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ROLE OF ZnO BULK AND NANOPOWDERS IN PHOTOCATALYTIC DECOLORISATION OF TEXTILE INDUSTRIAL DYES

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Abstract

We report on comparison of zinc oxide nanoparticles with bulk powders as candidates for decolorisation of organic dyes in the textile industry. X-ray diffraction showed pure phase catalysts; while ultraviolet-visible (UV-vis) spectroscopy showed larger absorbance in a wide visible range of spectrum for bulk, compared to nanopowders. Two dyes, Methylene Blue (MB) and Methyl Orange (MO) were treated with these catalysts in solar light. UV-vis studies showed ZnO bulk to completely decolorise both the dyes in < 20 min; as against its nano form. When decolorised components were evaluated it was found that the treated components were much in the safety regime as prescribed by WHO standards and were found to be Na, Zn, S, SO_4^{2-}, NO_2 and NO_3^-. Cell line studies performed on these treated samples showed the cell viability of ~ 100% on SiHa and B16F10 cell lines as well as on mouse primary fibroblasts, giving evidence of non-toxicity of the catalyst, as well as the byproducts upon treatment, with bulk nanopowders to be better than their nano-counterparts. Defects-driven wider absorption of the bulk samples in the visible optical regime is envisaged to be the probable reason for better decolorisation efficiency of ZnO bulk samples.

1. Introduction

It has been established that about 15% of the total world production of dyes is lost during the dyeing process and is released in the textile effluents [1]. The release of those colored waste waters in the ecosystem is a dramatic source of toxic pollution, which leads to perturbations in aquatic life, and is also hazardous to human beings. As international environmental standards are becoming more stringent, development of technological systems for the removal (or degradation into non-toxic forms) of organic dyes have been recently on the rise. These include physical methods (e.g. adsorption), [2] biological methods (e.g. biodegradation) [3, 4] and chemical methods (e.g. chlorination, ozonation) [5].

Wide-band gap semiconductor materials have been the focus in this context for quite some time, as photocatalysts for dye-degradation processes, [6-8] are commonly referred to as the materials which involve Advanced Oxidation Processes (AOPs). The higher mobility of the photogenerated carriers (including holes and electrons) and deeper valence bands of a semiconductor can enhance its photocatalytic oxidative activity leading to the decomposition of the organic dyes [9-10]. Among such different AOPs, most preferred photocatalysts include TiO_2 [11], CdS, ZnS [12-13], ZnO [14], Fenton [15] and polyoxometallates [16]. Photocatalyst-assisted degradation is reported to be achieved better with nanomaterials upon exposure of the catalyst-cum-dye solutions to ultra-violet (UV) light [17-21]. This is primarily due to higher energy imparted by UV source as compared to the visible region and the blue-shifted absorption band for nanomaterials. However, as it is easy to realize, UV occupies merely ca. 4% of whole solar energy, which makes the technology difficult, if not impossible, to further widen the application. Therefore, it is indispensable and urgent to develop a particular photocatalyst sensitive to sunlight for wastewater treatment.

In this context we report on the study of decolorisation of two classic dyes, namely Methylene Blue (MB) and Methyl Orange (MO) using zinc oxide as photocatalyst in ambient sunlight. Nanoparticles of ~20 nm were synthesized using citrate gel route and were compared with commercially obtained bulk powders. Dye to catalyst ratio was kept constant and the data was taken until one of the catalyst-subjected solutions showed complete decolorisation. The process showed ZnO bulk to completely decolorise both the dyes in less than 20 min, whereas ZnO nanopowders could not show complete decolorisation in the comparable time span. The results have been depicted using UV-visible spectroscopy analysis. The decolorized components were found to be Na, Zn, S, SO_4^{2-}, NO_2 and NO_3^-. To evaluate the decolorised components for water safety, an elemental and color analysis was done and it was found that the treated components were much in the safety regime prescribed by World Health Organisation (WHO) and Pollution Control Board (PCB) standards. To evaluate the toxicity issues, cell line studies were performed on these samples which showed the cell viability of ~ 100% on SiHa and B16F10 cell lines as well as on mouse primary

fibroblasts. Thus bulk materials, rather than nanoparticles can be regarded as potential candidates for efficient mineralization of organic pollutants at higher discharge rates.

