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Catalytic Degradation of Organic Dyes in Aqueous Medium

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Abstract

Water pollution by the textile industry is an emerging issue. Textile industry is the major industrial sector which contributes to water pollution. Textile industry releases a huge amount of unfixed dyes in wastewater effluents. About 20% of the dye production all over the world is discharged as waste in industrial effluents by textile industry. These dyes are highly stable and colored substances which disturb the aqueous ecosystem significantly. Therefore, there is a need for methods to remove organic dyes from textile industrial effluents. Photo catalysis and catalytic wet oxidation are best practices for degradation of dyes in wastewater. In photo catalysis, the dye molecules can be completely degraded into inorganic non-toxic compounds by irradiation of the dye solution under visible or ultra-violet light in the presence of semiconductor metal-oxide photo catalysts. In catalytic wet oxidation, various metal-based catalysts in supported or unsupported form can be used as heterogeneous catalysts for degradation of dyes in the presence of oxygen or hydrogen peroxide. These processes have several preferences like easy separation of the catalyst from reaction mixture and recycling of the catalyst.

Keywords: catalysis, degradation, dyes, Langmuir-Hinshelwood mechanism

1. Introduction

Water is an important resource in our society. In our planet, Earth, less than a 0.7% of the total of water is fresh water and only 0.01% is available to be used. Today, some of the most discussed issues around the world are sanitation, soil, air and water pollution [1]. Wastewater can be divided into four broad categories, according to its source, namely domestic, industrial, public service and system loss/leakage. Among these, industrial wastewaters

occupy a 42.4% of the total volume and households a 36.4% of volume. Industrial effluents are the major sources of water contamination. These industrial effluents contain a wide variety of complex, biodegradable and non-biodegradable organic substances like dyes, pesticides and herbicides and dyes with different concentrations [2]. A large amount of water is being used in the textile industry for preparing fabric and dyeing process. Other industries like plastics, pharmaceutical, pulp, leather and food industries also use dyes; however, textile industry is considered as a major water consumer as well as the largest dye consumer sector. The wastewater coming out of these industries contains a huge amount of dyes. Textile industry releases about 20% of the total world production of dyes in wastewater effluents.

Dyes are complex organic compounds which are used to impart color to materials. Dyes are categorized into different classes like anthraquinone, azo, reactive, disperse, acidic, basic and neutral dyes. Most commonly employed dyes are anthraquinone and azo dyes and more than 60% of these dyes are reactive dyes [3]. Reactive azo dyes are extensively used in the textile industry. Azo dyes consisting of a diazotized amine coupled to an amine or a phenol and contain one or more azo ($-N = N-$) linkage comprise about half of all textile dyes used in the present textile industry. The concentrations of these dyes in textile wastewater are significantly high, as about 20% of dye residues are released into effluents [4]. These industrial effluents are released directly into receiving waters without much effective treatment. The dye discharge into the environment poses serious threat to sustainability of ecosystems because they are highly resistant to natural degradation. These dyes have been declared as carcinogenic and tumorigenic material by the International Agency for Research on Cancer (IARC) and National Institute for Occupational Safety and Health; however, these dyes are still in use in textile dyeing processes. These dyes possess a complex nature due to a large degree of aromatics and synthetic origin. These dyes are highly stable, resistant towards photo and biological degradation and refractory against chemical oxidation. These characteristics make conventional biochemical and physiochemical techniques ineffective. Therefore, elimination of such dyes from textile effluents is of considerable interest and importance. Hence the textile effluents should be effectively treated before final disposal [5–7].

2. Photo catalytic degradation

Increase of recalcitrant organic pollutants in industrial effluents developed the law and regulations related to environment more forceful. As a response, advancement in new, more powerful and eco-friendly protocols for degradation of organic pollutants in industrial effluents turned into an important task. For the treatment of industrial effluents, various physical and chemical processes, such as ion exchange, adsorption, flocculation, UV radiation, electrochemical reduction, ozonisation and so on, have been used for elimination of dyes in the past few decades [8–12]. However, most of these processes face secondary pollution problems, complicated procedures and high cost. Hence, the development of an effective and eco-friendly protocol for treatment of industrial effluents is needed.

