

**CARBON NANOSTRUCTURE-BASED
MATERIALS FOR REMOVAL OF ORGANIC
CONTAMINANTS FROM WASTEWATER**

BY

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Dedication

All this effort is dedicated to my beloved people and the scientific community. To my parents, grandparents, brothers, and sisters. To researchers, scientists, doctors, engineers, teachers, students, writers, and readers (you).

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My gratitude and all praises to Allah, Glory to Him, first and foremost for giving the continuous and unlimited grace, health, strength, peace, resources, guidance, and success not only during this research but also throughout my life. I ask Allah to forgive and protect me and believers throughout our lives and after.

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LIST OF ABBREVIATIONS

$1/n$	:	Heterogeneity factor
A	:	Absorbance
A_b	:	Equilibrium binding constant (L/mg)
AOPs	:	Advanced oxidation processes
B	:	Temkin constant
b	:	Length of light path
b_s	:	Scatchard constant (L/g)
b_T	:	Sorption heat (J/mol)
C	:	Concentration of methylene blue (ppm)
C_a	:	Amount of methylene blue adsorbed onto PG (ppm)
C_e	:	Final concentration of methylene blue (ppm)
C_o	:	Initial or inlet concentration of methylene blue (ppm)
CNTs	:	Carbon nanotubes
COPs	:	Catalytic ozonation processes
c	:	Adsorption step constant (mg/g)

DG	:	Diethylenetriamine modified graphene
DWTP	:	Drinking water treatment plants
E	:	Energy needed to remove an adsorbate molecule (kJ/mol)
EG	:	Ethylenediamine modified graphene
FTIR	:	Fourier transform infrared
GAC	:	Granular activated carbon
GO	:	Graphene oxides
HG	:	Hydroxylamine modified graphene
h	:	Initial rate of adsorption (mg/(g•min))
K_d	:	Thermodynamic equilibrium constant
K_e	:	Freundlich constant (L/g)
K_L	:	Langmuir constant (L/mg)
K_{YN}	:	Yoon and Nelson rate constant (1/min)
k_1	:	Pseudo-first-order rate constant (1/min)
k_2	:	Pseudo-second-order rate constant (g/(mg•min))
k_i	:	Rate constant of intraparticle diffusion (mg/(g•min ^{1/2}))
MB	:	Methylene blue

m	:	Mass of adsorbent (mg)
OAG	:	Oxalic acid modified graphene
OPE	:	Organophosphate ester
PG	:	Polyethylenimine modified graphene
Q	:	Flow rate (mL/s)
q_t	:	Quantity of methylene blue adsorption at time t (mg/g)
q_e	:	Equilibrium adsorption capacity of methylene blue (mg/g)
q_m	:	Monolayer adsorption capacity (mg/g)
q_s	:	Scatchard adsorption capacity (mg/g)
R	:	Universal gas constant (J/(mol•K))
R^2	:	Correlation coefficient
R_L	:	Factor of separation
SEM	:	Scanning electron microscopy
T	:	Temperature (K)
TEM	:	Transmission electron microscope
TGA	:	Thermogravimetric analysis
t	:	Time (min)

V	:	Solution volume (L)
WHO	:	World Health Organization
WWTPs	:	wastewater treatment plants
XRD	:	X-ray diffraction
ΔG°	:	Standard Gibbs free energy (kJ/mol)
ΔH°	:	Standard enthalpy change (kJ/mol)
ΔS°	:	Standard entropy change (J/(mol•K))
α	:	Initial adsorption rate (mg/(g•min))
β	:	Desorption constant (g/mg)
β_a	:	Activity coefficient (g/mg)
ε	:	Molar absorptivity
ε_p	:	Polanyi potential (J/mol)
τ	:	The time needed for 50 % adsorbate breakthrough (min)

ABSTRACT

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Thesis Title : Carbon nanostructure-based materials for removal of organic contaminants from wastewater
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Water pollution from industrial wastewater is one of the major environmental concerns, that has been recognized as a global challenge. Major contributors to water pollution are organic chemical contaminants that are continuously being released into the environment. The objectives of this research are to design and synthesize functionalized carbon nanostructure-based materials including graphene, and polymer/graphene and to characterize the developed materials using state-of-the-art instrumentations such as scanning electron microscopy (SEM), transmission electron microscope (TEM), Fourier transform infrared (FTIR) spectroscopy, thermogravimetric analysis (TGA), and x-ray diffraction (XRD). The materials were evaluated to demonstrate their efficiency for the sorption and separation of toxic organic contaminants from water. This work also includes optimization of the treatment conditions in the batch mode including initial concentration, contact time, temperature, pH, and metals. Several models were applied to study the equilibrium isotherms, kinetics, and thermodynamics. This was followed by testing the materials in dynamic mode using real wastewater mixed with contaminants to investigate the effects of changing the flow rate and applying a dynamic model. Polyethylenimine modified graphene (PG) was found to have the highest efficiency in adsorbing methylene

blue and it was selected for further batch and dynamic experiments as well as the characterization. The results show that this material has a high adsorption capability with a maximum adsorption capacity q_m of 161.29 mg/g. It can remove methylene blue and metals simultaneously and work well at a wide range of temperatures and pH. This material has excellent structural stability even after use in the adsorption process. It was found to perform well in the dynamic mode which is more convenient for treating larger amounts of wastewater.

ملخص الرسالة

الاسم الكامل : علي هاشم محمد الناصر
عنوان الرسالة : المواد القائمة على الهياكل النانوية الكربونية لإزالة الملوثات العضوية من
المخلفات المائية
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تلوث الماء الناتج عن مخلفات المياه الصناعية هو أحد الاهتمامات البيئية الرئيسة والتي صارت تعتبر تحدي عالمي. الملوثات الكيميائية العضوية هي المساهمة الرئيسة في تلوث الماء والتي يتم تسريبها بشكل مستمر إلى البيئة. يهدف هذا البحث إلى تصميم مواد وظيفية قائمة على الهياكل النانوية الكربونية تشمل الجرافين وبوليمر/جرافين، وإظهار خصائص المادة المطورة باستخدام أجهزة من أحدث التقنيات مثل الفحص المجهر الإلكتروني الماسح ومجهر الانتقال الإلكتروني والتحليل الطيفي التحويلي الفوري بالأشعة تحت الحمراء والتحليل الحراري والأشعة السينية الحيادية. تم تقييم المادة لإثبات كفاءتها في امتصاص وفصل الملوثات العضوية السامة من الماء. هذا العمل يتضمن أيضا تحسين موازنة ظروف المعالجة كالتركيز الابتدائي للملوث وفترة الاتصال ودرجة الحرارة والحمضية والقاعدية (الرقم الهيدروجيني) ووجود المعادن. تم تطبيق بعض النماذج لدراسة التوازن الحراري والحركي والديناميكا الحرارية. يأتي بعد ذلك دراسة المادة في الوضع الديناميكي (المتحرك) باستخدام مخلفات مائية حقيقية مخلوطة مع ملوثات لتقصي التأثيرات الناتجة عن تغيير معدل التدفق ولتطبيق نموذج ديناميكي. المادة التي تسمى بولي إيثيلين المعدلة من الجرافين أظهرت أعلى كفاءة في امتزاز الميثيلين الأزرق وتم اختيارها لإجراء التجارب المغلقة (الدفعاتية) والديناميكية (التدفقية)، فضلا عن إظهار الخصائص (التوصيف). أظهرت النتائج أن هذه المادة تمتلك قدرة عالية في الامتزاز مع أقصى سعة امتزازه مقدارها 161.29 mg/g. يمكنها إزالة الميثيلين الأزرق والمعادن تزامنا في وقت واحد وتعمل بشكل جيد عند نطاق واسع من درجة الحرارة والحمضية والقاعدية (الرقم الهيدروجيني). هذه المادة لديها استقرار هيكلي ممتاز حتى بعد استخدامها في عملية الامتزاز. وجدت أنها تعمل بشكل ممتاز في الوضع الديناميكي (المتحرك) الذي هو أكثر ملاءمة لعلاج كميات أكبر من المخلفات المائية.

CHAPTER 1

INTRODUCTION

Currently, stricter regulations for water quality are being considered and implemented. Consequently, it is expected that water treatment plants worldwide will need to improve their treatment approaches to achieve the new standards. Consequently, there is a need to improve the efficacy of technologies toward water treatment [1-3]. Even at low levels, pollutants, inorganic or organic, are toxic to the environment and to humans [4]. Heavy metals and dyes are two classes of pollutants in wastewater that are causing poisoning in humans [5-8]. Sources of heavy metals and dyes include paints and petrochemical activities [9-11].

The World Health Organization (WHO) is making efforts to reduce the maximum contaminant level of heavy metals in drinking water by setting higher standards [3]. Likewise, according to the Drinking Water Standards and Health Advisories 2012 Edition from the US Environmental Protection Agency, the maximum allowable contaminant levels in drinking water are 0.006 mg/L (ppm) antimony, 2 ppm barium, 0.005 ppm cadmium, 0.1 ppm chromium (total), 1.3 ppm copper, 0.05 ppm selenium, 0 ppm arsenic and 0 ppm lead [11-12]. Organic pollutants like dyes are recommended to be completely removed from the water since they are toxic and may cause harmful side-products.

Major problems encountered in water treatment plants are the persistence of pollutants, resistance to microbial degradation, and temperature [13]. Due to the importance of the

subject, several conventional methods are used to deal with the dye's contaminants from the water. These methods are consisting of various physical and chemical processes to get rid of the dye pollutants from the water. The conventional methods include biodegradation, filtration, and floatation [14–16]. In some cases, chemical dispersants are used to deal with the removal of organic pollutants from water [17]. The marine environment contained a wide range of micro-organisms that helps in degrading organic pollutants contaminants [18]. The chemical dispersants suppress the activity of the organic pollutants' microorganisms [19]. The major issues associated with them are their high operating cost, complexity, and low separation efficiency that demands new separation methods for organic pollutants removal.

Unfortunately, effluents are often discharged from industrial sources containing high levels of pollutants. To remediate contaminated wastewater, various technologies have been developed including adsorption, coagulation, precipitations, reverse osmosis, solvent extraction, ion exchange, membrane separation, and flotation [20]. Recently, the applications of magnetic particles and other nanoparticles were reported by Farid et al in a similar fashion for the removal of pollutants from water [21]. The fundamental requirements for water purification are using appropriate materials that possessed high separation capacity, cheap, excellent porosity, and recovery [21]. Graphene is one of the materials that have a high surface area and strong mechanical stability [12-15].

Of the various water treatment technologies currently available, adsorption and membrane processes are considered the most efficient water remediation technologies [18-21]. For instance, the adsorption process has advantages over the other methods because of its simple design and can involve low investment in terms of both initial cost and space

required. The adsorption process is widely used for the treatment of industrial wastewater from organic and inorganic pollutants and meets the great attention of researchers. Polymeric materials are the most promising materials to be used as adsorbents in the treatment of wastewater [19, 20].

1.1 Statement of Problem

Pollution is becoming a worldwide major problem. Due to the increase in industries, industrial wastewater is in increase significantly. This puts a lot of pressure on the environment and water resources. The environment is being more polluted, and consumed water is increasing. Therefore, different solutions and efforts have to be introduced to reduce pollution and to remove pollutants from wastewater.

1.2 Significance of the Study

Treatment of wastewater and industrial wastewater can save the environment and enable the reuse of water for other applications. This will be important for industries to recycle the used water in different industrial units.

1.3 Research Objectives

The main objectives of this research are:

1. To evaluate different prepared graphene-based materials as adsorbents for the removal of dye pollutants.
2. To optimize the adsorption parameters for the best adsorbent.

3. To investigate the adsorption data using different related models.
4. To study the efficiency of the adsorbent in a dynamic mode.

CHAPTER 2

LITERATURE REVIEW

2.1 Adsorbent Materials

Adsorption is a physical process in which dissolved molecules or small particles in water (the adsorbate) are attracted and become attached to the surface of something larger (the adsorbent). Energy differences and electrical attractive forces, known as van der Waals forces, cause molecules of the adsorbate to physically fasten and stick onto the adsorbent. Due to its low cost and ease of implementation, adsorption is one of the key methods in the removal of pollutants from wastewater. Many adsorbent materials have been developed such as carbon active, residues of agro-industrial, sand, titanium oxide, chitosan, mesoporous materials, and its modifier [7][8]. These can be used to remove contaminants from wastewater [9]. Removal of ionic dyes and heavy metal ions simultaneously was applied using modified carbon active, groundnut shells and sawdust, fly ash, carbon fibers, carbon nanotubes [10].

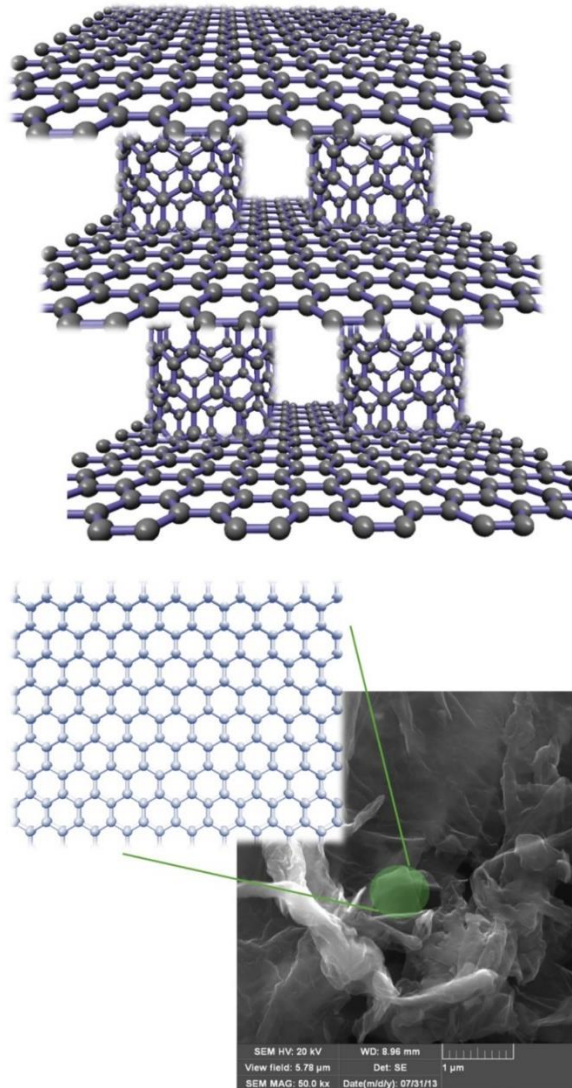


Figure 1 Typical scanning electron microscopy (SEM) image of graphene nanosheet and its structure as an example of 2-D nanostructured materials

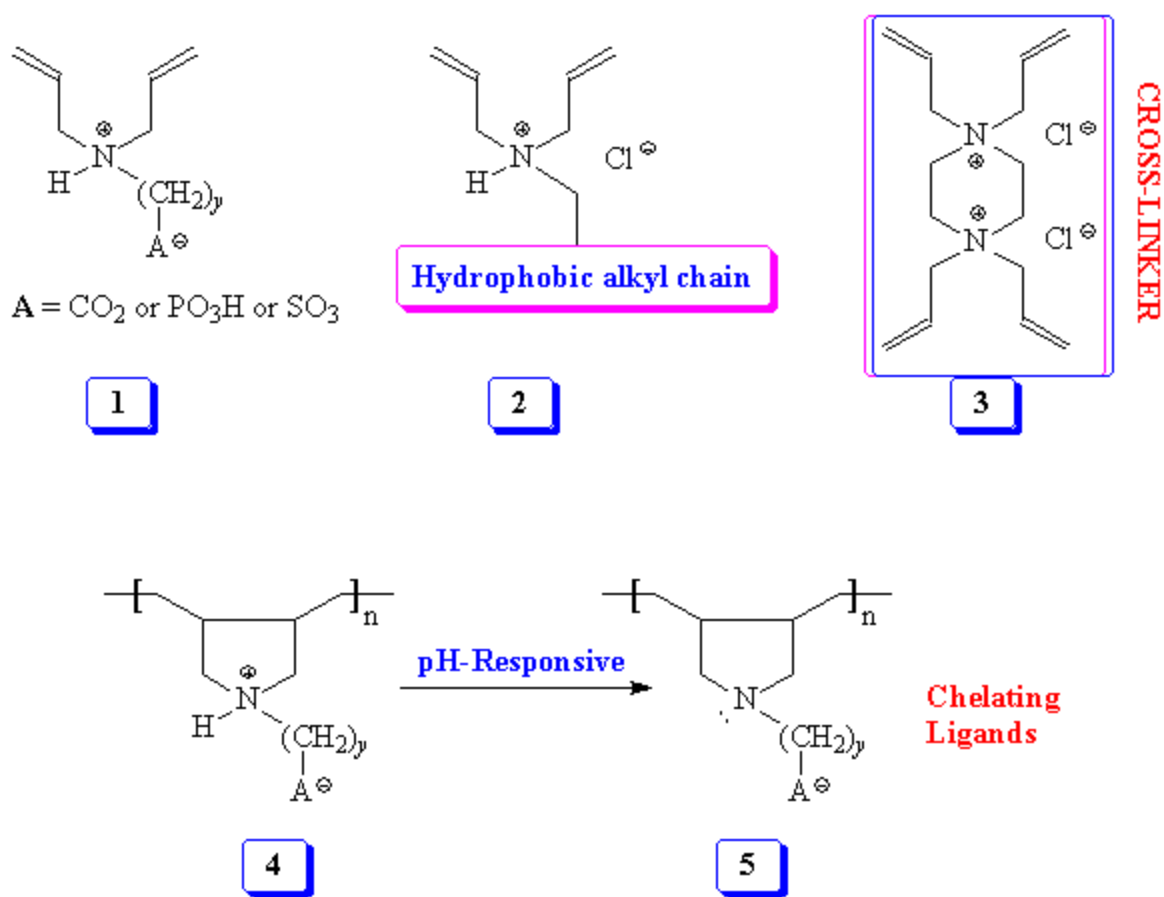


Figure 2 Butler's cyclopolymerization protocol to synthesize chelating adsorbents.

