

## Application of synthesized graphene in the treatment of wastewater

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### ABSTRACT

This research study presents an academic investigation on the development of a facile, low-cost, rapid and efficient method for the synthesis of highly expanded graphene using the thermal shock technique in an air atmosphere. The obtained samples were subjected to analysis using Fourier-transform infrared spectroscopy, X-ray diffraction spectroscopy and thermogravimetric analyses. A comparative analysis was conducted at three critical temperatures (750°C, 820°C and 870°C). The results demonstrated the effectiveness of the thermal shock technique in promoting rapid and significant expansion of the graphene structure by enhancing the internal forces within a remarkably short duration. Furthermore, the prepared samples exhibited outstanding thermal stability, along with a notable retention capability for green malachite (98%) and alizarine red (up to 100%).

*Keywords:* Expanded graphite; Synthesis; Thermal shock; Thermal stability; Filtration; Retention

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### 1. Introduction

Since its discovery, graphene, a single layer material formed by the sp<sup>2</sup> electron orbital hybridization tightly packed into a two-dimensional honeycomb lattice of carbon atoms with an atomic spacing of 1.42° [1–3], has attracted extensive focus from academic and industrial fields due to its specific surface area and storage modulus being two of the highest values reported at about 2,600 m<sup>2</sup>/g and 130 GPa, respectively [4], superior thermal, mechanical, electronic, optical characteristics [3,5,6]. Researchers incorporated this nanomaterial in various disciplines including electronics and batteries, energy storage, water treatment and many more [4]. However, the introduction of high-quality single layer graphene sheets free of defects into the industrial life still persists [5,6]. Hence, it is crucial to refine the manufacturing process in order to maximize the quality of graphene while insuring exceptional quality. Moreover, the key to future advancements lies on embracing easy-to-use, cost effective and environmentally sustainable approach [1].

Nowadays, most bulk-scale graphene is produced by a top-down approach [1], exfoliating graphite [7], oxidizing graphite via the Hummers' method or Brodie's method [8], followed by chemical or thermal reduction of graphite oxide (GO) which has always been one of the most advantageous and preferred method to obtain graphene in significant yields [2,9].

Effort has been performed to engineer the structure of GO materials for various specific applications, such as reduction (removing oxygen groups) and functionalization (adding other functionalities) [10,11]. The process of polymer functionalization of graphite oxide with dopants (acids or polymer molecules) has been proved to promote the self-exfoliating ability of graphene [8,12]. The addition of heat sensitive component is also effective for enhancing the inner pressure. Higher oxygen content can generate excessive gases which accelerate the exfoliation [5,8,13] confirmed that the functionalization of GO with PEG promoted its exfoliation into thin exfoliated nanosheets, also enlarge the basal spacing of the

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GO. Only recently considerable attempts have been conducted to prove the effect of heat-treatments on thermal reduction and exfoliation of graphite compounds. Bannov et al. [14] tested the efficiency of programmable heating and thermal shock as methods of producing expanded graphite at temperatures of 800°C–1,200°C. Song et al. [11] subjected graphene oxide to thermal reduction treatment in temperature range of 1,100°C–2,000°C. Ahmed et al. [12] reported the effect of treatment at high temperature (2,000°C) on the exfoliation of a graphene. However, all of their studies are time-consuming, need either pre-treatments, water rinsing, purification steps and desiccation, also often require sophisticated materials such as vacuums and large amounts of solvents with high-energy mixing, shearing, sonication or electrochemical treatment [7]. Additionally to chemical and thermal exfoliation, microwave assisted exfoliation of graphite compounds has been also reported to be efficient and rapid [15,16].

Providing access to drinking and affordable water for a large human population is one of the major global challenges of the 21st century [17]. For that, huge research interest has been focused for removal of toxic contaminants released from battery manufacturing, chemical manufacturing, textile, pesticides and other industries such as dyes, heavy metals, pharmaceuticals, oils and solvents causing numerous serious problems for living organisms and the natural environment [10,18,19]. It is demonstrated that graphite-based materials, due to their important properties, can effectively remove dyes from wastewater [19,20].

