

Impact of Hexavalent Chromium in Leather Goods and Chrome-tanned Waste on Human Health and to the Environment

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Abstract—Issue of waste, its formation, disposal and possible secondary processing as one of current global problems is dealt in this paper. Hazardous waste represents a potential threat to the environment and human health. The paper is focused on an area of waste containing hexavalent chromium arising especially from leather industry. Hexavalent chromium the element occurring in various amounts in tannery waste is classified as a carcinogen. Its repeated exposure to human organism has hazardous impact. New possible risk connected with the use of disinfectants on shoes containing oxidizers have been revealed and is introduced. The menace consequences are based on the known potency of conversion trivalent to hexavalent chromium in leather in different conditions. The oxidation is supported by experimental data gained by UV-visible spectrophotometry. Although the level of chromium in various ambient is controlled, it is often a total amount of chromium i.e. trivalent together with hexavalent chromium what can be indeed misleading from the hazardousness point of view. An innovative method Raman spectroscopy is proposed for identification of the valence state of chromium contained in investigated material. Raman spectroscopy renders an inner structure of a matter hence it has an ability to recognize the form of an element. Finally the process of collagen protein hydrolysis gained from tannery wastes as a mean of secondary processing of waste material is introduced. The final product of the process is intended to be used as inducer of resistance for crop plants.

Keywords—Closed-loop technology, hazardous materials, hexavalent chromium, leather manufacture, tannery wastes.

I. INTRODUCTION

WASTE can be regarded definitely as human products as there appears to be no such thing as waste in nature. The waste products created by a natural processes or organisms become quickly the raw materials used by other processes or organisms. This life cycle is a strategy of nature for ensuring stability and sustainability in its systems. The system created by man emphasizes different values as those economic which are largely incompatible with the stability of nature.

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Production and a pursuit of disposal of waste are as old as a human society. Trash holes were filled with different types of waste and broken tools ever since the prehistoric periods. Due to them we have today information about the modus vivendi of an ancient man, what can be really interesting in light of history and mankind progression.

People are accompanied by an occurrence of waste for centuries, but only for decades waste has become a problem that should be systematically solved and be organized. As a logical result of long-term situation the issue of waste reduction and ways of their safe, environmentally and economically favorable disposal is one of the most actual and pressing problems worldwide. The production of various waste types has an upward trend for decades in a manufacturing sector and even in the public sphere.

For turning the trend it is necessary for all producers of waste to changes their attitudes and approaches. Both industrial areas and general public need to comprehend meaning of the risks arising from cumulating waste. Especially risks in the sense of endangering the environment and human health.

Sorting-composting approach in the household waste disposal brings certain benefits as reduction of the volume of waste to be treated by incineration after sorting recyclable and compostable materials or utilization of compost in agriculture [1].

Closed-loop and low-waste technologies represent one of the ideal solutions for protecting the environment. Residues in single processes of closed-loop technologies are used as secondary raw materials for further use or as sources of energy. No waste is formed or eventually just in a less quantity. It is a kind of preventive access with the view to restrict production of waste but particularly hazardous waste. A prevention of waste production is profitable also economically. It brings the advantage of savings of raw materials or decreasing a cost of waste disposal. Moreover closed-loop technologies may advance competitive strength.

Both municipal and industrial waste generally contains a wide range of contaminants. Some of contaminants as toxic metallic elements or presence of microorganisms can represent serious threat for the environment and human health. These metallic elements form soluble compounds and make a waste hazardous. Released toxic elements as arsenic, cadmium,

asbestos, lead, mercury, nickel, or hexavalent chromium are dangerous by a reason of leaking into a soil or water.

Large problems with ground water and water sources contaminated by hazardous hexavalent chromium had appeared in USA or China in the past [2, 3]. These situations had negative impact on human health and even claimed lives of. Dangerous or tragic incidents generally have to happen to start looking for solutions how to claim preventions. Mentioned cases lead in the discussions about the permitted limits of toxic elements and emphasized the necessity of its control.

