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RESEARCH ARTICLE

Eco-friendly assessment of photocatalysis process for organic pollutants treatment

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ABSTRACT

Large volumes of contaminated water should not be dumped without being cleaned beforehand. The water contained a significant number of biological contaminants. The pollution of color usually causes harm for living organisms. The photocatalytic removal of methylene blue (MB) and crystal violet (CV) from aqueous solutions is explored. TiO2 concentration as a catalyst in both dark and light scenarios, pH value and the concentration of contaminants are the optimization factors. The results demonstrated that the photocatalysis method was quite effective in eliminating these contaminants. Following treatment in a basic solution with a pH of 9, the typical clearance durations for CV and MB are 30 and 60 minutes, respectively. The influence of different photocatalyst concentration. (o.5-1.5mg/l) on dissociation rate, Effect of pH on breakdown speed(3-9) and the initial concentration of the pollutant (10^{-5}-10^{-}4 M) For studied CV and MB. The best concentrations for each case are 1 mg/l of TiO_2 in dark and light applied and $5*10^{-5}$ M of the pollutant. According to the findings of the kinetics study conducted on the dyes CV and MB, the observed quantities at steady-state step (qe) values are quite similar to the experimental TiO_2 adsorption capacity. Based on the outcomes of the Langmuir and Freundlich studies, TiO_2 is a suitable option for removing the dye pollution since it is a good adsorbent with a high capacity for sorption. The results show that the equilibrium data fitted to the Freundlich model with R^2 =0.981 and 0.919 for studied CV and MB within the concentration range studied.

Keywords: Concentration , pH , Photocatalysis, Organic pollutants, TiO_2 .

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1. Introduction

In the last years of the 20th century, several warnings were issued regarding the future of life on Earth. Concern has grown as a result of human use of effective, which has been widely criticized for interfering with the natural equilibrium. must do all possible effort to prevent the issues that are being caused by the rapid development of industry and technology from getting worse. The environment, namely the global issue of environmental pollution, which encompasses any alteration to or influence on the natural equilibrium. Without establishing any ecosystems, which alter or influence their constituent parts, the pollution issue has grown to be one of the major issues that cannot be resolved. A remedy for it [1] as well as the many forms of environmental pollution, such as air pollution with disease-causing sulfur and nitrogen oxides. It is the primary contributor to acid rain in the respiratory system as well as soil pollution brought on by agricultural chemicals like fertilizers. Chemicals, pesticides, household and industrial waste, as well

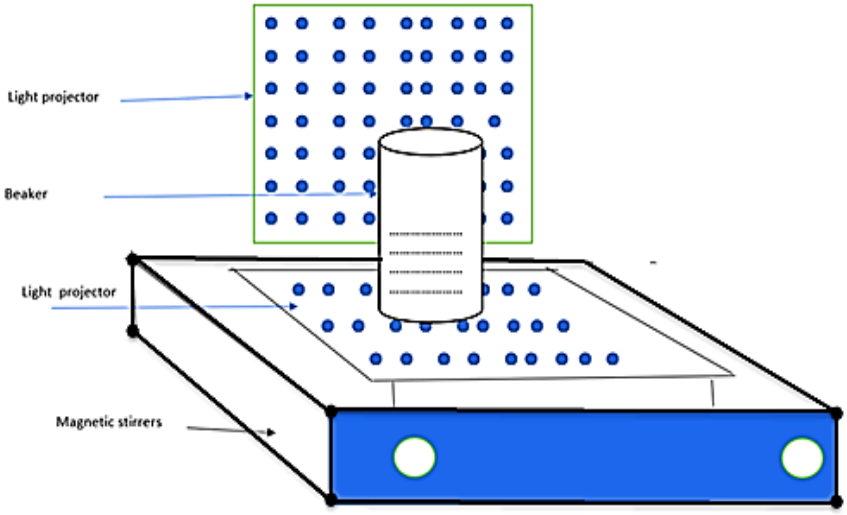
as sewage, pollution, and oil spills all contribute to water contamination. With agricultural residues such as pesticides [2-7]. Large The result of dumping polluted water without treatment processes is dangerous. The high percentage of organic pollutants in the water. On living organisms in general, dyes are among these pollutants, such as methylene blue and crystal violet. 7 mg/kg as an agent of little toxicity, but it can cause various harmful effects [8], and it is also used in doses or concentrations less than Exceeding this value may cause harm to humans, such as nausea, abdominal pain and confusion. As for the violet crystal, it is considered as an antibacterial and antifungal, and it was previously used as a local disinfectant [4], and it was used to dye paper and as a component of dark blue and black inks for printing and inkjet printers [5], as well as severe damage to the Eyes, and in case of ingestion, it has a carcinogenic effect as well as very toxic to aquatic organisms, which causes a long-term harmful effect in the environment Aquatic [9]. In fact, it was found that burning waste caused an increase in the rate of carbon dioxide emission into the atmosphere, or the so-called phenomenon. It has actually increased global warming, and it is wise here not to continue using this method as a countermeasure to combat pollution because The problem of pollution, and in such circumstances it is necessary to search for an alternative to solve this dilemma by finding a new method that does not cause.

