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Immobilized Thiosalicylic Ligand System Potentials for the Detoxification of Some Heavy Metals from Tannery Wastewater

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Abstract: Polysiloxanes are characterized by silicon and oxygen backbone and are hydrophobic in nature with low moisture uptake widely used for medical applications. Polysiloxane immobilized thiosalicylic acid ligand system has been prepared through sol-gel method, gelation was observed after 40 minutes. The immobilized ligand was characterized using FTIR, the spectrum showed characteristic absorption bands (cm^{-1}) at: 3377 (OH), 2981 (C-H stretch); 2631 (SH); 1587 to 1684 (C=C, C=O); 1032 to 1144 (Si - O) respectively. SEM analysis showed irregular particle sizes of the polysiloxane matrices while EDX elemental composition gave (wt %): 3-CPPS; Si (50.45), O (25.02) and Cl (24.57). F - 3CPPS showed, O (58.68), Si (41.32); thiosalicylic (7.14 of S). The extraction of metal ions (Cr^{3+}, Fe^{3+}, Pb^{2+}, Cu^{2+} and Zn^{2+}) were studied using Microwave Plasma Atomic Emission Spectrophotometer (Agilent MPAES-4200) at pH 6.0. Thermodynamic range with respect to Cr^{3+}, Fe^{3+}, Pb^{2+}, Cu^{2+} and Zn^{2+} yielded negative values forΔG^o: Cu^{2+}-(11.483 to 14.842) to Zn^{2+} -(14.368 to 14.842)$KJmol^{-1}$; positive values for ΔH^o: Fe^{3+} (0.000) to Pb^{2+} (105.130)$KJmol^{-1}$ and ΔS^o: Zn^{2+} (47.421) to Pb^{2+} (389.328)$Jmol^1K^1$ respectively, indicating spontaneous, endothermic reactions and high degree of disorderliness with respect to metal ion binding capacity to the ligand system.

Keywords: Tannery Wastewater, Detoxification, Polysiloxane, Nanomers, Thiosalicylic Ligand

1. Introduction

Leather industry generates harmful wastes into water bodies [1]. During tanning alone about 300 kg of chemicals are added per ton of hides or skins with large volume of water and sludge generated [2, 3]. Not more than 20% of the chemicals are absorbed by leather; the remainder flows out with the effluent [4]. Conventional methods used have limitations such as production of toxic sludge [5] and inability to remove heavy metals at trace level, this prompted the use of polymeric modified surfaces with good thermal, mechanical and chemical stability properties such as polysiloxane immobilized with ligands [6] have been employed as a recyclable extractants for heavy metals. These immobilized ligand system could be synthesized directly by sol gel or by chemical modification of the prepared functionalized polysiloxane [6]. A variety of analytical techniques have been employed such as Fourier Transform

Infra-red (FTIR) [7, 8], Nuclear Magnetic Resonance (NMR), Scanning Electron Microscopy (SEM) [9, 10] and Energy Dispersive X-ray Analysis (EDX) [9, 10]. This study described the Immobilization of thiosalicylic acid ligand system and its potential in the purification of tannery wastewater.

2. Location of the Study Area

Kano state covers an area extending between latitudes 120° 40' and 100° 30' and longitudes 70° 40' and 90° 30'. 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°50'S to 12°N and longitude 8°24'W to 8°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 [11, 12].

3. Experimental

3.1. Preparation of Polysiloxane Immobilized Thiosalicylic Acid Ligand System (PITSLS)

The methods of [13, 8, 14], were adopted. 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 cm^3) in a solution of sodium hydroxide (NaOH, 0.42 mol/dm^3, 4.95 cm^3) [6], 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 cm^3) for 12 h at 110°C (RAYPA Digital Drying Oven) [7]. The functionalized product was measured (3.200 g) and modified using thiosalicylic acid (0.05 mol; density 1.49 g/cm^3; volume 7.959 g) in ethylchloroacetate (0.244 mol; density 1.145 g/cm^3; volume 26.20 cm^3) and 5 cm^3 of triethylamine in a round-bottomed flask (250 cm^3) and refluxed for 12 h at 383 K, the product formed was filtered, washed successively with 50 cm^3 portions of de-ionized water, methanol and diethyl ether, dried at 383 K in an oven for 10 h, labelled and dried over $CaCl_2$.

