Journal Homepage: http://ijcpe.uobaghdad.edu.iq
Iraqi Journal of Chemical and Petroleum Engineering
Vol. 26 No. 2 (June 2025) 83 – 91
EISSN: 2618-0707, PISSN: 1997-4884

Comparative study for degradation of Congo red dye from synthetic wastewater by photocatalytic redox reactions using various nanoscale semiconductors

Rusul A. Jassim [a], **Ammar S. Abbas** [a, *]

a Department of Chemical Engineering, College of Engineering, University of Baghdad, Baghdad, Iraq

Abstract

A comparative study for two nanoscale semiconductors (TiO_2 and WO_3) was conducted as heterogeneous photocatalysts to degrade about 50 ppm of Congo red dye in an aqueous solution. The reaction was carried out in a batch reactor placed in a dark box and equipped with an air pump. The dye solution and 0.2 g/L of the catalyst were mixed, firstly, in a dark environment to monitor the amount of adsorbed dye, then the ultraviolet light was turned on with two different powers (15 and 30 W) to study the photocatalytic degradation reactions. The results showed that TiO_2 had higher photocatalytic activity to degrade the dye. The CRD removal values for TiO_2 and WO_3 were 99.67 and 72.16 %, respectively, using 15 W, and the UV power did not have a significant effect on redox reactions according to the observations and the electrical energy consumption. The reaction kinetics study showed that the results obtained followed a first-order kinetics model. A mathematical model was developed based on the recycle ratio approach to study the effects of the recycle ratio and space-time on the Congo red dye removal through the different types of reactors. The simulated results showed that the ideal plug flow reactor performance gave the highest removal in less space-time than the recycle plug flow reactors. The recorded reactor performance decreased with the increasing recycling ratio, and the worst reactor performance was reported for the mixed-flow reactor.

Keywords: Photocatalyst; Advanced oxidation process; Energy consumption; Kinetic study; Reactor design; Recycle ratio.

Received on 10/10/2024, Received in Revised Form on 06/12/2024, Accepted on 06/12/2024, Published on 30/06/2025

https://doi.org/10.31699/IJCPE.2025.2.9

1- Introduction

Heterogeneous photocatalysis is a chemical process that is catalyzed by a semiconductor solid under appropriate lighting conditions. In 1972, Fujishima and Honda began studying the use of semiconductors in solutions, which led to the development of new advanced oxidation processes (AOPs) based on semiconductor photocatalysis and involved irradiation with near-UV-light [1-3]; then researchers studied semiconductors for the potential to the decomposition of many organic waste materials through photocatalysis processes in the last decades [4-6].

AOPs have shown a significant feature as a low-cost, green treatment technology, and in consideration, do not have secondary waste and environmentally friendly products (CO_2 + H_2O), so photocatalysis is a sustainable treatment [7-9]. AOPs are categorized into homogeneous and heterogeneous catalyst reactions; homogeneous catalysts are in the same phase as the reactant, and heterogeneous catalysts have different phases [9, 10]. In most cases, heterogeneous photocatalysis is preferable because of its higher stability, easy separation of catalysts, and the possibility of reusing photocatalysts [11].

Many n-type semiconductors are used as photocatalysts for instance, titanium dioxide (TiO_2), tungsten trioxide (WO_3), cadmium sulfide (CdS), lead sulfide (PbS), zinc oxide (ZnO), ferric oxide (Fe_2O_3), and zinc sulfide (ZnS) in the degradation of various environmental contaminants in wastewater [8, 12, 13]. At the atomic level, semiconductors contain a top void region, the valence band (VB), and a bottom void region, the conduction band (CB). Between VB and CB, there is a void energy region called band gap energy (E_g) [14, 15]. The band gap energy for each semiconductor provides information about the required wavelength of light to excite electrons from the VB to the CB [16]. The considerations of heterogeneous reaction to occur depend on the solid catalyst (semiconductors) and photons absorbed on the catalyst to generate reducing agent holes (h^+) and electrons (e^-) on VB and CB, respectively, led to the formation of hydroxyl radicals ($OH^{\bullet}$) and superoxide anions ($O_2^{-\bullet}$) to degradation organic contaminants [17]. Heterogeneous catalysts can accelerate chemical reactions without any permanent chemical changes in the catalyst, and the process continues to work even at very low concentrations. The advantages mentioned provide savings in water production costs and maintaining the environment clean [18-20].

Binary metal sulfide semiconductors such as CdS, PbS, and Fe_2O_3 are regarded as insufficiently stable for catalysis; they readily undergo corrosion. CdS is also

---

*Corresponding Author: Email: ammarabbas@coeng.uobaghdad.edu.iq known to be toxic. ZnO in illuminated aqueous solutions is also considered unstable due to its being significantly affected by process conditions. While WO_3 has been investigated as a potential photocatalyst, it is generally less active catalytically than TiO_2 [18, 21, 22]. Among the metal oxide photocatalyst materials, TiO2 is a semiconductor considered a superior photocatalytic material because of stability, UV-light activity, low wavelengths in optics, a wide bandgap (3.2 eV), less toxicity, low cost, high reactivity, and chemical stability. The advantages of using TiO_2 as a catalyst have encouraged scientists to conduct research in the field of photocatalysis for the treatment of wastewater [8, 23, 24]. WO_3 is considered inexpensive, earth-abundant, with photocatalytic activity under visible light, a narrow band gap (2.8 eV), low toxicity, and high-oxidizing ability of the h+ in the VB, showing promising photocatalytic performance [25, 26].

Environmental pollution of water sources is caused by rapid population growth and development in different industries [27-30]. The presence of dye could hinder light penetration and oxygen transfer in water bodies and affect human health, producing carcinogenic, mutagenic, allergic reactions, dermatitis, and renal disease [31, 32]. Congo red dye (CRD) is one of the most common synthetic dyes; it belongs to azo dyes, which are known to be non-biodegradable because of the existence of diazo groups [33]. Therefore, more attention is needed to reduce pollutants from industrial wastewater before discharge and ensure degradation is complete [34, 35].

