Entry to the Stockholm Junior Water Prize 2018

A Novel, Eco-friendly Synthesis of Reduced Graphene Oxide from Durian Rind and Sugarcane Bagasse for Water Filters

By:

Johnny Xiao Hong Yu
Caleb Liow Jia Le

Hwa Chong Institution
Singapore

Mentor: Mrs Sow-Peh Yoke Keow

Abstract

Graphene oxide (GO) and reduced graphene oxide (rGO) have great potential as adsorbents for water purification purposes and can be made into membranes. .However, the conventional method of synthesis, Hummers' method, involves the oxidation of graphite using corrosive chemicals such as concentrated sulfuric acid and potassium manganate(VII). Although Hummers' method is effective, it is extremely expensive and produces toxic gases such as nitrogen dioxide which causes acid rain.

In this study, reduced graphene oxide (rGO) was synthesized from agro-wastes (durian rind and sugarcane bagasse) using an eco-friendly, simple and low-cost process. Agro-waste was added to ferrocene and the mixture was oxidised in a furnace under normal atmospheric conditions. Some of its oxygen functional groups were reduced by ferrocene in the furnace to produce rGO. After synthesis, the rGO was characterized using X-Ray Diffraction (XRD), Raman Spectroscopy, Energy Dispersive Spectroscopy (EDS) and Scanning Electron Microscopy (SEM). Batch mode adsorption studies of the synthesized rGO was carried out with methylene blue, a toxic dye, and copper(II) ion, a toxic heavy metal ion. To explore the applications of the rGO, it was coated onto MCE filter paper, as well as packed into a syringe which acts as a column filter. Both types of filters were tested for their effectiveness in removing methylene blue and copper(II) ions.

Results showed that rGO was successfully synthesized from durian rind. In contrast, sugarcane bagasse resulted in the formation of a mixture of both GO and rGO.

For the batch mode study on the removal of pollutants, rGO was comparable to commercial activated carbon in removing methylene blue and 33% more effective than commercial activated carbon in removing copper(II) ions. When coated onto MCE filter papers, rGO filter was able to remove 97% methylene blue and close to 100% of copper(II) ions. When packed into a column, rGO was able to remove almost 100% of both methylene and copper(II) ions across 6 cycles of filtration. rGO synthesized from durian rind has great potential to be incorporated into filters and be used to remove organic dyes and heavy metal ions from polluted water.

Content

List of Abbreviations

Abbreviation	Meaning
rGO	Reduced Graphene Oxide
GO	Graphene Oxide
MCE	Mixed Cellulose Ester
SEM	Scanning Electron Microscope
EDS	Energy Dispersive Spectrum
XRD	X Ray Diffraction

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1. Introduction

1.1 Literature review

Graphene materials have grown to prominence in recent years due to their exceptional electronic, thermal, and mechanical properties (Zhu *et al*., 2010). Graphene oxide (GO), in particular, has a broad range of applications ranging from electromagnetic interference shielding (Liang et al, 2009) and biomedical application such as biosensors (Chung *et al*., 2013), to water purification, specifically to create membrane filters, due to its ultrafast permanence, outstanding mechanical properties and high chemical stability (Jung, Woo, Lee, & Han, 2015). A reduced form of graphene oxide, known as reduced graphene oxide (rGO), has recently attracted increasing attention in liquid and gas separation (Liu, Wang, & Zhang, 2014). Both GO and rGO have been made into membranes for water purification purposes as they contain nanosheets, allowing gases and ions with smaller sizes than those of the channels to permeate, while blocking all other larger species. However, rGO membranes, with a similar layered structure as GO membranes, exhibit better stability in water as they can retain the compact interlayer spacing due to the significantly reduced amount of hydrated functional groups (Liu, Wang, & Zhang, 2014).

rGO is commonly derived from the reduction of graphene oxide. Graphene oxide is formed when graphite is oxidised, introducing oxygenated functionalities in the graphite structure which not only expand the layer separation, but also makes the material hydrophilic or water-loving. The most typical method of synthesizing graphene oxide is Hummers' Method, which involves the oxidation of graphite through treatment with potassium manganate (VII) and sodium nitrate in concentrated sulfuric acid (Hummers & Offeman, 1958). However, this method results in the production of toxic gases such as nitrogen dioxide and dinitrogen tetroxide, which is harmful to the environment and human health (Latza, Gerdes & Baur, 2008). Hence, there is a need to explore more eco-friendly methods of synthesizing reduced graphene oxide.

