

Enhancement of the photocatalytic activity of modified ZnO nanoparticles with manganese additive

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Abstract ZnO nanoparticles were synthesized under mild hydrothermal conditions ($T = 150\text{ }^{\circ}\text{C}$, $P = \text{autogenous}$, experimental duration = 18 h). Manganese was added as an additive to ZnO nanoparticles in different molar percentages. In situ surface-modification was successfully carried out for these manganese-added ZnO nanoparticles using *n*-butylamine as a surface modifier. The modified manganese-added ZnO nanoparticulates are hydrophilic in nature and are well dispersed in various solvents. The modified nanoparticles were characterized using powder XRD, FTIR, SEM, Zeta potential, and UV–Vis spectrophotometry. The characterization results indicated tailoring of the morphology and size of the nanoparticles, and changing the surface chemistry of the nanoparticles synthesized. The SEM results show that the surface modified manganese-added ZnO nanoparticles have a very thin layer of organic coverage around the inorganic nanoparticles, thus, giving rise to hybrid nanoparticles. The photodegradation of Brilliant Blue dye under

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sunlight showed the higher efficiency of the modified manganese-doped ZnO nanoparticles compared to the reagent-grade ZnO.

Keywords Photodegradation · Brilliant Blue · Surface modification · Doping · *n*-butylamine · Manganese-added ZnO nanoparticles

Introduction

Recently, zinc oxide (ZnO) has attracted much attention within the scientific community as a ‘future material’ and, hence, it has been widely studied since 1935 [1]. The applications of zinc oxide powder are numerous, and the principal uses are piezoelectric, luminescence [2], electronics [3], dye-synthesized solar cells [4], chemical sensors [5], transparent electrodes [6], and the photodegradation of water [7] and removal of wastewater pollutants [8]. Conventional methods of treatment of toxic organic and industrial effluents like activated sludge, trickling filters, etc. not only produce concentrated sludge but are also, in most cases, incomplete [9]. Therefore, photodegradation, as an eco-friendly technique, could be used as an alternative for the treatment of these toxic organic compounds. Different parameters are involved in enhancing the photodegradation efficiency, including light source, photocatalyst size, morphology, surface charge, dispersion, agglomeration, etc. In situ surface modification of ZnO using a suitable surface modifier and a dopant under mild hydrothermal conditions could overcome these problems. The mild hydrothermal method is one of the best techniques which can be used for the synthesis and modification of different nanoparticles, including TiO₂ and ZnO [10], known for their photodegradation application.

Therefore, the present authors have selected *n*-butylamine as the surface modifier to control the particle size, morphology, agglomeration, hydrophilicity, and dispersibility of ZnO. In addition, manganese oxide was used as an additive to alter the bandgap energy and optical properties of the ZnO nanoparticles. Moreover, Brilliant Blue FCF (BBF) was used as a model dye for photodegradation studies.

Experimental

Preparation of in situ surface-modified manganese-added ZnO nanoparticles

Manganese-doped ZnO nanoparticles were fabricated under hydrothermal conditions ($T = 150\text{ }^{\circ}\text{C}$, $P = \text{autogenous}$). 1 M of reagent-grade ZnO (Loba Chemie, India) was taken as the starting material and the additive (MnO₂, 2 mol%; 5 mol%) was added into it. A certain amount of 1 N NaOH was added as a mineralizer to the precursors. *n*-butylamine (Sisco Research Laboratories Pvt., Ltd., Mumbai, India) with different concentrations (0.8, 1.0, 1.2, and 1.4 M) was added into the above mentioned mixture and it was stirred vigorously for a few minutes. The final mixture was then transferred to the Teflon liner ($V_{\text{fill}} = 15\text{ mL}$), which was later placed inside a general-purpose autoclave. Then, the autoclave was kept in an oven

with a temperature programmer controller. The temperature was programmed and kept at 150 °C for 18 h. After the experimental run, the autoclaves were cooled to room temperature. The product in the Teflon liner was then transferred to a clean beaker, washed with double-distilled water, and later the product was allowed to settle down. The surplus solution was removed using a syringe and the remnants were centrifuged for 20 min at 1,500 rpm. The product was recovered and dried in a hot air oven at 40–50 °C for a few hours. The dried particles were subjected to a systematic characterization using XRD, FTIR, SLS, Zeta potential, SEM, and UV–Vis spectrophotometric techniques.

