

Slow Release of Menthol Using Sorbents Developed from Microwave Graphene Oxide

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Abstract

Menthol is a key ingredient in many of the traditional Thai aroma products such as potpourri and herbal air freshener. However, it suffers from the rapid evaporation and sublimation loss. In this work, microwave graphene oxide (mGO) has been prepared as sorbent and tested for the slow release of menthol. Menthol was loaded into microwave graphene oxide at loading ratios of 1:0.5 and 1:1. The release performance of the mGO as compared to traditional essential oil reed diffuser and the pure menthol was studied by monitoring the menthol weight loss at the temperature of 80°C until all of the menthol evaporated using thermogravimetric analysis. It was found that mGO can significantly slow down the menthol release rate compared to that of the pure menthol by up to eight times slower. The interaction and adsorption mechanism of the menthol-loaded microwave graphene oxide was also studied using Fourier Transform Infrared Spectroscopy (FTIR) which indicates that menthol adsorbs strongly onto the mGO leading to the slow release rate.

Keywords: Graphene oxide, Microwave graphene oxide, Menthol, Slow release

1 Introduction

Aroma compounds are useful in many products such as fabric softener, air freshener and fragrance. Menthol is one of the most popular aroma used. However, menthol evaporates rapidly, leading to short product lifetime

especially for air freshener applications. Jun Zhang *et al.* have reported preparation of nanoporous silica materials adsorbent for controlled release of the volatile menthol [1]. Controlled release of menthol have also been investigated using mesoporous silica [2] and bee wax [3]. Cellulosic system for general purpose

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controlled release of aroma compounds has also been reviewed [4]. Menthol has been widely used in food, pharmacy, and cosmetics, due to its unique fragrance and cooling effect. However, menthol is high volatility. Hence, the development of good materials for use as sorbent are required.

Graphene oxide is the graphite that has been oxidized and exfoliated into a few-layer stack. It contains a range of reactive oxygen functional groups and it is highly hydrophilic [5]. The popular method to synthesize graphene oxide is the Hummers' method [6]. Once the graphite stack has been exfoliated by oxidation, the oxidized graphene oxide can also be reduced back using chemical or thermal treatment to remove oxygenated functional groups, producing materials with large surface area. This state may be called reduced graphene oxide which can have high potential for adsorption or slow release applications. Many methods to prepared reduced graphene oxide have been developed such as the thermal reduction method, chemical reduction method, and multi-step reduction, for instance, the combination of the hydrazine reduction and low temperature annealing [7]. These conventional methods have disadvantages of often using dangerous chemicals which are toxic to environment, or slow, and high energy consumed.

Among them, thermal treatment by microwave irradiation is a friendly method that involve no toxic chemicals, has low cost, and very rapid. Conventional thermal annealing would be rather slow and high energy consumption. It has been reported that microwave irradiation can create reduced graphene oxide in a short time. The disadvantage may be that the microwave heating is difficult to control or to have uniform distribution of microwave radiation in the materials. There are reports about rapidly and efficiently method to prepare exfoliated graphite materials [8] and the exfoliation and reduction of graphite oxide [9] by microwave irradiation. The rapid and mild thermal reduction of graphene oxide to graphene induced by the assistance of microwaves in a solution [10]. Dejian Chen *et al.* proposed an extraction of essential oils, using graphene aerogel fabricated by the hydrothermal technique as extracting reagent that can bind well to essential oils enabling good separation of the oil [11]. The good binding between essential oils and graphene was explained in terms of hydrophobic interaction between the oil and the graphene.

Due to the adsorption property of reduced graphene oxide, the absorption of aroma compounds onto the reduce graphene oxide by microwave irradiation seems quite possible. The microwave graphene oxide also has combination of both hydrophobic surface due to the aromatic benzene ring part as well as some remaining oxygenated species are expected to interact quite well with essential aroma such as menthol that has both the hydrophobic benzene ring as well as the alcohol group. Here microwave graphene oxide is utilized as sorbent for the slow release of menthol. The release rate of menthol from the sorbents were studied by monitoring the weight loss of the menthol-loaded sorbents using thermogravimetric analysis. Their interactions are also characterized by the FTIR techniques.

