International Journal of Chemical and Biochemical Sciences
(ISSN 2226-9614)

Journal Home page: www.iscientific.org/Journal.html

A review on recent advancements in the removal of phenol and pharmaceutical compounds

Ho Soonmin[*,1], Sie Yon Lau[2], Abdul Zahir[2,3], Sankha Chakrabortty[4], Ajala Oluwaseun Jacob[5]*

[1,*]*Faculty of Health and Life Sciences, INTI International University, 71800, Putra Nilai, Negeri Sembilan, Malaysia.*

[2]*Department of Chemical and Energy Engineering, Faculty of Science, Curtin University Malaysia, CDT250, 98009 Miri, Sarawak.*

[2,3]*National Textile Research Centre, National Textile University, Faisalabad, 37610, Pakistan.*

[4]*Kalinga School of Biotechnology/Chemical Technology, Kalinga Institute of Industrial Technology (Deemed to be University), Bhubaneswar 751024, Odisha, India.*

[5]*Department of Pure and Applied Chemistry, Ladoke Akintola University of Technology, Ogbomoso, Nigeria.*

Abstract

Water pollution caused by several reasons such as global warming, fuel spillages, intensive farming, septic tank, nuclear waste, industrial wastes, and household wastes. When water supply was contaminated by fertilizers, herbicides, hazardous materials, heavy metal and organic pollutants, threat to plant, human and animal. Currently, adsorption method has been used extensively to remove pollutant or unwanted materials if compared to other techniques. In general, there are several advantages have been highlighted included low maintenance costs, simple design, insensitivity for toxic substances and high efficiency. Adsorption capacity was strongly depending on various factors such as surface area of adsorbent, porosity structure, and the pore diameter. Graphene oxide has large surface area, showed good electron transport capability, suitable for photocatalytic applications. Many researchers have reported that photodegradation of phenol compounds using this material in different specific conditions. Also, other metal oxide materials such as zinc oxide, copper oxide and titanium oxide could be employed to eliminate phenol compounds due to appropriate band gap value, good photocatalytic properties, and larger surface area, respectively. On the other hand, pharmaceutical compounds (ibuprofen, carbamazepine, sulfamethazine, chloramphenicol, diphenhydramine, sulfamethoxazole, and tetracycline) have been removed using graphene based material and biological treatment method. Moreover, graphene-based composites showed excellent visible light activity, and can capture solar radiation, could be used widely to reduce number of pharmaceutical compounds in wastewater.

Keywords: Water quality, Phenol compounds, Adsorption, wastewater treatment, water pollution, pharmaceutical compounds.

**Corresponding Author*, e-mail: soonmin.ho@newinti.edu.my

1. Introduction

Adsorption methods have been used for removing dye, heavy metal, herbicides, pesticides, organic compounds, and pharmaceutical compounds a few decades ago. In general, all these pollutants or unwanted materials will be absorbed into absorbent [1]. Unique properties of these adsorbents such as high surface area [2], well-developed porosity [3], and appropriate pore size distribution [4]. Based on the literature survey, granular activated carbon [5, 6], hydrated ferric oxide, single-walled carbon nanotubes, aluminum oxide, multiwalled carbon nanotubes [7], graphene oxide, montmorillonite, chitosan [8], and silica-supported iron nanocomposite have been used to prepare adsorbent. Graphene oxide (GO) is used for adsorption process due to chemical stability [9], high surface area (600-900 m^2/g), high adsorption kinetics, availability of functional groups, and

ease of regeneration [10]. However, several disadvantages including easily to form aggregates, and low thermal stability [11] have been reported using graphene oxide. In the phytostabilization technique [12], plant species were used to ensure that the contaminants remain immobile in soil and groundwater. Further, accumulation and adsorption occurred in botanical tissues, and the roots, respectively. In the rhizodegradation process, microbes were utilized to decompose contaminants to less hazardous or nontoxic substance. Following that, this less harmless substances will be released to atmosphere through leaves. Also, generated waste could be stored in shoots and roots via phytoaccumulation process [13]. Membrane incorporated bioreactor has been used to remove inorganic compounds and organic pollutants. It is combination of biological method with membrane filtration, happened in bioreactor [14]. Smaller pores could be seen in membrane, therefore, can produce high quality treated effluent. This technique showed low maintenance costs, produce less sludges, and tolerate high organic loading [15]. However, some limitations such as membrane fouling occurred, blockage, and high energy requirement [16].

The main purpose of this work is to study the removal of phenol and pharmaceutical compounds through different techniques. The adsorption process was conducted in water treatment due to its simple design, low maintenance cost, high efficiency, and cost-effectiveness. Percentage removal and photodegradation efficiency of these pollutants was reported according to the literature review. Selection of these techniques depending on operating cost, efficiency, simplicity, and investment cost.

2. Removal of pharmaceutical compounds

It was noted that biodegradation of pharmaceutical pollutants happened in two channels. In the primary metabolic, microorganisms degrade the pollutants, so that, to obtain carbon and energy source for the cell growth. While, in the co-metabolism [17], this compound will be chemically changed by bacteria (heterotrophic and autotrophic). Anerobic biological treatment did not need oxygen conditions to decompose the pharmaceutical drugs and the removal efficiency has been highlighted (Table 1). Several advantages have been described such as improved degradation efficiency, producing less waste sludges, need fewer chemicals, showed good stability and robustness [18]. Graphene oxide is carbon-based material, showing hydrophobicity properties [25]. It was noticed that the electrical properties [26] could be improved up to several times through chemical and thermal treatment process. These compounds can transport the electrons easily and photoexcited charges to the target locations. In addition, they play a role as surface modifier when deposited on the catalyst surface, enhanced better interaction between the pharmaceutical compounds and photoexcited charges [27]. Moreover, these modified graphene oxides can protect catalyst from the adverse effect of chemicals in the wastewater [28]. Several graphene oxide composites have been produced for removal of pollutants and the degradation efficiency was reported. Graphene oxide has been utilized to remove pharmaceutical compounds (Table 2). Unique properties in the prepared graphene oxide such as excellent visible light activity and was able to capture solar radiation. It was proven that several drawbacks (in conventional methods) could be solved through addition of photocatalysts into graphene compounds. As a result, the obtained graphene-modified photocatalysts showed great adsorption capacity, good performance activity, and successfully reduced the recombination of electron-holes.