Characterization of the in situ surface-modified manganese-added ZnO nanoparticles

The experimental run products were characterized using different analytical techniques. FTIR spectra were recorded using a Jasco 460 Plus (Japan) at a resolution of 4 cm^{-1} . Powder X-ray diffraction patterns were recorded using the Bruker D8 ADVANCE (Germany) with Cu $K\alpha$, $\lambda = 1.542 \text{ \AA}$ radiation, voltage = 30 mV, current = 15 mA, and scan speed $\sim 5 \text{ min}^{-1}$. The data were collected in the 2θ range 20–80°. The optical properties were studied using a UV–Vis spectrophotometer (Mini Spec SL 171, Elico, India). The particle size and its distribution were estimated using a HORIBA LB-550 (Japan). SEM images of the manganese-added ZnO hybrid nanoparticles were recorded using a Hitachi S-4200 (Japan). The Zeta potential was measured using a Zetasizer 2000 instrument (Malvern Instruments, UK).

Photoreactor and experimental procedure

A cylindrical flow photoreactor (Fig. 1) was designed and fabricated in our laboratory for the photodegradation studies. At the center of this cylindrical vessel, a 6-W low-pressure mercury lamp was placed inside a quartz sleeve with an emission peak at 264 nm (Philips, Netherlands). This was surrounded by a circulating water

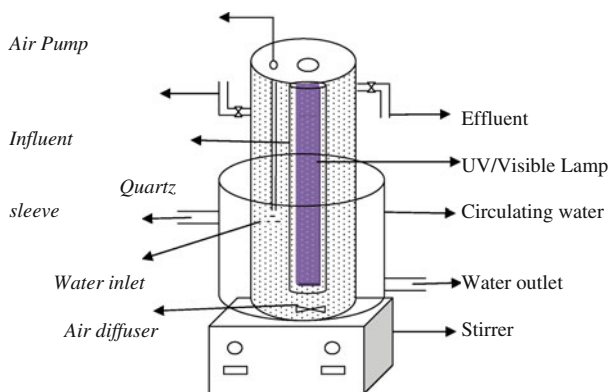


Fig. 1 Flow photoreactor

jacket intended to control the temperature during the reaction. For visible-light irradiation, sunlight was used. The reaction suspension was prepared by adding different amounts of photocatalyst powder (0–2.0 g) per liter of dye solution. An external aerator was used as an oxygen source and air was continuously pumped into the reactor through air diffusers to fully fluidize the surface-modified manganese-added ZnO hybrid nanoparticles during the photoreaction. For the purpose of application potential in practice, the initial pH was adjusted to 7.5 using 0.02 M HCl solution and 0.02 M NH_3OH solution before reaction. The surface-modified manganese-added ZnO hybrid nanoparticles were mixed with the Brilliant Blue FCF (BBF) solution and placed in darkness for 30 min to ensure balance of adsorption and desorption. The suspensions were sampled at specific intervals to monitor the changes of BBF concentrations. Suspensions sampled were centrifuged at 1,500 rpm for 30 min to remove the modified manganese-added ZnO hybrid nanoparticulates and then analyzed by a UV–Vis spectrophotometer.

Results and discussion

The powder XRD data reveal a highly crystallized wurtzite structure and there is no new peak, which confirms that manganese has been added to ZnO without changing the structure (Fig. 2). There is a slight change in the lattice parameters of the in situ surface modified manganese-added ZnO hybrid nanoparticles (ZnO- X , $X = 2, 5$ mol% manganese) at the a -axis and c -axis when compared to pure ZnO; this confirms the existence of manganese atoms in ZnO hybrid nanoparticles. The radii of the Mn (VI) ion (46 pm) is smaller than that of Zn (II) (72 pm) [11], so the addition of Mn (VI) has not changed the cell parameters of ZnO significantly (Table 1). The powder XRD pattern of (2 mol%; 5 mol%) in situ surface-modified manganese-added ZnO hybrid nanoparticles shows seven primary peaks, which can be attributed to different diffraction planes of ZnO [12].

