ACTA CHROMATOGRAPHICA, NO. 14, 2004

PREPARATION, CHARACTERIZATION, AND METAL-SORPTION STUDIES OF A MORDANT YELLOW 10-LOADED WOOL, A NEW STABLE CHELATING MATERIAL BASED ON BLEACHED WOOL

*L. Vladescu**, *M. Costache*, and *I. Badea*

Department of Analytical Chemistry, University of Bucharest, Blvd Regina Elisabeta 2-14, 70346 Bucharest, Romania

SUMMARY

A new stable chelating material has been prepared by loading bleached wool with mordant yellow 10. The sorption capacity of the bleached wool for the organic reagent and the stability of the new material in acidic solutions were established. The sorption capacity of the new material for Fe^{3+}, the effect of pH on adsorption of Fe^{3+}, and conditions for the removal of Fe^{3+} were established. The new material has been tested for separation and concentration of Fe^{3+} at trace levels in synthetic solutions and natural waters.

INTRODUCTION

The direct determination of metal ions at trace levels in samples remains a challenging problem because of interferences from the matrix. Preconcentration or selective separation of the metal ions must usually be performed and for this purpose selective and quantitative retention of metal ions on many materials has been investigated. The most extensively studied materials are conventional and chelating ion-exchange resins, inorganic ion exchangers, solvent-impregnated resins, controlled-pore glass, and plastic foam [1,2]. Highly selective unconventional resins have been prepared by modifying common anion-exchange resins with aromatic chelating agents containing sulphonic acid groups. The potential of anionic chelating agents loaded on anion-exchange resins and important aspects of retention of organic reagents on non-ionic and anionic conventional exchangers have been discussed in thorough reviews [3,4].

Analysis of the chemical structure of wool reveals it is made almost solely of keratin proteins. It has been reported that wool contains 22 different amino acids. Some absorb water, some repel water, some contain sulphur and form sulphur bridges. Lateral chains containing cationic groups are attached to arginine, lysine, and histidine and others containing anionic groups are attached to glutamic acid and asparagine [5]. Critical study of the literature reveals that few studies have focused on the behaviour of pretreated wool in the presence of ionic solutions [6,7] and there are no reports of the use of wool as support to furnish a new ion-exchange material based on chelating agents loaded on to wool fibre.

This paper reports results from a study of the preparation and use of a new chelate-forming material based on natural wool loaded with mordant yellow 10 (C.I. 14010). The behaviour of mordant yellow 10-loaded wool in the presence of solutions of Fe^{3+} has been studied. On the basis of the results obtained a new method suitable for separation and concentration of Fe^{3+} has been elaborated and validated.

EXPERIMENTAL

Materials

The wool, obtained from S.C. Laceca S.A. (Romania), was a Romanian type called Merinos of Baragan. Hydrochloric acid fuming 37%, hydrochloric acid 1 mol L^{-1} (Titrisol), nitric acid 65%, hydrogen peroxide 30% (Perhydrol), sodium hydroxide pellets, potassium bromide (Uvasol), iron ICP standard (CertiPUR), buffer solution, pH 8.00 (CertiPUR), and CCl_4 were purchased from Merck (Darmstadt, Germany). Mordant yellow 10 was purchased from Town End Industrial Dyestuffs (Leeds, UK) and the non-ionic detergent Sintaniol BV from OAO Ivchimprom (Moscow, Russia). Water was purified by use of a MilliQ Biocel A10 ultra-pure water system from Millipore (Yvelines, France).

Equipment

A Spectro Analytical Instruments (Germany) Spectroflame Model P inductively coupled plasma atomic emission spectrometer was used. Spectrophotometric studies were performed with a Jasco V 530 spectrometer (Budapest, Hungary) and pH was measured with a Consort P901 pH/mV meter (Turnhout, Belgium) provided with a combination glass electrode. IR spectra were recorded by means of a Jasco FT/IR 410 spectrometer

(Budapest, Hungary). A Kern 770 (Balingen, Germany) electronic analytical balance was used to weigh the wool.