This study aims to perform a comparative study of the degradation of CRD by different suspension photocatalysts (TiO_2 and WO_3), then change the power supply of UV light in the batch reactor to study the effect of power and energy consumption. The kinetics of the redox reaction CRD in aqueous solution will be studied. Also, a simulation model will be developed to study the performance of the ideal plug flow reactor (PFR), recycle PFRs, and ideal mix flow reactor (MFR) based on variation recycle ratio value from zero (ideal PFR) to infinity (MFR), then the effect of different reactor type, catalyst, and the reaction space-time on the CRD removal will be studied.

2- Mathematical model

Mathematical models are essential in chemical engineering, research, and the improvement of plant operations. In this study, a mathematical model was developed for an ideal PFR, recycle PFRs, and MFR to predict and understand the effect of space-time (τ) and recycle ratio (R) on the removal of the dye. The definition of R for recycle PFR was described in Eq. 1 [36].

$$R = \frac{\text{volume of fluid returned to the reactor entrance}}{\text{volume leaving the system}} \tag{1}$$

The general performance equation for PFR can be written as in Eq. 2.

$$\frac{V}{F_{CRDo}} = \int_{X_{CRDo}}^{X_{CRDf}} \frac{dX_{CRD}}{-r_{CRD}} \tag{2}$$

Where V (L) represents PFR volume, F_{CRDo} (L/min) feed rate of the initial concentration of CRD solution, X_{CRDo} initial conversion equals zero at the entrance point, X_{CRDf} final conversion at the output from PFR, and r_{CRD} is the rate of reaction (ppm/min). Eq. 2 can be expressed in terms of τ as shown in Eq. 3.

$$\tau = C_{CRDo} \int_{X_{CRDo}}^{X_{CRDf}} \frac{dX_{CRD}}{-r_{CRD}} \tag{3}$$

Fig. 1 shows a recycle PFR, where F'_{CRDo} would be the feed rate of the initial concentration of CRD solution, and X_{CRD1} of CRD (fresh inlet reactor stream plus recycle stream) as in Eq. 4.

$$F'_{CRDo} = (R+1) F_{CRDo} \tag{4}$$

So Eq. 3 was rewritten by replacing F_{CRDo} by F'_{CRDo} and X_{CRDo} by $X_{CRD1,}$ then substituted Eq. 4 to get Eq. 5.

$$\tau = \frac{C_{CRDo} V}{(R+1) F_{CRDo}} = C_{CRDo} \int_{X_{CRD1}}^{X_{CRDf}} \frac{dX_{CRD}}{-r_{CRD}} \tag{5}$$

The mass transfer did not affect the redox reaction rate of dye degradation utilizing a catalyst with a nanometer particle size, so the r_{CRD} equation is apparently like a first-order reaction, as shown in Eq. 6.

$$-r_{CRD} = k C_{CRD} \tag{6}$$

Where k is the reaction rate constant (min^{-1}), and C_{CRD} is the concentration of the CRD (ppm). For the liquid reactions, the change in density is negligible, so Eq. 7 could be used as a general relation between CCRD and XCRD, and Eq. 6 could be substituted in Eq.5 to get Eq. 8.

$$C_{CRD} = C_{CRDo} \left(1 - X_{CRD}\right) \tag{7}$$

$$\tau = \frac{C_{CRDo} V}{(R+1) F_{CRDo}} = C_{CRDo} \int_{X_{CRD1}}^{X_{CRDf}} \frac{dX_{CRD}}{C_{CRDo} k \left(1 - X_{CRD}\right)} \tag{8}$$

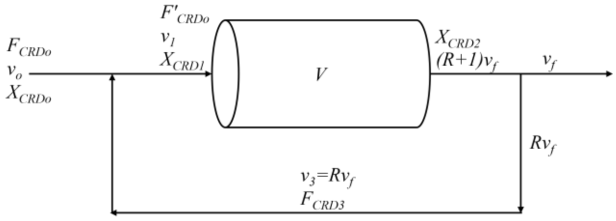

Fig. 1. Notations for the recycle PFR

Then, to get X_{CRD1}, it must be found at the beginning of C_{CRD1} from Eq. 9.

$$C_{CRD1} = \frac{F_{CRD1}}{v_1} \tag{9}$$

C_{CRD1} is the concentration of CRD (ppm) fresh inlet reactor stream plus the recycle stream of PFR F_{CRD1} is the feeding rate (L/min), and v1 is the superficial velocity (m/s).

After that, a material balance for F_{CRD1} and v_1 to substitute in Eq. 9 could be obtained by $C_{CRD1,}$ as shown in Eq. 10.

$$C_{CRD1} = C_{CRDo}\frac{\left(1+R-RX_{CRDf}\right)}{1+R} \tag{10}$$

Therefore, X_{CRD1} can be obtained by substituting Eq. 10 in Eq. 7 to find Eq. 11.

$$X_{CRD1} = \left(\frac{R}{R+1}\right)X_{CRDf} \tag{11}$$

Finally, Eq. 11 is substituted in Eq. 8 and integrated to get Eq. 12, which represents a useful form for the performance equation for the recycle PFR for the first-order kinetics model.

$$k\tau = \left(R+1\right)In\left(\frac{1-X_{CRD1}}{1-\left(\left(\frac{R}{R+1}\right)X_{CRDf}\right)}\right) \tag{12}$$

MFR represents the infinity situation of R, and the general formula is Eq. 13 [36].

$$F_{CRDo}X_{CRD} = \left(-r_{CRD}\right)V \tag{13}$$

The CRD degradation can be found using X_{CRD}, as shown in Eq. 14.