3.2. Digestion of Tannery Effluent

Tannery wastewater sample of 1000 cm^3 was transferred into a conical flask and evaporated till dried. The dried sample was digested in 10:1 HNO_3:$HClO_4$ (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 [15]. The total metal contents were determined as described by Parven *et al.,* [16]. No specific speciation was conducted to ascertain the various valencies of the species at the pH values of 2, 4, 6, 7 and 9 as used in this study.

3.3. Effect of Adsorbent

A volume of 60 cm^3 solution of the tannery wastewater adjusted at pH 6 (optimum) was transferred into 150 cm^3 conical flask and 10 mg of the polysiloxane immobilized thiosalicylic 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 (Cr^{3+}, Fe^{3+}, Pb^{2+}, Cu^{2+} and Zn^{2+}) using Agilent MPAES-4200 [17, 18, 19] This procedure was repeated for 20 and 30 mg of polysiloxane immobilized thiosalicylic ligand with mesh size of (125-150 μm) respectively.

3.4. Thermodynamic Studies

A volume of 60 cm^3 solution of the tannery wastewater adjusted at pH 6 (optimum) was transferred into 150 cm^3 conical flask and 20 mg of the polysiloxane immobilized thiosalicylic 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 (Cr^{3+}, Fe^{3+}, Pb^{2+}, Cu^{2+} and Zn^{2+}) using Agilent MPAES-4200. [17, 19, 20]. This procedure was repeated for temperatures of 35 and 40°C respectively.

4. Results and Discussion

PITSLS was employed to extract heavy metals in tannery wastewater due to the availability of reactive sites in the polysiloxane matrix (Figure 1.), the protonation of COOH to COO^- by triethylamine, SH to S^-, and the presence of oxy ions contributes to the removal of these heavy metals.

4.1. SEM/EDX Analysisof PITSLS

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 thiosalicylic immobilized ligand (200) in Figure 3, with the EDX (EVO/LS10-ZEISS). The morphology shows a rough surface with a pore volume of 52.9940 nm^3 in Table 1, which provides a better adsorption environment. EDX data of functionalized 3-CPP with immobilized thiosalicylic acid ligand gives 7.14 wt% of S (Table 2). 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 by Brad B [21], which the sulphur atom was originally not on the polymer framework with 7.14 wt %, within the range of 6.1-10.4 wt % reported by Issa M. E. [7]; 8.0 wt %, [6]; 4.30-11.30 wt % El-Nahhal I. M [22]; 3.90- 6.80 wt % [23] for similar synthesis. The value of 7.14 wt% was obtained because of the availability of reactive sites in Figure 3, which assisted in the immobilization process, with particle size of 3.4397 ± 1.5659 nm. This agreed with the nano-particle sizes of silica in the range of 2–5 nm with an extraordinary surface-to-volume ratio El-Nahhal I. M [22]. This particle size plays a vital role in adsorption of heavy metals in the tannery wastewater. This is in agreement with the suggested structure of the targeted system and is an indication of successful immobilization of the ligand in the polymer matrix as originally there was no sulphur atom on the polymer framework. The 7.14 wt % was. The presence of thiol in the matrix agrees with the FTIR results presented in Figure 1, as follows: thiol (SH, 2631cm^{-1}); silicone (Si-O-Si, 1032 cm^{-1}) Figure 2.

