International Journal of Engineering & Technology, 7 (4.42) (2018) 89-92

International Journal of Engineering & Technology

Website: www.sciencepubco.com/index.php/IJET

Research paper

The Effect of Different Concentration of 2-Methyl-4-Chlorophenoxy Acetate Acid on Graphite Oxide Intercalation Nanohybrid

N. I. Hasanuddin[1], N. N. Dzulkifli[1]and S. A. I. S. M. Ghazali[1*]

[1]Faculty of Applied Sciences, Universiti Teknologi MARA, Kuala Pilah, Malaysia
**Corresponding author E-mail: sheikhahmadizaddin@ns.uitm.edu.my*

Abstract

In this study, the effect of different concentration of 2-methyl-4-chlorophenoxy acetate acid (MCPA) was investigated to synthesis the successful intercalated herbicide nanohybrid by using graphite oxide (GO) as a nanocarrier. Through this experiment, a well-organized nanohybrid was obtained at the concentration of 0.3 M of MCPA. 2-methyl-4-chlorophenoxy acetate acid- graphite oxide (MCGO) nanohybrid was characterized by using FTIR, PXRD and CHNS. From the results obtained, the expansion of d-spacing of MCGO nanohybrid has indicated the presence of MCPA in the GO interlayer with the loading percentage around 98 %. Besides, FTIR spectra of the nanohybrid shown a resemblance peaks of the MCPA and GO that could confirm the formation of nanohybrid. Furthermore, the controlled release of MCPA into sodium carbonate solution (Na_2CO_3) was found to be reliant on concentration of Na_2CO_3 solution.

Keywords: *Graphite oxide; MCPA; Nanohybrid; Concentration; Herbicide*.

1. Introduction

Through the advance of current technologies, the development of graphite especially material based graphite oxide (GO) had received a huge of attention and funding across the countries to improve our daily life. By drawing a work of reference [1], a few giant countries had spent a big amount of funding on this field such as Korea, European Union, United Kingdom and Huawei Technologies, a Chinese company. This magnificent nanomaterial has been explored mainly in drug and gene delivery system [2-6], biosensors [7], fabrication of supercapacitors [8] and nanoelectronics [9-11]. In addition, graphite oxide as a nanocarrier also has possess remarkable characteristic as it has a large number of surface area, huge layers number and high purity [12-14]. Besides, layers number of graphite oxide plays an important part by increasing the rigidity of nanocarriers while a large surface area of graphite oxide significant in high drug/herbicides loading capacity compared with other nanomaterial [15]. Owing to these specialties, graphite oxide is the most ideal nanocarrier in providing an efficient loading of drugs/herbicides molecules based on non-covalent dynamic bonding interactions such as hydrogen bonding, π–π stacking, and electrostatic forces [16].

Intercalation reaction of nanocarrier with guest species can dramatically change the chemical and physical properties of graphite oxide. It is due to reversible insertion of guest species as in an ions, atoms or molecules state into the interlayer region of graphite oxide [17]. The guest anion could come from drug, herbicides, pesticide or plant regulator. 2-methyl-4-chlorophenoxy acetate acid (MCPA) is the example of herbicide that can intercalate into the nanocarrier. Fig 1 shown the molecular structure of MCPA. It is selective chemical herbicide that used to diminish or inhibit the growth of broadleaves weeds in wheat, paddy, corn and potatoes field [18]. However, World Health Organization (WHO) has categorized MCPA as slightly hazardous herbicide with class III classification because it can lead to soil and water pollution. It also can irritate human's skin upon direct exposure. Therefore, MCPA was chosen to intercalate into the GO nanocarrier for the formulation of new herbicide delivery system to minimize these problems. Different concentration of MCPA ranging from 0.1 M to 0.5 M were used to identify the most successful intercalation process to form MCGO nanohybrid. The controlled release property of this novel nanohybrid, MCGO was also investigated.

