



Received: 01 December 2018  
Accepted: 17 February 2019  
First Published: 07 March 2019

\*Corresponding author: Thi Thuong Nguyen; Long Giang Bach, NTT Hi-Tech Institute, Nguyen Tat Thanh University, Vietnam  
E-mail: [nthithuong@ntt.edu.vn](mailto:nthithuong@ntt.edu.vn);  
[blgiangntt@nttu.edu.vn](mailto:blgiangntt@nttu.edu.vn)

Reviewing editor:  
Nguyen Dinh Duc, Vietnam National University, Hanoi, Vietnam

Additional information is available at the end of the article

## CIVIL & ENVIRONMENTAL ENGINEERING | RESEARCH ARTICLE

# The application of expanded graphite fabricated by microwave method to eliminate organic dyes in aqueous solution

Ngoc Bich Hoang<sup>1</sup>, Thi Thuong Nguyen<sup>1\*</sup>, Tien Sy Nguyen<sup>2</sup>, Thi Phuong Quynh Bui<sup>2</sup> and Long Giang Bach<sup>1\*</sup>

**Abstract:** Recently, organic contaminants from textile and dye industry have adversely affected on human's health and living things. Hence, the development of effective contaminated water treatment is one of the most crucial tasks. Expanded Graphite (EG) has been considered as efficient platforms to remove of organic dyes from aqueous solution due to its excellent performance. The main objective of the present work is to investigate adsorption behavior of methylene blue (MB) and Congo Red (CO) on exfoliated graphite fabricated using flake graphite from Yen Bai province. The exfoliation of graphite was carried out using potassium permanganate and perchloric acid as oxidant agent and anhydride acetic as intercalating agent via microwave-assisted technique. The properties of EG were characterized by



Thi Thuong Nguyen



Long Giang Bach

### ABOUT THE AUTHORS

Thi Thuong Nguyen belong to the NTT Hi-Tech Institute, Nguyen Tat Thanh university, whose one of the specializations is development of new materials for treatment of contaminated water. Up to now, she has published in various reputable journals including *Desalination and Water Treatment* and *Journal of Nanoscience and Nanotechnology*. Currently, she is a PhD student of Faculty of Chemistry, University of Science, University of Science - VNUHCM, Viet Nam.

Dr. Long Giang Bach took his PhD degree in Pukyong National University, Busan in 2014. Up to now, he has expertise in polymer chemistry, nanotechnology, green chemistry. Now, he works as a head of Department of Technology and Science and a researcher of the NTT Hi-Tech Institute, Nguyen Tat Thanh University, Viet Nam.

### PUBLIC INTEREST STATEMENT

Organic contaminants, especially dyes, discharged from the textile industry pose a serious risk to the environment and human health. In this study, we attempted the fabrication of a type of exfoliated graphite from flake graphite, which is a locally available and inexpensive material in Vietnam. We also examined the produced material using various characterization methods and investigated its adsorption capacity against two common types of dyes, namely methylene blue and Congo red. It is found that the expanded graphite provided efficient and fast adsorption against the two dyes. Although capacity degradation of the material was observed after repeated uses, these manufacturing protocols are still suggested to be viable due to cost-efficiency.

X-ray diffraction, scanning electron microscopy, Fourier-transform infrared spectroscopy and nitrogen adsorption/desorption analysis. In batch adsorption experiments, various factors including initial dye concentration (50–600 ppm), adsorbent dosage (0.5–3 g/L), contact time (10–120 min) and pH of solution (4–10) were also studied. It is found that as-prepared EG provided high removal efficiency and fast adsorption rate for MB and CO. The maximum adsorption capacity of EG for CO and MB was found at 201.21 and 47.62 mg/g, respectively. These results demonstrate that the as-synthesized EG appears as an efficient and low-cost platform for remediation of colored effluents via adsorption route.

**Subjects:** Materials Science; Adsorption Science; Civil, Environmental and Geotechnical Engineering

**Keywords:** adsorption; expanded graphite; dye-contaminated water; microwave-assisted technique

## 1. Introduction

Recently, Vietnam has faced increasing water pollution due to waste streams from the processing and consumption of organic dyes in the textile industry. The massive discharge of untreated organic dyes is detrimental to aquatic life and human health (Roy, Chakraborty, Kundu, Adhikari, & Majumder, 2012). The existence of highly organic dye compounds in hydrosphere results in considerable increase in chemical oxygen demand, limitation of light penetration into the water, undesirable interference in photosynthesis of hydrophyte and prevention of growth of microbes in the aquatic ecosystem. In addition, the selective toxicity of organic dyes is carcinogen and mutagen (Arami, Limaee, Mahmoodi, & Tabrizi, 2005). There have been a variety of physical and chemical treatment method available for the treatment of colored effluents, namely adsorption, coagulation, flocculation, ozonation, membrane filtration, ion exchange and chemical precipitation (Arami et al., 2005; Avetta, Sangermano, Lopez-Manchado, & Calza, 2015).

Expanded graphite (EG) has drawn much attention lying on excellent properties, namely multiporosity, large-specific surface area, low density and hydrophobic nature. Thanks to this, EG has been considered as an important sorbent possessing a high sorption capacity especially for organic compounds (Goshadrou & Moheb, 2011; Yagub, Sen, Afroze, & Ang, 2014; Zheng, Wang, Kang, Wang, & Inagaki, 2004). There were several synthesis methods of EG from graphite intercalation compounds (GICs) in order to enhance its pores size range. GICs were complex materials containing alkali metals and acid molecules, i.e. Na-THF, K-THF, Co-THF, H<sub>2</sub>SO<sub>4</sub>, HClO<sub>4</sub> and HNO<sub>3</sub> inserted between oppositely charged carbon layers and GICs were then heated to exfoliate graphite layers (Altıntig, Altundag, Tuzen, & Sari, 2017; Goshadrou & Moheb, 2011; Yagub et al., 2014; Zheng et al., 2004). It is well known that the EG gave high oil removal efficiency due to suggested outstanding properties (Asfaram et al., 2015). Moreover, the EG has considered as an excellent candidate in removing organic dyes. The obtained results revealed that EG produced by using mixture of graphite, perchloric, potassium permanganate and acetic anhydride following weight ratio 1:1.4:1:0.5 under rapidly heating to 1,000°C had the expansion volume of 300 mL/g. The as-prepared EG could eliminate 94.05% azo direct scarlet 4BS with initial concentration of 100 mg/L at optimum conditions, namely dosage of 0.6 g/L, contact time of 120 min, pH = 2 and 50°C (Li, Li, Li, & Sun, 2007a). Additionally, such EG materials showed 96.9% removal for Blue 2BLN at initial concentration of 200 mg/L using 600 mg/L adsorbents at 45°C for 120 min and 99.5% removal for Acid Black 210 with initial concentration of 60 mg/L at pH = 1 and 51°C for 120 min (Li, Li, Li, & Sun, 2007b). The removal of Reactive red 24 using graphite-based adsorbents in combination with H<sub>2</sub>O<sub>2</sub> was found at 98.44% removal (pH = 2) using 600 mg/L EG at 50°C within 120 min (Li, Li, & Sun, 2008b). Accordingly, EG prepared by exfoliation of acid-treated graphite flake (with volume ration of H<sub>2</sub>SO<sub>4</sub>/HNO<sub>3</sub> = 4:1) was an efficient adsorbent for removal of methylene blue (MB) with the

