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Abstract: Multi-walled carbon nanotubes/titanium dioxide nanocomposites MWCNTs/x%TiO₂ with different weight ratios of TiO_2 (x = 3, 6 and 10%) have been synthesized using a simple modified evaporation method. The structure of the synthesized nanocomposite photocatalysts were characterized using XRD, SEM, N₂ adsorption-desorption and diffused reflectance UV-Vis spectroscopic techniques. The photocatalytic activity of the synthesized photocatalysts toward decontamination of two local textile dyes (Dianix Blue and Vat Green 1 Dyes) as an industrial organic pollutants commonly used in dyeing factories in Egypt. Moreover, the suggested possible mechanism of the photodegradation processes was studied. Also optical band gap was estimated by Kubelka-Munk equation for MWCNTs and MWCNTs/x%TiO₂ (x = 3, 6 and 10%) giving rises values 3.51, 2.89, 2.80, 2.69 eV respectively. The photodegradation of the two textile dyes after complete degradation were measured using chemical oxygen demand processes.

Keywords: MWCNTs/x%TiO₂ Nanocomposites, Dipping Method, Photocatalytic Activity, Dianix Blue Dye, Vat Green 1 Dye.

I. INTRODUCTION

Carbon nanotubes (CNTs) have attracted a lot of attention as a result of their mechanical properties, novel 1D (nanotube) character, unique properties and promising potential applications [1-7]. The uniformity in diameter, the dearth of purity, chirality and alignment has hindered searching of the intrinsic properties such as electronic, mechanical, sorption properties of CNTs in addition to their applications in novel electronic systems [8-12]. In last decades, various researches have been devoted to study the structure of CNTs and their high level surface area, stability toward electrochemical processes, thermal and electrical properties. Due to their exceptional properties, CNTs were introduced as applicants for excellent environmentally friendly uses such as filtration in separation techniques. CNTs have been used in removing hazardous pollutants from wastewater in industrial field such as leather and textile [13]. Due to its effectiveness, ideally producing nontoxic end products and easy operation, photocatalysis has been commonly used as a technique for the removing of industrial hazardous pollutants. TiO_2 (anatase) as a semiconductor with direct bandgap of 3.18 eV (wavelength, lower than 388 nm), has been used as an active photocatalyst. The quick recombination problem of photogenerated charge carriers (electron-hole pairs), alters photocatalytic efficiency and reduces the quantum efficiency of the photocatalytic process. Therefore, in recent years, many authors have been designed and developed nanocomposites including TiO₂ to avoid this problem and the pairing effect of MWCNTs with TiO_2 has been presented to provide a synergistic effect which can enhance the overall reaction of the dyes photodegradation [14-20], also TiO_2 can combined with other materials to like multi-nano walled carbon nanotubes to obtain good performance as photocatalyst [16]. The prepared nanocomposites were evaluated for the photodegradation of the Dianix Blue and Vat Green 1 Dyes under Sunlight, UV and Xenon lamps as well as the degree of complete mineralization of the two dyes were assessed.

A. Materials

II. EXPERIMENTAL

Dianix Blue Dye (4,8-diamino-1,5-dihydroxy-2-(4-hydroxyphenyl)-4a,9a-dihydroanthracene-9,10-dione) molecular weight 362.34 and the molecular formula $C_{20}H_{14}N_2O_5$ and Vat Green 1 Dye (Anthra[9,1,2-cde] benzo[rst]pentaphene-5,10- dione, 16,17- dimethoxy) with molecular weight 516.54 and the molecular formula $C_{36}H_{20}O_4$, both of these dye used in dyeing process in Egyptian Spinning & Weaving Company, Cairo, Egypt. Sulphuric acid (H₂SO₄) 3M, nitric acid (HNO₃) 2M, TiO₂ (Degussa P25) and deionized water. All purchased from SCRC, China and Merck and all chemical reagents were of analytical grade and used without further purification.



