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Antibiotics Removal from Aqueous Environments: A Mini Review on Graphene Oxide-based Nanomaterials Application

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Abstract: *Antibiotics are pharmaceutical emerging contaminants (ECs) that contaminate the environment and jeopardize public health. More dangerously, the widespread consumption of antibiotics and their impact on water contamination foster the formation and evolution of antibiotic-resistant genes in microbes. Graphene Oxide (GO) is an emerging carbon material with a great potential to operate as an adsorbent to remove antibiotics from water due to its unique physical and chemical properties. Thus, this study briefly reviews topics related to antibiotic removal from water using GO-based materials. This research also summarizes the benefits of GO structural properties, adsorption mechanisms, and the affinity of the GO synthesis method to the quality of the GO produced.*

Keywords: Graphene oxide, antibiotics, adsorption, water treatment.

1. INTRODUCTION

Water pollution is one of the world's most pressing concerns today because this pollution threatens national development, public health, and environmental sustainability. Water pollution due to Emerging contaminants is one of the most severe environmental challenges threatening humans worldwide [1]. These emerging contaminants significantly pollute water due to rising industrialization and the use of chemicals in the community to satisfy today's contemporary lifestyle. The industrial process does not eliminate all these emerging contaminants throughout the treatment phase, and then the contaminants enter the environment. Likewise, these chemicals used by humans remain in wastewater and end up in natural water sources because conventional treatment plants are not designed to remove these chemicals. These toxins can contaminate drinking water and pose an uncertain health risk, particularly to youngsters. More severe facts, over 121 uncontrolled chemicals, and microbes have been reported in wastewater and at least 25 in water treatment plants [2]. As more people became aware of the hazards of emerging contaminants pollution to humans and even flora and fauna, many provincial, federal, international, and intergovernmental environmental preservation agencies made policies to regulate the use of emerging contaminants to prevent worse pollution.

Emerging contaminants (ECs), sometimes known as contaminants of emerging concern (CECs) in particular articles or journals, can refer to a wide variety of artificial or naturally occurring chemicals or materials that are harmful to human health after long-term disclosure. These contaminants can be classified into several classes, including agricultural contaminants (pesticides and fertilizers), medicines and antidote drugs, industrial and consumer waste products, and personal care and household cleaning products [3]. Antibiotics are one of the ECs that have raised concerns in the previous two decades because they have been routinely and widely used in human and animal health care, resulting in widespread antibiotic residues discharged in surface, groundwater, and wastewater. The rampant and increasingly widespread misuse of antibiotics exacerbates the water pollution due to the ECs. These contaminants are often detectable in water systems at concentrations ranging from ng/L to µg/L and can even exist in any drinking water system [4]. According to the World Health Organization (WHO), surface and groundwater, as well as partially treated water, containing antibiotics residue and other pharmaceuticals, typically at concentrations of <100 ng/l, whereas treated water has concentrations of less than 50 ng/l [5]. However, the discovery of these contaminants in numerous natural freshwater sources worldwide is growing yearly. Several antibiotic residues have been reported to have been traced at concentrations greater than their ecotoxicity endpoints in the marine environment, specifically in Europe and Africa [6]. Thus, the European Union's Water Framework Directive enumerated certain antibiotics as priority contaminants [7]. As previously noted, the drinking and wastewater plants are typically not intended to remove these contaminants. Therefore, several strategies must be arranged to ensure that these contaminants do not enter any water sources to avoid adverse effects on human health.

Material engineering and nanomaterials technology are the engineering alternatives with the interweaving of scientific approaches that can be engineered to solve ECs pollution issues in the world's water resources. Numerous materials have been reported to have the potential and capacity to treat water or wastewater polluted with these antibiotics residue by applying the processes of adsorption and catalytic oxidation during the last few decades. The reported materials include mesoporous carbon beads [8], biochar [9]–[11], clay minerals [12], activated carbon [13]–[15], cellulose [16], [17], and chitosan [18]–[20]. As a result of engineering and science evolution, and in complement to the urgent need to increase the adsorption capability of antibiotic contaminants, more advanced materials such as carbon nanotube (CnT) [21]–[24], nano-zero valent iron (nZVI) [25]–[29], nanoporous carbons [30], porous graphene [4], [31] and graphene oxide [3], [32]–[34] to date have been analyzed and improved in their ability to remove these contaminants from water.

Graphene oxide (GO), one of the carbon nanomaterials, has piqued the widespread attraction of environmental specialists worldwide in recent years since it was first exfoliated from graphite in 2004 [35]. This material has been proven as a prospective material for treating water contaminated with ECs [36]. With its superior mechanical qualities and unique physicochemical features, GO promises a significant adsorption impact when employed alone or as a supporting material, particularly in water treatment applications [37]. Therefore, this paper provides a brief review of subjects relevant to eliminating ECs or antibiotics from water using GO-based materials. In addition, this paper is expected to assist future researchers in understanding the basis of GO characteristics and production, as well as gaining an early understanding of this material's benefits and capabilities in the remediation of antibiotic-contaminated water.

