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Abstract. Cephalexin (CFX) antibiotic concentration has been used as a marker for identifying emerging pollutants (EPs) in the non-medical setting due to its significant ability to cause antimicrobial resistance with the highest risk quotient. This study aimed to determine the characteristics of Eco-Zinc Oxide-Graphene Oxide (Eco-ZnO/GO) nanocomposite (NC) from green synthesis of *Musa Acuminata* by using Field Emission Scanning Electron Microscope (FESEM) coupled with Energy Dispersive X-ray Spectroscopy (EDX). The focus of the study is to optimize the efficiency of Eco-ZnO/GO NC from green synthesis of *M. Acuminata* for removal of CFX by using adsorption. The Response Surface Methodology (RSM) will be used as well to analyzed the adsorbent dosage, irradiation time, and pH value to obtain the optimum condition of the efficiency of Eco-ZnO/GO for the removal of CFX. The average particle sizes for Eco-ZnO and GO were determined to be 10 nm and 300 nm, respectively, by using FESEM. It is deduced that the optimization factors of adsorbent dosage to 100 mg/L, irradiation time to 120 min, and intial concentration of CFX to 100 mg/L could achieve the mean removal of CFX by 22.17 %. The study contributed to the new knowledge of using nanocomposite materials to remove CFX in the water. However, more thorough studies are needed to obtain higher removal capacity.

1. Introduction

A first-generation cephalosporin antibiotic with a molecular weight of 365.40 g/mol, cephalexin (CFX) is used globally [1]. Scientists are exploring non-clinical chlorofluorocarbon (CFX) issues in line with sustainable water management. Due to its simplicity and large spectrum of adsorbents, the study emphasized adsorption to remove water contaminants [2]. Time and effort are needed for photocatalytic degradation using direct sun radiation or UV and visible light. Nanotechnology's use in CFX removal shows a realistic solution to pollutant degradation.

Zinc oxide (ZnO) nanoparticles' nanotechnology and broad use have drawn attention. Green ZnO NP production using plant extracts instead of harmful chemicals is popular among researchers [3]. ZnO NP production using plant, fruit, and vegetable extracts is green and waste-free. M. Acuminata,

or banana, is an effective green ZnO NP producer. ZnO NPs from banana peel green synthesis have not been tested for CFX elimination. Graphene oxide (GO) was extensively studied for water contamination removal due to its high aspect ratio, conductivity, heat resistance, low friction, and imperviousness [4]. It is one of the most studied wastewater adsorption carbon nanomaterials. The nanoparticle chemical agent exhibited a high surface-to-volume ratio and a fast breakdown rate, removing CFX and its intermediate intermediates [5].

The adaptability and variety of adsorbents make adsorption a potent water purification method. Many CFX-absorbing adsorbents have been investigated, with mixed results. Graphene nanoparticles are unique and promising adsorbents, according to comprehensive research. Natural graphite yields considerable amounts of these chemicals [2]. Table 1 shows how fruit peels efficiently remove and produce ZnO NPs greenly. M. Acuminata, C. sinensis, and H. undatus showed near 100% dye removal efficiency. After durians and pineapples, bananas will make up 14.6% of Malaysia's fruit production in 2020 [6].

Table 1. Fruit Peels Facilitated Green Synthesis of ZnO NPs and its Relevance with Removal Efficiency

Plant	Common Name	Application	Removal of concern	Removal Eff. (%)	Ref.
M. Acuminata	Banana	Photocatalytic degradation of BB9 dye	BB9 dye	100	[7]
Lyco-persicon esculent-tum	Tomato	Degradation of Methylene Blue (MB)	Methylene Blue dye	97	[6]
Citrus auranti-folia	Lemon	Degradation of Methylene Blue (MB)	Methylene Blue dye	97	
Citrus sinensis	Orange	Removal of *E. coli* and *S. aureus*	*E. coli* *S.aureus*	100	[2]
Hyloce-reus undatus	Dragon fruit	Removal of pathogens	Pathogen	100	[4]

Eco-friendly ZnO nanomaterial production has been extensively explored. The development of biomass waste extracts like banana peels for antibiotic elimination was still underway. Previous research showed that M. Acuminata peels may generate ZnO NPs in a non-toxic, ecologically acceptable way. Eco-ZnO/GO also removed water and effluent contaminants better than single nanomaterials. The work intends to characterize and optimize M. Acuminata's green synthesis Eco-ZnO/GO for CFX elimination.

