

Synthesis and Characterization of Immobilized Thiolactic Ligand System for the Detoxification of Tannery Wastewater

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ABSTRACT

A porous solid polysiloxane immobilized thiosalicylic acid ligand system has been prepared by hydrolytic polycondensation of tetraethylorthosilicate with a mixture of 3-chloropropyltrimethoxysilane, methanol and sodium hydroxide as a catalyst, gelation formed after 40 min. The product formed was functionalized with excess ethylchloroacetate, triethylamine and immobilized with thiosalicylic acid. The immobilized ligand was characterized using FTIR, the spectrum showed characteristic absorption regions (cm^{-1}) at: 3384 (OH), 1587 to 1722 (C=C, C=O); 900 to 1038 (Si - O) respectively. SEM-EDX showed irregular particle sizes of the polysiloxane matrices with elemental composition (wt %): 3-CPPS; Si (50.45), O (25.02) and Cl (24.57). F - 3CPPS showed, O (58.68), Si (41.32); thiolactic (0.00 of S). The competitive sorption characteristic of the metal ions (Cr^{3+} , Fe^{3+} , Pb^{2+} , Cu^{2+} and Zn^{2+}) were studied using Microwave Plasma Atomic Emission Spectrophotometer (Agilent MPAES-4200). The immobilized thiolactic ligand exhibits high potential for the extraction of heavy metals in tannery wastewater at pH 6.0, this development would improve the treatment of tannery wastewater at a low cost; batch or column systems of extraction of metal could be employed. Thermodynamic range for the parameters with respect to Cr^{3+} , Fe^{3+} , Pb^{2+} , Cu^{2+} and Zn^{2+} yielded negative values for ΔG° , (Cu^{2+} - (8.650 to 11.962) to Fe^{2+} - (14.368 to 14.842) KJmol^{-1} ; positive values for ΔH° : Zn^{2+} (0.000) to Cu^{2+} (21.047) KJmol^{-1} and ΔS° : Zn^{2+} (47.421) to Fe^{3+} (245.869) $\text{Jmol}^{-1}\text{K}^{-1}$ respectively, indicating spontaneous, endothermic reactions and high degree of disorderliness with respect to metal ion binding capacity to the ligand system.

Key Words: tannery wastewater, detoxification, polysiloxane, thiosalicylic ligand, thermodynamic

1 Introduction

Leather industries play very important role in the economy of many countries, but also generates harmful wastes into water bodies [1,2,3]. During tanning alone about 300 kg of chemicals are added per ton of hides or skins [4] and requires large amount of water, about 35 L of water is consumed per kilogram of raw hide or skin processed, and an average of 35,000 L of wastewater is produced per ton of raw hide or skin [5]. Not more than 20% of the chemicals are absorbed by leather; the remainder flows out with the effluent [6]. Conventional methods used in the tannery wastewater treatments have limitations such as production of toxic sludge [7] and inability to remove heavy metals at trace

level. There is need for innovative technologies which require low maintenance, high energy efficiency, low cost and better operational techniques than the conventional methods, this prompted the use of polymeric modified surfaces with excellent thermal, mechanical and chemical stability properties such as polysiloxane functionalized or immobilized with ligands [8] have been employed as a recyclable extractants for heavy metals and in stationary phases in chromatographic techniques using simulated water but have not been tried on tannery wastewater. These immobilized ligand system could be synthesized directly by sol gel or by chemical modification of the prepared functionalized polysiloxane [8]. A variety of spectroscopic techniques such as Fourier Transform Infra-red (FTIR) [9], Nuclear Magnetic Resonance (NMR), Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray Analysis (EDX) [10,11], have been employed to study the ligand modified polysiloxane systems. This study described the synthesis and characterization of polysiloxane Immobilized thiolactic acid ligand system and its potential in the detoxification of tannery wastewater.

