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Dye wastewater treatment by using ozonation/ photocatalyitc processes

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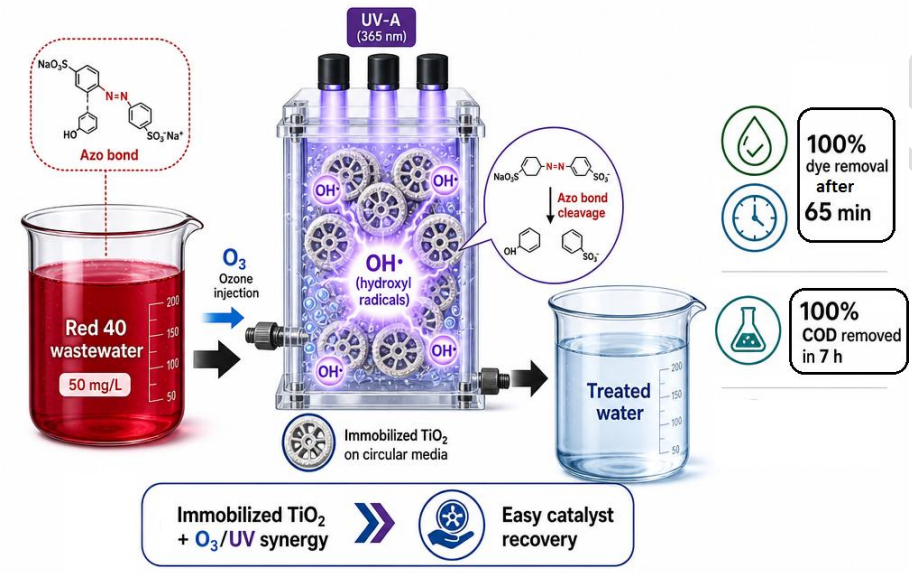
GRAPHICAL ABSTRACT



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ABSTRACT

In this research, the capability of two improved photocatalytic (immobilized-suspended) and hybrid (ozonation/Improved photocatalytic) methods were studied to treat wastewater containing azo dye of Red 40. Hybrid process had the best efficiency for dye concentration of 50 mg/L with pH of 9 and TiO_2 concentration of 40 g/m^3 with light source power of 120 W and ozone injection rate of 20 mg/min. In these conditions, dye and COD were removed completely after 65 min and 7 h. Based on the kinetic studies, pseudo first order model was applied for dye degradation. According to the results, immobilization of nano materials not only solved their recovery problem, but also improved the efficiency of conventional photocatalytic process. Addition of ozonation to the photocatalytic system for the purpose of having hybrid process was also resulted in an increase of the efficiency to over 30 times and production of safe products. The results have been showed the advantages of hybrid process.

1. Introduction

Papers Treatment of dye wastewater is an important issue in invironmental researches, specially using advanced oxidation processes are used in this field recently. Annually, over 7×105 tons of dyes is generated in the world (Gomes, Nunes, and Simões, 2010). Dye wastewaters have usually color and high temperature (Hu, Lin and Chiang, 2004). Azo dyes have been used in the color paper printing, textile, paper making, food, leather and cosmetic industries (Prahba and Lathasree, 2013). Moreover, some azo dyes have been found to be human carcinogens (Behnajady *et al*., 2009). These kinds of compounds are classified as environmental hazardous materials, due to their toxicity and hard biodegradation (Lu *et al*., 2009) which have to be treated before discharging to the environment. Different physical methods such as adsorption (Khani *et al*., 2013), ultra-filtration (Kasperchik, Yaskevich and Bil'dyukevich, 2010), reverse osmosis (Behnajady *et al*., 2009) and electro coagulation are widely used for dyes removal but they transport contaminants from water to sludge (Behnajady *et al*., 2009). Conventional biological treatment methods are ineffective for decolorization and degradation of dyes, because of

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presence of hard biodegradable aromatics in wastewaters (El-Ashtoukhy, 2013). Advanced Oxidation Processes (AOPs) such as ozonation and photocatalytic methods are proper to mineralize dye wastewater (Zuorroa and Lavecchia, 2013; Peng *et al*., 2008; Qaderi and Tamadoni, 2024; Ghasemi, Zoqi and Zanganeh Ranjbar, 2024; Ayati, 2018; Qaderi and Abdolalian, 2022; Farzinfar and Qaderi, 2022). They are characterized by production of hydroxyl radicals (Weng, Zhou and Zhang, 2013). Radicals are extremely reactive oxidants (Moradianfard, Ghorbani and Bakhshy, 2013). Ozone has been seen as an effective agent to remove the color of dye wastewater especially azo dyes (Turhan and Turgut, 2009; Rabieian and Qaderi, 2024; Tamadoni and Qaderi, 2019; Khourshidi and Qaderi, 2023; Qaderi and Banisheykholeslami, 2025). Ozonation of textile wastewater with 600 mg/L of initial COD resulted in 80 percent efficiency in 140 minutes (Chu *et al*., 2008). 120 L/hr ozone injection flow with 24 gr/m3 ozone concentration decolorized 2000 mL of 800 mg/L Sirius Blue SBRR during 26 minutes (Turhan and Turgut, 2009), but ozonation is an expensive and unsafe process (Peng *et al*., 2008).

