Long-Term Releasing Kinetics of Chromium from Leather

by

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Abstract

The release of chromium from leather inevitably results in potential risks and this study is conducted to investigate the long-term releasing behavior. The leaching tests proceed using water at solid to liquid ratio of 1:20 and rotational speed 60 r/min for 240 hours to simulate the release of chrome leather under natural conditions. The experimental data successfully fit with the Pseudo-second-order equation, Elovich equation, and Weber-Morris model, indicating the long-term leaching behavior of chromium in heterogeneous leather is controlled by liquid-solid film, while the interparticle and intraparticle diffusion also play important roles. The leachable chromium accounts for 2.8-4.5% total chromium in leather and increases with temperature. The Three-compartment model depicts the releasing process as rapid, slow, and very slow stages, and temperature mainly affected the very slow stage. The amount of released chromium in rapid and slow stages slightly increases with temperature, which could be used to assess the hazard of chrome leather.

Introduction

Now leather has been an indispensable item in the form of shoes, clothing, belting and other upholstery articles.[1,2] It is estimated the leather output every year is about 1.67×10^9 m^2 in the worldwide and perhaps 90% of leather is manufactured by using chromium(III).[3,4,5] During leather production, a large amount of leather waste containing chromium is also generated.[6,7] Typical full-chrome tanned leather generally contains 2.0 wt% to 3.0 wt% of chromium, and of this amount 2% chromium is simply adsorbed by the collagen matrix according to Brown et al findings,[8] in spite of washing following chrome tanning during the manufacturing process. Theoretically such chromium loosely bound would release easily from leather during the process of utilization as product or waste. Under certain conditions, low toxicity Cr(III) could be oxidized to highly toxic Cr(VI)[9] which is hazardous and toxic to both environment and health.[10-14] Indeed, leather attracts more and more attention for this alleged environmental impact and potential health risk of chromium. The kinetic behavior of chromium releasing from leather plays a key role in the assessment of the safety of chrome leather.

Although there are many efforts to minimize the release and conversion of chromium in leather,[15] little attention has been paid to the releasing process. Zhou et al. focused on the release of chromium in chrome tanning and post tanning processes in order to reduce chromium discharge in leather processing,[16] and Erdem et al.[17] investigated the effects of liquid/solid ratio, contact time, pH and sequential extraction on the leaching behavior of chromium in chrome shavings to indicate the pollution potential. In the production process of chrome leather, Cr(III) is attached to collagen fibers by dominant strong covalent complexation and weak adsorption, which is similar to chemisorption accompanying physical adsorption.[18] Then the release process of chromium is opposite to the adsorption.[17] The leaching kinetics of metal such as cobalt, vanadium from waste are studied by Pseudo-first-order kinetic equation, Pseudo-second-order kinetic equation, Webber-Morris and Elovich equation,[19-21] and the main control factor of leaching process was obtained.

In this study, the kinetics of chromium release from chrome leather and the main factors of chromium releasing are investigated. This research would contribute to waste management and assessing the risk of chrome leather.

Materials and Methods

Materials and reagents

The chrome leather sample was supplied from a tannery in Hebei (China). The leather sample was homogenized by oven at 40±5°C in standard laboratory atmosphere (20±2°C and 65±5% relative humidity) for 48 hours, ground by Retsch SM100 (Retsch GmbH, Germany) with 4×4mm sieve and thoroughly homogenized for this experiment. All chemicals were of analytical grade or better, provided by Chengdu Jinshan Chemical Reagent Co Ltd.

Experimental method

Leaching experiment

Four grams of leather powder and 80 mL ultrapure water (18.2 MΩ/cm, Milli-Q system, Millipore, USA) were added to 250 mL-conical flask, then shaken at 60 r/min by using the thermostatic oscillator (ZWY-2102C, shanghai, China) with contact time from 1 h to 240

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h at 20, 25, 30,35°C with the precision of ±0.1°C, respectively. The filtrate passed through 0.45μm membrane to analyze at once. All the tests were done in duplicate.

