Adsorption of Copper Ions from Environmental Water Samples by Graphene Oxide/Cellulose Acetate- Mixed Matrix Membrane

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Nowadays, the removal process of heavy metal ions by utilizing membrane technology, such as mixed matrix membrane (MMM), has many advantages, such as high effectiveness in adsorption performance and cost, rapid and simple procedures. In this study, a composite mixed matrix membrane, namely graphene oxide-cellulose acetate (GO/CAM-MMM) is developed. Cellulose acetate (CA) is a biodegradable polymer, and graphene oxide (GO) has high abundancy with oxygen-containing functional groups and has been widely utilized as an adsorbent. The GO/CAM-MMM has been characterized using Fourier transform Infrared (FTIR) spectroscopy and field emission scanning electron microscopy (FESEM) and used as an adsorbent to remove Cu^{2+} ions in water samples. A maximum adsorption capacity of 143 mg/g at 30 min of contact time for the removal of 50 ppm of Cu^{2+} ion at pH 5 of water samples was achieved by the best-performing MMM, which was fitted with a Langmuir isotherm and a pseudo-second-order kinetic study. Thus, the developed membrane has good potential for Cu^{2+} ions removal from aqueous solution and can be utilized for real waste water treatment due to its simple preparation, low cost and time.

Keywords: Mixed matrix membrane; graphene oxide as fillers; cellulose acetate as polymer matrix; removal of Cu^{2+} ion

Copper, one of the most critical toxic heavy metals, has many applications in industries [1]. Copper contamination in water occurs mainly from metal cleaning and plating bath, paper and pulp, fertilizers, refineries, and wood preservatives [2]. The contamination of industrial water that contains toxic metal ions has become a critical issue not only to the aquatic living but also to human health [3]. Over time, the accumulation of heavy metals in human bodies can cause severe damage to the kidney, liver, reproductive system, lungs, and blood composition and sometimes leads to cancer [4].

Consequently, many water/wastewater treatment techniques have been used to enhance water quality, such as ion exchange, adsorption, chemical precipitation, filtration, and coagulation [5]. The adsorption method is reported as the most widely used among these methods due to its simple procedure and setup, high removal efficiency, and cost-effectiveness.

Adsorption is a process where attractive forces associate a solute (adsorbate) to a solid surface (adsorbent), and it is a common practice for the removal of heavy metal ions for water and environmental remediation by utilizing various types of adsorbents [6]. Activated carbon [7], molecular organic frameworks (MOFs) [8], agricultural waste-derived adsorbents [5], carbon nanotubes [9] and graphene [10] are examples of conventional and commercial adsorbents that have been utilized for water remediation. Currently, the research aims to develop removal methods with high adsorption capacity while minimizing cost and time to fulfil the economic factors to meet both the technical and economic requirements. In this era, pollution control costs depend on the system characteristics and the application. Thus, the adsorptive membrane method is preferable due to its highly effective removal of heavy metal ions and is also cost-effective in the long run [15]. Most importantly, this method offers design and operating conditions flexibility, which leads to

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139   Sazlinda Kamaruzaman, Nur Najihah
        Mohammad Nasir, Noorfatimah Yahaya,
        Saw Hong Loh and Ili Syazana Johari

Adsorption of Copper Ions from Environmental
Water Samples by Graphene Oxide/Cellulose
Acetate- Mixed Matrix Membrane

in-situ real water application [16].

Recently, membrane separation technology has gained attention in lab-scale experiments and in industrial applications. Many studies have been developed by using membrane filtration for the removal of heavy metal ions such as microfiltration (MF) [11], ultrafiltration (UF) [12], nanofiltration (NF) [13] and reverse osmosis (RO) [14]. Adsorptive membrane (AM) owing to specific adsorption groups and exclusive morphological properties on the membranes to contribute support adsorption removal of heavy metal ions from wastewater [14].

The search for membrane material with tailored properties is still an urgent task for AD development. To solve these set tasks, not only membranes based on pristine polymers are actively used, but also mixed matrix membranes (MMMs). Mixed matrix membranes (MMMs) as adsorbents have been reported to be used for the adsorption of organic compounds such as drugs and pesticides [17] [18] [19]. MMMs are made from polymer-based matric and inorganic materials as the continuous and filler/dispersed phase, respectively. MMMs are easily made by casting a mixture of the dissolved polymeric matrix, mixed with particulate material, and then solidified to produce a thin film/membrane [20]. There are three crucial criteria for MMMs production to determine the selectivity and adsorption capability of the resultant membrane, such as (i) the choice of the base polymer matrix; (ii) the selection of inorganic fillers and (iii) the loading amount of dispersed particles [21].

Graphene oxide (GO), which has a high abundance of oxygen-containing functional groups, has been widely used as an adsorbent to remove various organic and inorganic pollutants in water samples. [10]. The high polarity of GO surface and ease of being dispersed in polar solvents are the most critical factors that lead to the improvement of the mechanical and physical properties of the membrane [11]. Besides that, GO has been more favourable in the adsorption process with high efficiency due to the high surface area. On the other hand, cellulose acetate (CA) is a biodegradable polymer that has been widely employed in various fields such as water purification, gas separation, and packaging. CA consists of hydroxyl-rich groups with beneficial physical and mechanical properties [22]. In the past few years, CA in the membrane has been extensively used in filtration and desalination processes but has poor chemical resistance, insufficient thermal stability, and low antifouling properties. Moreover, the lifetime of CA membrane is short and leads to decreasing membrane performance [23]. Thus, incorporating GO as filler in the CA polymer membrane could ensure high membrane performance and has been reported for high-flux desalination [23].

Based on our findings, the use of MMM to remove Cu^{2+} ions is still lacking. Tetala and Stamatialis have reported the utilization of MMM based on ethylene vinyl alcohol/chitosan for Cu^{2+} ion removal the first time. The finding showed the high maximum adsorption capacity, q_m, which is 225 mg/g. However, the adsorption study between the MMM and the analyte is not discussed in detail [24]. The same goes for the study in 2017 by He et al. using polysulfone/biochar as MMM [25]. Thus, in this study, we conducted an exploratory study of applying graphene oxide (GO) immobilized in cellulose acetate (CA) to form MMMs for the adsorption of Cu^{2+} ions from water samples. GO with different percentages of loading (v/v%) in MMM were evaluated thoroughly as potential adsorbent filler to adsorb targeted Cu^{2+} ion present in water samples. MMM was prepared by casting a solution of the desired proportions of cellulose polymer matrix and adsorbent graphene oxide on a flat glass surface. FTIR and FESEM spectroscopy were used to determine the chemical composition and morphology of the membrane, respectively. To the best of our knowledge, this is the first time the development of graphene oxide-MMM is introduced to remove Cu^{2+} ions from water samples by utilizing cellulose acetate as a polymer matrix. The adsorption parameter, kinetic, isotherm and reusability study of the graphene oxide/cellulose acetate-MMM (GC/CA-MMM) were comprehensively investigated. Then developed adsorbent are utilized in three type of real water samples and the percentage removal of Cu^{2+} ion is calculated. This research's outcomes enables the research community to utilize the high versatility of membrane in adsorptive removal of pollutants in wastewater samples, like the usage of the chemical modifications to not only increase the performance for a specific application, but also to increase the stability, which is an important step in making industrial applications possible.

METHODOLOGY

Reagent and Materials

Cellulose acetate (CA) used to synthesize membrane was purchased from Sigma-Aldrich, which exists in white solid form. Cu^{2+} ions standard solution, hydrochloric acid and nitric acid was supplied by Merck while GO was purchased from GO Advanced Solution. The details of the GO properties are as follows: GO (99% purity) contains 77% carbon, 22% oxygen and 1% other elements. It is black with 1 to 3 layers having a thickness of about 2 to 4 nanometers.