Therefore, novel methods of graphene synthesis must be developed in order to improve the important characteristics for further applications. In this work, we propose a one-step approach that integrates oxidation, reduction and exfoliation processes for graphene synthesis enhanced by polyvinyl alcohol functionalization in order to optimize the exfoliation process. The key aspect of this method involves rapid heating at three carefully selected critical temperatures.

## 2. Experimental set-up

### 2.1. Materials

Graphite (purity of 99% 80 µm of particle size) used in this study was in the form of graphite powder provided by a local company. Nitric acid HNO<sub>3</sub> (68%), sulfuric acid (98%) H<sub>2</sub>SO<sub>4</sub> and potassium permanganate KMnO<sub>4</sub> were purchased from Sigma-Aldrich, Germany. Malachite green (MG) and alizarin red (AR) were provided from Biochem Chemopharma, France.

Rapid heating was carried out in a tubular furnace provided by Nabertherm GmbH, Germany.

### 2.2. Characterizations

The as-obtained samples were characterized by the following methods:

The surface chemical properties were determined by a FTIR spectrometer ((IR Prestige-21, Shimadzu) via KBr tablets containing 0.5% of the analyte, with the spectra collected in the range of 4,000 and 400 cm<sup>-1</sup>.

Thermogravimetry (TG) were carried out using a TA, SDT Q600 thermal analyzer (NETZSCH, Selb, Germany). The heating was conducted in an Al<sub>2</sub>O<sub>3</sub> crucible. The stability of samples was analyzed at a heating rate of 10°C/min up to 1,000°C under azote gas flow of 50 mL/min.

The interlayer spacing of the obtained carbon materials was examined using X-ray diffractometer (600 Miniflex, Rigaku, Japan) equipped with a Cu X-ray tube (λ = 1.54 Å, 40 kV and 15 mA) was run at with 10°/min scan speed in the range of 2θ = 5° to 80°.

UV-Visible spectrophotometer SPECORD® 210 was used to determine the concentration of the treated dyes in each sample at a given wavelength (617 nm for GM, 480 nm for AR) using calibration curves.

### 2.3. Sample preparation

For the synthesis procedure, natural graphite powder (NG), intercalation agents (H<sub>2</sub>SO<sub>4</sub>) and oxidant (KMnO<sub>4</sub>) were combined in a weight ratio of 1:2:1 and mixed for a short duration. Subsequently, after 24 h, the resulting mixture was subjected to thermal heat shock treatment in a pre-heated furnace at three distinct critical temperatures (750°C, 820°C, 870°C), enabling rapid accomplishment of oxidation, intercalation and exfoliation processes witting a few seconds [15]. The heat treatment experiments were carried out under ambient atmosphere conditions using a furnace, employing a gradual heating rate of 10°C/min. Afterward, the samples were exposed to rapid heating at the specific temperatures of 750°C, 820°C and 870°C for only few seconds.

Based on the different expansion temperatures, the EGs were labeled as EG-750, EG-820 and EG-870.

### 2.4. Filtration

This study aims to investigate the effectiveness of a specialized vertical filtration system for the separation of water from synthetic wastewater containing malachite green (MG) and AR dyes. The filtration system, based on a PVC-FPT union and PVC coupling [21], incorporates graphene synthesized at 750°C (Gr-750) as the filtering material. By utilizing a support layer of gravel and cotton to prevent material loss, a stable mass of 2 g of Gr-750 is placed within the assembly. Synthetic wastewater models comprising various concentrations (10<sup>-5</sup> M, 10<sup>-4</sup> M, and 10<sup>-3</sup> M) of MG and AR dyes are used to assess the filtration system's consistency and performance, providing insights into the potential application of graphene-based filters in efficient dye removal from wastewater.