$$CRD\ degradation\ ,\% = X_{CRD} \times 100 \tag{14}$$

3- Experimental work

A cylindrical vessel was used as a photoreactor, which is placed in a closed and dark box made of an aluminum sheet reactor with dimensions 40*50*50 cm^3, as shown in Fig. 2. The 50 ppm CRD solution was prepared by dissolving CRD (analytical grade and purchased from Merck Company) with distilled water. 500 mL of the prepared CRD solution and 0.2 g/L of the suggested catalyst were placed in the reactor. Two semiconductors were suggested as photocatalysts to degrade the CRD in its aqueous solution by a redox reaction: Anatase nano-TiO_2 (Anatase phase, 10-30 nm particle size, purchased from Sky Spring Nanomaterial, Inc.) and nano-WO_3 (particle sizes 30-50 nm, purchased from Hongwu International Group Ltd). Also, a constant flow of air (0.2 L/min) was supplied to the photoreactor to provide dissolved oxygen. Before photocatalyst reactions, a 0.2g/L catalyst powder (TiO_2 or WO_3) was suspended in the natural pH of the CRD solution and stirred in the dark for 60 min. Then, photocatalytic reactions were carried out for 255 min by switching the immersed UV light (wavelength 254 nm) with different powers (15 and 30 W). Stirring the reaction solution continued during the photocatalytic runs to ensure a homogenized suspension of catalysts. A sample of 5 ml was taken at an interval, and the catalyst was separated by centrifuging the sample at 3000 rpm for 30 min. The concentration of CRD was measured by a UV-visible spectrometer (UV-9200, Biotech Engineering Management Co. Ltd., UK) at a wavelength of 500 nm. All experiments were repeated thrice, and the average values were reported.

The degradation of the CRD solution was calculated according to Eq. 15.

$$CRD\ degradation,\ \% = \frac{C_{CRD_o} - C_{CRD}}{C_{CRD_o}} \times 100 \tag{15}$$

Where C_{CRDo} is the initial concentration of CRD (ppm), and C_{CRDf} is the final concentration of CRD (ppm).
The power of UV light is an important factor during the photodegradation process of CRD because, as power increases, the electrical energy consumption (E_{EC}) is calculated according to Eq. 16.

$$E_{EC} = \frac{P \times t \times 10^6}{V \times \left(C_{CRDo} - C_{CRDf}\right)} \tag{16}$$

Where E_{EC} = electrical energy consumed in kWh/kg, P= power of the system UV lamp in kW, t = time in h, and V = treated sample volume in L [27, 37].

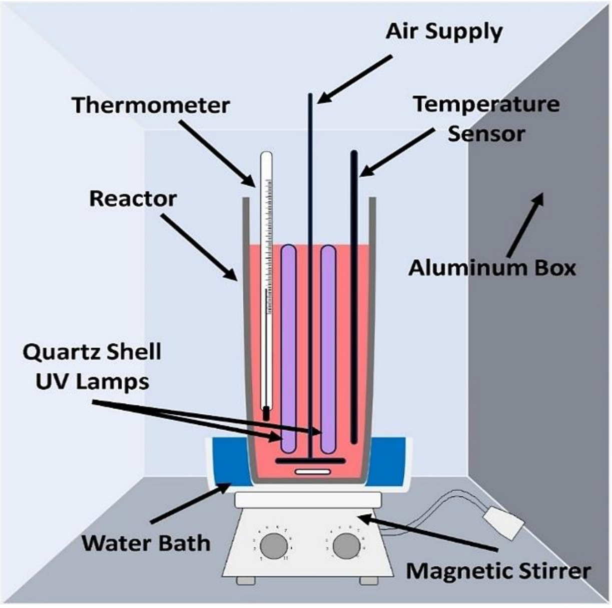

Fig. 2. Schematic system for CRD photocatalytic redox reactions

4- Results and discussion

4.1. The effect of catalyst type, UV power, and E_{EC}

Photocatalytic experiments were carried out to degrade 50 ppm of CRD using a dose of 0.2 g/L of the suggested photocatalysts (TiO_2 and WO_3) to evaluate their performance. Fig. 3 shows the degradation of CRD using TiO_2 and WO_3 with different UV powers. TiO_2 showed a remarkable ability to adsorb the dye (adsorbed about 20 ppm), unlike WO_3, which did not adsorb a large amount of the dye (only 5 to 7 ppm) during the adsorption period, which lasted for about an hour, during which the concentrations reached stable values, indicating saturation of the catalyst surface.

When UV light was applied, the photoreaction time was recorded. A continuous decrease in the CRD concentration was observed after the concentration stabilized during the adsorption stage. TiO_2 showed excellent photocatalytic activity for CRD removal as the dye concentration decreased from about 33.85 and 33.35 ppm to 0.11 ppm after 255 min of irradiation for both UV intensities used (15 and 30 W). Meanwhile, WO_3 showed less effectiveness in removing the dye as the concentration was reduced from 48.7 ppm to 13.56 and 12.66 ppm when using irradiation intensities of 15 and 30 W, respectively. The degradation of the dye can be attributed to the photocatalytic effect of irradiation by UV light, which results in the generation of h^+ and e^-, which participate in the photocatalysis pathway resulting in the generation of radicals ($OH^\bullet$ and $O_2^{-\bullet}$), the radicals were the precursors of the degradation of any organic pollutant. The decomposition of the CRD by radicals can form intermediate compounds of dye, which, on long-term exposure to UV, mineralization, result in the final products CO_2 and H_2O [38-40]. The higher observed photocatalytic activity of TiO_2 for the degradation of CRD is attributed to the wide bandgap energy that absorbs shorter wavelengths, which can produce more energetic reducing agents, h+, and e, on the surface. At the same time, WO_3 has a narrow band gap that can absorb only a small amount of energy.

