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Cytotoxicity reduction of wastewater treated by advanced oxidation process

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In this experiment the removal of printing dyes from textile printing industry effluents was carried out by Advanced Oxidation Process (AOP) in which heterogeneous photocatalytic treatment of textile printing wastewater using $UV/H_2O_2/TiO_2$ system was studied. For the treatment of textile effluents different concentration of titanium dioxide (TiO_2) and effect of application time of UV radiation was investigated. The degradation of treated wastewater was estimated spectrophotometrically. To check the extent of mineralization and decolorization after treatment water quality parameter such as percentage degradation, COD, BOD, TOC, pH, DO and toxicity were studied. Before treatment the values of water quality parameters were as; COD (1950 mg/L), BOD (963 mg/L), TOC (3410 mg/L), pH (9.6) and DO (1.77 mg/L). After application of $UV/H_2O_2/TiO_2$ degradation was observed to be 72% and reduction in COD, BOD, TOC were 58%, 57%, 48%, and increase in DO level was up to 49% respectively. For the evaluation of the toxicity of photocatalyticaly treated wastewater, *Allium cepa* and brine shrimp test were also carried out before and after treatment of printing wastewater.

Capsule Summary: Photo-degradation of textile printing wastewater was investigated and the treatment efficiency was evaluated on the basis of degradation, improvement of water quality parameter and cytotoxicity removal. The $UV/H_2O_2/TiO_2$ showed promising efficiency to hit the goal.

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INTRODUCTION

Environmental pollution is the discharge of any material or energy into land, water, or air that causes severe or persistent problems to the environmental balance. The random dispose of domestic and industrial effluents into water bodies and the use of newly invented chemicals without considering potential risks have resulted in main environmental calamities (Pera-Titus et al., 2004). Pollution is causing imbalance in ecosystems and today textile wastewater is severe threat to environment because of its toxic nature (Malato et al., 2009).

The textile industry produces large quantity of effluents and wastewater in dyeing and printing process which contains massive amount of coloring agents because of the remaining of reactive dyes, complex components and binders which are hard to be degraded. The textile printing wastewater contains high values of BOD and COD. As aquatic organisms require light in order to generate energy, the coloration in water prevents the penetration of light causing imbalance of ecosystem (Iqbal and Bhatti, 2014).

Now a day's different technologies are used for the treatment of textile industry printing wastewater. Different treatment includes flotation method, adsorption method, membrane separation method, nanofiltration method and electrochemical oxidation which have been used to minimize the toxicity that is caused by toxic substances present in textile wastewater (Prasad et al., 2011). But the most efficient of all is advance oxidation process (AOPs) due to its high degradation and mineralization efficiency.

In AOPs strong oxidizing agents such as hydroxyl radicals are produced at room temperature, which are very effective for the removal of chemical substances from industrial wastewater. There are different techniques to perform AOPs like by using Fenton reaction, Ozone oxidation process but photo-catalytic method is most promising among of all due to its high efficiency and cost effectiveness (Pang and Abdullah, 2013).

In photo-catalytic method gamma (γ rays), ultraviolet or visible radiation are used with some metal oxide like TiO_2 or ZnO_2 etc. as catalyst with H_2O_2 for the degradation of real textile effluents. But UV light is mostly used because these radiations are cheap and are less hazardous than the gamma (γ) radiations. The main objective of present study was to test $UV/H_2O_2/TiO_2$ on cytotoxicity reduction of textile printing wastewater.

MATERIALS AND METHODS

Wastewater samples were collected from three different textile printing industries in Faisalabad, Pakistan. The fabric printing consists of following steps: a) designing of fabric, b) scouting of fabric, 3) bleaching, 4) mercerizing, 5) printing of fabric with dyes, 6) mechanical finishing and 7) chemical finishing. In all these steps many inorganic and organic chemicals are used like dyes, detergents, softeners, binders and fixing agents. The color of samples was red, gray and indigo. The pH of samples was 10.1, 9 and 9.2, respectively.