Ultimately, researchers focused on advanced oxidation processes (AOPs) to eliminate these stable pollutants from the aqueous medium. Advanced oxidation processes involve the production of active radicals like OH. These active radicals take part in decomposition of macromolecules of pollutants into less harmful and smaller substances [13–14]. Fenton process, sonolysis, ozonation process, radiation-induced degradation, biodegradation and heterogeneous photo catalysis are techniques which are employed in the AOP approach [15–19]. The heterogeneous photo catalysis, which can be used for degradation of organic pollutants by initiation of redox transformations, has been proved as an efficient tool for degradation of aqueous as well as atmospheric organic pollutants. This technique involves the initiation of photo reactions in the presence of a semiconductor photo catalyst. A number of photo-sensitive semiconductors such as ZnO, V₂O₅, ZnS, CdS, TiO₂, ZnO, oxides of Mn and so on can be employed as photo catalysts for aqueous-phase photo degradation of organic pollutants due to their environmental-friendly benefits [20–25].

3. Mechanism of photo catalytic degradation

Irradiation excites an electron from valence band to conduction band of the semiconductor photo catalyst leaving behind a positive hole in valence band. Electron from the conduction band is taken up by oxygen adsorbed at the surface of photo catalyst and produces superoxide anion (O₂^{•−}). This super oxide anion further reacts with water and produces the OH radical. Similarly, the positive hole moves to the surface of catalyst and reacts with water and produces OH radical. These OH radicals take part in decomposition of the pollutants. This mechanism has been illustrated in **Figure 1**.

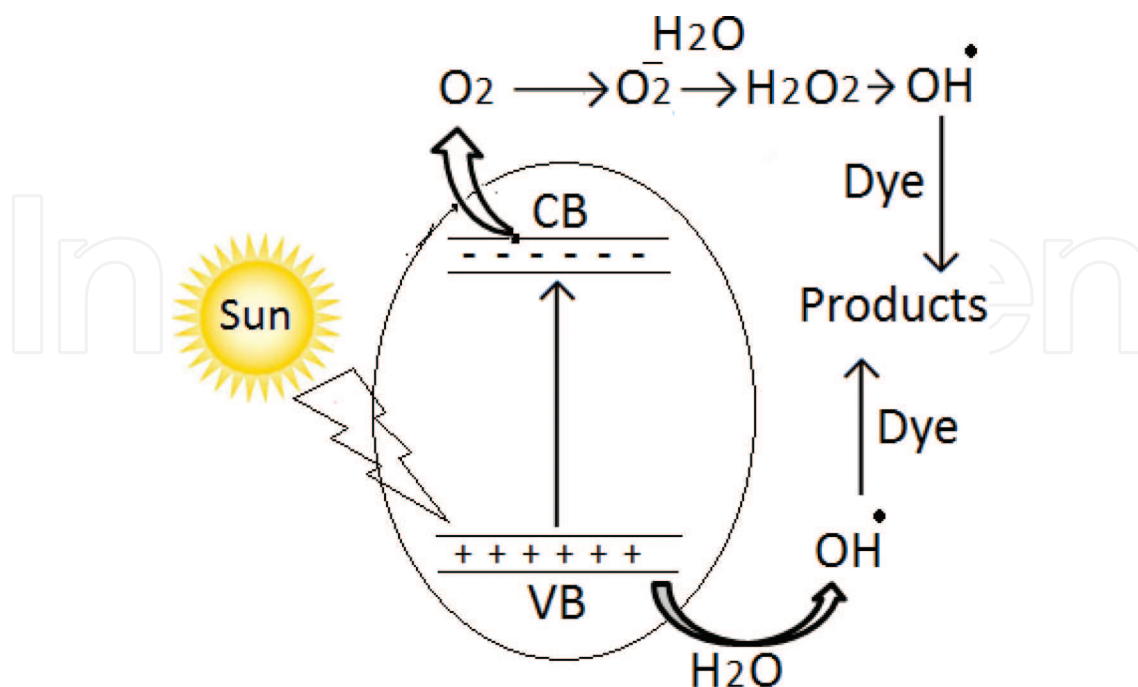


Figure 1. Mechanism of photo catalytic degradation of dyes.