2 Location of the Study Area

Kano state covers an area extending between latitudes $12^{\circ} 40^1$ and $10^{\circ} 30^1$ and longitudes $7^{\circ} 40^1$ and $9^{\circ} 30^1$. Climate is tropical wet and dry with mean annual rainfall of 850 mm, and a population of 9.3 million, it is a flat city drained by the Jakara river and several streams (Niger river watershed) and River Challawa (Lake Chad watershed) all are severely polluted by urban and industrial effluents. Kumbotso local government is the area of study and it lies between latitudes $11^{\circ}50'S$ to $12^{\circ}N$ and longitude $8^{\circ}24'W$ to $8^{\circ}40'E$. It falls within the Kano State settlement zone bordering the south and west by Madobi Local Government Area, in the Northern west; Rimin-Gado, in the North by Gwale and East by Tarauni local government areas respectively [12,13].

3 Experimentals

3.1 Reagents and Materials

Tetraethylorthosilicate, 3-chloropropyltrimethoxysilane, thiolactic acid and methanol, where purchased from Sigma-Aldrich Chemical Company and used without further purification. Triethylamine, ethylchloroacetate, sodium hydroxide (LOBA Chemie). Diethyl ether (spectroscopic grade). Different pH values in the range of 2.0 – 9.0 were control using 0.1 Mol/dm³ HCl and NaOH (Carson 2000pH Model) respectively.

3.2 Synthesis of Polysiloxane Immobilized Thiolactic Acid Ligand System (PITLLS)

3-Chloropropylpolysiloxane (CPPS) was prepared by reacting tetraethylorthosilicate (0.1 mol, 20.8 g) with 3-chloropropyltrimethoxysilane (0.05 mol, 9.936 g) in the presence of methanol (35 cm³) in a solution of sodium hydroxide (NaOH, 0.42 mol/dm³, 4.95 cm³) [8], stirred for 5 min at 40 °C and pH 10 (Tricolour Universal pH Paper). Gelation formed after 40 min. CPPS was functionalized by refluxing with ethylchloroacetate (0.122 mol; 15 g) and triethylamine (10 cm³) for 12 h at 110 °C (RAYPA Digital Drying Oven) [9]. The functionalized product was measured (3.200 g) and modified using thiolactic acid (0.05 mol; density 1.196 g/cm³; volume 4.44 cm³) in ethylchloroacetate (0.244 mol; density 1.145 g/cm³; volume 26.20 cm³) and 5 cm³ of triethylamine in a round-bottomed flask (250 cm³) and refluxed for 12 h at 383 K, the product formed was filtered, washed successively with 50 cm³ portions of de-ionized water, methanol and diethyl ether, dried at 383 K in an oven for 10 h, labelled and dried over CaCl₂.

3.3 Digestion of Tannery Wastewater

Tannery wastewater sample of 1000 cm³ was transferred into a conical flask and evaporated till dried. The dried sample was digested in 10:1 HNO₃:HClO₄ (v/v). White crystals were found in the digested samples and were dissolved in 150 ml double distilled water. The supernatant were filtered using Whatman No.41 filter paper and was read directly with Agilent MPAES-4200 [14] for Cr³⁺, Fe³⁺, Pb²⁺, Cu²⁺ and Zn²⁺. The total metal contents were determined as described by [15]. No specific speciation was conducted to ascertain the various valencies of the species at the pH values of 2, 4, 6, 7 and 9 which were used in this study.

3.4 Effect of Adsorbent

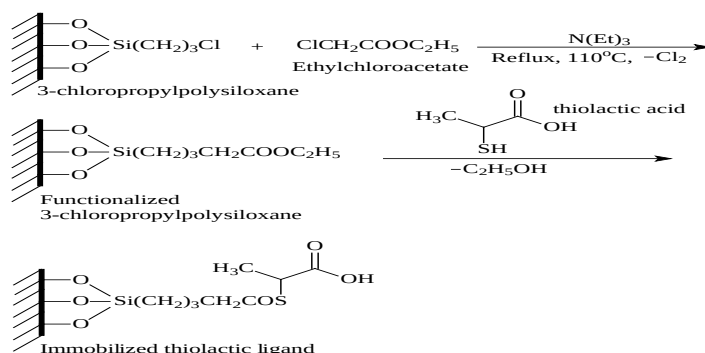
A volume of 60 cm³ solution of the tannery wastewater adjusted at pH 6 (optimum) was transferred into 150 cm³ conical flask and 10 mg of the polysiloxane immobilized thiolactic ligand was added and adjusted in a thermostatic multi-shaker (Gallenkamp Model) at 100 rpm for 2 h at 30 °C. The resultant solutions were filtered using Whatman No.41 and the residual metal concentrations analysed (Cr³⁺, Fe³⁺, Pb²⁺, Cu²⁺ and Zn²⁺) using Agilent MPAES-4200 [16,17,18]. This procedure was repeated for 20 and 30 mg of polysiloxane immobilized thiolactic ligand with mesh size of (125-150 µm) respectively.

