

SULPHOSALICILIC ACID LOADED WOOL NEW CHELATING SORBENT FOR IRON (III)

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abstract: A new chelating material has been prepared based on bleached wool loaded with sulphosalicylic acid. The sorption capacity of the bleached wool for the organic reagent and the stability of the new material in acidic solutions have been established. The sorption capacity of the new material for iron (III) and the conditions for removal of them from the material have been established. The new material has been tested for the separation and concentration of iron (III) found at traces level in synthetic solutions and natural waters.

Introduction

Determination of trace metal ions by inductively coupled plasma-atomic emission spectrometry (ICP-AES) and inductively coupled plasma – mass spectrometry (ICP-MS) have been selected as techniques of choice. However, pre-concentration or selective separations of the analyte before its determination are frequently required in order to avoid interferences caused by the matrix. The selective and quantitative retention of metal ions has been investigated on a great number of materials. The most extensively studied materials are ion exchange resins both conventional and chelating, inorganic ion exchangers, solvent impregnated resins, controlled pore glass and foamed plastics [1÷3]. The potential of anionic chelating agents loaded on anion exchange resins and important aspects of organic reagents retention on non-ionic and anionic conventional exchangers have been discussed in literature [4,5]. New materials having the wool fibre as support have been reported in the literature [6]. The wool is almost solely made of keratin proteins and contain up to 22 different amino acids. The cationic groups of the lateral chains are placed on the arginine, lysine and histidine rests and the anionic ones on the glutamic acid and asparagine rests [7]. A new material based on wool loaded with Mordant Yellow 10 has been studied and reported in a previous paper [8]. Sulphosalicylic acid (further noted by SSA) is an organic compound, having similar structure to Mordant Yellow 10, and it forms with iron (III) stable complexes having the stoichiometry Fe(III) : SSA = 1 : 1, 1 : 2 and 1 : 3 at pH : 2.50, 4.50 and 8.00 respectively [9]. As proteic support the bleached wool having the functional groups activated by chemical treatment has been used. Thus the optima

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working conditions for the preparation of a new chelating material based on natural wool loaded with Sulphosalicylic Acid are presented in this paper. The both SSA – loaded wool and the bleached wool activated in acidic conditions have been used for concentration and recuperation of iron (III) from diluted solutions.

Experimental

Reagents

The wool was obtained from S. C. LACECA S.A. (Romania) and was a Romanian type called Merinos of Bărăgan. Water was double distilled and all chemical reagents were of analytical reagent grade. Hydrochloric acid fuming 37%, hydrogen peroxide 30% (Perhydrol[®]), sodium hydroxide pellets, iron ICP standard (CertiPUR[®]) and sulphosalicylic acid were purchased from Merck. Diluted HCl solutions having the concentration of 0.100, 1.000, 4.000 and 6.000 mol.L⁻¹ have been prepared using HCl 37%. Stock solutions of sulphosalicylic acid 0.020 mol.L⁻¹ has been prepared. Aqueous stock solutions of iron (III) 0.020 mol.L⁻¹ (in HNO₃ 0,0144 mol.L⁻¹) has been obtained by diluting Merck atomic absorption standard metal ion solutions with distilled water. CHEMIX DBS used as detergent has been obtained from CHIMOPAR (Romania). Chloroform has been purchased from Aldrich.

Apparatus

A spectroflame Spectro Analytical Instruments Model P inductively coupled plasma atomic emission spectrometer has been used. The spectrometric studies were performed on a Jasco V 530 spectrometer coupled with a PC running a Jasco software. An electronic analytical balance Kern 770 was used for weigh wool. A microwave oven MILESTONE MLS - 1200 MEGA has been used for the digestion of bleached wool samples activated in acid medium and loaded with iron (III).

Procedure

Bleaching of wool. Purification and activation

The wool has been bleached in the laboratory using a procedure as follow: 300 g of raw wool has been washed several times using a solution containing 6 g of detergent in 1000 mL water. Samples of washed wool weighing each 20 g have been immersed into chloroform for 75 minutes and then dried at room temperature. Thus grease has been removed from the wool. Samples of degreased wool weighing each 30 g have been treated with hydrogen peroxide 30% at pH 8.00 and 80°C during 60 minutes. After that the bleached wool obtained has been washed with distilled water until the pH of waste water was equal to the pH of distilled water. The bleached wool weighing each 0.5 g were mixed with 35 mL of HCl 1 mol.L⁻¹ and 15 mL distilled water and shaken with a mechanical shaker for about 2 h. After being stirred the wool has been decanted and washed with distilled water until the pH of waste water was equal to the pH of distilled water. The washed wool has been pressed with a glass rod and dried up in the same Erlenmeyer flask used for the mechanical stirring. Thus the bleached wool has been activated.

