Materials Research Express

PAPER

Synthesis of immobilized ZnO over polyurethane and photocatalytic activity evaluation for the degradation of azo dye under UV and solar light irradiation

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Keywords: immobilization, ZnO, photocatalysis, acid black 1, optimization

Abstract
Zinc oxide (ZnO) nanoparticles were immobilized on polyurethane foam (PUF) and employed for the degradation of Acid black 1 dye (AB1). The ZnO/PUF was characterized by x-ray diffraction (XRD), scanning electron microscope (SEM) and energy dispersive x-ray (EDX) techniques. Process variables i.e., dye concentration, pH, concentration of H2O2, irradiation time were optimized for maximum degradation of dye. ZnO/PUF showed promising efficiency for the degradation of AB1 dye and up to 86% and 65% dye degradation was achieved under UV and solar light irradiation at neutral pH, 4% H2O2, 240 min/sunlight and 75 min/UV irradiation time using 40 mg l−1 dye initial concentration. The optimum conditions were applied for the treatment of textile wastewater and biological oxygen demand (BOD) and total organic carbon (TOC) were reduced up to 70% and 80%, respectively. In view of promising photocatalytic activity (PCA), ZnO/PUF could possibly be used for the treatment of wastewater contains dyes.

1. Introduction

Water contamination due to anthropogenic discharge of pollutants is a critical issue that must be resolved to ensure water quality and healthy environment. Among pollutants, synthetic dyes are of major concern because of their high production and disposal rate and severe toxicity. Dyes bearing effluents from paper, textiles, plastics and rubber industry are discharged into water bodies without any treatment, which pollute the water bodies and is responsible for different diseases like cancer, respiratory illness and endocrine diseases [1–5]. Various methods i.e., chemical process, physical techniques and biological process have been used for the removal of dye from industrial effluents [6–12]. Ultrafiltration, chlorination, coagulation by chemical agents, adsorption on activated carbon, ion exchange and reverse osmosis on synthetic adsorbent resins were previously used methods [6, 12–17]. These aforementioned methods have some drawbacks i.e., toxic compounds are not completely removed by these methods, but only trapped and transferred to another phase from water, thus create secondary contamination and disposal problems [18–21]. However advanced oxidation process is an eco-friendly and more efficient than the other existing technologies, during advanced oxidation process (AOP), the pollutants are degraded in to less toxic components rather than just being transferred to another phase [22–27].

In AOP, reactive species such as hydroxyl radicals (·OH) are produced that degrade the pollutants in aqueous medium non-selectively to harmless end products. Among different methods, photocatalytic based AOP
processes are considered as a promising for degrading the pollutants and also kill microbes in contaminated water [28–34]. This process resulted in complete mineralization of noxious pollutants into CO₂ and H₂O at ambient conditions [22, 26]. Various semiconductors along with other metal oxides have been evaluated as catalyst for AOP i.e., zinc oxide (ZnO), zinc sulfide (ZnS), iron(III) oxide (Fe₂O₃), cobalt iron oxide, BiFeO based nanocomposites, cadmium sulfide (CdS) titanium and dioxide (TiO₂) [24–26, 35–42]. Semiconductor nanoparticles are considered suitable for wastewater treatment due to their non-toxic behavior, chemically and biologically inert and inexpensive [43–45]. ZnO is one of promising catalysts to carry out the AOP process for the production of radicals to degrade the toxic organic pollutants in pure [26] and modified catalysts showed excellent efficiency in this regard [27]. However, separation and regeneration of catalysts for repeated cycles is difficult task. This problem can be overcome by immobilizing photocatalyst (ZnO) over some support [46].

Based on the aforementioned facts, ZnO NPs were immobilized on polyurethane foam via seeding method and characterized by XRD, SEM and EDX techniques. The photocatalytic activity (PCA) was evaluated by degrading the AB1 dye. The process variables i.e., pH, concentration of H₂O₂, irradiation time and dye concentration were optimized for the maximum degradation of dye.

