

PREPARATION, CHARACTERIZATION AND TESTING OF GRAPHITE NANOCOMPOSITES IN WATER TREATMENT

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ABSTRACT

The application of nanomaterials and composites in the field of treating water pollution with dyes has begun to take an important place in scientific research with the great development of the industrial sector. Therefore, this study aimed to prepare two composites of graphite and nano titanium dioxide (G2T1, G2T2) using different chemical methods. The active groups, graphite oxidation, and the ratio of the elements composing the composites were diagnosed using several techniques (Fourier transform infrared, X-ray diffraction and Energy disperse X-ray spectroscopy). The composites (G2T1, G2T2) were applied in the field of adsorption of Congo red dye (CR) from aqueous solutions using a continuous method, where the amount of CR dye adsorbed by the composites (G2T1, G2T2) were (107, 68) mg/g respectively. The adsorption process data were subjected to kinetic models, and it was found that the adsorption process data for Congo red dye follow the kinetic model of the pseudo second order, which indicates that the type of adsorption for both composites is chemical. This demonstrates the success of the preparation process of the composites and their use in the process of treating water pollution from dyes represented by Congo red dye.

Keywords: graphite, nanocomposites, congo red dye, adsorption, water treatment.

تحضير وتشخيص واختبار متراكبات الكرافيت النانوية في معالجة المياه

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الخلاصة

بدأ تطبيق المواد النانوية والمركبات في مجال معالجة تلوث المياه بالصبغات يأخذ مكانة مهمة في البحث العلمي مع التطور الكبير في القطاع الصناعي، لذا هدفت هذه الدراسة إلى تحضير متراكبين من الكرافيت وثنائي أوكسيد التيتانيوم النانوي (G2T1, G2T2) باستخدام طرق كيميائية مختلفة، وتم تشخيص المجموعات الفعالة وأكسدة الكرافيت ونسبة العناصر المكونة للمترابكين باستخدام عدة تقنيات (تحويل فورييه بالأشعة تحت الحمراء، حيود الأشعة السينية، مطيافية الأشعة السينية ذات الطاقة المشتتة)، وتم تطبيق المترابكات (G2T1, G2T2) في مجال امتزاز صبغة الكونغو الحمراء (CR) من المحاليل المائية باستخدام الطريقة المستمرة، حيث بلغت كمية صبغة الكونغو الحمراء الممتزة بواسطة المترابكات (G2T1, G2T2) تساوي (68, 107) ملغم/غم على التوالي. تم إخضاع بيانات عملية الامتزاز للنماذج الحركية، وتبين أن بيانات عملية الامتزاز لصبغة الكونغو الحمراء تتبع النموذج الحركي للمرتبة الثانية الكاذبة، مما يدل على أن نوع الامتزاز لكلا المترابكين كيميائي، وهذا يدل على نجاح عملية تحضير المترابكات واستخدامها في عملية معالجة تلوث المياه من الصبغات المتمثلة بصبغة الكونغو الحمراء.

الكلمات المفتاحية: كرافيت، مترابكات نانوية، صبغة الكونغو الحمراء، امتزاز، معالجة المياه.



INTRODUCTION

Graphite and diamond are considered natural forms of carbon that differ in terms of the bonding and organization of the carbon atoms to form diversely organized structures. Graphite is an industrial mineral that possesses unique properties that qualify it for multiple applications that aid technological innovation. It was discovered at the beginning of the sixteenth century in the form of a piece of high-quality graphite in Borrowdale, England (**Ivancev et al., 2020**). With the development of industry, graphite was used in various fields such as military industries, steel, and smart materials (**An et al., 2016**). One of the uses of graphite is in the field of carbon steel and the manufacture of filters that are used in the fields of gas masks and water purification (**Pierce & Ewing, 1967**). Dyes play an important role in various industries such as textiles, printing, feathers, cosmetics, and plastics (**Wong et al., 2020**).

Nanomaterials are advanced materials at the nano level, as they represent the bridge between macro materials and molecular materials. These are materials that have at least all or one of their dimensions ranging from 1 to 100 nanometers and have different shapes. As a result of their shapes and sizes, they give a large surface area, causing high effectiveness. Nanoparticles are used in everyday life, and can be used in various healthcare, chemical applications (**Nabi et al., 2018**), Water treatment (**Abd & Abbas, 2019**), (**Mizhir et al., 2022**).

Titanium dioxide (TiO₂) exists in many forms, including rutile, which is uniformly crystalline and stable and is formed at a high temperature of up to 800 °C. While in the amorphous form, another form is called Anatase, which is a random irregular form that forms at an average temperature of 350 °C. TiO₂ NPs have distinctive properties in terms of stability and stability and are cheap and are considered strong oxidizing materials, which makes them applied in several fields. (**Nabi et al., 2020**), (**Al-Kazragi & Al-Heetimi, 2021**).

