

Recycled-Wool-Based Nonwoven Material as a Sorbent for Lead Cations

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ABSTRACT: The aim of this study was to investigate the sorption properties of a recycled-wool-based nonwoven material for lead cations. To improve sorption properties, the material was treated with low-temperature air plasma and/or the biopolymer chitosan. The rate and extent of the uptake of lead cations by wool, the kinetics of adsorption, and the influence of concentration, pH, temperature, and mechanical agitation on the sorption process were deter-

mined. Changes in the electrokinetic properties of the sorbent were also investigated. Wool, even as a recycled material, efficiently bound lead cations in all of the investigated cases. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 90: 379–386, 2003

Key words: adsorption; fibers; cold plasma; biopolymers

INTRODUCTION

It has been known for decades that wool has the ability to effectively bind some metal ions.^{1–4} As far as we know to date, there have been no significant attempts to use this property in commercial applications. Nowadays, strict ecological legislation concerning the concentration of heavy metal ions requires the rigorous effluent control and purification of wastewater. Thus, increasing environmental concern has resulted in renewed interest in research on the use of wool as a possible sorbent for the removal of metal pollutants from industrial effluents and contaminated water.^{5,6} To address this, we developed a nonwoven material based on recycled wool that could be used for the removal of metal ions from effluents.⁷

The aim of this study was to highlight the influence of different treatments of wool on the sorption of lead cations from water. To improve the sorption properties of the recycled-wool-based nonwoven material, we treated the material with the biopolymer chitosan (CHT) and low-temperature air plasma (LTP). The main problem with CHT applications is that chitosan is weakly bound to wool. It is assumed that protonated amino groups of CHT interact electrostatically with the available anionic groups in wool and that

hydrogen bonding between hydroxyl or amide groups of wool and similar groups of CHT is established.⁸ Therefore, to enhance CHT binding, it could be useful to promote the formation of new anionic and hydroxyl groups on the fiber surface.⁹ To achieve this, the LTP treatment of wool was applied.^{10,11} Thus, the recycled-wool-based nonwoven material was pretreated with LTP and subsequently treated with CHT (LTP+CHT).

The polysaccharide-based cationic biopolymer CHT is poly(1,4)-2-amino-2-deoxy- β -D-glucan with a structure similar to cellulose. It is usually produced by the deacetylation of chitin, which is widely present in nature as a component of some fungi and in the exoskeletons of insects and crustaceans, such as crabs and shrimp. CHT is insoluble in water but is soluble in weak acids such as 5% formic or acetic acid and in dilute mineral acids. It shows polyelectrolytic properties in dilute aqueous acids due to protonation of the primary amino group. The existence of the amino group and primary and secondary hydroxyl groups makes CHT very reactive. Until recently, most research on the application of CHT to wool has focused on imparting shrink resistance.⁸ Furthermore, CHT has been well established as a relatively cheap and extremely good metal cation sorbent. Several studies have demonstrated a high affinity of CHT for different heavy metal cations.^{12,13}

A *plasma* is defined as a quasineutral gas that consists of charged and neutral particles.¹⁴ The appropriate control of the electric field, gas pressure, composition, and other plasma parameters allows operation in

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TABLE I
Physical and Mechanical Properties of Untreated Nonwoven Material

Weight (g/m ²)	Breaking strength (N) ^a	Bursting strength (N)	Thickness (mm)
235	19.23	21.97	1.56

^a Machine direction.

nonequilibrium conditions where the gas temperature is close to room temperature and where the electron temperature is high enough to initiate dissociation as the precursor of plasma-chemical reactions. This is the so-called LTP. Different plasma constituents, such as electrons, ions, free radicals, metastables, and ultraviolet photons, directly or indirectly take part in plasma-chemical reactions that cause a superficial modification of the wool fiber, leaving the bulk properties more or less unchanged.

EXPERIMENTAL

Materials

The experiments were performed with a recycled-wool-based nonwoven material. Secondhand knitted pullovers (85% wool/15% polyester) of the same quality and characteristics were torn off, washed, decolorized with reducing agent, dried, and garneted in industrial conditions. To avoid the effect of chemical binders on Pb²⁺ ion adsorption, the needlepunch process was chosen to produce the nonwoven material. The material was produced from recycled fibers on a Dilo (Eberbach, Germany) needle loom. The machine was equipped with a 4.5-m working-width needle board containing 20,000 needles. The processing speed was 1.2 m min⁻¹ with a stroke frequency of 200 min⁻¹.

The content of wool after application of the needlepunch process was reduced to 78% compared to the primary material. The physical and mechanical properties of the obtained material were good enough for the purpose of a sorbent material (Table I).

