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RESEARCH ARTICLE

Synthesis, Characterisation and Catalytic Behaviour of NiO Nanoflowers for the Photo Degradation of Norflaxacin in Aqueous Medium

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Abstract: NiO nanoparticles stabilized with starch was synthesized and characterized using UV-Vis, FT-IR, FESEM and XRD techniques. From FESEM analysis the morphology of the prepared NiO nanoparticles was found to be flower shaped. XRD analysis showed that the NiO nanoparticles corresponds to phase pure cubic crystals and from scherer formula the particle size was calculated to be 9±0.5 nm. Using optical absorption spectra, tha band gap energy was obtained. Photocatalytic activity of the synthesized nanoparticles was investigated by carrying out the degradation studies of norfloxacin under UV light irradiation.

Keywords: NiO nanoparticles, Starch, Degradation, Norfloxacin, pH studies

Introduction

For the few decades, number of studies have been focussed on the degradation of toxic organic compounds in waste water[1-10]. Pharmaceuticals such as antibiotics enter the water system through human, agricultural and veterinary practices[11-13]. Because of its widespread use and poor biodegradability, these drugs get accumulated in the aquatic environment causing adverse effects on the aquatic organisms. Norfloxacin(NF) is a fluoroquinolones class of antibiotic used in the treatment of urinary tract infections. NF has polar structure and therefore not sorbed in subsoil and leached significantly into water resources. Numerous methods are available in the literature for the treatment of waste water[14-17]. However, recently semiconducting material has attracted much attention in treating waste water containing pharmaceuticals[18-20].

NiO nanoparticles have been studied extensively for their optical, electronic, magnetic, thermal and mechanical properties and potential application in catalyst, gas sensors and photo-electronic devices[21-25]. NiO has played important role in catalysis and as *p*-type semiconductor. Recently Gondal *et al.*, used NiO nanoparticles in the photocatalytic degradation of phenol[26]. Among the different methods reported for the synthesis of NiO nanoparticles such as evaporation, sputtering, electrodeposition and sol gel techniques[27-31], sol-gel technique is more advantageous than other techniques since the chemical and physical properties of the nanomaterials can be tunned suitably by adjusting the operational parameters. In the present work, we have synthesized NiO nanoparticles with biostabilizer starch and used for the photocatalytic degradation of the antibiotic NF. The as prepared NiO nanoparticles are characterized using FESEM, UV-Vis, FT-IR and XRD measurements. Progress of the photo degradation of NF in the presence of NiO nanoparticles was monitored by using time dependant UV-Vis spectra. The reaction followed pseudo first order kinetics. Rate coefficient values at different pH and the optimum pH for degradation of NF was determined.

Experimental

Norfloxacin was purchased from Fluka Co. Ltd. Triple distilled water was used for solution preparations. $NiCl_2$. $6H_2O$, NaOH and pH buffer tablets are purchased from SRL, India ltd. Starch belong to the Fischer chemicals India Ltd. All working solutions are freshly prepared. UV-Vis spectrometer, double beam, Techcom with 1 cm path length quartz cuvettes was used. Bruker tensor 27 instrument was used for FT-IR measurements. Bruker D8 advance diffractometer was used for XRD data. FESEM of the nanoparticles were measured using SU6600, HITACHI model operating at an accelerating voltage of 100KV.

Synthesis of NiO nanoflowers and its characterization

3 g of the stabilizer starch was added to 200 mL ethanol. The mixture was heated at 40 °C for about 10 min with constant stirring for dissolution of the stabilizer. $NiCl_2.6H_2O$ (1.0 g) was added to the solution, which was then heated at 50 °C under nitrogen purging. 0.1 M NaOH solution was added drop wise and the pH of the final mixture was controlled in the range of 10-11. The mixtures were held at 50 °C for 2 h and green gel was obtained. The gel was washed several times using triple distilled water to remove by-products and excess stabilisers. The obtained gel was heated at 200 °C for 1 h. A black powder was formed and subjected to FESEM, UV-VIS, FT- IR and XRD characterization.

