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Enrichment of Chromium(III) from Tannery Sludge in the Presence of Calcium†

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In recent years, development of the leather industry and rapid increasing of the centers of leather production has caused to focus on control of the pollution consisting of tannery wastes. The sludges of the leather waste are main sources of the pollution in the leather industry. In this study, removal of chromium and calcium ions from sludges of the leather waste and developing an enrichment method to recover of chromium in the presence of calcium was conducted in the acidic range. The method is based on enrichment of chromium(III) by means of solubility of samples of the sludge with sulphuric acid solution at pH 1 following multi extraction by solutions of the previous extracts. The release behaviour of chromium and calcium ions from the sludges and separation of each other was characterized by using synthetic and real sludges such as biological sludge and pre-treatment output sludge of the wastewater of leather. The amount of the satisfactory enrichment of chromium from sludges has been obtained while significant amount of calcium remains in sludge.

Key Words: Chromium, Calcium, Tannery, Sludge, Recovery, Enrichment.

INTRODUCTION

Leather industry is one of the most polluting industries producing large amount of wastewater and sludge, which contain high organic pollutants and hazardous metals[1,2]. In tanning industry raw skin is transformed into leather by means of a series of chemical and mechanical operations. Organic and inorganic pollutants consist of chemical reactions that they are carried out between the skin and different chemicals such as chromium salts, acids, alkalines, tannins, solvents, sulfides, dyes, auxiliaries in aqueous solution[3].

The wastewater streams of tanning industry are generally mixed and chemical, physical and biological treatments are applied by the formation of sludge[3]. The chemical precipitation is required to remove the chromium and chemical oxygen demand (COD) from wastewater before the wastewater flows into a biological treatment unit[4,5]. The sludges are classified such as primary sludge, biological sludge and chemical sludge depending on sources of generation[6]. The wastewater composition, chemicals and treatment units mainly determine the amount and properties of chemical sludge. The chemical sludge from a tannery consists mostly of calcium and chromium hydroxides with other components such as magnesium, precipitates, inert solids, oil, grease and debris[7,8]. Biological sludge has small size of colloidal and fine particles. Therefore, it flows through the primary clarifying and it is removed in the secondary clarifying[9]. The activated sludge is a heterogeneous mixture of particles, microorganisms, colloids, organic polymers and cations[10].

According to the American (California) regulation, tannery sludges contain the concentration of chromium in the range of 1 to 40 mg/kg on a dry weight basis and American (California) regulation defines total chromium above a concentration of 2.5 mg/kg in sludge as hazardous waste[11].

Waste sludges are generally disposed of by pumping into the sea, or by storing or by land application for agricultural purposes by considering the environmental impacts and economic costs[12]. However, there are some problems associated with land applications of sludges including odors and aesthetics, potential pathogens in sludge, suitable site and soil and sludge quality with respect to toxic organic chemicals, salts and heavy metals[13,14-18]. The another problem is the high concentrations of heavy metals in sludge. As the heavy metals are adsorbed by soil they accumulate in soil[19,20]. Hence, some problems including metal toxicity to plant, microbial population of soil and the accumulation of metals in the food chain will be developed[21]. Therefore, the minimization of amount of tannery waste and the treatment of tannery waste is very important by recycling, biogas production, materials or energy recovery. The priority for waste sludge management and treatment is

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respectively prevention, reduction, re-use, recycling and recovery, thermal treatment for certain types of waste and landfill. There is some studies for treatment of sludge of leather waste. A study has existed as an ecological alternative to the pollution generated by tanneries with maximum recovery of Cr_2O_3[22]. A study has been carried out by application of ozonation and ultrasonication as pretreatment processes on primary and secondary sludge generated during treatment of tannery wastewater[23]. An environmentally friendly leather process involving a lime-free liming process and a nano SiO_2 tanning process based on silica chemicals was investigated in recovery processes[24]. In a study microemulsion systems were used to remove chromium from leather tannery sediments by a solid-liquid extraction process and efficiency of chromium removal was considered[25].