2. Experimental Procedures

Commercial bulk powders were obtained from two different sources- CDH, India and Sigma Aldrich, USA to doubly check the results. Double distilled water was used throughout the experiments to prepare solutions. Dyes, MO and MB were procured from Thomas Baker, India. The X-Ray Diffraction (PHILIPS X-PERT) technique was used to ensure the phase formation and particle size estimation. UV-visible spectroscopy measurements were carried out on a Jasco (model V-570) dual-beam spectrophotometer for both the characterization of the catalysts and decolorisation studies. The materials and procedures for treated water analysis and the cytotoxicity studies are mentioned in the following paragaraphs.

2.1 Synthesis of zinc oxide nanoparticles: The citrate gel method was used for synthesis of ZnO, wherein zinc acetate, citric acid and nitric acid were used as precursors. 4 gm zinc acetate was dissolved in 40 ml distilled water. Independently, 8 gm citric acid was dissolved in distilled water and was later added to zinc acetate solution. 10 ml nitric acid was added to the above solution. This solution was then heated at 100^0C in a water bath to get yellow gel which, on further heating at the same temperature, converted into a yellow fluffy mass. This was then furnace dried at 110^0C. The product was crushed and annealed at 400^0C for 4 hours and then at 600^0C for 4 hours to remove carbon content, if any. This resulted into white powder, which was subjected to further characterizations.

2.2 Decolorisation studies: MO was dissolved in water in the ratio of 6.8 mg/L. This concentration was maintained the same throughout the decolorisation experiment. 0.5 gm/L of the catalyst (ZnO bulk or nanopowder) was then added to this dye solution and kept in a sunlight ambient for a time span of 0 – 20 minutes. The time of 20 min was carefully selected after several trial experiments ranging from 0 min to several hours. 3 ml aliquots were removed carefully from a period interval of 5 min until one of the solutions was completely decolorised. The aliquots were subjected to 10000 rpm centrifugation to ensure that no catalyst particles remain in the aliquots. The samples were then subjected to UV-visible spectrophotometer and percent absorption was noted at the characteristic absorption wavelength of the dye. A similar experiment was carried out to see the decolorisation of MB. The decolorisation efficiency was determined using:

$$\text{Decolorisation efficiency (DE) (\%)} = \frac{C_0 - C}{C_0} \times 100$$

where C_0 is the initial concentration of dye and C is the concentration of dye after photo irradiation at varying reaction time (0 – 20 min).

2.3 Procedure used for ions identifications in the treated water: The two dye solutions viz. MO and MB were analyzed for various parameters using the standard procedures [22]. The different parameters analyzed were, color (platinum cobalt method), suspended solids (gravimetric method), COD (close reflux method), Na (Flame photometer), Zn (Zencon colorimetric method at 620nm), S (Iodometric titration), SO_4 (Nephalometric), NO_3 (brucin sulphanilic acid method, estimation at 410nm), NO_2 (Colorimetric at 543 nm), ammonical nitrogen (Nessler's reagent estimation at 400-425nm), Chloride (Argentometric titration), and Total Nitrogen (Jehldal's method).

2.4 Cytotoxicity studies: The cytotoxicity studies were performed on SiHa and B16F10 cell lines as well as on mouse primary fibroblasts isolated from skin epithelium of Swiss albino mice. The cell lines as well as primary cells were grown in DMEM supplemented with 2 mM L-glutamine, 100 μl/ml of penicillin/streptomycin, and 10% fetal calf serum. The cells were seeded at $1x10^5$ cells/ml density in 96-well plates (Nunc, Roskilde, Denmark). After 24 h, the cells were incubated with fresh medium containing (ZnO bulk/nanoparticles) treated dye (MO/MB) solutions that were added at concentrations ranging from 0-3.4 μg/ml in each well (in triplicates) and the plates were incubated for 24 h at 37°C in 5% CO_2 incubator. The experiments were repeated at least three times with each cell line. Cell viability was determined by MTT assay. The MTT solution (5 mg/ml) was added to each well, and the cells were incubated for another 4 h at 37 °C in 5% CO_2 incubator. The intensity of the colored formation derivative was determined by measuring optical density (OD) with the ELISA microplate reader (Biorad, Hercules, CA) at 570 nm. The mean OD value of three wells was used for assessing the cell viability expressed as percentage of control [% Viability = (Nanoparticle treated cells / Control cells) x100].

