ADSORTION PERFORMANCE OF GRAPHENE NANO PARTICLE TO REMOVE VOLATILE ORGANIC COMPOUNDS IN ENVIRONMENT

ĐÁNH GIÁ KHẢ NĂNG HẤP PHỤ CỦA HẠT GRAPHENE KÍCH THƯỚC NANO ĐỂ XỬ LÝ HỢP CHẤT HỮU CƠ BAY HƠI TRONG MÔI TRƯỜNG

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Abstract - In this study, graphene nano particles were synthesized chemically - modified Hummer method and used as the adsorbent to remove toluene and benzene in environment. Obtained nano adsorbents were characterized using Scanning electron microscopy (SEM), Transmission electron microscopy (TEM), Fourier transform infrared resonance spectroscopy (FTIR), Brunauer-Emmett-Teller analysis (BET), X-ray diffraction (XRD) and X ray photoelectron spectroscopy (XPS). The results showed that oxidation of graphite leading to the adding oxygen-contained functional groups on the surface of graphite and forming graphene oxide (GO). Ascorbic acid has been used to reduced GO forming reduced graphene oxide (rGO). Adsorption capacity of rGO for toluene and benzene was 180 mg/g and 150 mg/g, respectively. rGO could be regenerated at 50°C in N_2 flushing. After regeneration, adsorbents could used in 4 times.

Key words - Reduced graphene; adsorption; volatile organic compound; modified Hummer method; adsorption capacity

Tóm tắt - Trong nghiên cứu này, hạt nano graphene được tổng hợp bằng con đường hóa học – Phương pháp Hummer cải tiến và được sử dụng làm chất hấp phụ hơi toluene và benzene trong môi trường. Chất hấp phụ nano được đặc trưng tính chất bằng kính hiển vi điện tử quét (SEM), Kính hiển vi điện tử truyền qua (TEM), Phổ Hồng ngoại biến đổi Fourier (FTIR), phân tích BET, phổ tán xạ tia X (XRD) và Phổ quang electron tia X (XPS). Các kết quả cho thấy quá trình oxi hóa graphite đã gắn được các nhóm chức chứa oxy lên bề mặt graphite tạo nên graphene oxide (GO). Sử dụng axit ascobic đã khử được GO thành graphene oxide dạng khử (rGO). Dung lượng hấp phụ toluene và benzene của rGO lần lượt là 180 mg/g và 150mg/g. Vật liệu rGO có khả năng tái sử dụng đến 4 lần sau khi tái sinh trong môi trường N2, ở 50°C.

Từ khóa - Graphene dạng khử; hấp phụ, dung môi hũu cơ bay hơi; Phương pháp Hummer cải tiến, dung lượng hấp phụ

1. Introduction

Nowadays, industry activities discharged many pollutants in the environment. In some cases, the situation of pollution has been out of control. It results the volatile organic compounds (VOCs) are present in the environment. The condition will be worse if the workers are in the defined space and exposure in VOCs for along time. The risk of occupational health for worker should be considered. Although, they are toxic, benzene, toluene and xylene have been used commonly in industry as solvent. They can be found in the industrial working place and environment. Benzene and toluene are among the toxic materials emitted from industrial processing and are subject to worldwide emissions regulations.

Ingestion, inhalation and dermal exposure to VOCs can lead to many bad health effects [1]. Due to volatile property, VOCs inhalation is the major route of exposure of workers. Many studies demonstrated that the respiratory exposure of VOCs via the inhalation leaded to the risk of diseases, including asthma [2, 3], chronic obstructive pulmonary disease (COPD) [4], cardiovascular diseases and various cancers [5]. Because not all the inhaled VOCs are remained in the respiratory system, only the small percentage of the inhaled VOCs absorbed inside the body can play an important role in health risks [6].

Up to now, many methods are suitable to apply for removal these pollutants such as ad-on-control techniques. They are divided into recovery methods and destruction methods based on whether or not the VOCs are recovered. Recovery methods are separation, absorption, adsorption, condensation, and the destruction technique include catalytic oxidation, biodegradation, thermal oxidation and plasma catalysis [7]. Adsorption technology uses materials to interact with VOCs physically or chemically. It is considered an effective method and economic control strategy. Both adsorbent and VOCs could be reused after absorption.