TiO_2 (Degussa P25) was utilized as a photo-catalyst whose particle size is 25nm. Other chemicals used in this research such as H_2O_2 (35%), silver sulphate, mercuric sulphate, $K_2Cr_2O_7$ were of analytical grade. A UV lamp of, 44 watts intensity was used as the irradiation source and CECIL CE 7200 UV/Vis double beam Spectrophotometer used for spectroscopic analysis. For the evaluation of BOD_{5days}, Lovibond Ox.Direct BSB/BOD, for COD Lovibond $PC_{CHECKIT}$ COD vario with Lovibond incubator and for DO and pH evaluation digital Lovibond meter Senso Direct 150 was utilized. Photocatalytic degradation process was carried out by varying experimental parameters like pH, concentration of photocatalyst, concentration of H_2O_2 and UV exposure time. After experimentation percentage degradation was analyzed spectrophotometrically. Different water quality parameters like COD, BOD, TOC, DO and pH were also investigated.

The BOD of printing wastewater was calculated before and after treatment. Wastewater first homogenized and filtered, then according to manual of Lovibond Ox.Direct BSB/BOD range of BOD selected for 5 days. 56ml of each wastewater sample is filled in bottles of BOD meter with some nitrification inhibitor and 4-5ml of potassium hydroxide (KOH) in the cap of bottles. Magnetic stirrers were placed in bottles for 5 days continuous stirring.

For the determination of COD of textile printing wastewater Lovibond ET108/CSB reactor was used. Following the procedure 1.5 ml of digestion solution (2.6g potassium dichromate + 8.33g $HgSO_4$ in concentrated H_2SO_4) and 3.5ml of the catalytic solution (2.53g of silver sulphate in 250ml concentrated H_2SO_4) were subjected into COD vials and then 2.5 ml of sample solution was added in it. After this the COD vials were inserted in Lovibond incubator for 2hr at 150˚C for digestion. Vials were cooled down at room temperature once the digestion was completed. Absorbance was taken at 600nm on double beam spectrophotometer. After subtracting the absorbance value of standard and digested from the blank COD of the samples before and after treatment was found by using formula,

$$\text{COD} = \frac{\text{Absorbance of solution}}{\text{Absorbance of standard}} \times \text{Concentration of standard}$$

TOC of wastewater was calculated spectrophotometrically using glucose solution as standard. Sulfuric acid (1.6ml) was taken in vials after which added 1ml potassium dichromate solution (2N) and placed for incubation at 110˚C for one and half hour. After digestion samples were cooled down to room temperature and their absorbance was taken at 590nm with reference glucose solution. Then TOC was calculated using formula,

$$\text{Standard factor} = \frac{\text{concentration of glucose}}{\text{absorbance after incubation}}$$

TOC of samples = Standard Factor × Absorbance after incubation

Photocatalytic activity

Photo-catalytic activity was examined with the help of response surface methodology (RSM) by using central composite design in which different experimental variables like TiO_2 conc., H_2O_2 conc., pH, UV irradiation time and other biological parameters like COD, BOD, TOC and DO were monitored.

Textile printing wastewater was first filtered to remove contamination like cellulose or other insoluble impurities and then its absorbance was taken with the help of spectrophotometer. Photocatalyst (TiO_2) was then added, stirred for 30 min and subjected to UV radiation of 257nm wavelength using UV lamps having 44 watt intensity for 60 and 120 minutes. After treatment the samples were then centrifuged at 8000 rpm to elute out catalyst. Degradation efficiency was calculated using following formula,

$$\text{Degradation (\%)} = \frac{Ai - AF}{Ai} \times 100$$

Where Ai and A_f represents the initial and final absorbance of the samples respectively. Using central composite design different ranges like TiO_2 (4-8 mg), UV irradiation (1-2 hours), pH (3-9) and H_2O_2 (3-9 ml) were optimized.