Carbon nanostructures such as graphene, Figure 1, and polymers, Figure 2, are other classes of materials that can be used in the removal of pollutants from water. Carbonaceous porous materials are used as adsorbents due to their molecular sieving and micropore effects [11]. Graphene, as porous carbon has a high surface area, is chemically stable and can establish good π - π interaction with aromatic groups in many ionic dye pollutants [12]. Utilization of graphene as directly as adsorbent for dyes is difficult because of the hydrophobic nature of graphene itself. The oxidation process of graphene-to-graphene oxide facilitates the incorporation of hydrophilic groups, negatively charged structural motifs, which in turn help to form a stable suspension and spread in solution. Because of this, graphene oxide is

thus very useful for the removal of heavy metal ions and ionic dyes from waste [13][14]. Magnetic graphene oxide, modified graphene, was successfully synthesized by Deng et al. and applied as an adsorbent for binary system Cd(II)-orange G and Cd(II)-methylene blue [15]. Sponge-like polysiloxane-graphene oxide with gel form has been synthesized via a sol-gel method and has demonstrated excellent performance for adsorbing cadmium [16]. A chitosan-based magnetic composite nanoparticle-containing silica, glutamine, and iron oxide have been synthesized and found to be eco-friendly, biodegradable, and efficient in uptake of acid green 25 and mercury(II) ion simultaneously [17]. Magnetic resorcinol-formaldehyde with carbon nanotubes adsorbent has also been shown to uptake methylene blue pollutants in wastewater [17, 18]. Several other pHs and temperature-responsive magnetic composites have also been developed as adsorbents [19].

An effective adsorbent in water treatment must have a high adsorption capacity and reach equilibrium quickly. Chelating ionic polymers are considered excellent adsorbents by virtue of having multiple ionic adsorption sites to sequester metal pollutants in wastewater. Hydrophobically modified crosslinked ionic resins have amphiphilic properties, which enable them to trap non-polar organic pollutants [20].

2.1.1 Cross-linked and Hybrid Materials

A cross-linked tetrapolymeric anionic polyelectrolyte has been found to remove chromium(III) ions from effluent water [20]. Hybrid materials are interesting because of their unique properties and promising characteristics for use as adsorbents. An efficient adsorbent comprised of an organic-inorganic hybrid compound between silica gel and organic acid was reported to adsorb Au(III) ions [21]. Zwitterionic cross-linked hybrid polymer can uptake pollutants due to electrostatic effects. Polymer modification via

cyclopolymerization protocol with nitrogen and carboxylate as a chelating agent has led to adsorbent having excellent adsorption capability to remove heavy metal ions, such as Pb(II) ions [22].

2.1.2 Zeolites

Zeolites are crystalline aluminosilicates that can occur naturally or can be produced industrially on a large scale. They are among the best adsorbents for the removal of heavy metal ions. Zeolites are composed of hydrated aluminosilicate minerals made from the interlinked tetrahedral of alumina (AlO_4) and silica (SiO_4) moieties [23]. Zeolites have good ion exchange properties, a high surface area, and a hydrophilic character, which make them suitable for extracting heavy metals from wastewater effluents. Clinoptilolite, the most abundant natural zeolite, and has been effective in removing heavy metals [24] [25] [26]. In sodium form, the selectivity sequence of clinoptilolite for various heavy metal ions was determined to be follows: $\text{Pb}^{2+} > \text{Cd}^{2+} > \text{Cu}^{2+} > \text{Co}^{2+} > \text{Cr}^{6+} > \text{Zn}^{2+} > \text{Ni}^{2+} > \text{Hg}^{2+}$ [27]. Modified zeolites typically have higher adsorption capacities compared to natural ones. A number of methods for zeolite modification have been developed to enhance the adsorption properties of zeolites. For instance, nanosized zeolites have more accessible pores which are more effective for heavy metal removal. Among nanosized zeolite adsorbents, NaX zeolite [28] has been widely used to remove heavy metals, especially Cd^{2+} , from wastewater [29] [30] [31] [32]. Rad et al. (2014) synthesized NaX nanozeolite using a microwave heating method proceeded at 90 °C [32]. Then, polyvinyl acetate polymer/NaX nanocomposite nanofibers were prepared using an electrospinning method under a voltage of 20 kV and feeding rate of 0.5 mL/h [32]. The potential of these composite nanofibers was studied regarding Cd^{2+} . The reported maximum adsorption capacity was found to be

838.7 mg/g with 80-% removal at the optimum pH 5.0. Choi et al. (2016) modified zeolite by replacing Si^{4+} and Al^{3+} sites in the lattice with exchangeable cations such as Na^+ , Mg^{2+} , K^+ , or Ca^{2+} , leading to a net negative charge [23]. Mg-modified zeolite demonstrated some advantages (non-toxicity, low cost, abundance, and availability) with larger pore sizes compared to the non-modified adsorbent. This modified adsorbent showed Ca^+ removal exceeding 98% at the optimum pH 7.0. Furthermore, its adsorption capacity was found to be 1.5 times higher than that of the K- and Na-modified zeolites, and up to 2.0 times higher than that of the natural zeolite. [33]

2.1.3 Clays

There are three main groups of clays: kaolinite, smectites (bentonites), and mica. Among them, bentonites (in particular, montmorillonite) possess the greatest cation exchange capacity, it is highly selective and regenerable, and it was found to be 20 times cheaper as compared to activated carbons [34] [35]. The heavy metal removal capacity of clay minerals is lower than zeolites. However, they are used for removing different heavy metal species from wastewater due to a number of advantages over other adsorbents such as high surface area, excellent physical (plasticity, bonding strength, shrinkage), chemical (large zeta potential, cation exchange property, monobasic) and structural/surface (load-bearing strength, resistance to wear, resistance to chemical attack) properties [36] [37] [38]. [33]

2.1.4 Biological Adsorbents

The use of biological adsorbents receiving renewed attention as a cost-effective and environmentally friendly approach for the removal of heavy metal contaminants from aqueous media. The major advantages of using biological adsorbents are their high efficacy and inexpensive cost. This process is particularly suitable for treating dilute wastewater.

Typical biological adsorbents may be derived from three sources: 1) non-living biomass such as bark, lignin, shrimp, krill, squid, crab shell, etc.; 2) algal biomass; and 3) microbial biomass such as bacteria, fungi, and yeast [39]. [33]

2.1.5 Fullerenes

Fullerenes were discovered in 1985 through spectrometric measurements on interstellar dust [39]. They represent closed-cage carbon molecules containing pentagonal and hexagonal rings. Their formula is C_{20+m} , where m is an integer number. Fullerenes comprise a wide range of isomers and homologous series - from the most studied C_{60} and C_{70} to the so-called higher fullerenes like C_{240} , C_{540} and C_{720} . The relatively high electron affinity, hydrophobic surface and high surface/volume ratio of these materials allow for employing them for extraction of different species from aqueous media [41] [42]. [33]

2.1.6 Advanced Oxidation Processes

Advanced oxidation processes (AOPs) are among the most effective methods for the removal of organic contaminants. These methods are based on the production of highly oxidizing free radicals such as hydroxyl radicals, capable of mineralizing various toxic organic compounds [43]. AOPs are operationally easy, low cost, and efficient while being able to stabilize organic compounds through converting them into water and carbon dioxide [44], [45], [46], [47] often using ozone [48]. AOPs are suitable for treating contaminants that are resistant to biological decomposition [49], [50]. Catalytic ozonation processes (COPs) are AOPs in which solid catalysts play a role in the overall ozonation process, facilitating the decomposition of ozone into free radicals. In fact, the use of catalysts may eliminate the most important limitations of simple ozonation, including the low solubility and stability of ozone in water, and its slow reaction with organic compounds [51], [52].

The high efficiency, as well as low operating costs influenced by the short duration of COPs [53], [54] also facilitates the implementation of these technologies, particularly, in developing countries. [55]

2.1.7 Titanium Dioxide

Titanium dioxide (TiO_2) has been used as a valuable photocatalyst because of its amusing properties such as non-toxicity, low cost, strong oxidizing power, biological and chemical inertness. The use of heterogeneous TiO_2 is categorized as one of the AOPs in swage purification [56], [57]. The presence of dissolved oxygen in the solution in the role of an electron acceptor in photocatalytic reactions is necessary to ensure the presence of electronic scavengers to trap the excited electrons of the conducting band and restrict the recombination of electrons and cavities [58], [59].

Research has indicated that TiO_2 photocatalysis has various advantages over other degradation methods. The only reagents needed for the oxidation process are light (solar) and oxygen; this method is practical in destruction a variety of organic contaminants in different concentrations of various wastewater. The oxidation process mostly leads to the complete mineralization of organic pollutants to CO_2 , H_2O and others [60]. The main problem in the use of titanium dioxide at photocatalytic processes has required the utilization of costly and unhealthy ultraviolet light sources, due to the wide bandgap of TiO_2 . This leads to restrictions in the use of titanium dioxide photocatalyst under visible and sunlight [61]. However, when TiO_2 is used in pure form, due to the large bandgap and high-rate recombination of the photogenerated electron-hole pairs, its photocatalytic activity is reduced under light [62], [59].

2.1.8 Magnesium Oxide

Metal oxides, such as magnesium oxide (MgO) nanoparticles, have a high potential to be used in wastewater treatments, due to their possible large surface areas and the low cost of recovery and production. MgO also provides advantages of having antibacterial properties and high adsorption and/or photocatalysis performance for toxic compounds [63], [64], [65]. Various studies have been conducted on using MgO in COPs for the removal of toluene [66], textile dyes [67] and humic acid [68]. Moosavi et al. [69] studied the effect of MgO-enhanced COP on the removal of Reactive Red 198 (a textile dye), indicating that the removal efficiency improves with the increase of the pH value, due to the increased rate of ozone decomposition into free radicals at higher pH values. The decomposition of the dye molecules was attributed to an indirect oxidation process brought about by the active radicals. [55]

2.1.9 Carbon and Boron Materials

Nowadays, carbon and boron materials are being intensively studied in the field of catalyses such as carbon nitride (C_3N_4) and boron nitride for photodegradation of organic pollutants [70], [71], [72]. In comparison to inorganic semiconductor catalysts, these are more extensively stable and environment-friendly in nature. Few of metal-free photocatalyst such as graphitic carbon nitride (g- C_3N_4) [73], [74], poly (p-phenylene) [75], $C_3N_3S_3$ [76], α -sulfur [77] and red phosphorus are also studied [78]. To get sufficient efficacy, these materials must be loaded with noble metal co-catalysts which is the drawback of these materials [79]. [80]

B_4C with a relative band gap of 1.5–2.6 eV [81], [82] and a strong visible light response has attracted lots of attention in the photo-degradation of organic pollutants [83]. Boron

carbide (B_4C), a p-type semiconductor makes it one of only a handful of known stable and efficient photocatalyst materials under visible light irradiation that does not require any noble metal co-catalyst. B_4C is a modern non-metallic (non-oxide) ceramic material that has been extensively investigated for its salient features [84]. Boron carbide possesses high hardness (due to characteristic B–B and B–C bonding), high melting point ($\approx 2300^\circ C$) [85], Young's modulus (ranges from 360–460 GPa), strength, excellent chemical stability [86] and thermal conductivity [87] as well as a high cross-section for neutron absorption [88]. The appealing electronic structure, chemical, and physical stability, and low cost make this material more fascinating in order to utilize these nanomaterials for various applications. The utilization of nanomaterials will be constrained by their inherent toxicity, though the rapid development of nanomaterials will definitely continue due to their fascinating properties [89], [90]. The prospective harmful influence of nanomaterials must be appropriately estimated prior to their use. [80]

2.1.10 Carbon-based Nanomaterials

Carbon-based nanomaterials have been broadly used in the field of heavy metal ions removal due to their large sorption tendencies and non-toxic nature [91], [92], [93]. For many years, activated carbon has shown excellent sorption efficiencies in the purification applications of water and air. For instance, Zhou et al. have reported the adsorption capacity of carbon black and nano size hydroxyapatite for Pd^{2+} , Cu^{2+} , Cd^{2+} , and Zn^{2+} [94]. Although in tap water the efficacy was limited for heavy metals at trace levels (ppb). Therefore, other materials such as carbon nanotubes (CNTs), graphene, and fullerene were used for this purpose. For high adsorption capacities of metal ions, CNTs are subjected to functionalization from a practical application point of view [95], [96]. Functionalization of

CNTs with certain groups onto their surfaces containing N, O, and P increases surface area and dispersibility [97]. Carbon nanospheres functionalized with layered double hydroxide nanocrystals onto the surface of carbon nanospheres were reported [100-98] for the removal of Cu^{2+} from an aqueous medium. [99]

The increasing use of tailored nanostructured cues may exert a favorable human health benefit given drinking water quality. Several researchers have emphasized their possible harmful effects or impacts on the entire living ecosystem [100], [101], [102]. It is speculated that the generation of waste during their synthesis and application will eventually appear in various settings, and might expose to humans through or ingestion, inhalation, dermal contact, and absorption. A range of several different assumptions has also been documented regarding the physicochemical properties of nanomaterials associated with detrimental health effects. Some of the characteristics are high reactivity and surface area, size, shape, and organization of the nanoparticle, surface modifications, and degree of aggregation or agglomeration and chemical composition [100], [103], [104]. Indeed, the persistence of the manipulated nano-constructs in the body largely influences the durable consequences of these nanomaterials, and hence theaters a profound role in triggering the disease [105]. [99]

2.2 Wastewater Treatment Stages

The conventional sewage treatment flow in wastewater treatment plants (WWTPs) is shown in Figure 3. Generally, WWTPs contain two types of processes. Physical treatment processes comprise the preliminary and primary treatment such as bar screening and sedimentation basins to remove most of the suspended solids. As the secondary treatment,

biological treatment processes, such as the activated sludge process, biological filter process and rotating biological contactor process, are the principal technologies in WWTPs that aim to degrade the complex organic compounds into non-toxic substances via microbial metabolism. Some WWTPs include tertiary treatment, for example, disinfection, sand filtration, constructed wetland, and soil aquifer treatment for deeper water purification. [106]

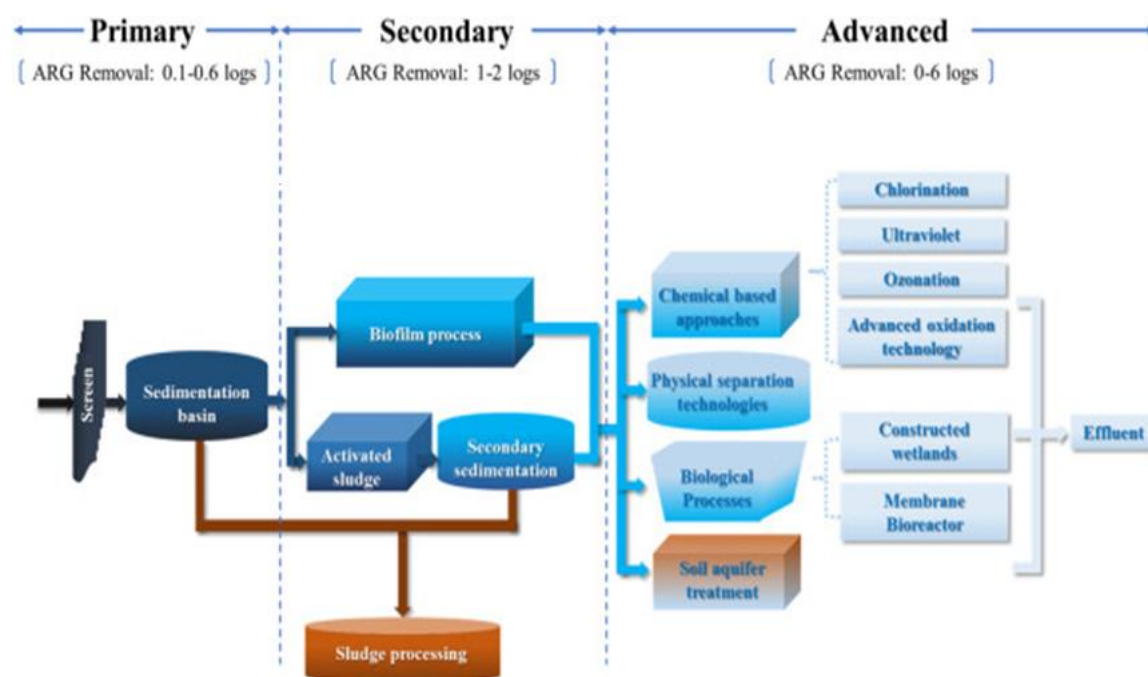


Figure 3 Flow of the traditional wastewater treatment crafts [106].

2.3 Adsorption Mechanisms

The adsorption process is a surface phenomenon in which adsorbates transfer onto adsorbents. Over the past decades, adsorption technology has been widely applied for water and wastewater treatment because it is low-cost, efficient, simple, and environmentally

friendly. The adsorption mechanisms mainly include chemical adsorption corresponding to the formation of chemical bonds, physical adsorption related to the van der Waals force, and ion exchange (Figure 4). The knowledge of adsorption mechanisms is of great importance to design the adsorbents and the adsorption systems. The adsorption mechanisms have been investigated by the modeling of the adsorption equilibrium data, the characterization of adsorbent before and after adsorption, the molecular dynamics study, and the density functional theory calculation [107] [108] [109]. Among these methods, modeling adsorption data by isotherm models are the most convenient and widely used one. In addition, the adsorption isotherm models can provide information on the maximum adsorption capacity, which is significant in the evaluation of the performance of the adsorbents. [110]

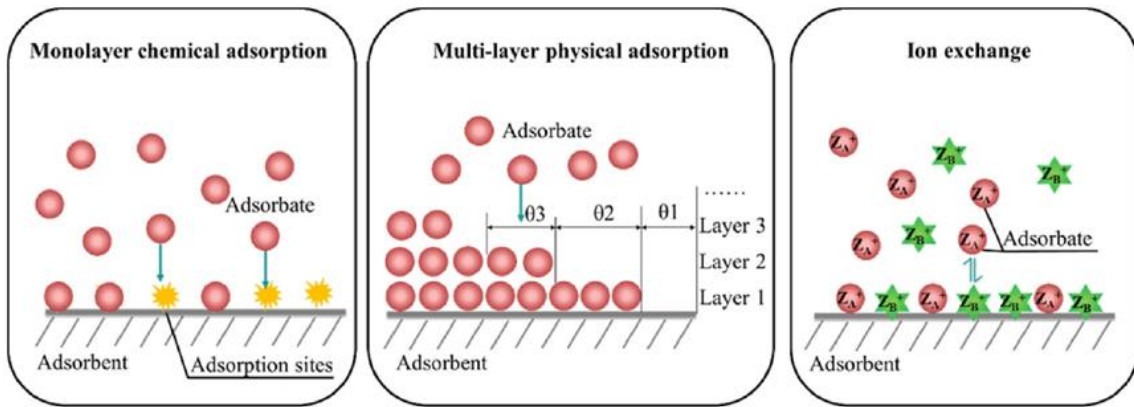


Figure 4 The possible adsorption mechanisms [110].

