water

MDPI

Article

Unveiling Distribution, Hydrogeochemical Behavior and Environmental Risk of Chromium in Tannery Wastewater

Fazila Younas [1], Irshad Bibi [1,*], Muhammad Afzal [2], Fahad Al-Misned [3], Nabeel Khan Niazi [1], Khalid Hussain [4], Muhammad Shahid [5], Qamar Shakil [6], Fawad Ali [7,8] and Hailong Wang [9]

1 Institute of Soil and Environmental Sciences, University of Agriculture Faisalabad, Faisalabad 38040, Pakistan
2 Soil and Environmental Biotechnology Division, National Institute for Biotechnology and Genetic Engineering (NIBGE), Faisalabad 38000, Pakistan
3 Department of Zoology, College of Science, King Saud University, Riyadh 11451, Saudi Arabia
4 Department of Agronomy, University of Agriculture Faisalabad, Faisalabad 38040, Pakistan
5 Department of Environmental Sciences, COMSATS University Islamabad, Vehari Campus, Vehari 61100, Pakistan
6 Fodder Research Sub-Station, Ayub Agricultural Research Institute, Faisalabad 38000, Pakistan
7 Centre for Planetary Health and Food Security, Griffith University, Nathan Campus, Brisbane QLD 4110, Australia
8 Department of Agriculture and Fisheries, Mareeba QLD 4880, Australia
9 Biochar Engineering Technology Research Center of Guangdong Province, School of Environmental and Chemical Engineering, Foshan University, Foshan 528000, China
* Correspondence: irshad.niazi81@gmail.com or irshad.niazi@uaf.edu.pk

Abstract: Chromium (Cr)-contaminated tannery wastewater is a major environmental concern, especially in developing countries, such as Pakistan, due to its use for crop irrigation, resulting in food-chain contamination and health issues. In this study, we explored the distribution, speciation, hydrogeochemical behavior and environmental risks of Cr in tannery wastewater collected from various tanneries of Kasur district in Punjab, Pakistan. Tannery wastewater samples were taken during the summer (TWW-summer; n = 82) and winter (TWW-winter; n = 82) seasons. The results showed that high Cr concentration was observed in TWW-winter (mean: 49 ± 32 mg L^{-1}) compared to TWW-summer (mean: 15 ± 21 mg L^{-1}). In TWW-summer and TWW-winter samples, the Cr concentration exceeded the National Environmental Quality Standard (1 mg L^{-1}), with the total Cr ranging from 2.8 to 125 mg L^{-1}. Hexavalent Cr (Cr(VI)) and trivalent Cr (Cr(III)) concentrations spanned 2.7 to 2.9 and 12.4 to 46 mg L^{-1}, respectively. The Piper plot showed that hydrogeochemistry of wastewater was dominated by Ca-Mg-SO_4 and Ca-Mg-Cl type water, and geochemical modeling indicated that the presence of Cr-iron (Fe)-bearing mineral phases—notably, $FeCr_2O_4$, $MgCr_2O_4$ and $Cr(OH)_3$) may control the fate of Cr in the tannery wastewater. Environmental risk assessment modeling categorized the tannery wastewater as the 'worst quality', which is not fit for use in crop irrigation without treatment. This study highlights that immediate monitoring, remediation and mitigation strategies are required to reduce the risk of Cr exposure from tannery wastewater in many areas of Pakistan.

Keywords: hydrogeochemistry; tannery industry; risk assessment; water; health

check for updates

Citation: Younas, F.; Bibi, I.; Afzal, M.; Al-Misned, F.; Niazi, N.K.; Hussain, K.; Shahid, M.; Shakil, Q.; Ali, F.; Wang, H. Unveiling Distribution, Hydrogeochemical Behavior and Environmental Risk of Chromium in Tannery Wastewater. *Water* **2023**, *15*, 391. https://doi.org/10.3390/w15030391

Academic Editor: Domenico Cicchella

Received: 20 October 2022
Revised: 1 January 2023
Accepted: 12 January 2023
Published: 18 January 2023

1. Introduction

Rapid industrialization and urbanization have drastically enhanced the production of wastewater containing various contaminants, including the potentially toxic elements (PTEs) [1–4], such as chromium (Cr), mercury (Hg), nickel (Ni), lead (Pb), zinc (Zn), copper (Cu), iron (Fe) and cadmium (Cd). These PTEs can cause severe environmental and human health issues, thus, becoming a major concern globally [5–7]. Among various PTEs, Cr is a highly toxic and carcinogenic metal and is used in different industries, including textile, Cr plating, refractories and particularly in the leather tanning industry [8].

Given the toxic and mobile nature of Cr, the maximum permissible limit of total Cr in wastewater has been set at 0.05 mg L^{-1} by the World Health Organization (WHO). The International Agency for Research on Cancer (IARC) has classified hexavalent Cr (Cr(VI)) as a Group-I human carcinogen [9]. Crop irrigation with wastewater containing PTEs is a common practice in developing countries, such as Pakistan, because it also has important nutrients, such as nitrogen and phosphorus [10–13].

Chromium-induced environmental and health hazards depend on its speciation and bioavailability. The most common Cr species are trivalent Cr (Cr(III)) and Cr(VI), which exist in water and soil environments [14]. The oxidation and reduction of Cr in water depend on the pH, redox potential (E_h) and presence of redox coupling agents, such as ferrous iron (Fe(II)), sulfide (S^{2-}) and organic carbon. The Fe(II) and S^{2-} may reduce Cr(VI) into Cr(III), while Cr(III) oxidizes into Cr(VI) by oxidizing agents, such as manganese oxide (MnO_2), hydrogen per oxide (H_2O_2) and dissolved oxygen (DO) [15,16].

Previous research has examined the fate of Cr by examining the oxidation and reduction of Cr-bearing minerals or precipitation/dissolution of Cr under varying redox potential and pH. The dissolution/precipitation of Fe-bearing minerals, such as pyrite (FeS_2), mackinawite (FeS_{1-x}), hematite (Fe_2O_3), goethite and magnetite (Fe_3O_4), present in wastewater and in subsurface systems may control the hydrogeochemical behavior and fate of Cr in tannery wastewater [17–19].

Previous research has been conducted to determine water quality attributes and Cr concentration in tannery wastewater, although it has not been directed to examine the hydrogeochemistry and fate of Cr in tannery wastewater [20–25]. Afzal, Shabir, Iqbal, Mustafa, Khan and Khalid [26] determined the aquatic chemistry of groundwater in Punjab, Pakistan and reported a high concentration of Cr (0.82–2.25 mg L^{-1}), which was possibly due to the discharge of Cr-contaminated wastewater from the surrounding leather tanning industry in the area. Joyia, Ashraf, Shafiq, Anwar, Nisa, Khaliq and Malik [27] reported a high concentration (72 mg L^{-1}) of Cr in tannery wastewater produced from various tannery industries of Harappa in Punjab, Pakistan. Most of the earlier research assessed the hydrogeochemistry of groundwater mainly contaminated with arsenic and fluoride and not wastewater, employing analytical and multivariate statistical tools.

While poorly understood, we investigated Cr distribution, speciation and assessed Cr-mediated environmental risk, using geochemical and multivariate tools to determine the fate of Cr in tannery wastewater. Moreover, the (hydro)geochemical behavior of Cr in wastewater was examined in the summer (TWW-summer) and winter (TWW-winter) seasons.

2. Materials and Methods

2.1. Description of the Study Area

Tannery wastewater samples (n = 82 in summer and winter each) were collected from Kasur in Punjab, Pakistan (Figure S1, Supplementary Information). Leather tanning has a long-standing tradition in Kasur district (Table S1, Supplementary Information) of Punjab, which is known as the biggest tannery industrial city in Pakistan [28]. The climate is comparatively cold in winter but hot in summer. In the months of May and June, the mean temperature may rise to 44 °C. The average annual rain of Kasur is 500 mm [29].

In Kasur, leather tanning is the most important industry where more than 300 active individual tanning industrial units are located. As a result of tanning activities, about 150 t solid waste and 13,000 m^3 of Cr-contaminated tannery wastewater are discharged on a daily basis to main water bodies and land, thus, contaminating the environment in the area and causing serious health hazards to humans and animals [30].

2.2. Tannery Wastewater Sampling

Tannery wastewater sampling points were selected considering their spatial distribution in different tanneries to represent major tannery areas with potential Cr-contamination in TWW-summer and TWW-winter samples. Wastewater was taken from 21 different tanneries during summer and winter seasons. Wastewater samples were collected in two replicates from each tannery wastewater site. The water samples were taken at a high loading rate during both seasons, although examining the impact of the loading rate was beyond the scope of the current study.

A total of 82 samples were taken in summer and 82 in winter from 21 different tanneries. In the summer season, tannery wastewater samples were collected in May 2018 and in winter season samples were collected in January 2019. Wastewater samples (250 mL each) were collected in clean plastic bottles and analyzed for the total Cr, iron (Fe), manganese (Mn), chemical oxygen demand (COD), biological oxygen demand (BOD), cations and anions.

Tannery wastewater was divided in two sets: (i) acidified with concentrated nitric acid (HNO_3) to bring the pH < 2 and used for Cr and major elemental analysis, and (ii) non-acidified to determine ions and other wastewater quality attributes. All the tannery wastewater samples were stored in a refrigerator at <4 °C prior to various physicochemical analyses.

During the collection of wastewater samples, various chemical and physical parameters, such as the pH, electrical conductivity (EC), redox potential (E_h), total dissolved solids (TDS) and dissolved oxygen (DO), were measured at the sampling time. The E_h, pH EC, TDS and DO of tannery wastewater samples were determined using a portable redox meter (Model 8424, Hanna, USA), pH meter (ST 300, Ohaus-USA), DO meter (model ST300, OHAUS, USA) and EC/TDS meter (Model 3100, OHAUS, USA), respectively.