Preparation of sulphosalicilic acid-loaded wool

The bath method was used for retention of sulphosalicilic acid on the wool. A weighed amount (~ 0,5 g) of bleached wool activated by bath method using HCl solutions of different concentrations was treated with 50 mL of 0.02 mol.L⁻¹ of SSA solution and shaken with a mechanical shaker for about 2 h. Then the loaded wool was filtered off in a fritted-glass funnel and washed with distilled water to remove the excess reagent. The supernatant solution and the rinsing water were collected in a 100 mL volumetric flask. The amount of SSA in supernatant solutions was determined by spectrometry ($y = 0,000124 + 0,008752x$, $r = 0,9997$). The SSA loaded on wool was determined by subtracting the quantity found in supernatant from the quantity used at the beginning of the shaking.

Acidity influence on the stability of the SSA-loaded wool

The bath method was used. An exactly weighed amount of SSA-loaded wool was treated with 50 mL of HCl solutions having different concentrations and shaken with a mechanical shaker for about 2 h. Then the loaded wool was filtered off in 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 water were collected in a 100 mL volumetric flask. The amount of SSA in supernatant solutions was determined by spectrometry.

Sorption of metal ions on the SSA-loaded wool

Weighed amount of SSA-loaded wool was treated with 50 mL of iron (III) solutions having different concentrations and shaken with a mechanical shaker for about 2 h. Then the loaded wool was filtered off in a fritted-glass funnel and washed with small volumes of distilled water to remove the excess of metal ion. The supernatant solution and the rinsing water were collected in a 100 mL volumetric flask. The amount of iron (III) found in supernatant solutions has been determined by ICP – AES. The quantity of iron (III) sorption on SSA–wool was calculated by subtracting the quantity found in supernatant from the quantity used at the beginning of the shaking.

Results and discussion*Retention of sulphosalicilic acid in wool*

As support for SSA-loaded wool the bleached wool has been used as this sort of wool loads a quantity of reagent greater than those fixed by the raw wool. After the activation stage ions from the fibre passed into solution, amine groups of wool became ammonium ions and are accessible to the organic reagent. The amount of SSA loaded on the bleached wool was determined by bath method. The results of sulphosalicilic acid retention in bleached wool are presented in Table 1. As it is shown the samples of bleached wool activated with HCl of 4 and 6 mol.L⁻¹ load a quantity of SSA greater than bleached wool activated with 0.100 and 1,000 mol.L⁻¹.

Table 1. Retention of SSA in bleached wool shaken with HCl of various concentrations

No.	Quantity of wool (g)	HCl (mol.L ⁻¹)	Quantity of SSA added (mg)	Quantity of SSA found in wool (mg)	SAA found in filtrate (mg)	Sorption Capacity (mmoli SSA /g wool)
1.	0.5502	0 (water)	230.0	15.4 ± 0.68	214.6 ± 1.32	0.028 ± 0.0030
2.	0.5598	0.10	230.0	40.3 ± 0.35	189.7 ± 1.68	0.072 ± 0.0050
3.	0.5498	1.00	230.0	53.3 ± 0.94	176.7 ± 1.59	0.097 ± 0.0020
4.	0.5465	4.00	230.0	95.6 ± 0.21	134.4 ± 1.09	0.175 ± 0.0001
5.	0.5524	6.00	230.0	99.4 ± 0.14	130.6 ± 0.29	0.280 ± 0.0003
6.	0.5396	6.00	230.0	149.9 ± 0.46	310.1 ± 0.83	0.652 ± 0.0002

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

Stability of SSA - loaded wool in acid solutions

In order to investigate the stability of the SSA-loaded wool in presence of acidic solutions, different concentrations of aqueous HCl solutions were used. The results are present in Table 2. The results in Table 2 show a different stability of SSA-loaded wool in acidic solutions. The occurrence of SSA has been noticed in HCl solutions having a concentration greater than 0.400 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 SSA was still retained on the wool even in 1.000 mol.L⁻¹ HCl solution due to the π - π interaction between the benzene ring of SSA and the structure of the wool fibre. The sorption of the organic reagent by its chelating groups has to be taken into consideration.