3.5 Thermodynamic studies

A volume of 60 cm³ solution of the tannery wastewater adjusted at pH 6 (optimum) was transferred into 150 cm³ conical flask and 20 mg of the polysiloxane immobilized thiolactic ligand was added and adjusted in a thermostatic multi-shaker (Gallenkamp Model) at 100 rpm for 2 h at 30 °C. The resultant solutions were filtered using Whatman No.41 and the residual metal concentrations analysed (Cr³⁺, Fe³⁺, Pb²⁺, Cu²⁺ and Zn²⁺) using Agilent MPAES-4200 [16,18]. This procedure was repeated for temperatures of 35 and 40 °C respectively.

4 Results and Discussion

The leather industry contributes immensely in the generation of wastewater without proper treatment thereby contaminating or polluting the eco-system. Hence the use of PITLLS was employed to adsorbed heavy metals present in the wastewater. This was made possible due to the availability of reactive sites in the polysiloxane matrix (Scheme 1.0.), the protonation of COOH to COO⁻ by triethylamine, SH to S⁻, and the presence of oxy ions contributes to the adsorption of these heavy metals. The particle size of the PITLLS, FTIR spectrum, SEM/EDX were analysed followed by pH, adsorbent dose and temperature effects on the adsorption of selected heavy metals in tannery wastewater.



Scheme 1: Reaction scheme for the preparation of thiolactic acid ligand system

4.1 Results of SEM/EDX Analysis of Immobilized Thiolactic Acid Ligand System

SEM (EVO/LS10-ZEISS) showed irregular particle sizes of the following polysiloxane matrices at various magnifications (μm): 3-chloropropylpolysiloxane (500); functionalized 3-chloropropylpolysiloxane (500) and thiolactic immobilized ligand (200) in Plate 1.0., with the EDX (EVO/LS10-ZEISS). The morphology shows a rough surface with a pore volume of 113.9992 nm^3 in Table 1.0., which provides a better adsorption environment. EDX data of functionalized 3-CPP with immobilized thiolactic acid ligand gives 4.08 wt % of S (Table 2.0). This is in agreement with the suggested structure of the targeted system and is an indication of successful polymerization by nucleophilic displacement of a halide anion [19], which the sulphur atom was originally not on the polymer framework with 4.08 wt %, within the range of 4.30-11.30 wt % [20]; 3.90- 6.80 wt % [21] for similar synthesis. The value of 4.08 wt % was obtained because of the availability of reactive sites in Scheme 1.0., which assisted in the immobilization process, with particle size of $4.5384 \pm 1.8640 \text{ nm}$. This is in agreement with the nanoparticle sizes of silica in the range of 2–5 nm with an extraordinary surface-to-volume ratio [20], this particle size plays a vital role in adsorption of heavy metals in the tannery wastewater. The presence of thiol in the matrix is not in agreement with the FTIR results in which the thiol group was absent, this could be because of the functional group being blocked due to steric hindrance or core shelling as presented in Figure 1.0., but the silicone matrix was available (Si-O-Si) at 1038 cm^{-1} as illustrated in Scheme 1.0.