The amount of CRD removal resulting only from the catalytic redox treatment was calculated and shown in Fig. 4. The amount of removal using TiO_2 is more than the amount of removal using WO_3, while the amount of CRD removal for each catalyst was not affected by the radiation intensity. The CRD removal values were recorded after 255 min of UV irradiation at two intensities (15 and 30 W). The removal rates were very close, with 99.67 and 72.16 % removal of TiO_2 and WO_3, respectively, reported at 15 W light intensity, and 99.67 and 74.00 % removal of TiO_2 and WO_3, respectively, when 30 W light intensity was used. Increasing the UV intensity will increase the photon generation per unit time; thus, the generated photons will enhance the activity of the catalyst surface. However, with increasing light intensity, the number of available active sites on the catalyst surface will remain the same; thus, an excessive increase in light intensity will not contribute to further increasing the reaction rate [38]. The results that were obtained agreed with the previous study on removing CRD [33], malachite green [41], and methyl orange [42].

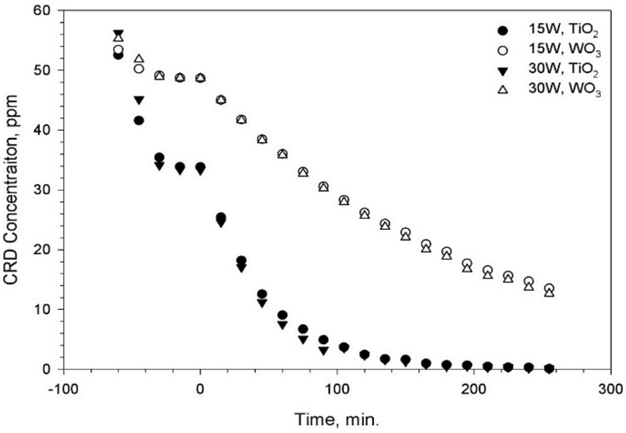

Fig. 3. Adsorption in the dark and the photocatalytic degradation of about 50 ppm CRD using 0.2 g/L of catalysts (TiO_2 and WO_3) under different UV irradiation power (15 and 30 W) at pH=7 and airflow=0.2 L/min

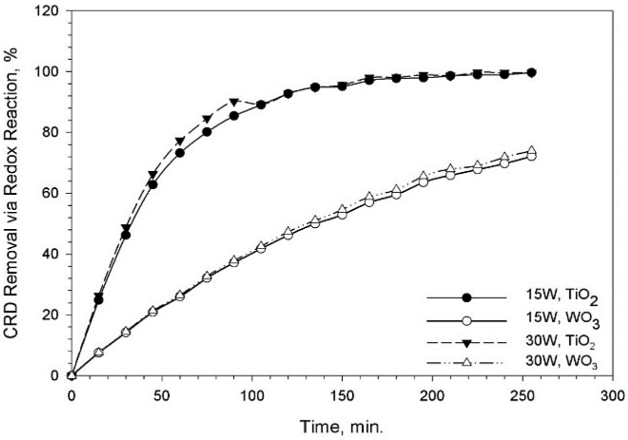

Fig. 4. The comparison of photocatalytic degradation of about 50 ppm CRD using 0.2 g/L of catalysts (TiO_2 and WO_3) under different UV irradiation powers (15 and 30 W) at pH=7 and airflow=0.2 L/min

The amount of E_{EC} was calculated, and the results were summarized in Table 1. The amount of E_{EC} was less when using lower radiation intensity. Using higher radiation energy had approximately no effect on the CRD removal values. Hence, the E_{EC} was a significant parameter to evaluate the efficiency, and 15W UV power was recommended to reduce the E_{EC} and to study the kinetics of the redox reactions.

Table 1. E_{EC} with different UV power and catalyst types

	E_{EC}, kWh/kg of CRD	
Power, W	TiO_2	WO_3
15	2329.72	3943.27
30	4632.41	6781.32

4.2. CRD degradation kinetics

A first-order model was used to investigate the photodegradation kinetics of CRD using TiO_2 and WO_3 semiconductor catalysts. Kinetic data extraction was done using the UV power recommended in the previous section (15 W). The linear form of the first-order kinetic model (Eq. 17) was used directly to determine the reaction rate constant depending on the concentration of the limiting reactant in the redox reaction (CRD).

$$ln\left(\frac{C_{CRDo}}{C_{CRD}}\right)=kt \tag{17}$$

The above model (Eq. 17) is plotted in Fig. 5 for the kinetic data using the two catalysts. The slope of the resulting straight line gives the rate constant (k) for each catalyst, and the correlation coefficient (R^2) was calculated for each of the available data. The results indicate that the rate constant for TiO_2 was 0.2090 min^{-1}, which is about four times higher than the rate constant for WO_3 (0.0051 min^{-1}), and the obtained R^2 was 0.9976 for TiO_2 and 0.9998 for WO_3, indicating the effectiveness of the first-order kinetic model in describing the redox reaction for CRD removal. Also, the resistance to mass transfer is small for these types of reactions and does not significantly affect the constant of the reaction rate [43].