2 Experimental

2.1 Materials

Graphite powder was purchased from ACROS (99% min). Potassium permanganate (KMnO_4 , UNIVAR, 99%), sulfuric acid (H_2SO_4 , Fisher Chemical, >95%), sodium nitrate (NaNO_3 , LOBA, 99%), and hydrochloric acid (HCl , LOBA, 35.4%) were purchased from Apex Chemicals. Hydrogen peroxide (6% w/v) was from government pharmaceutical organization (GPO). L(-)-menthol used was from ACROS (99.5%). Filter papers (WhatmanTM, No.4) and reed diffusers (from rattan plant) were used as traditional sorbent materials for comparison.

2.2 Preparation of microwave graphene oxide

First, graphene oxide is prepared by Hummers' method [6]. In brief, 3 g of the graphite powder and 1.5 g of sodium nitrate were mixed with 69 ml of sulfuric acid in 1000 ml beaker under stirring in an ice-bath. Then 9 g of potassium permanganate was added slowly and the reaction temperature was kept below 20°C. The system was warmed to 35°C and stirred for 30 minutes. Next, 138 ml of water was slowly added and maintained at the temperature of 98°C for 15 minutes. After that, the reaction was cooled using an ice-bath for 10 minute, 420 ml of the water and 3 ml of hydrogen peroxide (30%) were added in order to stop the reaction. The obtained products were centrifuged at 4000 rpm for 5 minute, multiple washed with 5% HCl and DI water, and dried in vacuum oven for 24 h. The dried solids

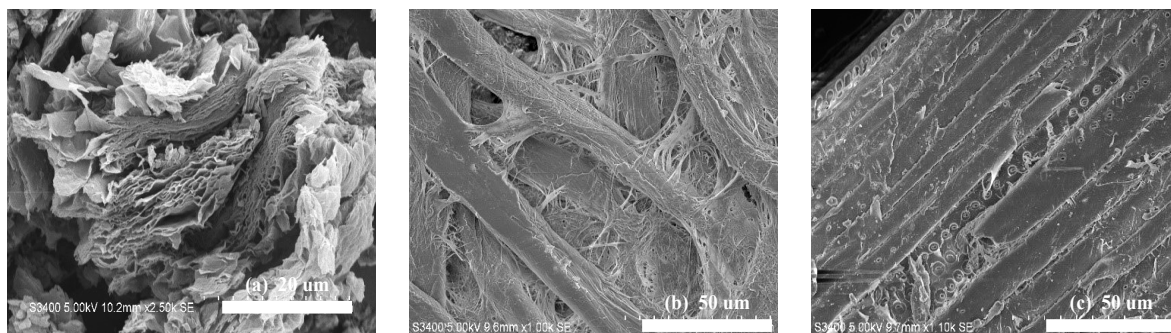


Figure 1: SEM images of (a) mGO, (b) filter paper, and (c) reed diffuser.

were treated by microwave irradiation at 700 watts (Samsung model ME81Y) for 1 minute. The dark brown solids of GO were turned into the black fluffy of the desired microwave reduced graphene oxide, or microwave graphene oxide (mGO).

2.3 Loading of menthol

In this experiment, mGO and solid menthol were mixed together at the two loading ratio of 1:0.5 and 1:1 (mGO:menthol, w/w).

The mixture was then heated up to melt the menthol and then sonicated in an ultrasonic bath maintained at the temperature of 40°C for 30 minutes. For comparison, traditional essential oil releasers, which are the reed diffuser (the wooden stem used for diffusion of fragrance oil into air) and the filter paper (representative of fragrance paper and dried scented flower leaves), were also prepared. These materials were cut into small pieces with a size of 2×2 mm for filter paper and 1×3 mm for reed diffuser and were loaded with menthol at the ratio of 1:0.5 (materials:menthol) using the same method as that with mGO described above. For the loading ratio of 1:1, the white crystal of excess menthol was visibly observed on the surface of the reed diffuser and the filter paper, indicating that they cannot adsorb all menthol into their structures at this loading ratio, thus the 1:1 ratio was neglected for reed diffuser and the filter paper.

