

Chromium recovery from chrome shaving generated in tanning process

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Abstract

In this study, the chromium recovery conditions in the form of soluble chromate from chrome shaving (chromium-containing solid waste) by oxidation with air, oxygen and Na_2O_2 were investigated and basic Cr(III) sulphate solution using in the tanning was prepared from the chromate obtained. It has been determined that the oxidation agent is the most effective parameter affecting the chromate formation. While maximum oxidation yields in air and oxygen atmosphere at 850°C were found to be 23.02 and 30.41%, respectively, the highest chromium recovery efficiency in the form of chromate (99.45%) occurred in the presence of eight times Na_2O_2 with respect to stoichiometric amount of chromium. The chromate generated in Na_2O_2 oxidation process where 99.45% of chromium in the chrome shaving can be recovered was leached with distilled water and pregnant chromate solution was prepared. The chromate ions in this solution were reduced by using Na_2SO_3 and Cr(III) sulphate solution was obtained.

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1. Introduction

Tanning is the main process that protects leather against some environmental effects such as microbial degradation, heat, sweat or moisture, etc. In the tanning process, stabilization of collagen, is the main stratum of the skin, is performed by using a convenient tannage material such as some mineral and vegetable-based substances and aldehyde.

While the skin is stabilized in the process, much greater quantities of by-product and wastes than leather produced generate. One tonne of wet hide yields only 200 kg of leather but over 600 kg of solid waste or by-product [1]. It has been stated that about 600,000 tonnes of solid waste each year worldwide generate by leather industry and approximately 40–50% of the hides are lost to shavings and trimmings [2]. Important quantities of the chemicals used in the tanning process together hides remain in the solid and liquid wastes. For example; when the chromium salts are used as tannage, only 60% of the total chromium reacts with the hides and about 40% of the chromium remains in the solid waste and spent tanning solutions [3].

Cr(III) salts are widely used among the mineral-based tannages because of the excellent properties of the chromium compounds in the tanning. When the taking into consideration amount of the wastes generated in the chromium tanning, it can be stated that the waste management is the most important issue. Particularly, economic benefit can be obtained from these wastes due to their chemical contents. For this purpose, some studies related to recovery or recycling of chromium from spent tanning liquors have been made [3–7]. The main procedure in the chromium recovery from spent tanning solutions is the precipitation of the chromium as chromium hydroxide by the addition of an alkali to spent tanning solution. Subsequently, the chromium hydroxide is redissolved by H_2SO_4 and basic Cr(III) sulphate is obtained. This compound is reused in tanning.

Protein and chemical-based solid wastes beside the liquid wastes also generate in the process. While untanned protein-based wastes are used in glue and gelatin production, the chemical-based wastes, include shavings and trimmings and splitting wastes, are generally disposed of in landfills or incinerated for elimination of organic residues and to reduction of volume of waste [8]. In the case of the incineration of these wastes, the gases and soluble toxic chemicals generate. These chemicals cause serious environmental problems such as air, soil and water pollution. When the solid wastes containing chromium are incinerated, Cr(III) can converted to its more soluble hex-

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avalent form in the air atmosphere. Wang et al. [9] and Kirk et al. [10] have verified this situation in their studies related to chromium behaviour during thermal treatment of municipal solid waste. Therefore, the solid wastes containing chromium must not be incinerated.

Chrome shavings constitute 75% of the solid wastes containing chromium in the tanning process. About 0.8 million tonne of chrome shavings could be generated per year worldwide [8]. This waste is partly used in the manufacture of leatherboard, but most are deposited in landfill. However, direct discharge is not also accepted in many countries because of the chromium content. The chromium recovery from this waste is necessary for environmental protection and economic reasons. Starting from this idea, in this study, the chromium recovery conditions in the form of soluble chromate from the chrome shaving by oxidation with air, oxygen and Na_2O_2 were investigated. In addition, pregnant chromate solution prepared at the conditions that maximum oxidation yield was achieved was reduced by using Na_2SO_3 and basic Cr(III) sulphate solution using in the tanning was obtained.