As adsorbents, carbon based material such as activated carbon, graphene, carbon Nano tube have been paid much more attention in research. Due to their unique properties, large specific surface area, graphene-based material have been used as an effective adsorbent for removal toxic substances in environment. It would be effective with hydrophobic organic compound in air atmosphere.

Graphene oxide (GO) is a graphene sheet, with carboxylic groups at its edges and epoxide groups and phenolic hydroxyl on its basal plane. Reduction of functional group on GO with many different oxidants will obtain reduced graphene oxide (rGO). It is possible to reduce GO by annealing, electrochemical method. So that, rGO can adsorb aromatic compound better than GO because they have smaller oxygen contained group, larger specific surface area, higher hydrophobicity [8].

L. Yu et.al. have studied the adsorption of VOCs on rGO. rGO synthesized chemically with modified Hummer method. Due to the higher surface area, rGO (292.6 m^2/g) showed higher adsorption benzene and toluene than that of GO (236.4 m^2/g). The rGO adsorption capacity of benzene and toluene was 276.4 and 304.4 mg/g, respectively [8]. J. Kim et. al have modified graphene with microwave irradiation and heat treatment near 800°C under KOH activation. Graphene was increased the surface area larger than that of pristine graphene; maximum volume capacity of 3,510 m^3/g for toluene gas and 630 m^3/g for acetaldehyde gas were observed. The high absorption performance for toluene (98%) versus acetaldehyde (30%) was due to π-π interactions between the pristine graphene surface and toluene molecules [9]. Mesoporous graphene adsorbents were used to adsorb toluene and xylene at various concentrations (30, 50, 100 ppm). rGO was produced by thermal exfoliated of GO. The obtained powder possesses high adsorption efficiency for toluene (92.7–98.3%) and xylene (96.7–98%) and its reusability is remarkable, being at least 91% [10]. Graphene/metal organic composite (also called graphene-based material) have been paid more attention as adsorbents for benzene and ethanol. The composites have high adsorption capacities for both benzene and ethanol, and the maximum uptakes reach 72 and 77 cm^3/g, respectively [11]. In Vietnam, there are some research publications of graphene-based material [12, 13, 14, 15, 16, 17, 18, 19]. The adsorption researches of benzene and toluene by graphene based material have not much been discussed in these literatures.

In this study, we used rGO with mesoporous structures as adsorbents. The rGO were synthesized by the chemical method and characterized by SEM, TEM, XRD, and XPS. We assessed the adsorption whilst varying the VOC concentration in the range 100 - 200 ppm and measured the adsorbed capacity.

2. Experimental

2.1. Chemical

Graphite flake (50 mesh) was purchased from Phu Binh Company, Vietnam with 94% C. All the chemicals such as: $KMnO_4$, H_2O_2, $NaNO_3$, acid ascorbic, toluene, benzene were analytic grade (from China) and did not purified before using.

2.1.1. GO preparation

GO was synthesized using modified Hummer's method. Graphite powder (3g) and $NaNO_3$ (3g) were stirred in 90 ml concentrated H_2SO_4 acid at 5°C. $KMnO_4$ (9g) was added in the mixture slowly and the temperature was kept below 10°C. After that, distilled water (200ml) was added carefully, the mixture temperature was controlled under 95°C. The mixture was still stirred in 30 min. Then 30% H_2O_2 was poured into the solution to oxidized residue $KMnO_4$. The solution continued to stir in 30 min. The brown solution of GO was obtained.

2.1.2. rGO preparation

The prepared GO solution was stirred in 30 min following adding 30g acid ascorbic (powder). The mixture color changed from brown to black and was filter to obtain rGO. After 24h drying, rGO products could be obtained.

