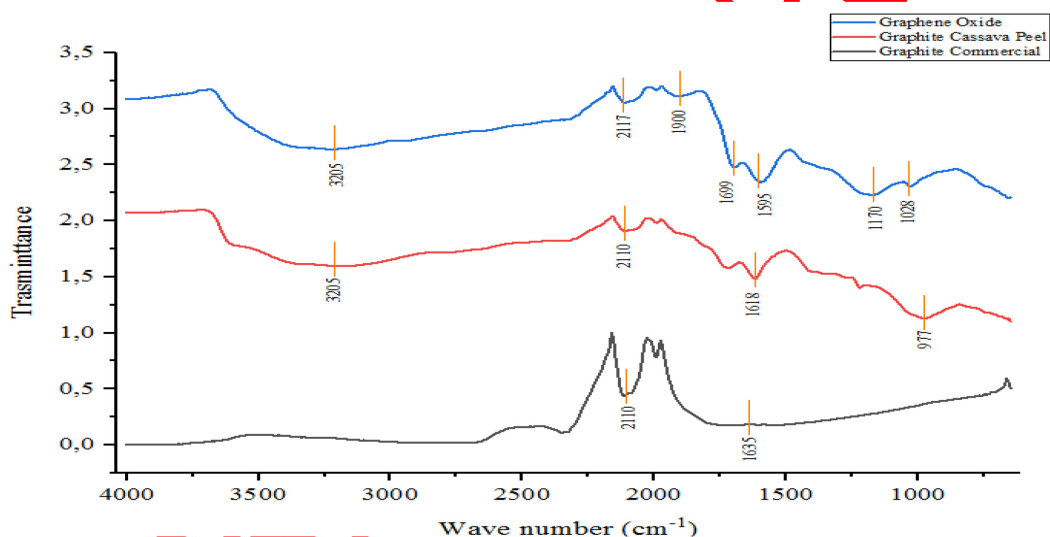


Figure 1. (a) FTIR Spectrum of graphite and GO and (b) SEM image of graphite and (c) GO made from cassava peel waste using modified Hummers method

The surface morphology of graphite and GO can be visualized in **Figure 1(b)** and **1(c)**. The results of the graphite surface morphology analysis (**Figure 1b**) appear to resemble chunks with flakes that have sharp edges, and there are wrinkled areas. The results of surface morphology analysis of GO at 5000x magnification (**Figure 1c**) exhibit a stack of thin sheets with a smooth surface and areas with slight wavy wrinkles. This image also shows that samples exhibit strata with different levels of transparency, as previously reported in [48]. In addition, the surface of GO has many curved shapes and protrusions. The formation of a pile sheets indicates that peeling has occurred during the oxidation and sonication process.

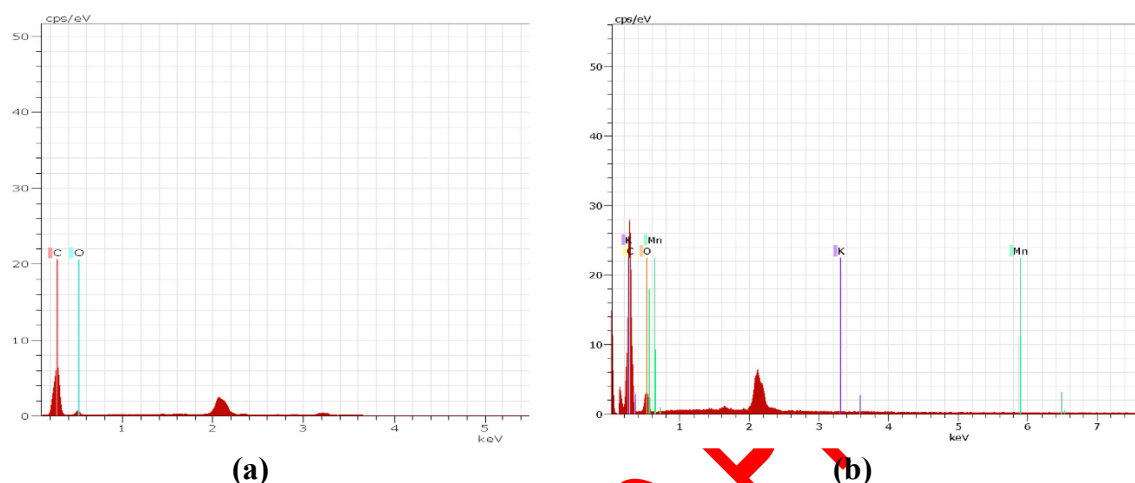


Figure 2. The EDX spectra of graphite (a) and GO (b)