II. SCOPE OF THE RESEARCH

The issue of hexavalent chromium in leather goods and tannery waste is solved. Hexavalent chromium has been classified as a carcinogen [4, 5] and hence it can cause serious health risks when coming into direct contact with human organism. This paper deals with a new potential health risk comprising the use of certain disinfectants on shoes that has been revealed and is introduced. The aim of this paper is to highlight that it is important attentively choose a disinfectant to be free of strong oxidizing agents as peroxides. Otherwise the main purpose to destroy bacteria would be probably fulfilled, but more serious health risk could be caused due to the repeated procedure.

Important connection to hexavalent chromium issue is the problem of chromium detection in the environment or industrial premises. The possibility of control of a presence of hexavalent chromium in common leather goods people are exposed to daily should be not less important. Raman spectroscopy as an innovative analytical method for determination and stating the valence of chromium compounds in leather is proposed.

Another related issue concerning the process of complex leather waste treatment and its possible further use as inducers of resistant is presented. The nature of this process allows ranking it among closed-loop processes. The ways of secondary processing of waste materials from various manufacturing industries are eco-friendly and desired in present technologies.

III. THEORY

A. Trivalent and hexavalent chromium

Chromium is a metallic element commonly occurring in nature. It can be found in rocks, volcanic dust, gases, sea water, but also as a part of living organisms including human bodies. In the environment chromium occurs in several different forms. The most common form of chromium in chromium compounds is trivalent (CrIII) and hexavalent (CrVI). Hexavalent chromium occurs naturally in the environment from the erosion of natural chromium deposits, but also as a product of industrial processes.

Biological effects of chromium are strongly dependent on the valence, in which chromium enters into the body. Trivalent

chromium is largely beneficial and necessary part of daily diet. Trace amounts are needful for humans for glucose and lipid metabolism. Trivalent chromium is benign due to poor membrane permeability in general [6]. On the contrary hexavalent chromium can negatively affect human health. Hexavalent chromium is toxic and is considered a carcinogen. In commercially available sources is often mentioned increase risk of irritation or damage to the respiratory tract and lung cancer when hexavalent chromium is inhaled in a large extend and also allergic contact dermatitis when coming into contact with skin [7].

When hexavalent chromium react with biological reductants free radicals participating in reactive oxygen species production are generated [4]. Excessive production of reactive oxygen species may cause DNA and proteins damage. These mutagenic characters can lead to cancerous growths in respiratory tract [7, 8].

A potential threat to the health could be hidden in chrome-tanned leather goods, mainly shoes, which are in daily contact with the human organism. If the goods contain even small amounts of carcinogenic chromium, there is a potential risk of cancer, especially kidney and urinary tract [9]. Upward trend in the incidence of urinary tract neoplasms not only in Czech Republic requires serious answer, if not caused by the content of hexavalent chromium in leather goods. According [5] there is a possible correlation between increasing mentioned cancer disease and rising import of relatively cheap and often disputable quality shoes. Hexavalent chromium can penetrate through the skin, amplified by the presence of sweat, into the organism, when wearing shoes on bare feet.

B. Tannery waste

A significant share of waste arises from manufacturing sector. Leather industry is one of the spheres that can be widely discussed. Leather products like shoes, belts, wallets, upholstery and others belong among the objects of everyday needs. Achieving the final products comprise a lot of waste arising from the raw material processing and creating specific items.

The majority of global leather production is chrome-tanned. Using complex salts of trivalent chromium in the process of tanning effectively influenced the desired functional properties of leather. Trivalent chromium stabilizes a hide by crosslinking the collagen fibers and supply required qualities. However, trivalent chromium contained in leather can be under various conditions in small amounts oxidized to another form – hexavalent chromium.

