A new approach to study the degradation of the organic pollutants by A-doped $\text{M}_x\text{O}_y$/B photocatalysts

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Abstract
This work presents a new approach and a comprehensive mechanism to study the kinetics of the photodegradation of the organic pollutants. The vital role of various operational factors on the degradation of the organic pollutants is explained using this method. The proposed approach is based on the simple strategies and a powerful computational method. Two new variables “the effective concentration of photon” ($I_{\text{eff}}$) and “the effective concentration of the reactive centers” (RC) are defined to better understand the effect of operational parameters on the organic pollutant photodegradation. The optimum conditions of the photocatalytic degradation can be determined with the help of this method. This approach was used to study the kinetics of photodegradation of the organic pollutants on the A – doped$\text{M}_x\text{O}_y$/B photocatalysts. The provided mechanism has been examined with some experimental data. The high correlations between the experimental data and the fitting results under different conditions prove this mechanism could be reliable.

Keywords Photodegradation · Organic pollutants · Comprehensive mechanism · Reactive centers · Effective charge carriers · Hybrid manual-automatic method

Introduction
Water is one of the essential needs of all life-supporting processes (Westall and Brack 2018). One of the most important challenges of today’s society is providing safe drinking water for all people (Khalifa and Bidaisee 2018, Reina et al. 2015). The water sources are at severe risk of pollution due to the growth of the various pollutant activities such as industrial waste effluents, agricultural runoff, pharmaceuticals disposal, urban sewage draining, and landfill seepage (Hu et al. 2013; Malakootian et al. 2019). Some authors have believed that textile industry wastewater is the most polluting among the various industrial fields (Liang et al. 2014; Verma et al. 2012). Waste effluents of the textile industry usually contain a high concentration of pigments, dyes, and toxic materials (Lau and Ismail 2009). It has been reported that synthetic dyes are among the major pollutants of water because of their toxic and carcinogenic characteristics (Lai et al. 2014).

The results of various researches show that advanced oxidation processes (AOPs) are suitable techniques for removing toxic materials (Ghatak 2014; Navarro et al. 2017; Samadi et al. 2017; Stets et al. 2018; Zhou et al. 2019). This technique is based on the in situ production of strong oxidizing intermediates such as superoxide radical anions ($\text{O}_2^-$), hydroxyl radicals ($\text{OH}^+$), hydrogen peroxide ($\text{H}_2\text{O}_2$), and singlet oxygen ($\text{O}_2^*$). AOPs include the different types of processes such as the chemical ($\text{Fe}^{2+}/\text{H}_2\text{O}_2$, $\text{O}_2/\text{H}_2\text{O}_2$), the photochemical ($\text{UV}/\text{H}_2\text{O}_2$, $\text{UV}/\text{O}_3$, $\text{UV}/\text{Fe}^{2+}/\text{H}_2\text{O}_2$, $\text{UV}/\text{TiO}_2$), the son-chemical ($\text{UV}/\text{H}_2\text{O}_2$, $\text{UV}/\text{O}_3$), and the electrochemical technologies (Al-Kdasi et al. 2004, Vagi and Petsas 2017).

Heterogeneous photocatalysis is an advanced technology to deal with environmental pollution (Al-Rasheed 2005, Ibhadon and Fitzpatrick 2013, Liu et al. 2014, Simon et al. 2020). It can be defined as “the acceleration of a chemical reaction by using a photocatalyst under light’s irradiation with adequate energy.” In recent years, many semiconductor metal oxides such as $\text{TiO}_2$ (Gupta et al. 2012), $\text{ZnO}$ (Chakrabarti and Dutta 2004), $\text{Fe}_2\text{O}_3$ (Hitam and Jalil 2020), $\text{NiO}$ (Sabouri et al. 2018), $\text{CdS}$ (Khan et al. 2016), and $\text{WO}_3$ (Yao...
et al. 2017) have been widely studied for the decomposition of the organic contaminants under visible light and UV irradiation. Titanium dioxide and zinc oxide have received much attention in the field of pollutant photodegradation research. These photocatalysts are non-toxic, low cost, highly efficient, and environmentally friendly (Xia et al. 2016).

In general, a photocatalytic process involves the following steps: (1) photon absorption with energy equal to or greater than the bandgap of the semiconductor, (2) the electron transfer from the valence band (VB) to the conduction band (CB) for the producing electron–hole pairs, (3) the trapping of the charge carriers on the effective reactive centers during light illumination, and (4) the degradation of toxic compounds by the powerful oxidizing agents:

$$A \rightarrow \text{doped } M_xO_y/B + h\nu \rightarrow e^- + h^+ \quad (1)$$

$$e^- + h^+ \rightarrow \text{The effective reactive -- centers} \rightarrow \text{The powerful oxidizing agents}$$

The powerful oxidizing agents + pollutant → intermediates \( \rightarrow \) The effective intermediates

Although the kinetics of photocatalytic reactions have been extensively investigated, more work is needed to gain the sufficient knowledge about the mechanism of these reactions. Many researchers have investigated the mechanism of photocatalytic reactions based on experiment results, identification of the reactive oxygen species, and studying the behavior of the reaction intermediates (Berberidou et al. 2016, Dror et al. 2020, El Mragui et al. 2019, Kaur and Sud, 2012).

To the best of our knowledge, some articles have discussed the mechanism of the photocatalytic reactions, and they have proposed the general mechanisms or the possible pathways for photocatalytic reactions (Huang et al. 2020, Turkten and Cinar 2017, Wang et al. 2018). Some articles have studied the kinetics of the photocatalytic process based on proposed mechanism (Emeline et al. 2000; Minero et al. 2013; Montoya et al. 2014). Unfortunately, the detailed mechanism at the atomic scale has been introduced for a limited number of photocatalysts (Nosaka and Nosaka 2017). However, only few articles describe the photodegradation mechanism involving the elementary steps of the reaction and their rate constant values (Bashiri et al. 2014, Bashiri and Pourbeiram 2016, Shams Ghamsari and Bashiri 2020).

In this paper, a new approach was proposed to study the kinetics and mechanism of the degradation of the organic pollutants by the various photocatalysts under UV–Vis light illumination. Without the use of common kinetic approximations, this approach helped us to gain a better understanding of the various steps of photocatalytic processes, such as the electron–hole generation step. The surface of semiconductors is a crucial factor for many applications such as pollutant photodegradation, solar cells, and microelectronic systems. A detailed understanding of their surface structure is essential for developing the mechanism of the pollutants photodegradation.

Our approach assumes the photodegradation of organic compounds occurs due to the effective charge carriers and the formation of the effective reactive centers on the \( A \rightarrow \text{dopedM_xO_y/B surface} \). Therefore, the two variables named the effective concentration of photon \( (I_{\text{eff}}) \) and effective concentration of the reactive centers \( (RC) \) are defined for a better understanding of the effect of operational parameters on pollutant photodegradation. Because a small number of the reactive centers and the charge carriers lead to the degradation of organic pollutant. Interestingly, these variables reach the maximum or minimum when the system is in optimal condition.

The \( A \rightarrow \text{dopedM_xO_y/B general formula was proposed} \)

$$I_{\text{eff}} \rightarrow \text{RC} \rightarrow \text{Degradation}$$

This method was used to demonstrate the flexibility of our method. The \( M_xO_y \) is a semiconductor, such as TiO_2 and ZnO, which can interact with water species, oxygen molecules, and other materials to form the various reactive centers. A is a metallic or nonmetallic element that can increase the photocatalytic activity of the \( M_xO_y \) photocatalyst.

The interaction of water species and the pollutant molecules with the \( A \rightarrow \text{dopedM_xO_y/B surface} \) is a critical step in the degradation mechanism (Thiel and Madey 1987, Vittadini et al. 2007). The adsorbed water species on the surface of photocatalysts are oxidized by the valence band holes to produce the hydroxyl radicals (Muhd Julkapli et al. 2014). These processes lead to the production of the reactive centers for the degradation of organic pollutant molecules.

The B component can be a compound such as graphic carbon nitride, reduced graphene oxide, ozone, montmorillonite, another photocatalyst, or even a mixture of them. The interaction of B component with some species in the system, such as oxygen molecules and water species, leads to the formation of the other reactive centers. The coupling of these materials with a photocatalyst can be a suitable method to achieve enhanced photocatalytic activity.

In the present investigation, MATLAB software was used as a computational tool to solve the differential rate equations by a deterministic method. Four sets of experimental data from some literature were used to examine this approach. These systems are listed in Table 1. The vital role of various operational parameters in the photodegradation of pollutants was easily explained using this approach. The values of rate constants for elementary reactions and the effective concentrations of the reactive centers were obtained by combining manual and automated methods. The conformity
between the experimental data and fitting results was examined under different operating conditions.

The production of the electron–hole pairs, dye adsorption on the photocatalyst surface, the trapping of the charge carriers to produce the reactive radicals, and the recombination of the charge carriers have the key effects on the photodegradation of the organic pollutants. In this study, a proposed approach has been used to theoretically investigate the effects of these factors on the degradation process of the organic pollutants without using the common kinetics approximations. Therefore, a non-approximation approach is proposed to study the kinetics and mechanism of the photocatalytic reactions. Obviously, a complex kinetics equation can be obtained using the proposed mechanism and the kinetics approximations such as the steady-state approximation. This complex kinetics equation can be reduced to a Langmuir–Hinshelwood equation by considering more approximations. It is not possible to solve this equation analytically by standard methods. However, a concise mechanism and multiple approximations must be used to derive a simple kinetics equation such as the first-order equation.

The real mechanism of the photodegradation of organic pollutants involves several steps, and their nature is not fully understood. These kinds of processes depend on various experimental conditions including the type of reactants, the solution pH, the concentration of reactants, and the photocatalyst surface structure. A suitable method for studying the mechanism of the photocatalytic reactions is to estimate the rate constants and to investigate the effect of different factors on their values. A detailed understanding of the photodegradation process of the organic pollutants by photocatalysis helps us to properly design a photocatalytic experiment. However, this approach provides more information about the generation process of the electron–hole pairs. On the one hand, the importance of our work is that it proposes the rate constants of a photocatalytic process without any approximation. The different samples can be compared in a photocatalytic system by using the rate constants of this step and the effective variables. In addition, a useful comparison between the rate constants of the first step and the rate constants of the other steps is provided by a proposed variable named as “the effective concentration of photons.”

### Methods: the estimation of the rate constants and the effective variables

The mechanism of a chemical reaction consists of a series of elementary chemical reactions. Usually, the rate constants and initial concentration of the sites are identified using the parameter estimation procedures. Mathematical methods for studying the kinetics and mechanisms of chemical reactions can be stochastic or deterministic.

