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Research Article

SOLAR LIGHT DRIVEN $Zn_3(PO_4)_2$/ZnO HETEROSTRUCTURE: ENHANCED PHOTOCATALYTIC MINRALIZATION OF BASIC VIOLET 10

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A B S T R A C T

Novel $Zn_3(PO_4)_2$ modified ZnO (ZnP/ZnO) photocatalyst was prepared and characterized by surface analytical techniques. The photocatalytic degradation of toxic dye Basic Violet 10 (BV 10) was carried out under natural sun light irradiation. This composite material signifies maximum photocatalytic activity (98%) at pH 7. The effect of operational parameters such as catalyst concentration, initial pH and dye concentration were discussed in details. The reusability of ZnP/ZnO was tested up to five runs, and there was no significant change in the activity at fifth run compared with fresh catalyst. Hence, this catalyst can be reused for continuous treatment of wastewater.

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INTRODUCTION

Nowadays water scarcity and pollution are still one of the most severe public health issues world wise; although tremendous effect have been dedicated to water treatment research and substantial progress has been made (Elimelec and Philips, 2011; Shannon *et al*., 2008). Semiconductor photocatalysis, as "green" technology, has been widely applied in solar water splitting, purifying air and eliminating the organic contamination of water (Chong *et al.,* 2010). However, most of semiconductor photocatalysis such as TiO_2 and ZnO require high energy ultraviolet (UV) radiation for photocatalytic activation because of their wide energy band gap (Anpo and Takeuchi, 2003). Degradation of pollutants over semiconductors under solar irradiation have attached more and more attention due to its potential as one of clean, low, cost, and environmental friendly strategies to solar the energy crisis and environmental contamination (Osterloh, 2013; Ibhadon and Fitzpatrick, 2013). ZnO is a good semiconductor photocatalyst due its unique up to electronic properties, environmental stability and low cost (Lizama *et al*., 2003). Its use under UV light, which is only 5% of the total solar spectrum. The effctive photocatalytic efficiency of the material strongly depends on the photogenerated electron hole recombination rate and solar energy utilization (Pian *et al.,* 2011). In this present study, we have prepared coupled $Zn_3(PO_4)_2$/ZnO catalyst (ZnP/ZnO) for the photocatalytic degradation of BV 10 under the natural sunlight irradiation. Basic Violet 10 is an organic dye which dissolves easily in water and widely used in the manufacturing of textile, printing, paper, pharmaceutical and food products (Mittal *et al*., 2007; Richardson *et al*., 2004). It is allergic to the respiratory system, skin and eyes. It is also a very well-recognized water tracer fluorescent. Basic Violet 10 is also an important representative of xanthene dyes, and it is usually used as a dye laser material because of its good stability. The ZnP/ZnO nanocomposite having excellent photocatalytic activity when compare to prepared ZnO. The effects of various experimental parameters such as pH, catalyst concentration and initial dye concentration have been analysed. Analysis of the stability of the catalyst reveals that the ZnP/ZnO nanocomosite can be reused.

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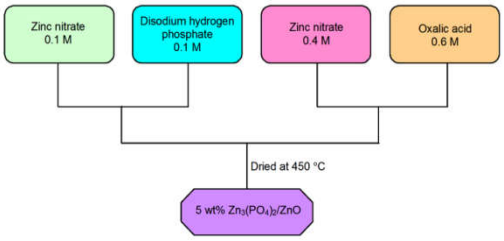
Experimental

Zinc nitrate hexahydrate, oxalic acid dihydrate, disodium hydrogen phosphate and ethanol were obtained from Himedia Chemicals, Basic Violet 10 (SD fine), molecular formula: $C_{28}H_{31}C1N_2O_3$ and molecular weight: 479.02 and was used as received. Double distilled water (DI) was employed throughout experiments.