2.4 Characterizations

The rate of menthol released were measured by following the weight loss of samples as a function of time at a constant temperature of 80°C using

thermogravimetric analysis (Mettler Toledo, TGA/SDTA851°). This temperature selected is in order to have appreciable released rate not taking too long time to measure. Isothermal release of menthol was studied until the weight of sample became stabled, the initial weight of sample was 15 mg. The normalized weight loss at Y-axis was calculated from the weight of the sample at time t divided by the initial weight of the sample. Fourier-Transform Infrared (FTIR) spectroscopy was used to examine the chemical characteristics as well as the interaction between the sorbent and the menthol. The FTIR spectra of the samples were measured in the Attenuated Total Reflectance (ATR) mode using diamond head with deuterated, L-alanine doped triglycine (DTGS) detector (Thermo Scientific, Nicolet iS5 FT-IR). FTIR spectra were obtained with the average of 32 scans from 4000 cm^{-1} to 525 cm^{-1} , with spectral resolution of 4 cm^{-1} . Brunauer-Emmett-Teller (BET) method were used to calculate the specific surface area of the sorbents.

3 Results and Discussion

3.1 Morphology

Surface morphology of mGO, filter paper, and reed diffuser are shown in Figure 1 (a), (b) and (c) respectively. SEM images of mGO shows that it consists of very small sheets crumpled together. For reed diffuser, it consists of fibrous like structure. In filter papers, the fibers appear to be smoother and more aligned than that of the reed diffuser. BET measurement shows that the specific surface area of the mGO is quite large of about 315 m^2/g while those of reed diffuser and filter paper are very small ($< 1\text{m}^2/\text{g}$).

3.2 Release rate and thermogravimetric analysis

Figure 2 shows the normalized weight loss of the samples as a function of time at a constant temperature of 80°C. The pure menthol weight constantly decreases as a function of time until all of the menthol completely evaporated at about 3,400 sec. The menthol released rate from each substance are in the order from the fastest to the slowest as follows: 0.16mg/min for pure menthol, 0.15 mg/min for filter paper:menthol (1:0.5), 0.13 mg/min for reed diffuser:menthol (1:0.5), 0.05 mg/min for mGO:menthol (1:1), and 0.02mg/min for mGO:menthol (1:0.5).

The menthol-loaded reed diffuser has a slightly faster rate of decrease initially, but the overall rate of decrease is slower than that of pure menthol with the final weight of about 65% due to the bare weight of the reed diffuser alone.

This is equivalent to the actual loading of menthol in the reed diffuser of about 1:0.5. The filter paper also has a similar rate of weight decrease to that of the reed diffuser but with a lower final weight of about 55% equivalent to the menthol loading ratio of about 1:0.8 higher than the ratio used in the preparation (1:0.5 of filter weight: menthol weight), which is probably due to some moisture or volatile content in the filter paper used. For the pure mGO, there is almost no weight change, the weight loss of the pure mGO is less than 0.5% during this time indicating that there is no significant content in pure mGO that can be volatile at this temperature similar to that observed also in [8]. The menthol-loaded mGO has a slower release rate with a final weight of about 75%, equivalent to the menthol loading ratio of about 1:0.25. This is lower than the ratio used in the preparation (1:0.5 of the mGO weight: menthol weight), which means that not all menthol was loaded into the mGO during mixing probably because some of the menthol was loss due to evaporation during the heating up, or some menthol was attaching to the container's wall. Similarly, the menthol-loaded mGO at the ratio of 1:1 also has a final weight of about 55%, equivalent to the menthol loading ratio of about 1:0.8 lower than the ratio 1:1 used in the preparation.

The 1:1 menthol-loaded mGO shows slower weight loss than those of pure menthol, reed diffuser or filter paper. Decreasing the menthol loading ratio from 1:1 to 1:0.5 decreases the rate even further. The