The EDX spectra and elemental weight percentages were obtained for graphite and GO derived from cassava peels, as illustrated in **Figure 2**. The EDX analysis of graphite only revealed the presence of carbon and oxygen atoms (**Figure 2(a)**), whereas GO exhibited the presence of carbon and oxygen atoms alongside potassium and manganese atoms (**Figure 2 (b)**). The latter may have originated from the reagents employed in the oxidation process. Upon subjecting graphite to oxidation via Hummer's method, the weight percentage of carbon decreased to 77.62%, while that of oxygen increased to 22.32%. This elevation in oxygen content suggests the occurrence of the oxidation process in graphite, resulting in the formation of GO.

The XRD spectra of GO is depicted in **Figure 3(a)**. The X-ray diffraction technique is a powerful method generally employed to examine the crystalline structure of a certain material. The crystalline compositions of the GO material indicated by the XRD diffractogram were shown in **Figure 3(b)**. The results revealed that the XRD diffractogram pattern of carbon peaks exists at 2θ values of 24.20° , and 38.91° , which are characteristic peaks for carbon materials [49]. The XRD diffraction patterns reveal an amorphous structure as evidenced by the broad peaks observed at 2θ values [50]. This XRD patterns obtained in this research coincide from those reported by Özgan and Eskalen [51], where the XRD pattern of GO exhibited a crystalline peak at 2θ of $12,78^\circ$. A comparison with the research conducted by Sujiono *et al.* [41], which involved the synthesis of GO from agricultural waste coconut shell graphite, reveals a similar amorphous peak at 2θ of 23.97° [41]. This distinction is attributed to the utilization of graphite derived from natural resources (agricultural waste) rather than commercial graphite [52].

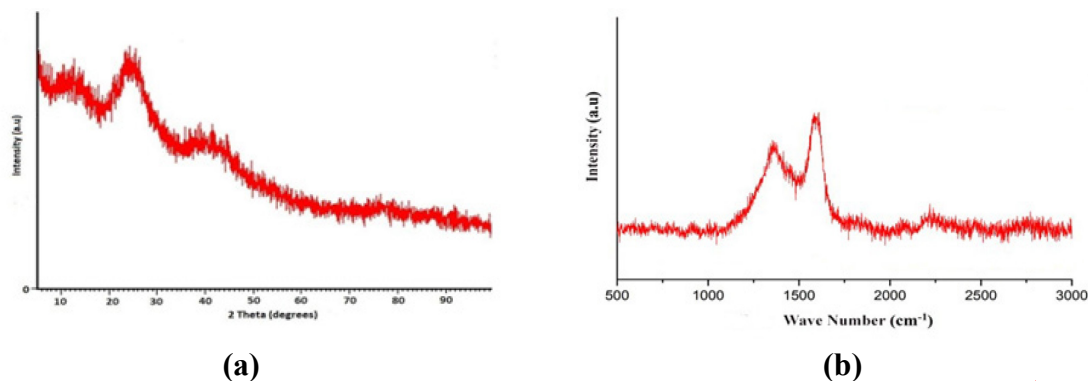


Figure 3. (a) The XRD spectrum of GO and (b) Raman spectra of GO made from cassava peel waste using modified Hummers method

The Raman spectra of GO is seen in **Figure 3(b)**. Two peaks, representing the D band and the G band, can be seen in the picture at wave numbers of 1363 cm^{-1} and 1598 cm^{-1} , respectively. In graphite, vibrational modes associated with edges, concomitant impurities, and structural defects give rise to the D band. The characteristic D-bands of graphene sheets indicate that the sp^3 carbons have been stretched. The graphic makes the G-bands, which are caused by vibrations in the normal graphite structure, more evident. It's like trying to stretch sp^2 carbon. These two peaks indicate the presence of sp^2 -hybridized carbon in the reported GO, which is consistent with conventional Raman vibrational modes for carbon-based materials. The Raman results of this study are in line with the approach used by Sujiono *et al.* [41] to characterize GO derived from leftover coconut shells and with the application of GO derived from sugarcane bagasse by Somanathan *et al.* [53].

