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Kinetics and Adsorption Isotherm Studies of Methylene Blue Photodegradation Under UV Irradiation Using reduced Graphene Oxide- TiO2 Nanocomposite in Different Wastewaters Effluents.

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ABSTRACT

In this study TiO_2@rGO nanoparticles was synthesized as an effective photocatalyst. Reduced graphene oxide (rGO) was mixed with TiO_2 with different doping ratio (1%, 3% and 5% wt) and utilized to remove MB dye as organic pollutants from different wastewater effluents and also from aqueous solution. The impacts of different factors, e.g. pH of solution, contact time, photocatalyst dose and initial MB dye concentration on the removal efficiency were studied. The results showed that the highest MB degradation occurred at pH 9, contact time = 120 min, dose of photocatalyst of 0.75 g/L at 30 mg/l dye concentration. Also, the prepared nanocomposites success in reducing COD values of wastewater in the range of 30 – 89.1 %. Moreover, the data of kinetics studies indicated that the adsorption process well obeys the pseudo-second order reaction model with q_e values ranged between 14.28 – 19.37 mg/L. Langmuir isotherm model well describes the behavior of adsorption behavior than Freundlich Model.

INTRODUCTION

Nowadays, the wide industrial progress, great using pesticides and fertilizers in agricultural process and enormous overpopulation especially in the developed countries lead to Aggravation of wastewaters effluents. These effluents carry different kinds of pollutants (Zuo *et al*., 2014). Industrial and domestic wastewaters are responsible for most pollutants in effluents include organic compounds; unbiodegradable materials and pathogens (Gajbhiye, 2012). These hazards materials must be removed, destroyed or controlled before pouring into the surface water bodies. Painting and textile industries are considered as the main coloured organic compounds sources between the different industries kinds (Alberici *et al*., 1998, Akram *et al*., 2016). However, dyes are used extensively in the textile factories during dyeing process, the excess of theses dyes are drained into the waste's effluent. Moreover, most these dyes are fairly stable under the sun light effect and consequently may turned to be a carcinogenic material (Khan *et al*., 2016, Kee, 2017).

The polluted wastewater by dyestuff and other organic compounds are mainly characterized with dense color, elevated values of COD and fairly stable with low biodegradability, so it causes seriously pollution concern of the drain water.

Moreover, the wastewater has low BOD/COD ratio and high levels of COD with an average range of 750- 1500 mg/l in some cases. Therefore, the wastewater needs to proper, effective and environmentally friendly treatment process before discharging into the effluent's drains (Liu *et al*., 2006, Sari *et al*., 2017)

Organic pollutants treatment and photodegradation in different colored wastewaters produced by the textile factories has attracted great attention in last decades, especially using nanoparticles of titanium oxide to eliminated the environmental pollutants, since it has been considered as one of the most photocatalysts has low economic cost, high photocatalytic effect, nontoxic and abundant resources (Sajan *et al*., 2016; Jiang *et al*., 2016; Wei *et al*., 2017). The photodegradation process using TiO_2 under UV irradiation have several advantages in comparison with other processes. Since the organic compound's degradation is happened at room temperature and normal pressure with CO_2 and H_2O as final products (Alberici *et al*., 1998, Ali *et al*., 2018).

Many recent studies were carried out for improving the efficiency of TiO_2 photocatalytic action, the incorporation with graphene as a carbonaceous substance which have large surface area is regarded as an effective way to enhance the photocatalytic performance of TiO_2 (Posa *et al*., 2016). Many various methods were used to prepares nanocomposites particle of TiO_2 with graphene, graphene oxide and reduced graphene oxide, such as physical mixing, electrochemical deposition, hydrothermal and sol-gel approaches (Lee *et al*., 2012, Pan *et al*., 2012, Williams *et al* 2008). The prepared of nanocomposites from TiO_2 and graphene combination have high advantages more than bare TiO_2, since it not only prevents h^+/e^- by transferring the photo-excited electron to graphene surface, but also improve the adsorptive capacity through increase TiO_2 surface area (Jiang *et al*., 2017).

The main aims for this paper to; 1) illustrates the factors affecting degradation process of methylene blue dye, 2) degradation of some organic pollutants from different wastewater types using the prepared TiO_2@rGO nanocomposites.

Material and Methods

Analytical grade chemicals were used in all steps of works as purchased form Loba Chemie (India), TiO_2 powder from Degussa Company (Germany).