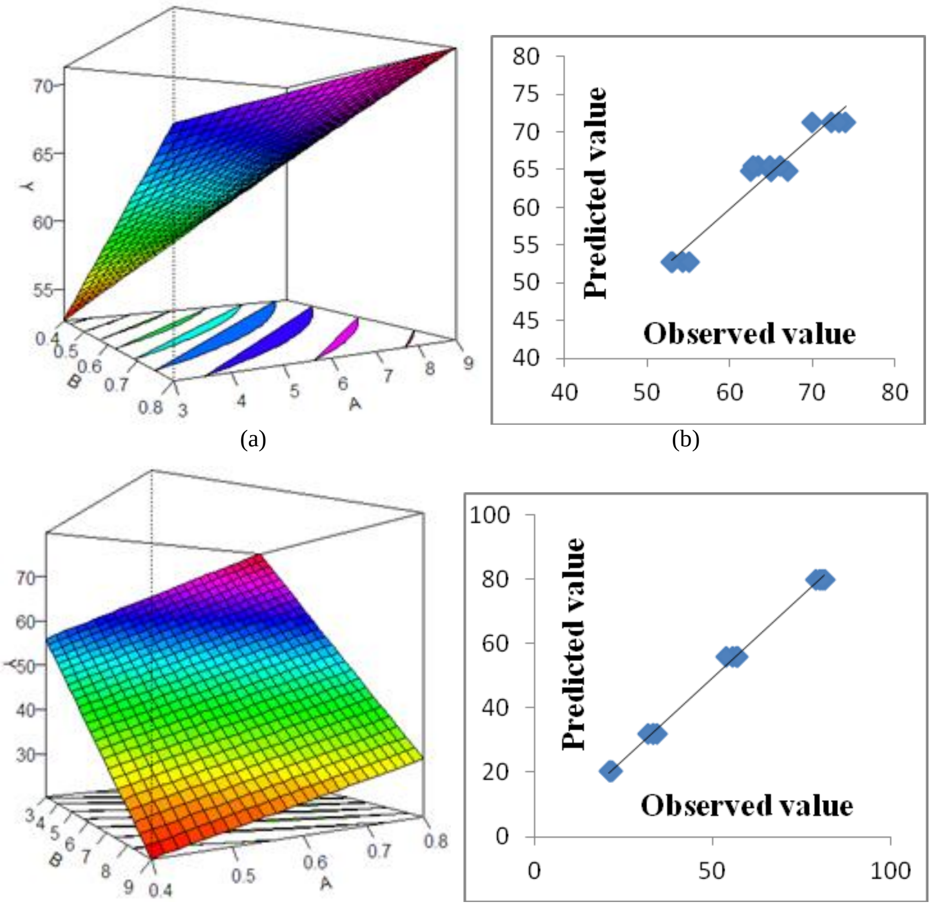

Fig. 1: (a) response surface (A-H_2O_2, B-TiO_2 and Y-degradation), (b) scatter plot (observed vs. predicted values, (c) response surface (A-TiO_2, B-H_2O_2 and Y-COD) and (d) scatter plot (observed vs. predicted values of COD removal)

Toxicity Evaluation

Hydroxyl radical generated from degradation of hydrogen peroxide, a bleaching agent, play a vital role in toxicity of textile wastewater which is catastrophic to aquatic life on exposure. To retard oxidizing effect of H_2O_2 manganese dioxide is added in treated samples and after 1 hr assessed for toxicity evaluation. Allium cepa test (abu and mba 2011) and Brine shrimp assay (Moshafi et al., 2010) were executed to analyze toxicity by reported methods.