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B. Measurements Techniques

- Scanning Electron Microscopy (SEM): Characterizations of the surface morphology of MWCNTs and MWCNTs/x%TiO₂ nanocomposites were observed through Scanning Electron Microscopy (SEM) performed using Philips XL-30 SEM analyzer (JEOL – JSM – T330 A) with an acceleration voltage 30 KV instrument.
- 2) X-ray Diffraction (XRD): XRD patterns were recorded by Philips Holland. Xpert MPD model using Cu-K α target. (Cu K α radiation = 0.154 nm, 50 kV, 40 mA; data recorded at a 0.017 \Box step size, 100 s/step).
- 3) UV-Vis Spectrophotometers: UV-Vis spectroscopy was conducted to monitor the concentration of some organics in liquid phase, which were being oxidized through photocatalytic degradation. The concentration of the investigated dyes after photodegradation was analyzed using a UV-Vis spectrophotometer (Schimadzu)
- 4) *Chemical Oxygen Demand (COD):* The chemical oxygen demand COD is based on the chemical decomposition of compounds, dissolved or suspended in water by using COD Hanna Professional Instrument.
- 5) *Photochemical Reactors:* The experimental setup was employed for the photocatalytic studies by using both of photoreactors 80-W UV-lamp and 50-W Xe-lamp (Eng. Co., Ltd., Egypt). Sunlight intensity for our photodegradation processes was nearly about 3.4 lux for UV light and 1009 lux for visible light, was measured by (Lx-102 light meter).

C. Synthesis of MWCNTs and MWCNTs/x%TiO2 nanocomposites

- 1) Synthesis of MWCNTs: High purity MWCNTs were synthesized according to the literatures previously reported with some modification [21]. In the present paper, MWCNTs were prepared by CVD method. The reactants were vaporized into a hydrogen/argon atmosphere at 720 \Box . The MWCNTs as well as residual iron catalyst particles were removed by annealing the as-grown MWCNTs in argon at 1750 \Box for 5 h. The production yield, which indicates the yield of multi-walled carbon nanotubes in the converted carbon, reaches 95%. One gram of MWCNTs was dispersed in the mixed acids consisting of 30 mL of concentrated H₂SO₄ and 10 mL of concentrated HNO₃ with ultrasonication for 7 h to activate the surfaces, then washing and drying at 100 \Box .
- 2) Synthesis of MWCNTs/x%TiO2 nanocomposites: MWCNTs/x%TiO₂ nanocomposites were prepared by a simple modified evaporation method. MWCNTs were dispersed in water in a 200-mL beaker and sonicated for 30 min. TiO₂ (Degussa P25) powder, Anatase and Rutile mixture (78%:22%) was added to MWCNTs suspension at different ratios of 1, 3, 6 and 10% (MWNT:TiO₂) during sonication. The suspension was filtered by using a vacuum evaporator to accelerate the water evaporation rate at 45 \Box . Then, the MWCNTs/x%TiO₂ composite was dried at 105 \Box for 24 h to avoid any probability of physicochemical change in the carbon materials may occurs in the presence of oxygen at higher temperatures.