The total Cr in wastewater was determined using a flame atomic absorption spectrometer (FAAS; Thermo-AA®, Solar Series, USA) at a 357.9 nm wavelength. The Cr(VI) in wastewater was determined using the 1,5-diphenylcarbazide (DPC) method at 540 nm using an UV-Visible Spectrophotometer (Lambda 25, Perkin Elmer, AA solar-series, USA) (APHA 2005). The concentration of Cr(III) was calculated by taking the difference between the total Cr and Cr(VI) in wastewater.

The Mn and Fe concentrations were analyzed using a FAAS. Concentrations of calcium (Ca), potassium (K) and sodium (Na) in the tannery wastewater were determined using a flame photometer (BWB Model BWB-XP, 5 Channel Flame Photometer, England). The analytical wavelengths of 589.0 nm (Na), 422.7 nm (Ca) and 766.5 nm (K) were used for analysis of these elements. The Ca and Mg hardness were determined using the standard titration method as described [31].

The sulfate (SO_4) in wastewater was determined following the barium sulfate ($BaSO_4$) precipitation method. A 1 N solution of barium chloride ($BaCl_2$) was prepared and added into wastewater samples and then allowed to precipitate SO_4–S as $BaSO_4$ following the method described elsewhere [32]. The concentrations of carbonate (CO_3^{2-}), bicarbonate (HCO_3^-) and chloride (Cl^-) were determined according to the method described by Estefan et al. (2013). The concentration of COD and BOD in tannery wastewater was analyzed according to the standard methods described by Saritha, Chockalingam and BIST [33].

2.3. Environmental Risk Assessment of Chromium-Bearing Wastewater

The comprehensive contamination index (CCI) and single-factor evaluation index (SFEI) were used to measure the wastewater quality and potential risk. The SFEI used to examine the contribution of every single water attribute to water contamination and CCI was used to assess the contributions of all the measured parameters in wastewater.

For this purpose, the National Environmental Quality Standards [34] of Pakistan were used to calculate the surface water quality attributes; and the United States Environmental Protection Agency and WHO standards were used to calculate the SFEI and CCI values [35].

The SFEI and CCI were computed by using Equations (1) and (2), respectively.

$$\mathrm{SFEI} = \mathrm{Mi}/\mathrm{Si} \quad (1)$$

$$\mathrm{CCI} = 1/\mathrm{n}\sum_{\mathrm{i}=1}^{\mathrm{n}} \mathrm{Mi}/\mathrm{Si} \quad (2)$$

where M_i is the measured concentration of each parameter, S_i is the corresponding maximum/environmental quality standard of surface water, and n is the total number of parameters.

The computed results by SFEI were interpreted as SFEI value < 1, the water quality meets the standards. If SFEI value > 1, the water quality exceeded the surface water quality standards. Based on the CCI value, the water quality was classified into five categories: (i) CCI is 0–0.20 (clean water), (ii) CCI is 0.21–0.40 (sub-clean), (iii) CCI is 0.41–1.00 (slightly contaminated), (iv) CCI is 1.0–2.00 (medium contamination) and (v) CCI is >2.01, highly contaminated. The heavy metal evaluation index (HEI) was used to determine the overall water quality concerning metal contamination.

The HEI was computed using Equation (3):

$$\mathrm{HEI} = \sum_{\mathrm{i=1}}^{\mathrm{n}} \mathrm{Hc/Hmax} \tag{3}$$

where H_c is the measured value, and H_{max} is the maximum permissible limit of each trace metal.

Based on the computed value of HEI, there are three levels of contamination: (i) HEI > 20, high contamination, (ii) HEI 10–20, medium contamination and (iii) HEI < 10, low contamination [35].

2.4. Quality Control and Analytical Precision

Quality assurance and quality control protocol was followed to ensure data reliability and analytical accuracy. After every 10 samples, a reference sample with a known total Cr or Cr(VI) concentration was run on the FAAS or UV-visible spectrophotometer, respectively, to check the analytical precision and accuracy. The chemicals used in this research were of analytical grade. All the glassware and plastic ware were soaked in diluted HNO_3 for 24 h and then washed with deionized water twice before use for analytical work.

2.5. Geochemical Modeling for Saturation Index

The saturation index (SI) values were calculated using geochemical modeling software, PHREEQC [36]. These values were used to estimate the equilibrium conditions of various mineral phases controlling the geochemistry of tannery wastewater. Based on the SI values, mineral-like phases/salts intensity can be classified into three categories: (i) SI > 0, oversaturated/precipitation, (ii) SI < 0, unsaturated/dissolution and SI = 0, equilibrium [37,38]. Geochemist Workbench software (version 9.0.8) was employed to make a E_h–pH stability diagram using the Cr and other relevant parameters data to predict Cr speciation in tannery wastewater and assess its fate in the environment.

2.6. Multivariate Analysis

The statistical analysis was performed using Excel 2016. Principle components analysis (PCA) and Pearson correlation were performed using the Minitab software®. The study area map to show the sampling sites was developed using ArcMap software version 10.4.1. The Piper plot and Durov diagram to show the wastewater type and (hydro)geochemistry were made using the Geochemist Workbench.

3. Results and Discussion

3.1. Distribution of Chromium and Speciation in Wastewater

Figure 1a shows the average concentration of Cr in tannery wastewater from summer and winter seasons collected from 21 tannery sites (hereafter referred as tannery wastewater summer (TWW-summer) and tannery wastewater winter (TWW-winter)) in the industrial zone of Kasur. A high Cr concentration was observed in TWW-winter (3.9–125 mg L^{-1}) compared to TWW-summer (2.8–94.6 mg L^{-1}) samples (Table 1). All the wastewater samples from summer and winter seasons exceeded the Cr concentration above the permissible limits set by the National Environmental Quality Standards (NEQS; 1 mg L^{-1}) and WHO

(0.05 mg L^{-1}) (WHO, 1999) (Table 2) as well as the USEPA safe limit of 2.0 mg L^{-1} for Cr (USEPA, 2012) (Table 2) (USEPA, 2012).

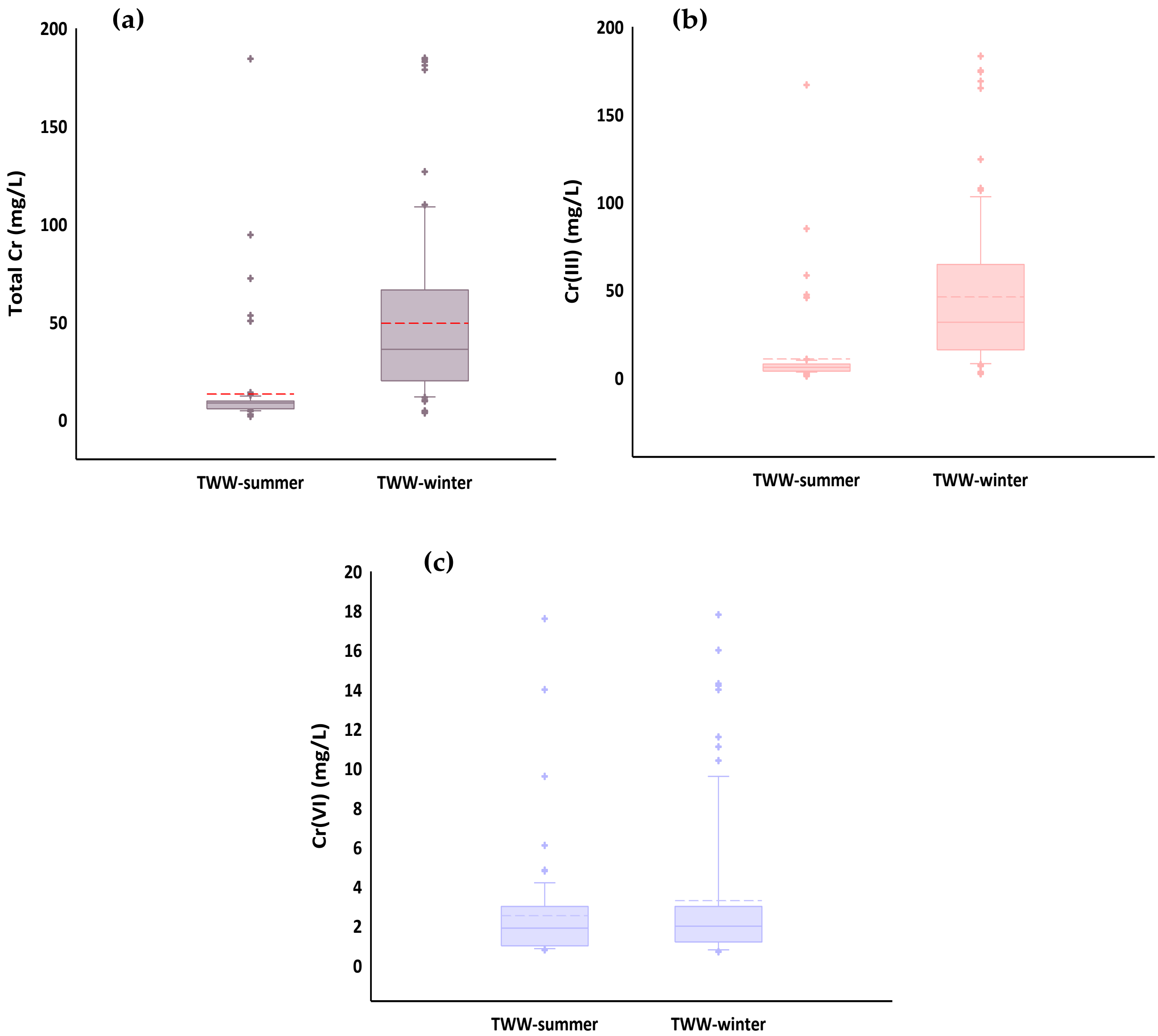

Figure 1. Box plot showing the quartiles and mean of the measured (**a**) chromium (total Cr), (**b**) trivalent Cr ((Cr(III)) and (**c**) hexavalent Cr ((Cr(VI)) values from the tannery industry wastewater samples collected from various tannery industries sites in summer and winter seasons from Punjab, Pakistan.