The catalytic activities of photo catalysts towards degradation of dye molecules can be enhanced by doping of semiconductor metal-oxide photo catalysts with metal nanoparticles of low fermi level like Ag. These metal nanoparticles doped on semiconductor photo catalysts prevent the recombination of the electron-hole pair by the well-known Schottky barrier effect which results in an increase in quantum efficiency of the photo catalysts [26, 27]. It has been reported, for example, that doping of Ag greatly enhanced the photo catalytic activities of the manganese oxide photo catalyst for degradation of rhodamine B dye in aqueous medium as shown in **Figure 2** [28]. It was observed that 11% (in 15 min of reaction) and 45% (in 120 min of reaction) of 40 mL (200 ppm) solution of rhodamine B degraded when using manganese oxide as the photo catalyst at 40°C. In the presence of Ag-doped manganese oxide, 28% (in 15 min) and 91% (in 120 min) degradation of rhodamine B dye were achieved under similar reaction conditions. The pH of the solution also affects the catalytic activities of photo catalysts. Higher pH favors the production of OH radicals; therefore, the photo catalytic activities of photo catalysts increase with pH. **Figure 3** shows the effect of pH on photo catalytic activities of Ag-doped manganese oxide [28]. Similarly, Ansari et al. [29] have reported that TiO₂ and Ag-doped TiO₂ catalyzed photo degradation of methyl orange and methylene blue dyes. It was found that 42% and 88% degradation of methyl orange and methylene blue dye was achieved after 6 h of reaction. In the presence of Ag-doped TiO₂, the degradation achieved was 78 and 96% for methyl orange and methylene blue dyes.

3.1. Kinetics of photo catalytic degradation

Eley-Rideal (E-R) mechanism, one of the three mechanisms of heterogeneous catalytic reactions (Langmuir-Hinshelwood, Mars van Krevelen and Eley Rideal), can be used to describe the kinetics of the photo catalytic degradation of dyes in the presence of oxygen. Eley-Rideal (E-R) mechanism states that surface-catalyzed reaction proceeds in two steps. In the first step, the gaseous reactant, oxygen, gets adsorbed at the surface of the catalyst followed by a reaction

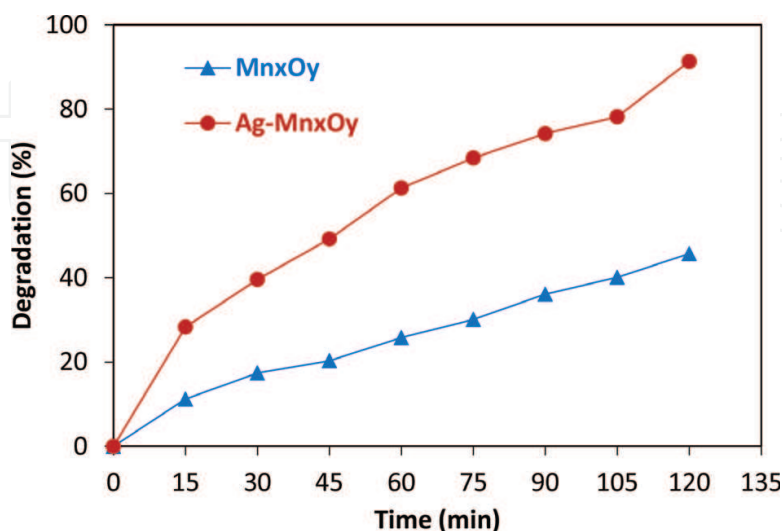


Figure 2. Effect of doping of Ag on photo catalytic activities of manganese oxide for photo degradation of rhodamine B dye in aqueous medium [28].