Chromium analysis

The leather powder and leachate were digested to measure total chromium content. For leather powder, 1.0 g sample was digested by mixed solution of 65% HNO_3 and 30% H_2O_2 with HNO_3-to-H_2O_2 volume ratio 3:1 in a 250 mL-conical flask using electric stove[22]. The filtered digestion liquor was diluted with ultrapure water to analyze the total chromium content by inductively coupled plasma optical emission spectrometer (ICP-OES, PerkinElmer Optima 8000, USA). The chromium standard stock solutions (1000 mg·L^{-1}) was obtained from National Nonferrous Metals and Electronic Materials Analysis and Testing Center (Beijing, China) and diluted to the calibration standards (1.0-50.0 mg·L^{-1}). For the leachate, 40 mL liquor was digested by 8.0 mL of the above mixed solution of HNO_3 and H_2O_2 in a 250 mL conical flask using an electric stove, and the operation was repeated till the solution was clear and transparent. The conical flask was washed three to four times by ultrapure water and mixed with digestion liquor, then set to 25 mL and measure the total chromium as the above. The chromium in leachate could be calculated based on C_t=0.625C, where C_t and C represent the chromium concentration of leachate (mmol/L) and that from ICP-OES (mmol/L) respectively, and 0.625 represents the dilute ratio.

Cr(VI) in leather is detected by ISO 17075-1:2017, and that in leachate by GB/T15555.4-1995 using colorimetric reagent 1, 5-diphenylcarbazide at 540 nm[23] (UV-1800 BPC, Mapada Instruments Co., Ltd.).

The organics released

The total organic carbon (TOC) analyzer (DKSH vario TOC, Germany) was used to analyze the dissolved organic carbon in leachates. For the leachate, 5.0 mL was transferred to 25-mL volumetric flask and set to volume by deionized water, and analyzed directly.

Scanning electron microscope and differential scanning calorimetry

The leather powder before and after leaching experiments were characterized by scanning electron microscope (SEM, FEI Nova Nano SEM 450, FEI Co.) and differential scanning calorimetry (DSC, NETZSCH 204 F1, Germany). Before the characterizations, the samples were homogenized in oven at 40±5°C about 48 h. The temperatures of DSC experiments range from 20°C to 200 °C under a nitrogen atmosphere with a heating rate of 10 K/min.

Nitrogen adsorption analysis

For nitrogen adsorption analysis, 0.3 g leather powder was used with a TriStar 3000 analyzer (Micromeritics, USA). The surface area, total pore volume and average pore size were obtained to characterize the leather fiber before and after leaching.

Result and Discussion

The characterization of chrome leather leached and unleached

The total chromium in chrome leather sample was measured to be 20.6721 g/kg leather, which is consistent with previous reports of about 2.0 wt% of chromium in full-chrome tanned leather[24]. No Cr(VI) was detected in leather. SEM characterization of leather powder is presented in Figure 1. It can be observed the improving dispersion degree of collagen fibers after 240-h leaching, and the voids between collagen fibers are enlarged, which could be further confirmed by the results of nitrogen adsorption (Figure 2). The surface area, total pore volume and average pore size increased from 3.34 to 3.57 m^2/g, 3.25 to 5.12 uL/g and 3.9 to 5.74 nm respectively after leaching. It is clear that the leaching of chrome leather in water had a good effect on separating fibers, which is also one of the tanning effects.[25] These results suggest leaching makes the chromium bound in lower level fibrils accessible for water, and indicate that the leaching of chrome leather involve complex physico-chemical interaction resulting in the further dispersion of fibers.