CHT (Vanson, Redmond, WA), with a viscosity of 16 cps and a deacetylation degree of 88.6%, was used without further purification. Pb(NO₃)₂ (Analar, Dorset, UK) was used for Pb²⁺ ion adsorption investigation. KNO₃ (1.00 × 10⁻¹ M; Laphoma, Skopje, Macedonia) was used as the supporting electrolyte.

Treatments and methods

The nonwoven material was treated with CHT by immersing it in a 0.1% CHT solution (liquor ratio 25:1), shaking it for 6 h, running it through a laboratory padder, and drying it at room temperature. The dry material was treated with a 5% ammonium hydroxide solution (liquor ratio 25:1) for 10 min at room

temperature and dried again. Finally, the samples were rinsed in tap water and dried.

LTP treatment was carried out in capacitively coupled, radio-frequency-induced (13.56 MHz) air plasma. The system had two asymmetric electrodes: the powered electrode was a rod 1 cm in diameter, and the grounded electrode was the walls of the vessel, which were 37 cm in diameter. This system allowed for the treatment of wool and other sensitive materials because the energy of ions bombarding the grounded electrode was expected to be very small. The vessel was pumped by a large-capacity mechanical pump and operated with a small gas flow controlled by a leak valve. Treatment time was 5 min, and pressure was 0.2 mbar with the power supply maintained at a constant level of 100 W.

The content of wool in the nonwoven material after the needlepunch process was determined in accordance with JUS F.S3.115.¹⁵ Breaking strength was determined with a dynamometer (TexTest, Zurich, Switzerland) in accordance with JUS F.S2.017.¹⁶ Bursting strength was determined with an AVK SZKG-2 dynamometer (AVK, Budapest, Hungary) in accordance with JUS F.S2.022.¹⁷ Thickness was determined with an AMES 414-10 instrument (Waltman, MA) in accordance with JUS F.S2.021 with a load of 170 g.¹⁸

Electrokinetic measurements were carried out with an electrokinetic analyzer (Anton PAAR, Graz, Austria). The pressure difference (ΔP) between the entrance and exit of the capillary system was produced by a pump. It induced the passing of electrolyte through the sample, which was placed in sample cell and led to the development of streaming potential (U_p). U_p was determined by silver/silver chloride electrodes.

The determination of ζ potential of samples in accordance with the Fairbrother and Mustin method was based on the measurement of U_p and specific electric conductivity of the electrolyte solution in the capillary system. In the case of electrolyte concentrations lower than 10⁻³ M and lower fiber surface conductivities, one is allowed to use the specific electric conductivity of the electrolyte solvent outside the diaphragm (κ_b) in the equation for the determination of ζ potential:

$$\zeta = \frac{U_p \eta \kappa_b}{\Delta P \epsilon \epsilon_0} \quad (1)$$

where ζ is the zeta potential, η is the viscosity of the aqueous solution, ϵ is the relative dielectric constant of the solution, and ϵ_0 is the vacuum dielectric constant.

As an electrolyte solution, 1.00 × 10⁻³ M KCl solution was applied. ζ potential values were determined in the pH range 3.00–10.00. To adjust the pH values, 1.00 × 10⁻¹ M HCl and 1.00 × 10⁻¹ M NaOH were used.

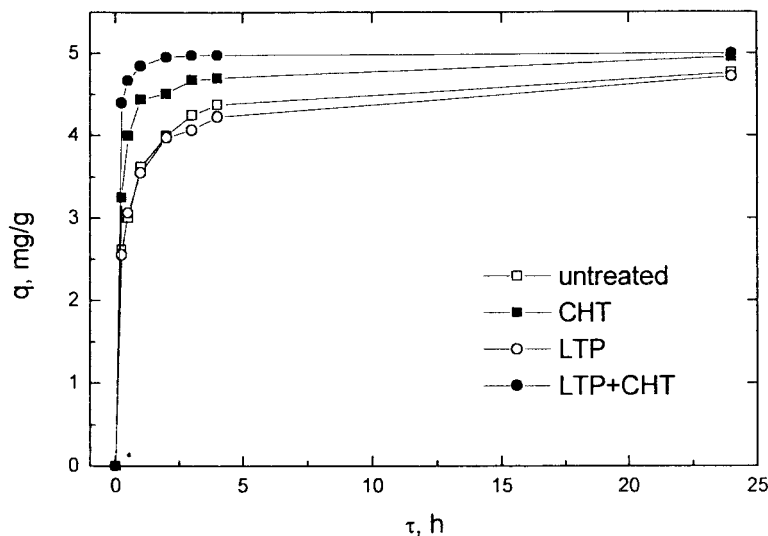


Figure 1 Adsorption kinetics –2 versus time (temperature = 20°C; pH₀ = 4.98; C₀ = 100 mg/L). ^aτ = time of sorption; h.

