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Graphite Oxide and Graphite Nanotubes with Rutile –TiO_2 for Combative Studies in Mineralization Process of Methyl Orange Dyes

Farqad Talib Ahmed[a], Ahmed Abdul Ismail[a]*, Hanaa H. Hussein[b], Zena M. Jassem[c] and Sajid M. Lateef[d,e]

[a]Chemistry Department, College of Education for Pure Science, Diyala University, Iraq
[b]Department of Chemistry, College of Science, Mustansiriyah University, Baghdad, Iraq
[c]Grain Board - Quality Control Department, Ministry of Trade, Iraq
[d]College of Science, Al-Ameen University, Iraq
[e]College of Education for Pure Science (Ibn Al-Haitham), Baghdad University, Iraq

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Abstract. Titanium dioxide TiO_2 (rutile) was impregnated with graphite and multiwall carbon nanotubes after being functionalized with H_2O_2/H_2SO_4. The binary composites were TiO_2/10% GO and TiO_2/10% MWCNT, which were characterized using X-ray diffraction, Raman spectroscopy and surface area BET. The pristine and modified rutile TiO_2 activates were tested with methyl orange dye removal, which accrued by two steps of adsorption and then photo (UV-A light) di-colourization. The kinetic studies showed that the first process follows the second-order reaction while the second process is behaving as a first-order reaction. The mechanism of reaction shows that carbon materials succeeded in enhancing the activities of the useful surface when creating more active sites to adsorb the MO molecules and then enhanced the process of transferring the electrons in photodecolourization.

Keywords: rutile, adsorption, di-colourization, photo reaction, MWCNT, GO

Introduction

The developments in all fields of life required synthesizing huge amounts of chemical compounds to ensure reaching the best benefits from these materials. The bad news was that many of these synthesized materials caused serious problems for the environments and that was represented by huge amounts of textile materials, such as dyes. It is reported that more than 10,000 dyes and pigments are used in many industrial processes, which required synthesizing more than 7 x 105 Tons of dyes (Jasim *et al*., 2024; Farah *et al.*, 2013). Many materials were tested for dye treatment of wastewater, which included materials reagents and biological reagents, such as carbon materials and microbes, respectively. The techniques required photocatalysis, chemical oxidation, adsorption and microbial degradation, which were used as mono-processes or poly-processes (Hussein *et al*., 2023). (Jiang *et al*., 2014) The common binary process that was used for purpose, aims to adsorb with photocatalysis as a heterogeneous reaction to remove the pollutants by withdrawing them on the active surface or discolouration, which could lead to mineralization (Rashed *et al*., 2017). Methyl orange (MO) is an example of a dye pollutant commonly used in the textile industry (Rabanimehr *et al*., 2022) and as a pH indicator for volumetric analysis (Guo *et al*., 2013). The last methods that were listed previously have specific requirements for application and that limits the abilities to use it, such as time-consuming operational costs and unit operations, as stated above (Abdul *et al*., 2020; Al Khazraji *et al*., 2019). Adsorption represents the simplest and cheapest design and operation choice for removing MO. Titanium dioxide is a nontoxic, stable structure material that is cheap in cost and friendly for the environment and three different structures Anatase, rutile and brookite were encouraged to use it in many applications (Bdewi *et al*., 2024; Abdul *et al*., 2020), Rutile behaviour shows less activity for photocatalytic reaction while having more adsorption abilities as compared with the other two types (Firas, 2016). Many materials were used to enhance the adsorption and photocatalytic abilities for removing the pollutant, such as carbon nanotubes (CNTs) with different types (multi-walled MWCNTs and single-

*Author for correspondence;
E-mail:ahmedabdullateefismail@gmail.com

walled SWCNTs), graphite (G), graphene (Gr) and fullerene (FL) (Rajni *et al*., 2017; Firas, 2016). In this work, TiO_2-rutile was modified with two types of carbon nanomaterials, which are multi-walled carbon nanotubes (MWCNTs) and graphite G. After activation, they were tested to remove MOs dye with two processes: adsorption and photo-reaction.

Materials and Methods

H_2SO_4 (70%) and H_2O_2 (50%) and graphite powder were purchased from Sigma-Aldrich and used without further purification. Carbon nanotubes, multi-walled, were provided from cheap tub com. USA with purifies 80% and titanium dioxide-Rutile phase (100%) were purchased from Ishihara Sangyo Kaisha-Japan.