2. Material and methods

2.1. Chemical and reagents

Zinc acetate dehydrate (Zn(CH₃COO)₂), sodium hydroxide (NaOH), zinc sulphate heptahydrate (ZnSO₄·7H₂O) with ≥98% purity were purchased from Sigma Aldrich. Acid Black 1 dye (AB1) was purchased from Sandal Dye Stuff, Pvt. Faisalabad, Pakistan. Textile wastewater was collected from Haaris Dyes and Chemicals Pvt. industry and Bismilla Textile Industry Pvt. Faisalabad, Pakistan.

2.2. Functionalization of PUF

To ensure the efficient growth of ZnO NPs over polyurethane foam, surface of polyurethane foam was made hydrophilic by chemical treatment. Polyurethane foam was stirred with 8% caustic soda for 20 min at 60 °C, then, washed with distilled water, dried and used for ZnO NPs immobilization.

2.3. Synthesis and immobilization of ZnO over PUF

ZnO/PUF was prepared by hydrothermal method by seeding of ZnO NPs. Typically, ZnO seed layer was prepared by refluxing solution of Zn(CH₃COO)₂ (90 mM⁻¹ in methanol) at 60 °C for 15 min followed by slow addition of NaOH (75 mM⁻¹ in methanol) until solution turned milky. Solution was refluxed till it becomes transparent. Later, the functionalized polyurethane foam was dipped in this solution and air dried afterwards. For even seeding, this dipping and drying process was repeated 10 times. After seeding, ZnO NPs were grown on PUF using ZnSO₄·7H₂O and NaOH at 90 °C for 3 h in Launder-o-meter (TC-M-25). Then, Launder-o-meter was quenched to room temperature and the ZnO grown on PUF was then transferred to a beaker and to remove the surplus solution, it was washed several times with distilled water. ZnO/PUF was allowed to dry at room temperature and undergone characterization and PCA studies.

2.4. Characterization

ZnO/PUF was characterized for morphological, elemental analysis and structure analysis by Scanning electron microscope (Quanta 250, FEG USA), Energy Dispersive x-ray Analysis (EDX) (INCA Oxford Instruments UK) and x-ray diffraction Analysis (XRD) (Jeol JDX-3532, Japan).

2.5. Photocatalytic activity evaluation

Reactor with dimension 50 cm³ fitted with four UV tube lights of low pressure mercury, each of 180 watt was used for UV irradiation. While natural sunlight during the month of May and June from 10 am to 3 pm, with solar flux ranges from 600–650 KWh m⁻² was used for solar irradiation. Experiments were conducted in glass containers with dimension 10 × 10 × 3 cm with working volume 50 cm³. The PCA batches were run as mentioned in Table 1. For PCA evaluation, the catalyst and sample (10:90 ratio) (at specific, pH, dye and H₂O₂ concentration) were kept in dark for 20 min and then, irradiated for stipulated time periods to UV and sunlight radiations. The absorbance (λmax = 617 nm) of dye sample was recorded before and after irradiation and dye degradation was estimated using relation shown in equation (2). Where, C₀ and Cᵣ are representing absorbance before and after treatment, respectively.

\[
\text{Degradation (\%)} = \frac{C₀ - Cᵣ}{C₀} \times 100
\]
The conditions optimized for AB1 dye were applied to treat textile wastewater. The textile wastewater was collected from Haaris Dyes and Chemicals Pvt. industry wastewater (HDCWW) and Bismilla textile industry wastewater (BTWW). The efficiency was evaluated on the basis of biological oxygen demand (BOD), chemical oxygen demand (COD) and total organic carbon (TOC) reductions. The COD and BOD were measured using digital meter (Lovibond® Water Testing system) and for TOC measurement, method reported elsewhere was followed [47]. Percentage reduction in TOC, BOD and TOC were measured using relation shown in equation (2). Where, \( V_0 \) and \( V_f \) are representing values (TOC, BOD and TOC) before and after treatment, respectively.

\[
\text{Reduction (\%)} = \frac{V_0 - V_f}{V_0} \times 100
\]