adsorption capacity to be 7.77  $\mu\text{g/g}$  at initial concentration of 16 mg/L and contact time of 180 min (Zhao & Liu, 2009). Amir et al. reported that EG fabricated by using mixture of  $\text{H}_2\text{SO}_4$  and  $\text{HNO}_3$  exfoliated at  $10,00^\circ\text{C}$  for 5 s could remove 95% CI Acid Blue 92 at initial concentration ranged 50–75 mg/L for 4 h (Goshadrou & Moheb, 2011). However, the preparation of EG by conventional thermal heating was limited due to long time to achieve desired temperature, consuming process and high energy requirement; and subsequently, a large amount of distilled water was used for washing. Microwave-associated heating is alternative method to fabricate EG rapidly from graphite intercalation compounds (GIC) without involvement of washing and drying (Wei, Liu, Zhang, Shi, & Guo, 2009). For instance, the exfoliation of GIC using graphite and  $\text{HClO}_4$  (with weight ratio 1:2) under microwave irradiation with 60–70 s showed superior performance in removal of organic dyes. The results exhibited that the maximum adsorption capacity for the removal of malachite green, Congo red (CR) and Rhodamine was found to be 384.6, 196.08 and 151.51 mg/g, respectively (Sykam, Jayram, & Rao, 2018). Till now, the investigations on the preparation of expanded graphite and its application for ionic dye removal have not yet studied adequately.

In the present work, the aim is to produce the EG using inexpensive intercalated compounds and microwave heating technique for 40 s. The as-fabricated EG-based adsorbents exhibited high removal efficiency of the MB and CR from aqueous solution. The experimental conditions affecting the dye adsorption including the contact time between adsorbents and adsorbates, the pH of the solution, dye concentration and the dosage of adsorbent were also investigated. Furthermore, the adsorption isotherm was described using Langmuir and Freundlich models.

## 2. Experimental

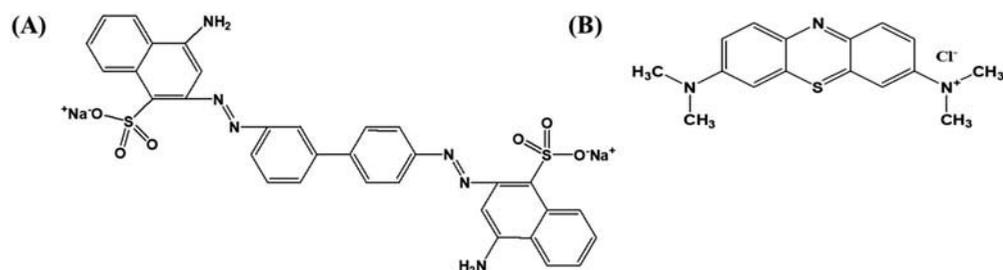
### 2.1. Materials

Natural graphite (NG) was originated from Yen Bai province in Vietnam with flake size  $>1.25$  mm and carbon component  $\geq 85\%$ . Potassium permanganate ( $\text{KMnO}_4$ ), perchloric acid ( $\text{HClO}_4$ ) and acetic anhydride ( $(\text{CH}_3\text{CO})_2\text{O}$ ) were obtained from commercial sources and used as received. Organic dyes including MB ( $\text{C}_{16}\text{H}_{18}\text{ClN}_3\text{S}$ ; molecular weight: 319.85 g/mol; maximum wavelength: 664 nm) and CR ( $\text{C}_{32}\text{H}_{22}\text{N}_6\text{Na}_2\text{O}_6\text{S}_2$ ; molecular weight: 696.665 g/mol; maximum wavelength: 500 nm) were purchased from HIMEDIA (Himedia Laboratories Pvt., Ltd.). Dye-polluted aqueous solution is obtained by dispersing commercial dyes in distilled water. The chemical structure of CR and MB is shown in Figure 1.

### 2.2. Preparation of the expanded graphite

The preparation of expanded graphite (EG) was performed via two steps including the fabrication of graphite intercalation compounds (GIC) and rapidly thermal processing under microwave irradiation. The GIC was prepared by mixing NG,  $\text{KMnO}_4$ ,  $\text{HClO}_4$  and  $(\text{CH}_3\text{CO})_2\text{O}$  according to the weight ratio of ingredients 1:0.5:1:0.4 for 10 s. Subsequently, the mixtures were placed directly into 2.45 GHz microwave irradiation (MW) operated at 720 W and for 40 s to produce EG. Finally, the obtained EG was stored in the desiccator at room temperature before use to prevent the material from absorbing steam outside the air.

Figure 1. The molecular structure of Congo red (a) and methylene blue (b).



### 2.2.1. Characterization

Scanning electron microscope (SEM) was used to observe the surface morphology of NG and EG on Hitachi S4800 instrument, Japan. Energy-dispersive spectroscopy mapping was determined during SEM analysis using Oxford instrument. In order to analyze structure of graphite after expansion, X-ray diffraction (XRD) patterns were determined using a Siemens D5000 diffractometer with a  $\text{CuK}\alpha$  radiation ( $\lambda = 1.5406 \text{ \AA}$ ) in the range between  $0^\circ$  and  $80^\circ$  at low speed of  $0.02^\circ/\text{s}$ . The Brunauer-Emmett-Teller (BET) surface area of graphite-based materials was determined using the  $\text{N}_2$  adsorption/desorption isotherm measurement on Micromeritics 2020 volumetric adsorption analyzer. The dye concentration in the aqueous solution was determined using an Evolution 60S UV-vis spectrophotometer (Thermo Fisher Scientific, USA). The functional groups of porous carbon material were identified using a Bruker Alpha FT-IR (Fourier transform infrared) spectrophotometer in the range of  $4,000\text{--}400 \text{ cm}^{-1}$  and using a KBr matrix.

### 2.2.2. Batch adsorption studies of EG for organic dyes

The batch adsorption experiments were performed to determine the optimum conditions for the elimination of cationic and anionic dyes. The EG with certain dosage (0.5, 1, 2 and 3 g/L) was added into 250 mL Erlenmeyer flasks containing 100 mL dye solution with known initial concentrations (50–600 mg/L) at adjusted pH value in the 4–11 range. The mixture was then shaken using an orbital shaker at 200 rpm for contact time range of 0–100 min and adsorption temperature of  $30 \pm 2^\circ\text{C}$ . Subsequently, the adsorbents and adsorbate were separated using centrifugation at 60,00 rpm for 10 min. The equilibrium dye concentration was measured by using the UV-vis spectrophotometer at the maximum absorbance wavelength value for each dye. Each experiment was triplicated to obtain the average data. The adsorption (%) of pollutant by graphite-based adsorbents was calculated by the following equation (Carvallho et al., 2016):

$$\text{Adsorption(\%)} = \frac{(C_i - C_e)}{C_i} \times 100 \quad (1)$$

The equilibrium adsorption capacity of dye  $q_e$  (mg dye/g EG) was described by the following equation (Sham & Notley, 2018):

$$q_e = \frac{V \times (C_i - C_e)}{m} \quad (2)$$

where  $C_i$  and  $C_e$  (mg/L) are the initial and the equilibrium concentration of the dye, respectively,  $V$  is the volume of aqueous dye solution in L and  $m$  is the adsorbent weight in g.