2. GRAPHENE OXIDE (GO)

2.1 Structure characteristics of GO

GO is one of the paramount graphene derivatives produced by treating graphene with strong oxidants such as sulfuric acid (H_2SO_4), sodium nitrate ($NaNO_3$), and potassium permanganate ($KMnO_4$) [38]–[40]. Graphene, which comprises carbon atoms as thick as a single atom and arranged in a hexagonal pattern sp^2 structure, has some constraints in some applications due to the absence of a bandgap in graphene and inadequate water-solubility properties [41], [42]. Therefore, this oxidation of graphene produces GO, which contains abundant functional groups on the basal plane and edges of graphene layers, including epoxide, hydroxyl, and carboxyl functional groups [43]–[45]. The existence of oxygenous functional groups (OFGs) overcomes the graphene's imperfection, resulting in a highly hydrophilic GO with outstanding dispersion properties in most solutions [46]. Moreover, the OFGs can provide reactive sites for the chemical modification of GO, which can be exploited to invent GO-based materials [47], [48]. Although this functional group gives many advantages to GO in its application, there are inter-functional solid bonds between graphene sheets, leading to the formation of a chemically inactive surface, lessening surface area, and increased agglomeration and poor dispersion in some aqueous solutions [35], [41]. These unfavorable elements restrict adsorption capacity performance and future utilization in wastewater treatment. Previous researchers have innovated the GO with chemicals to address this issue and created GO/metallic composites and GO/organic compound composites to effectively remove antibiotics from the environment [49], [50].

2.2 GO production

Although the novelty of graphene and graphene oxide has drawn widespread interest among material scientists in recent years, the GO production process has a lengthy evolution history that spans several decades. Bulk graphite oxide, seen as an accumulation of GO flakes, was synthesized for the first time in 1855 by Brodie at Oxford University using potassium chlorate ($KClO_3$) and fuming nitric acid (HNO_3) as precursors [51]. Graphite and the mentioned precursors are mixed in a distiller, and the temperature is held at 60°C using a water-bath system. Staudenmaier enhanced Brodie's approach in 1898 by adding concentrated H_2SO_4 to boost acidity [52]. This approach, however, was time-consuming and dangerous due to the creation of hazardous volatile chlorine dioxide (ClO_2). Later in 1958, Hummers and Offeman introduced an alternative method for lessening the harmful level of GO production by using H_2SO_4 and $KMnO_4$ [51]. To date, the Hummers method is the best approach that most researchers have widely employed.

In brief, the Hummer method mixes a certain amount of graphite, sodium nitrate ($NaNO_3$), and concentrated H_2SO_4 in an ice-bath system with the ambient temperature of the mixture maintained at 0–4 °C. A quantity of $KMnO_4$ is added slowly to the mixture under vigorous stirring. The mixture's temperature is then kept at 35–38 °C for some specific periods, and an amount of deionized or distilled water is added before being raised to 98 °C and sustained for roughly 30–60 minutes. A 30% hydrogen peroxide (H_2O_2) solution is added to the mixture to convert the remaining manganese dioxide and permanganate to soluble manganese sulfate. The resultant GO was then rinsed many times with distilled water.

Each parameter and precursor used during the production of GO affects the reaction and gives different GO qualities to its application. Therefore, many researchers have explored modifying this Hummer method for GO production. For instance, Cao et al. [53] and Lebron et al. [54] have used phosphoric acid (H_3PO_4) in the process of GO production in their studies. In addition to utilizing $NaNO_3$ as an extra oxidizing agent, Han et al. [38] eliminated several steps and shortened the GO synthesis time. Yuan et al. [55] presented ultrasonic in their study's rate-determining step of the oxidation reaction and discovered that the oxidation and exfoliation processes play an essential role in producing more functional GO. Arabpour et al. [56] refined the sonication technique to increase oxidation and create high-quality GO in ECs (Methylene Blue) removal. Muzyka et al. [44] investigated the effect of different oxidative conditions on the oxygen content and distribution of OFGs on GO. They discovered that the chemical structure of GO could be adjusted by changing the reaction conditions even when using the same oxidation method. According to F et al. [57], the GO sonication period is essential in manufacturing high-quality GO nanocomposite films for UV light blocking applications. Yoo & Park [58] has proven that the addition of the H_2O_2 process in the Hummers method could intensely influence the properties of GO.

Even though many researchers have improved the GO synthesis by adjusting various temporal aspects, steps, and precursors, the method presented was not significantly different and was still parallel to the primary method introduced by Hummer. Despite researchers introducing several strategies to enhance GO synthesis, research on low-cost GO manufacturing processes, creating high-quality GO according to current requirements, and environmental friendliness is still ongoing.

Thus, this paper generally defines and describes the graphite-to-GO transformation process, which can be divided into four main stages before the washing process, as illustrated in Fig. 1. The first stage involves transforming graphite into H_2SO_4 intercalated graphite compounds. The second stage uses concentrated oxidizing agents such as $KMnO_4$ to transform graphite intercalated compounds into oxidized graphite. The third stage is to transform graphite oxide to GO via water reaction, and the fourth stage is to use H_2O_2 to reduce the remaining manganese dioxide and permanganate by producing a colorless solution. All the parameters described above are critical in creating high-quality GO that fulfills the application's needs.