The stochastic method regards the time evolution of the chemical reaction as a random-walk process that is described by a differential equation (the chemical master equation) (Bashiri and Mohamadi 2016, Bashiri and Pourbeiram 2016, Rafiee and Bashiri 2019, Rafiee and Bashiri 2020a, b, Shams Ghamsari and Bashiri 2020). The deterministic method regards time evolution of the chemical system as a continuous process that can be governed by a series of coupled ordinary differential equations (ODEs). In our work, the deterministic method was used to solve a series of rate equations that describe the photocatalytic process. The fitting data of the organic pollutants concentration versus time are obtained by integration of the ODEs. For the implementation of the deterministic method, the numerical techniques can be used to solve the differential rate equations. The results of various researches showed that the performance of stochastic and deterministic methods strongly depends on the studied system (Lerkkasemsan 2010, Safieddine et al. 2012, Zheng and Ross 1991).

We used MATLAB code framework based on the following parts: (1) experimental data, initial concentrations, and initial guesses of rate constants are the inputs, (2) the rate equations of the elementary steps are written, (3) odes15s solver is used, (4) the commands for the drawing curves are used, (5) the codes related to the minimization are applied.

| The studied system | [Photocatalyst] | [Pollutant] | [The other materials] | pH | Ref |
|--------------------|----------------|-------------|-----------------------|----|-----|
| Acid Orange 7/Fe-doped TiO2/UV light | 100 mg L⁻¹ | 50 mg L⁻¹ | 3 wt. % | 3–9 | (Han et al. 2018) |
| Congo Red/Ni-doped ZnO/UV light | 0.5 g L⁻¹ | 10 mg L⁻¹ | Ni-to-Zn weight ratios (2%, 3%, 5%, and 10%) | 6 | (Mousavi et al. 2017) |
| Tetracycline hydrochloride/N-doped TiO2 and N-doped TiO2/RGO/visible light | 1 g L⁻¹ | 10 mg L⁻¹ | - | Neutral | (Tang et al. 2018) |
| Phenol/ZnO/O3, Ag-doped ZnO and Ag-doped ZnO/O3/UV light | 0.5 g L⁻¹ | 50 mg L⁻¹ | [O3(gas)] = 10 mg L⁻¹ [Ag] = 1.5 wt. % | 6.8 | (Peng et al. 2019) |
ODEs. Ordinary differential equations can be classified as stiff and non-stiff. Shampine et al. (Shampine and Reichelt 1997) believed that this classification plays a crucial role in selecting the solvers. Stiffness is an essential and efficient concept in the numerical integration of the ODEs. It is generally accepted that a differential equation is stiff if the explicit numerical methods do not provide the appropriate solutions to the given equation. The stiffness phenomenon depends on the initial conditions, the ordinary differential equations, and the numerical algorithm. Some algorithms are defined for non-stiff equations and some others for stiff equations.

MATLAB documentation suggests the ode45 is the best solver for solving problems in the first step. Many problems have been solved by the ode45 solver, which is based on a Runge-Kutta method (Forsythe 1977). The next suggestion is that the ode15s solver can be used if the ode45 fails or is extremely slow. In this work, the integration of the ODEs was performed by using the ode15s solver from MATLAB version, R2015b. The ode15s is a variable-order and multi-step solver that is used to solve stiff differential equations. The ode15s algorithm is based on the implementation of the backward differences of a set of numerical differentiation formulas (NDFs) (Shampine and Reichelt 1997).

Several numerical methods such as Euler, Runge-Kutta, Adams–Bashforth, and Adams–Moulton are used for solving the system of differential equations. These methods are divided into two categories single-step and multi-step methods. The backward difference formula (BDF) is a general method for solving stiff differential equations. The BDFs are a set of implicit methods for the numerical solving of the differential equations. A system of differential equations can be written as follows:

$$ F(t, x(t), x'(t)) = 0; x(t_0) = x_0 $$

(4)

The simplest BDF method is the backward Euler method, which involves replacing the x derivative by a backward difference:

$$ F(t_n x_n, \frac{x_n - x_{n-1}}{h}) = 0; h = t_n - t_{n-1} $$

(5)

where $h$ is the step size. MATLAB implements an ode15s solver based on the BDF method. Therefore, MATLAB solves the ODEs using the ode15s algorithm in this work. Then, the results were compared with experimental data. If there was no good fit, the input values were readjusted to obtain a coefficient of determination close to 1.

Generally, the rate constants for each step and the effective variables are the adjustable parameters obtained through the fitting process in the MATLAB environment. In this study, two methods of parameter estimation are employed to examine the final mechanism: the hybrid manual-automatic method and the optimization technique. The first method is the estimation of parameters in two steps: (1) the rate constants and initial concentrations of the reactive centers are manually adjusted to obtain a coefficient of determination close to 1; (2) the minimization function of the “fminsearch” is used to optimize the rate constants. In the second method, the rate constants are estimated in one step using the “fmincon” minimization function. The fminsearch function minimizes an unconstrained multivariable function by using the Nelder–Mead simplex method. This method is a direct algorithm, which is used to minimize the nonlinear functions. The “fmincon” function is an iterative method that starts from an initial point and converges to a constrained local minimum. In our simulations, the “fmincon” function implements the “interior-point” algorithm at each iteration using second-order gradient methods. The interior-point algorithm solves a sequence of unconstrained minimization problems to approach the constrained optimization.

In this work, the sum of squared errors (SSE) between the fitted and experimental data is used as an objective function of the optimization process.

**Objective function**

$$ SSE = \sum (x_{\text{pred}}(i) - x_{\text{exp}}(i))^2 $$

(6)

where, the variables $x_{\text{pred}}$ and $x_{\text{exp}}$ are the predicted and experimental data of $x$, respectively. In each run, the program calculates the coefficient of determination ($R^2$-square) using the mean-square error for easy comparison of the results. The coefficient of determination of the collection of the $(t, C)$ points can be defined as

$$ R^2 = 1 - \frac{\text{SSE}}{\text{SST}} $$

(7)

where, SST is the total sum of squares (variance), which is obtained as follows:

$$ \text{SST} = \sum (x_{\text{exp}}(i) - \bar{x}(i))^2 $$

(8)

where, $\bar{x}$ is the mean of the experimental data.

**Results and discussion**

**Basics of the proposed approach**

The photodegradation process of the pollutant depends on several intrinsic and extrinsic factors. The photocatalyst properties such as surface area, crystallinity, morphology, and the doping of other elements into its lattice refer to the intrinsic factors (Friedmann et al. 2010). The other factors such as irradiation light source, the concentration of organic pollutants, catalyst loading, reaction temperature, pH value,
and the presence of dissolved substances are related to extrinsic factors (Wan et al. 2014).

The interaction of the catalyst with other substances in the solution under UV/vis light illumination leads us to define a set of the reactive centers on the photocatalyst surface. The basic assumption of our approach is that photodegradation process is controlled by the effective reactive centers on the surface of the photocatalyst. The formula of the reactive centers is shown in Table 2.

In addition, the proposed approach is based on several other strategies as follows: (1) effective concentration of photon and the effective concentration of the reactive centers can be considered as an efficiency criterion of the photocatalytic process, (2) the trapping of the photogenerated electrons and holes plays a vital role in the degradation of organic pollutants, (3) the adsorption of dissolved species on the catalyst surface is one of the crucial factors in the photocatalytic activity, (4) surface-adsorbed radicals (OH’(ads) and O2−(ads)) are main reactive species formed in the photodegradation process, (5) the doping of the other elements into the photocatalyst lattices can significantly promote the destruction of the organic pollutants molecules, (6) the inactivation parameters in the photocatalytic system have a critical impact on the performance of the degradation reaction, (7) intermediates have a crucial effect on the rate of organic pollutants degradation due to the simultaneous reaction with reactive oxygen species formed in the solution.

As shown in Fig. 1, our approach to the photodegradation of organic pollutants involves the following steps: (1) a certain number of the reactive centers are defined on the surface of the TiO2, (2) based on the proposed model, the reaction pathway is decomposed into a series of elementary reactions, (3) a suitable software with high computing power (MATLAB) is selected, (4) an initial value is suggested for each rate constant and the effective concentration of the reactive centers, (5) the required codes were written in MATLAB environment to run the data fitting process, (6) the data fitting program was performed to examine the reaction mechanism, (7) the fitted and experimental data were compared by plotting the pollutant concentration versus time and computing the $R^2$, (8) if the fitting is not right, the kinetics factors (elementary steps and the rate constants) or the effective concentration of reactive centers will be changed, (9) the fitting process is terminated when the best fitting is obtained. In other words, an initial mechanism is constructed based on the proposed approach. The fitting codes are written in a MATLAB computing environment.

### Table 2 Proposed formulations of the reactive centers on the photocatalyst surface in contact with the pollutant aqueous solution

| The type of reactive center | Formula |
|---------------------------|---------|
| RC1                       | M − OH, M − OH2+, M − O2, M − OH2, M − OH(bridge)H − M, and M − O(bridge)(H2O) − M |
| RC2                       | A − OH, A − OH2+, A − O2, A − OH2, A − O(bridge)H − X, and A − O(bridge)(H2O) − X |
| RC3                       | M − O2(Ti − O2 or Zn − O2) |
| RC4                       | A − O2(Fe − O2 or Ag − O2 or Ni − O2) |
| RC5                       | B − O2(rGO − O2) |
| RC6                       | Species adsorbed (C) on the surface of the photocatalyst (such as O2) |
| RC7                       | The effective reactive centers such as Ti4+ and Zn2+ for the trapping of photogenerated electrons |
| RC8                       | The effective reactive centers such as O2 and OH− for the trapping of photogenerated holes |
| RC9                       | The other effective reactive centers (A0+) such as Fe3+, Ni2+, and Ag+ for the trapping of photogenerated electrons |
| RC10                      | S_{inactive} (for hydroxyl radicals) |
| RC11                      | S_{inactive} (for superoxide radicals) |
| RC12                      | S_{inactive} (for other species) |
| RC13                      | Adsorption sites |
The reliable fitting results are obtained by adjusting the rate constants of the elementary steps and the concentrations of the reactive centers. If a good fit is not found, another mechanism should be proposed. The initial guess for the rate constants is generated using the literature’s values (Bashiri et al. 2014) or our suggested values.

However, it is impossible to propose a unique and comprehensive mechanism for photocatalytic reactions due to the various factors and their influence on the degradation process. Therefore, to obtain the best conformity between the experimental and the simulated data, it is necessary to examine the different mechanisms of pollutant degradation.

**The mechanism of the pollutant photodegradation**

In general, three categories of mechanisms have been proposed for the degradation of organic pollutants by photocatalysts under UV–Vis light.

In the first category of mechanisms, the hydroxyl radicals are the main oxidant of the pollutant’s degradation. Achieving this mechanism requires the production of powerful holes. These holes are produced by the action of the UV light on the surface of a photocatalyst with the suitable bandgap. The systems of the TiO$_2$/UV, Ni-doped ZnO/UV, and Fe-doped TiO$_2$/UV are considered in this category.

In the second category of mechanisms, the superoxide radicals are the main oxidant of the pollutant degradation. In these systems, there are not powerful photogenerated holes to oxidize the water species. The systems of the TiO$_2$/Vis, N-TiO$_2$/Vis light, and N-TiO$_2$/RGO/Vis light are in the second category of the mechanisms.