2. Materials and methods

2.1. Materials

Chrome shaving used in the study was supplied from a Leather Plant in Elazığ (Turkey). Fresh chrome shavings were dried at room temperature for 3 days prior to use in the experiments. It has been characterized for moisture, chromium and ash contents. The amounts of moisture, chromium (as Cr_2O_3 on dry weight basis) and ash (on dry weight basis) of the chrome shaving have been found to be 57, 3.32 and 4.75%, respectively.

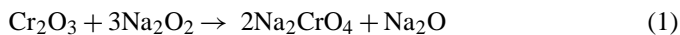
All reagents used in the study were in the analytical reagent grade.

2.2. Experimental procedure

The chromium recovery conditions from chrome shaving in the form of chromate were investigated by using both dried chrome shaving and its ash. For this purpose, two stages experiments were performed. In the first stage experiments, oxidation yield of chromium to chromate was studied in air and oxygen atmosphere by using dried chrome shaving. In these experiments, an appropriate amount of dried chrome shaving was placed in a porcelain dish and incinerated in a muffle furnace at different temperatures for 60 min. In order to sweep gases out of the furnace and supply fresh gas required for oxidation, air and oxygen were blown at a rate of 3 l/min during the incineration period.

In the second stage experiments, oxidation of the chromium to the chromate with Na_2O_2 was investigated by using chrome shaving ash (CSA) obtained at the temperature optimized from results of the first stage experiments. Predetermined amounts of CSA were mixed with varying amounts of Na_2O_2 . The amount of Na_2O_2 to be added to the CSA was calculated with respect to stoichiometric amount of chromium content of the CSA by considering Eq. (1). The mixtures were placed in porcelain dishes

and heated up to melting temperature and waited at this temperature about 15 min:



After the all oxidation stages, the porcelain dish contents cooled at room temperature were leached with distilled water at the liquid/solid weight ratio of 5 at 25 °C. Extracts were analyzed for chromate.

In order to obtain basic Cr(III) sulphate solution using in the tanning, pregnant chromate solution produced at the conditions that maximum oxidation yield was obtained was acidified with H_2SO_4 and reduced by using Na_2SO_3 .

The experiments were performed in duplicate and mean values were taken into account.

2.3. Methods of analysis

The samples obtained after the each oxidation were characterized by Mattson 1000 FTIR spectroscopy. An infrared spectrum of pure $\text{Na}_2\text{CrO}_4 \cdot 4\text{H}_2\text{O}$ (Merck) was also recorded to compare with those of samples.

The concentration of chromate in the extracts was determined colorimetrically with 1,5-diphenyl carbazide method [11] by using Jenway 6105 Spectrophotometer.

3. Results and discussion

3.1. Chromium recovery

In order to produce energy from solid wastes containing organic substances and to reduce volume of wastes, incineration is widely applying procedure. While organic constituents of wastes are removed by oxidizing to CO_2 and H_2O , inorganic matters generally convert to their oxides and remain in the ash during the incineration period.

In the case of incineration of the solid waste containing chromium, it has been stated that the chromium can oxidize to its more soluble and more toxic hexavalent form [9,10]. In the our preliminary experiments, when the chrome shaving is directly incinerated in air atmosphere, we have determined that the chromium in the tanned waste is converted to Cr(VI) and Cr_2O_3 . Also, the results obtained showed that the oxidation of Cr(III) to Cr(VI) depends on incineration temperature and type of the oxidative atmosphere. Therefore, in the first group systematic experiments, effects of the oxidative atmosphere and incineration temperature on the oxidation yield of Cr(III) to Cr(VI) were investigated. For this purpose, dried chrome shaving was incinerated in air and oxygen atmosphere at different temperatures in the range of 500–1000 °C.

Oxidation yields in the both atmosphere increase with increasing temperature up to 850 °C, and then it decreases probably due to quick incineration of waste affected high temperature (Table 1). Maximum oxidation yields of chromium to chromate in air and oxygen atmosphere at 850 °C were found to be 23.02 and 30.41%, respectively. It can be concluded that the chromium recovery from chrome shaving in the form of chro-

Table 1

The variation of chromium oxidation yield depending on incineration temperature and oxidation atmosphere

Incineration temperature (°C)	Oxidation yields of chromium (%)	
	Air atmosphere	Oxygen atmosphere
600	3.77	11.84
700	8.61	14.95
800	14.47	17.24
850	23.02	30.41
900	17.16	19.85
1000	4.92	6.39

mate by incineration of the waste in air and oxygen atmosphere is not satisfactory.