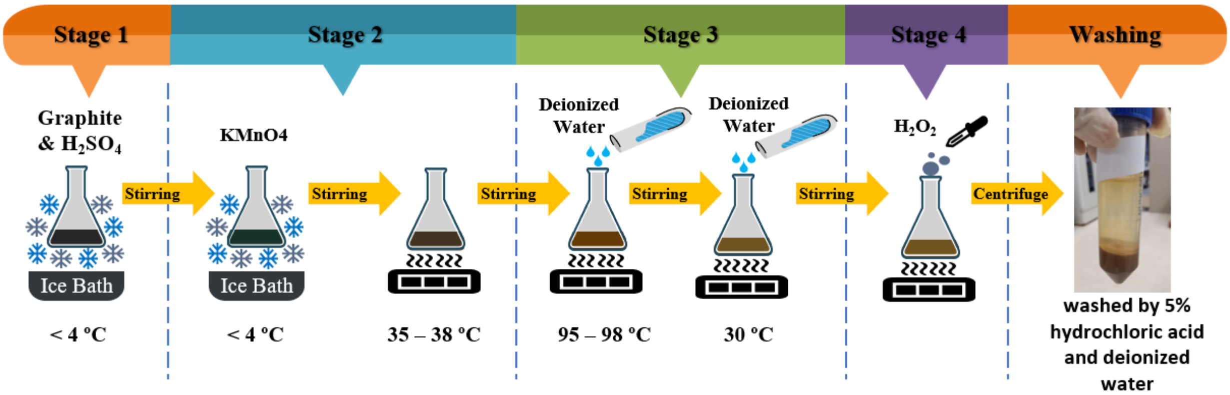

Fig. 1. Graphite-to-GO transformation process

3. ADSORPTION MECHANISM OF ANTIBIOTICS

Adsorption is one of the most appropriate physical approaches to removing antibiotics from water because of its low cost, flexibility, and exceptional efficiency. Graphene and GO having vast surface area characteristics make them beneficial for a more practical antibiotic reaction and faster adsorption [11], [51]. The unique structure of graphene and GO-based material also dramatically influences the performance of antibiotic removal through the adsorption approach. The single-layered carbon structure constituted in graphene oxide allows all atoms to be exposed to the environment and easily interact with antibiotic molecules, mainly by π-π interaction between antibiotic molecules and π-electron of graphene aromatic ring [59]. Moreover, the presence of high-density OFGs such as hydroxyl and carboxyl in the GO carbon lattice due to graphene functionalization creates more opportunities for hydrogen bonding between the antibiotic molecule and the functional group, making the antibiotic adsorption mechanism more effective and stable [43], [60]. In addition, this adsorption mechanism can also occur owing to the hydrophobic interaction of antibiotic molecules with the GO adsorbent's hydrophobic group and the antibiotic molecule's electrostatic interaction with the carboxyl group of GO at different pH [61].

4. ANTIBIOTICS ADSORPTION BY GO-BASED MATERIAL

Graphene has previously been utilized as an adsorbent in research to remove various antibiotics from environmental aqueous solutions [62]. However, its removal performance was still deemed mediocre in practical applications due to some drawbacks, such as surface hydrophobicity and facile aggregation in aqueous solutions [63], [64]. Thus, graphene is functionalized through a chemical or thermal approach and becomes an alternative material, such as GO and reduced GO (rGO), to address the drawbacks. The different chemical structures and the variety of functional groups present in the GO make it preferable to be employed as an adsorbent because it could provide a variety of antibiotic adsorption effects. Khalil et al. [4] performed a comparative study on the adsorption of several antibiotics on graphene and its derivatives (GO and porous graphene). They found that GO performance outperforms graphene in the adsorption of atenolol (ATL), ciprofloxacin (CIP), diclofenac (DCF), and gemfibrozil (GEM), but porous graphene outperforms GO in most of the studied antibiotics.

Covalent modification on the GO structure is usually performed due to the presence of hydrophilic functional groups such as hydroxyl, single bond -COOH, and epoxide. These hydrophilic functional groups allow small organic molecules such as nitrilotriacetic acid, diethylenetriaminepentaacetic acid, alginate, and chitosan to be easily attached to GO and provide more adsorption sites to improve the antibiotics' adsorption capacity. According to M. fang Li et al. [61], [65], GO functionalized with nitrilotriacetic acid and diethylenetriaminepentaacetic acid provided a high absorption capacity for CIP and tetracyclines (TC), and even the adsorption capacity of CIP has been significantly enhanced with coexisting Cu(II) in the solution.

The unique properties of graphene oxide have opened up a new chapter in developing various GO-based nanocomposites to raise antibiotic removal efficiency. Interestingly, nanoparticles can be incorporated directly onto GO without needing a specific molecular linker to bind the nanoparticle to GO. Tabrizian et al. [66] fabricated bimetallic-nanoparticles (nZVI/copper) supported by GO and found that the nanocomposite outperformed the single material in terms of TC removal. In comparison, Qiao et al. [34] reported that magnetic GO/Zink Oxide (ZnO) nanocomposite could adsorb TC with a remarkable adsorption rate, with a maximum adsorption capacity of 1590.28 mg/g.