Preparation of Graphene Oxide / Cellulose Acetate-Mixed Matrix Membrane (GO/CA-MMM)

The GO/CA-MMM was prepared by mixing 1 g of CA powder with 15 ml of a 2:1 mixture of acetone and dimethylformamide (DMF). The mixed solution was then loaded with three graphene oxide percentages of

140   Sazlinda Kamaruzaman, Nur Najihah
        Mohammad Nasir, Noorfatimah Yahaya,
        Saw Hong Loh and Ili Syazana Johari

                                    Adsorption of Copper Ions from Environmental
                                    Water Samples by Graphene Oxide/Cellulose
                                    Acetate- Mixed Matrix Membrane

graphene oxide (GO), namely 1% GO/CA-MMM, 10% GO/CA-MMM, and 15% GO/CA-MMM. The acquired homogeneous solution was pipetted and cast onto a glass plate to create a flat transparent membrane. The membrane was allowed to evaporate and dry at room temperature for 30 min. The resulting membrane was peeled and cut to 5mm x 5mm for an adsorption experiment with distilled water. A cellulose acetate membrane (CAM) was also designed without incorporating GO. The membrane was formed at room temperature.

Characterization of GO/CA-MMM

FTIR spectrometer was used to obtain the appropriate information on the functional groups and the chemical structure in the membrane. The pressure was applied to a solid sample on the universal diamond top plate, Attenuated Total Reflectance (ATR) to produce spectra. The percentage of transmittance against wavelength (cm^{-1}) was plotted. Wavelength (cm^{-1}) was plotted in the range of 4000-400 cm^{-1} at room temperature. The analysis was determined by using Perkin Elmer FTIR spectrometer, Spectrum 100. FESEM was used to produce enlarged images and obtain the surface morphology of the membrane. The analysis was determined by using FEI NOVA NANOSEM 230. The sample's small piece was coated with an extremely thin layer (1.5 – 3.0 mm) of gold or gold palladium to achieve conductivity and vacuum durability. After a conductive layer had covered the sample, it was mounted on a unique holder and then scanned with an electron beam.

MMM Adsorption Procedure

The adsorption experiments were performed to investigate the adsorption process of Cu^{2+} ion removal by using different adsorbents (CA-MMM and GO/CA-MMM). The experimental setup is illustrated in **Figure 1**. In detail, the 5 mm^2 MMM was added into the 30 mL of Cu^{2+} ions solution (100, 75, 50, 20, 10 and 5 ppm). The solution was adjusted to acidic conditions (pH 1-5) by dropping a certain amount of hydrochloric acid. Next, the solution was stirred for a certain adsorption time (10-90 mins). After completion of the adsorption process, the membrane was removed, rinsed with ultrapure deionized water to remove any possible surface contamination and then dried with a lint-free tissue. The used MMM were tested for desorption and reusability study. The solution's initial and final concentrations were determined by inductively coupled plasma-optical emission spectrometry (ICP-OES). The amount of adsorption capacities were calculated by using the equation below:

$$\text{Adsorption capacity } \left(\frac{mg}{g}\right), q_e = (C_o - C_e)\frac{V}{M} \qquad \text{Equation 1}$$

Where q_e the amount of metal is adsorbed at equilibrium (mg/g), C_o and C_e are the initial and final concentrations of the metal ions in the solution (mg/L). V is the volume of the heavy metal ions solution (L), while M is the mass of the adsorbent (g). The percentage of removal of heavy metal from the solution can be calculated by using the equation below:

$$\% \text{ Removal efficiency} = \frac{C_o - C_e}{C_o} \times 100 \qquad \text{Equation 2}$$
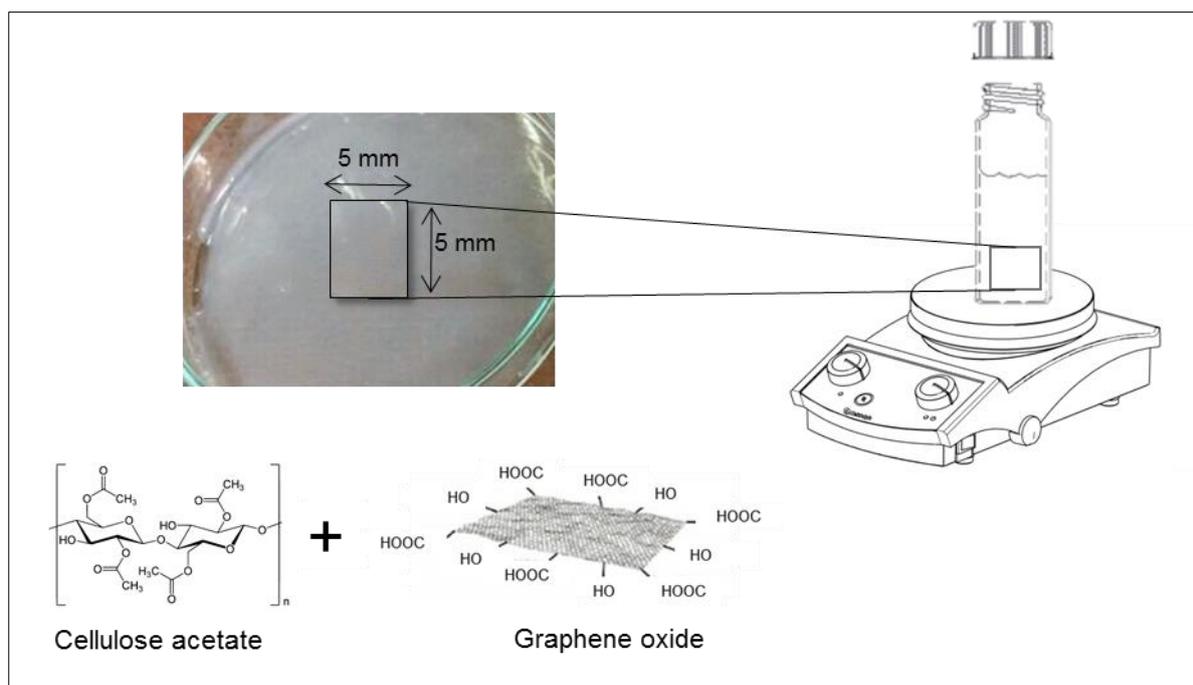

Figure 1. Schematic illustration of the MMM adsorption set-up.

141   Sazlinda Kamaruzaman, Nur Najihah
Mohammad Nasir, Noorfatimah Yahaya,
Saw Hong Loh and Ili Syazana Johari

Adsorption of Copper Ions from Environmental
Water Samples by Graphene Oxide/Cellulose
Acetate- Mixed Matrix Membrane

Desorption and Regeneration Study

The reusability of MMM for Cu^{2+} ion removal was examined utilizing the adsorption-desorption technique. After completing the Cu^{2+} ion adsorption experiment, MMM saturated with Cu^{2+} ions was soaked for 30 mins in 0.1 M HCl solution and then washed with deionized water. The adsorption technique was then used to re-evaluate the membrane's adsorption capabilities.

Real Water Sample Study

Three real water samples were collected for environmental application: Bahau lake water, Pahang river water and mineral water (Brand X). The samples (adjusted to pH5) were filtered using filter paper and kept at 4°C in the dark. Five mm^2 15%GO/CA MMM was added to the samples and stirred for 30 min for the removal process. The sample before and after the adsorption was measured using inductively coupled plasma-optical emission spectroscopy (ICP-OES).