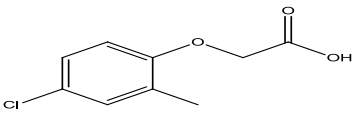


Fig.1: Structural formula for MCPA

2. Results and Discussion

2.1. FTIR Spectra

The spectra of MCPA, GO and MCGO nanohybrids at various concentration were demonstrated in Fig 2. For MCPA spectrum, a peak located at 2910 cm^{-1} was representing the hydroxyl group (O-H) due to vibration of the COOH [20]. There was also a peak observed at 2878 cm^{-1} that ascribed to methyl group. Next, the peak at 1707 cm^{-1} indicated the presence of C=O stretching while the peaks at 1494 cm^{-1} and 1428 cm^{-1} were corresponding to the C=C vibration of the aromatic ring. In addition, the symmetric and asymmetric stretching mode of C-O-C vibration can be seen at the peak of 1298. The functional group of para-disubstituted ring have been observed at 802 cm^{-1} that defined the presence of methyl

Copyright © 2018 Authors. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

group and chlorine atom. Lastly, the C–Cl stretching vibration was pointed out at the peak of 751 cm^{-1}.

As for GO, an intense broad peak found at 3362 cm^{-1} contributed to the stretching O-H band while the peak at 1730 cm^{-1} was attributed to the stretching vibration of C=O bond which displayed the presence of carboxylic acid. Furthermore, the C=C bonds was detected at 1626 cm^{-1} and the peaks at 1221 cm^{-1} and 1050 cm^{-1} represent the functional group of epoxy (C-O) and alkoxy group (C-O) respectively.

For the MCGO nanohybrids, spectrum at 0.1 M does not shown any significant peak that could relate to the intercalation process while spectrum at 0.3 M and 0.5 M did show the exhibited peaks obtaining from spectra of MCPA and GO. However, some peaks may slightly shifted compared to those pure MCPA and GO. Even though 0.5 M MCGO nanohybrid did exhibited some peaks as MCPA and GO, but the intercalation process did not completely successful. In the other hand, spectrum of 0.3 M MCGO nanohybrid has shown the disappearance of C=O peak of the carboxylic acid and a new peak has appeared at 1308 cm^{-1} that attributed to the C=O vibration of the carboxylate anion. This peak is significance to imply the loading of MCPA in the GO interlayers. Furthermore, a broad absorption peak at 3376 cm^{-1} indicated the O-H stretching vibration due to the absorbed and interlayer water molecules in the nanocomposite [21].

