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Oxidative degradation of Methyl Orange catalyzed by lab prepared nickel hydroxide in aqueous medium

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ABSTRACT

This study is focused on oxidative degradation of Methyl Orange, a common azo dye, catalyzed by nickel hydroxide in aqueous solution at 303, 313, 323, and 333 K. Sodium hypochlorite, sodium hydroxide, and nickel sulfate hexahydrate in distilled water were used as starting material for preparation of nickel hydroxide. Pyrex glass batch reactor was used to study the effect of various conditions such as temperature, concentration, agitation, and catalyst dose on catalytic degradation of Methyl Orange in aqueous medium. About 80% Methyl Orange was degraded in 120 min. Experimental data were subjected to kinetic analysis using CurveExpert software. Degradation reaction was taking place according to Langmuir–Hinshelwood mechanism. According to this mechanism, the reactants adsorb at the surface of catalyst in first step followed by reaction between adsorbed reactants in second step. Adsorption of Methyl Orange on surface of catalyst followed Langmuir adsorption isotherm. Apparent activation energy, true activation energy, and heat of adsorption were determined as 13.2, 32.7 and –23.5 kJ mol^{-1}, respectively.

Keywords: Methyl Orange; Nickel hydroxide; Kinetic analysis; Langmuir–Hinshelwood mechanism; Langmuir adsorption isotherm; Activation energy

1. Introduction

Rapid industrialization has increased the production of wastewater containing a wide variety of contaminant in high concentration, including dyes, phenol and its derivatives, hydrocarbons, sulfur, nitrogen, and halogen containing organic compounds and heavy metals [1,2]. Textile industry is considered as the most polluting among all industrial sectors on the basis of volume and composition of the generated wastewater effluents. Textile industry releases about 20% of the total world production of dyes in wastewater effluents. These organic dyes are highly colored and stable compounds and are resistant toward chemical, biochemical, and photochemical degradation

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[3,4]. These dyes have given birth to significant environmental problems due to their intense color and resistance to chemical, biochemical, and photo degradation. Adsorption on porous solids such as activated carbon, and advanced oxidation processes are commonly employed for removal of organic dyes from wastewater effluents. However, the adsorption process is non-destructive, since it just transfers organic compounds from aqueous phase to another phase, thus causing secondary pollution [5,6]. Therefore, exploration of different alternatives for the elimination of dyestuff from wastewater has received great attention. One of the most convenient, economically feasible, and technologically viable techniques is the wet oxidation process. It is the oxidation of dyestuff in aqueous medium at high temperature (398–593 K) and pressure (0.5–20 MPa) in the presence of oxygen. However, high temperature and pressure in wet oxidation process appeals high machinery and practical costs which can be reduced using a proper homogeneous or heterogeneous catalyst. This technique is referred as catalytic wet oxidation [7]. Heterogeneous catalytic wet oxidation is best practice for degradation of dyes in wastewater in which various metal-based catalysts in supported or unsupported form can be used as heterogeneous catalysts. This process has several preferences such as easy separation of catalyst from reaction mixture and recycling of the catalyst [8–12]. Precious metal-based catalysts such as Pt and Pd are sufficiently active toward the oxidative degradation of organic dyes in aqueous medium. However, due to economical point of view, the use of cheap metals Ni, Co, Mn, Cu, and Nb etc. as catalysts have gained great attention [13–15]. Certain heterogeneous catalysts have been pursued for removal of Methyl Orange dye from water [16–20]. In this paper, lab prepared nickel hydroxide has been employed as catalyst for degradation of Methyl Orange dye in aqueous medium. This paper is therefore aimed to evaluate the catalytic efficiency and practical feasibility of lab prepared nickel hydroxide toward degradation of Methyl Orange dye in aqueous medium. Moreover, the influence of various parameters such as time, temperature, catalyst dose, speed of agitation, and initial concentration of dye on degradation of dye has been examined. CurveExpert software was employed for kinetic analysis of experimental data.

2. Material and methods

2.1. Materials

The commercially available Methyl Orange 38 dye (FW: 327.33 g/mol, λ_{max}: 483 nm) was obtained from local dyestuff market of Faisalabad Pakistan and was used without any further purification. Analytical grade sodium hypochlorite (Merck), sodium hydroxide (Merck), nickel sulfate hexahydrate (Scharlau), silver nitrate (Merck), potassium iodate (Scharlau), potassium iodide (Merck), sodiumthiosulfate pentahydrate (Acros), acetic acid (Merck), and hydrogen peroxide (Merck) were used as received.