Tannery wastewater samples, which were taken from the main channels receiving wastewater from all the tanneries, showed the highest Cr concentration in both TWW-winter and TWW-summer samples (up to 72 and 44 mg L^{-1}, respectively). Among all the tanneries, tannery 2 had the highest Cr concentration (39 mg L^{-1}) in TWW-summer and tannery 20 had the maximum Cr concentration (125 mg L^{-1}) in the TWW-winter samples. The tannery 1 and tannery 13 samples showed the lowest Cr concentrations (2.8 and 4.0 mg L^{-1}) in summer and winter seasons, respectively (Table 1).

Table 1. Physico-chemical parameters of tannery wastewater collected in summer (TWW-summer) and winter (TWW-winter) seasons from the tannery industry area of Kasur, Punjab, Pakistan.

	TWW-Summer Sampling: n = 82				**TWW-Winter Sampling: n = 82**			
Parameters	**Mean**	**Median**	**Range**	**S.D (±)**	**Mean**	**Median**	**Range**	**S.D (±)**
pH	7.3	7.2	6.0–8.8	0.95	7.0	6.9	6.0–8.1	0.7
EC (mS/cm)	8.7	5.2	2.0–24.4	6.22	14.5	13.8	8.5–21.8	3.1
TDS (g/L)	4.2	2.7	1.0–11.9	3.05	7.6	8.0	5.0–11.9	2.7
DO (mg/L)	5.1	5.2	3.3–6.4	0.88	5.2	5.2	3.2–6.4	0.8
E_h (mv)	−3.4	−20.3	−74.5–198	66.0	−20.7	−19.0	−304–180	99.1
Ca (mg/L)	96.1	69.5	48.1–220	53.2	97.5	84.2	48.1–219	40.4
Mg (mg/L)	477.3	462.3	257.7–1161	165.1	509.1	483.1	358–774	112.4
Total hardness (mg/L)	573.2	531.7	350.0–1380	202.2	606.7	566.6	433.3–993.3	129.4
Na (mg/L)	324.3	295.9	147.0–564.5	127.5	345.7	351.0	117–643	122.1
K (mg/L)	151.7	129.4	62.9–283	55.2	184.6	163.0	91.3–354	63.6
CO_3 (mg/L)	512.8	518.2	192.0–750	190.9	622.1	640.0	260–870	157.3
HCO_3 (mg/L)	3119.9	3105.9	2199–4270	523.1	3301.7	3233.0	2623–4209	491.0
Cl (mg/L)	4136.6	4263.0	2408–5431	773.5	4542.8	4431.6	3147–5739	551.1
SO_4 (mg/L)	1033.2	686.5	446–4097	881.1	1294.0	922.5	425–5161	938.9
COD (mg/L)	3340.4	2583.3	471–9286	2654.7	3509.0	2324.0	356–9397	3124.9
BOD (mg/L)	1712.2	1416.6	235–4693	1346.5	1954.0	1273.7	178–5400	1758.7
Fe (mg/L)	12.8	12.0	3.6–21.0	4.7	15.3	14.4	4.5–29.0	5.5
Mn (mg/L)	2.8	2.8	1.1–6.1	1.1	5.3	5.3	2.1–11.6	2.1
Total Cr (mg/L)	15.0	7.5	2.8–94.6	21.1	49.3	43.6	3.9–125	32.2
Cr(VI) (mg/L)	2.7	2.0	1.0–9.6	2.1	2.9	2.2	1.0–7.2	1.8
Cr(III) (mg/L)	12.4	5.8	1.7–85.0	19.1	46.3	38.8	2.5–122	31.4

Note(s): TDS: total dissolved solids; DO: dissolved oxygen; E_h: redox potential; Ca: calcium; Mg: magnesium; Na: sodium; K: potassium; CO_3: carbonates; HCO_3: bicarbonates; Cl: chloride; SO_4: sulfate; COD: chemical oxygen demand; BOD: biochemical oxygen demand; Fe: iron; Mn: manganese; Cr: chromium; Cr(VI): hexavalent Cr; and Cr(III): trivalent Cr. S.D (±) indicates the standard deviation.

Table 2. Chromium concentration and maximum permissible limits for Cr and other wastewater quality parameters set by NEQS, WHO and USEPA.

Parameters	**TWW-Summer**	**NEQS Safe Limit**	**% Number of Samples >NEQS Limit**	**WHO**	**USEPA**	**TWW-Winter**	**% Number of Samples >NEQS Limit**
pH	7.3	6–10	0	6–9	6–9	7.0	0
EC (mS/cm)	8.7	NG	-	-	1.0	14.5	-
TDS (mg/L)	4200	3500	30	2100	500	7600	100
DO (mg/L)	5.1	6–9.5	-	-	-	5.2	-
E_h (mV)	−3.4	NG	-	-	-	−20	-
Ca (mg/L)	96	NG	-	-	-	97	-
Mg (mg/L)	477	NG	-			509	-
Total hardness (mg/L)	573	NG	-	-	-	606	-
Na (mg/L)	324	250	46	-	-	345	84
K (mg/L)	151	NG	-	-	-	184	-
CO_3 (mg/L)	512	NG	-	-	-	622	-
HCO_3 (mg/L)	3119	NG	-	-	-	3301	-
Cl (mg/L)	4136	1000	100	-	-	4542	100
SO_4 (mg/L)	1033	NG	-	-	-	1294	-
COD (mg/L)	3340	150	100	250	500	3509	100
BOD (mg/L)	1712	80	100	30	300	1954	100
Fe (mg/L)	12.8	2.0	100	-	5.0	15.3	100
Mn (mg/L)	2.8	1.5	80	-	-	5.3	100
Total Cr (mg/L)	15.0	1.0	100	0.05	1.0	49	100
Cr(VI) (mg/L)	2.7	0.25	100	-	-	2.9	100
Cr(III) (mg/L)	12.4	0.75	100	-	-	46	100

Note(s): TDS: total dissolved solids; DO: dissolved oxygen; E_h: redox potential; Ca: calcium; Mg: magnesium; Na: sodium; K: potassium; CO_3: carbonates; HCO_3: bicarbonates; Cl: chloride; SO_4: sulfate; COD: chemical oxygen demand; BOD: biochemical oxygen demand; Fe: iron; Mn: manganese; Cr: chromium; Cr(VI): hexavalent Cr; Cr(III): trivalent Cr; NEQS: National Environmental Quality Standards of Pakistan; WHO: World Health Organization; and USEPA: United State of Environmental Protection Agency.

These data concur with previous studies where researchers investigated the Cr concentration in wastewater collected from different areas of Punjab, Pakistan [39–41]. Parveen, Ashfaq, Ali, Qadri and Zeb [42] reported that the Cr concentration in tannery wastewater ranged from 15 to 186 mg L^{-1} in the Karachi district of Sindh, Pakistan. The authors revealed that the Cr concentration in all the tannery wastewater samples was above the NEQS safe limit of 1 mg L^{-1} in wastewater.

Recently, Ashraf, Naveed, Afzal, Seleiman, Al-Suhaibani, Zahir, Mustafa, Refay, Alhammad, Ashraf, Alotaibi and Abdella [43] reported that the Cr concentration in tannery wastewater was above the threshold limit with an average Cr concentration of 134 mg L^{-1}. The results from the current study demonstrated that greater Cr concentration was found in TWW-winter compared to TWW-summer samples, which may be due to more tanning processing in the winter season or due to inefficient tanning processes. Khalid, Rizvi, Yousaf, Khan, Noman, Aqeel, Latif and Rafique [44] revealed that tannery wastewater had a high Cr concentration (up to 1.45 mg L^{-1}) that exceeded the safe limits of NEQS (1 mg L^{-1}) in the city of Sialkot in Punjab, Pakistan. Our data indicated that the wastewater from all the tanneries collected in summer and winter seasons did not meet the legal requirements of discharge to drain or sewer without Cr treatment.

3.2. Chromium Speciation in Wastewater

Chromium speciation data of the tannery wastewater showed that the percentage distribution of Cr(III) ranged from 40% to 90% and from 2% to 98% of total Cr in the TWW-summer and TWW-winter samples, respectively (Figure 1b,c). The percentage distribution of Cr(VI) ranged from 1% to 70% and 1% to 35% in the TWW- summer and TWW-winter season samples, respectively.

The percentage abundance of Cr(III) and Cr(VI) was in the order of TW-winter > TW-summer (Table 1; Figure S2, Supplementary Information). In this study, Cr(III) was the dominant Cr species in tannery wastewater of Kasur in both seasons (Figure S2, Supplementary Information). This indicates that reducing conditions prevail in the tannery wastewater, which is also agreement with the presence of a negative redox potential (E_h) (TWW-summer: -3.4 ± 66; TWW-winter: -20.7 ± 99).

Neelam, Alamgir and Kanwal [45] reported that the basic pH of wastewater might induce Cr(VI) transformation to Cr(III), which settles down in the surface as oxides and in sludge. The results from the current study revealed that high concentration of Cr(III) in wastewater may make precipitates with Fe and settle down in bottom sediments or remain in tannery wastewater residues [46]. The presence of Cr(VI) in wastewater indicated that Cr(III)-compounds released from tanning processes could possibly be oxidized into Cr(VI) by oxidizing agents, such as manganese oxide (MnO_2) and dissolved oxygen [15,16].

3.3. Tannery Wastewater Attributes

In both seasons, tannery wastewater samples showed slightly acidic to alkaline pH (TWW-summer pH: 6.0–8.8 and TWW-winter pH: 6.0–8.1), which were within the permissible limit set by WHO and NEQS (pH 6–10 and 6–9, respectively) (Table 2). The EC of tannery wastewater ranged from 2.0 to 24.4 mS cm^{-1} (mean: 8.7 mS cm^{-1}) in TWW-summer and from 8.5 to 21.8 mS cm^{-1} (mean: 14.5 mS cm^{-1}) in TWW-winter samples, which were significantly greater than the USEPA's permissible limit (1.0 mS cm^{-1}). The results showed that the TWW-summer and TWW-winter samples had high concentrations of cations, such as Ca (96 and 97 mg L^{-1}, respectively) Mg (477 and 509 mg L^{-1}), Na (324 and 345 mg L^{-1}) and K (151.7 and 184.6 mg L^{-1}). Among various cations, the Na concentration of 46% (TWW-summer) and 84% (TWW-winter) samples exceeded the safe limit of NEQS (Table 2).