In a nutshell, it is clear that most researchers treated graphene chemically or thermally and embedded the GO surface with other molecules or particles such as magnetic oxide, nanoparticles, and polymers to realize the antibiotic removal with a remarkable adsorption capacity. Table 1 shows different antibiotic removal capacities by graphene and GO-based materials.

5. CONCLUSION

Graphene and GO are novel carbon nanomaterials with unique features that allow them to be widely used in developing high-quality adsorbents to adsorb contaminants in environmental aqueous solutions. Some facets must be considered and well understood to produce graphene and its derivatives with remarkable adsorption quality. Therefore, this review summarizes the advantages of GO structural characteristics that affect antibiotic adsorption performance and the prospect of improving the material by covalent modification and other molecules or nanoparticle decoration on the surface. This study also highlights past studies on the affinity between the GO synthesis process and the quality of the produced material and summarizes the four main steps of GO production. Four principal mechanisms may be involved in the adsorption of antibiotics to GO-based material, including π-π interaction, which is the specific dispersion forces from van der Waals forces, hydrophobic and electrostatic interaction, and hydrogen bonding. In addition to synthesis optimization, GO was improved by most researchers through functionalization and integration with other compounds or nanoparticles. Even so, there are many challenges today in producing GO with high performance in antibiotic removal by considering cost, time, reusability, and environmentally friendly processes.

Table 1. Different antibiotic removal capacities by graphene and GO-based materials.

Graphene and GO-based adsorbents	Antibiotic	Wavelength (nm)	Adsorbent dose (g/L)	Maximum sorption capacity (mg/g)	Ref.
Graphene	Sulfamethoxazole (SMX)	295	1	103	[67]
Graphene	SMX	285		239	[68]
graphene–NH_2	SMX	285		40.6	[68]
graphene–COOH	SMX	285		20.5	[68]
graphene–OH	SMX	285		11.5	[68]
GO	SMX	295	1	122	[67]
GO	SMX	285	0.02	240	[69]
GO	CIP	278 & 445	0.2	379	[69]
GO	CIP		0.02	409	[70]
GO	Levofloxacin (LEV)		0.02	303	[70]
GO – biochar	Sulfamethazine (SMT)		1	6.5	[71]
Mesoporous silica – magnetic GO	SMX		0.57	15.46	[72]
MnO_2 – graphene	TC			198	[73]
Fe – graphene	TC			422	[74]
GO – nZVI/copper bimetallic-nanoparticles	TC	260 & 360	0.25	201.9	[66]
Cobalt-based ferrite ($CoFe_2O_4$) – GO	DCF	278	0.74	32.4	[75]
magnetic GO/ZnO	TC	358		1590.28	[34]

6. REFERENCES

[1] I. Maamoun, R. Eljamal, O. Falyouna, K. Bensaida, M. F. Idham, Y. Sugihara, O. Eljamal, Radionuclides Removal from Aqueous Solutions: A Mini Review on Using Different Sorbents, Proc. Int. Exch. Innov. Conf. Eng. Sci. 7 (2021) 170–177.

[2] M. Achparaki et al., Classification, Potential Routes and Risk of Emerging Pollutants/Contaminant, Intech, p. 13, 2012, [Online]. Available: http://dx.doi.org/10.1039/C7RA00172J%0Ahttps://www.intechopen.com/books/advanced-biometric-technologies/liveness-detection-in-biometrics%0Ahttp://dx.doi.org/10.1016/j.colsurfa.2011.12.014.

[3] Mohd Faizul Idham, O. Falyouna, O. Eljamal, Effect of Graphene Oxide Synthesis Method on The Adsorption Performance of Pharmaceutical Contaminants, Proc. Int. Exch. Innov. Conf. Eng. Sci., 7 (2021) 232–239.

[4] A. M. E. Khalil, F. A. Memon, T. A. Tabish, D. Salmon, S. Zhang, D. Butler, Nanostructured porous graphene for efficient removal of emerging contaminants (pharmaceuticals) from water, Chem. Eng. J. 398 (2020) 125440.

[5] D. S. Maycock, C. D. Watts, Pharmaceuticals in Drinking Water, Encycl. Environ. Heal. (2011) 472–484.