2. Materials and Methods

2.1. Preparation of M. Acuminata peels

M. Acuminata was collected from banana peel waste at a Parit Raja, Johor food booth. First, tap and deionized water were used to clean the peels to remove impurities [8]. Thus, the peels were sun-dried for 24 hours. At 80° C, 100 g finely chopped peels and 100 ml purified water cooked for 20 minutes. After cooling to room temperature, two layers of Whatman No. 1 filter paper filtered the aqueous extract. Synthesizing Eco-ZnO/GO nanocomposites with filtrate was environmentally friendly.

2.2. Green Synthesis of Eco-ZnO/GO

Dissolving 1.6 g zinc acetate dihydrate in 100 ml distilled water and stirring at 200 rpm for 10 minutes produced Eco-ZnO NPs greenly. After adding 1 ml of M. Acuminata extract, pH was adjusted to 12

with NaOH. After 20 minutes at 1000 rpm, a pale white aqueous solution formed. For 25 minutes at 4000 rpm, the white precipitate was centrifuged. Rinse the precipitate with 5 ml of distilled water and 5 ml of ethanol and centrifuge at 4000 rpm for 25 min to generate NP ionic bonds. Finally, a drying oven at 100 °C dried the precipitate overnight to generate pale white ZnO NPs powder. Figure 1 shows ZnO NP production.

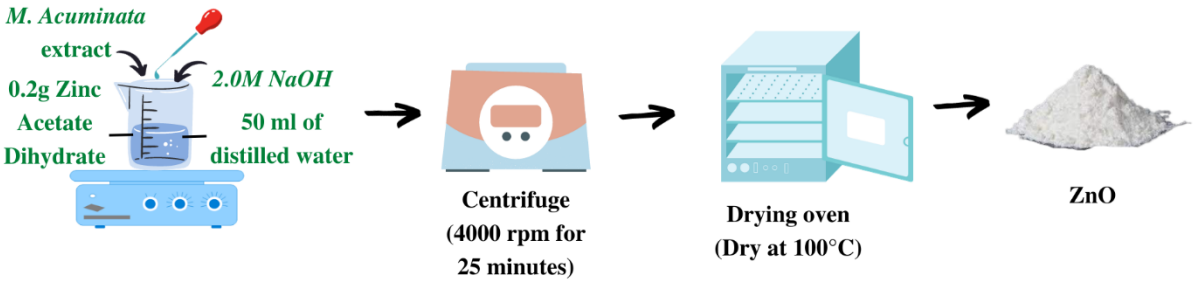

Figure 1. Schematic Representation of Green Synthesis of ZnO

The synthesis of Eco-ZnO/GO was conducted as the schematic diagram shown in Figure 2. 0.50 g GO powder was mixed with 0.50 g of Eco-ZnO powder in 5 ml of ethylene glycol (CH_2OH). Next, the mixture was stirred at 1000 rpm for 1 hour and centrifuged at 4000 rpm for 25 minutes. Centrifuged precipitates were rinsed with ethanol and centrifuged at 4000 rpm for 25 minutes. Finally, Eco-ZnO/GO powder was obtained by drying precipitates for one night at 100 °C in a drying oven.