Photodegradation studies

Photocatalytic activity of the as prepared NiO nanoparticles were evaluated by studying the photodegradation of NF using NiO nanoparticles under UV light. Photodegradation experiments were carried out with a solution of 10 mg/L of NiO nps and 50 mg/L of NF. The mixture was then exposed to UV light of 365nm wavelength from xenon lamp for variable time intervals. The change in absorption spectrum of NF was recorded for different UV irradiation time.

Results and Discussion

Structure characterisation

Figure 1 gives the XRD pattern of NiO nps stabilised with the biopolymer starch. All the diffraction peaks may be assigned to pure cubic NiO phase which is in agreement with the reported value (JCPDS 47-1049) readily indexed as (111), (200) and (220) crystal planes[32,33]. No impurity peaks were detected which confirms the formation of phase pure NiO nps. Using Debye–Scherrer equation, the average size of the NiO nps was found to be 9±0.5 nm.

FESEM was used to study the morphology of the NiO nanoparticles. FESEM image was given in Figure 2b, which shows the formation of NiO nanoflowers. FT-IR spectrum of pure starch and NiO nps stabilized with starch were shown in Figure 3. Pure starch shows peaks at 3351 cm^{-1}, 2928 cm^{-1}, 1645 cm^{-1} corresponding to –OH, C-H and >C=O stretching frequencies which are completely vanished in the NiO np spectrum. The prominent peaks at 1400 cm^{-1} to 575 cm^{-1} are completely diminished in the nano particle spectrum. There is a peak at 528cm^{-1} corresponding to NiO. The FT-IR spectrum of NiOnp confirms the binding of starch to the np. In the NiOnp surface, strong H-bonding interactions hold the OH groups of the stabilizing agent, starch.

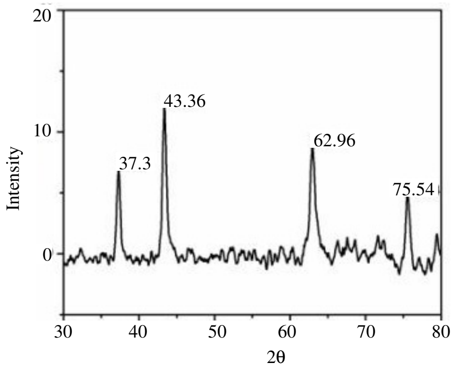


Figure 1. XRD pattern of NiO nps

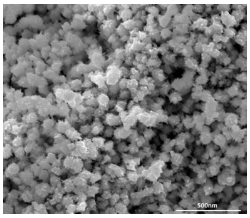


Figure 2a. FESEM image of NiO nps

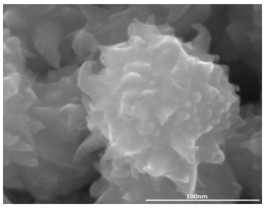


Figure 2b. FESEM image of NiO nps

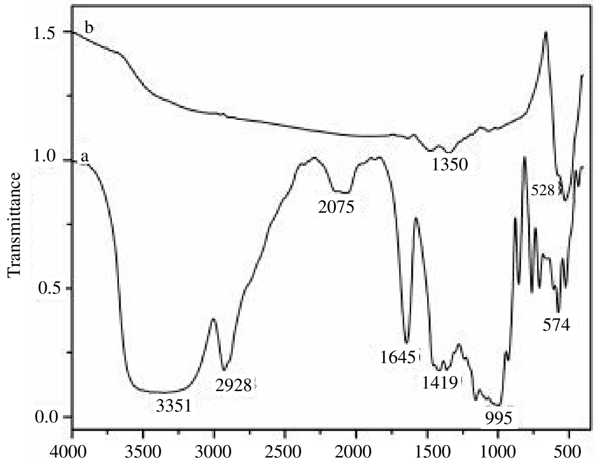


Figure 3. FT-IR spectrum of pure starch and NiO nps stabilized with starch

Figure 4 shows the optical absorption spectrum of the NiO nps. The absorption band gap E_g can be calculated by the following equation:

$$(\alpha h\nu)^n = B(h\nu - Eg) \quad (1)$$

In which hν is the photo energy, α is the absorption coefficient, B is a constant relative to the material and n is either 2 for a direct transition or 1/2 for an indirect transition. Eg can be calculated as shown in Figure 4b, by plotting $(\alpha h\upsilon)^2$ *versus* photon energy and extrapolating the linear portion of the curve to the photon energy axis. The direct band gap of the prepared NiO nps was found to be 3.2 eV[34].

