Removal of metal cations from wastewater using recycled wool-based non-woven material

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Abstract: In this study, the effect of low-temperature air plasma, biopolymer chitosan and hydrogen peroxide treatment of recycled wool-based non-woven material on metal cation uptake was investigated. Recycled wool-based material either as an untreated or modified material showed ability to bind all investigated metal cations in the following order: $Pb^{2+}>Cu^{2+}>Zn^{2+}>Co^{2+}$. Material performed good selectivity due to distinct sorption rates of studied metal cations.

Keywords: recycled wool, adsorption, lead, copper, zinc, cobalt.

INTRODUCTION

In spite of some limitations, adsorption is still commonly used for the removal of metal cations from industrial effluents.[1] Thus, many different sorbent materials have been developed.[1,2] For decades, it is well known that wool shows outstanding sorption properties for a wide range of metal cations.[3–7] Different rates of heavy metal uptake on wool provide the possibility of separation of metal cations. Some efforts have been made to improve metal cation uptake by modifying raw wool with different oxidizing and reducing agents.[4] However, wool as a raw material is too expensive for such purposes, which could be the reason why it has not been commercialised to date. Bearing in mind the high sorption efficiency of wool and the current request for the use of recycled and waste materials, a recycled wool-based non-woven material with multifunctional sorption properties has been developed.[8–11]

A prevous study indicated that recycled wool-based non-woven material shows a great ability to bind lead cations.[10] Nevertheless, the results revealed that even the

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untreated sorbent was sufficiently good and no further superficial modification with the biopolymer chitosan and/or a low-temperature plasma was required to improve its sorption properties. Intrigued with obtained results, it was decided to explore the possibility of the application of hydrogen peroxide treatment to facilitate the binding of chitosan to wool and hence, improve the sorption capacity. In addition, the study considered the uptake of other toxic metal cations (copper, zinc and cobalt) in order to evaluate further potential utilization of this sorbent material. Therefore, the aim of this study was to investigate the uptake of metal cations by untreated and modified recycled wool-based non-woven material from aqueous medium, as well as to follow the influence of time on the sorption behavior of the material.

EXPERIMENTAL

The recycled wool-based non-woven material was produced from secondhand military knitted pullovers (85 % wool/15 % polyester) of constant quality and characteristics. The pullovers were torn of, washed, decolorized with a reducing agent, dried and garneted under industrial conditions. In order to avoid the negative effect of chemical binders on the sorption of metal cations, needlepunch process was chosen for the production of the non-woven material. Needlepunching was performed on a Dilo (Eberbach, Germany) needle loom. The machine was equipped with a 4.5 m working width needle board containing 20000 needles. The processing speed was 1.2 m min^{-1} with a stroke frequency of 200 min^{-1}.

The content of wool in the final material was reduced to 78% compared to the primary material (85 %), due to a shortening of the wool fibres during the garneting. These fibres were discarded because they were too short to be incoporated into the material. Some physical and mechanical properties of the manufactured material are presented in Table I.

TABLE I. Some physical and mechanical properties of the untreated non-woven material

Weight/g m^{-2}	Breaking strength[a]/N	Bursting stength/N	Thickness/mm
235	19.23	21.97	1.56

[a]Machine direction

Chitosan (CHT) (Vanson, Redmond, WA, USA), with a viscosity of 16 mPa s and deacetylation degree of 88.6 % was used without further purification for the treatment of the non-woven material for investigation of the sorption of lead, copper and zinc ions. Chitosan ChitoClear$^®$ (Primex, USA) with a viscosity of 102 mPa s and deacetylation degree of 96 % was applied for the study of cobalt ions. Acetic acid (96 %, Lach-Ner, Czech Republic) was used for the preparation of the chitosan solution. $Pb(NO_3)_2$ (MP Hemija, Serbia), $Cu(NO_3)_2 \cdot 3H_2O$, $Zn(NO_2)_2 \cdot 6H_2O$ and $Co(NO_3)_2 \cdot 6H_2O$ (all from Centrohem, Serbia) were used for the investigation of the sorption of cations. 0.0100 M KNO_3 (Centrohem, Serbia) was applied as the supporting electrolyte. For hydrogen peroxide treatment, H_2O_2 (30 vol %, Centrohem, Serbia), $Na_4P_2O_7 \cdot 10H_2O$ (Kemika, Croatia) and NH_3 (aq) (Zorka, Serbia) were used.