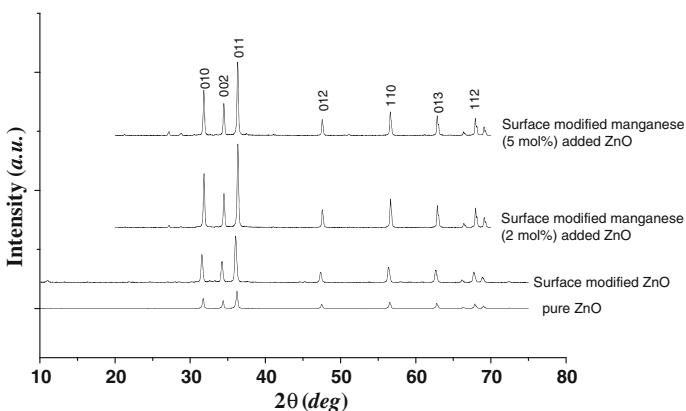


Fig. 2 Powder XRD pattern of in situ surface-modified manganese added ZnO hybrid nanoparticles

Table 1 Cell parameters of ZnO

Catalyst	a (\AA)	c (\AA)	$a:c$ ratio	V (\AA^3)	Reference
Pure ZnO	3.249	5.207	0.6239	47.60	[13]
Used ZnO	3.2525	5.2166	0.6241	47.88	Present work
2 mol% MnO_2 added ZnO	3.2510	5.2065	0.6244	47.66	Present work
5 mol% MnO_2 added ZnO	3.2510	5.2065	0.6245	47.65	Present work

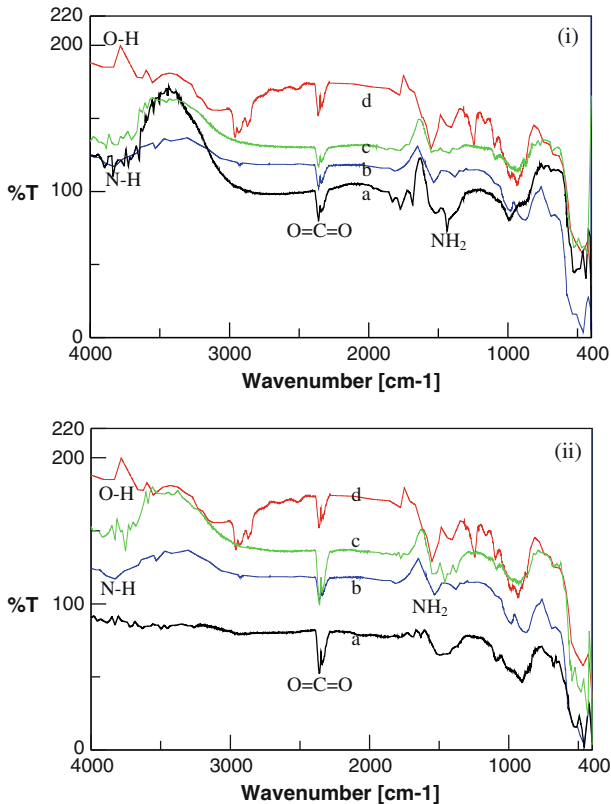


Fig. 3 FTIR spectra of: **a**) reagent grade ZnO, **b**) surface modified ZnO; manganese added ZnO hybrid nanoparticles modified with **c**) 0.8 M, and **d**) 1.6 M *n*-butylamine: **i**) 2 mol% additive and **ii**) 5 mol% additive

The functional groups present in the modified nanoparticles can be studied using FTIR spectroscopy. Figure 3 shows the FTIR spectra of the reagent-grade ZnO, in situ surface-modified pure ZnO, and in situ surface-modified manganese-added ZnO nanoparticles modified with *n*-butylamine as the surface modifier, respectively. The intensity of the peaks was greater for 1.4 M in situ surface-modified manganese-added ZnO hybrid nanoparticles compared to 0.8 M surface-modified manganese-added (2 and 5 mol%) ZnO hybrid nanoparticles. The FTIR spectra of the modified

hybrid nanoparticles show the presence of new peaks, implying that the reagents were chemically immobilized on the surface of nanoparticles. Thus, it can be concluded that the manganese-added ZnO hybrid nanoparticles, which were synthesized with the above mentioned modifier, have organic coverage on their surfaces, which has changed the surface property of the nanoparticles. The peaks around $1,516$ and $3,680\text{ cm}^{-1}$ correspond to the presence of NH_2 and N–H stretching bands. In addition, the appearance of new peaks around $2,965$ and $3,400\text{ cm}^{-1}$ correspond to O–H and N–H stretching bands [14].