The possibility of the spontaneous oxidation of CrIII into CrVI can occur both in alkaline and acidic medium in the wide range of pH what complicate the right conditions specification [5].

Known prerequisite factors for the formation of hexavalent chromium in leather are [10]:

- Oxidizing agents – the fundamental for the conversion is presence of oxygen.

- Energy in a form of heat and ultraviolet light, because the conversion requires energy supply.
- Fatty acids as catalysts for peroxide formation.

Although knowledge of trivalent to hexavalent chromium conversion is well described in literature, the precise mechanism is complex and details are not clearly explained [11].

A menace arising from chrome-tanned waste may be therefore related both to the environment and to human health. Chrome tanned waste can be sectionalized into three categories:

- Tannery waste comprising solid (shavings or trims) and liquid form (the waste water containing chromium).
- Manipulation waste e.g. leather scraps in the manufacture of footwear or leather goods.
- Used leather goods, such as old shoes, which are often a part of municipal waste at the dumps.

The third group can represent slightly underestimated problem. A considerable amount of trivalent chromium contained in these discarded leather items may succumb to uncontrolled oxidation and make the waste hazardous. Not to mention the possibility of leakage into the soil and groundwater.

C. Raman spectroscopy

Raman spectroscopy is an innovative analytical tool that becomes a valuable part of laboratories around the world in recent years. In principle, Raman spectroscopy as a vibrational spectroscopic method has the potential to answer a number of questions related to chemical details of molecular structure what makes this technique definitely proper for material identification [12].

Raman spectroscopy provides very specific chemical „fingerprint“ of every single chemical substance in the form of the Raman spectrum.

Raman scattering, the fundamental principle of Raman spectroscopy and the whole technique are named in honour of one of its discoverers, the Indian scientist Sir Chandrasekhara Venkata Raman (1888 - 1970), who searched out the effect together with Kariamanikkam Srinivasa Krishnan (1889 - 1961) in 1928. Sir C. V. Raman was awarded a Nobel Prize in physics in 1930 for the discovery of the effect and his work on the scattering of light.

Raman effect remained for a long time only on a theoretical level and practically was marginalized because of low sensitivity and difficulties with overcoming fluorescence phenomena. However, renaissance of Raman spectroscopy is coming even in the last two decades hand in hand with technical advancements and latest developments in the field of new extremely sensitive detection devices, efficient filters for filtering Raman scattered light from the Rayleigh scattering, and also innovative laser technology designs [13].

As is known, molecules have an ability to absorb or emit photons – an electromagnetic radiation with specific energy and by this way change their own energy. According to the quantum theory the energy of a photon E is given by the equation:

$$E = h\nu \quad (3)$$

or

$$E = hc\bar{\nu} \quad (4)$$

where h is Planck's constant, ν is its frequency, $\bar{\nu}$ is the wavenumber, thus the reciprocal wavelength. Mentioned specific energy ΔE have to fulfill following quantum condition

$$\Delta E = |E_p - E_q| = h\nu = \frac{hc}{\lambda} \quad (5)$$

E_p and E_q are energies of different quantum states in which a molecule can exist, c is the velocity of light and λ is the wavelength. The energy of a molecule will be changed by an amount ΔE , if molecule absorbs or emits the photon.

Raman effect occurs when a researched material is irradiated by an intense monochromatic light. A major part of light beam usually from near infrared, visible or near ultraviolet range is scattered without changes in frequency, no energy is gained or lost, i. e. Rayleigh (elastic) scattering, a part is absorbed and a remained tiny fraction, important for the origin of the spectra, is non-elastically scattered. After interaction of the photon with the molecule, particularly with the electron cloud and the bonds of the molecule, the photon evokes molecule excitation from the ground state to a virtual energy state.

Molecule relaxes, emits a photon, and returns to a different vibrational or rotational state. The energetic difference, between the ground state and the final state, results in a shift in the emitted photon's wavelength. Energy level diagram illustrates Fig. 1.