Atomic absorption spectroscopy as inherently a single-element method was applied to determine the Pb²⁺ ions. A series of standards (from 0.25 to 1 mg/L and from 10 to 100 mg/L) and the sample were prepared, and lead was measured at 217 and 283.3 nm. The limit of detection was 0.05 mg/L. The relative standard deviation of all of the determinations was 0.5%.

In the experiments, the metal cation uptake (*q*; mg/g) by nonwoven material was calculated from the difference between the initial concentration of metal cations in solution (*C*₀; mg/L) and the final concentration of metal cations in solution (*C*_{*f*}; mg/L), as determined by the atomic absorption method with a PYE Unicam SP9 atomic absorption spectrophotometer (Philips, UK). The following equation was used:

$$q = \frac{(C_0 - C_f)V}{m} \tag{2}$$

where *V* is the solution volume (L) and *m* is the mass of sorbent material (g).

The percentage of metal cation adsorbed was determined as:

$$\frac{q}{q_{max}} 100\% \tag{3}$$

where *q*_{max} is the maximum possible metal cation uptake (mg/g).

The following processes and parameters were investigated:

- The kinetics of adsorption: 1 g of material was shaken in 50 mL of metal salt solution (*C*₀ = 100 mg/L) for 0.25, 0.5, 1, 2, 3, 4, and 24 h.
- The influence of concentration on adsorption process: 1 g of material was placed in 50 mL of metal salt solution of different concentrations (*C*₀ = 10, 25, 50, 75, 100, 500, and 1000 mg/L) and was shaken in a laboratory shaker for 2 and 24 h.

TABLE II
q and Percentage of Metal Cation Adsorbed After 24 h

Treatment	<i>q</i> (mg/g)	Δ <i>q</i> (%) ^a	Metal adsorbed (%)
Untreated	4.76		+95.2
CHT	4.95	3.99	+99.0
LTP	4.72	-0.84	+94.4
LTP-CHT	5.00	5.04	+100

^a Compared to untreated, Δ*g* = $\frac{2(\text{treated}) - 2(\text{untreated})}{2(\text{untreated})} 100\%$

^b Temperature = 20°C; pH₀ = 4.98; C₀ = 100 mg/L.

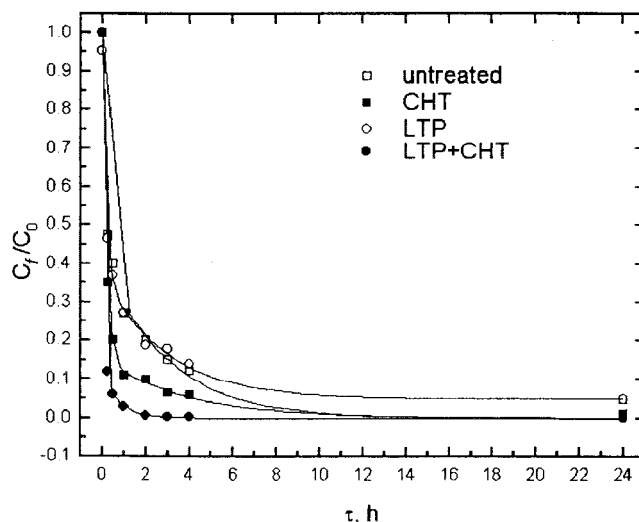


Figure 2 *C*_{*f*}/*C*₀ versus time (temperature = 20°C; pH₀ = 4.98; C₀ = 100 mg/L).

TABLE III
Double Exponential Functions for the Sorption of Pb²⁺ Ions

Treatment	Function $C_f/C_0 = f(\tau)$	R^2
Untreated	$C_f/C_0 = 0.59 \exp(-\tau/0.15) + 0.41 \exp(-\tau/2.97)$	0.9934
CHT	$C_f/C_0 = 0.85 \exp(-\tau/0.18) + 0.15 \exp(-\tau/4.01)$	0.9993
LTP	$C_f/C_0 = 0.06 + 0.61 \exp(-\tau/0.16) + 0.34 \exp(-\tau/2.91)$	0.9976
LTP+CHT	$C_f/C_0 = 0.70 \exp(-\tau/0.01) + 0.30 \exp(-\tau/0.32)$	0.9992

^a Temperature = 20°C; pH₀ = 4.98; C₀ = 100 mg/L.

^b R²—coefficient of determination.