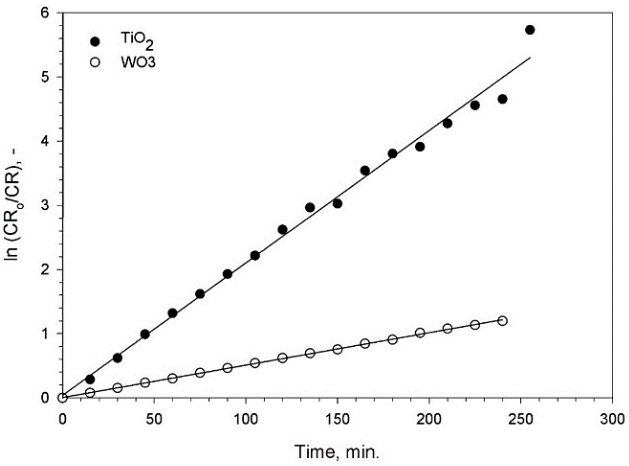

Fig. 5. kinetics for photocatalytic degradation of about 50 ppm CRD using 0.2 g/L of catalysts (TiO_2 and WO_3) under d UV irradiation power 30 W at pH=7, and airflow=0.2 L/min

4.3. Simulation of CRD degradation in continuous reactors

The performance of continuous reactors to degrade CRD by the two photocatalysts (TiO_2 and WO_3) was simulated using the built models. The model described in Eq. 12 was used to simulate the CRD removal via an ideal and recycle PFR, while Eq. 13 was used to simulate the performance of MFR to degrade the CRD in its aqueous solution.

The effect of τ for reactors (up to 300 minutes) was studied on CRD degradation using TiO_2 and WO_3, as shown in Table and Table 3, respectively. Increasing τ caused more CRD degradation for the two catalysts used for all values of R (from zero to infinity). In the ideal PFR (R=0), the CRD degradation values were the highest obtained compared to those obtained in other reactors. The ideal PFR used a TiO_2 catalyst that was able to remove 71.46 % of the CRD within 60 minutes and remove more than 99 % of the dye after 240 minutes. In contrast, when the WO_3 catalyst was used, the ideal PFR was only able to remove 26.36 % within 60 minutes and 78.35 % after 300 minutes. In general, the ability of the PFR with recycle ratios to degrade CRD decreased with increasing R (0.2, 0.5, and 1). However, the decrease in this ability was insignificant when using TiO_2, especially at high treatment times, as the reactor's ability to remove 97.92 % of the CRD within 300 minutes was recorded when using R equal to 1. Whereas the effect of increasing R was more evident in the decrease in reactor performance when using the WO_3 catalyst. The worst performance was observed for the MFR reactor, which is a PFR reactor with an excessive (infinite) recycling ratio. The decomposition ratio was 55.63 % at 60 minutes and reached 86.25 % after 300 minutes when using titanium as a catalyst. The lowest conversion ratios were recorded when using tungsten in the mixing reactor, which was 23.43 % after 60 minutes and increased to 60.45 % after 300 minutes.

The adverse effect of increasing the recirculation ratio on the reactor performance can be explained by the fact that recirculation provides different degrees of back mixing, and therefore, mixing the output stream with the input stream hinders the conversion and decomposition of CRD into intermediate products and then into final products (CO_2, H_2O). Therefore, for the high conversion of CRD to products for all positive orders, PFR is always the more efficient choice because it requires a smaller volume of the reactor for the highest CRD removal [36].

Table 2. CRD degradation for different reactor types (ideal PFR, recycle PFRs, and MFR) using TiO_2

	CRD degradation, % over TiO_2				
τ, min	R=0 (ideal PFR)	R=0.2	R=0.5	R=1	R=∞ (ideal MFR)
60	71.46	68.98	66.29	63.86	55.63
120	91.86	89.87	87.25	83.64	71.49
180	97.68	96.54	94.94	91.98	79.00
240	99.34	-	97.38	95.97	83.38
300	99.81	-	-	97.92	86.25

Table 3. CRD degradation for different reactor types (ideal PFR, recycle PFRs, and MFR) using WO_3

	CRD degradation, % over WO_3				
τ, min	R=0 (ideal PFR)	R=0.2	R=0.5	R=1	R=∞ (ideal MFR)
60	26.36	25.96	25.27	25.03	23.43
120	45.77	44.50	43.63	41.17	37.97
180	60.07	57.92	55.97	53.75	47.86
240	70.59	68.18	65.91	63.40	55.04
300	78.35	75.92	73.68	69.21	60.47

5- Conclusion

The degradation of CRD in the presence of photocatalyst suspensions of TiO_2 and WO_3 was investigated under different UV power irradiation (15 and 30 W). TiO_2 was found to have more photocatalytic degradation than WO_3 for CRD degradation via photo redox reactions because TiO_2 has a wide-bandgap energy, which means good absorption of UV light, then they can produce more radicals, OH• and O2−•, to attack the CRD molecules to degradation by photocatalytic redox reactions. The optimum E_{EC} for the performance of the photocatalytic process at the TiO_2 and 15 W after 255 min was 2329.72 kWh/kg of CRD. Based on the optimum results at 15 W for the two catalysts, the kinetics model of a first-order reaction was studied, and the results show it is perfect to describe the redox reactions for the CRD degradation using the two semiconductors' catalysts. The ideal PFR (R=0) gave the best degradation of CRD by using two catalyst types. Simulated results for increasing R in the recycle PFR from 0.2 to 1 reduced the degradation CRD due to the increased back-mixing and impeded the conversion of CRD to final products, which reduced the concentration distribution throughout the reactor. An increase in the value of the recycle ratio (R=infinity) in MFR showed the worst efficiency for CRD degradation and required a longer space-time to achieve the exact conversion of CRD that could occur during less space-time when an ideal or recycle PFR.