As a result of these industries, their waste is released, including used and untreated liquid dyes, and these dyes leave a negative impact on the aquatic environment and human life. Therefore, the process of removing them has become one of the major challenges facing researchers through the use of many techniques, the most important of which is adsorption for its high efficiency, ease of application, and low cost. Many carbon adsorbent surfaces were used, including activated graphite (**Bradder et al., 2011**), activated carbon (**Faraj & Abbas, 2021**), graphene oxide (**Jingjie et al., 2022**), carbon nanotubes (**Rajabi et al., 2017**), nano-titanium dioxide (**Hwang et al., 2016**), attapulgite-graphene oxide composite (**Abbas & Merza, 2020**), and CNT-TiO₂ composite (**Yu et al., 2005**), in order to remove dyes from their aqueous solutions under ideal experimental conditions (temperature, adsorbent surface weight, initial concentration, contact time). These surfaces have proven their efficiency in the removal process because they have a large surface area and many adsorption sites. This research aims to activate graphite, prepare a composite with titanium dioxide nanoparticles, and apply them in the field of dye adsorption.



MATERIALS AND METHODS

Chemicals

The chemicals required were graphite, hydrogen peroxide, ammonium hydroxide, sulfuric acid, Titanyl sulfate (Sigma-Aldrich), and congo red ($C_{32}H_{22}N_6Na_2O_6S_2$, Merck), and distilled water was used as a solvent.

Preparation of nano titanium dioxide -graphite-composite (G2T1)

The preparation process is done by dispersing (2g) of titanyl sulfate in a 400 ml beaker containing 50 ml of hydrogen peroxide (50%) at 10 °C for 30 min, then gradually adding (2g) of graphite with continuous stirring for 1h at laboratory temperature, then gradually adding 10 ml of ammonium hydroxide with continuous stirring for 1h, then gradually adding 60 ml of sulfuric acid for 5h. where it was observed that it was an exothermic reaction, and then the composite was washed with distilled water several ones , filtered, and dried at a temperature of 80 °C for a period of 1 h , then burned. The precipitate is kept at a temperature of 400 ° C (Furnaces oven Vindon LTD, Oldham, England) for 1h and kept in a tightly closed container away from moisture. It is diagnosed using several techniques (FT-IR , XRD ,EDX).

Preparation of nano titanium dioxide -graphite-composite (G2T2)

The preparation process is done by dispersing (2g) of titanyl sulfate in a 400 ml beaker containing 50 ml of ammonium hydroxide for 30 min, then gradually adding (2g) of graphite with continuous stirring for 1h at laboratory temperature, then gradually adding 10 ml of hydrogen peroxide (50%) with continuous stirring for 1h, then gradually adding 60 ml of sulfuric acid for 5h. where it was observed that it was an exothermic reaction, and then the composite was washed with distilled water several ones , filtered, and dried at a temperature of 80 °C for a period of 1 h . then burned. The precipitate is kept at a temperature of 400 ° C (Furnaces oven Vindon LTD, Oldham, England) for 1h and kept in a tightly closed container away from moisture. It is diagnosed using several techniques (FT-IR , XRD ,EDX).

Adsorption experiments

Adsorption of congo red dye by graphite nanocomposites (G2T1, G2T2).

The adsorption experiment was conducted by applying a continuous system by taking a range of weight (0.01-0.07) g of graphite nanocomposites (G2T1, G2T2) , bringing it into contact with the volume (100ml) of (CR) dye solution (50) mg/L by using a water bath shaker (Labtech, South Korea) at 298 K, 150 rpm agitation speed, and over time periods (5–120) min, and each sample is separated by a centrifuge in order to be measured. Each solution is used by the spectrometer (Shimadzu 1800, Japan), and the amount of adsorbed dye and the percentage of adsorption (A%) are calculated through the following equations (1, 2), respectively (Jasim *et al.*, 2021) :

$$q_e = \frac{(C_o - C_t)V}{m} \text{----- (1)}$$

$$\%A = \left(\frac{C_o - C_t}{C_o} \right) \times 100 \text{----- (2)}$$



Where C_o and C_e are the (CR) dye concentrations at time ($t = \text{zero}, t$) respectively. The V (L) represents the volume of (CR) aqueous solution, q_e the amount of adsorbent at equilibrium, whereas m (g) symbolizes the graphite activated adsorbent dose.

RESULTS AND DISCUSSION

Characterization of graphite nanocomposites.

Fourier Transform Infrared Analysis (FT-IR)

Infrared technology is used to determine the active groups of chemicals. (Figure 1, 2) show the FT-IR spectra of G2T1 and G2T2 composites. There are clearly many bands within the range between 400 and 4000 cm^{-1} of G2T1 and G2T2 composites respectively, (Figure 1,2) show that the weak broad peak at (3122) and (3231) cm^{-1} that belong to the stretch group (OH) which refer to graphite after oxidation process and refer to Ti-OH group of TiO_2 NPs, at (1716) cm^{-1} that belongs to the (C=O) group of oxidant graphite, at (1562, 1581) cm^{-1} that belongs to the (C=C) group of oxidant graphite, at (1133, 1199) cm^{-1} that belongs to the (Ti-O-Ti) group of TiO_2 NPs, at (450, 601) cm^{-1} that belongs to the (Ti-O) group of TiO_2 NPs which indicates the formation of all the composites under study (Visca *et al.*, 2022), (Mugundan *et al.*, 2015).