- The influence of temperature on adsorption process: 1 g of material was immersed in 50 mL of metal salt solution (C₀ = 100 mg/L) for 30 min without any agitation. The temperature was controlled with a thermostatic bath (UH 16, VEB MLW, Freital, Germany).
- The effect of pH on the adsorption process: 1 g of material was placed in 50 mL of metal salt solution (C₀ = 100 mg/L) and was shaken for 24 h. The appropriate initial pH values of the solutions (pH₀) were adjusted with 1.00 × 10⁻¹ M HNO₃ and 1.00 × 10⁻¹ M KOH. After 24 h of sorption equilibrium, pH values of the solution (pH_e) were measured. Both pH₀ and pH_e were measured with a HI8314 membrane pH meter (Hanna Instruments, Singapore).

RESULTS AND DISCUSSION

The influence of time on the Pb²⁺ ion uptake for the untreated and CHT-, LTP-, and LTP+CHT-treated samples is shown in Figure 1. It was obvious that after

rapid adsorption in the first 2 h, the process slowed down until equilibrium was reached (after 24 h). The CHT- and LTP+CHT-treated samples demonstrated better sorption properties than the untreated sample. The untreated and LTP-treated samples demonstrated similar behavior in the whole range of time. The *q* and the percentage of metal cations adsorbed after 24 h for Pb²⁺ ions and differently treated sorbent material samples are given in Table II.

To elucidate the trend of sorption, the dependence of C_f/C₀ versus time for the untreated and CHT-, LTP-, and LTP+CHT-treated samples was plotted and is shown in Figure 2. Experimental values were approximated as double exponential functions. The double exponential functions, which consisted of two terms, are given in Table III. They fit all of the investigated samples well, indicating that the sorption of Pb²⁺ ions was a diffusion-controlled process.

The first term of the functions corresponded to a very fast adsorption with a time constant that could not be determined accurately from these data (i.e., the time constant that we obtained was determined by the

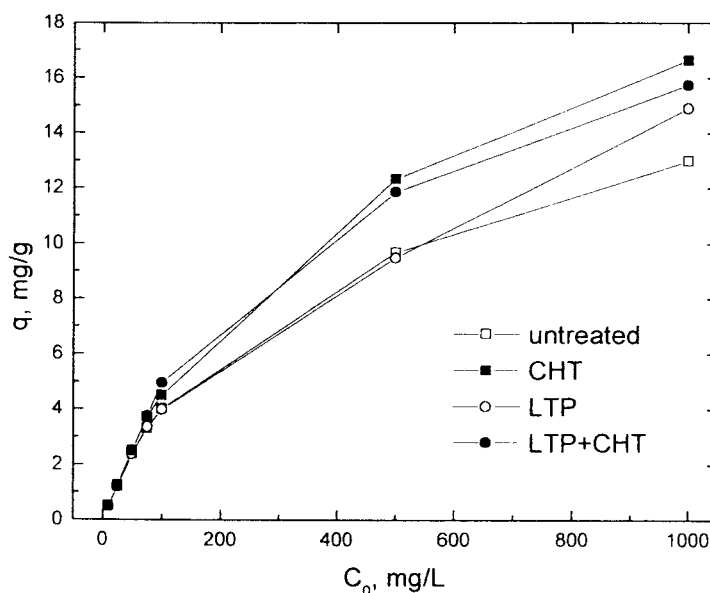


Figure 3 Influence of C₀ on Pb²⁺ ion uptake of untreated and CHT-, LTP-, and LTP+CHT-treated samples (temperature = 20°C; τ = 2 h; pH₀ = 4.98).

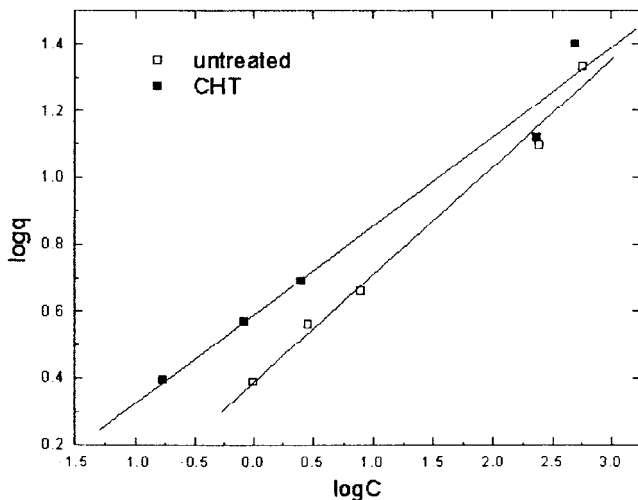


Figure 4 Linearized Freundlich isotherms of Pb^{2+} ions on untreated and CHT-treated samples (temperature = 20°C; τ = 24 h; pH_0 = 4.98). ^a C-equilibrium concentration of metal cations in solution; mg/L.

discretization of temporal measurements). The second term dominated the time dependence from 0.25 to 24 h and was probably controlled by the diffusion of ions. The time constant of the second term could be determined accurately from these data. For the LTP+CHT-treated sample, the time constant of the second term was significantly smaller compared to the other samples, clearly indicating that it was the fastest to achieve equilibrium.