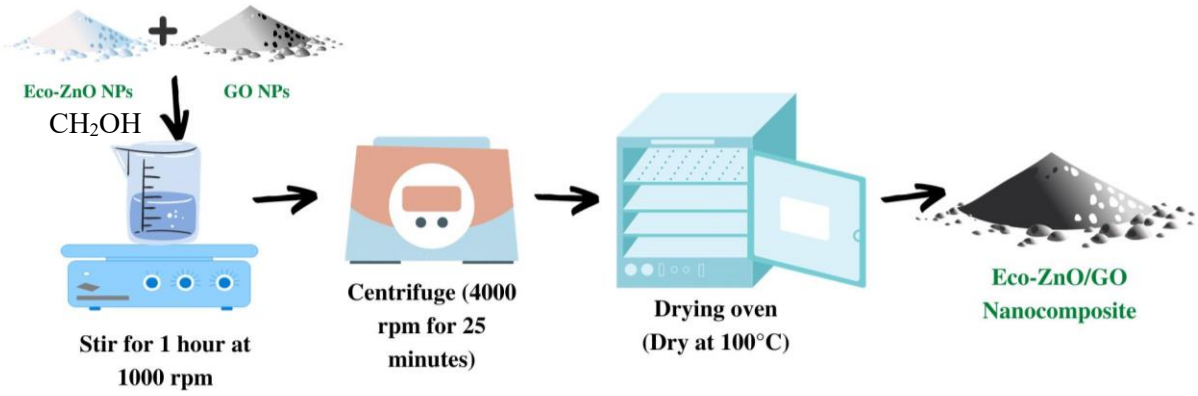

Figure 2. Schematic Representation of Green Synthesis of Eco-ZnO/GO

2.3. Characterisation of Eco-ZnO/GO

FESEM/EDX was used to analyse Eco-ZnO/GO samples. These tests examined Eco-ZnO/GO NC's shape, particle size, and elemental composition. After the operation, UV-Vis was used to evaluate Eco-ZnO/GO's CFX removal efficiency. Spectroscopy model HACH DR600 enabled high-speed wavelength scanning across the UV and visible spectra from 190 to 1100 nm.

2.4. Optimization of the Eco-ZnO/GO for CFX Removal

CFX photocatalysis-optimized Eco-ZnO/GO Nanocomposites are shown in Figure 3. Erlenmeyer flasks contained Eco-ZnO/GO Nanocomposites and CFX aqueous solution. Magnetised, heated plate stirrers mix solutions quickly. The combination will be sun-exposed to boost photocatalysis. Coupled-redox reactions activate catalysts through electron transfer to or from reactants due to light. Sunlight removes CFX solution.

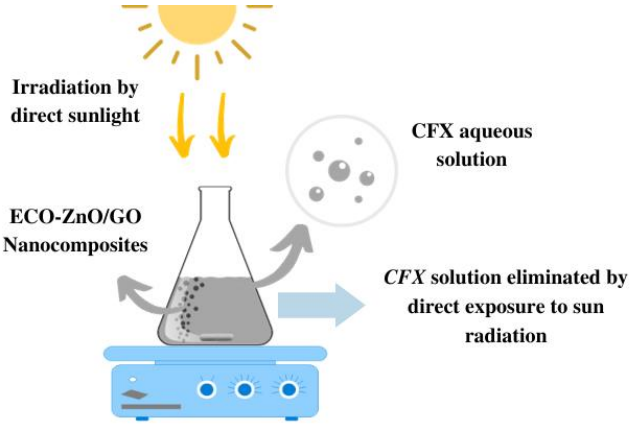

Figure 3. Optimization of the Eco-ZnO/GO for CFX Removal

Several independent factors were analyzed using Response Surface Methodology (RSM) based on adsorbent dosage, irradiation time, and pH value to obtain the optimum condition of the efficiency of Eco-ZnO/GO for the removal of CFX. The efficiency of adsorption or photocatalytic degradation (E) and the adsorption capacity (Q_c) of the Eco-ZnO/GO was calculated according to [9] by using Eq. (1) and Eq. (2).

$$E = \left(\frac{C_i - C_f}{C_i}\right) \times 100\ \% \quad (1)$$

$$Q_c = \frac{(C_i - C_f)}{A} \quad (2)$$

Where:

C_i	=	Initial concentration of CFX (mg/L)
C_f	=	Final concentration of CFX (mg/L)
A	=	Adsorbent dosage (g/L)

3. Results and Discussion

3.1. Characterisation of Eco-ZnO/GO

The FESEM test examined Eco-ZnO/GO NC particle size and shape. Figure 4 shows that ImageJ programme confirmed that Eco-ZnO/GO has a standard size of 15 nm and 300 nm for GO. The diameters match ZnO NP standards of 20–50 nm [3, 10]. The typical GO size was 100–500 nm [11]. The Eco-ZnO/GO was successfully synthesised because ZnO nanoparticles homogeneously aggregated on platelets were GO.

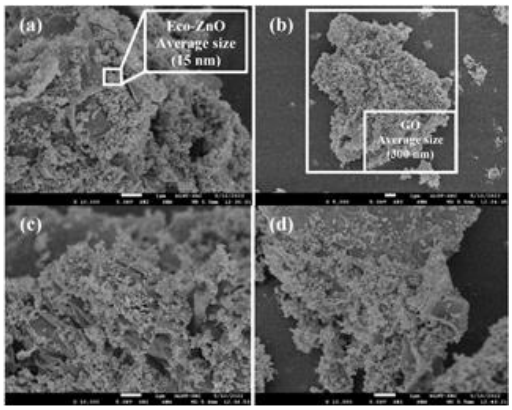

Figure 4. FESEM images of ECO- ZnO/GO NC (a) Average Size of ECO-ZNO (b) Average Size of GO (c,d) images of ECO-ZNO/GO

Table 2 shows C, O, and Zn in the Eco-ZnO/GO NC sample from EDX analysis. The Eco-ZnO/GO NC is mostly C, with 51.04% weight, followed by O and Zn with 25.33% and 23.62%, respectively. Table 2 compares ZnO/GO NP EDX measurements from previous studies. The result was similar to [10]. Figure 5 shows Eco-ZnO/GO NC element particle percentages. As expected, Eco-ZnO/GO NC contained C, O, and Zn.

Table 2. EDX Analysis of ECO-ZnO/GO NC

Weight (%)			Researchers
Carbon (C)	**Oxygen (O)**	**Zinc (Zn)**	
51.04	25.33	23.62	This study
46.30	30.00	23.70	[10]
32.73	22.80	44.47	[11]
14.93	23.99	61.08	[11]

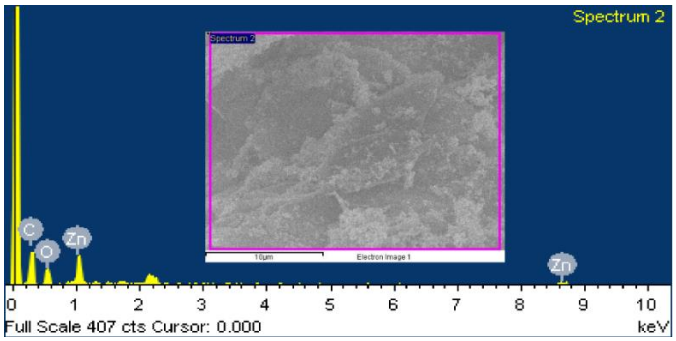

Figure 5. EDX Spectrum of ECO-ZNO/GO NC

3.2. Optimization of Efficiency of Eco-ZnO/GO for Removal of CFX

This study found that Eco-ZnO/GO removed 13.1% of CFX at 100 mg/L adsorbent, 60 minutes of irradiation, and 65 mg/L CFX. Additionally, the lowest CFX removal efficiency is 2.4% for 10 mg/L adsorbent, 120 minutes of irradiation, and 30 mg/L CFX. Figure 6 shows the absorbance profiles and initial CFX concentrations from UV-Vis Spectroscopy for each experiment run. Figure 6 shows the resonant peak absorbance of three initial CFX concentrations from 270 to 300 nm. According to Figure 6(a), sample No.17 removed 7.90% of CFX, while sample No.2 removed 2.42%. According to Figure 6(b), sample No.13 removed 13.1% of CFX, while sample No.3 removed 3.0%. Figure 6(c) shows that sample No.9 removed 12.6% of CFX, while samples No.1 and No.11 removed 7.4%. The

Response Surface Methodology (RSM) was used to examine the relationship between absorbance dosage, irradiation period, and CFX concentration and elimination efficiency.