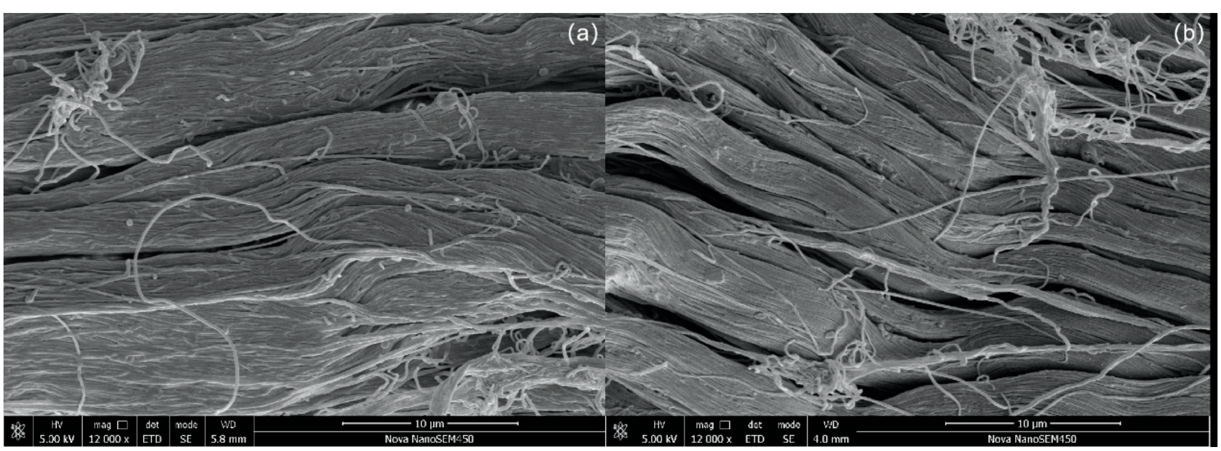

Figure 1. SEM images of chrome leather [(**a**)12000×] and after10-day leach[(**b**)12000×]

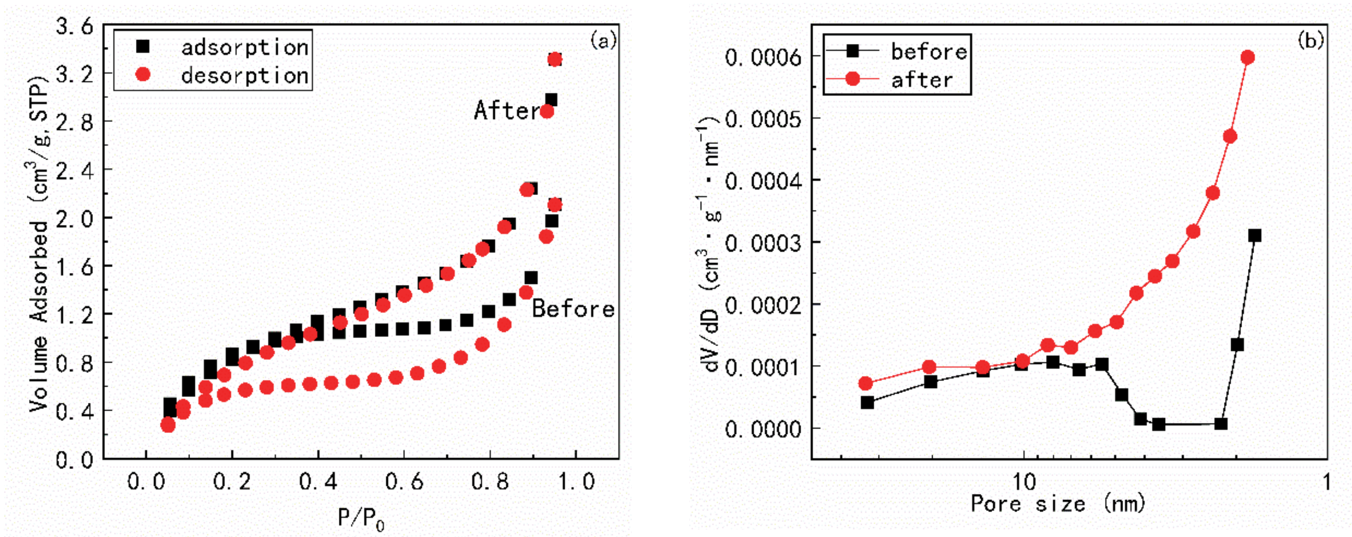

Figure 2. N_2 adsorption-desorption isotherms **(a)** and pore size distribution **(b)**

The denaturation temperature of leather powder before and after leaching is found to be similar around 72°C as shown in Figure 3, much lower than that of chrome leather(> 90°C),[26] which may be ascribed to the grinding in the sample preparation. The DSC results suggest no essential structure changes in the collagen fiber matrix during leaching.