The study of adsorption kinetics showed that approximately 80–99% of cations were adsorbed after 2 h, depending on the investigated sample. Therefore, a time of 2 h was chosen for the study on the influence of the initial metal cation concentration on material adsorption properties. The dependence of the q on C_0 for the untreated and CHT-, LTP-, and LTP+CHT-treated samples is shown in Figure 3. The best adsorption properties were achieved for the CHT-treated sample. LTP-treated samples behaved almost identically to untreated samples in solutions of lower metal cation concentrations (>500 mg/L). Differences between the untreated and LTP-treated samples became obvious at concentrations over 500 mg/L.

Despite the better sorption properties of LTP-treated sample for higher initial concentrations of Pb^{2+} ions compared to the untreated sample, its sorption capacity did not exceed the capacity of CHT-treated sample. Although, the applied plasma treatment resulted in a slight improvement of sorption properties, further investigations were focused on the sorption behavior of untreated and CHT-treated samples.

In the investigation of sorption properties of the material at the equilibrium conditions, the Freundlich model gave a good fit to the obtained adsorption

TABLE IV
Constants of the Freundlich Isotherms for Untreated and CHT-Treated Samples

Treatment	K_F (mg/g)	$1/n$
Untreated	2.45	0.102
CHT	3.88	0.121

^a Temperature = 20°C; τ = 24 h; pH_0 = 4.98.

isotherms of untreated and CHT-treated samples, as shown in Figure 4. Constants of the Freundlich isotherms for the untreated and CHT-treated samples are given in Table IV. The constant K_F is an indicator of adsorption ability, and it is proportional to the adsorption capacity. The larger the value of K_F is, the higher the adsorption capacity is. The constant $1/n$ is an indicator of the concentration dependence of adsorption. Low values of $1/n$ for untreated and CHT-treated samples indicated that concentration in the equilibrium state did not have a strong influence on the sorption of Pb^{2+} ions.⁵

The results demonstrate that CHT treatment of material caused an improvement in sorption properties. The effect of the concentration of the CHT solution applied to wool on the sorption capacity for different initial concentrations of Pb^{2+} ions in solution is shown in Figure 5. Obviously, for the initial concentrations lower than 100 mg/L, both samples, treated with 0.1% CHT solution and 0.2% CHT solution, behaved identically. However, for higher concentrations, the sample treated with a 0.2% solution of CHT had slightly better sorption properties.

The dependence of percentage Pb^{2+} ions adsorbed on the untreated and CHT samples on pH_e values after 24 h of adsorption is presented in Figure 6. As ex-

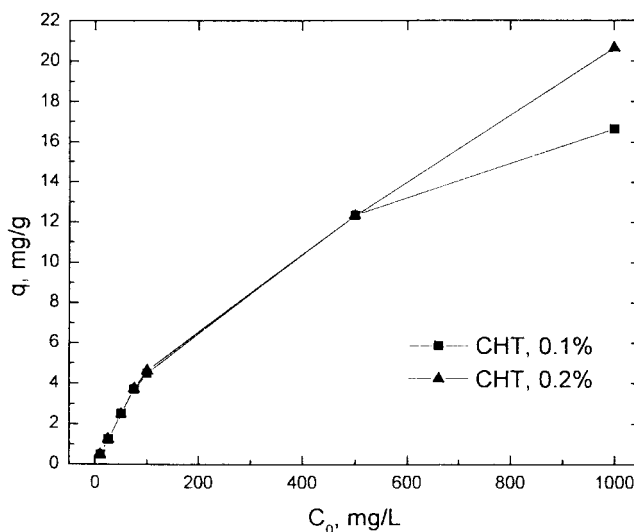


Figure 5 Effect of CHT concentration on the sorption properties of the materials (temperature = 20°C; τ = 2 h; pH_0 = 4.98).