Spectrophotometric Studies

Solutions to be studied were prepared in 25-mL volumetric flasks. Exactly measured volumes of metal ion stock solution (1 mL) and mordant yellow 10 stock solution (5 mL) were placed in the flasks and diluted to volume with distilled water. The spectra of the solution of the complex against reagent blank, and of mordant yellow 10 against water as blank, were recorded. The mole ratio method and the method of continuous variations were used for determination of the stoichiometry of the most stable complex formed between the metal ion and the organic reagent.

Separation Studies

Bleaching of Wool

The wool was bleached in the laboratory. Raw wool (300 g) was washed several times with a solution containing 2 g detergent in 1000 mL water. Samples (20 g) of washed wool were immersed in chloroform for 75 min and then dried at room temperature. These operations removed grease from the wool. Samples of degreased wool (30 g) were treated with hydrogen peroxide (30%) at pH 8.00 and 80°C for 60 min. The bleached wool obtained was then washed with distilled water until the pH of the waste water was equal to that of the distilled water.

Activation of Bleached Wool

Samples of bleached wool (0.5 g) were mixed with HCl (1 mol L^{-1}, 35 mL) and distilled water (15 mL) and shaken with a mechanical shaker for approximately 2 h. The wool was then decanted and washed with distilled water until the pH of waste water was equal to that of the distilled water. The washed wool was then pressed with a glass rod and dried in the Erlenmeyer flask used for mechanical stirring.

Preparation of Mordant Yellow 10-Loaded Wool

The bath method was used to load the wool with organic reagent. A weighed amount (~0.5 g) of bleached activated wool was treated with organic reagent solution (0.01 mol L^{-1}, 50 mL) and shaken with a mechanical shaker for approximately 2 h. The loaded wool was then isolated by filtration through a fritted glass funnel and washed with distilled water to

remove excess reagent. The supernatant solution and the rinsing water were collected in a 100-mL volumetric flask. The amount of mordant yellow 10 in these solutions was determined by UV spectrometry at $\lambda = 360$ nm, by means of a calibration plot with the equation $y = -0.000597 + 0.002314x$ ($r = 0.9995$). The quantity of the reagent loaded on the wool was then calculated as the difference between the quantity added and the amount found in the supernatant.

Study of the Effect of Acidity on the Stability of the Mordant Yellow 10-Loaded Wool

The bath method was used. A weighed amount (~0.5 g) of mordant yellow 10-loaded wool was treated with different concentrations of HCl solution (from 0.001 to 1 mol L^{-1}, 50 mL) and shaken with a mechanical shaker for approximately 2 h. The loaded wool was then isolated by filtration through a fritted glass funnel and washed with HCl solution of the same concentration as the solution used for the equilibration. The supernatant solution and the rinsing waters were collected in a 100 mL volumetric flask and the amount of reagent in the supernatant solution was determined by UV spectrometry (see above).

Studies of the Adsorption of Metal Ions on Mordant Yellow 10-Loaded Wool

A weighed amount (~0.5 g) of mordant yellow 10-loaded wool was treated with 50 mL metal ion solutions at concentrations between 2×10^{-2} and 2×10^{-5} mol L^{-1} and shaken by means of a mechanical shaker for approximately 2 h. The loaded wool, which had turned brown – the colour of the complex formed between the metal ion and the mordant yellow 10 – was isolated by filtration through a fritted glass funnel and washed with small volumes of distilled water (until the waste water was colourless) to remove excess metal ion. The supernatant solution and the rinsing water were collected in a 100-mL volumetric flask. In supernatant solutions the amount of reagent desorbed and the amount of metal ion complexed with mordant yellow 10 were determined by UV spectrometry and the amount of free iron by ICP–AES. For UV spectrophotometric determination of reagent and for UV spectrophotometric determination of Fe^{3+}–mordant yellow 10 complex calibration plots with equations $y = -0.0507 + 0.339x$ ($r = 0.9996$) and $y = 0.0245 + 0.259x$ ($r = 0.9998$), respectively, were used. The quantity of the iron retained by the wool was determined by ICP–AES after elution with HCl (1 mol L^{-1}).