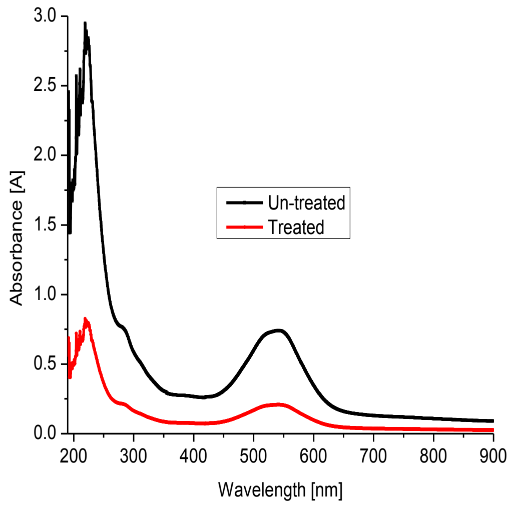

Fig. 2: UV-vis spectra of treated and untreated wastewater

Allium cepa test

Allium cepa (onion) was used to conduct toxicity test by its growth in wastewater before and after treatment. Similar sized and shaped onion bulbs were purchased from local market, Faisalabad. After gentle scrapping root primordia, onions were placed in tap water for germination. Five germinated bulbs were taken and subjected for analysis in positive control (methyle methane sulphonate) and negative control (Ultra-pure water) for 48 hours. The roots were then removed and put into acetone alcohol (1:3) solution. Afterword, under acidic conditions of 1 N HCl and at 60ºC

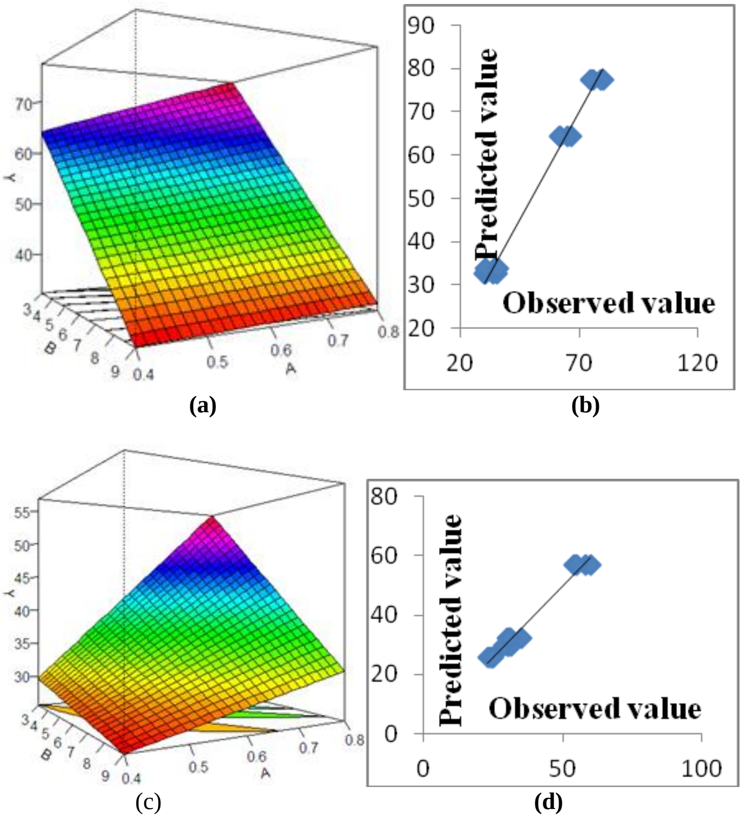

Fig. 3: (a) response surface (A-TiO_2, B-H_2O_2 and Y-BOD) and (b) scatter plot (observed vs. predicted values of BOD removal), (c) response surface (A-TiO_2, B-H_2O_2 and Y-DO) and (d) scatter plot (observed vs. predicted values of DO)

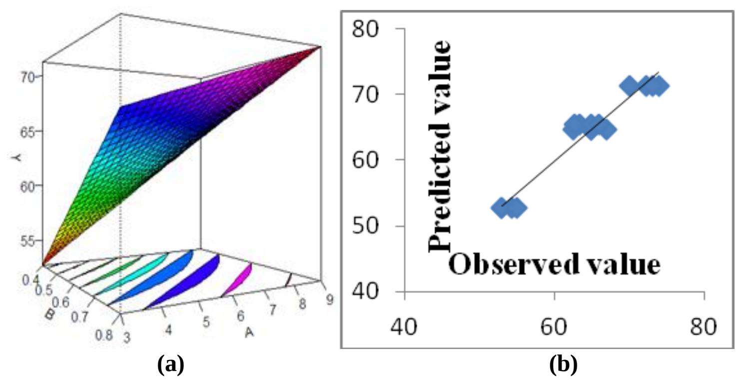

Fig. 4: (a) response surface (A-H_2O_2, B-TiO_2 and Y-TOC) and (b) scatter plot (observed vs. predicted values)

the root tips were hydrolyzed. Roots count, roots length and their average was then measured.