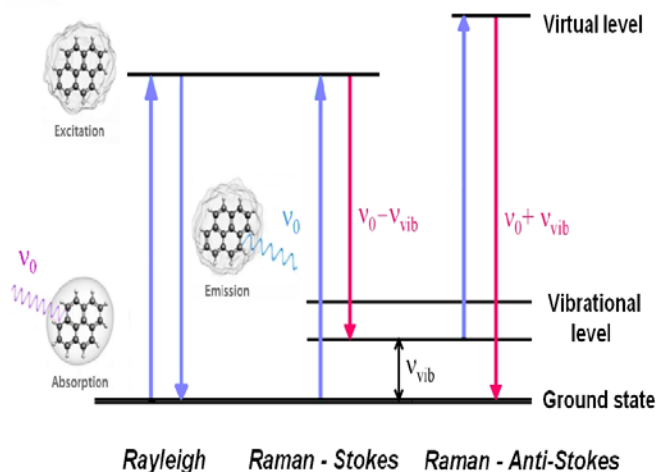


Fig. 1 Energy level diagram of Rayleigh and Raman scattering

The schematic principle of the Raman spectroscopy is shown in Fig. 2.

Wavenumber (Raman) shifts carry analytical information on differences between the individual quantum levels and play the key role in substance identification. These Raman shifts depend on the specific molecular geometry of the material and are independent on the incident photon wavelength, i.e. on the

excitation wavelength of the laser [14]. There can exist several characteristic shifts for certain material which originates the Raman spectrum. Distribution of the lines in the spectrum informs about a sort of the bonds in the molecule. Every individual substance has its own unique Raman spectrum characteristic only for the respective substance.

Raman spectrum represents a dependence of intensity of the scattered light (in arbitrary units) on wavelength or on a Raman frequency shift (measured in cm^{-1}). Intensity of the Raman scattering depends on several factors as the excitation wavelength of the used laser, used excitation power, changes in polarizability, the amount of Raman active molecules illuminated by the laser beam and temperature. The intensity of a Raman band is theoretically described by George Placzek [15].

In spite of the fact, that the particularity of Raman spectroscopy is remarkable, the conversion efficiency of Raman effect is rather poor, since only a scarcity (about 10^{-7}) of the initial photons are non-elastically scattered on molecules. Hence the detection of very low concentrated molecules is limited.

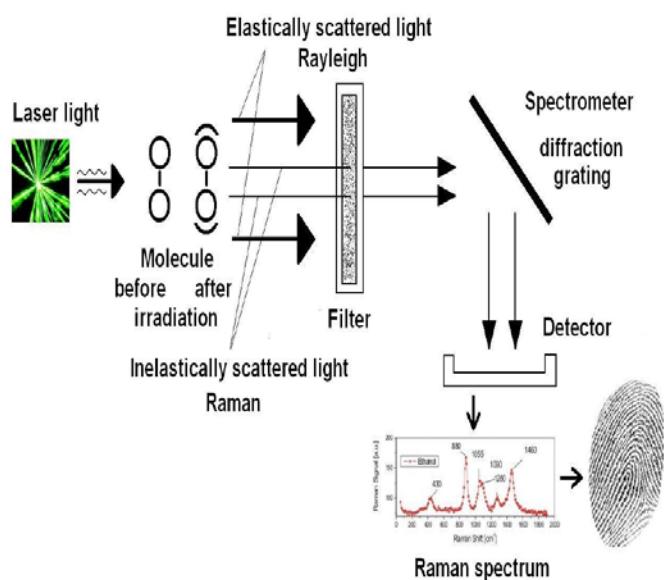


Fig. 2 The sample is irradiated with laser, molecule vibrates, filter eliminates intense Rayleigh scattering, the grating disperses the light onto a detector to generate a spectrum, which gives the information about molecule bonding and provides a chemical fingerprint utilizable for identification.

