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Impacts of tanneries wastewater on the vicinal flora of Sheikhupura and Kasur, Pakistan

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Abstract. It is of paramount concern that some leather tanneries around the world are disposing waste in environment which are a cause of destruction of flora and fauna in vicinity. Especially chrome tanning poses a major threat due to the release of chromium in wastewater (WW). Hexavalent chromium (Cr^{6+}) is a potential carcinogen and thus demands stern quality control measures. The present investigations focused on the quality of WW released from leather tanneries of two cities *i.e.*, Sheihupura and Kasur, Pakistan, and its effect on the vicinal flora. Cr^{6+} and total chromium (Cr) in all the samples were determined through UV visible spectroscopy and atomic absorption spectroscopy (AAS). Wastewater samples (WWS) were collected at head and at a distance of 50 – 200 m at specific intervals, at edge and inward towards middle of WW streams. WWS of both Sheihupura and Kasur tanneries showed comparable Cr^{6+} content at head but much higher total Cr *(in parenthesis)* in later *i.e*., 89.7 ppm (1440.57 ppm) and 94.9 ppm (3527.95 ppm). Cr^{6+} content declined inward stream and with the increasing distance down the stream falling exponentially in Sheikupura and steeply at Kasur. The soil samples (SS) at 3 m *i.e*., at edge of WW streams showed higher Cr^{6+} content for Sheikhupura than WWS i.e., 94.8 ppm (1041.8 ppm) falling with distance to 44.8 ppm at 150 m. It is less at Kasur *i.e*., 80.5 ppm (4465.9 ppm) falling sharply with distance at 150 m to 25.1 ppm. This showed buildup of Cr^{6+} ions in soil of Sheikupura with time. As the distance off stream on the ground increased, both Cr^{6+} and the total Cr declined and much more at Kasur site i.e., 23.8 ppm (880 ppm) and reached close to Sheikhupura 32.7 ppm (610 ppm) at 150 m. Plausibly, the Sheikhupura tannery is older and/or the soil in vicinal area is more porous. Plant vegetation examined in soil at edge only, show the uptake of both Cr^{6+} and total Cr. Roots and grass leaf at Sheikhupura and the potato leaf at Kasur showed the highest Cr^{6+} uptake of the total Cr i.e., 4.6% 3.5% and 6.4 %, respectively. The results show that tanneries WW has drastically affected soil and consequently the plants with Cr^{6+} ions and total Cr above the permissible levels of 0.1 ppm. To ratiocinate, these will finally incorporate in food chain ultimately damaging the fauna and henceforth calls for adoption of effective removal methodologies and greener routes for a sustainable environment.

***Keywords*:** tannery wastewater; chromium (VI); total chromium; flora.

1. Introduction

Global industrialization has brought economic stability and has thereby raised the living standards of masses. On one hand industrialization has benefitted humans immensely but on the other hand uncontrolled emissions from industrial plants have added pollution to the mother earth that has serious consequences on environmental sustainability. High pollution levels have not only injured the flora and fauna but are also a source of threat to human race. Several pollutants especially heavy metals are potential carcinogens which are directly or indirectly consumed by humans which not only limit their life span but also add misery to the destined journey. Tanneries are one of such industries: though good contributors in job creation and value-added goods. Pakistan is rich in arable land and 22.04% to GDP was contributed by agriculture in 2019 [1] with 56% of value addition by its subsector livestock i.e., 11% [2]. Animal husbandry is growing at a fast pace generating capital through providing raw material to germane industries [3]. With production numbers of 47.4 million hides per annum tanneries are one of such associated industry that directly or indirectly employs over 500,000 people [4] fetching $850 million in FY19 [5]. There are over 800 tanneries in Pakistan located mainly in the cities of Karachi, Multan, Kasur and Sheikhupura. The tanneries are making reasonable profits but many of these are not in the queue of sustainable industries.

