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ORIGINAL RESEARCH ARTICLE

Synthesis and characterization of nickel oxide and evaluation of its catalytic activities for degradation of methyl orange in aqueous medium

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ABSTRACT

This study focuses on synthesis of nickel oxide catalyst and exploration of its catalytic activities for degradation of methyl orange in aqueous medium. Nickel oxide was prepared sole-gel method using nickel nitrate haxahydrate and citric acid as precursor materials. X-ray diffractometry and scanning electron microscopy were used for characterization of prepared nickel oxide particles. The prepared particles were used as the catalysts for the degradation of Methyl Orange in aqueous medium. The effects of different parameters on degradation of methyl orange were investigated. The degradation of methyl orange followed the Eley-Rideal (E-R) mechanism. The apparent activation energies for degradation of methyl orange determined was found as 36.4 kJ/mol.

Keywords: Nickel Oxide; Methyl Orange; Degradation; Eley-Rideal Mechanism

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1. Introduction

Metal based oxides have been investigated for several years, because these materials are widely used in many technological applications, such as electrochemistry, optical fibers, sensors, coating, and catalysis. Nickel is higher in abundance, economically feasible and suitable for a number of applications as compared to other metals. It exists in different form of oxides[1]. Oxides of nickel have gained much attention since these materials are important for many electrochemical systems especially alkaline systems like fuel cells, electrolyzers and batteries. These materials are also important due to low price, good stabilities and appreciable catalytic activities. These oxides are oxygen rich species in which Ni can exist in various oxidation states in addition to its normal oxidation state of 2+. NiO, $Ni(OH)_2$, NiOOH, NiO_2, Ni_2O_3 are different types of oxides of nickel[2,3]. NiO and $Ni(OH)_2$ have been used as an important electrode material in the field of energy storage, especially in super capacitors and lithium ion batteries. The energy storage capability is due to redox process occurring at the electrode/electrolyte interface. P-type and semiconductor nickel oxide thin films have been investigated for gas sensor, light emitting diodes (LED) and electrochromic devices[4–8]. These oxides can also be used as catalysts for different processes. In 1962, Nakagawa *et al.*,[9] reported the use of nickel oxides as useful oxidizing agent for oxidation of alcohols, amines, nitriles, phenols and sulfur compounds.

Konaka *et al.*[10] used nickel peroxide as catalyst for oxidation of diphenylacetonitrile and benzyl alcohol. Nickel peroxide was prepared from nickel sulfate and sodium hypochlorite. Similarly, in 1970s, Fleischmann and co-workers investigated the electrochemical oxidation of some organic compounds like carboxylic acids, ketones, amines, alcohols and nitriles at Ni anode in alkaline solution[11]. In present study nickel oxide particles prepared by sol-gel method were employed as catalysts for degradation of methyl orange in aqueous medium effectively.

2. Experimental

2.1 Preparation of nickel oxide

A solution of citric acid was prepared by dissolving 4.2 g of citric acid in 100 mL distilled water. Another solution of nickel nitrate hexahydrate, was prepared by dissolving 5.8 g of nickel nitrate hexahydrate in 100 mL distilled water. The solution of nickel nitrate hexahydrate was added dropwise into the solution of citric acid under constant stirring. Then, the mixture was heated up to 343 K until water evaporates which resulted in green gel. Finally, the gel was calcined at 673 K for 4 hours. After calcination black powder of nickel oxide was stored for further study.

2.2 Characterization

XRD analysis was carried out on X-Ray Diffractometer, JEOL (JDX-3532) Japan. SEM analysis was carried out with JSM-5910 Japan Scanning Electron Microscope.

2.3 Catalytic experiment

Nickel oxide catalyzed degradation experiments of methyl orange was carried out in a Prex glass beaker as batch reactor. For a typical run, the reactor was charged with 50 mL solution of known concentration. 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 minutes at desired temperature, 0.5 mL sample was taken to observe any variation in concentration of methyl orange during heating and stirring period. Then pre-determined amount of nickel catalyst was added to reaction mixture and stirred continuously. At appropriate time intervals, 0.5 mL samples were taken from reactor. UV-Visible spectrophotometer (Shimadzu UV-160A, Japan) was used for analyses of reaction mixture. Percent degradation of dye was calculated using following equation.

$$Degradation(\%) = \frac{(R)_o - (R)_t}{(R)_o}(\times)100 \qquad \text{(Eq. 1)}$$

where $(R)_0$ and $(R)_t$ represent initial concentration and concentration of dye at various time intervals respectively.