2.2. Preparation of catalyst

Nickel hydroxide catalyst was prepared by precipitation method. A solution was prepared dissolving sodium hydroxide (42 g) in sodium hypochlorite (6%, 300 mL). Another solution was prepared by dissolving nickel sulfate hexahydrate (130 g) in double distilled water (300 mL). Solution of sodium hydroxide and sodium hypochlorite was added dropwise to nickel sulfate hexahydrate solution while stirring continuously at 298 K. Black nickel hydroxide was precipitated. The resultant precipitate of nickel hydroxide was filtered and washed several times with double distilled water till negative test of chlorine in drain was observed with silver nitrate. Finally, nickel hydroxide was ground and sieved after drying at 383 K for 24 h.

2.3. Characterization of the catalyst

The prepared nickel hydroxide was characterized by FTIR, XRD, SEM and surface area, and pore size analysis as described earlier [7]. For FTIR analysis, IR Prestige 21, Shimadzu, Japan was used in the range of 400–4,500 cm^{-1}. For XRD, X-Ray Diffractometer, JEOL (JDX-3532) Japan was used. For determination of surface area, Quantachrome (Nova 2200e) surface area and pore size analyzer was used. Catalyst sample was degassed at 383 K for 2 h prior to analysis. Nitrogen gas was used for surface area and particle size analysis. To determine the total oxygen content of the nickel hydroxide, about 2 g of potassium iodide was dissolved in 20 mL of 36% acetic acid solution. About 0.2 g nickel hydroxide was added to this solution and left for 15 min under inert atmosphere to release iodine. After filtration, released iodine was titrated with sodium thiosulfate solution (0.1 N). Starch was used as indicator. Similarly about 0.2 g nickel hydroxide and 2 g potassium iodide were mixed in 15 mL buffer of pH 7.1 and mixture was stirred for 15 min in inert atmosphere for exploration of surface oxygen content of nickel hydroxide. After filtration, 2 mL of 1 N HCl was added. Iodine was titrated with sodium thiosulfate solution. Following equation was used to determine the oxygen content.

$$\text{Oxygen}_{(\text{g-oxygen/g catalyst})} = \frac{\text{Na}_2\text{S}_2\text{O}_3\ (\text{mL}) \times \text{N}(\text{Na}_2\text{S}_2\text{O}_3)}{1{,}000 \times \text{catalyst (g)} \times 2} \quad (1)$$

3.5×10^{-4} and 2.9×10^{-4} g-atom oxygen g^{-1} were determined as total oxygen content and surface oxygen content of nickel hydroxide, respectively.

2.4. Degradation protocol

Nickel hydroxide catalyzed oxidative degradation experiments of Methyl Orange dye were carried out at four temperatures (303, 313, 323, and 333 K) and three different initial concentrations (100, 200, and 300 ppm) of Methyl Orange. For a typical run, the reactor was charged with 40 mL solution of Methyl Orange. The temperature of the reaction mixture was kept constant at a desired value using hot plate while stirring the solution continuously. After stirring the solution for 30 min at desired temperature, 0.5 mL sample was taken to observe any variation in concentration of dye during heating and stirring period. Hydrogen peroxide (1 mL) was added as oxidant to reactor while stirring the mixture continuously. After 30 min stirring, again 0.5 mL sample was withdrawn to observe any variation in concentration of dye solution. Then 0.1 g nickel hydroxide was added to reaction mixture and stirred continuously. At appropriate time intervals, 0.5 mL samples were taken from reactor. UV–vis spectrophotometer (Shimadzu UV-160A, Japan) was used for analyses of reaction mixture. The absorbance of the sample was measured by spectrophotometer at 483 nm, which corresponds to the maximum absorbance of Methyl Orange dye. The absorbance was converted to concentration using standard curve of Methyl Orange dye. HPLC (Agilent Technologies) was used to determine inorganic products and the reaction intermediates. Percent degradation of Methyl Orange was calculated using following equation.

$$\text{Degradation}\,(\%) = \frac{[\text{MO}]_0 - [\text{MO}]_t}{[\text{MO}]_0} \times 100 \quad (2)$$

where $[\text{MO}]_0$ and $[\text{MO}]_t$ represent initial concentration and concentration of Methyl Orange at various time intervals, respectively.

3. Results and discussions

3.1. Characterization of catalysts

The XRD spectrum is dominated by sharp and intensive diffraction peaks corresponding to hexagonal crystalline structure. The crystallite size calculated by Scherer's equation was 6.2 nm. BET surface area of nickel catalyst was found as 87 $\text{m}^2\,\text{g}^{-1}$. Porosity was estimated by BJH method considering the desorption branch of nitrogen isotherm. Average pore volume and average pore diameter were 0.04 cc g^{-1} and 24. Å, respectively. Diameter of the 90% pores is ≥ 24.1 Å.