Figure 4 shows the characteristic SEM images of 2 and 5 mol% in situ surface-modified manganese-added ZnO hybrid nanoparticles modified with (0.8 and 1.4 M) *n*-butylamine, respectively. The agglomeration was less when a higher concentration of the surface modifier was used. The surface modification has led to the controlling of growth direction, and also the particle size and preventing agglomeration. It was found that the surface modifier could not only affect the dispersibility of the synthesized manganese-added ZnO hybrid nanoparticles, but it can also change their morphology and size of particles. The morphology achieved is quite suitable for the photodegradation purposes, since the manganese-added ZnO hybrid nanoparticles are small, disperse well, and are hydrophilic, so they can be more active in the photodegradation of the organic pollutants present in industrial effluents. The SLS technique is one of the most popular methods used to determine the size of particles. Figure 5 shows the particle size distribution of the in situ surface-modified manganese-added ZnO nanoparticles synthesized, confirming the nano-range of the particles. The range is narrower in the case of 2 mol% manganese-added ZnO nanoparticles.

Zeta potential of in situ surface-modified manganese-added ZnO hybrid nanoparticles

Zeta (ζ) potential measurement was performed for ZnO nanoparticles in order to characterize the surface charge of nanoparticles and Fig. 6 shows the results as a

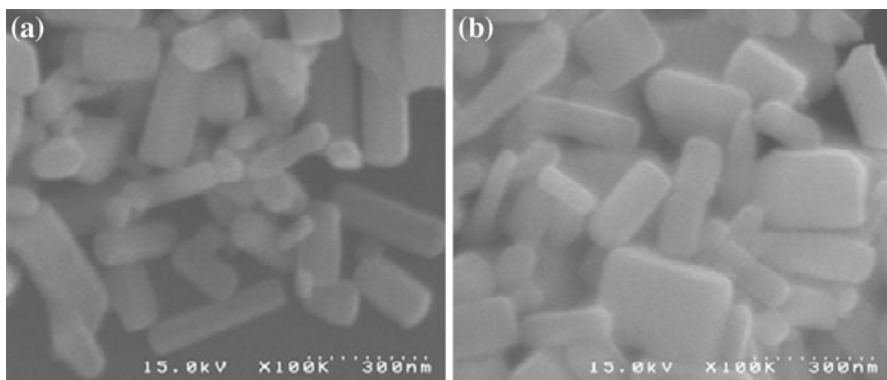


Fig. 4 Characteristic SEM images of in situ surface-modified manganese-added ZnO hybrid nanoparticulates using 1.0 M *n*-butylamine: **a** 2 mol% additive and **b** 5 mol% additive

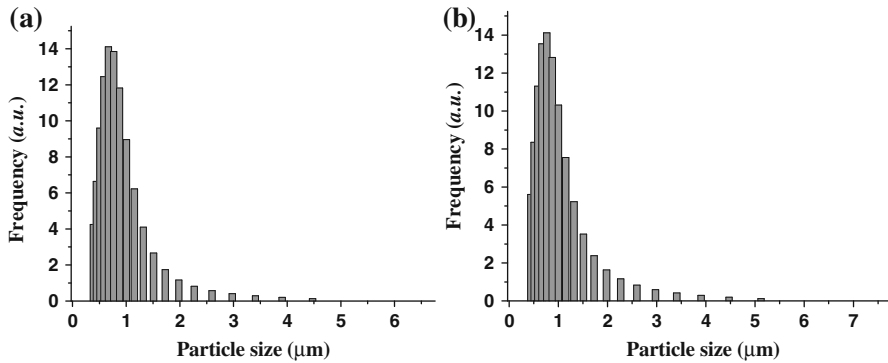


Fig. 5 Particle size distribution using SLS for in situ surface-modified manganese-added ZnO hybrid nanoparticles modified using 1.4 M *n*-butylamine: **a** 2 mol% additive and **b** 5 mol% additive