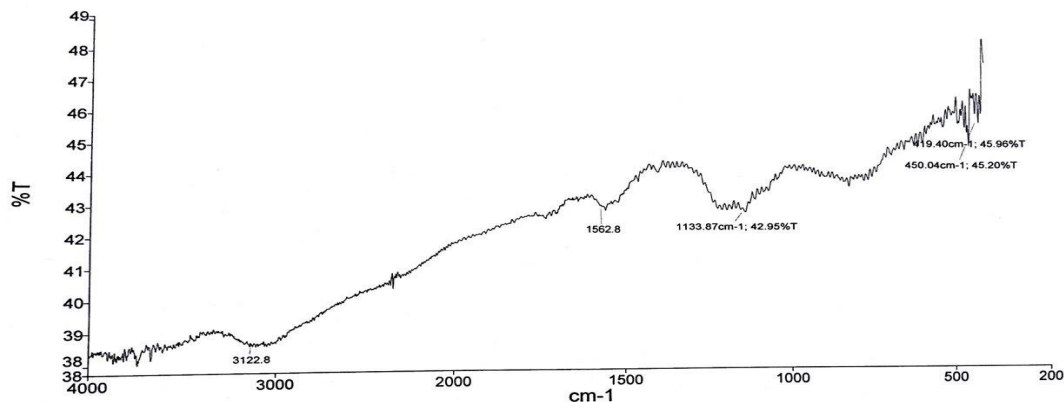


Figure (1): FT-IR of G2T1 surface.

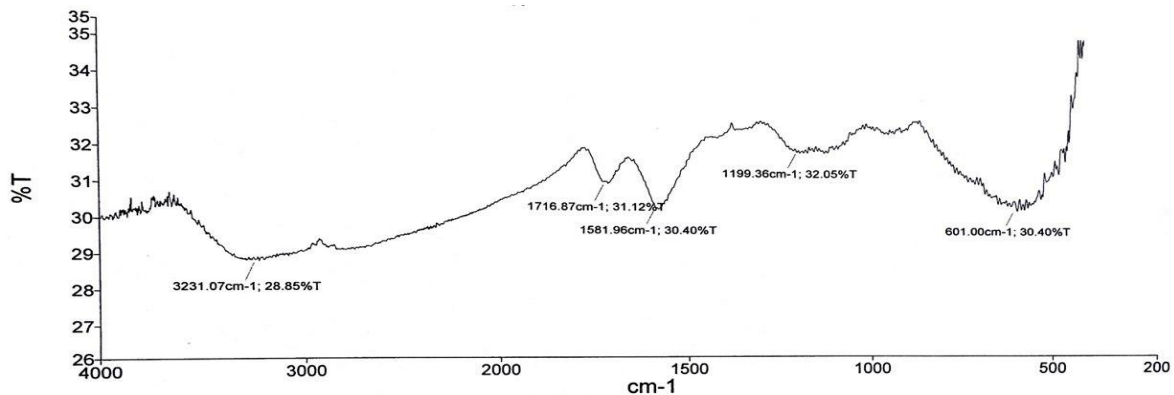




Figure (2): FT-IR of G2T2 surface.

X-ray diffraction Analysis (XRD)

X-ray diffraction technology is used to determine the crystallinity and purity of graphite nanocomposite (G2T1, G2T2) through the (Figure 3,4) respectively within the range (2θ :10–80). (Figures 3,4) show broad peaks at (24, 48°) overlapping due to oxidized graphite and TiO₂ NPs, and Figure 4 includes sharp peaks at (26 ,38°) due to TiO₂ NPs and in agreement with the JCPDS (Joint Committee on Powder Diffraction Standards) card No. 78-2486. This indicates the formation of anatase nano-titanium dioxide particles in both composites with oxidant graphite. On the other hand, the shape and size of the peaks of the G2T1 composite are broader and overlapping than those of the G2T2 composite, indicating that G2T1 is less crystalline and pure than the G2T2 composite (**Ratih & Siburian , 2018**) ,(**Chen & Zhang , 2009**). We used the Debye-Scherrer equation to obtain the crystallite size (**Zhang et al., 2014**):

$$S_{hkl} = \frac{k \lambda}{b \cos \theta} \text{----- (3)}$$

S_{hkl} is the average crystallite size (nm), K is the Scherrer constant (0.89), λ the incident X-ray wavelength, θ the Bragg diffraction angle, and b the FWHM (full width high maximum). The average crystallite size of G2T1, G2T2 are 5.7, 7.9 nm respectively.