3.2. Oxidative degradation

Oxidative degradation of Methyl Orange dye over nickel hydroxide catalyst is given in Fig. 1. This investigation was accomplished with 200 ppm as initial concentration of Methyl Orange dye in the presence of 1 mL hydrogen peroxide and 0.1 g nickel hydroxide catalyst while stirring the reaction mixture at 500 rpm. Separate experiments were carried out at 303, 313, 323, and 333 K. It was noted that about 31% of 200 ppm Methyl Orange dye degraded within first 15 min and gradually degradation increased to 65% after 120 min at 303 K. Degradation achieved after 15 min was 34% at 313 K, which was increased to 69% after 120 min. Similarly degradation of Methyl Orange increased from 37% in 15 min to 78% after 120 min at 323 K. Finally, at 333 K, 40% degradation was achieved in first 15 min and gradually increased to 80% after 120 min of reaction time as given in Fig. 1.

The cleavage often takes place on the azo linkage (–N=N–) of the aromatic azo compounds because these π bonds are comparatively more diffusive than other parts within the molecule. Ultimately Methyl Orange dye was completely mineralized to water and carbon dioxide; however, existence of benzene sulfonate, naphthoquinone, and carboxylic acids such as

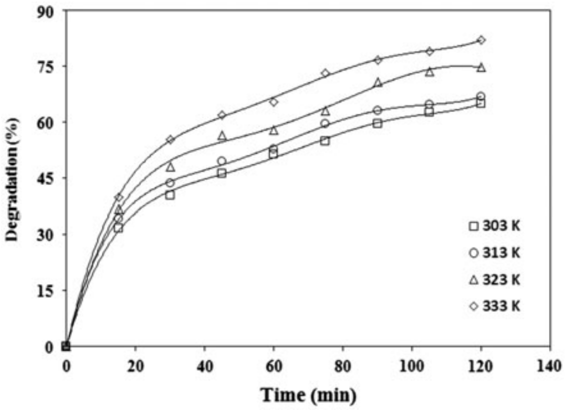

Fig. 1. Time profile investigation of nickel hydroxide catalyzed degradation of Methyl Orange in aqueous medium. Reaction conditions: Methyl Orange 40 mL (200 ppm), nickel hydroxide 0.1 g, agitation 500 rpm.

pthalic, fumaric, succinic, maleic, malonic, oxalic, and formic acids was observed with HPLC, which were then mineralized to water and carbon dioxide. FTIR analyses also support these predictions. In FTIR spectra (Fig. 2) various peaks can be observed. Bands in the range of 480–680 cm^{-1} were assigned to Ni–O bond. Peaks at 1,500–1,700 cm^{-1} represent physisorbed water molecules. Peak at 3,698 cm^{-1} represents OH group coordinated to nickel [7,12,21]. As Methyl Orange was degraded to carbon dioxide, therefore peak at ~2,400 cm^{-1} produced in spectra *b* and *c* [7]. Hua et al. [22] have assigned this peak to N–H bond and carbonyl group. Band at 1,482 cm^{-1} in spectrum *b* and *c* was attributed to characteristic azo (–N=N–) functional group. Kim and Lee [23] have assigned the band at 1,183 cm^{-1} to SO_3Na group of Methyl Orange. Band at 1,637 cm^{-1} in spectrum *c* was observed which was attributed to stretching vibration of C=O of carboxylic acids formed in degradation reaction. Peak appearing at 1,383 cm^{-1} was attributed to N–O stretching and N–H bending vibrations. Peak at 992 cm^{-1} in spectrum *b* is due to benzene ring [23]. Furthermore, it can be concluded from FTIR spectra that structure/composition of catalyst does not alter during the degradation reaction, hence the catalysts under investigation is stable and can be reused again in degradation experiment. XRD spectra also confirm the stability of catalyst.

To investigate the reusability of nickel hydroxide catalyst, used catalyst was first washed with ethanol and then with water. After drying at 383 K for 12 h, it was reused in degradation experiment. Used catalyst exhibited same performance as fresh catalyst (32% degradation of 40 mL, 200 ppm in 15 min at 313 K). In another experiment, the used catalyst was employed without washing. It also maintain its activity, but to lesser extent (25% degradation of 40 mL, 200 ppm in 15 min at 313 K). The observed results show that nickel hydroxide can be used as an efficient catalyst for degradation of Methyl Orange in aqueous medium.