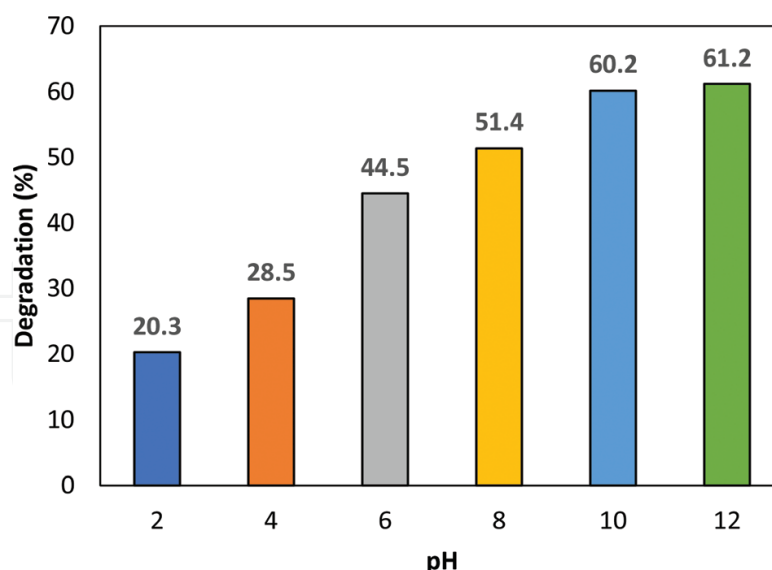


Figure 3. Effect of pH on photo catalytic activities of Ag-doped manganese oxide for photo degradation of rhodamine B dye in aqueous medium [28].

with a fluid phase reactant, the dye in second step. The adsorbed oxygen scavenges the electrons generated in the conduction band by the irradiation of catalyst and yields superoxide anions ($O_2^{\cdot-}$). Super oxide anions transform to OH radicals by protonation. The positive holes in valence band also generate OH radicals by reaction with water. These OH radicals play a significant performance in the mineralization of B dye [29]. The rate expression for the Eley-Rideal mechanism can be written as:

$$-\frac{dR}{dt} = k_r R \theta_{O_2} \quad (1)$$

R , θ_{O_2} and k_r indicate concentration of dye, surface concentration of oxygen and rate constant of reaction, respectively. Rate of reaction becomes independent of oxygen under constant flow of oxygen; hence

$$-\frac{dR}{dt} = k_{Ap} R \quad (2)$$

k_{Ap} is the apparent rate constant,

Equation (2) can be expressed in integral form as

$$\ln \frac{R_0}{R_t} = k_{Ap} t \quad (3)$$

R_0 and R_t is the concentration of dye at time zero and time t , respectively. The plot of $\ln(R_0/R_t)$ versus t gives a straight line. The slope of this straight line gives the apparent rate constant for photo catalytic degradation of dyes in the aqueous medium.

The time-profile data of Ag-doped manganese oxide catalyzed photo-degradation of rhodamine B dye and was subjected to kinetics analysis according to Eq. (3). It was noted that fitting Eq. (3) to experimental data gave the best straight lines as given in **Figure 4**. The apparent rate constants determined from the slopes of straight line were 0.0136, 0.0151 and 0.0216 per minute at 303, 313 and 323 K, respectively [28]. Similarly, we studied the ZnO-catalyzed photo degradation of methyl orange in aqueous medium [30]. The data obtained was subjected to kinetics analysis according to Eq. (3). The data gave a best fit to kinetics expression as given in **Figure 5**. The rate constants determined from the slopes of straight lines were 0.0098, 0.0128 and 0.0163 per minute at 303, 313 and 323 K, respectively. In another study [31], ZnO was used as a photo catalyst for degradation of rhodamine B dye in the aqueous medium. The experimental data was analysed according to expression 3. It was found that the data gave best fit to