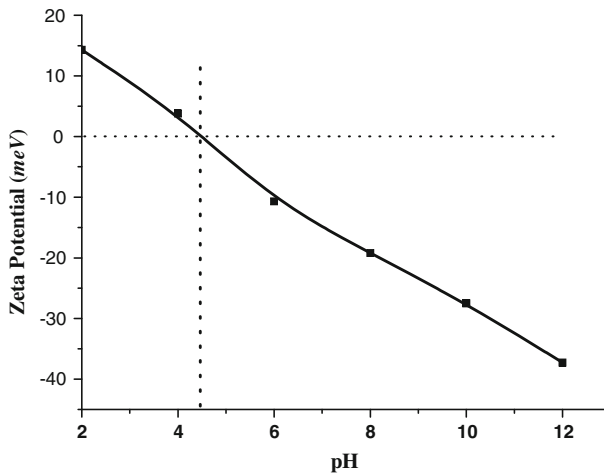


Fig. 6 Zeta potential of ZnO nanoparticles modified with *n*-butylamine as the surfactant

function of pH. The obtained ζ potential of the nanoparticles was found to decrease with an increase of pH as is expected for a surface with acid-base group. The isoelectric point or point of zero charge (PZC) for ZnO nanoparticles was found to be 4.2 for modification by *n*-butylamine. For smaller nanoparticles, a high ζ potential will confer stability, i.e., the solution or dispersion will resist aggregation [15, 16].

Band gap energy of modified manganese-added ZnO hybrid nanoparticles

The effect of metal addition was studied by UV–vis spectroscopy in the range of 200–600 nm. Figure 7 shows that pure ZnO had no absorption in the visible light region ($\lambda > 400$ nm). The in situ surface-modified manganese-added ZnO hybrid nanoparticles using ethanol as the solvent showed a remarkable absorption band

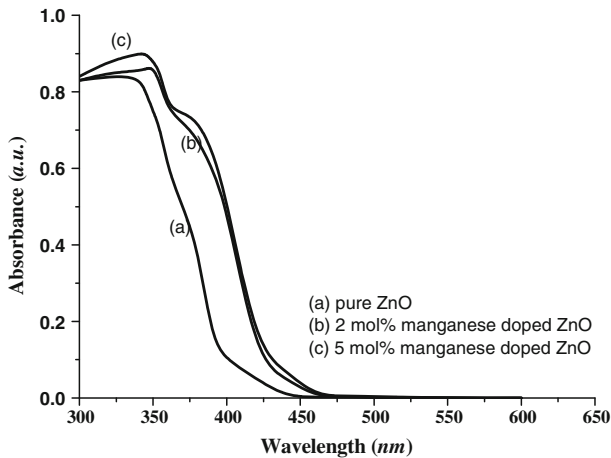


Fig. 7 Effect of doping on the band gap energy of the in situ surface-modified manganese-added ZnO hybrid nanoparticles modified with *n*-butylamine

shift towards the longer wavelength region, which indicates a decrease of the band gap energy.

Photodegradation of BBF

The absorption of BBF (Loba Chemie) was measured at 630 nm (λ_{\max}) of the remaining solution. The absorption was converted to the relative concentration of the photodegraded dyes ($\ln C/C_0$), where C and C_0 represent the concentration after reaction and the initial concentration, referring to a standard curve, and displayed linear behavior between the relative concentration and absorption at this wavelength, respectively. For comparison, the photocatalysis of BBF on pure ZnO powders from Loba Chemie were conducted under the same operating conditions.

Effect of in situ surface-modified manganese-added ZnO nanoparticles on the photocatalytic degradation of BBF

In a slurry photocatalytic process, the catalyst dosage is an important parameter. Photocatalytic degradation of 20 mg/L BBF was carried out with in situ surface-modified manganese-added (2, 5 mol%) ZnO hybrid nanoparticles and reagent-grade ZnO catalyst loading of 0–2.0 g/L under the sunlight irradiation, respectively. The degradation of BBF as a function of the fabricated ZnO nanoparticles and pure ZnO dosage is presented in Fig. 8a.