TiO_2 photocatalytic process is safe and does not require expensive oxidants (Ranjbar, Ayati and Ganjidoust, 2022; Azizi, Ebadi and Qaderi, 2022; Gholamian *et al*., 2025). It is based on exposure to a photocatalyst (Pratap Reddy *et al*., 2004; Augugliaro *et al*., 2004) which can be carried out at moderate temperature and pressure (Barka *et al*., 2008; Ranjbar, Ayati and Ganjidoust, 2019). TiO_2 nano particles were used in slurry and immobilized manner for wastewater treatment (Zhu, Zhang and Chen, 2010; Delnavaz *et al*., 2011). It has been reported that 90 percent of 50 mg/L Red 40 (R40) has been removed by modified TiO_2 with Fe and carbon atoms (Wu *et al*., 2010) and 20 mg/L R40 wastewater decolorized 80% by $Bi_{12}TiO_{20}$ (Zhu, Zhang and Chen, 2010).

According to the successful application of media in the attached biological systems (Qaderi, Ayati and Ganjidoust, 2011; Delnavaz, Ayati and Ganjidoust, 2010) and necessity of nano-materials separation in slurry systems, before discharging to the environment and lower efficiency of immobilized manner than systems (Delnavaz *et al*., 2012), a new method must be used.

Two main aims of this study were to apply a new improved photocatalytic system and a combination of ozonation and improved photocatalytic systems to troubleshoot the drawbacks and use the capabilities of both methods.

2. Materials and methods

2.1. Reactor set-up

A schematic diagram of the reactor is presented in Fig. 1. The reactor was a plexiglas cube with internal size of (W, L and H) 10, 15 and 27 cm and effective volume of 2.6 L. TiO_2 nanoparticles with a specific surface area of 20 g/m² were coated on circular plexiglas media (20 mm diameter and 2 mm thickness) by Hec-8 epoxy binder (Azar Resin Chemical Industrial Co.). The coated media were suspended in the reactor by stirrer (IKA, RH basic 2 models). UV-A lamps were used as the irradiation sources.

Ozone was produced from oxygen (99.9% purity) by ozone generator; Arda COG-5S model. The outlet stream from the ozonizer with 1 L/min flow rate, 1.2 g O_3/h and the pressure of 1 bar was injected to the solution from the diffusers. The gas flow rate was measured by air flow meters (Fischer Porter Co.). The temperature was fixed at 22±1°C during all experiments. Unused ozone was injected into 2% KI (Merck) solution, to provide safety conditions.

2.2. Reagents and catalysts

P25 TiO_2 with specific surface area of 55 m^2/g and 70 % anatine crystalline form was procured from Degussa Corporation. R40, H_2SO_4, $K_2Cr_2O_7$, Ag_2SO_4 (Merck), $HgSO_4$ (DBH Company), Potassium hydrogen phthalate (Hach Company) was used for chemical oxygen demand (COD) measurement. The pH was adjusted by aqueous solutions of HCl (Merck) and NaOH (Merck). The two distilled water was used in all steps of research.

2.3. Analytical methods

The dye concentration was measured using a spectrophotometer at the maximum absorption wavelength of 485 nm (Agilent/Varian Com., USA). COD and pH measurement were accomplished in accordance with 5220-B and 4500-H^+B instructions, respectively, presented in the "Standard Methods for the Examination of Water and Wastewater" (APHA, 2005). All laboratory tests were repeated at least three times and relative standard deviation of the measured data was within 2%. Gas chromatography– mass spectrometry (GC-MS) system was used for identifying intermediate products and kinetic study. GC (Agilent Co., 7890a model) had a Chrompak CP-Sil 8 CB capillary column (50 m× 250 µm× 0.12 µm film thickness) and interfaced to the MS (Agilent Co, 5475c model). The GC column was operated in a temperature programmed mode. It had an initial temperature of 50 °C held for 2 minutes, rise at 290 °C with a 6 °C/min rate, and maintained at that temperature for 10 min.

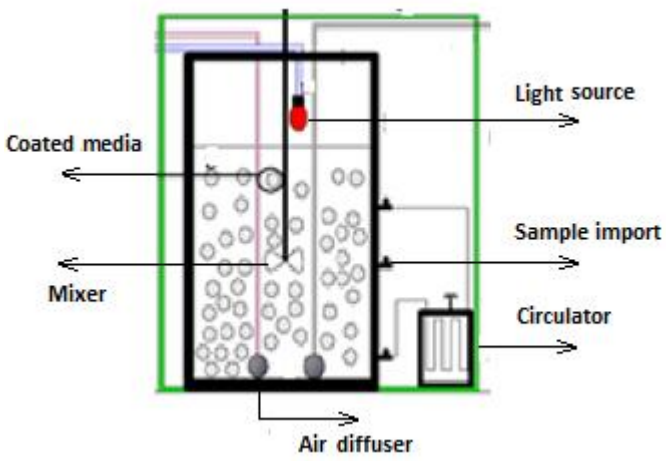


Fig. 1. A schematic diagram of the reactor

2.4. Experimental procedures

In the present research, the photocatalytic and hybrid processes were compared from the stand point of Red 40 removals. The independent variables of dye concentration, pH, and nano-materials concentration and radiation source were investigated. The optimum conditions of both processes were determined (see Table 1). The dye removal intermediates and kinetic considerations were also studied in optimum conditions of hybrid process.

