# Adsorption Behaviours of Anionic Azo Dye (Congo Red) from Aqueous Solution on Magnetic Expanded Graphite Material (EG@CoFe₂O₄) Composites

LAM VAN TAN[1,2,3], NGUYEN THI HONG THAM[1,2,3,*], VAN THUAN TRAN[1,2,3], DAO THI TO UYEN[1,2,3], PHAM GIA VU[4],
DO TRUNG SY[5], VO THANH DANH[6], NGUYEN ANH TIEN[7], DAI VIET N. VO[2] and TRINH DUY NGUYEN[2,3,*]

[1]Center of Excellence for Functional Polymers and NanoEngineering, Nguyen Tat Thanh University, Ho Chi Minh City, Vietnam
[2]Center of Excellence for Green Energy and Environmental Nanomaterials, Nguyen Tat Thanh University, Ho Chi Minh City, Vietnam
[3]NTT Hi-Tech Institute, Nguyen Tat Thanh University, Ho Chi Minh City, Vietnam
[4]Institute for Tropical Technology, Vietnam Academy of Science and Technology, Ha Noi, Vietnam
[5]Institute of Chemistry, Vietnam Academy of Science and Technology, Ho Chi Minh City, Vietnam
[6]BKU Institute of Advanced Applied Science and Technology (BKIST), Ho Chi Minh City, Vietnam
[7]Ho Chi Minh City University of Education, Ho Chi Minh City, Vietnam

*Corresponding authors: E-mail: ndtrinh@ntt.edu.vn; nguyenduytrinh86@gmail.com

In this paper, a potentiality of magnetic expanded graphite material (EG@CoFe₂O₄) for the adsorptive removal of Congo red, an anionic azo dye, from aqueous solution was studied. The experiments were carried out in batch mode in which various experimental conditions including contact time, initial dye concentration, adsorbent dosage and pH were varied and their influences on the adsorption yield were investigated. The surface of the adsorbent before and after the removal of the dye was characterized by using FT-IR analysis. Maximum adsorption of dye was achieved at pH 6. The adsorption capacity of Congo red onto EG@CoFe₂O₄ was found to be as high as 101.2 (mg/g), which is higher than the adsorption capacity of the CoFe₂O₄ (45.7 (mg/g)). These results suggested the use of expanded graphite materials as an efficient adsorbent for decontamination of Congo red dye from factory effluents.

**Keywords: Magnetic expanded graphite, Congo red dye, Adsorption, Batch mode.**

## INTRODUCTION

The widespread applications of organic dyes especially azo dyes in various industries such as textile, leather treatment, paper, printing, plastics, pharmaceuticals, tannery, solar cells, *etc*. [1-8] has resulted in a vast amount of contaminated effluents. Out of 800,000 tons of synthetic dyes that are produced annually, approximately 30 % of which has been deprived directly into the environment. Since the such effluents are highly toxic, colour-persistent, have high chemical oxygen demand and low bioavailability, thus untreated wastewater containing toxic dyes could cause serious water pollution and when being used for irrigation, render the soil uncultivable. In addition, dye wastewater is also harmful for human health as they reportedly the cause for various types of cancer, allergy, dermatitis, mutation and skin irritation [9,10].

Among various treatment techniques for dye wastewater adsorption emerges due to its advantages including improved efficiency, potentially low cost and effortless implementation [11-16]. However, the cost of techniques depends mainly on the sorbent material used and its requirements on pre-treatment processes, making material selection for adsorption applications for Congo red dyeucial. One of the notable adsorbents emerging in recent literature is expanded graphite. An expanded graphite is porous and especially effective when it comes to adsorption of organic compounds such as organic dyes and heavy oils [17-20]. However, the main drawback of expanded graphite, which is the small particle size and high dispersion, might restrict recovery, recyclability and in turn the scalability of the material in practical applications. To remedy, manipulation of magnetic properties has been proposed as a feasible strategy to extend its applications by electromagnetic collection.

In previous reports, successful introduction of $CoFe_2O_4$ magnetic particles to expanded graphite *via* sol-gel method has been found to enhance magnetism of as-synthesized $EG@CoFe_2O_4$ [21,22]. In addition, further sorption evaluation of $EG@CoFe_2O_4$ revealed that in comparison with diesel and Congo red dyeude oil, a material showed greater sorption capacities against fuel oil, suggesting its suitability for oil spill treatment [23,24]. Despite that such reported capabilities were insufficient for organic dye removal from water and required further improvement.