For non-doping TiO$_2$ under visible light irradiation, it has been suggested (Liu et al. 2000) that an adsorbed pollutant molecule is excited to the singlet or triplet states; subsequently, an electron is injected from the excited pollutant molecule to the TiO$_2$ conduction band to produce a pollutant cationic radical (pollutant$^{**}$). This excited molecule undergoes the degradation process to produce the intermediates. The visible-light-induced electrons react with O$_2$ molecules and produce the superoxide radicals. This mechanism is also called the photosensitized oxidation mechanism.

When N-doped TiO$_2$ or N-doped TiO$_2$/RGO are exposed by the visible light irradiation, the photogenerated electrons are transferred from the localized N levels in the TiO$_2$ bandgap (the mid-gap states) to the conduction band. These electrons in the conduction band are trapped by the O$_2$ pre-adsorbed on the TiO$_2$ surface or the RGO surface to produce the superoxide radicals.

The electron spin resonance (ESR) experiments using the spin-trap, 5,5-dimethylpyrroline-1-oxide (DMPO), showed (Rengifo-Herrera et al. 2009) the oxidative potential of the photoinduced holes associated with the mid-gap states has no high power to produce the hydroxyl radicals (2.38 V (SHE)). Some researchers ignore this argument and consider the reaction of water species to visible light-induced holes (Chen and Liu 2016). For the systems of the N-doped TiO$_2$ and N-doped TiO$_2$/RGO, the reaction of the visible-light-induced holes with water species was neglected in our method. However, the reaction of the holes with the adsorbed pollutant molecules on the photocatalyst surface is considered.

In the third category of mechanisms, the free photogenerated holes are the main factor of degradation of organic pollutants. In some systems that follow the first type mechanism, adding new material to the photocatalyst structure may change the main oxidant. For example, the presence of the ozone in the Ag-doped ZnO/UV photocatalyst plays this role.

The general proposed framework for the mechanism of the degradation process of the organic pollutants in (A – dopedM$_x$O$_y$/B/UV – Vis) aqueous systems is shown in Table 3. In the present study, several mechanisms were examined, and among them, the final mechanism presented in Table 4 had the best agreement with the experimental data. Three general conclusions can be deduced from the final mechanism: (1) a general framework can be proposed for the degradation process of organic pollutant by the photocatalysts; (2) the rate constants of the elementary reactions in different systems have similar values; (3) the excellent conformity in the fitting process indicates that the proposed approach can be verified using the experimental data (Han et al. 2018; Mousavi et al. 2017; Peng et al. 2019; Tang et al. 2018) under different conditions.

Two methods of the optimization and manual adjustment were implemented simultaneously for the TiO$_2$/visible light/TC system to compare the correlation results (Fig. 2). The correlation analysis on the fitting results shows that there is not much difference between the $R^2$ values in the optimization and the manual adjustment methods. For this system, the elementary reaction steps and their rate constants are presented in Table 5. Perfect conformity between the adjusted and optimized values was found in this table. This result shows that the MATLAB optimization method can be used well for simple systems.

However, the fitting results show that manual adjustment of the parameters leads to reliable values than the optimization-based procedure for the complicated systems. The main reasons can be explained as follows: (1) the number of parameters estimated in each run is large, (2) many operational factors are considered for the selection of an appropriate mechanism, (3) the detailed mechanism of photocatalytic reactions involves many elementary steps. For this reason, we proposed a hybrid manual-automatic method.
The analysis of the curve of pollutant concentration versus time and the effect of the intermediates on the degradation process

The analysis of the plot of the concentration versus time is slightly complicated. The shape of this curve qualitatively reflects the behavior of the photocatalytic system. In general, the curves of pollutant concentration versus time can be divided into three steps. In the first step, the ROSs mainly react with the organic pollutant molecules. The fitting investigations show that in the initial times, the curve of organic pollutant concentration versus time is mainly affected by the interaction between the pollutant and ROSs. In other words, regardless of the intermediates reaction with the \( \text{OH}^- \) radicals, only the initial parts of the fitting curve have good conformity to the experimental points. The reaction of ROSs with the initial intermediates, which is produced in the photocatalytic process, is considered as the second step. The effect of other intermediates is taken into account in the third step.

From this view, the two types of mechanisms can be defined: degradation mechanism without and with the reactions of intermediates. The first type is only suitable to describe the concentration vs. time at the initial times. The other type shows more agreement between the experimental and the fitting results after passing the time. In other words, a set of consecutive reactions occurs in which the produced intermediates are oxidized by the ROSs. The number of these reactions in the real system is large, but one or two reactions can be appropriate to obtain a good agreement. The rate constant of these consecutive reactions depends on the conditions of the studied system. After passing the time, the interaction between the intermediates of the degradation of organic pollutants and ROSs is also influential.

However, the steps of the hybrid manual-automatic adjusting of the system parameters and the concentrations of reactive centers can be explained as follows: (1) Based on the experimental results, the percentage of the ROS participation in the pollutant degradation is approximately adjusted. The fitting process starts without considering the intermediate reactions. The values of the effective variables should be adjusted, and the fitting results should be as close as possible to the first experimental data. (2) The reaction of the first intermediate with the ROSs is considered, and the program is executed. The rate constant of this step is adjusted to obtain good conformity between the model predictions and the other experimental points. (3) The reactions of one or more intermediates with the ROSs are considered to obtain the excellent fitting results. (4) Finally, the values

| Part 1: The generation of charge carriers:          | A − dopedM, \( \text{O}_x/\text{B}/\text{UV} − \text{Vis} \) aqueous systems |
|-----------------------------------------------|--------------------------------------------------------------------------------|
| Part 2: Adsorption of the organic pollutant on the photocatalyst surface:               | RC7 + pollutant ↔ pollutant(ads)                                                |
| Part 3: The trapping of the charge carriers:                                             | RC1 + h\(^+\) → OH\(^+\)(ads)                                                   |
| Part 4: The reaction of ROSs with the organic pollutant molecules                       | \( \text{OH}^+(\text{ads}) + \text{pollutant} \rightarrow \text{Intermediates} \) |
| Part 5: The reaction of ROSs with the intermediates:                                     | \( \text{Intermediates} + \text{OH}^+(\text{ads}) \rightarrow \text{products} \) |
| Part 6: The recombination of the e\(^-\)/h\(^+\) pairs:                                | \( \text{h}^+_{\text{trapped}} + e^-_{\text{trapped}} \rightarrow \text{heat} \) |
| Part 7: The inactivation of the ROSs by the inactive species:                           | RC10 + \( \text{OH}^+(\text{ads}) \rightarrow \text{Inactivatedspecies} \)      |
|                                               | RC11 + \( \text{O}_x^-\)(ads) → Inactivatedspecies                            |
|                                               | RC12 + Theotherradicals → Inactivatedspecies                                   |

Table 3 The general proposed framework for the mechanism of the degradation process of the organic pollutants in \( \{ \text{A − dopedM,} \text{O}_x/\text{B}/\text{UV} − \text{Vis} \} \) aqueous systems
Table 4 The elementary reaction steps and their rate constants (the fitted results and the reported values in the literature) for the mechanism of the degradation process of the organic pollutants in the studied systems

