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Solar photocatalytic treatment of wastewater with zinc oxide nanoparticles and its ecotoxicological impact on *Channa punctatus* –a freshwater fish

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Abstract
Azo dye and hexavalent chromium are two carcinogenic and toxic pollutants present in industrial wastewater. Zinc oxide nanoparticles can be used for the treatment of these pollutants with solar energy. However the nanoparticles themselves generally have some inherent toxicity for aquatic life. In this work, we have selected *Channa punctatus* as the model aquatic animal and examined whether the net toxicity to which it was exposed in wastewater before treatment, decreases after photocatalytic treatment of dye and hexavalent chromium using ZnO nanoparticles as photocatalyst under sunlight. *Lipid Peroxidation* (TBARS) and *Reduced Glutathione* (GSH) have been used as measures of toxicity in fish. We have compared these parameters under different experimental conditions comprising organic and heavy metal pollutants with and without nanoparticles.

Keywords: Trypan Blue dye; Hexavalent chromium; ZnO -nanoparticle photocatalysis; Ecotoxicity; TBARS and GSH of fish

1. Introduction
Nanoparticles (NP) having at least one dimension below 100 nm [1; 2] are not a human invention and have existed naturally from the beginning of the Earth's history. Natural water contains nanoparticles of minerals and humic substances. Hence the aquatic organisms have adapted to live with these materials, though their endurance level depends on the duration of exposure, dose, and the speed of change in habitat conditions. Many natural NPs are transient in the environment, often disappearing through dissolution, or becoming larger through particle growth or aggregation. On the other hand, engineered NPs are stabilized by capping and fixing agents [3] and therefore more persistent than the natural ones. They also may contain toxic components in concentrations or structural forms that do not occur naturally. There are many products and applications of engineered NPs in the various fields including water and wastewater treatment, fuel cells, catalysts, biosensors and for environmental remediation [1; 4-7]. Approximate production of engineered nanomaterials was 2000 tonnes in 2004 and increasing to 58,000 tonnes (estimated) by 2020 [8].
The size and shape dependent properties of nanoparticles made the environmentalists interested to explore their role in environmental remediation processes [9-13]. Nanosized zerovalent iron for reducing heavy metals, nanosized iron oxides for adsorption and /co-precipitation of arsenic and advanced oxidation processes (AOP) with oxide nanoparticles [14] are some of the examples. Formation of undesirable and toxic reaction intermediates is one of the major concerns in any AOP. Sometimes the intermediates or conjugates are more toxic than the parent compound itself.
Among the semiconductors used in AOPs, TiO_2 is the most popular choice in the published reports on photocatalysis. UV/visible light excitation induce separation of hole and electron within the catalyst particle. In aqueous solutions, the holes are scavenged by surface hydroxide groups to generate •OH radicals, which then lead to oxidation and mineralization of organics [15-19]. ZnO is a better candidate as a photocatalyst especially under the visible light excitation. Kabra et al. (2004) presented a review on the application of the photocatalytic technique for remediation of inorganic and organic pollutants in wastewater [20]. Oxidation of organic pollutants has been widely used for the treatment of drinking water and industrial wastewater [21-23].

The reducing capacity of the photocatalyst using the excited electron is comparatively less explored. Hexavalent chromium, Cr(VI) is a carcinogenic and toxic heavy metal ion often present in industrial wastewater. Effluents containing Cr(VI) must be treated to convert it to less toxic Cr(III) [24] before discharging to the surface water. A few reports are there on the photoreduction of hexavalent chromium with bulk-ZnO and UV or solar radiation [24; 25]. Fewer reports are available on the photocatalytic reduction of Cr(VI) employing ZnO-nanoparticles with solar radiation. Yang and Chan (2009) studied photocatalytic reduction of Cr(VI) in aqueous solution using dye-sensitized ZnO-NP under visible light [26]. Reduction of 75% with lamp and 90% with solar radiation were achieved after 17h with 20mg/L initial concentration of Cr (VI).