The data demonstrated that the tannery wastewater of the study area was dominated by major cations and anions in the following order of percentage abundance: Mg > Na > K > Ca and Cl > HCO_3 > SO_4 > CO_3 (Table 1). These results concur with other researchers, who reported acidic to basic pH and EC of tannery wastewater in various industrial zones of Pakistan and other countries [14,45,47,48]. An alkaline pH of tannery wastewater may be because of high anions and cations concentration which are possibly produced from different tannery industrial processes [49].

The manganese concentration was higher than the permissible limit set by NEQS (1.5 mg L^{-1}) in tannery industry wastewater samples of TWW-summer and TWW-winter season, with about 80% summer and 100% of winter samples. The iron concentration ranged from 3.6 to 21 and from 4.5 to 29 mg L^{-1}, respectively, in the summer and winter seasons samples, which was above the permissible limit of 2.0 mg L^{-1} set by NEQS. The COD values ranged from 1660 to 8330 and from 471 to 9286 mg L^{-1}. The BOD concentration spanned 885 to 4374 and 235 to 4693 mg L^{-1}, respectively, in TWW-summer and TWW-winter samples, respectively, thus, exceeding the WHO safe limits in all the wastewater samples (Table 2).

The results showed that the wastewater had low E_h and DO concentrations, which indicated reduced aqueous conditions. Due to the elevated concentration of dissolved organic contaminants or organic matter, microbes consume huge oxygen and enhance the level of BOD, which produces anaerobic conditions causing toxic greenhouse gas formation [50,51]. The results concur with the previous findings where researchers showed high BOD levels and low DO in tannery wastewater [52].

Afzal, Rehman, Shabir, Tahseen, Ijaz, Hashmat and Brix [53] reported high concentrations of COD because of a high number of organic compounds, which are not degraded by the microbes. Due to reduced conditions, microbes, Fe- and sulfur-bearing minerals reduced the Cr(VI) species into Cr(III), which might make precipitates, such as Cr_2O_3, $CrPO_4$ and $Cr(OH)_3$ or isomorphic substitution for Fe(III) in oxides, such as goethite [54]. At pH > 4, Cr (III) can adsorb on Fe oxide mineral surfaces (Fe_3O_4 and Fe_2O_3) or make complex through the chelation of organic matter [55,56].

3.4. Multivariate Analysis of Various Attributes in Tannery Wastewater

The chemical nature of the water was determined by plotting the major anions and cations concentrations on a Piper plot [57,58] (Figure 2).

It is important to examine the hydrogeochemistry of the water based on the abundance of the selected cations and anions [59]. There are two types of triangles—one is for cations, and the other is for anions. In addition, chemical nature of wastewater was also examined by plotting the TDS concentration on a Durov diagram. The Durov diagram shows that all the wastewater samples had a TDS less than 10 g L^{-1} with Cl and HCO_3 as the major anions (Figure S3, Supplementary Information).

The Piper plot shows the ionic supremacy of Mg over Na, K and Ca and of Cl over SO_4 and HCO_3 pointing to a Ca-Mg-Cl-SO_4 wastewater type (Figure 2a,b). During the summer and winter seasons, the major dominant wastewater type was Ca-Mg-SO_4 (non-carbonates hardness (secondary salinity) exceed 50%), mixed Ca-Mg-Cl (no cation-anion pairs exceed 50%) and Na-Cl (salinity). Other main dominant wastewater types were mixtures of SO_4-Cl, Cl-SO_4-HCO_3 and Na-K-Mg. These findings may reflect the highly saline type of tannery wastewater [60] as high concentrations of Ca, Mg, Na, Cl and SO_4 were present in the samples.

The Durvo and Piper plots specify the variability of the chemical composition in wastewater contributed by local geochemical conditions, mineral–water interaction, dissolution of minerals and use of salts in tannery industries [61,62]. The Piper plot demonstrates that alkaline ions (Mg and Ca) were not higher than the alkalis (Na and K) but strong acid anions (Cl and SO_4) exceeded week acids (HCO_3 and CO_3). Ghazaryan and Chen [59] reported the same type of water with high concentration of strong acid anions and cations. In the current study, high levels of EC with elevated COD and BOD, as well as an abundance of Cr(III) were an indication of the reduced aqueous environment in wastewater and as such may support Cr(VI) reduction by redox sensitive agents.

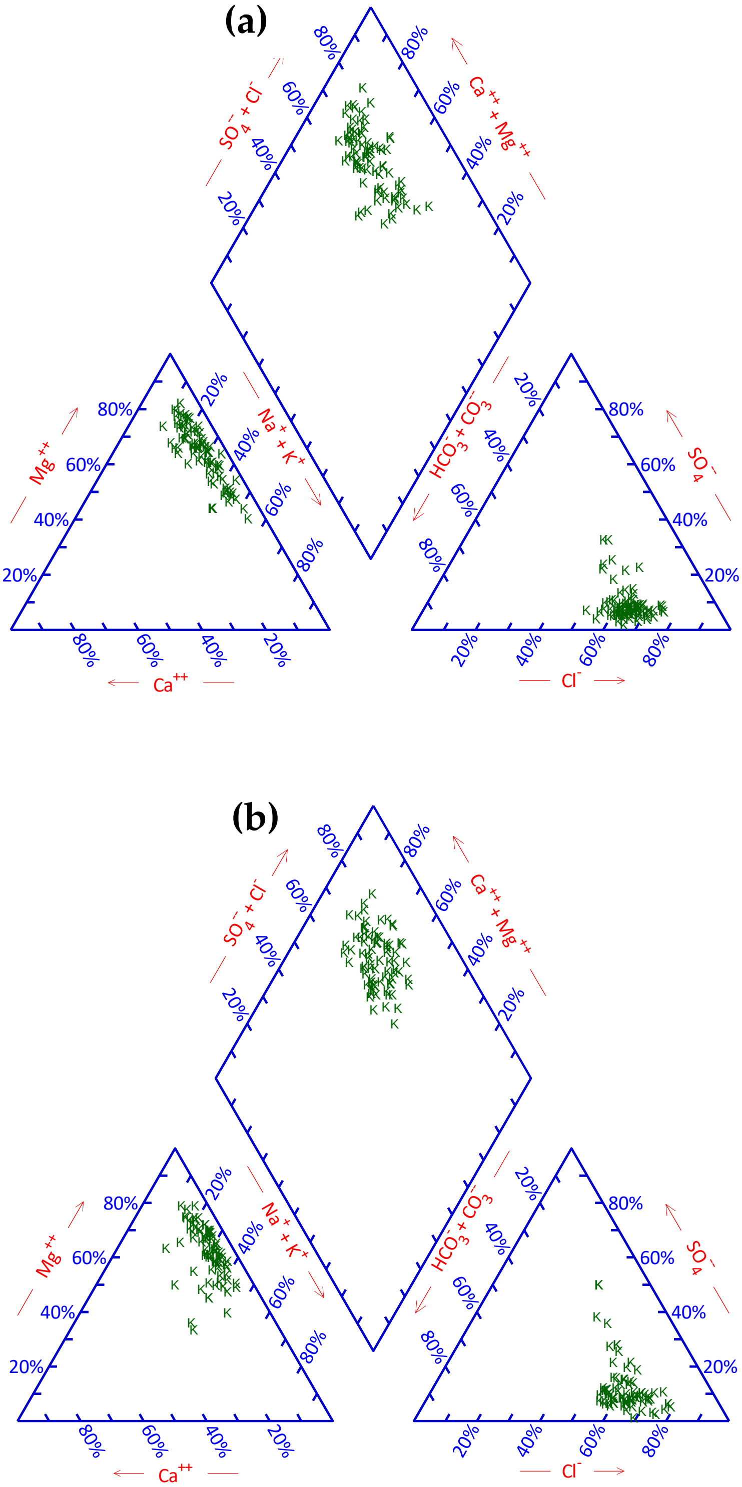

Figure 2. Piper plot showing the tannery industry wastewater chemistry of (**a**) summer (TWW-summer) and (**b**) winter (TWW-winter) season samples, collected from Kasur in Punjab, Pakistan.

In this study, the Pearson correlation matrix shows a correlation between Cr and other attributes in wastewater of TWW-summer and TWW-winter samples. In TWW-summer, a positive and significant correlation was found between EC-TDS (r = 0.99), HCO_3-Cl (r = 0.75), Ca-Mg (r = 0.61), Mg-Cr_T (r = 0.69), Na-K (r = 0.79), Cr_T-Cr(III) (0.99), Cr(III)-Cr(VI) (r = 0.90) and SO_4-E_o (r = 0.63) (Table S2, Supplementary Information). In TWW-winter, a significant and positive correlation was found between EC-TDS (r = 0.81),

CO_3-Cr_T (r = 0.55), TH-Mg (r = 0.95), Na-K (r = 0.62), Cr_T-Cr(III) (r = 0.99) and Cr(VI)-Cr(III) (r = 0.45) (Table S3, Supplementary Information).

Inter-elemental relationships in wastewater provide the information on pathways and sources of various variables in hydro-geoenvironments. A significant positive correlation was found between the total Cr and Cr(III), indicating the main source of Cr in tannery wastewater was Cr(III)-containing mineral phases. The pH has a positive correlation with Cr indicating that Cr speciation and the precipitation/dissolution depends on pH [62].

