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# RE-UTILIZATION OPTION OF INDUSTRIAL WASTEWATER TREATED BY ADVANCED OXIDATION PROCESS

**Munawar Iqbal[1] and Ijaz Ahmad Bhatti[2,*]**
**[1]National Centre of Excellence in Physical Chemistry, University of Peshawar, Peshawar-25120, Pakistan**
**[2]Department of Chemistry, University of Agriculture, Faisalabad-38040, Pakistan**
**[*]Corresponding author's e-mail: ijazchem@yahoo.com**

Present study was conducted to appraise the possibility of photo-catalytic detoxification of industrial wastewater samples. The waste water samples were subjected to ultra violet radiation in the presence of hydrogen peroxide and titanium dioxide in order to evaluate the treatment effect on the basis of cytotoxicity, mutagenicity, microbial load reduction and improvement in water quality parameters. The bioassays such as *allium cepa*, heamolytic and Ames tests were used to assess the cytotoxicity and mutagenicity. The photo-catalytic treatment, a state of the art technique, reduced the cytotoxicity and mutagenicity significantly and brought them within the permissible limit. Water quality parameters i.e. BOD, COD, DO, pH, TDS and TSS of waste water samples were also considerably improved. It is revealed that the advanced oxidation process can be successfully used for toxicity removal, improvement in water quality parameters and therefore, the processed wastewater could possibly be used for irrigation purposes.
**Keywords:** Photo-catalysis; water quality parameter; industrial waste water; bioassays and toxicity reduction

## INTRODUCTION

The discharge of industrial waste water containing broad spectrum of organic pollutants in the environment has been widely recognized as a potential environmental threat. The compounds usually reported in the aquatic environment are not only priority organic pollutants but also emerging pollutants (Camacho-Muñoz *et al*., 2014). The water bodies serve as temporary or final receptors of broad spectrum of organic pollutants, which are contaminating the watersheds and adjoining territories due to their ecotoxicological effects (Sponza, 2003; Bianchi *et al.*, 2011). Among the damages caused by chemical agents to exposed organisms, genotoxic and mutagenic effects have shown to be worrying, which can lead to several health problems and also affect future generations due to inheritable alterations in genetic material. Genetic toxicology involved in detecting compounds capable of causing genetic damage with the aim of understanding potential biological effects (Leme and Marin-Morales, 2008; Leme and Marin-Morales, 2009).

The waste discharged from industries enter into the water bodies in several different ways, either dumped directly or from waste water treatment plants that do not fulfill their obligations. Almost all kinds of substances can be transported and distributed more easily in the water cycle due to nature of water that makes it universal solvent (Oller *et al.*, 2011; Bai *et al.*, 2012; Bilal *et al.,* 2014). The safe disposal of industrial waste water is one of the major ecological challenges. Therefore, environmental degradation has now become a global problem and maintains the ecosystem is a serious issue. Due to mixing of untreated waste water with watersheds, the water bodies become polluted and are responsible for negative impacts on soil and aquatic life. Disposal of industrial effluents into fresh water bodies disturb water quality parameters such as BOD, COD, DO, color, pH etc., which are necessary to sustain aquatic life, primary productivity and food chain (Rao *et al.*, 2001; Auriol *et al.*, 2006). If the safety of waste water discharged from industries is assured by industrialists or by pollution control boards, then treated industrial waste water may be potentially used for fish production, irrigation for non-edible cash crop, industrial re-use and for many other multifarious uses (Singh and Singh, 2006; Molinos-Senante *et al.*, 2011; Iqbal *et al.,* 2013ab; Manzoor *et al.,* 2013).

As a result of exposure to contaminated water containing toxic agent, negative impact ranging from cytotoxicity to mutagenicity in various models (plants and animal) have been documented well (Grisolia *et al.*, 2004; Leme and Marin-Morales, 2008; Hoshina and Marin-Morales, 2009; Leme and Marin-Morales, 2009). Toxic pollutants screening in environmental samples using method *in vitro* are reliable to measure the extant of pollution load and this biological assessment is compulsory for effluent monitoring, discharged from industries before being mixed with water bodies (Rodrigues *et al.*, 2010; Margot *et al.*, 2013). To manipulate with these problems, different waste water treatment technologies have been proposed and efforts have been devoted to develop the analytical methods for emerging contaminants in environmental samples. In addition, various bioassays using aquatic organisms or recombinant cells have also been applied to assess the toxicity elicited by mixtures of wastewater-related contaminants, such as oxidative stress, estrogenicity, cytotoxicity, mutagenicity and genotoxicity (Chou *et al*., 2014).