Table 1.0: Polysiloxane Immobilized Thiolactic Ligand Particle Size (nm)

	Area (nm)	Mean	Min	Max	r ²	r (nm)	d (nm)	v (nm ³)
Mean	18.8776	255	255	255	6.0089	2.2692	4.5384	113.9922
Standard Error	1.6084	0	0	0	0.5119	0.0956	0.1912	14.8413
Median	13.974	255	255	255	4.4480	2.1090	4.2180	58.9435
Mode	9.316	255	255	255	2.9653	1.7220	3.4440	32.0848
Standard Deviation	15.6773	0	0	0	4.9902	0.9320	1.8640	144.6556
Sample Variance	245.7777	0	0	0	24.9024	0.8686	3.4745	20925.25
Range	74.53	0	0	0	23.7236	3.8029	7.6058	783.7973
Minimum	4.658	255	255	255	1.4826	1.2176	2.4353	11.3436
Maximum	79.188	255	255	255	25.2063	5.0205	10.0411	795.141
Sum	1793.373	24225	24225	24225	570.8484	215.5777	431.1554	10829.26
Count	95	95	95	95	95	95	95	95
Confidence Level(95.0%)	3.1936	0	0	0	1.0165	0.1898	0.3797	29.4678

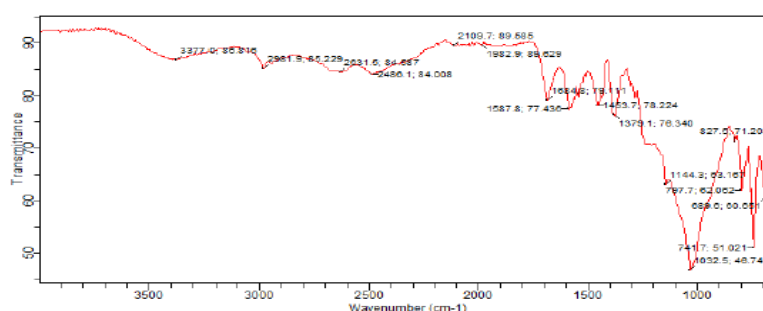
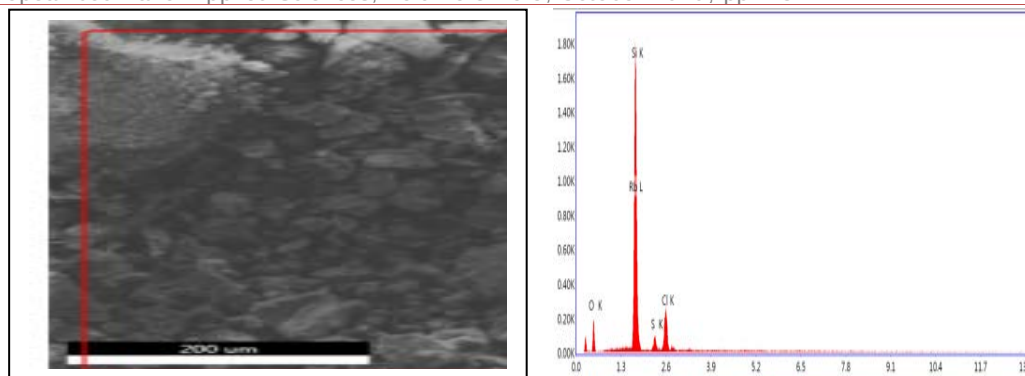


Figure 1: FTIR Spectrum for Thiolactic Immobilized Ligand



Plates 1: SEM/EDX, Morphology and Elemental Composition for Immobilized Thiolactic Ligand

Table 2: Elemental Composition of Polysiloxane, Functionalized and Immobilized Ligand Systems

Compounds	ELEMENTS				
	O (K)	Si (K)	Cl (K)	S (K)	Rb (L)
3-Chloropropylpolysiloxane (3CPP)	25.02	50.45	24.57	-	-
Functionalized 3CPP	58.68	41.32	-	-	-
Immobilized Thiolactic Ligand	20.18	36.09	13.61	4.08	18.04

Note: K, L and M Represent shells or orbitals. O (Oxygen); Si (Silicon); Cl (Chlorine); S (thiol); Rb (Rubidium)