Amitriptyline is used to treat several illnesses such as mental disorders and nerve and back pain. It could be excreted with urine due to very short half-life values (10 to 28 hours). Over the past 10 years, it has been observed in different water sources in Canada, China, France, China, and United Kingdom. It can be identified as emerging pollutants, harmful to humans and oceanic life because of stable melting point and very strong chemical structure. Wan and co-workers [53] have synthesized boron doped three-dimensional graphene oxide with central composite design. In the morphology study, there are different morphologies could be seen in graphene oxide, boron doped graphene oxide (less smooth, and more cracking), three-dimensional/boron doped graphene oxide (thin sheets, and wrinkled edges), and after the adsorption (smooth surface), based on the FESEM images (figure 1). The results confirmed that the highest removal efficiency was 87.72% in specified conditions (dosage=12.5 mg, adsorption time=32 minutes, temperature=30 °C, initial concentration=70 ppm). Researchers also concluded that higher influent concentration would increase the adsorption capacity, because of created a stronger driving force to improve the adsorbate uptake. Cetirizine is identified as antihistamine drugs, could be employed for treat allergies, fever, and angioedema. In general, about 80% of cetirizine was excreted because of poor metabolism. Other properties such as high solubility, stable, low volatility, low biodegradability and lipophilic in nature. Research has shown that very low concentration of cetirizine has been identified in drinking water and wastewater. Mechanism of adsorption onto adsorbent (figure 2) has been described by Tuhin and co-workers [54] and the influence of pH on the adsorption of cetirizine was investigated. Faster kinetics could be observed in acidic conditions and cetirizine removal was finished within 10 minutes. While relatively slower process (the highest removal was 81.3 mg/g) in neutral conditions. However, cetirizine could not be removed in basic conditions after 1 day. According to the thermodynamic parameters, entropy, enthalpy, and free energy were 33 J/K.mol, -16.984 kJ/mol, and -26.852 to -28.002 kJ/mol, respectively. Monolayer formation was observed, as highlighted in Langmuir model (rate constants=0.766 L/mg). The R^2 (R^2=0.999) indicated good agreement with the pseudo second order kinetics if compared to pseudo first order kinetic (R^2=0.885). Quercetin can be utilized to treat inflammation, allergy, cardiovascular disorders, and cancer. The quercetin was not produced in human body and was identified as flavonol group. Moreover, this flavonol can improve the biogenesis of mitochondria and platelet aggregation. Magnetic mesoporous silica Fe_3O_4 graphene oxide was produced to remove quercetin [55].

Table 1: Removal efficiency of various pharmaceutical drugs using different anerobic biological treatment

Anerobic treatment type	Pollutant	Removal efficiency (%)	Researcher(s)
Upflow anaerobic sludge blanket [19]	Amoxicillin	21.6	Chen et al., 2008
Upflow anaerobic sludge blanket [19]	6-Aminopenicillanic Acid	26.3	Chen et al., 2008
Upflow anaerobic sludge blanket [20]	Tylosin	95	Chelliapan et al., 2006.
Anerobic membrane reactor [21]	Erythromycin	40	Aydin et al., 2014.
Anerobic membrane reactor [21]	Sulfamethaxazole	37	Aydin et al., 2014.
Anerobic membrane reactor [22]	Amoxicillin	97.2	Chen et al., 2011.
Anerobic membrane reactor [23]	Etodola	99	Kaya et al., 2017.
Anaerobic sequencing batch reactor [24]	etracycline	85-95	Aydin, 2016