| I.D  | Elementary reactions                                                                 | Fe-doped TiO₂ | Ni-doped ZnO | N-doped TiO₂ | N-doped TiO₂/RGO | Ag-doped ZnO/O₂ |
|------|---------------------------------------------------------------------------------------|---------------|--------------|--------------|------------------|-----------------|
| 1    | A - dopedM₆O₉/B/C + Iᵣff → e⁻ + h⁺                                                   | 1.49×10⁻³     | 1.032×10⁻³   | 1.18×10⁻¹    | 1.78×10⁻¹        | 1.71×10⁻³       |
|      |                                                                                      | (M⁻¹ min⁻¹)   | (M⁻¹ min⁻¹) | (M⁻¹ min⁻¹) | (M⁻¹ min⁻¹)      | (M⁻¹ min⁻¹)     |
| 2    | h⁺ + M - OH → OH⁺ₕ_ads                                                               | 6.30×10⁰      | 8.39×10⁰     | -            | -                | 8.30×10⁰        |
|      |                                                                                      | (M⁻¹ min⁻¹)   | (M⁻¹ min⁻¹) |             |                  | (M⁻¹ min⁻¹)     |
| 3    | h⁺ + pollutant_ads → 2intermediate1                                                  | 1.00×10⁰      | 1.00×10⁰     | 9.53×10⁷     | 9.53×10⁷         | 2.10×10⁹        |
|      |                                                                                      | (M⁻¹ min⁻¹)   | (M⁻¹ min⁻¹) | (M⁻¹ min⁻¹) | (M⁻¹ min⁻¹)      | (M⁻¹ min⁻¹)     |
| 4    | h⁺ + A - OH → OH⁺₅_ads                                                                | 6.30×10⁰      | 8.30×10⁰     | -            | -                | 7.30×10⁰        |
|      |                                                                                      | (M⁻¹ min⁻¹)   | (M⁻¹ min⁻¹) |             |                  | (M⁻¹ min⁻¹)     |
| 5    | h⁺ + s_trapping₂ → h_trapped                                                          | 3.92×10⁰      | 3.92×10⁰     | 1.49×10⁹     | 1.49×10⁹         | 1.89×10⁹        |
|      |                                                                                      | (M⁻¹ min⁻¹)   | (M⁻¹ min⁻¹) | (M⁻¹ min⁻¹) | (M⁻¹ min⁻¹)      | (M⁻¹ min⁻¹)     |
| 6    | e⁻ + A → A⁻                                                                          | 1.73×10⁰      | -            | -            | -                | 7.86×10⁰        |
|      |                                                                                      | (M⁻¹ min⁻¹)   |             |             |                  | (M⁻¹ min⁻¹)     |
| 7    | M - O₂ + e⁻ → O²⁻₂ads                                                                | 6.20×10⁰      | 6.20×10⁰     | 5.49×10⁹     | 5.49×10⁹         | 7.70×10⁹        |
|      |                                                                                      | (M⁻¹ min⁻¹)   | (M⁻¹ min⁻¹) | (M⁻¹ min⁻¹) | (M⁻¹ min⁻¹)      | (M⁻¹ min⁻¹)     |
| 8    | A - O₂ + e⁻ → O²⁻₂ads                                                                | 7.30×10⁵      | 7.30×10⁵     | -            | -                | -               |
|      |                                                                                      | (M⁻¹ min⁻¹)   | (M⁻¹ min⁻¹) |             |                  |                 |
| 9    | e⁻ + M - C → C⁺(O⁺₃₃(ads))                                                           | -             | -            | -            | -                | 9.00×10⁹        |
|      |                                                                                      |               |               |             |                  | (M⁻¹ min⁻¹)     |
| 10   | e⁻ + s_trapping₁ → e_trapped                                                         | 4.89×10⁹      | 4.82×10⁹     | 5.49×10⁹     | 4.49×10⁹         | 3.02×10⁹        |
|      |                                                                                      | (M⁻¹ min⁻¹)   | (M⁻¹ min⁻¹) | (M⁻¹ min⁻¹) | (M⁻¹ min⁻¹)      | (M⁻¹ min⁻¹)     |
| 11   | e⁻ + B - O₂ → O⁻₂_ads                                                                 | -             | -            | -            | 6.53×10⁶         | -               |
|      |                                                                                      |               |               |             | (M⁻¹ min⁻¹)     |                 |
| 12   | O²⁻₂_ads + 2H⁺ + e⁻ → H₂O₂_ads                                                       | 1.42×10₁²     | 1.42×10₁²    | 9.53×10¹¹    | 9.53×10¹¹        | 2.30×10¹²       |
|      |                                                                                      | (M⁻¹ min⁻¹)   | (M⁻¹ min⁻¹) | (M⁻¹ min⁻¹) | (M⁻¹ min⁻¹)      | (M⁻¹ min⁻¹)     |
| 13   | H₂O₂_ads + e⁻ → OH⁺₅_ads + OH⁻                                                       | 2.59×10⁹      | 2.59×10⁹     | 2.53×10⁹     | 2.53×10⁹         | 2.80×10⁹        |
|      |                                                                                      | (M⁻¹ min⁻¹)   | (M⁻¹ min⁻¹) | (M⁻¹ min⁻¹) | (M⁻¹ min⁻¹)      | (M⁻¹ min⁻¹)     |
| 14   | A⁺ + M - O₂ → O⁺₂_ads                                                                 | 9.20×10⁵      | -            | -            | -                | 9.20×10⁸        |
|      |                                                                                      | (M⁻¹ min⁻¹)   |             |             |                  | (M⁻¹ min⁻¹)     |
| 15   | A⁺ + M - O₃ → O⁺₃_ads                                                                 | -             | -            | -            | -                | 9.50×10⁸        |
|      |                                                                                      |               |               |             |                  | (M⁻¹ min⁻¹)     |
| 16   | O⁺₃₃(ads) + H⁺ → HO⁺₅(ads)                                                           | -             | -            | -            | -                | 3.23×10¹⁰       |
|      |                                                                                      |               |               |             |                  | (M⁻¹ min⁻¹)     |
| 17   | HO⁺₅(ads) → O⁺₃(ads) + H⁺                                                            | -             | -            | -            | -                | 3.45×10⁴        |
|      |                                                                                      |               |               |             |                  | (M⁻¹ min⁻¹)     |
| 18   | HO⁺₅(ads) → OH⁺₅_ads + O₂                                                            | -             | -            | -            | -                | 3.20×10⁷        |
|      |                                                                                      |               |               |             |                  | (M⁻¹ min⁻¹)     |
| 19   | O⁺₂_ads + M - O₃ → O⁺₃_ads                                                           | -             | -            | -            | -                | 6.00×10⁹        |
|      |                                                                                      |               |               |             |                  | (M⁻¹ min⁻¹)     |
| 20   | pollutant + Site → pollutant_ads                                                     | 4×10⁻¹        | 2.1×10⁻²     | 7.92×10²     | 1.20×10³         | 2.75×10²        |
|      |                                                                                      | (M⁻¹ min⁻¹)   | (M⁻¹ min⁻¹) | (M⁻¹ min⁻¹) | (M⁻¹ min⁻¹)      | (M⁻¹ min⁻¹)     |
| 21   | pollutant_ads → pollutant + Site                                                     | 1×10⁻⁳        | 1.59×10²     | 7.50×10²     | 8.5×10³          | 2.12×10²        |
|      |                                                                                      | (min⁻¹)       | (min⁻¹)      | (min⁻¹)      | (min⁻¹)          | (min⁻¹)         |
| 22   | pollutant + OH⁺₅_ads → 2intermediate2                                                | 9.20×10⁶      | 5.02×10⁷     | 9.53×10⁷     | 9.53×10⁷         | 8.70×10⁷        |
|      |                                                                                      | (M⁻¹ min⁻¹)   | (M⁻¹ min⁻¹) | (M⁻¹ min⁻¹) | (M⁻¹ min⁻¹)      | (M⁻¹ min⁻¹)     |
| 23   | pollutant + O⁺₂₂_ads → 2intermediate3                                                | 5.03×10⁷      | 8.30×10⁴     | 9.53×10³     | 3.79×10³         | 7.30×10³        |
|      |                                                                                      | (M⁻¹ min⁻¹)   | (M⁻¹ min⁻¹) | (M⁻¹ min⁻¹) | (M⁻¹ min⁻¹)      | (M⁻¹ min⁻¹)     |
| 24   | pollutant + M − C → 2intermediate4                                                   | -             | -            | -            | -                | 2.52×10²        |
|      |                                                                                      |               |               |             |                  | (M⁻¹ min⁻¹)     |
| 25   | intermediate2 + OH⁺₅_ads → Products                                                  | 5.18×10⁶      | 6.90×10⁶     | -            | -                | 6.68×10⁶        |
|      |                                                                                      | (M⁻¹ min⁻¹)   | (M⁻¹ min⁻¹) |             |                  | (M⁻¹ min⁻¹)     |
| 26   | intermediate₃ + O⁺₂₂_ads → Products                                                  | 6.03×10⁷      | 5.38×10⁴     | 9.79×10⁳     | 2.11×10⁵         | 1.60×10³        |
|      |                                                                                      | (M⁻¹ min⁻¹)   | (M⁻¹ min⁻¹) | (M⁻¹ min⁻¹) | (M⁻¹ min⁻¹)      | (M⁻¹ min⁻¹)     |
The rate constants are optimized by using the `fminsearch` function.

The fitting results show the first intermediate competes significantly with the organic pollutant molecule to consume the hydroxyl radicals. These reactions are symbolically represented in the fifth part of the general mechanism. The rate constant of the consecutive steps is a function of the operational parameters and varies from $10^6$ to $10^9$ in the different conditions. The following reason can be used to explain this behavior. The ROS reaction with pollutants may lead to the production of two types of intermediates. Since each of the intermediates tends to react with the ROSs, the rate constant for these reactions varies slightly for the samples under study.

In this paper, four systems have been considered to examine the comprehensive mechanism of the degradation of the organic pollutant on the surface of the photocatalysts under different conditions. Figures 3 and 4 represent the fitting results for the studied samples. Figure 3 shows the trend of changes in the effective concentration of photon and the effective concentration of reactive centers based on the proposed approach. Figure 3 shows the trend of changes in the effective concentration of photon and the effective concentration of reactive centers based on the proposed approach. In an overview, Figs. 3 and 4 show that there are significant correlations between degradation efficiencies and the different parameters. In this paper, the effect of some operational parameters on the degradation efficiency will be discussed using these figures.

### Table 5

| LD | Elementary reactions | The adjusted rate constants (M$^{-1}$ min$^{-1}$) | The optimized rate constants (M$^{-1}$ min$^{-1}$) |
|----|----------------------|-----------------------------------------------|-----------------------------------------------|
| 1  | Site + TC $\rightarrow$ TC(ads) | 1.12$\times$10$^2$ | 1.13$\times$10$^2$ |
| 2  | TC(ads) $\rightarrow$ Site + TC | 6.30$\times$10$^1$ | 6.46$\times$10$^1$ |
| 3  | TC(ads) + $I_{eff}$ $\rightarrow$ TC(ads)$^*$ + e$^-$ | 2.70$\times$10$^4$ | 1.56$\times$10$^4$ |
| 4  | O$_2^*$ + e$^-$ $\rightarrow$ O$_2$(ads) | 5.49$\times$10$^8$ | 5.49$\times$10$^8$ |
| 5  | O$_2$(ads) + TC $\rightarrow$ Intermediates | 6.79$\times$10$^3$ | 6.79$\times$10$^3$ |
| 6  | Intermediates + O$_2$(ads) $\rightarrow$ products | 1.53$\times$10$^4$ | 1.53$\times$10$^4$ |
| 7  | TC(ads)$^*$ + e$^-$ $\rightarrow$ heat | 6.48$\times$10$^7$ | 6.48$\times$10$^7$ |
| 8  | S$_{inactive}$ + O$_2$(ads) $\rightarrow$ Inactivatedspecies | 1.63$\times$10$^5$ | 1.63$\times$10$^5$ |
Fig. 3  The effective concentration of the reactive centers obtained from implementing the fitting process for all the studied samples

Fig. 4  The curves of the organic pollutant concentration vs. time for the studied systems (the experimental and the fitted results)
The production step of the photogenerated charge carriers

The first part of the proposed framework is the production of the charge carriers. Similar to other photocatalytic reactions (Galindo et al. 2000; Rauf et al. 2011), the proposed mechanism is initiated by photoexcitation of the photocatalyst or the pollutant under the UV–Vis light illumination. This step is very fast with a timescale in the order of $10^{-14}$ s (Dou et al. 2004; Friedmann et al. 2010). Nevertheless, our results showed the rate constant for the photoexcitation by the UV light is in the order of $10^{-3}$ M$^{-1}$ min$^{-1}$, while the rate constant of the photoexcitation by visible light is in the order of $10^{-1}$ M$^{-1}$ min$^{-1}$. One reason for this difference may be that UV beams are more powerful than visible light. However, it seems that there is a mismatch between the timescale of charge carrier generation and the relatively low efficiency of photocatalytic reactions (Qian et al. 2019). This conclusion is an interesting result, because the fitting results show a significant difference between the physical and chemical understanding of the electron–hole generation process. In other words, the pollutant photodegradation can result from a balance between the processes of adsorption, recombination, trapping, and interfacial transfer of the charge carriers.

As a result, the generation of effective electrons and holes is the first step of the proposed mechanism, and the rate constant of the production of the effective charge carriers may be reduced. In our previous work (Arabameri and Bashiri 2021), we investigated the effect of light intensity on the photocatalytic degradation of the crystal violet by the TiO$_2$ using kinetic Monte Carlo simulation. The entering light intensity in the reaction vessel is estimated by the chemical actinometry method. The simulation results showed that the photodegradation percent and the effective concentration of photons increase with the light intensity increasing until an optimum value and then, it remains almost constant. As the light intensity increases, the number of incoming photons on the surface increases, and it causes more production of CB electrons and VB holes.

Based on the proposed approach, two categories of factors affect the rate of the photodegradation process. The first category of factors, such as the active sites, depends on the photocatalyst properties. The second category of factors, such as the light scattering, depends on the system properties.

The light scattering increases with increasing light intensity. As the incident photons on the photocatalyst surface decrease, the effective concentration of photons decreases. The result of these factors determines the rate of photocatalytic degradation. In addition, the scattering rate is a function of the geometry of the photoreactor. The light scattering affects the production step of charge carriers. This step is considered a crucial step of the dye degradation mechanism. In other words, it is part of a general process, not a separate step. Therefore, the reduced rate constant of this step can also be attributed to the limitations of the dye degradation process.

On the one hand, the rate of photocatalytic reactions is relatively low, and on the other hand, hydroxyl radicals react rapidly with pollutant molecules. Consequently, the rate constant of the first step is expected to be lower than the other steps of the mechanism. Therefore, it can be concluded the rate constant of this step is a complex parameter, and it is influenced by various factors. These factors depend on the operating conditions of the pollutant degradation. These factors lead to a decrease in the rate constant of charge carrier generation. The simulation and fitting results showed the value of the rate constant of the electron–hole productions step is lower than other steps.