Table 1. Conditions of decolorization experiments.

Variable	Levels
Dye concentration (mg/L)	5, 35 ,50
pH	3, 5, 7, 9
Nano TiO_2 concentration (g/m^2)	20, 40, 60, 80
Irradiation source power (W)	40, 80, 120, 160
Ozone injection rate (mg/min)	12, 20

3. Results and discussion

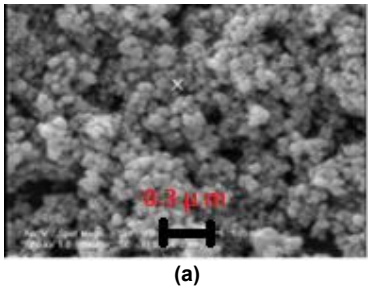
3.1. Immobilized media surface characteristics

The structure and shape of coated TiO_2 is shown in SEM micrographs with magnification of 30000 times (see Fig. 2a). According to the Fig. 2, the coated particles were in nano scale. Energy-dispersive X-ray (EDX) results were also confirmed the presence of TiO_2 on media surface (see Fig. 2b).

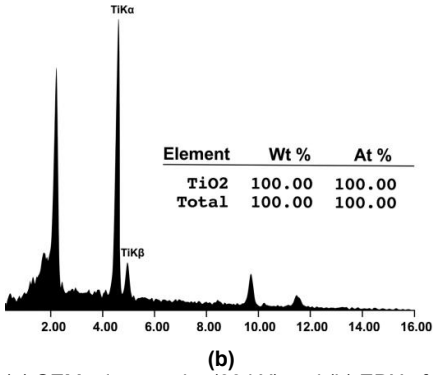
This result confirmed that this method of using nano particles in dye wastewater treatment can be used widely and this method is useful for coating of nanoparticles on the surface.

3.2. Effect of solution pH

The dye removal efficiency in different pH conditions are shown in Fig. 3. As shown, when pH increased, the dye removal was increased in photocatalytic and decreased in hybrid system, respectively. Time required to complete the elimination of dye is decreased from 120 minutes in pH=3 to 65 minutes in pH=9. Regarding the higher efficiency of dye removal in acidic pH in photocatalytic process, the hybrid process has a higher efficiency in alkaline pH.



(a)



(b)

Fig. 2. (a) SEM micrographs (30 kX) and (b) EDX of coated TiO_2 on media.

The pH effect on photocatalytic process efficiency is based on the oxidation capability of produced holes with pH increase and TiO_2 amphoteric behavior (Papadam *et al*., 2007) According to the literatures, the ozonation and photocatalytic processes have the higher efficiencies in alkaline (Turhan and Turgut, 2009; Somensi *et al*., 2010) and acidic conditions (Papadam *et al*., 2007), respectively. Thus, the ozonation is recognized as the dominant process in the hybrid method.

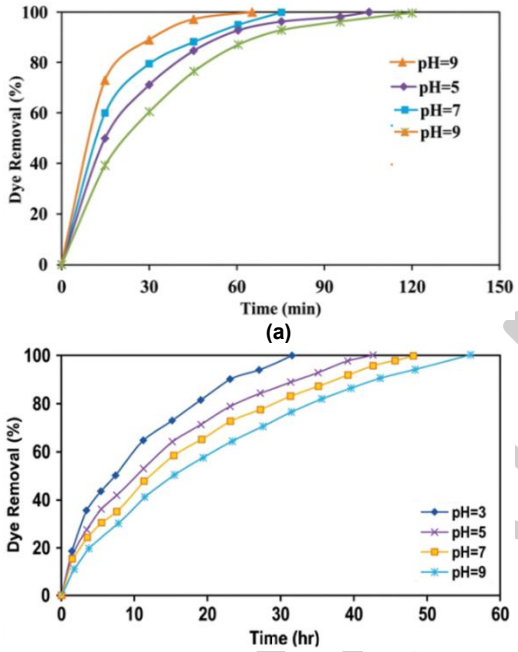


Fig. 3. Dye removal efficiency of (a) hybrid and (b) photocatalytic processes in different pH conditions. ([O_3]= 20 mg/L, [R40]=50 mg/L, [TiO_2]=40g/m^2, P_{UV-A}=120 W).