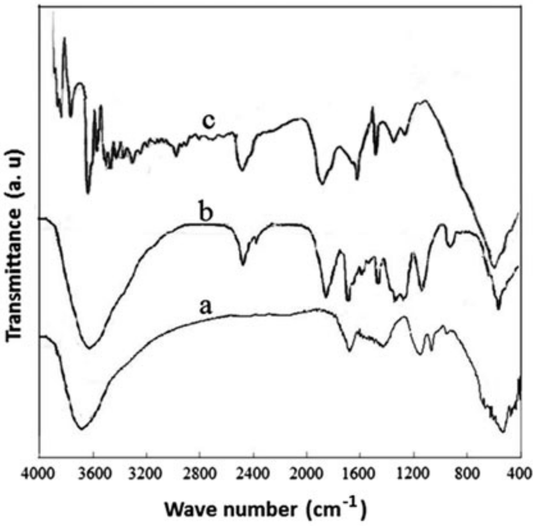

Fig. 2. FTIR spectra of catalysts (a) fresh catalyst (b) catalyst used for 2 min, and (c) catalyst used for 120 min.

3.3. Role of hydrogen peroxide on degradation

To investigate the effect of hydrogen peroxide on degradation of Methyl Orange dye, separate experiments were carried out in presence and absence of hydrogen peroxide at 313 K. The initial concentration of dye was 200 ppm. The dosage of nickel hydroxide catalyst was 0.1 g for 40 mL of dye solution. It was noted that in the absence of hydrogen peroxide, about 18% degradation was achieved in 15 min which was increased to 28% after 60 min. In the presence of hydrogen peroxide, 32% degradation was noted after 15 min, which was increased to 52% after 60 min. Hydrogen peroxide decomposes to oxygen and water. Oxygen is used in degradation process. Degradation in the absence of hydrogen peroxide is due to dissolved oxygen in water. Fig. 3 shows the comparison of degradation of Methyl Orange in presence and absence of hydrogen peroxide. It can be concluded that hydrogen peroxide acts as an efficient oxidant in this investigation and therefore it was used in all experiments.

3.4. Leaching of the catalyst

Leaching of the catalyst is an obstacle in reactions, where reactants in liquid phase and catalyst in solid phase are involved. To confirm whether nickel ions leaches to aqueous phase or not, following procedure was adopted. First reactor was charged with 40 mL water and 0.1 g nickel hydroxide catalyst and stirred at 323 K for 1 h. After separation of catalyst by filtration, 0.02 mmol Methyl Orange dye was added to get 200 ppm solution in second step. Finally, hydrogen peroxide was added to the solution and the mixture was stirred at 500 rpm for 1 h while keeping the temperature constant at 323 K. There was no change in concentration of Methyl Orange after 1 h, which confirms the absence of leaching of the nickel hydroxide. Hence, it was concluded that nickel hydroxide in present investigation is heterogeneous in nature.

3.5. Effect of initial concentration

The dye concentration is a very important parameter in wastewater treatment. The influence of various

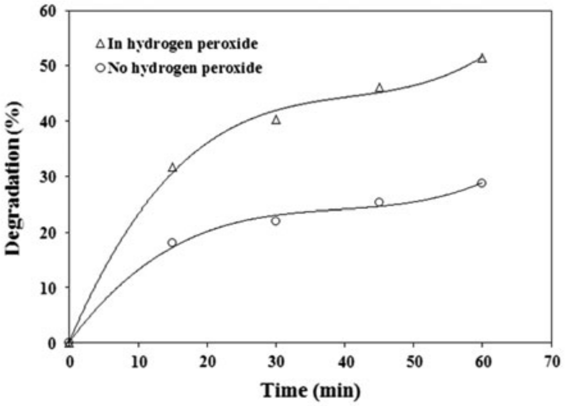

Fig. 3. Effect of hydrogen peroxide on nickel hydroxide catalyzed degradation of Methyl Orange in aqueous medium. Reaction conditions: Methyl Orange 40 mL (200 ppm), nickel hydroxide 0.1 g, agitation 500 rpm, temperature 303 K.

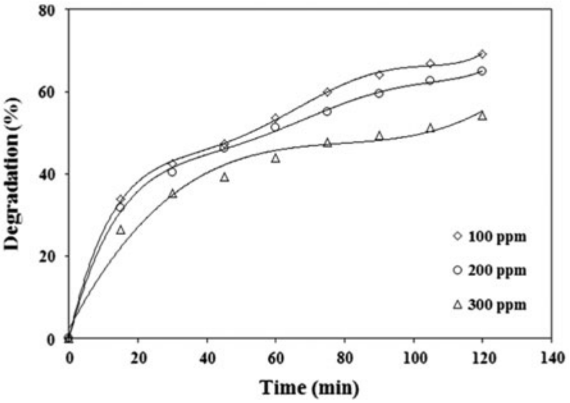

Fig. 4. Time profile of oxidation/degradation of Methyl Orange over nickel hydroxide catalyst at various initial concentration of Methyl Orange dye. Reaction conditions: temperature 313 K, catalyst 0.1 g, stirring speed 500 rpm, hydrogen peroxide 1 mL.

initial concentrations of Methyl Orange on the degradation process was investigated between 100 and 300 ppm Methyl Orange solution at 313 K over 0.1 g of catalyst while stirring the reaction mixture at 500 rpm. It was found that the increase in Methyl Orange concentration decreases the rate of degradation of Methyl Orange because the increase in concentration of dye increases the number of molecules and competition with hydrogen peroxide for active sites of the catalyst. This investigation is given in Fig. 4. The effect of decrease in degradation of Methyl Orange with increase in initial concentration of dye can be indicative of some kind of dye self-inhibition. For this reason the effect of the catalyst loading and speed of agitation has been investigated.