The permeance recovered at time intervals were subjected to UV-visible analysis.

The retention rate of the permeates of the different samples is given by the following relationship:

$$R(\%) = 1 - \frac{C_p}{C_o}$$

where  $R(\%)$ : the retention,  $C_o$ : the concentration of the initial solution,  $C_p$ : the concentration of the permeate at a defined time.

### 3. Results and discussion

#### 3.1. Synthesis

Rapid heating at the high temperatures leads to rapid decomposition and vaporization of the intercalated reagents that induces strong formation of a gases that instantaneously generates a strong driving force to strip the structure of graphite layers [14,20]. These procedures may help to produce channels and pore structures for adsorption [20].

#### 3.2. Fourier-transform infrared spectroscopy analysis

Fig. 1 shows Fourier-transform infrared spectroscopy (FTIR) spectra of graphite and the as obtained carbon materials Gr-870°C, Gr-820°C, Gr-750°C.

The visualization of the spectra shows the presence of a broad band between 3,400 and 3,200  $\text{cm}^{-1}$  corresponding to the hydrogen elongation vibrations of the O–H hydroxyl groups due to water, carboxyl, phenol or alcohol. While the small bands between 1,650 and 1,500  $\text{cm}^{-1}$  is attributed to elongation vibrations of C=C groups, the spectra also show an intense band around 1,140  $\text{cm}^{-1}$  due to deformation vibrations of C–O bonds. The small band around 1,400  $\text{cm}^{-1}$  results from C–H deformation vibrations. The deformation vibration bands between 800 and 600  $\text{cm}^{-1}$  correspond to C–H bonds (adjacent =C–H). Nearly a flat line with no obvious peak was detected for graphite, suggesting no significant amount of oxygen functional groups was found in this carbon material [22]. Therefore, the oxygen-containing functional groups were successfully removed partially and the low amounts of residue of functional groups are still remain at the edge and basal plane of rGO [23]. It is also noticeable that peaks are less intense than those peaks at the same location in FTIR spectra of GO, which were also due to the removal oxygen.

#### 3.3. X-ray diffraction analysis

Structural properties of the carbon materials were studied using X-ray diffractometer as presented in Fig. 2.

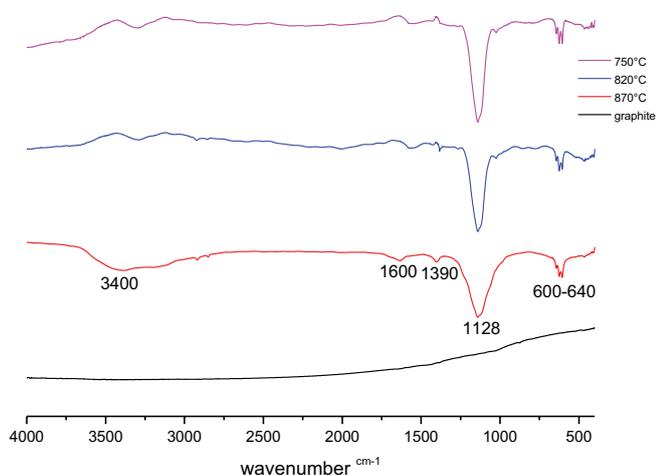


Fig. 1. Fourier-transform infrared spectra of graphite, Gr-870°C, Gr-820°C and Gr-750°C.

Fig. 2 shows X-ray diffraction (XRD) pattern of pristine graphite. It reveals that graphite sample are well arranged with a characteristic sharp (0 0 2) diffraction peak located at  $2\theta = 26.515^\circ$  corresponding to an interlayer spacing of ( $d_{002} = 3.3589 \text{ \AA}$ ). Fig. 2 shows the XRD patterns of the as-obtained graphene treated at 750°C, 820°C and 870°C. This is evidenced by the reappearance of the ( $d_{002}$ ) diffraction line at  $2\theta = 21.5^\circ$ ,  $2\theta = 26.43^\circ$  and  $2\theta = 26.46^\circ$  corresponding to a spacing of 4.14, 3.369 and 3.66  $\text{\AA}$  for Gr-750°C, Gr-820°C and Gr-850°C, respectively.