RESULTS AND DISCUSSION

Spectrophotometric Studies

The mordant yellow 10 (henceforth denoted R) has three functional groups. One ($–SO_3Na$) ensures its solubility in water and the others act as chelating groups. The structure of the reagent is presented in Fig. 1. It has the structural pattern of salicylic acid, which forms complexes with many cations and is an analytical reagent used especially for spectrophotometric determination of Fe^{3+} [8]. Spectrophotometric studies showed that R forms a complex with Fe^{3+} with an absorbance maximum at $\lambda = 490$ nm, a wavelength at which R absorbs little, but sufficient for use as a proper blank during spectrophotometric studies. The stoichiometry of the complex formed by Fe^{3+} and R was found to be 1:1.

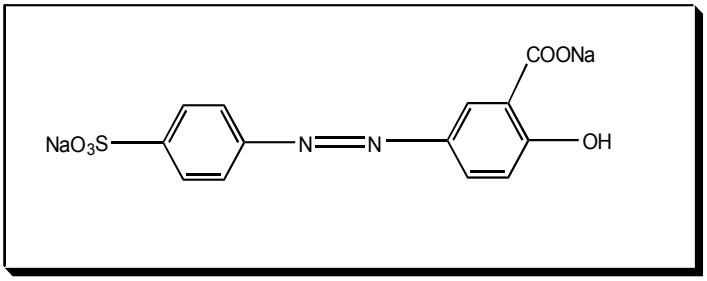

Fig. 1

The structure of mordant yellow 10

Retention of the Organic Reagent R in Wool

The bleached wool used as support for R was treated chemically to activate its functional groups. This type of wool fixes a quantity of reagent greater than that fixed by raw wool. The bleached wool was purified and activated by the bath method, by use of HCl of different concentrations. On activation of wool with HCl solution metal ions from the fibre pass into solution and the amino groups of the wool are converted to ammonium. Thus the reactive sites of the wool become accessible to the organic reagent. The amount of reagent loaded on the bleached wool was determined by the bath method. The results obtained are presented in Table I, from which it is apparent that the greater the concentration of HCl in which the wool was activated, the greater the amount of reagent loaded.

The use of 6 mol L^{-1} HCl ensures maximum activation of the wool and loading of the reagent with greater efficiency. The maximum adsorption capacity, C_S, of wool activated in acid aqueous solution was found to be 0.6473 mmol R g^{-1} wool. It is apparent that activation of the wool before loading with the reagent is essential.

Table I

Retention of the organic reagent by bleached wool

No.	Quantity of wool (g)	HCl (mol L^{-1})	Quantity of R added (mg)	Quantity of R found		C_S (mmol R g^{-1} wool)
				In wool (mg)	In filtrate (mg)	
1.	0.5500	0 (water)	94.50	5.81 ± 0.02	88.73 ± 0. 67	0.0278 ± 0.002
2.	0.5598	0.10	94.50	15.93 ± 0.03	78.65 ± 0.53	0.075 ± 0.003
3.	0.5441	1.00	94.50	18.54 ± 0.01	76.03 ± 0.24	0.089 ± 0.001
4.	0.5291	4.00	94.50	30.27 ± 0.02	64.34 ± 0.06	0.151 ± 0.003
5.	0.5121	6.00	94.50	34.15 ± 0.03	60.41 ± 0.09	0.176 ± 0.002
6.	0.5073	6.00	189.00	121.30 ± 0.71	67.11 ± 0.17	0.64730 ± 0.002