Additional damage to the environment and at the same time working to restore environmental conditions to their original status, so researchers and scientists have been guided to the importance of photocatalysis Increasing the rate of a chemical reaction without having a role in the reaction itself, the catalyst process depends on a substance that increases the rate of Any photocatalyst, the photocatalyseur transforms the reactants without being affected by this substance or being depleted. The name of this drug is It has been quite successful in eliminating numerous contaminants at the level of fields when it comes to pollution. Numerous research have demonstrated the effectiveness of this method [10]. The purpose of the present study is to examine and improve photocatalytic elimination of organic contaminants.

2. Materials and method

2.1 Model description

The photocatalysis reactor is an open-faced cardboard box. It is covered from the inside with black paper where a thin projector cells, magnetic stirrer and the beaker are located inside it as shown in Figure 1. The bar of magnetic stirrer is placed inside the beaker. At the same time, the side of the beaker is exposed to lighting from a second projector installed on the wall of the system, as the pollutant inside the beaker is exposed to lighting from the bottom and from the side. Cell characters are LED driver, 50W, DC:100-160 and output current is 300mA.



(a)

(b)

Figure 1. Photocatalysis reactor: (a). experimental setup (b). reactor photo.

2.2 Source of TiO_2

Titanium dioxide is a semiconductor that works well as a photochemical catalyst as it has a number of benefits, including thermal stability, non-toxicity, corrosion resistance, and a low cost due to the fact that it needs less processing and preparation than other semiconductors. The physical and chemical characteristics of TiO_2 are listed in Table 1.

Table 1. physical and chemical characteristics of TiO_2

molecular mass	**79.87 g/mol**
Appearance	White
Density	4.23 g/cm^3
Specific heat	298.13 J/(mol °C)
Solubility	Insoluble
Melting point	1870 °C
Boiling point	2972 °C

Optical reactions occur in the presence of semiconductors being photocatalysts and possessing an energy gap. The TiO_2 has an energy gap between the valence band and the conduction band equal to Eg=3.2eV. This energy is equivalent to the energy of a photon with a wavelength of 388 nm. This photon is in the ultraviolet range. The figure 2 shows the reaction mechanism [8].

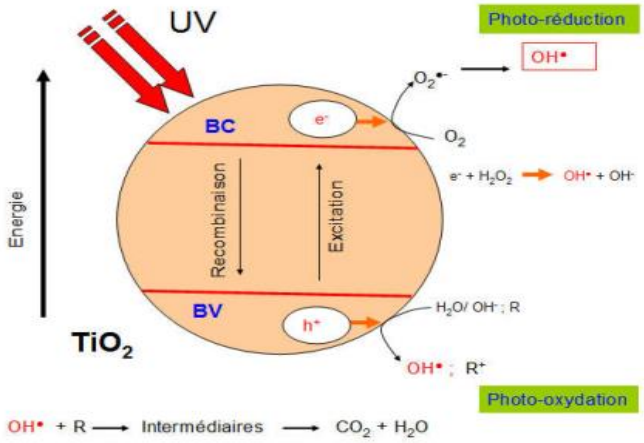


Figure 2. Mechanism of photocatalysis using TiO_2[8].

2.3 Tools of analysis

The compounds and materials used during all stages of work have specifications and analytical properties indicated in the following: 10 g/L methylene blue solution, Violet crystal is solid crystals (99.8 %) and titanium dioxide powder (99.9 %, Degussa p25). During the work, many devices were used, including analysis and measurement and separation devices. pH meter using Hanna type. The centrifuge device is Apagee type in which the components of the mixture in a test tube are separated, where the solid part of TiO_2 is concentrated at the bottom and the liquid part at the top. The separation is due to the generation of centrifugal forces resulting from a high rotational speed of up to 3000 rpm. Optimzen 2120UV is used for Ultraviolet Vis Spectrometer which it is a dual system reference spectrometer, with a cell width of 1cm. This spectrometer is conducted to obtain the absorption spectrum of impurities and measurements. Some of the characteristics of the devices used are summarized in Table 2.