### 2.2.3. Langmuir and Freundlich isotherms

In order to clearly identify the adsorption mechanism and predict the optimum parameters of adsorption process, the adsorption isotherm experiments were performed. Langmuir and Freundlich isotherms were used to characterize the adsorption of dyes from aqueous solution by graphite-based adsorbents. Documented in the literatures, the Langmuir adsorption model was explained on the ground of assumption of monolayer coverage on a uniformly surface with identical adsorption sites and negligible interaction between adsorbate molecules (Asfaram et al., 2015; Esfandiari, Nasernejad, & Ebadi, 2014). The linear equation for Langmuir adsorption model is given as follows (Yagub et al., 2014):

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{K_a q_m} \quad (3)$$

where  $q_m$  represents the maximum adsorption capacity of EG (mg/g) and  $K_a$  is the isothermal constant for Langmuir adsorption (L/mg) related to the affinity of the adsorption energy. The slope and intercept of the linear plot of  $C_e/q_e$  versus  $C_e$  will give  $q_m$  and  $K_a$  values (Yagub et al., 2014).

The important features of the Langmuir isotherm model can be expressed through the dimensionless constant separation parameter,  $R_L$ , defined as follows (Hameed & Hakimi, 2008):

$$R_L = \frac{1}{1 + K_a C_i} \tag{4}$$

where  $C_i$  (mg/L) is the initial dye concentration. Based on obtained  $R_L$  values, the adsorption process of dye on EG may be presumed to be favorable if  $0 < R_L < 1$ . In case of  $R_L > 1$ , the process shows unfavorable adsorption and  $R_L = 0$  represents irreversible for adsorption (Yagub et al., 2014).

The Freundlich model was described on the assumption that dye molecules are adsorbed on the different energy sites on the heterogeneous adsorbent surface. The interaction between adsorbate molecules is taken into consideration in this adsorption model. The linear equation of Freundlich model is given as follows:

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \tag{5}$$

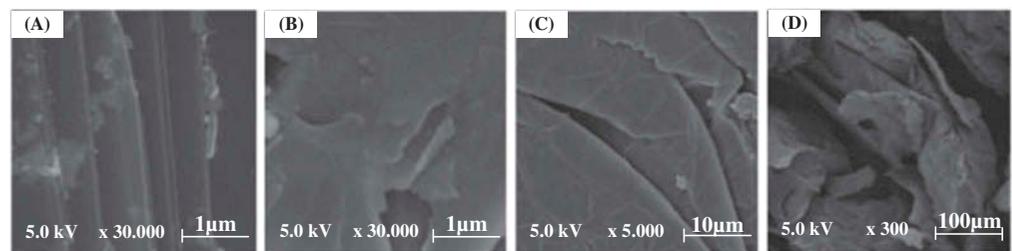
where  $1/n$  presents adsorption intensity which is related to the relative distribution of the bond energy and heterogeneity on adsorbate sites; for instance, the stronger adsorption bond is found in decreasing  $1/n$  value.  $K_F$  (L/mg) represents adsorption capacity of the adsorbents.

### 3. Results and discussion

#### 3.1. Fabrication and characterization of the exfoliated graphite

The surface morphology of graphite-based materials before and after using the microwave method was observed by SEM analysis as found in Figure 2. It can be seen that the morphology of NG presents rough surface with multilayered crystalline structure. After the adequate MW process, the interlayer structure of the NG flakes was fully broadened to the exfoliated graphite layers as found in

**Figure 2.** SEM of natural graphite (a) and expanded graphite (b–d).



**Figure 3.** XRD spectra of graphite and expanded graphite. The shift of (0 0 2) peak was observed in the inset image.

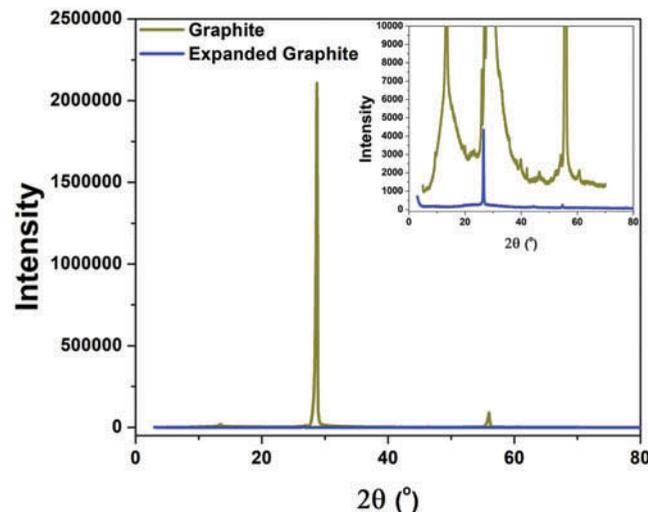


Figure 2(b-d). Many packed layers and formation of wrinkles, furrows appear on the surface of EG. In addition, EG was found in worm-like images with inner porous structure which facilitate the transport of dye effluents. These changes can be on the ground of intercalation and exfoliation of natural flake graphite. Therefore, it is expected that EG fabricated by destroying GICs under rapid and uniform local heating of MW irradiation may become efficient adsorbents for dye removal.

XRD patterns of the NG and the EG were shown in Figure 3. The peaks at 28.6° and 54.68° were characteristic diffraction peaks of graphite, in accordance with (0 0 2) and (0 0 4) plane (Badenhorst, 2014). Noticeably, the shift of peak at 28.6° to lower angle in EG spectrum suggests that interlayer distance at ( $d_{0\ 0\ 2}$ ) significantly raised. This can be ascribed to successful exfoliation of graphite sheets via microwave technique which well agreed with SEM analysis. Moreover, it is clear that EG presented weaker and narrower diffraction peaks at 26.60° than those graphite lying on broadening along *c*-axis of carbon layers. Some findings indicated the decline of peak intensity ( $d_{0\ 0\ 2}$ ) related to the stacked rearrangement of graphite layers (Li, Li, & Sun, 2008a; Zhao & Liu, 2009). Hence, it may be expected that the graphite exfoliation favors for dye adsorption.

Figure 4 reveals N<sub>2</sub> adsorption/desorption isotherms of NG and EG. It can be seen that the type IV isotherm was determined for NG and EG which indicates the existence of a large number of mesopores and very little micropores in graphite-based adsorbents. The BET surface area and total pore volume of EG were measured as presented in Table 1. The results show much higher total pore volume and surface area of EG compared to flake graphite; for instance, the total pore volume and surface area of EG were 46.10<sup>-3</sup> cm<sup>3</sup>/g and 30 m<sup>2</sup>/g while those of NG were 7.10<sup>-3</sup> cm<sup>3</sup>/g and 3 m<sup>2</sup>/g, respectively. Based on obtained results, the enhancement of total pore volume and surface area may be expected to be in favor with dye adsorption.

