

Removal of Brilliant Orange from Aqueous Solution by Prepared and Commercial ZnO

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Abstract

Removal of brilliant orange (BO), a typical textile dye from aqueous solution by adsorption as well as photodegradation has been studied by two ZnO samples, one prepared (*p*-ZnO) and the other commercial (*c*-ZnO). The *p*-ZnO having flaky and porous structures has the capacity to adsorb the BO, whereas the *c*-ZnO having crystalline structures has not. Nature of the isotherm also supports the existence of porous structures of the *p*-ZnO. However, the BO undergoes photodegradation by both the samples. The overall dye removal efficiency comprising adsorption and photodegradation of the *p*-ZnO is slightly higher than that of the *c*-ZnO. Most interestingly, about 62 % removal of BO from 12.0×10^{-5} M aqueous solution with the *p*-ZnO is reported to occur by only 10 min, whereas 35% removal is found in the case of *c*-ZnO under the same conditions.

I. Introduction

Wastewater comes out as effluent from the textile industry contains a large amount of azo dyes which owing to their non-biodegradability, toxicity and carcinogenic nature constitute a major threat to the ecosystem¹. The azo dyes are commercially available important class of textile dyes for which losses through processing operations are significant and their treatment before discharging into the aquatic environment is problematic. During the washing process, the exhausted reactive dyes are about 50% in their hydrolyzed and unfixed form^{2,3}.

Various physical⁴⁻⁷, chemical⁸⁻¹⁰ and biological^{11,12} methods are presently available for the treatment of textile wastewater. It has been reported that most of the reactive dyes are not biodegradable owing to their carcinogenic nature. Physical methods such as adsorption, coagulation, ion-exchange, etc. have limited applicability because of their high operational costs. Moreover, these methods do not result in dye degradation but merely transfer the dye material from one phase to another leaving the problem essentially unresolved. Chlorination and ozonation also lead to degradation by chemical reaction. However, discharging chlorinated organic compounds into the environment causes serious problems. Ozonation is a much cleaner process but due to the instability of ozone, its on-site preparation is required which involves significant capital costs.

Photocatalysis initiated by semiconducting oxides such as TiO₂, ZnO etc. has drawn considerable attention over the last three decades in view of their potential applications in environmental related problems¹³⁻¹⁵. Fascination about the use of these materials has mainly arisen due to the cost effectiveness, photostability, and having high redox activity and selectivity. However, the people are still in search of preparing cheaper materials having different but higher capacity of removing these dyes from textile effluents. Present study is an effort to explore the potential of preparing ZnO from its precursors and applying this oxide to remove a typical anionic dye, brilliant orange (BO, Fig. 1), from aqueous solution. The removal efficiency comprising both adsorption and photodegradation of the prepared ZnO (*p*-ZnO) will be compared with the

commercially available ZnO (*c*-ZnO).

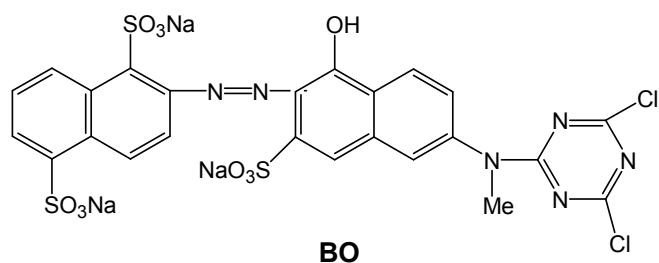


Fig. 1. Structure of the dye molecule, BO

II. Experimental

Commercial grade brilliant orange was obtained from BDH, England and was used here without further purification. All other chemicals were purchased from Fluka, Switzerland. The double distilled water was used throughout the present study.

The preparation of ZnO was carried out in a 1000 mL beaker. About 500 mL of 0.25 M zinc sulphate solution was taken into the beaker. 250 mL 0.5 M ammonium carbonate solution was added drop by drop to it under constant stirring at 60 °C. Zinc carbonate was precipitated which was aged for 2 hours under the experimental conditions. The precipitates that obtained were then filtered and washed with distilled water to remove the impurities including dissolved SO₄²⁻ ions. The precipitates were dried in an oven at 110°C for 2 hours. The samples were kept in a furnace at 600 °C for 3 hours for calcination^{16,17}. The resulting dried product was then ground and sieved using 140 mesh sieves and was stored in a desiccator.

Both the ZnO samples, one synthesized (*p*-ZnO) and the other commercially available (*c*-ZnO), were analyzed by attenuated total reflection (ATR) FTIR spectroscopy. In the ATR assembly of the spectrophotometer, the transparent crystal of ZnSe was used. The solid samples were put above

the crystal and spectra were recorded by IR Prestige (Shimadzu) spectrophotometer. Surface morphologies of both the oxide samples were analyzed using a scanning electron microscope (Philips XL 30, Holland).