Synthesis of binary composites. The MWCNT and G were activated by addition 50 mL of H_2SO_4/H_2O_2 (3:1) and stirring for 1 h before heating in a round flask with condensation at 100 °C for 3 h. Filtering and washing the product many times until reaching a pH about 7. The equivalent weight of MWCNTs or GO was dispersed with 0.025 mole of TiO_2-Rutile in 250 mL of distilled water with stirring for 1 h before separating by centrifuge and washing the product, then dried at 100 °C for 3 h.

Photocatalytic experiment. Removal of MOs dye was carried out in two steps. The first was adsorption, while the second was photoreaction. Removal experiments were done by adding 180 mg of pristine rutile TiO_2 or modified with 10% GO and MWCNTs into 100 mL of 20 ppm aqueous MOs solution. At first the mixture was stirred in the dark in order to reach adsorption/desorption equilibrium and calculate the ratios of MO dyes that were removed under the influence of adsorption. The second process was accrued after impregnating O_2 gas in the solution and then irradiating with UVA. The stirred suspensions were withdrawn 2 mL out in each 30 min and the catalyst was separated from the suspension by centrifuge before and after irradiation and the absorbance of the solution was measured at 5467 nm.

Characterization. The pristine TiO_2-rutile before and after doping with 10% GO and MWCNTs was identified by Raman spectroscopy and X-ray diffraction. The function groups and nature of bonding were done by Horiba Jobin Yvon LabRAM HR Raman spectroscopy with 514 nm by Arclaser from 100/cm to 2000/cm. The change in morphology and distributions of active groups on the TiO_2-rutile was made by PA Nalytical x'pertPRO -x- with 1.5406 A by Cu Ka radiation.

Raman spectra were carried out to investigate the crystalline phase of TiO_2 and the carbon type in the nanotubes (Fig. 1). Three peaks with strong intensities at 219, 425 and 605 can be observed in the Raman spectra for TiO_2 in the rutile phase, which witnesses an increase in width and intensity after adding MWCNTs and GO (Firas *et al*., 2020) and that was more intense with MWCNTs (Hind *et al*., 2021).

Figure. 1a and 1b, two weak peaks, the D and G band at about 1325/cm and 1615/cm correspond to disorder carbon and graphite carbon in the MWCNT/TiO_2, respectively. The binary composites GO/TiO_2 did not show the first peak at 1325/cm (D), while the second peak at 1620/cm was very weak as compared with MWCNT/TiO_2 (Firs *et al*., 2021).

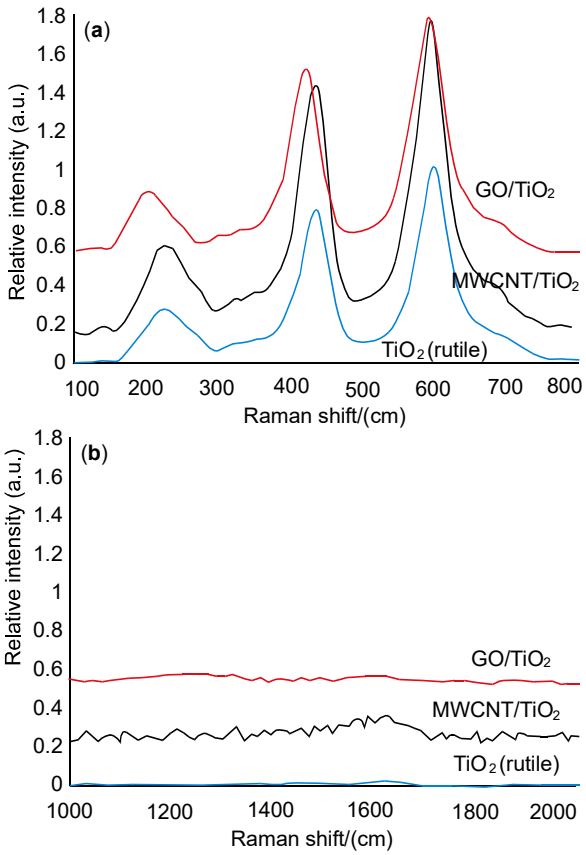

Fig. 1. Raman spectroscopy for pristine TiO_2-rutile and modifying with 10% GO and MWCNTs, (**a**) from 100-800/cm and (**b**) from 1000-2000/cm.