2.1.3. Characterization techniques

The structure and morphology properties of rGO, GO were characterized using many analytic and spectroscopy techniques. Transmission electron microscopy (TEM) was carried out by using JEM-2100 (Japan). Scanning electron microscopy (SEM) was obtained with JEOL-530 (Japan). X-ray diffraction (XRD) patterns of the samples were collected using X Ray Diffraction D8 Advanced Eco (Bruker). Fourier transform infrared (FTIR) spectra were recorded with FT-IR model Nicolet IS10, Thermo (Swiss). The specific surface area results were calculated using the BET (Micromeritics –ASAP 2020). Concentrations of VOCs were analysised with GC 2010 (Shimadzu - Japan). XPS spectra were obtained with ThermoVGMultilabESCA3000 spectrometer (Thermo Fisher Scientific, Waltham, MA, USA).

2.1.4. Adsorption experiments

The adsorption experiments of toluene and benzene on rGO were carried out in the adsorption column made from stainless steel at room temperature. The diameter of column, bed depth was 14mm, 5cm, respectively. rGO was filled in the column (1g) and then purged by supplying pure nitrogen air in 20 min before adsorption experiment.

Preparation of toluene or benzene vapor (VOC's vapor) at 500 ppm concentration in the HDPE bag: filling in the vaporized flask with the calculated amount of liquid toluene or benzene; then N_2 gas was pumped through vaporized flask at 5 l/min until total volume of bag reached 60 litters. N_2 stream could bring all VOC's vapor into the bag.

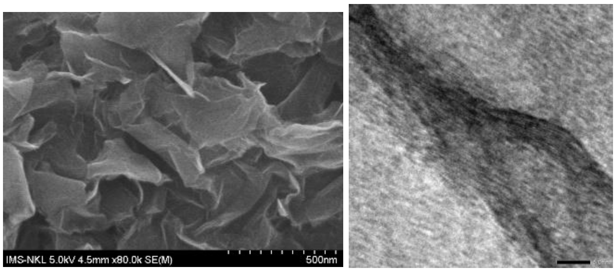
The adsorption experiment was carried out in a batch. VOC's vapor in the bag was pumped through the adsorption column at 0.5 l/min. After a certain time the air sample was collected to the air bag (Tedlar bag-USA, 3 litters) and was analyzed with gas chromatography.

The adsorption capacity for VOCs was calculated at the time that outlet concentration of VOCs was smallest or the adsorption efficiency got maximum value. The change of concentration of VOCs before and after adsorption could be used to calculate the amount of VOCs adsorbed by graphene.

2.2. Results and discussion

2.2.1. Characterization of GO, rGO

The TEM and SEM of GO, rGO are shown in Figure 1.



a *b*

Figure 1. *SEM (a) and TEM (b) pictures of rGO*

It could be seen the typical ripples on the surface of rGO (Figure 1,a). From these wrinkles, nano sheets are slight aggregated. From TEM picture (Figure 1,b), the nano sheet of rGO could be observed. Both flat surface and wrinkled region are both potential adsorption sites [1,5]. The surface of GO seemed flatter than that of rGO (Figure 2).

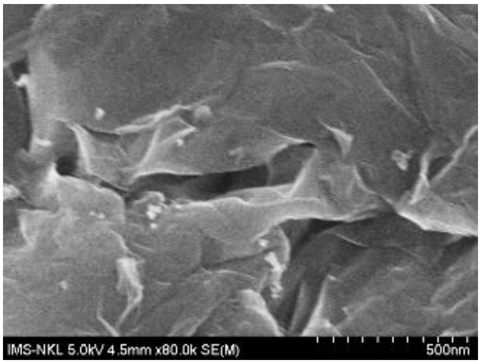


Figure 2. *SEM picture of GO*

The oxidizing with ascorbic acid could separate the nano sheet of rGO but in a cluster about 10 sheet of 1-2nm thickness.

Figure 3 shows the XRD pattern of graphite and GO

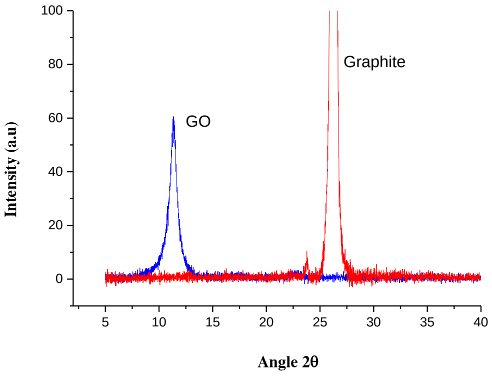


Figure 3. *XRD pattern of graphite and GO*

The interlayer distance of GO obtained was ~0.78nm (at 11.55°), which is much larger than that of graphite about 0.34nm (at 23°). Oxidizing with $KMnO_4$ in concentrated H_2SO_4 acid could graft some oxygen-containing functional groups on the graphite structure and the inlayer increased.

