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Radiation induced decontamination of Cr(VI), Cu(II) and phenol in some tannery effluents

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Abstract Industrialization has led to a number of environmental problems, such as release of toxic metals and other toxic organic and inorganic compounds to the environment. Among all, the rapid expansion of leather related industries in Pakistan have resulted in considerable environmental problems and effluents from processing of both domestic and imported hides and skins have increased pollution to alarming levels. Some tannery effluents of Peshawar area investigated in the present study showed high concentrations of Cr(VI) (2.7-12.6 mg/L), Cu(II) (2.6-11.4 mg/L) and phenol (0.1-4.2 mg/L). These contaminants are very toxic and must be removed from effluents before releasing into water bodies. A new technique of gamma irradiation has been investigated to decrease the load of COD and concentrations of Cr(VI), Cu(II) and phenol associated with tannery effluents to the permitted values. It was observed that concentration of Cr(VI) in the effluents can be brought to the permitted level by applying radiation dose of 3 kGy. A radiation dose of 2.5 kGy was required to remove more than 95% of Cu(II) and 100 % degradation of phenol in tannery effluents could be achieved by only one kGy of radiation dose.

Key words Radiation induced decontamination, Tannery effluents, Cr(VI), Cu(II), Phenol

CLC numbers X832, X794, Q691.1

1 Introduction

Because of large world-wide demand for tanned leather, there is a large growth in the tannery industries in Pakistan and it has become the second largest foreign exchange earner for the country. About 90% of its products are exported in finished form and there are more than 600 tanneries in the country that are mostly concentrated in Kasur, Karachi and Sialkot.[1]

In Pakistan the chrome tanning method for leather processing is the most widely used process. However, the vegetable tanning method and a combination of chrome and vegetable tanning is also applied. The process includes a number of different steps during which large quantities of water and chemicals are applied to the skins. About 130 different chemicals are used in leather processing, depending on the type of raw material used and finished product. These may be divided into four major classes: pre-tanning chemicals, tanning chemicals, wet finishing chemicals and finishing chemicals. In Pakistan, groundwater is normally used as the major source of water in leather industry.

Leather tanneries in Pakistan produce all three categories of waste, i.e. wastewater, solid waste and air emissions. However, wastewater is by far the most important environmental challenge being faced by Pakistan's tanneries. The current practice is to discharge this wastewater into the local environment without any treatment. The solid wastes from tanneries also have secondary users in the local market, such as glue manufacturing and poultry feed makers. However, the use of chrome contained solid waste for poultry feed preparation could cause serious health problems for poultry consumers.

Tanning process produces a very obnoxious and smelly waste, which contains chromium, copper, sulfides, ammonia, chloride, phenol and large quantity of other organic components and salts.[2,3] As a large

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amount of water is being used in the tanning process, a large volume of wastes is produced. The effluents, rich in suspended and dissolved impurities plus toxic chemicals, are normally discharged either to open lands or into waterways, polluting them to a very high extent.[1]

Chromium is one of the major toxic pollutants in tannery wastes. Cr(VI) is more toxic and water soluble contaminant present in tannery waste. On the other hand, Cr(III) is relatively less toxic and less water soluble form of chromium present in tannery effluents.[1] It is, therefore, necessary to remove the toxic Cr(VI) from the waste stream of tanneries before releasing the water into the environment.[2]