More eco-friendly techniques of synthesising graphene oxide include modifications of Hummers' Method, such as by removing the use of sodium nitrate to eliminate the production of toxic gases (Chen *et al*., 2013), or mechanical exfoliation techniques. However, most of these techniques are complicated and expensive (Guo & Dong, 2011).

In this study, reduced graphene oxide was synthesized from durian rind and sugarcane bagasse and its feasibility to be incorporated into filters used for water treatment was evaluated. The proposed method involves the carbonization of durian rind and sugarcane bagasse which are rich in cellulose (Manshor *et al*., 2012) in a furnace to form carbon which is then oxidized by air to form GO. Addition of ferrocene, a reducing agent, reduces some of the oxygen functional groups, yielding rGO. Compared to the current method of synthesis, the proposed method in this study has a shorter reaction time, does not produce toxic gases and is of lower cost.

Durian (*Durio zibethinus*) is a fruit (Figure 1) commonly found in Southeast-Asia and is a delicacy to most local populations. In 2016, Singapore imported as much as 16600 tonnes of durian for consumption (Soh, 2018). The edible portion of the fruit accounts for about 15-30% of the mass of the entire fruit (Brown, 1997). Therefore about 70-85% of the fruit is discarded as waste and would result in environmental problems such as land pollution if not disposed of in a proper manner (Hameed & Hakimi, 2007). Sugarcane bagasse is the fibrous remains of sugarcane stalks after being crushed for juice extraction. It can be easily obtained from hawker stalls selling sugarcane drinks. 54 million tonnes of bagasse are produced annually throughout the world (Khadija *et al.*, 2008). It would be meaningful and useful if both durian rind and sugarcane bagasse can be converted into rGO which can be used in water purification.

(a) (b)

Figure 1: (a) Durian fruit and (b) Discarded durian rind

Copper (II) ions and methylene blue are common water pollutants and hence they are chosen to evaluate the effectiveness of the rGO synthesized in water purification. Copper(II) ions are often discharged by industries involved in electroplating, batteries manufacturing, mining, metal finishing and many more (Aguilera et al., 2010). From November 2017 to January 2018, 17 companies from various industries such as printing and electroplating in Singapore were found to discharge industrial effluents containing high levels of copper into the public sewer illegally, negatively impacting the quality of feedstock for reclaimed water production (Ng, 2018). Although tiny amounts of copper are essential for human health, excess amounts can cause adverse health effects, including anaemia, kidney failure and liver damage (Abbas et al., 2014). Methylene blue is a common dye mostly used by industries involved in textile, paper, rubber, plastics, and leather (Mohammed, Shitu, & Ibrahim, 2014). About 15% of the total world production of dyes is lost during the dyeing process and is released as liquid effluents, thus causing pollution (Zollinger, 1987). For example, in Bangladesh, wastewater from textile industries is being discharged into a canal in Savar, resulting in serious water pollution (The Straits Times, 2013). Dyes are harmful as they interfere with the normal photosynthetic activities of aquatic life and the majority of them take a very long time to biodegrade. When ingested in high doses, methylene blue may cause hypotension, nausea, vomiting, abdominal pain and hemolysis (Wiklund, 2010).

1.2 Scope and Objectives

The overarching aim of this study is to enhance the quality of life through water and wastewater treatment. The scope of this study is not only relevant to the local context of Singapore, but is also a global issue that is affecting millions around the world. This study involves looking into two common water pollutants, which are methylene blue and copper (II) ions. It encompasses both the synthesis of rGO, as well as its application in the domain of water filtration, through creating water filters and investigating their ability to treat polluted water for domestic and industrial uses.

The objectives included:

1. To synthesize and characterize rGO from durian and bagasse waste via a novel and eco-friendly method.
2. To evaluate the effectiveness of the synthesized rGO in removing copper (II) ions and methylene blue dye from water
3. To coat rGO onto Mixed Cellulose Ester (MCE) filter and pack rGO into a syringe to create filters.
4. To evaluate the effectiveness of the rGO filters in removing copper (II) ions and methylene blue dye from water

2. Materials and Methods

2.1 Materials

Ferrocene ($Fe(C_5H_5)_2$) was purchased from Sigma Aldrich. Methylene blue and commercial activated carbon were purchased from Unichem while copper(II) sulfate was purchased from GCE Chemicals. Durian rind and sugarcane bagasse were collected from local fruit stalls and hawker stalls respectively.

