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Investigating the toxicity of acid dyes from textile effluent under UV/ZnO process using *Daphnia magna*

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ABSTRACT

Some of textile wastewater dyes and their raw materials are carcinogenic for humans due to production of toxic aromatic amines. The toxicity measurement of the textile wastewater was analyzed using zinc oxide nanoparticles under ultraviolet irradiation process (UV/ZnO) and *Daphnia magna* bioassay was performed. *D. magna* has been evaluated as indicator to test effluent toxicity in dyes effluent. The impact of effective parameters such as zinc oxide nanoparticles load, pH, and exposure time were well investigated and optimized. It was found that increase in toxicity during the process is possibly due to the production of intermediate toxic compounds, presence of excessive hydrogen peroxide in the solution, presence of excessive ZnO in the solution, or ZnO toxicity or presence of excessive hydrogen peroxide in wastewater and consequent death of *D. magna.* Obtained experimental results revealed that toxicity increases during the nanophotocatalytic process.

Keywords: Acid dye; *Daphnia magna*; Nanophotocatalytic process; Textile effluent

1. Introduction

Acidic dyes are treated as major environmental pollutants nowadays, the discharge of wastewater containing dye effluents is the significant source of pollution in the ecosystem, these effluents are proved to be the carcinogenic agents, in terms of esthetic and prevailing aquatic flora and fauna. Discharge of these dyed effluents into the environment can be origin of dangerous byproducts that are produced from oxidation or other chemical reactions in the effluent [1–4].

Toxicity evaluation of aquatic environment is quite necessary due to the production of intermediate toxic compounds. Several studies have been conducted for assessing the efficiencies of advanced oxidation processes in reduction of toxics concentrations present in aquatic environments using various organisms such as bacteria, fungi, and zooplanktons. According to the study conducted using *Daphnia magna*, microalgae, and *Vibrio fischeri*, the former was found to be the

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most sensitive and the latter was found to be the second most sensitive organism to environmental pollution [5–29].

D. magna has been widely used in bioassays; the use of *D. magna* for bioassays is more advantageous than any other organism, because it can be extensively used as receptor for the evaluation of noxious effluents discharged in the water bodies. Recently, much attention has been paid to this organism due to its low reproduction cycle time, high sensitivity, simplicity of the experiments, low laboratory experiment costs, and more importantly its ability to reproduce genetically same organisms, which highly increases the validity of the results obtained [2,30–32].

The aim of the present study was to evaluate acidic dyes solution toxicity after UV/ZnO-mediated nanophotocatalytic process using *D. magna* bioassay.

2. Materials and methods

2.1. Daphnia culture

One of the most straightforward cultures is humus which is periodically enriched with yeasts. This culture is produced by combination of 5 g animal fertilizer, 25 g soil or fertilizer combined with sand, and lake or tap water, which was kept at room temperature for two days, the culture is filtered with a fabric filter having 0.15 mm mesh size; however, some of the soil grains pass through the filter. The filtered liquid is kept for one week for depositing the suspended solids present in the solution. These deposits are then discarded. Final culture can be used for either individual or for herd cultivation. For individual cultivation, 100 ml of the synthesized culture is poured into a glass bottle, and then a *D. magna* is released into it. The next day, 1 ml of suspension containing 1 mg dry active yeast is added to each bottle every other day. For herd cultivation, a 3.8 L glass bottle is used which contains 3 L of the synthesized culture. In this case, the dry active yeasts are also added every other day. When the cultivation starts, the culture should not be changed. However, water is occasionally added to neutralize the effect of evaporation. In order to decrease the evaporation, a porous bonnet is used, through which the air can pass.

Aeration is not necessary since critical dissolved oxygen level for *D. magna* is less than 15% in 20˚C. Using 100 female *D. magna* cultured individually, a 300 new-born *Daphnia* can be daily obtained. When the female *Daphnia* starts reproducing, young *Daphnia* should periodically be separated. This should be preferably done every 24 h in 20˚C or every 12 h in 25˚C. When the production rate of the first generation of the female *daphnia* decreases, they are replaced by young female *D. magna* in a new culture. It should be noted that glass bottles were used for cultivation since the light necessary for algal growth can pass through them; besides, separation of the female *D. magna* becomes easier when the bottle is transparent.