Based on these arguments, the proposed approach assumes a significant fraction of the incident light beams is scattered into the reaction vessel and does not lead to electron–hole generation. Therefore, a minor fraction of the photogenerated carriers leads to degradation of the organic pollutants, due to performance-limiting factors, such as the recombination process, and the photoreactor geometry. In other words, a small number of electron–hole pairs generated by the intensity of the absorbed light contributes to the destruction of organic pollutants, and many of them are ineffective.

This discussion proposes two variables: “the effective concentration of photon ($I_{\text{eff}}$)” and “the effective concentration of reactive centers (RC).” Based on the proposed mechanism, the effect of limiting factors appears on $I_{\text{eff}}$ and RC. The concentration of reactive centers on the photocatalyst surface is constant during light irradiation. Therefore, with increasing light intensity, the RC involved in the degradation process increases until a certain amount, and after that, it does not increase. Still, the electron–hole recombination dominates over the production of charge carriers and prevents the increase of the pollutant photodegradation. Therefore, the optimum amount of light intensity was easily determined by plotting $I_{\text{eff}}$ versus light intensity.

These variables depend on the system operational parameters, such as the initial pollutant concentration, photocatalyst loading, light intensity, the solution pH, and the volume of the reaction vessel. The effective concentration of photon refers to the effect of the charge carriers in the pollutant degradation. Besides, the effective concentration of reactive centers indicates the role of the photocatalyst and its interaction with the other dissolved species in the degradation process. In our approach, the effective reactive centers refer to the sites that play a direct role in the destruction of the organic pollutant. The structure and effective concentration of the reactive centers depend on the following factors: (1) the structure of the photocatalyst; (2) the pH of the solution; (3) the species dissolved in the solution.
The pH of the solution is a critical parameter in the degradation of the pollutants under UV/visible irradiation. Because the medium pH determines the charges on the catalyst surface and the organic pollutant molecules. It is affected by various factors such as the charge values on the semiconductor surface and organic pollutant molecules, ROS concentration formed during the destruction process, and the aggregates’ size. The influence of pH on the photocatalytic activity of the organic pollutant molecules has been investigated by several researchers (Alkaim et al. 2014, Kazeminezhad and Sadollahkhani 2016). Therefore, the structure of the reactive centers depends on the solution’s pH. In some cases, the degradation rate of the cationic organic pollutants in an acidic medium is greater than that of an alkaline solution (Devi et al. 2017). In the proposed method, this behavior is ascribed to the increase in the concentration of the hydroxyl groups originated from the interaction of the protons (or water molecules) with the surface oxygen sites.

For the A−dopedMxOy/B photocatalyst, the concentration of reactive centers of M−OH2+, M−ObridgeH−M, A−OH2+, and A−ObridgeH−A increases in the acidic pH due to the availability of sufficient protons. Also, the concentration of the M−OH: M−OH− A−OH, and A−O− reactive center increases at alkaline conditions. In a neutral medium, the reactive centers produced by the interaction between non-dissociated water molecules and the MxOy surface are responsible for the degradation of the organic pollutant. It is worth noting that if A was not a metallic element, there is no effective interaction between this component and water species. The effective variables, especially \( I_{\text{eff}} \), can be used to determine optimal operating conditions. During the fitting process, the rate constants, \( I_{\text{eff}} \) values, and the effective concentration of reactive centers are adjusted simultaneously to obtain the best fitting between the experimental data and simulated results. Two significant results are obtained by the plotting of \( I_{\text{eff}} \) data against the values of operational parameters: (1) the optimum degradation conditions and (2) the effect of each parameter on the production process of the charge carriers.

**The adsorption of the pollutant on the photocatalyst surface**

The second part of the proposed mechanism refers to the adsorption process. The adsorption of the pollutant on the catalyst surface is one of the important factors in photocatalysis (Li et al. 2016). Generally, the organic pollutant adsorption on the photocatalyst surface depends on two factors: the electrical charge of the photocatalyst and the electrical charge of the organic pollutant molecules. Therefore, the adsorption capacity of the photocatalyst is known to be pH dependent (Grzechulska and Morawski 2002). In this work, the adsorption process refers to the adsorption of organic pollutant molecules on the catalyst surface during the photocatalytic reaction.

As seen in Tables 4 and 5, the values of the rate constants for the adsorption step indicate the following comments. (1) The pollutant adsorption on the surface of the photocatalyst under visible light irradiation plays a more prominent role in the degradation process; (2) the amount of TC adsorbed on the N-TiO2/RGO surface was high in the dark (without light) due to the presence of the RGO; (3) the pre-adsorption of the pollutant on the TiO2 surface is an essential factor to initiate the photodegradation process under visible light; (4) based on the mechanism proposed in Table 5, TC adsorbed on the TiO2 surface can be an important factor for the transfer of electrons to the TiO2 conduction band (Li et al. 2014). These observations are in agreement with the experimental results.

Furthermore, the photocatalytic processes are complicated and consist of many elementary steps. One of these steps is the adsorption of pollutant molecules on the catalyst’s surface. The adsorption process can be divided into two parts: (1) adsorption in dark conditions and (2) adsorption during the photocatalytic process. The experimental study of these two parts simultaneously is complicated due to their synergistic effects. For this reason, in most photocatalytic studies, dark adsorption is first investigated to evaluate the equilibrium constants of the adsorption of pollutants on the photocatalyst surface. The Langmuir–Hinshelwood model has been widely used to study the degradation kinetics of organic pollutants by various photocatalysts (Barka et al. 2008). This model states that the adsorption of pollutant molecules on the surface of the photocatalyst is an important factor that must be considered before any chemical reaction (Zhao and Yang 2003). Based on these arguments, the equilibrium constant of adsorption in the dark conditions cannot be considered exactly equal to the equilibrium constant of adsorption during the photocatalytic degradation process. For this reason, the calculated equilibrium constant in dark conditions cannot be used as the equilibrium constant for the adsorption step in Tables 4 and 5.

However, the fitting results indicate the critical role of the AOPs in the high degradation of the pollutants. The following possible reasons can be used to explain these results: (1) the powerful holes are produced in the photocatalyst/UV light system that can rapidly oxidize the pollutants. Therefore, adsorption seems to be less important in these conditions. The experimental results show that only 3.51% of the CR concentration and 5.31% of the AO7 concentration were adsorbed on the surface of the photocatalyst during the adsorption process in dark conditions.

However, the nature of the dark adsorption is different from the adsorption process during the photocatalytic reaction. If organic pollutant molecules were adsorbed on the photocatalyst surface, they might be more easily oxidized...
by the valence band holes or ROSs (Hossain et al. 2018). The adsorption step of organic pollutant on the TiO₂ surface is one of the elementary reactions of photocatalytic degradation in the proposed mechanism. Here, it is assumed that the reactive centers are the sites where the reaction can take place on the catalyst surface. The strategy considered for the adsorption process in the proposed approach can be described as follows: “the degradation of the adsorbed pollutant after light irradiation and then the adsorption of new molecules on the photocatalyst surface.”

The trend of changes in the concentration of the adsorption sites obtained from the fitting process can be observed in Fig. 3. In agreement with the literature (Yoneyama and Torimoto 2000, Yu et al. 2000), the fitting results indicate that increasing the number of adsorption sites improves the pollutant degradation on the photocatalyst surface. A relative correlation is observed between the degradation efficiency and the adsorption of the pollutant on the photocatalyst surface. The enhanced photocatalytic performance of the 3 wt.% Fe-doped TiO₂ (100 mg L⁻¹, pH = 3), 3 wt.% Ni-doped ZnO, and N-doped TiO₂/RGO compared to the other samples could be ascribed to the adsorption ability increasing of these catalysts. In agreement with the experimental results, the effective concentration of adsorption sites in N-doped TiO₂/RGO is increased in virtue of the presence of RGO.

It was found (Sathishkumar et al. 2011) that the catalysts with the higher surface areas provide more reactive centers, which could increase the organic pollutant adsorption and the incident UV light on the TiO₂ surface. Since more charge carriers will be generated when the catalyst surface interacts with more photons, the effective photon concentration is maximum in these samples (Fig. 3). Therefore, the surface area increasing can lead to high photocatalytic activity and improved pollutant degradation efficiency.

However, the fitting process indicates that the relatively small changes in the rate constant of the adsorption step have a significant effect on the fitting results. One possible reason for this behavior is the strong effect of the adsorption site concentration on the photodegradation process.

The effect of the modification of the photocatalyst on the degradation process

The various studies clearly show the doping of semiconductors with non-metallic atoms, transition metals, and organic compounds play a vital role in their photocatalytic performance (Gomez-Ruiz et al. 2018; Haque et al. 2013; Kumar et al. 2016). These strategies are proposed to overcome the limitations of semiconductors, prevent the recombination of the electron–hole pairs, and improve the ROSs production process. By implementing the above strategies, the photocatalytic system provides several possible paths to achieve these goals.

The fitting results show the modification of the TiO₂ and ZnO by the different materials, such as the Fe, Ni, Ag, and RGO lead to the following beneficial effects in the photocatalyst: (1) higher surface area; (2) the more effective trapping of the carriers; (3) the narrowing of the bandgap; (4) the increasing of the concentration of water species and oxygen molecules on the photocatalyst surface. These results are in agreement with the experimental findings. The incorporation of the nickel into the zinc lattice produces more electron–hole pairs without altering the crystal structure of the ZnO (Gnanamozhi et al. 2020).

The Fe and Ni dopant introduce the impurity states in the band gap of the TiO₂ and ZnO. Also, silver acts as an acceptor material to alter ZnO band gap energy. The results of the X-ray spectroscopy (DRS) showed the band gap of the TiO₂ is narrowed by the N-doping (Peighambardoust et al. 2018). Besides, the coupling of the TiO₂ with RGO decreases the bandgap energy (Li et al. 2020). Therefore, the doping process in these semiconductors leads to a decrease in their bandgap energy. The narrowing of the bandgap increases the efficiency of these photocatalysts for using the visible part of the solar spectrum in pollutant degradation.

Chen et al. (Chen et al. 2015) observed that an appropriate amount of Fe³⁺ ions could act as the reactive centers for trapping of the charge carriers on the TiO₂ surface. Reddy et al. (Reddy et al. 2018) showed the doping of the Ni²⁺ ions into ZnO lattice improves the interfacial charge transfer by the red shift in Fermi level position. Wageh et al. (Wageh et al. 2018) showed the rate constant of 7% wt. Ag-doped ZnO for the photocatalytic degradation of methyl orange was 38 times more than pure ZnO. They attributed this Ag-doped ZnO behavior to enhanced absorption in visible-light range and improved interfacial charge transfer. Beltrán et al. (Garrafa-Gálvez et al. 2019) found the photocatalytic performance of the TiO₂/RGO nanocomposite under solar light irradiation was ~5 times that of pure TiO₂. The improvement of the photocatalytic activity of the TiO₂/RGO was attributed to RGO role as a charge transporter and acceptor.

