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Heavy Metals Removal and Recovery from Hazardous Leather Sludge

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The tanning industry is one of the oldest industries in the world and is known for the production of a wide variety of toxic waste (aqueous and solid) containing chromium salts and other heavy metals. Solid waste is produced during the conversion of putrescible collagen fibres into finished non-putrescible leather products. In this process, the use of a variety of chemicals during the fleshing or trimming phases, results in different hazardous waste, such as wet blue leather, crust leather, chrome shaving, finished leather off-cuts, and unusable chrome spilt.

In the present study, we deal with the treatment of these hazardous leather sludge and the recovery of heavy metals contained in them. The leather sludge was pyrolyzed in a torch plasma reactor at a temperature of 1,400-1,500 °C producing an inert solid residue. However, the high temperatures involved induce the volatilization of some metals, which condense to form hazardous dusts (21.8% Zn, 0.70% Cr, 4,080 ppm Pb and 123 ppm Cd) that have to be properly dealt with. Numerous leaching tests have been conducted to maximize the amount of the individual components solubilized from the powder. Then, different treatment strategies have been combined for the recovery of the main metals: precipitation for Pb and Zn, and adsorption on chitosan for Cd.

1. Introduction

The technological tanning cycle consists in the transformation of the animal skin (subject itself to putrefaction after a bacterial attack) into leather (unalterable and not putrescible substance) used to produce goods such as shoes, leather products and clothing items. This activity represents a relevant sector of the Italian industry both by tradition and by economic importance. With over 2,600 production units and 35,000 employees (Tiravanti and Santori, 1993), Italy is the world leader in the quantity (about 1.050 Mt/y of tanned leather) and in the quality of the finished product: about 66 % of the tanned product produced in EEC countries is produced in Italy, equal to about 16 % of world production (Alibardi and Cossu, 2016).

During the conversion of putrescible collagen fibres into finished non-putrescible leather products, a variety of chemicals is used, leading to the production of a wide variety of high toxic waste such as wet blue leather, crust leather, chrome shaving, finished leather off-cuts, and unusable chrome spilt. It is possible to identify two main production cycles: (i) chrome tanning, and (ii) natural and synthetic tanning. The most common process uses chromium as the main tanning material, but the performance of the tanning baths does not generally exceed 50 – 60 % and this leads to a waste of raw materials (raw skin and chemical products) and high amounts of chromium in the drains.

Indeed, only 20 – 25 % by weight of the raw leather entering the tannery is transformed into products. The remaining weight, combined with chemical additions, ends up as waste or by-products (on average, a 60 % of raw material constitutes solid waste and sludge). Residues can be solid or liquid and include salt, hair, leather scraps, flesh, shaving powders, residual mud from wastewater treatment, residual chemicals and more. Usually, a ton of raw material (leather) produces about 600 kg of solid waste and 20 - 30 m^3 of wastewater; moreover, about 500 kg of chemical substances are used during the process (Mella et al., 2015). These and other factors are at the origin of the environmental impact that the tanning activity entails.

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Tannery residues can be classified as non-hazardous or hazardous waste depending on the legal context of the individual states, but also on the markets and the available treatments and reuse / recycling facilities. In particular, the leather waste material containing chromium is considered one of the most hazardous and harmful waste if discharged in the environment without treatment (Kanagaraj and Elango, 2019).

Despite this, a lot of waste is currently disposed of in landfills because of the simplicity and economy of this solution, with the risk of severe impacts on both environment and humans in case of improper disposal. For instance, the undesired migration of the metals towards other matrices can lead to different forms of persistent contamination that require to be properly quantified (Ferrucci et al., 2017) before being treated by applying specific strategies, based e.g. on phytoremediation (Franchi et al., 2019), or electrokinetic approaches (Vocciante et al., 2017). Although it is always possible to consider at least a cheap and non-invasive control of water movements (Vocciante et al., 2015) to monitor of the displacement of contaminants in soil and avoid groundwater contamination by toxic leachate, the possibility to recover raw materials from this type of waste is certainly attractive (Selvaraj et al., 2019). Since also mining activity causes severe effects on environment, the recovery of the metals from waste should be a priority (Pietrelli et al., 2018a). This is also in agreement with the latest European laws that promote the development of processes in line with the strategies of the Circular economy, BAT techniques, and the “near-zero discharge” of hazardous wastes (see, for example, Pietrelli et al., 2018b).

From the technical point of view, the choice of further treatments for both reuse and disposal depends on the nature and quantity of chemical substances and heavy metals present in the respective fractions, which vary according to the process chosen for tanning or for wastewater treatment.