2.2. Origin of the daphnia used for cultivation

The first generation of the *daphnia* used was preyed from its natural habitat. In the first step, one of the preyed *D. magna* was cultivated according to the above-mentioned instructions. *D. magna* were then nourished to reach to their reproductively active life cycle. At 20˚C *D. magna* reach sexual maturity in 6–8 d releasing their eggs into a brood chamber. The embryos complete their development inside the brood chamber and hatch as free-swimming neonates at day 8–10. In the following 2–4 d the mature females release a second brood of neonates with reproduction peaking around the third brood (day 12–14) or fourth brood (day 14–17). As the adult daphnids become older the time between broods will increase and the size of the brood will decrease [33]. This generation having the same mother was used for herd cultivation. Therefore, all of the *D. magna* used in the present study were genetically quite the same.

2.3. Conditions of culture environment

Cultivation was performed in the microbiology laboratory. Cultures were exposed to sunlight during the day. Temperature was constantly monitored by a thermometer placed in the culture. Temperature was kept in 20 ± 1˚C during the whole cultivation period.

2.4. Experiments using solution containing acid dye

After preparation of the solutions containing different concentrations of 0.5, 1, 1.5, and 2 mg/l of the acid 4092 dye ($C_{22}H_{14}N_6Na_2O_9S_2$), two separate 200 ml containers were provided for each concentration, one as the experimental bottle, and the other as the control. Young female *D. magna* were then collected and cultured in the both bottles (10 daphnia in each bottle) using a Pasteur pipette. Afterwards, observations were regularly performed in 2, 4, 6, 24, 48, and 96 h after cultivation. Number of dead (immobile) *D. magna* in each bottle was recorded. The *D. magna* was considered as dead if it did not move after the rotation of the bottle.

2.5. Experiments on the samples taken during the nanophotocatalytic process

This experiment was conducted for assessing the efficiency of the nanophotocatalytic process in decreasing the toxicity of the dyed solutions. After preparation of the synthetic sample with concentration of acid dye having the best efficiency with respect to the nanophotocatalytic process, it was placed in the reactor. Having passed the time required, various volumetric percentages (from 10 to 100%) of the sample underwent toxicity tests. As the previous experiments, one of the bottles was taken as control, with zero toxic concentrations. Careful considerations were performed after 2, 4, 6, 24, 48, 82, and 96 h and the number of immobile *D. magna* was recorded.

To determine the dye removal by nanophotocatalytic process experiments were conducted under different conditions. This is due to excitation of zinc oxide nanoparticles, which led to the formation of paired e-h in the surface of these particles (Eq. (1)). Direct oxidation of dye in solution is due to the high oxidation ability of h^+_{VB} (Eq. (2)). In fact, hydroxyl radicals produced through the breakup of water molecule (Eq. (3)) and the reaction between h^+_{VB} and hydroxide (Eq. (4)) cause degradation of dye [34,35]

$$ZnO + h\nu \rightarrow ZnO(eCB^- + h^+_{VB}) \quad (1)$$

$$h^+_{VB} + \text{dye} \rightarrow \text{oxidation of the dye} \quad (2)$$

$$h^+_{VB} + H_2O \rightarrow H^+ + {}^\circ OH \quad (3)$$

$$h^+_{VB} + OH^- \rightarrow {}^\circ OH \quad (4)$$

Hydroxyl radicals are super strong non-selective oxidants for the degradation of dye. Electrons in the conduction band of catalyst surface (eCB^-) reduce molecular oxygen to superoxide anions (Eq. (5)). The radicals, in the presence of dye, may lead to the formation of organic peroxide (Eq. (6)) or hydrogen peroxide (Eq. (7)).

$$eCB^- + O_2 \rightarrow {}^\circ O_2^- \quad (5)$$

$${}^\circ O_2^- + \text{dye} \rightarrow \text{dye} - oo^\circ \quad (6)$$

$${}^\circ O_2^- + HO_2^\circ + H^+ \rightarrow H_2O_2 + O_2 \quad (7)$$

Also, the electrons in the conduction band are responsible for the production of hydroxyl radicals that can cause mineralization of dye (Eq. (8)):

$${}^\circ OH + \text{dye} \rightarrow \text{degradation of dye} \quad (8)$$

All the experiments were performed according to the Standard Methods for the Examination of Water and Wastewater (2012) and USEPA-method 821-R-02-012 [36]. Data analysis and computation of LC_{50} were performed using pro-bit analysis. Toxicity unit was calculated by dividing 100 by LC_{50} [37–42].