Figure 4. The N<sub>2</sub> adsorption/desorption isotherm curves of graphite and expanded graphite.

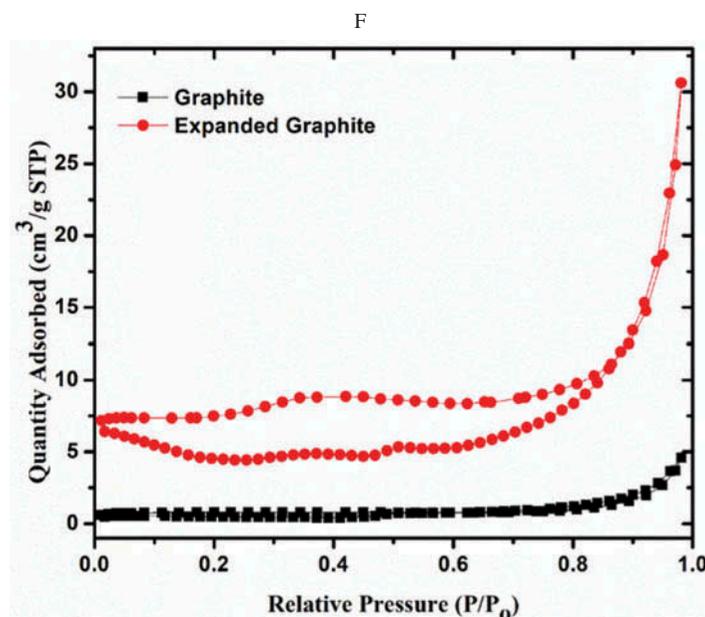
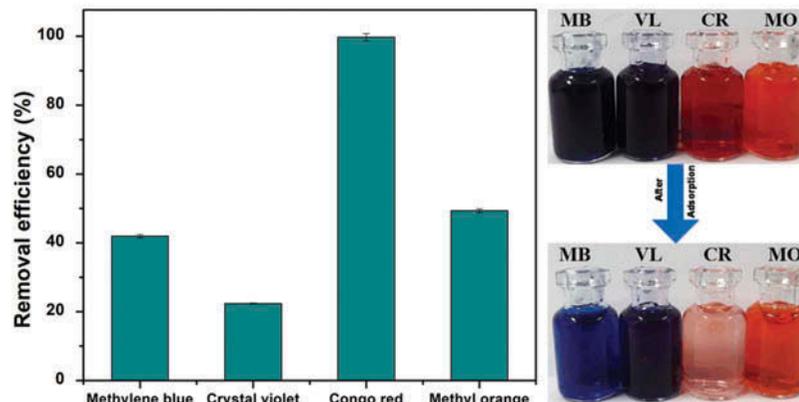


Table 1. Pore parameters of the graphite-based adsorbents

Sample	$S_{BET}$ (m <sup>2</sup> /g)	$V_{total\ pore}$ (cm <sup>3</sup> /g)	$V_{micropore}$ (cm <sup>3</sup> /g)
Natural graphite	3.1348	7.181.10 <sup>-3</sup>	1.037.10 <sup>-3</sup>
Expanded graphite	29.9523	45.520.10 <sup>-3</sup>	7.997.10 <sup>-3</sup>

**Figure 5. The adsorption capacities of expanded graphite for cationic and anionic dyes.**



### 3.2. Adsorption behavior of cationic and anionic dyes on EG

Figure 5 was exhibited the adsorption capacities of EG for cationic and anionic dyes including Methylene Blue (MB), crystal violet (VL), CR and methyl orange (MO) at fixed initial concentration of 200 mg/L, contact time of 120 min and adsorbent dosage of 2 g/L. It was found that EG favored with the adsorption of anionic dyes than cationic dyes. Comparably, the adsorption capacity was observed from Figure 5 for dyes following the order: 99.59% for CR > 49.32% for MO > 41.92% for MB > 22.37% for VL. These results indicated that the EG exhibited highest adsorption capacity for CR among anionic dyes and MB among cationic dyes used for the further investigation.

One of the crucial factors affecting the adsorption efficacy is the exposure time between adsorbents and adsorbates. It is given that the contact time is related to equilibrium adsorption time (Badenhorst, 2014), the influence of the contact time was performed in the range from 10 to 120 min with fixed adsorbent dose of 2 g/L and initial dye concentration of 200 mg/L. The results from Figure 6 show that the adsorption capacity for CO increased rapidly in the first 20 min with 98% removal (86 mg/g) and keep stability after 20 min indicating reached balance state, whereas the removal of MB increased gradually and reached the adsorption balance at 80 min with 51% removal (51 mg/g). Thus, equilibrium time has been taken as 20 min for CO and 80 min for MB considered in further studies.

The pH value plays an instrumental role in the adsorption process of organic dyes on EG. Effect of pH on the removal of MB and CO is carried out from 4 to 10 with fixed initial concentration of 200 mg/L and fixed adsorbent dosage of 2 g/L. The results reveal the adsorption capacity and removal efficiency increased with increasing pH values as found in Figure 7. With increasing pH value from 4 to 9, the adsorption capacity increased steadily and achieved highest value for MB (42 mg/g) and CO (100 mg/g) at pH = 9. However, the adsorption capacity increased at pH of 9–10. Hence, the pH of 9 was selected for further work.

**Figure 6. The effect of the contact time for EG with the adsorption capacity (a) and the removed efficiency (b).**

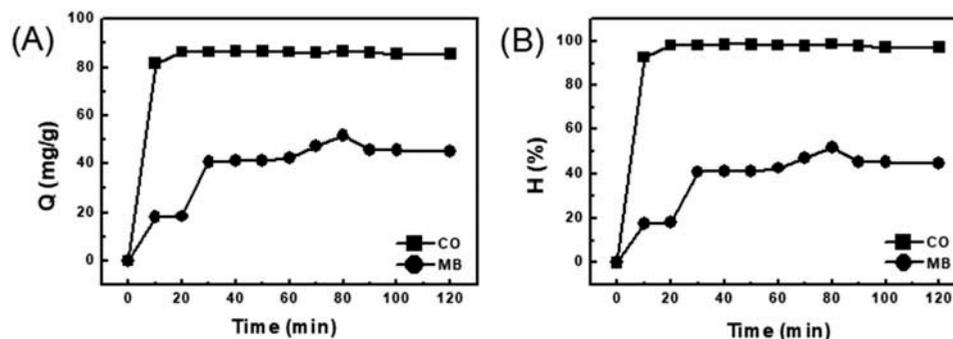


Figure 7. Effect of pH in the aqueous solution for EG with the adsorption capacity (a) and the removed efficiency (b).