Comparing the XRD patterns of pristine TiO_2-rutile with those of samples modified with GO and MWCNTs in new binary composites, as reported in Fig. 2. the following points are to be noted: The crystallized patterns in pristine TiO_2-rutile were significantly higher than those in binary composites after being impregnated with GO or MWCNTs. All major peaks of the rutile phase (2θ at 27.4°, 36.6°, 41.8°, 54.8° and 69.2°) appeared in the diffractogram of the rutile form (Jingang *et al*., 2012), which excited in binary composites. The primary peaks of utile-TiO_2 in binary composites were shown to be wider and less intense, especially the peak at 27.4° due to overlap with primary peaks for GO and MWCNTs, as shown in figure 2b. The size of the crystals was 83 nm based on estimation using the Scherrer equation (Al Khazraji *et al*., 2024; Hind *et al*., 2021) which witnesses reduced to 75 nm and 68 nm for GO/TiO_2 and $MWCNT/TiO_2$, respectively.

Photocatalytic activity. The adsorption and photocatalytic activities for pristine and modified rutile TiO_2 with GO and MWCNTs were evaluated in the removal of MO solution in the dark and under UV-A irradiation. The absorbance of dye solutions before and after irradiation for different durations was measured. Fig. 3a and 3b illustrate the removal of dye by absorption and removal by photocatalytic reaction of MO at different time intervals using pristine TiO_2-rutile catalyst, GO/TiO_2 and $MWCNT/TiO_2$, respectively.

The percentage of adsorption and photoreaction was estimated by deriving the value of change in concentration C_t/C_o with time, where C_o is the initial concentration and C_t is the absorbance of the dye after time t. In the case of pristine TiO_2-rutile, the adsorption activities are slow as compared with cases after modifying with carbon materials; however, note that MWCNTs were better in stimulating TiO_2-rutile than GO after reaching the equilibrium adsorption in 75 min. After irradiation, the activities of TiO_2-rutile for removing MOs but the two binary composites with irradiation were witnessed to have high activities as compared with TiO_2-rutile without modifying. At the same time, after 3 h, still the activities of $MWCT/TiO_2$ are the best when compared with GO for all times of irradiation.

According to Fig. 3a, for removal by adsorption, the results show that 31% was removed by pristine TiO_2-rutie, which increased to 34% and 40% after modifying with GO and MWCNTs, respectively, which can be

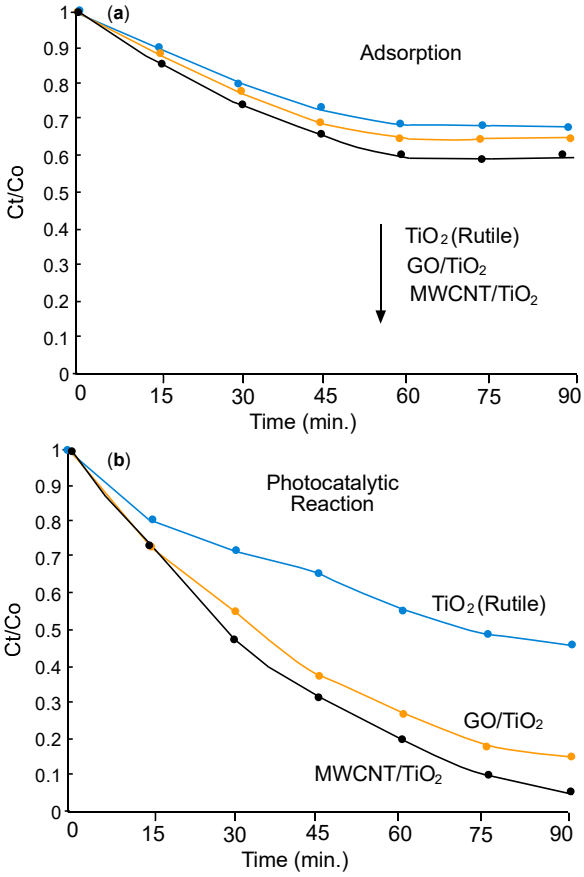

Fig. 3. The skim between Ct/Co with time for decolourization of MOs by pristine TiO_2-rutile and modifying with 10% GO and MWCNTs with, (**a**) adsorption and (**b**) photocatalytic reaction.

