MODIFICATION OF SURFACTANT CHEMICAL STRUCTURE FOR OPTIMISING GRAPHENE OXIDE SYNTHESIS AS AN EFFICIENT REMOVAL OF METHYLENE BLUE

NUR AMIRAH JAMALUDDIN

UNIVERSITI PENDIDIKAN SULTAN IDRIS

2023

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ABSTRACT

This research aimed to optimising the properties of surfactant-exfoliated graphene oxide (sEGO) as adsorbent and photocatalyst for methylene blue (MB) removal in aqueous solution. Modification of surfactants were made by increasing chain branching and exchanged in counter-ion with aromatic groups namely 1-butyl-3-methyl-imidazolium (BMIM) and anilinium. The role of these modified surfactants were compared to commercial surfactants. The mechanism in the stabilisation of sEGO, sEGO incorporated with nanofibrillated kenaf cellulose (NFC) and sEGO fabricated with titanium dioxide (TiO_2) were systematically compared. Modified surfactants have been studied via proton nuclear magnetic resonance (^1H NMR) spectroscopy, air – water (a/w) surface tension measurement, zeta potential measurement and dynamic light scattering. The morphology of the synthesised adsorbents and photocatalytic materials were observed by field emission scanning electron microscopy (FESEM), Raman spectroscopy and high-resolution transmission electron microscopy (HRTEM). The performance of adsorbents (sEGO and sEGO/NFC) and photocatalysts (sEGO/TiO_2) were also monitored through ultraviolet-visible (UV-vis) spectroscopy. The aggregation behaviour of modified surfactants in aqueous phase and in sEGO presence were analysed using small-angle neutron scattering (SANS) analysis. Results showed that increasing surfactant chain branching and exchange with counter-ions (BMIM and anilinium) enhance the graphite surface affinity and sheet exfoliation. Thus, contribute increment of adsorption sites of sEGO for MB removal (up to 99%) in aqueous solution. SANS analysis revealed that addition of chain branching and exchanged in counter-ion influenced micelle structure formation of modified surfactant similar with lamellar layered of graphene. In conclusion, the chain branching and counter-ions exchange modification in surfactant chemical structure optimise sEGO properties as efficient MB removal in aqueous solution. As implications, modification of surfactant in sEGO as adsorbents and photocatalysts opens up new alternative approach for wastewater treatment.

PENGUBAHSUAIAN STRUKTUR KIMIA SURFAKTAN UNTUK MENGOPTIMUMKAN SINTESIS GRAFENA OKSIDA SEBAGAI PENYINGKIR EFEKTIF METILINA BIRU

ABSTRAK

Kajian ini bertujuan untuk mengoptimumkan sifat surfaktan-pengelupasan grafena oksida (sEGO) sebagai bahan penjerap dan pemangkin-foto untuk penyingkiran metilina biru (MB) dalam larutan akueus. Pengubahsuaian surfaktan dilakukan dengan menambah cabang rantai dan menukar ion-balas dengan kumpulan aromatik iaitu 1-butil-3-metil-imidazolium (BMIM) dan anilinium. Peranan surfaktan terubahsuai dibandingkan dengan surfaktan komersial. Mekanisma dalam penstabilan sEGO, sEGO digabungkankan dengan nanofibril kenaf selulosa (NFC) dan sEGO digabung jalin dengan titanium dioksida (TiO_2) dibandingkan secara sistematik. Surfaktan terubahsuai telah dikaji menggunakan spektroskopi resonan magnetik nuklear (^1H NMR), pengukuran tegangan permukaan udara – air (a/w), pengukuran potensi zeta dan serakan dinamik cahaya. Morfologi bahan penjerap dan bahan fotokatalisis yang telah disintesis diperhatikan melalui mikroskopi pengimbas pancaran medan elektron (FESEM), spektroskopi Raman dan mikroskopi penghantaran elektron resolusi tinggi (HRTEM). Prestasi bahan penjerap (sEGO dan sEGO/NFC) dan pemangkin-foto (sEGO/TiO_2) juga telah dipantau melalui spektroskopi ultralembayung-nampak (UV-vis). Kelakuan pengagregatan surfaktan terubahsuai dalam fasa akueus dan dengan kehadiran sEGO dianalisa menggunakan analisis serakan neutron sudut kecil (SANS). Dapatan kajian menunjukkan penambahan cabang rantai surfaktan dan penggantian ion-balas (BMIM dan anilinium) meningkatkan keafinan permukaan dan pengelupasan lembaran grafit. Ini menyumbang kepada peningkatan tapak jerapan sEGO bagi penyingkiran MB (sehingga 99%) dalam larutan akues. Penganalisaan SANS membuktikan penambahan cabang rantai dan ion balas mempengaruhi pembentukan struktur misel surfaktan terubahsuai menyerupai struktur lapisan lamelar grafena. Kesimpulannya, pengubahsuaian cabang rantai dan penggantian ion-balas dalam struktur kimia surfaktan mengoptimumkan sifat sEGO sebagai penyingkir MB yang berkesan dalam larutan akueus. Implikasinya, pengubahsuaian surfaktan dalam sEGO sebagai bahan penjerap dan pemangkin-foto membuka pendekatan alternatif baharu dalam rawatan air buangan.