2.4 Drinking-Water Treatment Study

Five drinking water treatment plants (DWTP A–E) along the Nakdong River (South Korea) that receive river water and another DWTP F, in the same province, that receives reservoir

water were selected to investigate organophosphate ester (OPE) occurrence from DWTPs with different drinking water sources. The location and treatment processes used in each DWTP are shown in Figure 5. Despite of using river water as a drinking water source, there are many point sources like WWTPs and industrial complexes etc. along the Nakdong River basin, resulting from the chemical contamination problems in the drinking water of this area. Especially, there are two large national industrial complexes near the DWTP C and D (Figure 4). DWTP A was a conventional DWTP using chlorination, coagulation, sedimentation, and filtration processes. DWTP B–F used conventional processes and also advanced processes such as granular activated carbon (GAC) filters and ozonation processes. [111]

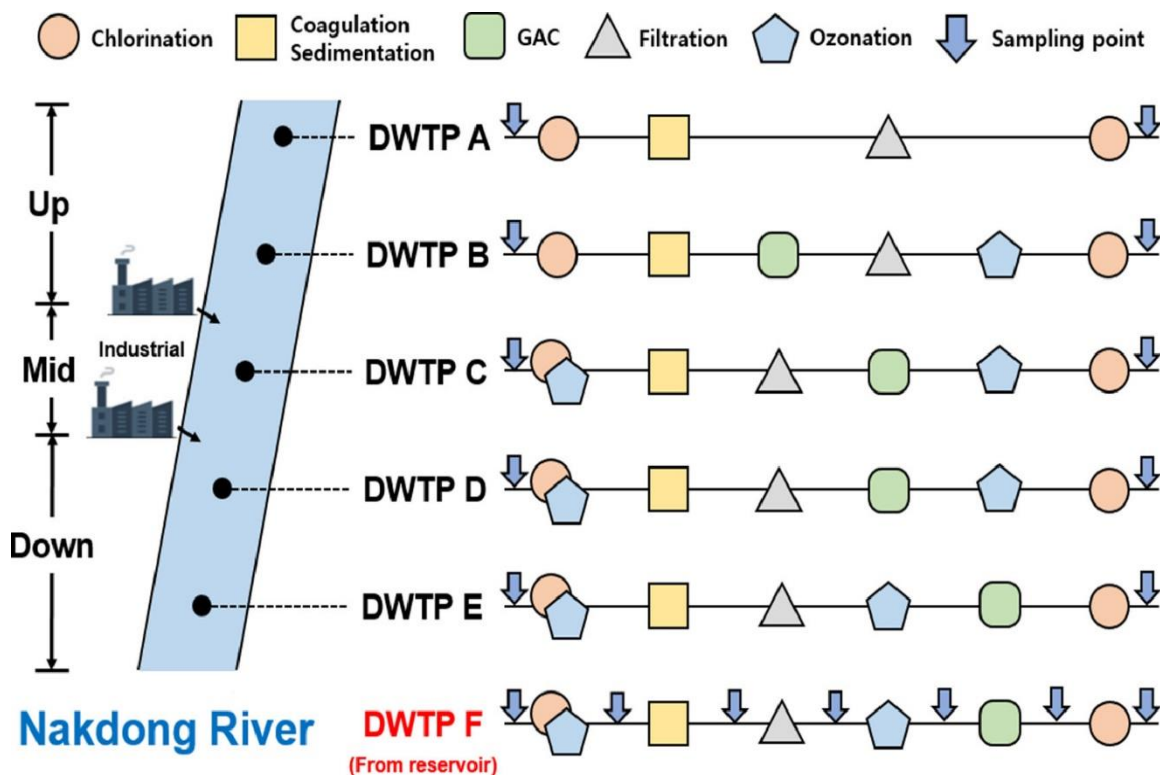


Figure 5 Purification processes used in the drinking water treatment plants (DWTPs) in the Nakdong River basin [111].

CHAPTER 3

EXPERIMENTS AND METHODOLOGY

3.1 Evaluation of modified graphene adsorbents using methylene blue as a model pollutant

0.500 g of methylene blue was taken and added to 1 L water to create a concentration of 500 ppm. 1 mL of this solution was added to 900 mL water to be diluted to 50 ppm. Graphene oxides (GO) can be prepared by many methods. Figure 6 illustrates how the different GO structures can be synthesized by Hummer's methods and this is the way how the materials were prepared in this work. Five different modifications of graphene (Oxalic acid (OAG), polyethylenimine (PG), ethylenediamine (EG), diethylenetriamine (DG), and hydroxylamine modified graphene (HG)) were tested to evaluate their ability to adsorb methylene blue. These adsorbents have different types of functional groups (Figure 7). The experiment was performed by adding 0.05 g from each one to a separate 20 mL of the diluted solution (50 ppm) and agitated 500 rpm by magnetic stirring. Two samples were taken from each one at 5 min and 60 min and the amount of blue color was compared. This experiment was done to choose one graphene modification that gives the highest purity (lightest blue color). Polyethylenimine modified graphene (PG) was chosen to be characterized and used throughout the next parts to experiment with some parameters including the ones in Table 1 and its chemical structure is shown in Figure 8.

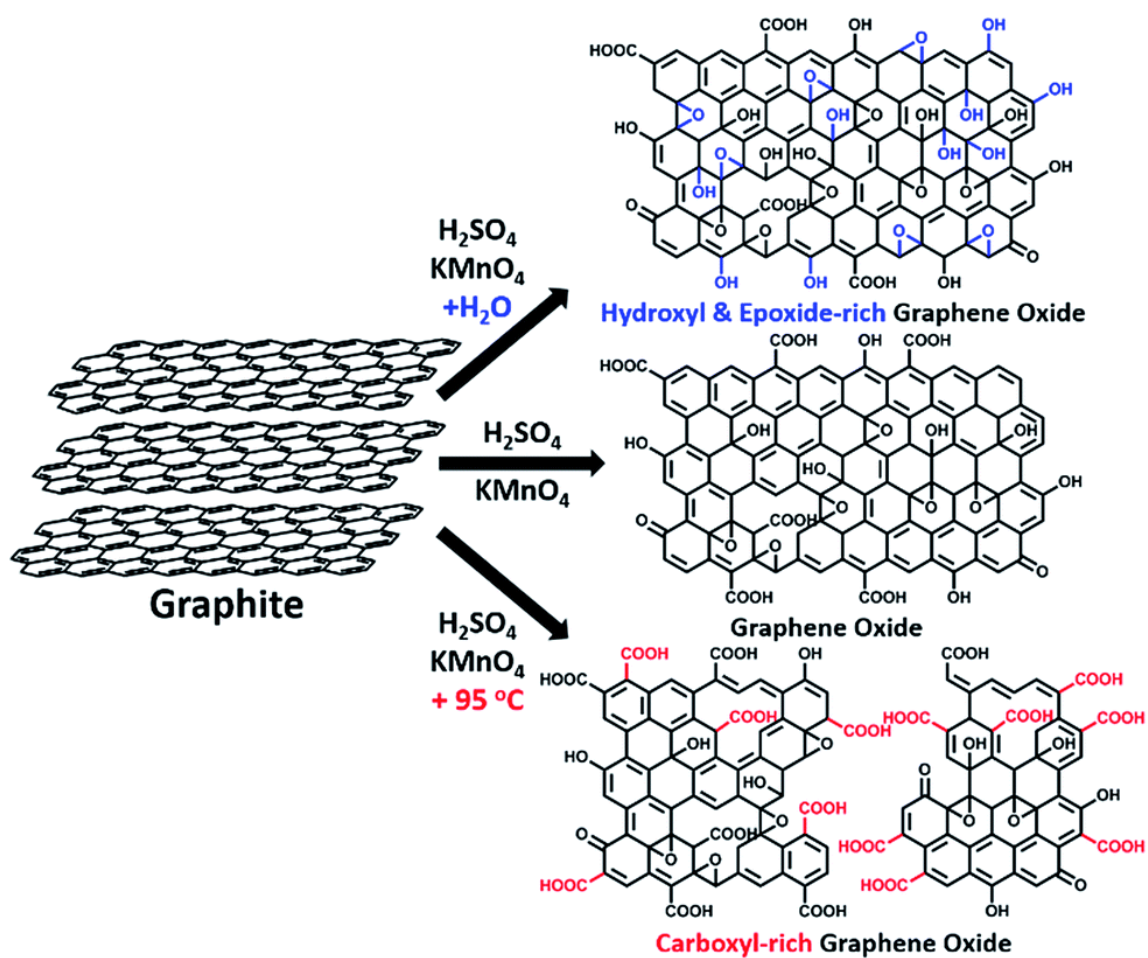


Figure 6 Hummer's methods for synthesizing graphene oxides (GO) from graphite.

- OC(=O)C(=O)O

- [illegible]

- NCCN

- NCCNC

- $$\text{HO}-\text{NH}_2$$

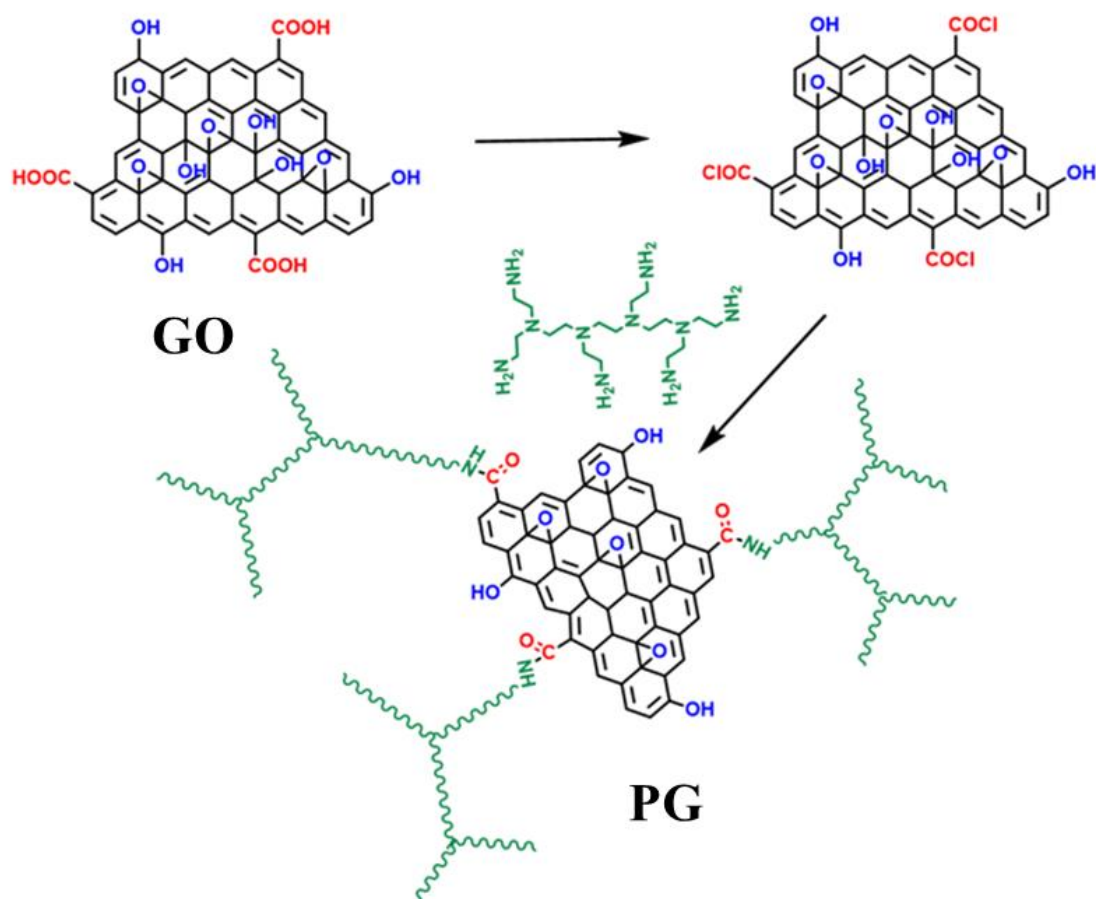


Figure 8 Chemical structures of graphene oxides (GO) and polyethylenimine modified graphene (PG).

3.2 Characterization

Several devices were used for the characterization of the prepared materials. This includes thermogravimetric analysis (TGA), Fourier transform infrared (FTIR) spectroscopy, and x-ray diffraction (XRD) instruments. TGA was carried out for 7.292 mg of PG using an instrument having the pan of alumina and nitrogen gas at 50 mL/min where the temperature was ramped at 5 °C/min to reach 700 °C in 135 min. FTIR was operated for PG before and after use in the adsorption process at wavenumbers from 500 to 4000 cm⁻¹ and data spacing

of 3.857 cm^{-1} with the number of scans of 46 and resolution of 32. XRD was also carried out for PG before and after use in the adsorption process where 2θ is from 5 to 80.7° with an increment of 0.1 and a total time of 798 s.

3.3 Investigation of Initial Concentrations

The 500-ppm methylene blue solution was diluted to 50, 75, 100, and 200 ppm and they were used as initial concentrations. 40 mL of each initial concentration was mixed with a separate 20 mg of PG at 500 rpm magnetic stirring for 60 minutes. Samples were taken and filtered after 2 minutes and every 5 minutes for further analysis.

3.4 Investigation of Temperature

This is similar to the previous experiment, but in this experiment, the initial concentration was fixed at 100 ppm. The 40 mL methylene blue solutions were heated up to 40 and 60°C . Both solutions were mixed with 20 mg of PG separately and a stopwatch was started. Samples were taken and filtered like in the previous experiment. The previous experiment was performed at 20°C that would be considered in the temperature-related calculations.

3.5 Investigation of pH

In this part, the PG was used to adsorb methylene blue at four different initial pH conditions (pH 2, pH 4, pH 7 and pH 10). The prepared concentrated methylene blue solution (500 ppm) was diluted five times in order to get 100 ppm by four buffered solutions separately. After that, 50 mL of each solution was mixed with a separate 20 mg of PG at 500 rpm by

a magnetic stirrer for 60 minutes. Samples were taken and filtered after 2, 5, 10, 20, 30, 40, 50, and 60 minutes.

3.6 Investigation of Metals

This is the last batch experiment. A solution containing Cr, Pb, Hg, and As was used in this experiment. Real water was spiked with this solution and methylene blue solution. Two 50 mL solutions were prepared at methylene blue concentrations of 50 and 100 ppm. Cr, Pb, Hg, and As are all at equal concentrations of 1 ppm. Both were mixed with a separate 20 mg of PG at 500 rpm by a magnetic stirrer for 60 minutes. Samples were taken and filtered at different times. The solution containing methylene blue at 100 ppm was prepared again in order to be mixed with 50 mg of PG for comparison.

3.7 Investigation of Dynamic Conditions

The PG bullets were prepared manually and placed inside a column. The column length, outer diameter and inner diameter are 14, 2 and 1.2 cm respectively. A higher amount of solution was prepared for this experiment. Real water was mixed with the concentrated methylene blue solution, 80 mg of $\text{Pb}(\text{NO}_3)_2$, 246.4 mg of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 384.8 mg of $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ in order to reach 50 ppm of methylene blue and 100 ppm of Pb, Ni, and Cr. This solution was diluted two times and used throughout this experiment. A peristaltic pump was operated at different flow rates passing the solution through the column from bottom to top vertically as shown in Figure 9. The PG adsorbent was regenerated by

washing with acetone several times. Samples were collected at the outlet at different times for further analysis.