3.3. Effect of dye concentration

Dye removal for both photocatalytic and hybrid processes in different dye concentrations and optimum pH conditions of 9 and 5 are shown in Fig. 4. Based on the results, this quantity was increased from 3.12 to 3.93 mg/hr when the dye concentration was increased from 5 to 50 mg/L in the photocatalytic process, but it was reached to 3.6 mg/hr as the dye concentration was increased to 60 mg/L. In hybrid process, it was increased from 30 to 115 mg/hr as the dye concentration was increased from 5 to 50 mg/L and reached 102 mg/hr as the initial concentration was increased to 60 mg/L. Because of the hydroxyl radicals' short lifetime, they have a very short time to oxidize the contaminants and the probability of collision with dye is decreased when the dye concentration is reduced.

As it was expected, the dye removal efficiency was decreased when the concentration was increased. For complete removal of 5, 35 and 50 mg/L of dye, the needed time were about 25, 55 and 60 min for hybrid process and 4.17, 22 and 33 hours for photocatalytic process, respectively. As the dye concentration to oxidant ratio is increased, a higher number of bonds should be broken which takes longer time regarding that the oxidant amount is constant. Similar results have been reported in ozonation and photocatalytic processes (Turhan and Turgut., 2009; Barka *et al*., 2008; Papadam *et al*., 2007). The removed dye amounts per unit of time for different concentrations in both systems are compared in Fig. 5.

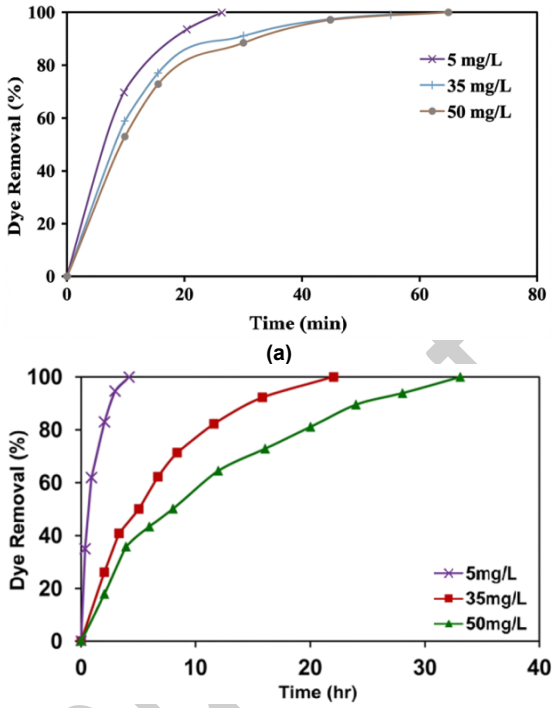


Fig. 4. Dye removal efficiency of a) hybrid and b) photocatalytic processes in different pollutant concentrations ([O_3]=20mg/L, $pH_{Hhybrid\ process}$=9, $pH_{photocatalytic\ process}$=3, [$TiO_2$]=40gr/m^2, P_{UV-A}=120 W).

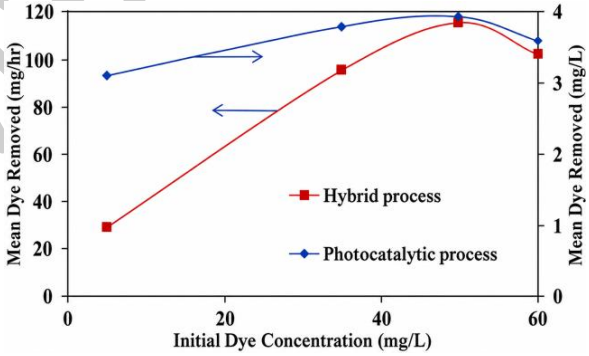


Fig. 5. Initial dye concentration effect on average removed in time unit ([O_3]=20 mg/L, $pH_{Hybrid\ process}$=9, $pH_{Photocatalytic\ process}$=3, [$TiO_2$]=40 gr/m^2 ,$P_{UV-A}$=120 W).

This resulted in a decrease of dye removal intensity (Turhan and Turgut, 2009; Barka *et al*., 2008). Moreover, the intermediate formed concentration was increased as the R40 concentration increased in which these compounds were also consumed the oxidant (Lackey, Mines Jr. and McCreanor, 2006). The interplay between two discussed phenomena specifies the optimum concentration of R40 in dye removal amount per unit of time. According to the results, 50 mg/L was chosen as the optimum concentration in both processes.

3.4. Effect of catalyst concentration

Nano TiO_2 concentration effect on the photocatalytic and hybrid processes efficiency is shown in Fig. 6. Based on the results, the hybrid process had higher efficiency (100 %) in 65 minutes for 40 gr/m^2 of TiO_2. This efficiency was attributed to an increase in active sites of TiO_2 photocatalyst as the concentration was increased up to 40 gr/m^2. The similar results have been reported in slurry photocatalytic studies (Kartal, Erol and Oguz, 2001). The enhancement of ozone oxidation in light presence has been reported which justified the higher efficiency of hybrid process as compared to the photocatalytic method (Amat *et al*., 2005). Based on the obtained results, the amount of 40 gr/m^2 was chosen as the optimum concentration.