2.2 Synthesis of reduced graphene oxide (rGO) from durian rind and sugarcane bagasse

Durian rind and sugarcane bagasse were washed with deionised water, dried, crushed and blended to produce fine powder. A sample of 0.5 g of ground durian husk or sugarcane bagasse powder was mixed with 0.1 g of ferrocene in a crucible which was then carbonized and oxidized in a furnace at 300 °C for 20 min under atmospheric conditions. The products obtained were characterized using Raman Spectroscopy, X-Ray Powder Diffraction (XRD), Scanning Electron Microscopy (SEM) and Energy Dispersive Spectroscopy (EDS).

2.3 Adsorption studies (Batch mode) of reduced graphene oxide (rGO)

0.05g of rGO (from both durian rind and sugarcane bagasse) was stirred on a magnetic stirrer with 20ml of solution containing 50 mg/l of methylene blue or copper (II) ion. After 24 hours, the mixture was centrifuged and the supernatant was analysed for the concentration of remaining pollutant. Methylene blue was analysed using a UV-VIS spectrophotometer at 664.5 nm while copper (II) ion was analysed using a colorimeter (Hach DR 890). Five replicates were conducted for each pollutant. The adsorption studies were also conducted on commercial activated carbon with the same mass as rGO and under the same conditions to compare the effectiveness of rGO synthesized with that of a commercial adsorbent.

2.4 Fabrication of rGO coated MCE filter

rGO suspension of 1g/100 ml was prepared and sonicated for 1 hour. The rGO suspension was filtered under vacuum through a MCE (mixed cellulose ester, 0.45 μm, Steritech) membrane filter. After filtration, the rGO coated MCE filter paper was dried at 45°C for 24 hours.

2.5 Determining the effectiveness of rGO coated MCE filter in filtering copper(II) ions and methylene blue

Solution containing 50 mg/l of methylene blue or copper (II) ion was filtered through the rGO coated MCE filter paper and MCE filter without rGO (control) using the set up shown in Figure 2. The filtrate was analysed for the remaining methylene blue and copper (II) ion.

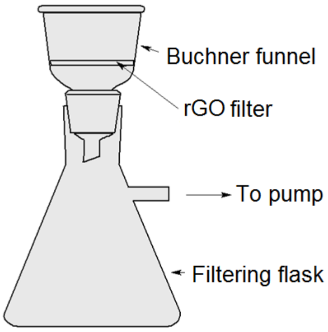


Figure 2: Filtration set up to evaluate the effectiveness of the rGO MCE filter

2.6 rGO column filter

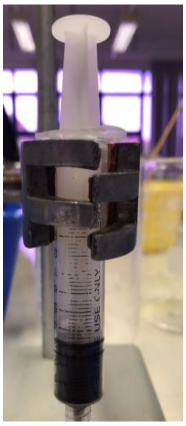


Figure 3: rGO column filter

In addition to the rGO coated MCE filter, the feasibility of using rGO in a column filter was also investigated. A 10 ml syringe was used as the column and it was packed with 1.0 g of rGO synthesized from durian rind. Aliquots of 10 ml of 50 mg/l methylene blue and copper (II) ion solution were passed through the filter. The syringe plunger was used to facilitate the filtration. The effluent was analysed for the amount of methylene blue and copper (II) ions remaining. A total of 6 rounds of filtration were carried out for each pollutant.

3. Results & Discussions

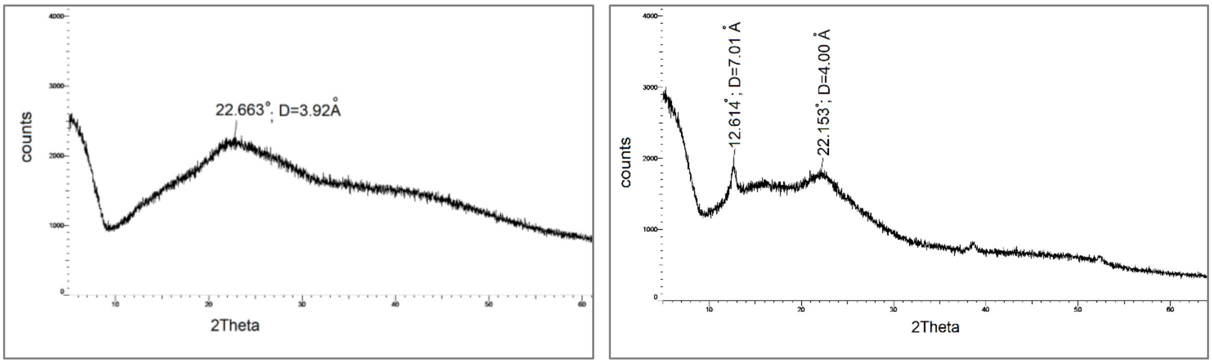
3.1 Characterisation of rGO

The rGO synthesized was characterised using 3 analytical methods: X-ray Diffraction (XRD), Raman Spectroscopy, Scanning Electron Microscopy (SEM) and Energy Dispersive Spectroscopy (EDS).