Low-temperature plasma (LTP) treatment was carried out in capacitively-coupled, radiofrequency (13.56 MHz) air induced plasma. The equipment used for the plasma treatment consisted of a chamber, RF power supply, matching box, vacuum pump and a gas supply with appropriate pressure gauges. The chamber was cylindrical (37 cm in diameter, 50 cm in length) with a central electrode, 14 mm in diameter, that was powered through the matching box. Plasma formed between the central electrode and the wall of the chamber, which was grounded. Such an asymmetric system was intentionally constructed since it provides operating conditions under which the sheath potential is not too high, but sufficient for optimum modification without permanent damage to the wool.[12] The

treatment time was 50 s at a pressure of 0.27 mbar with the power supply maintained at a constant level of 100 W.

Two different procedures for the treatment with the biopolymer chitosan were applied. Procedure A (CHT A) was based on the immersion of samples in 0.1 % CHT solution (liquor ratio 30:1), shaking for 6 h, squeezing out through laboratory squeeze rolls and drying at room temperature.[8] Subsequently, the samples were treated with 5 % solution of NH_3 (liquor ratio 30:1) for 10 min at room temperature in order to enhance the binding of the chitosan to the wool. The squeezed samples were dried at room temperature, washed with tap water and dried again at room temperature. A 0.1% solution of chitosan was prepared according to the following procedure: 1.00 g of chitosan was thoroughly stirred with 1 mL of acetic acid and distilled water which was added six times in portions of 2 mL. After homogenisation, the formed gel was left overnight. Then, the volumetric flask of 1 L was filled to the mark with distilled water and the solution was applied to the samples.

Procedure B (CHT B) was based on the immersion of the samples in 0.3 % CHT (liquor ratio 30:1), shaking for 20 min, squeezing out through laboratory squeeze rolls and dried at room temperature. Subsequently, they were washed with tap water and dried at room temperature. A 0.3 % solution of chitosan was prepared according to the following procedure: 3.00 g of chitosan was stirred in 0.4 % acetic acid in a 1 L volumetric flask. Then, the volumetric flask was filled to the mark with 0.4 % acetic acid and solution was left overnight before application to the material.

Hydrogen peroxide treatment (H_2O_2, 20 mL/L; $Na_4P_2O_7$, 1.5 g/L and NH_3 (aq), 2.5 mL/L) was performed under 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 content of wool in the non-woven material after the needlepunch process was determined in accordance with JUS F.S3.115.[13] The breaking strength was determined using a dynamometer (TexTest, Switzerland) in accordance with JUS F.S2.017.[14] The bursting strength was determined using an AVK SZKG-2 Dynamometer (AVK, Hungary) in accordance with JUS F.S2.022.[15] The thickness was determined using an AMES 414-10 (Waltman, USA) in accordance with JUS F.S2.021 with a load of 170 g.[16]

The metal cation uptake (q, mg/g) was determined as the difference between the initial concentration of metal cations in the solution c_0, mg/L and the final concentration of metal cations in the solution (c_f, mg/L) (Eq. (1)). Atomic Absorption Spectrometer (AAS 403, Perkin Elmer, USA) was used for the determination of the concentration of metal cations in the solution.

$$q = \frac{(c_0 - c_f)V}{m}$$ (1)

In Eq. (1) V is the solution volume (L) and m is the mass of sorbent material (g). The precentage of metal cation adsorbed (*MCA*, %) was determined using Eq. (2):

$$MCA = \frac{q}{q_{max}} 100 \quad [\%]$$ (2)

where q_{max} is the maximum possible metal cation uptake (mg/g), which was calculated from Eq. (3):

$$q_{max} = \frac{c_0 V}{m}$$ (3)

The following processes and parameters were studied:

* the influence of time on the metal cation uptake: 1.00 g of material was shaken in 50 mL of metal salt solution ($c_0 = 100$ mg/L) at pH 4.50 for 0.25, 0.5, 1, 3, 4, 12 and 24 h. The appropriate initial pH value of the solution was adjusted with 1.00 M HNO_3, 0.100 M HNO_3 and 0.100 M KOH. The pH values of the solutions were measured using an Inolab 730 (WTW, Germany) pH-meter.