Chrome tanning is favored in Pakistan due to easy and cheap availability of raw materials. However, uncontrolled emissions from some of the tanneries though not all, have impinged drastic effects on flora and fauna disturbing the balance of environment and causing illness in human beings. G.J. Hashmi and coworkers [6] have presented a concise review of scenario of Leather Industry in Pakistan that highlights the dangers of contaminated wastewater and gaseous emissions on human health. The highest risk arises from chromium sulfate use in the tanning process for interlocking collagen in leather. About 30-40% of chromium sulfate remains unused and (if untreated) released in waste WW imposing threat for soil and land species [7-8]. This matter is also of grave concern in other countries.

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Leather tanneries generate significant quantities of waste that contains degenerated hides, hair shavings, leather trimmings, flesh, lime, fatty material, splits, sulfides and salts. Total chromium released in WW generally contains Cr^{3+} and Cr^{6+}, the later being about 500 times more toxic than the former and hence of much more concern. The potential risks of Cr^{6+} are well established [9, 10] ranging from contact allergy [11, 12] to cancer [13-16].

The present paper focuses upon the release of chromium in tannery WW from two major tanneries situated in Sheikhupura and Kasur located in the province of Punjab, Pakistan. The soil and the plant analyses were also done to see the impact of released WW on the vicinal areas of tanneries. This study will be one of the whistle blowers for the business community to pay attention to the pollutant levels in WW and refine the processes at tanneries to minimize the risk of disaster in the affected areas.

2. Experimental

2.1. Sample collection and preservation

Samples of wastewater, soil and plants were collected from vicinal areas of tanneries situated in the cities of Kasur and Sheikhupura, Pakistan. The disposal sites are shown in Figure 1 (a, b and c).

a.

b.

Figure 1. a) Discharge of effluent from tannery Sheikhupura. b) Ineffective effluent treatment plant in Kasur. c) Wastewater contaminated area in Kasur

Wastewater samples (WWS) were collected from 9 different points starting from 0 m i.e., the discharge point/source/head, 50 m at stream edge and then moving 50 m inward from the stream edge, 100 m at stream edge and moving 100 m inward from the stream edge, 150 m at stream edge and moving 150 m inward and 200 m at stream edge and moving 200 m inward from stream edge. A total of 6 samples were picked for each distance. Thus, a total 54 WWS were collected for each tannery. The samples were stored in airtight glass bottles and labeled. Each sample was filtered several times on Whatman 42 to obtain clear solution i.e., removing suspended particles, hair and sludge, for further analyses. The final concentration of chromium was calculated from the average of the 6 samples within a standard deviation (SD) of < 0.5.

Soil samples (SS) were collected at a depth of 30 cm at the boundary of effluent stream i.e., at stream edge down the stream and off stream edge, on ground, at a distance of 50 m, 100 m and 150 m and placed in plastic Ziploc bags and labeled. The first SS off stream was taken where the WW started to disperse on ground at a distance of 3 m. The collected SS were oven dried at 105±5 ºC for 4 hours till constant weight and kept in desiccators. The dried SS were ground and thoroughly mixed and then passed through sieve number 36 to obtain constancy in size of particles. The samples were re-dried for 1 hour to avoid any moisture entrapment during the process of grinding and sieving. 0.5 g SS was acid digested in 30 ml of 37% HCl 70% HNO_3 (3:1) in 100 ml beakers with continuous stirring for about 15 to 20 minutes at 130 ºC to almost dryness (ISO 11466:1995). The mass was dissolved in 25 ml deionized water and then filtered. The filtrates were placed in airtight polythene bottles till further dilution for analyses. 5 determinations were done for each distance and average within an SD of <0.5 has been taken.