3. Results and discussions

3.1 Characterization

Figure 1 shows XRD pattern of prepared nickel oxide. The XRD is dominated with intense and sharp peaks which shows the purity and crystallinity of prepared nickel oxide particles. Peaks appeared at $2\theta = 27°, 40°, 45°, 53°$ and $57°$ are indexed to face-centered cubic structure (fcc) of NiO in accordance with the standard spectrum[12].

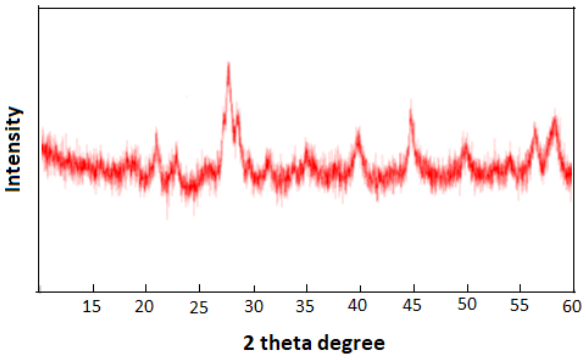

Figure 1. XRD pattern of prepared nickel oxide.

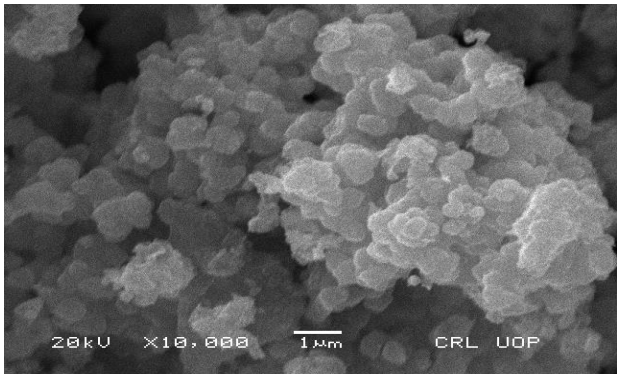

Figure 2. Scanning electron micrograph of prepared nickel oxide.

Figure 2 shows the scanning electron micrographs of prepared nickel oxide particles. The micrograph shows that particles are regular in morphology with spherical shape. It can also be concluded that particles are non-agglomerated and dispersed.

3.2 Catalytic degradation of methyl orange

To investigate the temperature effect on the degradation of methyl orange, reaction was carried out with initial concentration of methyl orange of 200 mg/L solution at temperature 313, 323 and 333 K separately. This effect was investigated by suspending 0.05 g of nickel oxide catalyst in 50 mL solution of methyl orange. Reaction mixture was stirred at speed of 500 rpm. 1 mL sample from the reaction mixture was withdrawn at regular intervals of 15, 30, 45, 60, 75, 90, 105 and 120 minutes. UV-visible spectrum of each sample was recorded. These absorbance values were used to determine the methyl orange concentration in reaction mixture at different time intervals using previously prepared calibration plot. The results revealed that degradation of methyl orange increases with temperature as given in **Figure 3**. It was noted that approximately 8, 10 and 15% of 200 mg/L methyl orange degraded in 15 minutes at 313, 323 and 333 K respectively. The degradation gradually increased to 45, 57 and 72% after 120 minutes of reaction time at 313, 323 and 333 K respectively.

Similarly, the effect of initial concentration of methyl orange was also investigated. For this purpose, separate experiments were performed at 323 K over 0.05 g of nickel oxide as catalyst with 100, 200 and 300 mg/L as initial concentration of methyl orange. Analysis of reaction samples taken from reactor at various interval of times confirmed that percent degradation of methyl orange decreases with increase in concentration as given in **Figure 4**. It was noted that approximately 7, 10 and 17% of methyl orange degraded in 15 minutes at with 300, 200 and 100 mg/L as initial concentration respectively. The degradation gradually increased to 55, 68 and 85% after 120 minutes of reaction time with 300, 200 and 100 mg/L as initial concentration respectively.