3.6. Effect of catalyst dose

The degradation of Methyl Orange on nickel hydroxide was studied by changing the amount of catalyst from 0.05 to 0.175 g in aqueous solution of 200 ppm at 303 K. It was observed that percentage degradation of Methyl Orange increases with increase in catalyst dose in the range of 0.05–0.125 g and then decreases in the range of 0.125–0.175 g of catalyst as given in Fig. 5. At higher catalyst dose, the reaction mixture cannot be homogenized properly at given speed of agitation. Therefore, the degradation decreases with increase in catalyst loading. Reaction mixture can be homogenized by increasing the speed of agitation; however, with increase in speed of agitation, splashing of the reaction mixture was observed. This also results in decrease of degradation of the dye. 0.1 g was selected as optimum catalyst loading.

3.7. Effect of agitation

Nickel hydroxide catalyzed oxidative degradation of Methyl Orange in present investigation is a typical slurry phase reaction. Experiments at different speed of agitation in the range of 300–600 rpm were carried out to examine the effect of the speed of agitation on the degradation rate of Methyl Orange dye (Fig. 6). With increase in speed of agitation from 300 to 500 rpm, the oxidative degradation of Methyl Orange increases indicating the mass transfer region. From 500 to 600 rpm, no appreciable differences on degradation were detected. Stirring speed of 500 rpm is the threshold value at which the resistance due to dye

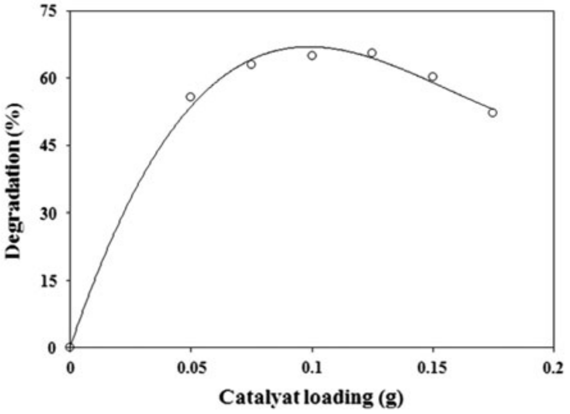

Fig. 5. Effect of catalyst dose on oxidation/degradation of Methyl Orange dye over nickel hydroxide. Reaction conditions: Methyl Orange 200 ppm (40 mL), temperature 303 K, time 120 min, hydrogen peroxide 1 mL, stirring speed 500 rpm.

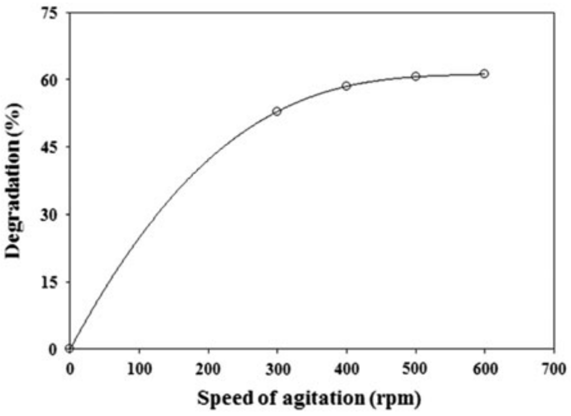

Fig. 6. Effect of stirring speed on oxidation/degradation of Methyl Orange over nickel hydroxide. Reaction conditions: Methyl Orange dye 200 ppm, catalyst 0.1 g, temperature 303 K, time 90 min, hydrogen peroxide 1 mL.

mass transfer to the catalyst particle has overcome. Stirring speed of 500 rpm was selected as optimum stirring speed.