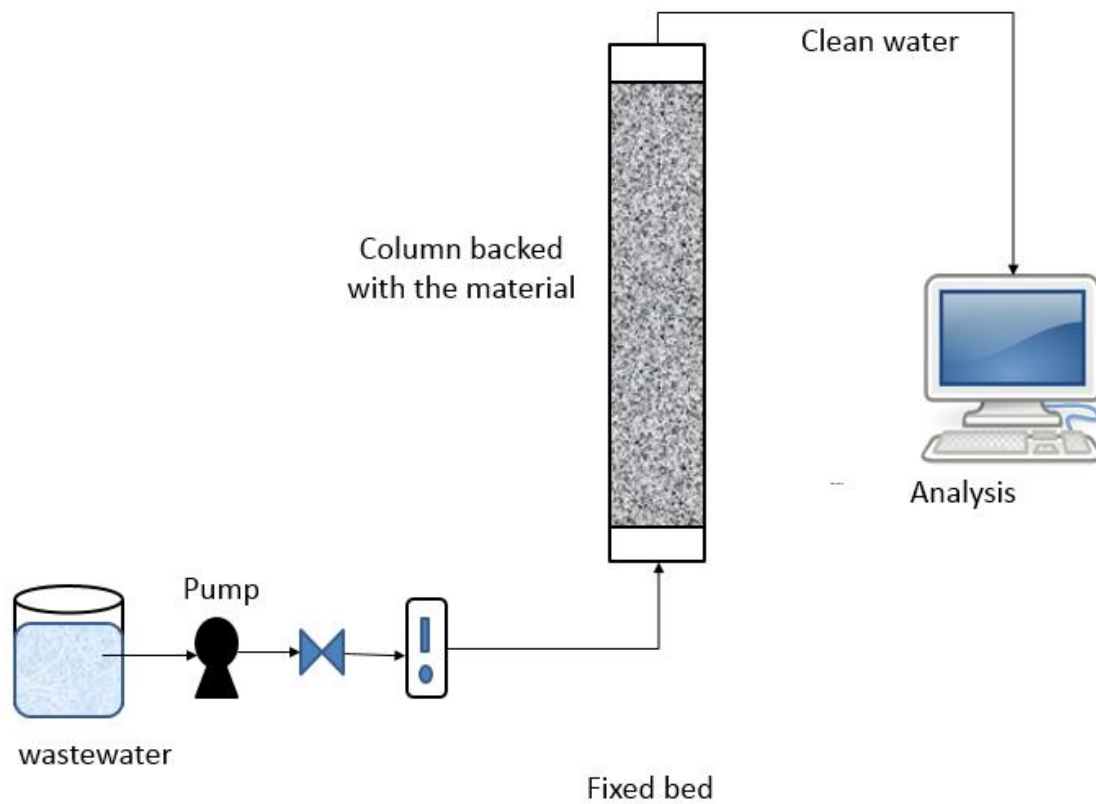


Figure 9 Fixed column system.

3.8 Concentration Analysis

The filtered samples were taken from the previous experiments in order to be analyzed by a UV-VIS instrument. The baseline was set, and water was used as the blank throughout the analysis. Cuvettes were used to hold the blank and the samples inside the instrument. This instrument was set up to find the photon wavelength at which methylene blue has the maximum absorption. This wavelength was found to be 665 nm and the absorbances at this wavelength were recorded for all samples. The Beer-Lambert law was applied to find the concentrations of these samples:

$$A = \epsilon b C \quad (1)$$

where A is the absorbance, ϵ is the molar absorptivity, b is the length of the light path and C is the concentration of methylene blue.

The amount of methylene blue dye adsorbed was determined according to the following equation:

$$q_t = \frac{(C_o - C)V}{m} \quad (2)$$

where q_t (mg/g) represents the quantity of methylene blue adsorption at time t ; m (g) is the mass of the adsorbent and V (L) is the solution volume. C_o and C (mg/L) are the concentration of methylene blue at initial and time t (min), respectively.

The % removal and the equilibrium adsorption capacity of methylene blue (q_e) were calculated based on the following:

$$\% \text{ removal} = \frac{(\mathbf{C_o} - \mathbf{C_e})\mathbf{100\%}}{\mathbf{C_o}} \quad (3)$$

$$\mathbf{q_e} = \frac{(\mathbf{C_o} - \mathbf{C_e})\mathbf{V}}{\mathbf{m}} \quad (4)$$

where C_e (mg/L) and q_e (mg/g) are the concentration of the adsorbate and adsorption amount of sample at adsorption equilibrium, respectively. [112]

CHAPTER 4

RESULTS AND CONCLUSION

4.1 Characterization

To have more information on the morphology of the prepared PG, a scanning electron microscope (SEM), a type of electron microscope that produces images of a sample by scanning the surface with a focused beam of electrons, was used. The image shows the morphology of PG as flakes structures (Figure 10). This indicates the formation of the polymeric chains on the surface of the graphene sheets.

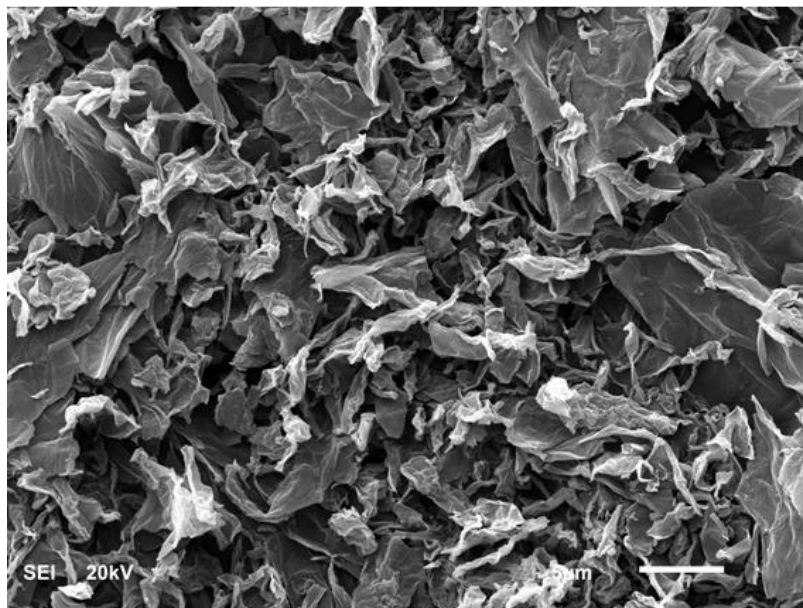


Figure 10 SEM and of PG.

In addition, and from the industrial application point of view, thermal stability up to 100 °C is a critical factor for the possible use of any adsorbent for the treatment of real industrial wastewater. TGA result for PG in Figure 11 shows that PG has excellent thermal stability up to more than 200 °C. This property is an indication of thermal stability and thus the prepared materials can possibly be used under high temperature for water treatment.

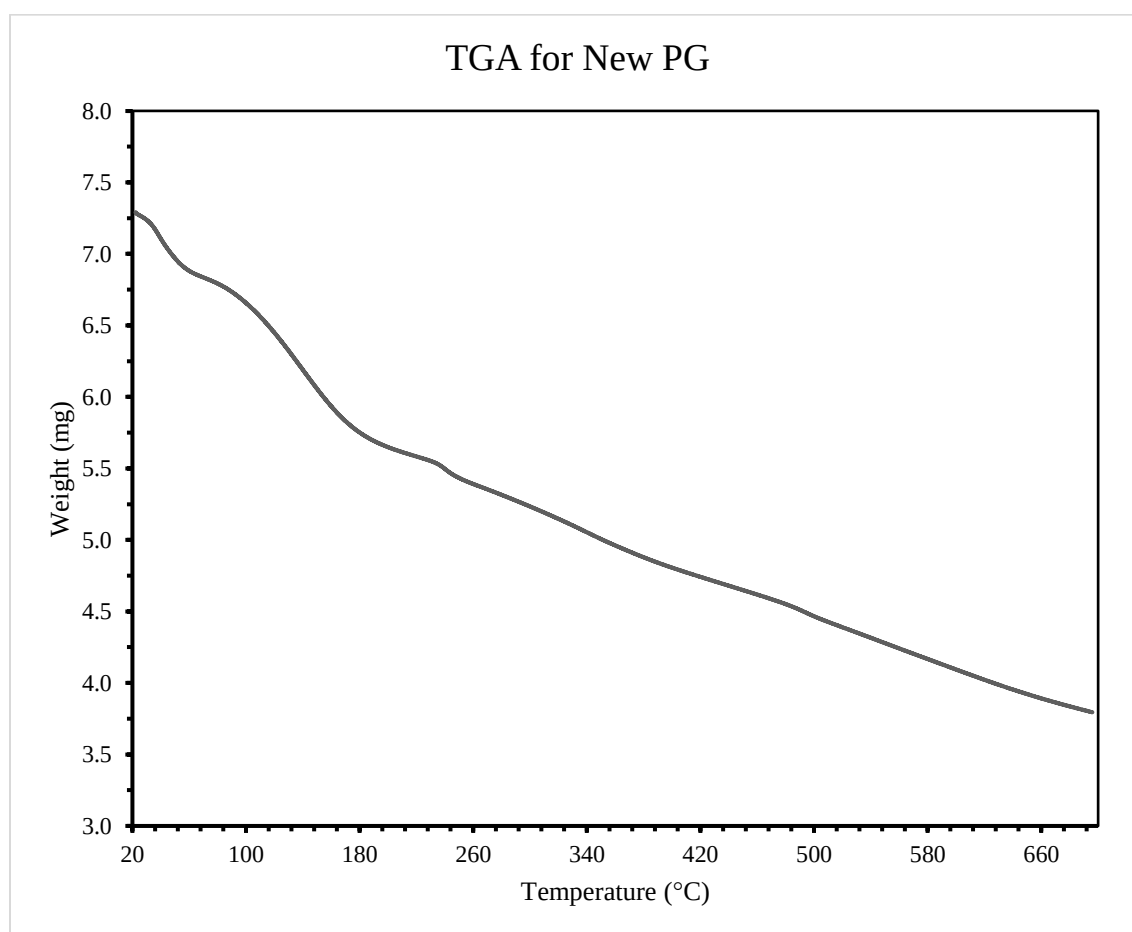


Figure 11 TGA result for new PG.

FTIR was performed for PG before and after use in methylene blue adsorption as shown in Figure 12. The band at around 3400 cm^{-1} can be ascribed to the O–H bond stretching in the hydroxyl group of GO. Bands at 2950 cm^{-1} can be attributed to the asymmetric stretching of the C–H bond in $-\text{CH}_3$. The bands at 2920 and 2860 cm^{-1} can be ascribed to asymmetric stretching and symmetric vibrations of the C–H bond in $-\text{CH}_2$. The band at 1070 can be ascribed to is the characteristic peak of epoxide groups on GO. The band at about 1720 cm^{-1} is assigned to the carbonyl C=O stretching. The bands at 1565 and 1460 cm^{-1} can be assigned to C=C backbone stretching and C–N stretching vibration present polymer. FTIR spectrum after the adsorption shows that the nature of characteristic bands does not change. However, there is some shift in some bands or changes in intensity like the band at 3400 cm^{-1} cm which can be explained by the presence of the dye on the PG surface.

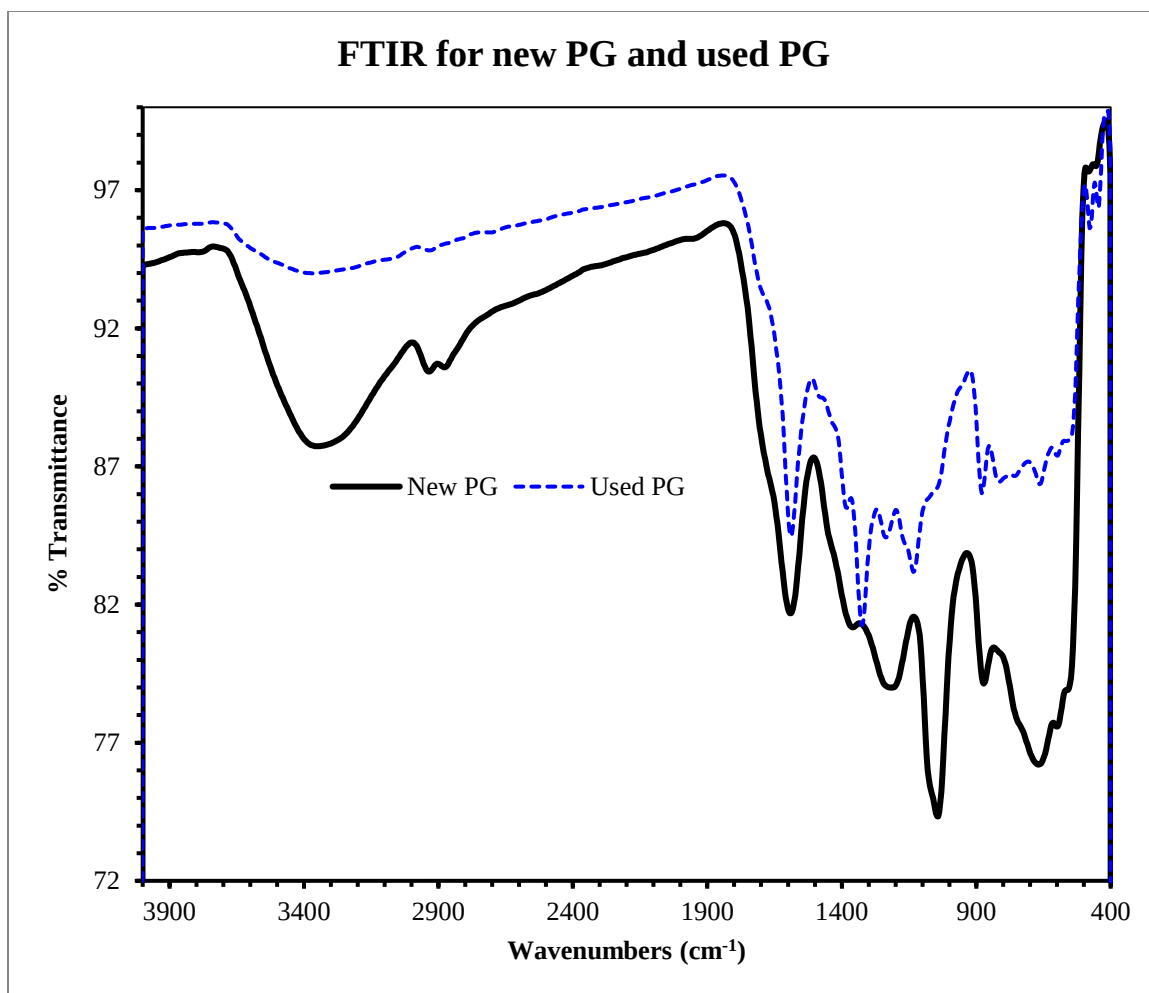


Figure 12 FTIR spectra for new PG and used PG.

X-ray diffraction (XRD) was also performed for characterization of structured PG before and after use in methylene blue adsorption as exhibited in Figure 13. It is well known that the interlayer spacing of GO sheets depends upon the degree of oxidation, which means attached functional groups as well as the number of intercalated water molecules during the growth. Variation (addition/removal) of these functional groups may change the interplanar (d-spacing values). The diffraction maxima at 2θ of about 11.2° can be observed. This peak is attributed to (001) plane of GO. A broad peak that appeared at around 25.6° can be assigned to (002) plane. The minor peak at 2θ of around 54.3° can be

assigned to (004) plane. Interestingly, it is clear from the XRD patterns of the prepared PG before and after its use for dye adsorption that PG has excellent structural stability even after use in the adsorption process.

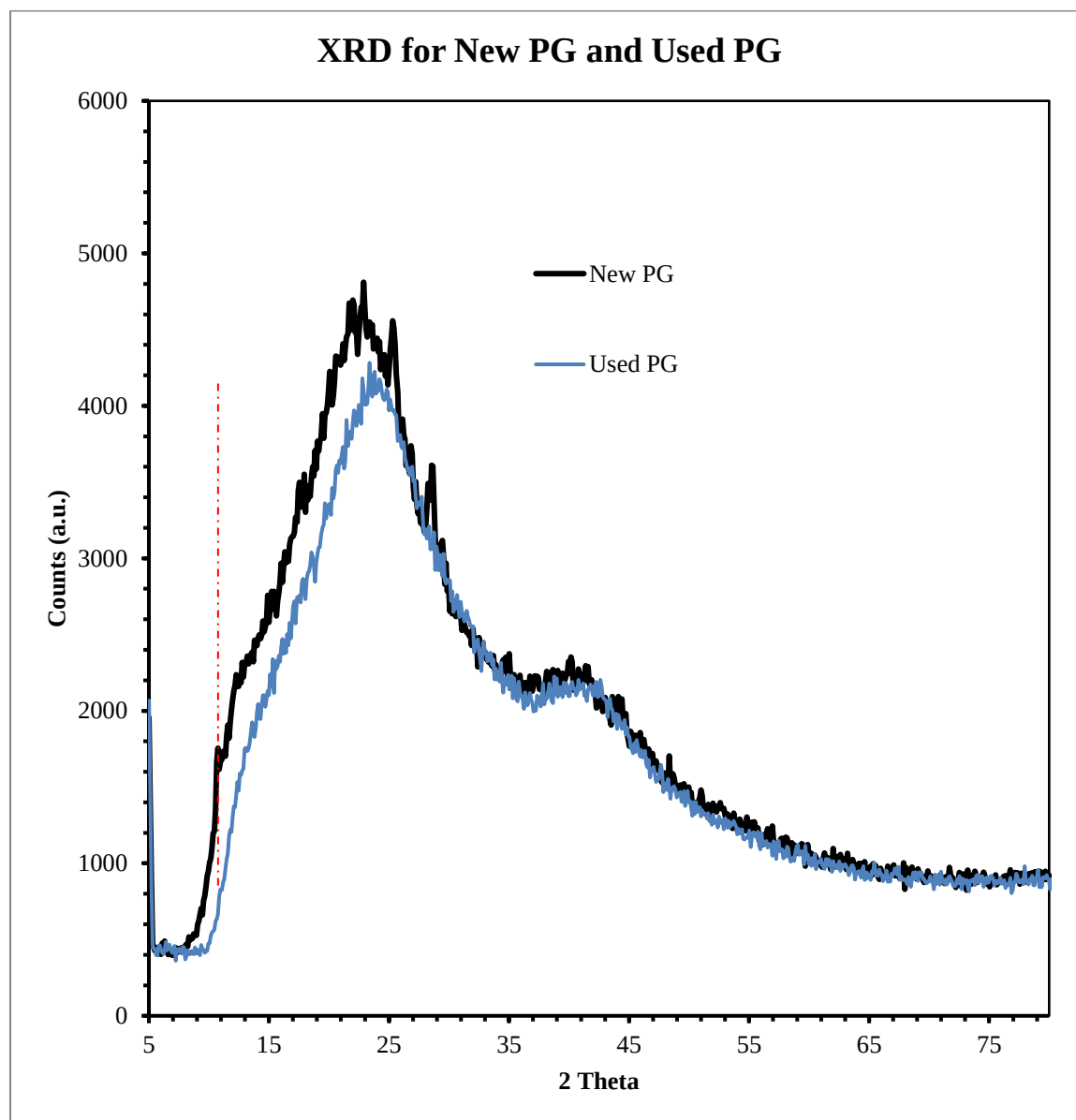


Figure 13 XRD results for new PG and used PG.