Synthesis of TiO_2@rGO nanocomposites

Modified Hummers method was used for synthesis reduced graphene oxide nanocomposites (Hummers and Offeman, 1958) using graphite powder (99.95%). Briefly, 15 g of graphite powder were added to 7.5g of $NaNO_3$ and 180 mL conc. H_2SO_4, this mixture transferred to 2L flask in an ice bath with continuous stirring for 30 min. after that, 45g of $KMnO_4$ were added slowly, temperature was kept below 15 ˚C for 12hr then, 210 mL of deionized water was added in careful with raising the temperature of mixture to 50˚C for another 12 hr, the mixture's color was turned to bright yellow. 66 mL H_2O_2 was added slowly was continuous stirring for 3 hr.

TiO_2 nanoparticles were pretreated in furnace at 500˚C for 2 hr, reduced GO was added to absolute ethanol with concentration of 0.5 mg/ml, weight ratio of rGO to TiO_2 of 1, 3 and 5 wt% were regulated in rGO/ethanol solution, this mixture was treated by ultrasound for 30 min. Finally, the obtained mixture was dried at 60 ˚C for 12 h to obtain the TiO_2@rGO nanocomposites.

Photocatalytic experiments

The photodegradation performances of TiO_2@rGO nanocomposites were assessed for MB dye with an initial concentration of 30 mg/L, using UV light source (six mercury lamps of 60 cm length and 11Watt for each lamp) with a cut-off filter (λ

> 400 nm) at room temperature 25°C, some factors e.g. pH effect, dose effect, degradation time and initial dye concentrations were be investigated in photocatalytic degradation process. The suspensions were stirred in the dark for 2 hr in order to establish the sorption-desorption equilibrium. For a given studied factor, 5 mL of the mixture solution was centrifuged at 10000 rpm for 10 min to get a clear supernatant. Then the concentrations of MB dye were determined from the maximum absorption (λ= 640 nm) by UV–vis spectrophotometer Jenway 6800UV/Vis double beam.

Collection and photocatalytic of wastewater samples

Wastewater samples representing different types of effluents were collected from major drains in Egypt; agricultural wastes (3 samples); domestic wastes (3 samples) and four samples represent industrial wastes Table 1). 100 ml of each waste sample was treated with different TiO_2@rGO nanocomposites (1, 3 and 5 % respectively) under UV irradiation for 150 min, then the mixture was centrifuged at 15000 rpm for 15 min. Determination of chemical oxygen demand was carried out for wastewater sample before and after treatment with closed reflux method using Lovibond COD RD125 thermoreactor (Boyles, 1997). Each sample was digested in the 6MM Ø vials of Lovibond COD VARIO. The resultant color was measured calorimetrically, using Lovibond MD 100 COD Photometer, before and after the degradation process.

Table 1: different wastewaters collected samples

Sample No.	Name of drain	Location	Type of waste
1	El-Wadi	El-Fayium Gov.	Agricultural drain
2	El-Bats	El-Fayium Gov	
3	El-Serw	Dakahlyia Gov	
4	El-Qalaa	Alexandria Gov.	Domestic drain
5	El-Rahawy	Qaulyobia Gov.	
6	Bahr El-Baqr	Dakahlyia Gov	
7	Textile factory	Menofiyia Gov.	Industrial wastes
8	Sugar factory	Giza Gov.	
9	Petrochemical factory	Alexandria Gov.	
10	Iron and Steel factory	Cairo Gov.	

RESULTS AND DISCUSSION

The degradation of methylene blue ($C_{16}H_{18}N_3SCl$) by the action of TiO_2@rGO nanocomposites (1, 3 and 5 wt%), at different pH values (3 - 9), UV irradiation time ranged from (15 - 120 min), different dose (0.1 – 1 g/L) and different initial dye concentration (5 – 30 mg/l) have been investigated. The temporal changes of MB concentration (C/C_o) were proportional to maximum absorbance (A/A_o, λ = 640 nm).

Effect of pH:

pH has a great influence in the photodegradation process, since it affects not only the charge of catalyst surface of photocatalyst but also the dye molecules dissociation, at alkaline conditions, hydroxyl radicals were formed and hence the dye decomposition was increased (Borhade *et al*., 2012).

Serial dye solutions of different pH ranged from 3 - 9 were used at fixed dye concentration (30 mg/l) and 0.75 g/L photocatalyst dose. The mixtures were stirred for 30 minutes in dark to ensure the sorption-desorption equilibrium attained. The results indicated an increase of photodegradation rate with gradual increase of pH values till pH = 6 then a noticeable steady state was observed at pH 7-8 followed by maximum degradation at pH equal 9. Furthermore, 5%TiO_2@rGO showed high degradation in comparison with other ratios (1 % and 3% TiO_2@rGO composites).