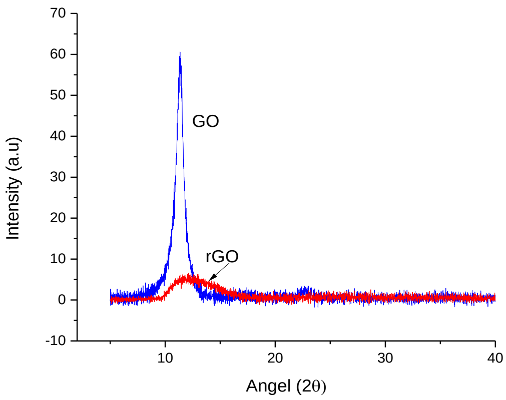


Figure 4. *XRD spectra of GO and rGO*

In Figure 4, it could be seen that GO exhibits a sharp peak, while rGO shows a broad and low peak at nearly 11°. Reduction of GO leaves aggregated and randomly packed RGO sheets with a broad and low intensity XRD [20].

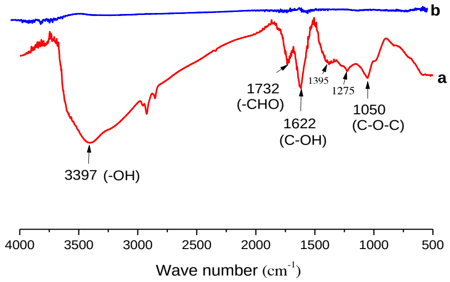


Figure 5. *FTIR spectra of GO (a) and rGO (b)*

The FTIR results are presented in the Figure 5. The peak at 3397 cm^{-1} is assigned to the bending and stretching of O-H group on GO. The peak located at 1732 cm^{-1} is attributed to carbonyl C=O of aldehyde, carboxylic acid or acetone. The peaks at 1622 cm^{-1} can be attributed to the stretching of O-H. The peaks 1395 cm^{-1}, 1274 cm^{-1} and 1050 cm^{-1} could be corresponded to C-O-C bonds (epoxy or alkoxy). It can be seen the intensities of all the peaks in rGO in FTIR spectra are lower than that of GO [21, 22]. All the groups on GO have been reduced leading to disappearing in the spectra pattern.

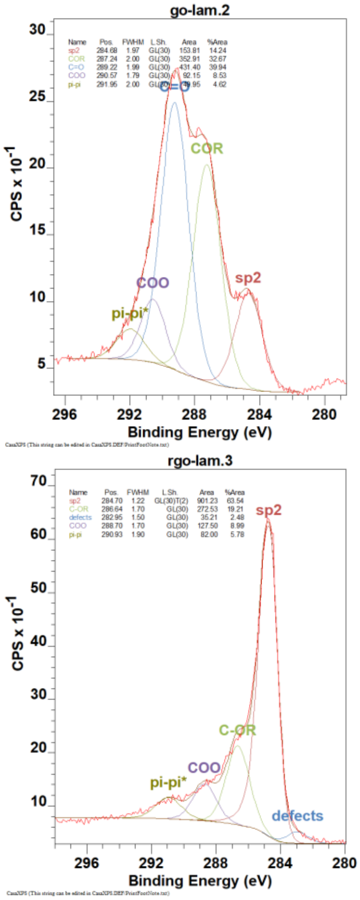


Figure 6. *XPS spectra of GO and rGO*

The XPS spectra of GO and rGO show on Figure 6. The C1s spectra of GO consists of functional groups such as C=C at 283.3 eV, C in C-O bond at 285.2eV, carbonyl C=O at 286.7 eV and carboxylate carbon (O-C=O) at 288.8eV with C/O ratio 1.94. It can be seen the sharp decreasing of intensity of all the groups in rGO. Most of the oxygen-contained functional groups are removed with the increase in C/O ratio is about 0.81.