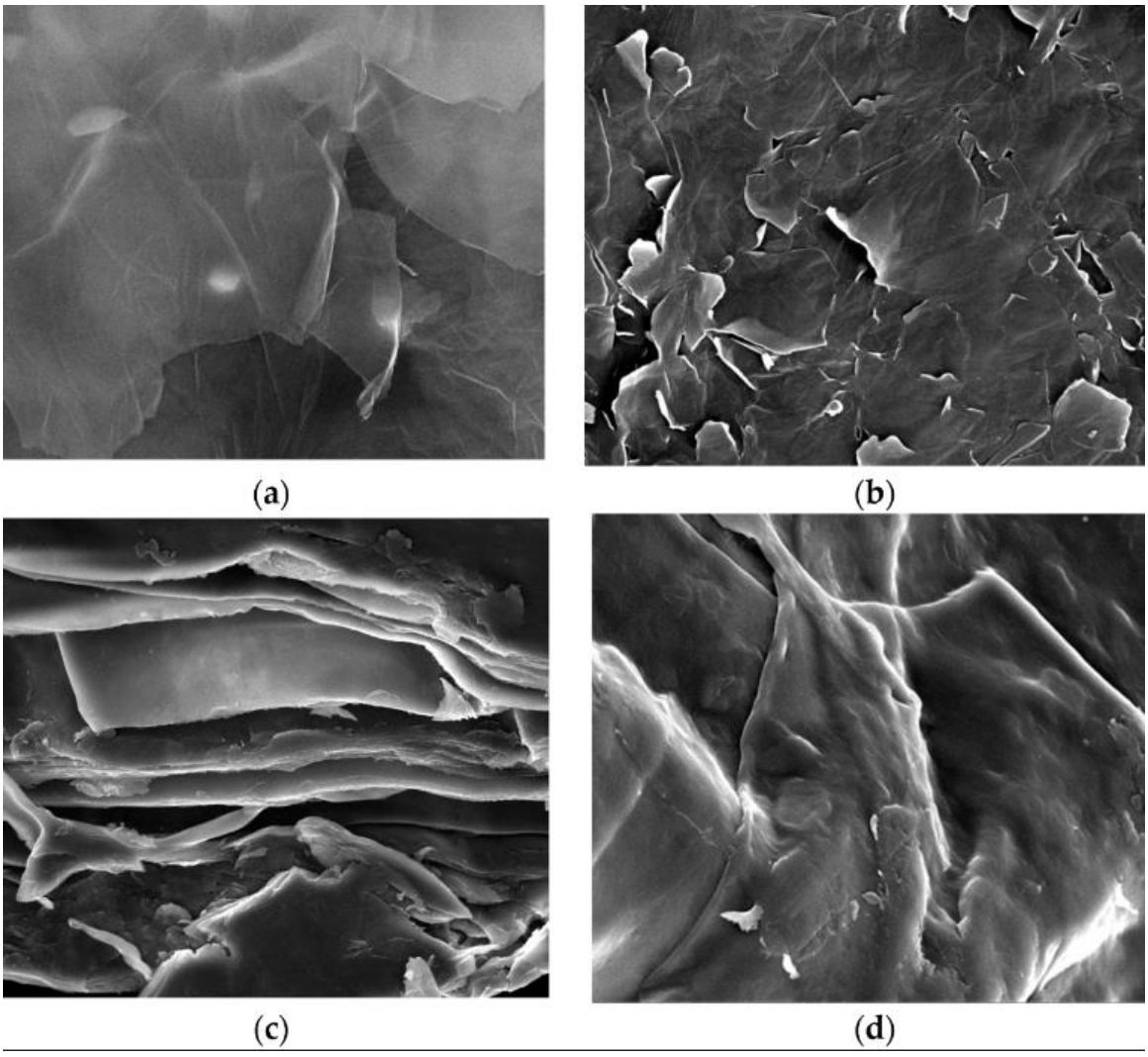

Figure 1. FESEM images for (**a**) graphene oxide (**b**) Boron doped graphene oxide, and (**c**) 3-dimensional/boron doped graphene oxide and (**d**) after AMI adsorption [53].

Table 2: Removal of different types of pharmaceutical compounds using graphene oxide.

Pollutants	**Highlighted experimental results**
Ibuprofen	Different removal rate [29] was observed in graphene oxide membranes (34.8%) and GO-EDA with ethylenediamine (44.9%).
Carbamazepine	Higher removal efficiency (sulfamethoxazole, ibuprofen, and carbamazepine) in TiO_2-rGO than TiO_2-Fe due to improved photocatalytic activity. [30]. $BiVO_4$ graphene quantum dots showed higher degradation efficiency than bare $BiVO_4$. [31]
Sulfamethoxazole	Removal rate was 98 % within 3 hours using rGO-WO_3 (RW-200) through visible light illumination [32].
Diphenhydramine	GO-TiO_2 (larger surface area) indicated higher adsorption capacity than P25 TiO_2. [33]. GO-TiO_2 (P25) composites showed the highest pseudo-first order rate constants ($56x10^{-3}$ min^{-1}) [34].
17-α-ethinylestradiol	$ZnFe_2O_4$-Ag/rGO showed minimize agglomeration, and improved charge carrier generation and separation, given that higher degradation efficiency value than $ZnFe_2O_4$ alone and $ZnFe_2O_4$-Ag [35].
Sulfamethazine	The percentage of removal achieved 99 % in Fe_3O_4/Mn_3O_4-rGO nanocomposite in specific conditions [36].
Tetracycline	An inorganic salts-assisted hydrothermal technique has been used to produce $Bi_{3.84}W_{0.16}O_{6.24}$-graphene oxide [37], showing additional active sites. Highly degradation rate could be seen using rGO-CdS/ZnS composites (15% RGO) due to facilitates the transformation of electrons [38].
Ciprofloxacin	Graphene oxide magnetite [39] shows good efficiency values if compared to bare Fe_3O_4. Degradation rate achieved 98.3% within 240 minutes and maintained for 80% (10 cycles) for Fe_3O_4@Bi_2O_3-rGO photocatalysts [40]. Excellent ciprofloxacin hydrochloride degradation [41] could be observed in ZnO-GO composite when the pH was 6 and experimental findings show it can be reused without significant loss of efficacy.
Chloramphenicol	$Ce(MoO_4)_2$/GO displayed good degradation performance under visible light irradiation. [42].
Metronidazole	Degradation efficiency was 72.5% for $ZnSnO_3$/RGO [43] Degradation efficiency reached 98% for Fe_3O_4/rGO/TiO_2 [44]
Levofloxacin	Degradation efficacy [45] achieved 99.2% for ZnONP
Oxytetracycline	Degradation efficiency was 84.7% for cobalt ferrite/reduced graphene oxide [46].
Cetirizine hydrochloride	Degradation efficiency [47] reached 89% for Graphene oxide decorated $ZnWO_4$
Diclofenac [48]	Degradation efficiency achieved 38.7% for pectin-graphene oxide-magnesium ferrite-zinc oxide nanocomposite
Bisphenol-A [49]	Degradation efficacy was 62% for $CoFe_2O_4$ nanoparticles decorated onto graphene oxide
Tetracycline [50]	Degradation efficiency reached 99% for $BiVO_4$/reduced graphene oxide
Ethenzamide [51]	Degradation efficiency achieved 99% for rGO/GNW hydrogel
Azithromycin [52]	Degradation efficiency reached 90% for GO@Fe_3O_4/ ZnO/ SnO_2 nanocomposites

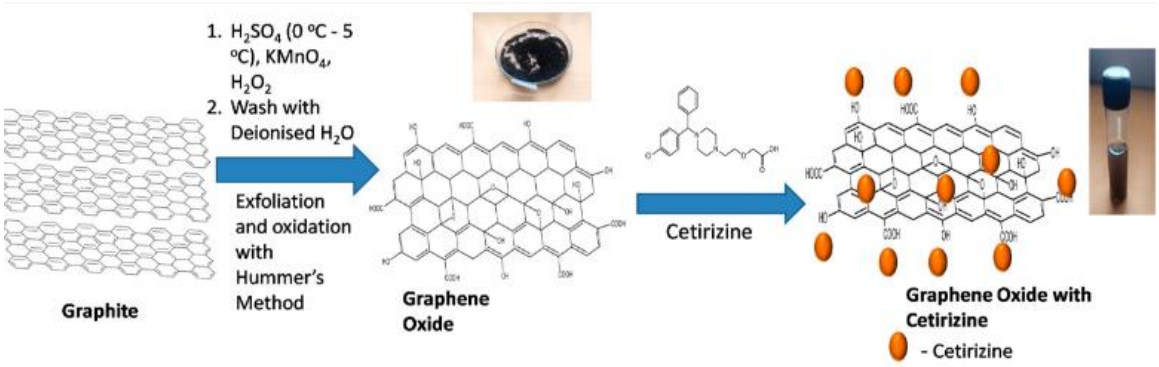

Figure 2: Adsorption mechanism of cetirizine on graphene oxide [54]