Plant samples (PS) were collected from the discharge point of tanneries and immediately cut into three portions i.e., roots, stems and leaves. These portions were placed in polythene sealed bags. Care was taken to place roots, stems and leaves of one plant together though in separate bags. All the plant samples were oven dried at 100 ºC for 1 hour and placed in desiccators. The samples were dried and weighed again till constant weight. After drying, the samples were ground to fine powder. 5 g of each sample was digested in 10 ml of *aqua regia* with continuous stirring in 100 ml beaker at 120 ºC till almost a dry mass. 25 ml water was added for dissolving and washing the beaker followed by filtration on Whatman 42. The filtrates were collected in beakers and transferred to airtight polythene bottles till further dilution for analyses. 5 determinations were done for each distance and average (SD of < 0.5) was taken.

2.2. Determination of Cr^{6+} in samples

Cr^{6+} content in the WWS, SS and PS was measured on UV-visible spectrophotometer. The method is based on the principle that Cr^{6+} reacts with 1, 5-diphenylcarbazide (DCP) and reduced to Cr^{3+} through complex formation. 1, 5-diphenylcarbazone complex is purple in color

which is estimated at a wavelength (λ) of 540 nm [17, 18].

The Cr^{6+} stock solution of 1000 mg/l, prepared from dried potassium dichromate ($K_2Cr_2O_7$), was used to make 0.2, 0.4, 0.6, 0.8 and 1 ppm standard solutions. The standard solutions were placed in sequence in 100 ml volumetric flasks and 1 ml DCP solution followed by 5 ml 1N H_2SO_4 was added. The blank solution was prepared by taking 1 ml DCP solution and 5 ml 5N H_2SO_4 in volumetric flask of 100 ml capacity making the final volume up to the mark with deionized water. The solutions were kept for 10 minutes and the intensity of the purple color, thus developed, was checked as absorbance at λ = 540 nm on a T80 UV- visible spectrophotometer, PG instruments U.K. A standard graph was constructed between the absorbance and the concentration of Cr^{6+} standard solutions. The standard graph showed a linear relationship between the selected concentrations of 0.2, 0.4, 0.6, 0.8 and 1 ppm and their respective absorbance taken at λ_{max} of 540 nm with an R^2= 0.999. This developed the equation y = 0.5969x where y is the absorbance and x is the concentration in mg/l. The standards graph was utilized to determine the concentration of Cr^{6+} in the unknown collected WWS.

2.3. Determination of total Cr in samples

Total chromium content of samples was estimated by Atomic Absorption Spectroscopy (AAS) [19]. Three standard solutions of 100 mg/l, 300 mg/l and 500 mg/l were made from thoroughly dried $K_2Cr_2O_7$ salt solution of 1000 mg/l. 1 ml aliquots of each was taken in a test tube, diluted with deionized water and labeled accordingly. The standards and the test samples were placed in the auto sampler and the absorbance was checked at λ 357.9 nm on AA240FS atomic absorption spectrometer, Varian USA, at a slit width of 0.2 nm using air/acetylene flame. Total chromium in the WWS, SS and PS was calculated from the calibration graph built from standards.

3. Results and discussion

WW from Sheikhupura and Kasur tanneries under study is thrown out via pipes into canals or directly onto the outside land creating radial drainage patterns forming pools of irregular shapes. Often, over the passage of time these turn into ponds of dirty obnoxious smelling yellow greenish waters. The pressure at point of emergence of WW i.e., the head directly affects the volume of WW passing at any point on a stream i.e., discharge. Water flow almost all the time from head and velocities of discharge keeps the WW spreading to nearby ground area as stream and later enter into water canals threatening water quality.

6 samples collected for each point showed good coordination with SD < 0.5. The WWS results (conferred as average of 6 samples) are presented graphically in Fig. 2.

The Cr^{6+} ion concentration at head (0 m) in WWS of tannery Sheikhupura and Kasur is almost the same. It can also be seen that Cr^{6+} ion content in WWS of tannery, Sheikhupura declined exponentially with the distance from the head, whereas, the Cr^{6+} ion concentration in WWS of tannery Kasur showed a linear trend. Plausibly, the pressure at head of tannery Sheikupura was low to carry the dissolved load to greater distances.