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^{1}H NMR	Proton Nuclear Magnetic Resonance
AOT	Aerosol-OT
AOT14	sodium 1,2-bis-(2,2-dimethyl-propoxycarbonyl)-ethanesulfonate
AOT14-AN	anilinium 1,2-bis-(2,2-dimethyl-propoxycarbonyl)-ethanesulfonate
BMIM-DS	1-butyl-3-methyl-imidazolium dodecylsulfate
BMIM-AOT14	1-butyl-3-imidazolium 1,2-bis-(2,2-dimethyl-propoxycarbonyl)-ethanesulfonate
BMIM-TC14	1-butyl-3-imidazolium 1,4-bis(neopentyloxy)-3-(neopentyloxycarbonyl)-1,4-dioxobutane-2-sulfonate
cmc	Critical micelle concentration
CVD	Chemical vapour deposition
DS-AN	anilinium *n*-dodecylsulfate
DLS	Dynamic light scattering
FESEM	Field emission scanning electron microscopy
GO	Graphene oxide
HRTEM	High-resolution transmission electron microscopy
ILs	Ionic liquids
MB	Methylene blue
rGO	Reduced graphene oxide
SAILs	Anionic surfactant ionic liquids
SANS	Small-angle neutron scattering

SDS	Sodium dodecylsulfate
SLD	Scattering-length density
TiO_2	Titanium dioxide
TMS	Tetramethylsiloxane
a/w	Air-water
A_{cmc}	Limiting area per molecule at cmc
D-band	Disorder band
G-band	Graphitic band
I(Q)	Scattering intensity
I_D/I_G	Ratio of defect and graphitic band intensity
L	Thickness of bilayer in lamellar
M	Number of bilayer in lamellar
P(Q)	Form factor
R_a	Polar radius for ellipsoidal micelle
R_b	Equatorial radius for ellipsoidal micelle
$R_{cylinder}$	Radius of cylindrical micelle
R_{disk}	Radius of stacked disk micelle
R_{sphere}	Radius of sphericak micelle
S(Q)	Structure factor
$V(h)$	Potential energy
Γ	Adsorption isotherm
γ_{cmc}	Surface tension atccmc
ζ-potential	Zeta potential
θ	Surface coverage

λ	Wavelength
ρ	SLD
Γ_m	Surface concentration of monolayer

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CHAPTER 1

INTRODUCTION

1.1 Rationale

The discovery of graphene in 2004 has gathered attention in the broader community since it was announced as the topic of the 2010 Nobel Prize in Physics. The potential market of graphene encouraged Malaysia to become a large scale graphene producer which realized through the National Graphene Action Plan 2020 (NGAP 2020). NGAP 2020 is a graphene commercialization program which was launched in July 2014 aimed to enhance relevant graphene application to the country. As has been outlined in the NGAP, Malaysia has the opportunity to become one of the early leaders in adopting graphene-based materials and at the same time maximizing the application of graphene. According to written report by Ministry of Science and

Technology (MOSTI), NGAP collaborating companies have stated their willingness to collaborate and take cooperative efforts in sharing positive ideas, initiatives, and implementations of collaborative projects aimed at boosting downstream use of graphene relevant to Malaysia by signing Memorandum of Understanding (MoUs) today (https://www.mosti.gov.my/en/berita/3-march-2016-ngap-2020-to-contribute-rm-20-billion-gni-impact-create-9000-jobs-for-malaysia/). As a result, a local graphene eco-system will be able to drive downstream adoption. These collaborations were expected to contribute RM 10 billion to Malaysia's Gross Domestic Product (GDP) and generate RM 20 billion in Gross National Income (GNI) effect. The collaborations are focused on developing downstream graphene-based applications for specialist and consumer items such as tyres, automotive components, water pipes, ultracapacitors including material for wastewater treatment.

MOSTI through NanoMalaysia Berhad have conducted to realised NGAP 2020 missions and till now, RM 28.3 million was utilised and successfully activate 61 projects with the concept of 'Triple Helix' which include commitment from from local agencies and industries including Small and Medium-Sized Enterprise (SMEs), 40 intellectual property were registered and 37 products of graphene industries were produced compared to 17 products among Europe Union (EU) countries (https://www.parlimen.gov.my/files/jindex/pdf/JDRBL16122021.pdf). Another graphene derivative which is graphene oxide (GO) has been a material chosen for water treatment. Among the challenges for GO application especially in wastewater treatment is to find the most cost effective method of production. There were many types of GO production available however not applicable for wastewater treatment. Therefore, finding cost-effective and direct application are both important. Here, NanoMalaysia provide supports in terms of scaling up and commercialisation including Research and Development (R&D) monitoring which are important for graphene properties utilisation in local industries. NanoMalaysia aim is to capitalise on revenue streams linked with nanotechnology products and applications. This is accomplished by directing financial and human resources toward commercial endeavours and projects that are practical (such as water treatment) and provide realistic and high-value returns over the medium to long term. Apart from that, emphasise the necessity of national objectives for job growth and a more environmentally sustainable future are important here as well (https://nanomalaysia.com.my/wp-content/uploads/2021/10/NanoMalaysia-Strategic-Report-2020-03082021_compressed.pdf). Thus, in order to complete the mission, projects included here in this thesis are very much important.

1.2 Water Treatment: Treatment Methods & Materials using Carbon Material

Water as a basic necessity is an influential factor in our everyday lives but water pollution, urbanization, and huge population growth has led humankind to the brink of water resource scarcity. Among the main sources of toxic pollution are textile (Gonzalez et al., 2015), dye and printing manufacturing including cosmetics (Yagub et al., 2014), food (Shabandokht et al., 2016; Al-Ghouti et al., 2016), polymer (Fleischmann & Lievenbruck, 2015), and chemical precipitation process (Cui et al., 2015). One of the main concern is in industrial area whereby water-soluble organic dye effluent contaminate our waterways. According to United Nation World Water Development Report (2017), over 80 % of the world’s wastewater and over 95 % in some least developed countries is released to the environment without treatment. The report also highlight the importance of wastewater management to generate social, environmental and economic benefits which are essential for sustainable development. Latest update on wastewater treatment by United Nation is to enhance water quality by minimizing pollution, abolishing dumping and reducing release of perilous chemicals and matter, subsiding untreated pollutant and significantly practicing recycling and reusing globally by 2030 (Alabaster et al., 2021). Thus, in order to contribute in achieving the global target, the work done here is important.