Chromium released from leather at various temperatures

Figure 4 shows the tendency of the leached chromium(a) and organics(b) from chrome leather powders varying with time at different temperatures. As seen from Figure 4(a), the released chromium increases parabolically with time at each temperature, indicating the leaching of chromium is controlled by the dissolution and diffusion.[17] No Cr(VI) was detected in leachate at each temperature. The release of chromium is substantially influenced by temperature especially after 24 hours. However, the release of organics is very different. In the initial 24 hours, the increasing temperature obviously intensifies the release of organics, which does not differ significantly with prolonged contact time after 48 hours. The results support the speculation that the solid-phase extraction techniques in the ISO 17075 protocol may result in underestimation of Cr(VI) in leather for the parallel release of organics as reducing agent.[27, 28]

In the initial 24 hours at each temperature, the released chromium increases rapidly, which might come from the diffusion of soluble chromium in void water. During the leaching time from 24 h to 168 h, the change of chromium content is comparatively small. This could be attributed to the release of chromium adsorbed onto the leather. 168 h later, the increase of chromium in leachate is very low, which might be derived from the shift of coordination equilibrium involving Cr(III) and collagen carboxyl groups, and

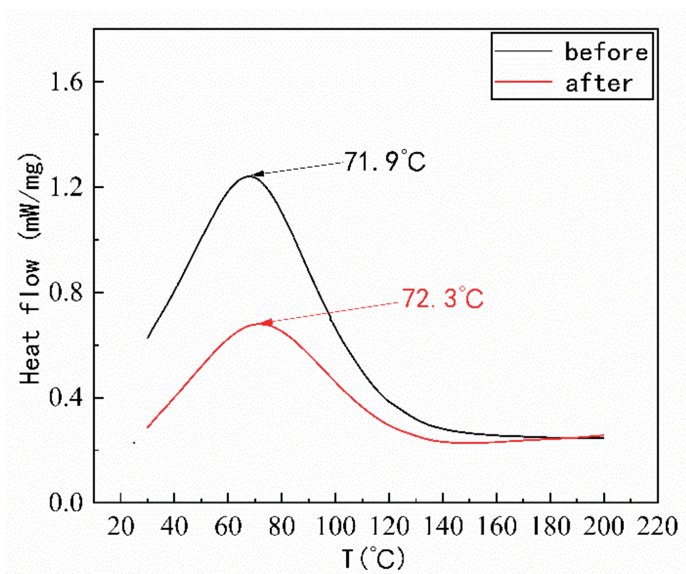

Figure 3. DSC of chromed leather shavings (before leaching and after leaching)