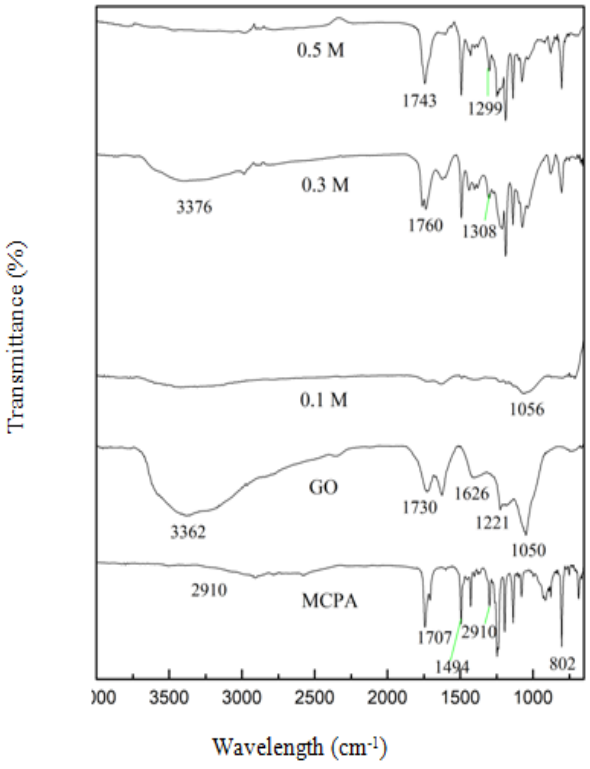


Fig. 2: FTIR spectra for MCPA, GO and various concentration of MCGO nanohybrids

2.2. PXRD Pattern

Fig 3 depicts the XRD pattern for GO and MCGO nanohybrids at various concentration of MCPA. Based on the pattern of GO, a very strong peak at 2θ = 9.54º was appeared which shown a good agreement with the researches reported previously [15, 22]. Next, a single peak in graphite oxide was observed at 2θ = 9.6º and its d-spacing was calculated to be 9.3 Å by using Bragg's law equation. The results of XRD pattern primarily proved the successful functionalization of graphite oxide that contained many oxygenated functional groups such 1 2-epoxides and hydroxyl groups are in the basal-plane while carboxyl and hydroxyl groups present at the edges.

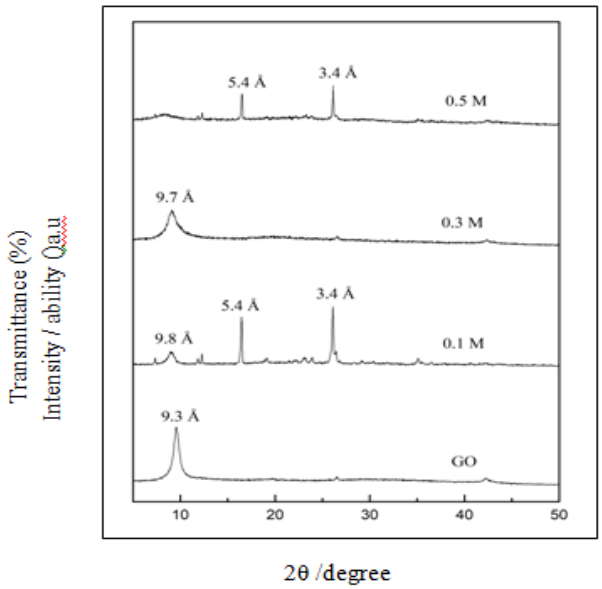


Fig.3: XRD pattern for GO and MCGO nanohybrid at various concentration of MCPA

These analysis were also be done for the further confirmation about the most succesful formation of nanohybrid at optimum concentration. As a result, a significant peak was shown in the XRD pattern of 0.3 M. In 0.3 M XRD pattern, the peak appeared was slightly shifted downwards to 9.10° than in GO and became wider with a d-spacing of 9.7 Å. The increases in the d-spacing of nanohybrid indicated that the intercalation process was occurred with the inclusion of a new guest anion, MCPA. Both GO and MCGO nanohybrid have exhibited similar properties in their XRD pattern which they only have one peaks appeared. This one peak became the indicator for the successful intercalation since there was an absence of any peak of pure MCPA in the XRD pattern of nanohybrid [16]. Meanwhile, 0.1 M and 0.5 M nanohybrids were said to be unsuccessful since they have the reflection peaks from GO and MCPA itself. In contrast, MCGO nanohybrids has showed an amorphous characteristic which lacks of crystallinity property than GO. It seemed evident that 0.3 M MCGO nanohybrid was being selected for futher characterization.

2.3. CHNS Analysis

According to the Table 1 shown below, the percentage of natural graphite powder was 75 % of carbon, 0.07 % of hydrogen and 0.35 % of sulphur while the prepared GO contained 54 % carbon, 1.76 % hydrogen and 1.97 % sulphur. After the oxidation of graphite, the percentage of the carbon decreases due to the presence of oxygen-containing functional groups implanted on the GO sheets. Besides, the composition of hydrogen and sulphur were increased. The composition of sulphur was increasing due to the usage of sulphuric acid in the experiment. In these result, the percentage of nitrogen was not obtained due to the absence of nitrogen atom throughout the process.