3.5. Principal Component Analysis

Five main principal components (PCs) (PC-1, PC-2, PC-3, PC-4 and PC-5) affecting the wastewater quality showed 70% and 57% variance of the data in the TWW-summer and TWW-winter samples, respectively (Table S4, Supplementary Information). The bold values in Table S4 of the Supplementary Information correspond to each variable that may control the hydrogeochemistry of the tannery wastewater. In the PC-1 of TWW-summer and TWW-winter samples (27% and 18%), Na, K, EC, TDS, total Cr, Cr(III) and EC, Na, K, TH, total Cr and Cr(III), respectively, were major contributing factors. In each PCA loading and score plot, the total Cr and its species were clustered together (Figures 3, S4 and S5, Supplementary Information). Thus, these attributes showed co-variance revealing an inter-correlation, and they may vary together in the tannery industry wastewater.

The PC-1, PC-2 and PC-3 may suggest the presence of possible sources and minerals of cation, anions and Cr, which may be associated with the dissolution of Na/Cl, Ca/Mg, Cr-minerals or other mineral phases in wastewater (Table S4, Supplementary Information). It could be inferred from the PC-4 that the high Cr(VI) concentration may be due to conversion of Cr(III) to Cr(VI) because of MnO and DO [56]. In wastewater, Cr(VI) may be present in the form of minerals in association with various cations released from tanneries [63].

3.6. Saturation Indices for Estimating Possible Mineral-Phases

The SI values from the geochemical speciation modelling of tannery wastewater samples are shown in Table S5, Supplementary Information. PHREEQC data revealed that the wastewater conditions were mainly under saturated for CO_3 containing minerals-phases, such as calcite [($CaCO_3$) (summer: −0.25; winter: −0.35)], aragonite, [($CaCO_3$) (summer: −0.36; winter: −0.46)] and gypsum [($CaSO_4$:$2H_2O$) (summer: −1.25; winter: −0.59)]. This indicates that CO_3 minerals are unlikely to precipitate as indicated by the negative SI values [57].

In contrast, the positive SI values were obtained for Fe-bearing phases, such as Fe(II)-chromite ($FeCr_2O_4$), ferrihydrite, goethite, hematite (Fe_2O_3), magnetite (Fe_3O_4), Mg-ferrite ($MgFe_2O_4$) and siderite ($FeCO_3$) (Table S5, Supplementary Information). This shows that Fe oxides and other Fe-bearing minerals could possibly control Cr speciation in tannery wastewater. Immobilization of Cr(III) may occur through the precipitation of $Cr(OH)_3$ or through the precipitation of mixed Fe(III)-Cr(III) (oxy)hydroxides [46].

The SI values for other Cr mineral phases were observed, such as $FeCr_2O_4$ (summer: 16.01; winter: 16.57)], $MgCr_2O_4$ (summer: 5.66; winter: 6.36)], $Cr(OH)_3$) (summer: 3.50; winter: 4.07)] and Cr_2O_3 (summer: 8.9; winter: 10.04)], with higher SI values in winter season wastewater compared to the summer season. This shows that, in summer season, there is a comparatively higher use and discharge of water in the leather tanning process than in the winter season, which may lead to greater solubility of ions in the winter season water. The results indicate that mainly Cr(III) compounds have been used in tannery wastewater for tanning purposes [8].

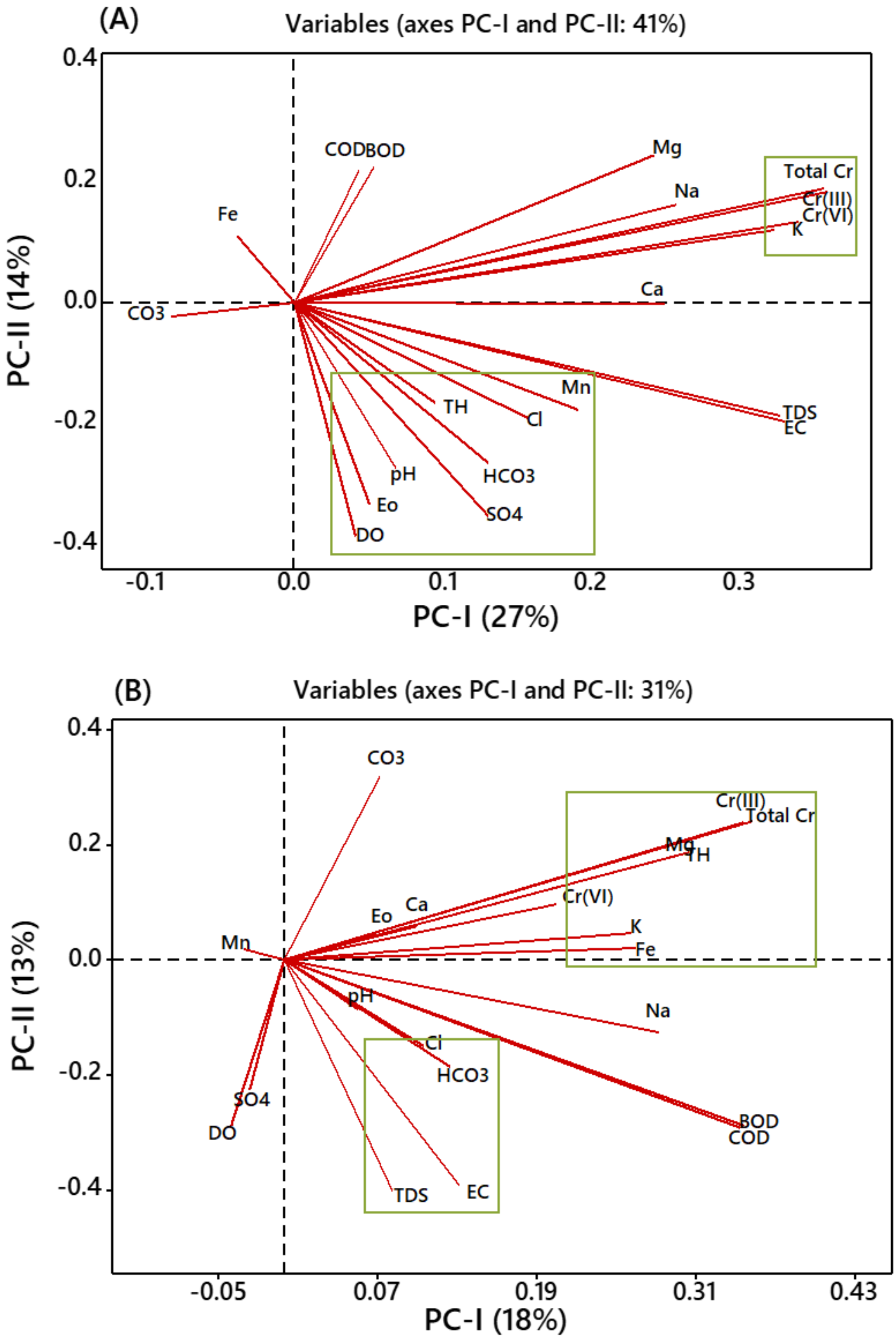

Figure 3. Loading plot of chromium (Cr) concentration and other physicochemical tannery industry wastewater parameters from Kasur, Punjab, Pakistan. (**A**) TWW-summer. (**B**) TWW-winter.

3.7. Geochemical Speciation and E_h–pH Relationship of Chromium-Contaminated Tannery Wastewater

The E_h–pH stability diagram illustrates various chemical forms of Cr that could be present within the specified E_h and pH range in wastewater (Figure 4). In this study, the E_h–pH diagram explained the stable and soluble forms of Cr in tannery wastewater.

Trivalent Cr was present in a wide pH and E_h range, while Cr(VI) exists in a specific pH and E_h range. Above the pH 3.5, Cr(III) hydrolysis in Cr-tannery wastewater system may produce Cr(III) as Cr_2O_3 and CrO_2 species. It is evident from the E_h–pH stability data that Cr fate is mainly controlled by Fe(III) oxides (i.e., magnetite, hematite and Mg-rich ferrite) and in the form of Fe(III)-Cr(III)-oxide precipitates in wastewater in both seasons.