Experimental design and optimization using Box-Behnken Design

Analysis on the Responses (ANOVA). The results of the optimization of CIP adsorption, conducted through a Box-Behnken Design (BBD) experimental approach involving 15 experiments, can be found in **Table 2**. The relationship between the response or CIP antibiotic adsorption and the three operational variables, namely adsorbent dosage, pH, and contact time, was evaluated using Response Surface Methodology (RSM). The use of RSM, specifically based on the BBD experimental design, aims to showcase the optimization process conditions for CIP antibiotic adsorption.

Table 2. The results of the Box-Behnken experimental design (BBD)

Run	Adsorbent dose (mg)	pH	Contact time (minute)	Adsorption (%)
1	27,5	4	40	85,10
2	20	4	30	84,07
3	35	2	30	75,12
4	20	2	30	60,02
5	20	3	40	83,40
6	35	3	20	91,71
7	27,5	3	30	80,25
8	27,5	4	20	88,28
9	35	4	30	83,41
10	27,5	3	30	84,97
11	27,5	2	20	78,51

12	20	3	20	86,92
13	27,5	3	30	77,13
14	27,5	2	40	76,90
15	35	3	40	90,24

The outcomes of the experimental design and the subsequent statistical analysis, employing a quadratic statistical model as derived from the software, are expressed in Equation 2. In this equation, a positive sign associated with a variable signifies a synergistic influence on the target, while a negative sign indicates that the variable exerts an antagonistic impact [54].

$$\% \text{ Adsorpsi CIP} = 80,78 + 3,26A + 6,29B - 1,22C - 3,94AB + 0,03925BC + 0,3708A^2 - 5,50B^2 + 6,91C^2 \dots\dots\dots(2)$$

Table 3. Results of analysis of variance (ANOVA)

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	788,90	9	87,66	7,56	0,0192	significant
A-Dosage adsorbent	84,96	1	84,96	7,33	0,0424	
B-pH	316,39	1	316,39	27,29	0,0034	
C-Contact time	11,96	1	11,96	1,03	0,3564	
AB	62,09	1	62,09	5,36	0,0685	
AC	1,05	1	1,05	0,0906	0,7755	
BC	0,6162	1	0,6162	0,0532	0,8268	
A ²	0,5078	1	0,5078	0,0438	0,8425	
B ²	111,66	1	111,66	9,63	0,0267	
C ²	176,47	1	176,47	15,22	0,0114	
Residual	57,96	5	11,59			
Lack of Fit	26,80	3	8,93	0,5735	0,6855	not significant
Pure Error	31,16	2	15,58			
Cor Total	846,86	14				

Std.Dev = 3,40. R² = 0,9316. Adj R² = 0,8084. CV% = 4,17. Pred R² = 0,4108. Adeq Precision = 10,7441.

It is evident from **Table 3** that the proposed model is statistically significant, with a total quadratic model sum of 788.90 and an F-value of 7.56. The P-value serves as a crucial indicator for evaluating the significance of each coefficient. The p-values less than 0.05 indicated a significant and well-fitting model [55]. In the present research, the operational variables such as adsorbent dosage (A), pH (B), the square of pH (B²), and the square of contact time (C²) exhibit P-values below 0.05, underscoring their significance. Conversely, the remaining variables display P-values exceeding 0.1, suggesting their lack of significance. Consequently, model refinement can be undertaken by eliminating the non-significant variables to enhance the model's performance.

The results indicated that the R-squared (R²) value was 0.9316, which signifies a good fit of the model with the experimental data. It is important to note that the difference between the predicted R² and the adjusted R² should be less than 0.2. The difference exceeding 0.2 indicated a potential issue with either the model or the experimental data. The Adeq precision value obtained in this research was 10.7441 (greater than 4), suggesting a favorable agreement between experimental results and predictions. With a coefficient of variation (C.V.%) of 4.17%

(less than 10%), there exists a notable correlation between the experimental response and model predictions. Moreover, the lack of fit, when compared to pure error, yields an insignificant F-value (0.6855). In order to establish a robust model, it is crucial for the lack of fit to be non-significant.