4.2 Batch Adsorption

4.2.1 Effects of Contact Time

The adsorption of PG for dye at different contact durations is essential for describing the adsorption rate and estimating the adsorption equilibrium time. As illustrated in Figure 14a, the PG can adsorb methylene blue and reach the maximum capacity relatively fast. The methylene blue can be adsorbed mostly within 30 minutes for an initial concentration of 75 ppm (Figure 14a). The effect of contact time on the adsorption capacity was further studied, as demonstrated in Figure 14b. In the first 20 minutes, the adsorption amount of PG for initial concentrations 75 and 200 ppm can reach 133.27 and 138.91 mg/g, respectively, which is a fast adsorption process at the stage. After 40 minutes, their adsorption roughly reached equilibrium. At 60 minutes, the adsorption capacities of PG for initial concentrations 75 and 200 ppm are 147.32 and 153.78 mg/g, respectively.

Compared with the adsorption capacity at 20 minutes, the adsorption capacity did not increase drastically. Overall, the adsorption process can be divided into 2 steps regarding the adsorption rate (Figure 14b): fast adsorption (first part) and slow adsorption (second part). In the first part, the methylene blue dye is adsorbed quickly because of numerous adsorption sites on the initial PG while in the second part, there is no major change in adsorption capacity caused by the steric hindrance which makes it hard for ions to occupy the remaining vacant surface sites. [112]

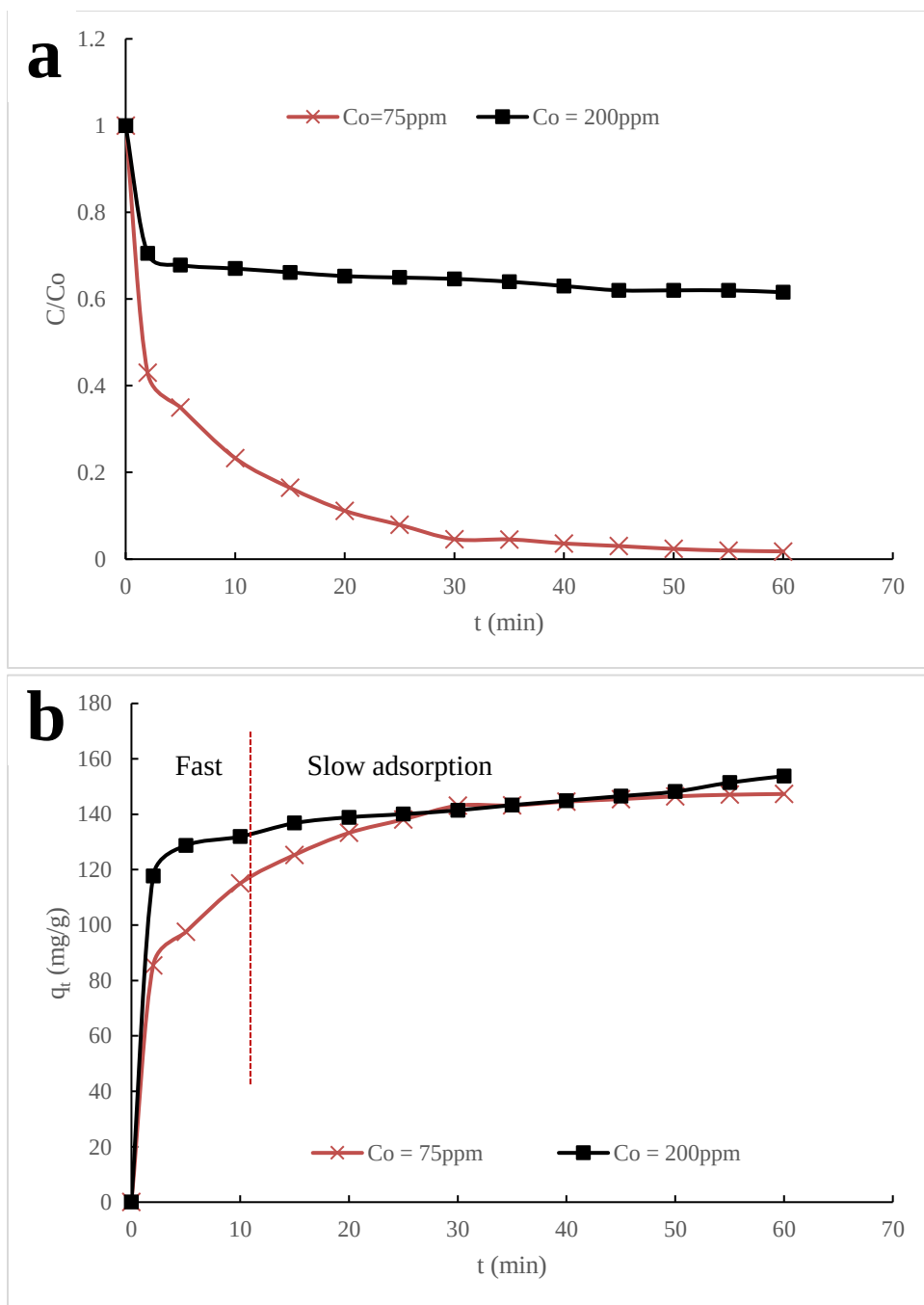


Figure 14 (a) Variation curves of methylene blue concentration versus time. (b) Effect of contact time on the adsorption capacities of PG.

4.2.2 Effects of Initial Concentration

To further understand the adsorption process, the influence of initial methylene blue concentration (50–200 ppm) on the adsorption performance of PG with high adsorption capacity was studied. As shown in Figure 15a, the adsorption capacity of PG increases and tends to become stable gradually with the increase of initial methylene blue concentration when maintaining the amount of adsorbent. Likewise, the equilibrium adsorption capacity q_e increases and becomes stable gradually with the increasing of the equilibrium concentration C_e (Figure 15b). The initial concentration of dyes is a major driving force for overcoming the diffusion resistance of dye molecules between the solid and aqueous phases. The available adsorption sites of PG are more than the amount of dye molecules at lower initial dye concentration. The adsorption capacity of PG for methylene blue in this case depends on how many available adsorption sites. At greater initial methylene blue concentrations, the number of dye molecules is more than the available adsorption sites of PG. Under the conditions, the concentration gradient driving force increases as the methylene blue concentration increases. This means that the greater the dye concentration is, the higher the interaction between dye molecules and adsorbents leading to the better adsorption capacity of the PG adsorbent. Therefore, the adsorbed dye largely depends on the initial concentration. [112]

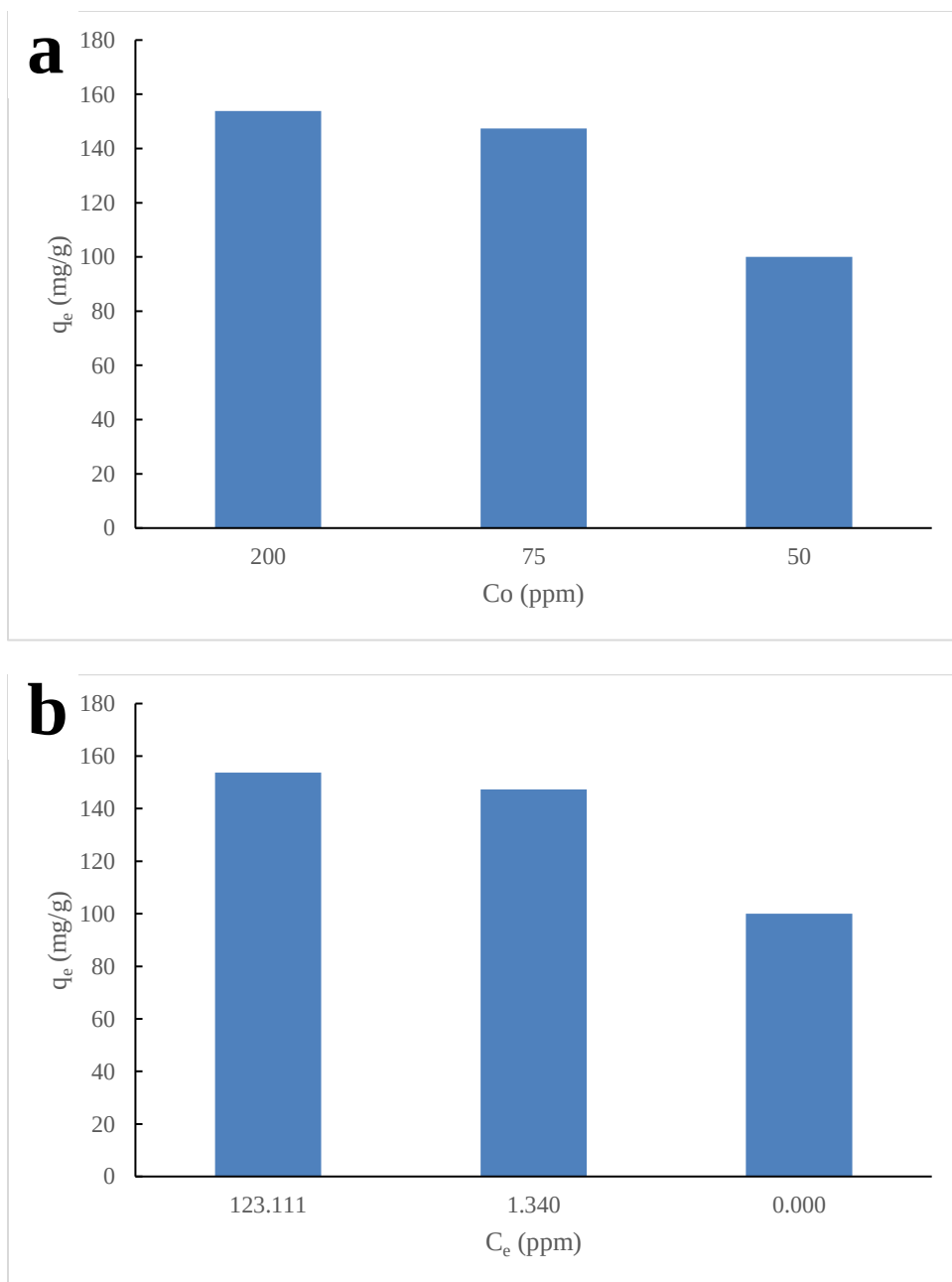


Figure 15 (a) Effect of initial methylene blue concentration on adsorption capacity of PG (adsorbent amount = 20 mg, time = 1 h, volume = 40 mL); (b) Adsorption isotherm of methylene blue on PG.

4.2.3 Effects of pH

The pH can impact the adsorption process as a result of the electrostatic forces. The effect of pH on the adsorption of methylene blue by PG was studied at the pH range of 2 - 10 for 60 minutes. The results in Figure 16 show that, although the pH has a variable effect on methylene blue adsorption by PG, the highest adsorption amount was achieved at the pH of 10. Naturally, the charges on the adsorbents' surface along with dominant charges in the solution impact the extent of adsorbate elimination from the solution. [113]

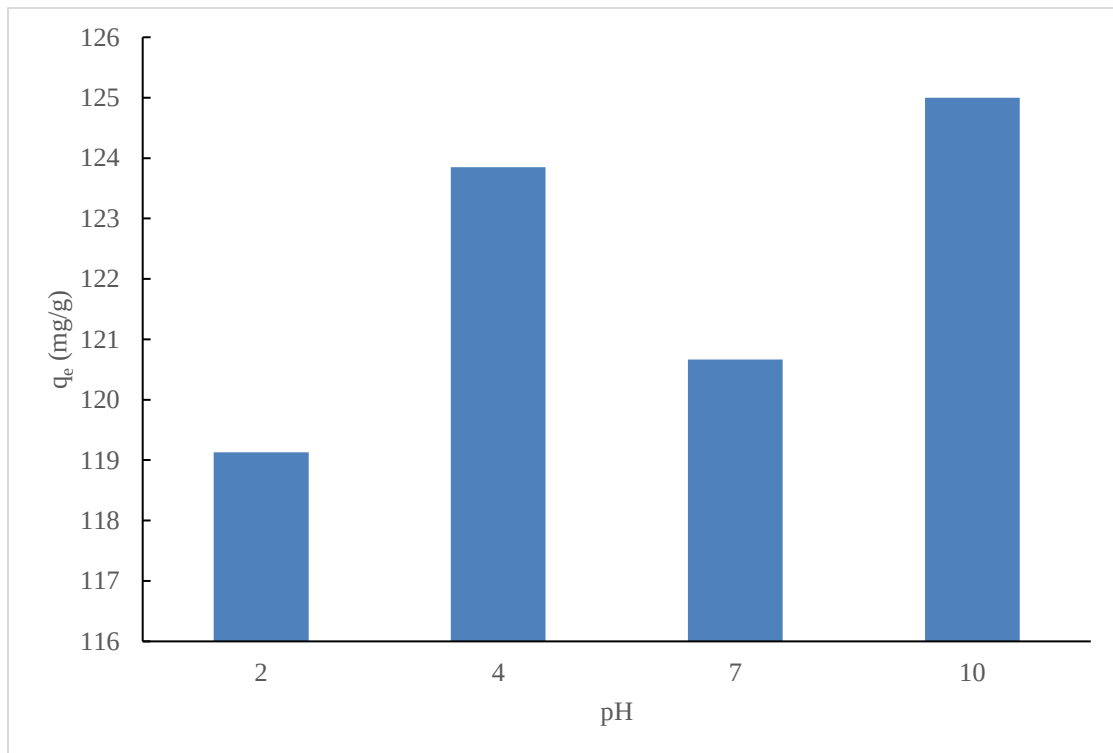


Figure 16 A plot of q_e (mg/g) at different pH values.

4.2.4 Simultaneous Removal of Dye and Metals

The simultaneous removal of dye and metals was investigated to understand the behavior of the adsorption process for the metals at low and high concentrations of methylene blue. In the first run, at an initial concentration of 50 ppm of methylene blue, 0.02 g of the PG adsorbent was able to remove most of the methylene blue from the solution as illustrated in Figure 17. Nevertheless, when the initial concentration was increased to 100 ppm, the removal increased but still much methylene blue remains in the solution. However, when the dosage of the PG adsorbent was increased to 0.05 g, the final methylene blue concentration is almost 0 ppm. Figure 18 is showing the behavior of the metals during the first, second, and third runs. The % removal of the metals in the first run (shown in Figure 18A) is stopped between 30% to 50%. This range is shifted when we have a high concentration of methylene blue in the second run to be from 20% to 40% in Figure 18B. This 10% shift indicates that there is a competition on the active sites between methylene blue and the metals because the metals occupied more active sites when there is a low concentration of methylene blue. Figure 18C confirms this observation, which is for the third run. It shows that the removal of all the metals reached more than 90% since the methylene blue was removed and there is no competition between methylene blue and the metals.

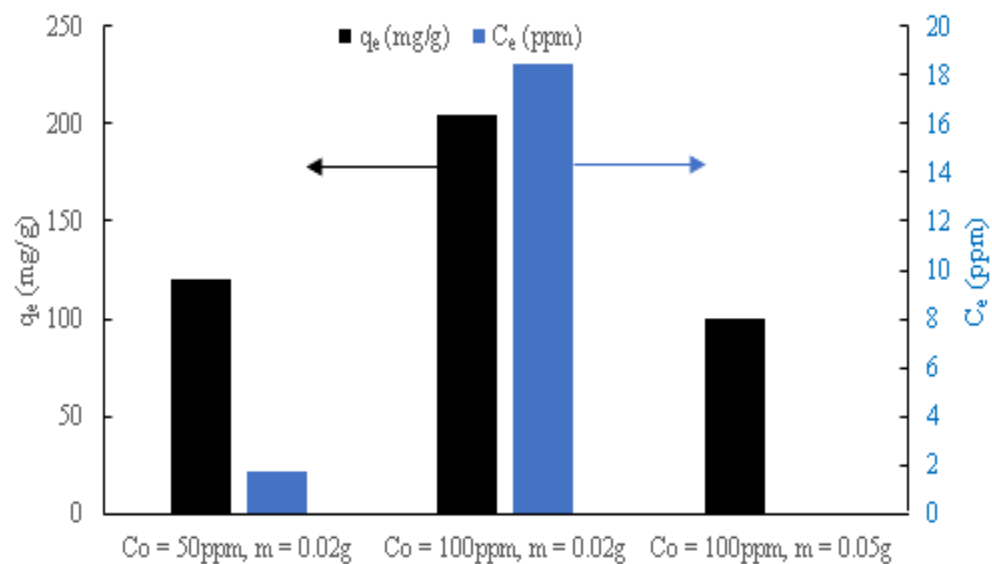
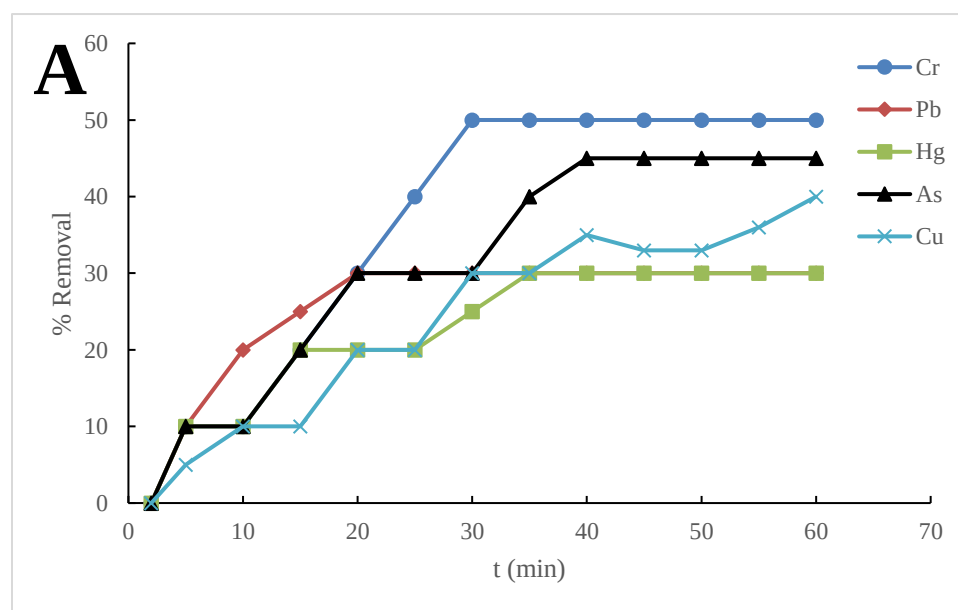


Figure 17 q_e (mg/g) and final concentrations of methylene blue at different methylene blue initial concentrations and PG amount.