However, after 120 min treatment at pH 9.0, the removal rate reaches 97.3, 97.9 and 98.3 % for 1%, 3% and 5 % TiO_2@rGO particles respectively (Figure, 1). It is well known that MB dye is cationic dye (carrying a positive charge in ionized form therefore, at relatively high pH range (alkaline conditions), the TiOH reacts with hydroxyl group forming TiO^- ions in the solution leading to attraction with MB dye. Thus, a remarkable high adsorption of dye was occurred (Houas *et al*., 2001).

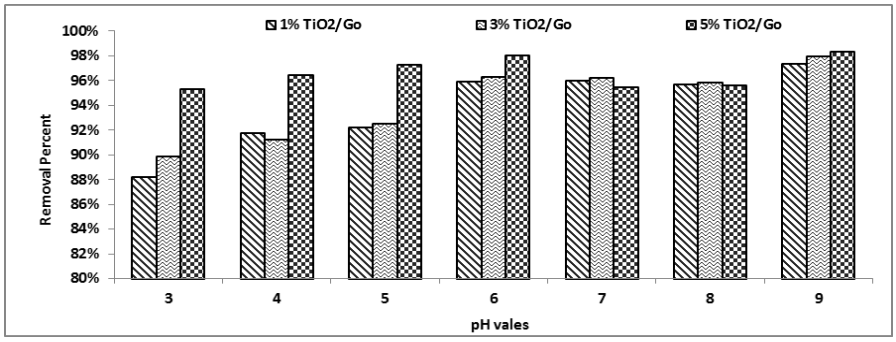


Fig. 1: Photocatalytic degradation of MB by TiO_2@rGO nanocomposites with various rGO doping ratio at different pH values

Effect of time

The effect of UV irradiation contact time from 15 to 120 min was carried out in standard 30 mg/L aqueous solution of MB dye, pH of solution was adjusted at 9 and catalyst amount of 0.75 g/L. The reaction started at dark condition for 30 minutes to attain sorption-desorption equilibrium between the catalytic surface and the dye. Figure 2 showed that a noticeable gradual increase of photocatalytic rate with increasing irradiation UV time. After 120 min irradiation time, the rate reached its maximum removal percent (98, 98.9 and 99.3% for 1%, 3% and 5% TiO_2@rGO nanocomposites respectively). The results revealed a regular relationship between degradation of MB dye with time increasing which explained on the basis of increasing time more and more light energy falls on the catalyst surfaces which induced formation of photon excited species and enhances the photocatalytic activities (Sahoo *et al*., 2012).

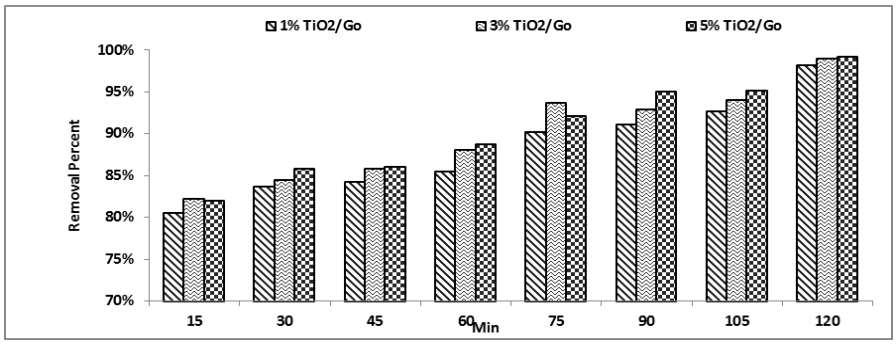


Fig. 2. Photocatalytic degradation of MB by TiO_2@rGO nanocomposites with various rGO doping ratio at different irradiation time

Effect of Catalyst Dosage:

Standard solution of MB 30 mg/l of pH = 9 was subjected to UV irradiation for 120 min with varying photocatalyst dosage ranged from 0.125 to 1 g/L. The photodegradation of MB dye results at different catalytic doses is shown in Figure 3. The degradation rate showed significant increase up to a dosage of 0.75 g/L and then

the reaction seems to be stable. The optimum catalyst dose was 0.75 g/L, beyond it the degradation rate was not significant.

The elevation of degradation rate with increase of photocatalytic dose may be attributed to greater surface area was available (Sahoo *et al*., 2012). Furthermore, the results showed low significant difference between the photodegradation effect of three used photocatalyst (Fig. 3).