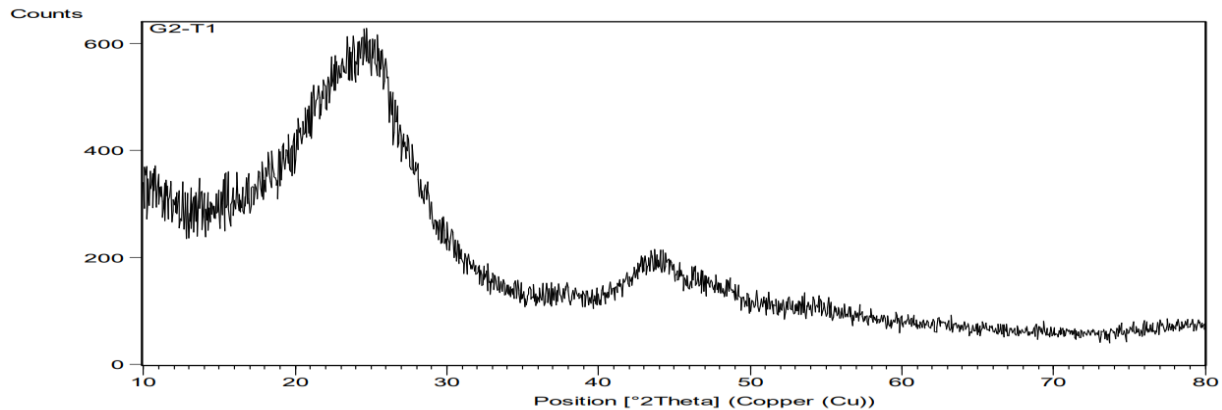


Figure (3): XRD of G2T1 surface.

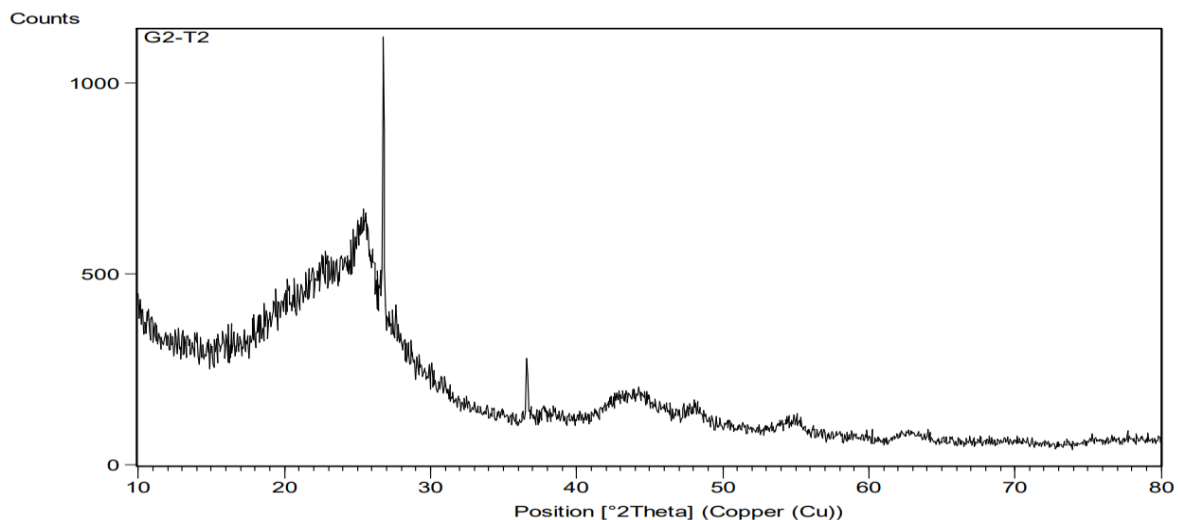


Figure (4): XRD of G2T2 surface.

Energy disperse X-Ray Analysis (EDX).

EDX analysis of graphite nanocomposites (G2T1, G2T2) were performed to determine the composition as shown in (Figure 5,6) respectively. The (Figure 5,6) show the presence of certain proportions of carbon, oxygen and titanium indicates the successful formation of the two composites (G2T1, G2T2). On the other hand, the decrease in the percentage of carbon and the increase in the percentage of oxygen and titanium of G2T1 composite compared to other composite indicates the presence of oxidized graphite and TiO_2NPs in a greater proportion in the G2T1 composite compared to G2T2 composite.

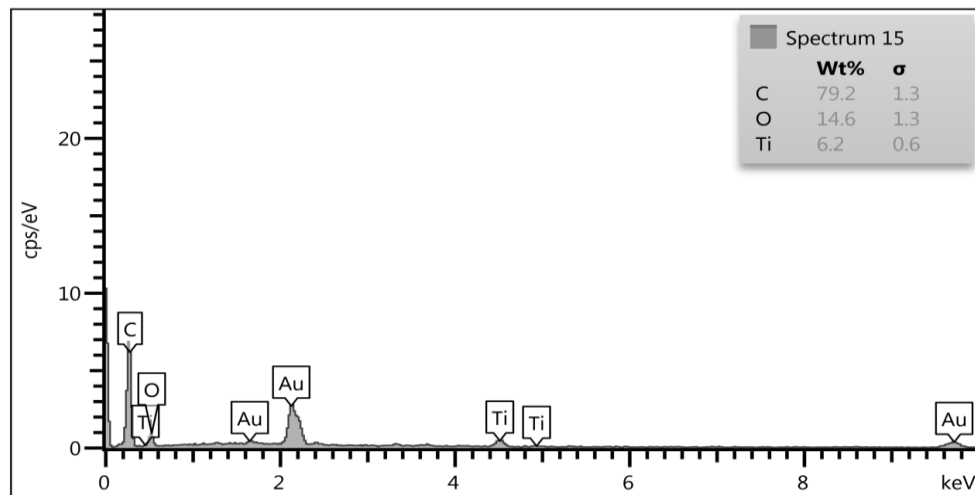


Figure (5): EDX of G2T1 surface.