In this study, an adsorption efficacy of magnetic expanded graphite material ($EG@CoFe_2O_4$) for Congo red dye, a typical anionic dye, from aqueous solution was explored. By performing batch operations, influence of various experimental parameters including initial dye concentration, material dosage, initial pH and contact time on the adsorption efficacy was determined. The obtained results are expected to contribute to improvements on the existing adsorption processes using $EG@CoFe_2O_4$ material.

## EXPERIMENTAL

Magnetic expanded graphite material ($EG@CoFe_2O_4$) was prepared by adding magnetic particles $CoFe_2O_4$ to expanded graphite through sol-gel process [25,26]. Congo red dye was purchased from Guangzhou Chemical Reagent Company. Other chemicals and reagents were of analytical reagent grade and used without further purification. A multi-parameter analyzer (Consort, Belgium) was utilized to measure pH of the solutions and NaOH (0.1 M) or HCl (0.1 M) was used to adjust the initial pH. The UV-visible spectra were recorded using the UV-visible spectrophotometer within the wavelength range of 200-800 nm.

**Batch experiments:** A pre-determined amount of dye was dissolved into distilled water to produce a stock solution of 100 mg/L. Adsorption experiments were performed by mixed 0.05g of $EG@CoFe_2O_4$ and $CoFe_2O_4$ with 100 mL of Congo red dye solution in a 250 mL beaker. The equilibrium adsorption capacity and removal efficacy was calculated as follows:

$$q_e = \frac{C_o - C_e}{m} V \qquad (1)$$

$$Removal\ (\%) = \frac{C_o - C_e}{C_o} \times 100 \qquad (2)$$

where $C_o$ and $C_e$ are the initial and equilibrium concentration of Congo red dye (mg/L), respectively; V is the volume of dye solution, and m is the mass of $EG@CoFe_2O_4$ and $CoFe_2O_4$, respectively.

## RESULTS AND DISCUSSION

**Effect of contact time:** Fig. 1 visualized adsorption variations of Congo red dye onto $EG@CoFe_2O_4$ and $CoFe_2O_4$ adsorbent with respect to different contact times (0-240 min) and concentrations (20-60 mg/L). In this experiment, a dosage was kept at 0.05 g. In general, adsorption of both adsorbents showed positive relationship with time and initial dye concentrations. In addition, an adsorption equilibrium was attained in both materials after 1 h of reaction. In comparison with $CoFe_2O_4$, a striking feature of $EG@CoFe_2O_4$ was the rapid increase in adsorption capacity, which almost reached the peak swiftly. This was mainly due to the abundance of active sites on $EG@CoFe_2O_4$ surface and weak internal diffusion resistance in the beginning. The time of 180 min was selected in further experiments because increasing the time post 30 min had negligible changes in adsorption.