In Malaysia, the legislation that is related to the prevention, abatement, control of pollution and enhancement of the environment is the Environmental Quality Act, 1974. The Act restricts the discharge of wastes into the environment in contravention of the acceptable conditions. Therefore, it is important for us researchers to find a way in implementing the act. According to Nair P. K. (2017) in Malay Mail article, the concern of freshwater supply and safely-treated wastewater return must be emphasized in Malaysia, especially in urban areas. As the *honorary secretary of the Bangsar Baru Residents' Association, Nair P. K. (2017)* also wrote that, despite being blessed with abundance of rainfall, water must be managed efficiently to ensure its sustainability and also to provide clean water for the generations to come. In conjunction with Green Technology Master Plan Malaysia 2017-2030, one of the six initial key sectors stated is wastewater treatment technology. Hence, Malaysian government aim on providing solutions through research, development and commercialization of wastewater treatment.

One material that has received substantial interest from both the scientific community and industry in this regard is graphene. Since the discovery of graphene in 2004, Malaysia has aspired to become a large scale graphene producer outlined through the vision of National Graphene Action Plan 2020 (NGAP 2020). Graphene presents a unique option for Malaysia to develop its capabilities as an innovation economy mentioned in the New Economic Model (2010) and the Economic Transformation Programme, ETP (2010).

With this, the government aim to create 9000 jobs in which among 3000 will be high-rise jobs. It is expected to contribute around 9 billion Malaysian Ringgit ($2.8 billion USD) to the country's GDP and $5.6 billion USD to the country's GNI. GNI measures our nation's economic activities through National Key Economic Area (NKEA). NKEA creates job opportunities through twelve core of ETP whereby NKEA 12 is Greater Kuala Lumpur/ Klang Valley. The primary goals of the wastewater management as one of the Entry Point Project under NKEA 12 are to clean up and beautify the river.

Up to now, several adsorbents that have been used for waste removal in aqueous environment namely are activated carbon (Nayak et al., 2017), biochar (Mohan et al., 2014), mesoporous silica (Pongkitdachoti & Unob, 2018), zeolite (Visa, 2016), chitosan (Riegger et al., 2018) and carbon nanotubes (CNT) (Ihsanullah et al., 2016). However, these available adsorbents are not efficient and effective in removing the pollutants as a large sum of these adsorbents needed for water purification. Therefore, finding a potential adsorbent for effectively purifying wastewater is crucial. To think that graphene materials possess high surface area, it is important to explore the application of this material for producing effective and efficient dye adsorbent. The main aspect of an adsorbent is undoubtedly its adsorption capacity. The choice of the graphene materials (whether in its oxidized form i.e. graphene oxide), the combined materials (which materials paired well with graphene oxide) and wastewater treatment technique that will give the best dye removal therefore must be evaluated.

Currently, there are various methods used for the removal of conventional pollutants from polluted water, such as submerged membrane bioreactor (Kaya et al. 2017), activated sludge treatment (Radjenović et al., 2009), constructed wetland (Li et al., 2014), photocatalytic oxidation (Martínez et al., 2013) and catalytic ozonation (Dai et al., 2014). Other treatment technologies such as precipitation (Hao et al., 2018), flocculation (Guo et al., 2018), heteroaggregation-sedimentation (Feng et al., 2018), acidification-coagulation (Rattanapan et al., 2011), nanofiltration (Chen et al., 2018a), chemical reactions (Silva et al., 2018), and ion exchange (Zhang et al., 2011) has accelerated progress in wastewater treatment research. However, the high waste disposal cost of charcoal is a major problem though its use is easier for dye removal. On the other hand, the problem in filtration is due to the low molar mass dyes which can easily pass through the filter system. The disposal of toxic sludge’s from coagulation technique has serious limitation in its application, similarly, ozone treatment, is very expensive (Byrappa et al., 2006).

Of major interest, adsorption process which include the development of adsorbent is highlighted in wastewater treatment current research. Adsorption is a surface phenomenon by which a multi-component fluid (gas or liquid) mixture is attracted to the surface of a solid adsorbent and forms attachments via physical (dominated by van der Waals interactions) or chemical bonds (ionic or covalent bonding between the adsorbate and adsorbent). The two major parts of adsorption are adsorbate and adsorbent. The adsorbent deal with substance which attaches the dye material on its surface and the material which gets attached to the adsorbent is called as adsorbate. It is recognized as the most favoured method for eliminating dye from aquatic environments due to simple and economical, offers high removal efficiency, generates minimal secondary by-products (e.g., sludge formation), and is able to separate a wide range of pollutants (Kumar et al., 2010; Sharma et al., 2016; Patra et al., 2016). Zhang et al. (2016) stated that adsorbents based separation process are widely used technology for polishing treatment of water and wastewater. Hence, researchers continuously exploring and developing new types of adsorbents for efficient waste removal methods by applying adsorption process.

Nevertheless, only organic pollutants adsorbs in adsorption process, causing secondary contamination thus, restricting its application (Sajna et al., 2022). Another alternative method in wastewater decontamination is photocatalytic degradation or photocatalysis (Upadhyay et al., 2014). The photocatalytic process primarily involves electron transfer and molecules undergoing transformation must associate with the surface of the particle. Hence, surface area as well as the chemical nature of the surface is important (Yuenyongsuwan et al., 2018). Photocatalysis shows advantages in the following aspects: gentle pH value of solution, mild reaction temperature, and high efficiency (Khataee & Kasiri, 2010). It is also considered as the most advantageous and green technology for eliminating effluents especially dye contaminants. Sajna et al. (2022) added that so as to solve the aforementioned problem, integration of adsorption and photocatalysis is required by enriching the adsorbed organic pollutants which later degraded and mineralized through photocatalytic mechanism.

1.2.1 GO as Adsorbent

The nanoscale structures formed by exfoliation of graphite by oxidizing agents are referred to as graphene oxide (GO) (Ray, 2015, p. 35; Gao, 2015, p. 61). As the name suggests, GO consists of carbon, hydrogen and oxygen atoms where oxygen functional groups can be on basal planes or on the edges of the sheets (Ray, 2015, p.35). GO has received increased focus (Sharma & Das, 2013, Robati et al., 2016a, Konicki et al., 2017; Sham & Notley, 2018). This is because GO possesses a high surface area to mass ratio (736.6 m^2g^{-1}) (Montes-Navajas et al., 2013) and includes polar oxygen functional groups. Therefore, GO is strongly hydrophilic and demonstrates good dispersibility in aqueous systems (Wu et al., 2013). Being negatively charged, GO is suitable for treating wastewater containing positively charged pollutants by promoting hydrogen bonding or electrostatic interactions (Kyzas at al., 2014).