Adsorption experiments were performed in batch mode. A typical experiment was carried out in the following way. 0.1 g sample of ZnO with 40 mL of dye solution having a concentration 12×10^{-5} M was taken in a series of reagent bottles with ground stopper. The bottles were shaken in a thermostated mechanical shaker maintained at 30 °C and each bottle was removed after a definite time interval. The concentration of each solution after removal of adsorbent was determined at the wavelengths of UV-maximum (λ_{\max}) at 448 nm of BO through the use of a UV-visible spectrophotometer (Shimadzu UV-2101PC). Adsorption experiments were also carried out to obtain the isotherms. During these experiments, 40 mL solutions of different concentration of dyes were taken into the reagent bottles. The suspensions were shaken in the thermostated shaker

maintained at 30 °C up to previously determined equilibrium time. Then the equilibrium concentration of the solution in each bottle is determined spectroscopically after removal of the adsorbent.

The photodegradation of the dye was carried out in a beaker of inside diameter 4.3 cm, height 5.5 cm. Light sources used were a UV lamp capable of emitting radiation of 254 nm. The reactor was placed on a magnetically stirred plates. The total system was enclosed in a wooden box called lamp house, inside surfaces of which were blacked. TiO₂ suspension was prepared by adding requisite amount of the oxide powder to appropriate volume of water. The powder was soaked overnight. A definite concentration solution of the dye was taken into the reactor and photodegradation was carried out. After degradation, the solution was centrifuged and the centrifugate was taken for UV visible spectroscopic analysis to monitor the change of the concentration with time.

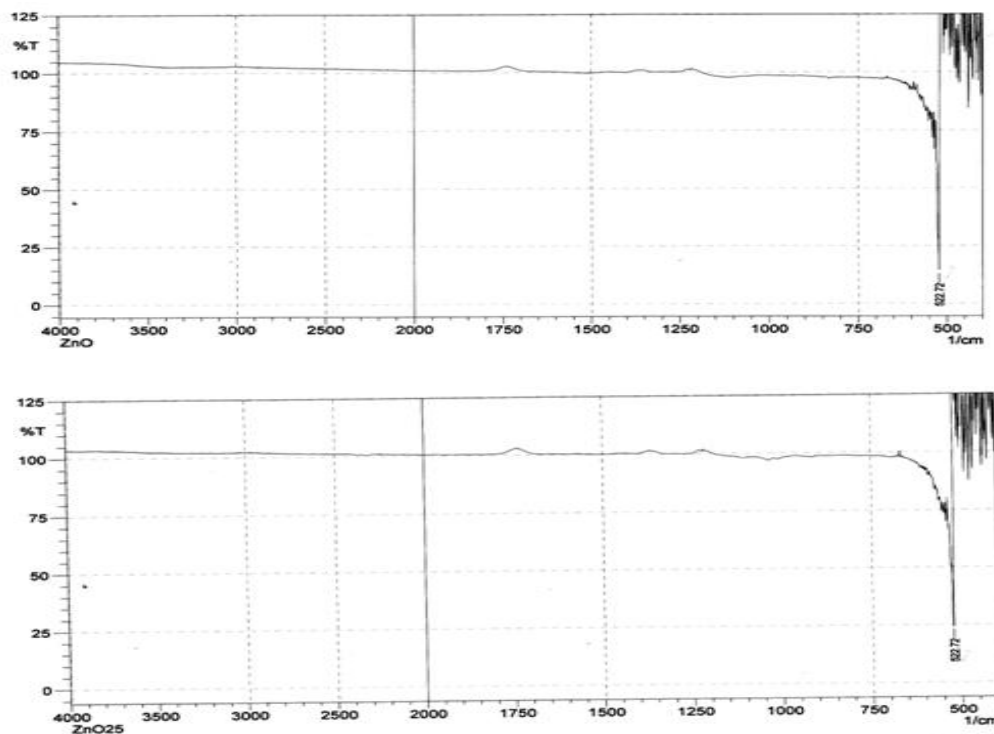


Fig. 2. ATR-FTIR spectra of *c*-ZnO (above) and *p*-ZnO (below).

III. Results and Discussion

Characterization by FTIR analysis

ATR-FTIR spectra of both the *p*-ZnO and the *c*-ZnO are presented in Fig. 2. The spectra of both the samples are almost identical. This ensures that the prepared sample is a pure ZnO having almost no impurity. The stretching frequency of vibration for Zn-O bond appears at about 523 ± 2 cm⁻¹, which is consistent the spectrum of ZnO reported elsewhere¹⁸. Moreover, absence of any other peaks in the measured range indicates that our prepared sample has similar purity to that of the *c*-ZnO.