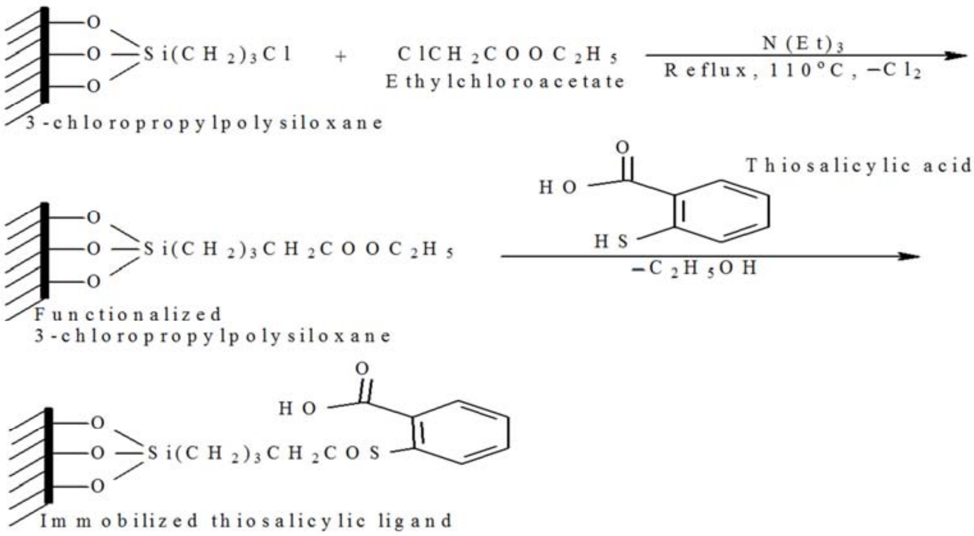


Figure 1. Preparation of thiosalicylic acid ligand system.

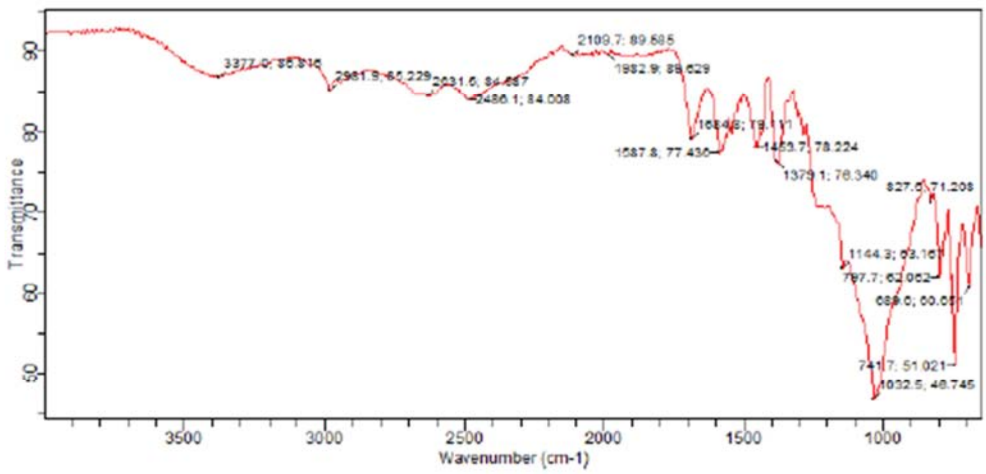
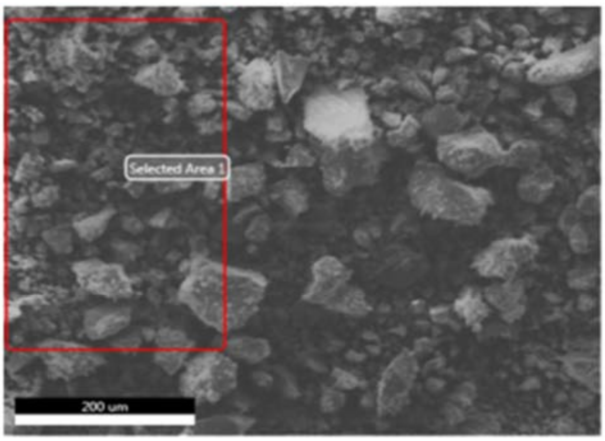


Figure 2. FTIR Spectrum for PITSLS.