Keeping in view the degradation efficiency of advanced oxidation process, it was hypothesized that it can be used for the detoxification of industrial waste water. The textile waste water collected from different industries were subjected to ultra violet radiation in the presence of hydrogen peroxide and titanium dioxide and the treatment effects were evaluated on the basis of toxicity reduction and improvement in water quality parameters.

## MATERIAL AND METHODS

***Sample collection*:** The waste water samples were collected from three different textile industries from the vicinity of Faisalabad following standard sampling methods (Eaton *et al*., 2005). Plastic gallon were pre-cleaned by soaking in nitric acid 1% v/v for 24 h and then rinsed with distilled water three times. The collected waste water samples were transported and refrigerated (4°C) in the Radiation Chemistry Laboratory, University of Agriculture, Faisalabad, Pakistan.

***Treatment procedure*:** The UV radiation source used for sample irradiation was a low pressure UV lamp having 44 Watt intensity emits radiation of wavelength 253.7 nm (Galvano Scientific, Pakistan). All samples were irradiated at room temperature and for irradiation; the solutions were projected at the bottom of the reactor at a distance of 6 cm. All independent variables were optimized using factorial design by analyzing the data through response surface methodology (Iqbal *et al.,* 2013c). For toxicity evaluation, the waste water samples were treated at optimized conditions.

***Water quality parameter measurement*:** The water quality parameters such as pH, DO, BOD and COD were measured using pre-calibrated pH, DO, BOD and COD and COD meters. The TSS and TDS were estimated following the methods reported elsewhere (Eaton *et al*., 2005). Briefly, well-mixed samples were filtered, evaporated to dryness in a pre-weighed china dish and dried to constant mass at 180°C. The increase in dish weight represents the TDS which was measured using relation given below. Where A = mass of dried residue + dish (mg) and B = mass of dish (mg). For the measurement of TSS, a well-mixed sample was filtered in filter paper of known mass. The filter paper was kept for 1 h at 105°C in an oven, cooled, weighed and TSS was measured by equation given below;

$$TDS\ or\ TSS = \left[\frac{A-B}{V(mL)}\right] x1000$$

All water quality parameter were reported as percentage decrease or increase and were calculated using following equation; where *A* and *B* are representing water quality parameter value before treatment and after treatment, respectively.

$$WQP\ (\%) = \left[\frac{A-B}{B}\right] x100$$

***Toxicity evaluation*:** To avoid the toxic effect of hydrogen peroxide, it was removed from treated samples by adding small amounts of $MnO_2$ (< 1 mg/mL) to the solution (Weihua *et al.*, 2002). After a reaction time of 1 h, the solutions were filtered and subjected to the toxicity tests such as microbial laod, *Allium cepa*, heamolytic, brine shrimp and Ames bioassays. The $TiO_2$ was also separated before toxicity evaluation by centrifugation at 14000 rpm for 5 min and supernatant thus collected, was used for toxicity evaluation.

**Cytotoxicity:**

***Allium cepa* test:** The onion bulbs of equal size of same species were purchased from local vegetable market, Faisalabad, Pakistan. The bases of the bulbs were gently scrapped and root primordia were exposed to the test solution. Before transformation of bulbs in tested solution, bulbs were germinated in tap water and finally, best five were transferred in waste water along with negative and positive controls. The germinated bulbs were kept in solution for 48 h and the tested samples were replaced with the gap of 6 h. Ultra-pure water was used as a negative control and methyl methanesulfonate (MMS) (Sigma-Aldrich) was used as a positive control. The roots were harvested after period of 48 h and transferred in aceto-alcohol (1:3). The root tips were hydrolyzed in 1N HCl at 60°C until they become soft and number of roots and their lengths were counted, measured and values thus obtained were averaged (Iqbal *et al.,* 2014).