Surface morphologies by SEM

The surface morphologies of both the samples were characterized by Scanning Electron Microscopy (SEM). The microphotographs of these samples are presented in Fig. 3. The micrograph of *c*-ZnO shows crystalline shape, but that of *p*-ZnO presents flaky and porous texture. Although the FTIR results represent similar chemical composition of both the samples, but their morphologies are different. This indicates that the prepared sample may have different adsorption characteristics and photocatalytic properties than the commercial sample.

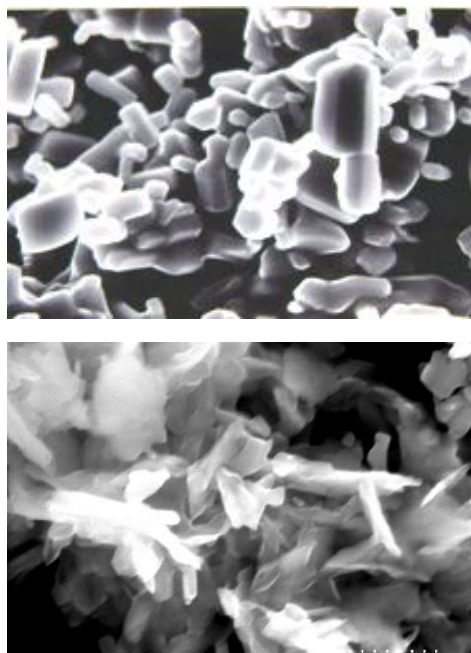


Fig. 3. SEM images of *c*-ZnO (above) and *p*-ZnO (below)

Adsorption studies

Fig. 4 shows the uptake of BO with time of adsorption on both the *c*-ZnO and the *p*-ZnO samples. The spectral characteristics before and after the adsorption for these samples are identical. BO solution having a concentration of 12×10^{-5} M shows negligible adsorption with time on the surface of *c*-ZnO, whereas the same solution evaluates a considerable amount of adsorption on the surface of *p*-ZnO. The time necessary to reach the equilibrium is found to be nearly 40 minutes. These results can be explained by the fact that the latter sample is flaky and porous in nature having a large number of sites where the BO molecules can easily be captured, whereas the crystalline form of *c*-ZnO has practically no such sites for adsorption which results in no significant adsorption of the dye molecules (Fig. 4).

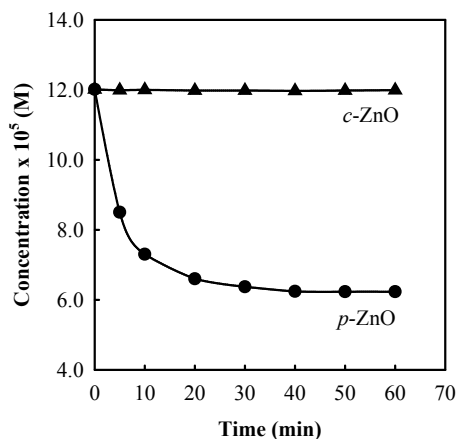


Fig. 4. Concentrations of unadsorbed BO on *c*-ZnO and *p*-ZnO with time.

Adsorption isotherm for BO on the surface of the *p*-ZnO has been determined at the room temperature (30 °C). The nature of the isotherm is shown in Fig. 5. Clearly, the observed S-shaped isotherm suggests the surface inhomogeneity of the *p*-ZnO. When the concentration of BO is low the amount of adsorption is considerably low. After attaining a slightly higher concentration of the solution, the extent of adsorption increases rapidly. With a further

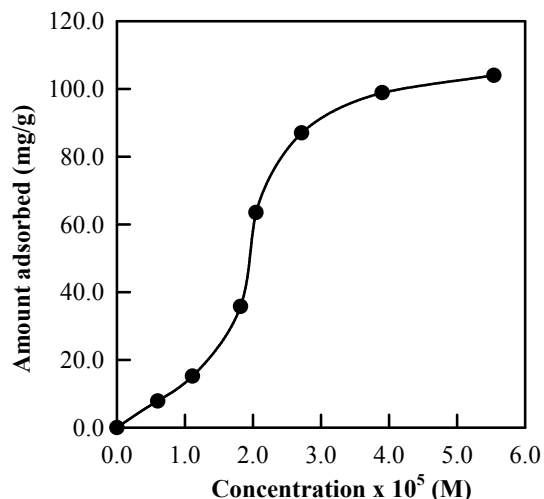


Fig. 5. Adsorption isotherm of BO on *p*-ZnO at 30 °C.

increase in the bulk concentration of the solution, the adsorption shows a limiting value. These results suggest that there are some capillaries present on the surface. When the concentration of the dye is low, the large BO molecules cannot enter into these pores. However, when the concentrations become higher, a dramatic increase in the extent of adsorption has been found. Finally, when these pores become saturated, the adsorption shows a limiting value¹⁹.