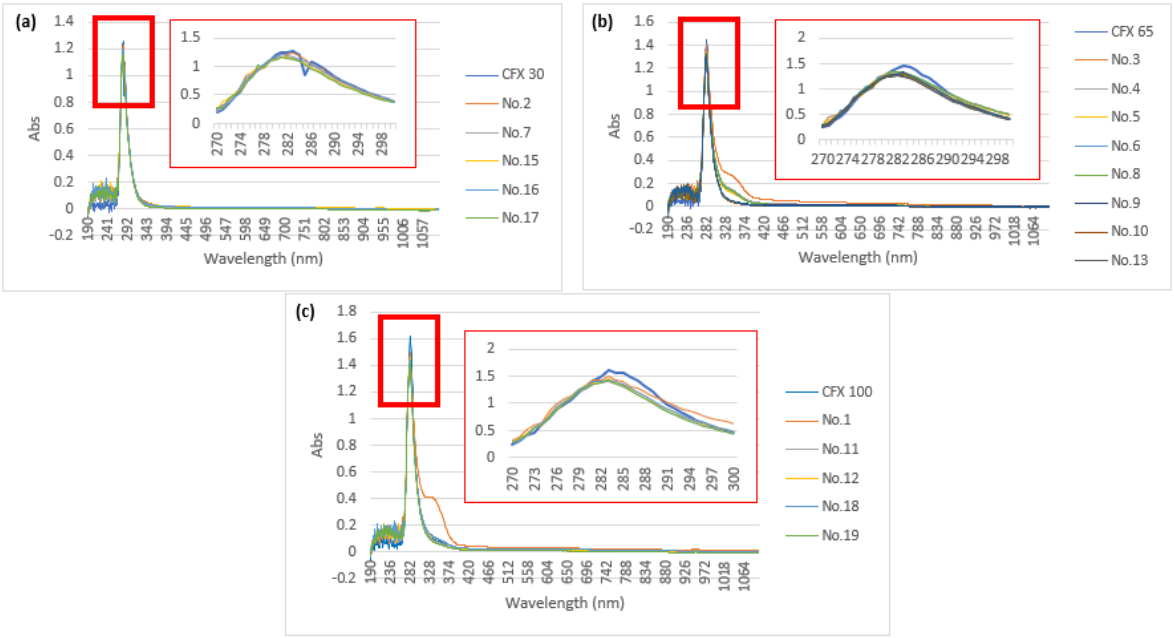

Figure 6. Absorbance profiles and initial CFX concentrations from UV-Vis Spectroscopy for each experiment run

Table 3 demonstrates CFX removal quadratic model ANOVA. Model terms with P-values ≤ 0.0500 are significant. In this model, CFX concentration was important. With a 3.03 F-value for lack of fit, the inaccuracy required to be more significant. A considerable lack of fit F-value was 12.48% likely due to noise. Some mismatch suggested a good model fit.

Table 3. ANOVA for Quadratic Model of Removal of CFX

Source	Sum of Squares	df	Mean Square	F-value	p-value
Model	126.38	9	14.04	2.14	**0.1264**
A-Absorbent Dosage	7.61	1	7.61	1.16	0.3074
B-Irradiation Time	15.24	1	15.24	2.32	0.1589
C-Concentration of CFX	67.10	1	67.10	10.21	0.0096
AB	0.3861	1	0.3861	0.0587	0.8134
AC	2.60	1	2.60	0.3958	0.5434
BC	13.48	1	13.48	2.05	0.1827
A^2	7.21	1	7.21	1.10	0.3198
B^2	13.42	1	13.42	2.04	0.1835
C^2	6.10	1	6.10	0.9276	0.3582
Residual	65.75	10	6.57		
Lack of Fit	49.42	5	9.88	3.03	**0.1248**
Pure Error	16.33	5	3.27		
Cor Total	192.13	19			