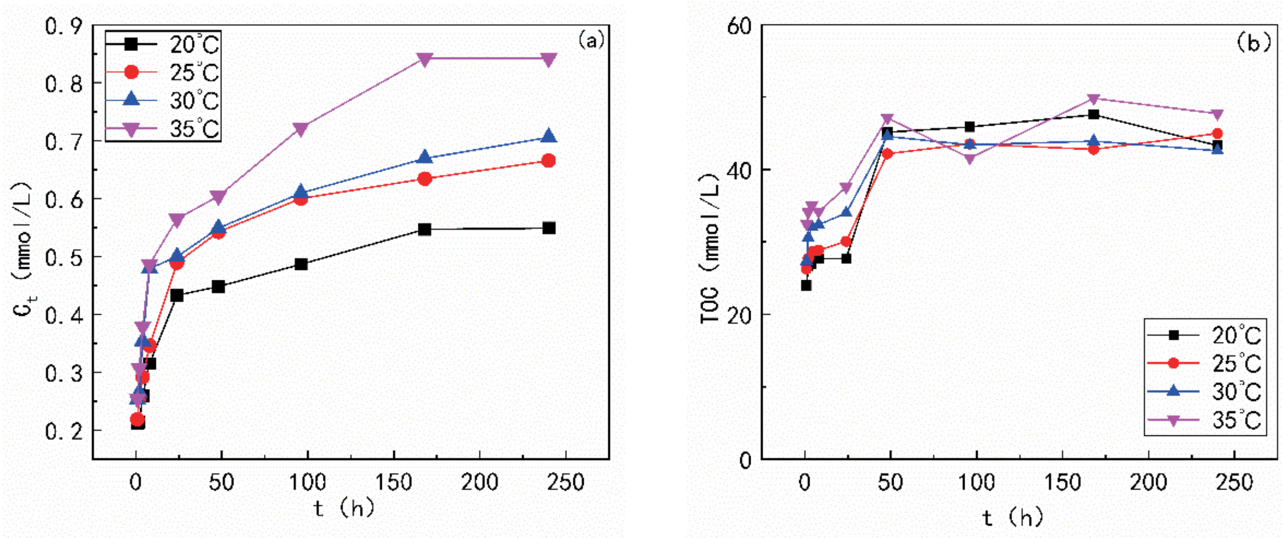

Figure 4. Releasing behavior of Cr**(a)** and organics**(b)**at different temperature

chromium concentration in leachate fluctuates slightly with time at each temperature. The released chromium concentration exceeds 10 mg/L after 1.0 h at each temperature, far beyond the maximum allowable limit 5 mg/L given by USEPA, indicating that the waste leather in this test is a pollutant. The released chromium content increases steadily as the leaching time, and is remarkably affected by temperature. For example, the released chromium concentration is beyond 15 mg/L after 4 h at 20°C and 2 h at 35°C. An increase of 15°C from 20°C to 35°C facilitates the chromium releasing, suggesting that the release of chromium from the leather scraps is an endothermic reaction. Obviously, it is very important to explore the mechanism of chromium releasing from chrome leather for the management of chrome leather wastes.

Kinetics analysis for Cr release

In order to investigate the kinetic mechanism involved in the long-term releasing process, four kinetic models namely Weber-Morris diffusion, Elovich, Pseudo-second-order and Three-compartment rate model have been adopted to fit the kinetic data. Results show that chromium releasing from the leather is successfully depicted by the kinetic models according to the significant R^2 values demonstrated in Table I.

As can be observed, R^2 values of Weber-Morris are lower than the other three models, indicating intra-particle diffusion should not always be rate-determining step in the long leaching process, which is very different from our previous short-term leaching behavior of chromium from leather.[24] The details of fitting are shown in Figure 5. Therefore, chromium release data are further analyzed by the Elovich, Pseudo-second-order, and Three-compartment rate equations, respectively.

Elovich equation

Elovich equation is suitable for highly heterogeneous media such as soil, and the adsorption systems of natural lignocellulose with Cr^{3+} has been well described by it.[29] The high heterogeneity implies the material fixes metal in multilayer manner, and each layer exhibits a different activation energy.[30] The dimensionless Elovich equation could be expressed as:[31]

$$\left(\frac{C_t}{C_{ref}}\right)=R_E 1n\left(\frac{t}{t_{ref}}\right)+1 \qquad (1)$$

Where C_t and C_{ref} are the concentration of chromium in leachate at time t and the longest operating time t_{ref} in leaching process respectively, R_E is an approaching equilibrium factor of the Elovich

Table I

Coefficients of determination (R^2) for the kinetic models of chromium leaching from leather

T(°C)	Weber-Morris diffusion	Elovich	Pseudo-second-order	Three-compartment
20	0.8616	0.9785	0.9973	0.9916
25	0.9043	0.9889	0.9977	0.9982
30	0.9229	0.9962	0.9958	0.9983
35	0.9289	0.9821	0.9933	0.9900