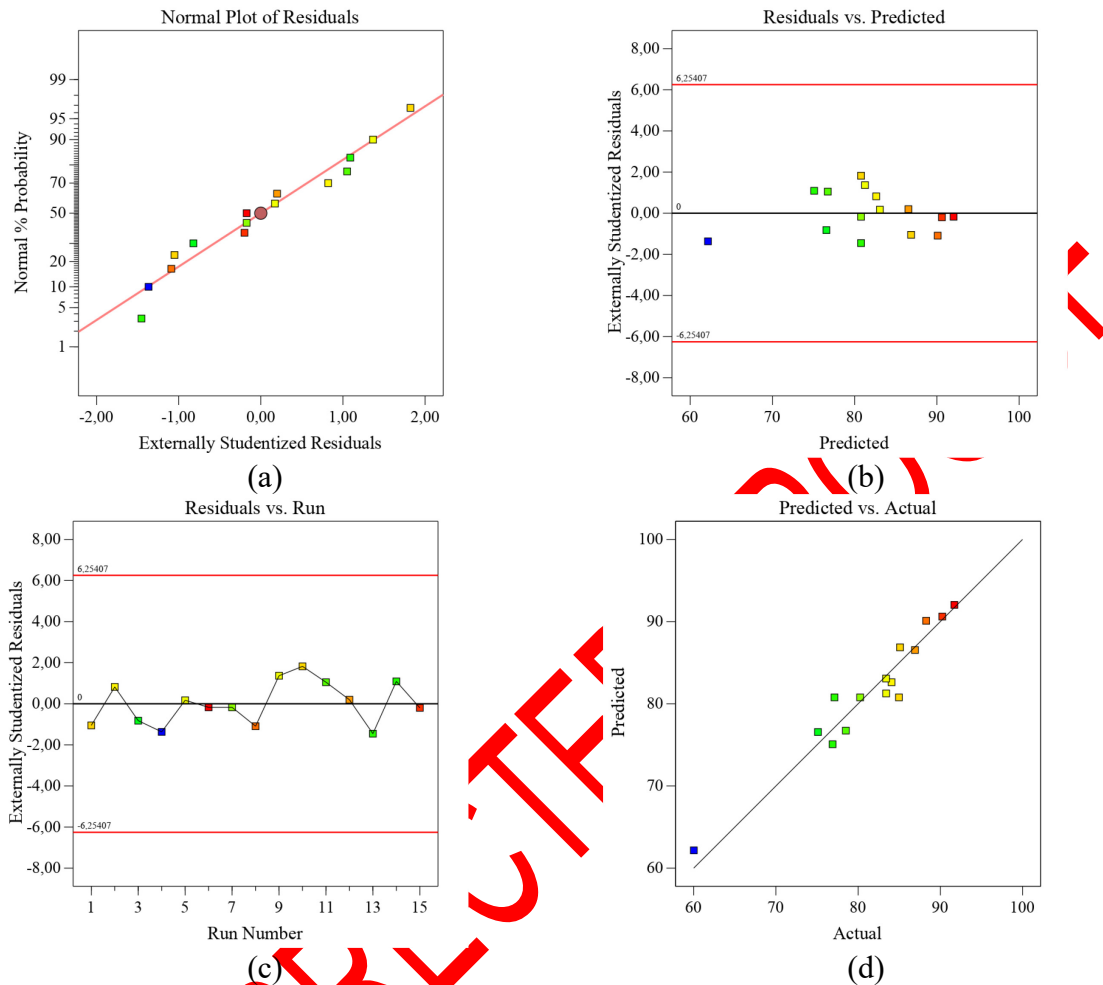


Figure 4. (a) Normal probability of student residuals. (b) Residuals versus predicted. (c) Residuals versus run number. (d) Measured values