3.1.1 By XRD

The XRD of rGO synthesized from durian rind (Figure 4 (a)) shows a peak at 22.663° corresponding to the interlayer distance of 3.92 Å which is characteristic of rGO. This result is in agreement with rGO synthesized by other methods (Chen et al., 2016; Pau et al., 2015).

The XRD of rGO synthesized from sugarcane bagasse (Figure 4(b)) however displays 2 peaks at 12.614° corresponding to the interlayer distance of 7.01 Å which is characteristic of GO synthesised by other researchers (Paulchamy, Arthi, & Lignesh, 2015; Somanathan et al., 2015) and 22.153° corresponding to the interlayer distance of 4.00 Å which is characteristic of rGO. This suggests that a mixture GO and rGO have been produced from carbonisation of sugarcane bagasse, unlike that of durian rind where only rGO has been synthesized.



(a) (b)

Figure 4: XRD pattern of (a) rGO synthesized from durian rind and (b) rGO synthesized from sugarcane bagasse

3.1.2 By Raman Spectroscopy

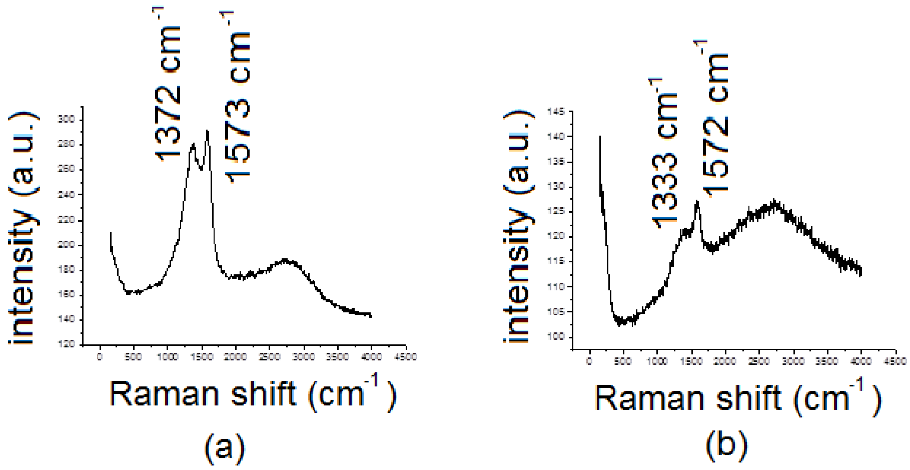
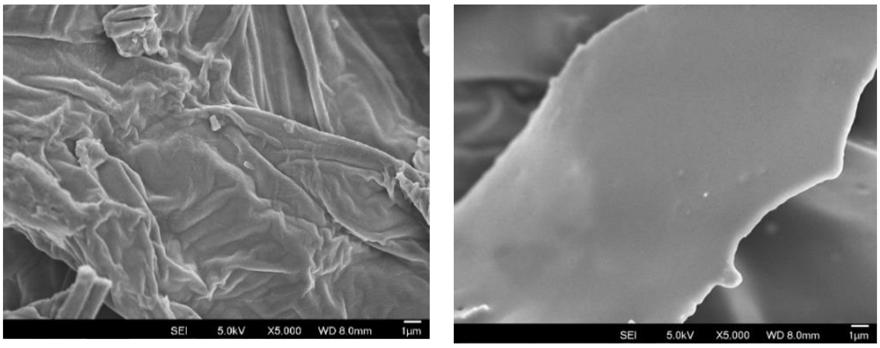


Figure 5: Raman spectrum of (a) rGO synthesized from durian rind and (b) rGO synthesized from sugarcane bagasse

Raman spectrum of rGO synthesized from durian rind (Figure 5(a)) displays 2 bands at 1372 cm^{-1} (D band) and 1573 cm^{-1} (G band) respectively. The G band is associated with the in plane vibrations of sp^2 bonded carbon atoms while the D band is due to the out of plane vibrations attributed to the presence of structural defects. Both bands are characteristic of rGO (Chen et al., 2016). Similarly, rGO from sugarcane bagasse also shows 2 bands at 1333 cm^{-1} (D band) and 1572 cm^{-1} (G band).

