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Municipal wastewater minimization through waste H_2O_2 from food industry

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ABSTRACT

In order to meet the water demands of ever-increasing human population, wastewater treatment is a challenging task. Advanced oxidation processes are promising technologies for wastewater treatment. The current study employed waste H_2O_2 (40%) collected from a food industry to treat municipal wastewater (MWW) of Abbottabad city in Pakistan. Various H_2O_2 doses (1, 1.5, 2, and 2.5 mL L^{-1}) were applied to evaluate its influence on water quality parameters like chemical oxygen demand (COD), biochemical oxygen demand (BOD_5), pH, conductivity, turbidity, and fecal coliforms. Using 2.5 mL waste H_2O_2, the initial concentration of BOD_5 200 mg L^{-1} and COD 327 mg L^{-1} were reduced to 70 and 93 mg L^{-1}, respectively; in addition to 51.72 and 50% reduction of turbidity and coliform populations. An increase in conductivity was noted after 30 min and at 90 min of peroxide dose application. No significant change occurred in pH at lower H_2O_2 dosing but it increased to 8.5 when higher dose of H_2O_2 was applied. The treatment strategy may effectively improve the quality of MWW rendering it suitable for its use in agricultural sector.

Keywords: Advance oxidation process; BOD_5/COD; Waste hydrogen peroxide; Waste minimization

1. Introduction

In view of scarce water supplies in Pakistan and its location in arid to semi-arid regions, there is dire need of wastewater collection and its treatment [1]. Available water resources are continuously depleting with ever-increasing discharge of wastewaters. Recycling of municipal wastewater (MWW) can be effectively measured to cope with irrigation water scarcity. In the coming decades, countries like Pakistan will face difficulty to meet the water demands for agricultural sector alone. It was reported that some farmers were irrigating their crops directly from MWW drains. There is significantly high risk of Giardiasis and other water-borne microbial infections when compared to regular (non-MWW) irrigation water [2]. In addition to agriculture, MWW has profound effect on the environmental quality, especially on the water bodies. Hence, sustainable use of available water will not only minimize adverse environmental impacts but will also minimize the scarcity of available freshwater resources.

To meet the demands of the ever-increasing human population, sustainable agriculture, and industrial development; wastewater treatment is a

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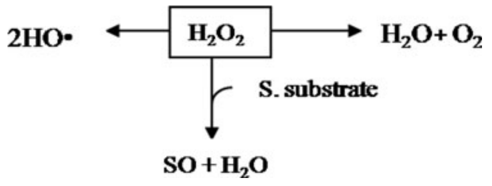
challenging task. There are several wastewater treatment options and the treatment strategies employed that largely depend on specific objectives of treated water reuse [3]. To treat moderately polluted waters, advanced physical treatment processes like chlorination and ozonation are handy techniques which guarantee better water quality [4,5], but they are expensive.

Oxidation potential of very reactive and short-lived hydroxyl radical has been utilized. The use of H_2O_2 is one of the Advanced oxidation process techniques. H_2O_2 can be used alone [5] or in the presence of some catalyst like iron [6], UV light [7,8] or ozone [9], which results in reduction of biological oxygen demand (BOD) and chemical oxygen demand (COD), coliforms, and other pathogens of wastewater. Minimization of wastewater by treating it with waste of another industry is an innovation. H_2O_2 is used in many industries for the disinfection of packaging materials. The use of H_2O_2, in tetra pack aseptic packaging of juices and milk is also accomplished to disinfect the packaging material. Use of 35% H_2O_2 is recommended for disinfection purpose [10]. After production period of 100 h, the concentration of H_2O_2 is increased up to 40%. It is not recommended to use the same H_2O_2 after 100 h production in tetra brik aseptic (TBA) machine. Therefore, it was drained into wastewater lines. The waste H_2O_2 can be reused as autonomous treatment of MWW. Being a suitable oxidizing agent H_2O_2 was used to produce effluent for irrigation. Hydrogen peroxide molecule has an extra oxygen atom bonded with other oxygen molecule. The most reactive components (hydroxyl radicals and perhydroxyl) generated from H_2O_2 have lethal or sub-lethal effects resulting in growth inhibition [5]. These radicals are very reactive with other substances like organic pollutants in municipal and domestic wastewaters and consequently produce CO_2, H_2O, N_2, and metal oxides [11]. Direct oxidation with H_2O_2 proceeds with free radical chain reactions as shown in reactions below [12].