Some studies involving minimization of amount of chromium(III) from sludge of tannery waste are available as below: A process for the treatment of tannery sludges was developed by acid leaching of the sludges and treating the leachate by a weak base anion exchanger resin and following by treating with a strong acid cation exchanger resin as selective to ferric species for separation and recovery of chromium and aluminum[26]. An another study on separation and recovery of chromium(III) from tannery sludge was presented by extraction of chromium(III) with sulphuric acid solution at pH 1 and oxidation of chromium(III) to chromium(VI) with H_2O_2 and separation of chromium(VI) from other cations by its subsequent reduction to chromium(III)[27]. The release behaviour of chromium(III) from tannery sludge was investigated as a function of pH and redox potential[28].

In recent years, the intensities of pollution have increased because of high technology and industrialization and waste sludges have been treated as a resource by considering the environmental impacts and economic cost.

The wastewater which is supplied from Organized Leather Tanning Industrial District, created in Tuzla, Turkey, has been generated with a flow rate of 36000 m^3/d, presently houses 107 tanneries processing both cattle hide and sheep skin, with resulting wastewater flow of 12000 to 15000 m^3/d[29]. The sludge of wastewater of leather has been produced as 59 ton/d in the plant of wastewater of leather. In this study the recovery and removal of chromium(III) from synthetic and real sludges of tannery waste, obtained from leather industry of Istanbul has been examined in the presence of calcium with composition of much more than chromium. The process is based on developing an enrichment technique to recover of chromium(III) while mostly amount of calcium remain in sludge. The method is characterized by solubility of the samples of real and synthetic sludge with solution of sulphuric acid (1:1) at pH 1 and developing an enrichment technique. The enrichment technique is based on subsequent extractions of the samples of dried sludges as 5 cycle with the solutions of previous extracts. The considerable contribution on enrichment and recovery of chromium(III) from tannery sludge has been achieved.

EXPERIMENTAL

Chromium chloride hexahydrate, calcium hydroxide and aluminum oxide were used for preparation of the synthetic sludges simulating sample of real sludges with respect to amount of chromium(III) and calcium. The pre-treatment output sludge of tannery and biological sludge were used as the samples of real sludge. Diluted sulphuric acid solution (1:1) was used for solubility of sludges at pH 1. Al_2O_3 was used as inert substance in the composition of synthetic biological sludge. The pH values of the extracts of sludge were measured by a pH meter with a model of knick 704. The solution of ferric(III) chloride was used for coagulation of solutions of the real sludges. All the chemicals are pure in analytical grade and from Merck, Germany. Bidistilled pure water was used throughout experiments. The solution of concentrated HNO_3 was used in acidification of samples before measurements.

Preparing of the real sludges: The sludge of pre-treatment output of the leather wastewater was pretreated with the procedures of respectively coagulation, precipitation, filtration by water tromp, drying at 105 ºC in oven and homogenization in ambient temperature. The biological sludge was used as another sample of real sludge and it was prepared by polymerization, precipitation, compression and drying at 105 ºC in oven and homogenization in ambient temperature.

Preparing of the synthetic sludges: The samples of the synthetic sludge simulating real sludges with respect to amounts of chromium(III) and calcium were named as synthetic sludge I and II. The samples of synthetic sludge I and II were prepared as equivalent to amounts of calcium and chromium in real sludges and they have simulated the samples of real sludge respectively as the sludge of the pre-treatment output [synthetic sludge I] and the sludge of biological [synthetic sludge II] of the leather wastewater. The synthetic sludges in the similar composition of amounts of the chromium and calcium of real sludges were composed of weighing of definite amounts of chromium chloride ($CrCl_3 \cdot 6H_2O$) and calcium hydroxide and aluminum oxide (Tables 1 and 2) and homogenization in ambient temperature. The samples of sludge were preserved as dried and closed in room temperature.