Model fit statistics are in Table 4. Negative projected R^2 indicates the overall mean could predict reaction better than the current model. Precision was used to measure signal-to-noise ratio. A signal

ratio of 5.486 was adequate since a ratio greater than four was preferred. Thus, this model may aid in developing space navigation. The 3D model graphs of variable components against CFX removal are shown in Figure 7. Figure 7(a) shows that since the resonant peak had not been noticed, the targeted absorbent dosage design point was 90 mg/L and above, and the irradiation time was 70–90 minutes. Figure 7(b) shows a substantial reaction on absorbent dosage from 90 mg/L and above, suggesting a larger value to reach the peak. In Figure 7(c), the irradiation time peaks between 90 and 100 minutes, while the CFX concentration responds better from 90 mg/L forward.

Table 4. Fit Statistics of the Model

Std. Dev.	**2.56**	R^2	**0.6578**
Mean	8.32	Adjusted R^2	0.3498
CV %	30.82	Predicted R^2	-1.9489
		Adeq Precision	5.4863

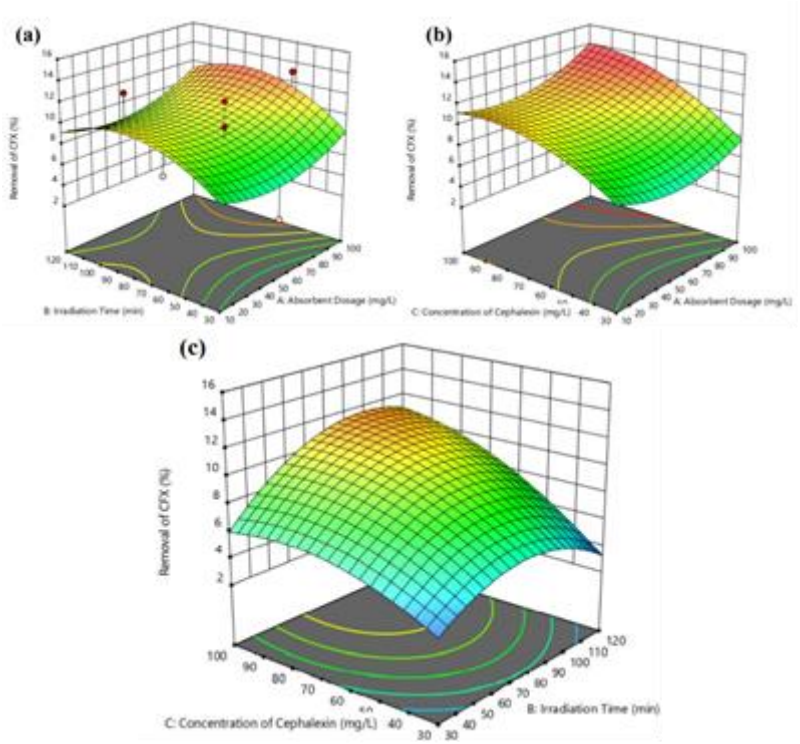

Figure 7. 3D Model Graph of Variable Factors Against Removal of CFX (a) Absorbent Dosage against Irradiation Time (b) Absorbent Dosage against Concentration of CFX (c) Irradiation Time against Concentration of CFX

The optimization study using RSM deduced that the removal of CFX was 100 mg/L absorbent dosage, 120 minutes' irradiation time, and 100 mg/L concentration of CFX. After conducting three optimization experiments, the obtained data mean for the removal of CFX was 22.17%. The interactions for the three independent factors could be more significant by adjusting the range value. Table 5 shows the optimal operating for removing CFX using Eco-ZnO/GO NC.