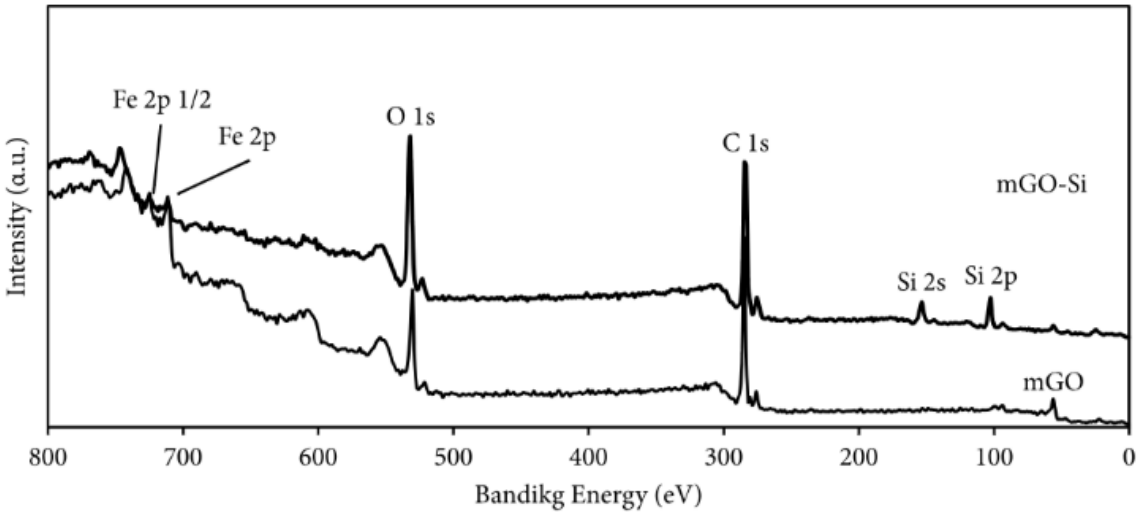

Figure 3: XPS analysis of Fe_3O_4-graphene oxide and Fe_3O_4@GO@mSiO_2 particles [55].

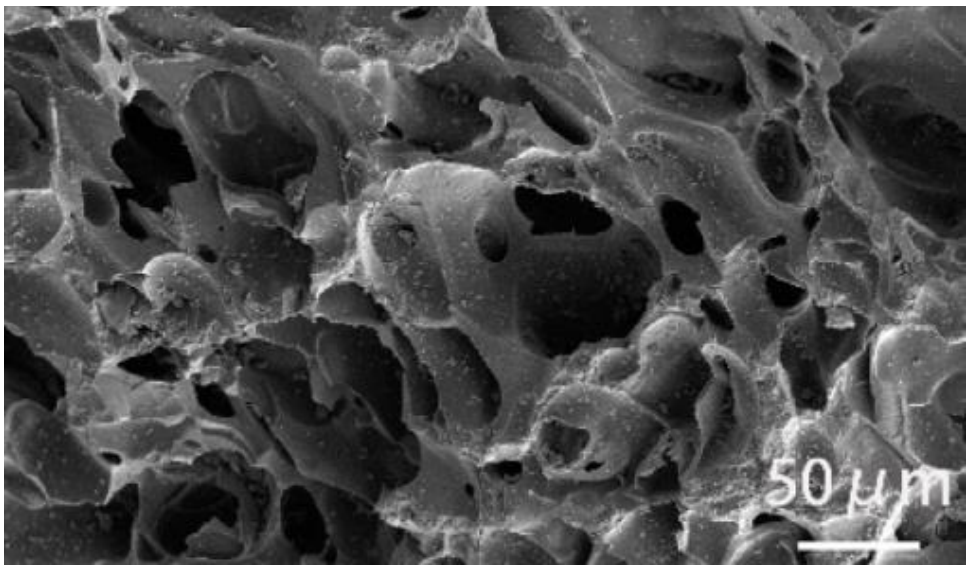

Figure 4: SEM image of coal derived granular activated carbon [79]

FTIR (peaks could be observed at 3444, 1238, 1731 and 2925 cm^{-1}), SEM (roughened structure), EDAX (carbon, oxygen, iron, and silicon were 33.8%, 8.26%, 2.2% and 81.21%), and XRD (diffraction peaks at (111), (220), (311), (400), (422), 9511), (440) and (533) planes) have been used to characterize the obtained nanoparticles. XPS technique (figure 3) have been conducted to investigate the chemical status of samples. Several peaks such as Fe2p, C1s and O1s could be seen in Fe_3O_4-graphene oxide. Additional peaks including Si2s and Si2p could be detected in Fe_3O_4@GO@mSiO_2 particles. Langmuir model has confirmed homogeneous process due to higher R^2 value (R^2=0.9959) if compared to Freundlich isotherm (R^2=0.9703). According to extraction capacity studies, the highest extraction capacity was 1.89 mg/g, and the amount of extracted adsorbate increases when the initial concentration (quercetin) was increased until 0.8 μg/mL, then remains constant value could be seen.

3. Removal of phenol compounds

Photodegradation of phenol compounds by graphene oxide (GO) due to higher surface area and good electron transport capability. It shows 2-dimesnional material, consisted of carbon atoms with honeycomb lattice. The highest degradation efficiency [56] reached 85% in optimized conditions (reaction time=240 minutes, concentration of graphene oxide=0.1 g/L, and initial phenol concentration=50 mg/L) and can described well using pseudo-first-order kinetics. Chen and co-workers [57] prepared nitrogen-doped graphene oxide to enhance visible light absorption. Photocatalytic degradation process could be explained by several steps. Phenol molecules will be directly adsorbed on graphene oxide through π-π interactions and hydrogen bonding. Then, phenol will be oxidized using photogenerated holes, to produce phenol radicals and other products [58]. While oxygen will be reduced to form superoxide radicals via photogenerated electrons [59]. Chen and co-workers [60] have synthesized silver decorated graphene oxide particles. The obtained results reflected higher degradation efficiency (92 %) in the presence of visible light irradiation. Photodegradation of phenol could be conducted using zinc oxide (ZnO) because of appropriate band gap (3.3 eV) value. In general, electron-hole pairs were generated when the ZnO was illuminated with UV light. Wang and co-workers [61] have highlighted that degradation efficiency was 92 % in the presence of UV light, within 2 hours. Li and co-workers [62] have pointed out that degradation efficiency achieved 80 % within 3 hours. Also, they explained that phenol molecules have been decomposed into non-toxic products.