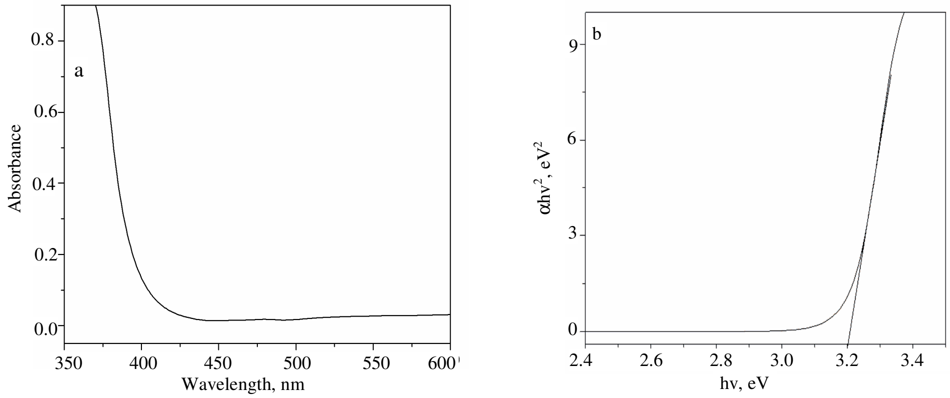


Figure 4. Optical absorption spectrum of the NiO nps

Photocatalytic activity of NiO nps

Figure 5 shows UV spectra of NF at various time intervals after irradiation. Absorbance at λ_{max} (272 nm) significantly decreased showing the degradation of NF. In order to confirm the photocatalytic activity of NiO nps, the sample was irradiated with UV light without NiO nps for 30 mins at 5 min increments. There is no appreciable decrease in absorbance at λ_{max} during direct photolysis of NF. Photodegradation of NF in the presence of NiO nps follows first order kinetics. The absorbance versus irradiation time plots determined from the spectra is shown in Figure 6. It may be seen that a gradual exponential decrease in the absorbance values with time are found out. The pseudo first order rate coefficient values for the degradation are determined from the kinetic plots which are obtained by plotting $\log(OD_0/OD_t)$ *versus* irradiation time.

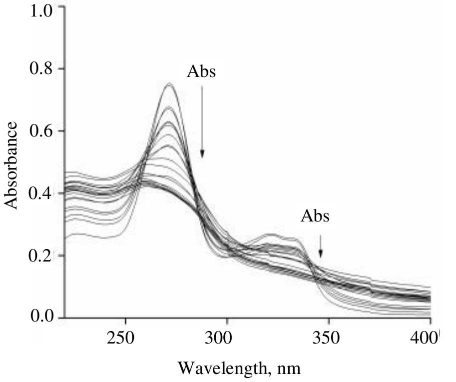


Figure 5. UV spectra of NF at various time intervals

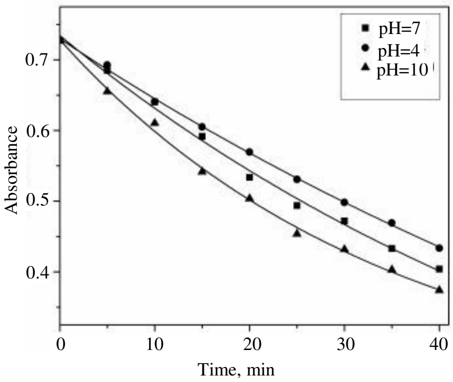


Figure 6. Absorbance *versus* irradiation time plot for the photodegradation of NF in the presence of NiOnps at various pH

Effect of pH on the catalytic activity of NiO nps was examined by adjusting pH of the reaction mixture at the values of 4, 7 and 10. Kinetic plots for different pH values of the reaction mixture were given in Figure 7 and the corresponding rate coefficient values are determined. From the k values, it is evident that the degradation rate is maximum in alkaline medium, shown in Figure 8.