RESULTS AND DISCUSSION

Characterization of Graphene Oxide / Cellulose Acetate-Mixed Matrix Membrane (GO/CA-MMM)

In this study, FTIR analysis was done to analyze the functional groups of cellulose acetate membrane (CAM) and the MMM when the GO with various loading percentages (1, 10 and 15%) were embedded into CA polymer matrix. Based on **Figure 2 (a)**, the FT-IR spectra of CAM exhibited bands at 1222, 1373 and 1733 cm^{-1} associated with the C–O–C, C–CH$_3$, and C=O, respectively. In the FT-IR spectra of GO/CA MMM in **Figure 2 (b-d)**, the intensity of the

cellulose acetate peak at 3000 cm^{-1} to 3400 cm^{-1} slightly decreases due to the incorporation of GO [26]. The peak at 3472, 3475 and 3472 cm^{-1} are attributed to the strong stretching mode of the OH group. This confirms the strong hydrogen bond interaction between CA and GO, which implies the composite compatibility the GO is successfully embedded into the cellulose acetate polymer matrix to form MMM.

In this study, one g of CA powder with 15 ml of a 2:1 mixture of acetone and dimethylformamide (DMF) were used to form the polymer matrix. This ratio is constant for preparing MMM with three different concentrations of GO. When > 15% GO is added into the polymer solution, the GO powder is not well-dispersed and leads to the adsorption results' inconsistency. Thus, 1, 10 and 15% of GO is used for the preparartion of MMM and further characterization and applications. The surface of the membrane was analyzed by FESEM analysis. Thus, the CAM and GO/CA-MMM microstructure can be directly observed. The observation of the membrane surface for CAM and various loading percentages of GO are illustrated in **Figure 3**. The produced cellulose acetate/graphene oxide MMMs (0.50 μm) displayed a sponge-like fibrous morphology. Three-dimensional nanoporous were assembled from CA embedded with GO. The adsorbent membranes demonstrated a low density, highly porous structural design, high surface area, and good mechanical characteristics. The surface morphology assessment, as well as the distribution of pores, was studied by the FESEM program, showing an average diameter of 0.25–0.50 μm after the addition of 15% of GO (**Figure 3(d)**). These characteristics of the developed membranes resulted in their potential applications as adsorbents in water treatment.
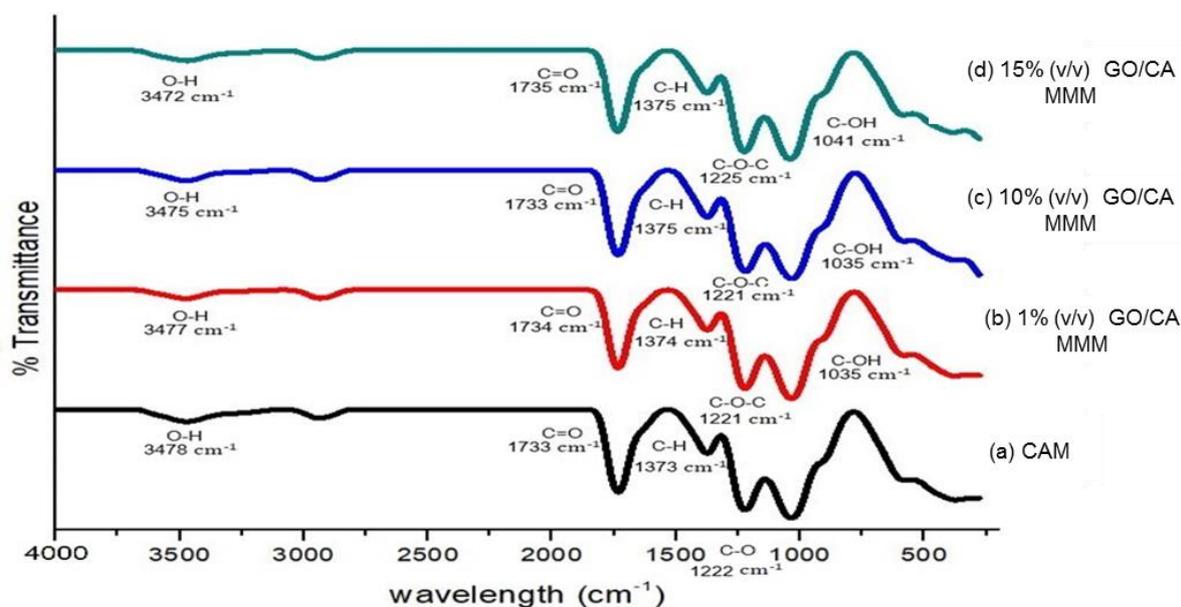

Figure 2. The FTIR spectrum of (a) CAM, (b) 1% (v/v) GO/CA-MMM, (c) 10% (v/v) GO/CA-MMM and (d) 15% (v/v) GO/CA-MMM.

142   Sazlinda Kamaruzaman, Nur Najihah
         Mohammad Nasir, Noorfatimah Yahaya,
         Saw Hong Loh and Ili Syazana Johari

Adsorption of Copper Ions from Environmental
Water Samples by Graphene Oxide/Cellulose
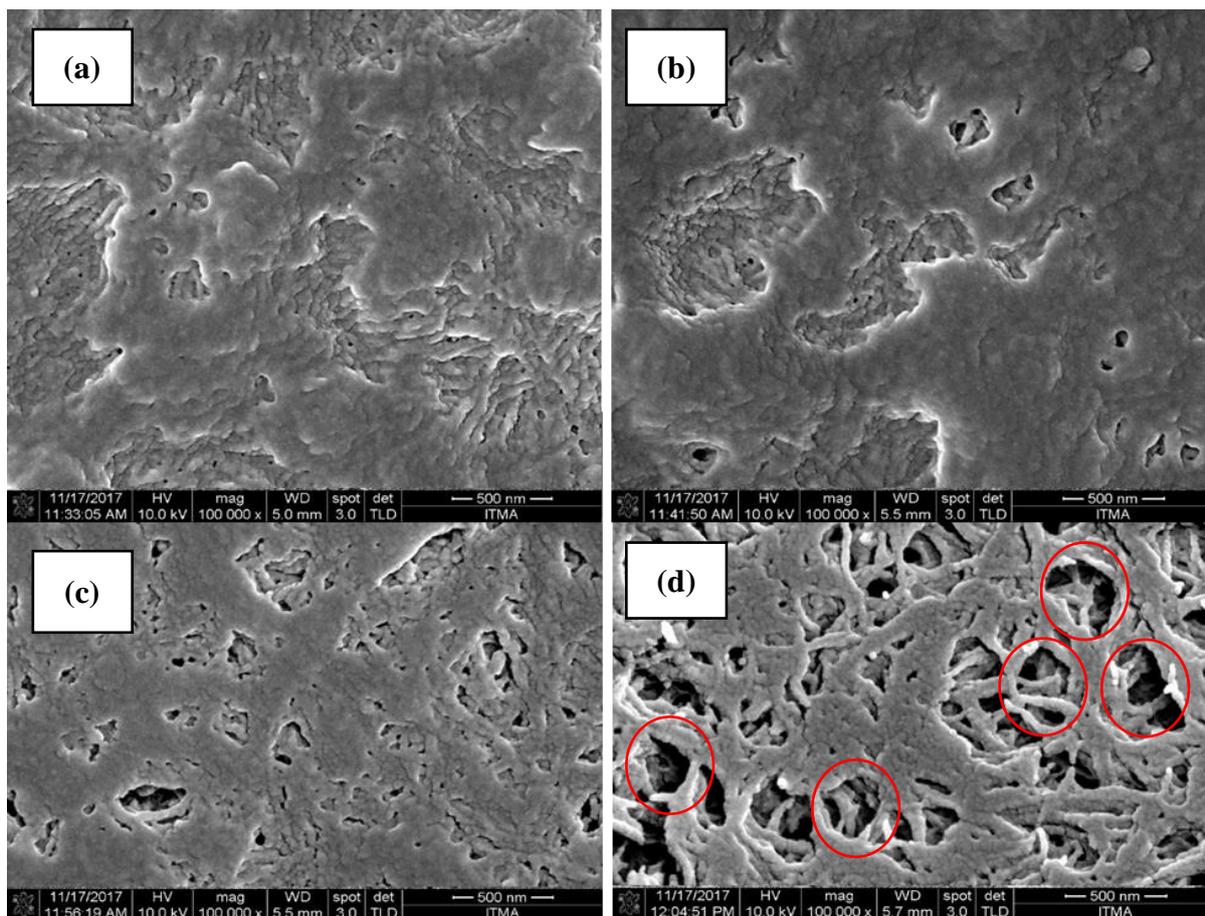Acetate- Mixed Matrix Membrane

Figure 3. FESEM images of the membrane surface for CAM and various adsorbent ratio of GO/CA-MMM (a) CA without GO (b) 1% of GO (c) 10% of GO and (d) 15% of GO.

