Preparation and Characterization of Polystyrene-Sulfonyl-Thiosemicarbazide Chelating Compound for Treatment of Wastewater Containing Heavy Metal Ions

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Abstract: ***This work studies the preparation of polystyrene-sulfonyl-thiosemicarbazide (PSS-TSC). Thio-polymer was characterized by IR, NMR, and elemental analysis. PSS-TSC was used fordetermination of metal capacity of Mn (II), Ni (II), Cu (II), Cd (II), metals ions. Hg (II) and Pb (II) in wastewater. Also the effect of pH (1-7) and shaking times (5 – 10 min) on the metal capacity were studied. Itwas found that the metal capacity values by PSS-TSC phase at pH 7 follow the following order: Hg(II) > Pb (II) > Cu (II) > Ni (II) > Cd (II) > Mn (II). The efficiency of metal ions extraction by PSS-TSC phase was studied by the distribution coefficient and separation factor of different metal ions.***

Keywords: Characterization, Polystyrene-Sulfonyl-thiosemicarbazide, Chelating compound, heavy metal ions

1. Introduction

Metal manufacturing is finishing and mining discharge heavy metal ions into the surface water. These heavy metal ions cause a significant pollution to the environment and human health. They are toxic and non-biodegradable, so their removal and extraction is very important before discharging into water.(1-3) One of the most convenient methods to remove the heavy metal ions is adsorption by chelating polymers due to their high adsorption capability, simplicity and selectivity. (4,5) This work involves preparation and characterization of polystyrene-sulfonyl-thiosemicarbazide (PSS-TSC). Stability test was investigated for the modified polystyrene phase (PSS-TSC). PSS-TSC was used for determination of metal capacity of Mn (II), Ni (II), Cu (II), Cd (II), Hg (II) and Pb (II) in wastewater. Also the effect of pH (1-7) and shaking times (5 – 10 min) on the metal capacity were studied. The efficiency of metal ions extraction by PSS-TSC phase was studied by the distribution coefficient and separation factor of different metals ions. Applications of PSS-TSC for extraction and removal of heavy metals ions from wastewater samples of Damanhour drug factory, Extracted oil company (Damanhour factory), Extracted Maryout (5000 fadan) and drinking tap water were studied by the prepared PSS-TSC phase.

2. Experimental Work

2.1 Chemical and Reagents

Polystyrene (M_n= 45000 g/mol) was purchased from Aldrich Chemical Company and used without purification. Chloroform, sulfuric acid, methanol, dioxane, and potassium iodide were purchased from Al-Gomhoria Co. and were used as received except dioxane, and chloroform. Pyridine, thiosemicarbazide (TSC), chlorosulfonic acid, HO and ammonium chloride were obtained from Aldrich. Metal ions (Nickel Chloride, Copper Chloride, Zinc Chloride, Cobalt Chloride and Ferric Chloride) were obtained from Fisher Co. whereas murexide, salicylic acid, ascorbic acid, EDTA, Erio-T and magnesium sulfate were purchased from Sigma Co. Buffer solutions used for pH adjustments, were prepared using glycine– hydrochloric acid pH (1–3), Sodium acetate–acetic acid pH (4–6), Ammonium acetate–ammonia pH (7–8) and ammonium chloride ammonia pH (9–10).

2.2 Solutions

The metal salts are all of analytical grade and purchased from Aldrich Chemical Company, USA and BDH Limited, Poole, England. The list of metal salts is given in Table (1). The metal ion solutions were prepared from doubly distilled water (DDW) and 0.1 M of metal solutions were prepared by dissolving 100 mmol of the following metal salts each in 1 liter DDW. These metal salts are lead acetate tri-hydrate (39.733 g), copper (II) chloride di-hydrate (17.048 g), nickel (II) chloride hexa-hydrate (**2**3.771 g), cadmium (II) chloride (**22**.834 g), manganese (II) chloride tetrahydrate (19.791 g), mercury (II) chloride (**2**7.15 g).

Table 1: List of metal Units

Selected metal	Formula	Formula weight
Pb(II)	$Pb(Ac)_{2.}$ 3 H_2O	397.33
Cu(II)	Cu $Cl_{2.}$ H_2O_2	170.48
Ni(II)	Ni Cl_2. $6HO_2$	237.71
Cd(II)	Cd Cl_2.5/2 HO_2	228.34
Mn(II)	Mn Cl_2. $4HO_2$	197.91
Hg(II)	Hg Cl_2	271.50

EDTA (0.1 M) solution was prepared by dissolving exactly 37.**22**5 g of EDTA after drying for one hour at 80 ^{0}C in one liter of DDW. This solution was diluted to 0.01 M and standardized against 0.01 M Zn^{+2}solution, prepared by dissolving appropriate amount of zinc metal in the least amount of sulfuric acid, followed by neutralization and dilution with DDW. Solution with pH 1.0, .0, 3.0, 4.0, 5.0 and 6.0 were prepared from 1.0 M hydrochloric acid solution and 1.0 M sodium acetate trihydrate solution by mixing the appropriate volumes of the two solutions and diluting to 1.0 liter. The pH value of each was adjusted by a pH meter.

2.3 Measurements

2.3.1. Infrared spectroscopy

IR- spectrum of the modified polystyrene (PSS-TSC) is recorded from KBr pellets using a Perkin- Elmer spectrophotometer, model 1430 in the micro-analytical central lab, City Of Scientific Research And Technological Application. Alexandria, Egypt

2.3.2 NMR spectroscopy

^{1}H NMR- spectrum of the polystyrene was recorded in $CDCl_3$, and also $PSSO_2Cl$, and PSS-TSC were carried out in DMSO using a Joel JUM ECA 500 MHz spectrophotometer, in the micro-analytical central lab, Faculty of Science, Alexandria, Egypt.