Regarding the wastewater from tanning industry, its treatment results in the production of tanning sludge, mainly obtained in purification plants from the primary sedimentation treatment, from the precipitation of exhausted effluents from the tanning operations in alkaline media, and from the biological treatment for the removal of organic substances. The amount of dried mud produced per unit weight of processed leather varies between 10 and 20 % (Simoncini et al., 1987).

Despite the high quantities of organic material, and the non-negligible quantities of chromium(III), according to the legislation currently in force in Italy (Ronchi Decree, 2/97), these sludge are classified as special non-hazardous residues, whose current destination is a second-class type B controlled landfill (D.Lgs. 04/06).

However, the organic material is subject to putrefaction phenomena, with the consequent development of methane responsible for the greenhouse effect to a much greater extent than CO_2, and Cr(III), once released into the water, can be converted into Cr(VI) even after purification treatments. All this has determined the sensitization of the scientific community towards the problem of the stabilization of tanning sludge before it is sent to some form of disposal or recovery.

Currently, the trend regarding the disposal of tanning sludge (or sludge deriving from the purification treatments of the tanning industry's wastewater) is that of reuse. Numerous are the investigations that foresee the utilization in agriculture of the tannery muds both directly as fertilizers (Silva et al., 2010), through the dispersion on agricultural lands, and for the production of compost with high content of nitrogenous substances (Vig et al., 2011). Some research works focused on the possibility to biologically extract valuable metals from tannery sludge to be recycled on tanning industry by using bioleaching processes (Ma et al., 2017). In other works, the possibility of using tannery sludge in ceramics (Abreu and Toffoli, 2009) and bricks manufacture (Giugliano and Paggi, 1985) or as substitute of construction aggregates (Celary and Sobik-Szołtysek, 2014) was evaluated.

Since not all these processes have been developed at an industrial level, disposal solutions alternative to landfills consider sludge combustion. Incineration has advantages as the significant reduction in the volumes of the treated masses and the destruction of the organic part that acts as fuel. However, the main problem linked to this solution consists in the production of ashes with a high content of Cr(VI), which makes their disposal particularly expensive, as well as the release of gaseous emissions containing aromatic hydrocarbons, such as dioxins and furans. On the contrary, pyrolysis offers some different benefits in the treatment of sewage sludge (Tôrres Filho et al., 2016). The advantages of this process include: i) the production of a high quality oil that can be used in various chemical processes; ii) the exclusion of the production of dangerous by-products, such as furans, due to the low operating temperatures (400 - 800 °C) in the absence of oxygen; iii) the entrapment of heavy metals in small volumes of inert residues (Werther and Ogata, 1999).

The solution considered in this work is a plasma pyrolysis process, which is becoming of increasing interest due to its manageability, fast heating, and relatively low power consumption (Czajczyńska et al., 2017). Plasma pyrolysis is essentially characterized by two distinct transformations: i) the conversion of the organic fraction of the waste into a synthesis gas with combustible characteristics; ii) the fusion of the inert (inorganic) part in a basaltic mass, which can be disposed of safely, in landfills, or in old abandoned mines.

For this to happen, it is necessary to transfer high amounts of energy to the mass of waste using the plasma torch that, due to the strong difference in potential applied, produces a "plasma discharge" or "arc discharge".

The purpose of this work was the study of physico-chemical treatments applied to the hazardous powders coming from the tanning sludge subjected to plasma pyrolysis. Although the solid residues produced are inert, the high temperatures involved induce the volatilization of some metals, unlike what happens in a normal pyrolysis process. Being a secondary effect, little attention is paid to this aspect, which tends to be overlooked. Yet in the subsequent stages of the process, these vapors condense to form hazardous dusts, which have to be recovered and properly disposed of, e.g. eliminating the cadmium present in quantities exceeding the law limits, and recovering the zinc, present in large quantities.

Numerous leaching tests have been conducted to maximize the amount of the individual components solubilized from the powder. Then, different treatment strategies have been combined for the recovery of the main metals. Based on the investigations and tests conducted, a fractional precipitation for Pb and Zn, and an adsorption on chitosan for Cd were found to be efficient and thus considered from the perspective of an integrated industrial activity.

2. Materials and methods

The powders here investigated come from the pyrolysis of tannery sludge performed with a plasma torch. The temperature inside the torch was around 1,500 °C, while the dust was collected immediately downstream of the first heat exchanger, where the temperature was around 200 - 250 °C. This solid residue, in the form of powder, contains 21.8% of Zn, 0.70% of chromium, 4,080 ppm of lead and 123 ppm of cadmium. Given the high temperatures reached in the combustion chamber, the metals having a relatively low boiling temperature pass to the gaseous state and are found in the heat exchanger as happens with zinc and cadmium. This is the reason why chromium is present only in traces, being characterized by a boiling temperature of about 2,600 °C.