In addition, the addition of graphene oxide inside the polymeric strands of the cellulose acetate matrix was found to influence the microporous film system signifying that the graphene oxide was fully immobilized within the composite matrix. The number of pores increased at the CAM surface with increasing the concentration of graphene oxide in the polymer matrix. The graphene oxide molecules located within the polymer strands result in shrinkage of the pore walls, and, consequently, result in increasing the diameter of the pore with increasing the graphene oxide concentration. The GO/CA-MMM showed high adsorption efficiency to Cu^{2+} ions due to its high surface area and porosity.

Optimization of Cu^{2+} Ions by Graphene Oxide / Cellulose Acetate Mixed Matrix Membrane (GO/ CA-MMM) Adsorption

pH Study

The pH optimization was essential to determine the degree of ionization of the metal ions and the charges on the membrane surface. **Figure 4a** shows

that pH influences the adsorption capacity of Cu^{2+} ions by the tested adsorbent in the solution. The adsorption capacity of the Cu^{2+} ion by the adsorbent can be calculated by using Equation 1. The pH tested ranged from 1 to 8 with four types of membranes (CAM, 1% CA/GO-MMM, 10% CA/ GO-MMM and 15% CA/GO-MMM). Because the hydroxide compound would be produced as pH was over 8.0 and lead to the formation of precipite in the solution, thus pH was varied from 2 to 8. The adsorption ability of all membranes improves dramatically from 7.63 to 67.4 mgg^{-1} for Cu^{2+} ion concentrations of 20 ppm when the pH increases from 1 to 5. This is attributed to the reason that the pH value affects the surface charge of the membrane adsorbent. The adsorbent's negative charge grows as the pH value increases. As a result, it may provide electrostatic attractions that favour the reaction of Cu^{2+} ion with the functional groups -COOH on the GO surface to produce a metal ion complex. As a result, H^+ and – COOH was released into the solution simultaneously. Because of this, it is possible to explain why the equilibrium pH is lower than the original pH value in a solution. [27].

143   Sazlinda Kamaruzaman, Nur Najihah
      Mohammad Nasir, Noorfatimah Yahaya,
      Saw Hong Loh and Ili Syazana Johari

Adsorption of Copper Ions from Environmental
Water Samples by Graphene Oxide/Cellulose
Acetate- Mixed Matrix Membrane

Additionally, it should be noted that when the pH value of the sample solution exceeds 6.0, precipitation of Cu^{2+} ion occurs. Thus, pH of 5 was selected as the optimum pH value of Cu^{2+} ion solution in the following adsorption experiments. While the adsorption capacity of Cu^{2+} ion rises with increasing GO loading percentages from 0 to 15% for pH 5, membrane adsorption rates decrease due to GO tending to agglomerate when embedded within the polymeric matrix, reducing accessible sites for adsorption activity. The schematic representation of the monolayer model for the adsorption of Cu^{2+} ions onto the MMMs is depicted in **Figure 4(b).**

Initial Concentration

The adsorption capacity of GO/CA-MMM as a function of initial Cu^{2+} ions concentration was investigated, as shown in **Figure 5**. When the starting concentration of Cu^{2+} ions was low (10 ppm), the adsorption sites of MMM adsorbent were not fully utilized, resulting in reduced adsorption uptake (50 mg/g) for all membranes. Furthermore, as the concentration increased from 20 to 50 ppm, the GO/CA-MMM adsorbent consumption rate continued to increase (q_e=113 mg/g) and remained constant at 100 ppm. It might be because the surface of the membrane is saturated with Cu^{2+} ions. Thus, 50 ppm of Cu^{2+} ions solution were used for further optimization.
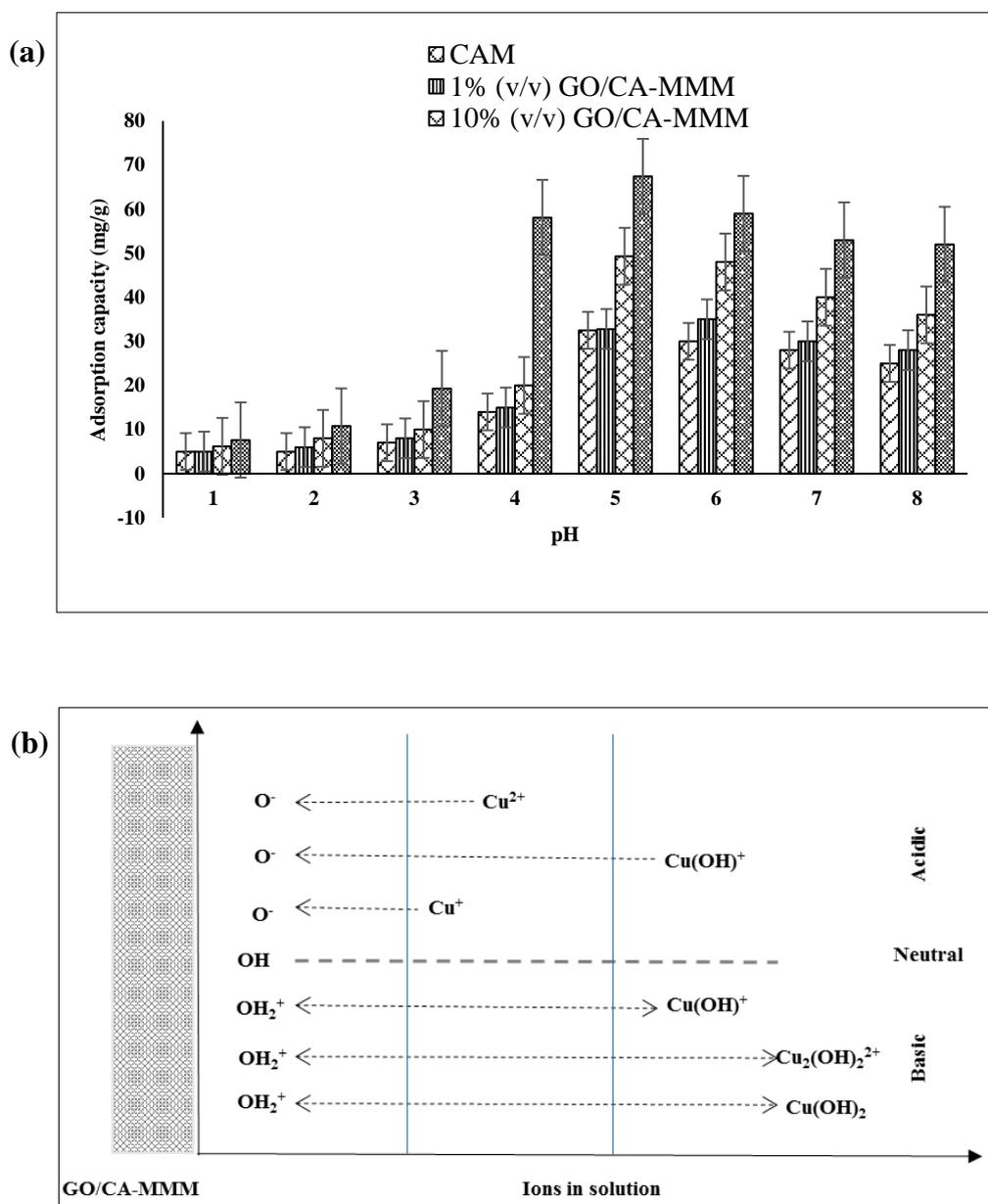