2.3.3. Elemental analysis

Elemental analysis was performed to study the quantitative conversion during each stage of resin functionalization using an Elementar Vario EL model CHN analyzer, in the micro-analytical central lab, faculty of science, Cairo, Egypt.

Determination of chloride content of chlorosulfonated polystyrene

a-Polystyrene (0.2 g) was added to 10% NaOH (20 ml) and boiled for 4h. After filtration 2 drops of BPB were added, and the solution was neutralized with 0.2 N HNO_3. When the color changed from violet to yellow another 4 ml excess of 0.2 N HNO_3 were added.(6) The content of chloride ion was determined by direct titration against standard Hg $(NO_3)_2$solution (0.01N) using drops of DPC (diphenyl carbazide) as an indicator. At the end point the color changed from yellow to pale violet orpink(7) .

b- by oxygen flask

0.02-0.03 g of dried chlorosulfonated polystyrene was burned in an oxygen flask in the presence of (1ml) H_2O_2 and (3 pellets) of KOH.(8) The resulting solution was heated for decomposition of HO then cooled. The content of chloride ion was determined by direct titration against standard Hg $(NO_3)_2$solution (0.01N) using drops of DPC (diphenyl carbazide) an indicator. At the end point the colour changed from pale yellow to pale violet or pink.(7)

2.3.4. Atomic Absorption Spectrometric Analysis

Determination of the metal concentration was performed using a Perkin-Elmer model **2**380 Atomic absorption spectrophotometer at appropriate wavelength for some metals in the micro-analytical central lab, Faculty of Science, Alexandria, Egypt and confirmed for these metals and others using SHIMADZU model AA-6650 Atomic absorption spectrophotometer at appropriate wavelength in central laboratory unit, High institute of public health, Alexandria, Egypt. The standard wavelength and working range for each tested metal ion is given Table (**2**).

2.3.5. pH – Measurements.

pH measurements of the metal ions and buffer solutions were carried out with an Orion 40. The pH-meter was calibrated against standard buffer solution of pH 4.0 and 9.**2.**

Table 2: Standard wavelength and working range of tested metal ions by atomic absorption spectrophotometer

Element	Wavelength λ (nm)	Working range (μg ml^{-1})
Mn	279.5	0.0-2.0
Hg	253.7	0.0-150
Ni	232.0	0.0-2.
Cu	324.8	0.0-5.0
Cd	228.8	0.0-2.0
Pb	283.3	0.0-20

2.4 Methods

2.4.1. Purification of solvents

a) Chloroform

Chloroform was washed three times with distilled water, separated by separating funnel, and was placed overnight with calcium chloride, and then distilled.(9)

b) Dioxane

One liter of dioxane, 14 ml of concentrated HCl and 100 ml of DDW were heated in fume cupboard under reflux for 6 -1 hours under slow stream of nitrogen to remove the acetaldehyde formed, the cold solution was treated with excess KOH pellets overnight. The strongly alkaline aqueous layer was run off by separating funnel. The residual dioxane was heated under reflux over excess sodium metal for 6 – 12 hours till the reaction was occurred, and then the remaining sodium removed by distillation with rotary system**. (10)**

2.4.2. Chlorosulfonation of polystyrene

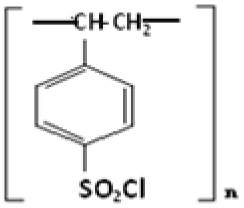
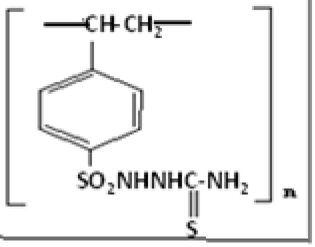
Polystyrene (**2** g) were dissolved in dried chloroform and stirred until the polystyrene was fully dissolved, and then placed in dropping funnel. Chlorosulfonic acid (11 ml, HSO_3Cl/polystyrene≥ 8 mole) was placed in three necked flask in an ice bath (-10 ^{0}C) under nitrogen atmosphere with constant stirring. The first solution of polystyrene was added dropwise to the chlorosulfonic acid. The addition time was about two hours to keep the temperature below 0 ^{0}C. After addition of polystyrene solution, the resulting precipitated polystyrene chlorosulfonic acid was maintained at 0 ^{0}C for about three hours under constant stirring. Finally the resulting precipitate was left at 0 ^{0}C overnight. The polystyrene chlorosulfonic acid was filtered, washed with chloroform several times and then with methylene chloride, then dried under vacuum (M.P = 130 – 140 ^{0}C).

2.4.3. Synthesis of polystyrene sulfonyl-thiosemicarbazide (PSS-TSC)

In 100 ml round bottom flask, 1.6 g of chlorosulfonated polystyrene (0.015 mole) was swelled in chloroform. To the swelled polymer (0.03 mole) of thiosemicarbazide, (dissolved in dioxane), was added. A few drops of pyridine were added to the reaction mixture to remove the resulting HCl. The reaction mixture was stirred for six hours at room temperature then refluxed for 6 h at 60 ^{0}C. The resulting polystyrene-sulfonyl- thiosemicarbazide (PSS-TSC) (Table

3) was precipitated in excess of methanol and dried under vacuum.

Table 3: Name, abbreviation and structure of the prepared polymer

Name	Abbreviation	Structure
Chlorosulfonated Polystyrene	CSPS	
Polystyrene-sulfonylthiosemi-carbazide	PSS -TSC	

2.4.4. Stability test the newly synthesized PSS-TSC in different buffer solutions

PSS-TSC phase (50 mg) was mixed with 20 ml of the selected buffer solutions (pH 1-7) in a 100 ml volumetric flask and automatically shaken for one hour. The mixture was filtered, and dried in at 70 0C. 25.0 ± 1 mg of PSS-TSC phase were added to a solution containing 9.0 ml of buffer solution (pH = 7) and 1.0 ml of 0.1 molar of Hg (II). The mixture was automatically shaken for 30 minutes by an automatic shaker and the degree of hydrolysis of PSS-TSC in different buffer solutions was determined from the metal uptake values of Hg (II).