Raman spectroscopy has a number of indisputable advantages which appreciate scientist from variety spheres and which makes this method attractive, convenient and support the growth of its popularity.

The method is:

- non-destructive
- non-contact
- rapid

- with no need for sample preparation prior the analysis is required
- applicable to a wide range of substances – in all states of matter and different forms - powders, crystals, fibers, thin layers, gel, solutions, etc. with no concern with sample size, shape or thickness
- for organic and inorganic compounds
- applicable to aqueous solutions - a great advantage in comparison with infrared spectroscopy where the presence of water or moisture is unfavorable
- granting highly specific chemical “fingerprint” - each compound gives arise to a unique Raman spectrum
- applicable to measuring through transparent covering layers and packaging
- highly sensitive

Currently the most commonly used Raman spectrometers are combined with microscopes. Then only very small volume (about ones of μm in diameter) of a sample is needed for collecting Raman spectra when using Raman microscopy. This interconnection yields many benefits e. g. for forensic science investigation of trace amounts of evidences.

Remote analyses can be also realized. Transmission of laser light and Raman scattered signal can be done by fiber optic probes.

In spite of many advantages of Raman spectroscopy a well known competing process can appear along with the Raman scattering: fluorescence. Fluorescence signal is generated by a part of matter that undergoes an electronic transition to an excited state what initiate emission of light at a wavelength which is changed from the excitation laser. A mechanism controlling both effects is similar and determines that if one of the phenomena occurs, the second will likely as well. Fluorescence initiation probability versus probability of Raman scattering initiation is in the order of 1 photon in $10^3 - 10^5$ versus 1 photon in $10^6 - 10^9$. Hence we always have to consider fluorescence interference. For sensitive samples it is necessary to have on mind eventual thermal degradation through the intense laser radiation.

The scope of application of Raman spectroscopy is continually expanding to a wide range of scientific branches in recent years, as is presented in [16, 17 18]

IV. EXPERIMENTAL PAR

A. Disinfectants containing oxidizers

People vulnerable to emergence of dermatological diseases (e.g. fungal infection) are recommended to disinfect the inner area of the shoes. It is important attentively choose a disinfectant to be free of strong oxidizing agents as peroxides. Otherwise the main purpose to destroy bacteria would be probably fulfilled, but more serious health risk could be caused due to the repeated procedure.

As was already said one of the prerequisite factors for the formation of CrVI in leather is the presence of oxidizing agents [11]. Hydrogen peroxide and its compounds are strong oxidants that are often used for disinfection or the process of sterilization.

Oxidation kinetics of CrIII to CrVI in the presence of hydrogen peroxide at normal temperature was studied. During the reaction hydrogen peroxide decomposes according the following equation:



O is highly reactive oxygen with the oxidation state -1, which can be also acquired by the effect of ultraviolet radiation:



The conversion of all trivalent to hexavalent chromium occurred very quickly particularly in alkaline medium.

There was made a survey of available disinfectant recommended specifically for disinfection of footwear in Czech Republic. Several disinfectants containing hydrogen peroxide were found.

To verify possible effects of disinfectant containing hydrogen peroxide to increase the level of hexavalent chromium in chrome-tanned leather eight different samples, mostly from pigskin and cow leather, were used as a source of trivalent chromium. The disinfecting agent (recommended on shoes) with the 0,1 grams of H_2O_2 per 100g of the product was purchased in a pharmacy.