Figure 4. (a) pH study on the uptake of Cu^{2+} ion (contact time = 20 minutes, initial concentration of Cu^{2+} ion 20 ppm, sample volume = 30 mL) and (b) Schematic representation of the monolayer model for the adsorption of Cu^{2+} ion onto the MMMs.
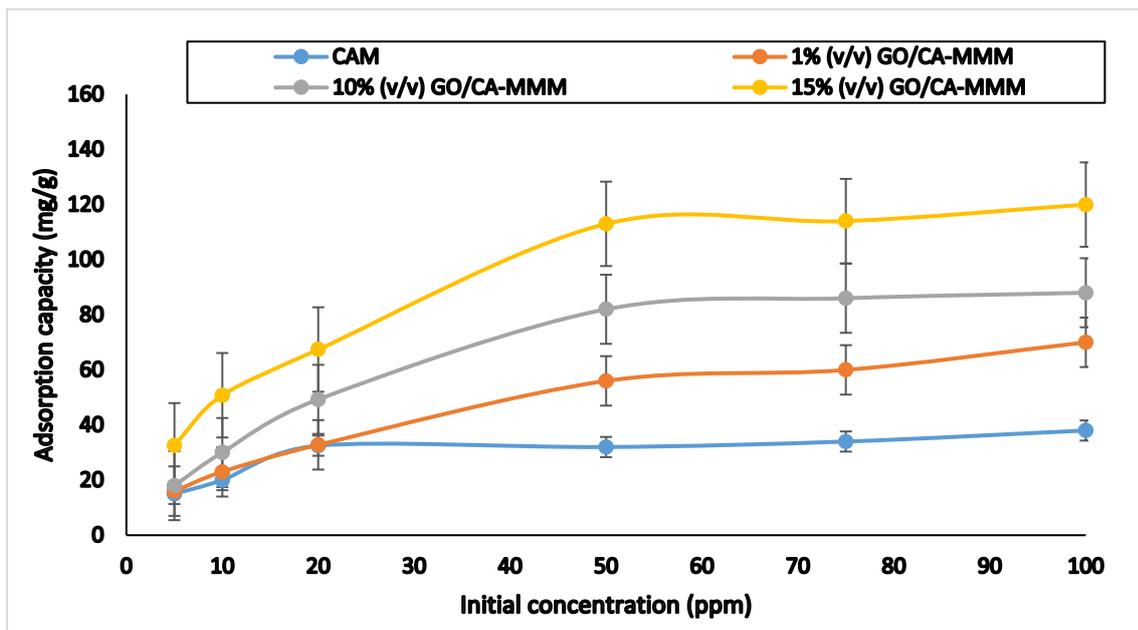
144   Sazlinda Kamaruzaman, Nur Najihah
      Mohammad Nasir, Noorfatimah Yahaya,
      Saw Hong Loh and Ili Syazana Johari

Adsorption of Copper Ions from Environmental
Water Samples by Graphene Oxide/Cellulose
Acetate- Mixed Matrix Membrane

Figure 5. Initial concentration study on the uptake of Cu^{2+} ion (contact time = 20 minutes, pH = 5, sample volume = 30 mL).

Adsorption Isotherm

Theoretically, adsorption is the most likely mechanism offered by the membranes to adsorb Cu^{2+} ions due to the electrostatic interaction between the MMM and Cu^{2+} cation. Two widely used equilibrium adsorption isotherms, Langmuir and Freundlich, were used to confirm the findings. The Langmuir isotherm model is based on the assumption of a finite number of active sites that are uniformly distributed across the adsorbent's surface [27]. According to its derivation, the Langmuir isotherm describes homogeneous adsorption in which each molecule has constant enthalpies and activation energies of sorption (all sites have equal affinity for the adsorbate) [28], with no adsorbate transmigration in the plane of the surface. The Langmuir model assumes uniform adsorption energies on the surface and no adsorbate transmigration in the plane of the surface. The Langmuir Isotherm is defined as the following equation:

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \qquad \text{Equation 3}$$

The transformation of the following equation into a linear form:

$$\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{C_e}{q_m} \qquad \text{Equation 4}$$

Freundlich model is an empirical equation based on sorption on various surfaces with varying affinities. The stronger binding sites are occupied first, and the binding strength decreases as site occupancy increases [27]. It is assumed that the amount adsorbed is the sum of adsorption on all sites (each with its bond energy), the stronger binding sites being occupied first until the adsorption energy is lowered exponentially after the adsorption process. The Freundlich isotherm model takes multilayer and heterogeneous adsorption into account. The Freundlich isotherm model is given by

$$q_e = K_F C_e^{1/n} \qquad \text{Equation 5}$$

The logarithmic form of the equation:

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \qquad \text{Equation 6}$$

Where q_e is the amount of initial metal adsorbed after adsorption per specific amount of adsorbent (mg/g), C_e is the equilibrium concentration of the adsorbate (mg/L), K_F and n are Freundlich equilibrium constants related to adsorption capacity (mg/L) and adsorption intensity. The solid/liquid adsorption system was defined using a Langmuir and Freundlich equilibrium adsorption isotherm model. The findings are presented in Table 1. **Figure 6** depicts the Langmuir adsorption isotherms for the Cu^{2+} ion. The removal of Cu^{2+} ions by MMMs is best fitted with the Langmuir adsorption isotherm (R^2 value near 1.000). The ability of MMMs to interact and bind on the adsorbent, as shown in the table, is independent of the active sites at the adsorbent surface that execute adsorption and adsorbate, resulting in a monolayer. Only one adsorbate molecule can occupy a single site until it is desorbed.

145   Sazlinda Kamaruzaman, Nur Najihah
    Mohammad Nasir, Noorfatimah Yahaya,
    Saw Hong Loh and Ili Syazana Johari

Adsorption of Copper Ions from Environmental
Water Samples by Graphene Oxide/Cellulose
Acetate- Mixed Matrix Membrane

Table 1. Linear regression, correlation coefficient, R^2 of Langmuir and Freundlich isotherm for GO/CA-MMMs.