Table 5. Fit Statistics of the Model

Response	Removal of CFX
Predicted Mean	14.294
Predicted Median	14. 294
Observed	-
Standard Deviation	2.56413
N	3
SE Prediction	2.76659
95% PI Low	8.12966
Data Mean	22.17
95% PI High	20.4584

4. Conclusion

Characteristics of Eco-ZnO/GO NC from the green synthesis of *M. Acuminata* indicating the nano size of the adsorbent composite of 10 nm and 300 nm by using FESEM analysis. Optimization factors of 100 mg/L adsorbent dosages, irradiation time to 120 min, and initial concentration of CFX to 100 mg/L achieved satisfactory mean removal of CFX with 22.17 %. Therefore, more in-depth investigation is needed with additional variable factors such as temperature, mixing speed, pH value of Eco-ZnO/GO NC from the green synthesis of *M. Acuminata*, as well as the kinetic adsorption model as the mechanism of the study.

Acknowledgment

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References

[1] Ali N E, Al-Gheethi A, Mohamed R M S R, Talip B A, Hossain M S, Ali H A W, & Ismail N 2021 Sustainable approaches for removal of cephalexin antibiotic from non-clinical environments: A critical review, *Journal of Hazardous Materials*, 417

[2] Moosavi S, Chin W L, Sinyee G, Golnoush Z, Omid A P, & Mohd R J 2020 Application of efficient magnetic particles and activated carbon for dye removal from wastewater, *ACS Omega* **5**, no. 33: 20684–97

[3] Zeghoud, Soumeia, Hadia H, Bachir B S, Ilham B A, Imane K, Abdelkrim R, Mohammad M, Shakeel A, Pawel P, & Simal-Gandara J 2022 A review on biogenic green synthesis of ZnO nanoparticles by plant biomass and their applications, *Materials Today Communications* **33**: 104747

[4] Asghar, Faiza, Bushra S, Saira F, Shamsa M, Humaira R, Shazia N, & Ian S B 2022 Fabrication and prospective applications of graphene oxide-modified nanocomposites for wastewater remediation, *RSC Advances* **12**, no. 19: 11750–68

[5] Ali N E, Al-Gheethi A, Mohamed R M S R, Balkis A T, Hossain M S, Wahid A H A, & Norli I 2021 Sustainable Approaches for Removal of Cephalexin Antibiotic from Non-Clinical Environments: A Critical Review, *Journal of Hazardous Materials* **417**: 126040

[6] Eskandari P, Farhadian M, Solaimany N A R, & Jeon B H 2019 Adsorption and photodegradation efficiency of TiO_2/Fe_2O_3/PAC and TiO_2/Fe_2O_3/Zeolite nanophotocata-lists for the removal of cyanide, *Industrial and Engineering Chemistry Research*

[7] Talib J, Aris A, Jaafar J, Majid Z A, & Syarmimi A 2020 Occurrence of emerging

pollutants in Skudai River in Johor Bahru region of Malaysia, *Indian Journal of Forensic Medicine & Toxicology* ***14***(3), 1098–1103

[8] Shenwari K A, Dhevagi P, Chitdeshwari T, & Avudainayagam S 2018 Biosorption of Cadmium from aqueous solutions by banana peel powder, *Madras Agricultural Journal* **105**, no. 1–3

[9] He S, Pengfu H, Evangelos P, Yanfang F, Yingliang Y, Lihong X, & Linzhang Y 2018 High efficient visible-light photocatalytic performance of cu/zno/go nanocomposite for decomposing of aqueous ammonia and treatment of domestic wastewater, *Frontiers in Chemistry* **6**

[10] Islam F, Sheikh S, Jalal M U, Rezaul I, Mohamed H. Nafady, A A, Saikat M, Arpita R, Talha E, & Simona C 2022 Exploring the Journey of zinc oxide nanoparticles (Zno-NPS) toward biomedical applications, *Materials* **15**, no. 6: 2160

[11] Khan, Ibrahim, Khalid S, & Idrees K 2019 Nanoparticles: properties, applications and toxicities, *Arabian Journal of Chemistry* **12**, no. 7: 908–31