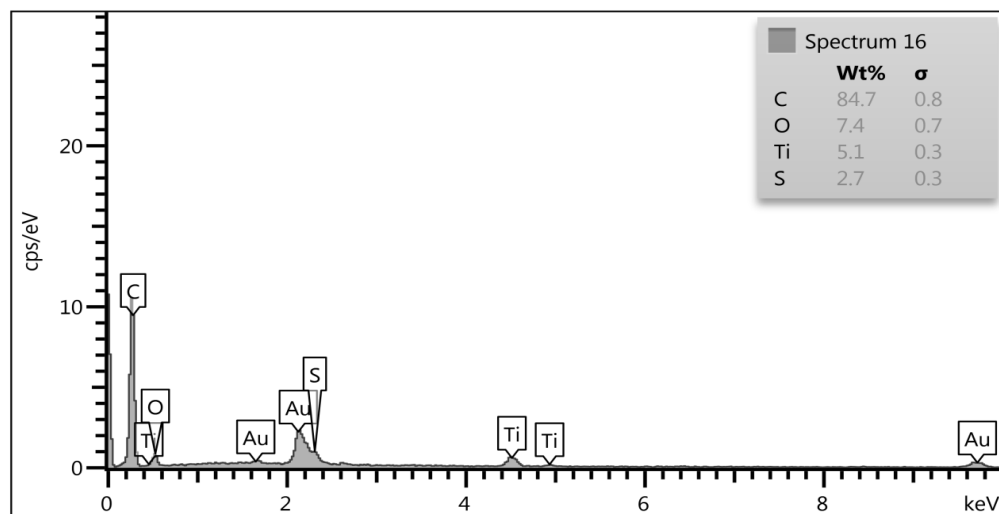


Figure (6): EDX of G2T2 surface.

Effect of weight

Different weights of graphite nanocomposites (G2T1, G2T2) were taken to study the effect of weight (0.01-0.07) g on congo red adsorption at 298 K and a fixed concentration of the dye (50 mg/L) at equilibrium time. (Figure 7) shows that the best weight of graphite nanocomposites (G2T1, G2T2) for congo red removal were (0.04, 0.06) g respectively (Abbas *et al.*, 2017).

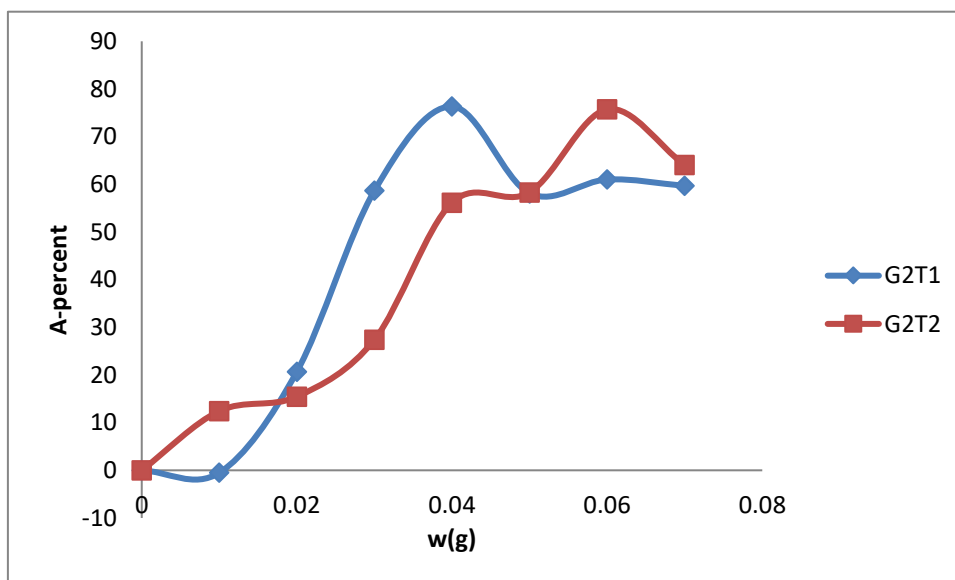


Figure (7): Effect of graphite nanocomposites on CR dye adsorption.