Leaching, or liquid-solid extraction, is necessary to solubilize the individual components of the powder. Numerous leaching tests have been conducted to maximize the amount of the individual components solubilized from the powder. The detection of the various metals was performed by atomic absorption spectrophotometry (AAS), with the aid of a Perkin Elmer series 5100 Flow Injection Analysis System 200.

The leaching agents used were HCl and H_2SO_4 at various concentrations (1, 3 and 6 M). From the chemical analysis of the powder, the percentage of calcium proved minimal, therefore a prewash in water was not considered necessary for its removal before performing leaching with sulfuric acid (CaO and carbonates would readily react with it, increasing its consumption).

The parameters studied were the contact time, the liquid-to-solid ratio (S/L) and the acid concentration. All the tests were performed in duplicate, that is two or more times with identical operating procedures, in order to minimize the incidence of possible errors and verify the reproducibility of the experiments.

3. Results and discussion

3.1 Leaching tests

Since none of the two leaching agents proved to be selective with respect to the metals taken into consideration, the choice was made with respect to the solution that leached in greater quantity zinc and cadmium.

Time-dependent tests, at constant stirring speed and temperature, have shown that both HCl and H_2SO_4, regardless of the concentration used, lead to a similar kinetic trend, with the extraction of about 70 – 80 % of the maximum extractable values (at that acid concentration), after 60 min. To achieve maximum extraction, it is necessary to reach at least 120 min for most of the metals considered. Cadmium and partly chromium show a different behaviour, a light and constant increase in the hydrochloric environment.

Table 1 shows the percentage extraction data of each metal at the end of the leaching cycle with different concentrations. As a verification, the solid leaching residue was dried at 60 °C for about 24 h and subsequently weighed, confirming that percentage of weight loss for the samples were consistent with extraction data. As expected, the best results were obtained at high concentrations (6M); moreover, at the same concentration, the best extraction was obtained with HCl, with which it is possible to recover almost the 100 % of the metals present.

Additional tests on the extraction yield as a function of the variation in the solid / liquid ratio using 3 M and 6 M HCl as leaching agents have shown that a S/L ratio of 1/15 with 6M HCl is the best in terms of efficiency of extraction for all metals – almost 100 % extraction against 23.7 % Zn and 43.7 % Cd extracted at 1/30 with 3M HCl. Consequently, an aliquot of solution obtained by using the 6M HCl and an S/L ratio of 1/15, after being filtered, was titrated to determine the residual acidity and have an estimate of the acidity consumed during the leaching process. The result of the titration, carried out with 0.1M NaOH, corrected for the buffer effect caused by the precipitation of heavy metal cations, showed a low consumption of acid, which was estimated in about 1 mol. Therefore, the residual acidity was sufficiently high to suggest its partial reuse.

Table 1: Percentage of metal extraction with HCl and H_2SO_4 after 5 hours

	Zn	Cd	Pb	Fe	Cr
HCl 1M	6.2	22.1	80.1	6.1	1.1
HCl 3M	17.3	50.8	98.2	12.9	2.4
HCl 6M	94.8	100	100	23.8	2.8
H_2SO_4 1M	4.6	10.6	9.8	9.8	1.5
H_2SO_4 3M	14.3	10.8	15.6	7.4	1.4
H_2SO_4 6M	20.7	12.8	32.8	8.6	0.9

3.2 Fractional precipitation

To recover the leached metals, the actual wastewater was subjected to fractional precipitation by addition of NaOH. Precipitation is usually accompanied by flocculation and coagulation, and the formation of large amounts of sediments could be a problem especially for solutions with low concentrations of metal ions. In this work, the application of precipitation is justified by the considerable amount of zinc; moreover, a good sedimentation capacity was noted.

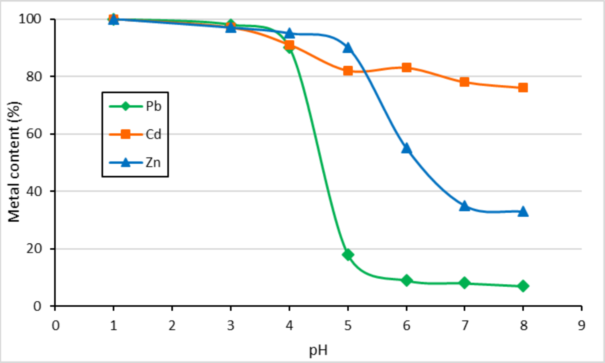

Figure 1: Percentage values of the three metals in the solution after fractional precipitation

Figure 1 shows how it is possible to first perform the separation of lead for pH values between 4 and 5; after filtration, continuing the addition of NaOH, it is possible to induce the precipitation of zinc, which corresponds to pH values between 5 and 7. The final solution contains mainly cadmium, at a concentration not too far from its initial value.