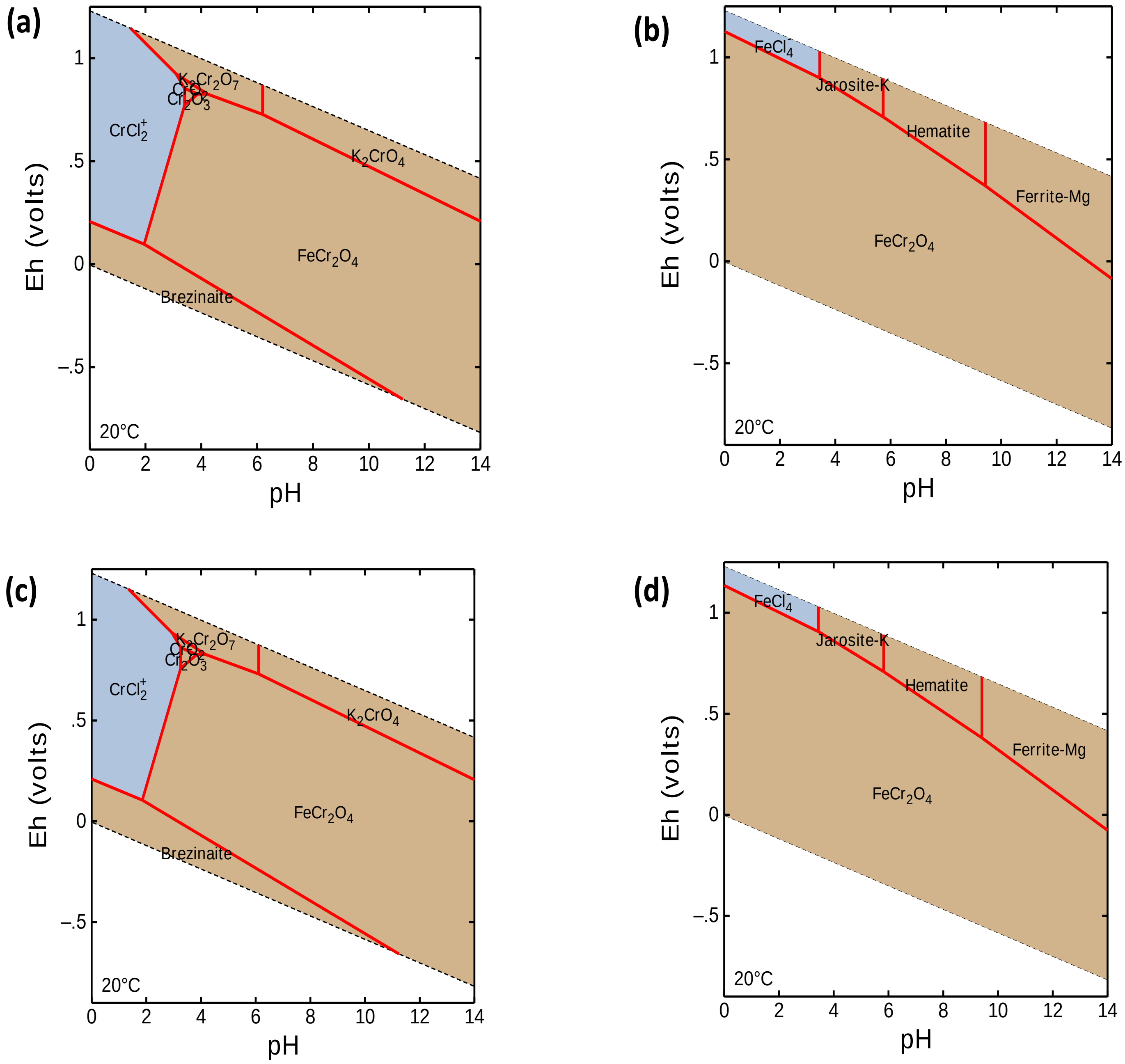

Figure 4. E_h-pH diagram for Cr-contaminated tannery wastewater collected in summer (**a**) Cr with other wastewater parameters and (**b**) Fe with other wastewater parameters); and winter (**c**) Cr with other wastewater parameters and (**d**) Fe with other wastewater parameters).

3.8. Environmental Risk Assessment of Tannery Wastewater

A single-factor evaluation index and CCI were used to identify the main attributes contributing to the contamination and to evaluate the overall status of water contamination [64] (Table 3). In tannery wastewater, the SFEI was above >1, and the CCI values of tannery wastewater exceeded the contamination standard category (Class V). The tannery wastewater was contaminated in the study area mainly due to anthropogenic processes related to leather tanning, causing enrichment with Cr, organic contaminants and other metals. Based on the quality classification [65], the CCI values were higher in all the wastewater samples, and its quality fell in Category V, i.e., 'heavily contaminated' [66].

Table 3. Single-factor evaluation index (SFEI), CCI and HEI index of tannery wastewater collected from Kasur, Punjab Pakistan.

Parameters	TWW-Summer (n = 82) SFEI	TWW-Winter (n = 82) SFEI	Single Factor Risk Category
TDS	1.2	2.1	SFEI > 1: Water is contaminated
Na	1.3	1.4	
Cl	4.1	4.5	
COD	22	23	
BOD	21	24	
Fe	6.4	7.6	
Mn	1.9	3.5	
Total Cr	15	49	
Cr(VI)	10	11	
Cr(III)	16	61	
Total	99	189	
CCI	9	18	
Tannery wastewater quality class	V	V	
HEI	23	60	
Chromium risk category	High contamination	High contamination	

Note(s): NG: Not given; TDS: total dissolved solids; Na: sodium; COD: chemical oxygen demand; BOD: biochemical oxygen demand; Fe: iron; Mn: manganese; Cr: chromium; Cr(VI): hexavalent Cr; Cr(III): trivalent Cr; SFEI: single-factor evaluation index; CCI: comprehensive water contamination index; and HEI: heavy metals index.

The HEI (summer: 23.3; winter 60.4) showed that tannery wastewater is highly contaminated with metals, especially with Cr produced from tannery industries in the study area. The HEI values of our study was lower than the reported values (up to 83) for contaminated water of Egypt [67]. Mekuria, Kassegne and Asfaw [35] reported that 60% of contaminated wastewater was within the low contamination class (HEI < 10), which may be because of low metal load in these sites. The major inputs of heavy metals include domestic wastes, tannery industries and agrochemicals. The results showed a warning situation of environmental risk from tannery wastewater for both seasons.

The highest SFEI, CCI and HEI values were recorded in the winter samples, which agrees with high load of BOD, COD, salinity and Cr inputs from different processes of tanneries. Future research is warranted on sustainable treatment of tannery wastewater using a low-cost and eco-friendly technology, such as floating treatment or constructed wetlands considering high values of risk parameters (SFEI, CCI and HEI).

4. Conclusions

This study shows that tannery wastewater had high concentrations of Cr, Fe and other ions (Cl^-, $CO_3{}^{2-}$, $HCO_3{}^-$ and $SO_4{}^{2-}$), as well as COD and BOD. All the tannery wastewater samples from the summer and winter seasons exceeded the Cr concentration above the permissible limits set by NEQS, USEPA and WHO. The chromium concentration in TWW-summer was lower compared to the TWW-winter samples (15 and 49 mg L^{-1}).

The Piper plot showed the ionic supremacy of Mg over Na, K and Ca and of Cl over SO_4 and HCO_3 pointing to a Ca-Mg-Cl-SO_4 wastewater type. These findings may reflect the highly saline type of tannery wastewater in the summer and winter seasons.

The PCA results were also supported by hydro-geochemical modelling data that showed that Cr association with Fe oxide phases might have a potential role in the adsorption and dissolution of Cr in tannery wastewater systems. According to the CCI and HEI values, the overall tannery wastewater quality is poor and not suitable for reuse without proper treatment.

Future research should be directed to develop and implement a suitable and eco-friendly remediation strategy to treat Cr-contaminated tannery industry wastewater, such as constructed wetlands technology. It is imperative to precisely understand Cr hydrogeochemistry in wastewater, which provides base knowledge to determine the fate of Cr in wastewater and potential threats to the ecosystem.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/w15030391/s1, Figure S1: Location map of study area showing the TWW-summer and TWW-winter sampling sites in Kasur, Punjab, Pakistan; Figure S2: Scatter plot showing the percentage speciation of total Cr in wastewater samples collected in summer (TWW-summer) and winter (TWW-winter) seasons from Kasur, Punjab, Pakistan; Figure S3: Durov plot showing the tannery industry wastewater chemistry with pH and TDS in (A) summer (TWW-summer) and (B) winter (TWW-winter) samples, collected from Kasur, Pun-jab, Pakistan; Figure S4: Score plot showing the Cr distribution in tannery industry wastewater samples collected in (A) summer (TWW-summer) and (B) winter (TWW-winter) from Kasur, Punjab, Paki-stan; Figure S5: Scree plot of PC-I and PC-II of the various tannery industry wastewater attributes and Cr determined in wastewater of different tannery industries (A: summer (TWW-summer); B: winter (TWW-winter)) in Punjab, Pakistan; Table S1 Location coordinates of wastewater samples collected in summer (TWW-summer) and winter (TWW-winter) seasons from Kasur, Punjab, Pakistan; Table S2 Pearson correlation matrix of various attributes of tannery wastewater samples collected in summer (TWW-summer) season from Kasur, Punjab, Pakistan; Table S3 Pearson correlation matrix of various attributes of tannery industry wastewater samples collected in winter (TWW-winter) season from Kasur, Pun-jab, Pakistan; Table S4 Principal component analysis of Cr and various other wastewater quality parameters for tannery wastewater samples collected in two different sea-sons from Kasur, Punjab, Pakistan; Table S5 Saturation indices of different mineral phases calculated by geochemical modeling using water attributes of tannery wastewater.

Author Contributions: F.Y. collected wastewater samples and prepared the initial draft. I.B., N.K.N., M.A. and M.S. conceptualized the idea, provided resources, read, edited and improved the paper. K.H., F.A.-M., Q.S., F.A. and H.W. read, edited and improved the paper. All authors have read and agreed to the published version of the manuscript.

Funding: Higher Education Commission (Project Nos. 6425/Punjab/NRPU/R&D/HEC/2016 and 6396/Punjab/NRPU/R&D/HEC/2016), Pakistan. COMSTEQ-TWAS research grant 2018 (18–268 RG/EAS/AS_C) and Researchers Supporting Project No. RSP-2021/24.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: All data are provided in paper.

Acknowledgments: The authors are thankful to Higher Education Commission (Project Nos. 6425/Punjab/NRPU/R&D/HEC/2016 and 6396/Punjab/NRPU/R&D/HEC/2016), Pakistan for providing financial support. I.B. acknowledges the support from COMSTEQ-TWAS research grant 2018 (18–268 RG/EAS/AS_C). The authors are grateful to the Researchers Supporting Project No. RSP-2021/24, King Saud University, Riyadh, Saudi Arabia.