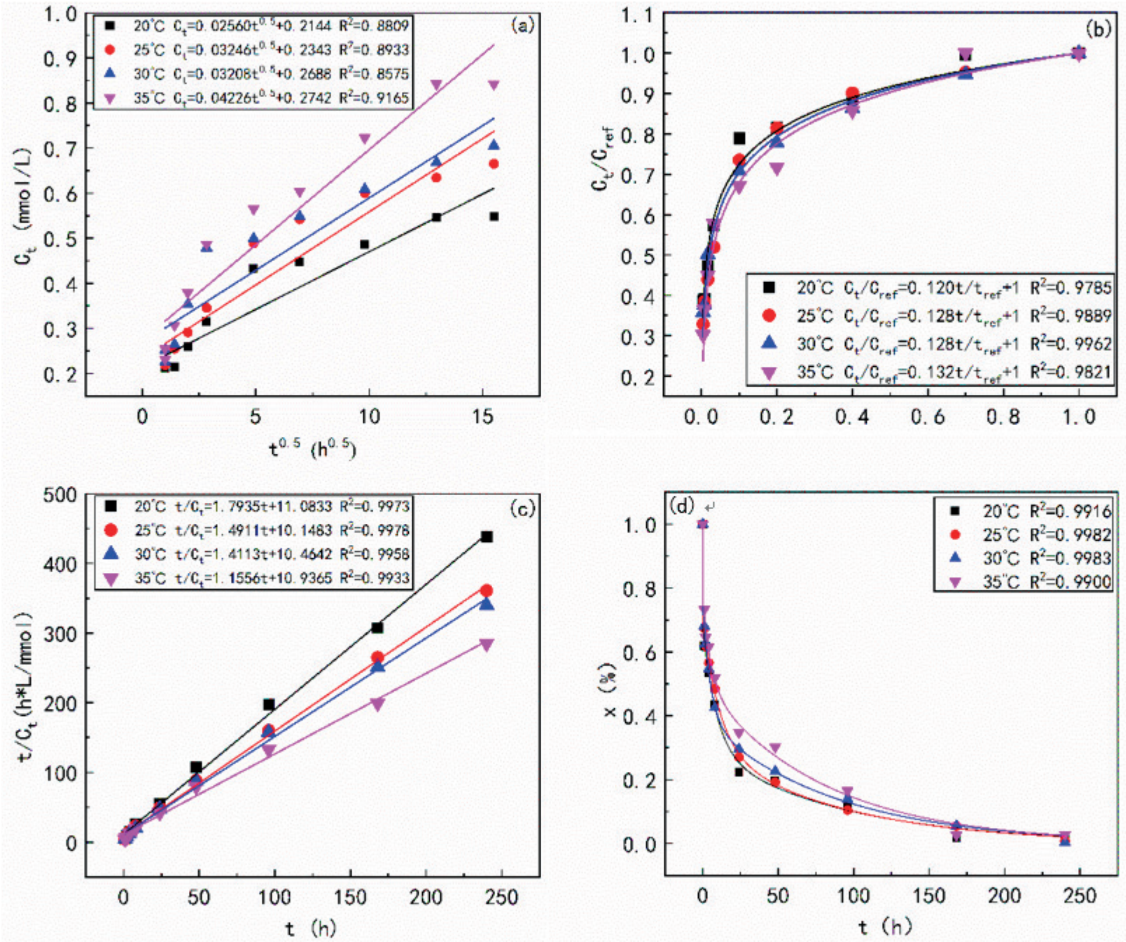

Figure 5. The fitting of Weber-Morris diffusion equation(**a**), Elovich equation(**b**), Pseudo-second-order equation(**c**) and Three-compartment rate model(**d**)

equation. Then the fitting of Elovich equation with experimental data is shown in Figure 5(b).

