

## Chapter 4: Study of photocatalytic property of pure and ZnO-BiVO<sub>4</sub> nanocomposites

### 4.1 Set-up for photocatalytic study

Photocatalytic activity was performed on Methylene Blue (MB) and Rhodamine B (RhB) to test dye degradation. The sample was prepared by taking 5mg of photocatalyst in 100 ml aqueous solution of 10  $\mu$ molar MB. The solution was ultrasonicated for 2hrs and further stirred for 1hr under dark to remove the agglomeration and uniformly disperse the photo catalyst nano particles in the solution. Same procedure was followed to prepare the solution with RhB. Samples were put under the simulated AM 1.5 solar illumination at 100 mW/cm<sup>2</sup> from a xenon arc lamp in ambient atmosphere and UV-vis spectrum were recorded after interval of every 15 minute to observe the change in the concentration of dye. This way several readings were collected starting from zero minute.  $C/C_0$  curve for each sample was plotted against time where  $C_0$  is the initial concentration of dye at zero minute and C is the concentration of dye at various time intervals. Dye degradation efficiency was calculated using the formula [197].

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### 4.2 Result and discussion

Fig 4.1(a) shows the  $C/C_0$  curves for ZnO, BiVO<sub>4</sub>, ZnO-BiVO<sub>4</sub> (1:1), ZnO-BiVO<sub>4</sub> (1:2) and ZnO-BiVO<sub>4</sub> (2:1) samples for MB dye solution. As indicated from the curves, the photocatalytic dye degradation efficiencies are (0%, 6.1%, 11.1%, 15.8%, 20%) for MB dye (without Photocatalyst), (0%, 17.4%, 27.6%, 39.9%, 45.2%) for BiVO<sub>4</sub>, (0%, 23.6%, 37.4%, 48.7%, 57.3%) for ZnO, (0%, 25.1%, 45.8%, 59.9%, 77.8%) for ZnO-BiVO<sub>4</sub> (2:1), (0%, 30.7%, 48.4%, 74.6%, 86%) for ZnO-

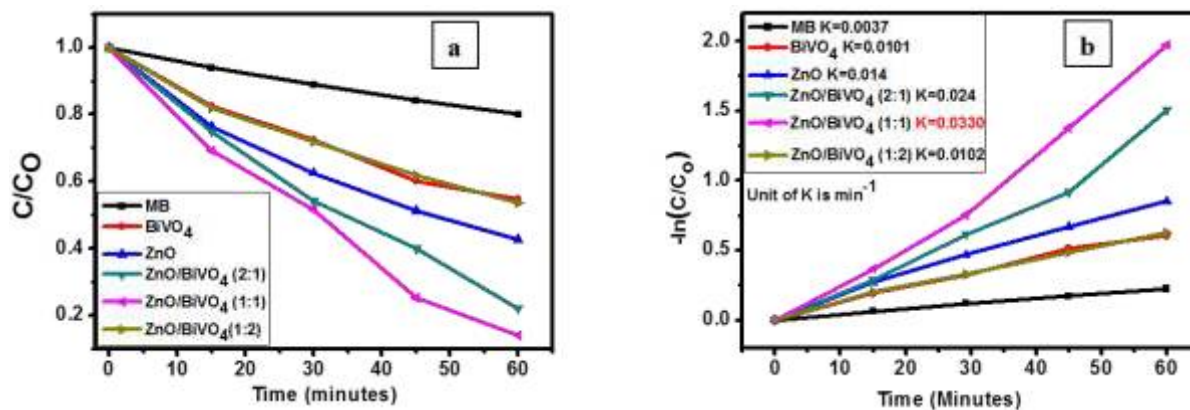
BiVO<sub>4</sub> (1:1) and (0%, 18.1%, 28.1%, 38.2%, 46.4%) for ZnO-BiVO<sub>4</sub> (1:2) at the intervals of 0, 15, 30, 45, 60 minutes, respectively. The above results indicate that ZnO-BiVO<sub>4</sub> (1:1) exhibits the highest dye degradation efficiency of 86% in 60 minutes.