TABLE -1
COMPOSITION OF THE REAL SLUDGES

Composition	% $Cr(OH)_3$	% $Ca(OH)_2$	% Other components	% Cr	% Ca
Pre-treatment output sludge of leather waste water	13.00	27.00	60.00	6.56	14.59
Biological sludge	9.88	57.84	32.28	4.99	31.26

TABLE-2
COMPOSITION OF THE SYNTHETIC SLUDGES

Composition	% $CrCl_3 \cdot 6H_2O$	% $Ca(OH)_2$	% Al_2O_3	% Cr	% Ca	% Al
Synthetic sludge (I)	36.09	27.99	35.92	7.04	15.13	19.02
Synthetic sludge (II)	25.72	54.63	19.65	5.02	29.53	10.40

Tables 1 and 2 have shown the compositions of sludge with respect to amounts of chromium and calcium respectively as the sludges of real and synthetic.

Enrichment method: The enrichment of chromium and recovery of calcium was based on subsequent extraction of samples of the sludge of real and synthetic with solution of previous extract-sulphuric acid (1:1) in the volume of 40 mL. The method was applied for as well as sludges of real and synthetic at pH 1 for 5 cycles.

Application of the enrichment method for first cycle: 5 g of the sample of sludge was taken in a beherglass and treated with 20 mL of distilled water. The pH of the solution was adjusted to 1 by adding solution of sulphuric acid (1:1). The solution of sludge was mixed with a magnetic stirrer for 1 h. The volume of the solution was completed to 40 mL with distilled water and filtered into a flask in the volume of 50 mL by quantitatively filter paper (5893 Blauband, ϕ: 150 mm, Ref. No.: 300212, Schleicher & Schüll). The remain sludge in filter paper was washed into the flask and the flask was completed to the volume by distilled water to obtain the first extract.

Application of the enrichment method for cycles between 2-5: 5 g of the sample of sludge was taken in a beherglass and treated with 40 mL of the previous-extract for each cycle by adding aqueous solution of sulphuric acid (1:1) up to the pH of the solution is 1. The solution of sludge was mixed by a magnetic stirrer for 1 h and filtered into a flask in the volume of 50 mL by quantitatively filter paper. The sample of the sludge in filter paper was washed into the flask and the flask was completed to the volume by distilled water to obtain the enrichment extract. The procedure was repeated for five time to form next extraction cycles between 2-5. The solutions of extract of the enrichment between the cycle of 2-5 were obtained by using the solution of the each previous extract in the volume of 40 mL as extract for the next extraction.

Preparation of samples for analysis: 1 mL of the solutions of enrichment extract was taken to the flask in the volume of 100 mL and flask were completed to the volume by distilled water. The solution was filtered by using millipore filters having size pore as 0.45 µm. The samples were acidified with the solution of ultrapure nitric acid. The content of chromium and calcium in the enrichment extract was determined by atomic absorption spectrophotometer with the model of Varian Spectra 300.

Effect of the contact time between solution of the enrichment extract and samples of real of biological sludge on enrichment of chromium in the presence of calcium: The enrichment procedure of chromium in the presence of calcium has been carried out at pH 1 depends on different contact times between solution of the enrichment extract in the volume of 50 mL and samples of sludge. The enrichment procedure was applied for 4 cycle with contact times of 15 and 60 min.

RESULTS AND DISCUSSION

The enrichment method of chromium from tannery sludge in the presence of calcium was conducted under same conditions by using samples of synthetic and real sludge. The samples of different kind of synthetic sludge simulating real sludges with the composition of chromium(III) and calcium were used for experiments as synthetic previous treatment output sludge [synthetic sludge (I)] and synthetic biological sludge [synthetic sludge (II)]. The biological sludge, which is provided from Tanning Industrial Sector of Turkey, Istanbul was used as sample of real sludge.