**Effect of initial concentration of dye:** Since the adsorbate species that could be adsorbed is limited and proportional to the adsorbent amount, determining the initial concentration plays a key role in optimizing the adsorption process. Fig. 2 demonstrates the relationship between the amount of dye adsorbed ($q_t$) at varying initial dye concentrations (20, 30, 40, 50 and 60 mg/L). Overall, in Congo red dye easing initial concentration of dye induces noticeable changes on the dye removal. However, an increase in dye removal slowed down at higher concentrations and started to diminish after reaching the equilibrium. When the initial dye concentration increased from 20 ppm to
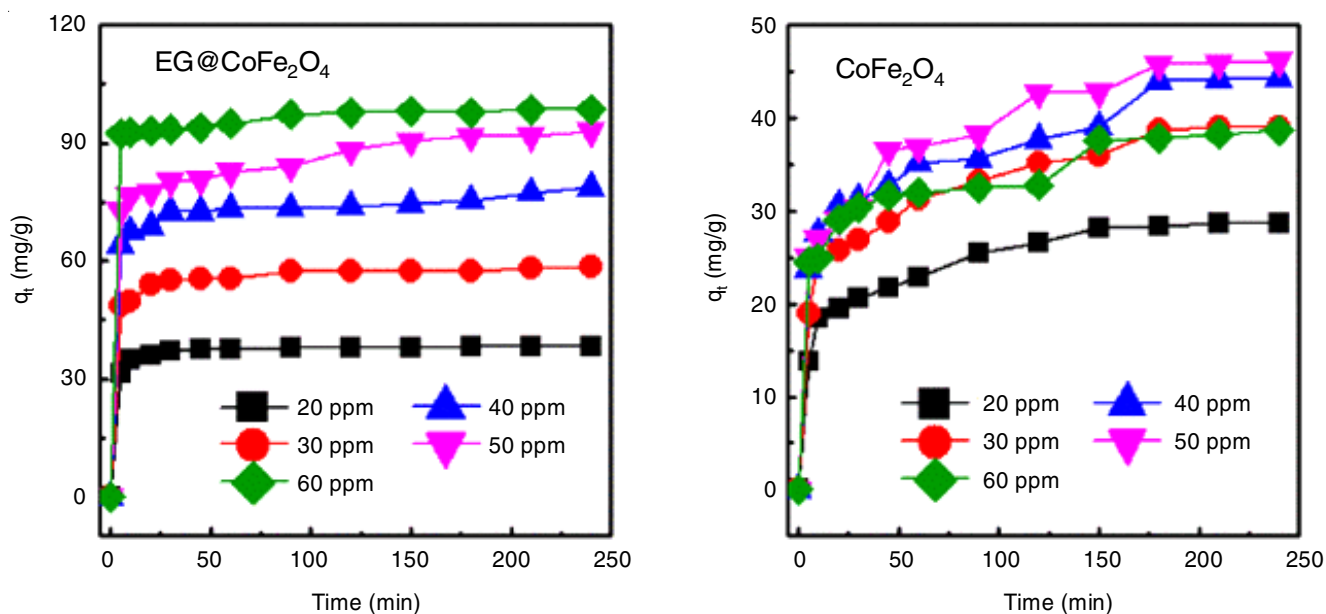


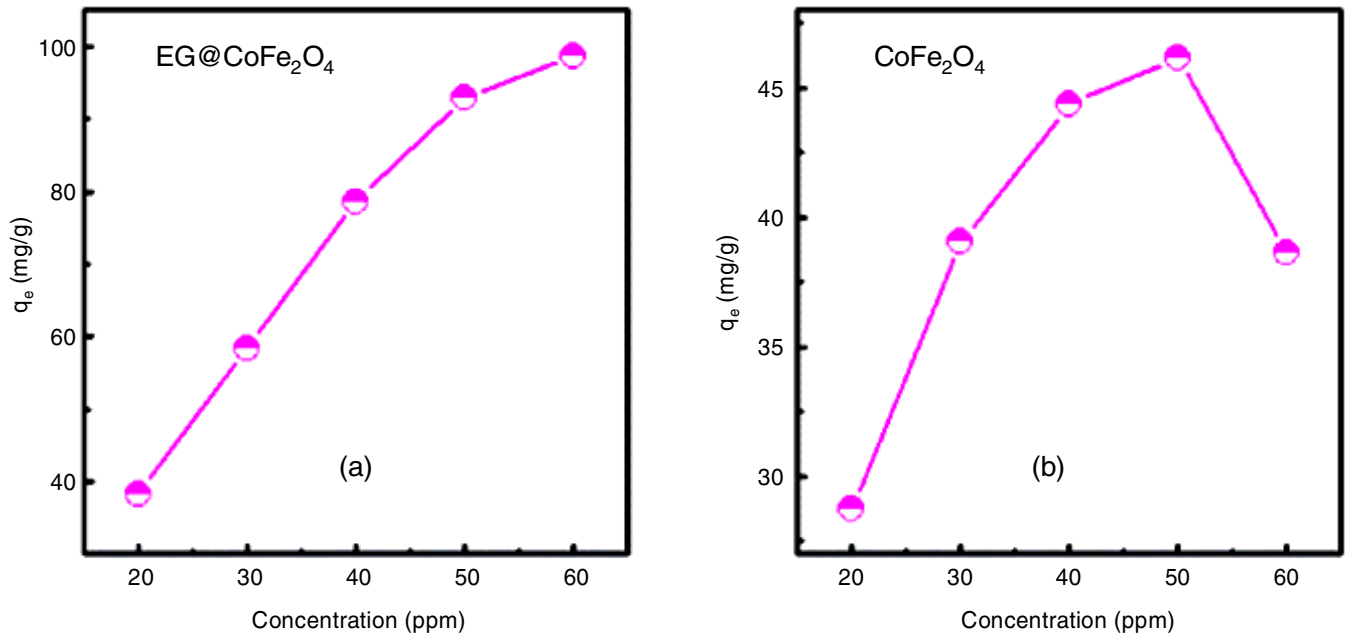Fig. 1. Effect of contact time on the adsorption of Congo red onto $EG@CoFe_2O_4$ and $CoFe_2O_4$