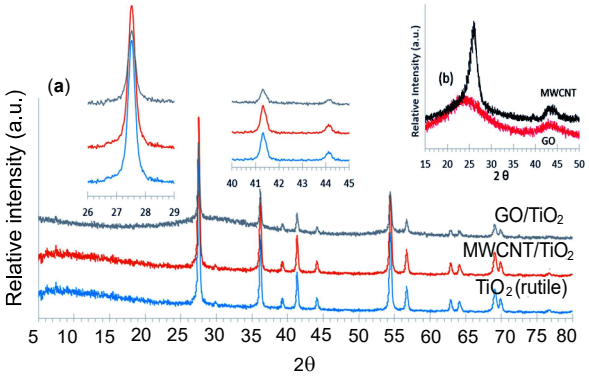

Fig. 2. The XRD patterns for (**a**), pristine TiO_2-rutile and modifying with 10% GO and MWCNTs from 5°- 80° and (**b**), for GO and MWCNTs from 15°-50°.

related to creating many active sites from carbon materials to TiO_2 (Gang *et al.,* 2016). The removal of MOs by photoreaction, as shown in Fig. 3b, witnessed more change when increased to 54% for the remaining MOs after adsorption by rutile TiO_2 and that refers to about 50% of the total concentration of 20 ppm MOs.

The binary composites GO/TiO_2 were the di-colourization of the remaining MOs after adsorption to 85%, which thus made the total activity was 85%, while the best di-colourization was related to $MWCNT/TiO_2$ when removal reached 95% (Zamani *et al*., 2020). The kinetic studies for the two processes, which are adsorption firstly and then photodecolourization, were reported in Fig. 4 and 5 which show mostly more acquisition for the second order, which may be related to the nature of the interaction between the catalyst and the day MOs. The rate of adoration was witness to the arrangement: $k\,(TiO_2) < k\,(GO/TiO_2) < k\,(MWCNT/TiO_2)$.

The kinetic studies for the photocatalytic reaction showed a preference for the second order due to applying the model of reaction kinetics with it according to the value of R^2. The estimation for the rate constant was shown in the same arrangement:

$$k\,(TiO_2) < k\,(GO/TiO_2) < k\,(MWCNT/TiO_2),$$

with an increase in the rate from 0.0003 for TiO_2-rutile to 0.0017 and 0.0026 M/s after modifying with GO and MWCNTs, respectively.

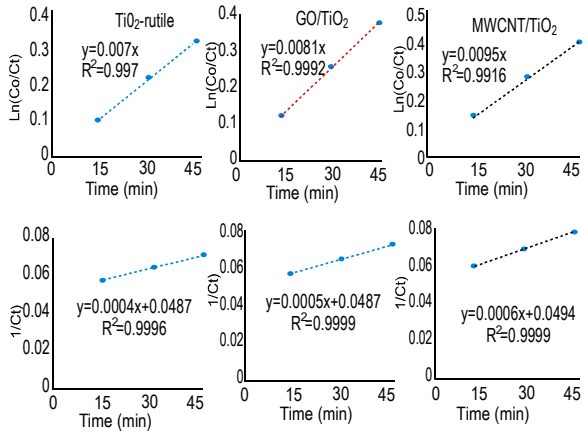

Fig. 4. The compare for removal of MOs by pristine TiO_2-rutile and modifying with 10% GO and MWCNTs with adsorption of first and second order reaction.

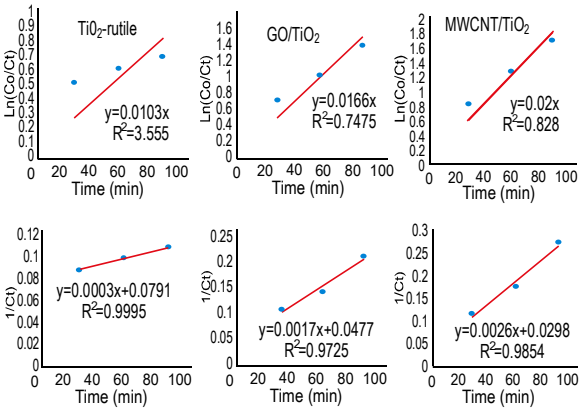

Fig. 5. The compare for removal of MOs by pristine TiO_2-rutile and modifying with 10% GO and MWCNTs with photo reaction of first and second order.