D. Photocatalytic Processes

The photocatalytic processes of Dianix blue and Vat green 1 dyes were carried out using advanced oxidation processes (AOP's) with different light sources such as Sunlight, UV and Xenon irradiation without photocatalysts, and With different amount of photocatalysts MWCNTs, MWCNTs/3%TiO₂-MWCNTs/6%TiO₂-MWCNTs/10%TiO₂ nanocomposites with the different illumination sources for various irradiation times to identify the most suitable and economical process for complete decolourization and substantial mineralization of the two textile dyes. The effect of various experimental parameters such as irradiation time, photocatalyst concentrations, substrate concentrations of the dyes were carried out to arrive the optimized experimental conditions. To study the effect of substrate concentration, the photocatalytic degradation experiments were carried out at the optimized photocatalyst concentrations. For this the substrate concentrations, i.e. concentrations of Dianix Blue dye were varied from 2.8×10^{-5} M to 2×10⁻⁵ M and concentrations of Vat Green 1 dye were varied from 2.2×10⁻⁵ M to 1.6×10⁻⁵ M. The photodegradation experiments were carried out in the photoreactors in which 100 ml of both of the two textile dye solutions were taken and the photocatalyst concentrations were 0.1g/100 ml for all photocatalytic processes. The solutions were agitated with the help of aeration pump and magnetic stirrer. On the other hand study of the effect of irradiation time of photocatalytic degradation experiments were carried up to 7 h. The effect of the catalyst concentration was studied by varying the amounts of MWCNTs/3%TiO₂, MWCNTs/6% TiO₂ and MWCNTs/10% TiO₂ nanocomposites with the irradiation with Sunlight, UV and Xenon lamps. For each experiment, the aliquot was taken out after a certain time with the help of the Pipet, which was then filtered and analyzed for its concentration with Schimadzu UV-Visible spectrophotometer to study the decolourization and degradation progress. The experimental setups were employed for the photocatalytic studies by using both of photoreactors 80-W UV-lamp and 50-W Xelamp (Eng. Co., Ltd., Egypt) and sunlight intensity of photodegradation processes was nearly about 3.4 lux for UV light and 1009 lux for visible light measured by (Lx-102 light meter). The concentration of the investigated dyes after photodegradation were



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analyzed by using a UV-Vis spectrophotometer (Schimadzu) by measuring the change in their maximum absorbance values at 625 nm for Dianix Blue dye and at 626 nm for Vat Green 1 dye. Also the mineralization of the dyes was confirmed by COD analysis.

III.RESULTS AND DISCUSSION

A. Characterizations and Measurements

 XRD patterns of MWCNTs and MWCNTs/x%TiO₂ Nanocomposites: The characteristic peaks around 25.7° and 41.9° appeared in XRD patterns as shown in (Figure - 1 (a)) were correspond to the (002) and (100) planes respectively reflected on the prepared MWCNTs. The obtained results were resemble to the previous works [19, 22]. On the other hand the characteristic peaks observed in XRD patterns for MWCNTs/x%TiO₂ nanocomposites as shown in (Figure - 1 (b), (c) and (d)) located at 20 = 25.17°,36.48°,48.84°,54.66° and 62.37°, correspond the (101), (004), (200), (211) and (204) planes respectively reflected on the prepared MWCNTs/x%TiO₂ nanocomposites. The shifts of the peaks is as a result for the trapping of the electrons at the active sites of the nanocomposites, which results in hindering electron-hole pair recombination [23, 24].



Fig.-1 Shows XRD patterns of the prepared MWCNTs and different MWCNTs/TiO2 nanocomposites.

2) Morphological study of MWCNTs and MWCNTs/x%TiO₂ nanocomposites surfaces: The surface morphologies of the prepared MWCNTs and MWCNTs/x%TiO₂ nanocomposites were measured by Scanning Electron Microscopy (SEM) as shown in (Figure - 2). It explains the different morphology between the prepared samples and indicates that the MWCNTs/x%TiO₂ nanocomposites present a homogeneous distribution of TiO₂ on the MWCNTs surface and less agglomeration of TiO₂ particles on MWCNTs surface, suggesting a strong interphase structure effect between TiO₂ and MWCNTs. So as to increase the surface area of the nanocomposites, so it was considered that MWCNTs/x%TiO₂ nanocomposites could perform much more activity and show a high photocatalytic activity. The patterns demonstrate the highly crystalline nature of the nanocomposites. It can be clearly seen that the surfaces of TiO₂ modified with MWCNTs are rough and little TiO₂ particles were dispersed on the MWCNTs enhancing the TiO₂ in photocatalytic activity of the nanocomposite.



Fig.-2 Shows SEM images of the prepared MWCNTs and different MWCNTs/TiO₂ nanocomposites.