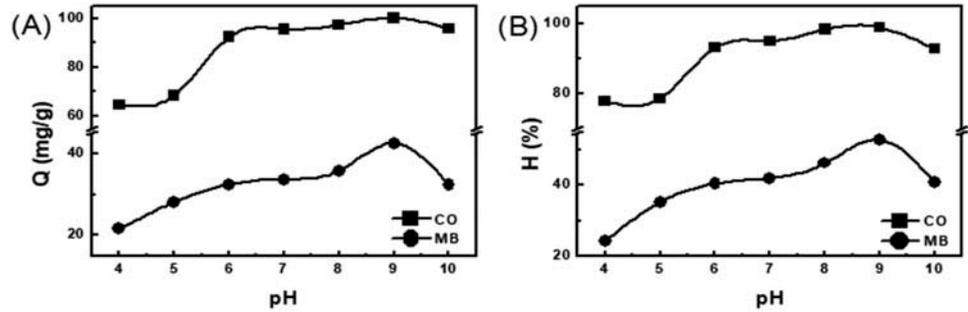
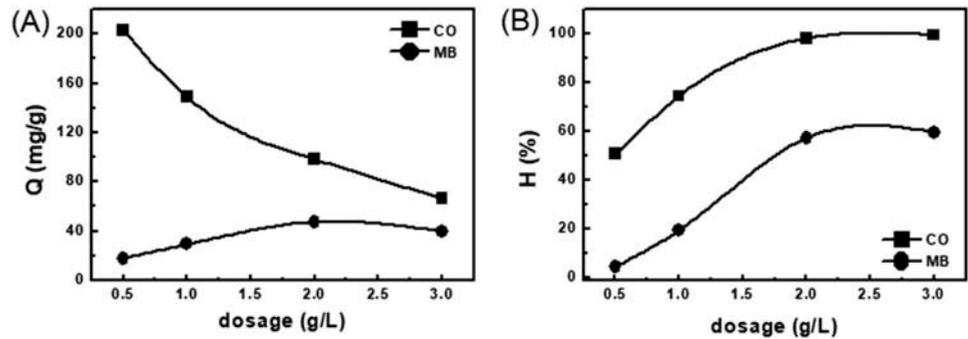


Figure 8. The effect of amount of adsorbent of EG with the adsorption capacity (a) and the removed efficiency (b).



The effect of adsorbent dosage was performed in the range from 0.5 to 3 g/L with fixed initial concentration of 200 mg/L and pH value of pH = 9. The obtained results show the increase in the removal efficiency but the amount of adsorbates per adsorbent unit mass decreased with increasing dosage of EG as shown in Figure 8. It is given that increasing adsorbent produce more uptake sites resulting in adsorption efficiency. It is clear that the removal efficiency of EG for CO is much higher than for MB; for instance, 98% CO was removed from aqueous solution while 57% removal for MB was found at 2 g/L EG adsorbed.

The initial concentration of dyes has a strong influence on the dye colorless due to efficient resistance for mass transfer between aqueous and solid phases. The effect of initial dye concentration on the removal rate of MB and CO was presented in Figure 9. It can be seen that the adsorption capacity increased with increasing initial concentration of dyes. For instance, the uptake amount of EG for CO increased significantly from 23 to 179 mg/g (78% removal) with increment of 500 ppm initial concentration. However, in higher initial concentration of 600 ppm, the adsorption capacity decreased due to lack of uptake sites on EG surface. The highest adsorption capacity was 57 mg/g for MB initial concentration of 300 mg/L and 179 mg/g for CO initial concentration of

Figure 9. Effect of the initial concentration of Congo red and methylene blue on EG's adsorption capacity (a) and removed efficiency (b).

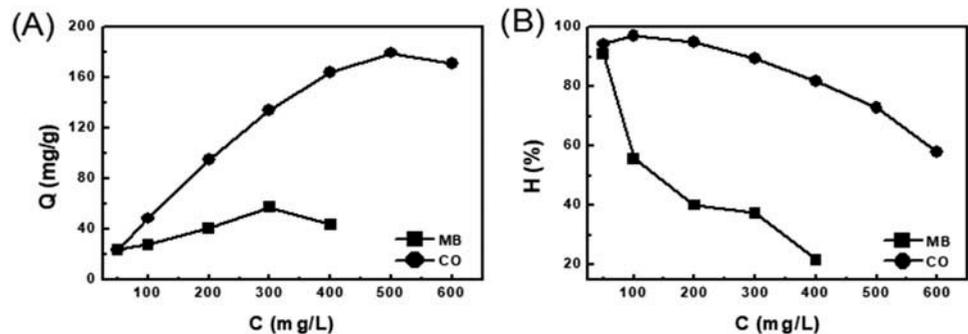
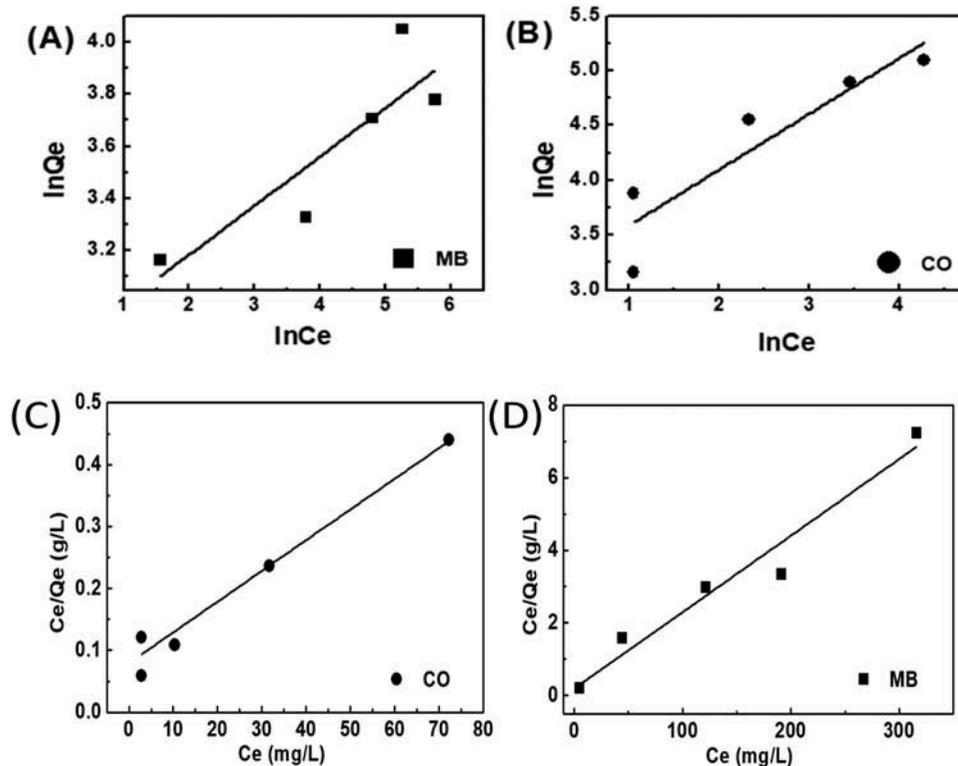


Figure 10. Freundlich (a,b) model and Langmuir (c,d) and of the dye adsorption onto EG with Congo red and methylene blue.



500 mg/L. These results clearly demonstrate that the adsorption capacity and removal efficiency are dependent on the initial concentration of CO and MB in aqueous solution.