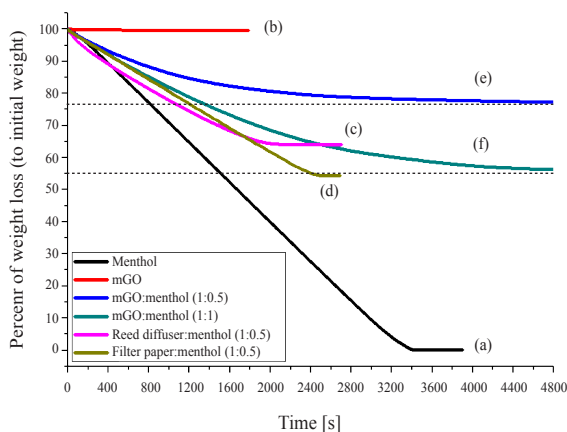


Figure 2: Normalized percent weight loss of the samples as a function of time at a constant temperature of 80°C. (a) pure menthol, (b) mGO, (c) menthol-loaded reed diffuser, (d) menthol-loaded filter paper, (e) menthol-loaded mGO at a 1:1 weight ratio (mGO:menthol), (f) menthol-loaded mGO at a 1:0.5 ratio.

average rate of menthol release calculated from the average slope of the graph. Using this, the rate of menthol release in menthol-loaded mGO at the 1:0.5 loading can be calculated to be about five times slower than that of the pure menthol and three times slower than that of traditional reed diffuser or filter paper. This indicates that mGO can help slow down the rate of menthol release from their structure compared to those of conventional sorbents.

3.3 FTIR

In order to understand the menthol adsorption on these sorbents further, FTIR was used to probe the interaction between menthol and mGO.

Figure 3 shows the FTIR spectra of menthol (a), mGO (b), menthol-loaded mGO (c), filter paper (d), menthol-loaded filter paper (e), reed diffuser (f), and menthol-loaded reed diffuser (g), respectively. Menthol has several strong and sharp peaks which can be assigned to characteristic functional groups of $-\text{CH}_2$ (2927, 2845, and 1447 cm^{-1}), $-\text{CH}_3$ (2954, 2869 cm^{-1}), and C-O bonds (1044, 1025 cm^{-1}) [12]. These peaks can still be seen in the menthol-loaded sorbent samples.

In order to see the difference clearer, subtraction spectra of the menthol-loaded samples in the region of strong menthol peaks around 950–1080 cm^{-1} are

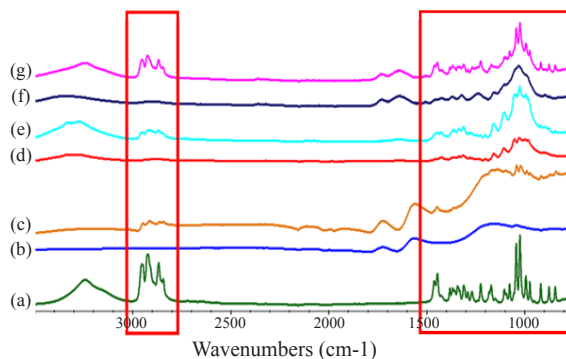


Figure 3: FTIR spectra of (a) menthol, (b) mGO, (c) menthol-loaded mGO (1:0.5 ratio), (d) filter paper, (e) menthol-loaded filter paper (1:0.5 ratio), (f) reed diffuser, and (g) menthol-loaded reed diffuser (1:0.5 ratio).

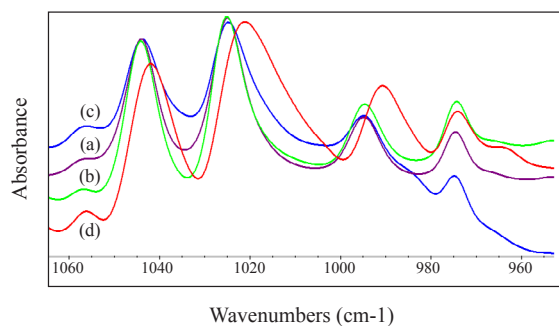


Figure 4: shows difference FTIR spectra of the menthol-loaded adsorbents to that of the bare adsorbents showing only the spectrum due to the menthol loaded on the sorbents compared with that of the pure menthol, (a) pure menthol, (b) menthol-loaded reed diffuser, (c) menthol-loaded filter paper, (d) menthol-loaded mGO.

shown in Figure 4. Here it can be seen that the strong peaks at 1025 and 1044 cm^{-1} in menthol are shifted to lower frequency in the mGO sample, while those of menthol in reed diffuser and filter paper show no shift. This indicates that menthol adsorbed onto the mGO interacts strongly with the mGO such that their peaks are shifted and also broaden, while those of traditional adsorbents such as the reed diffuser and the filter paper interact less strongly. Menthol has a planar aromatic benzene ring structure. The strong interaction between menthol and microwave graphene oxide may come from

the good interaction between the menthol molecule and the planar structure of the reduced graphene oxide plane [13]. The result that is also in the same trend as that of the menthol release rate observed in the TGA result.