Nomenclature

Symbols	**Description**
AOPs	Advanced oxidation process
CRD	Congo red dye
CB	Conduction band
e^-	Electron
E_g	Band gap energy
h^+	hole
$OH^{\bullet}$	hydroxyl radicals
$O_2^{-\bullet}$	superoxide anions
TiO_2	titanium dioxide
VB	Valances band
MFR	Mix flow reactor
PFR	Plug flow reactor
WO_3	Tungsten trioxide

Symbols	**Description**	**Units**
C_{CRD}	Concentration of the CRD	ppm
CRD degradation	Congo red dye degradation	%
E_{EC}	Electrical energy consumption	W
F_{CRDo}	Feed rate of the initial concentration of CRD	L/min
F'_{CRDo}	Feed rate of fresh inlet reactor stream plus recycle stream	L/min
K	Rate constant	min^{-1}
P	Power of the system UV lamp in	kW
R^2	Correlation coefficient	-
T	Space-time	Min
V	Reactor volume	L
V	Superficial velocity	m/s
X_{CRD}	Conversion of CRD	-

References

[1] M. J. Muñoz-Batista and R. Luque, "Heterogeneous Photocatalysis," *Chemical Engineering*, vol. 5, no. 2, p. 26, May 2021. https://doi.org/10.3390/chemengineering5020026

[2] C. Chee, A. Abd, S. Ibrahim, M. Matheswaran, and P. Saravanan, "Heterogeneous Photocatalytic Oxidation as an Effective Tool for Wastewater Treatment – A Review," in *Studies on Water Management Issues*, InTech, 2012. https://doi.org/10.5772/30134

[3] M. A. Oturan and J. Aaron, "Advanced Oxidation Processes in Water/Wastewater Treatment: Principles and Applications. A Review," *Critical Reviews in Environmental Science and Technology*, vol. 44, no. 23, pp. 2577–2641, Dec. 2014. https://doi.org/10.1080/10643389.2013.829765

[4] M. B. Tahir *et al.*, "Photocatalytic performance of hybrid WO_3/TiO_2 nanomaterials for the degradation of methylene blue under visible light irradiation," *International Journal of Environmental Analytical Chemistry*, vol. 101, no. 10, pp. 1448–1460, 2021. https://doi.org/10.1080/03067319.2019.1685093

[5] Z. Zhao, "Research progress of semiconductor photocatalysis applied to environmental governance," *IOP Conference Series: Earth and Environmental Science*, vol. 631, no. 1, 2021. https://doi.org/10.1088/1755-1315/631/1/012022

[6] M. Yasmina, K. Mourad, S. H. Mohammed, and C. Khaoula, "Treatment heterogeneous photocatalysis; Factors influencing the photocatalytic degradation by TiO_2," *Energy Procedia*, vol. 50, pp. 559–566, 2014. https://doi.org/10.1016/j.egypro.2014.06.068

[7] A. A. L. S. Duarte and M. T. P. Amorim, "Photocatalytic Treatment Techniques using Titanium Dioxide Nanoparticles for Antibiotic Removal from Water," *Application of Titanium Dioxide*, 2017. https://doi.org/10.5772/intechopen.69140

[8] F. H. Kamil, S. K. A. Barno, F. Shems, A. Jihad, and A. S. Abbas, "Photocatalytic Degradation of Sulfamethoxazole from a Synthetic Pharmaceutical Wastewater Using Titanium Dioxide (TiO_2) Powder as a Suspended Heterogeneous Catalyst," *Iraqi Journal of Industrial Research*, vol. 10, no. 1, pp. 26–33, 2023. https://doi.org/10.53523/ijoirvol10i1id314

[9] S. K. Kamal and A. S. Abbas, "Fenton oxidation reaction for removing organic contaminants in synesthetic refinery wastewater using heterogeneous Fe-Zeolite: An experimental study, optimization, and simulation," *Case Studies in Chemical and Environmental Engineering*, vol. 8, no. July, p. 100458, 2023. https://doi.org/10.1016/j.cscee.2023.100458

[10] A. Buthiyappan, A. R. Abdul Aziz, and W. M. A. Wan Daud, "Recent advances and prospects of catalytic advanced oxidation process in treating textile effluents," *Reviews in Chemical Engineering*, vol. 32, no. 1, pp. 1–47, 2016. https://doi.org/10.1515/revce-2015-0034

[11] M. B. Tahir, T. Iqbal, M. Rafique, M. S. Rafique, T. Nawaz, and M. Sagir, "Nanomaterials for photocatalysis," in *Nanotechnology and Photocatalysis for Environmental Applications*, Elsevier, 2020, pp. 65–76. https://doi.org/10.1016/B978-0-12-821192-2.00005-X

[12] M. I. Sari, T. E. Agustina, E. Melwita, and T. Aprianti, "Color and COD degradation in photocatalytic process of procion red by using TiO_2 catalyst under solar irradiation," in *AIP Conference Proceedings*, 2017. https://doi.org/10.1063/1.5011536

[13] M. M. Khan, S. F. Adil, and A. Al-Mayouf, "Metal oxides as photocatalysts," *Journal of Saudi Chemical Society*, vol. 19, no. 5, pp. 462–464, 2015, https://doi.org/10.1016/j.jscs.2015.04.003

[14] A. L. Linsebigler, G. Lu, and J. T. Yates, "Photocatalysis on TiO_2 Surfaces: Principles, Mechanisms, and Selected Results," *Chemical Reviews*, vol. 95, no. 3, pp. 735–758, May 1995. https://doi.org/10.1021/cr00035a013

[15] J. T. Richardson, *Principles of Catalyst Development*. in Fundamental and Applied Catalysis. Boston, MA: Springer US, 1989. https://doi.org/10.1007/978-1-4899-3725-4

[16] P. Makuła, M. Pacia, and W. Macyk, "How To Correctly Determine the Band Gap Energy of Modified Semiconductor Photocatalysts Based on UV–Vis Spectra," *The Journal of Physical Chemistry Letters*, vol. 9, no. 23, pp. 6814–6817, Dec. 2018. https://doi.org/10.1021/acs.jpclett.8b02892

[17] E. A. Alvarez-Aguiñaga, M. P. Elizalde-González, and S. A. Sabinas-Hernández, "Unpredicted photocatalytic activity of clinoptilolite–mordenite natural zeolite," *RSC Advances*, vol. 10, no. 64, pp. 39251–39260, 2020. https://doi.org/10.1039/D0RA06421A