3. Results and Discussion

The XRD analysis of bulk (a) and synthesized ZnO nanoparticles (b) is shown in Fig. 1. Characteristic reflections corresponding from various planes depicted in the figure confirmed the phase formation of the nanopowders, which match well with the bulk wrutzite structure (as reported in JCPDS Powder Diffraction data). The broadening of peaks in the synthesized sample indicated the presence of nanoparticles, and the Scherrer equation estimated the size to be 20 nm, as against the bulk of ~ 70-200 nm (polydispersed).

Fig. 2 shows the UV-visible spectroscopy data of ZnO bulk (a) and ZnO nanoparticles (b). We observed that the bulk sample showed an absorption edge at 382 nm, while the nanopowder samples show an absorption peak at 378 nm. This absorption was fairly sharp in

nanopowder sample, indicating that the synthesized nanoparticles had relatively narrow particle size distribution. The shifting of absorption towards blue region as compared to bulk ZnO could be explained on the basis of the quantum confinement effect of nanomaterials. The second point to note here is that the absorption range of bulk sample was much larger and higher than the nanoparticles (shown elaborately in the inset), which has been envisaged below to be one of the reasons for the observed phenomenon.

Fig. 3 shows photocatalytic decolorisation of MO with ZnO samples after 20 minutes of solar exposure using UV-vis spectrum. Fig. 3 (a) shows the initial signature of MO, (c) shows MO after subjecting the sample with ZnO nanopowder and (d) shows the sample with ZnO bulk. Fig. 3 (b) shows the bare MO solution subjected to sunlight for 20 min without using any catalyst. The results clearly demonstrated that MO shows some decolorisation (46% reduction) without any catalyst, which has already been reported in the literature [23]. However, with ZnO bulk, in less than 20 mins, the dye gets completely decolorised (99%), while with nanoparticles the decolorisation percentage is merely 58%. This result depicted the ZnO bulk to be a better dye-decolorising agent as compared to its nanoparticles. Further, the solution became clear with no orange molecules being adsorbed on the powder, indicating that the dye gets degraded (and not adsorbed). The inset shows time dependent decolorising efficiency (DE) with ZnO bulk (a) and nanoparticles (b) for MO. This showed that within the first minute itself, the dye gets decolorised to about 49% and 90% with ZnO nanopowder and bulk, respectively. The latter part shows a very slow rise, indicating that the rate of decolorisation drops rather rapidly. The picture in another inset also exhibits a clear visual decolorising effect.

Fig. 4 shows a similar photocatalytic decolorisation of MB with ZnO samples after 20 minutes of solar exposure. Fig. 4 (a) shows the initial signature of MB, (c) shows MB after subjecting the sample with ZnO nano and (d) shows the sample with ZnO bulk. Fig. 4 (b) shows the bare MB solution subjected to sunlight for 20 min without using any catalyst. The results once again demonstrate that MB shows some decolorisation (49% reduction) without any catalyst, which has already been reported in the literature [24]. However, with ZnO bulk, within 20 mins, the dye gets completely decolorised (99%), while with nanoparticles the decolorisation percentage is ~ 77%. The inset shows time dependent DE with ZnO bulk (a) and nanoparticles (b) for MB. On similar lines of MO, MB dye, also showed a similar trend with the values to be about 67% and 89% with ZnO nanopowder and bulk, respectively. The picture in another inset also exhibits a clear visual decolorising effect. These results depict that ZnO bulk proved to be better a dye-decolorising agent as compared to its nanoparticles.