4 Conclusions

Microwave graphene oxide (mGO) prepared by microwave thermal method is a very simple and rapid method to achieve reduced graphene oxide. The obtained mGO can be used as a novel adsorbent for a slow release of aroma compounds such as menthol. mGO can decrease the release rate of menthol compared to pure menthol and other commonly used substrates such as filter paper and reed diffuser. From the FTIR spectra, mGO shows strong interaction with the menthol, causing the peak vibrations to be shifted to lower wavenumber, which may be due to a good packing of menthol molecule with the planar structure of the reduced graphene oxide.

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References

- [1] J. Zhang, M. Yu, P. Yuan, G. Lu, and C. Yu, "Controlled release of volatile (–)-menthol in nanoporous silica materials," *Journal of Inclusion Phenomena and Macrocyclic Chemistry*, vol. 71, pp. 593–602, 2011.
- [2] X. Y. Ming Dong, Y. Y. Li, F. Wei, Y. Zhou, S. L. Zhou, and J. H. Zhu, "Novel menthol releaser derived from as-synthesized mesoporous silica," *RSC Advances*, vol. 5, pp. 5494–5500, 2015.
- [3] L. Zhu, H. Lan, B. He, W. Hong, and J. Li, "Encapsulation of menthol in beeswax by a supercritical fluid technique," *International Journal of Chemical Engineering*, vol. 7, 2010.
- [4] S. B. Todorova, C. J. S. M. Silva, N. P. Simeonov, and A. Cavaco-Paulo, "Cotton fabric: A natural matrix suitable for controlled release systems," *Enzyme and Microbial Technology*, vol. 40, pp. 1646–1650, 2007.

- [5] D. R. Dreyer, S. Park, C. W. Bielawski, and R. S. Ruoff, "The chemistry of graphene oxide," *Chemical Society Reviews*, vol. 39, pp. 228–240, 2010.
- [6] W. S. Hummers and R. E. Offeman, "Preparation of graphitic oxide," *Journal of the American Chemical Society*, vol. 80, pp. 1339–1339, 1958.
- [7] S. Pei and H.-M. Cheng, "The reduction of graphene oxide," *Carbon*, vol. 50, pp. 3210–3228, 2012.
- [8] T. Wei, Z. Fan, G. Luo, C. Zheng, and D. Xie, "A rapid and efficient method to prepare exfoliated graphite by microwave irradiation," *Carbon*, vol. 47, pp. 337–339, 2009.
- [9] Y. Zhu, S. Murali, M. D. Stoller, A. Velamakanni, R. D. Piner, and R. S. Ruoff, "Microwave assisted exfoliation and reduction of graphite oxide for ultracapacitors," *Carbon*, vol. 48, pp. 2118–2122, 2010.
- [10] W. Chen, L. Yan, and P. R. Bangal, "Preparation of graphene by the rapid and mild thermal reduction of graphene oxide induced by microwaves," *Carbon*, vol. 48, pp. 1146–1152, 2010.
- [11] D. Chen, G. Zhu, J. Lin, J. Liu, and S. Huang, "Renewable reduced graphene oxide-based oil-absorbent aerosols: preparation and essential oils absorption ability," *ACS Sustainable Chemistry & Engineering*, vol. 3, pp. 1428–1433, 2015.
- [12] F. A. Al-Bayati, "Isolation and identification of antimicrobial compound from mentha longifolia L. leaves grown wild in Iraq," *Annals of Clinical Microbiology and Antimicrobials*, vol. 8, pp. 20–20, 2009.
- [13] B. Wang, W. Chen, H. Fu, X. Qu, S. Zheng, Z. Xu, and D. Zhu, "Comparison of adsorption isotherms of single-ringed compounds between carbon nanomaterials and porous carbonaceous materials over six-order-of-magnitude concentration range," *Carbon*, vol. 79, pp. 203–212, 2014.