Results and Discussion

Photocatalytic activity. The photocatalytic activities of pristine and modified TiO_2-rutile were evaluated through the removal of MO dye. The results are shown in Fig. 3. For adsorption, pristine TiO_2-rutile removed 31% of MO, while GO/TiO_2 and $MWCNT/TiO_2$ removed 34% and 40%, respectively. Upon UV-A irradiation, the photocatalytic removal increased significantly: pristine TiO_2-rutile removed 54% of MO, GO/TiO_2 removed 85%, and $MWCNT/TiO_2$ achieved the highest removal at 95%.

Kinetic studies. Fig. 4 and 5 present the kinetic studies for adsorption and photocatalytic reactions. The adsorption data fitted better to a second-order kinetic model, with rate constants (k) arranged as follows:

$$k(TiO_2) < k(GO/TiO_2) < k(MWCNT/TiO_2)$$

For photocatalytic reactions, the second-order model also provided a better fit, with rate constants increasing from 0.0003 M/ s for TiO_2-rutile to 0.0017 M/s and 0.0026 M/s for GO/TiO_2 and $MWCNT/TiO_2$, respectively.

The enhanced activity of TiO_2-rutile modified with GO and MWCNTs can be attributed to several factors. The reduction in agglomeration of TiO_2 particles and increased surface area due to the incorporation of carbon materials significantly boost adsorption and photocatalytic efficiency. The presence of GO and MWCNTs creates additional active sites, improving the adsorption of incident light and facilitating electron

transfer, thus enhancing the photocatalytic reaction. The carbon materials act as electron bridges, enhancing the conductivity and electron mobility within the composites. This enhancement is crucial for improving the photocatalytic activity, as it allows for more efficient generation and transfer of reactive species such as O_2 radicals, which play a key role in the degradation of MO dye.

Mechanism of enchantment. The proposed mechanism for enhancing the activity of TiO_2 includes two sections: the first can be related to the nature of the morphology for the synthesized groups, and that is decided by reducing the agglomeration of TiO_2 particles after impregnating them with GO or MWCNTs, and that was reported from many works in this field (Tuka Mahroos Searan *et al*., 2024; Firas *et al*., 2018; Chao *et al*., 2014). The effect of GO and MWCNTs can be seen in increasing the surface area that forces the absorbed incident light on the solution of the reaction. At the same time, the enhancement in activity that is related to morphology factors also includes creating many bridges that increase the conductivity for electrons and that accrues with increasing the abilities to absorb light (Khaled *et al*., 2020).

The ether reason that may explain the increase in the activity of photo-reaction can be related to the increase in the adsorption activities of the surface after modifying it with carbon materials, which enhance the speed and transfer the electrons from ground state to active state to endure illumination. The critical parameters that influence dirtily in the photocatalytic properties can be due to the electronic structure, excess electrons and holes located in charge transport at the surface defects, in addition to the efficiency of the adsorption of active species such as O_2. All of these parameters are responsible for the formation of free radicals in the second step of removing color MOs. Practically, the two materials, MWCNTs and GO, succeeded in playing the best role for enhanced TiO_2 for photo-reaction (Thakur *et al*., 2024; Luttrell *et al*., 2014). However, this section refers to forming defects with high ratios of disorders on the surface of TiO_2 and that accrued after doping with fictionalized MWCNTs and GO when behaving as an active site for oxygen vacancy. Absolutely increase the size of materials (Jeevanandam *et al*., 2018), decreasing the surface area of the nano-catalyst and while increasing the size of the crystalline, more surface area leads to higher catalytic activity as compared with a larger agglomerate of catalyst.

Conclusion

The behaviour of binary composites can be related to the abilities of MWCNTs with TiO_2-rutile to show: The strongest interaction between MWCNTs and rutile TiO_2 as compared with GO and that it could be related to the successful dispersion of MWCNTs to more effective interfacial charge transfer. The last two causes produce—the highest electron-hole separation rate. All of these reasons are causing the highest photo-catalytic activity and stability for TiO_2-rutile with MWCNT and then GO. May be one of the most influential parameters that decided the activities of nanomaterials is that the crystallites tend to agglomerate and that represents critical behavior for nanomaterials due to forming bigger crystal particles.

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