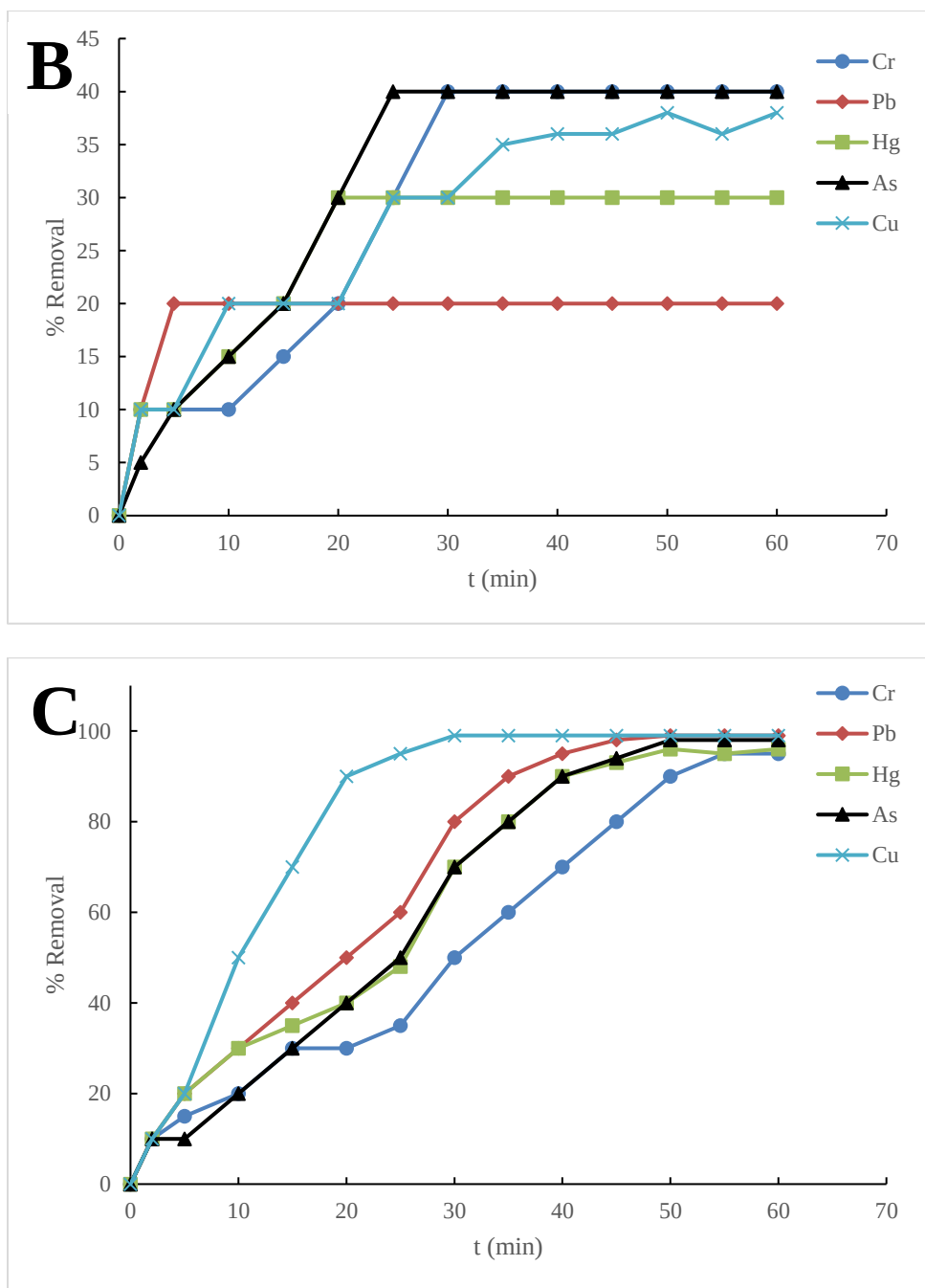


Figure 18 Plots of % removal versus time (min) for different methylene blue concentrations and PG dosages (A) $C_o = 50\text{ppm}$, $m = 0.02\text{g}$, (B) $C_o = 100\text{ppm}$, $m = 0.02\text{g}$ and (C) $C_o = 100\text{ppm}$, $m = 0.05\text{g}$.

4.3 Adsorption Equilibrium, Kinetics, and Thermodynamic Studies

4.3.1 Equilibrium Isotherms

Studying the adsorption equilibrium is essential to completely understand the characterization of the adsorbent and for the aim of designing for practical use. The data acquired from the batch experiments were fitted to five isotherm models which are Langmuir, Freundlich, Temkin, Scatchard plot, and Dubinin-Radushkevich isotherm models. Langmuir isotherm assumes that adsorbates bind on the surface onto monolayer active sites and that the adsorbent has a homogenous surface. This is the linearized Langmuir equation:

$$\frac{1}{q_e} = \frac{1}{K_L q_m} \frac{1}{C_e} + \frac{1}{q_m} \quad (5)$$

where q_m in mg/g is monolayer adsorption capacity while K_L is Langmuir constant in (L/mg). K_L is an important constant to determine the separation factor, R_L in the following equation:

$$R_L = \frac{1}{1 + K_L C_o} \quad (6)$$

R_L is dimensionless that provides information about whether the adsorption is favorable or not. Figure 19a shows the Langmuir plot and Table 2 contains Langmuir model parameters of PG. The data fitted the model with $R^2 = 0.9365$, which implies the presence of monolayer

adsorption. The capacity of the monolayer was obtained to be 161.29 mg/g. Since R_L values are between zero and 1, the adsorption process is favorable.

Unlike Langmuir, Freundlich adsorption isotherm assumes multilayer adsorption on heterogeneous adsorbent surfaces. The linearized equation of this model is written as:

$$\ln q_e = \ln K_e + \frac{1}{n} \ln C_e \quad (7)$$

where K_e in L/g denotes the Freundlich constant. $1/n$ refers to the heterogeneity factor. Smaller values (close to zero) would indicate heterogeneous binding sites. The data is not well fitted to the Freundlich model ($R^2 = 0.589$) as shown in Table 2. The heterogeneity factor, $1/n$ is close to 0, suggesting that there are heterogeneous binding sites.

Temkin isotherm assumes that the adsorption heat energy is a function of the surface coverage. By assuming that the binding sites on the adsorbent are uniformly distributed, it considers adsorbent-adsorbate interaction. The linear equation of this model could be expressed as:

$$q_e = B \ln A_b + B \ln C_e \quad (8)$$

where A_b in L/mg is equilibrium binding constant and B is the Temkin constant that is related to sorption heat b_T (J/mol) by the equation:

$$B = \frac{RT}{b_T} \quad (9)$$

R is the universal gas constant that has a value of 8.314 J/(mol•K), and T (K) is the absolute temperature. The correlation coefficient, R^2 of 0.549 is obtained indicating that it does not have an acceptable fit. This means that the binding sites are uniformly distributed on the adsorbent.

Scatchard plot provides more information about the heterogeneous assumption of Freundlich isotherm. If adsorption data shows a good fit in the Scatchard plot with a high correlation coefficient, R^2 , then the adsorbent has identical or only one type of binding site. If the R^2 is low, then there are more than one type of binding sites. The linear equation of Scatchard plot is written as:

$$\frac{q_e}{C_e} = q_s b_s - q_e b_s \quad (10)$$

where q_s is Scatchard adsorption capacity in mg/g and b_s is Scatchard constant in L/g. The adsorption data are not fitted very well. This indicates that the adsorbent does not have uniform binding sites.

Dubinin-Radushkevich isotherm model is used in order to describe the sorption of molecules onto microporous solids as a pore-filling process rather than layer-by-layer coverages. It is useful in categorizing sorption mechanisms into physical and chemical

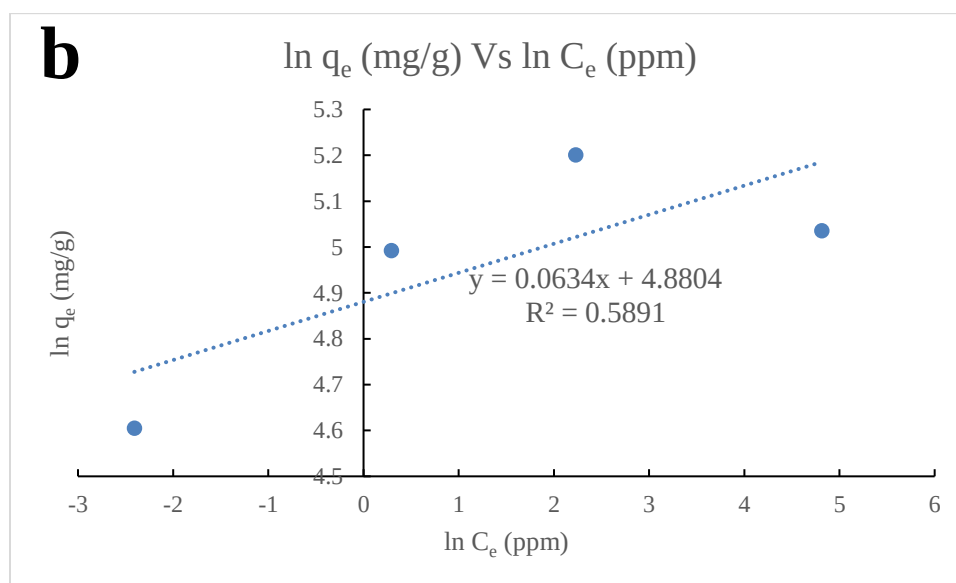
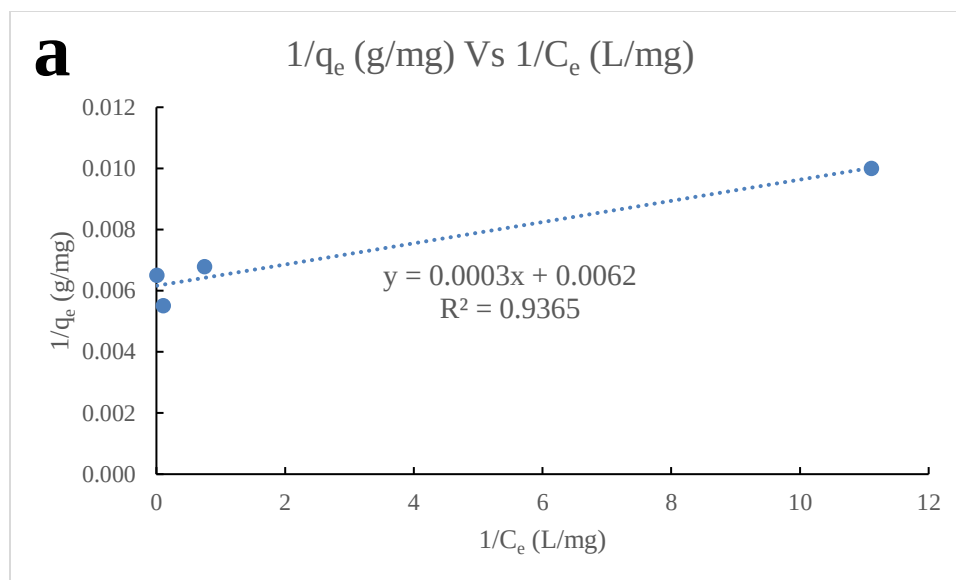
sorption because of the free energy component. The linearized equation can be expressed as:

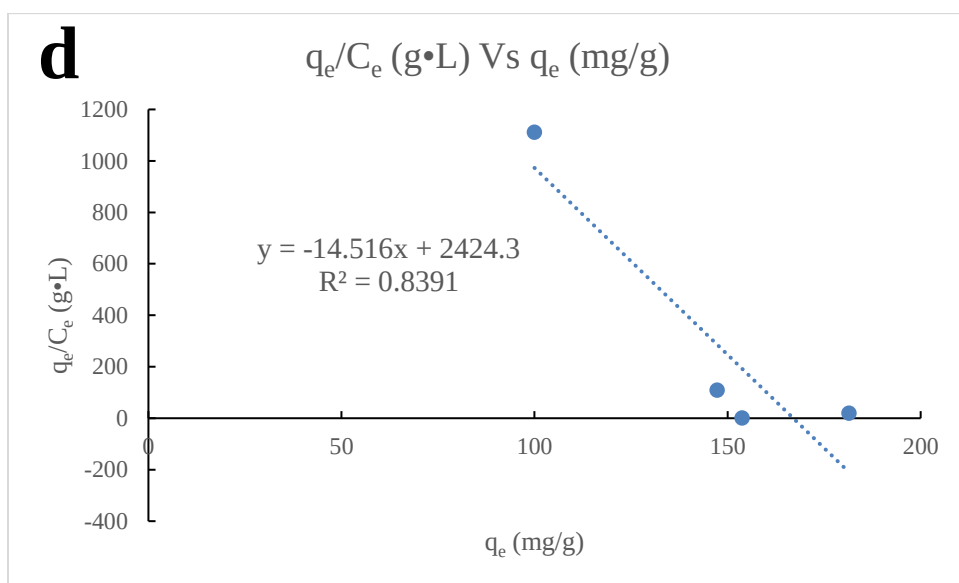
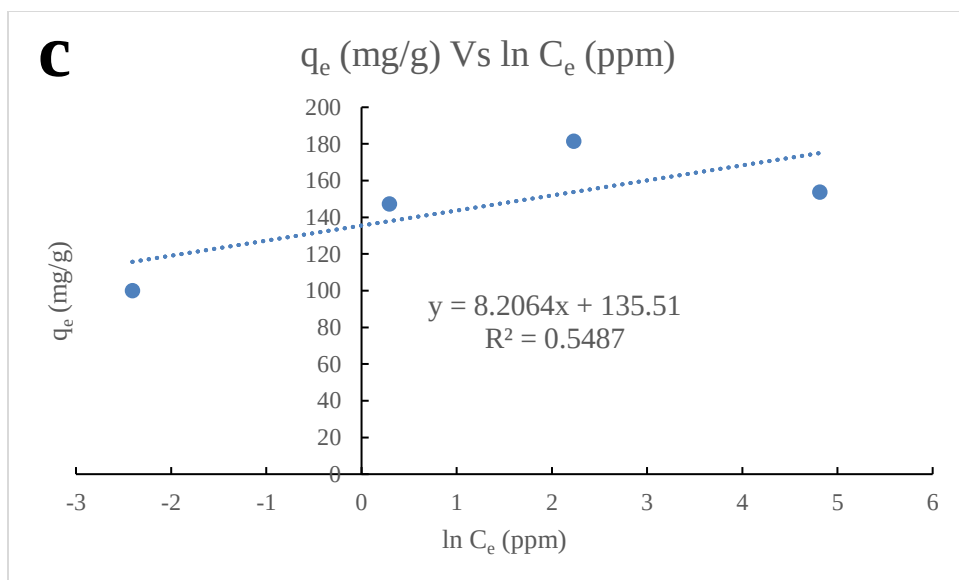
$$\ln q_e = \ln q_m - \beta_a \varepsilon_p^2 \quad (11)$$

where ε_p is Polanyi potential expressed as $\varepsilon_p = RT \ln(1 + 1/C_e)$ and β_a in mol^2/J^2 is a constant connected to adsorption free energy and q_m in mg/g is the theoretical saturation capacity otherwise identified as D-R constant. β_a is a constant useful in calculating the energy E in kJ/mol needed to remove an adsorbate molecule. The value of E provides information about the kind of adsorption process. E is calculated using the equation:

$$E = \frac{1}{\sqrt{2\beta_a}} \quad (12)$$

The correlation coefficient acquired from the plot of the data is poorly fitted to the model ($R^2 = 0.891$). From the value of desorption energy E in Table 2, the adsorption process is mainly physical adsorption. [113]





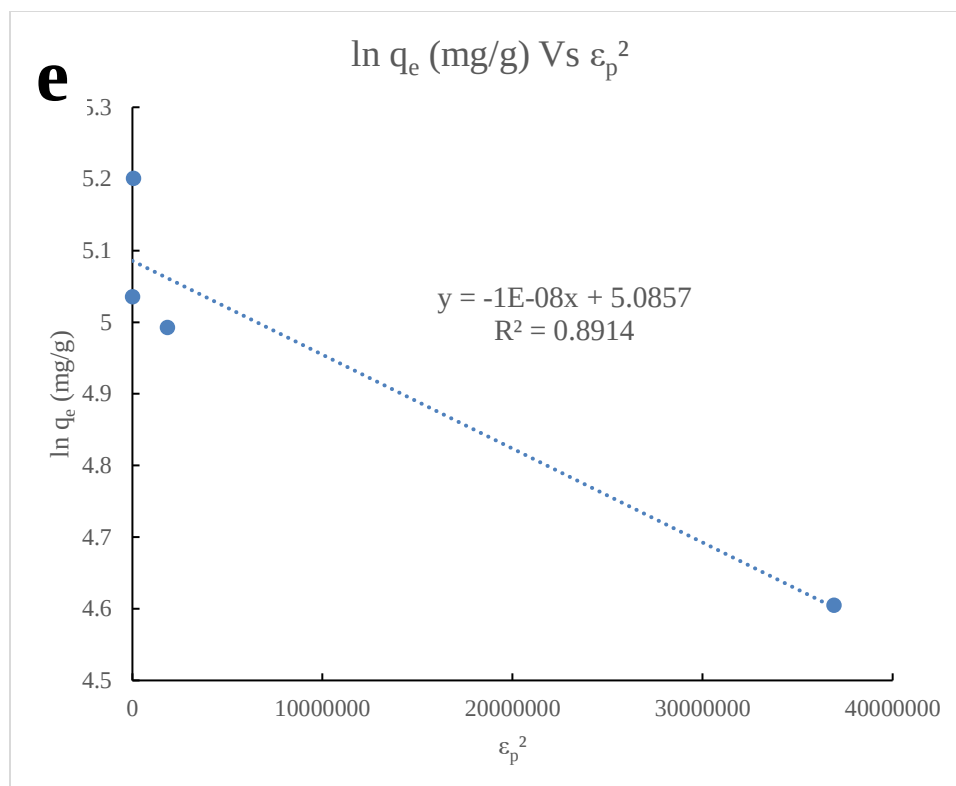


Figure 19 Isotherm plots for the adsorption of methylene blue on PG: (a) Langmuir isotherm plot; (b) Freundlich isotherm plot; (c) Temkin isotherm plot; (d) Scatchard plot; (e) Dubinin- Radushkevich isotherm plot.