Therefore, the degradation rate increases by modifying the TiO₂ and ZnO due to these important factors: (1) it leads to more effective separation of the hole-electron pairs, and (2) the synergistic effects between the new materials and semiconductors are seen. In other words, the dopants (Fe, Ni, Ag) and the RGO can form intermediate pathways for the transport and interfacial transfer of charge carriers. Therefore, this proposed approach uses many pathways for the degradation of pollutants.

$$\text{Fe}^{3+} + \text{Ag} + e^- \rightarrow \text{Fe}^{2+} + \text{Ag}^- \quad (9)$$
As shown in Table 4, the fitting results showed the rate constant for Eq. (18) is slightly higher than the rate constant of Eq. (19). However, the rate constant of the holes’ trapping by the first type of the effective reactive centers has a more significant effect on the conformity of the simulated results and experimental data. This result can be ascribed to the higher power of hydroxyl radicals generated by the valance band holes.

Water species are a crucial factor in forming some reactive centers on the surface of the TiO2 and ZnO. In the proposed approach, water is adsorbed on the TiO2 surface in two forms, i.e., the dissociative and the molecular. In molecular adsorption, the oxygen atom electrostatically interacts with a Ti5c site, and the hydrogens form the H bonds with two surface O2c sites on the next ridge. The formation of the hydrogen bonds between water molecules and the TiO2 surface expands a strong network of high-ordered configurations (Mattioli et al. 2008). In dissociative adsorption, the hydroxyl group bonds to a Ti5c atom, and hydrogen ion bonds to an O2c atom. Therefore, two distinct hydroxyl groups can arise from the water dissociation on the TiO2 surface, i.e., terminal and bridging hydroxyl species (Patrick and Giustino 2014, Wahab et al. 2008). Because the fivefold coordinated Ti atoms act as Lewis acid sites able to form powerful bonds with electron pairs of water molecules, and twofold coordinated oxygen atoms act as Lewis base sites able to share a pair of the electrons with empty orbitals. Walle et al. (Walle et al. 2011) showed that the amount of molecular and dissociated species of the adsorbed water on the surface are comparable. Dissociative adsorption of water molecules can produce hydroxyl groups and protons bonded to the TiO2 surface. The hydrogen and hydroxyl ions of the aqueous solution are adsorbed on the TiO2 surface and create the reactive centers of the RC1. On the other hand, the interaction of water species and Fe2+ and Ni2+ ions leads to the formation of the RC2 reactive centers on the surface of the Fe-doped TiO2 and Ni-doped ZnO. It was reported (Carneiro et al. 2011) that the iron doping into the TiO2 lattice leads to more surface hydroxylation.

In the past decades, the water interaction with the ZnO surface has been studied using both experimental and computational methods. Martins et al. (Martins et al. 1996) investigated the adsorption of the H2O molecules on a (ZnO)22 cluster by using some semi-empirical procedures. Their results indicated the weak interaction of the hydrogen atom of water with the oxygen atom of the ZnO surface leads to the formation of the O–H …O band.

Kharche et al. (Kharche et al. 2014) analyzed the microscopic structure of the ZnO aqueous interfaces using the
first-principles density functional theory. They concluded that protons of the dissociated water molecules interact with the oxygen anions of the ZnO surface, while the hydroxide ions interact with Zn cations. The presence of hydroxyl groups is confirmed by the FT-IR spectroscopy (Gnannozhi et al. 2020). The interaction of H2O molecule with the oxygen-terminated polar surface of ZnO was investigated by Kunat et al. (Kunat et al. 2003). They suggested that two OH species are formed by the dissociation of water molecules at the O-vacancy. Therefore, water is adsorbed on the ZnO surface in both physisorption and chemisorption forms (Nagao 1971; Yue et al. 2018).

The FT-IR spectra exhibit the presence of Zn–O–Ni bonds for all the Ni-doped ZnO samples (Mousavi et al. 2017). Water molecules and hydroxyl ions can interact with nickel ions on the Ni-doped ZnO surface to form the reactive centers of the RC2 (Assowe et al. 2012; Cappus et al. 1993; Simion et al. 2017). According to the proposed approach, these reactive centers have a synergistic effect on the organic pollutant photodegradation. The concentrations of the reactive centers are considered as a function of the pH solution. At the isoelectric point, the molecular form of water is effective in the formation of the reactive centers due to the low concentration of hydroxyl and hydrogen ions.

Since the report of the photocatalysis phenomena, many authors (Montoya et al. 2013; Salvador 2007) confirmed that electrons and holes are trapped in bulk or on the surface of photocatalyst. It has been debated whether the VB free holes are trapped by surface-adsorbed water species, or by the surface oxygen ions (Liu et al. 2014). The analysis of the electronic structure showed (Bahnemann et al. 1984) the HOMO levels of the adsorbed water on the rutile TiO2 (110) are much less than the top of the TiO2 VB level. For this reason, Salvador (Salvador 2007) explained the photogenerated holes do not have enough power to oxidize the adsorbed water species, and the oxidation of the water molecules by photogenerated holes is prohibited. The photo-induction process may change the position of the molecular orbitals in the electronic structure of the adsorbed water species. Therefore, some authors still believe the photocatalytic process is initiated through the oxidation of the adsorbed water on the surface by the valence band holes (Tan et al. 2012).

The formation of surface-adsorbed hydroxyls in the A–dopedM1O3 photocatalyst can be written as follows:

$$
\text{OH}^\bullet (\text{ads}) + \text{H}^\bullet (\text{ads}) \rightarrow \text{OH}^\bullet (\text{ads}) + \text{H}^\bullet (\text{ads})
$$

(20)

Photo-induced holes generated under UV illumination are simultaneously trapped with the conduction band electrons (Bahnemann et al. 1997). The trapped hole on the surface is considered as an adsorbed OH− radical (Nagao and Nosaka 2017, Schneider et al. 2014). The holes trapped are transferred to water species, resulting in the formation of OH′(ads). Researchers believe the hydroxyl radicals or the surface-adsorbed holes are the main oxidizing intermediates for the degradation of the organic pollutants (Andreozzi et al. 1999; Kuang et al. 2016). Several groups were presented the experimental evidence of the production of hydroxyl radical in photocatalytic reactions (Al-Ekabi et al. 1989; Carraway et al. 1994; Mao et al. 1991; Okamoto et al. 1985). Hydroxyl radicals (OH′) are short-lived and strong oxidants in an aqueous medium that react quickly with many of the dissolved compounds. The reaction between ROSs and an organic pollutant is symbolically represented in the fourth part of the general mechanism.

According to the experimental conditions, it has been reported (Qian et al. 2019) the trapping timescale of the VB holes varies between picosecond and nanosecond. As shown in Table 4, the rate constants of the trapping the valence band holes by the reactive centers of RC1 or RC2 are in order 107. Our findings show a good correlation between the rate constant and the timescale of the trapping process. The trapping step of VB holes is the most important step of pollutant degradation due to the high reactivity of hydroxyl radicals (Munter 2001). The fitting results showed that the rate constant of the hole trapping step by the reactive centers has a significant impact on the fitting curve.

Therefore, it is easy to understand the importance of water species and dopant level in the photocatalytic degradation of the pollutant using the proposed mechanism. As shown in Fig. 3a, the fitting results indicate that the effective concentration of reactive centers of the RC1 and RC2 is at their maximum value in a sample with the highest photocatalytic performance. Therefore, these variables can be used to find the optimal condition of the studied system.

An important pathway for the organic pollutant oxidation in photocatalytic reactions is the direct attack of VB holes to the pollutant molecules adsorbed on the catalyst surface. This step competes with the reaction of hydroxyl radicals and the pollutant molecules, because these charges have high oxidation potential (2.9 V vs. SHE in pH=0). The main pathway of the organic pollutant degradation is determined by the type of the catalyst and the pollutant’s nature. However, the fitting results confirm the adsorbed pollutants on the TiO2 surface are destroyed by the direct attack of the VB holes, and the rate constant of this step affects the fitting curve.

Chen et al. (Chen et al. 2005) indicated the AO7 degradation is primarily initiated by photo-induced holes. Sivalingama et al. (Sivalingam et al. 2003) investigated the photocatalytic degradation of the various dyes in the TiO2 suspension under UV light irradiation. They assumed that
dyes are oxidized by direct attacks of holes and hydroxyl radicals. Bahnemann et al. (Bahnemann et al. 1997) found a mechanism for the photocatalytic oxidation of dichloroacetate and thiocyanate on the TiO$_2$ (anatase). They stated the strongly adsorbed molecules react with the free VB holes, whereas the weakly adsorbed species react with long-live trapped holes.

The adjusted value of the rate constant (Table 4) shows the rate of this step is comparable with the trapping the holes in the reactive centers of RC1 and RC2. In other words, the rate constant confirms the claim that direct attack of holes supports the pollutant destruction by hydroxyl radicals. The computational results demonstrate that the rate constant of this step has a lower effect on the fitting process than the trapping of the holes by the reactive centers of RC1 and RC2. Therefore, there are two distinct pathways for the degradation of organic pollutant: (1) the free degradation by the charges trapped on the photocatalyst surface and (2) degradation of pollutants adsorbed on the surface of the photocatalyst by free holes. The role of these pathways in eliminating of pollutants depends on the photocatalyst nature, the pollutant structure, and the solution pH. The fitting results indicate the second pathway is less important because its proceeding depends on the adsorption reaction. One possible reason is that reactive centers are more accessible than adsorbed molecules.

The photogenerated holes have a short life-time, which can attack and destroy the adsorbed dye molecules on the photocatalyst surface. The intermediates produced during the AO7 photodegradation process may be adsorbed on the photocatalyst surface or diffuse into the solution. It is possible that the absorbed intermediate molecules on the surface are destroyed by the free VB holes. However, the simulation results show that the reaction of the photogenerated holes with intermediates has no effect on the AO7 degradation process. In other words, the curve of the AO7 concentration versus time is not affected by a change in the rate constant of this reaction. Therefore, the reaction of the photogenerated holes with intermediate molecules was ignored in the proposed mechanism.

On the other hand, excess electrons are usually available on the photocatalyst surface due to various factors such as intrinsic defects, the other element doping into the TiO$_2$ lattice, and the photo-induction by UV/Vis light illumination. These electrons may be trapped by some adsorbed species on the photocatalyst surface.

Oxygen molecules can play an essential role in the formation of the reactive centers. The ability of the charged oxygen molecule production is an influential factor in photoactivity. Wu et al. (Wu et al. 2003) suggested two molecular and one dissociated adsorbed configurations for the O$_2$ adsorption on the TiO$_2$ surface. In the most stable molecular configuration, the oxygen molecule is adsorbed on the vacancy site and binds to the two nearest Ti cations. In the other molecular configuration, O$_2$ molecule is located on top of a Ti$_{5c}$ atom. The binding energy of this configuration is $\sim 2$ eV smaller than the binding energy of the first configuration.