Fig. 2. Effect of concentration on the adsorption of Congo red onto EG@CoFe$_2$O$_4$ and CoFe$_2$O$_4$

60 mg/L, the sorption capacity of EG@CoFe$_2$O$_4$ increased from 38.25 to 101.2 mg/g while for CoFe$_2$O$_4$ an increase from 28.74 to 38.65 mg/g was observed. Thus, magnetic CoFe$_2$O$_4$ decorated-exfoliated graphite for adsorptive removal of Congo red dye can used as adsorbent at higher concentrations than magnetic CoFe$_2$O$_4$.

**Influence of pH:** Fig. 3 showed an adsorption capacity of Congo red dye onto EG@CoFe$_2$O$_4$ and CoFe$_2$O$_4$ at different pH levels. In solution, an existence of molecular ions in the form of ionization/dissociation can influence on absorbability of EG@CoFe$_2$O$_4$ and CoFe$_2$O$_4$ for Congo red dye. As seen from Fig. 3, an adsorption capacity of Congo red dye onto EG@CoFe$_2$O$_4$ and CoFe$_2$O$_4$ declined rapidly as the pH was elevated from 2.0 to 12.0. The optimum pH that induces the maximum

adsorption of Congo red dye was 6 and 4 for EG@CoFe$_2$O$_4$ and CoFe$_2$O$_4$, respectively. This result can be explained due to the prevalence of proton in aqueous solution at low pH, which might results in the formation of positive charges on the surface of EG@CoFe$_2$O$_4$, leading to enriched electrostatic repulsion between surface of EG@CoFe$_2$O$_4$ and dye molecules [25-27]. This result also suggested that low pH can be unfavourable for the adsorption of Congo red dye. Similarly, on increasing the pH of Congo red dye solution induces a decline in the adsorption yield. The main reason is due to electrostatic repulsion between negative charge Congo red dye molecules and surface of EG@CoFe$_2$O$_4$. Hence, a weak or neutral acid is a suitable condition for Congo red dye adsorption toward EG@CoFe$_2$O$_4$.
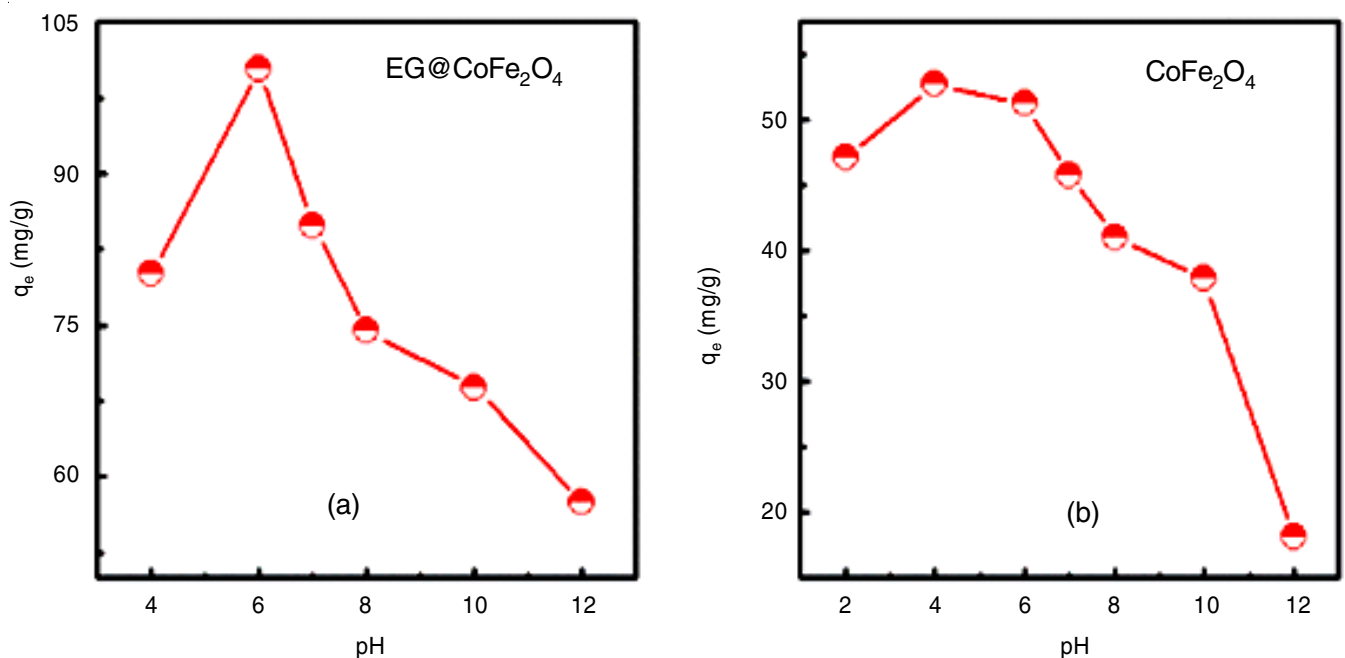


