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Highly effective graphene membrane for transformer oil purification

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ABSTRACT

A highly effective adsorbent comprised of the Graphene membrane was created using the sonification method in this study. For all we know, the resulting Graphene membrane was employed as an adsorbent for transformer oil purification for the first time. The quality of the treated oil was evaluated through several factors, such as acid number TAN(mg KOH/g), color, breakdown voltage, and viscosity. The results indicated that the Graphene membrane exceeded the other commercial adsorbents in terms of purifying capacity. Several reasons, including the unreduced oxygen functional groups, vacancy defects on the surface of the Graphene flake, the high specific surface area, and the proper pore size of the Graphene membrane for oil refining, might explain this exceptional outcome. Furthermore, the 3D structure of the Graphene membrane can extend the residence purification time of the transformer oil, assisting in the improvement of the purification capability of the Graphene membrane.

Introduction

Transformer oil is an essential component of a high-voltage transformer because it ensures dependable isolation and removes heat from hot sections. However, various conditions such as high working temperatures (70-80°C), the presence of ambient moisture, and the presence of metallic compounds such as iron, copper, and lead can degrade the hydrocarbons in the oil. This deterioration is the principle of lowering the oil-insulating qualities of the transformer [1,2]. It is generally understood that produced sludge can form on the transformer surface, preventing oil circulation and lowering oil dielectric strength. As a result, the sludge may cause the power transformer to fail during its operation. Furthermore, the acidity causes corrosion of the transformer's metal surface. Also, the water created in oil may lower the dielectric strength of the oil [3,4]. As a result, the old oil in the transformer must be purified to remove produced sludges, water, and regular acidity levels in the oil transformer.

The following are examples of how the oil is degrading: The creation of the hydrocarbon radical is the first step in the degrading process. Peroxy radicals are created when the air's oxygen interacts with the hydrocarbon radical. As the hydroperoxides degrade, ketones, alcohols, aldehydes, and organic acids are created. Organic acids can also create esters and resin. Therefore, after the oxidation process, the oil acidity will increase, and several products such as sludges, and oil coagulating are created. Adsorbent materials have recently emerged as the ideal choice for the

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purification of transformer oils. Many adsorbents, such as activated bauxite [5], and carbonated calcium phosphate (CACP)-biopolymers of chitosan polysaccharide [6], activated carbon [7], zeolite [8], and Kaolin clay [9], are commonly employed. However, the usage of the adsorbent materials discussed above has several limitations, such as high waste volume [5], high cost [6], and poor specific surface area [6].

In recent times, because of its high adsorption capacity, reduced graphene oxide (rGO) has recently emerged as an ideal adsorbent material for wastewater treatment [10–13]. Furthermore, its unreduced oxygen functional groups and surface vacancy defects give a high adsorption capability. The enormous specific surface area is also the primary reason for the success of rGO as an adsorbent [14].

Sonification is a possible alternate method for producing Graphene material [15]. In this study, we coupled the reduction of GO in the presence of a reductor with sonification process to produce a monolayer of reduced Graphene Oxide. After that, we produce the membrane based of rGO by vacuum filtration process. The material produced in this work was employed to cleanse aging transformer oil. The purifying capability of Graphene membranes was compared to that of activated carbon, a commercial carbon material, which is commonly used for refying oil.

Experimental

The preparation of Graphene Oxide

Graphene Oxide (GO) was synthesized utilizing Graphite flake as a raw material for the Graphene membrane through the modified Hummer technique [14]. The lateral size of the graphite flake ranges between 50 and 100 m.

Mechanical agitation was used to mix 20 g of graphite and 20 g of sodium nitrate with 500 mL of 98 wt.% sulfuric acid. The combination was placed in an ice bath to cool it down to 5°C. The chilled liquid was then progressively supplemented with 70 g of potassium permanganate. It is critical to keep the mixture temperature below 50°C throughout the potassium permanganate addition.

The reaction mixture was handled at 40°C for 5 hours after adding potassium permanganate to finish the oxidation process. The process was then halted by adding 200 mL of demineralized water to the mixture. As a result, 10-15 mL of H_2O_2 (30% in water) was added to eliminate the remaining potassium permanganates. The reaction mixture has now become a light-yellow tint. Following that, 100 mL of 20% HCl was added to remove the manganese oxide generated during the oxidation reaction. Finally, a brilliant yellow graphite oxide was formed. To get dried powder Graphite Oxide, the synthesized material was dried in an oven at 40°C for three days.

The GO dispersion was obtained by exfoliating Graphite Oxide in demineralized water using ultrasonic equipment 750 W. The unexfoliated Graphite Oxide was separated by a centrifugation step at 3000 rpm for 10 minutes. The concentration of the GO dispersion was adjusted to 2 g/L.