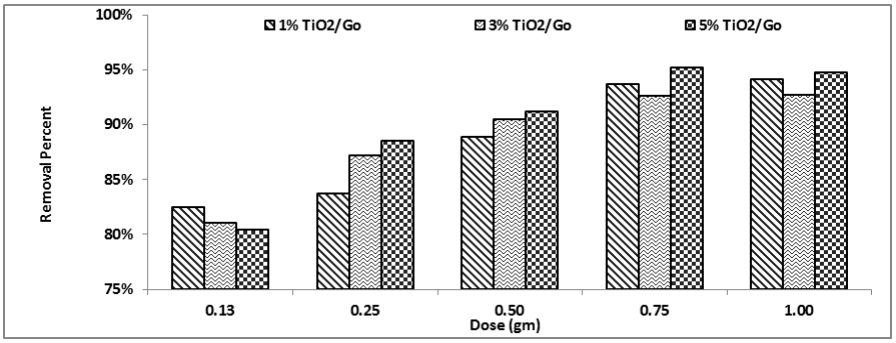


Fig. 3: Photocatalytic degradation of MB by TiO_2@rGO nanocomposites with various rGO doping ratio at different irradiation time

Effect of Initial Dye Concentration

Serial standard solution of MB dye with concentration ranged from 5 to 30 mg/l with adjusted pH = 9, catalyst dosage 0.75 g/L, 120 min duration time was used to study the effect of initial dye concentration of photocatalytic adsorption process (Fig 4). There is significant relationship between photodegradation rate and initial MB concentration, with increasing of dye concentration there is a decrease in the degradation rate was obvious. This is attributed to the increase of the dye molecules number the amount of penetrating light to reach the catalyst surface is reduced because of the light hindrance path, consequently, the formation of the reactive hydroxyl radicals is almost reduced. At higher concentration upon 10 to 30 mg/l, there was insignificance changes of degradation rate of removal percent which ranged between 94 to 97 % for all used nanocomposites due to existence of high amount of adsorbed dye results in lack of direct contact with the holes or hydroxyl free radicals this could have an inhibitive effect on the dye degradation (Gajbhiye, 2012).

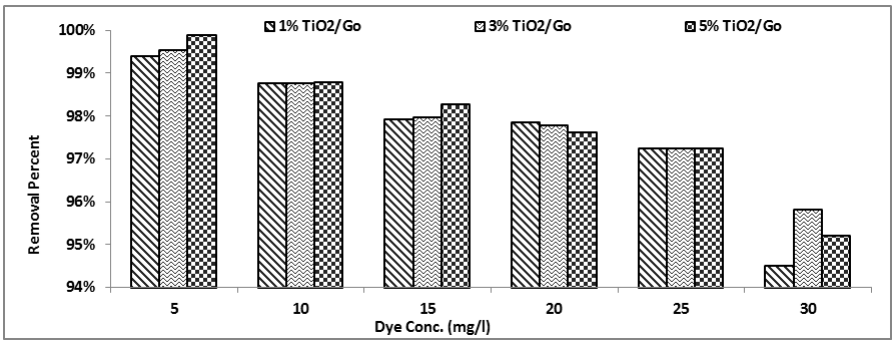


Fig. 4: Photocatalytic degradation of MB by TiO_2@rGO nanocomposites with various rGO doping ratio at different initial dye concentration.

Adsorption study

Langmuir and Freundlich isotherms were used to describe the adsorption process, either homogenous adsorption as Langmuir postulate or nonhomogeneous adsorption as assumption of Freundlich. The constants and isotherms graphs for Langmuir and Freundlich were showed in Table 2 and Figs. 5 and 6.

Langmuir Equation $q_e = \frac{q_{max}\, bC_e}{1+bC_e}$

Freundlich equation $q_e = K_f C_e^{1/n}$

Where: q_{max} (mg g^{-1}) maximum uptake of sorbate, b (L mg^{-1}), Langmuir constant, q_e (mg g^{-1}), amount of metal adsorbed; and C_e gL^{-1} the metal concentration at equilibrium K_f is the adsorbent capacity and n is the adsorption intensity.

Table 2: Constants of Langmuir and Freundlich isotherm for MB dye adsorption by different nanoparticles photocatalysts.