UV-visible spectrophotometric method was applied on our leather samples. Basically this method is colorimetric technique using 1,5 diphenylcarbazide reacting with the CrVI extracted from leather to form colored (magenta) complexes that are consequently measured on spectrophotometer at a wavelength 540 nm. Higher amount of CrVI in the solution



Fig. 3 Increasing (from left to right) color intensity of resulting solutions caused by increasing an amount of CrVI in these solutions

means more intense colored tone of the solutions as is shown in Fig. 3. Detection limit of this method is about $1 \mu\text{g/l}$. [19] Opponents of this method have expressed reasonable doubts about the reliability of the method. They argue that CrIII to CrVI oxidation can occur just by the extraction

The disinfectant was applied on three-gram pieces of leathers several times always in quantities of 1.25 ml and with the same time intervals. Specifications of sets of measurements are displayed in Table 1. The ambient conditions were maintained at the same level. Samples were left to air 24hours and then placed in distilled water for 120 hours. One more set of measurements was done without disinfection to determinate the content of CrVI on the untreated samples. Solutions were assessed according to CSN ISO 11083.

Table 1 Specifications of sets of measurements

EXPERIMENT NO.	TREATED OR UNTREATED	NO. OF DISINFECTANT APPLICATION
1	Untreated	0
2	Treated	1
3	Treated	2
4	Treated	4

V. RESULTS

A. Disinfectants containing oxidizers

Firstly a calibration curve, the dependence of absorbance on the content of hexavalent chromium in solution was measured. Evaluated data are shown in Fig. 4. The graph shows an increase in the content of hexavalent chromium in leather samples with repeated application of disinfectant. In half of the samples the increase is direct. Values pertaining to four times cured leather pieces are on average triple in comparison with untreated samples. The results clearly confirm the fact, that strong oxidizing agents facilitate the conversion of CrIII to CrVI in leather. With regard to the fact, that effects of repeated exposure, even to low concentrations, to CrVI have hazardous impact on human health it is necessary to take the issue of hexavalent chromium very seriously.

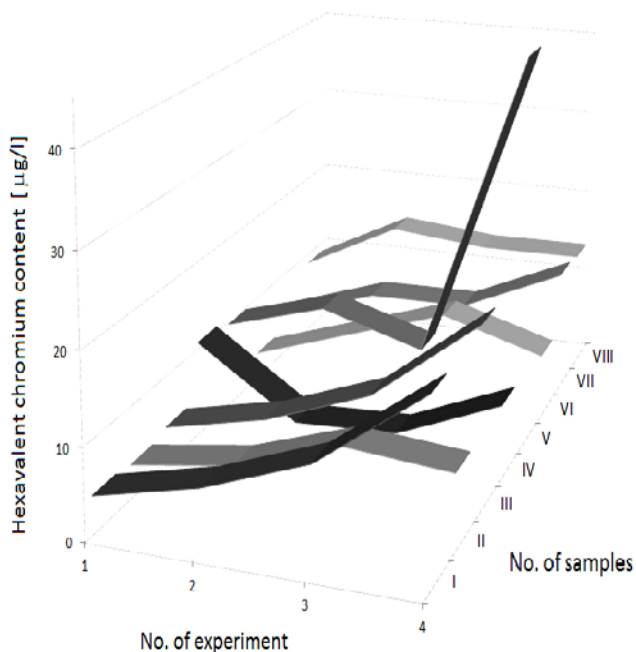


Fig. 4 The increase of hexavalent chromium content in leather samples after application of disinfectant containing hydrogen peroxide.

B. Raman spectra of chromium compounds

Raman spectra of trivalent and hexavalent form of chromium were measured on InVia Basis Raman microscope. Important for acquiring Raman was the choice of laser. It was found that chromium compounds are generally fairly well measurable with excitation in visible region, but for determination of chromium in leather samples is more suitable less energetic near infrared laser than laser using visible light (Argon ion laser, 514nm) because of the complication with luminescence caused by leather. Raman spectra were acquired using near infrared diode laser with the excitation wavelength 785 nm and maximum output power 300mW. Samples were scanned in range 100 – 1300 cm^{-1} with 2 cm^{-1} spectral resolution.