Table 1. *BET results of graphite, GO and rGO*

	Graphite	GO	rGO
BET surface area (m^2/g)	3.7566	72.9367	285.0957
Pore volume (cm^3/g)	0.0237	0.0619	0.3430
Pore size (Å)	253.2043	33.7597	48.1382
Average particle size (Å)	15972.068	817.437	210.456

Table 1 show that the specific surface areas of pristine graphite GO and rGO were 3.7566, 72.9367 and 285.0957m^2/g, respectively. Oxidizing and reduction have developed the surface area of rGO. The insertion of oxygen group and exfoliation of graphene nano sheet could be the reason of increasing the surface area. Addition, the pore volume was improved; particle size in nano scale could be observed.

2.2.2. Adsorption performance studies

Figure 7 shows the adsorption efficiency curves of toluene and benzene on the graphene bed. After 2.5h, toluene adsorption of graphene seemed saturated. The adsorption efficient could be kept in constant in some time before decrease. The adsorption capacity of rGO for toluene, benzene was 150 mg/g, 120mg/g, respectively. The micro-structure of rGO is important factor in adsorption. Electrostatic interactions, pi-pi bonds and hydrophobic interaction between the aromatic substance and rGO should be main mechanism of adsorption [8]. The methyl group of toluene can interact with oxygen-containing functional group on rGO via H bond. It leads to the stronger interaction between toluene and rGO. It should be the reason of increasing adsorption capacity of toluene.

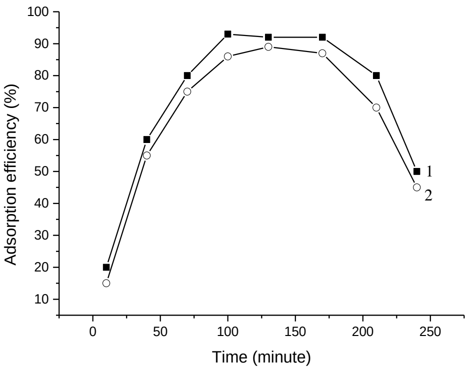


Figure 7. *Adsorption efficiency- time curves for toluene (1), benzene (2)*

After the first run, rGO was regenerated by flushing N_2 through the adsorption column at the flow rate 2 l/min, in 30 min. The column was kept at 50°C by thermostat to ensure all the toluene was desorbed totally. The second run of adsorption was carried out in the same condition of the first run. The change of adsorption efficiency of graphene for toluene after each graphene reuse is shown in Figure 8.

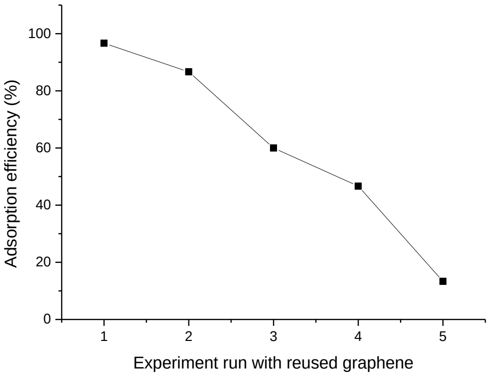


Figure 8. *Adsorption efficiency for toluene after each regeneration of graphene*

The results show that most of toluene was desorbed in 30 min. The adsorption efficiency at the second run could reach nearly 97%. After 5 cycles adsorption-desorption, the efficiency of adsorption felt down to 14%. rGO could not adsorb toluene any more.

3. Conclusion

These results presented the preparation of rGO by modified Hummer's method. rGO showed the sheet-like morphology. After reduction with ascorbic acid, the interlayer spacing of rGO decreased. It could be seen clearly in TEM, XRD pictures. The reduction chemically could not be exfoliated GO to single sheet of graphene. The cluster of about 10 layers could be obtained. The BET surface of rGO was 285.09 m^2/g. The adsorption capacity of rGO for toluene and benzene was 150 mg/g, 120 mg/g, respectively. Desorption experiment results showed that rGO could be regenerated in N_2 atmosphere at 50°C and should be used in 2-3 times of adsorption.

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