4.2 Effect of pH

The leather industry contributes immensely to the generation of wastewater without proper treatment, thereby contaminating or polluting the eco-system [22,23]. Hence, the PITLLS was employed to adsorb heavy metals (Cr^{3+} , Fe^{3+} , Pb^{2+} , Cu^{2+} and Zn^{2+}) present in the wastewater. This was made possible due to the availability of reactive sites in the polysiloxane matrix in Scheme 1.0. The mechanism could be surface adsorption or chemisorption. The deprotonation of COOH to COO^- by triethylamine, SH , to S^- , and the presence of oxy-ions contributed to the adsorption of these heavy metals. The results for the effect of pH on the adsorption of the metals are presented in Table 3.0. There was a gradual increase in absorption from pH 2 to a maximum at pH 6 mostly, which was within the limit of 5.5–7.0 [23], recorded using aminopolysiloxane for similar adsorption studies [24]. Above pH 6, the removal efficiency decreased as the pH increased to pH 9, which promoted the precipitation of metal hydroxide in solution.

Table 3: Adsorption Equilibrium for Immobilized Thiolactic Acid Ligand System after Treatment of Tannery Wastewater

METAL	Conc.	2	4	pH 6	7	9
Cr (ppm)	Cia	17.112	14.854	10.952	5.897	3.693
	Cib	17.112	14.854	10.952	5.897	3.693
	Cfa	9.901	13.532	0.932	1.312	3.244
	Cfb	9.901	13.532	0.932	1.312	0.449
	%ADS	42.140	8.900	91.490	77.751	12.158
Fe (ppm)	Cia	4.442	1.619	0.328	0.732	0.272
	Cib	4.442	1.619	0.328	0.732	0.272
	Cfa	0.467	0.408	0.000	0.000	0.000
	Cfb	0.467	0.408	0.000	0.000	0.000
	%ADS	89.487	74.799	100.000	100.000	100.000
Pb (ppm)	Cia	2.852	1.940	1.609	1.484	0.418
	Cib	2.852	1.940	1.609	1.484	0.418

	Cfa	0.816	0.652	0.000	0.046	0.409
	Cfb	0.816	0.652	0.000	0.046	0.009
	%ADS	71.388	66.392	100.000	96.900	2.153
Cu (ppm)	Cia	0.811	0.480	0.404	0.426	0.153
	Cib	0.649	0.318	0.242	0.264	0.009
	Cfa	0.409	0.233	0.036	0.102	0.205
	Cfb	0.247	0.071	-0.126	-0.060	0.043
	rCfb	0.247	0.071	0.000	0.000	0.043
	%ADS	61.941	77.673	100.000	100.000	94.117
	Cia	0.177	0.020	0.051	0.039	-0.003
Zn (ppm)	Cib	0.177	0.020	0.051	0.039	-0.003
	Cfa	0.134	0.012	0.000	0.000	0.000
	Cfb	0.134	0.008	0.000	0.000	0.000
	%ADS	24.294	40.000	100.000	100.000	

Note: Cia =Initial sample result before subtraction, Cib= Initial sample result after subtraction Cfa= Final sample result before subtraction, Cfb= Final sample result after subtraction, %ADS= Percentage adsorption

4.3 Effect of Thiolactic Immobilized Ligand Dose on the Adsorption of Heavy Metals

The results in Table 4.0., shows that increase in adsorbent dose from 20-30 mg/60 cm³ increased the adsorption of metal ion in the solution due to large availability of the surface area at higher concentration of the adsorbent in thiolactic with respect to Cr³⁺. Increase in the adsorbent dose from 10-30 mg/ 60 cm³ had no significant effect on the adsorption of Fe³⁺ and Zn²⁺ metal ion in the solution because any further addition of the adsorbent beyond this did not cause any significant change in the adsorption due to overlapping adsorption sites of the adsorbent particles, discrepancy was recorded with respect to Pb²⁺, and Cu²⁺ showed significant adsorption at 10 mg/60 cm³ and remained constant from 20-30 mg/cm³ due to complete overlapping of adsorption sites.