Fig. 3. Effect of pH solution on the adsorption of Congo red onto EG@CoFe$_2$O$_4$ and CoFe$_2$O$_4$

**Effect of adsorbent dosage:** The effect of EG@CoFe$_2$O$_4$ and CoFe$_2$O$_4$ dosage on the removal of Congo red dye in aqueous solution is shown in Fig. 4. Visually, an optimal dosage for the highest adsorption yield of Congo red dye (101.2 and 38.9 mg/g for EG@CoFe$_2$O$_4$ and CoFe$_2$O$_4$, respectively) could be optimum at 0.05 g/L. With the addition of sorbent mass from 0.03 to 0.05 g, it was found that an absorbability of EG@CoFe$_2$O$_4$ increased from 70.8 to 101.2 mg/g. However, further increasing a dosage amount from 0.06 and 0.07 g decreased the adsorption capacity to 90.7 and 80.1 mg/g, respectively. This trend was also observed similar for CoFe$_2$O$_4$ (Fig. 4b). According to previous studies [28,29], the initial dose of dye can provide a limited adsorption site and absorb a fixed amount of adsorbate. Meanwhile, excessively high adsorbent dosage will decrease the utilization ratio of active sites, therefore hindering the equilibrium adsorption capacity of EG@CoFe$_2$O$_4$ adsorbent. Therefore, a dosage of 0.05 g/L was selected as the optimal EG@CoFe$_2$O$_4$ dosage for removal of Congo red dye.

**FT-IR spectra of EG@CoFe$_2$O$_4$ after adsorption of Congo red dye:** Fig. 5 displayed FT-IR spectra of the as-synthesized EG@CoFe$_2$O$_4$ and the Congo red dye loaded adsorbent in the wavelength ranging from 4000 to 400 cm$^{-1}$. The existence of several peaks could be assigned to various functional groups that form EG@CoFe$_2$O$_4$ and contribute to the binding of dye molecules. The characteristic absorbance bands at 3400, 1639 and 1191 cm$^{-1}$ corresponds to the stretching of O-H, carbonyl C=C and both C-O-C & C-O, respectively. The absorption peaks and peak intensity in the spectrum of Congo red dye loaded EG@CoFe$_2$O$_4$ were different from bare EG@CoFe$_2$O$_4$. This was consistent with a previous study where saw dust was used as an adsorbent to remove tartrazine dye from aqueous solution [30-32]. To be specific, a peak at 1511.9 cm$^{-1}$ and the peaks ranges from 698.41 to 880.64 cm$^{-1}$ found to disappear from EG@CoFe$_2$O$_4$ spectrum, indicated the degradation Congo red dye molecules. While a peak at 1511.9 cm$^{-1}$ represents the material bond and peaks from 880.64 to 698.41 cm$^{-1}$ could be assigned to the benzene ring structures of the parent Congo red dye. These results suggested the role of functional groups on the surface of adsorbent in the adsorption process of dye ions. Since weak electrostatic interaction or van der Waals forces might be involved in the adsorption process and also concluded that chemical bonding did not take place.