### 3. Results and discussion

#### 3.1. Characterization of ZnO/PUF

ZnO morphology was studied by SEM and the ZnO grown over PUF homogeneously and uniformly (figure 1(a)), exhibiting the symmetrical arrangement of ZnO in closely packed assembly. Furthermore, purity and elemental analysis of ZnO/PUF was confirmed by EDX (figure 1(b)). The EDX analysis revealed Zn and O with 97.02 and 2.98 percentages, which revealed the high purity of ZnO. The crystallinity was analyzed through XRD analysis. By scanning the sample through a range of 2\( \theta \) angles, all possible diffraction directions of the lattice can be attained due to the random orientation of the powdered material. XRD pattern showed peaks
associated only with ZnO, which also revealed purity of ZnO. The diffraction pattern of ZnO matched with JCPDS card 36–1451 (hexagonal, wurtzite crystal) with highest peak at 2θ = 36.30° (figure 1(c)). Moreover, the FTIR analysis of ZnO/PUF was also recorded (figure 1(d)). Peak associated with stretching vibrations of ZnO was found at 482–520 cm⁻¹. A broad peak in the region 3000 to 3600 cm⁻¹ is due to free –OH, while narrow peak at 2800–3000 cm⁻¹ was associated with bonded –OH functional group. The optical property of ZnO/PUF was estimated by DRS and band gap measurements. The DRS revealed that up to 40% of sunlight was absorbed by ZnO photocatalyst in the visible region from 380–500 nm, while 30% was harvested throughout in the visible region. The enhanced absorption of solar radiation is based on the intrinsic crystal defects due to oxygen vacancies. The role of oxygen vacancies in enhanced solar radiation harvesting tendency has also been explained in already reported study [5]. The convenient excitation of electron and generation of electron–hole pair can be attributed to the introduction of interband energy levels within the band gap region. Using the Kubelka-Munk relationship, based on the data obtained by DRS provided with the band gap energy of 3.05 eV (figure 2). This band gap energy further explained that partial harvesting of visible radiation was possible in addition to UV absorption to carry out photocatalysis.

3.2. Photocatalytic degradation of dye
The process variables i.e., pH, H₂O₂ concentration, AB1 dye concentration and irradiation time were optimized for maximum degradation of dye. The quadratic models (equations (3), (4), for sunlight and UV irradiation, respectively) revealed the effect of process variables on dye degradation.

\[
Y \text{ (Solar)} = 90.63 - 1.88X_1 - 0.54X_2 - 4.86X_3 + 9.29X_4 \\
  + 1.56X_1X_2 - 1.44X_1X_3 - 0.94X_1X_4 \\
  + 3.06X_2X_3 + 0.56X_2X_4 + 3.81X_3X_4 \\
  - 16.08X_1^2 - 9.83X_2^2 - 13.50X_3^2 - 13.33X_4^2 \quad (3)
\]

\[
Y \text{ (UV)} = 90.26 - 2.99X_1 + 3.96X_2 - 5.04X_3 + 10.86X_4 + 2.94X_5 \\
  - 0.81X_1X_3 + 0.063X_1X_4 + 2.19X_2X_3 - 2.19X_2X_4 \\
  - 0.44X_2X_4 - 6.44X_3^2 - 7.56X_4^2 - 4.64X_5^2 - 11.68X_6^2 \quad (4)
\]