The flat structure of GO gives it additional dimension as compared to other carbon allotropes and makes it an excellent adsorbent material for dye removal (Liu et al., 2012a; Zhu et al., 2010). The hydrophilic nature of GO is another important advantages for its choice/selection as dye adsorbent material. The hydroxyl, carboxyl and epoxy groups are found after the oxidation of graphite into layered graphene oxide (Ramesha et al., 2011). There are two distinct region in GO, one region is with sp^2 hybridized carbon domain and another region is decorated by different oxygenated groups (Duan et al., 2014).The carboxylic groups are found at the edges of the GO where as epoxy and hydroxyl groups are found on its basal plane. The oxygen containing functional groups are the major reason for getting a stable dispersion of GO in water or polar solvents through easy exfoliation. The carboxylic group exchanges ion with metal cations or positively charged organic molecules. The GO swells in contact with water (Duan et al., 2014). The ultra large oxygen containing group and excellent water dispersibility made GO a promising candidate for dye removal (Cheng et al., 2015). They added that water molecules can easily penetrate the space between the layers of GO nanosheets, which is one of the driving forces for the high adsorbing nature of GO toward dyes and other pollutants from wastewater. Besides functioning as dye adsorbent, there are reports on the use of graphene and graphene oxide for heavy metal ions removal (Yusuf et al., 2015).

Recent publication by Mao et al. (2020) reported that GO synthesized through modified Hummers Method were compared to graphite with removal efficiency at 99% and 16% respectively. The distinct result was due to the fact that GO contains functional groups which interact with cationic dye (MB) through adsorption process. They added that graphite possess low surface area with zero functional groups which make MB adsorption almost impossible. Studies on GO for dye removal from aqueous solution by Robati et al. (2016a) applied commercial single layer graphene oxide while basic red 12 (BR12) and methyl orange (MO) dyes as adsorbates. It was found that the optimized values of initial concentration of dyes, contact time, pH and adsorbent dose were found to be 0.2 mg/L in 100 minutes at pH 3 and 20 mg.

Another findings for GO (synthesized according to modified Hummer's method) application on Acid Orange 8 (AO 8) and Direct Red 23 (DR 23) removal was by Konicki et al. (2017). Later, study of GO by Lv et al. (2018) showed adsorption process towards neutral red (NR) and amido black 10B (AB) by π-π stacking, hydrophobic interaction, van der Waals forces and electrostatic interactions. Furthermore, another study by Gao et al. (2018) demonstrated that combined effects of GO-heavy metal ion complexes show different bioavailability and toxicity compared to GO and metal ions separately. In particular, the complex formed after adsorption process presented a significantly reduction in toxicity, an important initial result to assess the ecological risk of carbon nanomaterials. Liu et al. (2012b) prepared graphene by Hummer's method and it was found that the maximum adsorption capacity toward methylene blue adsorption was 153.85 mg/g which was a high value indicating good adsorbent. Basic Red 46 (BR 46) dye removal by purified natural graphene (monolayer graphene film) was studied by Elsagh et al. (2017) with adsorption capacity of 30.52 mg/g and equilibrium was reached after 90 minutes of contact time. Other findings specifically on MB removal by graphene-based materials are presented in Table 1.1.

From the studies reported, it is noted that the most promising results in terms of adsorption capacity were obtained at ambient temperature and neutral pH as experimental conditions. The fact could be comprehended as an advantage since it would exempt the treatment process from chemical inputs, for a pH adjustment, or high energy demand, for temperature control; therefore, lowering operation expenditures when GO is applied for water treatment.

Table 1.1

Various Reported Graphene-Based Adsorbents for MB Comparison

Adsorbent	Source & Method	Adsorbent Dosage (mg)	Removal Percentage (%)	Adsorption Capacity (mg/g)	Initial Dye Concentration (ppm)	pH	Temperature	Contact Time (min.)	Reference
SDS-exfoliated graphene	Ultrasonic exfoliation of graphite & dispersion	1.1	86.5	782.3	10, 50 and 100	3 – 9	25°C	2880	Sham & Notley, 2018
Exfoliated graphene oxide (EGO)	Modified Hummers & dispersion	11	95	-	40	6	-	160	Ramesha et al., 2011
Exfoliated graphene	Graphite exfoliation & freeze dried	10	105	511.70	500	6	Room temperature	60	Xue et al., 2016
Graphene	Modified Hummers & dispersion	20 - 170		153.85	20 – 120	3 – 10	293 K	0 - 1500	Konicki et al., 2017
Graphene oxide (GO)	Modified Hummers & dispersion	25	98	243.90	40 - 120	6	-	0 – 350	Li et al., 2013a

The adsorption for ionic dyes mainly relies on electrostatic interaction and covalent bonding. GO presented high adsorption efficiency of cationic dyes, but low affinity for anionic dyes due to the strong electrostatic repulsion (Zhang et al. 2016). On the other hand, graphene and graphene-based composites are good adsorbents for anionic dyes due to their ion exchange and covalent bonding capacity (Liu et al., 2012b).

1.2.2 GO Composite as Adsorbent

Both GO and GO-based nanomaterials have limits as adsorbents for pollutant removal from aqueous solution (Shen & Chen, 2015). Specifically, the broken *sp*^{2}-hybridized carbon skeleton eliminates the conjugated *p* region and weakens the affinity for aromatic pollutants (Shen & Chen, 2015). The dispersion-stable GO nanosheets are difficult to separate from solutions due to its strong hydrophilicity and nano-scaled size, resulting in undesirable effects for the efficient removal of pollutants (Chen et al., 2012a). Multiple layers of GO are found to aggregate in aqueous suspension leading to inefficient separation of pollutants from adjacent aqueous phases (Chen et al., 2012a; Wei et al., 2017). Since GO was present as a nanomaterial and presents high dispersibility in aqueous solution (Stankovich et al., 2007) practical applications are hindered: collection of GO sheets is difficult after adsorption, meanwhile, the unprecipitated GO may lead to potential nanotoxicity (Chen et al., 2016) to aquatic creatures. These problems restrict large scale practical applications of GO as adsorbents. Apart from that, the basic criteria to be met for a good adsorbent to fulfil the existing global demands are low price with easy availability, guaranteed superior adsorption performance, and flexibility in the structure that allows modification.