Effect of Time

The equilibrium time for CR dye adsorption was determined by studying the adsorption process at 298 K and a fixed concentration of the dye (50 mg/L) with different periods (5-180) min. (Figure 8) suggests that the quantity of CR adsorption on both adsorbents (G2T1 and G2T2) increased with increasing contact time, up to the time (90) min and beyond, at which the amount of adsorption stabilizes, which indicates the occurrence of equilibrium. (Naief *et al.*, 2017)

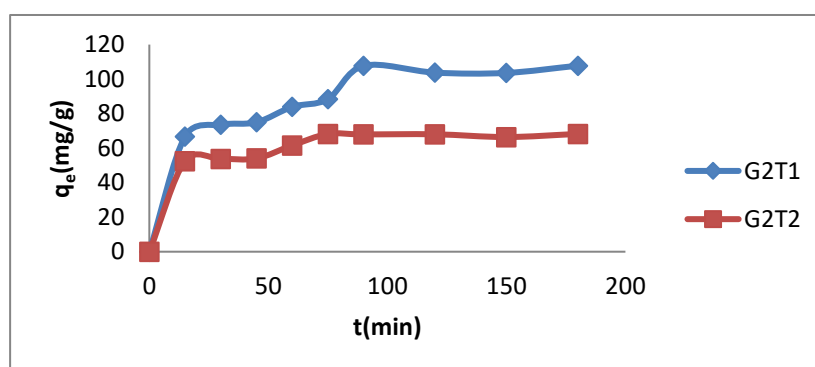


Figure (8): effect of contact time on CR dye adsorption by G2T1, G2T2 composites at 298 K.



Kinetics of Adsorption.

The experimental data were analyzed by kinetic models. The linearized pseudo-first-order (PFO) and pseudo-second-order (PSO) models have been applied. (Benjelloun *et al.*, 2021)

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad \text{-----(4)}$$

$$\frac{1}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad \text{-----(5)}$$

Where q_t and q_e are the amounts of (CR) dye molecules adsorbed on the TiO_2 NPs at time t and at equilibrium (mg/g). k_1 (min^{-1}), k_2 ($\text{g} \cdot \text{mg}^{-1} \cdot \text{min}^{-1}$) are the rate constants of PFO and PSO, respectively. The linear plots of $\ln(q_e - q_t)$ versus t and t/q_t versus t are employed to calculate k_1 , q_e values for PFO, and k_2 , q_e values for PSO, as shown in (Figure 9,10). Table 1,2 lists the PFO and PSO constants for the adsorption process. As shown in Table 1, the values of correlation coefficient R^2 for PSO were higher than those for PFO. Also, the values of q_e experimental ($q_{e \text{ exp}}$) and q_e calculated ($q_{e \text{ cal}}$) were matched well using PSO kinetic models, suggesting that the mechanisms of adsorption are related to both adsorbent and adsorbate (Bentahar *et al.*, 2016), (Saeed & AL-Mammar, 2021), (Jawad & Abbas, 2021).

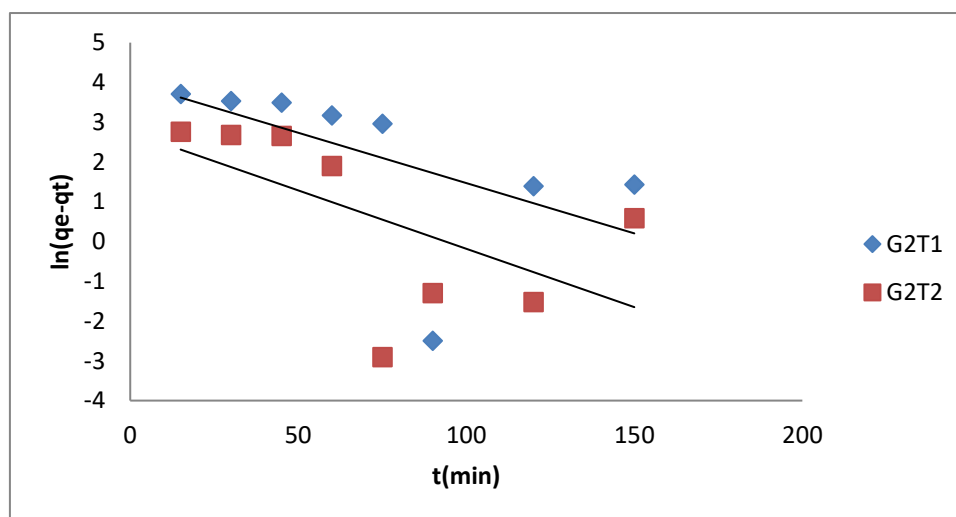


Figure (9): Graphical representation of the first-order equation model for dye Congo red adsorption on surfaces (G2T1, G2T2) at 298 K.



Table (1): displays the pseudo-first-order equation for the adsorption of a dye Congo red on surfaces(G2T1,G2T2) along with the amount of adsorbed dye (q_e), the adsorption rate constant (k_2), and the correlation coefficient (R) at a temperature of 298 K .