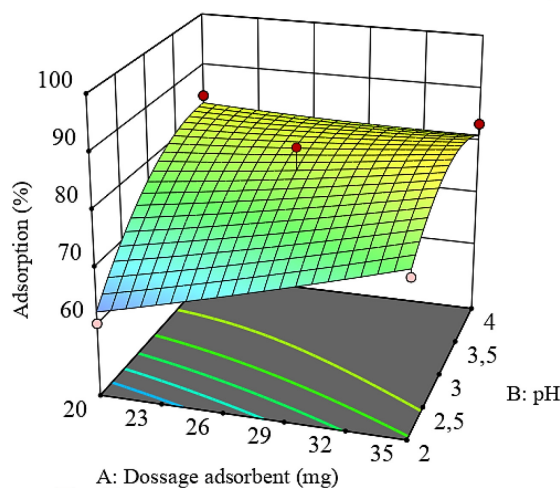
The results obtained from the diagnostic tests shown in **Figure 4** provide insight into the model's adequacy. These diagnostic assessments include (a) the normal probability plot of student residuals, (b) residuals versus predicted, (c) residuals versus run number, and (d) measured values. These diagnostics collectively support the notion that the model performs well. The diagnostic test results also support the ANOVA test results obtained in **Table 3**. The normal distribution graph shows favorable outcomes for the experiments conducted on % adsorption because the generated values align closely with the linear line. **Figure 4 (b)** and **(c)** also indicate that the experiments performed on % adsorption exhibit a homogeneous distribution because the spread of values generated approaches zero. The residual values show a normal distribution of the applied variables, approaching the mean value. Therefore, one of the proposed models for predicting CIP adsorption efficiency is a regression model [54]. The regression value obtained is 0.9316 as evident in **Figure 4 (d)**. The R^2 value indicates the quality of fit in a model. The criteria for a good fit model are $R^2 > 0.8$, and R^2 approaching 1 indicates a high level of agreement between experimental data and the proposed model [56].

Interaction Effects Within Process Variables and Their Effect on CIP Removal (%)

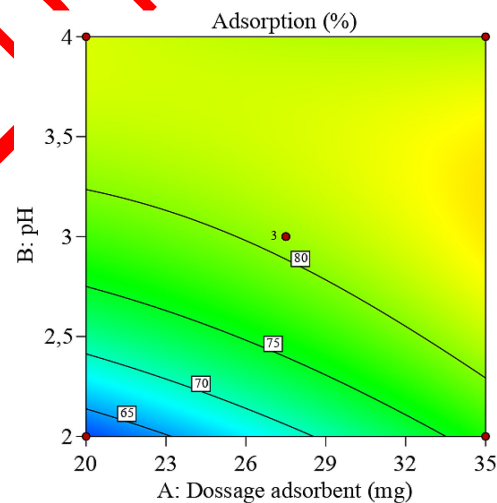
The three-dimensional reaction surface plots offer insights into the primary influences of three key factors. To assess the impact of adsorbent dosage on adsorption efficiency, a series of experiments were conducted using adsorbent quantities ranging from 20 to 35 mg, at pH levels of 2.0, 3.0, and 4.0, with contact times set at 20, 30, and 40 minutes. The interactive effect of pH and dosage on CIP removal is illustrated in **Figure 5 (a,b)**. The results revealed that higher levels of adsorbent dosage, exceeding 29 mg, and elevated pH levels beyond 2.5, are associated with increased CIP removal.

Konkena and Vasudevan (2012) reported a high correlation between the pH value and different functionalities on GO with pK values of 4.3, 6.6, and 9.8. Below a pH of 2, carboxyl groups remain undissociated, while above pH 4, they start to dissociate. This indicates that the surface of GO becomes negatively charged under acidic conditions, especially after the pH exceeds 4. The negatively charged surface of GO enhances interactions with positively charged CIP under acidic conditions. Therefore, even though the pH range in this study was selected as pH 2-4, it is necessary to test the adsorption capacity of GO over a wider pH range to maximize the potential for CIP adsorption onto GO. However, selecting pH conditions from acidic to neutral is more favorable as it corresponds to the positively charged nature of CIP and the negatively charged of the surface of GO. Under acidic conditions, GO is advantaged due to its stable dispersibility compared to other conditions [57].

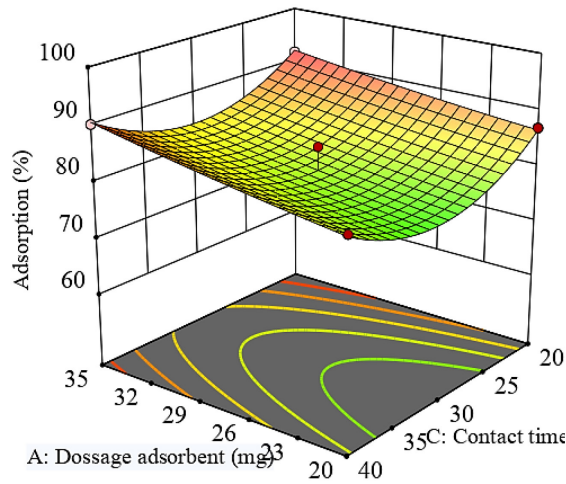
Furthermore, the interactive effect of dosage and contact time on CIP removal is depicted in **Figure 5 (c,d)**. These plots reveal that a higher dosage leads to improved CIP removal efficiency. At lower contact times (less than 2.5 minutes) or longer contact times (greater than 3.5 minutes), higher dosages of the adsorbent are preferable to achieve higher CIP removal efficiency.