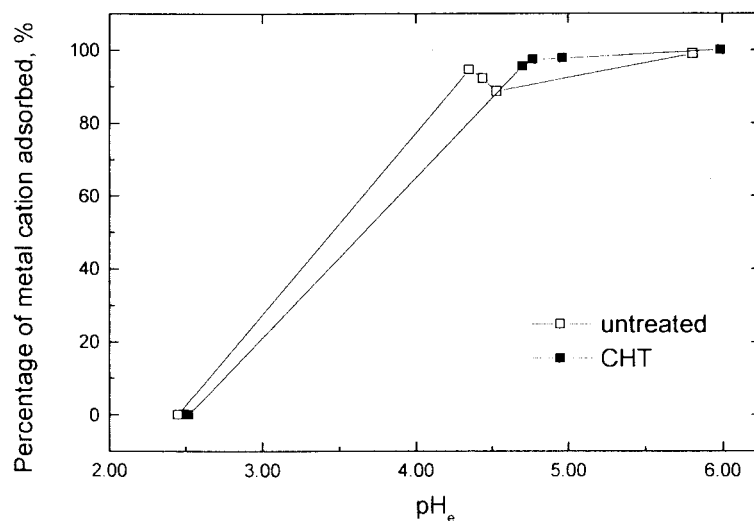


Figure 6 Dependence of the percentage Pb^{2+} ions adsorbed on untreated and CHT samples on final the pH values after 24 h of adsorption (temperature = 20°C ; $C_0 = 100 \text{ mg/L}$).

pected, the adsorption improved with increasing pH. At highly acidic conditions, Pb^{2+} ions were not adsorbed. Significant differences between the curves of the untreated and CHT-treated sample were not noticed. However, the results, as shown in Figure 3, indicate that remarkable differences in sorption capacity between the untreated and CHT-treated samples were introduced only cases of higher initial concentrations of Pb^{2+} ions in the solution.

It is well established that carboxylate anions are the main sites for the binding of metal cations to wool.^{8,19} However, metal cations can also be bound to wool via the free amino groups, as has been shown with chitin and CHT.^{8,20,21} Muzzarelli reported that good sorption of CHT for heavy metal ions can be attributed to the nitrogen electrons in the amino and substituted amino groups that can establish dative bonds with transition and some other metal ions, such as Pb^{2+} ions.²² CHT has an ability to chelate ions of some metals, and the type of complex is highly influenced by pH.²¹

It is likely that the better sorption properties of the CHT-treated sample arose from the increase of amino groups on the wool surface. Therefore, an increase in the concentration of the CHT solution applied to wool (Fig. 5) resulted in improved sorption properties, probably due to the introduction of a higher amount of amino groups.

It is well known that electrokinetic studies provide important information about the changes at the surface of the fiber.²³ The ζ potential of the material is highly influenced by the material surface composition and polarity, surface morphology, swelling in the water medium, temperature, and pH of the applied electrolyte.²⁴ Therefore, ζ potential is not a constant of the material, and changes in this parameter are certain indicators of fiber surface modification.

The dependence of ζ potential versus pH for the untreated and CHT-treated samples is shown in Figure 7. The untreated wool was negatively charged almost in the whole range of investigated pH. Merten

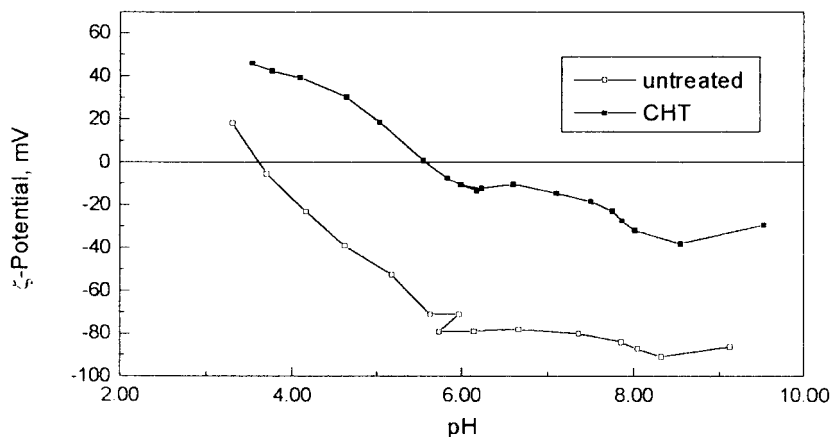


Figure 7 ζ potential as a function of pH for the untreated and CHT samples.

indicated that negative values of ζ potential of the wool surface could be the result of easier sorption of less hydrated anions compared to cations on the wool surface, making the wool negatively charged.²⁵ The lower the pH is, the greater will be the decrease in ζ potential due to the protonation of functional groups on the wool surface. The isoelectric point of the untreated sample was around 3.6. CHT treatment of the material led to a decrease in negative values of ζ potential. The isoelectric point of the CHT-treated sample shifted toward the pH around 5.6. A more positively charged surface was attributed to the increasing content of amino groups on the wool surface.