3. Results and discussion

After time periods of 2, 4, 6, 24, 48, 72, and 96 for all volumetric percentages, no dead *D. magna* was observed. For the time period of 72 h and under volumetric percentages of 10–100%, numbers of dead *D. magna* were 0, 0, 0, 0, 0, 0, 1, and 1, respectively. Corresponding values for the time period of 96 h were 0, 0, 0, 0, 0, 0, 1, 1, 2, and 2, respectively. For control samples, no dead *D. magna* was found. Variation in the toxicity indicators (LC_{50} and TU) were assessed using probit analysis. According to the results of the experiments, probit analysis was conducted only for the time periods of 72 and 96 h, since no dead *D. magna* was observed in other time periods.

Fig. 1 illustrates the death probability of *D. magna* in different volumetric percentages for the time period of 72 h. As shown in the Fig. 1, LC_{50}–72 h is determined to be 120.45 mg/l, implying that the dye solution is to some extent toxic.

The death probability of *D. magna* in different volumetric percentages for the time period of 96 h is illustrated in Fig. 2. According to the Fig. 2 LC_{50}–96 h of the sample is 118.6 mg/l, which revealed that the toxicity of the dyed compound has increased.

Table 1 presents the overall results of the bioassays conducted on the acid-4092 dye in different time periods of 72 and 96 h. As can be seen, LC_{50} values for the time periods of 72 and 96 h are 120.5 and 118.6 mg/l, respectively. Corresponding values for TU are 0.82 and 0.84, respectively. Fig. 3 shows LC_{50} values for *D. magna* in time periods of 24, 48, 72, and 96 h.

In this study, the results of the toxicity test on the samples taken from effluent of the nanophotocatalytic process in optimum operational conditions (ZnO = 0.2 mg/l, sample concentration of 2 mg/l, contact time of 12 min, and pH 10) were investigated. No dead *D. magna* was observed in all volumetric percentages for the time periods of 2, 4, and 6 h. For the time period of 24 h, numbers of dead *D. magna* in volumetric percentages of 10–100% were 0, 0, 0, 0, 0, 1, 1, 1, 2, and 2, respectively. Corresponding values for the time period of 48 and 72 h were 0, 0, 0, 0, 1, 1, 2, 2, 3, 3

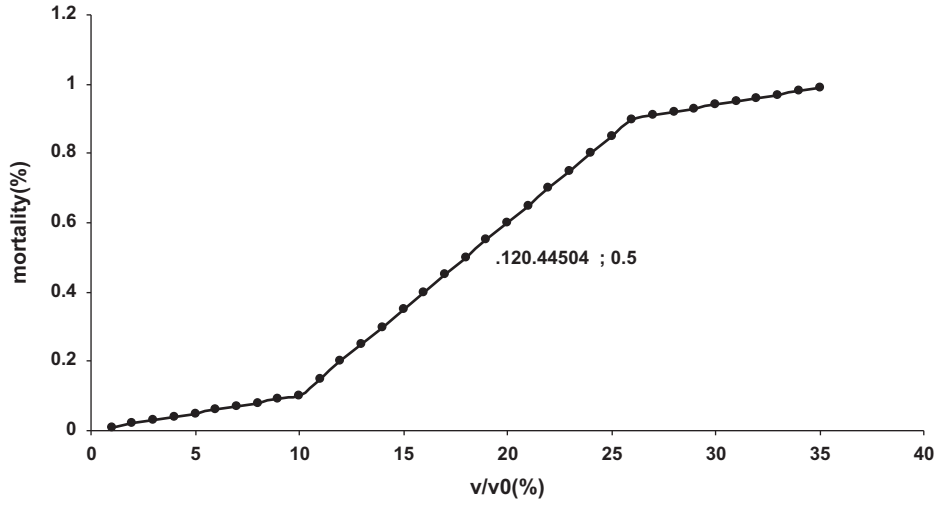

Fig. 1. Different volume percentages of death risk of dye and determination of LC_{50}–72 h.