Table 2. Characteristics of the equipment used.

pH meter	spectrophotometer uv/visible	Centrifugeuese
Microprocessor pH meter	uv/visible spectrophotometer	Horizontal centrifuge
Model : Hanna Instruments HI 2221 Digital	Model :Optizen 2120UV	Model :Apagee
pH :(0.00-14.00)Ph	Rated voltage :Freevolta	Speed setting :2700
Temperature :(0.00-100) °C	Rated current :1A	Swing-3000
Accuracy :+-0.01	Serial Number :240101-150416-05	Timer Control :30 mn

The main solution of each of crystal violet (CV) and methylene blue (MB) with a volume equal to 250 ml was prepared using distilled water and two measuring flasks of each (V=250ml) and each flask was covered with aluminum foil for The solution was not exposed to light. The dilation method was used to prepare standard volume solutions 250ml and in different concentrations ($0.5*10^{-6}$M ; 10^{-6} M ; $0.5*10^{-5}$ M ; 10^{-5} M ; $0.5*10^{-4}$ M and 10^{-4} M). These standard solutions were prepared using a Beacher and a graduated tube, and then each standard solution was placed in an opaque vial in order not to expose to light.

2.4 Experimental procedure

The experiments were conducted to investigate the factors influencing the rate at which the two pollutants (crystal violet and methylene blue) disintegrate. All stages of the work were completed at room temperature in a glass reactor that was exposed to the air. The first stage was completed after the preparation of the mother solutions for both crystal violet and methylene blue as well as the standard solutions. The pH is monitored and measured the absorbance of each standard solution, in order to obtain the calibration curve and absorption spectrum. The second stage, A suspension solution (100mg of TiO_2, C = 0.5*10^-4M and V=100ml from the aqueous solution of the contaminant) is prepared after weighing a quantity of TiO_2 using an analytical balance. The solution is prepared in a 100ml measuring flask, then the solution is shaken for an hour with a magnetic shaking device to reach the state of equilibrium. The first sample is taken by means of a 10ml pipette.Considering, the initial concentration is (C_o) before irradiation, then the solution is placed in the reactor after which the latter is placed in the center of the irradiation system with continuous shaking until the solution is homogeneous and exposed to the largest possible light intensity. Each time samples are taken after similar time periods in order to track the dissociation kinetics. After that, the solution is separated from the solid phase of TiO2 by centrifuge, and finally the solution is taken for analysis by visible spectrometer to measure its absorbance. In the third stage, the effect of the catalyst concentration on the reaction kinetics in dark and light applied was studied, by taking 0.5 mg/l of TiO_2 photocatalyst and preparing the suspension solution, then studying it in the same method as before, and again taking for 1 and 1.5 mg/1 of the TiO_2 catalyst concentration and studying it using same previous method. In the fourth stage, the same steps as the second stage only, the pH value of the suspension was modified after equilibrium and studying the effect of pH on the dissociation kinetics once at pH = 9 by adding NaOH at a concentration of 0.1 M and once at pH = 3 by adding HCl at a concentration of 0.1 M. In this fifth stage, the effect of the initial concentration of the pollutant on the rate of disintegration was studied while maintaining the optimal concentration of the photocatalyst for the solution by applying the same previous steps (preparation of the suspension solution, shaking, irradiation, sampling, separation and analysis). Isotherm and kinetic studies have been conducted to evaluate the performance of the TiO_2 in removing CV and MB from aqueous solution and to comprehend the potential adsorption process.

3. Results and discussion

3.1. Effect of photocatalyst concentration

To study the effect of the concentration of the photocatalyst on the rate of dissociation, three concentrations of the catalyst were taken (0.5, 1 and 1.5mg/l) TiO_2 in the solution under two case dark and light applied as shown in Figures 3 and 4.

The dissociation rate of the two pollutants (MB and CV) with time passing when applied light is better compared with in dark case as revealed in former studies[9, 10, 11]. In both cases of pollutants, the completely removal is obtained at 1 mg/l of TiO_2 concentration. This can be explained by the increase in the concentration of TiO_2, which leads to blocking the rest of the molecules from exposure to radiation, which means a decrease in the number of excited molecules from the catalyst. Also, a decrease from the ideal concentration means fewer TiO_2 molecules and thus less stimulation, which leads to a decrease in the dissociation rate [12]. In contrast to earlier research, 5.0 mg of a nanocomposite [ZrSiO 4 NPs-SDS] comprising zirconium silicate nanoparticles with surface modification using SDS was administered after 60 minutes. Both CV and MB had removal efficiencies of 80% and 83%, respectively [13]. The current outcomes are superior in terms of more removal effectiveness with the least amount of catalyst necessary, leading to in cheaper costs.