The treated samples were analysed for their by-products using standard water-analysis procedures. The results have been shown in Table 1. All the values are in mg/l, except the color, which is in hazen units. The last column depicts the standards prescribed by World Health Organisation [25] and also by Pollution Control Board of India [26]. As can be

seen clearly, there was a ~100% reduction in the color of the samples when they were treated with bulk ZnO bulk photocatalyst in ambient sunlight, whereas some color contribution remains with nanoparticles treatment (this matches well with the observed results shown in Figs. 3 and 4). It was also observed that the samples show an opening of benzene rings, thereby exhibiting different ions like Na, Zn, S, SO_4^{2-}, NO_2 and NO_3^- in MB and MO samples, where bulk catalyst particles show a better percentage of final products as compared to the nanopowders. The detailed pathway for this degradation has been very well reported for both MO [27] and MB [11, 28]. The important point to be noted here is that along with the oxide species we do see the elemental species as well, which gives us a hint for the reason that COD has not decreased much upon treatment. Indeed, there have been references pertaining to incomplete oxidation in such degraded samples of dyes, which do not show the reduction in COD values [29-30]. In that sense, COD may not be a good tool to evaluate the quality of water. Nonetheless, the comparison with the standards recommended by pollution control boards do point out to the useful strategy adopted in our work.

Fig. 5 (a) shows the cytotoxicity data for the MB sample treated with bulk ZnO (i) and with ZnO nanopowders (ii). The samples were those which were treated for 20 mins. It was observed that with bulk ZnO catalyst, the cell viability was ~100% upto the dose of 1.7 μg/ml for all the three cell lines and reduced to about 80, 60 and 50% on higher dosages for primary mouse fibroblasts, SiHa and B16F10, respectively. On similar lines, with nanoparticles of ZnO the cell viability was 85, 87 and 100% upto the dose of 1.7 μg/ml for all the three cell lines and reduced to about 60, 80 and 85% on higher dosages for primary mouse fibroblasts, SiHa and B16F10, respectively. With MO (Fig. 5(b)), the bulk ZnO (i) showed the values as 100% for all cell lines at the dose of 1.7 μg/ml for all the three cell lines and reduced to about 75, 85 and 95% on higher dosages, respectively. When treated with nanopowders of ZnO (Fig. 5(b) (ii)), the cell viability was maximum till 3.4μg/ml and went down to 80% thereafter. These results depicted that both nanopowders as well as bulk particles of ZnO did not offer any toxicity to the treated water systems, promising their applicability for water treatment; however, the bulk samples were better. In our past attempts, we have already studied the efficacy of ZnO for their cytotoxicity evaluation, which had given us a similar message [31]. It is also important to specify here that if ZnO bulk powders are used for such applications, their separation from clean water system becomes quite easy (say, by centrifugation), inviting yet another advantage of bulk system. The powders, so separated from the treated water, when reused, showed us exactly similar behavior with the fresh dye, indicating that neither dye molecules, nor their degraded components are adsorbed on the grains of this catalyst. Indeed, studies are underway to develop ZnO thin films, which are strongly adhered to the surface, and which would work in such treatment plants wherein the contaminated water could be rotated for multiple cycles, before it can be let out as safe water for the environments.

The photocatalytic process usually involves the following well-known steps: (1) photogenerated electrons in the conduction band (CB) are trapped by a recipient (such as oxygen); (2) photogenerated holes in the valence band (VB) are consumed by donors (such as dye organics). The higher the mobility of the photogenerated carriers (including holes and electrons), the better is the performance of the photocatalyst. Additionally, the valence band position of a semiconductor also plays an important role in deciding the photocatalytic activity of the semiconductor. The deeper the valence band of a semiconductor, the stronger is its oxidative activity, and the higher is the photocatalytic property of the material for decomposition of the organics. Therefore, in order to develop a sunlight sensitive photocatalyst, we either need an appropriately band-gap engineered material, or we need the material to possess these characteristics which are brought out by its defect nature. Zinc oxide, in its pure form has high excitonic energy, with its spectra showing a characteristic signature at 380 nm. It has been observed S. Singh et al. [32] and also by many others [33-34] that a broad green emission is seen around 500 nm, which also suppresses the signature at 380 nm (shown by an arrow in the inset of Fig. 2). This has been attributed to defects in the ZnO structure. As has been discussed in the elaborate review by S. Singh et al., these defects in ZnO play an important role in controlling the emission characteristics, which has been studied using first principle calculations. Since these defect states dominate in our bulk samples, we do get excellent photocatalytic dye decolorisation with these samples. Nanopowders, on the other hand show a blue shift in their UV-vis spectra, which makes it a better candidate for UV-assisted degradation, but not in the visible range. Indeed, the defect states in bulk ZnO powders can give much practical solution for industrial dye effluent treatments. Efforts are being made to introduce these broad emission characteristics in the visible range, in a more controlled way.