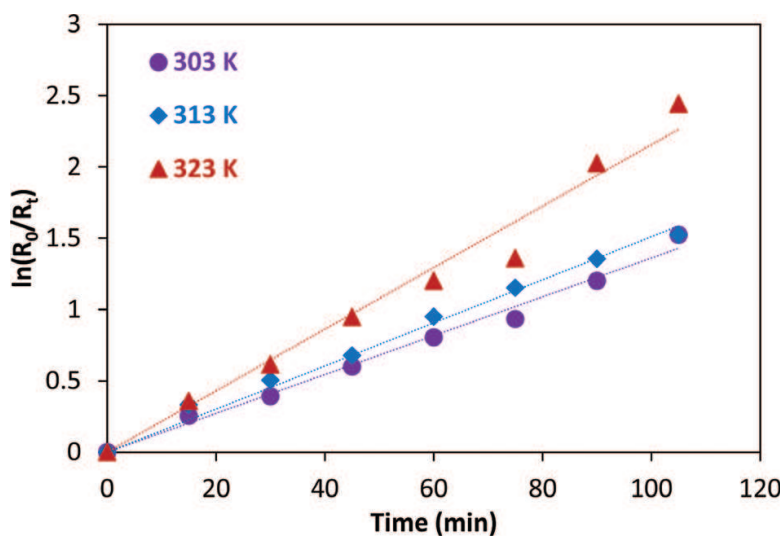


Figure 4. Kinetics of Ag-doped manganese oxide catalyzed photo degradation of rhodamine B dye in aqueous medium.

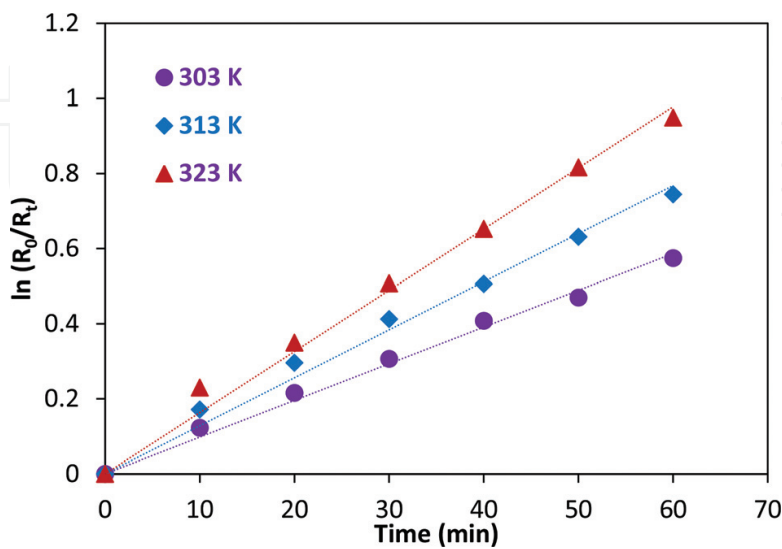


Figure 5. Kinetics of ZnO catalyzed photo degradation of methyl orange in aqueous medium.