Both Gr-820°C and Gr-850°C have quite similar peak where interlayer distance values are close to 3.35  $\text{\AA}$  for pristine graphite indicating that carbon materials has been restored considerably with two dimensional ordered stacks after heat treatment [11]. While Gr-750°C d value (4.14  $\text{\AA}$ ) is quite greater indicating that some oxygen is still intercalated into the interlayer spacings of graphite.

Also, a small (0 0 2) diffraction peaks can be observed on the XRD patterns of the graphene samples but with a weaker and lower intensity showing that the graphite lattice is still retained during the conversion from graphite to graphene. However, these peaks intensity is remarkably weaker compared with that of graphite, indicating the few-layer feature of the resultant grapheme [9,24,25].

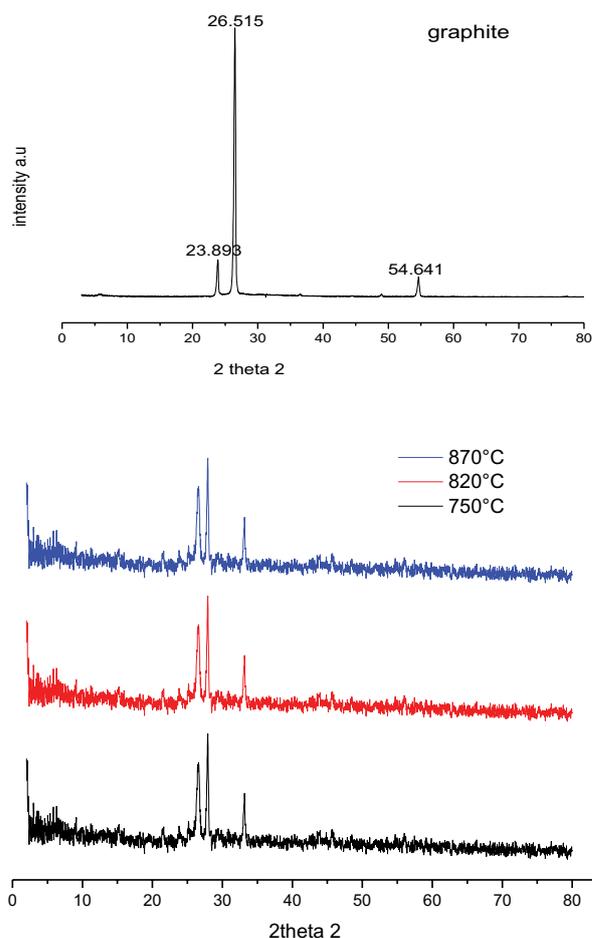


Fig. 2. X-ray diffraction spectra of graphite, Gr-870°C, Gr-820°C and Gr-750°C.