Langmuir												Freundlich								
1 % TiO_2@rGO				3 % TiO_2@rGO				5 % TiO@rGO				1% TiO2@rGO			3 % TiO_2@rGO			5 % TiO_2@rGO		
b	q_{max}	R_L	R^2	b	q_{max}	R_L	R^2	b	q_{max}	R_L	R^2	K_f	n	R^2	K_f	n	R^2	K_f	n	R^2
5.5	16.6	0.006	0.92	9.71	3.03	0.003	0.91	14.30	2.32	0.002	0.92	19.0	2.0	0.73	5.4	1.6	0.83	4.3	1.8	0.94

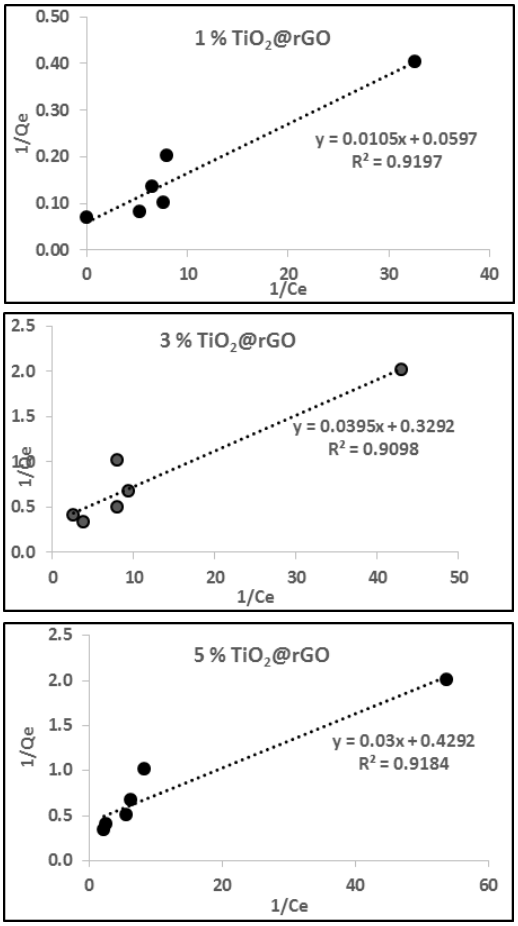


Fig. 5: Langmuir isotherm plot for adsorption of MB dye by TiO_2@rGO photocatalysts

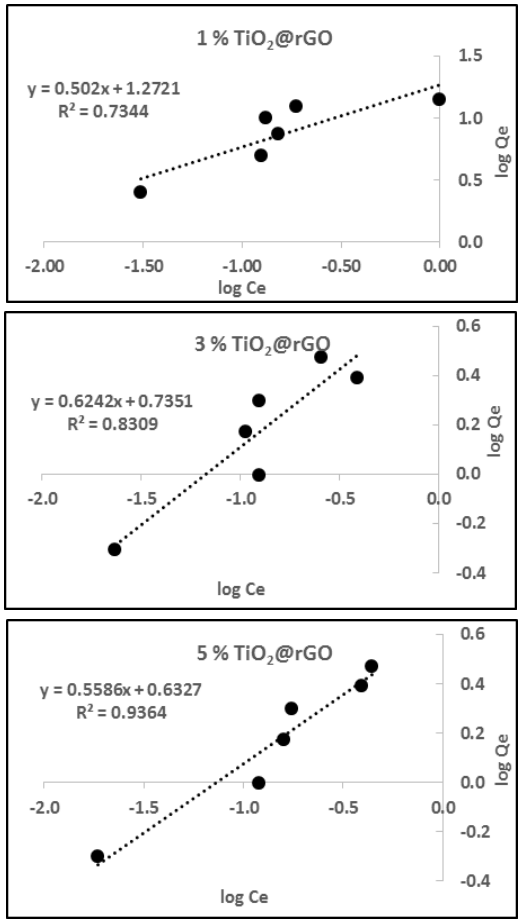


Fig. 6: Freundlich isotherm plot for adsorption of MB dye by TiO_2@rGO photocatalysts

It is clear that Langmuir model isotherms with $R^2 > 0.91$ were well best fitted in case using TiO_2@rGO with doping ratio of 1 % and 3 % respectively, while Freundlich mode isotherm is well best fitted in case of using 5% TiO_2@rGO with corresponding $R^2 = 0.94$ (Table, 2; Figs. 5 & 6). The dimensionless constant (R_L) which also known as separation factor which used to detected the Langmuir isotherm

type, if ($R_L = 0$) irreversible mode, ($R_L = 1$), linear mode, ($R_L > 1$), unfavorable mode or ($0 < R_L < 1$) favorable adsorption (McKay *et al*., 1982), R_L expressed as:

$$R_L = \frac{1}{1 + bC_i}$$

Where b is the constant of Langmuir and C_i is initial concentration of dye. The R_L values in the recent study ranged from 0.002 to 0.006 (Table, 2), thus, the favorable adsorption MB dye onto all used photocatalysts surface were occurred. Moreover, Freundlich intensity parameter ($1/n$) defined as function of the adsorption strength in the adsorption process (Voudrias *et al*. 2002), in case of $n = 1$ adsorption is linear, $n < 1$ adsorption is a chemical process and adsorption is a physical process if $n > 1$ (Desta, 2013). n values of the present data always > 1 (Table 3) which represent physical adsorption of MB dye onto the surface of the three photocatalysts.