***Heamolytic assay*:** For heamolytic assay, Powell *et al.* (2000) procedure was adopted with slight modification. The sheep blood cells were gently mixed, poured into a sterilezed polystyrene (15 mL) screw-cap tube (15 mL) and centrifuged for 5 min at 4000 rpm. The supernatant was decanted and the viscous pellet was washed three times with chilled sterile isotonic phosphate buffer saline (PBS) solution (NaCl, 8 g/L; $KH_2PO_4$, 0·2 g/L; $Na_2HPO_4$, 1·2 g/L; and KCl, 0·2 g/L). The pH was adjusted to 7·4 using 1M NaOH and 1% HCl solution. The washed cells were suspended in 20 mL chilled, sterile PBS and the cells counted on a haemacytometer. The blood cell suspension was maintained on wet ice and diluted with sterile PBS to $7{\cdot}068 \times 10^8$ cells m/L for each assay and sample (20 µL) was aseptically poured into 1.5 mL appendrof tubes. For each assay, 0·1% Triton X-100 and PBS were used as the positive negative control, respectively. Diluted blood cell suspension (180 µL) were aseptically poured into tube and gently mixed. Appendrof tubes were incubated for 35 min at 37°C with agitation (80 rev/min) and were immediately placed on ice for 5 min and finally centrifuged for 5 min at 1310 x *g*. The supernatant was collected, placed into a sterile appendrof tube and diluted with 900 µL chilled and sterile PBS. All tubes were maintained on wet ice after dilution and absorbance were measured at 576 nm (BioTek, Winooski, VT, USA). All the samples were run in triplicate and results

were averaged. The percentage lysis of RBC was calculated using following relation; where A and B are representing absorbance of sample and triton X-100, respectively (Iqbal *et al.,* 2014).

$$RBC\ lysis\ (\%) = \left[\frac{A}{B}\right] x100$$

***Brine shrimp assay*:** Brine shrimp (*Artemia salina* L.) eggs were hatched in artificial seawater. After 48 h of incubation at 26-30$^0$C under constant aeration, the larvae (nauplii) were attracted to one side of the vessel with a light source, collected and transferred to the tested solution. Waste water samples diluted two times with artificial seawater and total volume was finally adjusted to 5 mL and 100 mL of suspension of nauplii containing 20 larvae were incubated for 24 h. The tubes were then examined under a magnifying glass and the numbers of dead nauplii were counted. Cyclophosphamide (10 µg/mL) was used as a positive control in all experiments. The percentage lethality was determined by comparing the mean surviving larvae of the test and controls (Iqbal *et al.,* 2014).

***Ames test (mutagenicity assay)*:** The Ames test was performed in agar plate as precisely reported elsewhere (Maron and Ames, 1983). The plates were sealed in plastic bags and incubated at 37 $^0$C for 4 days. The blank plate was observed first and the rest of plates were read only when all wells in the blank plate showed purple color indicating that the assay was not contaminated. The background, standard, and test plates were scored visually and all yellow, partial yellow or turbid wells were considered as positive wells (Iqbal *et al.,* 2014).

## RESULTS AND DISCUSSION

The observed values of pH, DO, COD, TDS and BOD were recorded to enough high in comparison to international standards and were beyond the permissible limits required for sustain aquatic life in aqueous environment (Table 1). The pH, DO, COD, TDS and BOD of textile waste water were found in the following range; 11.4-11.8, 1.5-2.2 mg/L, 1700-2100 mg/L, 1380-1590 mg/L, TSS 400-505 mg/L and 635-800 mg/L, respectively. After evaluation of water quality parameters, textile waste water samples were treated photo-catalytically at pre-optimized conditions for the evaluation of detoxification. The detoxification effect was evaluated on the basis of biological and toxicological tests such as microbial load, heamolytic, shrimp, *allium cepa* and Ames tests.