### 3.3. Langmuir and Freundlich isotherm

The Langmuir isotherm is on the ground of the assumption that the adsorption occurs at homogeneous sites on the surface following monolayer mechanism while Freundlich theory is related to the heterogeneity on adsorbent surface with a multilayer adsorption mechanism. The model parameters for the Langmuir and Freundlich were determined from isotherm curves in Figure 10 and Table 2. It is noticed that Langmuir model fits well with the adsorption behavior of CO and MB on EG with  $R^2 > 0.956$  while the lower compatibility was found in Freundlich model. Based on parameters calculated from the Langmuir isotherms, the maximum adsorption capacities of CO (201.208 mg/g) exhibited much higher than that of MB (47.619 mg/g). The obtained RL value to be less than 1 indicate the adsorption process is favorable.

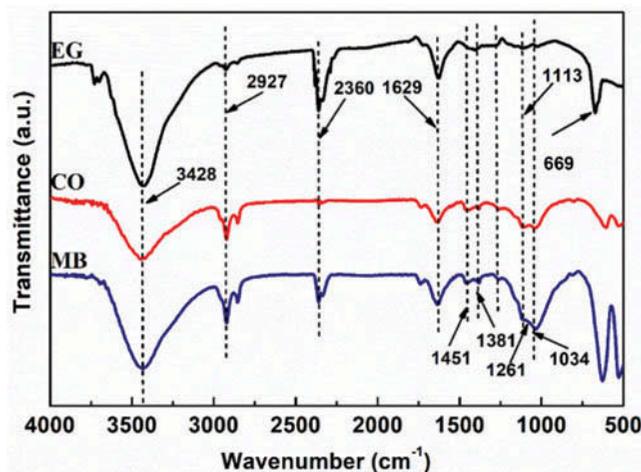
### 3.4. FT-IR analysis

Figure 11 shows FT-IR of EG, EG-MB and EG-CO. In case of EG, the existence of O-H groups and adsorbed water was confirmed by stretching vibration of broad band around  $3,425\text{ cm}^{-1}$ ; the absorbance peaks centered at  $1,628\text{ cm}^{-1}$  were ascribed to the presence of the C=O group;

Table 2. Langmuir and Freundlich isotherm model constants for adsorption of CO and MB

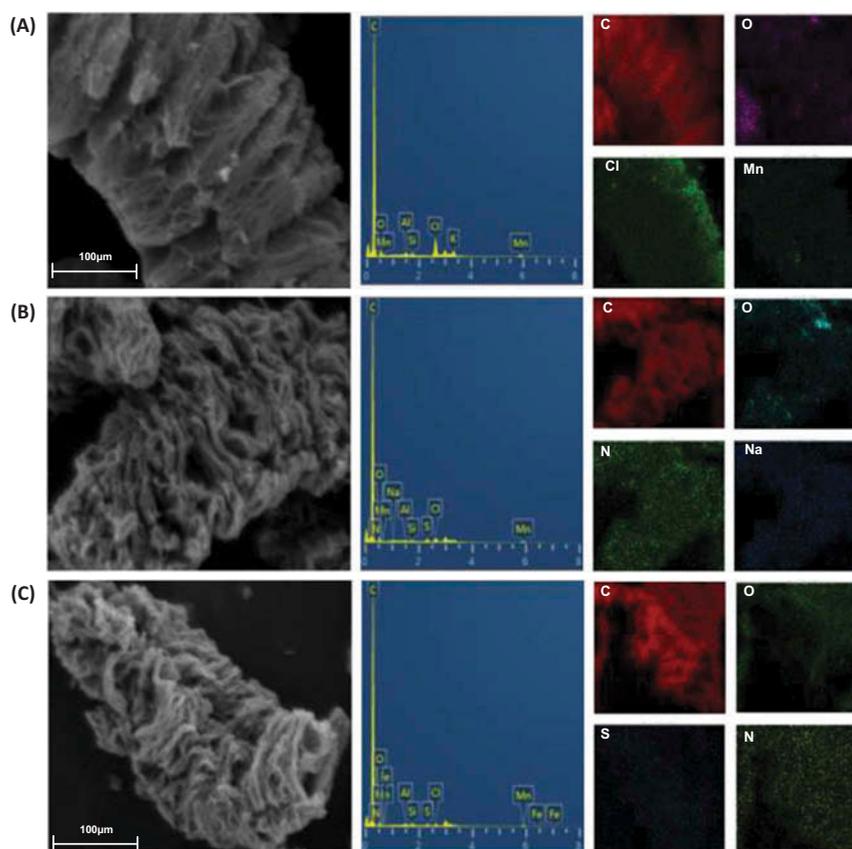
Organic dye	Langmuir				Freundlich		
	$Q_m$ (mg/g)	$K_a$ (L/mg)	$R_L$	$R^2$	$K_F$	$n$	$R^2$
CO	201.208	0.063	0.038	0.956	0.046	1.968	0.796
MB	47.619	0.106	0.023	0.959	0.060	5.319	0.690

**Figure 11. FT-IR analysis of EG with and without adsorption of Congo red and methylene blue.**

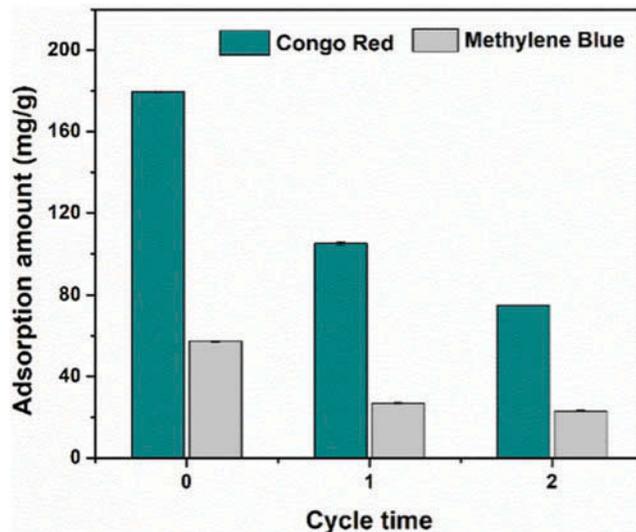


registered at  $2,360\text{ cm}^{-1}$  represents the C–O–C stretch vibration, registered at  $669\text{ cm}^{-1}$  represents the C–H stretch vibration. The  $-\text{CH}_3$  stretch vibration could be observed by the existence of the peak at  $2,927\text{ cm}^{-1}$ . After adsorption for MB and CO, there are some noticeable changes. In details, the new peaks at  $1,034$ ,  $1,261$ ,  $1,381\text{ cm}^{-1}$  attributed to characteristic vibration of the C–O, C–H and C–N group in benzene ring peaks of CO and MB. Additionally, the peaks observed at  $1451\text{ cm}^{-1}$  and  $1113\text{ cm}^{-1}$  was assigned to S=O and C–N< in branching of CO; the sharp absorbance at  $1404\text{ cm}^{-1}$  can be ascribed to C–H in Methyl group of MB (Altıntig et al., 2017; Ion, Alpatova, Ion, & Culetu, 2011). Moreover, the shifts of  $2,927$ ,  $2,360$ ,  $1,628$ ,  $669$ – $2,923$ ,  $2,356$ ,  $2,361$ ,  $1,633$ ,  $1,635$ ,

**Figure 12. SEM–EDAX mapping of expanded graphite before (a) and after adsorption for Congo red (b) and methylene blue (c).**



**Figure 13. Regeneration data of the expanded graphite in removal of Congo red and methylene blue.**



628 and 606  $\text{cm}^{-1}$ , respectively, can be easily recognized. These shifts may be attributed to the interaction between EG and organic dyes (MB and CO) (Sykam et al., 2018).