[6] S. Fekadu, E. Alemayehu, R. Dewil, B. Van der

Bruggen, Pharmaceuticals in freshwater aquatic environments: A comparison of the African and European challenge, Sci. Total Environ. 654 (2019) 324–337.
[7] X. Wang, A. Wang, M. Lu, J. Ma, Synthesis of magnetically recoverable Fe0/graphene-TiO2 nanowires composite for both reduction and photocatalytic oxidation of metronidazole, Chem. Eng. J. 337 (2017) 372–384.
[8] N. A. Ahammad, M. A. Zulkifli, M. A. Ahmad, B. H. Hameed, A. T. Mohd Din, Desorption of chloramphenicol from ordered mesoporous carbon-alginate beads: Effects of operating parameters, and isotherm, kinetics, and regeneration studies, J. Environ. Chem. Eng. 9 (2021) 105015.
[9] Q. Jiang, Y. Zhang, S. Jiang, Y. Wang, H. Li, W. Han, J. Qu, L. Wang, Y. Hu, Graphene-like carbon sheet-supported nZVI for efficient atrazine oxidation degradation by persulfate activation, Chem. Eng. J. 403 (2020) 126309.
[10] Z. Shirani, H. Song, A. Bhatnagar, Efficient removal of diclofenac and cephalexin from aqueous solution using Anthriscus sylvestris-derived activated biochar, Sci. Total Environ. 745 (2020) 140789.
[11] H. Li, J. Hu, Y. Meng, J. Su, X. Wang, An investigation into the rapid removal of tetracycline using multilayered graphene-phase biochar derived from waste chicken feather, Sci. Total Environ. 603–604 (2017) 39–48.
[12] M. B. Ahmed, J. L. Zhou, H. H. Ngo, W. Guo, Adsorptive removal of antibiotics from water and wastewater: Progress and challenges, Sci. Total Environ. 532 (2015) 112–126.
[13] T. Zhang, Y. Yang, J. Gao, X. Li, H. Yu, N. Wang, P. Du, R. Yu, H. Li, X. Fan, Z. Zhou, Synergistic degradation of chloramphenicol by ultrasound-enhanced nanoscale zero-valent iron/persulfate treatment, Sep. Purif. Technol. 240 (2020) 116575.
[14] Y. Ji, C. Zhang, X. J. Zhang, P. F. Xie, C. Wu, L. Jiang, A high adsorption capacity bamboo biochar for CO2 capture for low temperature heat utilization, Sep. Purif. Technol. 293 (2022) 121131.
[15] T. Avcu, O. Üner, Ü. Geçgel, Adsorptive removal of diclofenac sodium from aqueous solution onto sycamore ball activated carbon – isotherms, kinetics, and thermodynamic study, Surfaces and Interfaces, 24 (2021) 101097.
[16] T. Shahnaz, V. Vishnu Priyan, S. Pandian, S. Narayanasamy, Use of Nanocellulose extracted from grass for adsorption abatement of Ciprofloxacin and Diclofenac removal with phyto, and fish toxicity studies, Environ. Pollut. 268 (2021) 115494.
[17] Z. Wang, L. Song, Y. Wang, X. F. Zhang, J. Yao, Construction of a hybrid graphene oxide/nanofibrillated cellulose aerogel used for the efficient removal of methylene blue and tetracycline, J. Phys. Chem. Solids. 150 (2021) 109839.
[18] Z. A. ALOthman, A. Y. Badjah, O. M. L. Alharbi, I. Ali, Synthesis of chitosan composite iron nanoparticles for removal of diclofenac sodium drug residue in water, Int. J. Biol. Macromol. 159 (2020) 870–876.