Graphically presentation of dye degradation as a function of process variables is shown in figure 3. An interactive effect of pH and H₂O₂ concentration on AB1 degradation under sunlight was observed. In UV/sunlight/H₂O₂ system, AB1 degradation was higher in 5–7 pH range with maximum at pH 7 that gradually decreased by increasing the pH from 8–9. Higher degradation rate in acidic pH is due to the charge over the surface of ZnO that is positive and it can effectively adsorb anions of AB1 dye, reverse is true at higher pH. Another reason for reduced degradation of AB 1 at basic pH is the instability of H₂O₂ in alkaline conditions, scavenging of OH radical by carbonate and bicarbonate ions produced from carbon dioxide (a mineralization product of organic compound and nature of organic pollutant) [26]. Higher AB1 degradation was attained at 4% H₂O₂ concentration, higher dosage of H₂O₂ beyond the optimum level results in decrease in AB1 degradation because of consumption of valence band holes by H₂O₂ itself and a very reactive OH radicals [43, 48, 49]. Furthermore, the dependency of the rate of dye degradation on the concentration of AB1 dye was also optimized and a negative
relation between AB1 dye degradation and AB1 dye concentration was observed (figures 3(c), (d)). Low rate of AB1 degradation at higher AB1 concentration is due to accumulation of dye intermediates over catalyst surface and degradation process was slowed down [22]. In addition, an increase in dye concentration results in the production of intermediates that may adsorb on the catalyst surface. The slow diffusion of the resulting intermediates from the surface of the catalyst can lead to deactivation of the active sites of the photocatalyst and thus, dye degradation rate was decreased [50]. sunlight and UV light exposure time also affected the rate of degradation of AB1 dye. The combined effect of irradiation time and pH (figures 3(e), (f)) and irradiation time and H2O2 concentration (figures 3(g), (h)) demonstrate that the rate of degradation increased with irradiation time to a certain level and beyond that the degradation rate remained constant. However, the degradation was faster under UV irradiation versus sunlight. The exposure time of 120 min of UV revealed more degradation versus 360 min, which is due to the ZnO bandgap of 3.2 eV (λ = 380 nm) and the PCA under sunlight can be due to crystalline defects in ZnO.

The addition of H2O2 also showed interactive effect for dye degradation (figures 3(i), (j)). Increasing H2O2 concentration from 2% to 4% the dye degradation rate was enhanced from 60% to 86% under UV and 50% to 65% under sunlight irradiation. At higher concentration of H2O2 (6%) the dye degradation rate was decreased due to scavenging and recombination of OH radicals [43]. After optimizing the process variables, it was revealed that neutral pH, 4% H2O2, 240 min/sunlight and 75 min/UV irradiation time and 40 mg l^-1 dye initial concentration are best levels for maximum dye degradation. The overall mechanism for PCA over ZnO is shown in equations (5)–(10). It can be seen from equations (7)–(9) [43–45, 48, 49, 51], that there are different sources of hydroxyl radicals, which degrade the dye via oxidative process. The AOP efficiency depended upon the generation of hydroxyl radicals [27, 33, 34, 52] and hence, the PCA of ZnO in the presence of H2O2 was promising.

\[
\begin{align*}
\text{ZnO} + \text{irradiation} & \rightarrow h^+ + e^- \quad (5) \\
\text{e}^- + \text{O}_2 & \rightarrow \text{O}_2^- \quad (6) \\
h^+ + \text{H}_2\text{O} & \rightarrow \text{HO} \quad (7) \\
\text{O}_2^- + \text{H}_2\text{O}_2 & \rightarrow \text{HO}^- + \text{HO}^- + \text{O}_2 \quad (8) \\
\text{H}_2\text{O}_2 + \text{irradiation} & \rightarrow 2\text{HO}^- \quad (9) \\
\text{HO}^- + \text{dye} & \rightarrow \text{CO}_2 + \text{H}_2\text{O} + \text{Inorganic ions} \quad (10)
\end{align*}
\]