$$RH + O_2 \rightarrow R^{\bullet} + HO_2^{\bullet} \tag{1}$$

$$RH \rightarrow R^{\bullet} + H^{\bullet} \tag{2}$$

$$H^{\bullet} + O_2 \rightarrow HOO^{\bullet} \tag{3}$$

$$H^{\bullet} + H_2O \rightarrow HO^{\bullet} + H_2 \tag{4}$$

$$HO_2^{\bullet} + RH \rightarrow R^{\bullet} + H_2O_2 \tag{5}$$

$$R^{\bullet} + O_2 \leftrightarrows ROO^{\bullet} \tag{6}$$

$$H_2O_2 \rightarrow 2HO^{\bullet} \tag{7}$$

Hydroxyl radicals are also produced due to the presence of aerobic and facultative aerobes, these organisms possess catalase enzyme which converts hydrogen peroxide into oxygen and water.

Statistics revealed that the cost of chemical treatment of domestic or MWW is quite expensive [13]; however, such treatment is very efficient and time-saving. The addition of H_2O_2 to treat domestic wastewater has been demonstrated previously [5,14]; though the use of synthetic H_2O_2 can be very costly. It was hypothesized that waste H_2O_2 generated from food industry in Pakistan could be employed to treat MWW which might be a cost-efficient and quite feasible idea.

The current research was conducted to check the effectiveness of H_2O_2 as strong oxidizing agent in the overall reduction of organic load of MWW from Abbottabad, Pakistan. The specific objective of the present research was to explore the effectiveness of used H_2O_2 (40%) to reduce the BOD, COD, and fecal coliform load of MWW for irrigation.

2. Materials and methods

2.1. Wastewater sampling

MWW samples were collected from Shaikhulbandi Abbottabad, Pakistan. For this purpose, a 50 L container was thoroughly cleaned and rinsed thrice with running MWW before taking the grab samples. After sample collection, it was corked and taken to the COMSATS lab for further analysis and treatment. The characteristics of MWW are given in Table 1. About 40% of waste H_2O_2 was collected from drain of TBA machine in a food factory located in Hattar Industrial Estate, Hattar near Abbottabad.

2.2. Optimization of H_2O_2 dose

The wastewater comprised of effluents from domestic, institutional, and small industrial sources. It contained a large quantity of organic pollution with 0.9 biodegradable fractions. In order to evaluate the

Table 1
Pre-experiment analysis of MWW

Parameter	Value
pH	8.14
Total acidity (mg L^{-1})	80
Total alkalinity (mg L^{-1})	720
Conductivity	270
BOD (mg L^{-1})	200
COD (mg L^{-1})	327
Total nitrogen (mg L^{-1})	20
Total phosphate (mg L^{-1})	3
Microbial population	Too numerous to be counted (TNTC)
Total coliform (#)	

optimum quantity of 40% H_2O_2 for BOD, COD removal, and fecal coliform reduction, a series of experiments were conducted with various H_2O_2 concentrations (1, 1.5, 2, and 2.5 mL L^{-1}). The samples were drawn at the intervals of 0, 30, 60, 90, and 120 min after the addition of waste H_2O_2 and analyzed for water quality parameters.

2.3. Treatment system

All experiments were carried out in a batch reactor. A mixer with variable rotational speed of 0–500 rotations per minute (rpm) was used to mix the sample thoroughly. Raw MWW (1 L) was treated in batch mode and mixed at 500 rpm. Four different concentrations of waste H_2O_2 i.e. 1, 1.5, 2, and 2.5 mL L^{-1} were applied to various samples of MWW. All the experiments were conducted at an ambient temperature of 25 ± 2°C.

2.4. Microbial count

Membrane filter technique was used for total and fecal coliform analysis under aseptic conditions [15]. For this purpose, various dilutions (10^{-3}–10^{-6}) of wastewater sample were made. Eosin methylene blue agar was used for total coliform count. Diluted MWW sample (100 mL) was passed through filter paper (0.45 μm porosity) and incubated at 35°C for 24 h [16,17]. The metallic sheen-colored colonies were counted for fecal coliforms under the compound microscope at a magnification power of 10–15×.