Table 2 Isotherm model parameters for PG adsorbent.

Langmuir Model					
R^2	q_m (mg/g)	K_L (L/mg)	R_L (Co=75)	R_L (Co=100)	R_L (Co=200)
0.937	161.290	20.667	0.000645	0.000484	0.000242

Freundlich model				Temkin model			
R^2	K_e (L/mg)	n	$1/n$	R^2	B (mg/g)	A_b (L/g)	b_T (KJ/mol)
0.589	131.683	15.773	0.063	0.549	8.206	16.513	296.842

Scatchard plot			Dubinin-Radushkevich isotherm model			
R^2	q_s (mg/g)	b_s (L/g)	R^2	q_m (mg/g)	β_a (mol ² /J ²)	E (KJ/mol)
0.839	167.009	14.516	0.891	161.693	1E-08	7.071

Table 3 Comparisons of adsorption capacity of different adsorbents for MB.

Adsorbent	Adsorption conditions		q_m (mg/g)
	Adsorbent dose	Contact time	
	(g/L)	(min)	
Fe-Mn binary oxide	1	120	72.3
Ti-SBA-15	0.5	20	186.2
Zeolite-rGO	0.1	15	53.3
Commercial WO ₃	—	—	12.3
Urchin-like W18O49	1	120	66.7
Cubic WO ₃	1	1440	30.3
Au/WO ₂ 72	0.1	360	133.9
Seaweed-ZnO-PANI	0.5	60	20.6
Coir activated carbon	5	110	16
PDA-rGO-kaolin	0.8	120	39.7
CaHAp-(Alg)10	1	30	142.9
30 wt% WO ₃ /g-C ₃ N ₄	0.5	10	72.3
MnOx@cotton fibers	2	10	46.3
PG (this study)	0.5	60	161.29

4.3.2 Equilibrium Kinetics

The adsorption kinetics normally can reflect the physicochemical properties of the adsorbent. These kinetic models, which include pseudo-first-order, pseudo-second-order, Elovich model and Weber's intraparticle diffusion model could predict the adsorption mechanism, rate and rate-limiting step as well as the diffusion process.

The pseudo-first-order kinetics assumes that the adsorption is controlled by the diffusion step and that, on the adsorbent surface, there is only one type of binding site. The corresponding formulas are represented as follows:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (13)$$

where q_t and q_e (mg/g) are the amount of methylene blue adsorbed at any time t (min) and equilibrium time, respectively; k_1 (1/min) represents the pseudo-first-order rate constant.

The pseudo-second-order kinetics is also used to identify the adsorption capacity of the sample. It supposes that there are two binding sites on the adsorbent surface. The liner form of the model is given below:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (14)$$

q_t and q_e (mg/g) in Eq. (14) represent the same meaning as those of Eq. (13); k_2 (g/(mg•min)) represents the pseudo-second-order rate constant, which can be utilized to

calculate the initial adsorption rate via the limit theorem. The initial rate of adsorption, h (mg/(g•min)), was determined from the following equation:

$$h = k_2 q_e^2 \quad (15)$$

The Elovich equation is another kinetic model equation based on the adsorption capacity. It is used to confirm the chemisorption process with the assumption that the surface of the solid system is energy heterogeneous in nature. The formulas are expressed as follows:

$$\frac{dq_t}{dt} = \alpha \exp(-\beta q_t) \quad (16)$$

$$q_t = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} \ln(t) \quad (17)$$

Eq. (16) is simplified by assuming $\alpha\beta \gg t$ to Eq. (17), where β (g/mg) and α (mg/(g•min)) are the desorption constant and initial adsorption rate, respectively.

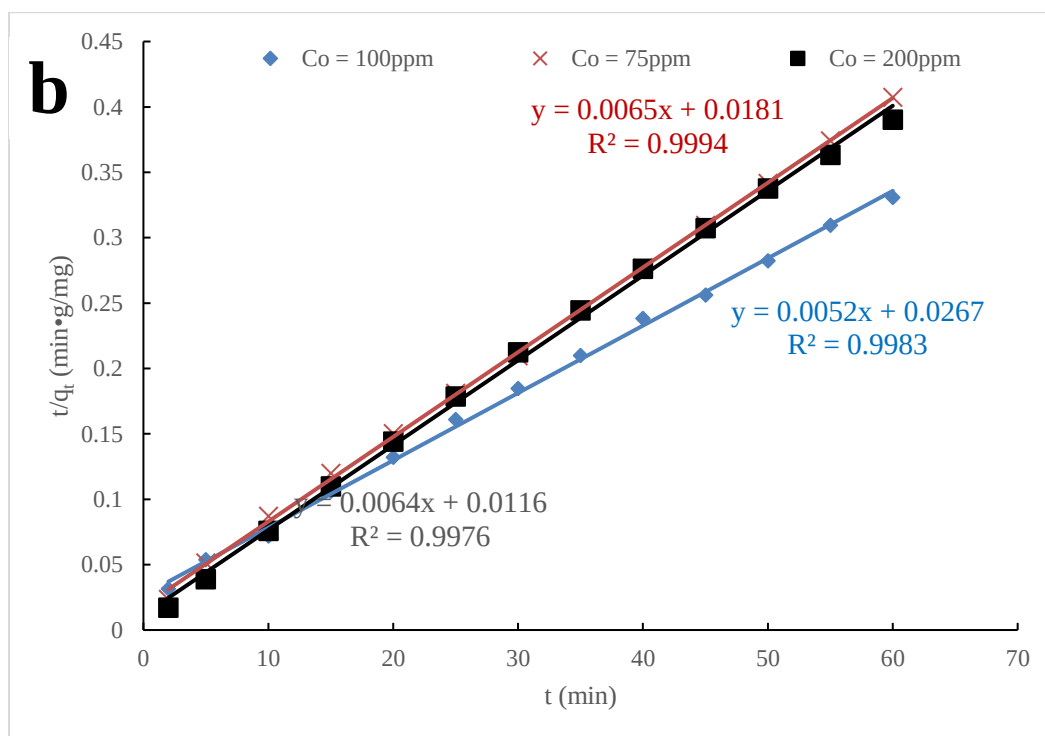
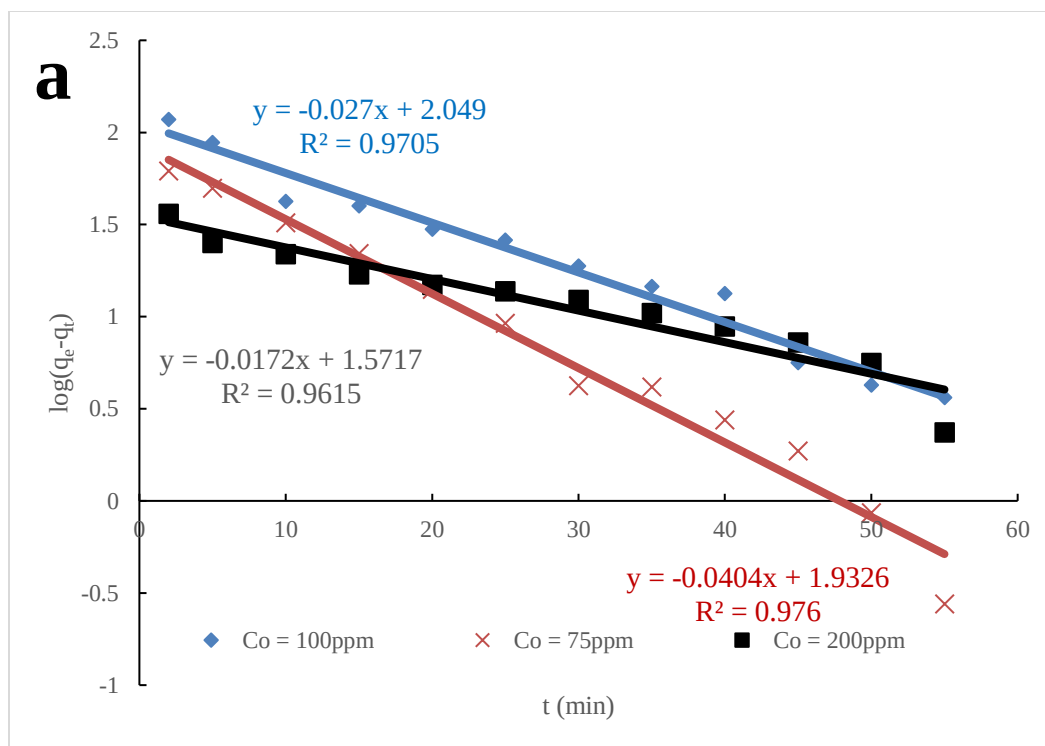
The adsorption process is actually through the diffusion effects of adsorbent, including film, surface, and pore diffusions, or any combination of those steps. To further understand the adsorption process, Weber's intraparticle diffusion model was employed. The formula is described as follows:

$$q_t = k_i t^{1/2} + c \quad (18)$$

where k_i ($\text{mg}/(\text{g}\cdot\text{min}^{1/2})$) is the rate constant of intraparticle diffusion; c (mg/g) is a constant related to the adsorption step.

Figure 20a-d shows the adsorption kinetic models of methylene adsorption by PG. It can be visually realized that pseudo-second-order kinetics fits better (Figure 20). Table 4 presents the kinetic parameters and correlation coefficients (R^2). The R^2 of pseudo-second-order kinetics is 0.999 that is greater than pseudo-first-order one (0.976) and Elovich adsorption kinetics one (0.977), meaning that this adsorption process is better represented by the pseudo-second-order model, which is consistent with the observation from Figure 20.

Figure 20c displays the Weber's intraparticle diffusion model of methylene blue adsorption onto PG. Clearly, the fitted lines do not go through the origin, meaning that the adsorption rate-limiting step is not only affected by the intraparticle diffusion but also controlled by other adsorption processes. [112] [114]



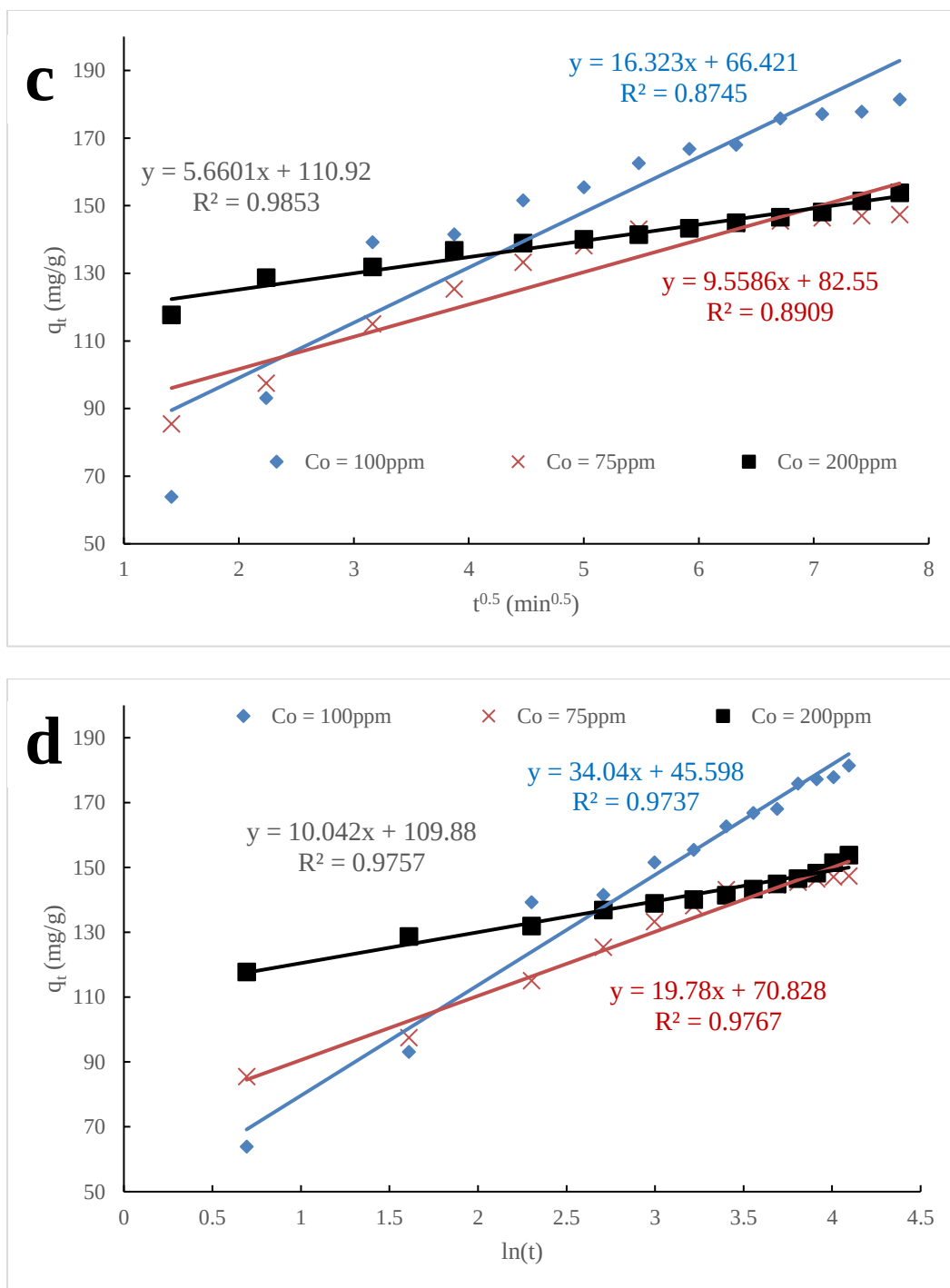


Figure 20 The kinetics model for the adsorption of methylene blue onto PG: (a) pseudo-first-order model, (b) pseudo-second-order model, (c) Weber's intraparticle, (d) Elovich model.

Table 4 Kinetic parameters of methylene blue adsorbed on PG.

Kinetic Models	Co (ppm)		
	75	100	200
Pseudo-First Order			
q_e (mg/g)	85.625	111.944	37.299
k_1 (1/min)	0.040	0.027	0.017
R ²	0.976	0.971	0.962
Pseudo-Second Order			
$q_{e,exp}$ (mg/g)	147.319	181.397	153.777
$q_{e,cal}$ (mg/g)	153.846	192.308	156.250
k_2 (g/(mg•min))	0.002	0.001	0.004
h (mg/(g•min))	55.249	37.453	86.207
R ²	0.999	0.998	0.998
Intraparticle Diffusion			
k_i (mg/(g•min ^{0.5}))	9.559	16.323	5.660
c (mg/g)	82.550	66.421	110.920
R ²	0.891	0.875	0.985
Elovich model			
α (mg/(g•min))	20.806	35.055	11.093
β (g/mg)	0.051	0.029	0.100
R ²	0.977	0.974	0.976

4.3.3 Thermodynamic Study

The temperature is a key parameter influencing the adsorption efficiency. Figure 21a shows the adsorption of PG for methylene blue at different temperatures. At 300 K, the adsorption amount of dye can reach roughly 186 mg/g, while it can be increased to nearly 195 mg/g at 340 K. The adsorption amount of methylene blue by PG manifests a trend of increase as the temperature increases, implying the endothermic nature of the adsorption process. For further understanding the adsorption behavior and mechanism, the thermodynamic parameters were utilized. These parameters were calculated as follows:

$$\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ} \quad (19)$$

$$\Delta G^{\circ} = -RT \ln K_d \quad (20)$$

$$K_d = \frac{C_a}{C_e} \quad (21)$$

$$\ln K_d = \frac{\Delta S^{\circ}}{R} - \frac{\Delta H^{\circ}}{RT} \quad (22)$$

where R (J/(mol•K)) is the universal gas constant and T (K) is the system temperature. ΔG° , ΔH° and ΔS° are standard Gibbs free energy in kJ/mol, standard enthalpy change in kJ/mol and standard entropy change in J/(mol•K), respectively. K_d (dimensionless) is the thermodynamic equilibrium constant. C_a in ppm is the amount of methylene blue adsorbed onto PG. ΔH° and ΔS° are determined by the intercept and slope of the plot of $\ln K_d$ versus

$1/T$ that is shown in Figure 21b. The thermodynamic parameters for the adsorption process are listed in Table 5. The ΔG° values are negative (-5.548 to -10.206 kJ/mol) suggesting that the adsorption of PG for methylene blue is spontaneous. The absolute value of ΔH° (29.159 kJ/mol) is between 20.9 and 80 kJ/mol, indicating that the adsorption of PG for methylene blue was attributed to a physicochemical adsorption process. Moreover, the ΔH° is greater than 0 confirming that the adsorption process is endothermic. Also, the positive ΔS° (120.212 kJ/(mol•K)) indicates the bonding of methylene blue to the surface of PG is not ionic and as such unstable. It can be removed simply for the re-use of the adsorbent. ΔG° is negative while ΔH° and ΔS° are positive, which means that the adsorption occurs spontaneously at higher temperatures. It verifies that the adsorption amount decreases with the temperature decreasing that was seen in Figure 21a. [112] [113]

