

4-TERT-BUTYLBENZOIC ACID-INCORPORATED POLYSTYRENE: AN EFFECTIVE CATION-EXCHANGE POLYMER MATRIX FOR THE REMOVAL OF METAL IONS FROM TANNERY EFFLUENT

ZDRUŽITEV 4-TERC BUTIL-BENZOJSKE KISLINE S POLISTIRENOM: UČINKOVITA ODSTRANITEV KOVINSKIH IONOV V ODPADNIH VODAH Z IZMENJAVO KATIONOV V POLIMERNI MATRICI

John Louis Louis Antoni^{1*}, Senthilkumar Ganapathy¹, Lekshmi Gangadhar²,
Mukesh Kumar Dharmalingam Jothinathan³, Lourdusamy Emmanuvel⁴

¹Department of Civil Engineering, Annamalai University, Annamalai nagar, Chidambaram, TamilNadu – 608002, India

²Department of Nanotechnology, NanoDot Research Private Limited, Nagercoil, TamilNadu-629001, India

³Centre for Global Health Research, Saveetha Medical College and Hospitals, Saveetha Institute of Medical and Technical Sciences (SIMATS),
Saveetha University, Chennai-602105, India

⁴Department of Civil Engineering, Government Polytechnic College, Valangaiman, Tiruvarur, TamilNadu-612804, India

Prejem rokopisa – received: 2024-04-23; sprejem za objavo – accepted for publication: 2024-06-24

doi:10.17222/mit.2024.1164

The preparation of a 4-tert-butylbenzoic acid-incorporated polystyrene matrix as the polymer matrix for removing the metal ions present in water is reported. The hydrophobic interaction between the polystyrene and the tert-butyl group of carboxylic acid was exploited to bind the carboxylic acid on polystyrene. Thus prepared polymer matrix was investigated for its ability to exchange and remove metal ions from water. Better efficiency was obtained with different metal ions, including copper, iron, calcium, magnesium, chromium (III), etc., during a batch process as well as a continuous process. The carboxylic acid was not leached out during the process and the hydrophobic force was strong enough to avoid leaching out. Further, it was employed to remove metal ions, particularly chromium, from tannery effluent.

Keywords: chromium, hydrophobic interaction, ion exchange, metal removal, tannery treatment

V članku avtorji opisujejo pripravo polistirenske matrice združene z 4-terc butil-benzojsko kislino. Tako izdelana polimerna matrica naj bi delovala kot učinkovit izmenjevalnik kovinskih ionov, ki so prisotni v odpadnih vodah strojarn živalskih kož. Avtorji so izkoristili hidrofobno interakcijo med polistirenom in terc-butilno skupino karboksilnih skupin za vezavo karboksilne kisline na polistiren. Nato so avtorji raziskovali sposobnost izdelane polimerne matrice za izmenjavo in odstranitev kovinskih ionov iz odpadne vode, uporabljene za strojenje kož. Avtorji so ugotovili večjo učinkovitost izmenjave za vrsto kovinskih ionov vključno z Cu, Fe, Ca, Mg, Cr(III) itd. Izmenjava je potekala učinkovito tako v šaržnem kot tudi kontinuirnem procesu. Karboksilno kislino niso izlužili med procesom in hidrofobna sila je bila dovolj močna, da ni prišlo do izluženja (ekstrakcije). Avtorji so uporabili izdelano matrico posebej uspešno za odstranitev različnih kovinskih ionov, predvsem ionov kroma iz odpadne vode v strojarnah živalskih kož.

Ključne besede: krom, hidrofobna interakcija, izmenjava ionov, odstranitev kovin, obdelava odpadnih voda strojarn živalskih kož