Photodegradation follows pseudo first-order kinetics and is given by:

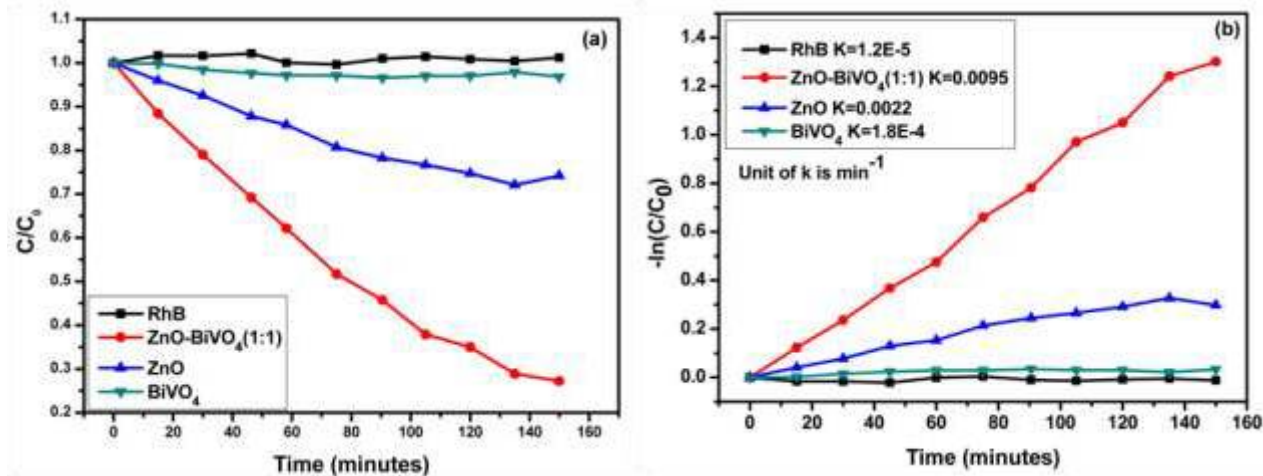
and

where  $C_0$  is the initial concentration,  $C_t$  is the concentration after time  $t$ , and  $k$  is the rate constant of pseudo first-order reaction [205,206].

Fig 4.1(b) shows the plot between  $-\ln(C_0/C_t)$  and time ( $t$ ) for various samples. The values for pseudo first-order reaction rate constants as given by the slope of the curves are  $k=0.0037 \text{ min}^{-1}$  for MB (without photocatalyst),  $0.0101 \text{ min}^{-1}$  for BiVO<sub>4</sub>,  $0.014 \text{ min}^{-1}$  for ZnO,  $0.024 \text{ min}^{-1}$  for ZnO/BiVO<sub>4</sub> (2:1),  $0.0330 \text{ min}^{-1}$  for ZnO/BiVO<sub>4</sub> (1:1) and  $0.0102 \text{ min}^{-1}$  for ZnO/ BiVO<sub>4</sub> (1:2). Thus, degradation rate of MB by ZnO/ BiVO<sub>4</sub> (1:1) is highest and is approximately 2.5 times faster as compared to pure ZnO.



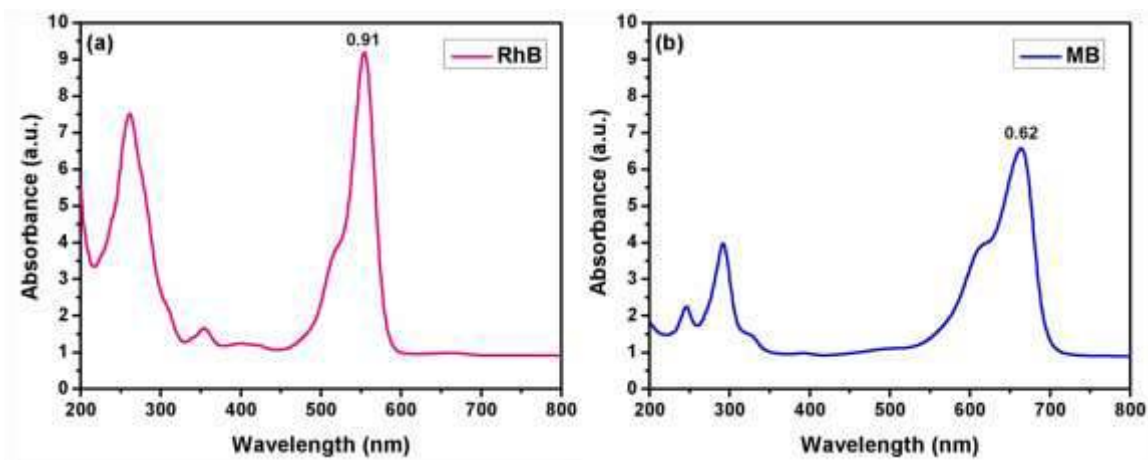
**Fig 4.1 C/Co curves for ZnO, BiVO<sub>4</sub>, ZnO-BiVO<sub>4</sub> (1:1), ZnO-BiVO<sub>4</sub> (1:2) and ZnO-BiVO<sub>4</sub> (2:1) samples for MB dye solution (a) and first order rate kinetics of MB dye degradation for various samples (b)**



**Fig 4.2 C/Co curve (a) and First order rate kinetics (b) of ZnO-BiVO<sub>4</sub> (1:1) sample for RhB dye degradation**

Dye degradation efficiency of ZnO-BiVO<sub>4</sub> (1:1) sample for RhB dye is 72.7% in 150 minutes as shown in Fig 4.2(a). Rate constant of pseudo first-order kinetics is 0.0095 min<sup>-1</sup> which is 4.3 times higher than ZnO as shown in Fig 4.2(b).