Spectra of both valences indicate their structural diversity, as is shown in Fig. 5 what simplify identification of valence forms. Presence of CrVI affects the dominant peak at 911 cm^{-1} in a spectrum. Other peaks pertaining to CrVI are at 231 cm^{-1} , in the region of 350 – 400 cm^{-1} and around 864 cm^{-1} . Characteristic for trivalent form of chromium is the most intense peak at about 541 cm^{-1} and two peaks in the area 350 – 400 cm^{-1} .

In Fig. 6 spectra of compounds of trivalent and hexavalent chromium which were not located in leather samples are displayed for comparison. These spectra were taken from freely accessible spectral database RASMIN [20].

The cardinal fact is that Raman spectroscopy can be used for the detection of compounds of different forms of chromium in leather. To the authors best knowledge there are very few reports on analytical methods for the detection of trace amounts of CrVI in leather samples.

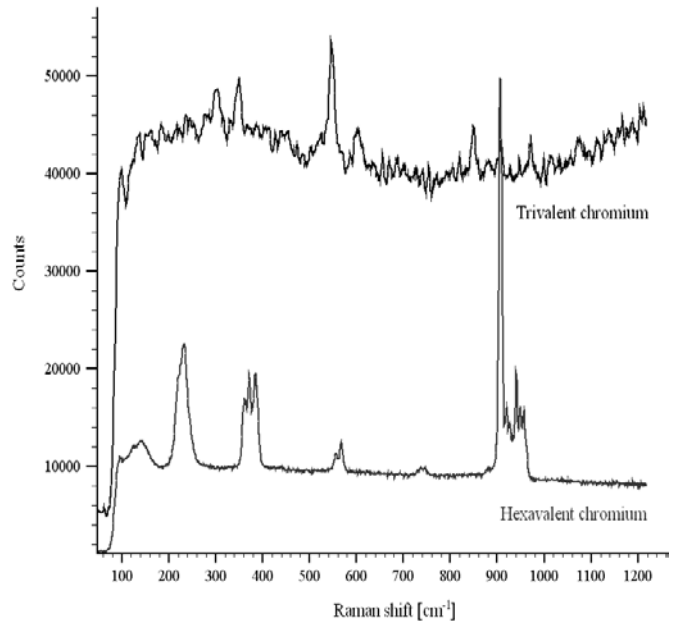


Fig. 5 Measured Raman spectra of trivalent and hexavalent chromium contained in leather samples

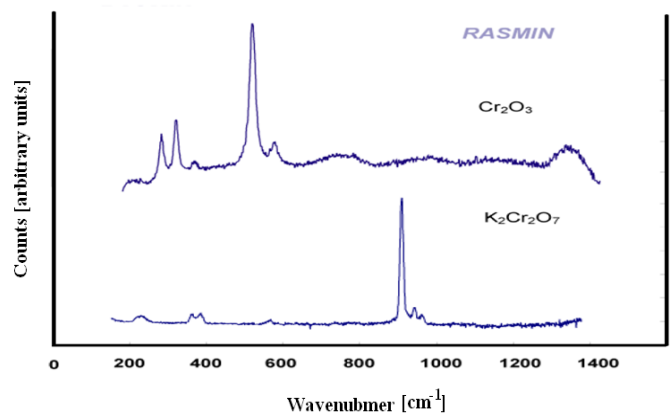


Fig. 6 Raman spectra of CrIII and CrVI compounds from RASMIN spectral database [20]

VI. PROCESS OF LEATHER WASTE TREATMENT

At the beginning of the process is first tannery waste material chromium tanned shavings. Along the treatment this initial matter is three times hydrolyzed under different conditions. The final product is then a protein with proper properties needful for further use as inducer of resistance, see Fig.7.