Copper oxide (narrow band gap) can be used as photocatalyst to remove phenol in aqueous solutions. Li and co-workers [63] have described that the highest degradation efficiency reached 75 % in the best conditions (time=240 minutes, concentration of CuO=0.5 g/L, and initial phenol concentration=100 mg/L) and the adsorption data was fitted well with pseudo-first-order kinetics. Yao and co-workers [64] have found that good interaction between pollutants and catalysts in the adsorption process. Photocatalytic degradation process has been improved using CuO/TiO_2 composites [65]. Similarly, nitrogen doped CuO composites have been produced by Xu and co-workers [66] to enhance the photocatalytic performance for phenol degradation,

Photodegradation of phenol using titanium dioxide (TiO_2) because of suitable band gap and larger surface area. Li and co-workers [67] have reported that the highest degradation efficiency achieved 95 % in specific conditions (180 minutes, under UV light irradiation, concentration of TiO_2=1 g/L, initial phenol concentration=50 mg/L) and the adsorption data were supported by pseudo-first-order kinetics. Liu and co-workers [68] have highlighted that mineralization of phenol molecules into less toxic products including carbon dioxide and water. Wang and co-workers [69] have confirmed that higher degradation efficiency in alkaline environment. Chen and co-workers [70] have modified TiO_2 with metals or nonmetals to improve its photocatalytic activity. Enzymatic treatment has been used to remove phenol due to cost-effectiveness if compared to traditional biological and chemical therapies [71]. Aromatic compounds have been treated using Horseradish peroxidase [72] in the early 1980s. Several advantages have been highlighted such as simplicity of control, reduced sludge volume, no shock loading limitation. Oxidoreductases (laccases, tyrosinases, and peroxidases) were chosen to enhance the elimination of phenolic compounds. The standard measure of activity per volume is utilized to describe enzyme concentration. The o-diphenols and monophenol could be converted to o-quinones and o-diphenols, through oxidation process and o-hydroxylation process, respectively in the presence of tyrosinases. The stability of this enzyme could be improved by covalently immobilizing it on nylon membranes, magnetic supports, or siliceous supports [73]. Soybean peroxidase (SBP) has been proven to be a reliable enzyme for phenol removal. Large-scale enzymatic treatments were carried out through immobilization approaches. Rezvani and co-workers [74] have reported the best conditions (concentration of H_2O_2=14 mM, initial phenol=1mM, temperature=56 °C, flow rate=5.5 mL/min) for removal of phenol (degradation was 97 %) through semi-permeable alginate membrane in bioreactor. Torres and co-workers [75] have studied the influence of polyethylene glycol and triton x-100 on the removal of phenol. They conclude that turnip peroxidase affected the removal of phenol in the presence of additions (50 % change in phenol oxidation). Peroxidase (potato pulp) has been used [76] to remove 2,4-dichlorophenol and degradation efficiency reached 90% (time=120 minutes, concentration of H_2O_2=2.59 mM, concentration phenol=0.02 to 1mM). Favorable pH values were found in the range of pH 4-8, however, significantly drops when the pH was 10.

Removal of phenol using activated carbon due to higher surface area and cheaper technique. Eucalyptus seed based activated carbon [77] treated with sodium hydroxide showed higher surface area (670-780 m^2/g), higher total basicity value (0.462-0.7 meq/g) and the adsorption data fitted well with Langmuir model. Moreover, the highest adsorption capacity was found to be 2.125 mmol/g, 2.568 mmol/g and 3.888 mmol/g for phenol, 4-nitrophenol and 4-chlorophenol, respectively using 30% of NaOH during the experiment. Micropore volume (0.18 – 0.43 cm^3/g), surface area (469-1113 m^2/g) and distribution of pore size (0.3 -1.4 nm) for coconut shell [78] based activated carbon (treated with phosphoric acid and nitric acid). The obtained results confirmed that the presence of nitrogen can enhance phenol

adsorption rate and reached 97% within 2 hours. Coal derived granular active carbon [79] showed surface area of 700.57 m^2/g with average pore size of 2.22nm and displayed skeletal structure (figure 4) with pores, so that, penetration of phenol into activated carbon occurred easily. Based on the FTIR studies, several peaks such as 3430 cm^{-1} (OH), 1200 cm^{-1} (CH stretching), 1500 cm^{-1} (C=O) could be observed, contribute to negative charge density if the surface of the adsorbent. Adsorption data could be described using Langmuir model (adsorption capacity was 214.13 mg/g) and pseudo second order kinetic isotherm (R^2=0.9861). Further, they explain that phenol adsorption happened via formation of donor (electron donor group in adsorbent) and acceptor (aromatic ring in phenol) interactions.

6. Conclusions

Water pollutant caused by human activities and industrial processes. Removal of pollutants was carried out using various techniques. In this work, removal of phenol and pharmaceutical compounds could be conducted using graphene oxide, activated carbon and copper oxide, titanium oxide, zinc oxide and enzymatic treatment. Degradation efficiency strongly depends on experimental conditions.

Acknowledgements:

One of the authors (HO SM) would like to thank you to INTI International University, Malaysia for the financial support.

References

[1] D. El-Sayed. (2023). Electronic band structure and density of state modulation of amphetamine and ABW type–zeolite adsorption system: DFT-CASTEP analysis. Journal of Molecular Modelling. https://doi.org/10.1007/s00894-023-05501-y.

[2] C. Lim, T. Seow and C. Neoh. (2016). Treatment of landfill leachate using ASBR combined with zeolite adsorption technology. 3 Biotech. https://doi.org/10.1007/s13205-016-0513-8.

[3] S.M. Ho and M. Saad. (2023). Review on heavy metal and dye removal via activated carbon adsorption process. Asian Journal of Chemistry. 35: 1-16.