About 25%—30% of total of the chrome applied goes into the wastewater that can be reused. A number of technologies exist to reduce and reuse the amount of chrome being lost to wastewater and sludge.[1] In addition, there are several end-of-pipe effluent treatments available for tanneries. The primary treatment system includes mechanical screening, pH equalization and physio-chemical processes. During this stage, coarse particulate flesh and hair can be removed by means of perforated screens which also reduce the BOD load; the amplitude of pH fluctuation can be reduced to a manageable and consistent range; and coagulation and flocculation can be applied to remove suspended solids. For secondary treatment, biological processes are used to remove most of the organic matter from the wastewater by converting it into different gases and into cell tissues.[1] The most widely used processes for secondary treatment tend to be aerobic. However, anaerobic process is also utilized to some extent. These treatments include anaerobic lagoons, which are not recommended due to large land requirement, odour problem and possible groundwater contamination. Trickling filter treatment is not preferred due to low efficiency and Upflow Anaerobic Sludge Blanket (UASB) treatment because of the complex characteristics of tannery wastewater and presence of sulphate. The low loaded activated sludge treatment, which is a proven technology for treatment of tannery wastewater is normally preferred and local climatic conditions in Pakistan, such as high temperature, also favours this type of secondary sludge treatment.

In all these treatments, there is normally phase transfer of contaminants from liquid to solid or gaseous phase, which eventually have to be treated. In the present study, ionising radiation from a gamma radiation source as a novel technique has been used to completely decontaminate these pollutants and specially to reduce the concentrations of Cr(VI), Cu(II) and phenol associated with tannery effluents to permissible levels.

2 Experimental

All chemicals used were analytical grade and were used without further purification. Triply distilled water, which was prepared by re-distillation of singly distilled water first from an alkaline $KMnO_4$ solution and then from an acidic $K_2Cr_2O_7$ solution, was used to make the solutions.

A Varian DMS-200 UV-visible spectrophotometer was used for the spectrophotometric determination of Cr(VI), Cu(II), phenol and for Fricke dosimetry. Absorbance and wavelength scales of the spectrophotometer were calibrated using standard solution of potassium dichromate.[3]

A ^{60}Co source at the Nuclear Institute for Food and Agriculture (NIFA) was used for irradiation. The source was calibrated using Fricke dosimetry[4] or radiochromic film dosimetry.[5] For radiolysis, 10 mL of sample solution was placed in Pyrex test tube and was irradiated by ^{60}Co γ-rays for desired interval of time (with a dose rate of about 1.03 kGy/h).

An indirect spectrophotometric method was used for the determination of Cr(VI).[6] The irradiated samples were analysed spectrophotometrically at 440 nm wavelength. The Cr(VI) concentration in the tannery effluents can vary over a wide range. Therefore, for calibration, the standard solutions were made in the range of 0.1 to 13 mg/L. Similarly spectrophotometric methods using DMS-200 UV-visible spectrophotometer were used for the analysis of Cu(II)[7,8] and phenol[9,10] in the tannery effluents. Each experiment was repeated three times or more and standard deviations were calculated.

Five tanneries at Charsaddah Road near Peshawar were selected for sampling. The effluent samples were collected from the point of discharge (POD) at the tannery and after about 100 and 200 m downstream from the POD. The samples were also collected after mixing of the effluent with local drain or canal water.

During collection of samples, careful attention was given to note down the location, time of sampling and the procedure to transfer samples with minimum chemical change to the laboratory for analysis. For each collected sample, name of tannery, distance from the point of discharge, colour and temperature were noted at the spot. The samples were collected in polyethylene storage bottles. The bottles were brand new and were washed with a detergent solution, then with distilled water and finally soaked in 1% HNO_3 for 24 h. After cleaning operation, the bottles were dried for 1 h. The samples were carefully collected and before filling, the bottles were washed with the same effluent sample. The bottles were filled in such a way that the air entrap was minimized. The samples, after capping and labelling, were brought to the laboratory on the same day and its pH was noted with pH meter. According to the preservation procedures, the samples were preserved by acidification.

3 Results and discussions

3.1 Radiation chemistry of aqueous solutions

The γ-rays interact with water and generate several reactive products. These include radical products as well as molecular products. The radiolysis of water or dilute aqueous solution can be represented as:[11]

$$H_2O \xrightarrow{\gamma\text{-rays}} e^-_{aq}, H, OH, HO_2, H_2O_2, H_2$$

Radiation yield of these species in terms of *G*-values is given below[11]:

e^-_{aq} (0.28), H (0.6), OH (0.29), H_2O_2 (0.07), H_2 (0.05).