3.3 Adsorption on chitosan

The adsorption of metal ions to chitosan is mainly due to its amino groups, yet also hydroxyl groups can contribute to the process (Fernandes et al., 2013). These functionalities can interact with metal ions through different mechanisms that depend on the metal, the pH, and the solution matrix. The free electron doublet of nitrogen can bind the metal cations at pH values close to neutral or slightly acidic. On the other hand, the protonation of the amino groups in acidic solutions gives the polymer a cationic behaviour and consequently the ability to interact with anionic species.

The effect of the initial concentration of metals plays an important role in the kinetics of adsorption on chitosan. As the initial concentration increases, the adsorption capacity of the metals increases too. The time required for the adsorption action of chitosan is about 120 min, especially for solutions with high concentrations. Lead and cadmium (Figure 2) at concentrations of 100 and 200 mg/L undergo maximum adsorption after 60 min.

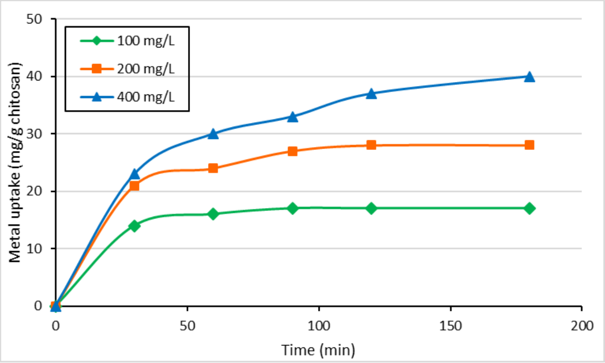

Figure 2: Adsorption kinetics of cadmium with 0.1g of chitosan and 50 mL of solution

The pH of the solution has a noticeable influence on the adsorption of metals; for this reason, the efficiency of adsorption of 0.1 g of chitosan in 50 mL of 200 mg/L solution of metal has been analysed varying the pH in the range from 4 to 9; values not shown are due to the formation of a precipitate.

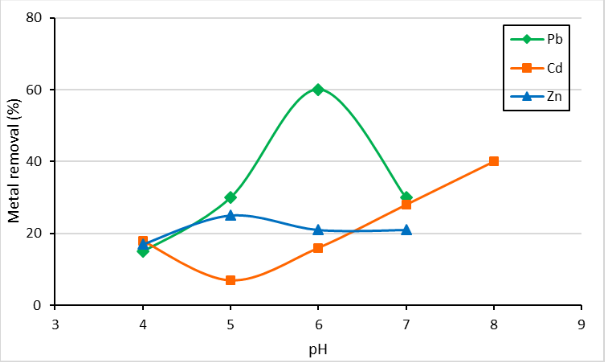

Figure 3: pH dependence of the removal (%) of the three metals by adsorption on chitosan

During the tests, a pH variation was noticed each time the chitosan was added to the solution. In fact, starting from an acidic pH, chitosan led to a slight increase of the initial value, and the opposite was seen for pH values greater than 7. It can be assumed that a competition takes place between the protons and the metal ions for the amino groups of chitosan at acidic pH, with consequent protonation of these groups (Lasindrang et al., 2015).
For pH values closer to neutrality or slightly alkaline, a lowering of the pH was noted, as a consequence of the release of protons by chitosan and subsequent complexation of metal ions. In fact, in the case of cadmium, a correlation between the lowering of the pH and the adsorption of the metal by chitosan was observed.
For the three metals, a common pH value that was favourable for adsorption was not observed. Conversely, this favours the selectivity of the separation: for zinc, the optimal pH value is about 5 ($ZnOH^+$ species prevails), while for lead it is around 6 ($PbOH^+$ and $Pb(OH)_2$ species prevail), and for cadmium it is around 8 ($CdOH^+$ and $Cd(OH)_2$ species prevail); the same trend can be found in literature (Karim et al., 2019). In particular, high removal yields (60 %) can be obtained for lead at pH 6. These evidences confirm that adsorption on chitosan may represent an effective method for the selective separation of these metals.

4. Conclusions

The first experimental part was carried out to optimize the operating modes of the leaching phase for the extraction of the metals contained in the powders. Subsequently, two selective separation processes were studied. Downstream of the fractional precipitation, the solution, containing metal residues, would need further treatments before being discharged into surface water or used as recycling water. Considering this, the results suggests that chitosan can be used in a complementary process to eliminate the amount of cadmium present in the solution, after removing lead and zinc by fractional precipitation. Further studies are underway to develop an integrated process that includes the two separation approaches investigated. In this perspective, strategies are being evaluated to best exploit the residual acidity found in the leaching solution used, in order to minimize waste and increase the economic and environmental sustainability of the treatment.

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