Photodegradation studies

To see the effectiveness of the *p*-ZnO as a photocatalyst, photodegradation of BO in the presence of 0.6 g/100 mL suspension of ZnO was carried out in the presence of UV light. The overall removal efficiency comprising adsorption and photodegradation of the *p*-ZnO is compared with that of the *c*-ZnO (Fig. 6). Both the ZnOs show very good removal efficiencies. However, the removal efficiency of *p*-ZnO is slightly higher than that of the *c*-ZnO. Since the adsorption is a rapid process, major portion of the BO dye undergoes adsorption which is followed by slow photodegradation in the case of *p*-ZnO. Most interestingly, about 62 % removal of BO from 12.0×10^{-5} M aqueous solution with the *p*-ZnO is reported to occur within 10 minutes, whereas 35% removal is found in the case of *c*-ZnO under the same conditions.

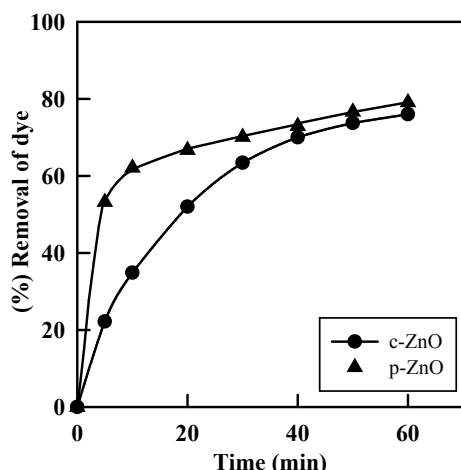


Fig. 6. Comparison of the dye removal efficiencies of the *c*-ZnO and *p*-ZnO. $[BO]_0 = 12.0 \times 10^{-5}$ M; $[ZnO] = 0.6$ g/100 mL

The characteristics related to the *p*-ZnO should be very important industrially because this sample can quickly capture the organic dyes during the continuous flow of the effluents into the river. This oxide can also photocatalyze the organics which will ultimately be degraded into the non toxic mineralized products.

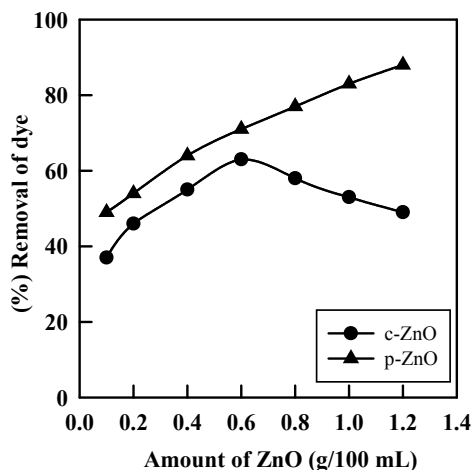


Fig. 7. Photodegradation of 12.0×10^{-5} M aqueous solution BO in the presence of different amount of ZnO after 30 min of irradiation.

The photodegradation of 12.0×10^{-5} M aqueous solution of BO was also carried out by varying the amount of ZnO to find out the optimum removal conditions. The results obtained after 30 minutes of photodegradation are shown in Fig. 7. In the case of *c*-ZnO, percent removal of the dye increases with increasing the amount of the oxide up to a concentration of 0.6 g/100 mL suspension. With a further increase in the amount of the oxide the percent removal of the dye decreases. It is well accepted that the semiconducting oxide mediated photodegradation is initiated by electron-hole pairs produced by the UV light.^{14,15} With an increase in the amount of ZnO, the electron-hole pairs are expected to increase in number.

These increased number of electron-hole pairs should increase the percent degradation of the BO. However, when the amount of ZnO becomes sufficiently high, the UV light cannot penetrate deep into the suspension. As a result, ZnO particles inside the bulk of the suspension remain inactive causing a decrease in the degradation with a further increase in the amount of oxide. On the other hand, the percent removal of the dye always shows an increasing tendency with an increase in the amount of *p*-ZnO. Because of flaky and porous characteristics of the surface of the *p*-ZnO, the amount adsorbed always increases with the amount of oxide which eventually increases the overall removal efficiency by the *p*-ZnO.

IV. Conclusions

Removal of BO, a typical textile dye, has been carried out by adsorption and photodegradation using two ZnO samples, one prepared (*p*-ZnO) and the other commercial (*c*-ZnO). Adsorption study shows no significant adsorption of BO on *c*-ZnO but a considerable amount of adsorption has been observed on *p*-ZnO because of its surface inhomogeneity. Both the samples have high removal efficiencies of the dye from aqueous solution, but *p*-ZnO is found to be the better photocatalyst than the *c*-ZnO. However, it is worth to mention that the overall dye removal efficiency of the *p*-ZnO is slightly higher than that of the *c*-ZnO.

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