4. Conclusions

In conclusion, two industrial textile dyes, namely Methylene Blue and Methyl Orange have been studied for their photocatalytic decolorisation in ambient solar light using zinc oxide particles as photocatalyst. Zinc oxide was either procured in their bulk forms, or was syntheised using citrate gel route. It was observed that these dyes show complete decolorisation more efficiently using ZnO bulk samples, as compared to their nano-counterparts. The decolorised components were found to be Na, Zn, S, SO_4^{2-}, NO_2 and NO_3^-. To evaluate the toxicity issues, cell line studies were performed on these samples which showed the cell viability of ~ 100% on SiHa and B16F10 cell lines as well as on mouse primary fibroblasts, giving an evidence of non-toxicity of the catalyst as well as the byproducts upon treatment, with bulk catalysts showing better results. Defects-driven wider absorption of the bulk samples in the visible optical regime is envisaged to be the probable reason for the observed phenomenon. If the defects could be meticulously engineered, ZnO bulk powders

could be considered to be better potential candidates for efficient decolorisation of organic pollutants.

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Table 1: The photocatalysts treated samples analysed for their by-products using standard water-analysis procedures. All the values are in mg/l, except the color, which is in hazen units.

Parameter *	**Control (MO)**	**with bulk ZnO**	**with nano ZnO**	**Control (MB)**	**with bulk ZnO**	**with nano ZnO**	**Tolerance Standard limit**
Color (Hezan Unit)	10	1	08	10	0	05	5
Suspended Solids	nil	54	128	nil	8	12	500
COD	6.4	25.6	22.4	35.2	19.2	32	250
Sodium as Na	-	**8**	3	nil	5	1	**< 20** extendable upto 200
Zinc as Zn	nil	nil	1.51	nil	3.35	3.92	5
Sulphide as S	-	1.42	1.68	nil	4.32	4.28	2
Sulphate as SO_4	0.9	1.4	2.1	1.1	1.3	0.8	200
Nitrate as NO_3	nil	2.87	nil	nil	1.905	1.1	1
chlorine as Cl	-	-	-	nil	14	14	250 (residual, free Cl, 0.2 mg/l)

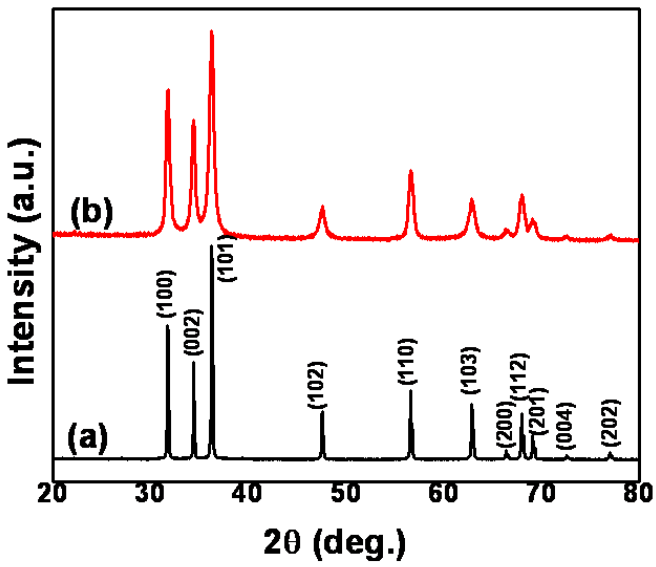

Fig. 1: XRD analysis of bulk (a) and synthesized ZnO nanoparticles (b). The spectrum show phase formation and peak broadening in case of nanoparticles.

