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## SORPTION OF LEAD, COPPER AND ZINC CATIONS ON RECYCLED WOOL-BASED NON-WOVEN MATERIAL

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### INTRODUCTION

It is well known that textile industry consumes huge amounts of water (approximately 200 dm<sup>3</sup> of water per 1 kg of textile product) [1]. The water consumption varies depending on the particular process, the equipment used and the prevailing management philosophy regarding the water use. Textile effluents typically contain a complex mixture of substances due to numerous processing stages.

Metal ions are usually found in textile effluents. They originate from fibres, processing water, dyes, plumbing and impurities present in chemicals and/or auxiliaries. Dyes may contain metals such as zinc, nickel, chromium and cobalt. In some dyes these metals are functional but in the most cases metals are generated as impurities during the dye manufacture. All classes of dyes contain a significant amount of copper, lead and zinc [2], this being the main reason to follow the sorption of these particular metals in this study.

Although there are other processes commonly applied for metal ion removal from wastewater, the possibility of using recycled wool as a sorbent for wastewater purification is of great importance from the resource preservation and cost-effectiveness point of view. Hence, the aim of this study was to investigate the sorption kinetics and influence of initial concentration on metal ion uptake on differently treated recycled wool-based sorbent.

### EXPERIMENTAL

#### Materials

The recycled-wool-based material was produced from secondhand military pullovers (knitted, 85% wool/15% polyester) having the constant quality and characteristics. Pullovers were torn off, washed, decolorized with reducing agent, dried and garneted on industrial equipment. The non-woven material was made from recycled fibers at Dilo (Eberbach, Germany) needle loom by the needlepunching process. The content of wool in the final material was reduced to 78% compared to primary material (85 %), due to shortening of the wool fibres during the garneting. These fibres were discarded because they were too short to be incorporated into the material.

Chitosan (CHT) (Vanson, Redmond - WA, USA), with a viscosity of 16 cps and deacetylation degree of 88.6% was used for wool treatment. Pb(NO<sub>3</sub>)<sub>2</sub> (MP Hemija, Serbia and Montenegro), Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O (Centrohem, Serbia and Montenegro) and Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (Centrohem, Serbia and Montenegro) were used for the investigation on ions adsorption. 0.0100 M KNO<sub>3</sub> (Centrohem, Serbia and Montenegro) was applied as a supporting electrolyte. For hydrogen-peroxide wool treatment H<sub>2</sub>O<sub>2</sub> (Centrohem, Serbia and Montenegro), Na<sub>4</sub>P<sub>2</sub>O<sub>7</sub>·10H<sub>2</sub>O (Kemika, Croatia) and NH<sub>3</sub> (Zorka, Serbia and Montenegro) were used. Distilled water was used for all experiments.

#### Treatments and methods

Low-temperature plasma (LTP) treatment was carried out in capacitively-coupled, radio-frequency air induced plasma. Treatment conditions were: treatment time of 50 s, pressure of 0.27 mbar and power of 100 W, indicated as optimal in previous studies [3].

Two different procedures for treatment with biopolymer chitosan were applied. The procedure A (CHT 0.1%) was based on immersion of samples in 0.1% CHT solution (liquor ratio 30:1) which were then shaken for 6 hours, squeezed out through laboratory squeeze rolls and dried at room temperature [3].

Subsequently, the samples were treated with 5% solution of NH<sub>3</sub> (liquor ratio 30:1) for 10 minutes at room temperature. Squeezed samples were dried at room temperature, washed with tap water and dried again at room temperature.

The procedure B (CHT 0.3%) was based on immersion of samples in 0.3% CHT (liquor ratio 30:1) which were shaken for 20 minutes, squeezed and dried at room temperature.

Hydrogen peroxide treatment (H<sub>2</sub>O<sub>2</sub>, 20 cm<sup>3</sup>/dm<sup>3</sup>; Na<sub>4</sub>P<sub>2</sub>O<sub>7</sub>, 1.5 g/dm<sup>3</sup> and NH<sub>3</sub>, 2.5 cm<sup>3</sup>/dm<sup>3</sup>) was done in static conditions (without shaking). Samples were treated in the solution for 1 h (liquor ratio 30:1) at 70°C and pH 9.40, washed with tap water and dried at room temperature.