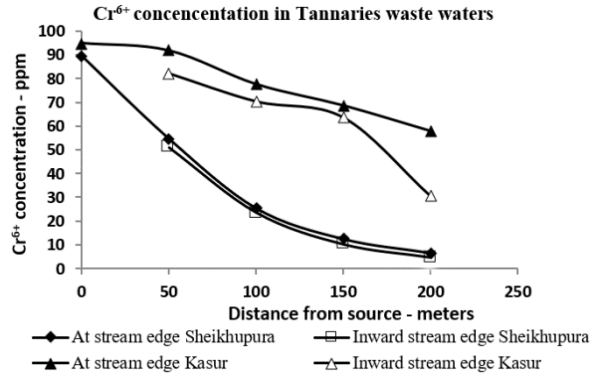

Figure 2. Cr^{6+} concentration in tanneries wastewater samples of Sheikhupura and Kasur

This is further evidenced by the Cr^{6+} concentration of 4.7 ppm at 200 m for tannery Sheikhupura as compared to 30.5 ppm for tannery Kasur for the same distance inward from stream edge. It is noticeable that WWS also carried suspended load comprising of hair, un-dissolved salts, hide scraps and fats especially in case of tannery Sheikhupura. Since, the tannery WWS were falling straight onto the soil ground, the seepage to the underground waterbed posed a severe threat to the drinking water table. EPA has set all forms of chromium to 0.1 mg/l in safe drinking water limits [20]. Both the tanneries under study are releasing Cr^{6+} in high amounts, which is alarming. The concentration of Cr^{6+} ion is higher at the edge of WW stream as compared to the inner flow. In the center, saltation slowly moves the bed load. Also, with the water flow, more dissolution occurs and as water disperses to the sides, the Cr^{6+} ion content builds up at edges with time due to stagnant conditions at boundaries. Henceforth, the severity of problem at stream edges rise. Total Cr in the same WWS is presented graphically in Figure 3.

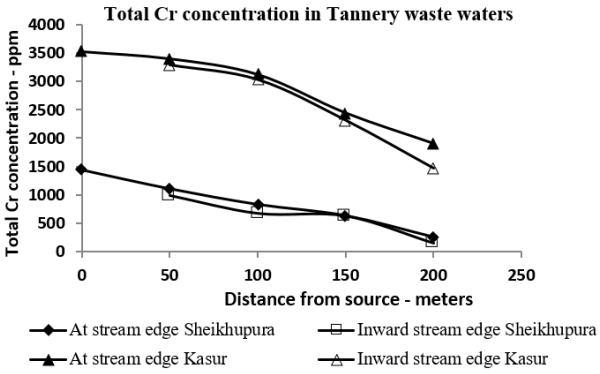

Figure 3. Total chromium content in tanneries wastewater samples (WWS) of Sheikhupura and Kasur

Total Cr content in tannery Kasur WWS is higher than double the amount in the tannery Sheikhupura. The total Cr content of tannery Sheihupura decreased linearly with distance i.e., 1441 ppm at head and falling to 155 ppm at 200 m inward from stream edge. The same tannery showed an exponential decline with distance for

Cr^{6+} (Fig. 2). Total Cr contained 6.2% Cr^{6+} ions in WW at head of the stream. Kasur tannery had total Cr of 3528 ppm at head and declined linearly with distance to 1475 ppm at 200 m inward from stream edge. This tannery had 2.7% Cr^{6+} ions in the total Cr released at head. It seems that the WW pressure at head of Kasur tannery was high and henceforth, the Cr content did not decline considerably low till 200 m. Kasur tannery had better performance in controlling Cr^{6+} ions in WWS. This tannery had a treatment plant which was not in effective use. In both the cases, there was uncontrolled release of heavily polluted water onto ground, see Fig. 1c. With such high total Cr content, in environment, no one can assure safe agriculture or safe drinking water availability to the people of these cities. This has been earlier investigated and reported by several researchers [21-24] that WW from several tanneries in Pakistan is untreated, highly contaminated and henceforth, creating a serious menace for the environment. The overview by Hashmi *et al.* [6] and M. Junaid *et al*. [25] through bio matrices have precisely highlighted the health hazards associated with tannery emissions and effluents.