2.5. Analytical procedures

All the analytical procedures used were the standard methods for water and wastewater analysis [15]. Wastewater samples were analyzed prior to and after the treatment with waste H_2O_2. BOD_5 was measured using the standard method [17], COD was determined by closed reflux colorimetric method using digester (HACH-LTG 082.99.40001) [17]. The wastewater sample, digestion solution, and sulfuric acid reagent were digested in vials for two hours at 150°C. After digestion, absorbance was measured at a wavelength of 605 nm in a spectrophotometer (LOVIBOND tintometer GMBH, 44287 DORTMUND). The pH meter (HANNA, HI-991003) was used for pH determination. Concentration of H_2O_2 was measured according to Tetra Pak Technical data manual using hydrometer and temperature. H_2O_2 value was obtained after connecting temperature and hydrometer reading on third scale of H_2O_2 [18].

2.6. Graphical work

Using Sigma Plot™ v.10 was used to illustrate the graphical work.

3. Results and discussion

3.1. BOD removal

The effects of various H_2O_2 concentrations on BOD removal have been shown in Fig. 1. It was evident that initial 200 mg L^{-1} BOD significantly changed after applications of waste H_2O_2 at different concentrations at various intervals throughout the reaction period.

Treatment of 1 mL L^{-1} waste H_2O_2 reduced BOD by 10 mg L^{-1}, in first 30 min. The highest decrease to 60 mg L^{-1} BOD was observed after 2 h of the application of 2.5 mL L^{-1} H_2O_2. With the increasing concentrations of waste H_2O_2 (1.5, 2, and 2.5 mL L^{-1}), BOD values were reduced at a very rapid rate in first 30 min. The maximum BOD reduction was observed at

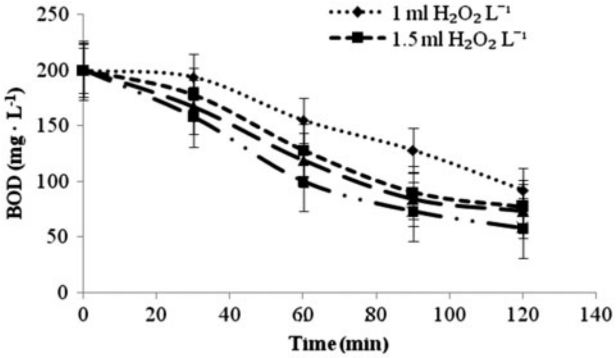


Fig. 1. BOD_5 reduction with increasing 40% H_2O_2 concentrations.

highest concentration of waste H_2O_2 increment during first 30 min and subsequent BOD reduction rate declined. It was speculated that most of the BOD reaction occurred in the first phase, and mixing and homogenization resulted in complete H_2O_2 consumption in 120 min (Fig. 1). The highest BOD reduction (70%) was evident with 2.5 mL L^{-1} H_2O_2 and was lowest with 1 mL L^{-1} after 120 min (Fig. 1).

3.2. COD removal

The results showed that the addition of H_2O_2 significantly reduced COD of MWW. The COD reduction had almost linear relationship with increasing doses of waste H_2O_2. The effects of H_2O_2 addition on the COD content of municipal MWW have been illustrated in Fig. 2. The results suggested that COD removal was strongly influenced by applied dose of H_2O_2. The application of 1 mL L^{-1} waste H_2O_2 reduced 36 mg L^{-1} COD (11%), in first 30 min. A dose of 1 mL H_2O_2 seemed quite insufficient in reducing COD burden of 250 mg L^{-1} (46%) after 2 h (Fig. 2). The maximum COD reduction was observed with 2.5 mL L^{-1} H_2O_2, where COD value reduced to 93 mg L^{-1} after 2 h which satisfied the National Environmental Quality Standards (NEQS). With increasing doses of waste H_2O_2 from 1 to 1.5, 2, and 2.5 mL L^{-1}, COD values rapidly reduced in first 30 min; however, subsequent COD reduction proceeded at a slower rate in next 2 h, revealing that mixing and homogenization may have affected COD reduction in comparison to BOD_5 of MWW (Fig. 2). These results prove the waste stabilization action of the waste H_2O_2 for the organic matter of the wastewater.