***Advanced oxidation treatment effect on toxicity reduction*:**

**Table 1. Water quality parameters of textile industry wastewater before and after treatment**

| S. No. | pH | DO (mg/L) | COD (mg/L) | TDS (mg/L) | TSS (mg/L) | BOD (mg/L) |
|---|---|---|---|---|---|---|
| **Industry I (n = 3)** | 11.8±0.63 | 1.5±0.5 | 2100±75.5 | 1380±51.10 | 400±95.00 | 800±55 |
| **Industry II (n = 3)** | 11.4±0.53 | 1.8±0.6 | 1800±81.5 | 1590±85.60 | 505±56.60 | 740±35 |
| **Industry III (n = 3)** | 11.6±0.58 | 2.2±0.9 | 1700±84.2 | 1425±70.00 | 460±54.55 | 635±60 |
| **WQP improvement** | 6.8 | 55% | 81% | 60% | 65% | 75% |

DO-dissolve oxygen, COD-chemical oxygen demand, BOD-biological oxygen demand, TDS-total dissolves solid, TSS-total suspended solid and WQP-water quality parameter

**Table 2. Microbial load and cytotoxicity profile of textile wastewater before and after treatment**

| | Microbial test | | *Allium cepa* | | *Heamolytic* | *Shrimp test* |
|---|---|---|---|---|---|---|
| **Before treatment** | **TBC** | **T coliform** | **RC** | **RL** | **Cell death** | **death** |
| | **CFU** | **CFU** | | **cm** | **%** | **%** |
| **Industry I (n=3)** | >1 x $10^6$ | 1 x $10^5$ | 10±0.15 | 4.1±0.06 | 81±1.6 | 68±0.80 |
| **Industry II (n=3)** | >1 x $10^6$ | 1 x $10^5$ | 9±0.25 | 3.9±0.04 | 78±1.8 | 64±0.85 |
| **Industry III (n=3)** | >1 x $10^6$ | 1 x $10^5$ | 11±0.20 | 3.8±0.05 | 72±1.9 | 54±0.81 |
| **PC** | ---- | ---- | 17±0.26 | 9.0±0.15 | 100±0.0 | 100±0.0 |
| **NC** | 0.000 | 0.000 | 08±0.20 | 2.5±0.04 | 0.0000 | 0.0000 |
| **After treatment** | | | | | | |
| **Industry I (n=3)** | ND | ND | 18±0.36 | 7.5±0.15 | 40±3.00 | 25±1.20 |
| **Industry II (n=3)** | ND | ND | 17±0.38 | 6.9±0.30 | 44±2.90 | 22±1.11 |
| **Industry III (n=3)** | ND | ND | 17±0.55 | 7.5±0.60 | 49±3.20 | 19±2.10 |
| **% reduction** | | | | | | |
| **Industry I (n=3)** | 100 | 100 | 44.44±0.9 | 45.33±1 | 50.61±1.20 | 63.23±1.00 |
| **Industry II (n=3)** | 100 | 100 | 47.05±0.8 | 43.47±1 | 43.58±1.23 | 65.62±1.50 |
| **Industry III (n=3)** | 100 | 100 | 54.54±1.0 | 49.33±1 | 32.00±0.90 | 64.81±1.03 |

TBC-total bacterial count, TC-total coliform, ACT-*Allium cepa* test, RC-root count, RL-root length, ND-not detected, PC-positive control, NC-negative control, n-sample seeded in triplicate; For heamolytic test, PC and NC were TritonX-100 (0.1%) and phosphate buffer saline, respectively; For ACT, PC and NC were distilled water and methyl methanesulfonate (MMS) (10 mg/L), respectively; For shrimp test, PC and NC were cyclophosphamide (10 µg/mL) and sea water, respectively