2.4.5. Determination of metal capacity

2.4.5.1. Effect of pH value of metal ion solution on the metal capacity.

The metal capacity values (μ mol g^{-1}) of PSS-TSC for the extraction **of these series of metal ions,** Mn (II), Ni (II), Cu (II), Cd (II), Hg (II) and Pb (II) in various buffer solutions (pH 1.0 – 7.0 and 1.0 M sodium acetate) were determined in triplicate by the batch equilibrium technique. In this method, 50 ± 1 mg of the dry phase were weighed and added to a mixture of 1.0 ml of 0.1 M metal ion and 9.0 ml of the selected buffer solution into 50 ml measuring flask. These flasks were then shaken at room temperature for 30 minutes by an automatic shaker. After equilibration, the mixture was filtered and washed three times with 100 ml of doubly distilled water (DDW). The unbounded metal ion by the studied modified polystyrene phases was subjected to complexometric titration using 0.01M EDTA solution or by atomic absorption analysis. (11-13)

2.4.5.2. Effect of shaking time on the metal capacity values and percentage of extraction

The effect of shaking time intervals (5, 10, 0, 30, 60 and 120 minutes) on the value of metal capacity and on the amount and percentage of the extraction was also studied for some selected metal ions by the batch equilibrium technique according to the following procedure:50 ± 1 mg of the dry PSS-TSC phase were added to a mixture of 1.0 ml of 0.1 M of each metal ion and 9.0 ml of buffer solution, which was found to exhibit the highest metal capacity in the previous study. This mixture was filtered, washed with 100 ml DDW and the unextarcted metal ion by PSS-TSC phase was determined by complexometric EDTA titration (14,15)

2.4.6. Determination of the distribution coefficient

The following metal ions were used to prepare the solutions used to determine the distribution coefficient of PSS-TSC phase. The metal ions are Mn (II), Ni (II), Cu (II), Cd (II), Hg (II) and Pb (II). The concentration of each metal ion solution is ~ 2.0 ppm in 0.1 molar sodium acetate solution. In a 25 ml measuring flask, 50 mg ± 1 mg of PSS-TSC phase were weighed. 50 ml of ~ 2.0 ppm metal ion were then added and the flask was shaken by an automatic shaker for 1-hour. This mixture was filtered through filter paper in a 100 ml measuring flask and washed with 10 ml DDW. The volume of the metal ion was completed to the 50 ml mark by using 5% hydrochloric acid solution. A standard solution of the metal ion was prepared by mixing 10 ml of the 1.0 ppm metal ion solution and 10 ml of DDW. The volume of this metal ion was completed to 50 ml in a measuring flask by 5% HCl solution. A blank solution was also prepared from 20 ml DDW and 30 ml of 5% HCl solution. The concentration of metal ions in the sample, standard and the blank solutions were determined by atomic absorption analysis. (14,16,17)

2.4.7. Applications of PSS-TSC for selective removal and extraction of some heavy metal ions from real drinking tap water and industrial water samples

The following water samples were collected from Damanhour Drug Factory, Extracted Oil Company (Damanhour factory), Industrial wastewater from Basin of Lake Maryout and Damanhour drinking tap water, and used to conduct this study:

2.4.7.1. Damanhour Drug Factory:

Industrial wastewater samples spiked with Pb (II), Ni (II) and Cu (II) were subjected to flame atomic absorption analysis. The chosen sample was prepared from ~ 1.0 ppm of Pb (II) and Cu (II) in 1.0 liter to study the suitability of application of PSS-TSC for selective removal and preconcentration of these metal ions.

2.4.7.2. Extracted Oil Company (Damanhour factory) Industrial wastewater

samples spiked with Pb (II), Ni (II), Cu (II), Cd (II) and Mn (II) were subjected to flame atomic absorption analysis. The chosen sample was prepared from ~ 1.0 ppm of Cu (II) and Ni (II) in 1.0 liter to study the suitability of application of PSS-TSC for selective isolation and preconcentration of these metal ions.

2.4.7.3. Industrial wastewater from Basin of Lake Maryout

1. Preparation of sample solution

Dry sediment was homogenized in its container, and an aliquot was dried and homogenized to a fine powder. In a Teflon reaction vessel 3 ml of HNO_3 are added. The vessel is heated in an oven (130 ^{0}C) for **24** hrs. **2** ml of hydrofluoric acid (HF) were added and the reaction vessel is heated again for 4 hrs. Boric acid 17 ml (5 %) were added and the reaction vessel is heated again for **24** hrs. Sample was then diluted to a final volume of **2**5 ml and transferred to 50 ml polystyrene bottle for storage until analysis.(18)

2. Application of Lake Maryout

Industrial wastewater sample was spiked with Pb (II), Ni (II), Cu (II), Cd (II), Hg (II) and Mn (II) prepared from ~ 1.0 ppm in 1.0 liter to study the suitability of application of PSS-TSC for selective removal and preconcentration of these metal ions followed by flame atomic absorption to this sample.

2.4.7.4. Damanhour drinking tap water

This samples were spiked with Cd (II), Pb (II), and Cu(II) followed by flame atomic absorption analysis study. The chosen sample was prepared from ~ 1.0 ppm of Cd (II), and Pb (II) in 1.0 liter to study the suitability of application of PSS-TSC for selective removal and preconcentration of these metal ions.

The extraction procedure of these metal ions from the selected water sample was accomplished by running the prepared solution over a column packed with 100 mg of PSS-TSC phase with a flow rate of 1 ml min^{-1}. The effluent solution was collected and acidified with hydrochloric acid and subjected for atomic absorption spectrophotometric analysis of the free unextracted metal ion by PSS-TSC phase. The water sample was subjected to atomic absorption spectrophotometric analysis for each specific metal ion before ruining over the tested column. A blank sample was also measured by atomic absorption spectrophotometric analysis for the direct comparison.