Table 2. Stability of the SSA-loaded wool in acidic solutions

No.	Quantity of wool (g)	Concentration of HCl (mol.L ⁻¹)	Concentration of SSA in filtrate solution mmol/100 mL
1.	0,5025	0,001	0
2.	0.5012	0,010	0
3.	0.5004	0,100	0
4.	0,5010	0,120	0
5.	0.5017	0,400	0.0015 ± 0.00021
6.	0,5002	1,000	0.0420 ± 0.00006

Note: each result represents the mean of five determinations ± standard deviation

Sorption of metal ions on the SSA-loaded wool

Both bleached wool activated with HCl of 4 and 6 mol.L⁻¹ and the SSA-loaded wool have been used for the sorption of iron (III) from synthetic samples. The results regarding the capacity of two kinds of wool to fix the iron (III) are presented in Table 3.

Table 3. Capacity of bleached wool and SSA-wool to fix the iron (III)

No.	Quantity of wool (g)	Quantity of Fe ³⁺ added (mg)	Quantity of Fe ³⁺ found		Sorption Capacity mmol iron (III)/g wool
			in filtrate (mg)	in wool (mg)	
1	0.5415	27.9	26.7 ± 0.17	1.2 ± 0.05	0.039 (a)* ± 0.0016
2	0.0230	27.9	22.3 ± 0.35	5.6 ± 0.06	0.199 (b) ± 0.0007
3	0.5064	27.9	21.9 ± 0.41	6.0 ± 0.08	0.212 (b) ± 0.0002
4	0.5023	27.9	22.1 ± 0.24	5.8 ± 0.02	0.206 (b) ± 0.0009

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

*after digestion of wool samples in a microwave four and determination of iron (III) by ICP-AES

The results obtained show that both bleached wool activated with HCl and the SSA-loaded wool fix the iron (III) from diluted solution. The sorption capacity of two sorts of wool is different. The SSA-loaded wool has a greater sorption capacity than the bleached wool activated with HCl.

Removal of iron (III) from SSA - loaded wool using HCl solutions

In order to establish the conditions for removal of iron retained by the SSA-loaded wool, solutions of HCl of different concentrations were used. Results obtained by the bath method showed that 1 mol.L⁻¹ HCl solution was efficient for iron recuperation without a substantial desorption of the sulphosalicylic acid from the wool.

Determination of iron from synthetic samples

The results obtained during the whole experiment ensure the use of the SSA-loaded wool for the separation and concentration of some iron traces from diluted solutions. The recoveries are between 99.48% and 100.87% and the RSD are below 2%. Using synthetic samples containing trace amounts of iron (III) the method has been validated [10] by regard to the accuracy and the precision. The accuracy and the precision (repeatability and intermediate precision) have been determined for sorption of iron (III) in SSA-loaded wool. The values obtained (expressed as % ± standard deviation) are: 99.05 ± 0.76 for accuracy, 98.82 ± 0.42 for repeatability and 99.63 ± 1.51 for day I and 98.58 ± 1.18 for day II.

Determination of iron from real samples

The new chelate forming material has been used for concentration and determination of iron (III) from real samples of running water. Samples of running water have been taken from North of Bucharest. The results obtained are summarised in Table 4. The quantity of iron (III) has been determined by the proposed procedure and by ICP-AES. It was noticed a good agreement between the results obtained. All the results are below the imposed value for iron (III) in running water [11]. Each value in Table 4 represents the mean of five determinations ± standard deviation.

Table 6 Determination of iron (III) in running water samples

Water	Quantity of iron (III) found		Quantity of iron (III) admitted [11] (ppm)
	proposed method (ppm)	ICP – AES[12] (ppm)	
Sample 1	0.182 ± 0.0012	0.1790 ± 0.0005	< 0.200
Sample 2	0.198 ± 0.0009	0.0195 ± 0.0014	< 0.200
Sample 3	0.141 ± 0.0017	0.0143 ± 0.0006	< 0.200

Conclusion

The bleached wool activated by bath method using 4 and 6 mol.L⁻¹ of HCl solutions and loaded with sulphosalicylic acid has been studied as a new chelating material for separation and concentration of iron (III) found at trace level. The sulphosalicylic acid can be loaded on the wool fibre at the N protonated atoms by means of its sulphonic group. Its structural pattern of salicylic acid stays free and can react with iron (III). This SSA-wool has been

used for separation and concentration of trace amounts of iron (III) from synthetic samples. The recoveries were between 99.48% and 100.87% with the RSD below 2%. The new chelate-forming sorbent based on the sulphosalicylic acid-loaded wool may be used for the separation and concentration of the traces of iron (III) from different samples with good accuracy and precision.

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