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

References

1. Laxmi, V.; Kaushik, G. Toxicity of Hexavalent Chromium in Environment, Health Threats, and Its Bioremediation and Detoxification from Tannery Wastewater for Environmental Safety. In *Bioremediation of Industrial Waste for Environmental Safety: Volume I: Industrial Waste and Its Management*; Saxena, G., Bharagava, R., Eds.; Springer: Singapore, 2020; pp. 223–243.
2. Yahya, M.D.; Obayomi, K.S.; Abdulkadir, M.B.; Iyaka, Y.A.; Olugbenga, A.G. Characterization of cobalt ferrite-supported activated carbon for removal of chromium and lead ions from tannery wastewater via adsorption equilibrium. *Water Sci. Eng.* **2020**, *13*, 202–213. [CrossRef]

3. Liang, T.; Li, L.; Zhu, C.; Liu, X.; Li, H.; Su, Q.; Ye, J.; Geng, B.; Tian, Y.; Sardar, M.F.; et al. Adsorption of As(V) by the Novel and Efficient Adsorbent Cerium-Manganese Modified Biochar. *Water* **2020**, *12*, 2720. [CrossRef]
4. Hasan, I.M.U.; Javed, H.; Hussain, M.M.; Shakoor, M.B.; Bibi, I.; Shahid, M.; Farwa; Xu, N.; Wei, Q.; Qiao, J.; et al. Biochar/nano-zerovalent zinc-based materials for arsenic removal from contaminated water. *Int. J. Phytoremediation* **2022**, *2022*, 2140778. [CrossRef]
5. Khan, M.U.; Malik, R.N.; Muhammad, S. Human health risk from Heavy metal via food crops consumption with wastewater irrigation practices in Pakistan. *Chemosphere* **2013**, *93*, 2230–2238. [CrossRef] [PubMed]
6. Czikkely, M.; Neubauer, E.; Fekete, I.; Ymeri, P.; Fogarassy, C. Review of Heavy Metal Adsorption Processes by Several Organic Matters from Wastewaters. *Water* **2018**, *10*, 1377. [CrossRef]
7. Sardar, M.; Ahmad, H.; Zıa-Ur-Rehman, M. Absorption of foliar-applied lead (Pb) in rice (*Oryza sativa* L.): A hydroponic experiment. *Fresenius Env. Bull* **2018**, *27*, 6634–6639.
8. Younas, F.; Niazi, N.K.; Bibi, I.; Afzal, M.; Hussain, K.; Shahid, M.; Aslam, Z.; Bashir, S.; Hussain, M.M.; Bundschuh, J. Constructed wetlands as a sustainable technology for wastewater treatment with emphasis on chromium-rich tannery wastewater. *J. Hazard. Mater.* **2021**, *422*, 126926. [CrossRef]
9. Kazakis, N.; Kantiranis, N.; Kalaitzidou, K.; Kaprara, E.; Mitrakas, M.; Frei, R.; Vargemezis, G.; Tsourlos, P.; Zouboulis, A.; Filippidis, A. Origin of hexavalent chromium in groundwater: The example of Sarigkiol Basin, Northern Greece. *Sci. Total. Environ.* **2017**, *593-594*, 552–566. [CrossRef]
10. Khalid, S.; Shahid, M.; Dumat, C.; Niazi, N.K.; Bibi, I.; Bakhat, H.F.S.G.; Abbas, G.; Murtaza, B.; Javeed, H.M.R. Influence of groundwater and wastewater irrigation on lead accumulation in soil and vegetables: Implications for health risk assessment and phytoremediation. *Int. J. Phytoremediation* **2017**, *19*, 1037–1046. [CrossRef]
11. Khalid, S.; Shahid, M.; Natasha; Bibi, I.; Sarwar, T.; Shah, A.H.; Niazi, N.K. A Review of Environmental Contamination and Health Risk Assessment of Wastewater Use for Crop Irrigation with a Focus on Low and High-Income Countries. *Int. J. Environ. Res. Public Heal.* **2018**, *15*, 895. [CrossRef]
12. Natasha; Bibi, I.; Niazi, N.K.; Shahid, M.; Ali, F.; Hasan, I.M.U.; Rahman, M.M.; Younas, F.; Hussain, M.M.; Mehmood, T.; et al. Distribution and ecological risk assessment of trace elements in the paddy soil-rice ecosystem of Punjab, Pakistan. *Environ. Pollut.* **2022**, *307*, 119492. [CrossRef] [PubMed]
13. Ali, A.; Hussain, M.M.; Niazi, N.K.; Younas, F.; Farooqi, Z.U.R.; Zeeshan, N.; Javed, M.T.; Shahid, M.; Bibi, I. A Comparison of Technologies for Remediation of Arsenic-Bearing Water: The Significance of Constructed Wetlands. In *Global Arsenic Hazard: Ecotoxicology and Remediation*; Niazi, N., Bibi, I., Aftab, T., Eds.; Springer International Publishing: Cham, Switzerland, 2022; pp. 223–245. [CrossRef]
14. Homa, D.; Haile, E.; Washe, A.P. Determination of Spatial Chromium Contamination of the Environment around Industrial Zones. *Int. J. Anal. Chem.* **2016**, *2016*, 7214932. [CrossRef] [PubMed]
15. Apollaro, C.; Fuoco, I.; Brozzo, G.; De Rosa, R. Release and fate of Cr(VI) in the ophiolitic aquifers of Italy: The role of Fe(III) as a potential oxidant of Cr(III) supported by reaction path modelling. *Sci. Total. Environ.* **2019**, *660*, 1459–1471. [CrossRef] [PubMed]
16. Vasileiou, E.; Papazotos, P.; Dimitrakopoulos, D.; Perraki, M. Expounding the origin of chromium in groundwater of the Sarigkiol basin, Western Macedonia, Greece: A cohesive statistical approach and hydrochemical study. *Environ. Monit. Assess.* **2019**, *191*, 509. [CrossRef] [PubMed]
17. Ma, H.; Li, X.; Zhu, C.; Chen, F.; Yang, Y.; Chen, X. Liberation and recovery of Cr from real tannery sludge by ultrasound-assisted supercritical water oxidation treatment. *J. Clean. Prod.* **2020**, *267*. [CrossRef]
18. Guo, S.-S.; Xu, Y.-H.; Yang, J.-Y. Simulating the migration and species distribution of Cr and inorganic ions from tanneries in the vadose zone. *J. Environ. Manag.* **2021**, *288*, 112441. [CrossRef]
19. Izbicki, J.A.; Ball, J.W.; Bullen, T.D.; Sutley, S.J. Chromium, chromium isotopes and selected trace elements, western Mojave Desert, USA. *Appl. Geochem.* **2008**, *23*, 1325–1352. [CrossRef]
20. Khan, M.; Ahad, S. Analysis Of Kasur Tannery Pre Treated Wastewater For Its Metal Toxicity. *J. Appl. Chem.* **2015**, *4*, 572–577.
21. Zaheer, I.; Ali, S.; Saleem, M.; Imran, M.; Alnusairi, G.; Alharbi, B.; Riaz, M.; Abbas, Z.; Rizwan, M.; Soliman, M. Role of iron–lysine on morpho-physiological traits and combating chromium toxicity in rapeseed (*Brassica napus* L.) plants irrigated with different levels of tannery wastewater. *Plant Physiol. Biochem.* **2020**, *155*, 70–84. [CrossRef]
22. Zaheer, I.E.; Ali, S.; Rizwan, M.; Bareen, F.-E.; Abbas, Z.; Bukhari, S.A.H.; Wijaya, L.; Alyemeni, M.N.; Ahmad, P. Zinc-lysine prevents chromium-induced morphological, photosynthetic, and oxidative alterations in spinach irrigated with tannery wastewater. *Environ. Sci. Pollut. Res.* **2019**, *26*, 28951–28961. [CrossRef]
23. Ashraf, S.; Naveed, M.; Afzal, M.; Seleiman, M.F.; Al-Suhaibani, N.A.; Zahir, Z.A.; Mustafa, A.; Refay, Y.; Alhammad, B.A.; Ashraf, S.; et al. Unveiling the Potential of Novel Macrophytes for the Treatment of Tannery Effluent in Vertical Flow Pilot Constructed Wetlands. *Water* **2020**, *12*, 549. [CrossRef]
24. Younas, F.; Bibi, I.; Afzal, M.; Niazi, N.K.; Aslam, Z. Elucidating the Potential of Vertical Flow-Constructed Wetlands Vegetated with Different Wetland Plant Species for the Remediation of Chromium-Contaminated Water. *Sustainability* **2022**, *14*, 5230. [CrossRef]
25. Shah, S.W.A.; Rehman, M.U.; Hayat, A.; Tahseen, R.; Bajwa, S.; Islam, E.; Naqvi, S.N.H.; Shabir, G.; Iqbal, S.; Afzal, M.; et al. Enhanced Degradation of Ciprofloxacin in Floating Treatment Wetlands Augmented with Bacterial Cells Immobilized on Iron Oxide Nanoparticles. *Sustainability* **2022**, *14*, 14997. [CrossRef]