Note: each result is the mean from five determinations ± standard deviation

Infrared Studies of the Loading Mechanism

Infrared spectrometry is a common technique for studying wool [9]. To obtain information about the way in which the reagent R became fixed to the wool the IR spectra of bleached wool, bleached wool activated with HCl, and activated and dyed wool were recorded both as pressed KBr disks and as wool film. The accuracy achieved was better for wool film than for KBr disk because the structure of the wool fibre is not modified by tossing and pressing and variation of the intensity and position of characteristic bands can be observed. This study focused on the evolution of the bands specific to phenolic OH, –COOH, –SH, $–SO_3R$, aliphatic and aromatic amines, –N=N–, RCOONH–, quaternary ammonium salts, and N protonated amino acids. The results obtained are presented in Table II. The bleached wool has an intense band at 3800 cm^{-1}, because of the presence of hydrogen peroxide used for bleaching. This band cannot be found in any other type of wool studied. The activated wool has bands characteristic of quaternary ammonium salts. These bands are less intense for wool dyed with reagent R, because the reagent can interact with quaternary ammonium salts by means of its sulphonic acid group (band found in dyed wool). Bands characteristic of –N=N– groups were observed in the IR

Table II

The IR characteristics of R-loaded wool

	–SH	$–SO_3R$	–N=N–	Amine		Quaternary ammonium salts		RCONH–	–OH	–COOH
				Alkyl	Phenyl					
Literature [10]	2600–2250	1720–1530	2260–1650	3800–3300 1650–1590	1340–1250	3000, 3200–2900, 2600–1900		3700–3500	3610–3500	3600–3400 3000–2500
Bleached wool	Less intense bands	–	–	Intense bands		–	–	3800–3500	Less intense bands	Less intense bands
Bleached activated wool	Intense bands	–	–	Intense bands		3100 2200–1950	3000	3800–3500	Less intense bands	Intense bands
Dyed wool	Intense bands	1800	2100	Intense bands		–	–	3800–3500	Intense bands	Very intense bands

Note: The position of the IR bands is in cm^{-1}

spectra of the dyed wool and the band of the quaternary ammonium salts groups was no longer present. On studying the intensity of the –COOH band it was noticed that this became intense in the activated wool and very intense in the dyed wool. This led to the conclusion that reagent R could be loaded on to the wool fibre at the N protonated atoms by means of its sulphonic acid group. The salicylic acid moiety in the molecule of R stays free, and is thus able to participate in complexation with metal cations.

Stability of R-Loaded Wool in Acid Solutions

To investigate the stability of the R-loaded wool in the presence of acidic solutions, different concentrations of aqueous HCl solutions were used. The results are presented in Table III. Analysis of the data in Table III shows how the stability of R-loaded wool varies in acidic solutions. Occurrence of R was noticed in HCl solutions of concentration greater than 0.359 mol L^{-1}. It was observed that the organic reagent was quantitatively held by the wool in the presence of 0.120 mol L^{-1} acid solution. Some R was still retained on the wool even in 1.000 mol L^{-1} HCl solution, because of π–π interactions between the benzene ring of R and the structure of the wool fibre. Adsorption of the organic reagent by its chelating groups must be taken into consideration.

Table III

Stability of the R-loaded wool in acidic solutions

No.	Quantity of wool (g)	Concentration of HCl (mol L^{-1})	Concentration of R in filtrate solution (mmol/100 mL)	Colour of R-loaded wool
1.	0.5034	0.001	0	No changes in colour
2.	0.5038	0.010	0	No changes in colour
3.	0.5059	0.100	0	No changes in colour
4.	0.5034	0.120	0	No changes in colour
5.	0.5035	0.359	$2.737 \times 10^{-3} \pm 4.08 \times 10^{-5}$	Small loss of colour
6.	0.5007	1.000	$5.46 \times 10^{-2} \pm 3.78 \times 10^{-4}$	Important loss of colour