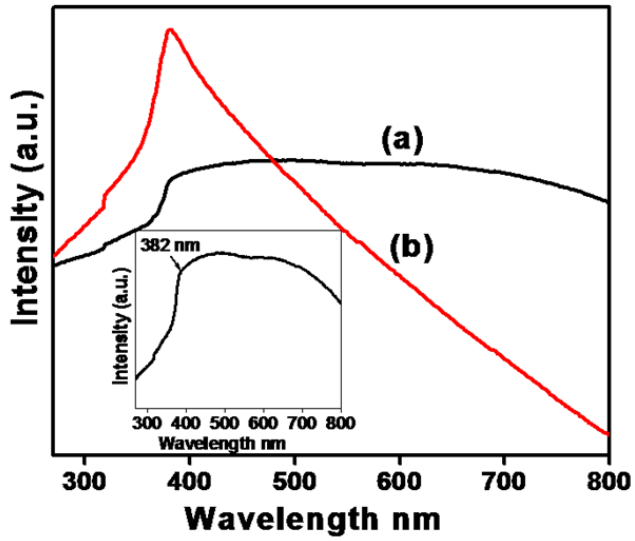

Fig. 2: The UV-vis spectroscopy data of ZnO bulk (a) and ZnO nanoparticles (b). Bulk sample shows an absorption edge at 382 nm, while the nanopowder samples show an absorption peak at 378 nm. The inset shows bulk sample data duly magnified. The arrow shows the absorption edge, which gets completely merged with the defect-state signature around 500 nm.

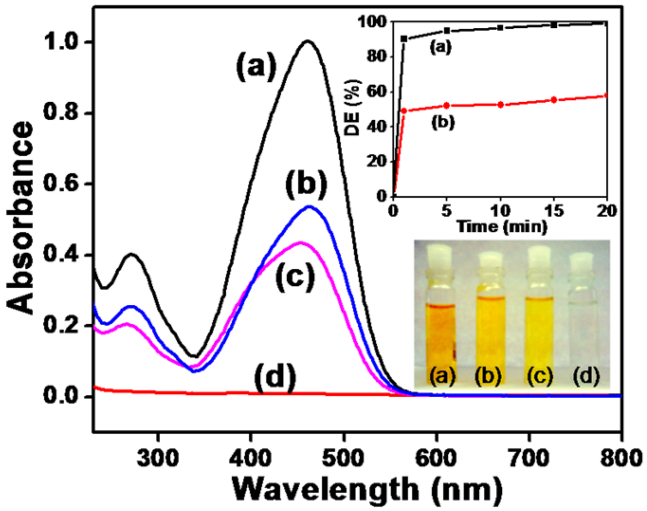

Fig. 3: UV-vis data for photocatalytic decolorisation of MO with ZnO samples after 20 minutes of solar exposure using UV-vis spectrum. Fig. 3 (a) shows initial signature of MO, (c) shows MO after subjecting the sample with ZnO nanopowder and (d) shows the sample with ZnO bulk. Fig. 3 (b) shows bare MO solution subjected to sunlight for 20 min without using any catalyst. The inset shows time dependent decolorising efficiency (DE) with ZnO bulk (a) and nanoparticles (b) for MO. The picture in another inset clearly exhibits visual decolorising effect.

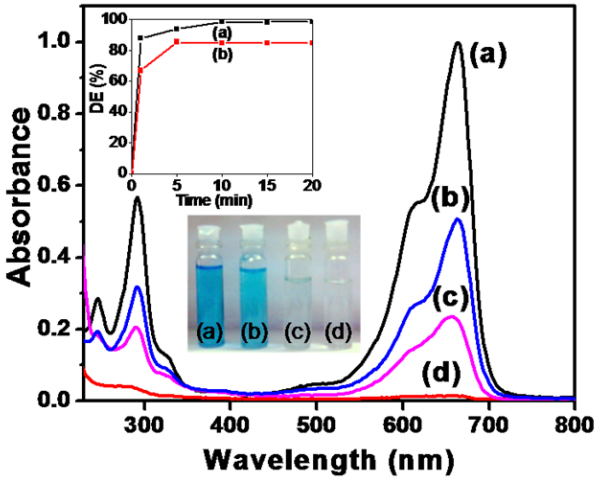

Fig. 4: Photocatalytic decolorisation of MB with ZnO samples after 20 minutes of solar exposure. Fig. 4 (a) shows initial signature of MB, (c) shows MB after subjecting the sample with ZnO nano and (d) shows the sample with ZnO bulk. Fig. 4 (b) shows bare MB solution subjected to sunlight for 20 min without using any catalyst. The inset shows time dependent DE with ZnO bulk (a) and nanoparticles (b) for MB. The picture in another inset also exhibits a clear visual decolorising effect.