The results of microbial load and cytotoxicity reduction are shown in Table 2. Pre-optimized conditions such as UV radiation intensity (44 Watt), $TiO_2$ (5.93%) and $H_2O_2$ concentration (4.39%) at shaking speed of 150 rpm and UV exposure for 100 min were used to treat waste water and subjected to toxicity evaluation. As a result of advanced oxidation treatment, the microbial load such as total bacterial count and total coliform reduced to zero. The total bacterial and total coliform population was recorded to be $>1 \times 10^6$ and $>1 \times 10^5$ CUF before treatment, whereas it reduce to zero when waste water was treated at optimized conditions (Table 2). Regarding cytotoxicity, very interesting results were obtained. The *allium cepa* test showed that the UV treatment in the presence of hydrogen peroxide and titanium dioxide showed promising efficiency to reduce the cytotoxic effect of textile waste water. Before treatment the number of roots and root lengths were recorded to be in the range 9-11 and 3.8-4.1 cm, respectively and after treatment, there was a significant increase in number of roots and root lengths. The maximum increase in root number and root lengths were recorded to be 54.54% and 49.33%, respectively. The significant reduction in cytotoxicity was also confirmed by heamolytic and brine shrimp assays. Before treatment, the red blood cell (RBC) death was up to 81% and after treatment, the value reduced considerably. The maximum reduction in RBC death was recorded to be 50.61% (Table 2). Brine shrimp test also showed a significant reduction in cytotoxicity. The brine shrimp nauplii death before treatment was recorded up to 68% and after treatment nauplii death rate decreased considerably and up to 65.62% reduction in shrimp death was observed (Table 2).

The waste water samples before treatment showed mild mutagenicity and after treatment, mutagenicity was not observed. A maximum of 62 plates in case of TA98 and 68 plates for TA100 were affected. After advanced oxidation treatment, the mutagenicity reduced significantly. Maximum number of plates affected in case of TA98 and TA100 were 31 and 36, respectively. The percentage reduction in mutagenic activity of treated waste water samples was recorded to be 54.83% (TA98) and 58.82% (TA100), respectively (Table 3). From the results of Ames assay, it can be concluded that advanced oxidation process has the ability to reduce the mutagenic activity of mutagenic agent.

In the last years, different AOP's have been investigated for the removal of emerging contaminants from urban waste water effluents (Naddeo *et al.*, 2011) and drinking water (Sanches *et al.*, 2010). Unfortunately, the partial oxidation of organic contaminants may result in the formation of more toxic intermediates than parent compounds. In order to avoid this drawback, AOP's are expected to be carefully operated and monitored, and toxicity tests should be used to evaluate toxicity of treated effluent (Rizzo *et al.*, 2009). Literature survey indicate that advanced oxidation processes based on photo-catalysis have been used successfully for the treatment of waste water and resultantly, a significant degradation and mineralization of organic pollutants have been reported. However, the studies regarding toxicities evaluation of treated wastewater by AOP are rare. On the other hand, the water quality parameters such as pH, DO, BOD, COD, TDS, and TSS are generally used for quality assurance. However, these parameters cannot be considered for evaluation of toxicity. Therefore, the bioassays application is the best way to evaluate the toxicity treated wastewater (Tchobanoglous *et al.*, 2003; Movahedian *et al.*, 2005; Leme and Marin-Morales, 2009). It is reported that the effluent meets all physicochemical requirements, may cause considerable negative effects on living organisms because during treatment some toxic compound may produce (Radix *et al.*, 2000; Movahedian *et al.*, 2005; Leme and Marin-Morales,

**Table 3. Mutagenicity of wastewater samples evaluated through Ames test**

| | TA98 | | TA100 | |
|---|---|---|---|---|
| | **Affected plates** | **Total plates** | **Affected plates** | **Total plates** |
| **Industry I (n=3)** | 62±2 | 96 | 68±2 | 96 |
| **Industry II (n=3)** | 59±2 | 96 | 63±2 | 96 |
| **Industry II (n=3)** | 60±1 | 96 | 61±3 | 96 |
| **PC** | 19±2 | 96 | 21±2 | 96 |
| **NC** | 00.000 | 96 | 00.000 | 96 |
| **After treatment** | | | | |
| **Industry I (n=3)** | 28±1 | 96 | 28±2 | 96 |
| **Industry II (n=3)** | 29±1 | 96 | 35±1 | 96 |
| **Industry III (n=3)** | 31±1 | 96 | 36±1 | 96 |
| **% reduction** | | | | |
| **Industry I (n=3)** | 54.83 | - | 58.82 | - |
| **Industry II (n=3)** | 50.84 | - | 44.44 | - |
| **Industry III (n=3)** | 48.33 | - | 40.98 | - |