Thus, preparing composite adsorbent is one of the option in order to solve the aforementioned issue.

Natural polymers, such as polysaccharides are known for possessing a wide range of functional groups (Zhou et al., 2013; Esquerdo, et al., 2014). The presence of functional moieties such as −OH, $-CONH_2$, $-SO_3$, $-NH_2$, and −COOH on the polysaccharide backbone gives them flexibility to be tuned or tailored for a varying range of applications (Wang & Yu, 2021). As for instance, incorporating or blending them with other substances having promising adsorption capacity such as graphene oxide (GO) has indeed led to the innovative design of numerous sustainable dye adsorbents. Hence, numerous polymeric dye adsorbents with different chemical compositions and a wide range of morphology variations with the potential to adsorb selectively cationic, anionic, or both types of dyes have been reported (Zhang et al., 2014; Gao et al., 2013; Shukla et al., 2012).

So far, there have been continuous attempts (Shi et al., 2016; Liu et al., 2017) to increase the surface area and enhance the removal of dyes by incorporating GO with various natural polysaccharides. GO, when combined with the polymer matrix of polysaccharide, demonstrates tremendous improvement in its electrical and mechanical properties. Hence, GO is used nowadays as a substrate modified with other substances, preferably biopolymers, to assemble 3D-graphene nanomaterials (Wang et al., 2017; Shen et al., 2017) that possess increased surface area. The resulting composites not only possess the intrinsic excellent properties of the original substrates, but also have a 3D porous structure exhibiting much superior adsorption capacity. It is also important here to mention that the escalation to the 3D assembled structures makes them easily separable from aqueous solutions by simple filtration. In addition, several useful properties such as high efficiency, abundance, and low cost (Pooresmaeil & Namazi, 2018; Dehghani et al., 2017; Namazi et al. 2012) of polysaccharides classifies them as an ideal source of sustainable materials for the purpose of water purification. They exhibit excellent performance as an ideal and sustainable eco-friendly material in the field of wastewater remediation through the removal of heavy metal ions (Musarurwa & Tavengwa, 2020; Pooresmaeil & Namazi, 2020) and dye contaminants because of their adsorption, oxidation, and catalytic properties.

For these reasons, a wide range of GO-based adsorbents have been developed over recent years, such as GO-based aerogels (Wei et al., 2017) and composites (Nayl et al., 2020). Nanofibrillated kenaf cellulose (NFC) in particular is extensively used as an adsorbent in dye wastewater treatment because it contains large proportions of intra- and inter-molecular hydrogen bonds and has high porosity (Samir et al., 2005; Roy et al., 2009; Moon et al., 2011). This biomaterial has the advantages of non-toxicity and biocompatibility (Tshikovhi et al., 2020). Cellulose can act as substrate (Wei et al., 2017) for GO and help form stable adsorbent structures. In particular, the successful introduction of GO into products and water treatment application requires simple and cost effective method of producing GO. Thus, a combination of exfoliated graphene oxide and nanocellulose to make hybrid material is seen as the most viable option to suit these needs. Table 1.2 summarizes previous reports on GO-composite for methylene blue (MB) removal.

Table 1.2

Comparison of Various Reported Adsorbents Based on Graphene Oxide–Composite for MB Removal

Adsorbent[a]	Source & method	W[b] (mg)	Removal (%)	q_e[c] (mg/g)	C_0[d] (ppm)	pH	T[e] (K)	t[f] (min.)	Ref.
CGO	Modified Hummers Method and wet-spinning technique	20	-	383	160	6	298	50	Chen et. al., 2016
GO/CNFs	Modified Hummers Method, easy blending and freeze-drying process	20	98	44	50	-	-	350	Wang et. al., 2021
Chitosan/CMC/GO	Hummers Method, vacuum filtered and hot-air oven process	100	100	122	10	7	303	180	Kaur et al., 2019
RCE/GO	Hummers method, solution mixing-regeneration and freeze-drying process	50	99	68	20	6	298	30	Ren et al., 2018

[a] CGO = cellulose/GO. CNF = cellulose nanfibrils. CMC = carboxymethyl cellulose. RCE = regenerated cellulose.
[b] Adsorbent dosage
[c] Adsorption capacity
[d] Initial dye concentration
[e] Temperature
[f] Contact time

1.2.3 GO/TiO_2 for Photocatalysis

According to studies in the last decade, photocatalytic products covered almost 1500 million pounds of the global market (Lacombe & Keller, 2012). Among various photocatalytic materials, titanium dioxide (TiO_2) is the most favourable photocatalyst for the degradation of organic pollutants from water. This is due to its distinctive properties such as high activity, economic, low toxicity and stability of chemical and physical properties (Andreozzi et al., 2018). The earliest display of water electrochemical photolysis by TiO_2 was executed by Fujishima & Honda (1972) lead to an enormous amount of research into the photocatalytic activity of diverse metal oxides. In addition to photolysis of water, metal oxides have been employed as a photocatalyst for the degradation of a variety of water contaminants, with encouraging results (Chatterjee & Dasgupta, 2005; Herrmann, 1999).

Despite the fact that it has a number of interesting features, TiO_2 did not able to compete with other water treatment materials (Upadhyay et al., 2014). The main reason for this is having a defect of the large band gap (band-gap energy 3.2 EV) (Mehta et al., 2019) which require light irradiation with a wavelength shorter than 387 nm (UVA) (Nada et al., 2018). Plus, the rapid recombination of photo generated carriers in TiO_2 limits its photocatalytic application (Upadhyay et al., 2014) On another note, adsorption capacity of contaminants plays a critical role in photocatalytic process (Shandilya et al., 2018).