3.3. BOD_5/COD ratios and biodegradability of MWW

The MWW was treated under operational conditions: initial pH 8.14 at room temperature (25˚C) using various concentrations of H_2O_2. BOD_5/COD ratios of the effluents obtained after each treatment were measured and have been presented in Fig. 3. The initial BOD_5/COD ratio of raw wastewater was around 0.6 which indicated its promising biodegradability. When effluent was treated with waste H_2O_2 2 mL L^{-1} then BOD_5/COD ratios increased to 0.78 after 30 min and started to decrease continuously till 120 min of mixing. Same kind of rise in BOD_5/COD ratio after 30 min was observed when treated with hydrogen peroxide 1, 1.5, and 2.5 mL L^{-1} and after 30 min it started to decrease till 120 min as indicated in Fig. 3. Therefore, biodegradability of MWW was improved greatly in first 30 min and afterwards decreased as chemical reaction proceeded during oxidation of organics. In this reaction, oxidants were released from hydrogen peroxide in the form of hydroxyl radical ($OH^•$) and per hydroxyl ($HO_2^•$) resulting in decrease in the BOD_5/COD ratio after 30 min [19].

The considerable increase of the BOD_5/COD ratio may also be attributed to the transformation by waste H_2O_2 of the mineral substances existing in the effluent such as sulfides, sulfites, and thiosulfate into sulfates that do not contribute to BOD_5/COD [5,13].

3.4. Turbidity removal

Fig. 4 shows the effect of various concentrations of H_2O_2 on turbidity after oxidation of organic matter. H_2O_2 is a weak acid and has strong oxidizing properties and is therefore a powerful bleaching agent.

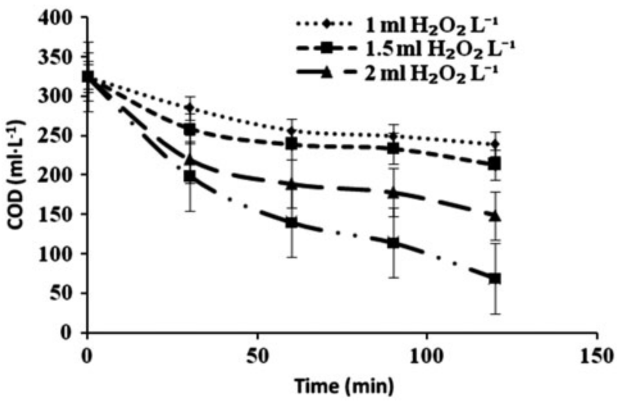


Fig. 2. COD removal with increasing concentrations of 40% H_2O_2.

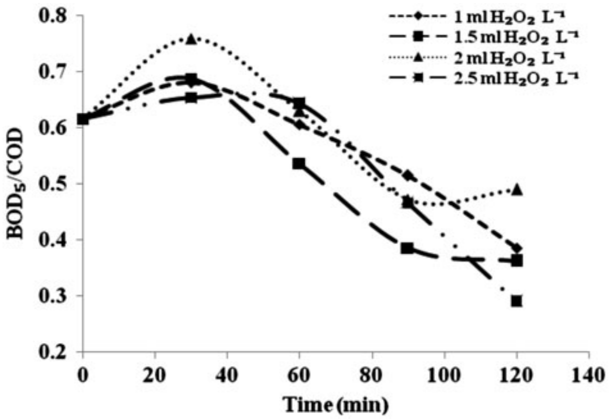


Fig. 3. The variations of BOD_5/COD during H_2O_2 per-oxidation process.

The rate of decomposition is dependent on the temperature and concentration of H_2O_2. Using 1 mL L^{-1} H_2O_2 treatment caused 74.13% reduction in turbidity (43 NTU). At 1.5 mL H_2O_2 per liter, 67.24% turbidity was reduced and only 51.72% (26 NTU) reduction was observed at 2 mL of H_2O_2. A sharp slope in Fig. 4 shows that the maximum effective dose in reducing turbidity was 2.5 mL L^{-1}. Turbidity decreased with decrease in COD which was an evidence of the oxidation of organics in wastewater. In Fig. 4, it shows that as dose of H_2O_2 increased the turbidity and the COD removal percentage was also increased.