After the pollutants are destroyed by the nanoparticles, partially or completely, the wastewater is to be generally discharged to the surface water body. Since separation of nanoparticles is expensive and quantity of nanoparticles is very small, one may choose to discharge the treated wastewater with the used nanoparticles.

In the present work, we report the combined toxicological effects of the pollutants and nanoparticles together on aquatic life when dye and Cr(VI) pollutants were partially removed from simulated wastewater using nanoparticles. In our previous paper, we reported such studies on a model aquatic alga, *Anabaena flos-aque* [27]. In the present work, we report the combined toxicological effects of the pollutants and nanoparticles together on aquatic life when dye and Cr(VI) pollutants were partially removed from wastewater using nanoparticles. Here we have used *Channa punctatus*, a common freshwater fish, as a model aquatic vertebrate. *Trypan Blue* dye has been used as model dye-pollutant and potassium dichromate has been used for hexavalent chromium.

Ecotoxicity of engineered nanoparticles on aquatic invertebrates has been reported by Baun et al. (2008) and that on aquatic plant, algae and fungi has been reported by Navarro et al. (2008) [28; 29]. Handy et al. (2008) presented a mechanistic analysis of the uptake and effect of engineered nanoparticles on fish [3]. They have used Trout and Zebra fish as models and TiO_2 and C60 fullerene for nanoparticles. Zhu et al. (2008) compared the toxicity of several metal oxide aqueous suspensions to Zebrafish (*Danio rerio*) early developmental stage [30]. Of the substances tested, ZnO was the most toxic material to zebrafish embryos and larvae. Wiench et al. (2009) reported the acute and chronic effects of nano- and non-nanoscale TiO_2 and ZnO particles on mobility and reproduction of the freshwater invertebrate, *Daphnia magna* [31]. They concluded that the acute effects of ZnO on the mobility of *Daphnia magna* are probably due to the ion-toxicity of Zn and are not an effect of exposure to the metal oxide ZnO. Cr (VI) has been known for inducing oxidative stress on fish [32]. Cr (VI) also severely affects the vital organs such as the liver and kidney [33]. Azo dyes are carcinogenic and they are also responsible for induction of oxidative stress [34; 35]. Zinc oxide (both in bulk phase and as nanomaterials) is capable of generating reactive oxygen species. The cytotoxicity of ZnO nanoparticles may be partially due to their induction of cellular oxidative stress through the generation of free radicals and reactive oxygen species. Redox active metals such as chromium (whose stable oxidation states are +3 and +6) may induce generation of ROS either through redox cycling or by getting involved in Fenton reaction [36].

In the present research, we have studied the oxidative stress induced by the initial or treated solutions and by the nanoparticles as well by measuring the lipid peroxidation (TBARS) and reduced glutathione levels (GSH). This is perhaps the first report on the combined or cumulative toxicological effect of the pollutants and semiconductor nanoparticles on fish.

2. Materials and Methods

2.1. Materials

2.1.1. For Solar energy photo-oxidation of Trypan Blue dye and photo-reduction of hexavalent chromium

Trypan Blue dye (Mol formula: $C_{34}H_{28}N_6C_{14}S_4$, Molecular weight 872.88, CI number: 23850) was procured from Loba Chemie. Potassium Dichromate ($K_2Cr_2O_7$) was procured from Sisco Research Lab, Mumbai. Micro sized ZnO catalyst was procured from SRL- Mumbai. Distilled water with conductivity 4–7 micromhos was used in the experimental work at a pH of 6.6–6.9. Intensity of solar radiation was measured using Metravi 1330 digital lux meter (China). The pH was measured using a Testr24 digital pH meter (Eutech Instruments, Singapore).