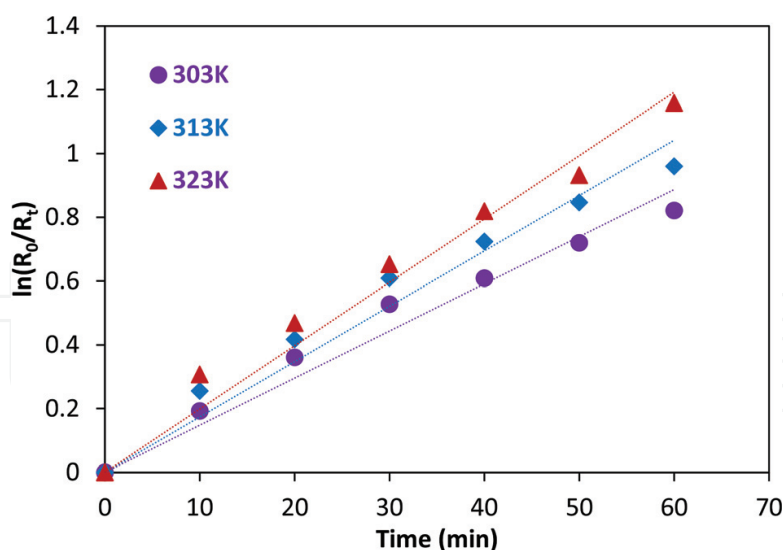


Figure 6. Kinetics of ZnO catalyzed photo degradation of rhodamine B dye in aqueous medium.

kinetic expression as given in **Figure 6**. The rate constants determined were 0.0148, 0.0174 and 0.0199 per minute at 303, 313 and 323 K, respectively.

4. Wet catalytic oxidation/degradation

In the recent years, the field of wastewater treatment and reuse of industrial processed water, for the suitable development of human activities, has achieved much attention. Chemical oxidation of organic wastes in water is one of the recommended and environmental-friendly methods to improve water quality. The wet-air or thermal liquid-phase oxidation process is known to have a great potential for the treatment of effluents containing organic toxic contaminants. The efficient removal of pollutants via the wet-air oxidation process requires very high temperature and pressure, typically in the range 473–573 K and 7–15 MPa, respectively, which leads to high installation costs, and practical applications for this process are limited. Therefore, the development of heterogeneous catalytic wet oxidation using various types of catalysts and oxidants has been attempted in order to reduce the severity of the oxidation conditions. The use of heterogeneous catalysts makes the process more attractive by achieving high efficiency for oxidation of organic wastes at considerably lower temperature and pressure. Compared to conventional wet oxidation, catalytic wet oxidation has lower energy requirements in which organic compounds are oxidized to inorganic compounds such as CO₂ and H₂O [32–34].

The catalytic degradation of dyes is a slurry-phase reaction having reactants in liquid phase and catalysts in solid phase. It is generally assumed that surface-catalyzed reactions occur by a reaction between reactants adsorbed at the surface of the catalyst. The surface-catalyzed reaction can be broken down into the following basic five steps. Any one of these steps can be the rate determining step:

1. Transport of reactants to the catalyst
2. Adsorption of reactants at the catalyst surface
3. Reaction between adsorbed reactants on the surface of catalyst
4. Desorption of the products from the catalyst
5. Transport of products away from the catalyst

Steps 2, 3 and 4 are chemical in nature. These steps jointly are regarded as the catalytic reaction. If any of these steps is slow step, that is, rate determining step, the reaction is said to be taking place in the kinetic-controlled region. Step 1 and 5, on the other hand, are physical processes which involve no chemical change. When either of these is slower, the reaction is said to be diffusion controlled or the rate is said to be diffusion limited. The diffusion control or kinetic control nature of the heterogeneous reaction can be confirmed by studying the effect of stirring on the rate of reaction [35, 36].

4.1. Kinetics of wet catalytic oxidation/degradation

As stated earlier, degradation of dyes takes place at the surface of catalyst. The kinetics of surface-catalyzed reaction can be described by one of the three possible mechanisms of heterogeneous catalysis [37]:

1. The Langmuir-Hinshelwood mechanism (L-H)
2. The Mars-van Krevelen mechanism (M-K)
3. The Eley-Rideal mechanism (E-R)

According to Langmuir-Hinshelwood (L-H), the reaction proceeds in two steps. In the first step the reactants get adsorbed on the surface of the catalyst and in the second step the adsorbed reactants react and give the final products. This whole process can be summarized in the following steps.