[18] A. Ibhadon and P. Fitzpatrick, "Heterogeneous Photocatalysis: Recent Advances and Applications," *Catalysts*, vol. 3, no. 1, pp. 189–218, Mar. 2013, https://doi.org/10.3390/catal3010189

[19] M. Campanati, G. Fornasari, and A. Vaccari, "Fundamentals in the preparation of heterogeneous catalysts," *Catalysis Today*, vol. 77, no. 4, pp. 299–314, Jan. 2003. https://doi.org/10.1016/S0920-5861(02)00375-9

[20] S. H. K. Ranjin, N. Pathak, and C. L. Dube, "Photocatalytic degradation of textile dye with titanium (IV) doped tungsten oxide nanoparticles," *Materials Protection*, vol. 65, no. 1, pp. 169–175, 2024. https://doi.org/10.62638/ZasMat1037

[21] S. Anandan, Y. Ikuma, and K. Niwa, "An Overview of Semiconductor Photocatalysis: Modification of TiO_2 Nanomaterials," *Solid State Phenomena*, vol. 162, pp. 239–260, Jun. 2010. https://doi.org/10.4028/www.scientific.net/SSP.162.239

[22] J. A. Rengifo-Herrera and C. Pulgarin, "Why five decades of massive research on heterogeneous photocatalysis, especially on TiO_2, has not yet driven to water disinfection and detoxification applications? Critical review of drawbacks and challenges," *Chemical Engineering Journal*, vol. 477, no. August 2023, 2023. https://doi.org/10.1016/j.cej.2023.146875

[23] V. H. Rathi, A. R. Jeice, and K. Jayakumar, "Green synthesis of Ag/CuO and Ag/ TiO_2 nanoparticles for enhanced photocatalytic dye degradation, antibacterial, and antifungal properties," *Applied Surface Science Advances*, vol. 18, no. August, p. 100476, Dec. 2023. https://doi.org/10.1016/j.apsadv.2023.100476

[24] A. Kumar, "A Review on the Factors Affecting the Photocatalytic Degradation of Hazardous Materials," *Material Science & Engineering International Journal*, vol. 1, no. 3, pp. 106–114, 2017. https://doi.org/10.15406/mseij.2017.01.00018

[25] M. S. S. Danish *et al.*, "Photocatalytic Applications of Metal Oxides for Sustainable Environmental Remediation," *Metals*, vol. 11, no. 1, pp. 1–25, 2021. https://doi.org/10.3390/met11010080

[26] H. Guo *et al.*, "Degradation of antibiotic chloramphenicol in water by pulsed discharge plasma combined with TiO_2/WO_3 composites: mechanism and degradation pathway," *Journal of Hazardous Materials*, vol. 371, pp. 666–676, Jun. 2019. https://doi.org/10.1016/j.jhazmat.2019.03.051

[27] S. K. Kamal and A. S. Abbas, "Decrease in the organic content of refinery wastewater by photocatalytic Fenton oxidation using iron-doped zeolite: Catalyst preparation, characterization, and performance," *Chemical Engineering and Processing - Process Intensification*, vol. 193, p. 109549, Nov. 2023. https://doi.org/10.1016/j.cep.2023.109549

[28] S. K. A. Barno, H. J. Mohamed, S. M. Saeed, M. J. Al-Ani, and A. S. Abbas, "Prepared 13X Zeolite as a Promising Adsorbent for the Removal of Brilliant Blue Dye from Wastewater," *Iraqi Journal of Chemical and Petroleum Engineering*, vol. 22, no. 2, pp. 1–6, 2021. https://doi.org/10.31699/ijcpe.2021.2.1

[29] M. S. Abdulrahman, A. A. Alsarayreh, S. K. A. Barno, M. A. Abd Elkawi, and A. S. Abbas, "Activated carbon from sugarcane as an efficient adsorbent for phenol from petroleum refinery wastewater: Equilibrium, kinetic, and thermodynamic study," *Open Engineering*, vol. 13, no. 1, 2023. https://doi.org/10.1515/eng-2022-0442

[30] S. K. Kamal, Z. M. Mustafa, and A. S. Abbas, "Comparative Study of Organics Removal from Refinery Wastewater by Photocatalytic Fenton Reaction Coupled with Visible Light and Ultraviolet Irradiation," *Iraqi Journal of Industrial Research*, vol. 10, no. 3, pp. 22–32, Dec. 2023. https://doi.org/10.53523/ijoirVol10I3ID370

[31] S. Dutta, B. Gupta, S. K. Srivastava, and A. K. Gupta, "Recent advances on the removal of dyes from wastewater using various adsorbents: A critical review," *Materials Advances*, vol. 2, no. 14, pp. 4497–4531, 2021. https://doi.org/10.1039/d1ma00354b

[32] R. H. Salman, E. M. Khudhair, K. M. Abed, and A. S. Abbas, "Removal of E133 brilliant blue dye from artificial wastewater by electrocoagulation using cans waste as electrodes," *Environmental Progress & Sustainable Energy*, vol. 43, no. 2, pp. 1–11, Mar. 2024, https://doi.org/10.1002/ep.14292

[33] S. A. Mousa, S. Tareq, and E. A. Muhammed, "Studying the Photodegradation of Congo Red Dye from Aqueous Solutions Using Bimetallic Au–Pd/TiO_2 Photocatalyst," *Baghdad Science Journal*, vol. 18, no. 4, p. 1261, Dec. 2021. https://doi.org/10.21123/bsj.2021.18.4.1261

[34] R. N. Abbas and A. S. Abbas, "Kinetics and Energetic Parameters Study of Phenol Removal from Aqueous Solution by Electro-Fenton Advanced Oxidation Using Modified Electrodes with PbO_2 and Graphene," *Iraqi Journal of Chemical and Petroleum Engineering*, vol. 23, no. 2, pp. 1–8, Jun. 2022. https://doi.org/10.31699/IJCPE.2022.2.1