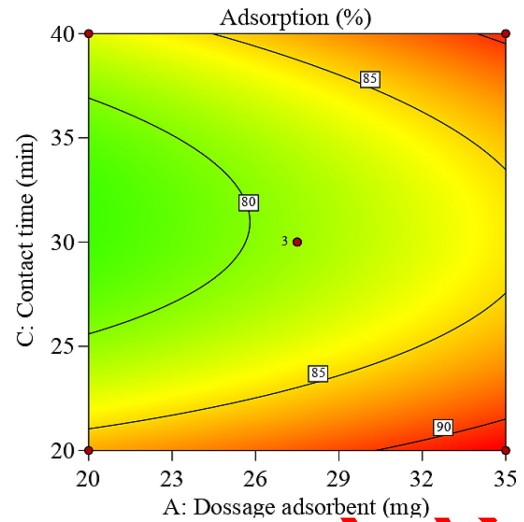
A: Dossage adsorbent (mg)
 X1 : A = Adsorbent dose (mg)
 X2 : B = pH
 Actual Factor
 C : Contact time (min) = 30
(a)



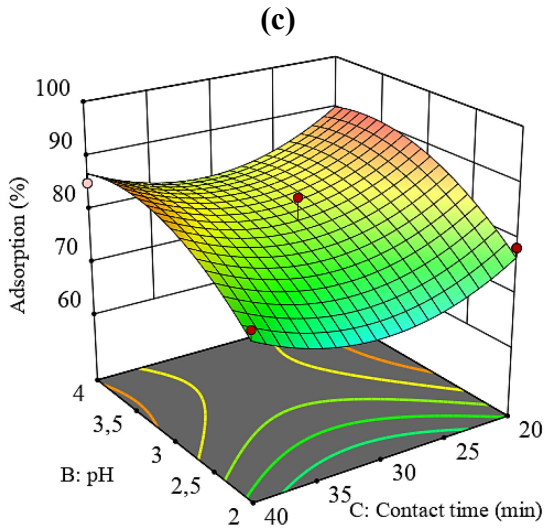
X1 : A = Adsorbent dose (mg)
 X2 : B = pH
 Actual Factor
 C : Contact time (min) = 30
(b)



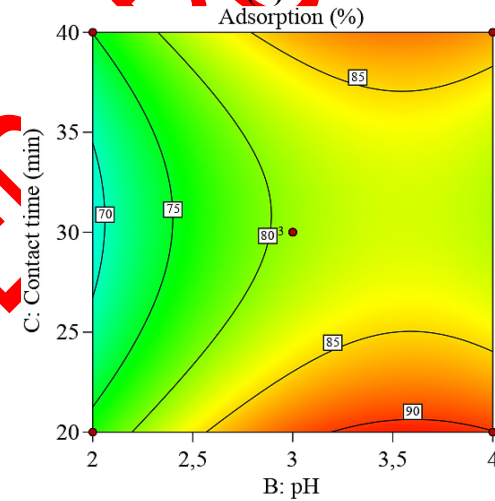
X1 : A = Adsorbent dose (mg)
 X2 : C = Contact time (min)
 Actual Factor
 B : pH = 3



X1 : A = Adsorbent dose (mg)
 X2 : C = Contact time (min)
 Actual Factor
 B : pH = 3



X1 : B = pH
 X2 : C = Contact time (min)
 Actual Factor
 A : Adsorbent dose (mg) = 27,5



X1 : B = pH
 X2 : C = Contact time (min)
 Actual Factor
 A : Adsorbent dose (mg) = 27,5

Figure 5. Response surface plots (3D) and contour plots (2D): (a,b) interaction between adsorbent dose (mg) and pH, (c,d) interaction between adsorbent dose (mg) and contact time (min), (e,f) interaction between pH and contact time (min)

Figure 5 (d) also indicates the possibility of achieving optimal CIP removal at adsorbent doses exceeding 35 mg. The curvature of the surface plot in **Figure 5 (e,f)** demonstrates the interactive effect of pH and contact time on CIP removal. It is evident that the removal efficiency is notably low within the range of 25-35 minutes of contact time and at lower pH levels. In contrast, at shorter contact times (below 25 minutes) or extended contact times (beyond 35 minutes), higher pH levels, specifically above 2.5, are preferred to attain higher CIP removal efficiency.