1 INTRODUCTION

The usage of leather for making various products like shoes and boots, belts, apparel, purses, luggage bags, sports materials, etc., has been known since the iron age.¹ The durability and elegant look make leather products a symbol of status. Leather production involves hide preparation, tanning and finishing. The tanning process can be carried out either with vegetable tanning or chrome tanning. Chrome tanning is a more preferred technique for the production of large quantities in industries since chrome tanning can be completed in one day while vegetable tanning requires two weeks.² In addition, chrome-tanned leather is softer than vegetable-tanned leather; it also exhibits high hydrothermal stability and good dying properties so that better finishing can be

achieved.^{3,4} The skin from a slaughter house is subjected to several step processes and treated with several organic and inorganic chemicals to get better finished leather products. The chemicals include chromium sulphate, biocides like DDT, formaldehyde, a base like calcium hydroxide, a reducing agent like sodium sulphide, aniline-based dyes and solvents like dichloromethane, benzene, ethanol, etc.^{5,6} During chrome tanning, chromium binds to and stabilizes the collagen, a peptide containing glycine, proline and 4-hydroxy proline in major along with other amino acids including aspartic acids and glutamic acids.⁷ The carboxylic acid group of collagen becomes bonded with chromium and thus chromium is incorporated into the hide. The chemistry behind this process is complex and it is given in **Figure 1**.

Chromium sulphate in a solution forms $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ which is an aqua acid (red violet in colour) and readily deprotonates at a higher pH to give $[\text{Cr}(\text{H}_2\text{O})_5\text{OH}]^{3+}$

*Corresponding author's e-mail:
sllouis1966@gmail.com (John Louis Louis Antoni)

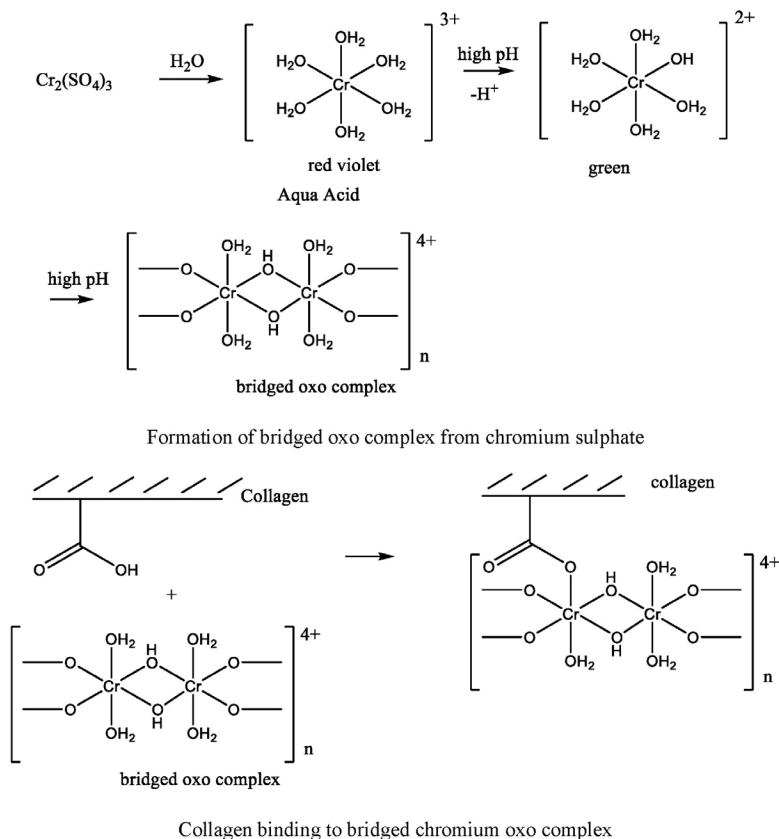


Figure 1: Chrome tanning process

(green colour). Further, this complex polymerizes at a higher pH, i.e., the basic condition allowing a polychromium complex.⁷ The carboxylic acid residue present in the glutamic acid and aspartic acid of collagen forms carboxylate ions upon treatment with lime ($\text{Ca}(\text{OH})_2$). The carboxylate anion displaces the water molecule from the polychromium complex via coordination and thus chromium is incorporated in the hide.⁸

The chromium that is bound to the collagen of leather gives softness, flexibility and suppleness to tanned leather. A study shows that 90 % of leather is processed with chrome tanning as it is quick and easy. In spite of its advantages, chrome tanning also poses a serious threat to the environment as chromium salt is not fully absorbed by the collagen and a portion of chromium is discarded in the effluent.⁹ Fortunately, Cr(III) is less toxic compared to Cr(IV) as Cr(III) is not readily absorbed by the body. While chromium (III) is essential for the regular operation of human vascular and metabolic systems as well as combating diabetes, too much chromium (III) may result in a severe skin rash, or other more serious symptoms. Also, Cr (III) can cause severe environmental issues and pose a severe threat to aquatic life.¹⁰