As shown in Fig. 8b, in the absence of ZnO, the removal percentage of this dye was almost zero. The addition of nanoparticles enhances the removal of BBF. The removal rate of this dye increases as the concentration of the dyes thickens. It should be mentioned that there was no difference in the extent of degradation based on the light source in the case of reagent-grade ZnO, but as this figure indicates, the

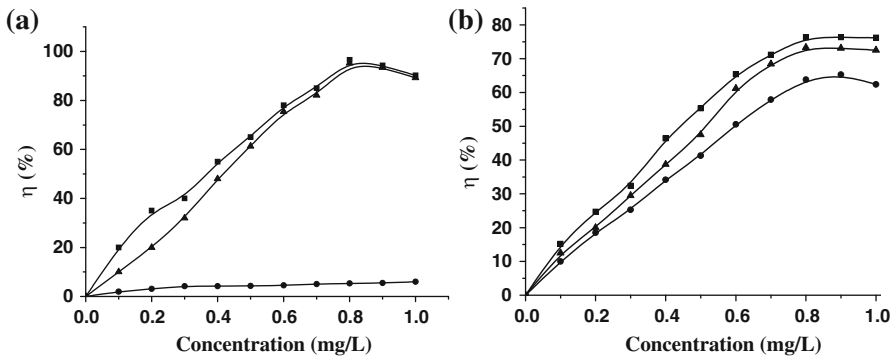


Fig. 8 Effect of catalyst dosage on the photodegradation of BBF under **a** sunlight and **b** UV light: in situ surface-modified manganese-added (filled triangles 2 mol% and filled squares 5 mol%) ZnO hybrid nanoparticles with 1.0 M *n*-butylamine, and filled circles reagent-grade ZnO

degradation also occurred in visible light, which can confirm the doping effect on the photodegradation of this dye. An optimal result was achieved at a ZnO dosage of 1.4 g/L. The removal then decreases with a further increase in the catalyst dosage.

Effect of light source and its duration on the photocatalytic degradation of BBF

Figure 9 shows a comparison of the photodegradation of BBF at different moments in the presence of in situ surface-modified manganese-added (2, 5 mol%) ZnO hybrid nanoparticles under sunlight and UV irradiation. The photodegradation ratio in the presence of in situ surface-modified manganese-added (2 and 5 mol%) ZnO hybrid nanoparticles increases along with the irradiation time and attains about 89.6 and 78.75% respectively, within 3.0 h of sunlight irradiation. In the case of UV irradiation, the efficiency was 61.5 and 55.6% respectively. The results indicate that the photocatalytic degradation reaction is a pseudo-first-order kinetic reaction.

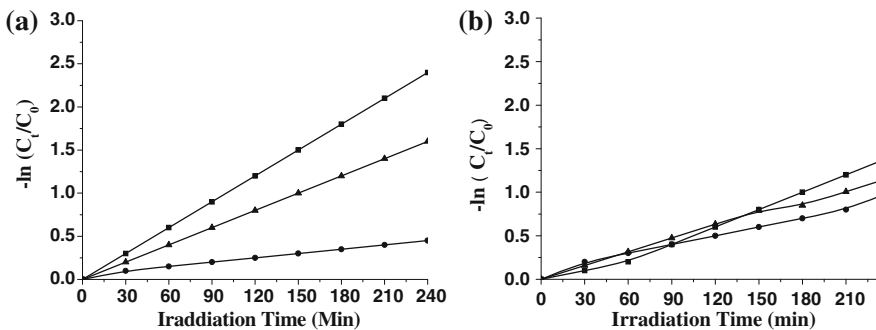


Fig. 9 Effect of irradiation time under **a** sunlight and **b** UV light on the photodegradation of BBF: in situ surface-modified manganese-added (filled triangles 2 mol% and filled squares 5 mol%) ZnO hybrid nanoparticles with 1.0 M *n*-butylamine, and filled circles reagent-grade ZnO