For the MCGO nanohybrid, the percentage of carbon was 52 % and the percentage of hydrogen was 3.24 % as well as the percentage of sulphur was 0.75 %. The changes in the results might be due to contribution of other functional groups from MCPA after the intercalation taken place. From the CHNS results, the percentage loading of MCPA that had been intercalated into the GO calculated to be 98 % which considerably higher compared to other nanohybrid. Reference [23] had informed in their journal that the delivery system using graphite nanohybrid could be reached up to 200 %. This shown that MCGO nanohybrid can be a great potential of herbicide delivery system.

Table 1: Composition of elements present

Samples	Carbon	Hydrogen	Sulphur	Nitrogen
Graphite	75	0.07	0.35	0
GO	54	1.76	1.97	0
MCGO	52	3.24	0.75	0

2.4. Controlled Release Study

Controlled release study was done to determine the amount of MCPA anions that was de-intercalated or released from the GO by using the UV-Visible instrument. The release profile of MCPA from the MCGO nanohybrid in sodium carbonate solution (Na_2CO_3) was displayed in Fig 4. The release of MCPA anion from MCGO nanohybrids was ascribed due to the π-π stacking interaction, hydrogen bonding and electrostatic attraction between MCPA and GO [21]. In this research, 0.1 M and 0.01 M of same solution were used for the controlled release study to investigate the crucial factor that could affect the percentage release of MCPA anion. Thus, the results obtained does proved that the higher concentration of anions can shorter the release time to de-intercalated from the nanohybrid.

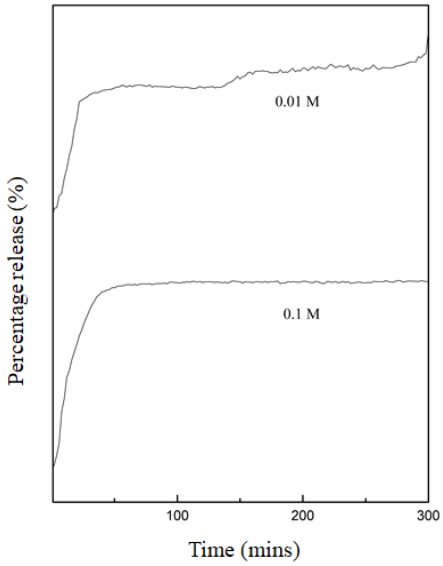


Fig.4: Release studies of 0.3 M MCGO nanohybrid at different concentration of Na_2CO_3 solution

The release percentage of MCPA from nanohybrid in the 0.1 M Na_2CO_3 solution was 66 % with the rapid release occurring until 60 mins before achieved an equilibrium. However, in 0.01 M Na_2CO_3 solution, the graph did not achieved an equilibrium as it has lower concentration of Na_2CO_3 solution and need more time to completely de-intercalated. These happened due to incorporated of carbonate anions that have high affinity towards interlayers of GO [18]. So, it would favor the exchanged of carbonate anions with the intercalated MCPA anions. As a result, carbonate ions moved into the interlayer of graphite oxide and simultaneously, the MCPA will be released into the aqueous solutions. By this exchange method, rate of the MCPA in the MCGO nanohybrid would eventually decrease after released into the aqueous solution.

3. Experimental

3.1. Chemicals and Reagents

Graphite powder and MCPA were purchased from Sigma Aldrich and being used without further purification. Sulphuric acid (98%), potassium permanganate, hydrochloric acid (35%), hydrogen peroxide and ethanol (98%), were obtained from R&M Chemical. All the solutions were prepared by using deionized water.

3.2. Synthesis of Graphite Oxide

Graphite oxide was prepared by using the improved Hummer's Method through the oxidation process. Firstly, about 1 g of graphite powder and 12 M of sulphuric acid (H_2SO_4) were mixed together in a beaker under mechanical stirring. Then, 3.0 g of potassium permanganate ($KMnO_4$) was added slowly into the beaker to keep the temperature of the suspension lower than 20 ^{0}C. Next, the reaction system was transferred to oil bath shaker for 30 minutes before being placed in a beaker. In the beaker, 50 mL of deionised water was poured into the mixture and the solution was stirred for 15 minutes at 95 ^{0}C. After that, 150 mL of deionised water was added and followed by a dropwise addition of 30 % hydrogen peroxide. During this step, the colour of the solution was changed from dark brown to yellow colour. The mixture was filtered and washed them with the hydrochloric acid aqueous solution to remove metal ions. Lastly, the precipitate was dried at 60 ◌C in the vacuum oven for 48 hours.