1. $R + * \rightarrow R^*$ Adsorption of dye on the surface of the catalyst
2. $O_2 + * \rightarrow O_2^*$ Adsorption of oxygen on catalyst surface
3. $R^* + O_2^* \rightarrow P_s^*$ Reaction at the surface of catalyst
4. $P_s^* \rightarrow P_s + *$ Desorption of the products

According to the Langmuir-Hinshelwood (L-H) theory, the rate of reaction can be given by following equation.

$$Rate = k_r \theta_R \theta_{O_2} \quad (4)$$

where θ_R and θ_{O_2} represent the surface covered by dye, R and molecular oxygen, respectively. Adsorption of dye, R and oxygen on the surface of the catalyst may take place according to

- Langmuir adsorption isotherm
- Temkin adsorption isotherm
- Freundlich adsorption isotherm

Langmuir adsorption isotherm may be either competitive or non-competitive. If adsorption of dye and oxygen takes place according to the competitive Langmuir adsorption isotherm, then fraction of the surface covered by reactant R and oxygen can be represented by expressions 5 and 6, respectively.

$$\theta_R = \frac{K_R[R]}{1 + K_R[R] + K_{O_2}[O_2]_g^n} \quad (5)$$

$$\theta_{O_2} = \frac{K_{O_2}[O_2]_g^n}{1 + K_R[R] + K_{O_2}[O_2]_g^n} \quad (6)$$

K_R and K_{O_2} represent adsorption coefficient for dye R and oxygen, respectively. The value of n can be taken as 1 or 0.5 for molecular or dissociative adsorption of oxygen, respectively.

Putting the values of θ_R and θ_{O_2} from Eqs. (5) and (6) in Eq. (4), we get Eq. (7).

$$Rate = k_r \frac{K_R[R]K_{O_2}[O_2]_g^n}{\left(1 + K_R[R] + K_{O_2}[O_2]_g^n\right)^2} \quad (7)$$

At constant flow of oxygen, the expression 7 transforms to.

$$Rate = \frac{ab[R]}{(c + b[R])^2} \quad (8)$$

where a , b and c are $k_r K_{O_2} [O_2]$, K_R and $1 + K_{O_2} [O_2]$, respectively.

If the adsorption of reactant R and oxygen at the catalyst surface is taking place according to the non-competitive Langmuir adsorption isotherm, then fraction of the surface covered by reactant R and oxygen may be represented by expression 9 and 10, respectively.

$$\theta_R = \frac{K_R[R]}{1 + K_R[R]} \quad (9)$$

$$\theta_{O_2} = \frac{K_{O_2}[O_2]_g^n}{1 + K_{O_2}[O_2]_g^n} \quad (10)$$

Putting the values of θ_R and θ_{O_2} from Eqs. (9) and (10) in Eq. (4), we get.

$$Rate = k_r \frac{K_R[R]K_{O_2}[O_2]_g^n}{(1 + K_R[R])(1 + K_{O_2}[O_2])} \quad (11)$$

At constant flow/pressure of oxygen, the expression 11 transforms to Eq. (12).

$$Rate = \frac{ab[R]}{1 + b[R]} \quad (12)$$

Similarly, if adsorption of dye and oxygen at the surface of catalyst follow Temkin or Freundlich isotherm, then the rate expression becomes Eqs. (13) and (14), respectively.

$$Rate = \bar{k}_r(K_1 \ln K_2 [R]) \quad (13)$$

$$Rate = \bar{k}_r K_R [R]^{1/n} \quad (14)$$

Like Langmuir-Hinshelwood mechanism, Mars-van Krevelen mechanism also comprises of two steps. In the first step, the lattice oxygen of the catalyst oxidizes the substrate molecule and hence produces a partially reduced catalyst. In the second step, the reduced catalyst is reoxidised by molecular oxygen. The rate equation for Mars-van Krevelen can be given by expression 15.