System	k_1 (min^{-1})	R^2	$q_{e, \text{cal}}$ (mg/g)	$q_{e, \text{exp}}$ (mg/g)
G2T1	0.0234	0.4032	56.940	107.778
G2T2	0.0294	0.3567	15.680	68.245

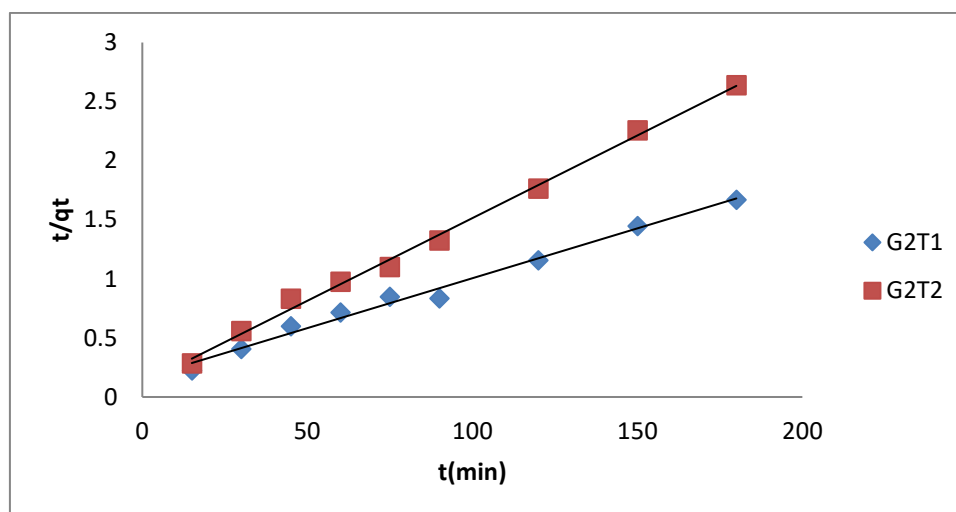


Figure (10): Graphical representation of the Second -order equation model for dye Congo red adsorption by surfaces of G2T1, G2T2 at 298 K.

Table (2): displays the Second -order equation for the adsorption of a dye Congo red on surfaces G2T1, G2T2 along with the amount of adsorbed material (q_e), the adsorption rate constant (k_2), and the correlation coefficient (R) at 298 K .

System	k_2 ($\text{g.mg}^{-1}.\text{min}^{-1}$)	R^2	q_e (mg/g)
G2T1	0.0004	0.9884	11.9047
G2T2	0.0017	0.9955	7.1428

CONCLUSIONS

We conclude according to the techniques (FT-IR, XRD, EDX) the success of the preparation process of the two composites (G2T1, G2T2), which included the graphite oxidation process and the implicit preparation of anatase-type nano-titanium dioxide particles in different proportions according to the chemical methods used to prepare each composite. As



a result of these differences between the two composites, this was reflected in their performance in the adsorption of Congo red dye, which gave an advantage to composite (G2T1) compared to composite (G2T2). The type of chemical adsorption was also renewed in order to follow the results of the Congo red dye adsorption process on both composites for the pseudo-second-order kinetic model.

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REFERENCES

1. Abbas, A. M., Mohammed, Y. I., & Himdan, T. A. (2017). Adsorption kinetic and thermodynamic study of congo red dye on synthetic zeolite and modified synthetic zeolite. *Ibn Al-Haitham Journal For Pure and Applied Science*, 28(1), 54-72.
2. Abbas, A., & Merza, S. (2020). Preparation and Characterization of Graphene Oxide–Attapulgite composite and its use in kinetic study of Alizarin Dye Adsorption from Aqueous Media. *Egyptian Journal of Chemistry*, 63(2), 561-572.
3. Abd, S. S., & Abbas, A. M. (2019). Preparation, characterization and adsorption capacity of bauxite-carbon nanotube composite. *Nature Environment and Pollution Technology*, 18(3), 863-869.
4. Al-Kazragi, M. A. U. R., & Al-Heetimi, D. T. (2021). Removal of toxic dye (Rhodamine B) from aqueous solutions by natural smectite (SMC) and SMC-nanoTiO₂. *Desalination and Water Treatment*, 230, 276-287.
5. An, S. J., Li, J., Daniel, C., Mohanty, D., Nagpure, S., & Wood III, D. L. (2016). The state of understanding of the lithium-ion-battery graphite solid electrolyte interphase (SEI) and its relationship to formation cycling. *Carbon*, 105, 52-76.
6. Benjelloun, M., Miyah, Y., Evrendilek, G. A., Zerrouq, F., & Lairini, S. (2021). Recent advances in adsorption kinetic models: their application to dye types. *Arabian Journal of Chemistry*, 14(4), 103031.
7. Bentahar, S., Dbik, A., El Khomri, M., El Messaoudi, N., Bakiz, B., & Lacherai, A. (2016). Study of removal of Congo red by local natural clay. *Scientific Study & Research. Chemistry & Chemical Engineering, Biotechnology, Food Industry*, 17(3), 295.
8. Bradder, P., Ling, S. K., Wang, S., & Liu, S. (2011). Dye adsorption on layered graphite oxide. *Journal of Chemical & Engineering Data*, 56(1), 138-141.
9. Chen, J., & Zhang, L. (2009). NH₄Cl-assisted low temperature synthesis of anatase TiO₂ nanostructures from Ti powder. *Materials Letters*, 63(21), 1797-1799.
10. Faraj, R. A. S., & Abbas, A. M. (2021, May). Loading and Activating a Carbon Surface and Applied for Congo Red Adsorption, Kinetic Study. In *Journal of Physics: Conference Series* (Vol. 1879, No. 2, p. 022076). IOP Publishing.