Shrimp bioassay

For shrimp lethality test, the procedure has been reported elsewhere (Iqbal et al., 2014).

RESULTS AND DISCUSSION

For statistical analysis and optimization of experiment response surface methodology was applied along with central composite design to get variable response within the ranged values and to optimize the experiment respectively (Table 2). Various experimental variables were optimized like TiO_2 concentration, H_2O_2 concentration, pH and UV exposure time as well as their effects on BOD, COD, TOC and DO was also investigated (Figs. 1-4).

Combined effect of TiO_2, H_2O_2 and UV on degradation of textile printing wastewater (TPWW)

Combined effects of H_2O_2, TiO_2 (Degussa P-25) and UV irradiation time as well as the relation between these parameters were studied and optimized using R. S. M. along with contour plots. Textile wastewater holds many toxic dyes, inorganic and organic salts that are hazardous to our ecosystem. The degree of degradation and mineralization of dyes depends upon the molar contaminant ratio. The maximum percentage of degradation and mineralization was achieved at ranges predicted by central composite design that are TiO_2 (0.8g/L), pH (3), H_2O_2 (9mL/L) and UV irradiation time (2 Hours). Some dyes present in wastewater are photo labile and often convert into more complex structure and hinders the complete degradation when exposed to UV radiations. So to increase the degradation process TiO_2/H_2O_2/UV system was implemented because a photocatalyst TiO_2 enhances the degradation process by many folds (Garcia et al., 2007). Photocatalyst acts as a precursor as it is thermally stable, have small band gap, and outstanding conducting properties for free electron generation which helps in hydroxyl radical, a strong oxidizing agent having oxidation potential 2.8eV. As radiations from visible region lack energy to excite electron from valence band to conduction band so radiation of wavelength below 365nm have shown increase in degradation efficiency. By the addition of a strong oxidizing agent i.e. H_2O_2 degradation increases by many folds as it clutches electron from conduction band and inhibits recombination of electron and positive hole. In current study maximum degradation was attained to be 72% which is comparable with results of literature surveyed (Ong et al., 2012). R. S. M. and contour

Table 1: Water quality parameters before treatment of wastewater obtained from three textile dyeing industries

Industries	pH	COD	TOC	BOD	DO
		mg/L	mg/L	mg/L	mg/L
1	10.1	1950	3100	963	0.92
2	9	1792	3255	895	1.13
2	9.17	1766	3410	874	1.77

Table 2: Experimental design

Runs	Conc.	Time	H_2O_2	TiO_2	pH
	mg/L	min	%	g/L	
1	50	60	3	0.4	9
2	100	60	3	0.4	3
3	50	120	3	0.4	3
4	100	120	3	0.4	9
5	50	60	9	0.4	3
6	100	60	9	0.4	9
7	50	120	9	0.4	9
8	100	120	9	0.4	3
9	50	60	3	0.8	3
10	100	60	3	0.8	9
11	50	120	3	0.8	9
12	100	120	3	0.8	3
13	50	60	9	0.8	9
14	100	60	9	0.8	3
15	50	120	9	0.8	3
16	100	120	9	0.8	9

plots help to study relations between independent variables and their interaction with dependent variables.

Effect of UV/H_2O_2/TiO_2 on water quality parameters

Various water quality parameters like BOD, COD, DO, TOC and pH were investigated before and after treatment of samples for ensuring the efficiency of the treatment using R.S.M. Contours and scatter plots explain treatment effectiveness, relation between dependent and independent variables as well as closeness between observed and predicted values. Results shown that COD, BOD, DO and TOC reduction by UV/H_2O_2/TiO_2 system was up to 80%, 77.5%, 57% and 72%, respectively.