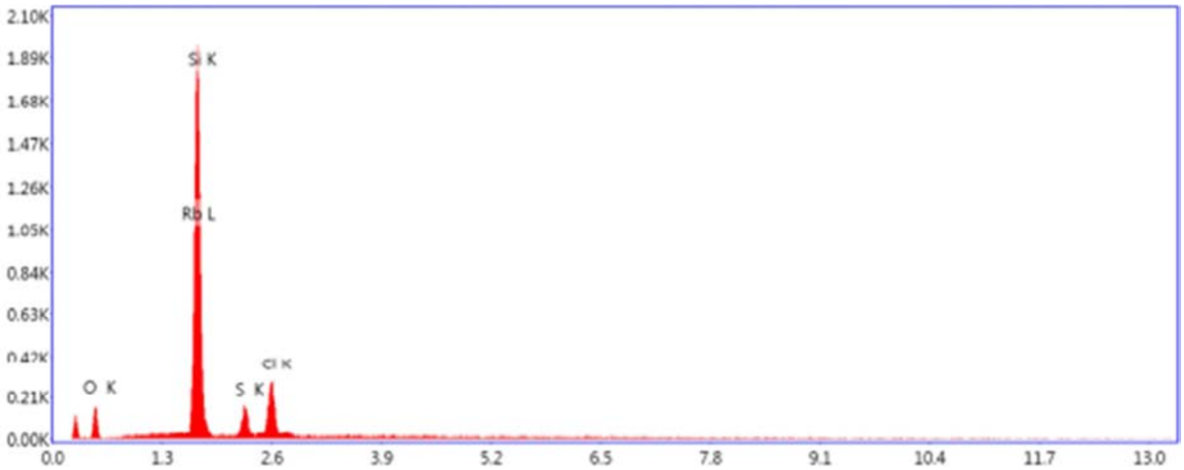


Figure 3. *SEM Morphology / EDX Spectrum of Immobilized Thiosalicylic Acid Ligand System.*

Table 1. *Polysiloxane Immobilized Thiosalicylic Ligand Particle Size (nm) Analysis.*

	Area (nm)	Mean	Min	Max	r^2	r (nm)	d (nm)	v (nm^3)
Mean	11.1706	255	255	255	3.5557	1.7198	3.4397	52.9940
Standard Error	1.5278	0	0	0	0.4863	0.1237	0.2475	9.9847
Median	7.932	255	255	255	2.5248	1.5889	3.1779	25.2074
Mode	2.644	255	255	255	0.8416	0.9173	1.8347	4.8511
Standard Deviation	9.6631	0	0	0	3.0758	0.7829	1.5659	63.1494
Sample Variance	93.3771	0	0	0	9.4610	0.6130	2.4522	3987.846
Range	29.083	0	0	0	9.2574	2.2605	4.5210	196.799
Minimum	2.644	255	255	255	0.8416	0.9173	1.8347	4.8511
Maximum	31.727	255	255	255	10.0990	3.1778	6.3557	201.6502
Sum	446.827	10200	10200	10200	142.2295	68.7954	137.591	2119.762
Count	40	40	40	40	40	40	40	40
Confidence Level (95.0%)	3.0904	0	0	0	0.9837	0.2504	0.5008	20.1961

Foot note: r= radius, d= diameter, v= volume

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

ADSORBENTS	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 Thiosalicylic Ligand	24.79	33.68	13.85	7.14	20.54

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 generates wastewater without proper treatment, thereby contaminating the eco-system [24, 25]. As a result of that PITSMCBLS was employed to extract heavy metals (Cr^{3+}, Fe^{3+}, Pb^{2+}, Cu^{2+} and Zn^{2+}) available in the wastewater. This was made possible due to the availability of reactive sites in the polysiloxane matrix in Figure 1. 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 their extractions. The results for the effect of pH on the purification of the metals are presented in Table 3. There was a gradual increase in the extraction from pH 2 to a maximum at pH 6 mostly, which was within the limit of 5.5–7.0 [25] recorded using aminopolysiloxane for similar adsorption studies [26]. 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 Thiosalicylic Acid Ligand System after Treatment of Tannery Wastewater.*

METAL	Conc.	pH				
		2	4	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	15.368	11.999	0.28	0.514	1.136
	Cfb	15.368	11.999	0.28	0.514	1.136
	%ADS	10.192	19.22	97.443	91.284	69.239

METAL	Conc.	pH				
		2	4	6	7	9
	Cia	4.224	1.619	0.328	0.732	0.272
	Cib	4.224	1.619	0.328	0.732	0.272
Fe (ppm)	Cfa	1.205	0	0	0	0
	Cfb	1.205	0	0	0	0
	%ADS	0.715	100	100	100	100
	Cia	2.852	1.94	1.609	1.484	0.418
	Cib	2.852	1.94	1.609	1.484	0.418
Pb (ppm)	Cfa	0.922	0.595	0.001	0	0
	Cfb	0.922	0.595	0.001	0	0
	%ADS	67.672	69.33	99.956	100	100
	Cia	0.811	0.48	0.404	0.426	0.153
	Cib	0.649	0.318	0.242	0.264	0.009
Cu (ppm)	Cfa	0.319	-0.329	0.036	0.043	0.002
	Cfb	0.319	0	0.036	0.043	0.007
	%ADS	50.847	100	85.124	83.712	77.777
	Cia	0.177	0.02	0.051	0.039	-0.003
	Cib	0.177	0.02	0.051	0.039	-0.003
Zn (ppm)	Cfa	0.115	-0.025	0	0	0
	Cfb	0.115	0	0	0	0
	%ADS	35.028	100	100	100	0