The correlation coefficients between Elovich equation and experimental data at four temperatures are all above 0.97, indicating the leaching process of chromium is not a single reaction mechanism process but a complex heterogeneous dispersion process with large changes in activation energy during the reaction process.[32] The hierarchical structure of collagen fiber makes chromium fixed into the leather matrix with different stability. For example, the dominate coordination interactions include mononuclear mono-coordination, mononuclear chelating coordination, polynuclear mono-coordination, polynuclear multi-coordination,[33] which leads to various activation energies during leaching process including the chemical equilibrium shift of coordination, as well as inter-, and intra-particle diffusion. The R_E values shown in Figure 5(b) of four temperatures are around 0.12, indicating the release of chromium proceeds mildly.[31]

The Pseudo-second-order rate equation

The finished leather contains sufficient voidage and shows excellent hydrophilicity,[34, 35] which is conducive to the free diffusion of water into the interior of the fiber, therefore the leaching of chromium could be viewed as occurring in liquid films throughout the fibers. The Pseudo-second-order model is extensively used in the leaching process of metal ions from inorganic material such as cement.[36, 37] The equation for the Pseudo-second-order kinetics can be expressed as follows:[38, 39]

$$\frac{t}{C_t} = \frac{t}{C_s} + \frac{1}{k_2 C_s^2} \tag{2}$$

Where C_t is the concentration of chromium in leachate at time t, and C_s is the concentration of chromium in leachate at the equilibrium state. While k_2 ($L \times mmol^{-1} \times h^{-1}$) is the rate constant of leaching reaction in Pseudo-second-order equation. The fitting of experimental data with Pseudo-second-order kinetic equations is shown in Figure 5 (c).

The linear coefficients R^2 of Pseudo-second-order rate equation are all above 0.99 for the four temperatures, indicating that the rate-determining step of the leaching process is liquid–solid film. Thus, the releasing process of chromium could be described as the following. At first, the driving force of the fresh water is enough to make chromium adsorbed on the surface of leather fiber release, which leads to the rapid increase of chromium in the leachate just as shown in Figure 4(a). Meanwhile a reacted layer with fewer chromium is formed, and the chromium inside the leather fiber could subsequently diffuse out through it and enter the leachate. In this stage, the driving force of the leachate is much weaker than the previous fresh water due to the higher concentration of chromium in the leachate, and the releasing rate of chromium becomes slower just as the case from 48 h to 168 h shown in Figure 4(a). Then the chromium on leather matrix might further release because of the equilibrium shifts to a new equilibrium. In this stage, the releasing rate of chromium should be much slower.

According to the Pseudo-second-order rate equation, we could obtain the equilibrium concentration of chromium in leachate at leaching equilibrium, which was 0.56, 0.67, 0.71 and 0.87 mmol/L respectively at 20, 25, 30, 35°C. The equilibrium concentration could be used to estimate the leachable chromium in leather under natural conditions. About 2.8-4.5% of total chromium in leather could be leached and increases with temperature. However, after leaching 168 h the released chromium exceeds 94% of the leachable chromium which could be calculated from the Pseudo-second- order rate equation at the four test temperatures. Obviously, the risk assessment of chrome leather and its waste should pay more attention to this period.

The better fitting of Pseudo-second-order kinetic equation and Elovich equation show the multi-step releasing process of chromium involving multi-phasic mass transfer with various activation energies. The collagen fiber network of the leather consists of modules of different dimensions in terms of diameter, length and surface area, which results in the leather matrix porosity and capillarity. Then the leather would contain two types of water, including those bound by hydrogen bond such as intramolecular water and multilayer water enveloped on the surface of the fibrils, elementary fibers and fibers, as well as the mobile capillary water. During the leaching process, the chromium desorbed firstly into the adsorbed water, then transferred to the capillary water by diffusion and liquid phase transport, ultimately leached out by the convective diffusion of eluent. The dissociation of chromium from coordination compound Cr-collagen is very difficult under mild conditions, so chromium desorption should play the key role during the long-term intermittent leaching process in nature.