$$Rate = \frac{k_1 [R] k_2 [O_2]_g^n}{\beta k_1 [R] + k_2 [O_2]_g^n} \quad (15)$$

k_1 , k_2 and β is the rate constant for degradation of dye, R is the rate constant for reoxidation of catalyst and stoichiometric coefficient of oxygen (0.5), respectively. At constant flow of oxygen, expression 15 changes to expression 16.

$$Rate = \frac{a[R]}{b + c[R]} \quad (16)$$

According to the Eley-Rideal mechanism (E-R) mechanism, the gaseous reactant gets adsorbed on the surface of the catalyst while the second reactant, dye, reacts with the adsorbed reactant from the fluid phase. In the present case, oxygen is adsorbed at the surface while reactant R remains in the fluid phase.

Rate expression for the Eley-Rideal mechanism (E-R) can be given by Eq. (17) as below:

$$Rate = k_r \theta_{O_2} [R] \quad (17)$$

In case of constant pressure of oxygen, the above equation can be transformed to Eq. (18) by lumping all the constants together as given below.

$$Rate = a[R] \quad (18)$$

All these equations can be applied to experimental data of heterogeneous catalytic degradation of dyes in the aqueous medium by linear and non-linear method of analysis. We studied the degradation of rhodamine B and methylene blue dyes catalyzed by $CoFe_2O_4$ in aqueous

medium [38]. The data obtained was subjected to kinetic analysis according to above equations using Curve Expert software. It was found that Eq. (12) was best applicable to the data indicating that reactions were taking place according to the Langmuir-Hinshelwood mechanism. The constants determined using Curve Expert are given in **Table 1**. In another study [39] we employed nickel hydroxide as catalyst for degradation of black dye in aqueous medium. The experimental data was analysed according to kinetics discussed above. It was found that the reaction followed the Langmuir-Hinshelwood mechanism. The constants determined by Curve Expert software are listed in **Table 2**. Similarly, the degradation of methylene blue dye catalyzed by nickel hydroxide was also investigated [40]. The experimental data was analysed using the Curve Expert software. The Langmuir-Hinshelwood mechanism was applicable in this study as well. The rate constants and adsorption equilibrium constants are listed in **Table 3**.

T (K)	k _r (/min)		k _x (L/mol)	
	RhB	MB	RhB	MB
303	0.028	0.031	1.61	1.74
313	0.066	0.069	1.60	1.71
323	0.098	0.098	1.58	1.69
333	0.128	0.131	1.55	1.67

Table 1. Kinetics parameter determined by application of Langmuir model (Eq. 12) to time profile data of CoFe₂O₄ catalyzed degradation of rhodamine B and methylene blue dyes using Curve Expert software.

T (K)	k _r (/min)	k _x (L/mol)
313	0.051	0.153
323	0.093	0.125
333	0.218	0.079

Table 2. Kinetics parameter determined by application of Langmuir model (Eq. 12) to time profile data of nickel hydroxide catalyzed degradation of direct black dye using Curve Expert software.

T (K)	k _r (/min)	k _x (L/mol)
313	1.12	0.0112
323	1.55	0.0093
333	2.05	0.0084

Table 3. Kinetics parameter determined by application of Langmuir model (Eq. 12) to time profile data of nickel hydroxide catalyzed degradation of methylene blue dye using Curve Expert software.

5. Conclusion

Water pollution by textile industry is an emerging issue. Textile industry releases about 20% of the total world production of dyes in wastewater effluents. Photo catalysis and catalytic wet oxidation are best techniques for elimination of these dyes from aqueous system. In photo catalysis, the dye molecules are degraded to inorganic non-toxic compounds by irradiation of dye solution under visible or ultraviolet light in the presence of semiconductor metal-oxide photo catalysts. In catalytic wet oxidation, various metal-based catalysts in supported or unsupported form can be used as heterogeneous catalysts for degradation of dyes in the presence of oxygen or hydrogen peroxide. These processes have several preferences like easy separation of catalysts from the reaction mixture and recycling of the catalyst.

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