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3) The optical band gaps of MWCNTs and MWCNTs/x%TiO₂ Nanocomposites: The band gap energy of the prepared MWCNTs and its composites was determined using UV-Vis diffuse reflectance spectroscopy in Kubelka-Munk units. The nanocomposite material can absorb almost the entire range of visible region, which is caused by the addition of MWCNTs. For a semiconductor materials, the investigation of optical absorption is considered as an appropriate method for calculation of the optical band gaps and determining the kinds of transitions. The diffuse reflectance (R) converted into equivalent absorption coefficient F (R) using Kubelka–Munk equation (equation 1) [25], it may be written as in (equation 2):

$$F(R) = \frac{(1-R)^2}{2R}$$
(1)

$$\left(\frac{(1-R)^2}{2R},E\right)^{1/n} = (F(R).E)^{1/n}$$
 (2)

Where (E) energy of light, n is an inter number = $\frac{1}{2}$ and 2 for direct and indirect allowed transitions, respectively, which characterizes the transition process, thus giving direct and indirect bandgaps. The band gap for the photocatalysts may be determined from the plot of $(F(R).E)^{1/n}$ versus energy of light (E) measured in eV, from the intersection of the tangent via inflection point in absorption band and the photon energy axis. Optical energy band gap was calculated using Tauc relation (see equation 3):

$$(\alpha hv)^{1/n} = B (hv - E_g)$$
(3)

Which may be written as the equation (4):

$$(F(R) \cdot E)^{1/n} = B(h\nu - E_g)$$
 (4)

where $n = \frac{1}{2}$ and 2 for direct and indirect transitions, respectively, α is (absorption coefficient), h is (a Planck constant), v is (light frequency), B is (a constant independent on the photon energy but depends on the transition probability) and E_g the optical band gap. The band gap energy for all the samples may also be measured by the same method from the plot of $(\alpha hv)^{1/n}$ versus (hv) energy of light, this also depended on the intersection of the tangent via inflection point in absorption band and the photon energy axis as shown in (figure - 3). Where for allowed direct transitions, $n = \frac{1}{2}$, equation (3) become:



Figure 3. Kubelka-Munk curves for estimating band gap of (a) MWCNTs and (b, c and d) MWCNTs with different TiO2 % (3, 6 and 10%), respectively.



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Photocatalyst	band gap (eV)
MWCNTs	3.51
MWCNTs/3%TiO ₂	2.89
MWCNTs/6% TiO ₂	2.80
MWCNTs/10%TiO2	2.69

Table-1: Band gap values of MWCNTs and different MWCNTs/TiO₂ nanocomposites

The optical band gap energy calculated values are shown in Table-1. The E_g value of MWCNTs was 3.51 eV; it decreases to 2.89 eV for MWCNTs/3%TiO₂ and to 2.80 eV for MWCNTs/6%TiO₂ until it reaches to 2.69 eV for MWCNTs/10%TiO₂. This effect may be due to two reasons, an increase in vacancies or chemical defects present in the intergranular areas, also due to the chemical interaction between MWCNTs and TiO₂ to generate a new energy level reducing the band gap E_g . MWCNTs/x%TiO₂ nanocomposites with less band gap energy are optically active, have been extensively used in photocatalytic degradation for environmental decontamination. The decrease in band gap values suggests high photocatalytic activity of the synthesized nanocomposites in visible light range. From the obtained values, it is clear that the band gap values depend on both MWCNTs support and the TiO₂ percentages in the binary nanocomposites. The variation of the band gap with increasing the particle size is an important feature for photocatalytic activity of MWCNTs/x%TiO₂ nanocomposites [26, 27]. The interaction between MWCNTs and TiO₂, so the photocatalytic efficiency of the nanocomposites was enhanced.

4) Brunauer-Emmett-Teller surface area of the synthesized MWCNTs and MWCNTs/x%TiO₂ nanocomposites: Table-2 presents the surface area Brunauer-Emmett-Teller (BET) (m²/g), Average pore diameter (nm), Total pore volume (cm³/g) and Monolayer adsorption amount V_m of the MWCNTs and MWCNTs/x%TiO₂ nanocomposites. The BET surface area of MWCNTs, MWCNTs/3%TiO₂, MWCNTs/6%TiO₂ and MWCNTs/10%TiO₂ are 95.201, 98.142, 104.251 and 117.125 m²/g respectively (see Table-2).