Molecular hydrogen (H_2) and hydrogen peroxide (H_2O_2) are molecular products, while radical products are hydrated electron (e^-_{aq}), hydrogen atom (H), hydroxyl radical (OH) and perhydroxyl radicals (HO_2). The hydrated electron and hydrogen radical are often described collectively as the reducing radicals while the hydroxyl radical and perhydroxyl radical are described as the oxidizing radicals.

The first three radicals shown in the equation (e^-_{aq}, H and OH**)** are very reactive and are produced in sufficient amount and, therefore, play important role in radiolysis of water and dilute aqueous solutions. On radiolysis of tannery effluents, the Cr(VI) and Cu(II) is expected to be reduced by hydrated electrons and H radicals (strong reducing radicals) to lower valance state, such as Cr(III) and eventually may lead to precipitation out of the metallic chromium from effluent solution.[12,13]

3.2 Cr(VI), Cu(II) and phenol in tannery effluents

The concentrations of different contaminants found in the samples collected from five different tanneries are summarised in Table 1. It is clear from the table that the concentrations of Cr(VI) in these samples were in the range of 2.7 to 12.6 mg/L, of copper in the range of 2.6 to 11.4 mg/L and of phenol less than 0.1 mg/L (lower detection limit for phenol) to 4.20 mg/L in the samples collected from the point of discharge of the selected tanneries.

The minimum value of 2.7 mg/L of Cr(VI) was recorded for the effluents of Hayat Tannery and maximum value of 12.9 mg/L was recorded for the effluents of Afzal Tannery. The maximum concentration of Cr(VI) in the effluents permitted by US Environmental Protection Agency and the Environmental Protection Agency (EPA) of Pakistan is 1 mg/L.[14]

It is clear from Table 1 that the concentration of Cr(VI) in all the effluents collected from tannery industries were considerably higher than permissible level. The concentration of Cr(VI) in Afzal Tannery is significantly higher than those in the samples collected from other tannery industries. The concentration of toxic chromium(VI) in effluents of several industries even after mixing with local drain or with canal water was higher than the maximum permissible value of 1 mg/L.

The higher concentrations of Cr(VI) in all the effluents investigated in the present study are alarming and severely pollute the water, which is dangerous for aquatic life and also make the water unfit for human and animal consumption. Ingestion of high concentration of Cr(VI) may results in severe acute effects, such as gastrointestinal disorder and convulsions. It is also reported that there is sufficient evidence of respiratory carcinogenicity in human exposed to chromium (VI).[15]

Table 1 Concentrations of Cr(VI), Cu(II) and phenol and COD values for some tannery effluents of Peshawar area

Name of Tannery	Sample No.	Sampling site	Cr(VI) /mg·L^{-1}	Cu(II) /mg·L^{-1}	Phenol /mg·L^{-1}	COD /mg·L^{-1}
City Leather Tannery	1	POD	6.8±0.2	7.4±0.0	3.7±0.2	882±17
	2	100 m from POD	6.3±0.2	7.0±0.1	3.2±0.1	808±20
	3	200 m from POD	5.8±0.1	5.6±0.0	2.8±0.1	724±26
	4	After mixing with local drains	2.9±0.2	2.3±0.0	0.8±0.2	376±8
Altawakkal Tannery	5	POD	9.0±0.2	4.7±0.0	4.2±0.1	1068±17
	6	100 m from POD	8.8±0.1	4.1±0.1	4±0.2	1012±10
	7	200 m from POD	6.4±0.3	3.8±0.1	2.7±0.2	922±26
	8	After mixing with local drains	1.5±0.3	1.7±0.1	0.8±0.1	464±10
Hayat Tannery	9	POD	2.7±0.3	11.4±0.1	BDL	693±14
	10	100 m from POD	2.5±0.2	10.7±0.1	BDL	672±20
	11	200 m from POD	1.8±0.1	9.1±0.1	BDL	554±10
	12	After mixing with canal water	0.5±0.2	2.7±0.1	BDL	288±17
Ittefaq Tannery	13	POD	7.0±0.2	6.1±0.1	2.0±0.1	537±10
	14	100 m from POD	6.6±0.3	5.8±0.1	1.9±0.2	503±20
	15	200 m from POD	4.7±0.1	3.0±0.1	1.2±0.1	362±26
	16	After mixing with canal water	1.5±0.2	1.2±0.1	0.3±0.1	187±17
Afzal Tannery	17	POD	12.6±0.3	2.6±0.1	BDL	549±10
	18	100 m from POD	12.0±0.1	2.3±0.1	BDL	503±10
	19	200 m from POD	10.3±0.2	1.8±0.1	BDL	401±20
	20	From river under Shah Alam Bridge	0.2±0.2	BDL	BDL	130±20