The amounts of chromium and calcium in the enrichment extract of 50 mL were determined with synthetic sludge (I), synthetic sludge (II) and real of biological sludge depend on number of enrichment cycle for each cycle. The atomic absorption spectrophotometric method was used for quantitative analysis of solutions of sludge sample.

The values of enrichment of chromium and recovery of calcium from sample of synthetic sludge (I) of 100 g have been obtained depend on number of enrichment cycle respectively as 83 and 65.46 % for fifth cycle (Fig. 1). Although synthetic sludge(I) has consisted of amount of chromium(III) as two times less than calcium the high amount of enrichment of chromium(III) has achieved. Al_2O_3 has acted as inert substance and it has not an effect on enrichment of chromium and recovery of calcium.

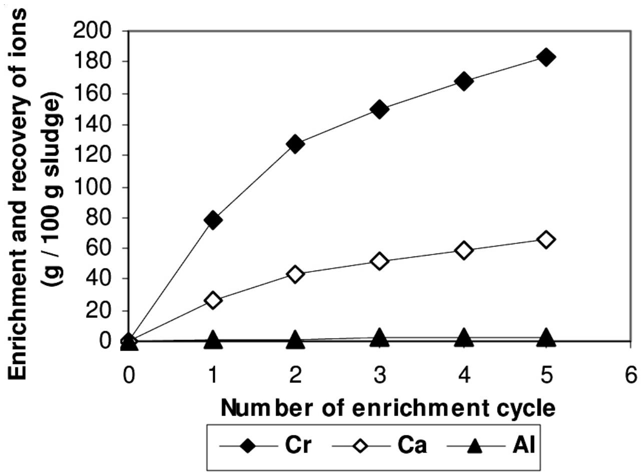

Fig. 1. Enrichment and recovery of ions of chromium(III) and calcium(II) and aluminium(III) depends on number of enrichment cycle from synthetic sludge (I) of 100 g

The values of recovery of chromium and calcium from sample of synthetic sludge (II) of 100 g have been obtained depend on number of enrichment cycle respectively as 60 and 20 % for fifth cycle (Fig. 2). Although the enrichment of chromium has not been obtained at pH 1 in the presence of amount of calcium as six times more than chromium with synthetic sludge (II) the recoveries of chromium were in agreement with different amounts of sludge samples such as 5.0 g and 2.5 g. The existence of calcium with high composition in sludge has shown interference effect on enrichment of chromium.

The enrichment of chromium and recovery of calcium were carried out as 5 cycle from real of biological sludge of 100 g. The biological sludge has consisted of amount of calcium as six times more than chromium. The values of enrichment of chromium and recovery of calcium have been obtained depend on number of enrichment cycle respectively as 43.49 and 1.46 % for last cycle of extraction (Fig. 3). While chromium has been recovered with effective enrichment amount calcium has a small recovery value with extraction of 5 g of dried biological sludge.

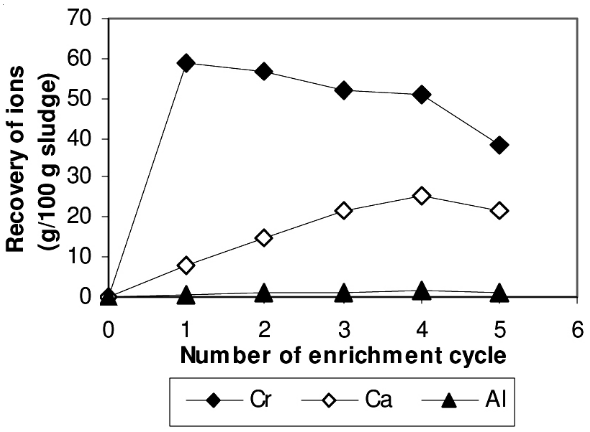

Fig. 2. Recovery of ions of chromium(III) and calcium(II) and aluminium(III) depends on number of enrichment cycle from synthetic sludge (II) of 100 g