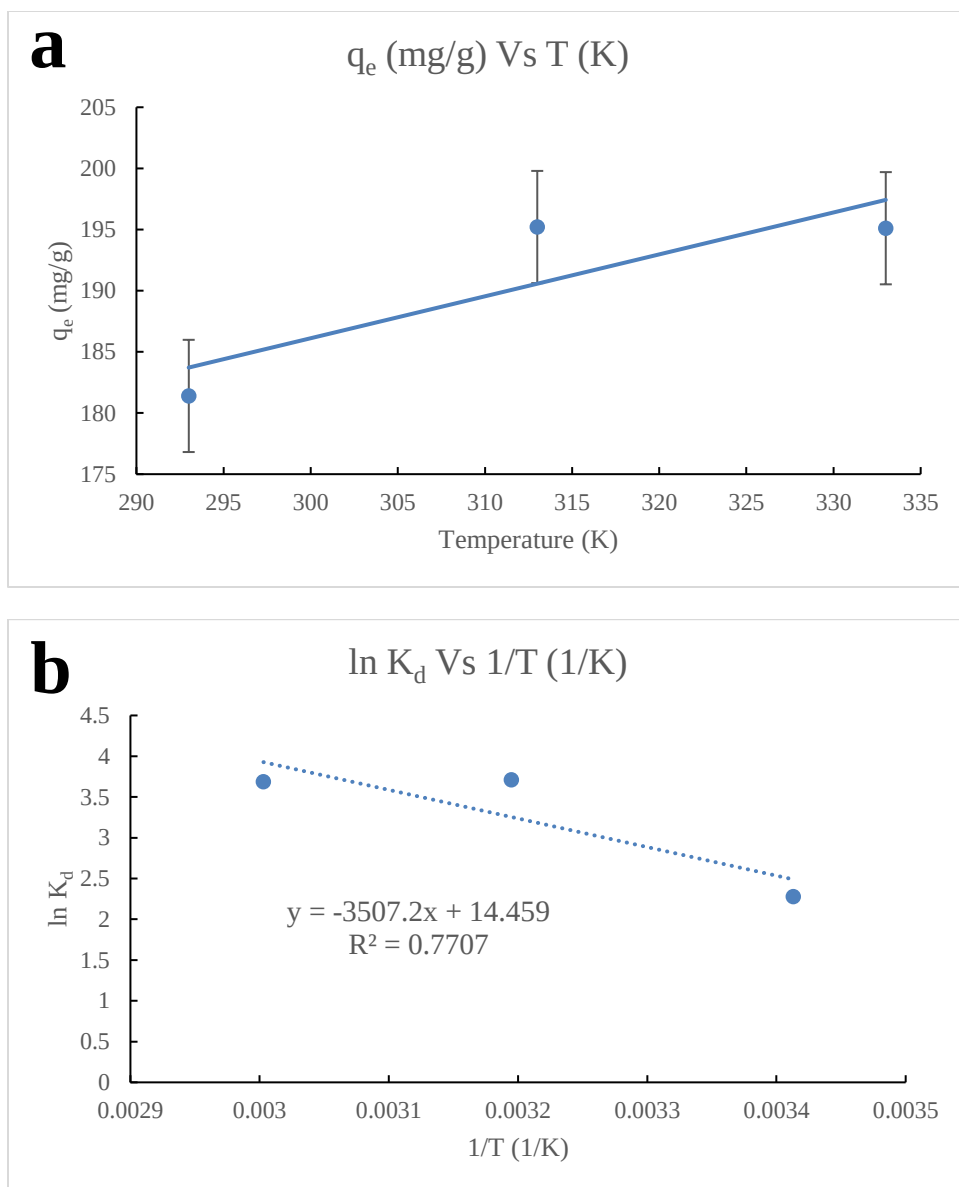


Figure 21 (a) Effects of temperature on the adsorption of methylene blue onto PG; (b) Van't Hoff plot of methylene blue removal by PG.

Table 5 Thermodynamic parameters of PG.

T	K_d	ΔG°	ΔH°	ΔS°
(K)		(kJ/mol)	(kJ/mol)	(J/(mol•K))
293	9.751	-5.548	29.159	120.212
313	40.729	-9.646		
333	39.897	-10.206		

4.4 Dynamic Adsorption

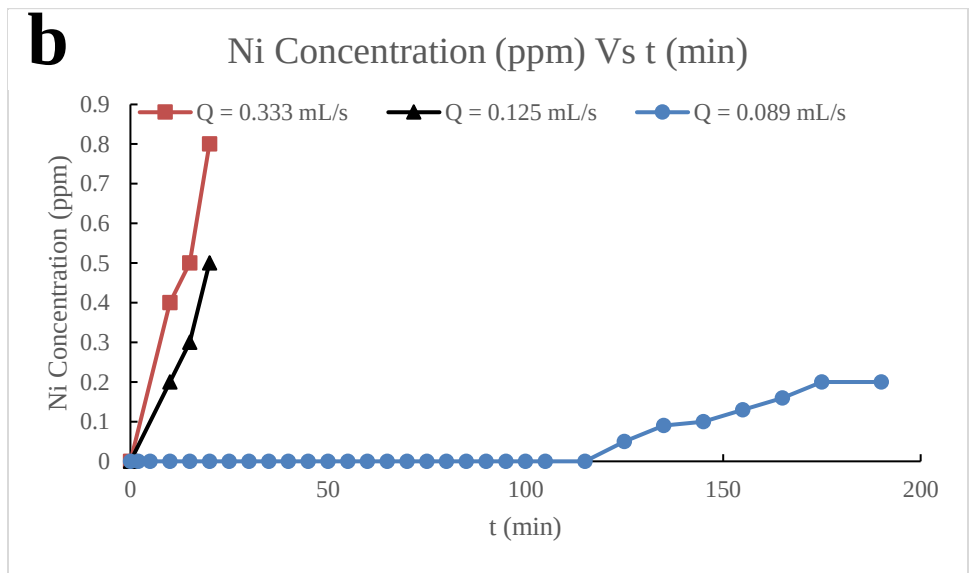
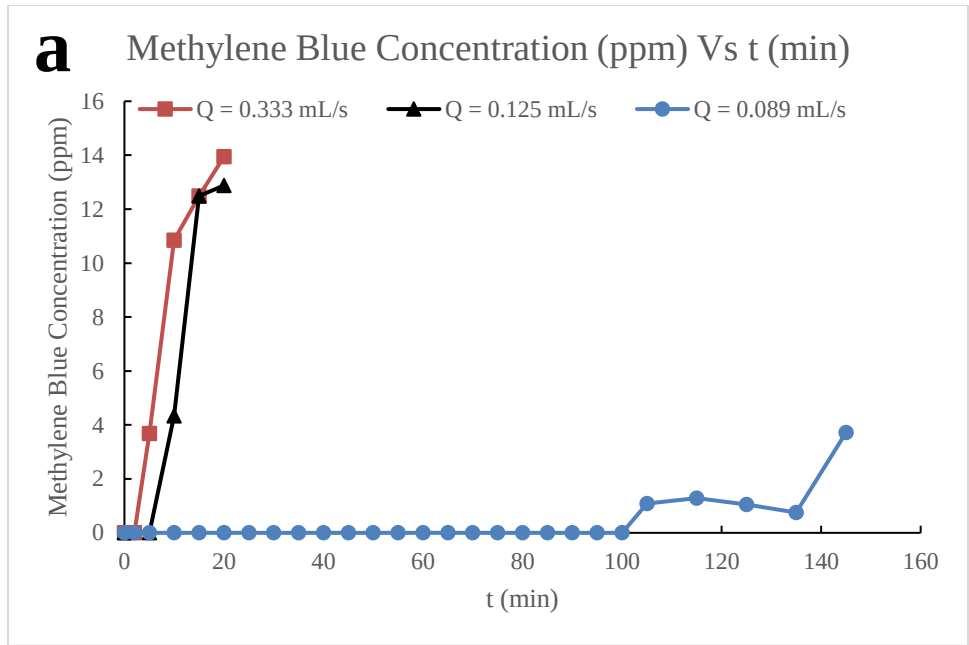
This study would give a better idea about the potential of using this material in large-scale adsorption. Flow rate influences significantly the performance of the column in continuous mode and this is a significant parameter for assessing the efficiency of an adsorbent in a continuous treatment of effluents on the pilot or industrial scale. The influence of the flow rate on the adsorption of methylene blue dye using PG was investigated by changing the feed flow rate ($Q = 0.333, 0.125, \text{ and } 0.089 \text{ mL/s}$) with the inlet methylene blue dye and metals concentrations of 25 and 50 ppm respectively and a constant bed height of 14 cm, as displayed by the breakthrough curves in Figure 22. In this work, the flow rate was changed to reach the maximum removal of methylene blue dye and metals, and it was found that the maximum uptake was accomplished at a flow rate of 0.089 mL/s. for the flow rates ranging between 0.089 and 0.333 mL/s, the breakthrough time decreased from 105 to 5 min, respectively. Methylene blue, Ni, Cr, and Pb ions have the same trend. As

the flowrate increases, the contact time becomes lower resulting in a less adsorption. Therefore, the adsorption is the highest for 0.089 mL/s that is the lowest flowrate.

Yoon–Nelson model was applied to the dynamic data acquired from methylene blue dye and metals adsorption by PG. The assumption of this model is based on the rate of decrease in the probability of adsorption for each adsorbate molecule being proportional to the probability of adsorbate adsorption and the probability of adsorbate breakthrough on the adsorbent. The linearized form of Yoon–Nelson model is written as:

$$\ln\left(\frac{C}{C_0 - C}\right) = K_{YN}t - K_{YN}\tau \quad (22)$$

Here K_{YN} (1/min) is the Yoon and Nelson rate constant, C_0 (ppm) is the inlet or initial concentration, C (ppm) is the effluent methylene blue concentration, t (min) is the time, and τ (min) is the time needed for 50 % adsorbate breakthrough. The values of the parameters, τ and K_{YN} were calculated from the plot of $\ln\left(\frac{C}{C_0 - C}\right)$ versus t at different flow rates (0.333, 0.125 and 0.089 mL/s). This plot will result in a straight line with an intercept of $K_{YN}\tau$ and slope of K_{YN} presented in Figure 23. The values of all determined parameters are presented in Table 6. It can be observed that simulation of the breakthrough curve is effective with the Yoon–Nelson model at a greater flow rate. From Table 6, the 50 % breakthrough time τ increased with decreasing flow rate. The results of the Yoon–Nelson model sufficiently match the experimental results indicating the suitability of this model for this proposed system. [115]



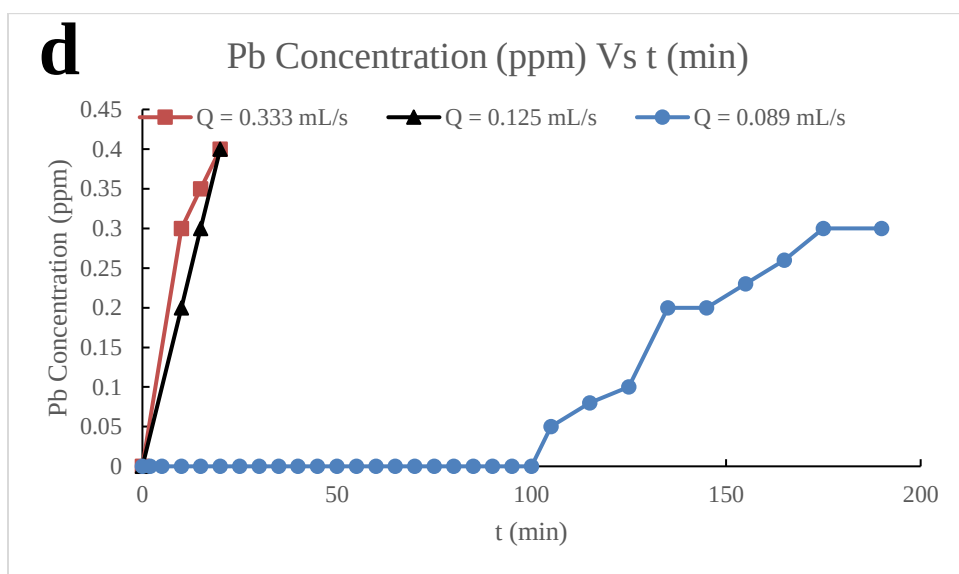
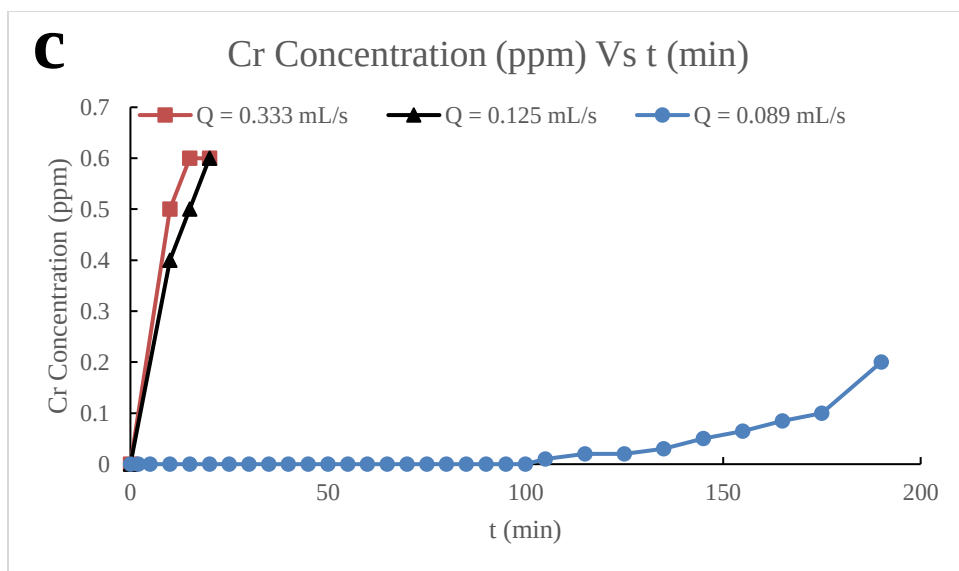


Figure 22 Plots of concentrations (ppm) versus time (min) at different flowrates for (a) methylene blue, (b) Ni, (c) Cr and (d) Pb.

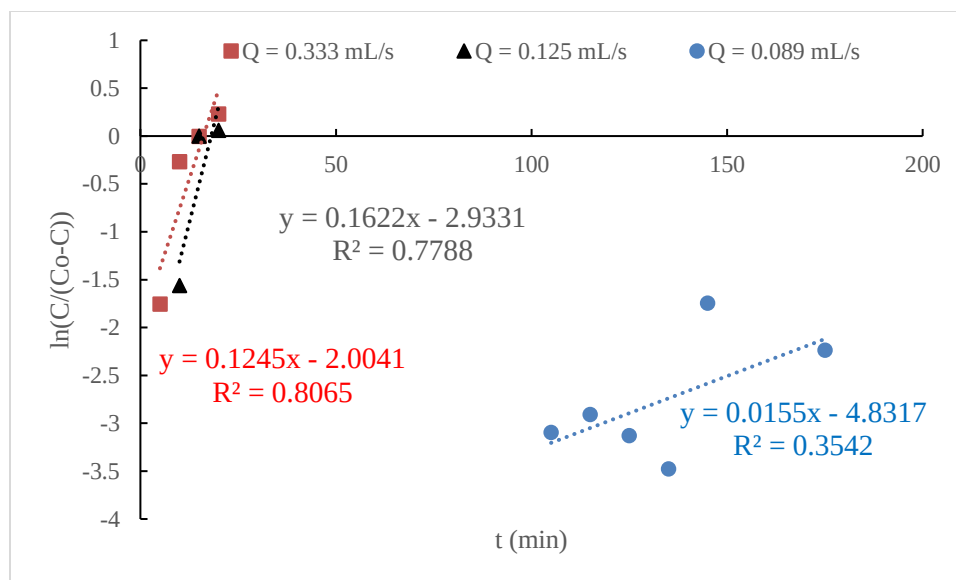


Figure 23 Yoon–Nelson kinetic plot for the adsorption of MB at different flow rates.

Table 6 Yoon–Nelson kinetic model parameters at different flow rates.

Yoon-Nelson	Q (mL/s)		
	0.333	0.125	0.089
K_{YN} (1/min)	0.125	0.162	0.016
τ (min)	16.096	18.083	311.723
R^2	0.807	0.779	0.354

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

The idea of having PG for methylene blue adsorption was analyzed. Five different adsorbents were evaluated for methylene blue adsorption from water and the results show that the best one was polyethylenimine modified graphene. The adsorption of methylene blue was further investigated in two modes which are the batch mode and the dynamic mode. In the batch adsorption, the effects of initial concentration, contact time, temperature, pH, and metals were investigated and some models were applied to study the equilibrium isotherms, kinetics, and thermodynamics of the adsorption process. The dynamic adsorption was investigated by changing the flow rate and applying a dynamic model. The results showed that the polyethylenimine modified graphene has a maximum adsorption capacity of 161.29 mg/g which means it has a high adsorption capability compared to other adsorbents. It can simultaneously remove the metals and methylene blue efficiently. It can perform well at room temperature and high temperature with faster adsorption. It can remove the methylene blue at a wide range of pH. The dynamic experiment was operated successfully indicating that there is a potential for this material to be used on a large scale in the industry.

5.2 Recommendations

The results in this study are promising that encourage us to recommend the materials toward larger-scale tests for real water treatment, using systems such as pilot-scale combined adsorption columns packed with the reported materials. Moreover, it is recommended that the prepared adsorbents be tested under real conditions such as real industrial wastewater. This will allow getting clear information on the reliability of the materials to be used in the real application. Furthermore, the materials can be tested under long-term experiments to make sure that they can stand the higher temperature produced by the continuous suitable pressure.

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