

## NEW TANNING TECHNOLOGIES BASED ON VALORIZATION OF INDUSTRIAL WASTES

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### 1. SUMMARY

Leather industry has to cope nowadays with major environmental problems because of the polluting processes (a World Bank report has placed the leather industry in the 10th place when considering the environmental impact). Therefore, increasing the environmental efficiency in the leather sector is the major aim of leather, auxiliary materials and equipment manufacturers. The development of new tanning agents and new technologies is required to cope with the increasingly higher environmental pressure on the current tanning materials and processes such as tanning with chromium salts. The original contribution of this work has involved the use of solid titanium wastes (cuttings) resulting from the process of obtaining highly pure titanium (ingots) in the preparation of new tanning compounds intended to increase the environmental efficiency of the leather sector.

### 2. EXPERIMENTAL

The main classification criterion for titanium wastes was their contaminant level (Buzatu M., 1994). The highest contaminant level in titanium wastes and titanium alloys is in cuttings resulting from the mechanical processing of ingots and cast articles.

Basic metal composition of the Titanium wastes (filings) used as raw materials for the production of the new Ti (III) tanning agents is given in Table 1.

Table 1 - Chemical composition

Element	Ti	Al	V	Fe
N	40.00	1.0	0.1	4
	0.0001			0.0005

The Aluminum salt used was  $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$  (15.3%  $\text{Al}_2\text{O}_3$ , 8.55% Al). The schematic outline of the synthetic pathway designed and applied for the generation of the mixed new tanning agents based on Titanium and Aluminum is shown in Figure 1 (Crudu M. et al., 2008, 2009).



Figure 1. Chemical synthesis pathway for obtaining the new tanning agents based on Ti and Al.

### 3. RESULTS AND DISCUSSIONS

The results of chemical analysis carried out for the novel tanning agents' solution and powder form are reported in Table 2.

Table 2 - Chemical analysis of the Tanning agents

Parameter	Value
Titanium (Ti)	15.3%
Aluminum (Al)	8.55%

The evaluation of new tanning agents' and in particular topographic distribution - mapping - of the metal species, was obtained by means of scanning electron microscope (SEM) and energy dispersive X-ray (EDAX) analyses (Figure 2).

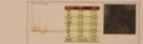


Figure 2. Mapping of scanning electron microscope (SEM) and energy dispersive X-ray (EDAX) analyses.

### New Wet-White leathers characterization and evaluation

Shrinkage temperature values determined for the different new tanning agent variants ranged from 18-20°C, whereas wet white leathers were successfully processed through the subsequent mechanical operations of splitting - steady grain, middle and bottom split were obtained, as well as shaving, as demonstrated with the photographic image of Figure 3.

Good hydrothermal stability of the prototype leathers was confirmed with measurements undertaken using the Micro-Fit table device, with T=70-80°C, as shown in Figure 3.



Figure 3. Hydrothermal stability using the Micro-Fit table device.

Another confirmation of the thermal behavior of the new semi-wet type of leather tanned with white pre-tanning agents was obtained by using DSC analysis (differential scanning calorimetric dynamic analysis). A typical example of the thermographs recorded for samples taken from the prototype wet-white leathers tanned with the new Ti-Al based tanning agents is shown in the Figure 4.



Figure 4. DSC analysis (differential scanning calorimetric dynamic analysis) for the tanned leather.

The evaluation of the modification of collagen by new tanning agents' and in particular topographic distribution - mapping - of the metal species in the prototype leathers, was obtained by means of scanning electron microscope (SEM) and energy dispersive X-ray analysis (EDAX). These are most appropriate methods for the characterization of surfaces and the results obtained confirm all previous assumptions about metal tanning agents uniform penetration and distribution, as well as provide semi-quantitative data of the mineral species topographic mapping (Figure 5).

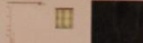


Figure 5. SEM - image of grain split of wet white leather.

### 4. CONCLUSIONS

Exploring the valorization of solid Titanium metallurgical wastes, as a low cost raw material has yielded new tanning agents for the replacement of Cr(III) tanning salts, a hitherto unthinkable or non technically feasible mission. In turn, as demonstrated here it is plausible to:

- increase of eco-efficiency in the leather manufacturing sector by making use of solid wastes, which cannot be recycled in the industry that generated them;
- total or partial replacement of chromium salts in the tanning process with cheap to produce and easy to apply in rapid full substance bovine leather manufacture, that, in turn required minimum process rationalization or modification; moreover, the new mineral tanning agents are free of restricted or regulated metals Cr, Pb, Cd, Hg and Ni;
- increase in articles diversity.