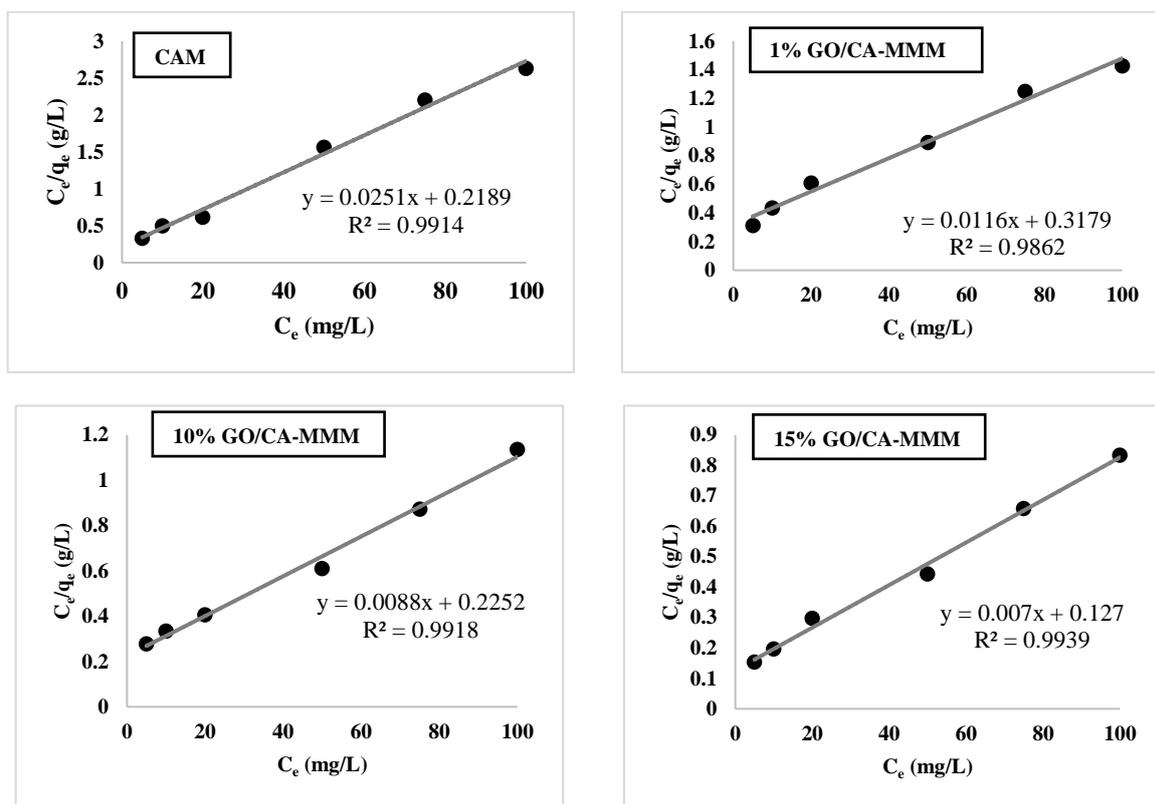| Membrane	Langmuir model		Freundlich model	
	Linear regression	R^2	Linear regression	R^2
CAM	y = 0.0251x + 0.2189	0.9914	y = 0.2864x + 2.36	0.8662
1% v/v GO/CA-MMM	y = 0.0116x + 0.3179	0.9862	y = 0.4968x + 1.993	0.8835
10% v/v GO/CA-MMM	y = 0.0088x + 0.2252	0.9918	y = 0.5432x + 2.134	0.7520
15% v/v GO/CA-MMM	y = 0.007x + 0.127	0.9940	y = 0.4418x + 2.8589	0.7901

Figure 6. Langmuir adsorption isotherm.

Contact Time

The optimum time of Cu^{2+} ion adsorption by MMMs was also investigated. According to **Figure 7**, over the first 30 mins, the adsorption capacity of MMMs considerably increases. The metal removal rate was high during the initial contact time. This could be attributable to the abundance of unoccupied binding sites accessible for metal ion adsorption to the MMM surfaces. After 30 mins, equilibrium adsorption was achieved, and the adsorption capacity did not considerably increase. As the outer surface got depleted, the adsorbate uptake rate dropped until an apparent equilibrium was reached. Due to the reduction of active sites on the adsorbent and the concentration of Cu^{2+} ions in the water sample, chelation potential is also reduced. The proton H^+ in MMM's reactive functional groups is also released into the solution. Thus, the ideal adsorption duration for GO/CA-MMM is 30 mins.
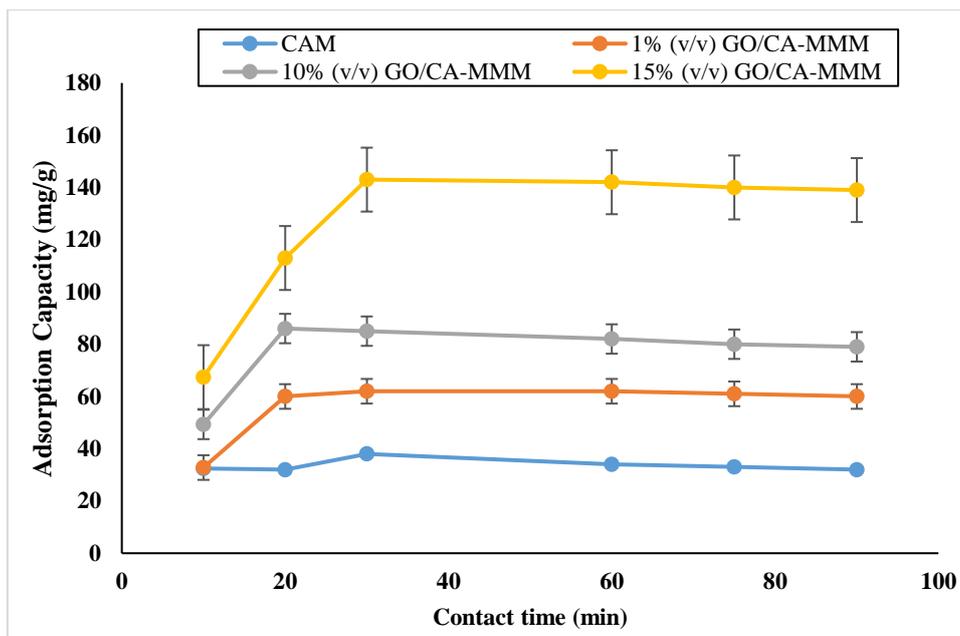
146   Sazlinda Kamaruzaman, Nur Najihah
      Mohammad Nasir, Noorfatimah Yahaya,
      Saw Hong Loh and Ili Syazana Johari

Adsorption of Copper Ions from Environmental
Water Samples by Graphene Oxide/Cellulose
Acetate- Mixed Matrix Membrane

Figure 7. Contact time study on the uptake of Cu^{2+} ion (Initial concentration of Cu^{2+} ion=50 mg/L, pH = 5, sample volume = 30 mL).

Adsorption Kinetics

The adsorption kinetics study is conducted to evaluate the time required for achieving adsorption equilibrium, where there is no change in adsorption capacity [28]. Traditional adsorption kinetics models, notably pseudo-first and pseudo-second-order rate models, were employed to explain the adsorption kinetics and rate-limiting phase.

The Pseudo-First Order kinetic model has been widely used to predict the metal adsorption kinetics, and it is a unimolecular reaction that depends only on the concentration reactant. For example, the metal adsorption kinetics following the pseudo-first-order model is given by [28].

$$\frac{d_{qt}}{d_t} = K_1 (q_e - q_t)$$ Equation 7

A linear form of an equation is:

$$\ln (q_e - q_t) = \ln q_e - K_1 t$$ Equation 8

Where K_1 (min^{-1}) is the rate constant of the pseudo-first-order adsorption, q_t (mg/g) denotes the amount of adsorption at time t (min) and q_e (mg/g) is the amount of adsorption at equilibrium. The adsorption kinetic data can be further analyzed using Ho's pseudo-second-order kinetics. This is expressed as:

$$\frac{d_{qt}}{d_t} = K_2 (q_e - q_t)^2$$ Equation 9

A linear form of the equation is:

$$\frac{t}{q_t} = \frac{t}{q_e} + \frac{1}{K_2 q_e^2}$$ Equation 10

Where K_2 (g/mg min) is the constant rate while q_t (mg/g) denotes the amount of the adsorption at time t (min) and q_e (mg/g) is the amount of adsorption at equilibrium. K_2 and q_e can be obtained from the intercept and slope.