Chrome shaving contains large amounts of more easily oxidizable organic substances than chromium. It is necessary to remove organic substances prior to recover of chromium in the form of chromate from this waste. For this purpose, the most suitable and practical method is incineration. The chromium content of the waste is enriched in its ash by incineration. In this case, recovery of chromium from the ash can be profit and put into practice. Starting from this idea, chrome shaving was incinerated at 850 °C in air atmosphere by taking into consideration results of the first group experiments and chrome shaving ash (CSA) was prepared.

Total chromium content of CSA was found to be 47.15%. 23.02 and 76.98% of the total chromium in the ash are in soluble hexavalent and insoluble trivalent form, respectively. In order to oxidize Cr(III), Na₂O₂ was used as oxidant. For this purpose, certain amounts of CSA were mixed different stoichiometric amounts of Na₂O₂ in the range of 1–10 and heated up to melting temperature and waited at this temperature about 15 min. Obtained results are presented in Table 2.

As seen from Table 2, oxidation yields of chromium increase with increasing amount of Na₂O₂. The highest chromate formation efficiencies occurred in the 8 and over eight times Na₂O₂ with respect to stoichiometric amount of chromium. Oxidation percentages in the 8 and over eight times stoichiometric amounts of Na₂O₂ are close to each other. Therefore, a further increase in Na₂O₂ dosage higher than 8 has a negligible effect on the chromate formation. 99.45% of chromium in chrome shaving is recovered under these conditions.

Table 2

The variation of chromium oxidation yield depending on amount of Na₂O₂

Stoichiometric amount of Na ₂ O ₂	Oxidation yields of chromium (%)
1	29.80
2	34.12
3	48.51
4	53.06
5	67.19
6	86.82
7	96.32
8	99.45
9	99.82
10	99.84

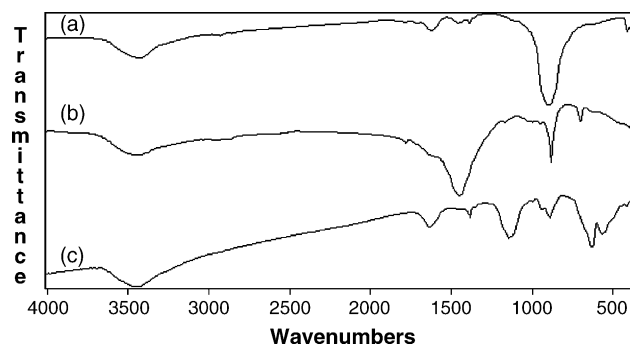


Fig. 1. Infrared spectra of the samples: (a) Na₂CrO₄·4H₂O; (b) product obtained from Na₂O₂ oxidation process; (c) CSA (product of air oxidation process).

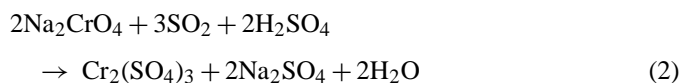
3.2. Characterization of the samples obtained in the oxidation processes

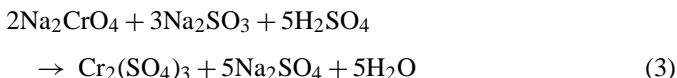
Chromium species by FTIR technique are characterized by presence of infrared bands. While Cr(III) displays characteristics absorptions of chromic oxide at <800 cm⁻¹, Cr(VI) displays in 850–950 cm⁻¹ region [12,13]. In order to determine structure of the chromium species in the samples obtained in the oxidation processes, the samples were subjected to FTIR analysis. The FTIR spectrums taken were compared with that of sodium chromate. The results are shown in Fig. 1.

CSA have characteristic absorption spectrums of chromic oxide at 632, 570 and 416 cm⁻¹ [12,14] and chromate spectrum at 887 cm⁻¹ [15]. The product which 99.45% of chromium in CSA has been recovered in the form of chromate in the Na₂O₂ oxidation process displays characteristics absorptions of chromate at 879 cm⁻¹ (sharp) and chromium oxide at 702 cm⁻¹ (weak). These results show that the most suitable oxidation process is Na₂O₂ process. Spectrum of the sodium chromate also confirms these situations.