As the nano materials were coated on the media, an increase in the photocatalyst concentration (media's number) was caused UV light penetration into the solution (Kartal, Erol and Oguz, 2001). This matter affects the TiO_2 excitation and synergetic effect of O_3/UV combination

(Amat *et al*., 2005; Chou and Chang, 2007) that is why the amount of removal efficiency wasn't changed considerably.

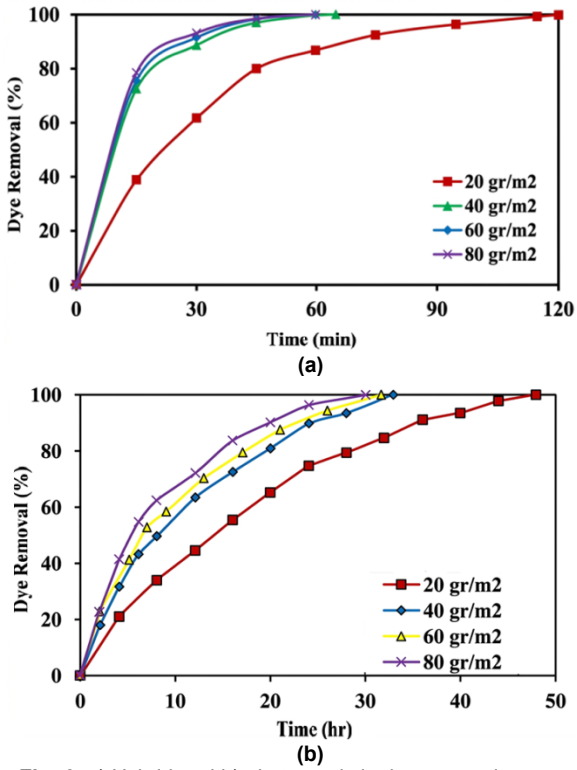


Fig. 6. a) Hybrid and b) photocatalytic dye removal processes efficiency in different nanomaterial concentration ([O_3]=20mg/L, pH $_{Hybrid\ process}$=9, pH $_{Photocatalytic\ process}$=3, [R40]=50 mg/L, P_{UV-A}=120 W).

3.5. Effect of radiation source power

The effect of different light sources power on the efficiency of hybrid and photocatalytic processes was shown in Fig. 7. It can be seen that the dye removal was increased as the light source power increased in both systems. As the light source power was increased from 40 to 160 Watt, the needed time to complete the dye removal was decreased from 75 to 52 hours and from 100 to 60 minutes in hybrid and photocatalytic processes, respectively. Because in the photocatalytic process, by rising the light source power, rate of the reaction (1) and the electron (e_{CB-}) and hole (h_{VB+}) will be increased and the reaction of pollutant oxidation is improved through reactions of (2) to (9) (Fujishima, Rao, and Tryk, 2000; Papadam *et al*, 2007; Mirkhani *et al*, 2009).

Also, in the hybrid system, O_3/UV combination had significant synergetic effect on the removal efficiency (Amat *et al*., 2005; Chou and Chang, 2007).

$TiO_2 + h\upsilon(UV) \rightarrow TiO_2(e_{CB}^- + h_{VB}^+)$ (1)

Pollutant+ $h_{VB}^+ \rightarrow$ Oxidation Products (2)

$TiO_2(h_{VB}^+) + H_2O \rightarrow TiO_2 + H^+ + OH^\bullet$ (3)

$TiO_2(h_{VB}^+) + OH^- \rightarrow TiO_2 + OH^\bullet$ (4)

Pollutant+$OH^\bullet \rightarrow$Degradation Products (5)

$TiO_2(e_{CB}^-) + O_2 \rightarrow TiO_2 + O_2^{\bullet-}$ (6)

$O_2^{\bullet-} + H^+ \rightarrow HO_2^\bullet$ (7)

$2HO_2^\bullet \rightarrow O_2 + H_2O_2$ (8)

$H_2O_2 + O_2^{\bullet-} \rightarrow OH^\bullet + {}^+OH^- + O_2$ (9)

Based on the results, increase in the efficiency was negligible as the power increased from 120 to 160 Watt due to high dye decomposition rate in high radiation intensities. Because, the light intensity effect of efficiency has a saturation level and no increase in efficiency is obtained in higher intensities (Chiou, Wu, and Juang, 2008). Thus, 120 Watt was applied as the optimum power.

3.6. Comparison of the processes

The comparison of two studied systems is summarized in Table 2. Based on the results, retention time was decreased 30 times as the slurry photocatalytic process was promoted to hybrid and the average removed dye per unit of time in optimum conditions was reached from 3.8 mg/hr in photocatalytic to 115.7 mg/hr in hybrid method.

Table 2. Comparison optimum condition of improved photocatalytic and hybrid processes.