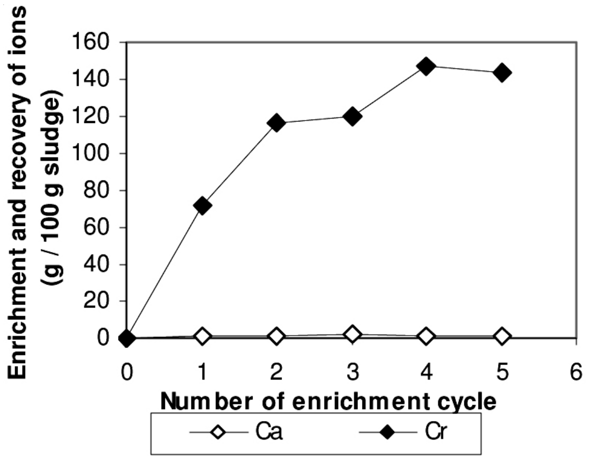

Fig. 3. Enrichment and recovery of ions of chromium(III) and calcium(II) depends on number of enrichment cycle from real of biological sludge of 100 g

The amounts of the chromium and calcium in the enrichment extracts in the volume of 50 mL have been examined as a function of contact times between samples of real of biological sludge and solutions of enrichment extract for 4 cycle. The enrichment and recovery of chromium and recovery of calcium were obtained from real of biological sludge of 100 g with respect to contact time of 15 and 60 min. The values have been shown in Figs. 4 and 5, respectively.

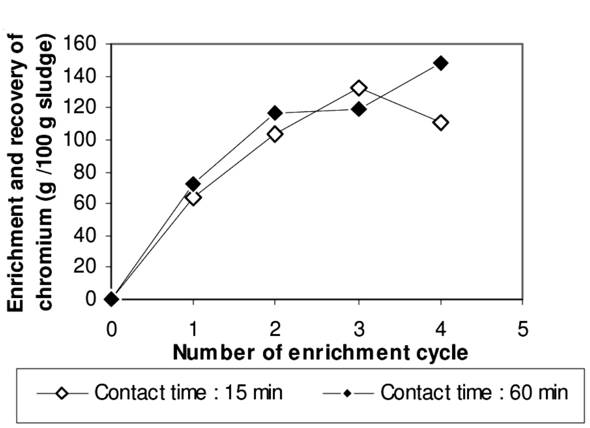

Fig. 4. Enrichment and recovery of chromium(III) depends on contact time between biological sludge and enrichment extract by using real of biological sludge of 100 g

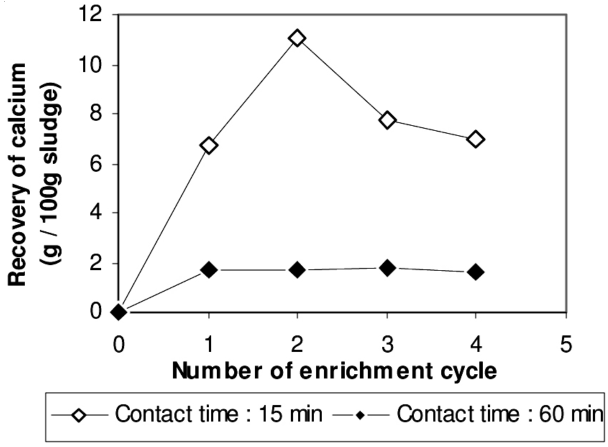

Fig. 5. Recovery of calcium depends on contact time between biological sludge and enrichment extract from real of biological sludge of 100 g

The enrichment percentage of chromium depends on number of enrichment cycle was determined by extraction of the samples of real of biological sludge with contact times as 15 and 60 min (Fig. 6).