BDL = Below Detecting Limit

The concentration of Cu(II) in the effluents of selected tanneries was in the range of 2.6 to 11.4 mg/L in the samples collected from point of discharge (POD). The maximum value of 11.42 mg/L of Cu(II) was recorded in the effluents collected from the point of discharge of Hayat Tannery, while the minimum value of 2.60 mg/L was recorded for the effluents taken from the point of discharge of Afzal Tannery.

The permissible level of Cu(II) in industrial effluents is 1 mg/L as recommended by the Environmental Protection Agency (EPA) of Pakistan.[14] It is clear from the results that the concentration of Cu(II) in all the effluents collected from tannery industries were several times higher than recommended level of 1 mg/L at the point of discharge and at 100 or 200 m downstream the discharge point. Even after mixing with the local drain or with canal water the level of Cu(II) was higher than the permissible value for most of the tannery industries investigated in the present study.

For phenol, the maximum concentration of 4.2 mg/L was recorded for the effluents collected from POD of Altawakkal Tannery (sample No.5 in Table 1). In the effluents of Hayat Tannery and Afzal Tannery, the concentration of phenol was below the detected limit (0.1 mg/L). In the effluents collected from Ittefaq Tannery, the concentration of phenol was 2.1 mg/L.

The permissible concentration of phenol in industrial wastewater recommended by Environmental Protection Agency (EPA) of Pakistan is 0.1 mg/L.[14] Phenol is highly toxic and some of phenols, especially chlorinated phenols, are reported to be carcinogenic.[15] Acute poisoning by ingestion, inhalation or skin contact may lead to death.

3.3 Radiation treatment of tannery effluents

Among the tannery effluents analysed in the present study, two tanneries, *i.e.* Ittefaq and Altawakkal tanneries, which showed high loads of all pollutants analysed in the present study were selected for radiation treatment. The effluents from these tanneries, situated at Charsadda road, Peshawar, Pakistan were collected and irradiated to different doses at NIFA. Effluents were analysed for the decontamination of Cr(VI), Cu(II), phenol and COD after radiation treatment. The results are given in Tables 2, 3 and 4, respectively.

Table 2 shows the results for the decrease in concentration of Cr(VI) with the irradiation dose. It is clear from the table that 2.5 kGy dose is needed for

96% removal of Cr(VI) in the effluents collected from Ittefaq Tannery while for Altawakkal Tannery, which contained somewhat higher load of Cr(VI), 3 kGy radiation dose was required for the same percentage decrease in the concentration of Cr(VI). This amount of radiation is sufficient to bring the concentration of toxic Cr(VI) to the permissible level.

