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Mutagenicity and cytotoxicity evaluation of photo-catalytically treated petroleum refinery wastewater using an array of bioassays

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HIGHLIGHTS

- Advanced oxidation processes for the treatment of refinery wastewater were investigated.
- Independent variables were optimized through response surface methodology.
- The toxicity and mutagenicity profiles of raw and treated wastewater were evaluated.
- The investigated method was found to be very promising for the de-contamination and detoxification of toxic agents in wastewater.

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ABSTRACT

Degradation and detoxification of petroleum refinery wastewater (PRW) was carried out by advanced oxidation processes (UV/TiO_2/H_2O_2 and gamma radiation/H_2O_2). Response surface methodology (RSM) was used to optimize the independent variables. The cytotoxicity was evaluated using *Allium cepa*, brime shrimp and haemolytic assays; whereas mutagenicity was tested by Ames tests (TA98 and TA100 strains). Maximum reductions in COD and BOD were recorded as 78% and 87% for UV/TiO_2/H_2O_2 and 77% and 86% for gamma ray/H_2O_2, respectively. Treatments with both methods at optimized conditions reduced the cytotoxicity and mutagenicity of PRW, however, UV/TiO_2/H_2O_2 system was found slightly efficient as compared to gamma ray/H_2O_2. From the results, it can be concluded that AOP's can successfully be utilized for the degradation of toxic pollutants in petroleum refinery wastewater. Moreover, the bioassays used in this study offered a good reliability for checking the detoxification of treated and un-treated PRW wastewater.

1. Introduction

Wastewater from petroleum refinery has high concentration of aliphatic and aromatic hydrocarbons, which could lead to heavy pollution of soil and rivers. The quantity and characteristics of wastewater generated depend on the process configuration (Shahrezaei et al., 2012a; Hassan, 2016; Majolagbe et al., 2016; Peter and Chinedu, 2016). Phenol and phenolic derivatives in the petroleum refinery effluents pose a significant threat to the environment

Abbreviations: PRW, Petroleum refinery wastewater; UV, Ultra violet; TiO_2, Titanium dioxide; H_2O_2, Hydrogen peroxide; RSM, Response surface methodology; COD, Chemical oxygen demand; BOD, Biological oxygen demand; AOP's, Advanced oxidation processes; •OH, Hydroxyl radical; CCD, central composite design; TDS, Total dissolved solid; TSS, Total suspended solid; WQP, Water quality parameters; DO, dissolved oxygen; kGy, kilo Gray.

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due to their extreme toxicity, stability, poor biodegradability and ability to remain in the environment for longer period (Kavitha and Palanivelu, 2004). As a result of exposure to contaminated water bodies from industries, negative impact ranging from cytotoxicity to mutagenicity in various models (plants and animals) have been documented (Leme and Marin-Morales, 2008; Hoshina and Marin-Morales, 2009; Leme and Marin-Morales, 2009; Iqbal, 2016). So, there is need to develop efficient and economical methods to treat PRW for the degradation of toxic pollutants before being discharged into water bodies (Sayed, 2015; Adesola et al., 2016; Babarinde and Onyiaocha, 2016; Jafarinejad, 2016; Ukpaka, 2016a, 2016b).

The PRW has a very complex nature (Wake, 2005; Al Zarooni and Elshorbagy, 2006; Diyauddeen et al., 2011) and for the degradation of pollutants, different methods and technologies have been practiced e.g. sedimentation/flotation (Thompson et al., 2001), coagulation and precipitation (Fu and Wang, 2011), adsorption (Mahmoodi et al., 2011; Manzoor et al., 2013; Ullah et al., 2013), oxidation (Oller et al., 2011) and membrane filtration (Judd and Judd, 2011), biological treatment-aerobic treatment (Chan et al., 2009), integrated treatment processes (Pokhrel and Viraraghavan, 2004) and bioremediation (Fratila-Apachitei et al., 2001). However, all these methods suffered with many drawbacks vis-à-vis disposal of spent contaminated activated sludge, control of appropriate reaction conditions, low efficiencies and operation within a narrow pH range (Shahrezaei et al., 2012a).

In recent years, the AOPs have been employed for wastewater treatment; especially for the degradation and mineralization of organic compounds. During AOPs treatment, strong oxidizing species like •OH are produced *in situ*, which break down the complex organic molecule into harmless end products such as CO_2, H_2O and inorganic ions through a chain reactions (Rauf et al., 2008; Rauf and Ashraf, 2009). The AOPs are very easy to handle, produce less residual as compared to classical treatment approaches and can successfully be employed for color removal, mineralization of toxic chemicals and industrial wastewater treatment (Rauf et al., 2008; Rauf and Ashraf, 2009). Hence, in view of the higher efficiency of AOPs, a number of studies have been undertaken for the treatmment of industrial wastewater (Hachem et al., 2001; Ledakowicz et al., 2001; Gupta et al., 2012; Sayed, 2015). Moreover, several researchers have also reported the effectiveness of AOPs for detoxification of industrial wastewater (Ledakowicz et al., 2001; Karci et al., 2013).