3.3 Kinetics analysis

For kinetics investigation, all the kinetics models were applied to time profile data for degradation of methyl orange as described in our previous study[13-17]. It was found that degradation of methyl orange follows pseudo 1st order kinetics expression according to Eley-Rideal (E-R)

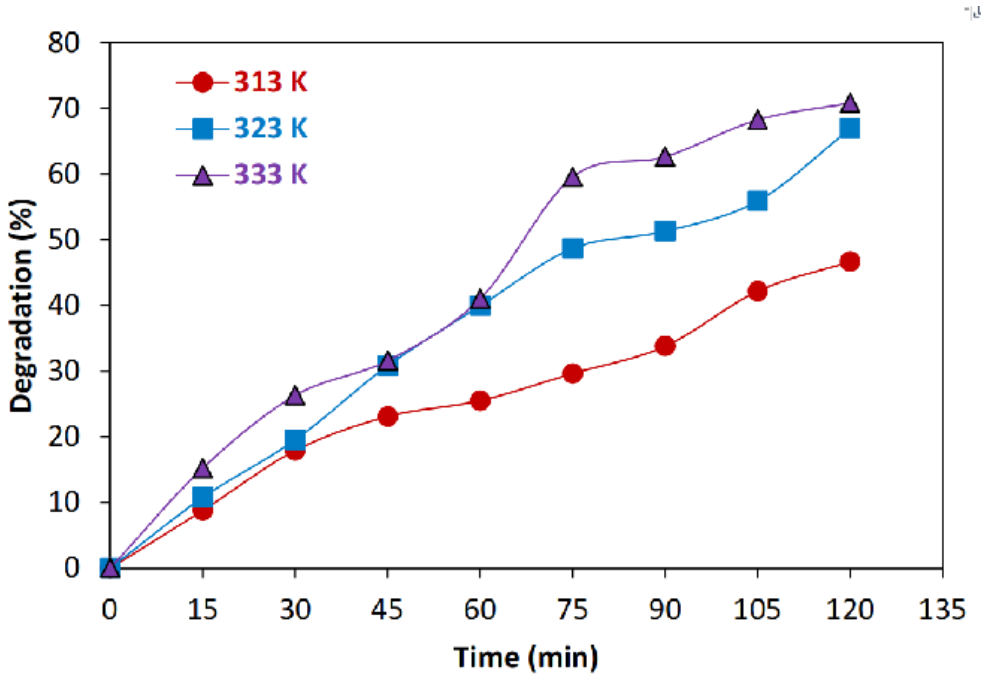

Figure 3. Time profile data of nickel oxide catalyzed degradation of methyl orange at various temperatures.

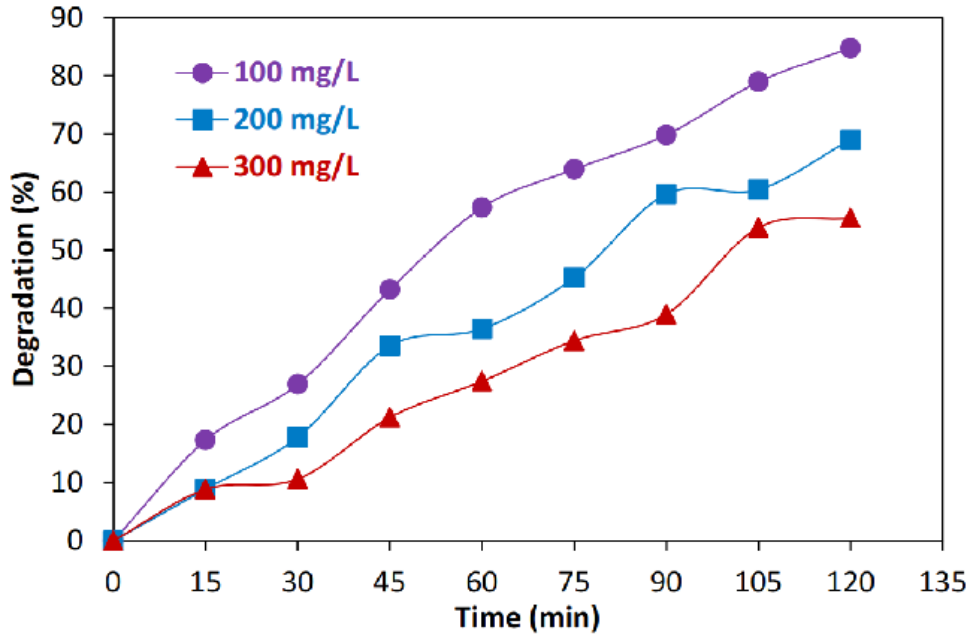

Figure 4. Time profile data of nickel oxide catalyzed degradation of methyl orange with various initial concentration.