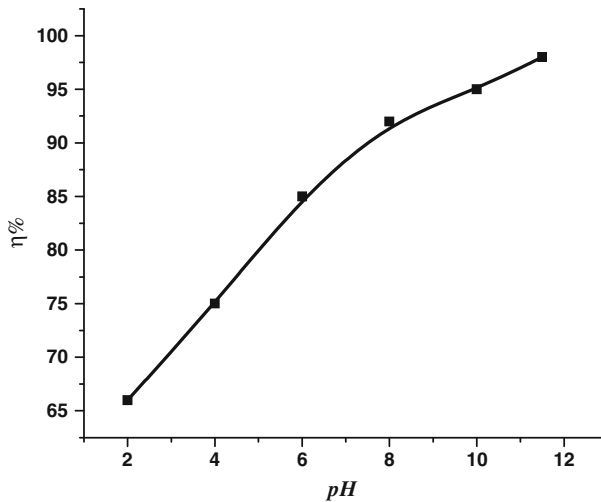


Fig. 10 Effect of pH on the photodegradation of BBF

Effect of pH on the photodegradation of BBF

The pK_a value of BBF is 5.63, 6.58, which means that the pH has an effect on its photodegradation. The pH was adjusted using varying concentrations of 0.02 N HCl or NH_3OH . The effect of pH is shown in Fig. 10. The maximum efficiency was observed at extreme basic conditions. The change in pH of the solution varies with the dissociation of the dye molecule and the surface properties of the nanoparticles used. The initial adsorption of the dye molecules onto the nanoparticles greatly depends on the solution pH [17]. Increase in the degradation efficiency under the alkaline condition could be attributed to the increase in hydroxyl ions, which induce more hydroxyl radical formation.

Effect of surfactant concentration on photocatalytic degradation

The surface modifier density and its concentration play a critical role in its suitability. The density of the surfactant should be less than water and the precursors, otherwise, its removal from the nanoparticles prepared will be very difficult. Figure 11 shows the effect of surfactant concentration on the photodegradation of effluents. As it shown, the optimum concentration of the surfactant is found to be 0.8 M for the surface modification of ZnO hybrid nanoparticles using *n*-butylamine.

Conclusion

Manganese-added ZnO hybrid nanoparticles were successfully modified under hydrothermal conditions. *n*-butylamine was used as the surface modifier. Surface

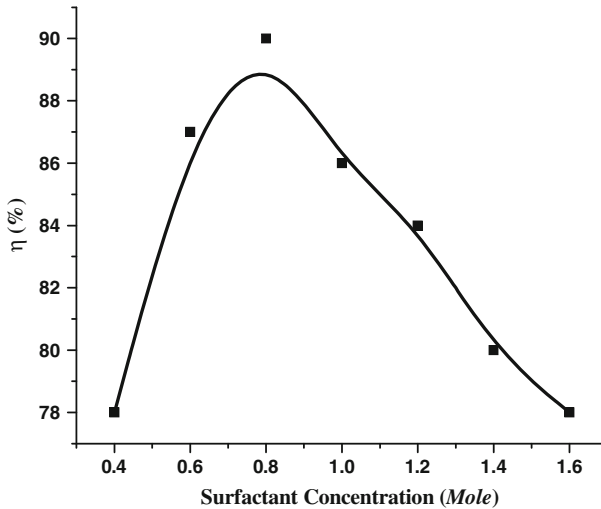


Fig. 11 Relationship between the concentration of *n*-butylamine applied to modify the surface of ZnO nanoparticulates and photodegradation efficiency

modification changed the morphology and size of the in situ surface-modified ZnO-added hybrid nanoparticles synthesized. In addition, it changed the surface charges and increased the stability of the nanoparticles, which is necessary to achieve higher photodegradation efficiency. Adding a suitable metal like manganese into the ZnO nanoparticles can reduce the band gap energy and enhance the feasibility of the photodegradation in the visible light range. Simultaneous surface modification and addition of manganese into ZnO nanoparticles not only change the surface morphology, size, and surface charges of the nanoparticles synthesized, but they also significantly shift the band gap energy to the visible region, where photodegradation efficiency is greater compared to the UV region.

The photodegradation efficiency of ZnO was enhanced by modifying these nanoparticles and the results of BBF photodegradation indicate that the activity of the in situ surface-modified ZnO hybrid nanoparticles has enhanced.

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