3.8. Kinetic studies

The kinetics of the oxidative degradation of Methyl Orange dye catalyzed by nickel hydroxide in present investigation can be expressed as power rate law.

$$\text{Rate} = k_r[\,\text{MO}]^m[\,\text{H}_2\text{O}_2]^n \qquad (3)$$

where k_r is rate constant and m and n are the reaction orders with respect to Methyl Orange and hydrogen peroxide, respectively. This representation has limited utility for mechanistic elucidation; however, it can be used to obtain a preliminary dependency of rate of reaction on concentration of dye and hydrogen peroxide. As hydrogen peroxide is in excess in present case; therefore, the rate expression becomes as

$$\text{Rate} = k[\text{MO}]^m \qquad (4)$$

On integration, Eq. (4) changes to

$$\ln\frac{[\text{MO}]_0}{[\text{MO}]_t} = kt \qquad (5)$$

where $[\text{MO}]_0$ and $[\text{MO}]_t$ represent initial concentration of Methyl Orange and concentration at time t, respectively. k is apparent rate constant.

Eq. (5) was applied to the time profile data at various temperatures from Fig. 1 as given in Fig. 7. The linearity of plots in Fig. 7 indicates first-order dependence of oxidation rate on the concentration of Methyl Orange dye. Slops of the graphs give rate constants, which are listed in Table 1. However, such representation has limited utility. Hence, we have followed the approach of fitting experimental data to Langmuir–Hinshelwood (L–H) mechanism of heterogeneous catalysis, which assumes that reaction between dye and hydrogen peroxide commence at catalyst surface. Initially, this mechanism was developed for surface catalyzed reactions involving gaseous reactants; however, it has been used recently for reactions involving reactants in liquid and gaseous phase [9,24–26].

According to L–H mechanism, first Methyl Orange and hydrogen peroxide molecules adsorb at the surface of catalyst. The adsorbed Methyl Orange and hydrogen peroxide commence the catalytic reaction and generate a number of products at the surface of catalyst. Finally, the products desorbs from the surface. This whole process can be summarized in the following steps.

1. $\text{MO} + \theta \rightarrow \theta_{\text{MO}}$
   Adsorption of Methyl Orange
2. $\text{H}_2\text{O}_2 + \theta \rightarrow \theta_{\text{H}_2\text{O}_2}$
   Adsorption of hydrogen peroxide
3. $\theta_{\text{MO}} + \theta_{\text{H}_2\text{O}_2} \rightarrow \theta_{\text{P}}$ Catalytic surface reaction
4. $\theta_{\text{P}} \rightarrow \text{P}$ Desorption of products

where θ represents the surface active sites.

According to L–H kinetic theory, the rate of reaction is proportional to the fraction of the surface covered by substrate, θ,

$$\text{Rate} = k_r\theta_{\text{MO}}\theta_{\text{H}_2\text{O}_2} \qquad (6)$$

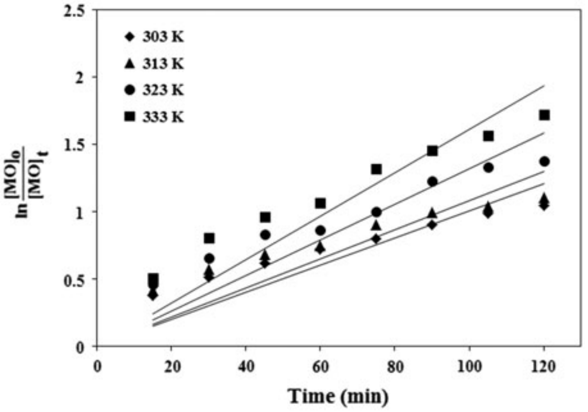

Fig. 7. Application of first order kinetic expression to time profile data of Methyl Orange.

Table 1
Apparent rate constants determined by application of first-order kinetic expression to time profile data

T (K)	$k \times 10^2$ (min^{-1})	R^2
303	1.01	0.54
313	1.09	0.47
323	1.32	0.67
333	1.61	0.73

where k_r, θ_{MO}, and $\theta_{H_2O_2}$ represents rate constant, surface covered by Methyl Orange and hydrogen peroxide, respectively.

Adsorption of Methyl Orange and hydrogen peroxide on the surface of catalyst may take place either according to Langmuir, Temkin, or Freundlich adsorption isotherm. Langmuir adsorption isotherm may be either competitive or noncompetitive. For competitive Langmuir adsorption of Methyl Orange and hydrogen peroxide, the rate of reaction can be expressed as:

$$\text{Rate} = k_r \frac{K_{MO}[MO]K_{H_2O_2}[H_2O_2]}{(1 + K_{MO}[MO] + K_{H_2O_2}[H_2O_2] + K_P[P])^2} \tag{7}$$

K_{MO}, $K_{H_2O_2}$and K_P represent adsorption coefficient for Methyl Orange, hydrogen peroxide, and products, respectively.