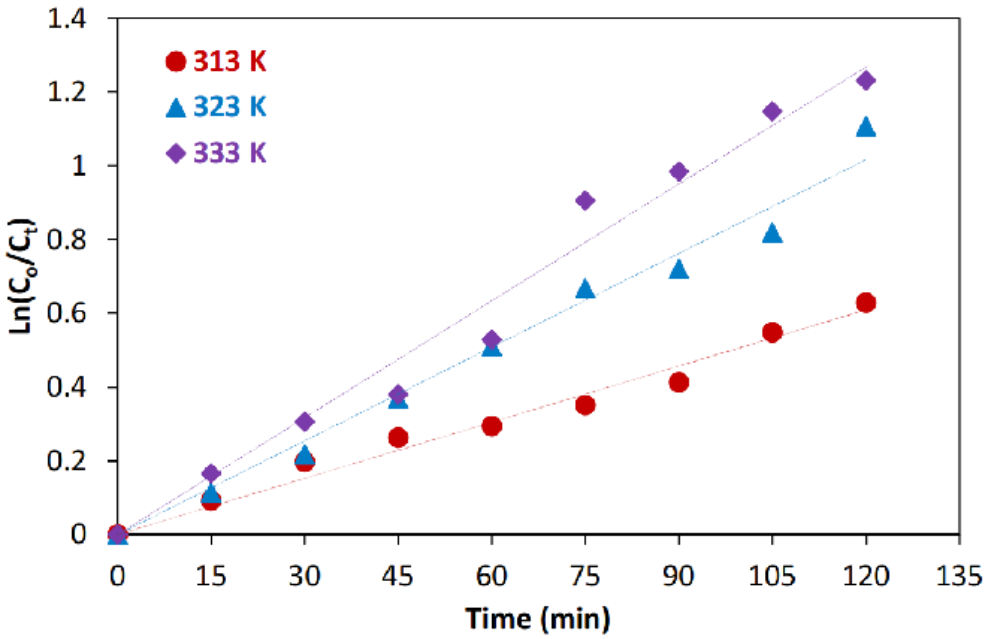

Figure 5. Application of kinetic expression (Eq. 4) to time profile data at various temperatures.

mechanism.

According to Eley-Rideal (E-R) mechanism, the rate expression can be given by Eq. 2.

$$-\frac{dC}{dt} = k_r \theta_{O2}[C] \qquad \text{(Eq. 2)}$$

where k_r, θ_{O2} and C represent the rate constant, surface of catalyst covered by oxygen and concentration of methyl orange respectively. As the oxygen is constant, Eq.2 changes to Wq. 3 as below.

$$-\frac{dC}{dt} = k_{Ap}[C] \qquad \text{(Eq. 3)}$$

where k_{Ap} is apparent rate constant. On integration, Eq. 3 changes to Eq. 4, a straight-line equation.

$$ln\frac{C_o}{C_t} = k_{Ap}t \qquad \text{(Eq. 4)}$$

where C_o and C_t represent the initial concentration of methyl orange, concentration after time t respectively.

Eq. 4 was applied to time profile data at various temperatures as given in **Figure 5**. The slops of straight lines in **Figure 5** gives the apparent rate constants. The apparent rate constants were found as 0.0046, 0.0075 and 0.0105 per minute at 313, 323 and 333 K respectively. For determination of energy of activation, Arrhenius equation was applied to apparent rate constant at various temperatures. The energy of activation was calculated as 36.4 kJ/mol.

4. Conclusions

Nickel oxide which is eco-friendly as compared to commonly used catalysts was successfully synthesized and employed as effective catalyst for degradation of methyl orange in aqueous medium. About 71% of methyl orange solution was degraded in 120 minutes under ambient experimental conditions. The catalyst was heterogeneous in nature which could easily separate from reaction mixture. Catalytic degradation of methyl orange in present investigation followed Eley-Rideal mechanism. The apparent rate constants were found as 0.0046, 0.0075 and 0.0105 per minute at 313, 323 and 333 K respectively. The energy of activation was calculated as 36.4 kJ/mol.

Conflict of interest

The authors declare that they have no conflict of interest.

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