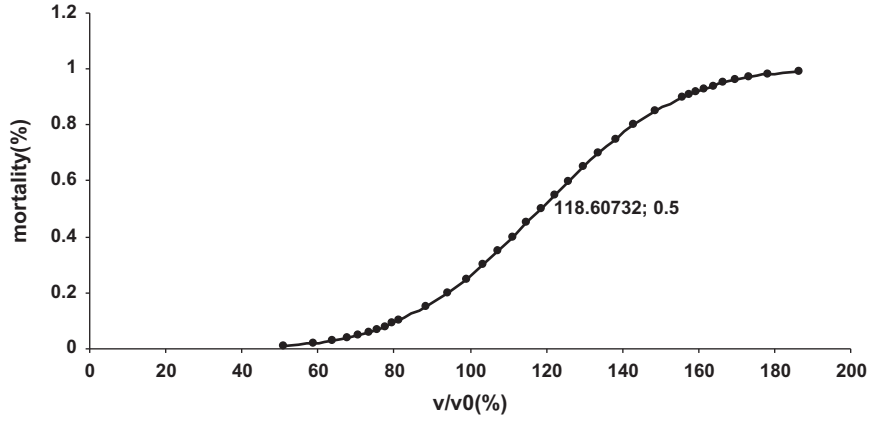

Fig. 2. Different volume percentages of death risk of dye and determination of LC_{50}–96 h.

Table 1
Data from toxicity testing on *D. magna* using synthetic samples

Parameters	Time(h)			
	96	72	48	24
LC_{50} (mg/L)	118.6	120.5	–	–
LC_{50} (mg/L) (95% confidence Limit; Upper bound)	310.1	–	–	–
LC_{50} (mg/L) (95% confidence Limit; Lower bound)	99.6	–	–	–
Toxicity Unit (TU)	0.84	0.82	–	–

and 0, 0, 0, 1, 2, 2, 2, 3, 3, 4, respectively. The values for the time period of 96 h were 0, 1, 2, 2, 3, 3, 3, 4, 5, and 5, respectively. No dead *D. magna* was observed in control samples.

Figs. 4 and 5 reveals the death probability of *D. magna* in the different volumetric percentages of the samples taken from the effluent of the nanophotocatalytic process for the time period of 24 and 48 h.

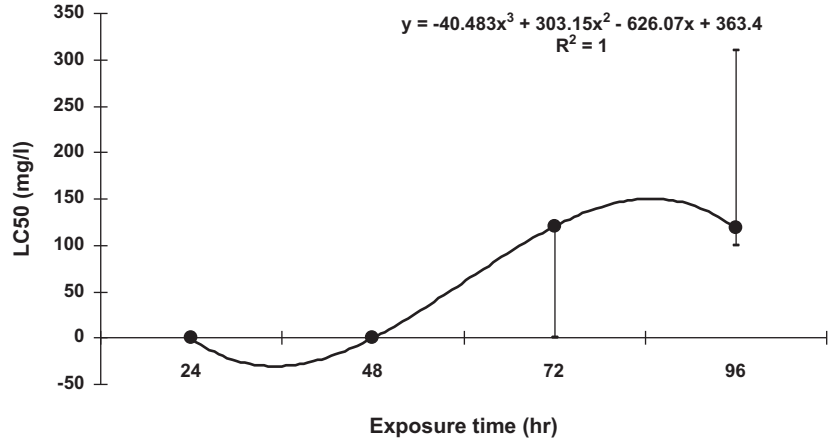

Fig. 3. LC_{50} samples obtained from the toxicity of synthetics on *D. magna* per time.