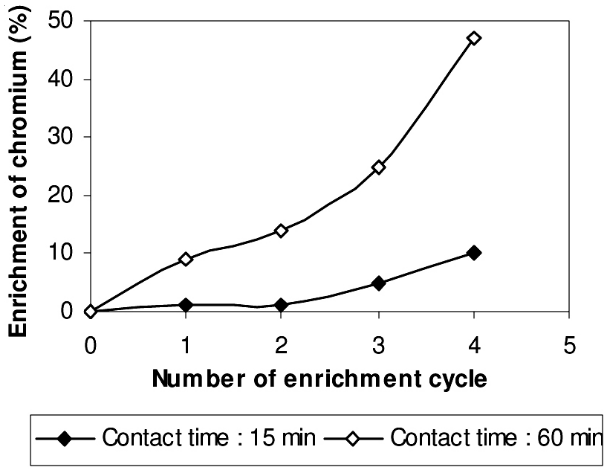

Fig. 6. Enrichment percentage of chromium(III) depends on contact time between biological sludge and enrichment extract from real of biological sludge of 100 g

The experimental data has shown that the enrichment amount of chromium has increased in the case of more contact time between real of biological sludge and enrichment extract while the recovery of calcium has reduced. The enrichment of chromium have been reached by raising as 8 % for first cycle; 13 % for second cycle; 20 % for third cycle and 37 % for last cycle with more contact time as 45 min. The recovery of calcium is under 12 % with contact time of 15 min and it has decreased with expanding of contact time as 5.02 % for first cycle; 9.32 % for second cycle; 5.5 % for third cycle and 5.32 % for last cycle. Increasing contact time has been resulted in favour of effective recovery and enrichment of chromium as the solubility of calcium sulphate and recovery of calcium is very low in sulphuric acidic media at pH 1. The method is efficient to recover and to enrich of chromium from synthetic pre-treatment output sludge and real of biological sludge even in the case of less amount of chromium(III) than calcium as six times.

The values of enrichment of chromium and recovery of calcium have been obtained which depend on number of enrichment cycle respectively as 43.49 and 1.46 % for last cycle of extrac-tion. While chromium has been recovered with effective enrichment amount calcium has a small recovery value with extraction of 5 g of dried biological sludge.

Conclusion

The sludge of the tannery is the major source of chromium pollution as it is classified as hazardous waste. The chromium content in sludges, which is supplied from Istanbul Organized Leather Tanning Industrial District, Tuzla, Turkey, is sufficiently high in the presence of calcium more than chromium. The compositions of chromium(III) in the samples of real sludge are 65.6 and 49.9 g/kg on a dry weight for respectively pre-treatment output sludge and biological sludge. This values are extremly high according to American regulation[12]. The tannery sludges containing toxic compounds of chromium(III) requires a safe treatment to make it harmless before release into the environment.

The aim of this study is to develop sludge management by recovery and removal of chromium from real and synthetic sludges of the tannery waste with application an enrichment technique. The method is based on enrichment and removal of chromium(III) from sludge samples at pH 1 by solubility of the sludges with sulphuric acid solution (1:1) and extraction with the solutions of previous enrichment extract for 5 cycle. The sulphate salts consist of treatment of sludges with sulphuric acid solution. The difference of solubility of the chromium(III) sulphate and calcium sulphate at pH 1 is an advantage to separate both metals. The method allows not only enrichment and recovery of chromium(III) from real and synthetic sludges of the wastewater of leather but separation of calcium and chromium(III) from tannery sludges. The another advantage of the method is to obtain less toxic sludge of tannery waste by removal of chromium(III) for safely disposal. The method is cheap and practical.

The effective enrichment of chromium(III) with real of biological sludge has been observed with higher enrichment data in comparison of the synthetic biological sludge. This different approach has occurred because of different structures of synthetic and real biological sludge. Some studies have taken place in literature on solubility of tannery sludges with solution of sulphuric acid at pH 1 to concentrate chromium(III) sulphate for direct reusing[30] and to separate of chromium(III) from other cations and recovery[27]. In this study, the recovery yield of chromium(III) has increased by application of enrichment technique. The produced solution of chromium(III) sulphate from the sludge of tannery waste can sufficiently be concentrated for direct reuse and recycling.

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