Keeping in view the previous studies, it was hypothesized that AOP would have promising efficiency for the detoxification and mineralization of toxic compounds present in PRW wastewater. Therefore, the present study was designed to explore the possibility of AOP's (gamma radiation/H_2O_2 and UV radiation/H_2O_2/TiO_2) for the degradation and detoxification of PRW. The treatment efficiencies were evaluated on the basis of degradation, water quality improvement and detoxification. The independent variables such as pH, TiO_2 concentration, H_2O_2 concentration, UV reaction time, shaking speed and gamma radiation absorbed doses were optimized through RSM.

2. Material and methods

2.1. Chemicals and reagents

The catalyst TiO_2 (80% anatase and 20% rutile, Degussa P25, surface area of 50 m^2/g), H_2O_2 (30%), TritonX-100 (laboratory grade), methyl methanesulfonate (99%), $K_2Cr_2O_7$ (99%), NaN_3 (99%), MnO_2 (≥99%), H_2SO_4 (98%) and NaOH (≥97%) were purchased from Sigma-Aldrich, whereas cyclophosphamide monohydrate (99%) was purchased from Wuhan Dahua Pharmaceutical Co., Ltd, China.

2.2. Petroleum refinery wastewater

The wastewater samples were collected from Karachi, Kot Addu and Rawalpindi, Pakistan. Dried plastic gallons (washed with distilled water and drenched in 1% HNO_3 for 24 h) were used for collection of water samples. Sampling was performed for three days for each industry and each sample was collected in triplicate at different times of the day. In this way total 9 samples (10 L each) were collected from 3 industries. The gallons were immediately sealed and transported to Toxicity and Radiation Chemistry Laboratories, Department of Chemistry and Biochemistry, University of Agriculture, Faisalabad, Pakistan. The wastewater samples were stored at −4 °C to avoid any type of change. The characteristics of the PRW wastewater are shown in Table 1.

2.3. Blood sample collection

For bovine blood sample, three healthy sheep (2 year age, weight 42 ± 2 kg), were selected at animal house, Department of Clinical Medicine and Surgery (CMS), University of Agriculture, Faisalabad, Pakistan. Blood sample (10 mL) from vein of each sheep was collected in heparinized tube and stored at −10 °C. For human blood collection, three male students (not involved in any clinical trials within 90 days prior to this investigation and not subjected to any medical treatment within 60 days prior to the present study) were selected from the Department of Chemistry and Biochemistry, University of Agriculture, Faisalabad. Before sampling, written consent was obtained from students (volunteers) by informing them about the nature of study. Study was designed in the supervision of Research Supervisory Committee and approved by Institutional Review Board (IRB), The University of Lahore. Blood samples were taken by medical officer (University dispensary) under the guidelines of WHO (WHO, 2010). Venous blood samples (10 mL) were collected in heparinized tubes and stored at −10 °C until haemolytic assay was performed.

2.4. Experimental design

The variables i.e., UV reaction time (40–140 min), pH (4–10), shaking speed (50–150 rpm), H_2O_2 (3.5–7.5%) and TiO_2 concentration (4–10 g/L) were selected and optimized. The un-coded and coded values with lower and higher levels of independent variables are shown in Table 2. The central composite design (CCD) was constructed using Design Expert software (version, 7.1.3, STAT-EASE Inc., Minneapolis, USA). The complete design consisted of six-factors (i.e., UV reaction time, pH, shaking speed, H_2O_2, TiO_2 concentration and gamma radiation absorbed dose), each at 3-levels (+1, 0, −1) was used for wastewater treatment. Expression shown in Eq. (1) was employed to describe the relationship between the coded and un-coded values.

$$X_i = \frac{X_i - X_0}{\Delta X} \tag{1}$$

Where, X_i is the un-coded value of the independent variable *i*th, X_0 is the value of X_i at the central point and Δ_X is the step change. A quadratic polynomial equation (Eq. (2)) was developed for the prediction of responses as a function of independent variables and their interactions. The RSM consists of a group of empirical techniques used to determine the relationship, existed between a cluster of independent experimental variables (process variables) and measured responses as shown in Eq. (2).