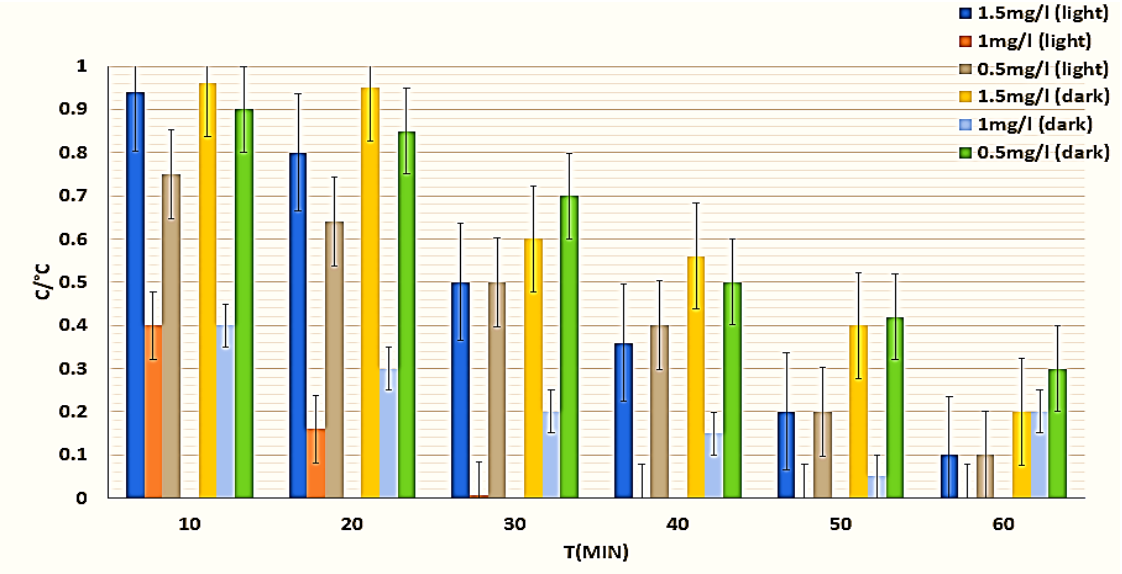


Figure 3. Effect of photocatalyst concentration on dissociation rate of MB in dark and light.

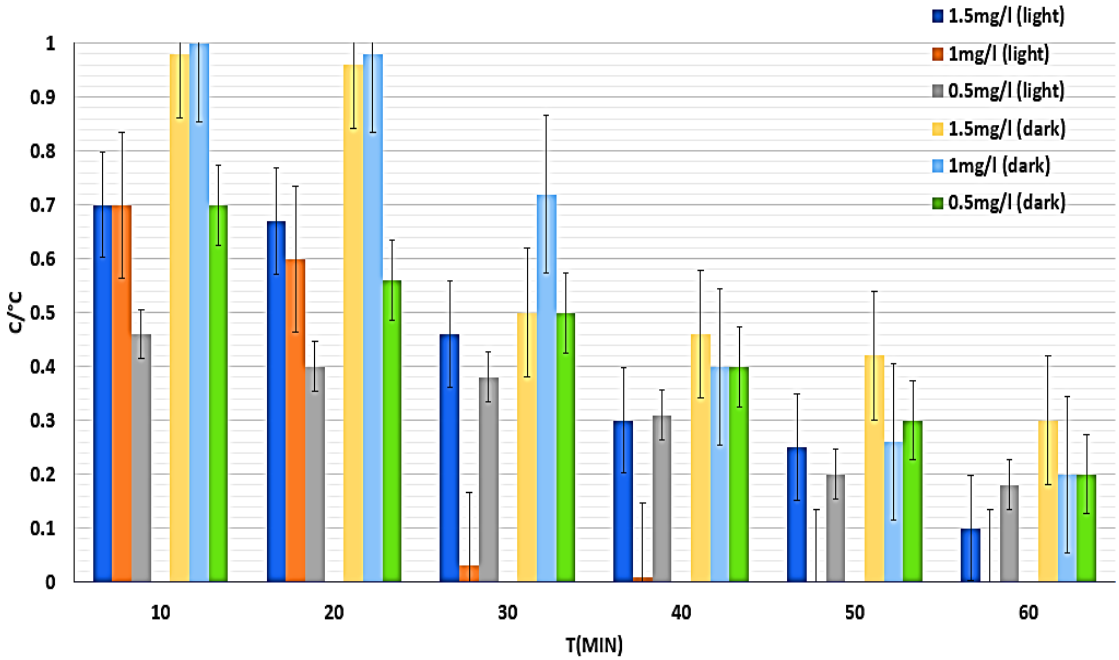


Figure 4. Effect of photocatalyst concentration on dissociation rate of CV in dark and light.