PC = positive control, NC = negative control: For Ames test, PC for TA98 and TA100 were $K_2Cr_2O_7$ (0.01 g/L) and $NaN_3$ (0.5 µg/100 µl), respectively and background (without standard and tested compound) was used as NC

2009; Oliveira-Martins and Grisolia, 2009). Few studies highlighted this issue that the toxicity of industrial waste water after the application of AOPs can be reduced (Gomes de Moraes *et al.*, 2000; Tezcanli-Guyer and Ince, 2003; Andreozzi *et al.*, 2004; Selcuk, 2005; Pérez *et al.*, 2006; Mahmoodi and Arami, 2009). In view of importance of AOP, the present study was performed whether the treated waste water samples were detoxified or not. The toxicity of effluents was evaluated through cytotoxicity and mutagenic assays. The microbial population before and after application of AOP treatment was also performed and it was found that the AOP was able to reduce the microbial load completely. Similarly, the cytotoxic and mutagenic assay also showed that the waste water samples were safe after treatment. Other than reduction in cytotoxicity and mutagenicity of waste water samples, the water quality parameters were also improved significantly. The maximum improvement in water quality parameter was recorded where sample were treated by UV radiation (44 watt) for 100 min using $H_2O_2$ (4.39%) at shaking speed of 150 rpm having 3% concentrations of $TiO_2$. As a result of degradation of pollutant present in waste water, the reduction in COD and BOD were observed up to 81% and 75% for 3% $TiO_2$ concentration. The pH of the solution reduced after advanced oxidation treatment which is considered as a good efficiency of the treatment because when pollutant are degraded and converted into organic acids, resultantly pH of solution may decrease slightly. Before treatment the pH of waste water was in the alkaline range reduced significantly after treatment and solution showed mild acidic pH (6.8) which is the indication of complete conversion of pollutant in to carbon dioxide and water. Similarly, the TDS and TSS values of waste water samples were also reduced considerably.

It has been reported that advanced oxidation treatment of waste water showed significant effect on toxicity reduction and improved the water quality parameters as well (Andreozzi *et al.*, 2004). In the present study, the efficiency of UV treatment in the presence of $TiO_2$ along with hydrogen peroxide was found promising and similar results have also been reported previously (Gomes de Moraes *et al.*, 2000; Tezcanli-Guyer and Ince, 2003; Andreozzi *et al.*, 2004; Selcuk, 2005; Pérez *et al.*, 2006; Mahmoodi and Arami, 2009). Some author studied the toxicity of treated water by other bioassays. However positive results have been reported. Toxicity of four types of industrial waste water, treated by Fenton's reagent, was analyzed using bioluminescent bacteria *Vibrio fischeri* NRRL B-11177 (Barbusiski, 2005), microtox test (Koparal *et al.*, 2007) and *Daphnia magna* for textile dyes synthetic solution (Selcuk, 2005). All these authors also pointed out that the AOPs could successfully be used for the detoxification of toxic pollutant in effluents and processed water can be re-utilized for sustainable agriculture production (Maqsood *et al.,* 2013; Iqbal *et al.,* 2014) and is also environmental friendly (Ullah *et al.,* 2013). Currently, the agriculturists are researching for eco-friendly agricultural practices (Perveen *et al.,* 2011; Iqbal *et al.,* 2012ab; Jamil *et al.,* 2012; Naz *et al.,* 2012; Jamil *et al.,* 2013; Zia *et al.,* 2012) and AOP application for the detoxification of wastewater is also one of the sustainable agricultural practices to conserve water resources for sustainable agriculture growth.

***Conclusions*:** The advanced oxidation process ($UV/H_2O_2/TiO_2$) showed promising efficiency for the detoxification of textile wastewater samples. The cytotoxicity, mutagenicity and microbial load reduced significantly. The water quality parameters were also improved considerably. However, to enhance the treatment efficiency, there is need to optimize the treatment conditions. From results of detoxification and improvement in water quality parameters, it is concluded that this treatment is able to detoxify the toxic pollutant and the treated waste water could possibly be suitable for industrial reuse, irrigation and for aquaculture etc.

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