2.2.2. For toxicological analysis

Sodium chloride, sodium hydroxide, sodium bicarbonate, sodium phosphate monobasic anhydrous, di-sodium hydrogen phosphate anhydrous, hydrochloric acid, copper sulphate, sodium potassium tartarate, Folin-Ciocalteu's reagent, trichloroacetic acid (TCA) were procured from Merck (Merck Specialities Private Limited, Mumbai, India) and Bovine serum albumin (BSA), thiobarbituric acid (TBA), 5, 5'-dithio-bis (2-nitro benzoic acid) (DTNB) and GSH from Sigma (St Louis, MO, USA). All these chemicals were used for different biochemical assays to estimate protein, GSH and lipid

peroxidation (LPO) level. All the chemicals used were of highest grade of purity available.

2.2.3. Characterization of nanoparticles
Characterization of the ZnO nanoparticles used in the experiments has been discussed elsewhere [37]. The major characteristics of the nanoparticles procured from Sigma-Aldrich are given below:
Average particle size: 40-50 nm; Specific surface area: 15 - 25m^2/g ; Grain size: ~29nm
Cell volume: 29.147 ± 0.019 Å; The average particle size of the micro sized ZnO catalyst was 146.7 nm and the BET surface area was 3.23m^2/g.

3. Experimental details
Solar photocatalytic degradation experiments for dye and Cr(VI) solutions were performed separately with 50mg/L of substrate solution and 2gm (max) of micro/nano ZnO particles and the resultant solution with the nanoparticles were added to the aquarium containing 25L water and fish. We did not filter the catalyst particles since filtration of nanoparticles is an expensive procedure and we examined the toxicity alongwith the catalysts so as to explore the possibility of discharging treated wastewater into the surface water as such after solar photocatalytic treatment.

3.1. Solar energy photo-oxidation of Trypan Blue dye and photo-reduction of Cr(VI)
Experiments for the solar photocatalytic oxidation of dye and reduction of Cr(VI) were carried out in separate experiments but in the same stainless-steel box reactor provided with a quartz glass cover and a cooling water circulation system through the jacket around it. The volumetric capacity of the reactor was 550 mL while 500 mL of the reaction mixture is taken. Dye or Potassium dichromate solution, weighed quantity of ZnO and methanol (used as hole-scavenger in case of reduction experiment only) were taken together in the reactor. The mixture was kept in suspension with the help of a magnetic stirrer for reduction experiment. For oxidation experiment, compressed air was passed through the reaction mixture using a sparger which kept the reaction mixture in suspension and the oxygen in air acted as an electron-scavenger. Schematic diagram of the experimental set-up has been provided elsewhere [37; 38]. Adsorption experiment was performed in the dark for both cases and after ensuring the adsorption equilibrium; the reactor was exposed to the sunlight (average 70 klux) for 2 hours. Aliquots of about 25mL were withdrawn at particular time intervals, filtered/centrifuged and the supernatant was analyzed spectrophotometrically (λ_{max} = 349nm for dichromate solution and 590nm for *Trypan Blue* solution) against standard calibration curves for the residual potassium dichromate and dye contents respectively [25; 39-42].

3.2. Sample-preparation with the test- species
Two hundred forty fishes were taken and divided into twelve groups. These groups were arranged into three different sets. Among the three sets Control group and Cr(VI) solution treated group were common for Set I and Set II. Three different sets were as follows (Table 1). The legends indicated in Table 1 are used in the Figures 1 and 2 later.

3.3. Selection and culture of the fish
The selected fish, *Channa punctatus*, has some distinctive characteristics such as wide distribution in the freshwater environment, cost-effectiveness, easy availability throughout the year and their quick adaptability to laboratory conditions to be considered as test species.
Samples of fresh water fish, *Channa punctatus* (Bloch) were obtained from local fresh water ponds (free from pollutants). Fishes weighing 50±1.30 gm with an average length of 25.5±1.21cm were maintained in a glass aquaria containing 25 litre of water, following standard fish maintenance procedure during acclimatization and exposure. Fishes were acclimatized for 3 days before use. The atmosphere and components of aquarium water were maintained according to standard protocol and are presented in Table 2.