3.2 Effect of pH

The effect of the pH factor on the rate of pollutant disintegration was studied in three media: the moderate medium, the acidic medium pH = 3 and the basic medium pH = 9, and the results were as shown in Figures 5 and 6.

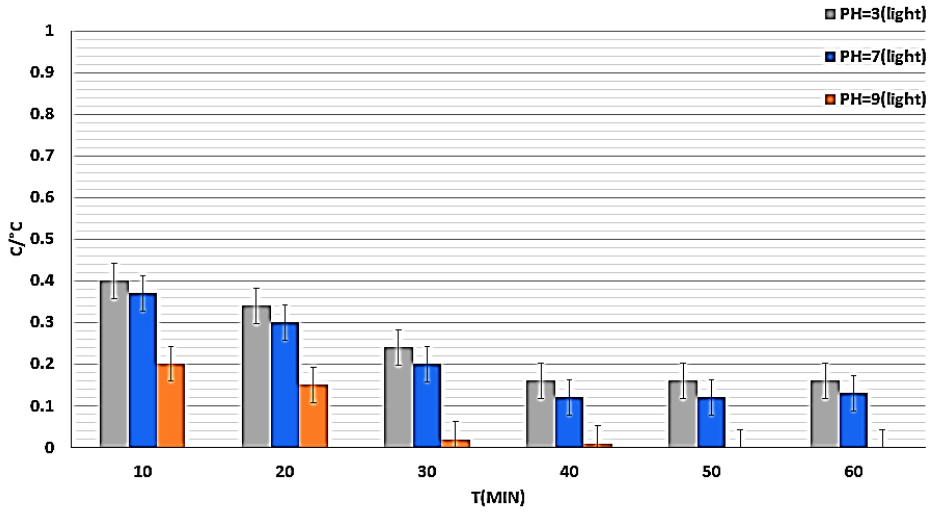


Figure 5. Effect of pH on breakdown speed CV.

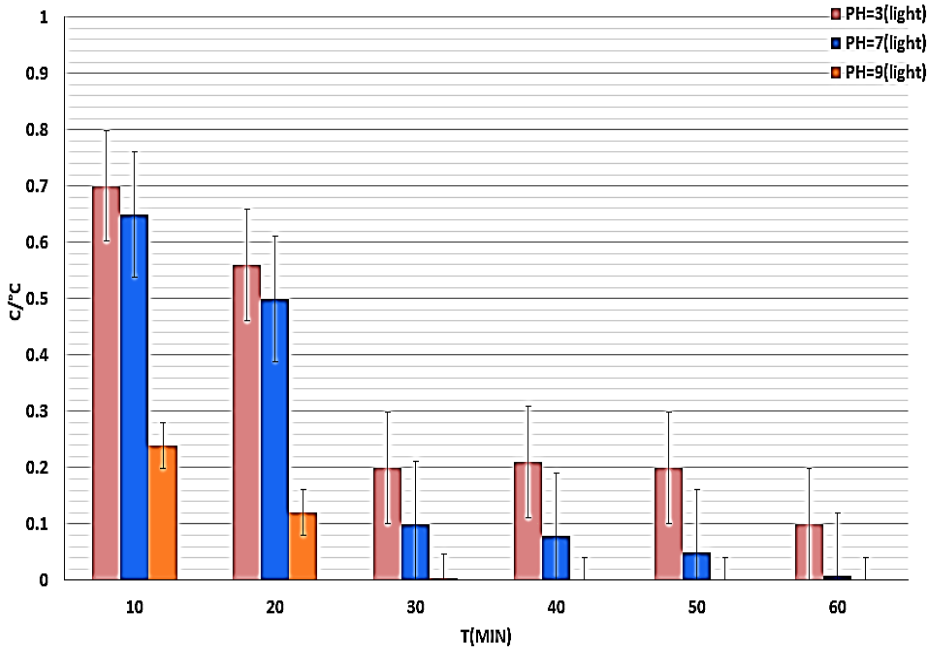


Figure 6: Effect of pH on breakdown speed MB.