Adsorption/desorption processes in the above steps are fast enough to be assumed at equilibrium. This assumption helps to simplify the above expression as

$$\text{Rate} = k_r \frac{K_{MO}[MO]K_{H_2O_2}[H_2O_2]}{(1 + K_{MO}[MO] + K_{H_2O_2}[H_2O_2])^2} \tag{8}$$

If H_2O_2 is kept constant, and combine all the constants together, Eq. (8) can be modified to

$$\text{Rate} = \frac{ab[MO]}{(c + b[MO])^2} \tag{9}$$

where a, b, and c are $k_r K_{H_2O_2}[H_2O_2]$, K_{MO}, and $1 + K_{H_2O_2}[H_2O_2]$respectively.

In case of noncompetitive adsorption of Methyl Orange and hydrogen peroxide, the rate expression is

$$\text{Rate} = k_r \frac{K_{MO}[MO]K_{H_2O_2}[H_2O_2]}{(1 + K_{MO}[MO])(1 + K_{H_2O_2}[H_2O_2])} \tag{10}$$

For constant concentration of hydrogen peroxide, rate can be given by expression (11).

$$\text{Rate} = \frac{ab[MO]}{1 + b[MO]} \tag{11}$$

Considering Temkin adsorption isotherm, the rate expression is given by

$$\text{Rate} = k_r(K_1 \ln K_2[MO])(\bar{K}_1 \ln \bar{K}_2[H_2O_2] \tag{12}$$

where K_1 and K_2 are constants related to heat of adsorption, which decreases linearly with surface coverage.

For constant concentration of hydrogen peroxide, the rate equation is modified as Eq. (13).

$$\text{Rate} = \bar{k}_r(K_1 \ln K_2[MO]) \tag{13}$$

Plot of ln [MO] vs. rate results in straight line.

Similarly in case of Freundlich adsorption isotherm, rate can be expressed by

$$\text{Rate} = k_r K_{MO}[MO]^{1/n} K_{H_2O_2}[H_2O_2]^{1/n} \tag{14}$$

where K_{MO} and $K_{H_2O_2}$ are the adsorption coefficient for Methyl Orange and hydrogen peroxide and n (>1) is a constant.

Expression (14) is simplified by keeping concentration of hydrogen peroxide constant.

$$\text{Rate} = \bar{k}_r K_{MO}[MO]^{1/n} \tag{15}$$

Plot of ln [MO] versus ln rate results in straight line. It is not necessary that both the reactants will adsorb on the surface according to same adsorption isotherm. Methyl Orange and hydrogen peroxide may follow different adsorption isotherms. Under this condition the rate expression may have various forms.

Time profile data at various temperatures from Fig. 1 were subjected to kinetic analysis according to Langmuir, Temkin, and Freundlich models by linear and nonlinear least square method. For nonlinear least square method CurveExpert 1.4 software was used. Rate of the reaction was calculated by applying third-order polynomial to the time profile data, using CurveExpert software. Noncompetitive Langmuir model (Eq. (11)) was applicable to the data. Fitting of Langmuir model shows that the Methyl Orange adsorbs at identical sites on homogeneous surface of catalyst. Langmuir model was fitted to experimental data in integral form (Eq. (16)). Wolfram Mathematica Online Integrator was used for integration of Eq. (11).

$$t = a(0.611 - x)(4b + a(0.611 - x) + 2b^2\ln(0.611/x))/(2c) \tag{16}$$

0.611 mM is the initial concentration of Methyl Orange. Fig. 8 shows the comparison of experimental rate of degradation reaction and rate of reaction determined by fitting of noncompetitive Langmuir model to experimental data using CurveExpert software. Straight lines with high regression coefficient values suggest the validity of the model. Values of rate constants and adsorption equilibrium constants were determined using CurveExpert software and are listed in Table 2. Rate constants determined by Langmuir model are true rate constants because the contributions of adsorption equilibrium constant of Methyl Orange have been excluded from these values.

3.9. Energy of activation

Activation energy was calculated by applying Arrhenius equation to rate constants at various temperatures. Rate constants determined by power rate law at various temperatures listed in Table 1 are apparent rate constant; hence, activation energy determined by application of Arrhenius equation to these rate constants is apparent activation energy, E_{Ap} which was found as 13.3 kJ mol^{-1}. Similarly rate constants determined by Langmuir model (listed in Table 2) are true rate constants (true in the sense that contributions of adsorption equilibrium constant of Methyl Orange have been excluded); hence, activation energy calculated using these rate constants is true activation energy, E_{T}, which was found as 32.7 kJ mol^{-1} (Fig. 9). Enthalpy (ΔH_a), entropy (ΔS_a), and Gibb's energy (ΔG_a) of adsorption for Methyl Orange dye were determined by applying vant's Hoff isochore (Eq. (17)) to the adsorption constants of Methyl Orange dye, K_{MO}, at various temperatures from Table 2 (Fig. 10) and were found as −23.5 kJ/mol, 115.9 J/mol, and −11.6 kJ/mol, respectively.