Due to the availability of adequate oxygen, our approach assumes the O$_2$ molecules primarily adsorb on the A – dopedM$_x$O$_y$/B surface, leading to the formation of RC3, RC4, and RC5. These reactive centers trap the excess electrons. When the photogenerated holes quickly migrate to the surface trapping centers, electrons are initially trapped in Ti$^{3+}$ lattice trapping states (Di Valentin et al. 2006). The photoexcited electrons in Ti$^{3+}$ defect sites were firmly confirmed by the electron paramagnetic resonance (EPR) technique (Hurum et al. 2003). The transfer of one or more trapped electrons to the oxygen molecules leads to the formation of adsorbed-surface oxygen, and consequently, the generation of the superoxide anion radicals. It was reported (Fujishima et al. 2008) the trapped electrons react with oxygen molecules faster than the free electrons.

Superoxide radicals (O$_2^-$) enable to act as the effective species for destroying many toxic organic pollutants (Carter et al. 2007, Ryu and Choi 2004). Kuang et al. (Kuang et al. 2016) found that 40% of the total degradation of orange II and methylene blue dyes could be attributed to O$_2^-$, and the UV photolysis in the TiO$_2$/UV system. The formation of O$_2^-$ during the photocatalytic reactions was confirmed by several techniques (Jaeger and Bard 1979, Nosaka et al. 1997). The characteristic time for trapping of the charge carriers varies depending on the experimental conditions from picosecond to nanosecond timescale (Friedmann et al. 2010). Tamaki et al. (Tamaki et al. 2007) reported that the electrons and holes are trapped on the surface of the anatase TiO$_2$ at $\sim$200-fs timescale.

Bahnemann et al. (Bahnemann et al. 1997) determined a rate constant of the reaction of the trapped electrons with oxygen molecules as $7.6 \times 10^7$ L mol$^{-1}$ s$^{-1}$. Gerischer (Gerischer 1995) reported the rate constants for transfer of free and trapped electrons to oxygen molecules are $4.5 \times 10^7$ and $4.5 \times 10^5$ s$^{-1}$, respectively.

In our study, it is assumed the concentration of dissolved oxygen (DO) remains constant during the photocatalytic reaction. Pan et al. (Li et al. 2019) investigated the various properties of the ZnO nanoparticle as a gas sensor. They found that oxygen molecules are rapidly pre-adsorbed on the surface of the ZnO (001). Wang et al. (Li et al. 2005) studied the sensing mechanism of the ZnO films by the transient photocurrent technique. Their results indicated that O$_2$ molecules are adsorbed on the surface of ZnO in both physisorption and chemisorption forms. When the Ni-doped ZnO is exposed to oxygen, the reactive centers of the Ni–O$_2$ are formed by the reaction of the adsorbed oxygen molecules with nickel ions (Norton et al. 1977; Qian et al. 2020).
In our provided mechanism, the photogenerated electrons are trapped by Ti$^{4+}$, Fe$^{3+}$, Zn$^{2+}$, and Ni$^{2+}$ ions in the reactive centers of Ti$^{4+}$ – O$_2$(ads), Fe$^{3+}$ – O$_2$(ads), Zn$^{2+}$ – O$_2$(ads), Ni$^{2+}$ – O$_2$(ads), and RGO – O$_2$(ads). Besides, silver is considered as a reactive center, which can accept and transfer the CB electrons of the semiconductor. Some studies (Sengunthar et al. 2020; Yu et al. 2018) showed the higher photocatalytic efficiency of RGO/TiO$_2$ and RGO/ZnO is attributed to RGO. It acts as (1) a charge separator, (2) a photosensitizer, and (3) a good adsorbent. The RGO sheets transfer the CB electrons to the adsorbed oxygen molecules on the nanocomposite surface to produce O$_2^-$ radicals.

As shown in Fig. 3c, the improvement of the photocatalytic efficiency of the N-doped TiO$_2$/RGO sample can be attributed to the presence of RC5 reactive centers, which can trap the CB electrons. The fitting results show the rate constant of the trapping of photo-induced electrons by the reactive centers of the RC3, RC4, and RC5 is in the order of $10^9$. The values of the rate constants are consistent with this strategy and to the timescale of the process of trapping the CB electrons on the TiO$_2$ surface (Friedmann et al. 2010).

The results of our work show the fitting process is affected by changing the value of the rate constant for the reaction of the CB electrons with the reactive centers of the RC3, RC4, and RC5. Therefore, using the proposed mechanism, the role of the following two factors in the pollutants photodegradation can be explained: (1) the synergistic effect of the Fe$^{3+}$, Ni$^{2+}$, RGO, and Ag$^+$ with TiO$_2$ and ZnO, and (2) the flow rate of the O$_2$.

The proposed mechanism is in good agreement with the experimental results. Trapping experiments showed that OH$^*$ and O$_2^-$ in the system of the Ag/ZnO/O$_3$/phenol play a major role in the degradation of pollutants, which is consistent with the EPR results (Peng et al. 2019). On the other hand, the radical quenching experiments clearly indicated that O$_2^-$ radicals have an important role in the TC photodegradation under visible light illumination (Tang et al. 2018).

Hydrogen peroxide (H$_2$O$_2$) is another important ROS in photocatalytic systems. It is produced from two pathways during the photocatalytic processes. Those are the two-hole oxidation of H$_2$O and the two-electron reduction of O$_2$(ads) (Hirakawa et al. 2001, Nosaka and Nosaka 2017, Sahel et al. 2016), as follows:

$$2\text{H}_2\text{O} + 2\text{h}^+ \rightarrow \text{H}_2\text{O}_2 + 2\text{H}^+ \quad (21)$$

$$\text{O}_2^-(ads) + \text{e}^- + 2\text{H}^+ \rightarrow \text{H}_2\text{O}_2 \quad (22)$$

The reduction pathway seems to be dominant due to the low reactivity of superoxide radicals. Li and Selloni (Li and Selloni 2013) found the generation of O$_2^-$ via the transfer of an electron to an oxygen molecule is barrier-less. In contrast, the transfer of the second electron to adsorbed superoxide to produce an adsorbed H$_2$O$_2$ is nonadiabatic, and it has a barrier of 0.3 eV at the anatase TiO$_2$. A low concentration of hydrogen peroxide has been detected in the aqueous suspension of the TiO$_2$ and ZnO under UV illumination (Mrowetz and Selli 2006, Nosaka et al. 1997). It can be formed by the reaction of the electrons with superoxide radicals in the presence of protons (Sahel et al. 2016):

$$\text{O}_2^-(ads) + \text{e}^- + 2\text{H}^+ \rightarrow \text{H}_2\text{O}_2(ads) \quad (23)$$

It was reported (Nosaka and Nosaka 2017) the quantum yield of the H$_2$O$_2$ generation is in the order of $10^{-7}$ for the TiO$_2$ powder, and in the order of $10^{-3}$ for the anatase TiO$_2$ films. Although the rate constant of this reaction is high, the fitting results show that this reaction has little effect on the fitting curve. The reason may be as follows: (1) the proceeding of this reaction depends on the presence of three species; (2) the concentration of hydrogen ions is low in the non-acidic solution.

The rate constant for the reaction of the aqueous electrons with H$_2$O$_2$ is in the order of $10^{10}$ M$^{-1}$ s$^{-1}$ (Gierer et al. 1994). This reaction is thermodynamically favorable ($\Delta E^0 = +0.73$ V at pH 7) (Nosaka and Nosaka 2017). The fitting results show the adjusted value of the rate constant for the electron reaction with H$_2$O$_2$ is in the order of $10^0$. This result is consistent with the trapping process of the CB electrons on the TiO$_2$ surface. Therefore, the reaction of electrons with H$_2$O$_2$ has a significant effect on degradation of organic pollutant. As a result, the effect of H$_2$O$_2$ on the degradation process in photocatalytic systems can be investigated with these explanations.

The recombination of the charge carriers

The sixth part of the general mechanism is the recombination of the charge carriers. In our approach, the degradation of the organic pollutants is prevented by both recombinations of the free and the trapped electron–hole pairs. The trapping of the charge carriers not only prevents the recombination of the charge carriers on the fitting process was investigated by changing the value of the rate constant. The fitting results show that the recombination of e$^-$/h$^+$ pairs has a determining role in the degradation of the organic pollutant. The recombination of the charge carriers is an important step of the photodegradation process that occurs in a femtosecond timescale. The quantum yields of the most photocatalytic reactions are less than 10%, and it can be due to the recombination process. After a certain time, the charge carriers are recombined to produce light and heat. The recombination of the charge carriers is one of the most
important factors in the fabrication of photocatalysts and the design of the photoreactors (Li and Li 2002, Visan et al. 2019; Wang et al. 2010).

The adjusted value of the rate constant for the recombination of the charge carriers shows that this step has a significant effect on the degradation process of organic pollutants. Besides, the fitting results indicate the following findings: (1) the free charge carriers recombine faster than the charge carriers trapped by the TiO$_2$ surface; (2) the value of $R^2$ changes significantly by changing the value of the rate constant for the trapping of the CB electrons by the semi-effective centers; (3) the fitting process is strongly influenced by the recombination of the charge carriers trapped in the reactive centers.

Figure 3 shows that the concentration of the semi-effective centers is highest in the following samples: 3% wt. Fe-doped TiO$_2$, pH = 3, 3% wt. Ni-doped ZnO, N-doped TiO$_2$/RGO, and Ag-doped ZnO/O$_3$. The fitting results are in agreement with the experimental results. Using the proposed approach, a deeper understanding of the recombination process is obtained, and the obtained results are in agreement with the previous studies (Krýsa et al. 2006; Qian et al. 2019; Rothenberger et al. 1985). Therefore, this study confirms the trapping of the charge carriers by the active sites is an acceptable strategy.

### Inactivation reactive centers

A prominent feature of the proposed mechanism is that hydroxyl radicals are consumed by the inactivation of the reactive centers (Barka et al. 2010; Daneshvar et al. 2004; Dutta et al. 2009). This step is symbolically represented in the seventh part of the general mechanism (Table 3). The nature of these centers is highly dependent on the type of catalyst and the reaction conditions. For instance, the following two reactions can be performed to form H$_2$O$_2$ (Guo et al. 2011, Pelizzetti and Minero 1993):

\[
\text{TiO}^\cdot\text{H} + \text{TiO}^\cdot\text{H} \rightarrow \text{H}_2\text{O}_2(\text{ads}) \tag{24}
\]

\[
\text{TiO}^\cdot\text{H} + \text{OH}^- \rightarrow \text{H}_2\text{O}_2(\text{ads}) + e^- \tag{25}
\]

Daneshvar et al. (Daneshvar et al. 2004) and Dutta et al. (Dutta et al. 2009) assumed the hydroxyl radicals produced in the photocatalytic reaction could be consumed by the inactivation species. They suggested that inactivation of the hydroxyl radicals with inactive centers is more important than other steps. According to Table 4, the fitting results show that the rate constant of the inactivation step is in the order of $10^6$. This study shows the fitting data is affected by changing the value of the rate constant for the reaction of the inactivation species with the ROSs. Therefore, this step has an essential impact on the degradation of the pollutant and competes with other reactions.