Table 2 Radiation-induced reduction of Cr(VI) in Ittefaq and Altawakkal Tanneries

Dose /kGy	Cr(VI) in Ittefaq Tannery /mg·L^{-1}	% decrease	Cr(VI) in Altawakkal Tannery / mg·L^{-1}	% decrease
0	7.1 ± 0.1	-	9.2 ± 0.1	-
0.17	6.8 ± 0.2	4	8.9 ± 0.1	3
0.33	6.6 ± 0.1	7	8.5 ± 0.2	8
0.67	5.8 ± 0.1	18	7.8 ± 0.4	15
1.0	5.0± 0.1	30	6.9 ± 0.1	25
1.5	3.6 ± 0.1	49	5.7 ± 0.2	38
2.0	2.0 ± 0.1	72	4.1 ± 0.2	55
2.5	0.3 ± 0.1	96	2.3 ± 0.2	75
3.0	BDL	-	0.4 ± 0.1	96

The concentration of Cr(VI) is reduced by hydrogen atoms and hydrated electrons, which are strong reducing agents, to lower valence state and eventually chromium may precipitate out of the solution:[13,16]

H + Cr(VI) → Cr(III), k=2.3×10^{10} m^3·mol^{-1}·s^{-1}
e^-_{aq} + Cr(VI)→ Cr(III), k=4.0×10^7 m^3·mol^{-1}·s^{-1}
OH + Cr(III) →Cr (IV) + OH$^-$, k=3.8×10^8 m^3·mol^{-1}·s^{-1}.

Table 3 summarizes the results for radiation induced reduction of Cu(II) in the tannery effluents. The results show that using irradiation dose of 2.5 kGy, 96% Cu(II) is reduced in the effluents of Ittefaq Tannery, while complete removal was achieved by the same dose in Altawakkal Tannery. The concentration of Cu(II) in the effluents of these tanneries can be brought to the permissible limit of 1.0 mg/L by irradiation of 2.5 kGy.

Table 3 Radiation-induced reduction of Cu(II) in Ittefaq and Altawakkal Tanneries

Dose /kGy	Cu (II) in Ittefaq Tanneruy /mg·L^{-1}	% decrease	Cu (II) in Altawakkal Tannery /mg·L^{-1}	% decrease
0	6.1 ± 0.1	-	4.7 ± 0.07	-
0.17	5.8 ± 0.0	5	4.4 ± 0.03	6
0.33	5.4 ± 0.0	11	4.0 ± 0.02	15
0.67	4.8 ± 0.1	21	3.4 ± 0.05	30
1.0	3.9 ± 0.0	36	2.6 ± 0.03	43
1.5	2.8 ± 0.0	52	1.7 ± 0.02	64
2.0	1.5 ± 0.0	75	0.4 ± 0.07	92
2.5	0.3 ± 0.0	96	BDL	-

Copper is reduced by hydrated electron to lower valance state and eventually precipitated out of solution. The following reactions are expected to contribute to the radiolysis mechanism:[16]

e^-_{aq} + Cu^{2+}→ Cu^+, k=3.3 ×10^7 m^3·mol^{-1}·s^{-1}
H + Cu^{2+}→ Cu^+ + H^+, k=9.1×10^4 m^3·mol^{-1}·s^{-1}.

Table 4 indicates that 100% degradation of phenol was achieved in the effluents collected from Ittefaq Tannery by irradiation of only 1 kGy, while for the same dose, 83% degradation of phenol was achieved in Altawakkal Tannery, which contained higher load of phenol. In Altawakkal Tannery complete removal of phenol was achieved by 1.5 kGy radiation dose. The probable mechanism of phenol degradation is given as follows:[17]

C_6H_5OH + OH$^-$ → Catechol + Hydroquinone
k=1.8×10^{10} m^3·mol^{-1}·s^{-1}
C_6H_5OH + H → Products, k=1.7×10^9 m^3·mol^{-1}·s^{-1}
C_6H_5OH + e^-_{aq}→ Products, k=3.0×10^7 m^3·mol^{-1}·s^{-1}
Catechol + OH$^-$ →Products, k=1.1×10^{10} m^3·mol^{-1}·s^{-1}
Hydroquinone+ OH$^-$ → Products, k=2.1×10^{10} m^3·mol^{-1}·s^{-1}.