3.4. Tests for toxicity
The concentration of the initial solution was 50mg/L for both Cr(VI)/ *Trypan Blue* dye. When diluted into the aquarium water, the same became 3mg/L. Solar photocatalysis with micro-ZnO reduced the concentration of Cr(VI) to 38.67mg/L whereas with nano-ZnO it became 27.91 mg/L. When these treated solutions were mixed in the aquarium, the resultant concentrations became 2.2 mg/L of and 1.8 mg/L of Cr(VI) respectively. Similarly, from an initial value of 50mg/L of *Trypan Blue*, solar photocatalysis reduced it to 26.67 mg/L and on dilution, the final concentration of the dye in aquarium water was 1.6 mg/L.With these concentrations of the pollutants, along with micro and nano ZnO particles, the toxicities were examined.
Tissue homogenate preparation: After 24 hrs of exposure, all fishes were sacrificed and liver was collected for toxicity study. Liver was homogenised using a tissue homogeniser (Sono Plus, Germany) in ice-cold 0.2 mM phosphate buffer (pH 7.4) containing protease inhibitors (0.1 mM EDTA, 1.0 mM PMSF, 1 mM DTT, 0.1 mM EGTA, 0.3% NP-40 and 1 g/ml pepstatin A) to obtain a 10% tissue extract. The tissue extract (1.5 ml) was centrifuged at 12,000 x g (30 minutes at 4°C) in a refrigerated centrifuge (Sorvall, USA). This tissue extract was used for different biochemical tests.

Table 1. Details of the three sets of ecotoxicity study

SET-I : Cr(VI) and micro ZnO			SET-II: Cr(VI) and NanoZnO		SET-III: Dye and NanoZnO	
No	Description	Legend	Description	Legend	Description	Legend
(i)	25 L water and Fish	Control	25 L water and Fish	Control	25 L water and Fish	Control
(ii)	1.5 L solution of 50 mg/L Cr(VI) added to 25L water containing fish	Cr(VI)	1.5 L solution of Cr(VI) added to 25L water containing fish	Cr(VI)	1.5 L solution of Trypan Blue dye added to 25L water containing fish	Dye
(iii)	1.5 L solution of Cr(VI) + 0.6g micro-ZnO added before solar treatment to 25L water containing fish	MicroZnOBT	1.5 L solution of Cr(VI) + 0.6g nano-ZnO added before solar treatment to 25L water containing fish	NanoZnOBT	1.5 L solution of Trypan Blue dye + 0.6g nano - ZnO added before solar treatment to 25L water containing fish	NanoZnOBT
(iv)	1.5 L solution of Cr(VI) +0.6 gm micro-ZnO added after solar treatment to 25L water containing fish	MicroZnOAT	1.5 L solution of Cr(VI) + 0.6 gm nano - ZnO added after solar treatment to 25L water containing fish	NanoZnOAT	1.5 L solution of Trypan Blue dye + 0.6 gm nano - ZnO added after solar treatment to 25L water containing fish	NanoZnOAT
(v)	0.6 gm microZnO added to 25L water containing fish	MicroZnO	0.6 gm nano ZnO added to 25L water containing fish	NanoZnO	0.6 gm nano ZnO added to 25L water containing fish	NanoZnO

Table 2. Physicochemical parameters of aquarium water

Characteristics	Unit	Mean	Range
Air temperature	˚C	26.20	25.6-26.6
Water temperature	˚C	24.40	24.2-25.4
pH		7.6	7.4-7.9
Dissolved oxygen	mg/L	6.8	6.7-7.8
conductivity	µM/cm	282	260-300
Total hardness	mg/L	220	200-300

The loading of catalyst was maximum 0.6g in 25L of aquarium water. The fishes were exposed to the pollutants for 24 hours and then sacrificed. It may be noted that the components imparting toxicity are Cr(VI), Cr(III) and ZnO particles (micro- or nano).