[19] G. Cui, J. Guo, Y. Zhang, Q. Zhao, S. Fu, T. Han, S. Zhang, Y. Wu, Chitosan oligosaccharide derivatives as green corrosion inhibitors for P110 steel in a carbon-dioxide-saturated chloride solution, Carbohydr. Polym. 203 (2019) 386–395.
[20] W. Phasuphan, N. Praphairaksit, A. Imyim, Removal of ibuprofen, diclofenac, and naproxen from water using chitosan-modified waste tire crumb rubber, J. Mol. Liq. 294 (2019) 111554.
[21] H. Zhao, X. Liu, Z. Cao, Y. Zhan, X. Shi, Y. Yang, J. Zhou, J. Xu, Adsorption behavior and mechanism of chloramphenicols, sulfonamides, and non-antibiotic pharmaceuticals on multi-walled carbon nanotubes, J. Hazard. Mater. 310 (2016) 235–245.
[22] C. V. T. Rigueto, M. Rosseto, M. T. Nazari, B. E. P. Ostwald, I. Alessandretti, C. Manera, J. S. Piccin, A. Dettmer, Adsorption of diclofenac sodium by composite beads prepared from tannery wastes-derived gelatin and carbon nanotubes, J. Environ. Chem. Eng. 9 (2021) 105030.
[23] S. Bellamkonda, N. Thangavel, H. Y. Hafeez, B. Neppolian, G. Ranga Rao, Highly active and stable multi-walled carbon nanotubes-graphene-TiO2 nanohybrid: An efficient non-noble metal photocatalyst for water splitting, Catal. Today. 321–322 (2019) 120–127.
[24] F. Yu, S. Sun, S. Han, J. Zheng, J. Ma, Adsorption removal of ciprofloxacin by multi-walled carbon nanotubes with different oxygen contents from aqueous solutions, Chem. Eng. J. 285 (2016) 588–595.
[25] M. B. Ahmed, J. L. Zhou, H. H. Ngo, W. Guo, M. A.H. Johir, K. Sornalingam, D. Belhaj, M. Kallel, Nano-Fe0 immobilized onto functionalized biochar gaining excellent stability during sorption and reduction of chloramphenicol via transforming to reusable magnetic composite, Chem. Eng. J. 322 (2017) 571–581.
[26] J. Zhao, X. Yang, G. Liang, Z. Wang, S. Li, Z. Wang, X. Xie, Effective removal of two fluoroquinolone antibiotics by PEG-4000 stabilized nanoscale zero-valent iron supported onto zeolite (PZ-NZVI), Sci. Total Environ. 710 (2020) 136289.
[27] C. H. Nguyen, M. L. Tran, T. T. Van Tran, R. S. Juang, Efficient removal of antibiotic oxytetracycline from water by Fenton-like reactions using reduced graphene oxide-supported bimetallic Pd/nZVI nanocomposites, J. Taiwan Inst. Chem. Eng. 000 (2021) 1–10.
[28] O. Falyouna, M. F. Idham, I. Maamoun, K. Bensaida, UPM Ashik, Y. Sugihara, O. Eljamal, Promotion of ciprofloxacin adsorption from contaminated solutions by oxalate modified nanoscale zerovalent iron particles, J. Mol. Liq. 359 (2022) 119323.
[29] O. Falyouna, I. Maamoun, K. Bensaida, A. Tahara, Y. Sugihara, O. Eljamal, Encapsulation of iron nanoparticles with magnesium hydroxide shell for remarkable removal of ciprofloxacin from contaminated water, J. Colloid Interface Sci. 605 (2022) 813–827.
[30] A. Mokhati, O. Benturki, M. Bernardo, Z. Kecira, I. Matos, N. Lapa, M. Ventura, O.S.G.P. Soares, A.M. Botelho do Rego, I.M. Fonseca, Nanoporous carbons prepared from argan nutshells as potential removal agents of diclofenac and paroxetine, J. Mol. Liq. 326