3.3. Chromate reduction by Na₂SO₃ and preparation of Cr(III) sulphate solution

Commercial chrome tanning products are generally used in powder form. They contain about 25% Cr₂O₃ of 33% basicity. Basic chrome sulphate liquors are also used. These liquors are prepared by reducing the Na/K chromates in the presence of sulphuric acid [16]. Hence, it can be stated that reuse of the chromium recovered in the form of chromate from chrome shaving will be more reasonable. In this case, it is necessary to reduce Cr(VI) to Cr(III). Although the reducing agents commonly used for hexavalent chromium in aqueous solutions are sulphur dioxide, sodium sulphites, iron and ferrous compounds and some organic substances [17–29], the most suitable reducing agents are sulphur dioxide and sodium sulphites. When these compounds are used, the solution obtained will be relatively pure and more suitable for tanning since it does not contain foreign ions:





Starting from knowledge mentioned above, 99.45% chromium recovered in the form of chromate in the Na_2O_2 oxidation process was leached with distilled water and a pregnant chromate solution was obtained. Chromate ion in the solution was reduced by using Na_2SO_3 . For this purpose, pH of the solution was adjusted to 2 ± 0.1 by using H_2SO_4 solution and a stoichiometric amount of Na_2SO_3 calculated (Eq. (3)) was added. Whole chromate ions in the solution were reduced at the end of contact period of 30 min and chrome sulphate solution was obtained. When this solution is basificated by adding a basification agent such as sodium hydrogen carbonate, it can be reused as a tannage in tanning.

4. Conclusion

This work shows the possibility of using chrome shaving as a source of chrome. For this purpose, in this study, chromium recovery conditions in the form of soluble chromate from the chrome shaving by oxidation with air, oxygen and Na_2O_2 have been investigated and following conclusions have been drawn by taking into consideration results obtained.

It has been determined that the oxidation agent is the most effective parameter affecting the chromate formation. While chromium oxidation yields in air and oxygen atmospheres are not satisfactory, the highest chromium recovery efficiency in the form of chromate (99.45%) occurred in the Na_2O_2 oxidation process.

It has been determined that it is possible to recover of chromium in the form of chromate by Na_2O_2 oxidation. This compound can be reused in tanning by reduction with Na_2SO_3 . Due to effective chromium recovery, environmental protection and economical benefit, it can be stated that Na_2O_2 oxidation process and using of chrome shaving will be advantage for leather plants.