[4] S.M. Ho. (2022). Low-Cost Adsorbents for the Removal of Phenol/Phenolics, Pesticides, and Dyes from Wastewater Systems: A Review. Water. https://doi.org/10.3390/w14203203.

[5] W. Low, S. Kevin, and H. Lee. (2023). Adsorption of zinc, copper, and iron from synthetic wastewater using watermelon (Citrullus Lanatus), Mango (Mangifera Indica L) and rambutan peels (Nephelium Lappaceum L) as bio-sorbents. Journal of Engineering Science and Technology. 18: 386-405.

[6] S.M. Ho, M. Akram, A. Rashid and U. Laila. (2022). Uses of activated carbon in medicine area: short review. EPRA International Journal of Research and Development. 7: 4-39.

[7] F. El-Sweify, I. Abdelmonem and M. El-Masry. (2019). Adsorption Behavior of Co(II) and Eu(III) on Polyacrylamide/Multiwalled Carbon Nanotube Composites. Radiochemistry. 61: 323–330.

[8] F. Ahmad, S. Hassan and Z. Imran. (2023). Green Approach to Water Purification: Investigating Methyl Orange Dye Adsorption Using Chitosan/Polyethylene Glycol Composite Membrane. Journal of Polymers and the Environment. https://doi.org/10.1007/s10924-023-02994-9.

[9] M. Raad, M. Kassir and W. El. (2017). A comparative adsorption study of trinitrotoluene onto graphene oxide, reduced graphene oxide and reduced graphene oxide-coated silica nanoparticles through equilibrium, kinetic and thermodynamic modeling. Graphene Technology. 2: 63–73.

[10] F. Wang, Z. Jia and W. Su. (2019). Adsorption of phenanthrene and 1-naphthol to graphene oxide and $_L$-ascorbic-acid-reduced graphene oxide: effects of pH and surfactants. Environmental Science and Pollution Research. 26: 11062–11073.

[11] F. Alamdarlo, G. Solookinejad and F. Zahakifar. (2021). Study of kinetic, thermodynamic, and isotherm of Sr adsorption from aqueous solutions on graphene oxide (GO) and (aminomethyl)phosphonic acid–graphene oxide (AMPA–GO). Journal of Radioanalytical and Nuclear Chemistry. 329: 1033–1043.

[12] J. Pérez, C. Escolástico and A. Moliner. (2014). Phytostabilization of metals in mine soils using Brassica juncea in combination with organic amendments. Plant Soil. 377: 97–109.

[13] G. Ondrasek, B. Jelovica and I. Peter. (2022). Humates and Chlorides Synergistically Increase Cd Phytoaccumulation in Strawberry Fruits, Heightening Health Risk from Cd in Human Diet. Exposure and Health. 14: 393–410.

[14] M. Pervez, M. Balakrishnan and S. Hasan. (2020). A critical review on nanomaterials membrane bioreactor (NMs-MBR) for wastewater treatment. NPJ Clean Water. https://doi.org/10.1038/s41545-020-00090-2.

[15] J. Cho, K. Song and H. Ahn. (2009). Contribution of microfiltration on phosphorus removal in the sequencing anoxic/anaerobic membrane bioreactor. Bioprocess and Biosystems Engineering. 32: 593–602.

[16] A. Jauneau, C. Morvan and J. Fenyo. (1988). Pectate lyase production by Bacillus subtilis in a membrane bioreactor. Applied Microbiology and Biotechnology. 29: 234–238.

[17] H. Dalton and D. Stirling (1982). Co-metabolism. Philosophical Transactions of the Royal Society B, Biological Sciences. https://doi.org/10.1098/rstb.1982.0056 (1982).

[18] X. Shi, K. Leong and Y. Ng. (2017). Anaerobic treatment of pharmaceutical wastewater: A critical review. Bioresource Technology, 245: 1238–1244 (2017).

[19] Z. Chen, N. Ren and A. Wang. (2008). A novel application of TPAD–MBR system to the pilot treatment of chemical synthesis-based

pharmaceutical wastewater. Water Research. 42: 3385–3392.

[20] S. Chelliapan, T. Wilby and P. Sallis. (2006). Performance of an up-flow anaerobic stage reactor (UASR) in the treatment of pharmaceutical wastewater containing macrolide antibiotics. Water Research. 40: 507–516.

[21] S. Aydin, B. Ince and Z. Cetecioglu. (2014). Performance of anaerobic sequencing batch reactor in the treatment of pharmaceutical wastewater containing erythromycin and sulfamethoxazole mixture. Water Science & Technology. 70: 1625–1632.

[22] Z. Chen, H. Wang and N. Ren. (2011). Simultaneous removal and evaluation of organic substrates and NH 3-N by a novel combined process in treating chemical synthesis-based pharmaceutical wastewater. Journal of Hazardous Materials. 197: 49–59.

[23] Y. Kaya, A. Murat and H. Hasar. (2017). Treatment of chemical synthesis-based pharmaceutical wastewater in an ozonation-anaerobic membrane bioreactor (AnMBR) system. Chemical Engineering Journal. 322: 293-301.

[24] S. Aydin. (2016). Enhanced biodegradation of antibiotic combinations via the sequential treatment of the sludge resulting from pharmaceutical wastewater treatment using white-rot fungi Trametes versicolor and Bjerkandera adusta. Applied Microbiology and Biotechnology. 100: 6491–6499.

[25] K. Lu, Y. Li and R. Tang. (2021). Roles of Graphene Oxide in Heterogeneous Photocatalysis. ACS Materials Au. https://doi.org/10.1021/acsmaterialsau.1c00022.

[26] K. Chua and M. Pumera. (2014). Chemical reduction of graphene oxide: a synthetic chemistry viewpoint. Chemical Society Reviews. 43: 291–312.

[27] K. Moon, J. Lee and R. Ruoff. (2010). Reduced graphene oxide by chemical graphitization. Nature Communications. https://doi.org/10.1038/ncomms1067.

[28] S. Stankovich, D. Dikin and G. Dommett. (2006). Graphene-based composite materials. Nature. 442: 282–286.

[29] L. Yanyan, S. Xia and J. Tan. (2020). Preparation of Cross-Linked Graphene Oxide on Polyethersulfone Membrane for Pharmaceuticals and Personal Care Products Removal. Polymers. https://doi.org/10.3390/polym12091921.