(2021) 115368.
[31] D. Shan, S. Deng, J. Li, H. Wang, C. He, G. Cagnetta, B. Wang, Y. Wang, J. Huang, G. Yu, Preparation of porous graphene oxide by chemically intercalating a rigid molecule for enhanced removal of typical pharmaceuticals, Carbon N. Y. 119 (2017) 101–109.
[32] F. Görmez, Ö. Görmez, B. Gözmen, D. Kalderis, Degradation of chloramphenicol and metronidazole by electro-Fenton process using graphene oxide-Fe3O4 as heterogeneous catalyst, J. Environ. Chem. Eng. 7 (2019) 102990.
[33] C. H. Nguyen, M. L. Tran, T. T. Van Tran, R. S. Juang, Efficient removal of antibiotic oxytetracycline from water by Fenton-like reactions using reduced graphene oxide-supported bimetallic Pd/nZVI nanocomposites, J. Taiwan Inst. Chem. Eng. 119 (2021) 80–89.
[34] D. Qiao, Z. Li, J. Duan, X. He, Adsorption and photocatalytic degradation mechanism of magnetic graphene oxide/ZnO nanocomposites for tetracycline contaminants, Chem. Eng. J. 400 (2020) 125952.
[35] Y. P. Liu, Y.-T. Lv, J.-F. Guan, F. M. Khoso, X.-Y. Jiang, J. Chen, W.-J. Li, J.-G. Yu, Rational design of three-dimensional graphene/graphene oxide-based architectures for the efficient adsorption of contaminants from aqueous solutions, J. Mol. Liq. 343 (2021) 117709.
[36] M. F. Idham, B. Abdullah, K. M. Yusof, Effects of two cycle heat treatment on the microstructure and hardness of ductile iron, Pertanika J. Sci. Technol. 25 (2017) 99–106.
[37] W. Peng, H. Li, Y. Liu, S. Song, A review on heavy metal ions adsorption from water by graphene oxide and its composites, J. Mol. Liq. 230 (2017).
[38] L. Han, B. Li, S. Tao, J. An, B. Fu, Y. Han, W. Li, X. Li, S. Peng, T. Yin, Graphene oxide-induced formation of a boron-doped iron oxide shell on the surface of NZVI for enhancing nitrate removal, Chemosphere. 252 (2020).
[39] Y. Sun, M. Gu, S. Lyu, M. L. Brusseau, M. Li, Y. Lyu, Y. Xue, Z. Qiu, Q. Sui, Efficient removal of trichloroethene in oxidative environment by anchoring nano FeS on reduced graphene oxide supported nZVI catalyst: The role of FeS on oxidant decomposition and iron leakage, J. Hazard. Mater. 392 (2020) 122328.
[40] J. Chen, B. Yao, C. Li, G. Shi, An improved Hummers method for eco-friendly synthesis of graphene oxide, Carbon N. Y. 64 (2013) 225–229.
[41] X. Liu, R. Ma, X. Wang, Y. Ma, Y. Yang, L. Zhuang, S. Zhang, R. Jehan, J. Chen, X. Wang, Graphene oxide-based materials for efficient removal of heavy metal ions from aqueous solution: A review, Environ. Pollut. 252 (2019) 62–73.
[42] R. Ghorbani, S. Behrangi, H. Aghajani, A. Taghizadeh Tabrizi, N. Abdian, Application of synthesized porous 3D graphene structure for electrochemical hydrogen storage, Mater. Sci. Eng. B. 268 (2021) 115139.
[43] B. Y. Z. Hiew, L. Y. Lee, X. J. Lee, S. Gan, S. Thangalazhy-Gopakumar, S. S. Lim, G.-T. Pan, T. C.-K. Yang, Adsorptive removal of diclofenac by graphene oxide: Optimization, equilibrium, kinetic and thermodynamic studies, J. Taiwan Inst. Chem. Eng. 98 (2019) 150–162.
[44] R. Muzyka, M. Kwoka, Ł. Smędowski, N. Díez, G. Gryglewicz, Oxidation of graphite by different modified Hummers methods, New Carbon Mater. 32 (2017) 15–20.
[45] J. Chen, G. M. He, G. Y. Xian, X. Q. Su, L. L. Yu, F. Yao, Mechanistic biosynthesis of SN-38 coated reduced graphene oxide sheets for photothermal treatment and care of patients with gastric cancer, J. Photochem. Photobiol. B Biol. 204 (2020) 111736.
[46]X. Sun, X. Yu, W. Li, M. Chen, D. Liu, Mechanical properties, degradation behavior and cytocompatibility of biodegradable 3vol%X (X = MgO, ZnO and CuO)/Zn matrix composites with excellent dispersion property fabricated by graphene oxide-assisted hetero-aggregation, Biomater. Adv. 134 (2022) 112722.
[47] Y. Yang, L. Xu, H. Shen, and J. Wang, Construction of three-dimensional reduced graphene oxide wrapped nZVI doped with Al2O3 as the ternary Fenton-like catalyst: Optimization, characterization and catalytic mechanism, Sci. Total Environ. 780 (2021) 146576.
[48] S. Georgitsopoulou, N. D. Stola, A. Bakandritsos, V. Georgakilas, Advancing the boundaries of the covalent functionalization of graphene oxide, Surfaces and Interfaces. 26 (2021) 101320.
[49] Y. Lin, S. Xu, J. Li, Fast and highly efficient tetracyclines removal from environmental waters by graphene oxide functionalized magnetic particles, Chem. Eng. J. 225 (2013) 679–685.
[50] M. fang Li, Y.-G. Liu, S.-B Liu, D. Shu, G.-M. Zeng, X.-J. Hu, X.-F. Tan, L.-H. Jiang, Z.-L. Yan, X.-X. Cai, Cu(II)-influenced adsorption of ciprofloxacin from aqueous solutions by magnetic graphene oxide/nitrilotriacetic acid nanocomposite: Competition and enhancement mechanisms, Chem. Eng. J. 319 (2017) 219–228.
[51] B. Y. Z. Hiew, L. Y. Lee, X. J. Lee, S. Thangalazhy-Gopakumar, S. Gan, S. S. Lim, G.-T. Pan, T. C.-K. Yang, W. S. Chiu, P. S. Khiew, Review on synthesis of 3D graphene-based configurations and their adsorption performance for hazardous water pollutants, Process Saf. Environ. Prot. 116 (2018) 262–286.
[52] M. fang Li, Y. guo Liu, G. ming Zeng, N. Liu, S. bo Liu, Graphene and graphene-based nanocomposites used for antibiotics removal in water treatment: A review, Chemosphere. 226 (2019) 360–380.
[53] M. li Cao, Y. Li, H. Yin, S. Shen, Functionalized graphene nanosheets as absorbent for copper (II) removal from water, Ecotoxicol. Environ. Saf. 173 (2019) 28–36.
[54] Y. A. R. Lebron, V. R. Moreira, G. P. Drumond, M. M. da Silva, R. de Oliveira Bernardes, L. V. de Souza Santos, R. S. Jacob, M. M. Viana, C. K. B. de Vasconcelos, Graphene oxide for efficient treatment of real contaminated water by mining tailings: Metal adsorption studies to Paraopeba river and risk assessment, Chem. Eng. J. Adv. 2 (2020) 100017.
[55] R. Yuan, J. Yuan, Y. Wu, L. Chen, H. Zhou, J. Chen, Efficient synthesis of graphene oxide and the