Graphene oxide (GO) also act as the best supportive component in photocatalyst for the zero-bandgap property. Doping (Yang et al., 2010; Choi et al., 1994), initiation of defects (Martyanov et al., 2004; Etacheri et al., 2011) and combination with band gap reduction was accomplished using electron acceptor materials (Li et al., 2013b; Jiang et al., 2013; Woan et al., 2009; Zhang et al, 2009). Among the aforementioned approach, one of the most common combinations is with electron acceptor materials. The use of graphene as an electron acceptor molecule in TiO_2 composites has been investigated, and some of the TiO_2/graphene composites reported in various research are included in Table 1.3. The combination of TiO_2 and graphene has been found to improve the catalyst's photocatalytic performance. When TiO_2 and graphene are combined, the band gap of the metal oxide is reduced due to energy-favoured hybridisation of the O 2p and C 2p atomic orbitals, resulting in the development of additional valence bands (Li et al., 2013). Thus, TiO_2 can be incorporated with carbon inorganic filler such as GO to decrease the recombination rate of the electrons and holes and tuning the band gap of TiO_2.

GO has been added to a titanium source when synthesizing TiO_2 by a hydrothermal method or a sol-gel method, and studies have shown that GO-TiO_2 catalysts have a broader spectral absorption range and higher photocatalytic performance than TiO_2 (Adamu et al., 2016). In a recent study, GO nanosheets with well embedded nanospherical TiO_2 hybrid (TGO) composite exhibits reduced recombination of charge carriers with remarkable catalytic activity for the photodegradation of organic dyes (Purkayastha et al., 2020). There are a lot of oxygen-containing functional groups in GO, which can serve as favourable anchoring centres and nucleation sites for active species or precursors (Garcia-Gallastegui et al., 2012). It can prevent the aggregation of TiO_2 and further enhance the photocatalytic activity due to the synergistic effects between GO and/or rGO nanosheets and TiO_2.

For this reason, it has been reported that GO/TiO_2 and/or rGO/TiO_2 nanocomposites can serve as a dye remover in aqueous solutions (Liu et al., 2011; Kim et al., 2012; Jiang et al., 2011; Shi et al., 2012).

The interface between TiO_2 and graphene, where there is an intensive coupling that allows charge separation and prevents recombination, is where the photocatalytic activity of hybrid materials is most dependent (Upadhyay et al., 2014). They stated that hybrid photocatalysts can be made much more effectively by in-situ growing graphene on TiO_2 or vice versa. In-situ synthesis of graphene on TiO_2 using a technique created by Wang et al. (2010a) exhibits about 2.5 times more MB photodegradation than pure Degaussa P25 TiO_2. Liang et al. (2010) reported on the uniform development of TiO_2 nanocrystals on GO substrate via hydrolysis and hydrothermal treatment. When compared to P25 TiO_2, the photocatalytic activity of the GO–TiO_2 hybrids demonstrated a three-fold increase in Rhodamine B dye degradation. This improvement was attributed to an increase in electronic interaction between GO and TiO_2 nanocrystals, as well as the hybrid material's increased surface area. Another aspect which rather important in finding a material for water treatment is the cost effectiveness which TiO_2/GO can offer since both materials are cheaper than other materials available (Wang et al., 2019)

Table 1.3

Comparison of the Photocatalytic Performance (Under UV-Light Irradiation) of Various Reported Graphene or GO/TiO_2 for MB Degradation

Photocatalytic material[a]	Source & method	W[b] (mg)	Removal (%)	C_0[c] (ppm)	pH	T[e] (K)	t[f] (min.)	Rate constant (min^{-1})	Ref.
GTNRA	Modified Hummers method & one-pot solvothermal	-	-	5	-	-	120	0.006	Wang et al., 2013
TiO_2/RGO-C	Modified Hummers method & one-step modified hydrothermal	30	98	12	-	-	120	0.020	Ju et al., 2017
TNS-GR	Hydrothermal pressurized oxidation method & solvothermal	50	82	50	-	-	120	0.009	Liu et al., 2018
GO/TiO_2 nanofibers	Ultrasonication	100	100	100	3	293	105	0.050	Hsu et al., 2020
GO/TiO_2	Improved Hummers & ultrasonic dispersion	50	85	10	5.5	298	450	-	Kurniawan, et. al., 2020

[a] GTNRA = graphene modified titania nanorod arrays. RGO-C = reduced graphene oxide/CTAB. TNS-GR = TiO_2 nanosheets-graphene.
[b] Adsorbent dosage
[c] Initial dye concentration

1.3 Producing Surfactant Exfoliated Graphene Oxide (sEGO)

In recent years, the production of graphene from graphite has been popularized by sonication assisted liquid-phase exfoliation (LPE) (Ciesielski & Samorì, 2014) in the presence of organic solvents (Hernandez et al., 2008; Coleman, 2009; Coleman, 2013; Wei & Sun, 2015; Johnson et al., 2015), ionic liquids (Wei & Sun, 2015; Wang et al., 2010b; Nuvoli et al., 2011; Ravula et al., 2015) and aqueous surfactant solutions (Ciesielski & Samorì, 2014; Wei & Sun, 2015; Johnson et al., 2015; Texter, 2014, Narayan & Kim, 2015). However, the production costs of GO are much lower compared to graphene (Hiew et al., 2018) which might be a reason for the extensive use of GO.

In order to keep the concept of environmental friendly and cost-saving process, it is important to find a production method which avoid using harsh chemicals such as organic solvents and strong acids (Wang & Zhang, 2019). Forming sEGO through a simple process along with the presence of surfactants that is compatible with graphene such as reported by Sham et al. (2018) is the answer to the previous dilemma. Surfactant assisted exfoliation offers advantages over the use of volatile organic solvents which are toxic and expensive. The presence of surfactants, stabilizer molecules of the dispersion, minimizes the surface energy, preventing the aggregation of the graphene sheets (Vera-López et al., 2018).