Optimization of the Responses

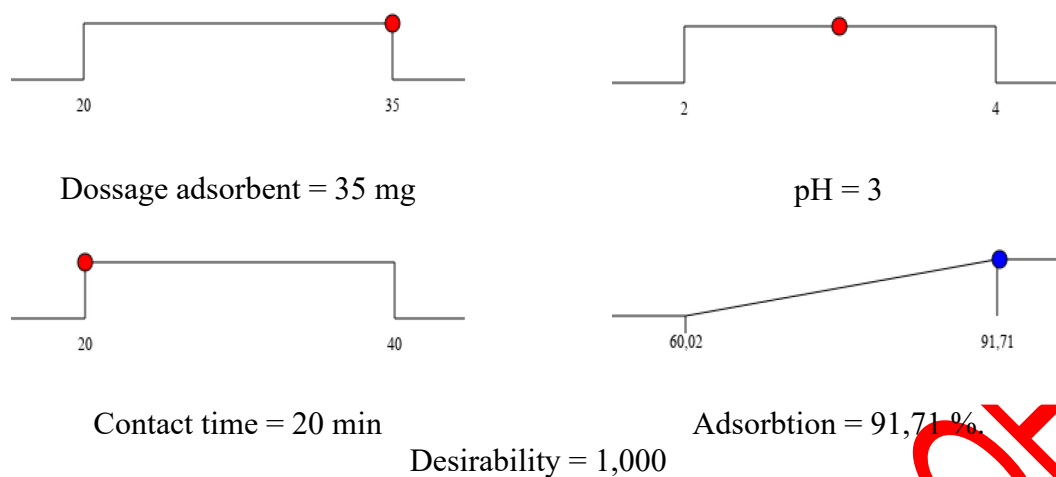


Figure 6. Ramp solution for desirability approach

The optimization of responses was carried out using the desirability approach. In this approach, the total desirability is calculated as the geometric mean of all individual desirability values, with individual desirability scores ranging from 0 (indicating the least desirable) to 1 (representing the most desirable) [55]. The highest desirability is depicted in a graphical form, as shown in **Figure 6**. The results obtained align with the experimental data, indicating that the ideal conditions for CIP removal were achieved at a pH level of 3 and a contact time of 20 minutes, using 35 mg of adsorbent. Under these conditions, the maximum CIP concentration removed was determined to be 91.71%.

Effect of Variables and Their Interactions. The amount of adsorbent used in the adsorption process varies depending on the specific adsorbate and is influenced by its physical and chemical characteristics. In the case of CIP (Ciprofloxacin) adsorption, the adsorbent dosage plays a significant role. When a dosage of 35 mg of adsorbent was utilized at pH 3 with a contact time of 20 minutes, the percentage of CIP adsorption reached 91.71%. This enhanced adsorption can be attributed to the greater number of active sites and increased surface area available on the adsorbent, facilitating more effective adsorption. Carbon-based materials are known to have outstanding adsorption characteristics, making them highly effective in eliminating antibiotics not only at low environmental concentrations but also at elevated concentrations. The presence of C=C functional groups in both carbon-based materials and antibiotics plays a crucial role in influencing the adsorption rate. An increased number of aromatic rings corresponds to a higher adsorption rate [58].

CIP exhibits a positive charge when the pH is below 5.90, transitions to a neutral or zwitterionic state between pH 5.90 and 8.89, and carries a negative charge at pH levels above 8.89, as depicted in **Figure 7** [59]. The highest adsorption of CIP is observed around neutral and acidic pH levels. In particular, under acidic conditions, the amine group in CIP will be protonated ($-\text{NH}_3^+$) and inhibit its ionic interaction with GO adsorbents containing carboxyl groups [60]. At pH 5, about 80% of the carboxyl groups are deprotonated (COO^-) and become negatively charged [43]. This phenomenon can be attributed to the ionic state and interactions occurring between the amine groups on CIP and the carboxylate groups on GO [60]. However, as the pH increases, the positive charge on CIP decreases, leading to a reduction in electrostatic interactions and consequently decreasing the adsorption capacity.