	1		-	1
Photocatalyst	MWCNTs	MWCNTs/3%TiO ₂	MWCNTs/6%TiO ₂	MWCNTs/10%TiO ₂
BET (m^2/g)	95.201	98.142	104.251	117.125
Total pore volume	0.2139	0.2089	0.2001	0.1939
(cm^{3}/g)				
Average pore	8.987	9.181	9.301	9.521
diameter (nm)				
$V_{\rm m} ({\rm cm}^3/{\rm g})$	21.843	22.148	22.800	23.113

Table-2: BET parameters of MWCNTs and different MWCNTs/TiO₂ nanocomposites

The BET surface areas and porous structures of MWCNTs and its nanocomposites were investigated using nitrogen adsorption-desorption isotherms.



Figure - 4 displays the nitrogen adsorption-desorption for all photocatalysts.



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All the photocatalysts represent type IV curves showing a typical hysteresis loop associated with capillary condensation of gases within mesopores [28]. Such mesoporous structure of photocatalysts provides efficient transport pathways to the interior, which may be useful for improving the photocatalytic activity. The smaller micro/mesopores are usually related to the primary intraagglomeration (the hysteresis loop located in the lower P/P_0 range), while the larger ones are associated with secondary interaggregation (the hysteresis loop located in the higher P/P_0 range). With a further increase in the amount of TiO₂, however, this peak increases and broadens. This phenomenon indicates that there is a correlation between the loading of TiO₂ and pore size distributions of MWCNTs/x%TiO₂ nanocomposites. The adsorption isotherms shifts upwards and the hysteresis loop as well moves to a relatively low pressure range. From pore size distribution analysis for all samples, it observed that the smallest average pore diameter for MWCNTs which have the smallest surface area while with increasing amount of TiO₂ led to increase surface area because of increasing its average pore diameter as shown in Table-2. These data confirmed that the band gap decreasing in presence of TiO₂ and in rising its amount. This indicates that the increase of specific surface area and average pore size of the nanocomposites (Table-2) increased the photocatalytic activity of the photocatalysts that accelerated the mass transfer and generated the more reactions sites which led to the photocatalysis.

B. Photocatalytic performance of MWCNTs and MWCNTs/x%TiO₂ as a photocatalysts

1) Study of the Effect of the Initial Dye Concentration: The maximum absorption peaks of Dianix Blue dye and Vat Green 1 dye were located at 625 nm and 626 nm respectively. Figure - 5 (a) and (b) show that there are a positive correlation between the absorbance and the corresponding concentration of the two dye solutions. From the following figure, the suitable concentrations of the two dyes (a) and (b) used in the photodegradation processes were 2.6×10^{-5} M and 2×10^{-5} M respectively.



Fig.-5 Effect of concentration of Dianix Blue and Vat Green 1 dyes

2) Photocatalytic degradation of Dianix Blue and Vat Green 1 dyes using different light sources (Sunlight, UV and Xenon irradiation).

The photocatalytic degradation rates of the two dyes Dianix Blue and Vat Green 1 using Sunlight, UV and Xenon irradiation was monitoring spectrophotometrically in UV–Vis range as shown in Figure - 6, according to equation (6).

$Ln (C_0/C) = k_{app}t$

(6)

where C_0 is the initial concentration of the dye, C is the concentration at time t and k_{app} is the apparent reaction rate constant of the photodegradation process [20]. From the Figure-6 a linear relationships were obtained between ln (C_0/C) and irradiation time. The photocatalytic experiments of the two dyes follow the pseudo first order kinetics. Three sets of experiments for each dye were performed using three types of light sources (Sunlight, UV and Xenon) respectively in presence of MWCNTs and MWCNTs/x%TiO₂ nanocomposites (where x=3, 6 and 10) to observe the adsorption and photocatalytic effects of MWCNTs on the synthesized nanocomposites, the BET surface area of MWCNTs and MWCNTs/3%TiO₂, MWCNTs/6%TiO₂,MWCNTs/10%TiO₂ are 95.201, 98.142, 104.251 and 117.125 m²/g respectively (see Table-2). There is rapid recombination between conduction band