The experimental results obtained so far in pre-tanning trials, are a clear witness that it is now possible at pilot scale to produce full substance bovine wet white with the desired smooth grain, that possesses the minimum hydrothermal stability for subsequent mechanical processing and further R&D ought to be carried out aiming at:

- improving the methods of waste processing to make them more efficient;
- a complete survey of environmental impact and LCA of the products, effluent and waste generated;
- obtaining quantitative yield and costing data from large scale lots;
- the diversification and rendering more efficient the tanning materials, application processes, and wet-white leather semi-processed commodity products.

### ACKNOWLEDGEMENTS

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# CRETE2012

## 3RD INTERNATIONAL CONFERENCE ON INDUSTRIAL AND HAZARDOUS WASTE MANAGEMENT

**3rd Award**

## New Tanning Technologies Based on Valorization of industrial Waste

by

**Crudu M., Deselnicu V.,  
Ioannidis I., Albu R.**

# CRETE2012

## 3<sup>RD</sup> INTERNATIONAL CONFERENCE ON INDUSTRIAL AND HAZARDOUS WASTE MANAGEMENT

### EVALUATION OF ASBESTOS DERIVED ZEOLITE AS AN ADSORBENT FOR Pb(II) AND Cd(II) REMOVAL FROM AQUEOUS SOLUTIONS

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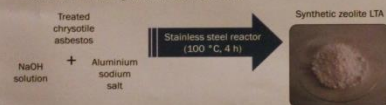
#### SUMMARY

The main objective of this study was the evaluation of Pb(II) and Cd(II) adsorption from aqueous solutions onto synthetic zeolite, produced from treated chrysotile asbestos. Batch sorption experiments were performed to investigate the influence of adsorbent dose, initial solution pH, agitation time and initial metal concentration, on the removal of Pb(II) and Cd(II) from aqueous solutions. The results showed that the synthetic zeolite used in the study presents itself as a valid alternative adsorbent for water and wastewater purification from metals. In fact, it was demonstrated that satisfactory results are achieved in a relatively short process duration period, as well as in a wide range of solution pH and metal concentration values.

#### MATERIALS AND METHODS

##### Zeolite synthesis:

Greek chrysotile asbestos was treated for several hours in aqua media using 2.5 N  $H_2SO_4$  in various temperatures under continuous stirring for 6 h, with a ratio of water solution and chrysotile asbestos equal to 20.

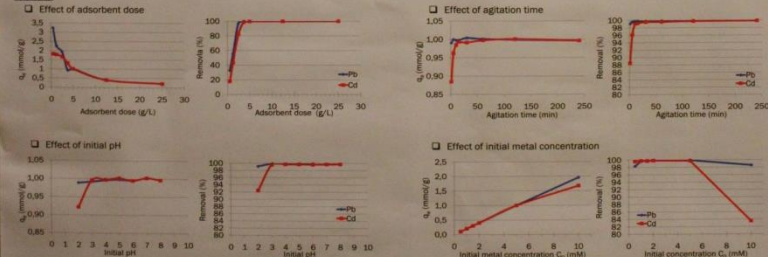


##### Adsorption experiments:

Table 2: Experimental conditions of adsorption studies

Experiments	Initial metal concentration (mM)	pH	Adsorbent dose (g/L)	Agitation time (min)
Adsorbent dose	5	5	0.5, 1.25, 2.5, 3.75, 5, 12.5, 25	120
pH	5	2, 3, 4, 5, 6, 7, 8	5	120
Agitation time	5	5	5	1.5, 10, 15, 30, 60, 120, 240
Initial metal concentration	0.5, 1, 1.5, 2, 5, 10	5	5	120

#### RESULTS



#### CONCLUSIONS

- The optimum conditions for lead and cadmium removal by using the studied material were: adsorbent dose 5 g/L, pH 5 and agitation time 2 h.
- The synthetic zeolite showed a satisfactory behavior regarding the removal of lead and cadmium from aqueous solutions even at low initial pH values, as well as at high initial metal concentration values.
- The zeolite showed similar affinity to both metals, nevertheless in some cases higher efficiency was noticed for lead.
- In general the synthetic zeolite that was examined in this study was proven to have great potential to be used as an alternative adsorbent for lead and cadmium removal from water and wastewater.