The preparation of Graphene membrane

The single stage of Graphene membrane production in our study is a mixture of two processes: the reduction of GO by urea [14] and the filtering to produce a membrane structure from the rGO dispersion. In an ultrasonic bath of 100 W, a typical combination onf 6 g urea and 300 mL dispersion of GO of 2 g/L was ultrasonicated. The resulting mixture was then sonicated for 5 hours at 80°C. The resulting material was then recovered by vacuum filtration to form the membrane and washing with massive amounts of demineralized water. Lastly, the membrane was dried in a 60°C oven for 6 days. The digital picture of Graphene membrane is presented in Fig.1. The Graphene membrane is durable and has a thickness around of 1 mm. The membrane can be resusable for many treatment cycles. The durability of the membrane will be studied in the next study.

Figure 1: The digital picture of Graphene membrane

Treatment process

Transformer oils (used for five years) were gathered from a substation in HABAC NITROGENOUS FERTILIZER & CHEMICALS COMPANY LIMITED and

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utilized in this study. The oil was extracted from a power transformer rated at 10 MVA and 30/10 kV.

At room temperature, the experiment was carried out. A different volume of oil: 50 mL, 100 mL, and 150 mL was passed over a 2g Graphene membrane. According to the volume of oil utilized, the treated oils were designated as G-oil-50, G-oil-100, and G-oil-150.

The purifying capability of the as-prepared Graphene membrane was compared to that of activated carbon. This material, having a specific surface area of 634 m^2/g, was obtained from Toan Cau Company. Several amounts of old oil were treated with 2 g of activated carbon: 50 mL, 100 mL, and 150 mL. The treated samples were noted as C-oil-50, C-oil-100, and C-oil-150 based on the amount of oil used.

Characterization of the Graphene membrane

The XRD spectra were examined using a Bruker D8 Advance instrument at 40 kV and 40 mA with Cu K radiation (= 0.15406 nm). Using Scherrer's equation, the crystal size values were derived from the XRD pattern (d_{XRD}). Scanning electron microscopy was used to investigate the morphology of the material (SEM, FEI Quanta FEG 650 model).

The N_2 isotherm data were collected using a Micromeritics ASAP 2020 analyzer. The Brunauer-Emmett-Teller (BET) equation was used to calculate the specific surface area of a graphene membrane.

Characterization of the treated oil

The International Electrotechnical Commission (IEC) and the International Organization for Standardization (ISO) standard standards were used to characterize the treated oil. The following approaches were used to characterize oils:

- The KEP OLT-80A tester was used to measure the breakdown voltage.
- The acidity index was calculated using the Burette TITRETTE. The quantity of acid in the oil was calculated by multiplying the number of mg potassium hydroxide (KOH) necessary to neutralize 1 g of old oil by the amount of acid present. To monitor the endpoint of the titration, phenolptaline was utilized as an indicator.
- The oil color was determined using OKATON C-105 Spectrophotometric Colorimeters.
- The viscosity was estimated using Ostwald's viscometer.

Results and discussion

Characterization of the Graphene membrane

Scanning Electron Microscope (SEM) analysis

To analyze the general morphology of the Graphene membranes, SEM method was employed. The typical high-resolution SEM pictures of the Graphene membrane are shown in Fig. 2. These membranes are made up of stacked laminar graphene sheets that are formed by random arrays of flakes, as can be seen. The wrinkled structure of the Graphene membrane is a typical morphology of reduced graphene oxide.