2.4.8. General procedure for the selective pre-concentration of some heavy metal from water samples

Pre-concentration of the metal ion(s) was performed according to this procedure. 1.0 liter sample of DDW was spiked with (~5.0 ppb) of selected metal ion. The metal ion solution was passed over a micro column packed with 100 mg of PSS-TSC phase with a flow rate of (~10.0 mL min^{-1}) under air pressure. The adsorbed metal ion(s) on PSS-TSC surface was desorbed by the flow of 5.0 mL of analar concentrated HNO_3 collected, and determined by atomic absorption analysis. (16, 18-1)

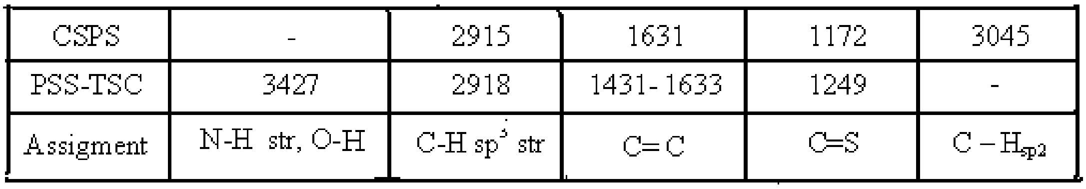
3. Results and Discussion

The modified polystyrene-sulfonyl- thiosemicarbazide (PSS-TSC is air stable and insoluble in most organic non – polar or weakly polar solvents and water, but slightly soluble in DMSO & DMF. The chlorosulphonated polystyrene (CSPS) and PSS-TSC are prepared and characterized by different techniques as IR, 1H-NMR spectroscopy and Elemental analysis.

3.1 IR spectra

The prepared chlorosulphonated polystyrene (CSPS) was characterized by the absorption at **2**915 cm^{-1} is attributed to C-H stretching vibration, while absorptions at 1450 – 163**2** are due to aromatic C=C. The infrared spectrum of PSS-TSC shown in table (4). The band at 347is due to NH stretching vibration of polystyrene-sulfonated- thiosemicarbazide (PSS-TSC). The band at **2**918 is assigned to C-H stretching, while the absorption band at 143 -1633 is due to the skeletal vibration of benzene ring for PSS-TSC. The bands of C=S for chlorosulfonated, polystyrene (CSPS) and PSS-TSC, appeared at 117**2** and 1**2**49 respectivel**2**y.

Table 4: IR bands assignments for CSPS and PSS-TSC



CSPS	-	2915	1631	1172	3045
PSS-TSC	3427	2918	1431-1633	1249	-
Assigment	N-H str, O-H	C-H sp^3 str	C=C	C=S	$C-H_{sp2}$

3.2 NMR spectra

^{1}HNR spectra for PS, CSPS and PSS-TSC are showed tables (5-7) respectively. The integration confirmed that 100 % substitution in case of CSPS as shown in table 6, and this attributed to SO_2Cl group. Table (7) show that the substitution for ligand resulted from the reaction between TSC and CSPS occurs completely, and also show that NH & NH_2 disappears after addition of D_2O.

Table 5: ^{1}H – NMR spectrum for polystyrene (PS)

Chemical shift	No. of protons	Multiplicity	Assignment
6.54 – 7.16 ppm	5H	m	Aromatic
1.2 – 1.8 ppm	3H	m	CH&CH$_2$Aliphatic

Table 6: ^{1}H- NMR spectra of CSPS

Chemical shift (ppm)	No. of protons	Multiplicity	Assignment
6.5 – 7.38	4H	m	Aromatic
1.1 – 1.67	3H	m	CH& CH$_2$Aliphatic

Table 7: ^{1}H – NMR spectra of PSS-TSC

Chemical shift (ppm)	No. of protons	Multiplicity	Assignment
8.67	2H	m	NH &NH exchangeable
6.9 – 7.35	2H& 4H	m	NHExchangeable& Aromatic
1.2 – 1.78	3H	m	CH&CHAliphatic

3.3 Elemental analysis

Table (8) shows the analytical data for prepared PSS-TSC . From the table, it was found that Chlorosulfonation of the polystyrene was successfully occurred. Also can be seen that the chloride was completely substituted with ligands. Elemental analysis data, it was found thatfrom the elememtal analysis datd and ^{1}H-NMR that chlorosulfonation occurred completely.

Table 8: Elemental Analysis of CSPS and PSS - TSC

Compound		Elemental analysis (%)					Chemical Analysis (%)
		%C	%H	%S	%N	%Cl	%Cl
CSPS	Th.	17.53	17.53	-	15.8	3.45	47.4
	Exp.	17.42	17.31	-	15.4	3.7	47.1
PSS-TSC	Th.	42.0	4.28	16.3	24.9	0.00	0.00
	Exp.	41.6	4.17	15,9	24,6	0.03	0.00

3.4 Stability of PSS-TSC phase in different buffer solutions

The stability of PSS-TSC was studied in different acidic standard pH solutions (pH 1-7) to identify the possible degree of leaching or hydrolysis of the organic chelating modifier (TSC) from the surface of modified polystyrene phase. The hydrolyzed PSS-TSC phase was then used to determine the µmol g^{-1} of Hg (II), which was found to exhibit the maximum metal uptake value within all the tested metal ions. The values of determined µmol g^{-1} for the hydrolyzed PSS-TSC phase were compared with those of the unhydrolyzed PSS-TSC phase to calculate the percentage values of stability for PSS-TSC phase in the tested solutions.(16, 22) Table (9) shows the results obtained for stability towards hydrolysis and leaching process of PSS-TSC phase. It is evident from the data given in Table (9) that the newly modified PSS-TSC is highly stable in most **Where Th: Theoretical calculated, and Exp: Experimental found that**
solutions at pH 5 and 6 with a percentage stability of 98 % while in the other buffer
solutions at pH 1, , 3, 4 and 7, the percent stability values were found to be 87.15 %,
91.8**2** %, 94.1%, 94.1 % and 91.8**2** % respectively**.**