Parameter	Improved photocatalytic	Hybrid system
pH	3	9
Dye concentration, mg/L	50	50
TiO_2 concentration, g/m^2	40	40
Light source power, W	120	120
Time of complete dye removal, h	33	1.08
Removed dye in a time unit, mg/h	3.8	115.7

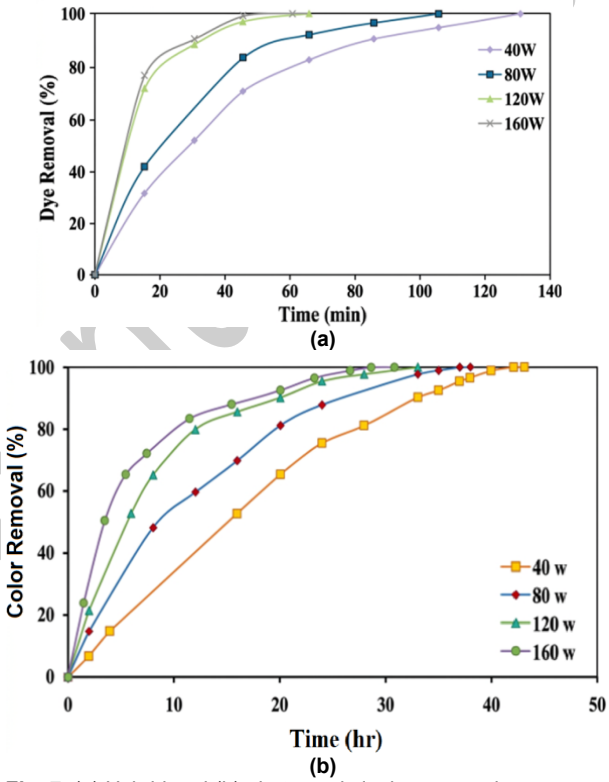


Fig. 7. (a) Hybrid and (b) photocatalytic dye removal processes efficiency in different light source powers ([O_3]=20 mg/L, pH$_{Hybrid\ process}$=9, pH$_{Photocatalytic\ process}$=3, [R40]=50 mg/L, [$TiO_2$]=40 gr/m^2).

Therefore, the hybrid process was selected as the appropriate method of dye removal and the capability of photocatalytic process was increased as the dye removed by ozonation process in system since the UV ray was completely received. All results are reported for hybrid process.

3.7. Effect of ozone concentration and injection flow rate

Considering the effect of ozone concentration and its injection flow rate on the system two cases of 12 mg/min ozone with flow rate of 0.5 L/min and 20 mg/min ozone with flow rate of 1 L/min were investigated (see Fig. 8). As shown in the figure, the hybrid process efficiency was improved as the ozone concentration and flow injection were increased. The figure also indicates that the complete removal for the ozone injection rate of 20 mg/min with flow rate of 1 L/min was achieved in less time (35 min) which was applied for the rest of the experiments.

3.8. COD removal and light penetration

Dye and COD removal efficiency in the optimum conditions of hybrid process is indicated in Fig. 9. As shown in the figure, the removal efficiency of dye (100 %) is higher than COD (18 %). This means that the chromophore functional azo dye group (–N=N–) were decomposed easier than the other dye structural bonds. It can also be seen that COD is increased in the first 15 minutes that can be attributed to the cleavage of cyclic compounds and non-cyclic intermediates.

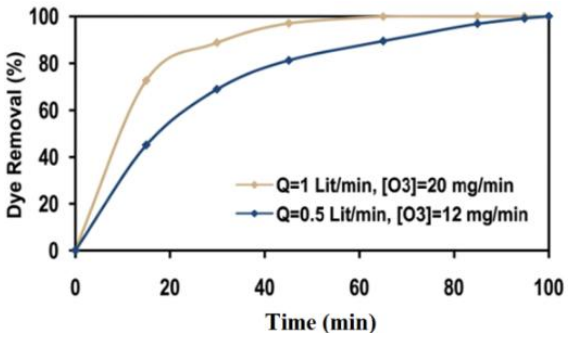


Fig. 8. Ozone injection effect on hybrid dye removal process efficiency (pH=9, [R40]=50 mg/L, [TiO_2]=40 gr/m^2 P_{UV-A}=120 W).

The absorbance curve variations in hybrid process are presented in Fig. 10. It can be seen that the peak of azo bond in 450-500 nm was normalized after 65 minutes while the absorbance in other wave lengths was not influenced noticeably. This means that azo bonds cleavage occurs more easily than the other bonds.

3.9. Intermediate compounds of the hybrid process

Fig. 11 shows the absorbance of different intermediates including benzene one-cyclic, di-cyclic naphthalene, and azo dye compounds in the wave lengths of 230, 485 and 310 nm, respectively. Based on the results, the azo bonds in the solution were broken in the first hour while 3 and 7 h were needed, respectively, for cleavage of naphthalene and benzene compounds. Moreover, it can be seen that after 7 hours, all cyclic compounds were completely broken.

According to the GC-MS coupled technique after 65 minutes (Fig. 12), the compounds of 5-amino 1-naphtol, 1-naphtol compounds, phenol, aniline and phathalic acid were formed. Based on the LD_{50} amounts (300, 275, 270, 464 and 550 mg/Kg for the mentioned organics, respectively), these compounds were more toxic than R40 with LD_{50} of 10000 mg/Kg that was why the process was continued 7 hours to complete COD removal. This important issue has not been considered in the previous studies.