Table 4: Effect of Adsorbent Dosage (PITLLS) on the Adsorption of Heavy Metals after Digestion of Tannery Wastewater

METAL	Conc.	Adsorbent (mg)		
		10	20	30
Cr (ppm)	Cia	10.952	10.952	10.952
	Cib	10.952	10.952	10.952
	Cfa	0.932	0.168	0.106
	Cfb	0.932	0.168	0.106
	%ADS	91.490	98.466	99.032
Fe (ppm)	Cia	0.328	0.328	0.328
	Cib	0.328	0.328	0.328
	Cfa	-0.076	-0.460	-0.959
	Cfb	0.000	0.000	0.000
	%ADS	100.000	100.000	100.000
Pb (ppm)	Cia	1.609	1.609	1.609
	Cib	1.609	1.609	1.609
	Cfa	-0.074	0.456	0.288
	Cfb	0.000	0.456	0.288
	%ADS	100.000	71.659	82.101
Cu (ppm)	Cia	0.404	0.404	0.404
	Cib	0.242	0.242	0.242
	Cfa	0.036	-0.037	-0.123
	Cfb	0.036	0.000	0.000
	%ADS	85.124	100.000	100.000
Zn (ppm)	Cia	0.039	0.039	0.039
	Cib	0.039	0.039	0.039
	Cfa	-0.012	-0.052	-0.069
	Cfb	0.000	0.000	0.000
	%ADS	100.000	100.000	100.000

Note: rC_{oi} = relative initial concentration; rC_{ef} = relative final concentration, %ADS = percentage adsorption

4.4 Thermodynamic Study of PITLLS

The distribution coefficients (K_D) for the extraction and percentage adsorption (% ADS) of Cr^{3+} , Fe^{3+} , Pb^{2+} , Cu^{2+} and Zn^{2+} metal ions from solutions of tannery wastewater by Polysiloxane immobilized thiolactic ligand system was studied at different temperatures of 303, 308 and 313 K in Table 5.0. The results for (K_D) and (% ADS) ranged from: Cr^{3+} 287.837 to 296.850; Pb^{2+} 226.165 to 286.202; Cu^{2+} 30.992 to 99.174 and % ADS for Cr^{3+} 96 to 99; Pb^{2+} 75 to 95; Cu^{2+} 77 to 100 respectively. This showed that, the distribution coefficients K_D and % ADS increased with increase in temperature because the rate of adsorbate diffusion across the external boundary layer and in the internal pores of the adsorbate particles increases with increase in temperature with a resultant decrease in liquid viscosity while Fe^{3+} and Zn^{2+} showed no significant change with increase in temperature. In order to determine the thermodynamic feasibility and the thermal effects of sorption, the thermodynamic parameters were evaluated using $\Delta G^\circ = -RT \ln K_D$ and $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$, where ΔG° , ΔH° , ΔS° and T are Gibbs free energy, enthalpy, entropy and absolute temperature respectively [8,25]. R is the gas constant ($8.314 \text{ Jmol}^{-1}\text{K}^{-1}$) and K_D is the equilibrium constant. Plots of $\ln K_D$ against $1/T$ gave the numerical values of ΔH° and ΔS° from slope and intercept respectively [26]. The values of ΔG° , ΔH° and ΔS° are given for Cr^{3+} , Fe^{3+} , Pb^{2+} , Cu^{2+} and Zn^{2+} in Table 5.0. The negative values of the Gibbs free energy ΔG° for all temperatures with reasonable affinity for Polysiloxane immobilized Thiolactic ligand system towards Cr^{3+} , Fe^{3+} , Pb^{2+} , Cu^{2+} and Zn^{2+} , suggests spontaneity of the adsorption process which does not required an external energy source for the system. The values for ΔG° ranged from (Cr^{3+} -14.264 to -14.815; Fe^{3+} - 14.368 to -14.843; Pb^{2+} -13.656 to -14.720; Cu^{2+} -8.650 to -11.962 and Zn^{2+} -14.367 to -14.843 kJmol^{-1}). Consequently, ΔG° of -15 kJ/mol are connected with physical interaction between adsorption sites and metal ions which was observed in this work to be less, whereas -30 kJ/mol involves charge transfer from adsorbent surface to the metal ion to form a coordination bond this is a total deviation from the results obtained in this work. The positive values: ΔH° (Cr^{3+} 2.444; Fe^{3+} 60.324 Pb^{2+} 18.640; Cu^{2+} 21.047 and Zn^{2+} 0.000 kJmol^{-1}), suggest variation of enthalpies accompanying sorption of metal ions on the Polysiloxane immobilized thiolactic ligand system (indicating an endothermic process) which is facilitated by higher temperatures. The positive entropy changes: ΔS° (Cr^{3+} 55.184; Fe^{3+} 245.869; Pb^{2+} 106,835; Cu^{2+} 114,958 and Zn^{2+} 47.421 $\text{Jmol}^{-1}\text{K}^{-1}$) is characterized by irregular increase in the randomness at the composite material -solution interface during adsorption procedure of the system [27]. The results above are characterized by chemisorption process, favoured at higher temperatures. The thermodynamic parameters considered are in agreement with the work of [28].