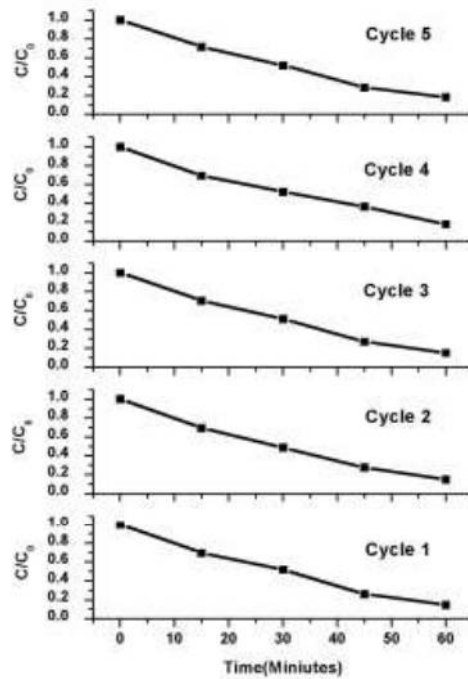
From above results it is clear that ZnO/BiVO<sub>4</sub> exhibits higher degradation efficiency on MB in comparison to RhB. The probable reason for this difference is discussed in Fig 4.3.



**Figure 4.3 UV-Vis spectra for (a) RhB and (b) MB dye**

This difference of efficiency of same photocatalyst on different dye could be attributed to several probable reasons. First, RhB dye has more complex structure than MB, making it more photostable and thus difficult to degrade. Another reason may be due to the absorbance of light photons by RhB dye itself resulting in reduction in the number of photons reaching the photocatalyst. As a result the photogenerated carriers and free radical production is reduced which indeed results in the decreased photo catalytic activity. This fact is also visible from the UV-vis spectrum of both the dyes at same dye molar concentration of 10uMolar in which RhB shows higher visible light absorption than MB.

Photostability of ZnO-BiVO<sub>4</sub> (1:1) nanocomposite was also investigated as shown in Fig 4.4. No significant loss in activity was observed up to five cycles and catalyst exhibited a highly stable photocatalytic performance towards MB degradation.