* sorbent selectivity: 1.00 g of material was shaken in 50 mL of solution which contained simultaneously Pb^{2+}, Cu^{2+}, Zn^{2+} and Co^{2+} ions ($c_0 = 100$ mg/L) at pH 4.50 for 1 h.

RESULTS AND DISCUSSION

The dependence of the uptake of Pb^{2+}, Cu^{2+}, Zn^{2+} and Co^{2+} ions by untreated and differently treated samples on time is shown in Figs. 1, 2, 3 and 4, respectively. It can be seen that after the rapid sorption of Pb^{2+} ions in the first hour, the process slowed down until equilibrium was reached after 24 h. On the contrary, the rate of sorption of Cu^{2+} and Zn^{2+} ions was considerably lower and equilibrium was not reached after 24 h for almost all the investigated samples. The exception were the H_2O_2 treated sample in case of Cu^{2+} and the CHT A and LTP+CHT A treated samples in case of Zn^{2+} ions. After the third hour of sorption, the uptake of Co^{2+} ions became slightly affected by the sorption time. The metal cation uptake and the percentage of metal cations adsorbed after 24 h for differently treated samples are presented in Table II.
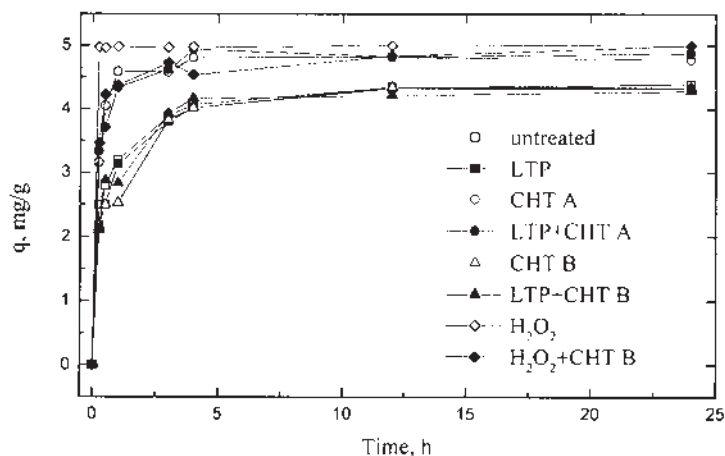

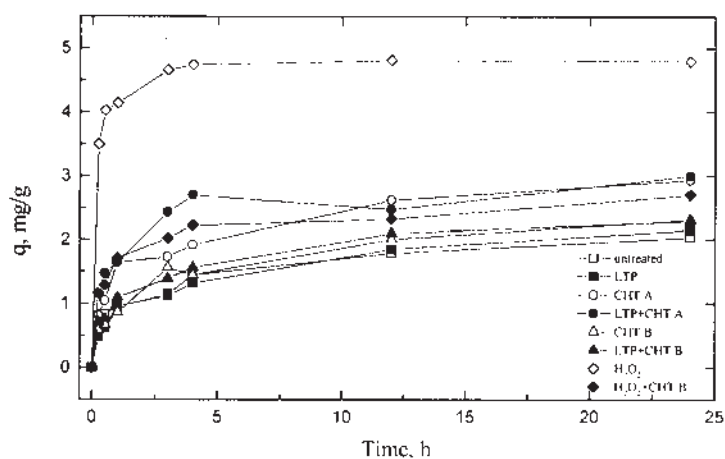Fig. 1. Uptake of Pb^{2+} ions *vs.* time (20 °C, pH_0 4.50, c_0 100 mg/L).