Table 9: Percentage Stability of PSS-TSC phase

Phase / pH	1.0	.0	3.0	4.0	5.0	6.0	7.0
PSS-TSC % Stability (µmol g^{-1})	1486.4 (87.15 %)	1566 (91.8 %)	1605.9 (94.1 %)	1605.9 (94.1 %)	1685.5 ((98%)	1685.5 (98%)	1566 (91.8 %)

3.5 Metal Capacity values of PSS-TSC phase.

3.5.1. Effect of the pH-value on the metal capacity of PSS-TSC.

Figure1 shows the determined metal capacity values for binding with each metal ion, expressed in µmol g^{-1} in buffer solutions with pH 1-7. It is evident from the data given in Figure 1 for PSS-TSC phase that Hg (II) and Pb (II) are the highest extracted metal ions in buffer solutions at pH 7.0. The maximum metal capacity value of Hg (II) was found to be 1705.4 µmol g^{-1}as the highest extracted metal ion. For Pb (II), the maximum metal capacity value determined for PSS-TSC phase was found to 1655.7 µmol g^{-1} at pH .0. The metal capacity values for Mn (II), Ni (II), Cu (II), Cd (II), Hg (II) and Pb (II) by PSS-TSC phase at pH 7 were found to be in the following order: Hg (II) > Pb (II) > Cu (II) > Ni (II) > Cd (II) > Mn (II).

Generally, in strong acidic media, two possibilities are probably occurred:

1. The polymer could be subjected to hydrolysis.
2. The polymer could be protonated.

These two lead to lower possibility for the interaction with the metal ions. This explains the lower value for metal capacity at lower pH 's (strong acidic media)(23-28}

3.5.2 Effect of shaking time on the metal capacity values determined by the batch equilibrium technique

The effect of shaking time is the second most important factor when the batch or static technique is used in the processes of determination of the metal capacity values by PSS-TSC. Six metal ions, Hg (II), Cu (II), Pb (II), Cd (II), Mn (II) and Ni (II), were selected to perform the effect of shaking time (5, 10, **20**, 30, 60 and 1**2**0 minutes) on the metal capacity values of these metal ions and this study is represented by Figures 1-3. pH 7.

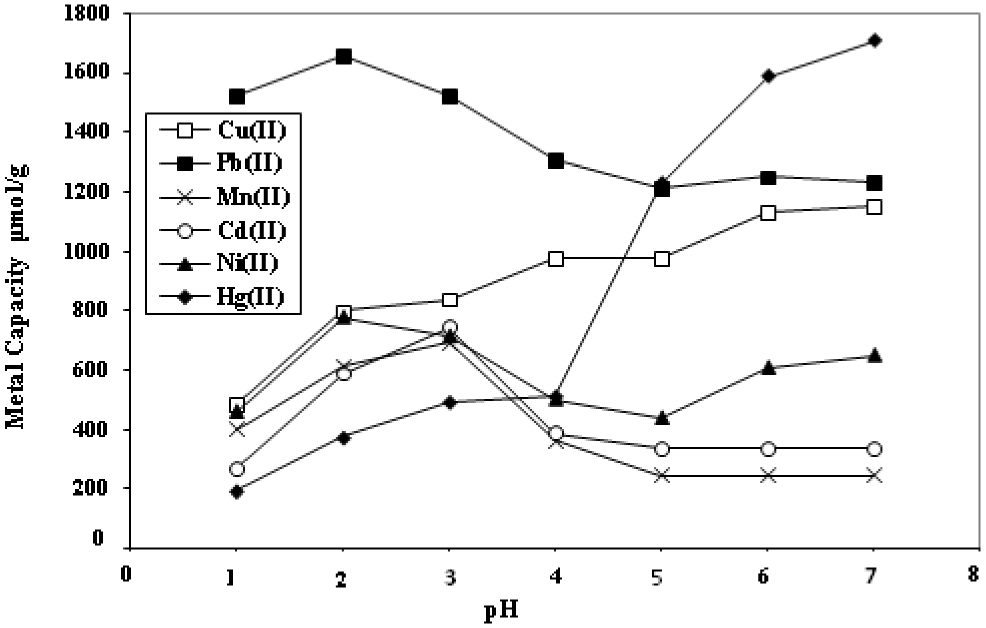


Figure (1): The effect of pH on the metal capacity values for PSS-TSC

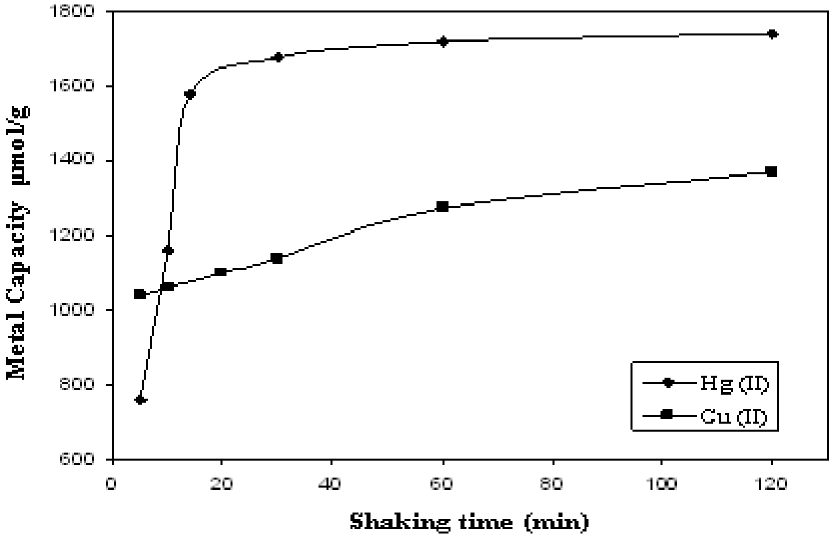


Figure (2): Effect of shaking time (min) for Hg (II) and Cu (II) ions by PSS-TSC phase at pH 7.