Several research efforts have been carried out to remove chromium (III) from the tannery effluent.¹¹ The techniques include adsorption¹² (rice husk, pumice, activated carbon from sugar industry, clay, zeolites, peat moss, chitin and agricultural wastes like neem bark, wal-

nut shell, rice husk, tea waste, sugar industry waste, banana rachis charcoal, chitin-humic acid, etc.), chemical precipitation (calcium hydroxide [$\text{Ca}(\text{OH})_2$], sodium hydroxide (NaOH), magnesium oxide (MgO), or calcium magnesium carbonate [$\text{CaMg}(\text{CO}_3)_2$], coagulation and flocculation (aluminium sulphate [$\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$] and ferric chloride ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$), calcium carbonate (CaCO_3), ammonium aluminium sulphate [$\text{NH}_4\text{Al}(\text{SO}_4)_2$], aluminium sulphate [$\text{Al}_2(\text{SO}_4)_3$], and sodium citrate ($\text{Na}_3\text{C}_6\text{H}_5\text{O}_7$), ferric chloride and organic polymer), ion exchange¹³ (zeolite, ion exchange resin, macroporous carboxylic resin), membrane filtration techniques like reverse osmosis (RO),¹⁴ nanofiltration (NF), ultrafiltration (UF), microfiltration (MF)¹⁵ and electrodialysis (ED) electrochemical treatment like electro-deposition,¹⁶ electrocoagulation,¹⁷ electro-disinfection, electro-oxidation,¹ electro-reduction, electro-osmosis, and electro-flotation. These are some of the many research methods for removing Cr from the tannery waste.¹⁸

Though several methods for removing metals from water are available, development of new methods that are cheap and carried out with a readily accessible material, is required. In this paper, we report on a simple and cost-effective method for removing transition metals from water, in particular Cr (III) ions from the secondary treated tannery water. This method involves a polystyrene film incorporated with 4-tert-butylbenzoic acid (TBBA) that binds to the surface of polystyrene through

a hydrophobic interaction and can exchange metal ions with protons.

2 EXPERIMENTAL PART

Substrates were purchased from Avra synthesis, SD fine, Spectrochem and Merck. AR grade methanol and CH_2Cl_2 were used as such without further purification. A rotary evaporator was used for evaporation under a reduced pressure. A SEM analysis was carried out with a TESCAN VEGA3. The analysis of metal ions was carried out following the standard procedure. Double-distilled water was used for preparing a solution of known salts. Complexometric titrations were carried out for the estimation of Cu, Ca, Mg, Zn using suitable indicators and buffer solutions. Fe (II) and Fe (III) were estimated using permanganometry and spectrophotometry, respectively.

2.1. General procedure for a TBBA-incorporated polymer matrix

Commercially available polystyrene (1 g) and 4-tert-butylbenzoic acid (0.1 mmol) were dissolved in 30 mL of CH_2Cl_2 and the solution was poured onto a Petri dish. Over time, the organic solvents became evaporated, leaving back flakes of TBBA-incorporated polystyrene. The flakes were washed with more polar methanol (20 mL) to remove any excess TBBA that was not tightly bound to the polymeric matrix.

2.2. General procedure for the removal of metal ions from the solution

A column with sintered disc (20 mm) is tightly packed with 10 g of TBBA-incorporated polystyrene. The height is approximately 8 cm. 20 mL of a metal-salt solution (with a concentration of 1000 ppm or 1 mg/mL) together with NaHCO_3 (0.05 mmol) is poured over the column through the inner walls without disturbing the column packing. The stopcock is partially open and the solution is allowed to flow dropwise and be collected in the conical. Thus collected solution is analysed for the presence of metal ions.

2.3. Batch process

A beaker is charged with 1 g of TBBA-incorporated polystyrene and 20 mL of the metal-salt solution (a concentration of 1000 ppm) together with NaHCO_3 (0.05 mmol) and a magnetic pellet. The mixture is stirred with the help of magnetic stirrer for 10 minutes and the mixture is decanted. Thus collected solution is analysed for the presence of metal ions.