Results of studies conducted to ascertain the ingress of Cr^{6+} ions and the total Cr down along the stream edge in the surrounding soil areas of tannery WW streams are presented in Figure 4 and 5. The changes in Cr^{6+} ions and the total Cr off stream edge (away on dry ground) in the vicinal areas of tanneries are shown in Table 1.

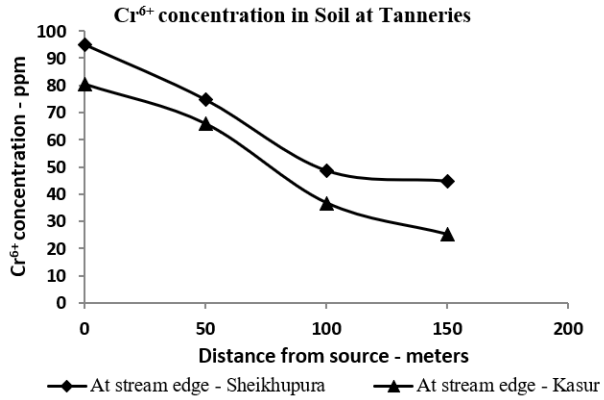

Figure 4. Cr^{6+} concentration in soil samples (SS) downstream at edge of tanneries Sheikhupura and Kasur

Table 1. The Cr^{6+} and total Cr off stream in soil in vicinal areas of tanneries Sheikhupura and Kasur

Distance off stream [m]	Sheikhupura Tannery		Kasur Tannery	
	Cr^{6+} [ppm]	Total Cr [ppm]	Cr^{6+} [ppm]	Total Cr [ppm]
3	94.8	1041.8	80.5	4466.0
50	67.0	939.1	61.0	2730.7
100	46.4	786.4	34.8	2611.6
150	32.7	610.2	23.8	880

Cr^{6+} in SS at stream edge of head of tannery Sheikhupura is a slightly higher i.e., 95 ppm than the WWS i.e., 90 ppm. Cr^{6+} content declined systematically down the stream edge in SS with increase in distance i.e., 75 ppm (50 ft), 49 ppm (100 ft) and to 45 ppm at 150 ft. The Kasur tannery showed less Cr^{6+}, 81 ppm at stream edge at head as compared to WWS having Cr^{6+} of 95 ppm (Fig. 2). Down the stream at edge, Cr^{6+} in SS declined with distance to 66 ppm (50 ft), 37 ppm (100 ft) and to 24 ppm at 150 ft. This tannery had comparatively higher Cr^{6+} in WWS than Sheikhupura tannery but the soil is showing less amounts. May be the Sheikhupura tannery is older and/or the vicinal soil is of different nature retaining more of Cr^{6+} in the soil. Vegetation is another factor that could have contributed in removal of Cr^{6+} from soil in vicinal area of Kasur tannery.

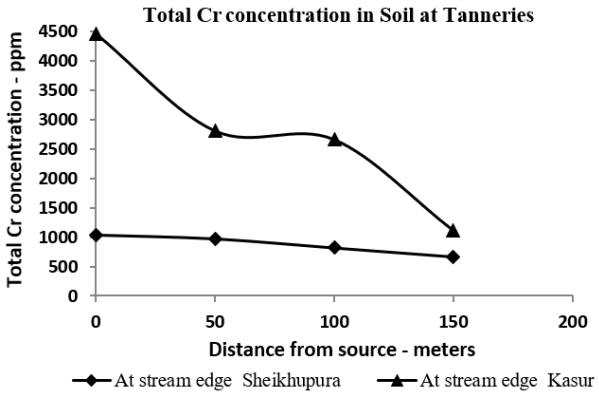

Figure 5. Total Cr content in soil samples (SS) at tanneries Sheikhupura and Kasur