Fig. 2. Uptake of Cu^{2+} ions *vs.* time (20 °C, pH_0 4.50, c_0 100 mg/L).
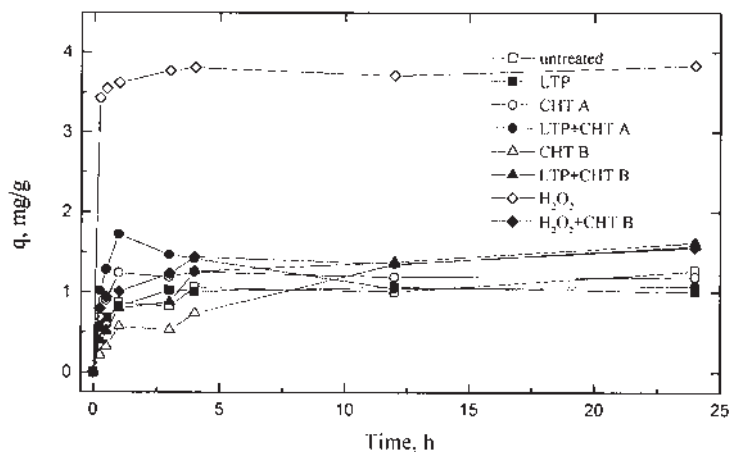
Fig. 3. Uptake of Zn^{2+} ions *vs*. time (20 °C, pH_0 4.50, c_0 100 mg/L).
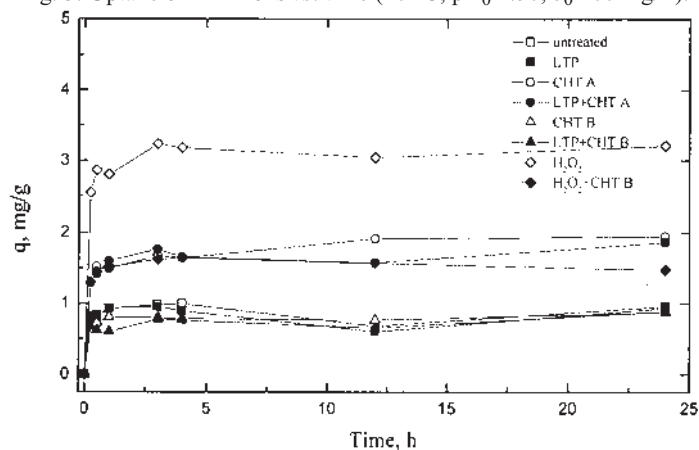

Fig. 4. Uptake of Co^{2+} ions *vs*. time (20 °C, pH_0 4.50, c_0 100 mg/L).

The untreated and LTP treated samples demonstrated almost identical sorption behaviour for Pb^{2+} ions over the whole range of investigated time. An analogue trend of sorption occurred in the case of the CHT B and LTP+CHT B treated samples, although these similarities became more obvious after the third hour of sorption. The CHT A, LTP+CHT A and, particularly, the H_2O_2 and H_2O_2+CHT B treatments significantly contributed to an increase in the uptake of Pb^{2+} ions. Moreover, the H_2O_2 and H_2O_2 + CHT B treated samples completely removed the Pb^{2+} ions from the solution.

Fig. 2 and Table II show that every treatment positively affected the sorption of Cu^{2+} ions. However, the uptake of Cu^{2+} ions was considerably lower in comparison to Pb^{2+} ions. The contribution of CHT A, LTP+CHT A, H_2O_2 and H_2O_2+CHT B treatments was remarkably more pronounced in case of Cu^{2+} ions compared to Pb^{2+} ions. The differences in the sorption kinetics of Cu^{2+} ions onto the H_2O_2 treated sample, on the one hand, and the CHT A and LTP+CHT A treated samples on another, were much more noticeable.

TABLE II. Metal cation uptake and percentage of metal cation adsorbed after 24 h (20 °C, pH_0 4.50, c_0 100 mg/L)