Figure **2** shows the effect of shaking time for Hg (II) and Cu (II) ions by PSS-TSC at pH 7.

It was found that the metal capacity increases with shaking time up to 30 min

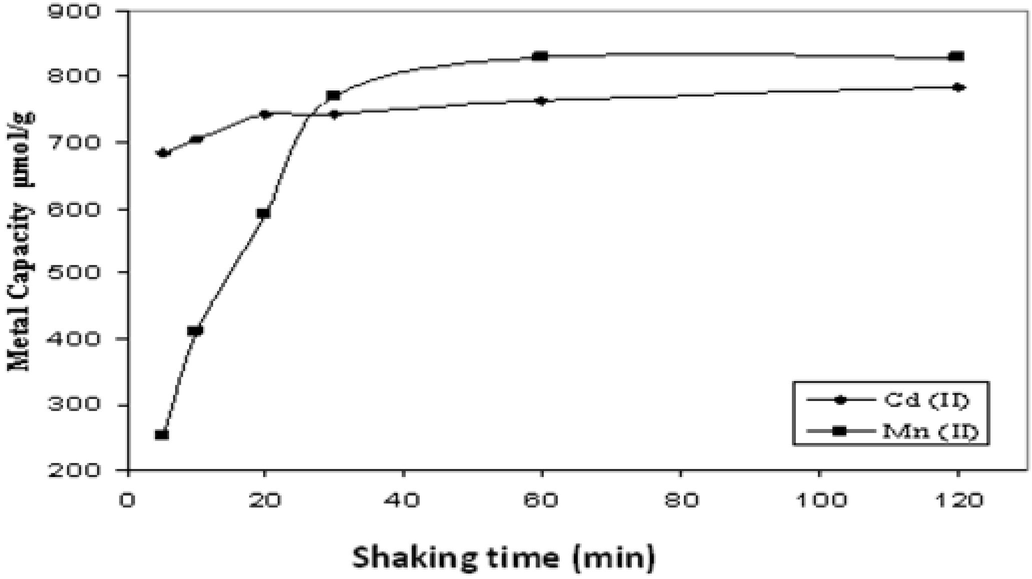


Figure (3) : Effect of shaking time (min.) for Cd(II) and Mn(II) ions by PSS-TSC at pH 3.

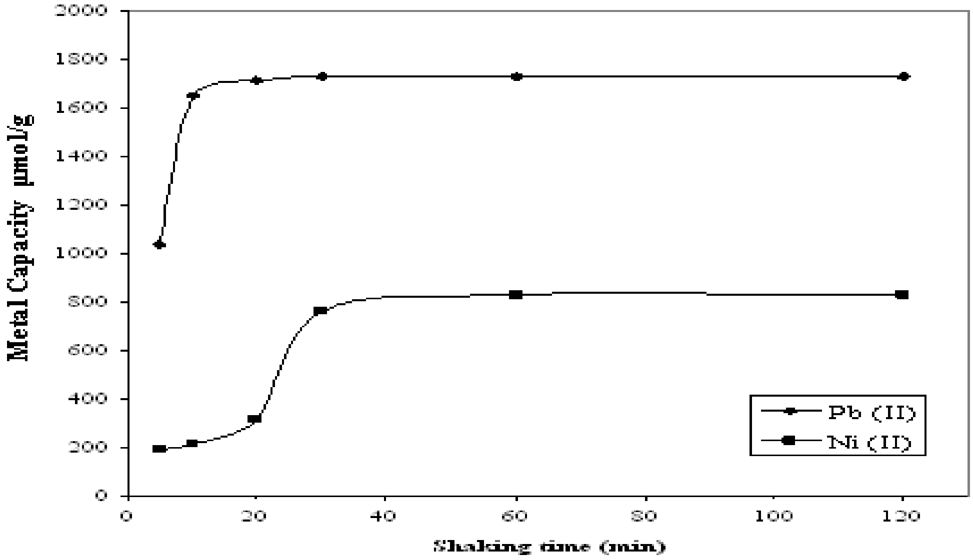


Figure (4): Effect of shaking time (min) for Pb (II) and Ni (II) ions by PSS-TSC phase at pH 2.

for Hg (II). The metal capacity value after 5 min was 45%. Increasing the shaking time from 30 to 120 min results in nearly a constant plateau. It can be seen that the metal capacity of Cu (II) increases with shaking time from 5 up to 120 min. The metal capacity was found to be 75% after 5 min, whereas the value was 92% after 60 min.

The effect of shaking time for Cd (II) and Mn (II) by PSS-TSC at pH 3.0 was shown in figure 9. It was found that the metal capacity increases with shaking time up to 30 min for Cd (II), the increasing was very small. The metal capacity after 5 min was 92%. For Mn (II) it can be seen that, the metal capacity increases with shaking time up to 30 min. Increasing the shaking time from 30 to 120 min results in a constant plateau. The metal capacity after 5 min was 33%.

3.6 Distribution coefficient values of metal ions by PSS-TSC phase

Evaluation of the metal binding properties is considered more convenient by the distribution coefficient (K_d) (18,20,24,29-31) when the possible concentrations of the tested metal ions are very low especially in the range of part per million (ppm) or part per billion (ppb).