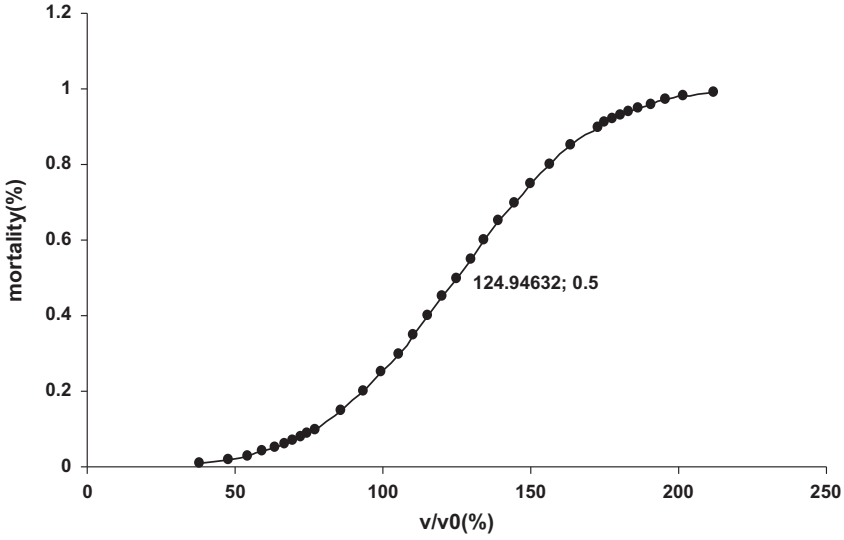

Fig. 4. Different volume percentages of death risk in samples of UV/ZnO nanophotocatalytic reactor and determination of LC_{50}–24 h.

According to the Figs. 4 and 5, LC_{50}–24 h is 124.95 mg/l (Fig. 4) and LC_{50}–48 h is 111.58 mg/L (Fig. 5), respectively.

Fig. 6 shows the expected results for the time period of 72 h. According to the Fig. 6, LC_{50}–72 h is 105.97 mg/L.

Fig. 7 presents the death probability of *D. magna* in different volumetric percentages of the samples taken from the effluent for the time period of 24 h. According to the Fig. 7, LC_{50}–96 h is 91.55 mg/l, which is lower than LC_{50}–24 h and LC_{50}–48 h, and LC_{50}–72 h.

Table 2 presents results of the bioassays conducted on the samples taken from effluent of the nanophotocatalytic process. LC_{50} and TU are given for all time periods of the experiments. LC_{50}–24, 48, 72, and 96 h are 124.9, 106, 111.6 and 91.55 mg/l, respectively. Corresponding values for TU are 0.8, 0.9, 0.94, and 1.1, respectively. According to the Table 2, LC_{50}–96 h is the lowest, implying that the toxicity is the highest in this time period. Fig. 8 illustrates LC_{50} values for the samples taken from the nanophotocatalytic process for different time periods of 24, 48, 72, and 96 h.

The results of the present study are consistent with those who decomposed dye and observed the increased toxicity [43]. Additionally, in case of black 5 dyes and disiprine orange 25 dyes [44] during advanced oxidation process, it was found that the toxicity increases after photolysis-hydrogen peroxide

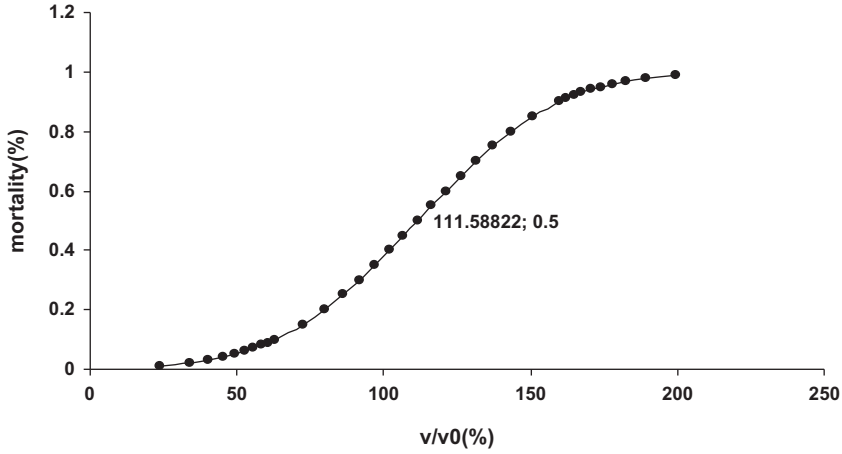

Fig. 5. Different volume percentages of death risk in samples of UV/ZnO nanophotocatalytic reactor and determination of LC_{50}–48 h.