### 3.5. SEM-EDAX mapping

Figure 12 exhibited SEM-EDAX mapping of EG-based adsorbents before and after decolonization process for CR and MB. It can be seen from Figure 12(a) that the EG shows the large crevice-like pores on the surface of particles and slit-shaped gaps between the graphite layers providing the channels which may facilitate the transport of working fluids. Combined with the EDAX analysis, the primary ingredient C was found in EG sheets in addition to other elements originated from chemicals used in the preparation process, namely O (from oxidation process), Mn (from adding  $\text{KMnO}_4$ ) and Cl (from adding  $\text{HClO}_4$ ). After adsorption process, the surface of worm-like graphite particles was filled with wrinkles and narrower slit-shaped gaps as a result of efficient captures of dye molecules (Figure 12(b,c)). Furthermore, the EDAX data of the EG after adsorption reveal not only normal ingredients of EG but also others, e.g. N, Na and S, which are the main ingredients of CR and MB, confirming the adsorption of CR and MB from aqueous solution on EG layers.

### 3.6. Desorption and regeneration

The investigation of possibility of recovery and reuse of EG was followed by the desorption process. The desorption of organic dyes from the resulted dye-adsorbed of EG was determined using 100 mL ethanol solution to wash several times until the adsorbates were released completely from adsorbents. The EG obtained from desorption process was regenerated and reused for two times in the fixed conditions, namely initial concentration of 200 mg/L, pH value of 7 and adsorbent dosage of 2 g/L. Figure 13 illustrates the changes in adsorption capacity of the EG after two regeneration cycles. It can be found that the adsorption capacity of EG for removal of CR and MB significantly decreased to 105.12 and 26.91 mg/g after the first reuse compared with the initial adsorption amount of 179 and 57 mg/g, respectively. The second regeneration caused a serious decrease of adsorption capacity and removal percentage for elimination of CR (74.97 mg/g, 31.16%, respectively). Lower reusing adsorption amount of EG was presumed due to the collapse of bulky structure and surface reconstruction during the adsorption and subsequent desorption of dye fluids from EG structure (Inagaki, Konno, Toyoda, Moriya, & Kihara, 2000; Vinh et al., 2018). Although the adsorption amount dramatically declined after second reuse, it is higher than other adsorbent with the quite similar sorption behavior in the first use (Phuong Quynh et al., 2017). These results demonstrated the removal efficacy of expanded graphite for organic dyes.

#### 4. Conclusions

In summary, this study shows that MB and CO can be eliminated from aqueous solution by using EG materials fabricated via facile microwave technique. The contact time, pH value in solution, adsorbent dosage and initial concentration of dyes showed important effect on the adsorption rate for MB and CO on EG. Possessing mesoporous structure with large surface area and total pore volume, the EG shows maximum adsorption performance for dyes with removal capacities of 47.5 mg/g MB and 201.2 mg/g CO per 1 g of adsorbent at pH = 9 and EG dose of 2 g/L. It has been found that the performance of EG was degraded in reuse tests; however, the adsorption capacities are still significant within three times of using. It is suggested that further investigation is necessary to find a proper desorption approach to improve the reusability of EG. These obtained results indicate that cost-efficient graphite-based adsorbents using simple manufacturing protocols exhibited remarkable efficacy for dye removal from aqueous solution.

#### Acknowledgements

This research was funded by the Science and Technology Development Funds of Nguyen Tat Thanh University in Ho Chi Minh City, Vietnam.

#### Funding

This research was funded by the Science and Technology Development Funds of Nguyen Tat Thanh University in Ho Chi Minh City, Vietnam.

#### Author details

Ngoc Bich Hoang<sup>1</sup>  
E-mail: [hnbich@ntt.edu.vn](mailto:hnbich@ntt.edu.vn)  
Thi Thuong Nguyen<sup>1</sup>  
E-mail: [nthithuong@ntt.edu.vn](mailto:nthithuong@ntt.edu.vn)  
ORCID ID: <http://orcid.org/0000-0003-0474-4317>  
Tien Sy Nguyen<sup>2</sup>  
E-mail: [synguyenars@gmail.com](mailto:synguyenars@gmail.com)  
Thi Phuong Quynh Bui<sup>2</sup>  
E-mail: [phuongquynh102008@gmail.com](mailto:phuongquynh102008@gmail.com)  
Long Giang Bach<sup>1</sup>  
E-mail: [blgiangntt@nttu.edu.vn](mailto:blgiangntt@nttu.edu.vn)  
<sup>1</sup> NTT Hi-Tech Institute, Nguyen Tat Thanh University, Ho Chi Minh City 755000, Vietnam.  
<sup>2</sup> Faculty of Chemical Technology, Ho Chi Minh City University of Food Industry, Ho Chi Minh City 705800, Vietnam.

#### Citation information

Cite this article as: The application of expanded graphite fabricated by microwave method to eliminate organic dyes in aqueous solution, Ngoc Bich Hoang, Thi Thuong Nguyen, Tien Sy Nguyen, Thi Phuong Quynh Bui & Long Giang Bach, *Cogent Engineering* (2019), 6: 1584939.