**Comparison with other adsorbents:** The maximum Congo red dye adsorption capacity (Q$_m$) of EG@CoFe$_2$O$_4$ composites and other synthesized adsorbents are summarized in Table-1. The maximum monolayer uptake capacity of EG@CoFe$_2$O$_4$ composite was superior to various types of sorbents (magnetic core-manganese oxide shell, chitosan/montmorillonite nanocomposite, acid-activated bentonite, magnetic (Fe$_3$O$_4$) cellulose activated carbon, magnetic nanocomposite of activated charcoal, anilinepropylsilica xerogel), *etc*. [33-41]. This highlight the high potential ability of EG@CoFe$_2$O$_4$ composites for the decontamination of Congo red dye from industrial discharges.

## Conclusion

Magnetic expanded graphite material (EG@CoFe$_2$O$_4$) was experimentally characterized for removal capacity of anionic azo dye Congo red from aqueous solutions. It was found that

TABLE-1
ADSORPTION CAPACITY OF CONGO
RED ON DIFFERENT ADSORBENTS

| Adsorbent | Q$_m$ (mg/g) | Ref. |
|---|---|---|
| Magnetic core-manganese oxide shell | 42.00 | [33] |
| Chitosan/montmorillonite nanocomposite | 54.52 | [34] |
| Mesoporous activated carbon | 189.00 | [35] |
| Fe$_3$O$_4$ particles | 97.62 | [36] |
| Acid-activated bentonite | 61.50 | [37] |
| Magnetic (Fe$_3$O$_4$) cellulose activated carbon | 66.09 | [38] |
| Nanosized rod-like hydroxyapatite particles | 337.33 | [39] |
| Magnetic nanocomposite of activated charcoal | 46.80 | [40] |
| Anilinepropylsilica xerogel | 22.62 | [41] |
| EG@CoFe$_2$O$_4$ composites | 101.20 | This study |
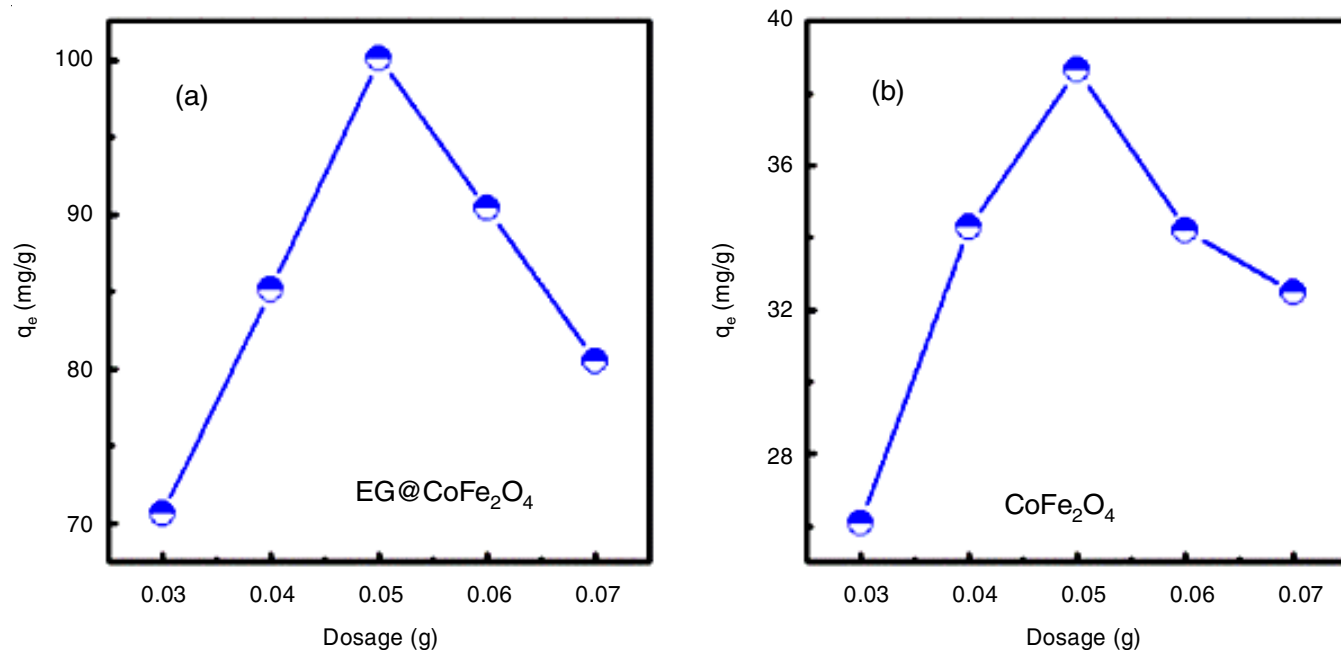