3.10. Kinetic study of the hybrid process

The kinetic relations and correlation coefficients in different experiment conditions are given in Table 3. According to the results, by increasing pH, nano TiO_2 concentration and light source power, the kinetic constant was increased whereas by increasing dye concentration, it was decreased. It can also be concluded that the pseudo first order kinetic is suitable to describe the dye removal in different conditions.

The Langmuir-Hinshelwood model is presented in the optimum conditions in Fig. 13. According to the results, there was an appropriate correlation coefficient between experimental and theoretical results. The kinetic constant and root mean square error (RMSE) were obtained 0.08 min^{-1} and 0.3, respectively.

Table 3. The kinetic relations in the hybrid process.

Experiments conditions					Function	k, min-1	n	R^2
pH	[R40], mg/L	Ozon, mg/min	[TiO_2], gr/m^2	Light source power, W				
3	50	20	128	120	$\log\left(\frac{-dC}{dt}\right) = -1.286 + 0.882 * \log(C)$	0.051	0.882	0.993
9	50	20	128	80	$\log\left(\frac{-dC}{dt}\right) = -1.219 + 0.861 * \log(C)$	0.06	0.861	0.978
9	50	20	58	120	$\log\left(\frac{-dC}{dt}\right) = -1.262 + 0.854 * \log(C)$	0.055	0.854	0.987
9	35	20	128	120	$\log\left(\frac{-dC}{dt}\right) = -1.086 + 1.014 * \log(C)$	0.082	1.014	0.95
7	50	20	128	120	$\log\left(\frac{-dC}{dt}\right) = -1.141 + 0.909 * \log(C)$	0.072	0.909	0.95
9	50	12	128	120	$\log\left(\frac{-dC}{dt}\right) = -1.428 + 1.023 * \log(C)$	0.037	1.023	0.996
9	50	20	128	40	$\log\left(\frac{-dC}{dt}\right) = -1.238 + 0.751 * \log(C)$	0.057	0.751	0.971
9	50	20	191	120	$\log\left(\frac{-dC}{dt}\right) = -1.13 + 1.06 * \log(C)$	0.074	1.06	0.988
9	5	20	128	120	$\log\left(\frac{-dC}{dt}\right) = -0.863 + 0.91 * \log(C)$	0.137	0.91	0.989
5	50	20	128	120	$\log\left(\frac{-dC}{dt}\right) = -1.154 + 0.887 * \log(C)$	0.07	0.887	0.97
9	50	20	243	120	$\log\left(\frac{-dC}{dt}\right) = -1.13 + 1.101 * \log(C)$	0.074	1.101	0.983
9	50	20	128	120	$\log\left(\frac{-dC}{dt}\right) = -1.133 + 1.009 * \log(C)$	0.073	1.009	0.952
9	50	20	128	160	$\log\left(\frac{-dC}{dt}\right) = -1.119 + 1.015 * \log(C)$	0.076	1.015	0.95

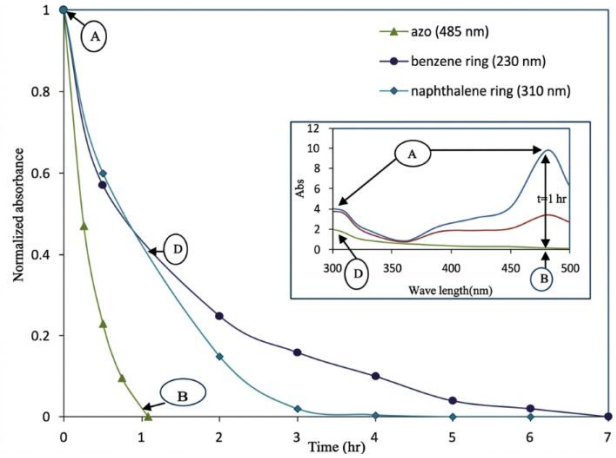


Fig. 11. Azo, naphthalene and benzene compounds absorbance in optimum conditions of hybrid process ([O_3]=20 mg/L ،pH=9 ,[R40]=50 mg/L-،[TiO_2]=40 gr/m^2, P_{UV-A}=120 W).

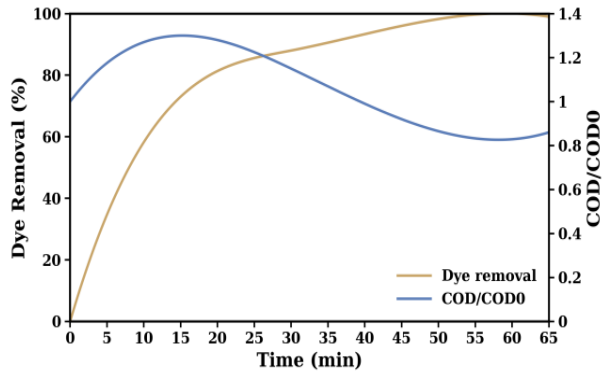


Fig. 9. Dye removal efficiency and COD removal in optimum condition of hybrid process ([O_3] = 20mg/L, pH=9, [R40]=50 mg/L, [TiO_2]=40 gr/m^2, P_{UV-A}=120 W).