3 RESULTS

Cationic ion-exchange resin was successfully employed to remove the metals like Ca, Mg, Cr, etc., from water. Though the process is promising, the cost of the ion-exchange resin is the major concern. The carboxylic acid incorporated onto the polystyrene through a hydrophobic interaction, rather than a covalent bond, could play the role in the cationic ion-exchange resin and might also be cost-effective. The choice was TBBA since it has a large lyophilic/hydrophobic part oriented opposite to hydrophilic carboxylic acid. Further, the aromatic part can impart rigidity to the whole molecule once it is bound to the polymer matrix. Initially, the carboxylic acid (4-tert-butylbenzoic acid, TBBA)-incorporated polystyrene flakes were prepared by simply dissolving and evaporating. In the Petri dish, the polystyrene solution with 1 mmol of 4-tert-butylbenzoic acid was dried to obtain flakes of a TBBA-incorporated polystyrene film. After drying, the film was washed with more polar methanol to remove any TBBA present on the surface and also washed with water before characterization. Upon evaporation of the methanol, 0.07 mmol (12 mg) of TBBA was obtained. This clearly indicated that the major portion of the TBBA was incorporated in the polystyrene film. The surface of the polystyrene film was studied with SEM at various magnifications, as shown in **Figure 2**. The TBBA-polystyrene flakes were soft, having an irregular shape and surface. Under a high resolution (1 μm), one can observe several tiny humps on the surface which are attributed to the binding of the TBBA to the surface. Further, the sample was analysed with infrared spectroscopy, i.e., by dissolving the it chloroform and using a NaCl crystal as the sample holder. The

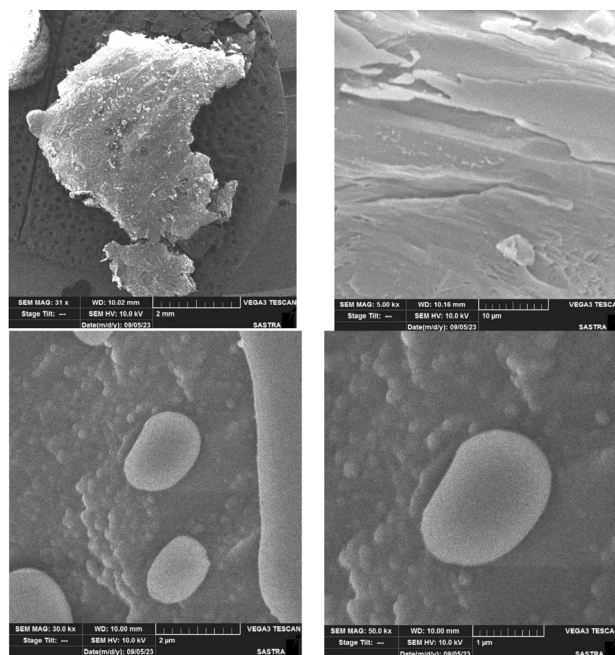


Figure 2: SEM images of 4-tert-butylbenzoic acid-incorporated polystyrene film

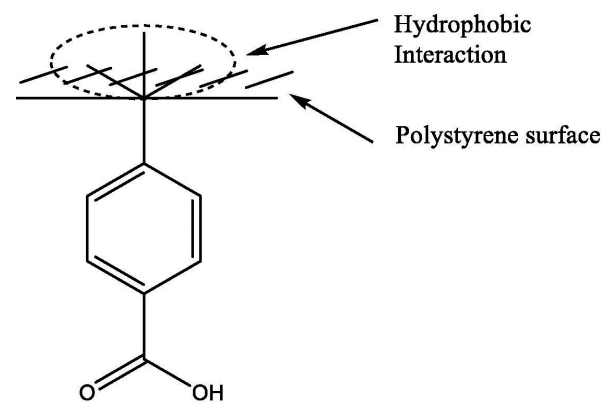


Figure 3: Proposed structure for the TBBA incorporation in polystyrene

carboxylic acid group appears as the intense peak at 1754 cm^{-1} .