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electrons and valence band holes in TiO_2 photocatalyst. However, after introducing the MWCNTs in the synthesized MWCNTs/x%TiO₂ nanocomposites, the photocatalytic activity was enhanced and increased, this can be attributed to the synergetic effects of adsorption on multi walled carbon nanotubes in MWCNTs/x%TiO₂ nanocomposites. This enhancement in photocatalytic activity of the nanocomposites supports the idea of formation of a common contact interface between the multi walled carbon nanotubes and TiO₂ in the nanocomposite, where MWCNTs acts as an efficient adsorption trap of the two dyes, this led to rapid photocatalytic degradation.

The slopes which represent the photocatalytic reaction rate constants (k_{app}) and the synergy factors (R) were calculated, the products of the photodegradation processes using Chemical Oxygen Demand (COD) values were measured, all values are listed in Table-3. Comparing the k_{app} for all photodegradation processes of the dyes using MWCNTs, MWCNTs/3%TiO₂, MWCNTs/6%TiO₂, MWCNTs/10%TiO₂ photocatalysts, The photodegradation rate increases greatly in the existence of MWCNTs and in the order of MWCNTs-MWCNTs/3%TiO₂-MWCNTs/6%TiO₂-MWCNTs/10%TiO₂ respectively, where The BET surface area of MWCNTs and MWCNTs/3%TiO₂, MWCNTs/6%TiO₂, MWCNTs/10%TiO₂ are 95.201, 98.142, 104.251 and 117.125 m²/g respectively (see Table-2) and depending on the TiO₂ percent in the nanocomposites, where increasing of the photogenerated charge carriers (electron-hole pair) led to high photocatalytic e ciency. As expected when TiO₂ is exposed to photons and the electrons are transfer from the valence band (VB) to the conduction band (CB) resulting in the formation of equal numbers of holes in the valence band, as in (equation 7).

$$\mathrm{TiO}_2 + \mathrm{h}\nu \to \mathrm{h}^+ + \mathrm{e}^- \tag{7}$$

The electrons in the CB react with O_2 to yield superoxide anion radicals O_2^{-1} that oxidize the two dyes under investigation according to (equation 8).

$$e^{-} + O_2 \rightarrow O_2^{-}$$
 (8)

On the other hand, the adsorbed water or hydroxyl anions were reacted with the holes of the VB to produce hydroxyl radicals as in equations (9) and (10).

$$\begin{array}{ll} H_2O + h^+ \rightarrow H^+ + OH & (9) \\ OH^- + h^+ \rightarrow OH & (10) \end{array}$$

The generated hydroxyl radicals attack the organic dyes adsorbed onto the photocatalyst surface in solution and oxidized them [29, 30]. The hydroxyl radical which produced from the oxidation of adsorbed water or OH during the degradation of the organic dyes is considered as the primary oxidant; as well dissolved oxygen in solution alter the recombination of (h⁺- e⁻ pairs). From the results of MWCNTs exist in the prepared nanocomposites, causing an increase in the decolourization rate as shown in Figure-6, multi-walled carbon nanotubes MWCNTs with excellent adsorption capacity enhance the lifetime of the separated charge carriers, hindering (electron e^{-} - hole h^{+} pair) recombination of the synthesized nanocomposites more than TiO₂ alone and provide an increase in synergistic effect in all photodegradation processes of the dyes using nanocomposites than TiO₂. The possible role of MWCNTs in the prepared nanocomposites on the photocatalytic processes could be investigated due to the generation of electrons (e) by different light sources which transferred to conduction band of TiO₂ (MWCNTs act as electron source), in the same time the electrons of TiO₂ were transferred to MWCNTs (MWCNTs act as electron sink) simultaneously. In other hand, the holes (h⁺) generated during the induced electrons migrated from MWCNTs to TiO₂. The transferred electrons (e) from MWCNTs to TiO₂ could react with the O_2 adsorbed on the surface of TiO_2 to produce very active superoxide anion radicals. The produced superoxide radical ions, the positive charged holes (h^+) could react with OH or adsorbed H₂O to produce hydroxyl radicals. The produced superoxide radical ions O_2 and hydroxyl radicals OH were responsible for the photodegradation of the dyes. The dominant contribution of MWCNTs in MWCNTs/x%TiO₂ nanocomposites is mainly determined by an increase in recombination time for photogenerated h⁺- e⁻ pairs. MWCNTs can act as an electron sink leading to (h⁺- e⁻ separation) because of its delocalized π electronic structure that facilitates the transfer of photogenerated electrons as shown in Figure-7. The injected electrons are transferred to the oxygen O_2 to generate the highly active superoxide anion radical O_2^{-} , helping the photodegradation process of the dyes adsorbed on MWCNTs surface. Also, due to the interphase interactions between TiO₂ and MWCNTs in the synthesized MWCNTs/x%TiO₂ nanocomposites, the photocatalytic activity of the nanocomposites were improved.