On the other hand, some inactivated OH$^-$ radicals may be reactivated by the participation of water molecules and activation sites. For example, the produced H$_2$O$_2$ in the photocatalytic reaction may be converted to hydroxyl radicals by the following reactions:

\[
\text{Ti}^{IV} + e^- + \text{H}_2\text{O} \rightarrow \text{Ti}^{III}\text{OH}_2 \tag{26}
\]

\[
\text{Ti}^{III}\text{OH}_2 + \text{H}_2\text{O}_2(\text{ads}) \rightarrow \text{TiO}^\cdot\text{H} + \text{OH}^- + \text{Ti}^{IV}\text{OH}_2 \tag{27}
\]

In this work, the effect of the re-activation step on the degradation of the organic pollutant was investigated by changing the values of the rate constants. The results indicated that the reactivation process in the studied systems is much less important than the generation of hydroxyl radicals or the inactivation reaction. For this reason, the reactivation steps were omitted in the final mechanism.

### Comparison of the pollutant photodegradation caused by different light sources

This approach can be used to investigate the photodegradation mechanism of the organic pollutants by photocatalysts with the general formula A-doped M$_x$O$_y$ under different irradiation sources. In this work, the AO7 photodegradation on the 2 wt.% Fe-doped TiO$_2$ surface induced by different light sources was simulated. The curves of the AO7 concentration versus time for these samples are plotted in Fig. 5. As can be seen in this figure, there is good conformity between...
the results of the simulation and the experimental data. The adjusted values of the rate constants of the first step for the irradiation sources of the UV, solar, and visible light are $1.47 \times 10^{-3}$, $7.33 \times 10^{-4}$, and $4.90 \times 10^{-4} \text{ M}^{-1} \text{ min}^{-1}$. The rate constant of the other steps is the same as the values given in Table 2 for the Fe-doped TiO$_2$ system. These results show the degradation efficiency of the UV light is greater than that of the solar light and visible light. The simulation results show the effective concentration of photons ($I_{\text{eff}}$) in the 2 wt.% Fe-doped TiO$_2$/visible-light/AO7 system is lower than other samples. The reason can be attributed to the lower power of visible-light photons. This decreases the effective concentration of the charge carriers and thus the rate of the AO7 degradation.

We predict the proposed approach can also be used to investigate the mechanism and kinetics of photocatalytic reactions using other photocatalysts such as sulfides. However, it should be examined in another study.

**Comparing the proposed approach with the first-order equation**

The Langmuir–Hinshelwood kinetic model is often used to describe the photocatalytic degradation of the organic pollutants (Ranjbar et al. 2019). Analytical solution of the Langmuir–Hinshelwood differential equation does not lead to an equation in which the pollutant concentration versus time is directly obtained. For this reason, researchers have approximated this model to the first-order kinetic equation (Nguyen et al. 2018). The first-order kinetic equation cannot provide a detailed description of the various elementary steps in the photodegradation mechanism of organic pollutants. When this equation is solved, the apparent rate constant is obtained. The apparent rate constant is a function of the operating conditions, and it changes by increasing the pollutant concentration. However, they cannot provide an accurate description of such processes. One of the obvious drawbacks of this equation is that the apparent rate constant changes by changing the pollutant’s concentration, whereas it should not happen from a kinetics point of view.

In contrast, our proposed approach provides a more reliable description of the various steps of the photodegradation process. A comprehensive mechanism for the degradation of organic pollutants by A-doped M$_x$O$_y$/B photocatalysts was developed with our approach. Adjusted values of the rate constants, the effective concentration of photons, and the effective concentrations of reactive centers are obtained from the fitting process by a hybrid manual-automat ic method. As the pollutant concentration increases, the values of the rate constants of the elementary steps are constant.

In this study, the effects of initial pollutant concentration on the effective concentration of photons and the effective concentration of reactive centers were investigated. For this purpose, an article was chosen which used ZnO plates to photocatalytic degradation of the Reactive Red 180 (RR 180) in an aqueous solution (Yasstepe et al. 2008). Based on the presented mechanism in this work, the elementary steps of the mechanism of RR 180 photodegradation are shown in Table 6. In Fig. 6a, the curve of the RR 180 concentration versus time is plotted for the initial dye concentrations 20 to 60 mg L$^{-1}$. As seen in Fig. 6a, there is good conformity between the fitted and experimental data, and it confirms the presented mechanism for the RR 180 photodegradation. When the initial concentration of the RR 180 increases, the degradation percent decreases. This behavior can be explained as follows: due to the screening effect of the RR 180 molecules and the decreasing of the penetration length of photons in the solution, less photon number is absorbed on the TiO$_2$ surface. The effect of the initial concentration of the RR 180 on the effective concentration of photon was investigated, and the results are shown in Fig. 6b. It can be seen when the initial concentration of the RR 180 increases, the effective concentration of photons decreases. This result shows the generation of effective electrons and holes decreases by increasing initial dye concentration. In the proposed approach, the production of hydroxyl radicals varies directly with the effective photon concentration. In other words, the photodegradation percent decreases as the effective concentration of photons decreases.

The fitting results show these results: (1) the rate constants of the elementary steps are constant for the systems with different initial concentrations, (2) the effective concentration of photon varies in these systems, (3) the optimum concentration of the RR 180 is 20 mg L$^{-1}$, and (4) because the other operating parameters are constant, no change was observed in the effective concentration of reactive centers. The fitting of the experimental data with the first-order equation leads to different values of the apparent rate constants. Meanwhile, using our proposed approach, the rate constants of the elementary steps do not change by changing the initial dye concentration. Therefore, using the proposed approach by introducing the two new variables to study the pollutant photodegradation is more reliable than the first-order equation.

**Conclusion**

In this study, a new approach and a general mechanism are provided to investigate the kinetics of the degradation of the organic pollutants by the photocatalysts under UV/Vis light irradiation. This approach was examined to find a suitable mechanism for the photodegradation of the four different empirical systems of acid orange 7 on Fe$^{3+}$-doped TiO$_2$ nanocatalysts, ozonation of phenol on Ag/ZnO nanocomposites, tetracycline hydrochloride on N-doped TiO$_2$/
Table 6 The elementary reaction steps and their rate constants for the mechanism of the RR 180 photodegradation process by ZnO plate in the studied samples

| No. | The elementary steps | The rate constants (obtained by a hybrid manual-automatic method) |
|-----|----------------------|-------------------------------------------------------------------|
| 1   | ZnO(plate) + I_{eff} → e^- + h^+ | 1.022×10^{-3} (M^{-1} min^{-1}) |
| 2   | h^+ + Zn − OH → OH^*_{ads} | 8.39×10^{9} (M^{-1} min^{-1}) |
| 3   | h^+ + (RR180)_{ads} → 2 intermediate 1 | 1.00×10^{9} (M^{-1} min^{-1}) |
| 4   | h^+ + S\text{trapping} \rightarrow h\text{trapped} | 3.92×10^{9} (M^{-1} min^{-1}) |
| 5   | Zn − O_2 + e^- → O^*_{2ads} | 6.20×10^{9} (M^{-1} min^{-1}) |
| 6   | e^- + S\text{trapping} \rightarrow e\text{trapped} | 4.82×10^{9} (M^{-1} min^{-1}) |
| 7   | O^*_{2ads} + 2H^+ + e^- → H_2O_{2ads} | 1.42×10^{12} (M^{-1} min^{-1}) |
| 8   | H_2O_{2ads} + e^- → OH^*_{ads} + OH^- | 2.59×10^{9} (M^{-1} min^{-1}) |
| 9   | (RR180) + Site → (RR180)_{ads} | 2.54×10^{2} (M^{-1} min^{-1}) |
| 10  | (RR180)_{ads} → (RR180) + Site | 1.87×10^{2} (min^{-1}) |
| 11  | (RR180) + OH^*_{ads} → 2 intermediate 2 | 5.02×10^{7} (M^{-1} min^{-1}) |
| 12  | (RR180) + O^*_{2ads} → 2 intermediate 3 | 8.30×10^{4} (M^{-1} min^{-1}) |
| 13  | intermediate 2 + OH^*_{ads} → Products | 6.90×10^{6} (M^{-1} min^{-1}) |
| 14  | intermediate 3 + O^*_{2ads} → Products | 5.38×10^{8} (M^{-1} min^{-1}) |
| 15  | e\text{trapped} + h\text{trapped} → heat | 7.86×10^{9} (M^{-1} min^{-1}) |
| 16  | e^- + h^+ → heat | 8.90×10^{9} (M^{-1} min^{-1}) |
| 17  | S1 inactive + OH^*_{ads} → inactive | 8.00×10^{6} (M^{-1} min^{-1}) |

Fig. 6 (a) The curves of the RR 180 concentration versus time for the studied samples (the experimental (Yassıtepe et al. 2008) and the fitted results), (b) the effect of the initial concentration of the RR 180 on the effective concentration of photon
reduced graphene oxide, and congo Red on Ni-doped ZnO. The production of the effective reactive centers and the trapping of the charge carriers are two main strategies used in the proposed mechanism. This mechanism describes the experimental data well, and it can be used to predict the behavior of the photocatalytic systems at different conditions. The fitting results showed the excellent conformities between the calculated and experimental data at various conditions.

Two methods were used to estimate the parameters: the hybrid manual-automatic method and the optimization-based techniques. The first method can be performed in two steps to obtain good agreement between the experimental data and the fitting results: (1) manual adjusting the system parameters and (2) the optimization by the fminsearch function. The fitting results show the hybrid manual-automatic method leads to reliable values than optimization-based procedure. Moreover, the fitting results showed:

1. the rate constant of electron–hole generation step in the proposed mechanism is in the order of $10^{-2}$ for UV light and $10^{-1}$ for visible light illumination. Therefore, a small fraction of the charge carriers can lead to the degradation of the organic pollutants;
2. the photocatalyst surface is composed of the different reactive centers in contact to the water species and the other materials. Depending on the reaction conditions, a certain number of these centers participate in the organic pollutant degradation. The synergic effect of dopants increases the surface area, the effective reactive centers, and the trapped $e^-/h^+$ pairs, and thus, it improves the pollutant photodegradation;
3. the photodegradation efficiency is highest when the effective concentration of the reactive centers and the effective concentration of photons are maximum. Therefore, the optimum conditions can be achieved by the plotting of the concentration curve of the reactive centers for different conditions;
4. the hydroxyl radicals and superoxide radicals are mainly responsible for the degradation of the organic pollutants;

The proposed mechanism in this work can be utilized to construct efficient photocatalysts, to study the kinetics of the organic pollutant photodegradation on the surface, and to optimize them.

**Author contribution** Conception and design of study: H. B.; M. A. Collected the data, analysis, and/or interpretation of data: M. A. Wrote the manuscript: M. A.; H. B. All authors read and approved the final manuscript.

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**Data availability** The datasets used and/or analyzed during the current study are available from the corresponding author on reasonable request. All data generated or analyzed during this study are included in this published article [and its supplementary information files].

**Declarations**

**Ethics approval and consent to participate** Not applicable.

**Consent for publication** Not applicable.

**Competing interests** The authors declare no competing interests.

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