Reduction of turbidity by waste H_2O_2 occurred at same rate as COD removal as shown in Fig. 4. The use of waste H_2O_2 efficiently reduced the COD and turbidity. Treatment of MWW with 2.5 mL hydrogen peroxide resulted in greater turbidity reduction compared with COD. Our preliminary experiments indicated that further addition of peroxide was not efficient to reduce the turbidity but was effective in COD and fecal coliform reduction.

3.5. Inactivation of total and fecal coliforms

The reduction in colony-forming units (CFU) mediated by the addition of increasing concentrations of 40% H_2O_2 is displayed in Fig. 5. It was in 2-log order, with initial 3.5 CFU.

At 1, 1.5, and 2 mL L^{-1} H_2O_2, the respective CFU reductions were 3.3, 3.2, and 3; at the highest dose of waste H_2O_2 (2.5 mg L^{-1}), it reached to 1.5 CFU, which was less than half of the initial value (Fig. 5). A relatively high rate of fecal coliform inactivation was observed with increasing dosage of H_2O_2. H_2O_2 exhibited strong germicidal effects. The cell-killing power of H_2O_2 is due to oxidation of intracellular constituents [20]. Hydroxyl and perhydroxyl species can have both lethal and sub-lethal effects on microbial genome and other intracellular molecules resulting in growth inhibition [21–23].

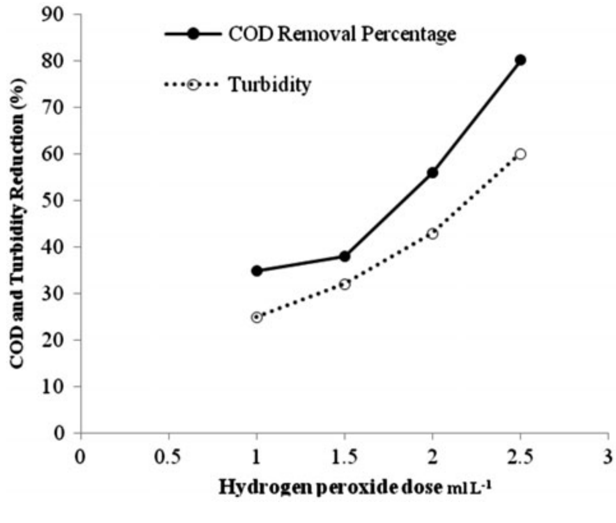


Fig. 4. The effect of H_2O_2 on percent reduction of COD and turbidity.

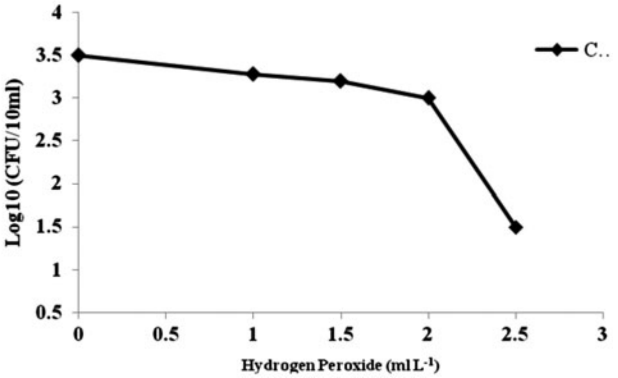


Fig. 5. Log_{10} reduction of fecal coliforms with increasing dose of H_2O_2.

3.6. Effect on pH after addition of H_2O_2

The changes of pH after the addition of waste H_2O_2 have been illustrated in Fig. 6. No significant change in pH was observed after dosing with 1 mL L^{-1} H_2O_2 and during first 30 min pH increased from 8.14 to 8.17 and reached up to 8.31 in 2 h. But at 1.5 mL L^{-1} pH increased from 8.14 to 8.37 in 2 h. Similarly, doses of 2 and 2.5 mL L^{-1} caused an increase in pH up to 8.46 (Fig. 6). Increase in pH at different doses of H_2O_2 was due to the release of OH^- radicals contributing to rise in pH. H_2O_2 has an extra oxygen atom which takes part in the oxidation of organics. Higher dose of H_2O_2 (2.5 mL L^{-1}) releases more OH^-

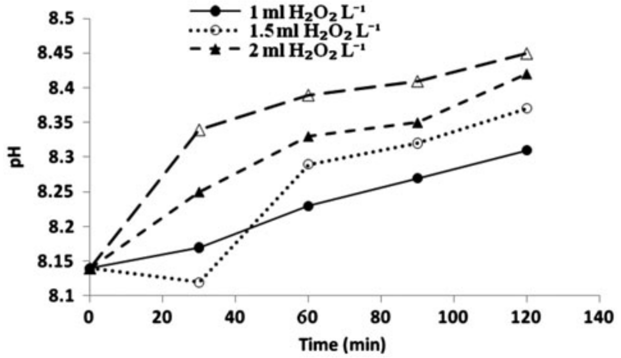


Fig. 6. Change in pH after the application of H_2O_2.