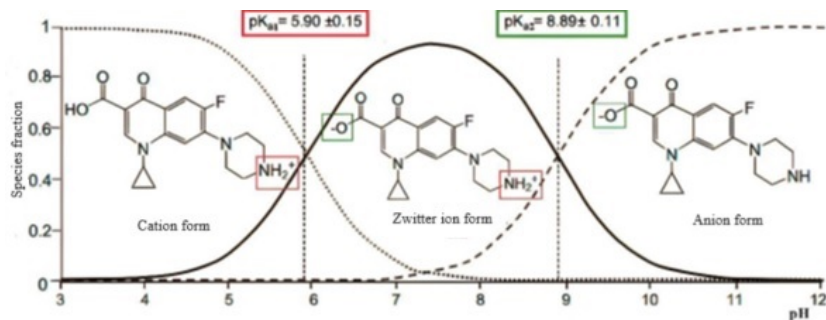


Figure 7. The variation of CIP into distinct forms or types at various pH levels [61]

The contact time also has a significant influence on CIP adsorption. When using an adsorbent dosage of 35 mg and a pH of 3, a 40-minute contact time resulted in a CIP removal efficiency of 90.24%. However, when maintaining the same conditions but reducing the contact time to 20 minutes, the CIP removal efficiency increased to 91.71%, as evident in Table 2. This phenomenon can be attributed to the initial abundance of available active sites on GO during the early stages of CIP uptake. Subsequently, the adsorption rate slows down after 40 minutes, likely due to a reduction in available active sites over time, ultimately leading to adsorbent saturation [62].

CONCLUSION

The optimization of CIP adsorption onto GO derived from cassava peel, employing a Box-Behnken Design (BBD) experimental approach, has yielded optimal conditions for CIP removal. These conditions include a pH level of 3, a contact time of 20 minutes, and the utilization of 35 mg of adsorbent material. The GO derived from cassava peel is rich in functional groups like hydroxyl, carboxyl, and epoxy, which provide robust adsorption capabilities through their active sites. Under these optimized parameters, a remarkable CIP concentration removal efficiency of 91.71% was achieved, highlighting the potential of the GO material obtained from cassava peel to be effectively used as an adsorbent for CIP from aqueous solutions. However, it is important to note that further research is needed to test the performance of GO on larger scales and various environmental conditions to ensure its sustainability in practical applications.

The restrictive pH range for effective adsorption is one of the key effective applications for CIP removal treatment in wastewater. This may involve adjusting the pH of the wastewater influent to maintain conditions favorable to GO adsorption. Implement pH adjustment strategies to ensure that the influent wastewater falls within the optimal pH range for GO adsorption. This could involve the addition of acids or bases to the influent stream to achieve the desired pH level.

The results of this research provide important implications in the context of environmental protection and public health. The use of CIP as an antibiotic can increase bacterial resistance and have a negative impact on aquatic organisms and human health if it accumulates in wastewater. Therefore, GO's effective ability to remove CIP can help reduce the risk of antibiotic contamination in the water cycle, as well as reduce its negative impact in the environment and public health.

Overall, this study highlights the significant potential of the GO material obtained from cassava peel to be effectively used as an adsorbent for CIP removal from aqueous solutions. By understanding the optimal conditions for CIP adsorption, we hope that these findings will provide a valuable contribution to the development of more effective and sustainable wastewater treatment methods in the future.

DECLARATION OF COMPETING INTEREST

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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NOMENCLATURE

Symbols

C_0	initial concentration of ciprofloxacin in solution	[ppm]
C_x	final concentration of ciprofloxacin in solution	[ppm]

Abbreviations

BBD	Box-Behnken Design
CIP	Ciprofloxacin
FTIR	Fourier Transform Infrared
GO	Graphene Oxide
RSM	Response Surface Methodology
SEM-EDX	Scanning Electron Microscopy-Energy Dispersive X-ray
UV-Vis	Ultraviolet Visible
XRD	X-ray Diffraction

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