3.3. Synthesis of MCGO Nanohybrids

The MCGO nanohybrid was done by using ion-exchange method [19] with various concentration of MCPA ranging from 0.1 M to 0.5 M. This method was run under the room temperature. Firstly, prepared graphite oxide was reacted with 25 mL aqueous solution of MCPA. As the mixture of graphite oxide and MCPA were mixed together, the mixture was stirred for 5 hours on the hot plate before aging for 18 hours in an oil bath shaker. Then, the slurry solution was taken for centrifuged and washed several times with deionized water. The product obtained was dried in an oven at temperature of 70 ^{0} C for 72 hours.

3.4 Controlled Release Study Method

The release of MCPA from 0.3 M MCGO nanohybrid were prepared with different concentration of sodium carbonate (Na_2CO_3) which were 0.01 M and 0.1 M. 3 mg of 0.3 M MCGO nanohybrid was placed in the cuvette on top of aqueous media contained 0.1 M Na_2CO_3 and being run for the certain period of time. Then, these steps were repeated by using 0.01 M Na_2CO_3 solution for the comparison. The percentage release of MCPA from 0.3 M MCGO nanohybrid was measured by using UV-Vis instrument with the wavelength of 237 nm.

4. Conclusion

MCGO nanohybrid was successfully attained through ion-exchange method by intercalating MCPA into GO interlayers. In fact, the optimum concentration of MCPA has to be 0.3 M to allow the complete intercalation process happened. PXRD, FTIR-ATR spectra and CHNS analysis were confirmed the existing of MCPA in GO nanocarrier with the percentage loading of 98 %. Moreover, the stimulation of MCPA in the soil was accomplished with the controlled release study with the percentage release of 66 % in 0.1 M Na_2CO_3 solution. The release of MCPA is dependent to the concentration of herbicide used in order to be an effective herbicide delivery system.

Acknowledgement

This research was funded by the Ministry of Higher Education (MOHE) under the FRGS grant no. 600IRMI/FRGS5/3(66/216). The authors also would like to thank department of Academic Affair of Universiti Teknologi Mara (UiTM) Kuala Pilah for providing the fund and the facilities to carry out this study.

References

[1] G. Lalwani, M. D'Agati, A. M. Khan, and B. Sitharaman, "Toxicology of graphene-based nanomaterials," Advanced Drug Delivery Reviews, vol. 105, pp. 109-144, 2016

[2] Wang, Y., Li, Z., Wang, J., Li, J., and Lin, Y. (2011). Graphene and graphene oxide : biofunctionalization and applications in biotechnology. Trends in Biotechnology, 29(5), 205–212

[3] Meng, N., Zhang, S., and Zhou, N. (2010). Biopolymer-modified graphite oxide nanocomposite films based on benzalkonium chloride – heparin intercalated in graphite oxide, Nanotechnology.185101

[4] Tran, T. H., Nguyen, H. T., and Pham, T. T. (2015). Development of a Graphene Oxide Nanocarrier for Dual-Drug Chemo-phototherapy to Overcome Drug Resistance in Cancer Article Development of a Graphene Oxide Nanocarrier for Dual-Drug Chemo- phototherapy to Overcome Drug Resistance in Cancer. Applied Materials & Interfaces

[5] Yu, D., Ruan, P. A. N., Meng, Z., Zhou, J., and Ber, P. (2015). The Structure-Dependent Electric Release and Enhanced Oxidation of Drug in Graphene Oxide-Based Nanocarrier Loaded with. Journal of Pharmaceutical Sciences, 104(8), 2489–2500

[6] Torbati, M. B., Ebrahimian, M., and Yousefi, M. (2016). GO-PEG as a drug nanocarrier and its antiproliferative effect on human cervical cancer cell line, 1401(April), 0–6.