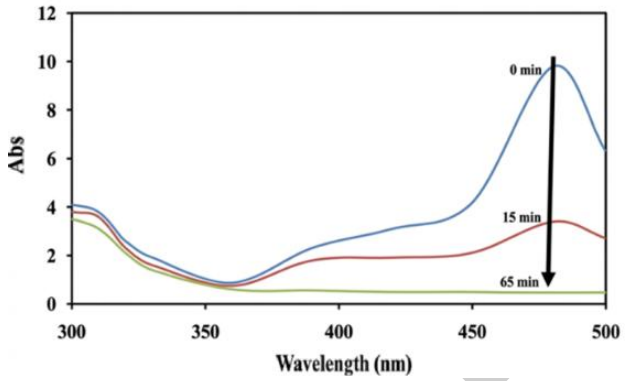


Fig. 10. Absorbance changes in optimum conditions of hybrid process ([O_3]=20mg/L, pH=9, [R40]=50 mg/L, [TiO_2]=40 gr/m^2,P_{UV-A}=120 W).

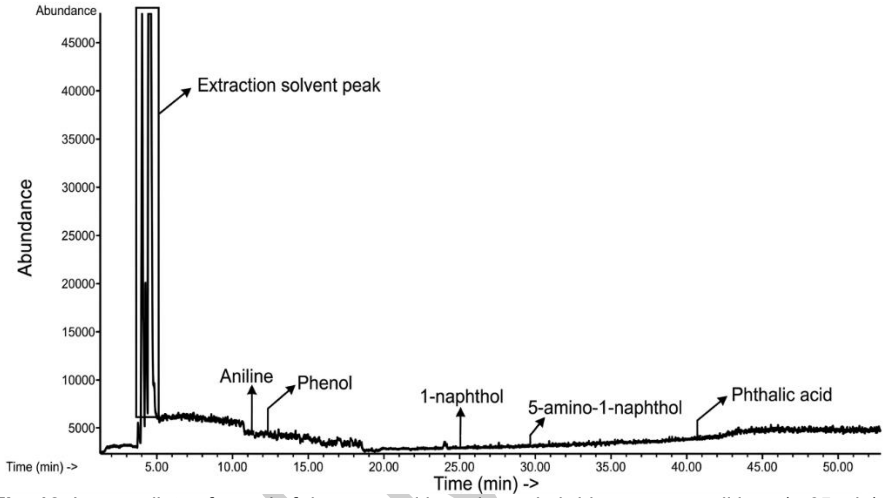


Fig. 12. Intermediates formed of dye removal in optimum hybrid process conditions (t=65 min).

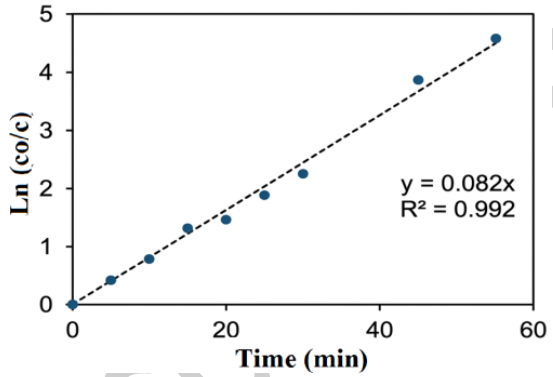


Fig. 13. Langmuir-Hinshelwood model consideration in optimum hybrid process ([O_3]=20 mg/L, pH=9, [R40]=50 mg/L, [TiO_2]=40 gr/m^2, P_{UV-A}=120 W).

4. Conclusions

Based on the results, improved photocatalytic (immobilized-suspended) and hybrid (Ozonation/Improved photocatalytic) methods can be used for treatment of wastewater containing azo dye of Red 40. Hybrid process had better efficiency than improved photocatalytic process and it had the best efficiency for dye concentration of 50 mg/L with pH of 9 and TiO_2 concentration of 40 g/m^3 with light source power of 120 W and ozone injection rate of 20 mg/min. In these conditions, dye and COD were removed completely after 65 min and 7 h, respectively. Based on the kinetic studies, pseudo first order model was the best model for dye degradation. Introduced hybrid process including improved immobilized-slurry photocatalytic and ozonation system not only solved recovery problem of the nano-particles but also improved the conventional process efficiency over 30 times and produced safe products to discharge. The results have been showed the advantages of hybrid process.

Author Contributions

Farhad Qaderi: Contributed to the study conception and design, conducted material preparation, data collection, analysis, and composed the original draft of the manuscript.
Amir Hossein Norouzi: Contributed to the study conception and design, data collection, and provided feedback on prior versions of the manuscript, and edited the manuscript.

Conflict of Interest

The authors have no competing interests to declare.

Data Availability Statement

Datasets employed and/or evaluated in this research are available from the corresponding author upon justifiable request.

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