Protein estimation: The protein content was determined from tissue extract by Lowry's method [43]. About 1 ml of Lowry reagent and NaCl was mixed with 4 µl tissue extract. After 10 minute of incubation, 100 µl Folin reagent was added. After 30 minute incubation, absorbance was measured at 612 nm.
Lipid peroxidation (LPO): LPO level in the homogenate was determined using standard protocol [44]**.** The homogenate was incubated for a brief period with 15% TCA, 0.375% TBA and 5 N HCl at 95ºC for 15 min, the mixture was cooled, centrifuged and the absorbance of the supernatant was measured at 535 nm against appropriate blank. The amount of lipid peroxidation was determined by using $\varepsilon=1.56 \times 10^5$ /M/ cm and expressed as amount of produced TBARS in nanomoles/gm tissue.

Reduced glutathione: Liver homogenate was treated with 0.1 ml of 25% TCA and the resulting precipitate was pelleted by centrifugation at 3900 x g for 10 minutes. Free endogenous sulfhydryl was assayed after adding 2 ml of 0.5 mM DTNB prepared in 0.2 M phosphate buffer (pH 8) to 1 ml of the supernatant. The GSH reacts with DTNB and forms a yellow complex with DTNB. The absorbance was measured at 412 nm [45].

4. Results and Discussions

As indicated before, solar photocatalytic degradation experiments were performed separately before the whole contents were added to the aquarium of fish for toxicity study. Salient features and outcomes of those experiments are given below.

4.1. Solar photo-catalytic reduction of hexavalent chromium

About 21% of the original Cr (VI) has been reduced with 50mg/L of Cr(VI) with micro ZnO suspension after 120 minutes exposure to 70 Klux of solar radiation. About 43 % reduction of the substrate could be achieved using nano ZnO over the same time-interval under otherwise identical experimental conditions. As stated earlier, Treated water contained 38.67 mg/L and 27.9 mg/L (before dilution) Cr(VI) respectively.
Blank experiments were conducted to ensure adsorption of the potassium dichromate solution onto the filter membrane or on the photocatalyst surface. No adsorption of the Cr(VI) was observed on the catalyst or on the

membrane. However substantial adsorption of methanol was noted on the zinc oxide nano and micro particles when adsorption experiment was conducted separately with a high concentration of alcohol. The residual concentration of methanol was measured spectrophotometrically at λ_{max} = 280nm. The reduction followed a Langmuir-Hinshelwood-type pseudo first order route. The details of the photoreduction of hexavalent chromium with ZnO photocatalyst has been separately described elsewhere [38].

4.2. Solar photo-catalytic oxidation of Trypan Blue azo dye

Trypan Blue dye can efficiently be photo-oxidized in wastewater using ZnO nanoparticles and solar energy. Dark experiments were conducted to examine adsorption of the dye solution on the photocatalyst surface before exposing it to sunlight. At equilibrium, 15% of dye was adsorbed from a starting solution of 50mg/l. About 50% dye was oxidized when initial dye concentration was 50mg/l and nano ZnO loading was 0.2gm/500ml of simulated wastewater. Concentration of dye after solar photocatalytic treatment was 24.6 mg/L. 27.53% of the initial COD (Chemical Oxygen Demand, determined by APHA standard total reflux method) was removed. Increase in initial concentration decreased the photo-oxidation. The reaction followed Langmuir-Hinshelwood model. The difference in the decrease of colour and COD indicates that by photo-oxidation, colourless intermediates with COD are formed [46].

4.3. Toxicity-studies of different solutions

Results of the toxicity-studies are discussed as below:

4.3.1. LPO

An increase in TBARS value indicates toxicity in the living being. The TBARS value of control group was 1.09±0.13 nanomoles/gm of tissue whereas in case of the group exposed to only Cr(VI) solution, the TBARS value was 3.39±0.23 nanomoles/gm of tissue (Fig. 1).