A comparison of the pH_0 and the pH_e values of solution are presented in Table V. It was obvious that for lower pH_0 values, pH_e was greater than pH_0 . However, above a certain value of the pH_0 , pH_e was much lower than pH_0 . The main changes in the sorption behavior occurred at pH values close to the isoelectric point of both the untreated and CHT-treated wool (Fig. 7). Below the isoelectric point, protons from the solution were bound to the wool, causing the protonation of amino groups, and consequently, the pH_e of the solution increased. The wool surface was positively charged, and only few Pb^{2+} ions were sorbed. Above the isoelectric point, wool became negatively charged when a more intensive sorption of Pb^{2+} ions began, and pH_e decreased due to the release of protons.

Temperature had a strong influence on the sorption of Pb^{2+} ions. An increase in temperature led to a considerable improvement in the sorption properties. The influence of temperature on the adsorption propensity of the untreated and CHT-treated samples for Pb^{2+} ions is shown in Figure 8. A temperature rise from 20 to 70°C resulted in an increase of sorption capacity by 132% for the untreated sample and 87% for the CHT-treated sample.

These results, compared to values related to the kinetics investigation for the same period of 30 min, show that the latter were higher. The effect of mechan-

TABLE V
Changes in pH Values for Untreated and CHT-Treated Samples

Sample	pH_0	pH_e
Untreated	2.24	2.45
	3.31	4.53
	4.53	4.44
	5.46	4.35
	6.60	5.81
CHT	2.26	2.52
	3.32	4.70
	4.53	4.96
	5.51	4.77
	6.08	5.99

^a Temperature = 20°C; C_0 = 100 mg/L.

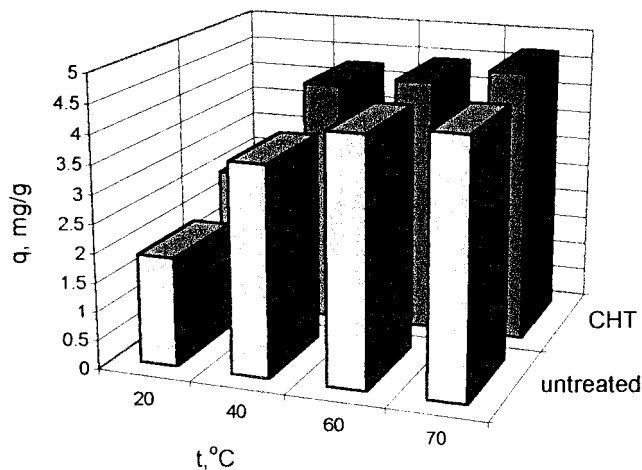


Figure 8 q versus temperature (untreated and CHT-treated samples; temperature = 30 min; pH_0 = 4.98; C_0 = 100 mg/L).

ical agitation on q for the untreated and CHT-treated samples is presented in Figure 9. Mechanical agitation induced an improvement of sorption of 60% for the untreated sample and 37.5% for the CHT-treated sample. The results obtained confirm that mechanical agitation significantly promoted the adsorption process.

CONCLUSIONS

Recycled nonwoven wool material was a good sorbent for Pb^{2+} ions, and it seemed that it did not need any modification to improve this property. However, at higher initial Pb^{2+} ion concentrations, CHT-treated wool material showed remarkably higher sorption properties than the untreated reference material. Additionally, the CHT treatment significantly changed the electrokinetic properties of the sorbent, which in-

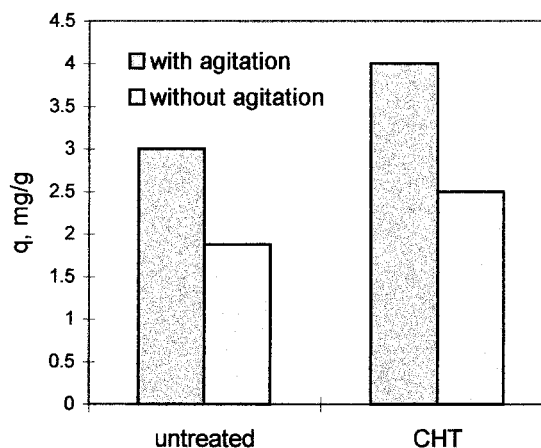


Figure 9 q of untreated and CHT-treated samples with and without mechanical agitation (temperature = 20°C; time = 30 min; pH_0 = 4.98; C_0 = 100 mg/L).

dicates appropriate surface modification of wool for the sorption of Pb^{2+} ions.