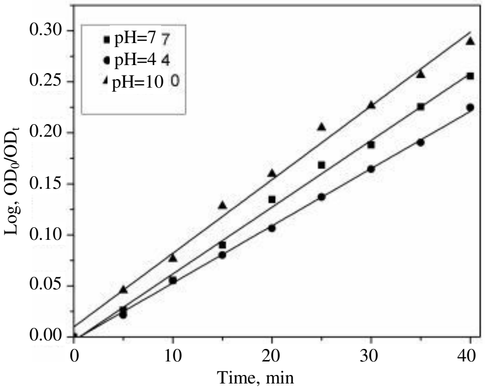


Figure 7. Kinetic plot for the photodegradation of NF in the presence of NiOnps at various pH

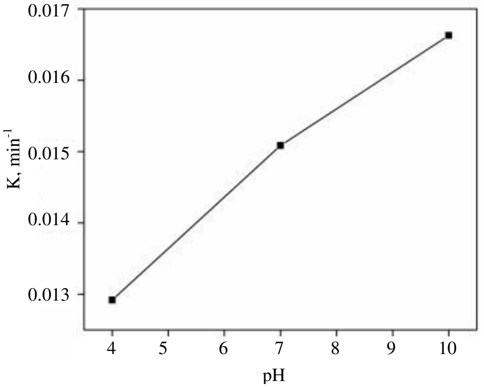
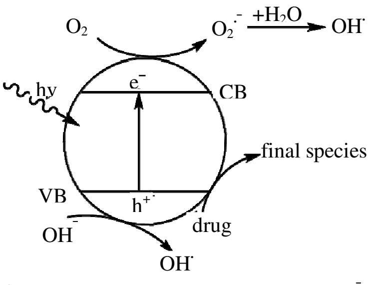


Figure 8. pH *versus* k plot for photodegradation of NF at various pH

Chemical structure of the drug and surface charge properties are strongly dependent on the pH of the reaction medium. NF has pKa values[18] at 6.34 and 8.75 corresponding to proton dissociation from carboxyl group and proton combination to N in the piperazinyl group respectively. Under different pH conditions, (pH = 4, 7 and 10) NF exists as positively charged, zwitter ionic and negatively charged. It is well documented that adsorption of reactants on the surface of catalyst is the basic step in photocatalytic reaction[18]. At the acidic pH, both the NiO nps and NF molecule are positively charged repelling each other resulting in low reaction rate. When the pH is between the pKa values, NF is in zwitter ionic form whereas NiO is negatively charged. Positively charged N atom of peperazinyl ring bound with the negatively charged NiO nps promotes the reaction resulting in increase of rate of the reaction. At the basic pH, optimal NF decay was observed. This may be due to higher concentration of hydroxyl ions resulting in more hydroxyl radicals. Further increase of pH decreases the rate of the reaction because both NF and NiOnps are negatively charged repelling each other retarding the reaction.



NiO + hυ → h_{VB}^{+} + e_{CB}^{-} h_{VB}^{+} + H_2O → $OH^{\bullet}$ e_{CB}^{-} + O_2 → $O_2^{\bullet -}$ + H_2O → $OH^{\bullet}$ Drug + h_{VB} + → mineralisation

Scheme 1. Proposed mechanism of drug degradation in the presence of NiO nanoparticles

It is evident from the earlier reports[35,36] that on irradiation of UV light, the metal oxide nanoparticles generate an excitation of electron from conduction band to valence band leading to electron hole formation. Transfer of generated electron to NF adsorbed on the NiO nanoparticle surface can be considered as the first step of photocatalytic degradation of NF. The photogenerated hole and hydroxyl radicals further acts on the drug NF leading to mineralization of the drug. The proposed mechanism of drug degradation in the presence of NiO nanoparticles is given in Scheme 1.

Conclusion

NiO nps stabilised with starch was prepared and characterized using UV-Vis, FT-IR, FESEM and XRD analysis. The band gap energy for the as prepared NiO nanoparticles was 3.2eV. The average size of the particles was found to be 10±1 nm. Photocatalytic activity of starch bound NiO nps was investigated for degradation studies of the drug NF. UV-Vis spectra was used to follow the degradation reaction. Kinetic plots were drawn and the rate coefficient values are determined. pH effect on drug degradation was studied and optimum pH was found to be 10. Thus, the biopolymer starch stabilised NiO nps were found to be efficient photocatalyst in the drug degradation. The results are encouraging and further studies can be carried out in drug waste water treatment using NiO nps as photocatalyst.

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