Note: each result is the mean from five determinations ± standard deviation

Adsorption of Metal Ions on the R-Loaded Wool

Because the stability of the R in the R-loaded wool depends on the acidity of the medium, the pH of the metal cation solution must be rigorously controlled. To determine the optimum working conditions for adsorption of metal ions by the R-loaded wool, the effects of iron concentration and acidity on the retention of iron by R-loaded wool were studied. As has already been shown, R forms a 1:1 complex with Fe^{3+}. The amount of iron(III) retained by R-loaded wool was determined by a batch method. The results are presented in Table IV. It was noticed that the filtrate solution contained excess Fe^{3+} and an insignificant quantity of Fe^{3+}–R complex. For most of the reagent chemically loaded on the wool fibre the functional groups were free to react with Fe^{3+}, thus these ions were fixed by the wool. The infrared spectra of such wool showed that the bands

Table IV

Determination of sorption capacity of R-loaded wool for Fe^{3+}

No.	Quantity of wool (g)	Quantity of Fe^{3+} added (mg)	Quantity of Fe^{3+} found		C_S (mmol Fe^{3+} g^{-1} wool)
			In wool (mg)	In filtrate (mg)	
1.	0.5138	55.90	6.92 ± 0.01	49.08 ± 0. 27	0.2411 ±0.02
2.	0.5672	55.90	7.21 ± 0.04	48.51 ± 0.34	0.2276 ± 0.01
3.	0.5315	55.90	6.89 ± 0.02	49.15 ± 0.21	0.2321 ± 0.04
4.	0.5475	55.90	7.02 ± 0.03	49.21 ± 0.19	0.2295 ± 0.01
5.	0.5711	55.90	7.15 ± 0.05	48.82 ± 0.49	0.2242 ± 0.02
6.	0.5749	55.90	7.09 ± 0.02	49.51 ± 0.19	0.2208 ± 0.01

Note: each result is the mean from five determinations ± standard deviation

specific to the phenolic and carboxylic OH groups disappeared in the spectrum of the R-loaded wool with fixed Fe^{3+}. The values obtained for the quantity of Fe^{3+} fixed by the new chelate-forming material corresponded to the theoretical value calculated for formation of a 1:1 stoichiometric complex between Fe^{3+} and the reagent in the wool, i.e. the same complex whose existence in solution had been demonstrated by UV–visible spectrophotometry.

Removal of Fe^{3+} from R-Loaded Wool by Use of Acidic Solutions

To establish conditions for removal of Fe^{3+} retained by the chelate-forming adsorbent, solutions of HCl of different concentration were used. Results obtained by the bath method showed that 1 mol L^{-1} HCl solution was efficient without substantial desorption of the reagent.

Determination of Iron in Synthetic and Real Samples

The results obtained during the whole experiment indicate that the R-loaded wool can be used for separation and concentration of traces of iron from dilute solutions. Results obtained for adsorption of iron from synthetic solutions, presented in Table V, were used to validate the accuracy and precision (repeatability and intermediate precision) of the method. The values obtained (% ± standard deviation) were 98.31 ± 0.48 for accuracy, 98.56 ± 1.16 for repeatability, 99.02 ± 1.41 for day I, and 98.29 ± 1.89 for day II.

Table V

Adsorption of traces of iron by R-loaded wool

No.	Quantity of wool (g)	Quantity of Fe^{3+} added (mg)	Quantity of Fe^{3+} found		$m_{Fe(III)}/m_{R\text{-}wool}$ (mmol Fe^{3+} g^{-1} wool)
			In wool (mg)	In filtrate (mg)	
1.	0.5312	5.5960	5.3261 ± 0.02	0.2716 ± 0.03	0.1794 ± 0.03
2.	0.5817	0.5596	0.5593 ± 0.01	$0.00024 \pm 4.35 \times 10^{-6}$	0.0172 ± 0.001
3.	0.5730	0.0559	0.0551 ± 0.0008	$0.00069 \pm 5.89 \times 10^{-6}$	$0.00174 \pm 5.80 \times 10^{-6}$

Note: each result is the mean from five determinations ± standard deviation

The new chelate-forming material was used for real samples of Romanian soda (Perla Harghitei), drinking water from Ploiesti town (60 km north of Bucharest), and water from Prahova river in Ploiesti and 50 km downstream from Ploiesti. The results obtained are summarised in Tab-

le VI. The quantity of Fe^{3+} was determined by this procedure and by ICP–AES. The results obtained were in good agreement.