The sorption capacity of the material ( $q$ , mg/g) was determined as a difference between the initial concentration of metal ions in the solution ( $C_0$ , mg/dm<sup>3</sup>) and the final concentration of metal ions in the solution ( $C_f$ , mg/dm<sup>3</sup>) (Equation 1). Atomic Absorption Spectrometer (AAS 403, Perkin Elmer, USA) was used for determination of the concentration of metal ions in the solution.

$$q = \frac{(C_0 - C_f) \cdot V}{m} \quad (1)$$

The symbol  $V$  presents the solution volume (dm<sup>3</sup>) and  $m$  is the mass of sorbent material (g).

Investigation on the sorption kinetics was carried out by shaking 1g of material in 50 cm<sup>3</sup> of metal salt solution ( $C_0=100$  mg/dm<sup>3</sup>) for 0.25, 0.5, 1, 3, 4, 12 and 24 h at pH 4.50.

Investigation on influence of the initial concentration on sorption capacity was done by shaking 1g of material in 50 cm<sup>3</sup> of metal salt solution of different concentrations (50, 100, 250 and 500 mg/dm<sup>3</sup>) for 3 hours at pH 4.50.

To adjust initial pH values of the solutions 0.010 M KOH and 0.100 M HNO<sub>3</sub> were used. pH values were measured with Inolab 730 (WTW, Germany) pH-meter.

## RESULTS AND DISCUSSION

As it is shown in Figures 1 and 2, after the rapid sorption of heavy metal ions (copper and zinc, respectively) during the first hour, the process was slowed down and equilibrium was not reached even after 24 hours for the most of investigated samples. The equilibrium was reached only in case of H<sub>2</sub>O<sub>2</sub> treated samples which showed excellent sorption properties and almost completely removed metal ions from the solution. The copper and zinc removal by H<sub>2</sub>O<sub>2</sub> treated wool was a bit less compared to removal of lead ions. Good sorption properties of samples treated with H<sub>2</sub>O<sub>2</sub> are likely due to the modification of the wool fibre surface i.e. oxidation and formation of appropriate groups that are potential sites for binding of heavy metal ions.

The CHT 0.1% and LTP+CHT 0.1% treated material demonstrated better sorption properties compared to untreated material in case of copper whereas CHT 0.3% and LTP+CHT 0.3% treatments caused better sorption in case of zinc. Noticeable increase in the sorption capacity of material treated with chitosan which was pre-treated with LTP can be contributed to improved binding of the biopolymer to the wool. In fact, LTP treatment promotes the formation of new anionic and hydroxyl groups on the wool surface which plays key role in binding of chitosan to wool fibres [4].

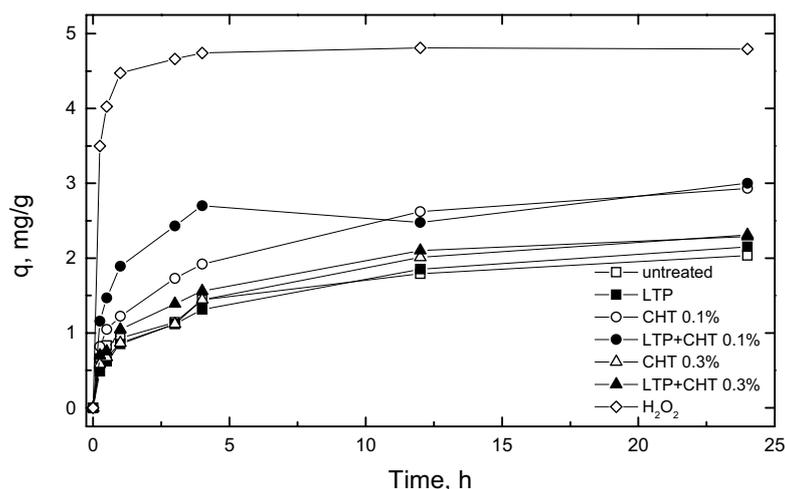


Figure 1. Sorption kinetics of  $\text{Cu}^{2+}$ -ions ( $t=20\text{ }^{\circ}\text{C}$ ,  $\text{pH}_0=4.50$ ,  $C_0=100\text{ mg/dm}^3$ )