It is noticeable that the total Cr down at stream edge of SS of tannery Sheikhupura is considerably lower than at tannery Kasur i.e., 1042 ppm and 4466 ppm, respectively, see Fig. 5. It declined with distance down the stream in both the cases i.e., 610 ppm at former and 880 ppm at later at 150 m. However, Kasur tannery showed 5 times reduction in total Cr. The off stream vicinal areas of tannery Sheikhupura retained more total Cr as compared to tannery Kasur. The Cr^{6+} concentration in soil at 3 m is 9.1% of the total Cr in Sheikhupura and 1.8% of total Cr in Kasur tannery, respectively. The pressure at head of tannery could also be one of the factors for more Cr^{6+} and total Cr retention in vicinal soils of Sheikhupura. Such high Cr is plausibly carried through WW running on topsoil that absorbed in soil with time. Diffusion processes in soil also played a role depending on several factors e.g., porosity of soil, plants, temperature and time. In both the cases, such high Cr^{6+} content in top layers of soil can be taken up by vegetation and may thus be incorporated in food chain.

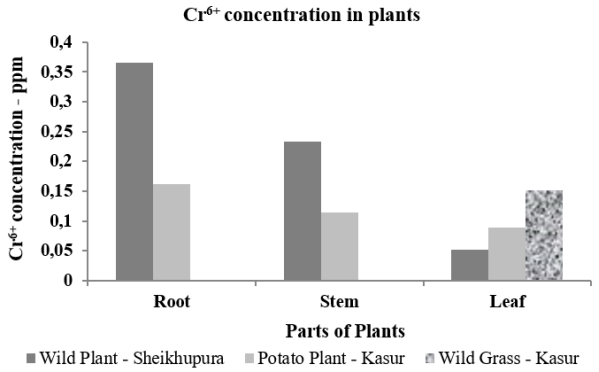

Figure 6. Cr^{6+}concentration in plants growing at tanneries Sheikhupura and Kasur

The impact of Cr laden soil on flora of tanneries area was studied by randomly picking the growing plants at

edge of tanneries at 3 meters near the source/head. The Cr^{6+} and the total Cr extraction results of plants are shown in Figures 6 and 7, respectively.

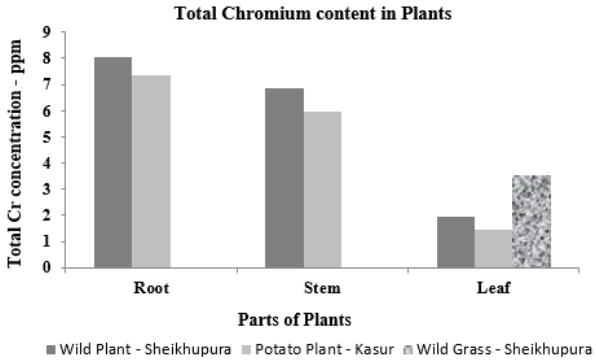

Figure 7. Total Cr concentration in plants growing at tanneries Sheikhupura and Kasur

The plants at Sheikhupura tannery site were some wild species whereas, the plants picked at the Kasur tannery site were identified as potato plants. It is seen that Cr^{6+} ions intake by the different parts of plants at the source/head of both Sheikhupura and Kasur tanneries is systematic i.e., roots > stem > leaf. Gheju *et al.* [26] also reported that Cr^{6+} ions slowly translocated within *Zea mays* plants from roots to stem, and further very slowly to leaves in controlled soils. It is seen that roots and stem at Sheikhupura tannery site contained higher concentration of Cr^{6+} as compared to potato plants at Kasur tannery. Cr^{6+} ions concentration in leaves is higher in potato plants of Kasur i.e., 0.09 ppm as compared to wild species 0.05 ppm at Sheikhupura. The Grass leaf samples collected at Kasur tannery site showed absorbance of Cr^{6+} ions up to 0.152 ppm.