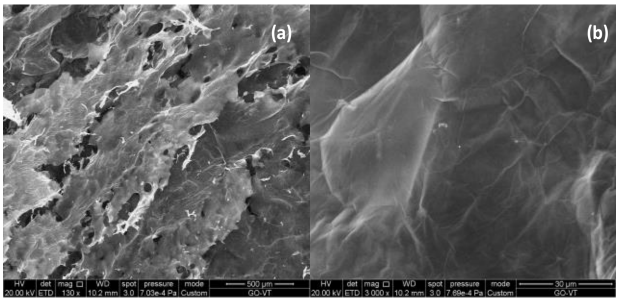

Figure 2: SEM characterization of Graphene membrane

The X-ray diffraction analysis

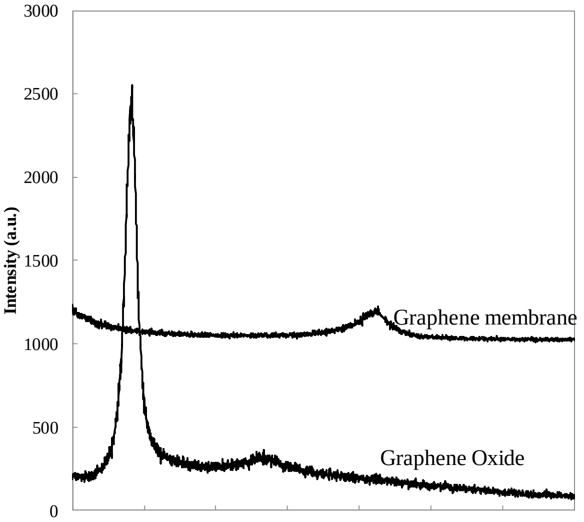

Figure 3: XRD pattern of Graphene oxide and Graphene membrane

The typical XRD patterns of the GO and Graphene membrane in a range of 2 from 5° to 40° are shown in Figure 3. The spacing between two layers of graphene is shown by the (001) diffraction peak in the as-prepared GO's XRD spectrum at 2 = 9.88° (0.89 nm) [16].

The results revealed that graphite was entirely oxidized to produce graphene oxide (GO) [17].

According to the XRD pattern for Graphene membrane, the (001) diffraction peak at 9.88 of GO moved to the (002) diffraction peak at 26, which is the characteristic peak for reduced Graphene Oxide (Graphene membrane) [14]. As a result, the XRD peak shows that GO was decreased to reduced Graphene Oxid , which is Graphene membrane [18]. However, the Graphene membrane diffraction peak (002) indicates that the stacking effect has a short-range order.

N_2 adsorption/desorption measurement

Through isotherm characterizations of the adsorbents, the effectiveness of the purification may be assessed. The N_2 adsorption/desorption isotherm of the two samples, GO and Graphene membrane, is shown in Fig. 4. The distinct texture structures of the two samples show that the isotherms are quite different, corresponding to H3 model. According to IUPAC categorization, the hysteresis loop H3 with aggregation of plate-like particles, which gave birth to the slit-shape pore, is responsible for the isotherms of GO and Graphene membrane samples.

The specific surface area of GO and Graphene membrane, total volume, and average pore diameter are displayed in Table 1. The Graphene membrane has the largest specific surface area 420 (m^2/g), while GO has smaller surface areas (190 m^2/g), according to the results. The specific surface area exposed by commercial activated carbon is greater, measuring 334 m^2/g (Table 1).

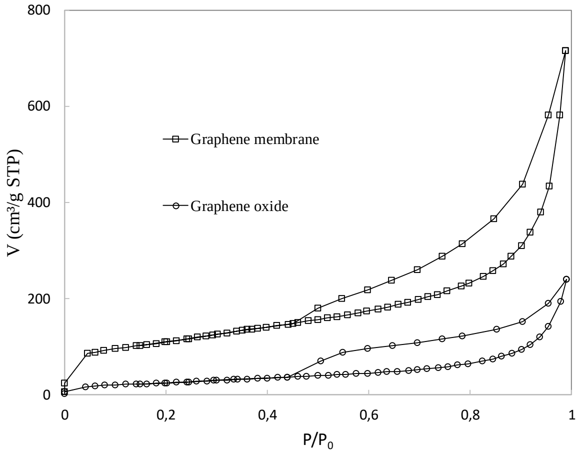

Figure 4: Isotherm of Graphene Oxide and Graphene membrane

According to the Table 1, the total pore volumes of the activated carbon and GO are both higher than those of the Graphene membrane, which have a smaller total pore volume of 0.23 cm^3/g. The Graphene membrane is a mesoporous substance, as evidenced by the average pore diameter indicated in Table 1 and IUPAC nomenclature [12]. With an average pore size of between 2.6 and 8.0 nm, the Graphene membrane may be suitable for oil purification [19].

Table 1: Parameters of specific surface area (S_{BET}), total pore volume (Vp) and the average pore diameter (L)

Material	S_{BET} (m^2/g)	Vp (cm^3/g)	L (nm)
GO	190	0.39	18.9
Graphene membrane	420	0.23	2.6; 8.0
Activated carbon	334	0.25	1.56

Characterization of the treated oil

Effect of treatment on acidity number of oil

Table 2: The acid number TAN (mg KOH/g, standard measurement IEC 62021) of the fresh, aged and treated oil

Oil sample	mg KOH/g
Fresh oil	0.100
Aged oil	0.380
G-oil-50	0.179
G-oil-100	0.258
G-oil-150	0.264
C-oil-50	0.230
C-oil-100	0.279
C-oil-150	0.304

It is well known that oil deterioration produces dissolved acids, which are harmful to power transformers. It is essential to eliminate the oil acidity number for the power transformer to function properly. The acidity of fresh oil, aged oil, and purified oil utilizing commercial activated carbon and Graphene membrane is shown in Table 2. According to the table, increasing the quantity of adsorbent materials reduces acidity. When compared to fresh oil, the oil sample treated with Graphene membrane, G-oil-50, delivers the closest value. As a result of utilizing a particular amount of absorbent, Graphene membrane, the dissolved acids were virtually fully eliminated.