LTP treatment alone did not significantly improve the sorption properties, but it was clearly shown that LTP-treated wool material that was subsequently treated with CHT had much better sorption kinetics than the other samples.

The results indicate that the investigated nonwoven recycled-wool-based sorbent material is a potentially useful low-cost substrate for the removal of lead cations from industrial effluents and other water sources.

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References

- Masri, M. S.; Reuter, F. W.; Friedman, M. *Text Res J* 1974, 44, 298.
- Friedman, M.; Masri, M. S. *J Appl Polym Sci* 1973, 17, 2183.
- Hartley, F. R. *Aust J Chem* 1968, 21, 1013.
- Hemrajani, S. N.; Narwani, C. S. *J Indian Chem Soc* 1967, 44, 704.
- Weltrowski, M.; Patry, J.; Beaudoin, B. In *Proceedings of the 9th International Wool Textile Research Conference, Biella, Italy, 1995; Citta degli Studi: Biella, Italy, 1995; Vol. 4, p 343.*
- Crighton, J. S. In *Proceedings of the 9th International Wool Textile Research Conference, Biella, Italy, 1995; Citta degli Studi: Biella, Italy, 1995; Vol. 1, p 345.*
- Radetić, M.; Jocić, D.; Jovančić, P.; Rajaković, L.; Potkonjak, B.; Petrović, Z. L. In *Proceedings of the 1st Autex Conference Technitex 2001: Technical Textiles: Designing Textiles for Technical Applications, Pova de Varzim, Portugal, 2001; Williams Lda. Portugal, 2001; Vol. 1, p 414.*
- Jocić, D.; Julià, M. R.; Erra, P. *J Soc Dyers Colour* 1997, 113, 25.
- Julià, M. R.; Cot, M.; Erra, P.; Jocić, D.; Canal, J. M. *Text Chem Colorist* 1998, 30, 78.
- Pavlath, A. E.; Lee, K. S. In *Proceedings of the 5th International Wool Textile Research Conference, Aachen, Germany, 1975; DWI an der RWTH-Aachen: Aachen, Germany, 1975; Vol. 3, p 263.*
- Kan, C. W.; Chan, K.; Yuen, C. W. M.; Miao, M. H. *Text Res J* 1999, 69, 407.
- Maslova, G.; Krasavtsev, V. In *Proceedings of the 7th International Conference on Chitin, Chitosan and Euchis '97, Lyon, France, 1997; European Chitin Society: Villeurbanne, France, 1997; p 554.*
- Kulak, Z.; Niekraszewicz, A.; Struszczyk, H. *Fibres Texts Eastern Eur Oct/Dec* 1999, 60.
- Grill, A. *Cold Plasma in Material Fabrication: From Fundamentals to Applications; IEEE Press: New York, 1994.*
- Testing of Textiles: Determination of Viscose Fibers Content in Mixture with Wool-Potassium Hydroxide Solution Method; Yugoslav Standard JUS F.S3.115; Federal Inst. for Standardization: Belgrade, Serbia and Montenegro, 1968.
- Physical Tests for Textiles: Determination of Elongation of Break; Yugoslav Standard JUS F.S2.017; Federal Inst. for Standardization: Belgrade, Serbia and Montenegro, 1958.
- Determination of Bursting Strength of Fabrics; Yugoslav Standard JUS F.S2.022; Federal Inst. for Standardization: Belgrade, Serbia and Montenegro, 1958.
- Determination of Fabric Thickness; Yugoslav Standard JUS F.S2.021; Federal Inst. for Standardization: Belgrade, Serbia and Montenegro, 1986.
- Maclaren, J. A.; Milligan, B. *Wool Science: The Chemical Reactivity of the Wool Fibre; Science Press: Marickville, Australia, 1981.*
- Masri, M. S.; Reuter, F. W.; Friedman, M. *J Appl Polym Sci* 1974, 18, 675.
- Rinaudo, M.; Desbrières, J.; Auzély, R. *Abstracts of the 3rd International Symposium on Chitin Enzymology and 4th Conference of the European Chitin Society, Ancona, Italy, Atec: Grottammare, Italy, 2002; S-03, 2001.*
- Muzzarelli, R. A. A. *Chitin, 1st ed.; Pergamon: Oxford, England, 1977.*
- Capablanca, J. S.; Watt, I. C. *Text Res J* 1986, 56, 49.
- Severich, B. Ph.D. Thesis, RWTH: Aachen, Germany, 1994.
- Merten, T. Ph.D. Thesis, RWTH: Aachen, Germany, 1998.