Influence of TiO_2 dosage

Metal oxides are widely used in heterogeneous AOPs due to their small band gap and hence the promotion of electron from valence to conduction band is facilitated under UV/Vis light therefore they act as precursor of reaction. TiO_2 is a splendid photocatalyst, as its band gap is 3.2eV so radiation below 365 nm can promote electron from valence to conduction band leaving a positive hole in valence band which is essentially responsible for the production of hydroxyl radicals on reaction with oxygen, hydroxide ion, water and other such species. Electron upheld to conduction band also takes part in production of strong oxidizing species like per hydroxyl and superoxide radicals on reacting with dissolved oxygen. Dissolved oxygen takes part in reaction by two ways. Initially it accepts electron from conduction band and inhibits its recombination with positive hole. Secondly it produces per hydroxyl and superoxide radicals which have strong oxidation potential to degrade organic and inorganic toxins completely. Reaction mechanism involved in whole process is briefly described below (Gad-Allah et al., 2009).

$$TiO_2 + h\upsilon \rightarrow h^+ + e^- \quad (1)$$

Electron transfers to the electron hole from the adsorbed substrate (RX_{ad}), H_2O_{ad} or the OH_{ad} ion.

$$h^+ + RX_{ad} \rightarrow RX^+_{ad} \quad (2)$$

$$h^+ + H_2O_{ad} \rightarrow OH^\bullet_{ad} + H^+ \quad (3)$$

$$h^+ + OH^-_{ad} \rightarrow OH^\bullet_{ad} + H^+ \quad (4)$$

The last step is of much importance because presence of high concentration of OH^- as a result of dissociation of water.

$$H_2O \rightarrow OH^-_{ad} + H^+ \quad (5)$$

Molecular oxygen also accepts electron to form superoxide radical anion.

$$e^- + O_2 \rightarrow O^{\bullet -}_2 \quad (6)$$

Finally $OH^\bullet$ radicals and superoxide radical anion oxidize dyes and other pollutants on the surface of TiO_2 into mineral acids including carbon dioxide and water.

$$OH^\bullet_{ad} + dye \rightarrow product \quad (7)$$

$$O^{\bullet -}_2 + dye \rightarrow product \quad (8)$$

For the optimization of TiO_2 concentration, required to complete mineralize dye stuff in wastewater, different concentrations of TiO_2 (0.4-0.8g) were employed as per designed experiment. Low concentrations of TiO_2 were not much effective ensuring almost 53% degradation however high concentration (0.8g) of TiO_2 ensured 72% degradation

Table 3: Cytotoxicity of wastewater before and after treatment

	ACT		Shrimp
Before treatment	RC	RL	death
		cm	%
Industry 1	10±0.33	3.5±0.11	62±0.75
Industry 2	11±0.20	3.9±0.15	59±0.85
PC	17±0.80	7±0.38	100±0.0
After treatment			
Industry 1	21±1.1	5.6±0.37	8±0.10
Industry 2	23±1.0	5.9±0.40	11±0.06
Reduction (%)			
Industry 1	52	60	87
Industry 2	52	51	81

ACT-Allium cepa test, RC-root count, RL-root length, PC-positive control, For ACT, PC was methyl methanesulfonate (MMS) (10 mg/L), while for shrimp test, it was cyclophosphamide (10 µg/mL).

which is very effective at room temperature and beyond this concentration the degradation rate remain constant and on further addition the rate decreases. When the concentration of TiO_2 was increased beyond the optimum value, the rate of degradation decreased because of aggregation of TiO_2 particles leading to less surface area and less transparency of photo-reactor causing less light penetration.