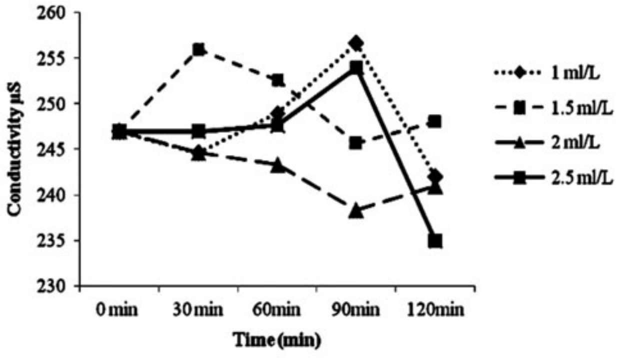


Fig. 7. Effect on conductivity.

which contributes to alkaline pH. A decrease in pH that may be due to incomplete mixing and reaction after 30 min was observed when 1.5 mL L^{-1} peroxide was added. In another study by Ksibi [5] pH increased gradually when hydrogen peroxide was used during domestic wastewater treatment. It resulted to basic by-products like HCO_3^- during degradation. In the same study, pH slightly decreased when hydrogen peroxide was used with Fe^{2+}.

3.7. Effect on conductivity during mixing with H_2O_2

Conductivity in water shows ability to flow the currents. There was increase in conductivity after 30 min and at 90 min of peroxide dose application. This rise in conductivity may be due to the production of some ionic species as a result of organic degradation using waste H_2O_2; further, temperature may aggravate the effect of H_2O_2 on the conductivity as temperature increases the ionic movement. The temperature increases due to oxidation reaction between organic compounds in MWW (like fat, protein, grease, and oil) and hydroxyl radical produced during mixing. The exothermic reaction was observed when 1 and 2.5 mL L^{-1} of peroxide were added, where the maximum values of conductivity were 256 and 254 µS. H_2O_2 oxidizes the organic-like oil and fat in wastewater. Mixing of 120 min with H_2O_2 resulted in conductivity values of 242, 248, 241, and 235 µS with respective peroxide doses of 1, 1.5, 2, and 2.5 mL L^{-1} (Fig. 7).

4. Conclusions

Waste H_2O_2 proved to be a powerful oxidant in minimizing the organic load of MWW. The optimum dose of waste H_2O_2 was found as 2.5 mL L^{-1} which significantly reduced pollution load in 120 min thus meeting the discharging NEQS for MWW. The results revealed that disinfection capacity of 40% waste H_2O_2 at 2.5 mL L^{-1} caused a significant reduction in the fecal coliform population to less than half of the initial value. Treating MWW with H_2O_2 can be a low cost option for direct irrigation to croplands.

Acknowledgment

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Nomenclature

AOPs	—	advanced oxidation processes
H_2O_2	—	hydrogen peroxide
MWW	—	municipal waste water
COD	—	chemical oxygen demand
BOD_5	—	biochemical oxygen demand
TBA	—	tetra brik aseptic
TNTC	—	too numerous to be counted
NEQS	—	national environmental quality standards
OH^-	—	hydroxyl radical
HO_2^-	—	per hydroxyl
NTU	—	nephelometric turbidity units
CFU	—	colony-forming units