Treatment	q/mg g^{-1}	Δq/%	MCA/%	q/mg g^{-1}	Δq/%	MCA/%	q/mg g^{-1}	Δq/%	MCA/%	q/mg g^{-1}	Δq/%	MCA/%
	Pb^{2+}			Cu^{2+}			Zn^{2+}			Co^{2+}		
Untreated	4.39		87.8	2.04		40.8	1.27		25.4	0.96		19.2
LTP	4.33	−1.37	86.6	2.15	+5.39	43.0	1.01	−20.5	20.2	0.93	−3.12	18.6
CHT A	4.78	+8.88	95.6	2.93	+43.6	58.6	1.19	−6.33	23.8	1.95	+103	39.0
LTP+CHT A	4.88	+11.2	97.6	3.00	+47.1	60.0	1.05	−17.3	21.0	1.87	+94.8	37.4
CHT B	4.34	−1.14	86.8	2.31	+13.2	46.2	1.58	+2.44	31.6	0.88	−8.33	17.6
LTP+CHT B	4.29	−2.28	85.8	2.29	+12.3	45.8	1.62	+27.6	32.4	0.89	−7.29	17.8
H$_2$O$_2$	5.00	+13.9	100	4.80	+135	96.0	3.84	+202	76.8	3.21	+234	64.2
H$_2$O$_2$+CHT B	5.00	+13.9	100	2.70	+32.4	54.0	1.56	+22.8	31.2	1.47	+53.1	29.4

$^{*}\Delta q = \dfrac{q - q_{untreated}}{q_{untreated}}\,100$

The sorption of Zn^{2+} ions differs significantly from the sorption of Cu^{2+} and, particularly, of Pb^{2+} ions. In additon to a decrease in uptake, the treatments which enhanced the sorption of Cu^{2+} and Pb^{2+} ions (CHT A, LTP+CHT A treatments) induced a negative effect on the sorption of Zn^{2+} ions and *vice versa*. Both the untreated and differently treated materials showed a lower affinity for Zn^{2+} ions compared to Cu^{2+} and Pb^{2+} ions, which is in accordance with literature data.[2,3,6,7]

The sorption behaviour of untreated, LTP, CHT B and LTP+CHT B treated samples for Co^{2+} ions was almost identical over the whole range of investigated time. Again, the CHT A, LTP+CHT A, H_2O_2 and H_2O_2+CHT B treatments led to an increase in metal cation uptake, although these values were very low compared to the other studied metal ions.[2]

It has already been established that metal cation uptake by raw wool changes in the following order: $Pb^{2+}>Cu^{2+}>Zn^{2+}>Co^{2+}$.[2,7] This study confirmed the same order in the case of recycled wool.

The results of the sorption kinetics indicated that all samples exhibited rates of sorption which were significantly influenced by the investigated metal cation. Such a behaviour can be utilized for the separation of various metal cations from an aqueous medium. The selectivity of recycled wool-based non-woven material for metal cations is presented in Table III. The presence of all metal cations in the same solution brought about competition between the cations. As expected the material exhibited the highest affinity for Pb^{2+} ions, followed by Cu^{2+}, Zn^{2+} and Co^{2+} ions.

TABLE III. Selectivity of recycled wool-based non-woven material for metal cations (20 °C, pH_0 4.50, c_0 100 mg/L, 1 h)

Treatment	q/mg g^{-1}			
	Pb^{2+}	Cu^{2+}	Zn^{2+}	Co^{2+}
Untreated	1.70	0.601	0.00	0.00
LTP	1.71	0.722	0.00	0.00
CHT A	2.63	1.31	0.00	0.00
LTP+CHT A	2.47	1.25	0.118	0.00
CHT B	1.56	0.797	0.00	0.00
LTP+CHT B	1.48	0.719	0.00	0.00
H_2O_2	3.76	2.86	0.937	0.404
H_2O_2+CHT B	2.43	1.58	0.265	0.00

The H_2O_2-treated material demonstrated the best sorption properties and the CHT A, LTP+CHT A and H_2O_2+CHT B treatments contributed significantly to an increase in the uptake of all metal cations. The good sorption properties of the samples treated with H_2O_2 are likely due to modification of the surface of the wool fibres, *i.e.,* oxidation and formation of appropriate groups that are potential sites for the binding of heavy metal cations.[17,18]

The results revealed that LTP treatment caused insignificant changes of the sorption properties. Generally, the content of hydroxyl, amino, carboxylate and sulphonate groups on the surface of the wool fibres increases after LTP treatment and the specific fibre surface is enlarged.[19–21] Consequently, an improvement of the sorption properties was expected. The lack of a positive effect of LTP treatment could be attributed to a remarkable increase in the fibre hydrophilicity. The wettability of wool is improved and water molecules are easily bound to the wool fibre surface hindering the sorption of metal cations.[22]