Effect of H_2O_2 dosage

Addition of strong oxidizing agent enhances the rate of photo-catalytic reaction. H_2O_2 plays duel role in reaction, it entraps electron from conduction band of TiO_2 to prevent electron hole recombination and primarily plays its part in production of $OH^•$ radicals by mechanism shown as under.

$$H_2O_2 + O^{-2} \rightarrow HO^• + OH^- + O_2 \quad (9)$$

$$H_2O_2 + h\upsilon \rightarrow 2OH^• \quad (10)$$

$$H_2O_2 + e^-_{cb} \rightarrow HO^• + HO^- \quad (11)$$

$$RH + OH^• \rightarrow H_2O + R^• \rightarrow CO_2 + H_2O \quad (12)$$

Hydrogen peroxide was utilized 3-9% in present experiment according to experimental design. By addition of H_2O_2 the rate of degradation enhances up to certain limits then its effect remains constant. Maximum degradation at 9% H_2O_2 was observed to be 72%. Addition of more H_2O_2 leads to formation of hydroperoxyl radical ($HO_2^•$) whose oxidation potential is less than $OH^•$ and is unfavorable for reaction.

$$OH^• + H_2O_2 \rightarrow HO_2^• + H_2O \quad (13)$$

It also showed chromatographic peaking effect as it competes with organic load to occupy catalyst surface.

Effect of pH

Printing house wastewater contains wide range of pH values. So pH plays a vital role in complete degradation textile wastewater. Its effect can be explained on the basis of surface charge. Since point zero charge of TiO_2 was reported as 6.8 (Gad-Allah et al., 2009), so its surface is positively charged in acidic media while negatively charged in basic media. This can be explained by following equations.

$$TiOH + H^+ \rightarrow TiOH_2^+ \qquad pH < pH_{pzc} \quad (14)$$

$$TiOH + OH^- \rightarrow TiO^- + H_2O \qquad pH > pH_{pzc} \quad (15)$$

Where $pH_{PZC} = 6.8$.

At acidic pH it is obvious that adsorption of anionic dyes will be very high as surface of catalyst is positively charged and also the dyes containing benzene ring favors adsorption due to high electron density. At basic pH adsorption has no role as the surface of catalyst is negatively charged. Acidic pH also facilitates the production of hydroxyl radical because positive holes act as precursors in acidic pH for the formation of strong oxidizing species. It was witnessed that maximum degradation was observed pH 3 with TiO_2/H_2O_2/UV because of the effects discussed. By increasing pH, reverse of the process occurred because of repulsion between anionic dyes and catalyst surface (data not shown).

Cytotoxicity

Cytotoxicity test indicated cytotoxic nature of textile wastewater before treatment. After treatment the cytotoxicity decreased considerably evidencing that advance oxidation treatment is helpful in detoxification of wastewater (Table 3). Cytotoxicity was detected by *Allium cepa* and brine shrimp test as sown in table 3. It was observed that before treatment Root Count (RC) was 10±0.33 and Root Length (RL) was 3.5±0.11cm while percentage death of brine shrimp was 62±0.75. After treatment RC and RL were 21±1.1 and 5.6±0.37 respectively whereas percentage death of shrimp was 8±0.10%. Cytotoxic results indicated that after the treatment of wastewater it was much detoxified that it could be disposed out into the environment.

CONCLUSION

The TiO_2/H_2O_2/UV system is proved to be efficient enough to treat printing house wastewater. The conditions optimized were found to be 0.8g TiO_2 catalyst dose, 9% H_2O_2, 3 pH and UV irradiation for 2 hours. More catalytic dose led to reduction in efficiency of reaction due to high opacity inside the reactor as well as due to aggregation of photocatalyst. Low pH enhances the adsorption of dyes on photocatalyst and hence increases the reaction rate. H_2O_2 above the optimized condition led to reduction the reaction rate due to its scavenging effect. Under optimized conditions degradations and decolorization was achieved in 2 hrs. Cytotoxicity test proved that TiO_2/H_2O_2/UV system is efficient enough to detoxify printing wastewater and hence the wastewater can be eluted out into the environment after treatment. This treatment is applicable on industrial scale as it is efficient and cost effective. Further studies required in order to investigate different aspects like removal, reuse and surface area enhancement of photocatalyst.

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