26. Afzal, M.; Shabir, G.; Iqbal, S.; Mustafa, T.; Khan, Q.M.; Khalid, Z.M. Assessment of Heavy Metal Contamination in Soil and Groundwater at Leather Industrial Area of Kasur, Pakistan. *CLEAN Soil, Air, Water* **2013**, *42*, 1133–1139. [CrossRef]
27. Joyia, F.A.; Ashraf, M.Y.; Shafiq, F.; Anwar, S.; Nisa, Z.-U.; Khaliq, B.; Malik, A. Phytotoxic effects of varying concentrations of leather tannery effluents on cotton and brinjal. *Agric. Water Manag.* **2020**, *246*, 106707. [CrossRef]
28. Abbas, M.; Rahman, M.A.U.; Safdar, A. Detection of Heavy Metals Concentration Due to Leather Tanning Industry and Prevalent Disease Pattern in Kasur, Pakistan. *Environ. Urban. ASIA* **2012**, *3*, 375–384. [CrossRef]
29. Andleeb, S.; Mahmood, T.; Khalid, A.; Akrim, F.; Fatima, H. Hexavalent chromium induces testicular dysfunction in small Indian mongoose (Herpestes javanicus) inhabiting tanneries area of Kasur District, Pakistan. *Ecotoxicol. Environ. Saf.* **2018**, *148*, 1001–1009. [CrossRef]
30. Bozlur Rahman, M. Design and Fabrication of Column Filtration Reactor for the Removal of Dissolved Dyes from Tannery Wastewater. Master's Thesis, Bangladesh University of Engineering and Technology, Dhaka, Bangladesh, 2004.
31. Spellman, F. *Water & Wastewater Infrastructure: Energy Efficiency and Sustainability*; Crc Press: Boca Raton, FL, USA, 2013.
32. Ryan, J.; Estefan, G.; Rashid, A. *Soil and Plant Analysis Laboratory Manual*; ICARDA: Beirut, Liban, 2001.
33. Saritha, B.; Chockalingam, M.; Bist, B. Evaluation and Characterization of Tannery Wastewater. *Int. J. Pure Appl. Math.* **2018**, *119*, 8479–8487.
34. NEQS. *The Gazette of Pakistan, Extraordinary, Islamabad*; Part II, Statutory Notification (SRO); Government of Pakistan, Environmental and Urban Affairs Division (Pakistan Environmental Protection Agency): Islamabad, Pakistan, 1999.
35. Mekuria, D.M.; Kassegne, A.B.; Asfaw, S.L. Assessing pollution profiles along Little Akaki River receiving municipal and industrial wastewaters, Central Ethiopia: Implications for environmental and public health safety. *Heliyon* **2021**, *7*, e07526. [CrossRef]
36. Bibi, I.; Singh, B.; Silvester, E. Dissolution of illite in saline–acidic solutions at 25 °C. *Geochim. Cosmochim. Acta* **2011**, *75*, 3237–3249. [CrossRef]
37. Dotro, G.; Larsen, D.; Palazolo, P. Preliminary Evaluation of Biological and Physical–Chemical Chromium Removal Mechanisms in Gravel Media Used in Constructed Wetlands. *Water, Air, Soil Pollut.* **2010**, *215*, 507–515. [CrossRef]
38. Shakoor, M.B.; Bibi, I.; Niazi, N.K.; Shahid, M.; Nawaz, M.F.; Farooqi, A.; Naidu, R.; Rahman, M.M.; Murtaza, G.; Lüttge, A. The evaluation of arsenic contamination potential, speciation and hydrogeochemical behaviour in aquifers of Punjab, Pakistan. *Chemosphere* **2018**, *199*, 737–746. [CrossRef]
39. Bhalli, J.A.; Khan, Q.M. Pollution Level Analysis in Tannery Effluents Collected From Three Different Cities of Punjab, Pakistan. *Pak. J. Biol. Sci.* **2006**, *9*, 418–421. [CrossRef]
40. Shakir, L.; Ejaz, S.; Ashraf, M.; Ahmad, N.; Javeed, A. Characterization of tannery effluent wastewater by proton-induced X-ray emission (PIXE) analysis to investigate their role in water pollution. *Environ. Sci. Pollut. Res.* **2011**, *19*, 492–501. [CrossRef] [PubMed]
41. Shafiq, M.; Shaukat, T.; Nazir, A.; Bareen, F.-E. Modeling of Cr contamination in the agricultural lands of three villages near the leather industry in Kasur, Pakistan, using statistical and GIS techniques. *Environ. Monit. Assess.* **2017**, *189*, 1–18. [CrossRef]
42. Parveen, R.; Ashfaq, M.; Qureshi, J.; Ali, S.M.M.; Qadri, M. Estimation of Chromium in Effluents from Tanneries of Korangi Industrial Area. *Pak. J. Chem.* **2013**, *3*, 29–33. [CrossRef]
43. Hadad, H.; Maine, M.A.; Bonetto, C. Macrophyte growth in a pilot-scale constructed wetland for industrial wastewater treatment. *Chemosphere* **2006**, *63*, 1744–1753. [CrossRef]
44. Khalid, N.; Rizvi, Z.F.; Yousaf, N.; Khan, S.M.; Noman, A.; Aqeel, M.; Latif, K.; Rafique, A. Rising Metals Concentration in the Environment: A Response to Effluents of Leather Industries in Sialkot. *Bull. Environ. Contam. Toxicol.* **2021**, *106*, 493–500. [CrossRef]
45. Neelam, A.; Alamgir, A.; Kanwal, H. Determination of chromium in the tannery wastewater, Korangi, Karachi. *Int. J. Environ. Sci. Nat. Resour.* **2018**, *15*, 122–125. [CrossRef]
46. Bibi, I.; Niazi, N.K.; Choppala, G.; Burton, E. Chromium(VI) removal by siderite (FeCO3) in anoxic aqueous solutions: An X-ray absorption spectroscopy investigation. *Sci. Total. Environ.* **2018**, *640–641*, 1424–1431. [CrossRef]
47. Chowdhury, M.; Mostafa, G.; Biswas, T.K.; Mandal, A.; Saha, A.K. Characterization of the Effluents from Leather Processing Industries. *Environ. Process.* **2015**, *2*, 173–187. [CrossRef]
48. Ashraf, S.; Naveed, M.; Afzal, M.; Ashraf, S.; Ahmad, S.R.; Rehman, K.; Zahir, Z.A.; Núñez-Delgado, A. Evaluation of Toxicity on Ctenopharyngodon idella Due to Tannery Effluent Remediated by Constructed Wetland Technology. *Processes* **2020**, *8*, 612. [CrossRef]
49. Nur-E-Alam, M.; Mia, M.; Ahmad, F.; Rahman, M. An overview of chromium removal techniques from tannery effluent. *Appl. Water Sci.* **2020**, *10*, 205. [CrossRef]
50. Mwinyihija, M.; Meharg, A.; Dawson, J.; Strachan, N.J.; Killham, K. An Ecotoxicological Approach to Assessing the Impact of Tanning Industry Effluent on River Health. *Arch. Environ. Contam. Toxicol.* **2006**, *50*, 316–324. [CrossRef] [PubMed]
51. Sardar, M.F.; Zhu, C.; Geng, B.; Huang, Y.; Abbasi, B.; Zhang, Z.; Song, T.; Li, H. Enhanced control of sulfonamide resistance genes and host bacteria during thermophilic aerobic composting of cow manure. *Environ. Pollut.* **2021**, *275*, 116587. [CrossRef] [PubMed]
52. Aregu, M.B.; Asfaw, S.L.; Khan, M.M. Developing horizontal subsurface flow constructed wetland using pumice and Chrysopogon zizanioides for tannery wastewater treatment. *Environ. Syst. Res.* **2021**, *10*, 1–13. [CrossRef]

53. Afzal, M.; Rehman, K.; Shabir, G.; Tahseen, R.; Ijaz, A.; Hashmat, A.J.; Brix, H. Large-scale remediation of oil-contaminated water using floating treatment wetlands. *NPJ Clean Water* **2019**, *2*, 3. [CrossRef]
54. Li, Y.; Cundy, A.B.; Feng, J.; Fu, H.; Wang, X.; Liu, Y. Remediation of hexavalent chromium contamination in chromite ore processing residue by sodium dithionite and sodium phosphate addition and its mechanism. *J. Environ. Manag.* **2017**, *192*, 100–106. [CrossRef]
55. Liang, J.; Huang, X.; Yan, J.; Li, Y.; Zhao, Z.; Liu, Y.; Ye, J.; Wei, Y. A review of the formation of Cr(VI) via Cr(III) oxidation in soils and groundwater. *Sci. Total. Environ.* **2021**, *774*, 145762. [CrossRef]
56. Dai, R.; Liu, J.; Yu, C.; Sun, R.; Lan, Y.; Mao, J.-D. A comparative study of oxidation of Cr(III) in aqueous ions, complex ions and insoluble compounds by manganese-bearing mineral (birnessite). *Chemosphere* **2009**, *76*, 536–541. [CrossRef]
57. Li, P.; Wu, J.; Qian, H. Assessment of groundwater quality for irrigation purposes and identification of hydrogeochemical evolution mechanisms in Pengyang County, China. *Environ. Earth Sci.* **2012**, *69*, 2211–2225. [CrossRef]
58. Natasha; Bibi, I.; Shahid, M.; Niazi, N.K.; Younas, F.; Naqvi, S.R.; Shaheen, S.M.; Imran, M.; Wang, H.; Hussaini, K.M.; et al. Hydrogeochemical and health risk evaluation of arsenic in shallow and deep aquifers along the different floodplains of Punjab, Pakistan. *J. Hazard. Mater.* **2020**, *402*, 124074. [CrossRef] [PubMed]
59. Ghazaryan, K.; Chen, Y. Hydrochemical assessment of surface water for irrigation purposes and its influence on soil salinity in Tikanlik oasis, China. *Environ. Earth Sci.* **2016**, *75*, 383. [CrossRef]
60. Kumar, P.S. Evolution of groundwater chemistry in and around Vaniyambadi Industrial Area: Differentiating the natural and anthropogenic sources of contamination. *Geochemistry* **2014**, *74*, 641–651. [CrossRef]
61. Kanagaraj, G.; Elango, L. Chromium and fluoride contamination in groundwater around leather tanning industries in southern India: Implications from stable isotopic ratio δ53Cr/δ52Cr, geochemical and geostatistical modelling. *Chemosphere* **2019**, *220*, 943–953. [CrossRef]
62. Shahid, M.; Shamshad, S.; Rafiq, M.; Khalid, S.; Bibi, I.; Niazi, N.K.; Dumat, C.; Rashid, M.I. Chromium speciation, bioavailability, uptake, toxicity and detoxification in soil-plant system: A review. *Chemosphere* **2017**, *178*, 513–533. [CrossRef]
63. Unceta, N.; Séby, F.; Malherbe, J.; Donard, O.F.X. Chromium speciation in solid matrices and regulation: A review. *Anal. Bioanal. Chem.* **2010**, *397*, 1097–1111. [CrossRef]
64. Mishra, S.; Lai, K.; Singh, V. Optimality and duality for minimax fractional programming with support function under (C,α,ρ,d)-convexity. *J. Comput. Appl. Math.* **2015**, *274*, 1–10. [CrossRef]
65. Son, C.T.; Giang, N.T.H.; Thao, T.P.; Nui, N.H.; Lam, N.T.; Cong, V.H. Assessment of Cau River water quality assessment using a combination of water quality and pollution indices. *J. Water Supply Res. Technol.* **2020**, *69*, 160–172. [CrossRef]
66. Matta, G.; Kumar, A.; Nayak, A.; Kumar, P.; Kumar, A.; Tiwari, A.K. Water Quality and Planktonic Composition of River Henwal (India) Using Comprehensive Pollution Index and Biotic-Indices. *Trans. Indian Natl. Acad. Eng.* **2020**, *5*, 541–553. [CrossRef]
67. Goher, M.E.; Hassan, A.M.; Abdel-Moniem, I.A.; Fahmy, A.H.; El-Sayed, S.M. Evaluation of surface water quality and heavy metal indices of Ismailia Canal, Nile River, Egypt. *Egypt. J. Aquat. Res.* **2014**, *40*, 225–233. [CrossRef]