As there is no possibility of chemical bonding between the polystyrene and TBBA, it is presumed that the hydrophobic part of TBBA is bound to the hydrophobic polystyrene while the more polar hydrophilic carboxylic acid group is exposed at the surface, as shown in **Figure 3**.

After successful preparation of the TBBA-incorporated polystyrene, focus was given to the exploitation of the ion exchange property of the carboxylic acid group, removing various metal ions from the solution. The efficiency in the batch process as well as the continuous process were studied. As the continuous process required more TBBA polystyrene it was limited to highly toxic copper and chromium.

Table 1: Removal of metal ions by TBBA-incorporated polystyrene^a

S. No.	Metal ions ^b	Concentration of metal ions after treatment (gm) ^c
1	Cu (I)	0.7 (0.8) ^d
2	Cu (II)	0.8 ^f
3	Fe (II)	1.1 ^h
4	Fe (III)	5.0 (4.5) ^{e, g}
5	Cr (III)	0.6 (0.8) ^d
6	Ni (II)	1.0
7	Zn (II)	0.3 ^f
8	Ca (II)	0.3 ^f
9	Mg (II)	0.3 ^f

^a refers to the experimental section, ^b metal sulphates with a concentration of 1 ppm/mL were used. ^c indicates the amount of metal ions after the treatment with a batch process. ^d 0.1 mol% NaHCO_3 was employed. ^e indicates a continuous process. ^f complexometric titration was used to measure the metal ions. ^g analysed by a spectrophotometer using KSCN. ^h permanganometry was used.

Initially, ion-exchange absorption with several most common metal-ion solutions and without any base ($\text{pH} \approx 7$) was attempted. The absorption was very poor which clearly indicates that $-\text{CO}_2\text{H}$ has a poor ligating property with the metal. Inspired by the collagen binding to Cr (III) under the basic condition, absorption with a small quantity of weak base NaHCO_3 ($\text{pH} \approx 8$) was car-

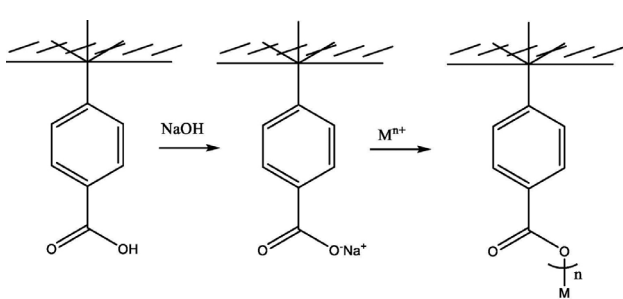


Figure 4: Metal-ion exchange with TBBA polystyrene

ried out. Surprisingly, the absorption increased drastically and only a small amount of metal ions was left unabsorbed in the water after treatment. This absorption property may be attributed to the formation of benzoate which coordinates with the metal salt, as shown in **Figure 4**. Encouraged by this result, several salt solutions were prepared from their metal sulphates with a concentration of 1 mg/mL and were studied for efficiency of the ion exchange under batch and continuous conditions, as shown in **Table 1**. From this table, it is clear that the batch process is more effective than the continuous process, which may be attributed to a shorter contact time in the continuous process (the flow time is only 2 min and 25 s).

After the batch process, the TBBA-incorporated polystyrene flakes were washed with water, dried and analysed with SEM. The surface had an entirely different nature as compared to the film before the absorption (**Figure 5**). The metal absorption was confirmed with flame photometry studies of the polystyrene film in CH_2Cl_2 . Several attempts to increase the absorption process by increasing the pH (up to 10) were not promising as the concentration of Na ions increased in the wastewater.