Preparation of ZnP/ZnO

Equimolar aqueous solution of zinc nitrate with Na_2HPO_4 is stirred using magnetic stirrer for an hour, and the obtained $Zn_3(PO_4)_2$ precipitate is filtered, washed with double distilled water, and dried at 100 °C for 3 h. 100 mL of 0.4 M zinc nitrate hexahydrate and 100 mL of 0.6 M oxalic acid dihydrate in deionized water are brought into boil separately, and zinc nitrate solution is added rapidly to the oxalic acid solution and then immediately 0.123 g of $Zn_3(PO_4)_2$ is added to this, and the mixed suspension is stirred for 3 h. The formed precipitate zinc oxalate dihydrate with $Zn_3(PO_4)_2$ is filtered, washed with DI water several times, dried in hot air oven at 80 °C for 6 h. $Zn_3(PO_4)_2$-zinc oxalate dihydrate-coupled system is taken in a silica crucible and calcined at 450 °C for 12 h in the muffle furnace at the rate of rising temperature 20 °C min^{-1} (Scheme 1). After 12 h, the furnace is allowed to cool down to room temperature. The ZnP/ZnO catalyst is collected and used for further analysis. This catalyst has 5 wt% of $Zn_3(PO_4)_2$, and catalysts similarly with 1, 3, and 7 wt% of $Zn_3(PO_4)_2$-coupled ZnO are prepared using appropriate amount of $Zn_3(PO_4)_2$. The bare ZnO catalyst is prepared this procedure without $Zn_3(PO_4)_2$.



Scheme 1 Schematic representation of preparation of ZnP/ZnO

Photocatalysis

All photocatalytic experiments were carried out under similar conditions on sunny days of April-May 2016 between 11 am and 2 pm. An open borosilicate glass tube of 50 mL capacity, 40 cm height and 20 mm diameter was used as the reaction vessel the suspensions were magnetically stirred in the dark for 30 min to attain adsorption desorption equilibrium between the dye and ZnP/ZnO irradiation was carried out in the open air condition. 50 mL dye solution with ZnP/ZnO was continuously aerated by a pump to provide oxygen and for the complete mixing of reaction solution during the illumination time no volatility of the solvent was observed. After dark adsorption the first samples was taken. At specific time intervals 2 mL of the sample was withdrawn and centrifuged to separate the catalyst. 1 mL of the centrifugation was diluted to 10 mL and its absorbance was measured at 553 nm (5×10^{-4}) for BV 10, respectively light intensity was measured for every 15 min and the average light intensity over the duration of each experiment was calculated. The intensity of each experiment was calculated. The intensity of solar light was measured using LT Lutron LX-10/A digital LUX meter and intensity was (1250×100) ± 100LUX (Krishnakumar *et al*., 2014). A Shimadzu UV-1650 PC UV-visible spectrophotometer was used for absorbance measurements.

RESULTS AND DISCUSSION

Characterization of ZnP/ZnO

ZnP/ZnO was characterized in our earlier paper (Rajasri *et al*., 2017). The summarized characterizations are given below. XRD analysis shows that the characteristic peaks of ZnO at 2θ values 31.77°, 34.49°, 36.23° and 56.60° correspond to (100), (002), (101) and (110) planes of wurtzite ZnO. The 2θ values 20.0°, 21.53°, 23.30°, 25.0°, 29.50°, 31.77°, 34.77°, 34.49° and 35.10° correspond to $Zn_3(PO_4)_2$. The high intense (001) peak is correspond to zinc phosphate [($Zn_3(PO_4)_2$) Card No. 33-1474, 37-0316 and 37-0465]. The diffraction pattern of ZnP/ZnO has no difference from that of ZnO. This reveals that ZnO in ZnP/ZnO also has a wurtzite structure. Aside from this, it should be noted that there were no observation of new peaks for $Zn_3(PO_4)_2$ in the ZnP/ZnO catalyst, while $Zn_3(PO_4)_2$ showed nine strong peaks at 20.0°, 21.53°, 23.30°, 25.0°, 29.50°, 31.77°, 34.77°, 34.49° and 35.10°. This may be due to the low concentration of $Zn_3(PO_4)_2$ on ZnO. The average crystalline size of ZnP/ZnO and it was found to be 44 nm. The PO_4^{2-} stretching vibrations are observed in the range of 947 to 1200 cm^{-1}. The band at 1640 cm^{-1} is ascribed as OH bending vibrations in $Zn_3(PO_4)_2$ and ZnP/ZnO. Symmetric PO_4^{2-} stretching vibration is observed at 1120 cm^{-1}, which confirms the formation of hybrid nanocomposite ZnP/ZnO. The absorption bands at 375 and 875 cm^{-1} were attributed to P–O bending and stretching vibrations, respectively in $Zn_3(PO_4)_2$. The N_2 adsorption-desorption isotherms of ZnP/ZnO exhibited a hysteresis loop, typical of type II pattern. This type of isotherm indicates the presence of macroporous structure in ZnP/ZnO. In HR-SEM analysis ZnP/ZnO exhibits a chain-like structure and ZnO particles are well dispersed on $Zn_3(PO_4)_2$ plates are nanochains. In HR-TEM analysis, the ZnP/ZnO particles are in nm sizes and are in the range approximately from 30–50 nm. In UV-DRS analysis and applying Kubelka-Munk analyses for allowed direct band gaps for prepared ZnO, $Zn_3(PO_4)_2$ and ZnP/ZnO. The estimated optical band gaps are ~3.20, 3.07 and 3.23 eV, respectively. In PL spectra, the loading of $Zn_3(PO_4)_2$ with ZnO does not change the emission of ZnO, but the PL intensity is less than ZnO. This is due to the suppression of recombination of electron-hole pairs by loaded $Zn_3(PO_4)_2$, which enhanced the photocatalytic activity of the catalyst.