The total Cr concentration in PS increased systematically i.e., leaf < stem < roots. Maximum 4.5% Cr^{6+} ions of the total Cr are absorbed by roots of wild species at the Sheikhupura tannery site. Grass leaves had comparable uptake of 4.24%. Most interestingly the potato leaves showed the highest Cr^{6+} i.e., 6.2% of the total Cr. The rate of transpiration from leaves as the function of leaf area, temperature, humidity and wind velocity can be the contributing factors. Anything conclusive requires controlled laboratory conditions. The experimental results obtained from the plant analyses are indicators that all the plant types can take up Cr^{6+} ions. This will also vary according to the plant type, age, species, weather conditions, soil texture etc. The ecosystem is severely affected as the contaminants along with other pollutant ions are spread, circulated and accrued both in abiota and biota.

The nexus leads us to the fact that both tanneries at Sheikupura and Kasur are releasing high levels of Cr^{6+} ions in soil and any existing treatment is not helpful to the required level. This scenario exists in other cities e.g., Karachi, Pakistan as observed by Omm-e-Hany *et al*. reporting TSS, TDS, pH, BOD and COD of WWS within acceptable limits but chromium exceeding the permissible levels in the months of May and June, respectively [27]. Similarly, F. Younas *et al*. observed total Cr concentration in WW from Kasur tanneries were much above the National Environmental Quality Standards (NEQS) of 1 mg/l [28]. In our studies, the Kasur tannery had a treatment plant but due to ineffective execution it is damaging the environment with excessive Cr release. Earlier S. Ahad and coworkers analyzed WW released from Common Effluent Pre Treatment Plant (CEPTP) at Kasur [29]. They declared the effluent water unfit for irrigation due to pH, EC, TDS, SAR, RSC, SO_4^{2-} and Cl^- above the permissible levels. We have focused on the much more serious issue of Cr that importantly needs attention. Surveys by Qureshi *et al.* have precisely covered the associated health risks. They interviewed and clinically examined 332 male and female tannery workers between the age of 20-50 from Sheikhupura and Peshawar, Pakistan [30]. They found quite higher infertility rate, still births and infant deaths in workers exposed to chromium as compared to controls.

The vicinal areas of tanneries both at Kasur and Sheikhupura are heavily laden with chromium. Consequently, the plants have taken up both Cr^{6+} and Cr^{3+}. Presence of these ions will negatively affect the growth of healthy plants [31-34]. The disquisition leads us to finally report that people must not pay such a heavy toll and tannery effluents need to be controlled. The quaesitum forces the adoption of green tanning processes [35, 36] or the use of multivocal end of pipe technologies combined or lone [37-40], and by low-cost waste materials through adsorption [41, 42]. Last but not the least is phytoremediation of soil. We have observed that wild grass picked up Cr from soil. Any vicinal areas of tanneries that are already spoiled through ignorance and or insouciance can be healed through specific plantation [43-45]. This issue can be resolved in many ways and henceforth, a slack attitude which is risking so many lives is indefensible and unjustified. The prolegomena is enough to incite nisus for sustainable green environment.

4. Conclusions

The wastewater released from the tanneries of Kasur and Sheikhupura, Pakistan, contains high amounts of Cr^{6+} and horrendous levels of total Cr though austere legislation exists against such ill practices. The study confirms that the soil in the vicinity of these tanneries is also exceedingly contaminated with chromium and henceforth, the vegetation has also taken up Cr^{6+}. The flora is spoiled. This problem is also of grave concern in other countries [46]. Strenuous efforts through use of multiple technologies and methods are required to treat the tannery wastewater before it is released in the area to safe guard environment and humans and to endorse goals of sustainable development.

Conflicts of interest. The authors declare no conflict of interest.

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