3.1.3 By SEM

The SEM image of rGO from durian rind at 1 μm magnification (Figure 6(a)) suggests that its surface is rough, uneven and wrinkled. In contrast, the surface of rGO from sugarcane bagasse is relatively smooth (Figure 6(b)).



(a) (b)

Figure 6: SEM image of (a) rGO from durian rind and (b) rGO from sugarcane bagasse

3.1.4 By EDS

Figure 7 shows the EDS spectra of rGO and commercial activated carbon. It is evident that both have different composition, with rGO having a much higher oxygen content but lower carbon content as compared to commercial activated carbon.

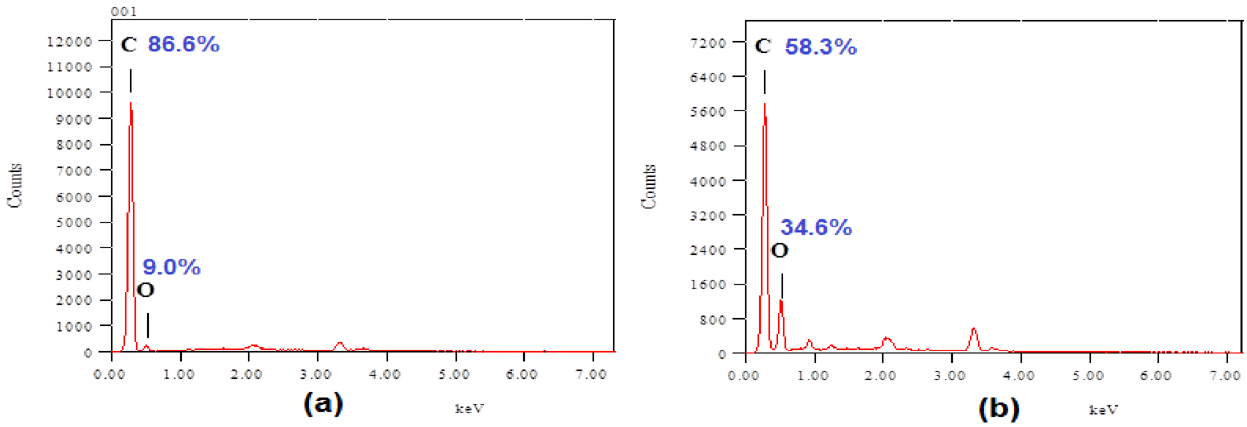


Figure 7: EDS spectrum of (a) commercial activated carbon and (b) rGO from durian rind

3.2 Adsorption studies (batch mode) of rGO

Batch adsorption studies were carried out with 0.05 g of rGO and commercial activated carbon with 20 ml of solutions containing either 50mg/l of copper(II) ion or methylene blue. Figure 8 shows that the rGO from durian is comparable to commercial activated carbon in adsorbing methylene blue while rGO from sugarcane bagasse is evidently less effective.