11. Hwang, K. J., Shim, W. G., Kim, D., An, J., Im, C., Kim, Y., ... & Cho, D. W. (2016). Dye adsorption mechanisms in TiO₂ films, and its effects on photodynamic and photovoltaic properties in dye-sensitized solar cell. *Phys Chem Chem Phys*, 18(7), 5659-5667.
12. Ivancev-Tumbas, I., Landwehrkamp, L., Hobby, R., Vernillo, M., & Panglisch, S. (2020). Adsorption of organic pollutants from the aqueous phase using graphite as a model adsorbent. *Adsorption Science & Technology*, 38(7-8), 286-303.
13. Jasim, M. A., Abbas, A. M., & Radhi, I. M. (2021, November). Preparation and characterization of biomass-alumina composite as adsorbent for safranin-o dye from aqueous solution at different temperatures. In *AIP Conference Proceedings* (Vol. 2372, No. 1). AIP Publishing.
14. Jawad, H., & Abbas, A. M. (2021). Study of Efficacy Adsorption of Methyl Green by Attapulgit and Modified Attapulgit Clay from Aqueous Solution. *Ibn AL-Haitham Journal For Pure and Applied Sciences*, 34(1).
15. Jingjie, Y., Siroos, S., & Saeed, S. (2022). Removal of drug and dye from aqueous solutions by graphene oxide: Adsorption studies and chemometrics methods. *NPJ Clean Water*, 5(1).
16. Mizhir, A. A., Al-Lami, H. S., & Abdulwahid, A. A. (2022). Kinetic, isotherm, and thermodynamic study of bismarck brown dye adsorption onto graphene oxide and graphene oxide-grafted-poly (n-butyl methacrylate-co-methacrylic acid). *Baghdad Science Journal*, 19(1), 0132-0132.
17. Mugundan, S., Rajamannan, B., Viruthagiri, G., Shanmugam, N., Gobi, R., & Praveen, P. (2015). Synthesis and characterization of undoped and cobalt-doped TiO₂ nanoparticles via sol-gel technique. *Applied Nanoscience*, 5, 449-456.
18. Nabi, G., Khalid, N. R., Tahir, M. B., Rafique, M., Rizwan, M., Hussain, S., ... & Majid, A. (2018). A review on novel eco-friendly green approach to synthesis TiO₂ nanoparticles using different extracts. *Journal of Inorganic and Organometallic Polymers and Materials*, 28, 1552-1564.
19. Nabi, G., Raza, W., & Tahir, M. B. (2020). Green synthesis of TiO₂ nanoparticle using cinnamon powder extract and the study of optical properties. *Journal of Inorganic and Organometallic Polymers and Materials*, 30(4), 1425-1429.
20. Naief, M. F., Hamoshi, E. A., Sadiq, A. J., & Ahmed, Y. N. (2017). Study of the kinetic and adsorption isotherm parameters for removing copper and iron ions from aqueous solutions by using agricultural by-products. *Iraq Journal of Market Research & Consumer Protection/Al-Mağalla al- 'Irāqiyya li-Buḥūṭ al-Sūq wa-Ḥimāya al-Mustahlik*, 9(2).
21. Pierce, C., & Ewing, B. (1967). Localized adsorption on graphite surfaces. *The Journal of Physical Chemistry*, 71(11), 3408-3413.
22. Rajabi, M., Mahanpoor, K., & Moradi, O. (2017). Removal of dye molecules from aqueous solution by carbon nanotubes and carbon nanotube functional groups: critical review. *Rsc Advances*, 7(74), 47083-47090.
23. Ratih, D., & Siburian, R. (2018). The performance of graphite/N-graphene and graphene/N-graphene as electrode in primary cell batteries.



24. Saeed, S. A., & AL-Mammar, D. E. (2021). Adsorption potential for a mixture of chemically and thermally treated clays to remove orange G dye from waste-water : *Iraqi Journal of Market Research and Consumer Protection*, 13(2), 10-31.
25. Visca, R., Dewi, M. N., Liviani, A., & Satriawan, B. D. (2022). Characterization of FTIR in Graphite from Palm Oil Waste with Ferric Chloride Catalyst. *Interdisciplinary Social Studies*, 1(11).
26. Wong, S., Ghafar, N. A., Ngadi, N., Razmi, F. A., Inuwa, I. M., Mat, R., & Amin, N. A. S. (2020). Effective removal of anionic textile dyes using adsorbent synthesized from coffee waste. *Scientific reports*, 10(1), 2928.
27. Yu, Y., Jimmy, C. Y., Chan, C. Y., Che, Y. K., Zhao, J. C., Ding, L., ... & Wong, P. K. (2005). Enhancement of adsorption and photocatalytic activity of TiO₂ by using carbon nanotubes for the treatment of azo dye. *Applied Catalysis B: Environmental*, 61(1-2), 1-11.
28. Zhang, J., Zhou, P., Liu, J., & Yu, J. (2014). New understanding of the difference of photocatalytic activity among anatase, rutile and brookite TiO₂. *Physical Chemistry Chemical Physics*, 16(38), 20382-20386.