[35] R. Abbas and A. S. Abbas, "PbO_2 /graphite and graphene/carbon fiber as an electrochemical cell for oxidation of organic contaminants in refinery wastewater by electrofenton process; electrodes preparation, characterization and performance," *Environmental Research and Technology*, vol. 7, no. 2, pp. 175–185, Jun. 2024. https://doi.org/10.35208/ert.1378232

[36] O. Levenspiel, "Chemical reaction engineering," *Industrial and Engineering Chemistry Research*, vol. 38, no. 11. pp. 4140–4143, 1999. https://doi.org/10.1021/ie990488g

[37] J. R. Bolton, K. G. Bircher, W. Tumas, and C. A. Tolman, "Figures-of-merit for the technical development and application of advanced oxidation technologies for both electric- and solar-driven systems," *Pure and Applied Chemistry*, vol. 73, no. 4, pp. 627–637, 2001. https://doi.org/10.1351/pac200173040627

[38] K. M. Reza, A. Kurny, and F. Gulshan, "Parameters affecting the photocatalytic degradation of dyes using TiO_2: a review," *Applied Water Science*, vol. 7, no. 4, pp. 1569–1578, Jul. 2017. https://doi.org/10.1007/s13201-015-0367-y

[39] M. A. Hassaan, M. A. El-Nemr, M. R. Elkatory, S. Ragab, V.-C. Niculescu, and A. El Nemr, "Principles of Photocatalysts and Their Different Applications: A Review," *Topics in Current Chemistry*, vol. 381, no. 6, p. 31, Dec. 2023. https://doi.org/10.1007/s41061-023-00444-7

[40] A. Fujishima, X. Zhang, and D. A. Tryk, "TiO_2 photocatalysis and related surface phenomena," *Surface Science Reports*, vol. 63, no. 12, pp. 515–582, 2008. https://doi.org/10.1016/j.surfrep.2008.10.001

[41] C. C. Chen, C. S. Lu, Y. C. Chung, and J. L. Jan, "UV light induced photodegradation of malachite green on TiO_2 nanoparticles," *Journal of Hazardous Materials*, vol. 141, no. 3, pp. 520–528, 2007. https://doi.org/10.1016/j.jhazmat.2006.07.011

[42] L. M. González Rodríguez *et al.*, "Synthesis, characterization and photocatalytic activity evaluation of WO_3, TiO_2 and WO_3/TiO_2 supported on zeolite faujasite," *International Journal of Chemical Reactor Engineering*, vol. 18, no. 10–11, pp. 1–15, Oct. 2020. https://doi.org/10.1515/ijcre-2020-0095

[43] S. K. Kamal, Z. M. Mustafa, and A. S. Abbas, "Reaction Kinetics and Mass Transfer of Photocatalytic Fenton for Phenol Degradation in a Petroleum Refinery Wastewater," *Tikrit Journal of Engineering Sciences*, vol. 32, no. 1, p. 1743, Mar. 2025. https://doi.org/10.25130/tjes.32.1.30

دراسة مقارنة لتحلل صبغة الكونغو الحمراء من مياه صرف مصنعة عن طريق تفاعلات الأكسدة والاختزال الضوئية باستخدام أشباه موصلات نانوية مختلفة

رسل احمد جاسم [١]، عمار صالح عباس [١، *]

١ قسم الهندسة الكيمياوية، كلية الهندسة، جامعة بغداد، بغداد، العراق

الخلاصة

تم أجراء دراسة مقارنة لشبه موصلين (ثنائي أكسيد التيتانيوم و ثلاثي أكسيد التنكستن) كعوامل مساعدة ضوئية غير متجانسة لتحلل حوالي ٥٠ جزء في المليون من صبغة الكونغو الحمراء في محلول مائي. تم حدوث تفاعل التحلل الضوئي للصبغة في مفاعل دفعات داخل صندوق مظلم مع استخدم مضخة هواء. في البداية تم خلط محلول الصبغة و٠,٢ جم / لتر من العامل المساعد، في بيئة مظلمة لمراقبة كمية الصبغة الممتزة، بعدها تم تشغيل ضوء الأشعة الفوق بنفسجية بقدرة مختلفة (١٥ و ٣٠ واط) لدراسة تفاعلات التحلل الضوئي. أظهرت النتائج أن ثنائي أكسيد التيتانيوم لديه نشاط ضوئي أعلى لتحلل الصبغة. كانت قيم إزالة صبغة الكونغو الحمراء ٩٩,٦٧ و ٧٢,١٦٪ لثنائي أكسيد التيتانيوم و ثلاثي أكسيد التنكستن على التوالي، باستخدام ١٥ واط. لم تظهر قوة الأشعة فوق البنفسجية تأثيرًا كبيرًا على تفاعلات الأكسدة والاختزال وفقًا للملاحظ من التحلل لصبغة و احتساب استهلاك الطاقة الكهربائية. أظهرت دراسة حركية تفاعل الاكسدة و الاختزال للصبغة ان النتائج التي تم الحصول عليها تطابق نموذج حركي من الدرجة الأولى. تم تطوير نموذج رياضي لمفاعلات مختلفة من خلال دراسة نسبة إعادة التدوير مع الزمن على إزالة صبغة الكونغو الحمراء. أظهرت نتائج المحاكاة ان أداء مفاعل التدفق المثالي حقق أعلى إزالة في زمن أقل من مفاعلات التدفق الذي تحتوي على نسبة اعادة تدوير و تم تسجيل أسوأ أداء للمفاعل في مفاعل الخلط المستمر.

الكلمات الدالة: العامل المساعد الضوئي، عمليات الأكسدة المتقدمة، استهلاك الطاقة، دراسة حركية التفاعل، تصميم المفاعل، نسبة إعادة التدوير.