4 DISCUSSION

Though only a few ppm of Cr were present in tannery wastewater, attempts were made to study the efficiency of the TBBA polystyrene (1 g) by employing the solutions with different concentrations (10–70 ppm). At a lower concentration the absorption was greater than

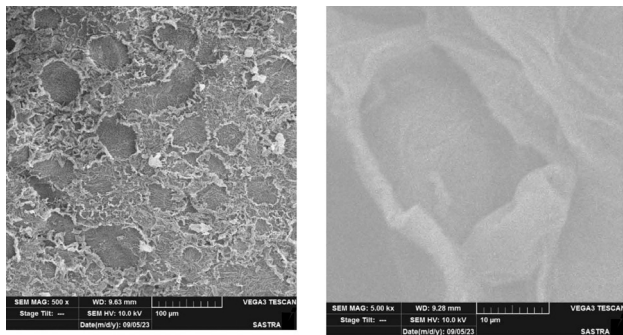


Figure 5: SEM images of 4-tert-butylbenzoic acid-incorporated polystyrene film after treatment

90 % and it decreased considerably with higher concentrations. This is attributed to the decrease in the available CO_2Na^+ sites on the surface (**Table 2**).

Table 2: Absorption of Cr (III) by TBBA polystyrene

S. No.	Initial Cr (III) concentration (ppm)	Cr (III) in the treated water (ppm)	Absorbed Cr (III) concentration (ppm)
1	10	1	9
2	20	3	17
3	30	4	26
4	40	7	33
5	50	10	40
6	60	16	44

With these promising preliminary results, the removal of Cr from the secondary treated tannery wastewater was carried out. The preliminary studies were conducted to measure the common parameters like pH, TDS, etc., as shown in **Table 3**. The tannery effluent was turbid with soil particles and several other chemicals. So it was centrifuged to remove the suspended solids and the supernatant was taken for analysis. A systematic analysis showed that the effluent contained several other chemicals in small quantities (**Table 2**). The pH of the tannery effluent was 8.7 which was enough for the benzoate ions to form during the absorption process. The absorption in the tannery wastewater was complex as there were several chemicals that could interact with the polymer matrix.

Table 3: Common parameters of the secondary treated effluent

S. No.	Parameters	Measured values with units	Permissible values for potable water ¹⁸
1	pH	8.8	6.5–8.5
2	Electrical conductivity	6.32 mmho/cm	800–2500 $\mu\text{S}/\text{cm}$
3	Colour	brown	colourless
4	Total dissolved solids (TDS)	4260 mg/L	50–150 ppm
5	COD	1470 mg/L	1–2 mg/L
7	Chromium	7.26 mg/L	trace
8	Chloride	1730 mg/L	250 mg/L

The tannery effluent (100 mL) was being stirred with the flakes of TBBA-incorporated polystyrene (5 g) and 0.1 mmol of NaHCO_3 for 10 minutes (the batch process). The effluent was then decanted and analysed for Cr(III) ions. The analysis clearly showed that the solution contained a negligible amount of chromium. The polymer matrix was not selective towards Cr (III) ions. In addition to chromium, other metals like Ca and Mg were also trapped during this process. The study was not complete without studying the leaching of TBBA from the polymeric matrix. An HPLC chromatogram of the effluent showed that the organic residues in the effluent were not absorbed by the polymeric matrix. From the HPLC studies of the solution, it was clear that TBBA was not

leached out from the polymeric matrix during this operation.

5 CONCLUSIONS

In conclusion, the absorption of metal ions from water using a polystyrene matrix that incorporated TBBA was demonstrated. The benzoic acid derivative bound on the surface via a non-covalent hydrophobic interaction. Hence, the hydrophilic carboxylic acid moiety was exposed on the surface and could bind with several metals. The ligation was more facile under the basic condition than in a neutral medium. This polymeric matrix was successfully used in both the continuous and batch processes to remove metal ions. Further, the scope of this process was extended to the removal of chromium ions from the tannery effluent. The studies showed that 4-tert-butylbenzoic acid was not leached out during the process and it is thus safe to handle.

Acknowledgement

The Authors thank the central facilities, SASTRA deemed to be university, Thanjavur for their support to analyze sample and the Head of the department, Civil Engineering, Annamalai University for constant support and infrastructure to carry out this research work.