For CV at pH = 9, and after 30 minutes of irradiation, the pollutant was completely removed, while the removal percentage was 76% in the moderate medium (pH = 7), but in the acidic medium (pH = 3) did not exceed the percentage 50% removal. As for MB, after 30 min, the contaminant was completely removed at pH=9. For the moderate and acidic medium, the removal did not exceed 48% after 30 minutes of irradiation.This result can be explained by the fact that the increase in the concentration of H^+ ions leads to the formation of N-H bonds on the chromophores in these two pollutants, which restricts the movement of free pairs on the N atom and leads to a reduction in the number of n-π* transitions [8]. Comparing to other investigation, the MMT-mAmCs composite (fabricated montmorillonite/magnetic NiFe2O4@amine-functionalized chitosan) is employed to extract CV and MB from aqueous solution. The percentage of elimination was 85% for CV and 87% for MB at pH=9 and 30 minutes [14]. The current obtained results according to the used methodology are better.

3.3. Effect of initial concentration of pollutant

To study the effect of the initial concentration of the pollutant (C_0) on the rate of decomposition, three concentrations were relied upon ($5*10^{-5}$, 10^{-5} and 10^{-4}) M, maintaining the moderate medium of the solution, and the results were as shown in Figures 7 and 8. The ideal concentration of the contaminant in the working conditions was $5*10^{-5}$M, which gave the greatest speed of disintegration in both cases, the CV pollutant is totally removed after half an hour of irradiation, while the highest disintegration rate for the MB pollutant after half an hour of irradiation did not exceed 50%. This could not be explained by the increase on $5*10^{-5}$M leads to a large density of pollutant particles that prevent radiation from reaching the TiO_2 particles, which means fewer excited TiO_2 particles, and this means a lower reaction (dissociation) speed. As for the decrease in the concentration of $5*10^{-5}$M of the pollutant, this leads to a relatively large density of TiO_2, which means that the phenomenon of effect decant or blocking will be repeated [15-24].

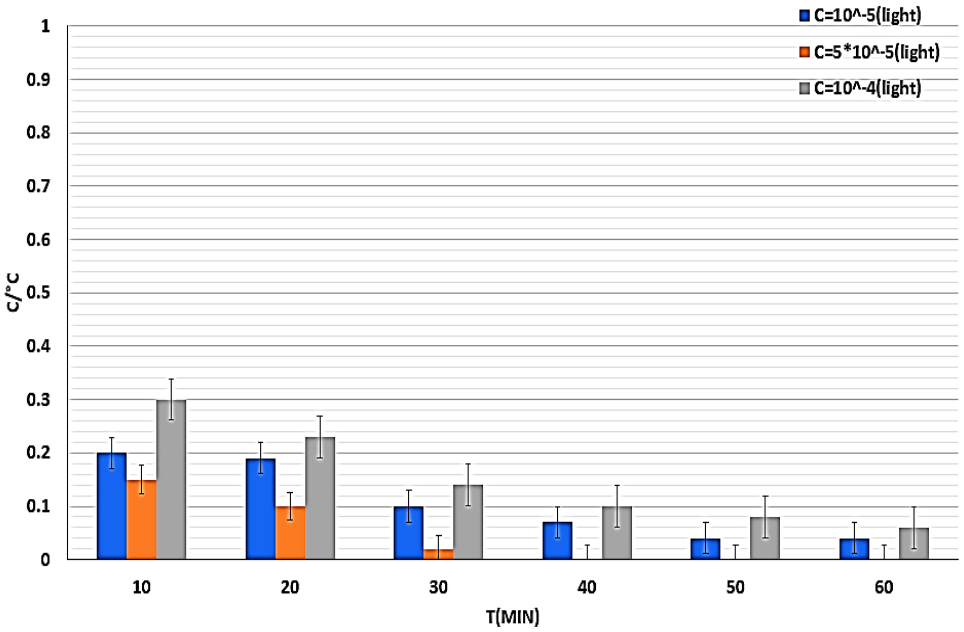


Figure 7. The effect of the initial concentration of the pollutant on CV decomposition rate.