Table 4 Radiation-induced removal of phenol in effluents from Ittefaq and Altawakkal Tanneries

Dose /kGy	Phenol in Ittefaq Tannery /mg·L^{-1}	% decrease	Phenol in Altawakkal Tannery/mg·L^{-1}	% decrease
0	1.9 ± 0.1	-	4.1 ± 0.18	-
0.17	1.6 ± 0.1	16	3.5 ± 0.14	15
0.33	1.2 ± 0.1	37	3.1 ± 0.19	24
0.67	0.5 ± 0.1	74	2.0 ± 0.06	51
1.0	BDL	-	0.7 ± 0.12	83
1.5			BDL	-

4 Conclusions

The present study has revealed that the tannery effluents have high load of Cr(VI), Cu(II) and phenol. The concentrations of these contaminants were found to be very high compared to the permissible limits,[14] which may affect the quality of surface as well as ground water in the area.

It was found out in the study that gamma irradiation is an efficient method for the cleaning of tannery effluents. Free radicals, produced using high-energy gamma radiation in aqueous solutions, are highly reactive and can effectively eliminate phenol, Cu(II) and Cr(VI) associated with tannery effluents.

In the effluents, more than 96% decrease in the concentration of Cr (VI) was achieved using radiation dose of only 3 kGy, more than 96% decontamination of Cu(II) using radiation dose of 2.5 kGy and complete decontamination of phenol was achieved using radiation dose of only 2 kGy.

References

1 ETPI, The Leather Sector, Environmental Report, Environmental Technology Program for Industry (ETPI), Islamabad, 1998.

2 Chasteem T G. A text book on qualitative and instrumental analysis of environmentally significant elements, Sam Houston State University Huntsiville, Taxas, 1993: 43.

3 Vinter E. Liquid absorbance standards, in Standards in absorbance spectroscopy, (Burgem C, Knowles A, Eds.), Vol.I, New York: Chapman and Hall, 1981.

4 Sechested K. The Fricke dosimeter, in Manual on radiation dosimetry (Holm N W, Berry R J, Eds.) New York: Marcel Dekker, 1970: 313.

5 Sayler M C, Taargo T T, McLaughlin W L, *et al*. Radiat Phys Chem, 1988, **31**: 529-536.

6 Anwar J, Aslam M A, Ahmad M. J Chem Soc Pak, 1996, **18**: 291-295.

7 Majeed A, Mustafa M M, Asma R N. J Chem Soc Pak, 1996, **18**: 291-295.

8 Vogel's text book of quantitive analysis, (Revised by Jeffery G H, Basseti J, Mendham J, *et al*.), 5th edition.1989, 707.

9 Norwitz G, Keliher P N. Analytica Chemica Acta, 1980, **119**: 99-111.

10 De A K. A text book of environmental chemistry, 3rd edition, New Delhi: Wiley Eastern, 1993: 270-271.

11 Woods R J, Pikaev A K. Applied radiation chemistry. New York: John Wiley and Sons, 1994.

12 Chaychian M, Al-Sheikhly M, Silverman J, *et al*. Radiat Phys Chem, 1998, **53**: 145-150.

13 Al-Sheikhly M, McLaughlin W L. Radiat Phys Chem, 1991, **38**: 203-211.

14 EPA, Revised National Environmental Quality Standards for Municipal and Industrial Effluents (NEQS), Environmental Protection Agency (EPA) of Pakistan, 1999.

15 WHO, Guidelines for drinking water quality, 2nd ed. Vol. 2. Health criteria and other supporting information, World Health Organisation (WHO), Geneva, 1966: 206-215.

16 Spinks J W T, Woods R J. An introduction to radiation chemistry. New York: John Wiley, 1976: 293.

17 Zele S R, Nickelsen M G, Cooper W J. Modeling kinetics of benzene, phenol and toluene removal in aqueous solution using high energy electron beam process, in Environmental application of ionizing radiation (Cooper W J et al. Eds), New York: John Wiley, 1998: 400.