Primary analysis

Photodegradation of Basic Violet 10 (BV 10) under different reaction conditions was carried out using solar light and the results are displayed in Figure 1. The dye is found to be resistant to self-photolysis by solar light. In the presence of dye/ZnO/dark, a small decrease in dye concentration (21%) occurs and remains almost constant up to 90 min (curve a). The dye irradiated with ZnO under solar light, 48% degradation was observed at the time of 90 min (curve b). A small decrease in dye concentration (20%) when it is treated with dye/ZnP/dark (curve c). The dye/ZnP/solar light process shows that 40% degradation of BV 10 (curve d). The dye on irradiation with ZnP/ZnO, catalysts of different wt% of $Zn_3(PO_4)_2$ loaded on ZnO shows that the degradation increases with increase in wt% of $Zn_3(PO_4)_2$ loading up to 5 wt% (curves

e, f and g) and then decreases (curve h). The maximum percentage of BV 10 removal was observed in the presence of 5 wt% ZnP/ZnO (93%). Hence 5 wt% ZnP/ZnO catalyst is the optimum catalyst for further studies. The mechanism of the coupled semiconductor heterojunction ZnP/ZnO mediated dye degradation mechanism has been discussed in our earlier paper (Rajasri *et al*., 2017).

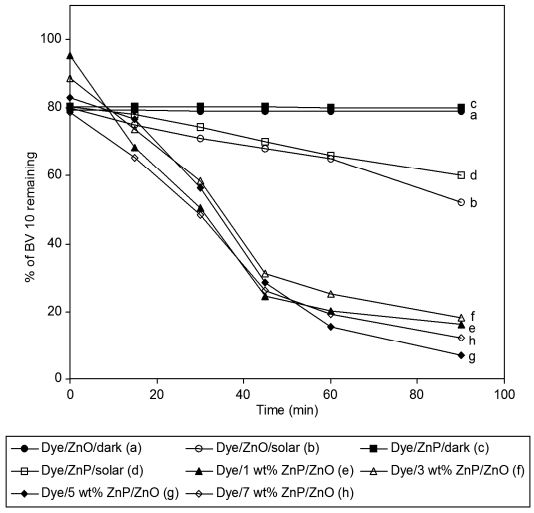


Figure 1 Primary analysis of BV 10 under solar light. [BV 10] = 5×10^{-4} M, catalyst suspended = 2 g L^{-1}, airflow rate = 8.1 mL s^{-1}, pH = 7.0, I_{solar} = (1250×100)±100LUX.