mechanisms of oxidation and exfoliation, Appl. Surf. Sci. 416 (2017) 868–877.
[56] A. Arabpour, S. Dan, H. Hashemipour, Preparation and optimization of novel graphene oxide and adsorption isotherm study of methylene blue, Arab. J. Chem. 14 (2021) 103003.
[57] H. L. F., C. P. Tan, Z. R.M., N. H. Nur, Effect of sonication time and heat treatment on the structural and physical properties of chitosan/graphene oxide nanocomposite films, Food Packag. Shelf Life. 28 (2021) 100663.
[58] M. J. Yoo, H. B. Park, Effect of hydrogen peroxide on properties of graphene oxide in Hummers method, Carbon N. Y. 141 (2019) 515–522.
[59] H. Karimi-Maleh, M. Shafieizadeh, M. A. Taher, F. Opoku, E. M. Kiarii, P. P. Govender, S. Ranjbari, M. Rezapour, Y. Orooji, The role of magnetite/graphene oxide nano-composite as a high-efficiency adsorbent for removal of phenazopyridine residues from water samples, an experimental/theoretical investigation, J. Mol. Liq. 298 (2020).
[60] A. Razaq, F. Bibi, X. Zheng, R. Papadakis, S. H. M. Jafri, H. Li, Review on Graphene-, Graphene Oxide-, Reduced Graphene Oxide-Based Flexible Composites: From Fabrication to Applications, Materials (Basel). 15 (2022)
[61] M. fang Li, Y.-G. Liu, S.-B. Liu, G.-M. Zeng, X.-J. Hu, X.-F. Tan, L.-H. Jiang, N. Liu, J. Wen, X.-H. Liu, Performance of magnetic graphene oxide/diethylenetriaminepentaacetic acid nanocomposite for the tetracycline and ciprofloxacin adsorption in single and binary systems, J. Colloid Interface Sci. 521 (2018) 150–159.
[62] F. Perreault, A. Fonseca De Faria, M. Elimelech, Environmental applications of graphene-based nanomaterials, Chem. Soc. Rev. 44 (2015) 5861–5896.
[63] N. A. Elessawy, M. H. Gouda, S. M. Ali, M. Salerno, M. S. M. Eldin, Effective elimination of contaminant antibiotics using high-surface-area magnetic-functionalized graphene nanocomposites developed from plastic waste, Materials (Basel). 13 (2020).
[64] H. Guo, Y. Wang, X. Yao, Y. Zhang, Z. Li, S. Pan, J. Han, L. Xu, W. Qiao, J. Li, H. Wang, A comprehensive insight into plasma-catalytic removal of antibiotic oxytetracycline based on graphene-TiO2-Fe3O4 nanocomposites, Chem. Eng. J. 425 (2021) 130614.
[65] M. fang Li, Y.-G. Liu, G.-M. Zeng, S.-B. Liu, X.-J. Hu, D. Shu, L.-H. Jiang, X.-F. Tan, X.-X. Cai, Z.-L. Yan, Tetracycline absorbed onto nitrilotriacetic acid-functionalized magnetic graphene oxide: Influencing factors and uptake mechanism, J. Colloid Interface Sci. 485 (2017) 269–279.
[66]P. Tabrizian, W. Ma, A. Bakr, M. S. Rahaman, pH-sensitive and magnetically separable Fe/Cu bimetallic nanoparticles supported by graphene oxide (GO) for high-efficiency removal of tetracyclines, J. Colloid Interface Sci. 534 (2019) 549–562.
[67] R. Rostamian, H. Behnejad, A comparative adsorption study of sulfamethoxazole onto graphene and graphene oxide nanosheets through equilibrium, kinetic and thermodynamic modeling, Process Saf. Environ. Prot. 102 (2016) 20–29.
[68] H. Chen, B. Gao, H. Li, Functionalization, pH, and ionic strength influenced sorption of sulfamethoxazole on graphene, J. Environ. Chem. Eng. 2 (2014) 310–315.
[69] H. Chen, B. Gao, H. Li, Removal of sulfamethoxazole and ciprofloxacin from aqueous solutions by graphene oxide, J. Hazard. Mater. 282 (2015) 201–207.
[70] K. Sun, S. Dong, Y. Sun, B. Gao, W. Du, H. Xu, J. Wu, Graphene oxide-facilitated transport of levofloxacin and ciprofloxacin in saturated and unsaturated porous media, J. Hazard. Mater. 348 (2018) 92–99.
[71] D. Huang, X. Wang, C. Zhang, G. Zeng, Z. Peng, J. Zhou, M. Cheng, R. Wang, Z. Hu, X. Qin, Sorptive removal of ionizable antibiotic sulfamethazine from aqueous solution by graphene oxide-coated biochar nanocomposites: Influencing factors and mechanism, Chemosphere. 186 (2017) 414–421.
[72] N. Ninwiwek, P. Hongsawat, P. Punyapalakul, P. Prarat, Removal of the antibiotic sulfamethoxazole from environmental water by mesoporous silica-magnetic graphene oxide nanocomposite technology: Adsorption characteristics, coadsorption and uptake mechanism, Colloids Surfaces A Physicochem. Eng. Asp. 580 (2019) 123716.
[73] Z. Song, Y. L. Ma, C. E. Li, The residual tetracycline in pharmaceutical wastewater was effectively removed by using MnO2/graphene nanocomposite, Sci. Total Environ. 651 (2019) 580–590.
[74] S. M. Alatalo, E. Daneshvar, N. Kinnunen, A. Meščeriakovas, S. K. Thangaraj, J. Jänis, D. C.W. Tsang, A. Bhatnagar, A. Lähde, Mechanistic insight into efficient removal of tetracycline from water by Fe/graphene, Chem. Eng. J. 373 (2019) 821–830.
[75] T. Van Tran, D. T. C. Nguyen, H. T. N. Le, D. V. N. Vo, S. Nanda, T. D. Nguyen, Optimization, equilibrium, adsorption behavior and role of surface functional groups on graphene oxide-based nanocomposite towards diclofenac drug, J. Environ. Sci. (China). 93 (2020) 137–150.