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 PITSLS Dose on the Adsorption of Heavy Metals

The results in Table 4, shows that, increase in adsorbent dose from 20-30 mg/60 cm^3 increased the adsorption of metal ion in the solution due to large availability of the surface area at higher concentration of the adsorbent in thiosalicylic with respect to Cr^{3+}. Increase in the adsorbent dose from 10-30 mg/60 cm^3 had no significant effect on the adsorption of Fe^{3+} and Zn^{2+} metal ion in the solution because any further addition of the adsorbent beyond this point did not cause any significant change in the adsorption due to overlapping adsorption sites of the adsorbent particles [27, 28], discrepancies were recorded with respect to Pb^{2+}, which showed significant adsorption at 10 mg/60 cm^3 and decreased from 20-30 mg/cm^3 due to complete overlapping of adsorption sites.

Table 4. *Effect of Adsorbent Dosage of PITSLS on the Adsorption of Heavy Metals after Digestion of Tannery Wastewater.*

METAL	Conc.	Adsorbent (mg)		
		10	20	30
	Cia	10.952	10.952	10.952
	Cib	10.952	10.952	10.952
Cr (ppm)	Cfa	0.280	0.198	0.172
	Cfb	0.280	0.198	0.172
	%ADS	97.443	98.192	98.430
	Cia	0.328	0.328	0.328
	Cib	0.328	0.328	0.328
Fe (ppm)	Cfa	-0.233	-0.668	-0.716
	Cfb	0.000	0.000	0.000
	%ADS	100.000	100.000	100.000
	Cia	0.418	0.418	0.418
	Cib	0.418	0.418	0.418
Pb (ppm)	Cfa	-0.014	0.233	0.325
	Cfb	0.000	0.233	0.093
	%ADS	100.000	44.258	22.248
	Cia	0.404	0.404	0.404
	Cib	0.242	0.242	0.242
Cu (ppm)	Cfa	0.036	-0.082	-0.109
	Cfb	0.036	0.000	0.000
	%ADS	85.124	100.000	100.000
	Cia	0.051	0.051	0.051
	Cib	0.051	0.051	0.051
Zn (ppm)	Cfa	-0.002	-0.069	-0.070
	Cfb	0.000	0.000	0.000
	%ADS	100.000	100.000	100.000

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

4.4. Thermodynamic Study of PITSLS

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 thiosalicylic ligand system was studied at different temperatures of 303, 308 and 313 K in Table 5. The results for (K_D) and (% ADS) ranged from: Cr^{3+} 287.838 to 296.384 and Pb^{2+} 193.788 to 300.000 and % ADS for Cr^{3+} 96 to 99; Pb^{2+} 65 to 100 respectively. This showed that, the distribution coefficients K_D and % ADS increased with increase in temperature while Fe^{3+}, Cu^{2+} and Zn^{2+} showed no significant changes with increase in temperature. In order to determine the thermodynamic feasibility and the thermal effects of sorption, the thermodynamic parameters were evaluated using $\Delta G^o = -RT \ln K_D$ and $\Delta G^o = \Delta H^o - T\Delta S^o$, where ΔG^o, ΔH^o, ΔS^o and T are Gibbs free energy, enthalpy, entropy and absolute temperature respectively [6, 29]. R is the gas constant (8.314 $Jmol^{-1}K^{-1}$) and K_D is the equilibrium constant. Plots of $\ln K_D$ against 1/T gave the numerical values of ΔH^o and ΔS^o from slope and intercept respectively [30]. The values of ΔG^o, ΔH^o and ΔS^o are given for Cr^{3+}, Fe^{3+}, Pb^{2+}, Cu^{2+} and Zn^{2+} in Table 5. The negative values of the Gibbs free energy ΔG^o for all temperatures with affinity for polysiloxane immobilized thiosalicylic 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. The values for ΔG^o ranged from (Cr^{3+} -14.264 to -14.811; Fe^{3+} - 14.368 to -14.842; Pb^{2+} -13.2676 to -14.8429; Cu^{2+} -11.4839 to -14.8429 and Zn^{2+} -14.3686 to -14.8429 $kJmol^{-1}$). Consequently, ΔG^o 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^o (Cr^{3+} 2.316; Fe^{3+} 0.000 Pb^{2+} 105.1305; Cu^{2+} 19.2569 and Zn^{2+} 0.0000 $kJmol^{-1}$), suggest variation of enthalpies accompanying sorption of metal ions on the Polysiloxane immobilized thiosalicylic ligand system (indicating an endothermic process) which is facilitated by higher temperatures. The positive entropy changes: ΔS^o (Cr^{3+} 54.750; Fe^{3+} 47.421; Pb^{2+} 389.328; Cu^{2+} 110.9670 and Zn^{2+} 47.4214J mol^1K^1) is characterized by irregular increase in the randomness at the composite material solution interface during adsorption procedure of the system [31]. The results above are characterized by chemisorption process, favoured at higher temperatures. The thermodynamic parameters considered are in agreement with the work of El-Ashgar *et al.,* [32].