Three-compartment model

Chromium in leather exists at equilibrium state before leaching, and the release curve shown in Figure 4(a) could be divided into three additional contributions dominated by the bulk eluent water, capillary water and adsorbed multilayer water based on the structural hierarchy of leather. Chromium adsorbed on fibers releases into eluent water firstly in the initial stage of leaching, then those adsorbed on fibrils, elementary fibers desorbed. Finally, very slow increase of Cr concentration in leachate could be ascribed to those adsorbed inside the microfibrils and then possibly dissociated from coordination compound Cr-collagen. Thus, the rapid, slow, and very slow leaching process could be described by the sum of three exponential functions as the following: [40]

$$C_t/C_0=F_{rap}\exp(-k_{rap}t)+F_{slow}\exp(-k_{slow}t)+F_{vs}\exp(-k_{vs}t) \quad (3)$$

where C_t is the concentration of Cr in leachate at time t, and C_0 is the leachable concentration of chromium in leachate at leaching equilibrium state, while F_{rap}, F_{slow} and F_{vs} are the chromium ratios of the rapid, slow, and very slow leaching stages respectively, and k_{rap}, k_{slow} and k_{vs} are the rate constant of the corresponding stage, h^{-1}. Using the equilibrium concentration fitted by Pseudo-second-order equation as the total leachable chromium in leather, the chromium ratios of three leaching stages should satisfy:

$$F_{rap}+F_{slow}+F_{vs}=1 \quad (4)$$

The correlation coefficients are all above 0.99, indicating the Three-compartment model gives a statistically significant improvement over Elovich. The fitting parameters are shown in Table II, and the fitting figure is listed as Figure 5(d).

With the increase of temperature, the leachable chromium increases, and the releasing fraction shifts from almost even distribution at 20°C to the very slow fraction. The total amount of chromium

Table II
The parameters of Three-compartment model

T(°C)	rapid stage		slow stage		very slow stage		R^2
	F_{rap}	$k_{rap}(h^{-1})$	F_{slow}	$k_{slow}(h^{-1})$	F_{vs}	$k_{vs}(h^{-1})$	
20	0.316	89.9	0.389	0.112	0.295	0.0108	0.9916
25	0.297	90.1	0.393	0.0912	0.310	0.0112	0.9982
30	0.248	90.6	0.364	0.193	0.387	0.0115	0.9983
35	0.230	91.0	0.271	0.185	0.498	0.0124	0.9900

released in rapid stage and slow stage at four temperatures is similar and increases slightly with temperature. Obviously, the increased leachable chromium with temperature is mainly derived from the very slow stage, which may be caused by the presence of more micropore and thermodynamically favorable regions of the leather from which trapped chromium cannot be easily released. The fitted rate constants for rapid, slow, very slow process are about 90, 10^{-1} and 10^{-2} h^{-1}, respectively, and generally increased with temperature. The magnitude of observed release rate constants demonstrates the rationality of the division of chromium release process into three releasing fractions.

Conclusion

The leachable chromium in leather is mainly in the form of weak binding or free state with water as extractant under natural conditions, accounting for 2.8-4.5% of the total chromium in leather. The long-term leaching behavior of chromium in heterogeneous leather is controlled by liquid-solid film fitted well by Pseudo-second-order kinetic equation, meanwhile the interparticle and intraparticle diffusion also play important roles. The releasing curve of chromium from leather is deduced to be three compartments: fast, slowly, and very slowly releasing fractions, and the rate constants of the three compartments are distinguished. The very slowly releasing compartment increases significantly with temperature, which may consist mainly of thermodynamically more favorable chromium in leather. The rapid and slow releasing compartment at four temperatures fluctuates slightly around 2% of total chromium in leather. This value could be used to assess the risk of chrome leather, such as the transport to ground water and uptake by organisms that feed from water, or the transport to the leather surface and contact with skin.

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Availability of data and materials

The data used to support the findings of this study are available from the corresponding author upon request.

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