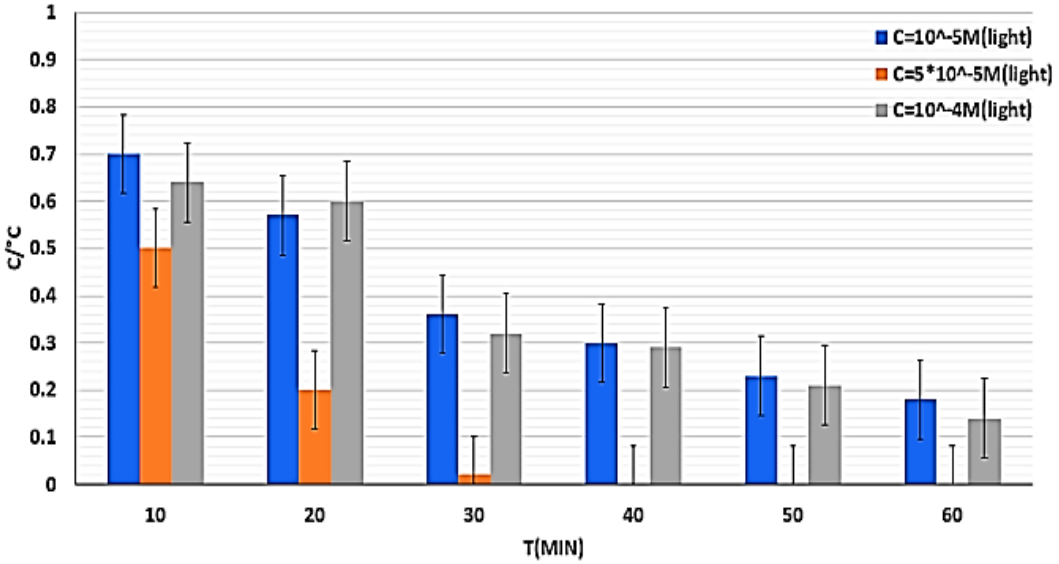


Figure 8. The effect of the initial concentration of the pollutant on MB decomposition rate.

Thus, it is noticed that there is a compatibility between the concentration of the pollutant and the concentration of the photocatalyst so that the largest possible dissociation speed is achieved, and the two best concentrations in working conditions are 1mg/ml of the photocatalyst and $5*10^{-5}$M of the pollutant. When the MMT-mAmCs composite is utilized as a catalyst, the optimal initial concentrations of CV and MB were $118*10^{-}4$ M and $137*10^{-4}$ M, respectively [14]. Another study is used Sn/Si mixtures as a catalyst, where the best initial concentrations of CV and MB were $36*10^{-}4$ M and $30*10^{-4}$ M, respectively [25]. As a result, the present model with a TiO_2 catalyst performs well in low pollution levels.

3.4 Kinetics models and isotherm

To characterize the sorption effectiveness in terms of stability over time, type of CV and MB interaction and binding mechanism with TiO_2, and adsorption rate, the kinetic research of MB and CV adsorption was explored. The elimination of CV and MB was carried out at starting concentrations of $5*10^{-5}$M ppm, pH = 9, and intervals of 30–60 min. According to the findings, the sorption was rapid in the first 30 minutes due to the large number of active surface locations. Comparatively, the adsorption to removal rate stabilized after 30 minutes, as previously discussed in the analysis of the time parameter. To suit the data and look into potential rate-controlling of CV and MB Removal mechanisms under ideal removal conditions, two typically kinetic versions the pseudo 1st and 2nd order versions were used in the following linear forms. The pseudo 2nd order paradigm is used to assess the nature of sorbent-sorbate interaction and a rate-limiting stage in accordance with the following equations, whereas pseudo 1st order type is typically employed to determine the sorption behavior in a solid-solution system [26-29]:

$$\text{Log}\,(q_e - q_t) = \text{Log}\,qe - (k_1/2.3) * t \quad (1)$$

$$t / q_i = 1 / k_2 q_e^2 + (1 / q_e) * t \quad (2)$$

The first and second rate invariables are denoted by k_1 and k_2, respectively. qe and qt are the adsorbed quantities of MB and CV at steady-state step and t is the time. The slope and intercept of the $\log(q_e-q_t)$ and t/q_t versus time plots can be used to find these constants. According to R^2 values, the adsorption of MB and CV dyes fulfills the pseudo 2nd order, as illustrated in Table 3. Therefore, chemical adsorption is employed by TiO_2 to adsorb and remove MB and CV. This trend could be caused by the MB and CV's quick binding to TiO_2 surface-active sites and the rising CV and MB transfer/diffusion rates. Similar to how the CV and MB's rate constants appear to be influenced by chemisorption interactions, where the higher sorption rate is further supported by the high value of k_2. The pseudo-first order's linear fitting is sufficient. ($R^2 \geq 0.79$). As an outcome, for CV and MB dyes, the observed q_e values are close to the experimental adsorption capacity of TiO_2.