References

[1] World Bank, worldbank.org.pk/WBSITE/EXTERNAL/COUNTRIES/SOUTHASIAEXT, 22 May 2011.
[2] M.A. Kahlown, M. Ashraf, Z. Zia-ul-Haq, Effect of shallow groundwater table on crop water requirements and crop yields, Agric. Water Manage. 76 (2005) 24–35.
[3] S.U. Geissen, Water demand in arid countries: An opportunity to reduce environmental pollution, Mediterranean area, in: M. Enabbli, R. Bennaceur, A. Bahri, L. Bousselmi, A. Ghrabi (Eds.), Proceedings of the International Conference WATRAMA, Tunis, 2000, pp. 25–28.
[4] A.R. Bull, J.T. McManamon, Destruction of Inorganic Pollutants in Wastewater with Hydrogen Peroxide, Emerging Technology in Hazardous Waste Management, American Chemical Society, Washington, DC, 1990, pp. 52–66.
[5] M. Ksibi, Chemical oxidation with hydrogen peroxide for domestic wastewater treatment, Chem. Eng. J. 119 (2006) 161–165.
[6] W.H. Glaze, The chemistry of water treatment processes involving ozone, hydrogen peroxide, and ultraviolet radiation, Ozone Sci. Eng. 9 (1987) 335.
[7] V. Lazarova, G. Cirelli, P. Jeffrey, M. Salgot, N. Icekson, F. Brissaud, Enhancement of integrated water management and water reuse in Europe and the Middle East, Water Sci. Technol. 42 (1–2) (2000) 193–202.
[8] F.J. Beltran, M. Gonzalez, J.F. Gonzales, Industrial wastewater advance oxidation, Water Res. 31 (2007) 2405–2414.

[9] F.J. Millero, A. Leferriere, M. Fernandez, S. Hubinger, J.P. Hershey, Oxidation of hydrogen sulfide with hydrogen peroxide in natural waters, Environ. Sci. Technol. 23 (1989) 209–213.

[10] M.D.I.A. Ansari, A.K. Datta, An overview of sterilization methods for packaging materials used in aseptic packaging system, Inst. chem. Eng. 81 (2003) 57–65.

[11] R. Robert, S. Barbati, N. Ricq, M. Ambrosio, Intermediates in wet oxidation of cellulose: Identification of hydroxyl radical and characterization of hydrogen peroxide, Water Res. 36 (2002) 4821–4829.

[12] F.J. Rivas, S.T. Kolaczkowski, F.J. Beltran, D.B. McLurgh, Hydrogen peroxide promoted wet air oxidation of phenol: Influence of operating conditions and homogeneous metal catalysts, J. Chem. Technol. Biotechnol. 74 (5) (1999) 390–398.

[13] N.T. Song, M. Hiraoka, Anaerobic treatment of sewage sludge treated by catalytic wet air oxidation process in up flow anaerobic sludge blanket reactors, Water Sci. Technol. 26 (1992) 867–895.

[14] T. George, Wastewater Engineering Treatment and Reuse, 4th ed., McGraw-Hill, New York, NY, 2004, pp. 1196–1200.

[15] W. Verstrate, Microbial Ecology, Practical Course Notes, Ghent University Belgium, Ghent, 1998, 20–30.

[16] F. Maqbool, Z.A. Bhatti, A.H. Malik, Q. Mahmood, Effect of landfill leachate on the water quality of the Salhad stream in Abbottabad, Pakistan. Int. J. Environ. Res. 5 (2011) 491–500.

[17] Standard Methods for the Examination of Water and Wastewater, 21st ed., APHA, AWWA & WEF, New York, NY, 2005.

[18] Tetra Pak Technical Data Manual, Hydrogen Peroxide, Doc. No. OM-2771726-0101, 2008, pp. 8–9.

[19] Metcalf and Eddy, Wastewater Engineering Treatment and Reuse, McGraw-Hill, 4th ed., New Delhi, 2003, pp. 1196–1202.

[20] J.L. DeMorais, P.P. Zamora, Use of advanced oxidation processes to improve the biodegradability of mature landfill leachates, J. Hazard. Mater. B123 (2005) 181–186.

[21] L.F. Liotta, M. Gruttadauria, G. Di Carlo, G. Perrini, V. Librando, Heterogeneous catalytic degradation of phenolic substrates: Catalysts activity, J. Hazard. Mater. 162 (2009) 588–606.

[22] H. Olmez, U. Kretzschmar, Potential alternative disinfection methods for organic fresh-cut industry for minimizing water consumption and environmental impact, LWT – Food Sci. Technol. 42 (2009) 686–693.

[23] A. Berkessel, Biomimetic Oxidation of Organic Substrates with Hydrogen Peroxide, Institut fur organische chemie der universitat zu Koln, Koln, 2001, p. 109.