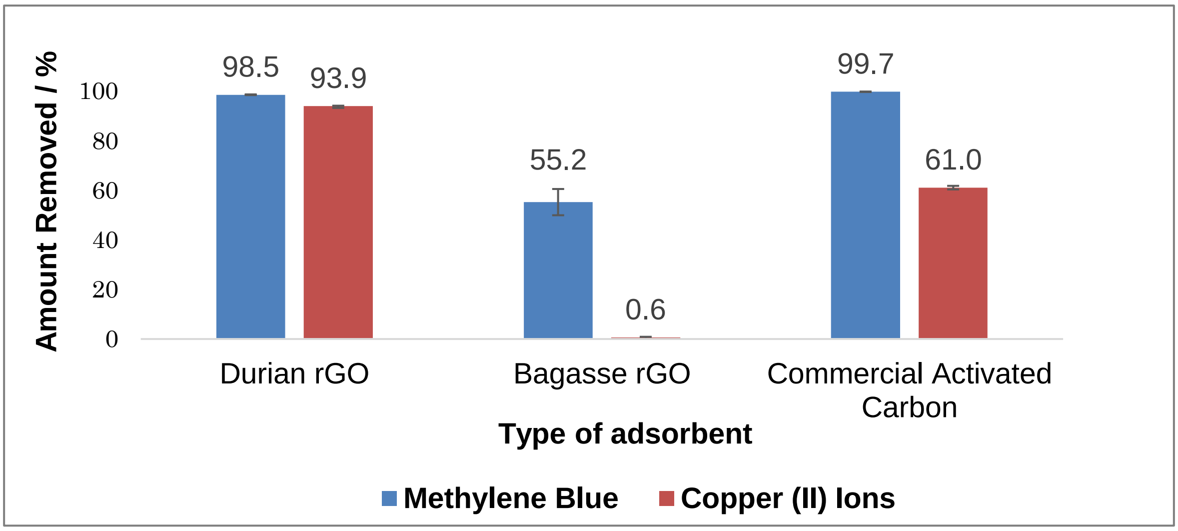


Figure 8: Adsorption of methylene blue and copper (II) ions by different adsorbents.

The stark difference in the performance between the durian rind rGO and the bagasse rGO is likely due to the difference in the structure of the two types of rGO, as supported by the SEM images shown in Figure 6. The surface of rGO from durian rind is rough and uneven and hence provides a large surface area for effective adsorption. In contrast, the surface of rGO from sugarcane bagasse is smooth, which may explain why adsorption is not so effective.

Interestingly, rGO from durian rind is able to remove 33% more copper(II) ions as compared to commercial activated carbon , hence showing great potential to be developed as filters for water purification. This is because rGO from durian rind contains a greater percentage of oxygen than commercial activated carbon, as shown in the Energy Dispersive Spectrum (EDS) spectra (Figure 7). While rGO contains 34.6% of oxygen, commercial activated carbon contains only 9.0% of oxygen. The oxygen-containing functional groups bind to copper (II) ions via dative bonds, thus removing them from solution. Again, rGO from sugarcane bagasse is least effective in adsorbing copper (II) ions; this finding is in agreement with the methylene blue results.

As rGO synthesized from durian rind shows promising results in the removal of both methylene blue and copper (II) ions, it is used for the subsequent filter studies.

3.3 Effectiveness of rGO-coated MCE filter in filtering methylene blue and copper(II) ions

Figure 9: rGO-coated MCE filter

The rGO-coated MCE filter (Figure 9) was used to filter solution containing 50 mg/l methylene blue and copper (II) ion. The filtrate collected was passed through the filter again for up to 4 cycles to determine the effectiveness of the filter.

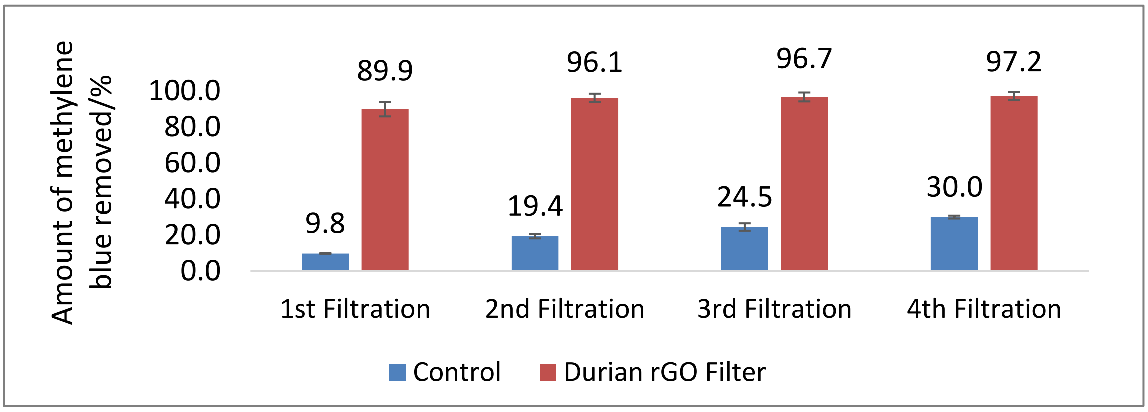


Figure 10: Adsorption of methylene blue by rGO-coated MCE filter.