The K_d -value is determined from the following equation:

$$K_d = \frac{\text{mmol of extracted metal ion / g – modified polystyrene phase}}{\text{mmol of unextracted metal ion / volume of solution}}$$

The distribution coefficient values for PSS-TSC are given in figure 11. It evident that surface modification of polystyrene phase with TSC as an organic chelating modifier has led to change the chemical properties of polystyrene surface toward binding and extraction of certain metal ions. It is clear from figure 11 that the order of metal ions extraction was as follows: Pb (II) > Hg (II) >Ni (II) > Mn (II) > Cd (II) > Cu (II) by PSS-TSC phase based on its K_d values.

This conclusion can be confirmed by evaluation of the separation factors for these tested metal ions

3.7 Separation factors of selected metal ions by PSS-TSC phase

The separation factor(32,33) is one of the key points in the evaluation process of selective solid phase extraction of target metal ions from other interfering ions. The separation factor ($\alpha_{A/B}$) of any two cations A and B is calculated from the distribution coefficient values K_d (A) and K_d (B), respectively as given in the following equation:

$$\alpha_{A/B} = \frac{K_d(A)}{K_d(B)}$$

The separation factor αA/B for Pb(II) versus other tested metal ions by PSS-TSC was shown and represented in figure 12. It is clear from the data given in Figure 12 that Pb (II) can be selectively extracted from other interfering metal ions as Hg (II), Ni (II), Cd (II), Mn (II) and Cu (II). Cu (II) can be selectively extracted from other interfering metal ions except Pb (II). Possible interference of some metal ions as Mn (II), Hg (II) and Ni (II), due to the low calculated separation factors for Pb (II) versus these three metal ions.

3.8 Effect of recyclability on adsorption of metal ions

The metallated resin used can be brought back to its original state by desorbing the metal ions using (6 M HCl) in tetrahydrofuran. The metal-free polymer can be reused after neutralization

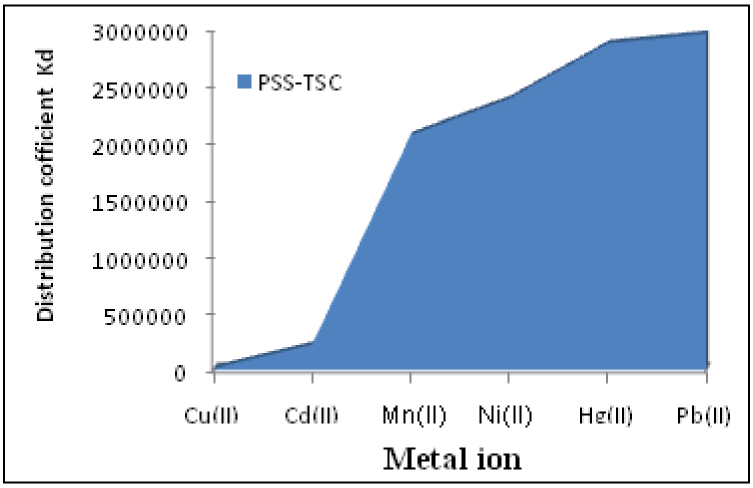


Figure 5: Distribution Coeficient of PSS-TSC

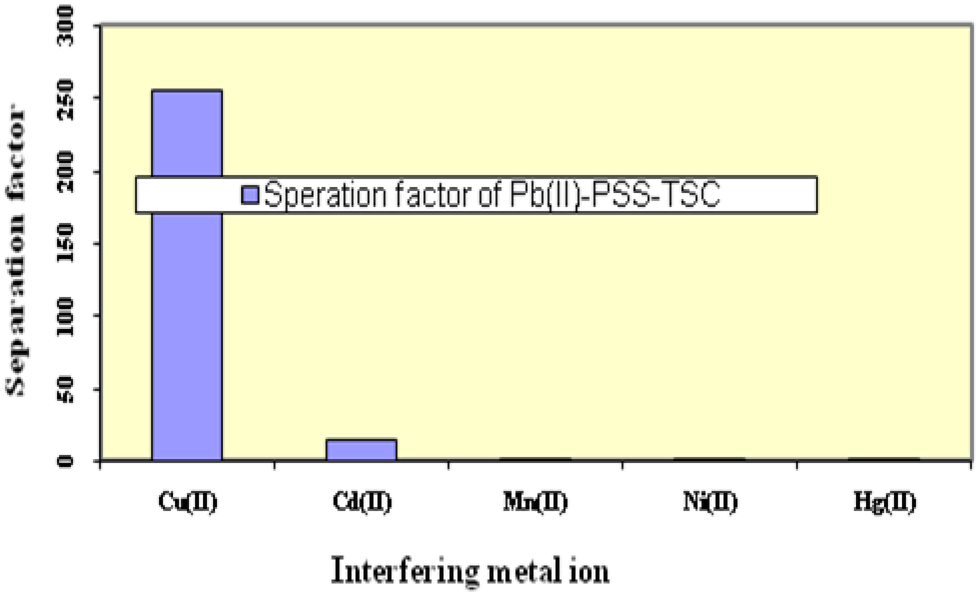


Figure (6) : The separation factors of Pb(II) versus other interfering metal ions by PSS-TSC

For every cycle the metal ion uptake and percentage desorption were studied. The metal ion uptake efficiency is found to be almost the same, even after five cycles using PSS-TSC phase.

3.9 Selective solid phase extraction and removal of heavy metal from water samples by PSS-TSC phase

Selective solid phase extraction and preconcentration of heavy metal ions from real samples is another dimension for application of newly modified polystyrene phase (PSS-TSC). (34,35) The preconcentration technique, also known as enrichment, is a generic term for the various processes employed to increase the ratio of determined analyte to the matrix. In the preconcentration procedures, the ratio of the trace amount of desired analyte to that of the original matrix is usually converted into a new matrix suitable for analytical determination and evaluation.