Table 3: Constants of Pseudo first order and pseudo second order reactions for MB dye adsorption by different nanoparticles photocatalysts

Pseudo first order reaction									Pseudo second order reaction								
1 % TiO_2@rGO			3 % TiO_2@rGO			5 % TiO_2@rGO			1 % TiO_2@rGO			3 % TiO_2@rGO			5 % TiO_2@rGO		
q_e	K_1	R^2	q_e	K_1	R^2	q_e	K_1	R^2	q_e	K_2	R^2	q_e	K_2	R^2	q_e	K_2	R^2
4.21	1.56	1.00	2.28	1.51	1.00	2.29	1.54	0.99	14.28	0.015	0.96	19.37	0.004	0.90	17.24	0.006	0.86

Kinetics studies of MB Degradation

Several factors have an important impact in determining the photocatalytic reaction kinetics, time is one of these factors which is necessary to establish the adsorption equilibrium (Kurajica *et al*., 2018). There are many models could be used to express the sorption of solute onto a sorbent mechanism. In this study we discussed pseudo-first-order and pseudo-second order models in order to their have great applicable manner in comparison with other models of adsorption (Ghasemi *et al*., 2014). The main assumption of the pseudo-first order model that there is a direct proportion between occupation rate of sorption sites with the unoccupied sites number. Generally, pseudo-first order equation is expressed as follows:

$$\frac{dq_t}{dt} = K_1(q_e - q_t) \quad or\ \log(q_e - q_t) = log\, q_e - \frac{k_1}{0.203}\, t$$

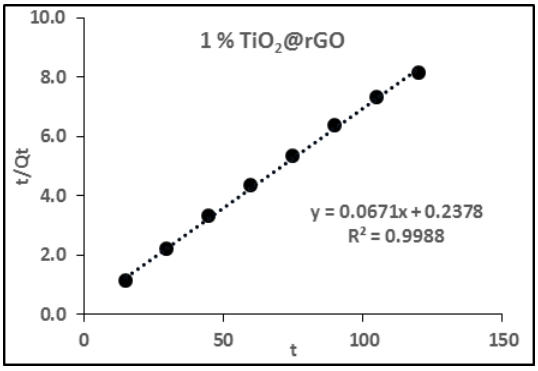
The pseudo-second order kinetic rate equation is expressed as follows:

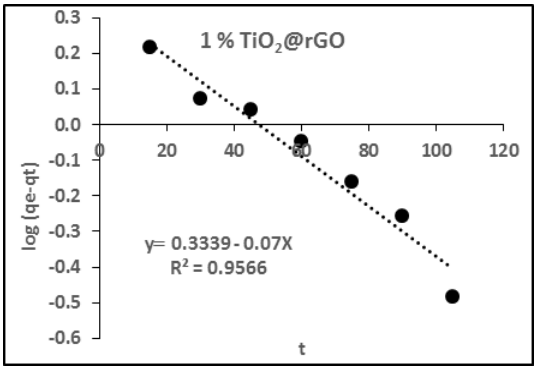
$$\frac{dq_t}{dt} = \boldsymbol{K_2(q_e - q_t)^2} \quad \text{or} \quad \frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}\, t$$

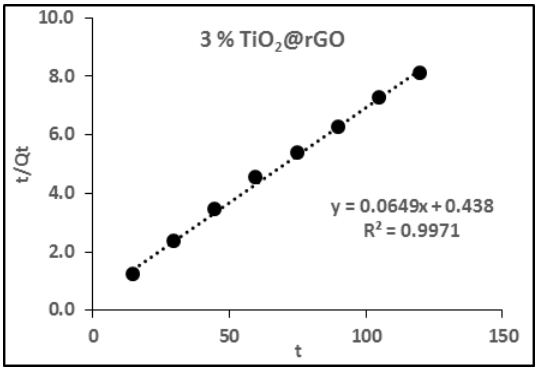
where q_t is MB amount (mg/g) adsorbed at irradiation time t, q_e is MB amount (mg/g) adsorbed at the equilibrium, and k_1 (min^{-1}) and k_2 (mg/g.min) are the rate constants of the first- and second-order kinetic, respectively.