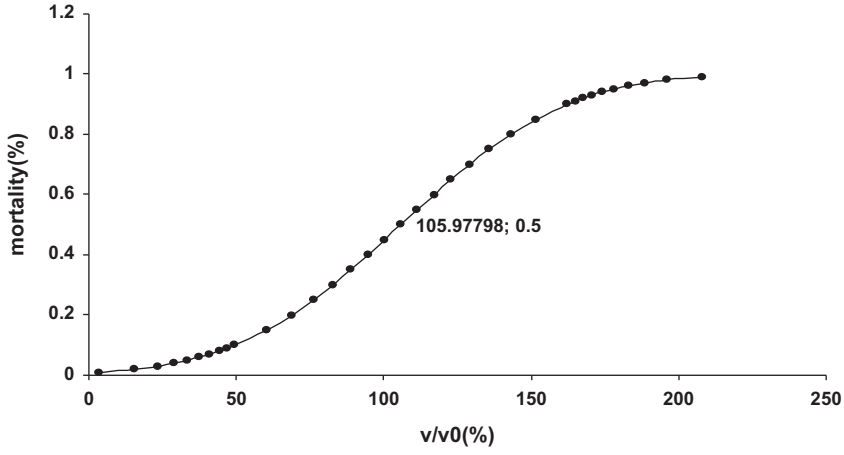

Fig. 6. Different volume percentages of death risk in samples of UV/ZnO nanophotocatalytic reactor and determination of LC_{50}–72 h.

process, even in 100% dye removal. This was reported to be possibly due to the presence of hydrogen peroxide in the samples.

3.1. Interpretation of the results of bioassay for determining the LC_{50}

In this step, three dye samples were synthesized in volumetric percentages of 10 to 100%. One sample was free of color (control sample). Each glass bottle contained 200 ml of the sample. Ten *D. magna* were released into each sample. When less than 10% of *D. magna* are dead in the control sample, the results can be considered as acceptable. However, no dead *D. magna* was found in the control sample.

LC_{50}–72 h and LC_{50}–96 h values were 120.44 and 118.6 mg/l, respectively. Corresponding values for TU were 0.82 and 0.84, respectively. The main objective for conducting these experiments was to determine LC_{50} values in different time periods and different volumetric percentages in dye concentration of 2 mg/L. According to this study, toxicity of the synthetic sample is lower than that taken from the reactor effluent.

According to LC_{50} and TU values, it can be concluded that toxicity increases during the nanophotocatalytic process. Besides, toxicity also increases with time. Nanophotocatalytic process is capable of destructing the color, so reduction of toxicity also decreases during the process. Increasing toxicity during the process is possibly due to production of

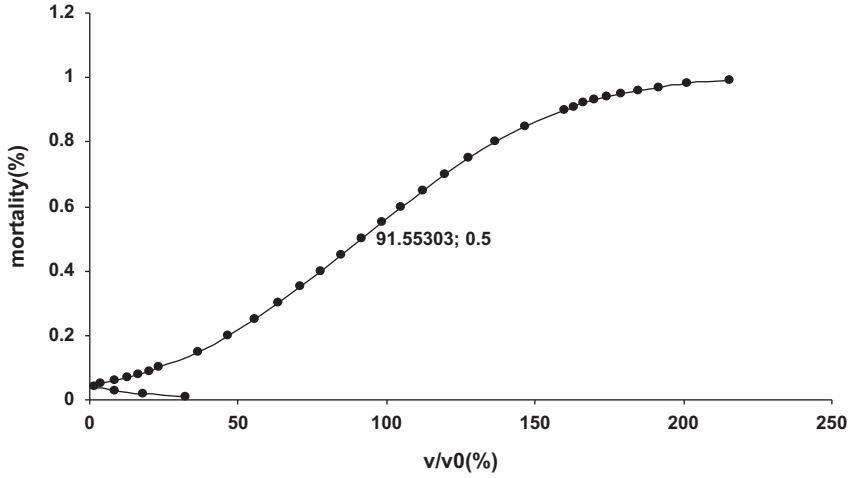

Fig. 7. Different volume percentages of death risk in samples of UV/ZnO nanophotocatalytic reactor and determination of LC_{50}–96 h.