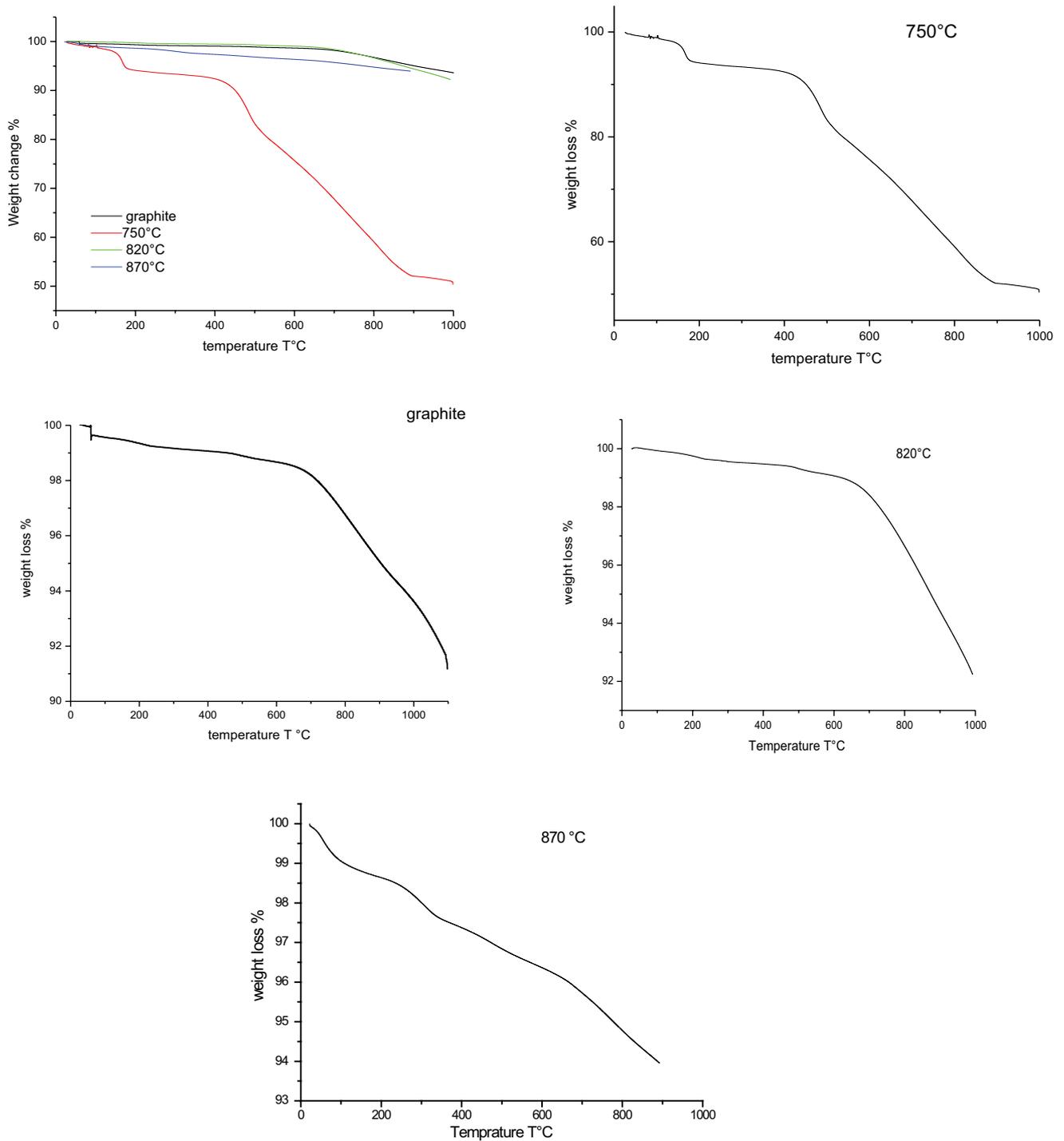


Fig. 3. Thermogravimetric analysis spectra of graphite, Gr-750°C, Gr-820°C and Gr-870°C.

The peak C(002) in the sharp graphene shows that the formation of graphene has not been single layer [25].

#### 3.4. Thermogravimetric analysis

The thermogravimetric analysis results illustrated in Fig. 3 offer useful insights to understand the thermal behavior of the carbonaceous decomposition of the as-obtained

materials. The as prepared graphene materials and graphite samples were subjected to thermal decomposition up to 1,000°C in the nitrogen atmosphere to probe thermal characteristics. Graphite start to decompose at 700°C~1,000°C the thermogram of Gr-750°C is similar to that of graphene oxide and highlights 3 significant thermal events corresponding to the evaporation of water below 100°C, 100°C–200°C for partial decomposition of some unstable oxygenated