Fig. 4. Effect of dosage on the adsorption of Congo red onto EG@CoFe$_2$O$_4$ and CoFe$_2$O$_4$
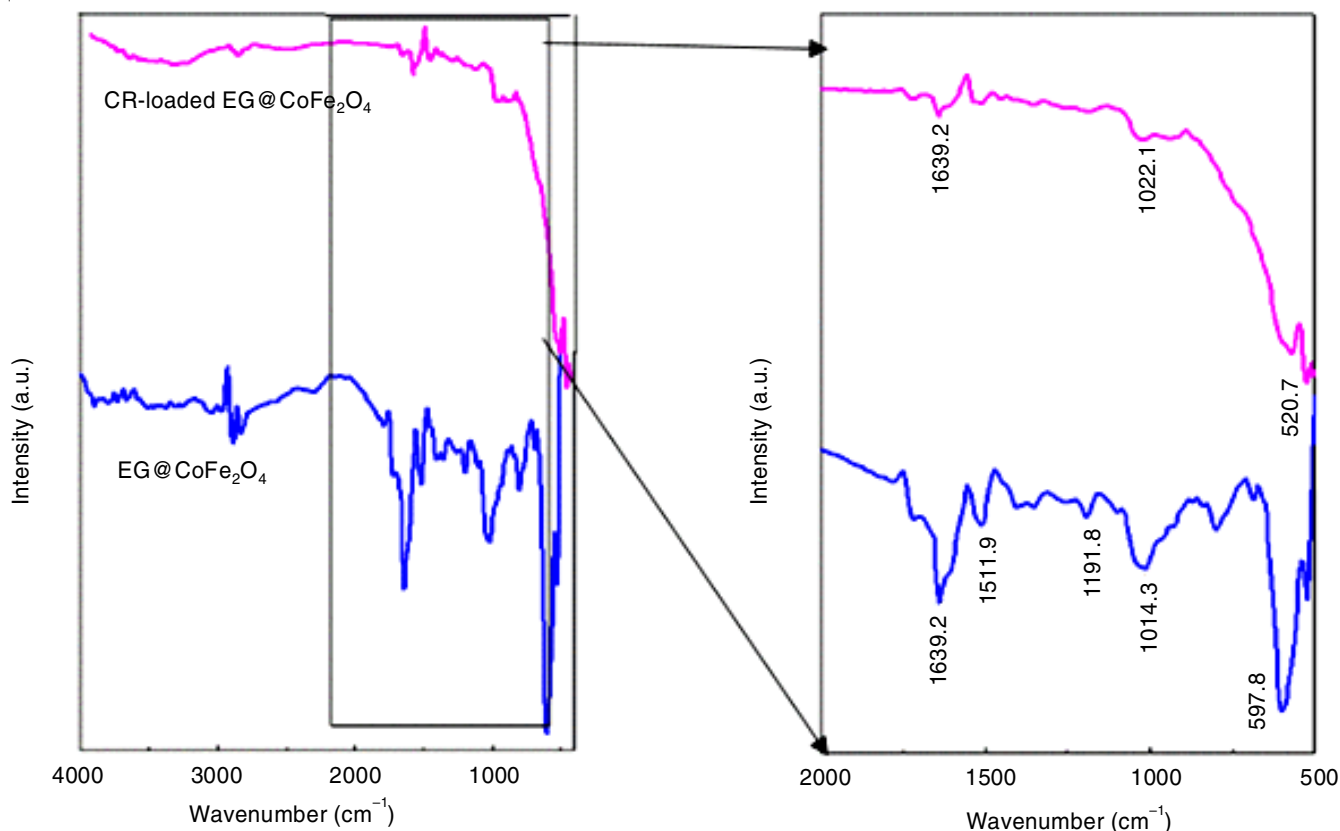
Fig. 5. FT-IR spectrum of EG@CoFe₂O₄ and Congo red loaded EG@CoFe₂O₄

initial solution pH, initial dye concentrations, contact time, and adsorbent dose all contribute to the variations in dye adsorption, where initial concentration and pH seemed to be important parameters. An optimum initial Congo red dye concentration was 60 mg/L and optimal pH was approximately 6 to achieve maximum adsorption. In comparison with reported adsorbents in terms of Congo red dye removal, EG@CoFe₂O₄ seems to be a an excellent candidate for removal efficiency of around 101.2 (mg/g) resulting in a nearly colourless solution when used.

## CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

## REFERENCES

1. Y. Dai, N. Zhang, C. Xing, Q. Cui and Q. Sun, *Chemosphere*, **223**, 12 (2019); https://doi.org/10.1016/j.chemosphere.2019.01.161
2. O.M.L. Alharbi, A.A. Basheer, R.A. Khattab and I. Ali, *J. Mol. Liq.*, **263**, 442 (2018); https://doi.org/10.1016/j.molliq.2018.05.029
3. M. Nagpal and R. Kakkar, *Sep. Purif. Technol.*, **211**, 522 (2019); https://doi.org/10.1016/j.seppur.2018.10.016
4. M. Bilal, T. Rasheed, H.M.N. Iqbal and Y. Yan, *Sci. Total Environ.*, **644**, 1 (2018); https://doi.org/10.1016/j.scitotenv.2018.06.274
5. A.H. Shalla, M.A. Bhat and Z. Yaseen, *J. Environ. Chem. Eng.*, **6**, 5938 (2018); https://doi.org/10.1016/j.jece.2018.08.063
6. R.M. El-Shishtawy, *Int. J. Photoener.*, **2009**, 434897 (2009); https://doi.org/10.1155/2009/434897
7. C. Fleischmann, M. Lievenbrück and H. Ritter, *Polymers*, **7**, 717 (2015); https://doi.org/10.3390/polym7040717
8. G.P. Kalaignan and Y.S. Kang, *J. Photochem. Photobiol. C*, **7**, 17 (2006); https://doi.org/10.1016/j.jphotochemrev.2006.03.003
9. B. Lellis, C-Z. Fávaro-Polonio, J.A. Pamphile and J.C. Polonio, *Biotechnol. Res. Innov*., **3**, 275 (2019); https://doi.org/10.1016/j.biori.2019.09.001
10. S. Sharma, V. Suryavathi, P.K. Singh and K.P. Sharma, *Australasian J. Ecotoxicol*., **13**, 35 (2007).
11. S. De Gisi, G. Lofrano, M. Grassi, M. Notarnicola, Sustain. Mater. Technol., 9, 10 (2016); https://doi.org/10.1016/j.susmat.2016.06.002
12. A. Ahmad, S.H. Mohd-Setapar, C.S. Chuong, A. Khatoon, W.A. Wani, R. Kumar and M. Rafatullah, *RSC Adv*., **5**, 30801 (2015); https://doi.org/10.1039/C4RA16959J
13. V.K.Gupta and Suhas, J. Environ. Manag., 90, 2313 (2009); https://doi.org/10.1016/j.jenvman.2008.11.017
14. M. Deaconu, R. Senin, R. Stoica, A. Athanasiu, M. Crudu, L. Oproiu, M. Ruse and C. Filipescu, *Int. J. Waste Resour*., **6**, 212 (2016); https://doi.org/10.4172/2252-5211.1000212
15. V.V. Ilyasov, L.G. Bach, A.V. Ilyasov, T.P. Zhdanova, G.A. Geguzina, H.V. Phuc, N.N. Hieu, C.V. Nguyen and K.D. Pham, *Superlattices Microstruct*., **123**, 414 (2018); https://doi.org/10.1016/j.spmi.2018.09.024
16. V.D. Thao, B.L. Giang and T.V. Thu, *RSC Adv*., **9**, 5445 (2019); https://doi.org/10.1039/C8RA10478F
17. T. Van Tran, D.T.C. Nguyen, H.T.N. Le, C.D. Duong, L.G. Bach, H.-T.T. Nguyen and T.D. Nguyen, *Chemosphere*, **227**, 455 (2019); https://doi.org/10.1016/j.chemosphere.2019.04.079
18. D.W. Kim, L.G. Bach, S.S. Hong, C. Park and K.T. Lim, *Mol. Cryst. Liq. Cryst.*, **599**, 43 (2014); https://doi.org/10.1080/15421406.2014.935919