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Figure-6 shows pseudo first order linear plots of $\ln (C_0/C)$ vs. irradiation time for the degradation kinetics of Dianix Blue dye (a, c and e) and Vat Green 1 dye (b, d and f) under different Sunlight, UV and Xenon irradiation, respectively.



Figure-7 shows schematic diagram of the proposed mechanism of photocatalytic degradation over MWCNTs /TiO₂ nanocomposite. 3) The synergy factor (R) of MWCNTs: The synergy factor (R) is expressed as in equation (11).

$$R = \left(\frac{\text{kapp}(\text{MWCNTs/x\%TiO2})}{\text{kapp}(\text{MWCNTs})}\right)$$
(11)

Where k_{app} (MWCNTs/x%TiO₂), k_{app} (MWCNTs) refers to the apparent rate constant for the photocatalytic activity in the existence of the nanocomposite and MWCNTs respectively [20, 27]. The photocatalytic activity of the dyes depends on the adsorption on the surface of photocatalysts. Table-3 shows photodegradation rates (k_{app}), synergy factors (R) and Chemical Oxygen Demand (COD) of the two dyes with MWCNTs and MWCNTs/3%TiO₂, MWCNTs/6%TiO₂, MWCNTs/10%TiO₂ nanocomposites in the existence of Sunlight, UV and Xenon irradiation respectively.

Generally, the organic pollutant dyes can't degraded completely under Sunlight irradiation and according to Egyptian Environmental Law (Law NO.9), The COD value allowed is less than 1000 ppm [31, 32]. From the above table, the photodegradation of the two



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dyes under Sunlight in presence of MWCNTs and MWCNTs/x%TiO₂ nanocomposites still had COD (ppm) values higher than the allowed value (1000 ppm). While the photodegradation of the two dyes on the MWCNTs/x%TiO₂ nanocomposites surfaces exposed to both of UV and Xenon light sources recorded COD values less than 1000 (ppm), especially the MWCNTs/10%TiO₂ samples which has COD values less than 1000 (ppm), this indicate that they are used as excellent photocatalysts. It can be seen from Table-3 that the photocatalytic degradation process of the dyes increases with increasing the TiO₂ weight percent in the nanocomposites from 3 to 10% and reaches its maximum at a 10%TiO₂ in the nanocomposite. Also the highest photodegradation rate was observed using Xenon irradiation with MWCNTs/10%TiO₂ nanocomposite, where the number of dye molecules adsorbed on the photocatalysts and the number of photons absorbed were increased which promotes the photodegradation rate.