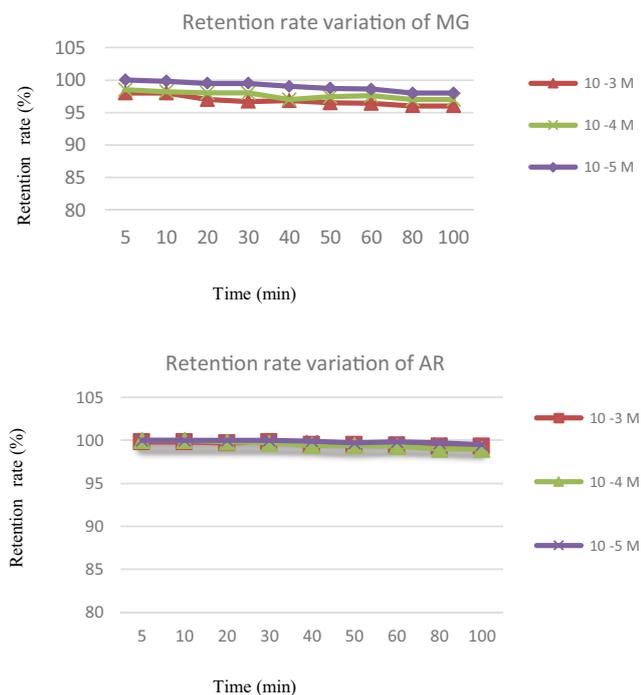


Fig. 4. Retention rate variation of VM and NR with time on Gr-750°C.

functional groups such as epoxide, hydroxyl and carboxyl and the oxidative pyrolysis of carbon skeleton at around 400°C [22]. Gr-750°C requires lower heat energy to overcome weaker non-graphitic sp<sup>3</sup> hybridized carbon and to decompose the high level of oxygen groups. Graphite and Gr-870°C show quite a similar thermographs with a starting decomposition temperature of beyond 600°C, resulting the most thermodynamically stable carbon materials studied in this work while they demand more heat energy to overcome its strongest 3D carbon network, consisting of a large number of graphene stacked layers held by additional Van Der Waals forces [22].

### 3.5. Filtration

The retention rate of permeances of MG and AR solutions through the filtration assembly using Gr-750°C is given in Fig. 4.

The retention of malachite green recorded is in the order of 99% up to 100% for the concentrations 10<sup>-5</sup> M and 10<sup>-4</sup> M. However, for a concentration of 10<sup>-3</sup> M, the retention rate varies between 97% and 98%.

The retention rate of the malachite green permeances, (10<sup>-5</sup> M and 10<sup>-4</sup> M), decreases during the first 30 min and stabilized until the end of the experiment. It can be seen that the retention rate of the 10<sup>-3</sup> M concentration of malachite green is lower than that of the 10<sup>-4</sup> M and 10<sup>-5</sup> M concentrations, decreasing to 97% during the first 10 min. Therefore, the retention of Alizarin Red S permeates recorded is in the order of 99% up to 100% for the concentrations 10<sup>-4</sup> M and 10<sup>-3</sup> M. This is due to the good absorption capacity of the activated carbon.

The uptake of the dye particles could be due to the  $\pi$ - $\pi$  interactions between the Gr-750°C and the benzene rings of MG and AR. Additionally, the adsorption of the dye particles on the provided adsorption sites could be due to the Van der Waals' forces and hydrogen bonding [21].

## 4. Conclusion

In conclusion, this research proposes a cost-effective and efficient approach to thermally exfoliate graphite into few layers of graphene. Our method involves a unique high-temperature shock treatment in a tubular furnace, enabling simultaneous oxidation, intercalation, and exfoliation within a matter of seconds. We investigated the impact of expansion temperature on the physicochemical properties of the resulting carbonaceous materials. Moreover, the filtration assembly we developed effectively retained organic dyes, with retention rates ranging from 97% to 99%, and achieving complete retention (100%) for malachite green and alizarin red, respectively.