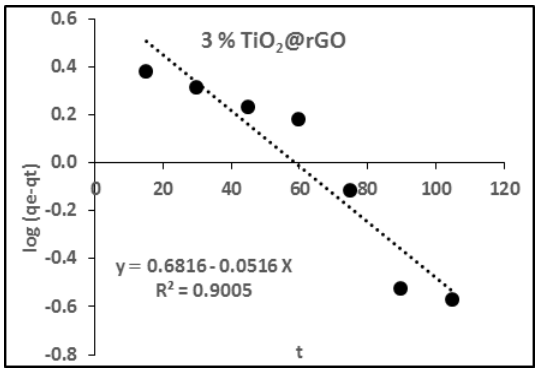
Fig. 7 showed a linear relation between t/qt versus time which represent the pseudo-first order kinetic reaction and Figure (8) showed a relation between log(q_t-q_e) versus time represented the pseudo-second order reaction. The kinetic constants (q_e, K_1 and K_2) were calculated from the intercept and slope of regression equations and tabulated in Table 3. Results indicated that the adsorption of MB dye will obeys a linear relation with R^2 values ranged between 0.86 – 0.96 with q_e values ranged between 14.28 – 19.37 mg/l. So, the removal kinetics of MB using TiO_2@rGO photocatalyst well fitted with pseudo-second order reaction. These results with in a good agreement with that obtained by Salehi *et al* (2012) who reported that the

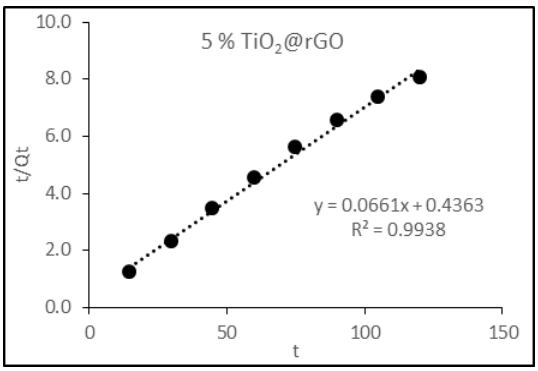
photocatalytic degradation of Mb followed the pseudo-second order using TiO_2 nano-tubes as photocatalyst.











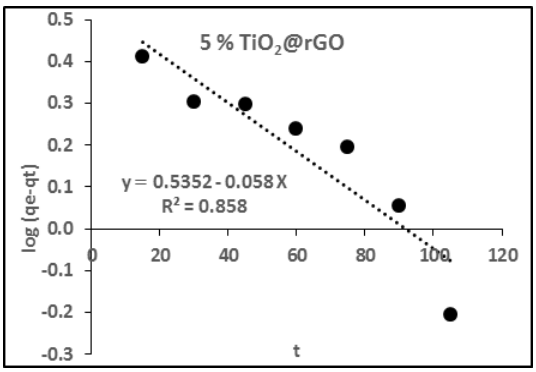


Fig. 7: Pseudo first order reaction plot for MB dye adsorption TiO_2@rGO photocatalysts

Fig. 8: Pseudo second order reaction plot for MB dye adsorption TiO_2@rGO photocatalysts

Chemical oxygen demand of wastewater effluents.

The collected wastewaters samples are characterized by high chemical oxygen demand values due to abundance of organic matter especially in in industrial wastes. The highest COD values were recorded at industrial wastes of textile and sugar factories with values of 900 and 335 mg/L, followed by domestic effluents in El-Rahway and Bahr El-Baqr and Drains, then the agricultural effluents have the lowest COD values ranged from 59 – 66 mg/l (Table, 4).

Degradability of wastewater effluents and decolorization of MB dye.

The study of degradability of different wastewaters samples was carried out, the efficiency of organic matter degradation was measured experimentally throughout chemical oxygen demand (COD) measured for wastewaters effluents after UV irradiation exposure. The results showed an acceptable success of used TiO_2@rGO catalyst in breakdown of organic matter, the reduction of COD ratios ranged between 30 % - 89.1 % (Table, 4). Industrial wastes attained high COD

reduction ratio followed by domestic wastes, while the agricultural wastes have the lowest reduction in its COD ratios.