Thus, the use of surfactants as aqueous media is the perfect choice in completing electrochemical exfoliation process. The significance of surfactants applied for exfoliation of graphite was to decrease the surface tension of aqueous solution to complement with graphene properties making exfoliation process practical. The surfactant plays a critical role in promoting the exfoliation and dispersion of graphene in aqueous surfactant solutions. In these systems, the purpose of the surfactant is two-fold, which is as graphite exfoliator to form graphene oxide and graphene aggregation inhibitor (Notley, 2012). Commercially available surfactant such as sodium dodecylsulfate (SDS), bearing single surfactant tail was chosen as benchmark since little to none research regarding surfactant-graphene was reported as wastewater adsorbent and catalyst.

1.4 Graphene-philic Surfactants

Graphene is a material which require "precursor" in order to perform as pollutant scavenger. Therefore to fully realize the potential application of graphene-based materials as adsorbent, this issue must be addressed. "Precursor" here refers to surfactant. The role of surfactant in dispersion is two-fold: (i) to ease graphite sonication thus forming sEGO and (ii) to homogenize the colloidal environment including maintaining the stability of graphene dispersion in the solution (Notley, 2012; Du, 2013).

Surfactants' capacity to adsorb at interfaces and self-assemble as micelles is advantageous for intercalation within graphene layers (Liu et al., 2013; Najafabadi & Gyenge, 2014) and it promotes extra sEGO surface area to further enhance adsorption. Earlier, the common surfactant sodium *n*-dodecylsulfate (SDS) has been applied in producing graphene with exfoliation was found optimum at surface tension of 41.0 mN ml^{-1} in aqueous solution with mixture of either methyl alcohol, ethyl alcohol or isopropyl alcohol as surface-tension-reducing-agents, STRAs (Yeon et al., 2015). Later, SDS has also been used for the production of exfoliated graphene in aqueous solution alone and subsequently applied in MB removal from aqueous solution (Sham & Notley, 2018).

Wang & Zhang (2019) produced graphene from graphite exfoliation technique using surfactant solutions as electrolytes such as dodecyl trimethyl ammonium bromide (DTAB) and sodium dodecyl benzene sulfonate (SDBS) with SDBS showed the best effect for exfoliation (highest graphene yield). However, these references were specifically focusing on graphene production using surfactant. The hydrophobic feature of graphene leads to agglomeration of graphene sheets into graphitic layered structures or better known as agglomerates, therefore spontaneous wetting by water is not possible (Mohamed et al., 2016).

Recent publication by Hu et al. (2019) provide information regarding implementation of anionic surfactant being better than cationic surfactant in producing GO from graphite exfoliation. Intercalation of anionic surfactants into the interlayers of graphite by hydrogen bonding and hydrophobic forces leads to weak electrostatic forces formation which resulting in exfoliation of graphite (Hu et al., 2019). Thus, the decision on choosing a series of anionic surfactants were appropriate in surfactant-assisted graphene oxide fabrication.

In order to achieve a thermodynamically stable colloidal system, surfactant is needed to lower the interfacial energy among two immiscible phases either by strongly bind the target compound or solvated by continuous phase (Goodwin, 2009; Mohamed et al., 2010). At the interface of graphene-solution, the surfactant tails adsorbed which facilitated by hydrophobic interactions to help separate the graphene sheets to avoid agglomeration by steric or electrostatic stabilization (Lotya et al., 2009). Applying concept of surfactants that display compatibility with graphene surface results in "graphene-philic" groups. This term was introduced by a Mohamed et al. (2016) where they used surfactants as stabilizing agents for the development of graphene nanocomposite for latex technology.

Using ionic surfactants, a prior study found that increasing the number of surfactant tails (from one to three) improves the compatibility of graphene surfaces with surfactant molecules, allowing better exfoliation (Zhang et al., 2014). Previous statement were proven by findings by Sagisaka et al. (2014) & Czajka et al. (2017) whom stated that surfactants or amphiphilic molecules featuring highly-methylated alkyl-tails would effectively reducing aqueous media surface tension which is expected to help in promoting graphite exfoliation. Further modification of surfactants by changing traditional sodium counter ion by Sagisaka et al. (2021) provide proof of further decrease of critical micelle concentration (cmc). Previously, Mohamed et al. (2018) stated that production of graphene decrease at a certain concentration after cmc (ideal surfactant concentration).

The micellisation of short-chain ILs such as [C_4mim][BF_4] leads to its aggregation aqueous environments (Bowers et al., 2004; Singh & Kumar, 2007). It was shown that imidazolium-based ILs have better surface-active properties compared with analogous common ionic surfactants (Dong et al., 2007). Graphene exfoliation by surfactant ionic liquids (SAILs) has also been achieved (Kaur et al., 2020). Kaur et al. (2020) provide results that by using SAIL at minimum concentration leads in effective graphene exfoliation with colloidal stability up to one month.

Recent work on graphene-philic surfactants was published by Mohamed et al. (2018a) which employed anionic surfactant ionic liquids as exfoliating and stabilizing agents that optimized the cellulose conductive paper produced for electrical properties enhancement. Surfactants were designed to meet the compatibility with graphene surface. Commercial phenyl surfactant, SDBS and SDS were compared to modified single chain anionic surfactant ionic liquids (SAILs) in order to achieve dissolution/dispersion. The relationship between surfactant molecular structures of conventional straight-chain anionic graphene-philic surfactants to SAILs for graphene dispersion stability were investigated. Results proved that the presence of imidazolium cation in the anionic surfactant appeared to cause exfoliation increment including stabilised graphene dispersion.

1.5 Problem Statement, Research Aim and Objectives

1.5.1 Problem Statement

Current available (commercial) surfactant in the market such as sodium dodecyl sulfate (SDS) and a few others are limited for improving graphene production dispersion in colloidal environment. In present time, optimised exfoliated graphene assisted by surfactant are not available especially for wastewater treatment applications. Thus, the studies and optimisation of surfactant chemical structures for wastewater treatment will be the main focus.