Future studies should aim to explore the exfoliation of graphite into defect-free single-layer graphene at elevated temperatures opening up opportunities for environmentally sustainable and economically viable approaches to address freshwater and wastewater remediation projects.

## References

- [1] A.L. Olatomiwa, T. Adam, S.C.B. Gopinath, S.Y. Kolawole, O.H. Olayinka, U. Hashim, Graphene synthesis, fabrication, characterization based on bottom-up and top-down approaches: an overview, *J. Semicond.*, 43 (2022) 061101, doi: 10.1088/1674-4926/43/6/061101.
- [2] C. Nethravathi, M. Rajamathi, Chemically modified graphene sheets produced by the solvothermal reduction of colloidal dispersions of graphite oxide, *Carbon N.Y.*, 46 (2008) 1994–1998.
- [3] M. Liu, X. Zhang, W. Wu, T. Liu, Y. Liu, B. Guo, R. Zhang, One-step chemical exfoliation of graphite to ~100% few-layer graphene with high quality and large size at ambient temperature, *Chem. Eng. J.*, 355 (2019) 181–185.
- [4] H. Jahandideh, J.-R. Macairan, A. Bahmani, M. Lapointe, N. Tufenkji, Fabrication of graphene-based porous materials: traditional and emerging approaches, *Chem. Sci.*, 13 (2022) 8924–8941.
- [5] C. Zhang, W. Lv, X. Xie, D. Tang, C. Liu, Q.H. Yang, Towards low temperature thermal exfoliation of graphite oxide for graphene production, *Carbon N.Y.*, 62 (2013) 11–24.
- [6] F.S. Al-Hazmi, G.H. Al-Harbi, G.W. Beall, A.A. Al-Ghamdi, A.Y. Obaid, W.E. Mahmoud, One pot synthesis of graphene based on microwave assisted solvothermal technique, *Synth. Met.*, 200 (2015) 54–57.
- [7] D.X. Luong, K.V. Bets, W.A. Algozeeb, M.G. Stanford, C. Kittrell, W. Chen, R.V. Salvatierra, M. Ren, E.A. McHugh, P.A. Advincula, Z. Wang, M. Bhatt, H. Guo, V. Mancevski, R. Shahsavari, B.I. Yakobson, J.M. Tour, Gram-scale bottom-up flash graphene synthesis, *Nature*, 577 (2020) 647–651.
- [8] Y. Hu, C. bao Sun, J. Kou, Exfoliation of poly(ethylene glycol)-intercalated graphite oxide composite in water without sonication, *Int. J. Miner. Metall. Mater.*, 27 (2020) 840–845.
- [9] B. Kartick, S.K. Srivastava, I. Srivastava, Green synthesis of graphene, *J. Nanosci. Nanotechnol.*, 13 (2013) 4320–4324.
- [10] E. Freitas, D. Janu, Y. Jaqueline, G. Wernke, G. Maria, M. Demiti, L. Bergamasco, S. Vieira, Chemosphere Application of activated carbon functionalized with graphene oxide for efficient removal of COVID-19 treatment-related pharmaceuticals from water, *Chemosphere*, 289 (2022) 9, doi: 10.1016/j.chemosphere.2021.133213.