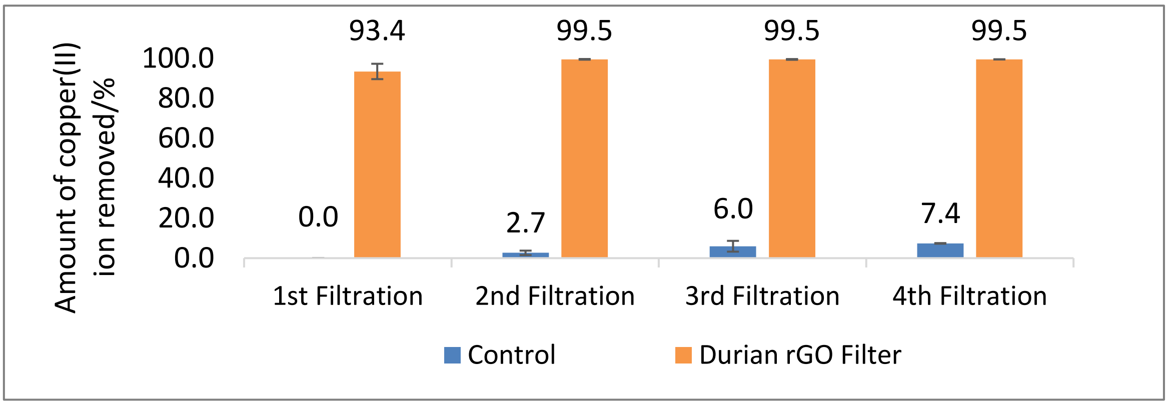


Figure 11: Adsorption of copper (II) ions by rGO coated MCE filter.

For methylene blue, after a large increase in percentage of methylene blue removed after the 2nd filtration, the effectiveness of the rGO filter remained relatively unchanged from the 3rd to the 4th filtration. A similar trend was also observed in the removal of copper (II) ions, where the effectiveness of the rGO membrane remained constant at 99.5% from the 2nd to 4th filtration (figure 11). Durian rGO filter is effective in removing both methylene blue and copper (II) ions from water, up to 97.2% for methylene blue and 99.5% for copper (II) ions. In contrast, the control (MCE filter paper without rGO) was only able to remove 30.0% of methylene blue and

7.4 % of copper (II) ions.

rGO is highly effective in adsorbing both organic dye and metal ions due to the presence of oxygen functional groups in its structure (Figure 12). These groups interact with the dye via electrostatic interaction and hydrogen bonds (Minitha et al., 2017). In addition, the conjugated carbon in rGO is able to interact with methylene blue via pi-pi interaction. The oxygen functional groups on rGO are also able to bind to metal ions via dative bonds (Sitko et al., 2013).