Table 3. Factors of the pseudo-first- and second-order paradigms for the elimination of dyes pollutant

Pollutant	Pseudo 1st order		Pseudo 2nd order	
CV	K_1 $(min)^{-1}$	0.033	K_1 $(min)^{-1}$	0.0011
	q_e (M)	0.00005	q_e (M)	0.000025
	R^2	0.83	R^2	0.88
MB	K_1 $(min)^{-1}$	0.025	K_1 $(min)^{-1}$	0.0125
	q_e (M)	0.00005	q_e (M)	1.6*10-5
	R^2	0.79	R^2	0.85

The present investigation uses two widely used isotherm versions (Langmuir and Freundlich) to examine the equilibrium between the TiO_2 surface-active sites and the MB and CV in aqueous phases throughout the process of adsorption. By examining the relationship between q_e and C_e, which illustrates the heterogeneous

character of the TiO_2 surface, Freundlich isotherm illuminates the adsorption nature of heterogeneous systems in multilayer physical interaction. Information on the equilibrium stage between the CV, MB, and TiO_2 adsorbent is provided via the Freundlich equation. The adsorption characteristic of homogeneous systems in monolayer is defined by Langmuir's model as a chemical interaction. Under the optimal conditions for sorption, the isotherm investigation for TiO_2's removal of polluting dyes was carried out at various CV and MB concentrations ranging from 10^{-4} to $5*10^{-5}$ M. At this point, using the linear Langmuir and Freundlich models, the essence of the CV and MB interaction with TiO_2 during the equilibrium phase was examined according to the following equations [30-32]:

$$C_e / q_e = (1 / k_L Q_o) + (1 / Q_o) C_e \quad (3)$$

$$R_L = 1 / (1+k_L C_o) \quad (4)$$

$$\ln q_e = \ln k_f + (1/n) \ln c_e \quad (5)$$

The maximum properties of TiO_2, the adsorption equipoise constant, constants relating to TiO_2's capacity for sorption and adsorption strength are Q_o, K_L, K_F and n respectively. These variables were established using the slope and intercept of the derived linear figures, and they were then documented in Table 4. According to correlation coefficients (R^2), the Langmuir isotherm model (0.995 and 0.997) suited the investigative data acquired precisely, in contrast to the Freundlich isotherm model, which showed a low value of R^2. The highest possible adsorption capacity Q_o is 0.00007 M. The Q_o value is close to the experimental values for both the CV and MB, which are 0.00005 M. According to the results, 1 mg/l of utilized TiO_2 adsorbent can therefore adsorb around 0.00007 M of CV and MB. According to the information acquired, CV and MB adsorption are reversible since their K_L values are less than 1, which is revealed by the data. Additionally, values of 1/n are less than 1, indicating that CV and MB are chemisorbent adsorption. The R_L value found below 1 suggests that adsorption is advantageous. The analysis concluded that the dyes CV and MB were adsorbed and formed a monolayer on the uniform TiO_2 surface. Through chemical bonding, the adsorbed CV and MB joined the active TiO_2 sites. TiO_2 is an excellent adsorbent with a high capacity for sorption, making it an ideal choice for removing the dyes pollutant.

Table 4. Factors of Langmuir and Freundlich isotherm for removal of dyes pollutant

Pollutant	Langmuir		Freundlich	
	k_L (l/mg)	0.045		
	q_m exp(M)	0.00005	K_F ($mg^{1-(1/n)}$ $l^{1/n}$ / g)	25.34
CV	Q_o (M)	0.00007	N	2.63
	R_L	< 1	1 / n	0.38
	R^2	0.995	R^2	0.981
	k_L (l/mg)	0.066		
	q_m exp(M)	0.00005	K_F (l/mg)	56.65
MB	Q_o (M)	0.00007	N	4.16
	R_L	< 1	1 / n	0.24
	R^2	0.997	R^2	0.919

4. Conclusions

Photocatalysis is one method that might be used to clean water, and it is particularly effective in getting rid of different organic pollutants like dyes, pesticides, and aromatic chemicals in general. The production of potent catalysts is necessary for photocatalysis, with hydroxyl radicals serving as the primary catalyst. The results of the investigation demonstrate that a wide range of organic pollutants are rapidly and vigorously oxidized. This study demonstrates the great effectiveness of the catalytic photochemical dissociation approach employing TiO_2 for the two pollutants in practical settings, where after an hour of irradiation the two pollutants had completely disappeared from their aqueous medium. The TiO_2 photocatalyst required a focus of 1 mg/l in two situations dark and light applied. By adjusting the medium's pH, the greatest speed is achievable, since an alkaline pH resulted in a rapid rate of dissociation. Since the pollutant concentrations are $5*10^{-5}$M, the technology's efficiency is dependent on the pollutant's beginning concentration. The findings of the kinetics investigation for the dyes CV and MB show that the measured q_e values are nearly equal to the experimental TiO_2 adsorption capacity. TiO_2 is a good adsorbent with a high capacity for sorption, making it an appropriate choice for eliminating the dyes pollution, according to the findings of the Langmuir and Freundlich analysis.

Conflict of interest

The authors declare that they have no conflict of interest.

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