[30] K. Lin, J. Pan and Y. Chen. (2009). Study the adsorption of phenol from aqueous solution on hydroxyapatite nanopowders. Journal of Hazardous Materials. 161: 231-240.

[31] L. Tang, J. Wang and C. Jia. (2017). Simulated solar driven catalytic degradation of psychiatric drug carbamazepine with binary $BiVO_4$ heterostructures sensitized by graphene quantum dots. Applied Catalysis B Environmnetal. 205: 587-596.

[32] Z. Wenyu, F. Sun and Y. Zhou. (2017). Facile fabrication of RGO-WO_3 composites for effective visible light photocatalytic degradation of sulfamethoxazole. Applied Catalysis B Environmental. 207: 93-102.

[33] M. Pastrana, S. Morales and V. Likodimos. (2012). Advanced nanostructured photocatalysts based on reduced graphene oxide-TiO_2 composites for degradation of diphenhydramine pharmaceutical and methyl orange dye. Applied Catalysis B Enviroinmental. 123-124: 241-256.

[34] S. Morales, M. Pastrana and J. Figueiredo. (2013). Graphene oxide-P25 photocatalysts for degradation of diphenhydramine pharmaceutical and methyl orange dye. Applied Surface Science. 25: 361-368.

[35] N. Khadgi, Y. Li and A. Upreti. (2016). Enhanced Photocatalytic Degradation of 17α-Ethinylestradiol Exhibited by Multifunctional $ZnFe_2O_4$-Ag/rGO Nanocomposite under Visible Light. Photochemistry and Photobiology. 92: 238–246.

[36] Z. Wan and J. Wang. (2017). Degradation of sulfamethazine using Fe_3O_4-Mn_3O_4/reduced graphene oxide hybrid as Fenton-like catalyst. Journal of Hazardous Materials. 324: 653–664.

[37] C. Song, X. Li and L. Wang. (2016). Fabrication, Characterization and Response Surface Method (RSM) Optimization for Tetracycline Photodegration by $Bi_{3.84}W_{0.16}O_{6.24}$-graphene oxide (BWO-GO). Scientific Reports. https://doi.org/10.1038/srep37466.

[38] Y. Tang, X. Liu and C. Ma. (2015). Enhanced photocatalytic degradation of tetracycline antibiotics by reduced graphene oxide-CdS/ZnS heterostructure photocatalysts. New Journal of Chemistry. 39: 5150-5160.

[39] P. Alicanoglu and D. Sponza. (2017). Removal of ciprofloxacin antibiotic with nano graphene oxide magnetite composite: Comparison of adsorption and photooxidation processes. Desalination and Water Treatment. 63: 293–307.

[40] Y. Zhu, J. Xue and T. Xu. (2017). Enhanced photocatalytic activity of magnetic core–shell Fe_3O_4@Bi_2O_3–RGO heterojunctions for quinolone antibiotics degradation under visible light. Journal of Materials Science Materials in Electronics. 28: 8519–8528.

[41] T. Anirudhan, R. Deepa and S. Nair. (2017). Fabrication of chemically modified graphene oxide/nano hydroxyapatite composite for adsorption and subsequent photocatalytic degradation of aureomycine hydrochloride. Journal of Industrial and Engineering Chemistry. 47: 415–430.

[42] R. Karthik, K. Vinoth and S. Chen. (2017). A Study of Electrocatalytic and Photocatalytic Activity of Cerium Molybdate Nanocubes Decorated Graphene Oxide for the Sensing and Degradation of Antibiotic Drug Chloramphenicol. ACS Applied Materials & Interfaces. 9: 6547–6559.

[43] S. Dong, Y. Li and J. Sun. (2014). Facile synthesis of novel ZnO/RGO hybrid nanocomposites with enhanced catalytic performance for visible-light-driven photodegradation of metronidazole. Materials Chemistry and Physics. 145: 357–365.

[44] F. Bashiri, M. Khezri and R. Kalantary. (2020). Enhanced photocatalytic degradation of metronidazole by TiO_2 decorated on magnetic

reduced graphene oxide: Characterization, optimization and reaction mechanism studies. Journal of Molecular Liquids. https://doi.org/10.1016/J.MOLLIQ.2020.113608.

[45] C. El, M. El and A. Naem. (2020). Effective Removal of Levofloxacin from Pharmaceutical Wastewater Using Synthesized Zinc Oxid, Graphen Oxid Nanoparticles Compared with their Combination. Scientific Reports. https://doi.org/10.1038/S41598-020-61742-4.

[46] J. Wang, L. Zang and Y. Wang. (2022). Magnetic cobalt ferrite/reduced graphene oxide (CF/rGO) porous balls for efficient photocatalytic degradation of oxytetracycline. Journal of Environmental Chemical Engineering. https://doi.org/10.1016/J.JECE.2022.108259.

[47] K. Qureshi, M. Ahmad and A. Bhatti. (2019). Graphene oxide decorated $ZnWO_4$ architecture synthesis, characterization and photocatalytic activity evaluation. Journal of Molecular Liquids. 285: 778–789.

[48] A. Bateni, K. Valizadeh and Y. Salahshour. (2022). Fabrication and characterization of pectin-graphene oxide-magnesium ferrite-zinc oxide nanocomposite for photocatalytic degradation of diclofenac in an aqueous solution under visible light irradiation. Journal of Environmental Management. Doi: 10.1016/j.jenvman.2022.116358.

[49] O. Görmez, E. Yakar and B. Gözmen. (2022). $CoFe_2O_4$ nanoparticles decorated onto graphene oxide and graphitic carbon nitride layers as a separable catalyst for ultrasound-assisted photocatalytic degradation of Bisphenol-A. Chemosphere. https://doi.org/10.1016/J.CHEMOSPHERE.2021.132663.

[50] T. Soltani, A. Tayyebi and B. Lee. (2019). Photolysis and photocatalysis of tetracycline by sonochemically heterojunctioned $BiVO_4$/reduced graphene oxide under visible-light irradiation. Journal of Environmnetal Management. https://doi.org/10.1016/J.JENVMAN.2018.11.133.

[51] Y. Hu, Y. Yang and J. Zhang. (2020). Efficient adsorption and full spectrum photocatalytic degradation of low concentration PPCPs promoted by graphene/TiO_2 nanowires hybrid structure in 3D hydrogel networks. RSC Advances. 10: 27050–27057.