The CHT A and LTP+CHT A treated material demonstrated better sorption properties compared to the untreated material in the cases of lead, copper and cobalt, whereas CHT B and LTP+CHT B treatments brought about better sorption of zinc cations. Obviously, the CHT treated samples showed better sorption properties than the untreated sample independent of the applied procedure. Muzzarelli[23] reported that the good sorption properties of chitosan for heavy metal cations could be attributed to the nitrogen electrons in the amino and substituted amino groups, which can establish dative bonds with transition and some other metal ions. Chitosan has the ability to chelate the ions of some metals and the type of complex is highly influenced by pH.

It is also a known fact that the ζ-potential is not a constant of the material and a change of this parameter is a certain indicator of a modification of the fibre surface as it is highly influenced by the composition of the material surface, as well as by the polarity, surface morphology, swelling in the aqueous medium, temperature and pH value of the applied electrolyte. Previous research on the ζ-potential of recycled wool-based non-woven material revealed that LTP, CHT A and LTP+CHT A treatments considerably affected the electrokinetic properties of the material surface.[8,10] Untreated material was negatively charged in the pH range 3.6–10. It was suggested that negative values of the ζ-potential of the wool surface could be the result of an easier sorption of less hydrated anions compared to cations on the wool surface, making the wool negatively charged.[19] The lower the pH, the greater was the decrease in the ζ-potential due to the protonation of the functional groups on the wool surface. The isoelectric point of untreated material was 3.6.

At lower pH values, the LTP treated material was more negatively charged in comparison to the untreated material and the extrapolated value of the isoelectric point was 3.1. This was due to plasma oxidation and plasma etching, which caused the formation of new anionic groups on the wool fibre surface. However, it should be emphasized that although the previous LTP treatment was performed in the same plasma system,[10] the treatment conditions differed. The pressure and power were the same, but the LTP treatment time was longer (5 minutes double-sided treatment was carried out). However, it appeared that changes of the LTP treatment time within $50-600$ s did not significantly affect the sorption properties.[10] In these terms, the results concerning the ζ-potential arising from the former study could be

used for consideration on the sorption mechanism since the exact values are less important than the trend of the electrokinetical changes of the material.

The CHT A and LTP+CHT A treatments brough about a reduction of the negative ζ-potential, indicating an increase in the positive charge of the material surface. The isoelectric points of the CHT A and LTP+CHT A treated samples was at pH 5.6 and 5.9, respectively. This could be due to the presence of amino grups originating from the chitosan which was bound to the wool fibre surface.

CONCLUSIONS

Recycled wool-based non-woven material is a good sorbent for lead, copper, zinc and cobalt cations. The best adsorbed metal is lead, followed by copper, zinc and cobalt. The sorbent shows satisfactory sorption behaviour and good selectivity even as an untreated material. The LTP treated samples exhibited similar behaviour to that of the untreated samples, whereas chitosan and particularly hydrogen peroxide treatments led to a significant increase in the uptake of all investigated metal cations.

In addition to its efficiency, the possibility of using recycled wool-based sorbent for wastewater purification is of great importance not only from the resource preservation standpoint but also from the cost-effectiveness point of view.

ИЗВОД

УКЛАЊАЊЕ КАТЈОНА МЕТАЛА ИЗ ОТПАДНЕ ВОДЕ НЕТКАНИМ МАТЕРИЈАЛОМ НА БАЗИ ВУНЕ КАО СЕКУНДАРНЕ СИРОВИНЕ

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У овом раду је испитан утицај обраде нетканог материјала на бази вуне као секундарне сировине нискотемпературном плазмом, биополимером хитозаном и водоник-пероксидом на сорпцију катјона метала. Материјал на бази вуне као секундарне сировине било као необрађен или модификован, поседује способност везивања катјона метала према следећем редоследу: $Pb^{2+}>Cu^{2+}>Zn^{2+}>Co^{2+}$. Материјал показује добру селективност услед различите брзине сорпције испитиваних катјона метала.

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