The mechanism involved in adsorption kinetics was determined using Lagergren's pseudo-first and second-order equations (Equations 8 and 10). Because of the higher R^2 values compared to the Pseudo-first order, the adsorption of Cu^{2+} ions is best matched with the Pseudo-second order, as shown in **Table 2**. This finding implies that chemisorption (Pseudo-second order) rather than physisorption is the primary source of Cu^{2+} ion adsorption (Pseudo-first order). Furthermore, the anticipated q_e values of MMMs computed using the Pseudo-second order linear equation are extremely similar to the experimental results, suggesting a good correlation between the experimental data and the Pseudo-second order.

Regeneration Potential of GO/CA-MMMs

The GO/CA-MMMs were loaded with Cu^{2+} ions solution (50 mg/L), and the aqueous EDTA solution was employed as a desorbing solvent in a regeneration investigation. For the regeneration of adsorptive membranes, EDTA is a particularly effective substance. The hexadentate ligand of EDTA interacts strongly with Cu^{2+} ions to form a sustainable octahedral complex [29]. **Figure 8** illustrates possible mechanisms/ interactions. As a result, the MMM was reused using this chemical. **Figure 9** demonstrates the findings of

147 Sazlinda Kamaruzaman, Nur Najihah
Mohammad Nasir, Noorfatimah Yahaya,
Saw Hong Loh and Ili Syazana Johari

Adsorption of Copper Ions from Environmental
Water Samples by Graphene Oxide/Cellulose
Acetate- Mixed Matrix Membrane

the adsorbent regeneration test. The regeneration study data indicated that 86% of the metal was recovered in approximately two cycles. However, the percentage of removal of Cu^{2+} ion using 15% GO/CA-MMM is decreased by 10-15% after three-six regeneration cycles. This might be due to the membrane fouling process. Since the adsorption process occurs, thus the solute ions are adsorbed onto the membrane pores and surface by chemical interactions or mechanical action, which results in smaller or blocked membrane pores [42]. Since the uncomplicated MMM preparation and adsorption set-up for each operation, and because only a tiny piece of the membrane (5 mm x 5 mm) is required for each adsorption process, it may be utilized as a single-use disposable membrane, preventing any analyte carry-over effects.

Table 2. Pseudo-first and Pseudo-second parameters for adsorption of Cu^{2+} ion membrane adsorbent.

Membrane	Pseudo-first order	Pseudo-second order		
	Correlation coefficient, R^2	Amount of adsorption, q_e calculated (mg/g)	Amount of adsorption, q_e calculated (mg/g)	Correlation coefficient, R^2
CAM	0.8115	43.76	41.90	0.9612
1% GO/CA-MMM	0.7621	59.36	63.23	0.9213
10% GO/CA-MMM	0.7512	80.610	83.214	0.9635
15% GO/CA-MMM	0.6981	143.06	141.38	0.9862
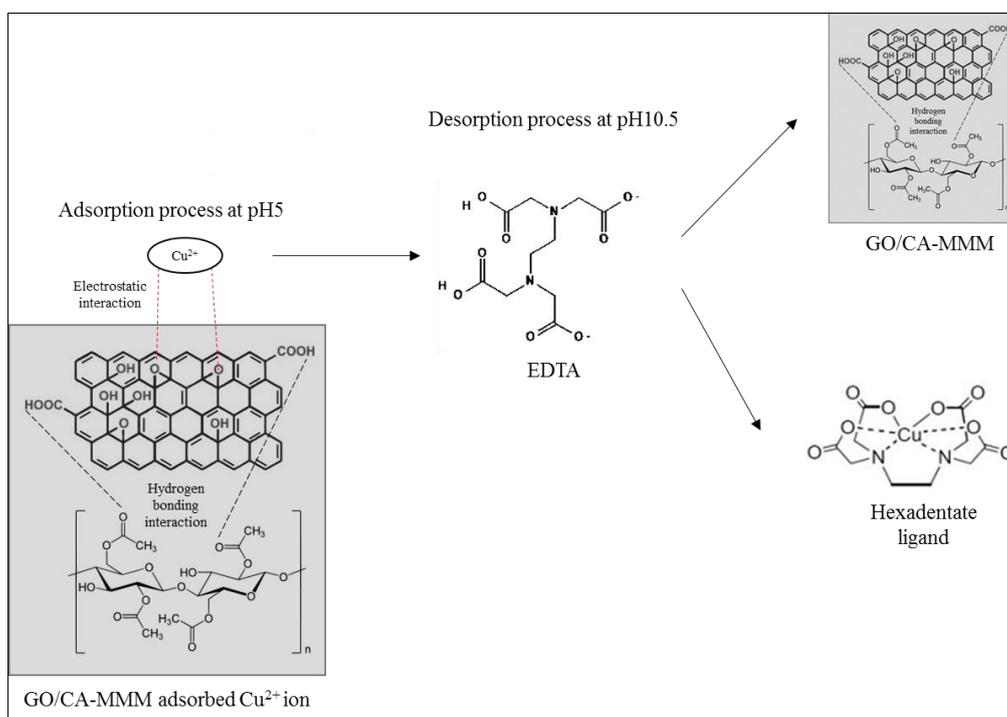
Figure 8. A possible mechanism/interaction during adsorption and desorption process.

148   Sazlinda Kamaruzaman, Nur Najihah
      Mohammad Nasir, Noorfatimah Yahaya,
      Saw Hong Loh and Ili Syazana Johari

Adsorption of Copper Ions from Environmental
Water Samples by Graphene Oxide/Cellulose
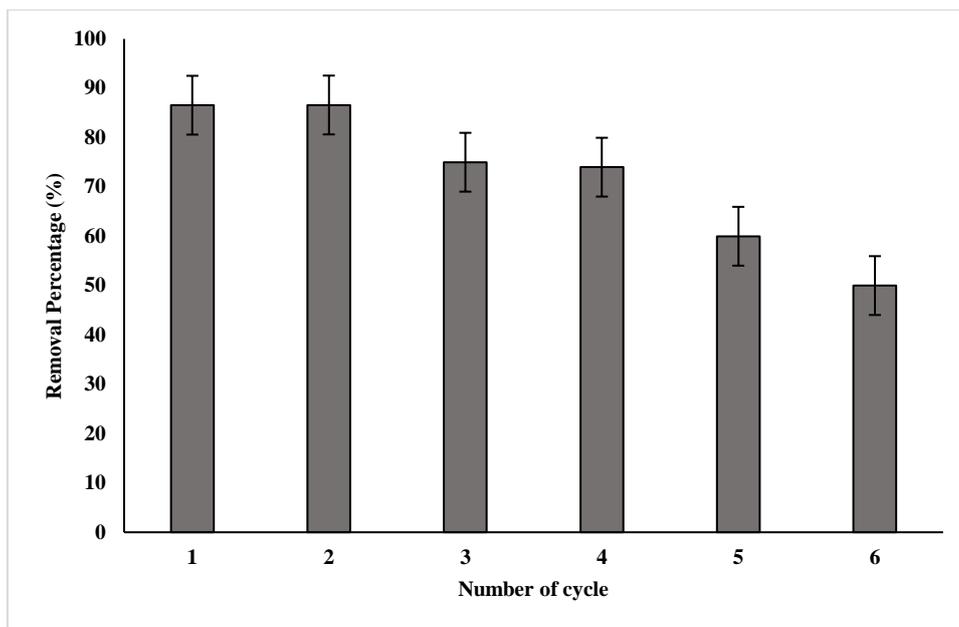Acetate- Mixed Matrix Membrane

Figure 9. Regeneration potential of 15% GO/CA-MMMs with six cycles

The developed membrane's adsorptive performance was compared with graphene oxide as an adsorbent for removing Cu^{2+} ions (**Table 3**) and numerous membranes for the removal of heavy metal ions (**Table 4**). The production of a flat sheet membrane using a casting technique can be described as a simple process in this work. Most importantly, this study's adsorption setup is substantially more straightforward than other adsorption/filtration configurations used in membrane development. Furthermore, the membrane matrix of cellulose acetate is derived from natural minerals as the source of embedded adsorbents in the polymer. Although the proposed membrane had a limited adsorption capacity, it had a shorter contact time (30 min) and an 86% removal rate compared to previously published heavy metal ion removal membrane technology. The study's findings suggested that the adsorptive membrane has massive potential for heavy metal treatment in adsorption/filtration applications.