Table 2
Data from toxicity testing on *D. magna* using samples of UV/ZnO nanophotocatalytic reactor

Parameters	Time(h)			
	96	72	48	24
LC_{50} (mg/L)	91.55	106	111.6	124.9
LC_{50} (mg/L) (95% confidence Limit; Upper bound)	129.9	156.3	173.9	303.5
LC_{50} (mg/L) (95% confidence Limit; Lower bound)	75.2	88.3	93.6	1.1
Toxicity Unit (TU)	1.1	0.94	0.9	0.8

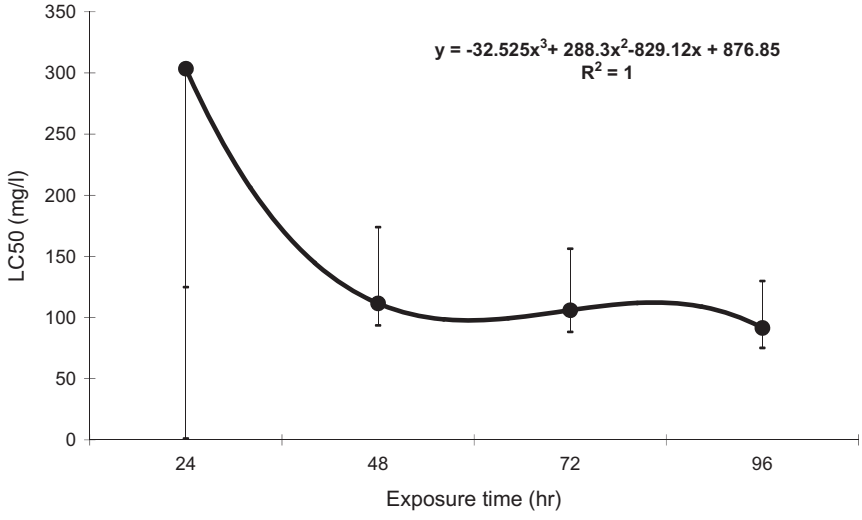

Fig. 8. LC_{50} samples obtained from the toxicity of samples of UV/ZnO nanophotocatalytic reactor on *D. magna* per time.

intermediate toxic compounds, presence of excessive hydrogen peroxide in the solution, presence of excessive ZnO in the solution, or ZnO toxicity [45–50].

4. Conclusion

Bioassays are considered as straightforward and inexpensive tests for determining the toxicity of the

samples. This approach can, therefore, be used for selection of the appropriate method for removal of the target pollutant. *D. magna* was used in this work for our objective. Dye removal in the UV/ZnO nanophotocatalytic reactor using ZnO nanoparticles leads to increased toxicity of the solution. Increasing toxicity during the process is possibly due to production of intermediate toxic compounds, presence of excessive hydrogen peroxide in the solution, presence of excessive ZnO in the solution, or ZnO toxicity or presence of excessive hydrogen peroxide in wastewater and consequent death of *D. magna*. The bioassays conducted on the acid-4092 dye in different time periods of 72 and 96 h. As can be seen, LC_{50} values for the time periods of 72 and 96 h are 120.5 and 118.6 mg/l, respectively. Corresponding values for TU are 0.82 and 0.84, respectively. The death probability of *D. magna* in different volumetric percentages for the time period of 72 h, the LC_{50}–72 h is determined to be 120.45 mg/l, implying that the dye solution is to some extent toxic. For the time period of 72 h and under volumetric percentages of 10–100%, numbers of dead *D. magna* were 0, 0, 0, 0, 0, 0, 1, and 1, respectively. Corresponding values for the time period of 96 h were 0, 0, 0, 0, 0, 0, 1, 1, 2, and 2, respectively. For control samples, no dead *D. magna* was found. Therefore, possible hazard of *D. magna* toxicity exists in any receptor ecosystem, raising the need for evaluating the toxicity of industrial dyes.

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