Table 5. *Adsorption Thermodynamics of Metal ions Chemisorbed by PITSLS.*

METAL ION	T (K)	q_e (mgg^{-1})	K_D (Lg^{-1})	$\ln K_D$	ΔG° ($KJmol^{-1}$)	ΔH° ($KJmol^{-1}$)	ΔS° ($Jmol^{-1}K^{-1}$)	Rel.C_i (ppm)	Rel.C_f (ppm)	Cd	% ADS
	303.00	3152.40	287.837	5.662	-14.264			10.952	0.444	10.508	96
Cr^{3+}	308.00	3233.70	295.261	5.687	-14.565	2.316	54.750	10.952	0.173	10.779	98
	313.00	3246.00	296.384	5.691	-14.811			10.952	0.132	10.820	99
	303.00	98.40	300.000	5.703	-14.368			0.328	0.000	0.328	100
Fe^{2+}	308.00	98.40	300.000	5.703	-14.605	0.000	47.421	0.328	0.000	0.328	100
	313.00	98.40	300.000	5.703	-14.842			0.328	0.000	0.328	100
	303.00	81.00	193.779	5.266	-13.267			0.418	0.148	0.270	65
Pb^{2+}	308.00	95.00	227.512	5.427	-13.897	105.130	389.328	0.418	0.101	0.317	76
	313.00	125.00	300.000	5.703	-14.842			0.418	0.000	0.418	100
	303.00	23.00	95.454	4.558	-11.483			0.404	0.003	0.239	99
Cu^{2+}	308.00	24.00	300.000	5.703	-14.605	19.256	110.967	0.404	0.000	0.242	100
	313.00	24.00	300.000	5.703	-14.842			0.404	0.000	0.242	100
	303.00	15.30	300.000	5.703	-14.368			0.051	0.000	0.051	100
Zn^{2+}	308.00	15.30	300.000	5.703	-14.605	0.000	47.421	0.051	0.000	0.051	100
	313.00	15.30	300.000	5.703	-14.842			0.051	0.000	0.051	100

5. Conclusion

The PITSLS has been prepared and subjected to instrumental methods of analysis such as: FTIR, SEM and EDX the PITSLS showed high potential for the extraction of Cr^{3+}, Fe^{3+}, Pb^{2+}, Cu^{2+} and Zn^{2+} 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 Cr^{3+}, Fe^{3+}, Pb^{2+}, Cu^{2+} and Zn^{2+} with polysiloxane immobilized thiosalicylic ligand System was accompanied by an absorption of heat.

Authors' Contributions

This study was conducted between all authors. BULUS HABILA (BH) and E. C. Ezeh (ECE) devised the concept and designed the study. The laboratory investigation, analysis and manuscript draft were performed by BH. Statistical analysis was performed by Jonathan D. G and T. N. B.

Shekarri (TNBS), S. T. Dahiru (STD), Paul O. Nsude (POS) Emmanuel Agboeze (EA), Ike Christian Ozoemena (ICO) Olajide J. Igbehinadun (OJI), participated in the laboratory work. The final version was written by BH, E C E and Simon Moses, critically reviewed the manuscript for its intellectual content. All the authors gave final approval of the revised version for publication.

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Conflicts of Interest

The authors declare they do not have a conflict of interest.

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