Effect of catalyst loading

The degradation of BV 10 with 5 wt% ZnP/ZnO at different catalyst concentration was studied under solar light. Increase the amount of catalyst from 1-4 g L^{-1} increases the dye removal (0.0141-0.0697 min^{-1}) (Figure 2), further increase in catalyst amount above 4 g L^{-1} decreases the dye removal rate. This may be due to i) the increase in the amount of catalyst weight which increases the number of dye molecules adsorbed, ii) the removal rate is decreased (above 4 g L^{-1} of catalyst) this may be due to the enhancement of light reflectance by the catalyst and decrease in light penetration. Thus the optimum amount of catalyst for efficient degradation of BV 10 is found to be 4 g L^{-1} (San *et al*., 2001; Saquib and Muneer, 2003; Wong and Chu, 2003; Daneshvar *et al*., 2004).

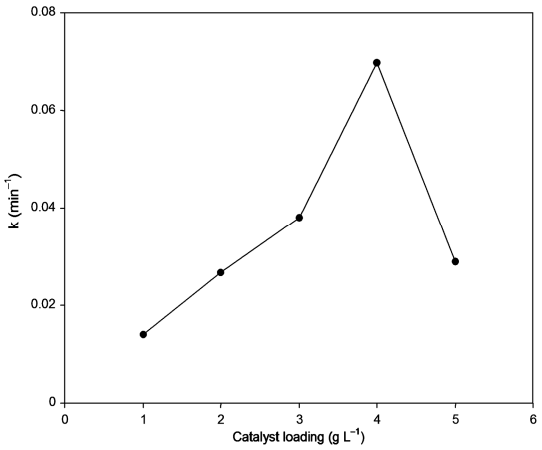


Figure 2 Effect of catalyst loading. [BV 10] = 5×10^{-4} M, airflow rate = 8.1 mL s^{-1}, pH = 7.0, irradiation time = 30 min, I_{solar} = 1250×100)±100LUX.

Influence of initial solution pH

The solution pH plays an important role in the photocatalytic degradation. The effect of pH in the photocatalytic degradation of BV 10 was studied in the pH range 3-9 and the results are shown in Figure 3. At pH 7, the maximum percentage of degradation was observed *i.e.,* 98% (90 min). Above pH 7 the degradation efficiency decreases. Reason for the maximum degradation was observed at pH 7. It was confirmed the adsorption experiment at different pH. The percentage of adsorption, after the attainment of adsorption equilibrium are 25, 17, 28 and 21 at pH 3, 5, 7 and 9, respectively. At higher pH values (above 7), surface of the catalyst is negatively charged and the electrostatic attraction between dye anions and negatively charged catalyst becomes weak resulting in reduced adsorption (Parks, 1965).

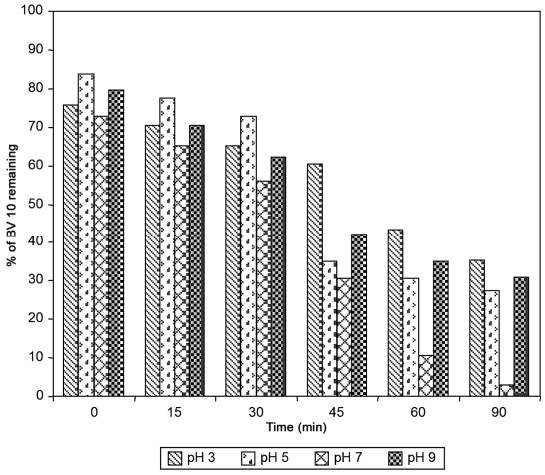


Figure 3 Effect of initial solution pH. [BV 10] = 5×10^{-4} M, 5 wt% ZnP/ZnO = 4 g L^{-1}, airflow rate = 8.1 mL s^{-1}, I_{solar} = (1250×100)±100LUX.