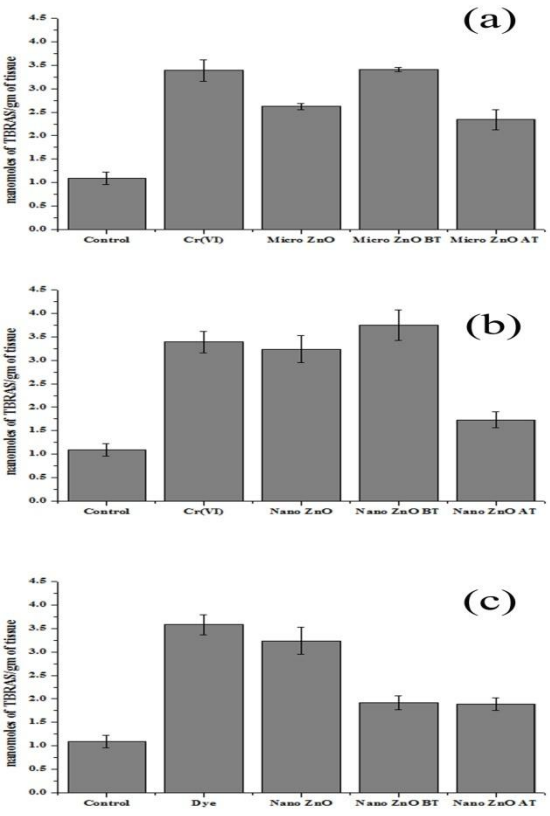

Figure 1(a,b,c): Levels of TBARS in sets I, II and III as nanomoles/g of tissue

It indicates Cr(VI) develops oxidative stress. For remediation of such pollution of the aquatic environment, if we add bulk-ZnO in view of solar photocatalytic reduction of Cr(VI), then, before it is exposed to sunlight, the water remains equally toxic for the fishes as indicated by the TBARS value (3.41± 0.05 nanomoles/gm tissue).

It was observed that only micro-ZnO induced less toxicity (2.62±0.06 nanomoles/gm tissue) than only ZnO-NP (3.39±0.23 nanomoles/gm tissue). Therefore when ZnO-NPs were used instead of the micro-ZnO, the toxicity of the mixture of Cr(VI) and ZnO, prior to sunlight exposure was even more, as indicated by a TBARS value of 3.75±0.33 nanomoles/gm tissue.

The toxicities of two mixtures, one with ZnO-NP and partially reduced Cr(VI) and the other with micro-ZnO and partially reduced Cr(VI), were assessed. It was observed that the TBARS level came down to 2.34±0.21 nanomoles/gm tissue for the micro ZnO (Figure 1a) and 1.73±0.17 nanomoles/gm tissue for the nano-ZnO (Fig. 1b). In the phtoreduction process, the toxic Cr(VI) has been reduced to the comparatively less toxic Cr(III) and hence the overall toxicity of these mixtures decreased. The overall toxicity is less in case of nano-ZnO since the reduction of Cr(VI) to Cr(III) was more with ZnO-NPs and hence less amount of more toxic Cr(VI) is present in the medium.

For the dye pollutant, the TBARS value for the group exposed to only dye solution was the maximum whereas the combined toxicity was found to reduce in the group exposed to the mixture of partially reduced Cr(VI) and ZnO-NP after solar photocatalysis.

4.3.2. Reduced glutathione

Reduced glutathione is a measure of the resistance of a living being towards oxidative stress and its decrease indicates that the subject is exposed to such stress. In an uncontaminated environment (Control), the average value of GSH in the fish samples was 81.59±2.76 micromoles of GSH/mg of protein. In a similar way of interpretation of lipid peroxidation data, it can be observed from Fig. 2a that toxic Cr (VI) decreased the GSH value to 40.35±4.0 micromoles of GSH/mg of protein.