## 2<sup>nd</sup> Award

## Evaluation of Asbestos Derived Zeolite as an Adsorbent for Pb(II) and Cd(II) Removal From Aqueous Solutions

by

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Gidararakos E.*



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## 3<sup>RD</sup> INTERNATIONAL CONFERENCE ON INDUSTRIAL AND HAZARDOUS WASTE MANAGEMENT

1<sup>st</sup> Award

### Development of magnetic nanoparticles for Cr (VI) removal from drinking water integrated by a magnetic separation system

by

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#### Development of magnetic nanoparticles for Cr(VI) removal from drinking water integrated by a magnetic separation system

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#### Outline

Iron-based magnetic nanoparticles are tested as potential reducing agents for the removal of hexavalent chromium species at the concentration range usually found in drinkable water (<1 mg/L). In particular, zero-valent iron, magnetite nanoparticles, as well as copper-magnetite nanocomposites prepared by solar physical vapor deposition exhibit a remarkable efficiency in removing chromates from water at pH 7. Results show that iron nanoparticles can remove 3 µg Cr(VI)/mg at residual concentration of 50 µg/L, much higher than the corresponding value for magnetite ones. Further improvement (up to 6 µg Cr(VI)/mg) was observed in the copper-magnetite nanocomposites since the electron coupling upon contact between the two phases extends the materials efficient lifetime before surface passivation occurs. Meanwhile, the sorbent can be readily separated from solution using an integrated water treatment magnetic device, leaving the water essentially free of sorbent and adsorbed chromium.

#### Experimental

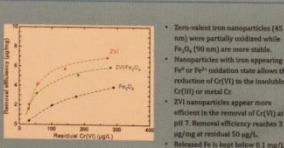
**Synthesis of nanoparticles**  
Solar physical vapor deposition under inert argon atmosphere (PROMES facilities in Bellevue-Fourieres). The arrangement is constituted of a "bellows" which tracks the sun and reflects the radiation on a parabolic concentration mirror.  
Target (solid pressed pellets prepared by single and mixtures of Fe, Cu and/or Fe<sub>3</sub>O<sub>4</sub>) is placed in the focus of a 2 kW solar concentrator and the flame produced is contained in a cold finger or trapped on a nanoscale ceramic filter.  
Chamber's dynamic pressure was set to 80 Torr.

**Characterization methods**  
• 100–200 mg/L of nanoparticles in water pH 7.  
• Initial Cr(VI) concentration: 100–2000 µg/L.  
• Claking for 24 h and measurement of the residual concentration by graphite furnace atomic absorption and UV/Vis spectrophotometry.  
• Evaluation according to the ability to reduce contaminants below the regulation limit for drinking water (50 µg/L Cr).

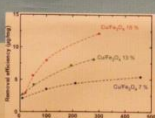
#### Magnetic separation tests

- Batch experiments using a 15 T/m field produced by a permanent magnet.
- Continuous flow separation tests at various rates and magnetic fields.

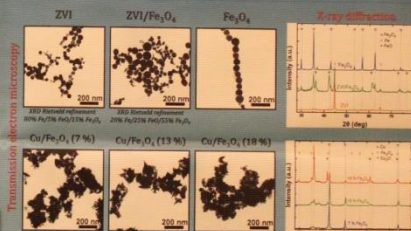
#### Cr(VI) removal



- Depending on the target's Fe:Cu ratio (0.5–2.0) Cu/Fe<sub>3</sub>O<sub>4</sub> nanocomposites with elongated shapes are formed.
- Fe-Cu coupling confers a higher potential for Cr(VI) reduction. Removal efficiency reaches 6 µg/mg at pH 7 and residual 50 µg/L.
- The dissolution of Fe and Cu is limited (<0.2 mg/L).

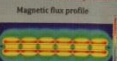


#### Nanoparticles structure



#### Magnetism and separation

##### Laboratory-scale continuous flow separator



Magnetic flux profile

Yield of separation for 90 nm Fe<sub>3</sub>O<sub>4</sub> nanoparticles

The yield of magnetic separation is proportional to the magnetization of nanoparticles, the field strength and distribution, the contact time and the particle's concentration.

As reported by their magnetic properties, the time of separation experiments was 21–24 s for Fe<sub>3</sub>O<sub>4</sub>, ZVI/Fe<sub>3</sub>O<sub>4</sub> and Fe<sub>3</sub>O<sub>4</sub> nanocomposites.

Simulation of the separation process predicts the optimum of magnetically induced aggregation which facilitates separation.

For a separation >100% at velocity 40 cm<sup>3</sup>/min particle size should be 800 nm.

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#### Conclusions

- Nanostructures with high electron donation ability (Fe, Cu/Fe<sub>3</sub>O<sub>4</sub>) are very efficient in Cr(VI) removal at drinking water levels.
- However, the long-term chemical stability and the possibility of easy discard are requirements for the practical application of nanoparticles in water treatment.
- Continuous-flow magnetic separation appeared a minimum cost method for high-yield removal and regeneration of magnetic nanoparticles. The system can be optimized according to solid's concentration, contact time and field intensity.