Table VI

Determination of Fe^{3+} in water samples

No.	Water	Quantity of Fe^{3+} found		Quantity of Fe^{3+} admitted [11] (mg L^{-1})
		Proposed method (mg L^{-1})	ICP–AES (mg L^{-1})	
1.	Perla Harghitei soda	0.0137 ± 0.008	0.0139 ± 0.007	0.0100
2.	Drinking water	0.13 ± 0.01	0.14 ± 0.02	0.10
3.	Prahova river in Ploiesti town	43.05 ± 0.42	44.13 ± 0.31	<10
4.	Prahova river 50 km downstream the Ploiesti town	17.52 ± 0.25	18.56 ± 0.17	<10

Note: each result is the mean from five determinations ± standard deviation

CONCLUSIONS

Bleached wool activated with 6 mol L^{-1} HCl solution by the bath method and loaded with mordant yellow 10 (R) has been studied as a new chelate-forming material for separation and concentration of traces of iron. Infrared studies have shown that the sulphonic acid groups of the mordant yellow 10 become attached to the N protonated atoms of the wool fibre. The salicylic acid part of the structure thus remains free to form complexes with metal ions. The maximum adsorption capacity of the wool is 0.6473 mmol R g^{-1} wool. Wool loaded with R is stable in acidic solution. This R-wool has been used for separation and concentration of trace amounts of Fe^{3+}. In solution Fe^{3+} forms a 1:1 complex with R. The sorption capacity of R-wool is 0.2292 ± 0.0070 mmol Fe^{3+} g^{-1} wool. The Fe^{3+} retained by the R-wool can be removed with 1 mol L^{-1} HCl solution without substantial desorption of the reagent. The accuracy and precision of the method are good.

This new chelate-forming adsorbent based on R-loaded wool was used for separation and concentration of Fe^{3+} from water samples. After adsorption on R-loaded wool then desorption with 1 mol L^{-1} HCl solution Fe^{3+} was determined by UV spectrometry. Results were in good agreement with those obtained by use of ICP–AES.

REFERENCES

[1] J.A. Marinsky (ed.) Ion Exchange, Vol. 1, Marcel Dekker, New York, 1966

[2] F.X. McGarvey and D. Tamaki, 52nd Off. Proc. Int. Water Conf., Selective Ion-Exchange Resins for Toxic Metal Removal, 1991, pp. 228–233

[3] C. Kantipuly, S. Katragadda, A. Chow, and H.D. Gesser, Talanta, **37**, 491 (1990)

[4] M. Torre and M.L. Marina, Crit. Rev. Anal. Chem., **24**, 327 (1994)

[5] L. Vladescu and Z. Moldovan, Roum. Chem. Quart. Rev., **8**, 233 (2000)

[6] J. Knott, Proc. Int. Wool Text. Res. Conf. I, vol III, Tokyo, 1985

[7] F.Yu. Telegin, I.Yu. Vashurina, A.V. Shormanov, E.N. Ivanova, Yu.A. Kalinnikov, and B.N. Melnikov, J. Phys. Chem., **97**, 752 (1993)

[8] T.N. McKenzie and E.M. Aicolina, Proc. RACI 14th Australian Symp. Anal. Chem. p. 365, 1997

[9] J. Fries and H. Getrost, Organic Reagents for Trace Analysis, E. Merck, Darmstadt, 1977, p. 186

[10] A. Pielesz, A. Włochowicz, and W. Biniaś, Spectrochim. Acta A, **56**, 1409 (2000)

[11] D.A. Skoog and J.J. Leary, Principles of Instrumental Analysis, 4th edn, Saunders College Publishing, Forth Worth, 1992

[12] Romanian STAS 1342-71