	1 0					
		Dianix Blue dye				
radiation	Photocatalyst	$k_{app} (s^{-1})$	R	COD (ppm)		
	MWCNTs	0.00571 ± 1.95619E-4	1	2645		
	MWCNTs/3%TiO ₂	0.00622 ± 9.45456E-5	1.089	2470		
	MWCNTs/6%TiO ₂	0.00658 ± 2.44397E-4	1.152	2108		
	MWCNTs/10% TiO ₂	0.00679 ± 1.52953E-4	1.189	1985		
ht i	Vat Green 1 dye					
Sunlig	Photocatalyst	$k_{app} (s^{-1})$	R	COD (ppm)		
	MWCNTs	0.00212 ± 7.95952E-5	1	3785		
	MWCNTs/3%TiO ₂	0.00248 ± 1.03928E-4	1.169	3205		
	MWCNTs/6%TiO2	0.00294 ± 1.11411E-4	1.386	2988		
	MWCNTs/10% TiO ₂	0.00366 ± 1.36129E-4	1.726	2645		
UV irradiation	Dianix Blue dye					
	Photocatalyst	k_{app} (s ⁻¹)	R	COD (ppm)		
	MWCNTs	0.017 ± 3.50919E-4	1	2258		
	MWCNTs/3%TiO ₂	0.02711 ± 0.00111	1.594	1310		
	MWCNTs/6%TiO2	0.03612 ± 5.76817E-4	2.124	1025		
	MWCNTs/10% TiO ₂	0.04213 ± 5.54871E-4	2.478	865		
	Vat Green 1 dye					
	Photocatalyst	k_{app} (s ⁻¹)	R	COD (ppm)		
	MWCNTs	0.00458 ± 1.21127E-4	1	2185		
	MWCNTs/3%TiO ₂	0.00653 ± 1.52995E-4	1.425	1764		
	MWCNTs/6%TiO2	0.00732 ± 2.23643E-4	1.598	1388		
	MWCNTs/10% TiO ₂	0.00929 ± 1.99737E-4	2.028	925		
	Dianix Blue dye					
adiation	Photocatalyst	k_{app} (s ⁻¹)	R	COD (ppm)		
	MWCNTs	$0.02114 \pm 5.88147\text{E-4}$	1	2101		
	MWCNTs/3%TiO ₂	0.03128 ± 0.00119	1.479	1156		
	MWCNTs/6%TiO ₂	0.04332 ± 0.00114	2.049	864		
	MWCNTs/10% TiO ₂	0.05126 ± 0.00168	2.424	714		
l iri	Vat Green 1 dye					
Xenor	Photocatalyst	k_{app} (s ⁻¹)	R	COD (ppm)		
	MWCNTs	0.00795 ± 1.53579E-4	1	1785		
	MWCNTs/3%TiO ₂	0.00973 ± 3.45827E-4	1.223	1325		
	MWCNTs/6% TiO ₂	0.01251 ± 3.55707E-4	1.573	1080		
	MWCNTs/10% TiO ₂	0.01491 ± 5.29326E-4	1.875	897		

Table-3: Photodegradation rates (k_{app}), synergy factors (R) and Chemical Oxygen Demand (COD) values of the two dyes with different photocatalysts in the existence of different irradiation sources.



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IV.CONCLUSION

Semiconductor photocatalysis seems to be a promising technology that encompasses a range of applications in environmental systems such as hazardous waste remediation, air purification. Photocatalytic oxidation using MWCNTs and MWCNTs/3%TiO₂, MWCNTs/6%TiO₂, MWCNTs/10%TiO₂ nanocomposites in the presence of Sunlight, UV and Xenon lights were effectively applied for the photodegradation of Dianix Blue and Vat Green 1 dyes. It can be deduced that the synergistic effect of MWCNTs, the percentage of TiO₂ in nanocomposites, polymorphs of TiO₂ due to the dominant structure which cause high levels of crystalline of the nanocomposites, and the synthesis method of the nanocomposites had a good photocatalytic effectiveness especially the samples MWCNTs/10%TiO₂. Both of the photodegradation rates k (s⁻¹) and the synergy factors (R) were increased, also the photodegradation processes using COD analysis revealed a higher degree of complete mineralization of the dyes from aqueous solutions and follow COD limits of Egyptian Environmental Law (Law NO.9).

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