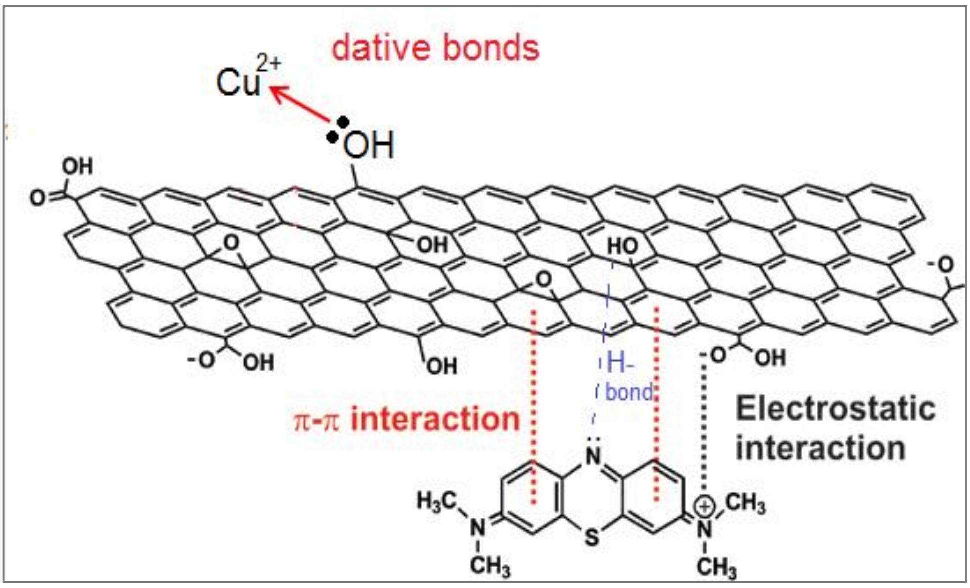


Figure 12: Adsorption mechanism of copper (II) ion and methylene blue by rGO

3.4 Effectiveness of rGO column filter in filtering methylene blue and copper (II) ion

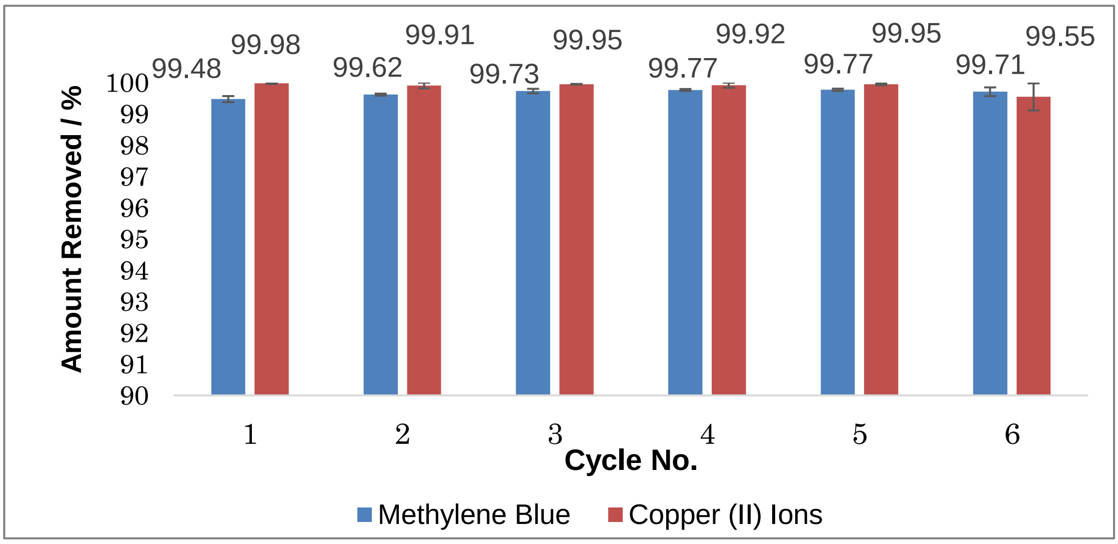


Figure 13: Effectiveness of rGO column filter in removing methylene blue and Cu^{2+}.

The durian rGO column filter is shown to be extremely effective in removing both methylene blue dye and copper (II) ions (Figure 13), achieving almost 100% removal for both pollutants across 6 cycles. The effectiveness of the column filter remained relatively constant across the 6 cycles of filtration. The concentrations of copper(II) ion remaining in the effluents after passing through the rGO column filter after each cycle were all below 1.3 mg/l, which is the maximum contaminant level set for copper by United States Environmental Protection Agency. Although methylene blue does not have a specified maximum contaminant level, the presence of even small amount of dyes (1-2 mg/l) is highly visible and aesthetically undesirable (Mishra and Soni, 2016). Concentrations of methylene blue remaining in the effluents were all below 0.5 mg/l.

4. Conclusions & Recommendations

Reduced graphene oxide (rGO), a useful product, has been successfully synthesized from durian rind via a novel, simple, rapid and eco-friendly method. The cost of rGO synthesized in this study is comparable to that of commercial activated carbon and a lot lower than commercial rGO as it requires only one step and only one chemical unlike the conventional Hummers' method which requires multi-stages and several chemicals. The rGO synthesized from durian rind is comparable to commercially available activated carbon in removing methylene blue and is more effective than commercial activated carbon in removing copper (II) ions. When coated onto MCE filter paper, the rGO filter is able to remove more than 95% of both methylene blue and copper (II) ions. When packed into a syringe, the rGO column filter is able to remove close to 100% of both methylene blue and copper (II) ions across 6 cycles of filtration. rGO synthesized from durian rind has great potential to be exploited as water filters to treat water containing dye and metal ions.

In future, the study could be extended to include other organic pollutants such as pesticides and other metal ions such as lead (II) ions so as to better determine the effectiveness of durian rGO in water purification. More studies could be conducted on the rGO filters to determine the maximum amount of polluted water it could filter as well as the reusability of the rGO filters. The rGO column filter also has potential to be scaled up and utilised in both domestic and industrial usage, such as in filtering industrial effluents before the release into water bodies. The rGO-MCE filter can be used in household water purification systems.

The physical structure of rGO lends itself easily to being used as a membrane. rGO consists of layers stacked on top of each other. These stacked sheets have interconnected channels running through them which act as nanosized membrane pores, filtering out undesirable substances such as pollutants and salts but allowing water molecules to permeate through (Wang et al., 2018). Hence rGO membranes have potential to be used in processes such as desalination and reverse osmosis. Therefore, durian rGO shows enormous potential in the field of water purification and filtration, and can be applied in a wide range of domestic and industrial uses.

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