- [11] L. Song, F. Khoerunnisa, W. Gao, W. Dou, T. Hayashi, K. Kaneko, M. Endo, P.M. Ajayan, Effect of high-temperature thermal treatment on the structure and adsorption properties of reduced graphene oxide, *Carbon N.Y.*, 52 (2013) 608–612.
- [12] M.M.M. Ahmed, T. Imae, J.P. Hill, Y. Yamauchi, K. Ariga, L.K. Shrestha, Defect-free exfoliation of graphene at ultra-high temperature, *Colloids Surf., A*, 538 (2018) 127–132.
- [13] N.D. Mao, H. Jeong, T.K. Ngan Nguyen, T.M. Loan Nguyen, T.V. Vi Do, C.N. Ha Thuc, P. Perré, S.C. Ko, H.G. Kim, D.T. Tran, Polyethylene glycol functionalized graphene oxide and its influences on properties of poly(lactic acid) biohybrid materials, *Composites, Part B*, 161 (2019) 651–658.
- [14] A.G. Bannov, A.V. Ukhina, E.A. Maksimovskii, I.Y. Prosanov, A.A. Shestakov, N.I. Lapekin, N.S. Lazarenko, P.B. Kurmashov, M.V. Popov, Highly porous expanded graphite: thermal shock vs. programmable heating, *Materials (Basel)*, 14 (2021) 1–17.
- [15] T. Wei, Z. Fan, G. Luo, C. Zheng, D. Xie, A rapid and efficient method to prepare exfoliated graphite by microwave irradiation, *Carbon N.Y.*, 47 (2009) 337–339.
- [16] W. Jiang, Z. Li, Y. Zhu, W. Xin, Y. Yu, Arc spectra of different solid reduced graphene oxide samples under microwave irradiation, *Diamond Relat. Mater.*, 109 (2020), doi: 10.1016/j.diamond.2020.108060.
- [17] H. Wang, X. Mi, Y. Li, S. Zhan, 3D graphene-based macrostructures for water treatment, *Adv. Mater.*, 32 (2020) 1–11.
- [18] W.T. Tee, N.Y.L. Loh, K.C. Lai, B.Y.Z. Hiew, S. Gan, L.Y. Lee, Application of 3D heteroatom-doped graphene in adsorptive removal of water pollutants: review on hydrothermal synthesis and its influencing factors, *Sep. Purif. Technol.*, 320 (2023) 124072, doi: 10.1016/j.seppur.2023.124072.
- [19] N. Chandra, P. Gururani, Advances of graphene oxide based nanocomposite materials in the treatment of wastewater containing heavy metal ions and dyes, *Curr. Res. Green Sustainable Chem.*, 5 (2022) 100306, doi: 10.1016/j.crgsc.2022.100306.
- [20] G. Yin, Z. Sun, Y. Gao, S. Xu, Preparation of expanded graphite for malachite green dye removal from aqueous solution, *Microchem. J.*, 166 (2021) 106190, doi: 10.1016/j.microc.2021.106190.
- [21] M. Zhao, M.T. Yang, M. Singh, T. Overturf, Y. Gao, G. Silva Hernandez, S. Ahmed, S. Banerjee, Fabrication and characterization of a water purification system using activated carbon and graphene nanoplatelets: toward the development of a nanofiltration matrix, *Water Environ. Res.*, 93 (2021) 1530–1542.
- [22] F. Farivar, P. Lay Yap, R.U. Karunakaran, D. Losic, Thermogravimetric analysis (TGA) of graphene materials: effect of particle size of graphene, graphene oxide and graphite on thermal parameters, *C*, 7 (2021) 41, doi: 10.3390/c7020041.
- [23] N.M.S. Hidayah, W. Liu, C. Lai, N.Z. Noriman, C.-S. Khe, U. Hashim, H.C. Lee, Comparison on graphite, graphene oxide and reduced graphene oxide: synthesis and characterization, *AIP Conf. Proc.*, 1892 (2017) 150002, doi: 10.1063/1.5005764.
- [24] W. Wu, M. Liu, Y. Gu, B. Guo, H. Ma, P. Wang, X. Wang, R. Zhang, Fast chemical exfoliation of graphite to few-layer graphene with high quality and large size via a two-step microwave-assisted process, *Chem. Eng. J.*, 381 (2020) 122592, doi: 10.1016/j.cej.2019.122592.
- [25] R. Siburian, D.R. Sari, J. Gultom, H. Sihotang, S.L. Raja, J. Gultom, M. Supeno, Performance of graphite and graphene as electrodes in primary cell battery, *J. Phys. Conf. Ser.*, 1116 (2018) 042034, doi: 10.1088/1742-6596/1116/4/042034.