[52] H. Sayadi, S. Sobhani and H. Shekari. (2019). Photocatalytic degradation of azithromycin using GO@Fe_3O_4/ ZnO/ SnO_2 nanocomposites. Journal of Cleaner Production. 232: 127–136.

[53] T. Wan, L. Lee and J. Yong. (2023). Remediation of Amitriptyline Pharmaceutical Wastewater by Heteroatom-Doped Graphene Oxide: Process Optimization and Packed-Bed Studies. *Separations.* https://doi.org/10.3390/separations10070392.

[54] B. Tuhin, B. Arnab and D. Deka. (2023). Adsorption Characteristics of Cetirizine on Graphene Oxide. *Sustainable Chemistry. 4:* 209-223.

[55] H. Delnia and S. Bahar. (2023). Synthesis of modified magnetic graphene oxide with mesoporous silica for extraction of the pharmaceutical compound quercetin. Journal of Analytical Methods in Chemistry. https://doi.org/10.1155/2023/8581986.

[56] T. Wang, Z. Xu and L. Wu. (2017). Enhanced photocatalytic activity for degrading phenol in seawater by TiO_2-based catalysts under weak light irradiation. RSC Advances. 7: 31921–31929.

[57] W. Chen, S. Chen and F. Li. (2017). Photocatalytic degradation of phenol using nitrogen-doped graphene oxide under visible light irradiation. Environmental Science and Pollution Research. 24: 12971-12981.

[58] X. Wang, Y. Liu and L. Zhang. (2016). Photocatalytic degradation of phenol using graphene oxide/BiFeO3 composite under visible light irradiation. Applied Catalysis B: Environmental. 180: 652-660.

[59] J. Liu, L. Zhang and S. Zhang. (2015). Photocatalytic degradation of phenol over reduced graphene oxide/TiO_2 composites under UV and visible light irradiation. Applied Surface Science. 356: 973-980.

[60] L. Chen, Y. Liu and H. Yu. (2018). Enhanced photocatalytic degradation of phenol by Ag-decorated graphene oxide under visible light irradiation. Chemical Engineering Journal. 331: 38-46.

[61] J. Wang, H. Wang and Y. Liu. (2018). Highly efficient photocatalytic degradation of phenol over ZnO nanoparticles under UV light irradiation. Environmental Science and Pollution Research. 25: 25252-25260.

[62] H. Li, J. He and J. Li. (2019). Photodegradation of phenol by ZnO nanorods under UV light irradiation. Materials Science in Semiconductor Processing. 91: 88-94.

[63] H. Li, J. Zheng and Y. Sun. (2018). Photodegradation of phenol by copper oxide nanoparticles under visible light irradiation. Journal of Environmental Chemical Engineering. 6: 5458-5467.

[64] K. Yao, L. Chen and C. Hu. (2016). Efficient photodegradation of phenol using copper oxide nanoparticles synthesized via a green approach. RSC Advances. 6: 46816-46824.

[65] H. Tang, X. Tan and G. Chen. (2017). Photocatalytic degradation of phenol by copper oxide/titanium dioxide composites. Journal of Environmental Sciences. 60: 102-112.

[66] Y. Xu, J. Zhang and L. Li. (2019). Visible-light-driven photocatalytic degradation of phenol by nitrogen-doped copper oxide nanoparticles. Applied Surface Science. 470: 1045-1053.

[67] H. Li, G. Zhang and T. Wu. (2018). Photodegradation of phenol using TiO_2 as a photocatalyst. Journal of Environmental Sciences. 65: 313-321.

[68] X. Liu, Y. Wang and H. Zhang. (2017). Characterization of phenol degradation intermediates by TiO2 photocatalysis using HPLC and GC-MS. Journal of Hazardous Materials. 324: 51-59.

[69] S. Wang, R. Li and R. Amal. (2019). The influence of pH on the photocatalytic degradation of phenol over TiO_2. Chemical Engineering Journal. 358: 1184-1192.

[70] L. Chen, Y. Chen and H. Liu. (2016). Enhancing the photocatalytic degradation of phenol by TiO_2 through metal/nonmetal doping. Applied Catalysis B: Environmental. 181: 333-340.

[71] M. Alshabib and S. Onaizi. (2019). A review on phenolic wastewater remediation using homogeneous and heterogeneous enzymatic processes: Current status and potential challenges. Separation and Purification Technology. 219: 186-207.

[72] A. Klibanov. (1989). Enzymatic catalysis in anhydrous organic solvents. Trends in Biochemical Sciences. 14: 141-144.

[73] P. García, F. Molina and A. Teruel. (2022). Considerations about the kinetic mechanism of tyrosinase in its action on monophenols: A review. Molecular Catalysis. https://doi.org/10.1016/j.mcat.2021.112072.

[74] F. Rezvani, H. Azargoshasb and O. Jamialahmadi. (2015). Experimental study and CFD simulation of phenol removal by immobilization of soybean seed coat in a packed-bed bioreactor. Biochemical Engineering Journal. 101: 32-43.

[75] J. Torres, P. Chagas and M. Silva. (2016). Evaluation of the protective effect of chemical additives in the oxidation of phenolic compounds catalysed by peroxidase. Environmental Technology. 37: 1288-1295.

[76] K. Kurnik, K. Treder and M. Twarużek. (2018). Potato pulp as the peroxidase source for 2, 4-dichlorophenol removal. Waste and Biomass Valorization. 9: 1061-1071.

[77] G. Nelson, C. Juan and G Liliana. (2015). Thermodynamic study of adsorption of phenol, 4-chlorophenol and 4-nitrophenol on activated carbon obtained from Eucalyptus seed. Journal of Chemistry. http://dx.doi.org/10.1155/2015/569403.

[78] M. Ana, L. Giraldo and J. Carlos. (2018). A study of the interactions of activated carbon phenol in aqueous solution using the determination of immersion enthalpy. Applied Sciences. https://doi.org/10.3390/app8060843.

[79] B. Xie, J. Qin and S. Wang. (2020). Adsorption of phenol on commercial activated carbons: modelling and interpretation. International Journal of Environmental Research and Public health. https://doi.org/10.3390/ijerph17030789.