Preconcentration of trace concentration levels of heavy metal ions is an essential step for the sake of increasing the concentration of the target metal ions in order to improve the sensitivity of the instrumentation used, atomic absorption (AA), to meet and match with the linear dynamic range assigned for each metal ion by the atomic absorption. In addition, preconcentration, increases the sensitivity by several orders of magnitude, enhances the accuracy of the results, offers high degree of selectivity and facilitates calibration.(36,37) The percentage concentration of metal ions on ion-exchanger at equilibrium, $C_{M,eqm}\%$ using one stage separation is given by the following equation:

$$C_{M,eqm}\% = \frac{K_d \cdot m_{i,ex} * 100}{K_d \cdot m_{i,ex} + V_{ml}}$$

Where, m $_{i,\ ex}$ is the mass of ion-exchanger, and V_{ml} is the volume of solution, cm^3.

Table 10 summarizes the results of selective metal extraction and removal of heavy metal ions as Pb (II) and Cu (II) from wastewater of Damanhour drug factory by PSS-TSC.

Table 10: Selective solid phase extraction and removal of heavy metal ions from wastewater of Damanhour drug factory

Modified polystyrene Phase	Sample volume	Metal ion	mg l^{-1} spiked	mg l^{-1} Detected	Percent Extraction
100-mg (PSS--TSC)	1.0L	Cu (II)	2.1167	0.1135	94.6 ±2 %
		Pb(II)	1.9561	0.0025	99.9 ±2 %

PSS-TSC. It evident from the percentage extraction values given in Table 10 that an excellent extraction of Cu (II) and Pb (II) by PSS-TSC was achieved with percentage recovery values of 94.6 % and 99.9 % respectively.

Table 11 summarizes the application results of selective solid phase technique for metal extraction and removal via PSS-TSC based on micro-column separation. It is evident from the values given in table 11 that PSS-TSC provided excellent selective extraction results for the tested heavy metal ions from water samples giving percentage extraction values of 92.8 and 97.7 % for Cu (II) and Ni (II), respectively.

Table 11: Micro-column application for selective heavy metal extraction and removal from Extracted oil company (Damanhour factory) industrial waste water samples by PSS-TSC

Modified polystyrene Phase	Sample volume	Metal ion	mg l^{-1} spiked	mg l^{-1} Detected	Percent Extraction
100-mg (PSS--TSC)	1.0L	Cu (II)	1.8728	0.1352	92.8 ±2 %
		Ni (II)	1.918	0.0432	97.7 ± 2 %

Table 12 summarizes the results of selective metal extraction and removal by PSS-TSC via micro-column application. It is evident from the values given in Table 1 that PSS-TSC was superior in the processes of selective extraction of heavy metal ions from natural drinking tap water samples giving 99.5 and 94.3% recovery values for removal of Pb (II) and Cd (II) respectively.

Table 12: Micro-column application for selective metal extraction and removal from Damanhour drinking tap water by PSS-TSC

Modified polystyrene Phase	Sample volume	Metal ion	mg l^{-1} spiked	mg l^{-1} Detected	Percent Extraction
100-mg (PSS--TSC)	1.0L	Cd(II)	1.553	0.007	99.5 ±2 %
		Pb(II)	1.4546	0.081	94.3 ± 2 %

Table 13: summarizes the application results of selective solid phase technique for metal extraction and removal via PSS-TSC phase based on micro-column separation. It is evident from the values given in Table 13 that the selective metal extraction for PSS-TSC were found to be in the following order: Hg (II) > Pb (II) > Mn (II) > Ni (II) > Cd (II) > Cu (II).

Table 13: Micro-column application for selective heavy metal extraction and removal from Extracted Maryout (5000 fadan) industrial wastewater samples by PSS-TSC

Modified polystyrene Phase	Sample volume	Metal ion	mg l^{-1} spiked	mg l^{-1} Detected	Percent Extraction
00-mg (PSS--TSC)	1.0L	Hg(II)	1.5324	0.0336	97.8 ±2 %
		Pb(II)	1.3564	0.0422	96.9 ±2 %
		Cu (II)	1.4356	0.2182	84.8 ±2%
		Mn(II)	1.2689	0.0835	93.4 ±2%
		Ni(II)	1.2985	0.0998	9.3 ±2 %
		Cd(II)	1.0235	0.1423	86 ±2 %

3.10 Selective solid phase extraction and preconcentration of selected metal ions by by PSS-TSC phase

Table 14 summarizes the results of selective metal extraction and removal by PSS-TSC phase via micro-column application using 5 ml conc. HNO_3 as a preconcentration reagent. The preconcentration factor is 00 one can conclude that

Table 14: Selective solid phase preconcentration of heavy metal from drinking tap water PSS-TSCphase

Modified polystyrene Phase	Sample volume	Metal ion	mg l^{-1} spiked	mg l^{-1} Detected	Percent Extraction
100-mg (PSS--TSC)	1.0L	Cu(II)	4.952	0.296	94 ±2 %

Excellent percentage recovery value of 94% was established for pre-concentration of Cu (II) by PSS-TSC phase.

4. Conclusions

This work studies the preparation of polystyrenesulfonyl-thiosemicarbazide (PSS-TSC). This polymer was characterized by IR, NMR, and elemental analysis. PSS-TSC was used for determination of metal capacity of Mn (II), Ni (II), Cu (II), Cd (II), Hg (II) and Pb (II) in wastewater. Also the effect of pH (1-7) and shaking times (5 – 10 min) on the metal capacity were studied. It was found that the metal capacity values by PSS-TSC phase at pH 7 follow the following order: Hg (II) > Pb (II) > Cu (II) > Ni (II) > Cd (II) > Mn (II). The efficiency of metal ions extraction by PSS-TSC phase was studied by the distribution coefficient and separation factor of different metals ions. Applications of PSS-TSC for extraction and removal of heavy metals ions from wastewater samples of Damanhour drug factory, Extracted oil company (Damanhour factory), Extracted Maryout (5000 fadan) and drinking tap water were studied by the prepared PSS-TSCphase.

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