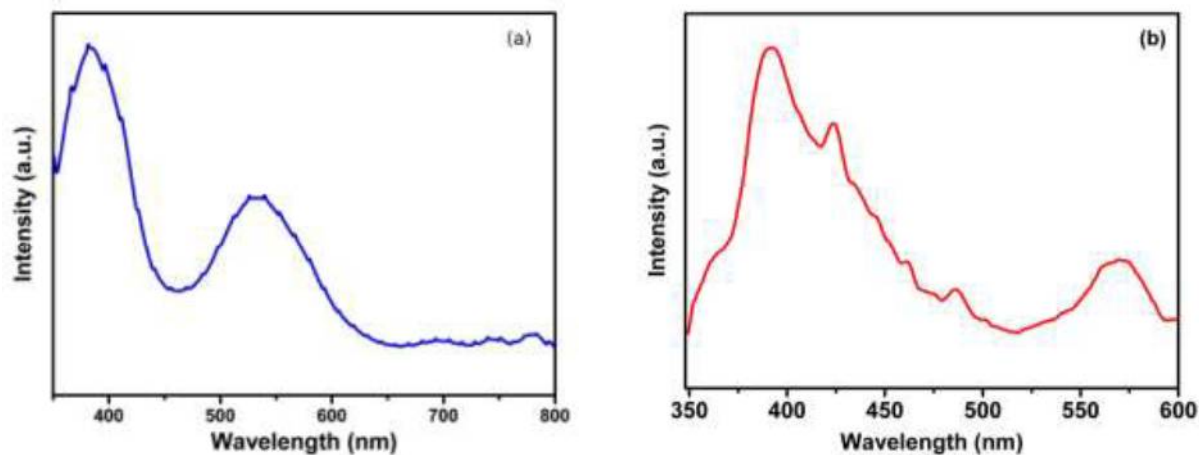


**Fig 4.4 Repeatability test for ZnO-BiVO<sub>4</sub> (1:1) nanocomposite using MB dye**

#### 4.3 Proposed Mechanism of photocatalysis in ZnO-BiVO<sub>4</sub> nanocomposite

A possible mechanism for improved photo catalytic activity of ZnO-BiVO<sub>4</sub> nano composite is presented in this section. It is well known that in ZnO, surface defects are common and various physical processes such as grinding and mechanical-milling generates more amount of such defects in the material that contribute in altering its surface chemistry, optical and electronic properties [207-209]. To verify this in our case too, we conducted PL study of pure ZnO, with and without mechanical milling process, as shown in Fig.4.5. It is clearly observed that ZnO after milling contains an overall increase in various surface defects as seen from the origin of multiple peaks in the defect band in PL. Therefore, when this ZnO is combined to a different material to form a composite, it establishes a bond of interaction with the later due to the presence of a large number of defects on its surface which proves to be a source of chemical interaction between the two [210,211]. Similarly in our case when ZnO is coupled to BiVO<sub>4</sub> through the process of milling followed by high temperature annealing, these defects act as active high energy sites favourable for adsorption of the BiVO<sub>4</sub> on ZnO surface through weak chemical bond. This existence of chemical interaction between the two materials was also revealed through the XPS spectra of composite

which shows a shift in the binding energies of Zn, Bi and V as compared to energies of their pure counterparts. Moreover, in PL study of the composite it was observed that ZnO near band edge & defect peaks were suppressed and only a major peak at 421 nm was present which corresponds to energy of 2.94 eV and could only be formed due to the major electron transition from VB of BiVO<sub>4</sub> and CB of ZnO supported by estimated band edge potentials of both the materials. Non appearance of defect PL peaks of ZnO in composite is attributed to the chemical adsorption of BiVO<sub>4</sub> on the defect sites of ZnO, so the presence of BiVO<sub>4</sub> in ZnO highly suppresses the defect inter band electron transition in ZnO and VB of BiVO<sub>4</sub> itself is acting as inter band for electron transition to take place. Such intermediate band formation in composites has been reported earlier [212,213]. Also in DFT calculations, ZnO sheet structure considered for calculations have terminated Zinc and Oxygen bonds at the edges. Band structure & density of states calculations performed considering terminated bond-ZnO sheet also confirmed the electron transition from VB of BiVO<sub>4</sub> to CB of ZnO.



**Figure 4.5** PL spectra for pure ZnO (a) without milling and (b) with milling process

So, presence of this intermediate band reduces the amount of energy to 2.94 eV from 3.23 eV band gap of ZnO) required for electron transition to the conduction band of ZnO thus making nanocomposite photoactive in visible region of solar spectrum. In photo catalytic process, when light falls on nanocomposite surface, electron transition takes place between newly formed intermediate band and CB of ZnO. These electrons in CB of ZnO reduce the adsorbed oxygen to form  $O_2^-$  super oxides [79,214,215].

These reactive ions undergo reaction with water to form hydrogen peroxide ( $H_2O_2$ ). Electron-hole pair in intermediate band and CB of ZnO has enough electrochemical potential to redox water to form  $H^+$  and hydroxyl ions ( $OH^-$ ). These  $OH^-$  ions produced loses their electron to holes in intermediate band (VB of  $BiVO_4$ ) to form  $\bullet OH$  radicals [47, 48]. These reactive species ( $O_2^-$ ,  $H_2O_2$ ,  $\bullet OH$ ) further react with the dye present in the solution and results in dye degradation.

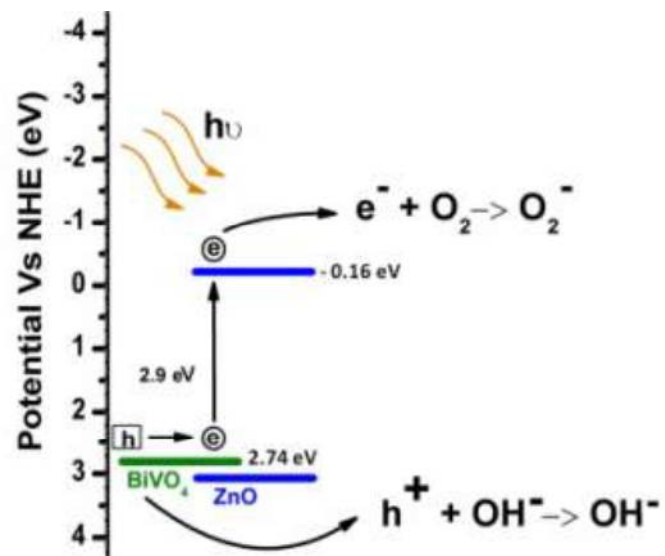


Fig 4.6 Mechanism of action of nanocomposite photocatalyst