[7] Kumar, A., and Lee, C. H. (2013). Synthesis and Biomedical Applications of Graphene : Present and Future Trends. *Wiley InterScience*. Vol. 94, 1420–1427

[8] Chowdhury, D. R., Singh, C., and Paul, a., (2014). RSC Advances graphite oxide synthesis, 15138–15145

[9] Cao, Y., Li, G. and Li, X., (2016). Graphene / layered double hydroxide nanocomposite : Properties , synthesis , and applications. Chemical Engineering Journal, 292, 207–223.

[10] Wu, Z., Ren, W., Gao, L., Liu, B., Jiang, C., and Cheng, H. (2008). Synthesis of high-quality graphene with a pre-determined number of layers. Carbon, 47(2), 493–499.

[11] Jeong, H., Lee, Y. P., Jin, M. H., Kim, E. S., Bae, J. J., and Lee, Y. H. (2009). Thermal stability of graphite oxide. Chemical Physics Letters, 470(4–6), 255–258

[12] Ceriotti, G., Romanchuk, A. Y., Slesarev, A. S. and Kalmykov, S. N., (2015). Rapid method for the purification of graphene oxide. RSC Adv., Nanoscale.5(62), 50365–50371.

[13] Chen, J., Li, Y., Huang, L., Li, C., and Shi, G. (2014). High-yield preparation of graphene oxide from small graphite flakes via an improved Hummers method with a simple purification process. Carbon, 81, 826–834.

[14] Chen, J., Yao, B., Li, C., and Shi, G. (2013). An improved Hummers method for eco-friendly synthesis of graphene oxide. Carbon, 64(1), 225–229

[15] Liu, J., Cui, L., and Losic, D. (2013). Acta Biomaterialia Graphene and graphene oxide as new nanocarriers for drug delivery applications. Acta Biomaterialia, 9(12), 9243–9257.

[16] Dorniani, D., Saifullah, B., Barahuie, F., Arulselvan, P., Zobir, M., Hussein, B. and Twyman, L. J. (2016). Graphene Oxide-Gallic Acid Nanodelivery System for Cancer Therapy. Nanoscale Research Letters.

[17] Braterman, P. S., Xu, Z. P., Yarberry, F., Auerbach, S. M., & Carrado, K. a. (2004). Handbook of layered materials: layered double hydroxides, 373–474

[18] Sarijo, Sheikh, S., Izaddin, A., and Mohd, S. (2012). Synthesis of nanocomposite 2-methyl4-chlorophenoxyacetic acid with layered double hydroxide : physicochemical characterization and controlled release properties, J Nanopart Res (3)

[19] Sarijo, S. H., and Hussein, M. Z. (2015). Synthesis of dual herbicides-intercalated hydrotalcite-like nanohybrid compound with simultaneous controlled release property. Porous Mater.

[20] Salleh N.M, Mohsin S.M.N, Sarijo S.H and Ghazali S.A.I.S.M. (2017). Synthesis and Physico-Chemical Properties of Zinc Layered Hydroxide-4-Chloro-2-Methylphenoxy Acetic Acid (ZMCPA). *Materials Science and Engineering.*

[21] Barahuie, F., Saifullah, B., Dorniani, D., Fakurazi, S., Karthivashan, G., Zobir, M., and Elfghi, F. M. (2016). Graphene oxide as a nanocarrier for controlled release and targeted delivery of an anticancer active agent , chlorogenic acid. Materials Science & Engineering C, 74, 177–185.

[22] Song, J., Wang, X., and Chang, C. (2014). Preparation and Characterization of Graphene Oxide, Journal of Nanomaterials. Volume 2014 : 276143, (6)

[23] Zhang, L., Xia, J., Zhao, Q., Liu, L., and Zhang, Z. (2010). Functional Graphene Oxide as a Nanocarrier for Controlled Loading and Targeted Delivery of Mixed Anticancer Drugs, 537–544.