1.5.2 Aim

The aims of this thesis were to systematically study the role and the stabilisation mechanism of graphene-philic surfactants for the production of graphene oxide and their applications for methylene blue removal.

1.5.3 Objectives

The objectives of this research were firstly the optimisation of surfactants into highly-branched, surfactant ionic-liquids (BMIM) and anilinium surfactants. Secondly is the production of surfactant-assisted exfoliated graphene oxide (sEGO) from electrochemical exfoliation method. Thirdly, preparation and characterisation of sEGO nanofibrillated kenaf cellulose (NFC) composites and sEGO/TiO_2 photocatalysts for methylene blue (MB) removal. Next is interfacial behaviour study between surfactants, sEGO and sEGO/TiO_2 through air-water surface tension measurement. Finally the relationship between self-assembly structure of highly-branched, BMIM and anilinium surfactants with colloidal stability studies of sEGO, sEGO/NFC & sEGO/TiO_2.

1.6 Scope of Study

In order to fulfil the research gap, the main focus of the projects here are modifying surfactants structure to optimize graphene oxide production which were then used for wastewater treatment through adsorption and photocatalysis. The graphene oxide was produced using electrochemical approach with the assistance of surfactant. The as-produced graphene oxide was used for methylene blue removal in its suspension form, as a composite with nanofibrillated kenaf cellulose, and embedded in TiO_2. The surfactants structure are based on commercial single chain (sodium dodecylsulfate), double chain Aerosol-OT (AOT) and triple chain custom-made surfactant. Modification on surfactant hydrophilic counterpart was done by exchanging the traditional sodium counter-ion with aromatic groups.

These custom-made surfactants was characterized using proton Nuclear Magnetic Resonance (^1H NMR) spectroscopy to ascertain the chemical structures. A Willhelmy tensiometer was used for air-water (a/w) surface tension measurement of surfactant solutions along with zeta (ζ) potential measurement for sEGO surface charge determination. Particle size of surfactants and sEGO were determined by dynamic light-scattering (DLS). Meanwhile, the shapes and sizes of the self-assembled materials were studied using small-angle neutron scattering (SANS).

All of the structural and morphology analysis for sEGO, sEGO composites and sEGO/metal oxide catalysts were characterized using Raman spectroscopy, Field Emission Scanning Electron Microscopy (FESEM) and High Resolution

Transmission Electron Microscopy (HRTEM). Batch-adsorption and photocatalytic studies were evaluated using UV spectrophotometer.

1.7 Significance of Study

There has been a vast research regarding adsorbents using GO with various methods of production and modification. Yet, less attention given on specifically producing GO through one-pot electrochemical exfoliation utilizing modified surfactant for water treatment. Thus, the main purpose of this work is to study the effect of modifying surfactant headgroup and the hydrophobic tails towards micelles formation on GO. Next, is to investigate the enhancement of adsorption and photocatalytic studies of methylene blue removal in aqueous solution using the produced GO. Although several studies have been performed (Ramesha et al., 2011; Lotya et al., 2009; McCoy et al., 2018), there is currently a lack of knowledge concerning the role of adsorbed surfactant in GO synthesis and dye removal. Furthermore, contemporary research has mostly focused on the efficacy and optimisation of exfoliation, with the surfactant serving simply as a stabilising factor (Sham & Notley, 2018), rather of addressing the principles of the contaminant and dye removal. The ultimate goal is to create surfactants that promote both efficient exfoliation and removal of dye at the same time.

The roles of sEGO as an efficient adsorbent and catalyst for methylene blue removal in aqueous solution were studied. Both adsorption and photocatalytic studies were conducted at various initial methylene blue concentration and contact time. UV-

Visible spectroscopy was used to collect the absorbance value data. The adsorption experiment data obtained from batch adsorption and photocatalytic studies were analysed and interpreted using different kinetic and isotherm models (adsorption studies) and photodegradation performance respectively to assess the removal behaviour of MB by sEGO and sEGO/metal oxide. The results presented here show new potential for using sEGO as an adsorbent and catalyst in direct (*in situ*) applications and provide a basis for the development of future surfactants for carbon nanomaterials-based water treatment. Apart from that, the relationship of surfactant structure-nanocomposite performance for the development of stabiliser/GO/nanocellulose dye adsorbents is highlighted. Finally, accomplishment in stabiliser/GO/metal oxide catalyst production for decontamination process.

1.8 Thesis Outline

Thesis is organized in five chapters. Chapter 1 is a preface on research background and aim of the study. This part bring forth general overview regarding graphene oxide (GO) function in water treatment including surfactant role for GO production and finally applied in water treatment. Chapter 2 is literature review which explains fundamental knowledge related to the topics studied in this thesis. This chapter includes the theory about surfactants, ionic liquids, graphene oxide, and colloidal stability of graphene oxide in surfactant solutions, adsorption and photocatalysis studies. Chapter 3 is experimental section which gives thorough details of the synthesize method and characterization of surfactant-assisted exfoliated graphene oxide (sEGO), sEGO composite and sEGO/metal oxide catalysts used in this study.

Discussion on the ^{1}H NMR spectroscopy of the synthesized surfactants also appeared in this chapter. Chapter 4 is composed of 3 sections. Varying the surfactant chain degree and methylation is reported in section 1 (4.1). The sEGO suspension which was obtained from surfactant-assisted graphite exfoliation was directly used as methylene blue adsorbent. In the second section (4.2), sodium counter-ion in surfactants were substituted with aromatic group counter-ion and sEGO produced through similar process as in (4.1) were composited and also used as adsorbent. Exchange in counter-ion but with different type of aromatic group can be found in the final section (4.3). sEGO produced by identical graphite exfoliation as the previous sections were made into catalyst along with metal oxide. This is followed by adsorption and photocatalytic studies. Finally, Chapter 5 summarizes the key research findings and also includes recommendations of the future work.