The degradation of AB1 dye by ZnO/PUF was monitored by UV/vis and FTIR techniques [53–56]. AB1 dye showed absorbance maximum at 617 nm (figure 3(a)) before treatment and the absorption at 617 nm was
disappeared after treatment under UV and sunlight (Figures 4(b), (c)), which revealed that no new by product was produced, but dye was degraded in to inorganic species. FTIR analysis also revealed similar behavior of AB1 dye before and after treatment (Figures 5(a)–(c)). The characteristic peaks in the fingerprint are of benzene ring, which is supported by the peaks at 1022 cm\(^{-1}\), 1078 cm\(^{-1}\) and 1097 cm\(^{-1}\) for the \(-\text{C–C–C}\) bending vibrations and with the asymmetric \(-\text{SO}_3\) stretching vibrations peak at 1242 cm\(^{-1}\). A peak at 1654 cm\(^{-1}\) for \(-\text{N} = \text{N}\)– stretching vibrations (azo group) and for \(-\text{OH}\) group, peaks are observed at 2937 cm\(^{-1}\) and 3421 cm\(^{-1}\). After treatment, a peak at 1597 cm\(^{-1}\) and 1570 cm\(^{-1}\) are the peaks that support loss of azo bond and formation of primary amine (\(-\text{NH}\)).

The quantitative assessment of the AB1 degradation was done by measuring water quality parameters i.e., COD, TOC and BOD before and after treatment. The COD reduced from 295 mg l\(^{-1}\) (before treatment) to 188

Figure 4. UV-visible analysis of AB1 dye before (a), after photocatalytic treatment with ZnO/PUF under UV (b) and sunlight irradiation (c).

Figure 5. FTIR analysis of AB1 before (a) and after treatment with ZnO/PUF under UV (b) and sunlight irradiation (c).
mgl$^{-1}$ and 150 mg$l^{-1}$, whereas TOC reduced from 132 mgl$^{-1}$ to 85 mgl$^{-1}$ and 57 mg$l^{-1}$ and BOD reduced from 310 mgl$^{-1}$ to 50 mgl$^{-1}$ and 100 mgl$^{-1}$ for UV and solar light irradiation, respectively, which revealed that the dye was degraded significantly by ZnO/PUF since water quality improved significantly (figure 6).

Degradation potential of ZnO/PUF for textile effluents was also evaluated. HDCWW and BTWW wastewater treated by ZnO/PUF showed significant reductions in TOC, BOD and TOC values (figure 7). The COD values 350–450 mgl$^{-1}$ after treatment decreased < 200 mgl$^{-1}$, TOC values ranging from 457–756 mgl$^{-1}$ reduced to < 400 mgl$^{-1}$ and BOD values ranging from 265–305 mgl$^{-1}$ were reduced to < 100 mgl$^{-1}$. The reductions in COD, TOC and BOD values after treatment of textile real wastewater revealed that immobilized ZnO over PUF is efficient to treat the wastewater containing textile dyes, which are otherwise difficult to treat. Under the current scenario of environmental pollution [6, 14–16, 57–62], there is need to develop and utilize efficient materials that are active under solar light and ZnO/PUF proved to be highly efficient since the activity was considerable under solar light that could possibly be used for the degradation of dyes in textile wastewater [63–67].

Figure 6. BOD, COD and TOC values of AB1 dye before and after treatment with ZnO/PUF under UV and sunlight irradiation.

Figure 7. BOD, COD and TOC values of HDCWW and BTWW sample before and after treatment with ZnO/PUF under UV and sunlight irradiation.
4. Conclusions

ZnO/PUF was prepared and employed for AB1 dye degradation and textile wastewater treatment. ZnO/PUF showed promising efficacy and up to 85% and 65% dye degradation was achieved under UV and solar light irradiation. The maximum AB1 dye degradation was achieved at neutral pH, 4% H2O2, 240 min/sunlight and 75 min/UV irradiation time and 40 mg l−1 dye initial concentration and these conditions were applied to treat the textile wastewater. The reductions in BOD, COD and TOC values confirmed that the ZnO/PUF was highly efficient for wastewater treatment. It has been shown that due to photodegradation of azo dye and textile wastewater is possible using ZnO/PUF since immobilization of ZnO on PUF furnished higher activity that could possibly be applied for the treatment of textile wastewater economically since the separation of catalyst is easy for next cycles.

Acknowledgments

The Endowment Fund Secretariat, University of Agriculture, Faisalabad is gratefully acknowledged for providing research grant to carry out this research work (time efficient cost effective and stand-alone nanophotocatalytic wastewater technology for irrigation, project identification No. 1553).

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