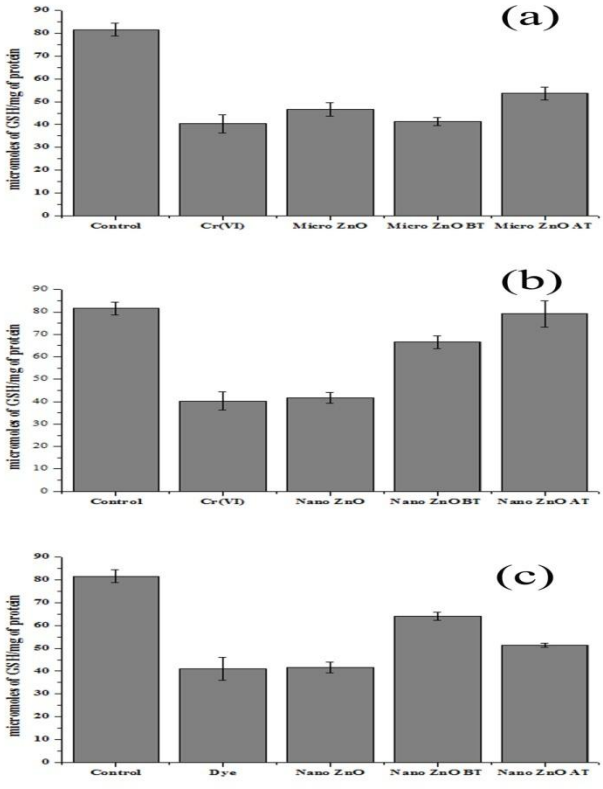

Figure 2(a,b,c) Levels of GSH in sets I, II and III as micromoles/mg of protein

Before exposure to sunlight, mixture of micro-ZnO and Cr(VI) imparted nearly equal toxicity as indicated by GSH of 41.35±1.71 mM/mg protein and after solar photocatalytic reduction, the mixture of micro-ZnO, Cr(VI) and Cr(III) induced GSH of 53.59±2.76 micromoles of GSH/mg of protein. With ZnO-NP, the GSH values before and after photocatalysis were 66.53±2.84 micromoles of GSH/mg of protein and 79.11±5.84 micromoles of GSH/mg of protein respectively (Fig. 2b). In case of contamination with dye pollutant, it was observed that in terms of GSH, ZnO-NP is more toxic than the dye- pollutant alone, but there was a decrease in

toxicity after solar photocatalysis of the dye-laden water with ZnO-NP as the GSH value increased from 51.33±1.01 micromoles of GSH/mg of protein to 64.03±1.89 micromoles of GSH/mg of protein (Fig. 2c). The possible explanations for variation of toxicities are as before.

5. Conclusion

Based on the above, it may be summarized that solar energy photocatalysis with ZnO, especially with ZnO-NPs, is an effective and energy-efficient technique to degrade organic pollutants like azo dyes and heavy metals like Cr(VI). If, after photocatalysis, the treated water is discharged to the surface water along with the catalyst-particles and degradation- products, it was observed that even after degradation of the pollutants, a resulting toxicity remains in the medium that can influence the lipid peroxidation and reduced glutathione in the aquatic vertebrates. Hence filtration is recommended before discharging, for separation of the catalyst particles. But the filtration of nanoparticles from the treated water is costly and might outweigh the savings of energy. It may be mentioned that the physico-chemistry of nanoparticles largely depends upon the conditions of the medium and hence the toxicity can seldom be generalized. In the experiment we have used only a small quantity (2.4% weight/volume only) of nanoparticles that was diluted in 25L of aquarium water. But in real-life, the volume of surface water where the treated effluent (and the nanoparticles) would be discharged is expected be huge compared to the experimental volume and the dilution would be much more. So it is expected that the toxicity can nearly be eliminated and the aquatic life will remain safe. Hence the energy-efficient technology of solar - photocatalysis using ZnO-NP can be used in a larger scale for treatment of wastewater containing Cr(VI) and azo- dye without compromising the safety of the aquatic life even if the nanoparticles are not separated from the treated water.

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