Breakdown Voltage

Because of the moisture, organic acids, and produced sludge, old oil has a greater breakdown voltage than new oil. If the breakdown voltage parameter of the oil in the transformer is less than the limit value, many failures may occur during its operation. The breakdown voltage of oil samples was evaluated in this study using a KEP OLT-80A oil breakdown voltage tester (According to IEC 60156). The breakdown voltage values of the fresh, aged, and treated oil samples are shown in Table 3. The breakdown voltage value of the oil samples treated by the Graphene membrane is greater than the breakdown voltage value of the oil samples treated by commercial activated carbon. The breakdown voltage of the Graphene membrane sample is extremely close to the value of fresh oil.

Table 3: The breakdown voltage values (kV, standard measurement IEC 60156) of the fresh, aged and treated oil

Oil sample	kV
Fresh oil	75
Aged oil	32.4
G-oil-50	71.8
G-oil-100	67.5
G-oil-150	65.8
C-oil-50	64.9
C-oil-100	51.8
C-oil-150	38.5

Viscosity

Low viscosity oil gives a greater cooling effect in power transformers. Because of its deterioration, old oil always has a higher viscosity than new oil. The viscosity of the old oil must be reduced. The viscosity values of the fresh, aged, and treated oil samples are shown in Table VI. Purified oil has a lower viscosity than old oil. Furthermore, oil treated with Graphene membrane has a higher viscosity than oil treated with conventional activated carbon. Moreover, the viscosity of the G-oil-50 sample treated with Graphene membrane is extremely near to that of fresh oil.

Table 4: The viscosity value (standard measurement 40ºC ISO 3104) of the fresh, aged and treated oil.

Oil sample	Measurement 40ºC
Fresh oil	6.45
Aged oil	7.79
G-oil-50	6.87
G-oil-100	6.90
G-oil-150	7.45
C-oil-50	7.24
C-oil-100	7.61
C-oil-150	7.70

Color

The oil colour shows the degeneration of the oil of the power transformer. Because new oil is colorless, the colour of the oil after it has been used in power transformers may be used to evaluate its degradation. Because of contaminants, old oil generally has a dark colour. The colour of the aged oil was determined in this work using Spectrophotometric Colorimeters OKATON C-105 in accordance with ASTM D1500 (Petroleum products-determination of colour - ASTM scale). Table 5 illustrates the colour variation after purification. The results show a significant improvement in the colour of the treated oil utilizing the Graphene membrane.

Table 5: The colour measurement of the fresh, aged and treated oil.

Oil sample	Value by OKATON
Fresh oil	0.45
Aged oil	3.02
G-oil-50	0.76
G-oil-100	1.24
G-oil-150	1.51
C-oil-50	1.34
C-oil-100	1.73
C-oil-150	2.21

The color of three oils is compared in Fig. 5: oil samples treated with Graphene membrane, aged oil, and oil treated with commercial activated carbon. When compared to the oil samples treated with activated carbon and aged oil, the oil sample treated with Graphene membrane has almost colouress appearace.

Figure 5: The colour of the aged oil, oil treatedby activated carbon and Graphene membrane

According to the findings, the Graphene membrane surpasses commercial activated carbon in terms of treatment effectiveness. When compared to the oil sample treated with activated carbon, all of the treated oil parameters using Graphene membrane are extremely near to the fresh oil. The results can be explained by the textural nature of the Graphene membrane, which has a greater specific surface area than commercial activated carbon [20]. Furthermore, the 3D structure of the Graphene membrane with strong mechanical resistance [21], adequate pore size, and low propensity to become stuck [22] may increase the Graphene membrane's purifying capability.

Conclusion

For the first time, the Graphene membrane was created by sonochemically reducing GO in the presence of urea and vacuum filtration. To reduce the GO, urea works as a reducing agent and vacuum filtration make the 3D structure of Graphene. The Graphene membrane created in this study has a larger specific surface area than many others created using different methods, 420 m^2/g. Furthermore, its average pore size, 0.23 cm^3/g, reveals that this material is a mesoporous material with the size required for old oil purification.

As far as we know, this is the first time a Graphene membrane has been employed as an adsorbent for transformer oil purification. The results reveal that when compared to the old oil sample treated with commercial activated carbon, the aged oil sample treated with the Graphene membrane has a greater enhanced property in team of color, viscosity, breaking voltage, and acid number KOH. This discovery might be attributed to graphene's mesoporous structure, 3D structure, unreduced oxygen functional groups, and vacancy defects on the surface of the reduced graphene oxide flake, which could give a high purifying capacity for old transformer oil.

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