Effect of initial dye concentration

As the dye concentration is an important parameter in wastewater treatment, the effect of initial dye concentration of BV 10 on the degradation investigated over the concentration of 1 to 6×10^{-4} M. Increase the initial dye concentration from 1 to 6×10^{-4} M decreases the degradation rate constant from 0.1812 to 0.0105 min^{-1} (Figure 4). Since the concentration of the catalyst, airflow rate and solar light intensity are same for all dye concentration, the generation of hydoxyl radical remains constant. The rate of degradation relates to the $^{\bullet}OH$ (hydroxyl radicals) formation on catalyst surface and probability of $^{\bullet}OH$ reacting with dye molecules. When the initial concentration of the dye increases, the path length of photon entering into the solution decreases, and the photocatalytic degradation efficiency decreases (Jothivel *et al*., 2011). While in low concentration the reverse effect is observed, thereby increasing the photon absorption by the catalyst the large amount of absorbed dye may also have a competing effect on the absorption of oxygen and OH^{-} on the surface of catalyst.

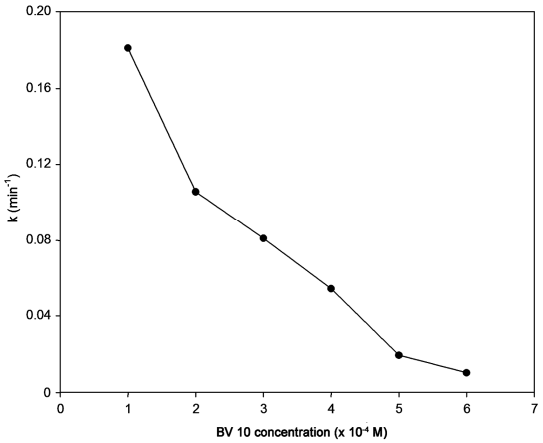


Figure 4 Effect of initial dye concentration. 5 wt% ZnP/ZnO = 4 g L^{-1}, airflow rate = 8.1 mL s^{-1}, pH = 7.0, irradiation time = 30 min, I_{solar} = (1250×100)±100LUX.

Long-term stability

The long-term stability of catalyst was tested and results are shown in Figure 5. The reusability of ZnP/ZnO was tested for the degradation of BV 10 under identical reaction conditions. After complete degradation, the catalyst was separated and washed with demonized water and ethanol, the recovered catalyst was dried in hot air oven at 100 °C for 90 min and used for further runs. The results BV 10 degradation for five runs ZnP/ZnO exist remarkable photostability as the BV 10 almost 98% degradation was observed for all the 5 runs at the time of 90 min. There is no significant change in the degradation efficiency of ZnP/ZnO after 5th run. Hence, this catalyst could be reused for multiple runs.

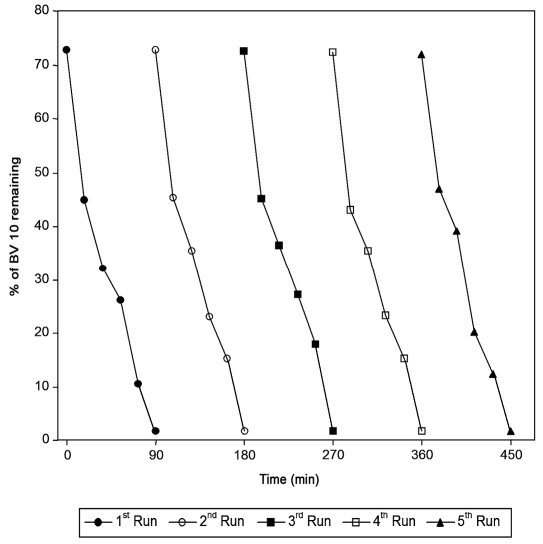


Figure 5 Effect of long-term stability. [BV 10] = 5×10^{-4} M, 5 wt% ZnP/ZnO = 4 g L^{-1}, airflow rate = 8.1 mL s^{-1}, pH = 7.0, I_{solar} = (1250×100)±100LUX.

CONCLUSIONS

Photocatalytic activity of synthesized ZnP/ZnO nanocomposites was evaluated under natural sun light irradiation in aqueous BV 10. The effect of various experimental parameters such as pH, catalyst concentration and initial dye concentration had been analysed. Analysis of the stability of the catalyst reveals that the catalyst can be reused. From this study, it is found that ZnP/ZnO catalyst is viable and efficient catalyst for the continuous treatment of dye wastewater under solar light.

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