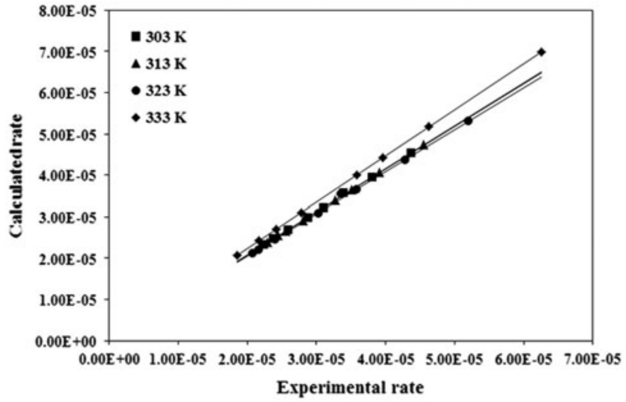

Fig. 8. Comparison of experimental rates of degradation reaction and rates determined by fitting noncompetitive Langmuir model to time profile data.

Table 2
Kinetics parameters determined by fitting of noncompetitive Langmuir model to time profile data using CurveExpert software

T (K)	k_{r}	$K_{\mathrm{MO}} \times 10^2$	R^2
303	1.04	1.04	0.98
313	1.76	0.67	0.95
323	2.17	0.52	0.99
333	3.56	0.44	0.95

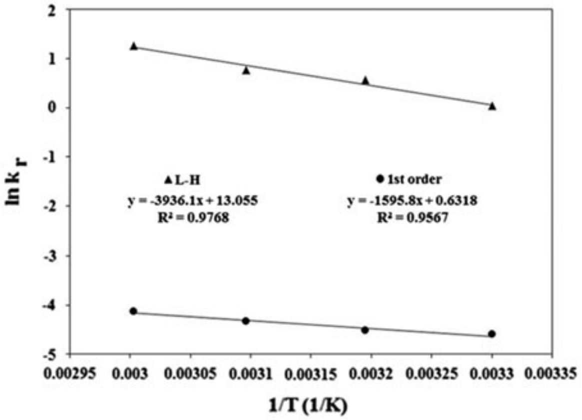

Fig. 9. Arrhenius plots.

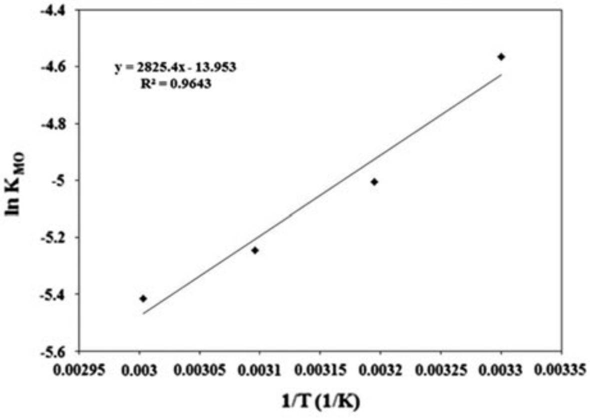

Fig. 10. vant Hoff plot.

$$\frac{d \ln K_{MO}}{dT} = \frac{\Delta H_a}{RT^2} \tag{17}$$

As adsorption is always exothermic, enthalpy of adsorption, ΔH_a is negative from the system's point of view, and $-H_a$ has a positive value. The true activation energy is thus obtained by adding the enthalpy of adsorption as a positive quantity to the apparent activation energy [8,27].

4. Conclusions

This study reveals that lab prepared nickel hydroxide which is much cheaper as compared to commonly used catalysts such as Pt and Pd can be used as an effective catalyst for oxidative degradation of Methyl Orange dye in aqueous system at milder conditions of temperature and pressure. Degradation of Methyl Orange 65, 69, 78, and 80% was observed at 303, 313, 323, and 333 K, respectively. The optimum catalyst dose was 0.1 g at 500 rpm. The catalyst was heterogeneous in nature and the oxidative degradation reaction was taking place in kinetic control regime, free from diffusion control regime. Catalytic oxidative degradation of Methyl Orange dye in present investigation follows L–H type mechanism. According to this mechanism, reaction proceeds in two steps. In first step reactants adsorb at the surface of catalyst, and in second step the adsorbed reactants react. Adsorption of Methyl Orange dye was taking place according to noncompetitive Langmuir adsorption isotherm. This shows that adsorption sites for Direct Black dye are homogeneous in nature. −23.5, 13.2 and 32.7 kJ mol^{-1} were determined as heat of adsorption, apparent activation energy, and true activation energy, respectively.

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