#### References

- Altıntig, E., Altundag, H., Tuzen, M., & Sari, A. (2017). Effective removal of methylene blue from aqueous solutions using magnetic loaded activated carbon as novel adsorbent. *Chemical Engineering Research and Design*, 122, 151–163. doi:10.1016/j.cherd.2017.03.035
- Arami, M., Limaee, N. Y., Mahmoodi, N. M., & Tabrizi, N. S. (2005). Removal of dyes from colored textile wastewater by orange peel adsorbent: Equilibrium and kinetic studies. *Journal of Colloid and Interface Science*, 288(2), 371–376. doi:10.1016/j.jcis.2005.03.020
- Asfaram, A., Ghaedi, M., Hajati, S., Rezaeinejad, M., Goudarzi, A., & Purkait, M. K. (2015). Rapid removal of Auramine-O and Methylene blue by ZnS:Cu nanoparticles loaded on activated carbon: A response surface methodology approach. *Journal of the Taiwan Institute of Chemical Engineers*, 53, 80–91. doi:10.1016/j.jtice.2015.02.026
- Avetta, P., Sangermano, M., Lopez-Manchado, M., & Calza, P. (2015). Use of graphite oxide and/or thermally reduced graphite oxide for the removal of dyes from water. *Journal of Photochemistry and Photobiology A: Chemistry*, 312, 88–95. doi:10.1016/j.jphotochem.2015.07.015
- Badenhorst, H. (2014). Microstructure of natural graphite flakes revealed by oxidation: Limitations of XRD and Raman techniques for crystallinity estimates. *Carbon*, 66, 674–690. doi:10.1016/j.carbon.2013.09.065
- Carvallho, M. N., Da Silva, K. S., Sales, D. C. S., Freire, E. M. P. L., Sobrinho, M. A. M., & Ghislandi, M. G. (2016). Dye removal from textile industrial effluents by adsorption on exfoliated graphite nanoplatelets: Kinetic and equilibrium studies. *Water Science and Technology*, 73(9), 2189–2198. doi:10.2166/wst.2016.073
- Esfandiari, N., Nasernejad, B., & Ebadi, T. (2014). Removal of Mn(II) from groundwater by sugarcane bagasse and activated carbon (a comparative study): Application of response surface methodology (RSM). *Journal of Industrial and Engineering Chemistry*, 20(5), 3726–3736. doi:10.1016/j.jiec.2013.12.072
- Goshadrou, A., & Moheb, A. (2011). Continuous fixed bed adsorption of C.I. Acid blue 92 by exfoliated graphite: An experimental and modeling study. *Desalination*, 170–176. doi:10.1016/j.desal.2010.10.058
- Hameed, B. H., & Hakimi, H. (2008). Utilization of durian (*Durio zibethinus* Murray) peel as low cost sorbent for the removal of acid dye from aqueous solutions. *Biochemical Engineering Journal*, 39(2), 338–343. doi:10.1016/j.bej.2007.10.005
- Inagaki, M., Konno, H., Toyoda, M., Moriya, K., & Kihara, T. (2000). Sorption and recovery of heavy oils by using exfoliated graphite Part II: Recovery of heavy oil and recycling of exfoliated graphite. *Desalination*, 128(3), 213–218. doi:10.1016/S0011-9164(00)00035-7
- Ion, A. C., Alpatova, A., Ion, I., & Culetu, A. (2011). Study on phenol adsorption from aqueous solutions on exfoliated graphitic nanoplatelets. *Materials Science and Engineering: B*, 176(7), 588–595. doi:10.1016/j.mseb.2011.01.018
- Li, J. T., Li, M., Li, J. H., & Sun, H. W. (2007a). Decolorization of azo dye direct scarlet 4BS solution using exfoliated graphite under ultrasonic irradiation. *Ultrasonics Sonochemistry*, 14(2), 241–245. doi:10.1016/j.ultsonch.2006.04.005
- Li, J. T., Li, M., Li, J. H., & Sun, H. W. (2007b). Removal of disperse blue 2BLN from aqueous solution by combination of ultrasound and exfoliated graphite. *Ultrasonics Sonochemistry*, 14(1), 62–66. doi:10.1016/j.ultsonch.2006.01.006

- Li, M., Li, J. T., & Sun, H. W. (2008b). Decolorizing of azo dye reactive red 24 aqueous solution using exfoliated graphite and H<sub>2</sub>O<sub>2</sub> under ultrasound irradiation. *Ultrasonics Sonochemistry*, 15, 717–723. doi:10.1016/j.ultsonch.2007.10.001
- Li, M., Li, J.-T., & Sun, H.-W. (2008a). Sonochemical decolorization of acid black 210 in the presence of exfoliated graphite. *Ultrasonics Sonochemistry*, 15(1), 37–42. doi:10.1016/J.ULTSONCH.2007.01.004
- Phuong Quynh, B. T., Kim, S. H., Que Minh, D. T., Mong Diep, N. T., Van Thinh, P., & Thuong, N. T. (2017). Magnetic NiFe<sub>2</sub>O<sub>4</sub> decorated-exfoliated graphite for adsorptive removal of anionic dyes and cationic dyes from aqueous solution. *Desalination and Water Treatment*, 82, 101–113. doi:10.5004/dwt.2017.20936
- Roy, A., Chakraborty, S., Kundu, S. P., Adhikari, B., & Majumder, S. B. (2012). Adsorption of anionic-azo dye from aqueous solution by lignocellulose-biomass jute fiber: Equilibrium, kinetics, and thermodynamics study. *Industrial & Engineering Chemistry Research*, 51(37), 12095–12106. doi:10.1021/ie301708e
- Sham, A. Y. W., & Notley, S. M. (2018). Adsorption of organic dyes from aqueous solutions using surfactant exfoliated graphene. *Journal of Environmental Chemical Engineering*, 6(1), 495–504. doi:10.1016/j.jece.2017.12.028
- Sykam, N., Jayram, N. D., & Rao, G. M. (2018). Highly efficient removal of toxic organic dyes, chemical solvents and oils by mesoporous exfoliated graphite: Synthesis and mechanism. *Journal of Water Process Engineering*, 25(January), 128–137. doi:10.1016/j.jwpe.2018.05.013
- Vinh, N. H., Hieu, N. P., Van Thinh, P., Diep, N. T. M., Thuan, V. N., Trinh, N. D., ... Quynh, B. T. P. (2018). Magnetic NiFe<sub>2</sub>O<sub>4</sub>/Exfoliated graphite as an efficient sorbent for oils and organic pollutants. *Journal of Nanoscience and Nanotechnology*, 18(10), 6859–6866. doi:10.1166/jnn.2018.15718
- Wei, X. H., Liu, L., Zhang, J. X., Shi, J. L., & Guo, Q. G. (2009). HClO<sub>4</sub>-graphite intercalation compound and its thermally exfoliated graphite. *Materials Letters*, 1618–1620. doi:10.1016/j.matlet.2009.04.030
- Yagub, M. T., Sen, T. K., Afroze, S., & Ang, H. M. (2014). Dye and its removal from aqueous solution by adsorption: A review. *Advances in Colloid and Interface Science*, 209, 172–184. doi:10.1016/j.cis.2014.04.002
- Zhao, M., & Liu, P. (2009). Adsorption of methylene blue from aqueous solutions by modified expanded graphite powder. *Desalination*, 249(1), 331–336. doi:10.1016/j.desal.2009.01.037
- Zheng, Y. P., Wang, H. N., Kang, F. Y., Wang, L. N., & Inagaki, M. (2004). Sorption capacity of exfoliated graphite for oils-sorption in and among worm-like particles. *Carbon*, 42, 2603–2607. doi:10.1016/j.carbon.2004.05.041



© 2019 The Author(s). This open access article is distributed under a Creative Commons Attribution (CC-BY) 4.0 license.

You are free to:

Share — copy and redistribute the material in any medium or format.

Adapt — remix, transform, and build upon the material for any purpose, even commercially.

The licensor cannot revoke these freedoms as long as you follow the license terms.

Under the following terms:

Attribution — You must give appropriate credit, provide a link to the license, and indicate if changes were made.

You may do so in any reasonable manner, but not in any way that suggests the licensor endorses you or your use.

No additional restrictions

You may not apply legal terms or technological measures that legally restrict others from doing anything the license permits.



**Cogent Engineering (ISSN: 2331-1916) is published by Cogent OA, part of Taylor & Francis Group.**

**Publishing with Cogent OA ensures:**

- Immediate, universal access to your article on publication
- High visibility and discoverability via the Cogent OA website as well as Taylor & Francis Online
- Download and citation statistics for your article
- Rapid online publication
- Input from, and dialog with, expert editors and editorial boards
- Retention of full copyright of your article
- Guaranteed legacy preservation of your article
- Discounts and waivers for authors in developing regions

**Submit your manuscript to a Cogent OA journal at [www.CogentOA.com](http://www.CogentOA.com)**