6 REFERENCES

- Y. Yu, Y. Lin, Y. Zeng, et al., Life cycle assessment for chrome tanning, chrome-free metal tanning, and metal-free tanning systems, *ACS Sustain. Chem. Eng.*, 9 (2021), 6720–6731, doi:10.1021/acssuschemeng.0c09663
- C. R. China, A. Hilonga, S. S. Nyandoro, et al., Suitability of selected vegetable tannins traditionally used in leather making in Tanzania, *J. Clean Prod.*, 251 (2020), 119687, doi:10.1016/j.jclepro.2019.119687
- S. D. Richardson, T. A. Ternes, Water analysis: emerging contaminants and current issues, *Anal. Chem.*, 94 (2021), 382–416, doi:10.1021/acs.analchem.9b04804
- J. M. Morera, R. Bartoli, C. Chico, C. Sole, L. F. Cabeza, Minimization of the environmental impact of chrome tanning: a new process reusing the tanning floats, *J. Clean Prod.*, 19 (2011), 2128–213, doi:10.1016/j.jclepro.2011.08.006
- K. S. Bhavya, P. Raji, A. J. Selvarani, A. V. Samrot, P. T. Mohamed Javad, V. V. S. S. Appalaraju, Leather processing, its effects on environment and alternatives of chrome tanning, *Int. J. Adv. Res. Eng. Technol.*, 10 (2019), 69–79, doi:10.24321/ijaret.2019.v10i6.2092
- S. Rýglová, M. Braun, T. Suchy, Collagen and its modifications—crucial aspects with concern to its processing and analysis, *Macromol. Mater. Eng.*, 6 (2017), 1600460, doi:10.1002/mame.201600460
- J. W. Harlan, S. H. Fearheller, Chemistry of the crosslinking of collagen during tanning, *Adv. Exp. Med. Biol.*, 86A (1977), 425–440, doi:10.1007/978-1-4684-3282-4_27
- K. H. Gustavson, The chemistry of tanning processes, Academic Press Inc., New York 1956
- T. A. Risco, B. Budiawan, E. I. Auerkari, Effects of chromium on human body, *Ann. Res. Rev. Biol.*, 13 (2017), 1–8, doi:10.9734/ARRB/2017/33462

- ¹⁰ A. Alebel, Impacts of chromium from tannery effluent and evaluation of alternative treatment options, *J. Environ. Prot.*, 1 (2010), 53–58, doi:10.4236/jep.2010.11007
- ¹¹ A. M. Álvarez, D. Bolaños, C. Montero Calderón, Natural zeolite as a chromium VI removal agent in tannery effluents, 7 (2021) 9, 07974, doi:10.1016/j.heliyon.2021.e07974
- ¹² A. K. Sengupta, Chromate ion exchange, In: *Ion exchange technology*, Technomic Publishing Co. Inc., Lancaster, PA, 1995
- ¹³ J. Kanagaraj, N. K. Chandra Babu, A. B. Mandal, Recovery and reuse of chromium from chrome tanning waste water aiming towards zero discharge of pollution, *J. Clean Prod.*, 16 (2008), 1807–1813, doi:10.1016/j.jclepro.2007.12.012
- ¹⁴ V. Neagu, S. Mikhalovsky, Removal of hexavalent chromium by new quaternized crosslinked poly(4-vinylpyridines), *J. Hazard Mater.*, 183 (2010), 533–540, doi:10.1016/j.jhazmat.2010.07.089
- ¹⁵ T. Z. Sadyrbaeva, Removal of chromium(VI) from aqueous solutions using a novel hybrid liquid membrane electrodialysis process, *Chem. Eng. Process.: Process Intensif.*, 99 (2016), 183–191, doi:10.1016/j.cep.2015.09.012
- ¹⁶ D. T. Moussa, M. H El-Naas, M. Nasser, M. J. Al-Marri, A comprehensive review of electrocoagulation for water treatment: potentials and challenges, *J. Environ. Manag.*, 186 (2017), 24–41, doi:10.1016/j.jenvman.2016.10.039
- ¹⁷ A. K. Golder, A. K. Chanda, A. N. Samanta, S. Ray, Removal of hexavalent chromium by electrochemical reduction-precipitation: investigation of process performance and reaction stoichiometry, *Sep. Purif. Technol.*, 76 (2011), 345–350, doi:10.1016/j.seppur.2010.10.021
- ¹⁸ Y. Zhao, D. Kang, Z. Chen, J. Zhan, X. Wu, Removal of chromium using electrochemical approaches: a review, *Int. J. Electrochem. Sci.*, 13 (2018), 1250–1259, doi:10.20964/2018.02.55