Table 5: Adsorption Thermodynamics of Metal ions Chemisorbed by PITLLS

METAL ION	T (K)	q_e (mg/g)	K_D (L/g)	$\ln K_D$	ΔG° (KJ/mol)	ΔH° (KJ/mol)	ΔS° (J/molK)	Rel.Ci (ppm)	Rel.Cr (ppm)	Cd	% ADS
Cr^{3+}	303.00	3152.40	287.837	5.662	-14.264	2.443	55.184	10.952	0.444	10.508	96
	308.00	3251.10	296.849	5.693	-14.578			10.952	0.115	10.837	99
	313.00	3251.10	296.849	5.691	-14.815			10.952	0.115	10.837	99
Fe^{2+}	303.00	81.60	300.000	5.703	-14.368	60.323	245.869	0.272	0.000	0.272	100
	308.00	81.60	300.000	5.703	-14.605			0.272	0.000	0.272	100
	313.00	81.60	300.000	5.703	-14.842			0.272	0.000	0.272	100
Pb^{2+}	303.00	363.900	226.165	5.421	-13.656	18.640	106.834	1.609	0.396	1.213	75
	308.00	448.50	278.744	5.630	-14.417			1.609	0.114	1.495	93
	313.00	460.50	286.202	5.656	-14.720			1.609	0.074	1.535	95
Cu^{2+}	303.00	7.50	30.991	3.433	-8.650	21.046	114.957	0.242	0.055	0.187	77
	308.00	21.00	86.77	4.463	-11.429			0.242	0.010	0.232	96
	313.00	24.00	99.173	4.596	-11.962			0.242	0.000	0.242	100

Zn ²⁺	303.00	11.70	300.000	5.703	-14.368			0.039	0.000	0.039	100
	308.00	11.70	300.000	5.703	-14.605	0.000	47.421	0.039	0.000	0.039	100
	313.00	11.70	300.000	5.703	-14.842			0.039	0.000	0.039	100

5 Conclusion

The PITLLS has been prepared by hydrolytic polycondensation of tetraethylorthosilicate with a mixture of 3- chloropropyltrimethoxysilane, methanol and sodium hydroxide as a catalyst. The instrumental analysis of FTIR, SEM and EDX confirmed that the ligand was chemically immobilized to the polysiloxane network. The PITLLS showed high potential for the extraction of Cr³⁺, Fe³⁺, Pb²⁺, Cu²⁺ and Zn²⁺ at an optimum pH of 6.0 in the tannery wastewater. This achievement could be employed in the treatment of tannery wastewaters in the industry. Extraction of metal ions increased with the increase in the adsorbent dose and temperature respectively. The thermodynamic parameters suggest a spontaneous and an endothermic affinity of the chelating ligand. The complex formation process is favoured at higher temperatures. The distribution coefficient values increased with increasing temperature indicating that the complex formation process of metal ions Cr³⁺, Fe³⁺, Pb²⁺, Cu²⁺ and Zn²⁺ with polysiloxane immobilized thiosalicylic ligand System was accompanied by an absorption of heat.

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