References

- [1] L.F. Cabeza, M.M. Taylor, DiMaio, E.M. Brown, W.N. Marmer, R. Carrio, P.J. Celma, J. Cot, Processing of leather waste: pilot scale studies on chrome shavings. Isolation of potentially valuable protein products and chromium, *Waste Manage.* 18 (1998) 211–218.
- [2] F.J. Berry, N. Costantini, L.E. Smart, Synthesis of chromium-containing pigments from chromium recovered from leather waste, *Waste Manage.* 22 (2002) 761–772.
- [3] C. Fabiani, F. Ruscio, M. Spadoni, M. Pizzichini, Cr(III) slats recovery process from tannery wastewaters, *Desalination* 108 (1996) 183–191.
- [4] T.F. O'Dwyer, B.K. Hodnett, Recovery of chromium from tannery effluents using a redox-adsorption approach, *J. Chem. Tech. Biotechnol.* 62 (1995) 30–37.
- [5] B.D. Pandey, G. Cote, D. Bauer, Extraction of chromium(III) from spent tanning baths, *Hydrometallurgy* 40 (1996) 343–357.
- [6] K.J. Sreeram, T. Ramasami, Sustaining tanning process through conservation, recovery and better utilization of chromium, *Resour. Conserv. Recycle* 38 (2003) 185–212.
- [7] R. Aravindhan, B. Madhan, J.R. Rao, B.U. Nair, T. Ramasami, Bioaccumulation of chromium from tannery wastewater: an approach for chrome recovery and reuse, *Environ. Sci. Technol.* 38 (2004) 300–306.
- [8] J.R. Rao, P. Thanikaivelan, K.J. Sreeram, B.U. Nair, Green route for the utilization of chrome shavings (chromium-containing solid waste) in tanning industry, *Environ. Sci. Technol.* 36 (2002) 1372–1376.
- [9] K.S. Wang, C.J. Sun, C.Y. Liu, Effects of the type of sintering atmosphere on the chromium leachability of thermal-treated municipal solid waste incinerator fly ash, *Waste Manage.* 21 (2001) 85–91.
- [10] D.W. Kirk, C.C.Y. Chan, H. Marsh, Chromium behavior during thermal treatment of MSW fly ash, *J. Hazard. Mater.* B90 (2002) 39–49.
- [11] APHA, Standard Methods for the Examination of Water and Wastewater, 17th ed., American Public Health Association/American Water Works Association/Water Environment Federation, Washington, DC, USA, 1989.
- [12] B.M. Abu-Zied, Structural and catalytic activity studies of silver/chromia catalysts, *Appl. Catal. A: Gen.* 198 (2000) 139–153.
- [13] M. Hoang, A.E. Hughes, J.F. Mathews, K.C. Prattz, Surface chemistry of supported chromium oxide on lanthanum carbonate, *J. Catal.* 171 (1997) 313–319.
- [14] A.M. El-Awad, B.M. Abu-Zied, The synergism of cadmium on the catalytic activity of Cd–Cr–O system. I. Preparation, characterization and electrical properties, *J. Mol. Catal. A: Chem.* 176 (2001) 213–226.
- [15] F.A. Miller, C.H. Wilkins, Infrared spectra and characteristic frequencies of inorganic ions, their use in qualitative analysis, *Anal. Chem.* 24 (8) (1952).
- [16] United Nations Industrial Development Organization, Regional Programme for Pollution Control in the Tanning Industry in South-East Asia, United Nations Industrial Development Organization, 2000.
- [17] M. Sittig, *Pollutant Removal Handbook*, Noyes Data Co, New Jersey, 1973.
- [18] J.W. Patterson, *Wastewater Treatment Technology*, Ann Arbor Inc, New York, 1975.
- [19] K.H. Lanouette, *Heavy Metal Removal*, Chemical Engineering Deskbook Issue, 1977.
- [20] A.V. Bridgwater, C.J. Mumford, *Waste Recycling and Pollution Control Handbook*, George Godwin Limited, London, 1979.
- [21] W.W. Eckenfelder, *Industrial Water Pollution Control*, 2nd ed., McGraw-Hill, New York, 1989.
- [22] I.J. Buerge, S.J. Hug, Kinetics and pH dependence of chromium(VI) reduction by iron(II), *Environ. Sci. Technol.* 31 (1997) 1426–1432.
- [23] L.E. Eary, D. Rai, Chromate removal from aqueous wastes by reducing with ferrous ion, *Environ. Sci. Technol.* 22 (1988) 972–977.
- [24] S.E. Fendorf, G. Li, Kinetics of chromate reduction by ferrous iron, *Environ. Sci. Technol.* 30 (1996) 1614–1617.
- [25] A. Özer, H.S. Altundoğan, M. Erdem, F. Tümen, A study on the Cr(VI) removal from aqueous solutions by steel wool, *Environ. Pollut.* 97 (1997) 107–112.
- [26] M. Erdem, F. Tümen, Cr(VI) reduction in aqueous solutions by using pyrite, *Doğa Tu J. Eng. Environ.* 20 (1996) 363–369 (in Turkish).
- [27] M. Erdem, H.S. Altundoğan, A. Özer, F. Tümen, Cr(VI) reduction in aqueous solutions by using synthetic iron sulphide, *Environ. Technol.* 22 (2001) 1213–1222.
- [28] P. Chebrolu, P.K. Sharada, Reduction of potassium chromate by D-fructose, D-galactose, D-mannose, D-glucose and L-sorbose, *Carbohydr. Res.* 244 (1993) 15–25.
- [29] S.J. Hug, H.U. Laubscher, B.R. James, Iron (III) catalyzed photochemical reduction of chromium (VI) by oxalate and citrate in aqueous solutions, *Environ. Sci. Technol.* 31 (1997) 160–170.