To compare between the degradability and decolorization of MB dye, 100 ml of serial standard solution of MB dye (20 – 100 mg/l) were treated with 0.1 g/L photocatalyst dose under 150 min UV irradiation. After that, the resulting solution was examined spectrophotometrically and its COD values were measured (Figures, 9&10). The results revealed that TiO_2@rGO photocatalyst have great success for breakdown the organic matter found in the wastes so, it is regarded as promising photocatalyst to treatment of wastes. From Figs (9 & 10) it is clearly that TiO_2@rGO have the highest degradation ratio ranged between 42-89 % at low dye concentrations (20-40 mg/l), while in gradual increasing of dye concentration the degradation removal percent also attained gradual decrease with lowest value of 26.2%.

Table 4: COD content (mg/l) in different types of wastewater and COD removal efficiency using 1%, 3% and 5% of TiO_2@rGO catalyst

Drain	COD of waste water mg/l	Removal % TiO2@rGO 1%	Removal % TiO2@rGO 3%	Removal % TiO2@rGO 5%
El-Wadi	59	40.7%	52.5%	57.6%
El-Bats	60	46.7%	56.7%	61.7%
El-Serw	66	60.6%	69.7%	37.9%
El-Qalaa	70	30.0%	72.9%	61.4%
El-Rahawy	136	59.6%	62.5%	66.9%
Bahr El-Baqr	135	79.3%	69.6%	67.4%
Textile factory	900	83.9%	85.1%	77.8%
Sugar factory	330	88.5%	88.8%	89.1%
Petrochemical factory	90	44.4%	56.7%	35.6%
Iron and Steel factory	85	74.1%	81.2%	69.4%

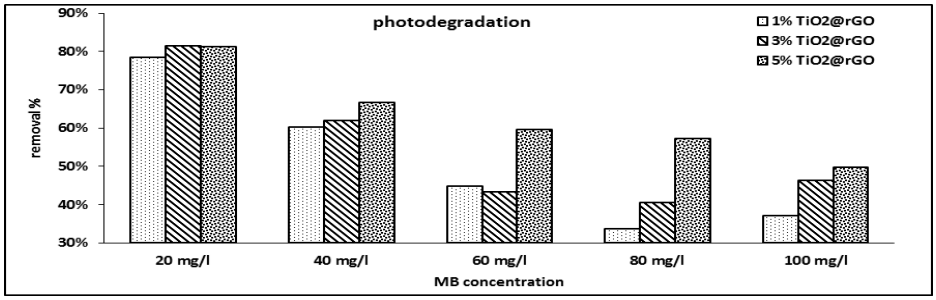


Fig. 9: Photodegradation of MB by TiO_2@rGO nanocomposites with various rGO doping ratio at different initial dye concentration.

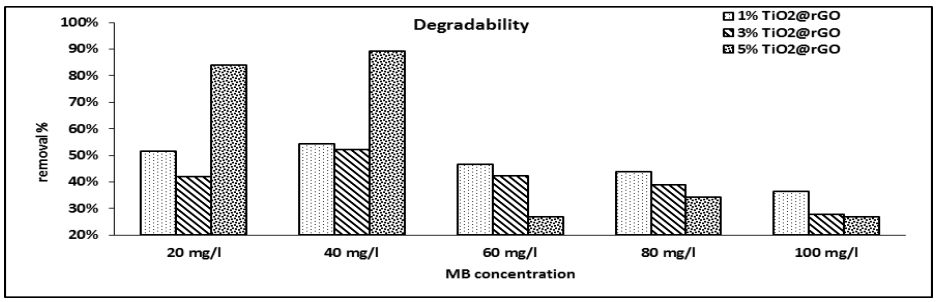


Fig. 10: COD removal percent of MB by TiO_2@rGO nanocomposites with various rGO doping ratio at different initial dye concentration.

CONCLUSION

TiO_2@rGO nanocomposites photocatalyst (1%, 3 % and 5% wt) were prepared and used for MB dye removal from different wastewaters effluents and aqueous solution using UV light. The prepared nanocomposites showed highest MB degradation at pH = 9, contact time = 120 min, dose of photocatalyst of 0.75 g/L at 30 mg/l dye concentration. The results revealed that, TiO_2@rGO catalyst have a considerable success in breakdown of organic matter in wastewater, the reduction of COD ratios ranged between 30 % - 89.1 %. The adsorption kinetics well fitted with pseudo-second order reaction model with q_e values ranged between 14.28 – 19.37 mg/L. Moreover, the isothermal studies indicated that Langmuir isotherm model well describes the adsorption behavior.

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