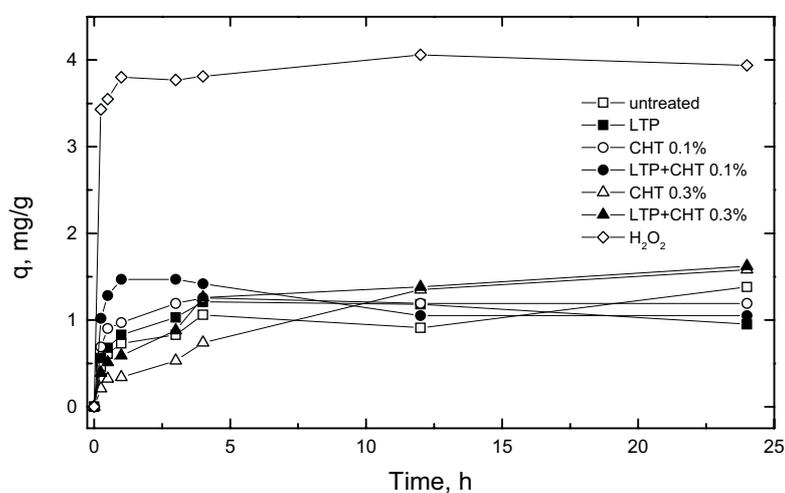


Figure 2. Sorption kinetics of  $\text{Zn}^{2+}$ -ions ( $t=20\text{ }^{\circ}\text{C}$ ,  $\text{pH}_0=4.50$ ,  $C_0=100\text{ mg/dm}^3$ )

The dependence of the sorption capacity on initial concentration of lead ions in solution for differently treated samples is presented in Figure 3. As we can see, both untreated and differently treated wool showed the high sorption capacity for lead ions and these results are in accordance with literature [5-6]. At low values of initial metal ion concentration ( $<100\text{ mg/dm}^3$ , approximately), there is almost no difference between the differently treated and untreated materials, except those treated with  $\text{H}_2\text{O}_2$ . However, at higher initial concentrations the treated sorbent materials start to show their advantages over the untreated sorbent material. This behaviour could be attributed to the different degree of the structural changes at the surface and/or interior of the sorbent material after applied treatments.

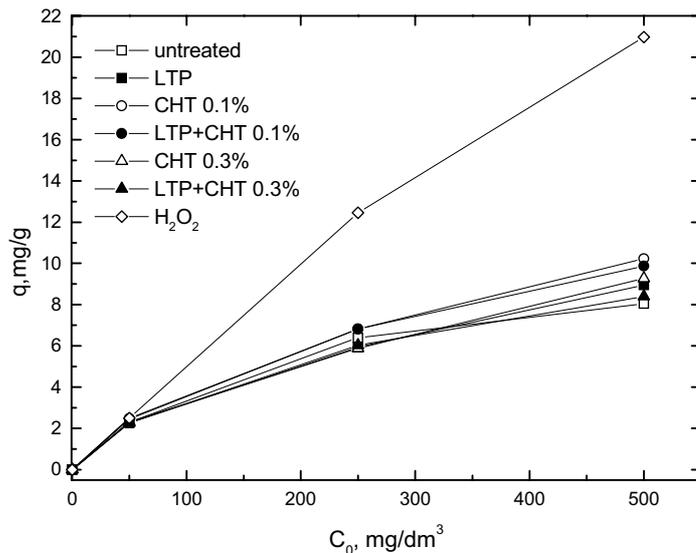


Figure 3. Influence of initial concentration on sorption capacity for Pb<sup>2+</sup>-ions ( $t=20$  °C,  $pH_0=4.50$ ,  $\tau=3$  h)

Achieved results indicate that recycled wool-based non-woven material can be used as an efficient and relatively inexpensive sorbent for removal of heavy metal ions. Obviously, treatment with H<sub>2</sub>O<sub>2</sub> in alkaline conditions, apart from treatment with low temperature plasma and chitosan, should be considered as viable and promising procedure for improvement of naturally good sorption properties of wool.

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