Table 3. Adsorption performance of graphene oxide as adsorbent for the removal of Cu^{2+} ions.

Sorbent type	q_{max} (mg/g)	Removal percentage (%)	Adsorption condition/Adsorption Study	Ref
GO powder	277.77	97	pH=6, contact time=60min, Initial concentration=700mg/L, Fitted to Langmuir isotherm and Pseudo-second order kinetic model.	[29]
Carboxylated-GO	357.14	99.4		
Cu(tpa).GO nanocomposite powder	200	-	pH=7, contact time=120min, Fitted to Langmuir isotherm and Pseudo-second order kinetic model.	[31]
EDTA-functionalized chitosan graphene oxide nanocomposites	207.26	-	pH=5, contact time=6h, Initial concentration=140mg/L, Fitted to Langmuir isotherm and Pseudo-second order kinetic model.	[32]
Manganese oxide nanoparticles-GO granular	-	93	pH=5, contact time=40min, Initial concentration=25mg/L, Fitted to Langmuir isotherm and Pseudo-second order kinetic model.	[33]
Chitosan/ GO nanofibre	423.8	-	pH=6, contact time=40min Fitted to Langmuir isotherm and Pseudo-second order kinetic model.	[34]
Chitosan/ GO powder	111.11	-	pH=7.5, contact time=150min, Initial concentration=80mg/L Fitted to Langmuir isotherm and Pseudo-second order kinetic model.	[35]
GO/CA-Mixed matrix membrane	143	85.67	pH=5, contact time=30min, Initial concentration=50mg/L, Fitted to Langmuir isotherm and Pseudo-second order kinetic model.	Present work

149 Sazlinda Kamaruzaman, Nur Najihah
Mohammad Nasir, Noorfatimah Yahaya,
Saw Hong Loh and Ili Syazana Johari

Adsorption of Copper Ions from Environmental
Water Samples by Graphene Oxide/Cellulose
Acetate- Mixed Matrix Membrane

Table 4. Performance of different MMMs for the removal of heavy metal ions from water.

Polymer matrix	Inorganic filler	Membrane process	Heavy metal ions	Reported on removal efficiency	Adsorption/ Filtration time	Ref
Polyethersulfone	Graphene oxide-manganese ferrite (GMF)	Adsorption-filtration	As(V)	75.5mg/g[a]	4h	[36]
Polyethersulfone (PES)	Polyaniline/iron (II, III) oxide (PANI/Fe_3O_4)	adsorption-filtration	Cu^{2+}	75%[b]	-	[37]
Purolite	Chitosan	Adsorption/ desorption	Hg^{2+}	5.516mg/g[a]	60min	[38]
Polyethersulfone	Manganese oxide (MnO_2)	Adsorption/ desorption	Cd^{2+}	51.7 mg/g[a]	48h	[39]
Polyethersulfone (PES)	Zeolite 13X	Adsorption/ desorption	NH^{4+}	55mg/g[a]	-	[40]
Polyvinylidene fluoride (PVDF)	Tin(IV) oxide SnO2	adsorption-filtration	Pb^{2+} Cu^{2+} Zn^{2+} Cd^{2+} Ni^{2+}	93.9%, 92.8%, 82.3%, 70.7%, 63.9%	-	[41]
Cellulose acetate (CA)	Graphene oxide	Adsorption/ desorption	Cu^{2+}	143mg/g	30min	Present work

a: Based on the adsorption capacity (q_{max}) of a heavy metal ion for the adsorption study; b: Based on the rejection of a heavy metal ion for the filtration

Real Water Sample Study

Real environmental water samples from a river, lake, and mineral water were used to test the 15% GO/CA-MMM application for Cu^{2+} ion adsorption. The ICP-OES technique was used to measure the changes in heavy metal concentration following adsorption through GO/CAM-MMM. The ICP-OES results of the real water studied before and after adsorption were provided in **Table 5.** The results demonstrate that the developed adsorption method using 15% GO/CAM-MMM is successful with a percentage removal of 49.24% to 85.82%. Even though the present concentration of Cu^{2+} ion in water samples are below the permitted limit (1 mg/L, Standard B) established by the Malaysian Department of Environment (DOE) [43]. Still, the accumulation of Cu^{2+} for the daily intake may be at risk. Thus, according to the experimental results, GO/CAM-MMM has several advantages in terms of simplicity and high adsorptive performance and can be used as one of the alternative adsorbents in the adsorption process.

Table 5. Concentration of environmental water samples before and after adsorption and the percentage of removal by using the synthesized membrane.

Environmental Water Samples	Concentration before adsorption (mg/L)	Concentration after adsorption (mg/L)	Percentage of removal (%)
Lake Water (Bahau)	0.17	0.06	65.78
Mineral Water (Brand Bleu)	0.21	0.11	49.24
River Water (Pahang)	0.17	0.02	85.82

150 Sazlinda Kamaruzaman, Nur Najihah
Mohammad Nasir, Noorfatimah Yahaya,
Saw Hong Loh and Ili Syazana Johari

Adsorption of Copper Ions from Environmental
Water Samples by Graphene Oxide/Cellulose
Acetate- Mixed Matrix Membrane

CONCLUSION

The prepared CAM and GO/CA-MMM adsorbent were successfully synthesized via the casting method using CA as polymer matrix and GO as fillers and verified by FTIR and FESEM. The incorporation of GO within the polymer structure of CAM has been proven to be attributable to the improved porosity and adsorption capacity compared with pristine CAM. The experimental results supported that the complexity of the adsorption system mechanism was fully explained through the investigation of solution pH, adsorption isotherm models, kinetic models and regeneration studies. The best adsorption conditions were found when Cu^{2+} ion solutions concentration was kept at 50 ppm, pH 5 and contacted for 30 mins with 15% GO/CA-MMM. Hence, the maximum adsorption capacity of Cu^{2+} ion was reported up to 143.06 mg/g. The equilibrium adsorption data of Cu^{2+} ion on the prepared GO/CA-MMM matches well with the Langmuir isotherm adsorption isotherm, which illustrates that the Cu^{2+} adsorption behaviour occurred on the monolayer of the adsorbent. The kinetics mechanism was best fitted with a pseudo-second-order kinetics model, which signifies the chemisorption mechanism's involvement. The possible chemical interaction mechanism of Cu^{2+} adsorption on the prepared GO/CA-MMM involves electrostatic interactions and ion exchange. In addition, the prepared GO/CA-MMM were investigated for six regeneration cycles and showed that the removal efficiency of Cu^{2+} on GO/CA-MMM was gradually depleted, possibly due to the membrane fouling phenomenon. Even though the result indicates that GO/CA-MMM is a single-used sorbent, however the developed membrane has good potential for Cu^{2+} ions removal from aqueous solution and can be utilized for real waste water treatment due to its simple preparation, low cost and time.

ACKNOWLEDGEMENTS

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Mohammad Nasir, Noorfatimah Yahaya,
Saw Hong Loh and Ili Syazana Johari

Adsorption of Copper Ions from Environmental
Water Samples by Graphene Oxide/Cellulose
Acetate- Mixed Matrix Membrane

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152   Sazlinda Kamaruzaman, Nur Najihah
Mohammad Nasir, Noorfatimah Yahaya,
Saw Hong Loh and Ili Syazana Johari

Adsorption of Copper Ions from Environmental
Water Samples by Graphene Oxide/Cellulose
Acetate- Mixed Matrix Membrane

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