Fig. 5(a)

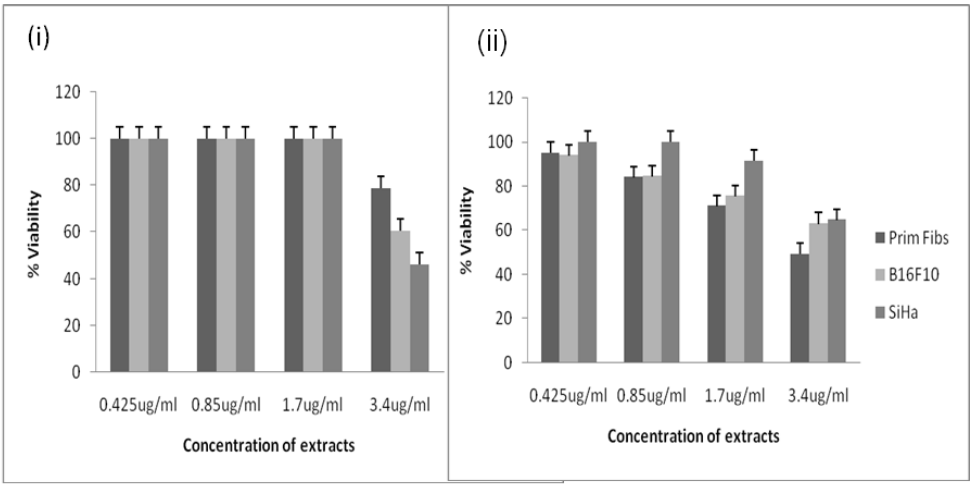

Fig. 5(b)

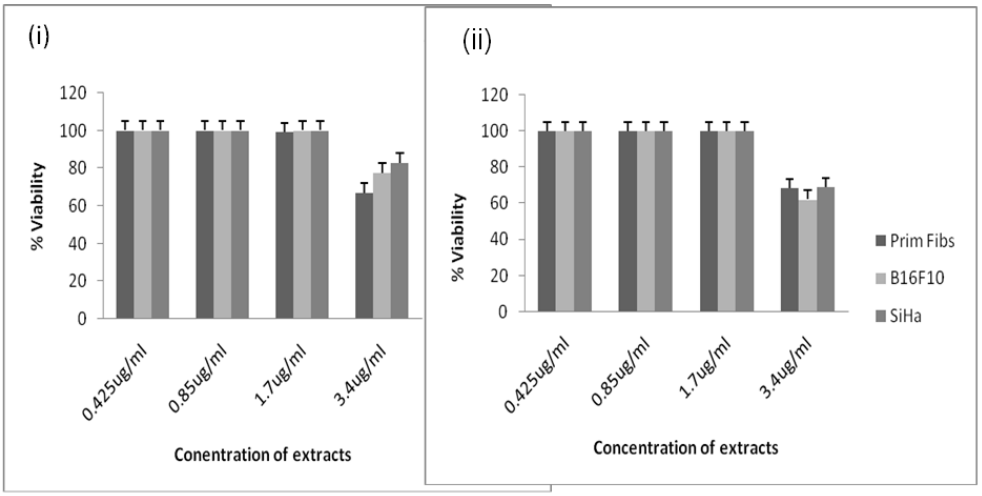

Fig. 5: The cytotoxicity data for the methylene blue sample treated with bulk ZnO (i) and with ZnO nanopowders (ii). Fig. 5 (b) shows the cytotoxicity data for the methyl orange sample treated with bulk ZnO (i) and with ZnO nanopowders (ii).