In the first step the collagen protein is hydrolyzed and separated from the chromium sludge. This waste product can be revitalized for obtaining chromium in a form of salts for further leather tanning [21]. The part of resulting gelatinous protein high-quality gelatin finds many applications in food industry, pharmacy or cosmetic etc. and therefore can be used cost-effectively. The rest of gelatinous protein is used for the

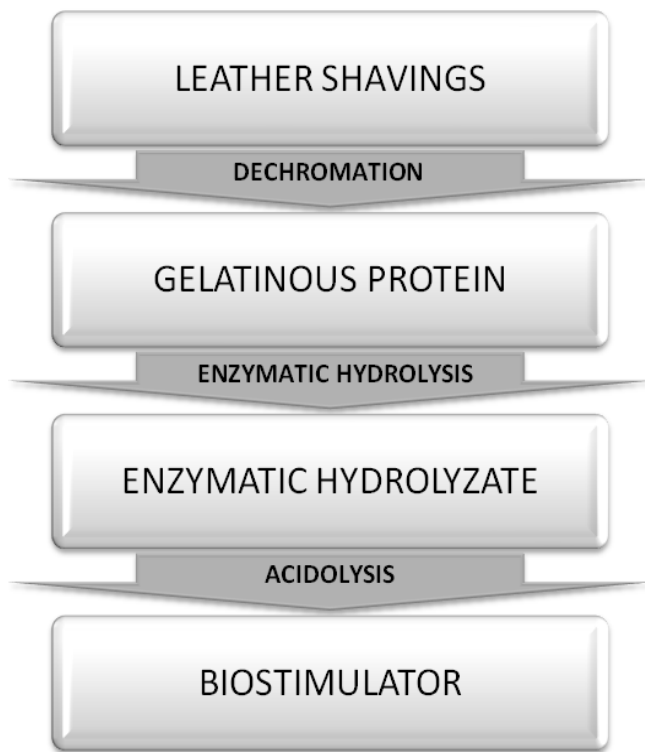


Fig. 7 Collagen protein hydrolysis process structure

purpose of further processing. Used enzyme causes in alkaline conditions splitting of a gelatinous hydrolyzate. However, enzymatic hydrolyzate is not still efficient for the use with a view to biostimulator for plant protection due to very slow diffusion the splitting of protein chain continues by the act of acid. Mathematical model for the acidolysis of enzymatic hydrolyzate is published in [22]

These successive hydrolyses are implemented because of reducing the molar masses. The initial molar mass is about 500 000 kg/kmol, the value of molar mass of the final

Table 2 Values of molar masses of proteins resulting during the hydrolysis process

SUBSTANCE	MOLAR MASS [kg/kmol]
Collagen protein in shavings	300 000 – 500 000
Gelatinous protein	100 000 – 150 000
Enzyme hydrolyzate	10 000 – 30 000
Biostimulator	2 000 – 5 000

substance is hundred times smaller. In Table 2 are listed the values for all the substances present in the process. Due to the low molar mass of biostimulator a plant is able to absorb this substance what helps to run its immune mechanism.

VII. CONCLUSION

The problem of waste disposal and possible secondary processing of waste is ranked among actual global issues. Non-utilization of secondary materials is not economical and is not environment-friendly. Probably it will have a great impact on the environment in the future but it can also bring potential threats for human health.

Both municipal and industrial waste contains a number of contaminants including toxic and dangerous compounds as is hexavalent chromium. The amount of hexavalent chromium in the environment can grow due to the known, but already clearly unexplained fact that harmless trivalent chromium contained e.g. in majority of leather products can under various conditions oxidize into this dangerous form. Hexavalent chromium can appear in leather goods as shoes using disinfectants containing oxidizers as is presented in this paper. The effects of repeated exposure to hexavalent have hazardous impact on human health. Significant on submitted demonstration is the fact that to this or similar situation people may be routinely exposed.

Raman spectroscopy seems to be a potential method for chromium valence identification, even in leather. It could be subservient to perform control analyses for the chromium content in leather, water or other ambient in the future.

Finally the closed-loop process of collagen protein hydrolysis gained from tannery wastes for the purpose of production inducers of resistance for crop plants was introduced.

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