Synthesis, Characterization of Immobilized Thiosalicylic-Mercaptoethanol Bi-Ligand System and its Application in Detoxification of Chromium III and Iron III ions from Tannery Wastewater

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Abstract

Background: Effective wastewater treatments are paramount to modern-day Scientists. The available methods are ineffective in detoxifying tannery wastewater.

Aim: This study synthesize and characterized polysiloxane-Immobilized thiosalicylic-mercaptoethanol ligand system (PITSMCBLS) and used in detoxification of Cr^{3+} and Fe^{3+} from tannery wastewater.

Method: Porous solid PITSMCBLS was prepared by hydrolytic polycondensation of tetraethylorthosilicate with mixture of 3-chloropropyltrimethoxysilane, methanol and sodium hydroxide as catalyst. The gelation formed (3-CPP) after 40 min, was functionalized (F-3CPP) with excess ethylchloroacetate, triethylamine and grafted with thiosalicylic-mercaptoethanol bi-ligand. The PITSMCBLS was characterized using FTIR and SEM-EDX. The competitive sorption characteristics of metal ions (Cr^{3+} and Fe^{3+}) were studied using Microwave Plasma Atomic-Emission Spectrophotometer.

Result: The FTIR spectrum of PITSMCBLS showed vibrational frequencies (cm^{-1}) at: 3339, (O-H); 2928, (C-H); 2685, (SH); 2497, (Si-H); 1587–1707, (C=O) and 1028, (Si-O). The SEM-EDX showed irregular particle sizes (4.4294 ± 1.7187 nm) and elemental composition (wt %): 3-CPP, Si (50.45); O (25.02) and Cl (24.57). The F-3CPP showed, O (58.68) and Si (41.32), while PITSMCBLS showed 11.94 of S. Gibbs free energy yielded negative range values for ΔG^{o} (Cr^{3+} -14.187 to -14.832 and Fe^{3+} - 14.369 to -14.843 $kJmol^{-1}$), positive values for: ΔH^{o} (Cr^{3+} 5.345 and Fe^{3+} 0.000 $kJmol^{-1}$) and ΔS^{o} (Cr^{3+} 64.459 and Fe^{3+} 47.421 $Jmol^{1}K^{1}$) respectively.

Conclusion: PITSMCBLS exhibits high potential for extraction of Cr^{3+} and Fe^{3+} in tannery wastewater. The Thermodynamic values indicate spontaneous, endothermic reactions and high degree of disorderliness with respect to metal ion binding capacity to the ligand system. This development would improve tannery wastewater treatment.

Keywords: Tannery wastewater; Detoxification; Polysiloxane; Thiosalicylic-mercaptoethanol ligand; Thermodynamic.

1. Introduction

Leather industries play very significant role in the economy of many countries, but also generate harmful wastes into water bodies (Bulus *et al.*, 2018; Igiri *et al.*, 2018; Evangelo and Ebel, 2007). The harmful wastes are generated from cleaning, fleshing, splitting, tanning, shaving and buffing of raw hides or skins (Onukak *et al.*, 2017). These waste materials in water bodies' results in environmental risks associated with health hazard (Okoduwa *et al*, 2017, 2019). Several living organisms in ecosystem including human have suffered severe toxicity threat emanating from untreated discharged of tanning chemicals in the environment (Okoduwa, et al 2019; Igiri *et al.*, 2018; Okolo *et al.*, 2016). During tanning alone about 300 kg of chemicals are added per ton of hides or skins (Durai and Rajasimman 2001). Additionally, large volume of water, 35 L 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 (Islam *et al.,* 2014). Not more than 20% of the chemicals used are absorbed by leather; the remainder flows out with the effluent causing environmental pollution when discharged untreated or partially treated (Muthukkauppan and Parthiban, 2018). These resultant wastewaters that are discharged contain toxic metallic components such as Cr^{6+}, Fe^{3+}, Cd^{2+}, Cu^{2+} (Machado *et al.*, 2009). Some of these toxic heavy metals are difficult to detoxify (Islam *et al*., 2014). Conventional methods used in the tannery wastewater treatments include electrochemical treatment, coagulation/flocculation, activated sludge process and sequential batch reactor (Ayoub *et al.*, 2011; Ganesh *et al*., 2006). All these technologies have limitations such as production of toxic sludge (Jahan *et al.,* 2014) and inability to remove heavy metals at trace level. It is therefore imperative to develop 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 (El- Ashgar, 2009). Although they have been employed as a recyclable extractant for heavy metals and in stationary phases in chromatographic techniques using simulated water but have not been used nor investigated on tannery wastewater. The immobilized ligand system could be synthesized directly by sol gel or by chemical modification of prepared functionalized polysiloxane (El- Ashgar, 2009; 2012). A variety of spectroscopic techniques such as Fourier Transform Infra-red (FTIR) (Issa *et al.*, 2002; Nizam and Salman, 2006), Nuclear Magnetic Resonance (NMR), Scanning Electron Microscopy (SEM) (Abdussalam *et al.,* 2012; Piotr *et al.,* 2016) and Energy Dispersive X-ray Analysis (EDX) (Abdussalam et al., 2012; Piotr *et al*., 2016), have been employed to study the ligand modified polysiloxane systems. This study therefore described the synthesis and characterization of polysiloxane-Immobilized thiosalicylic acid ligand system and its potential in the detoxification of tannery wastewater.

2. Materials and Methods

2.1 Reagents and Chemicals

Tetraethylorthosilicate, 3-chloropropyltrimethoxysilane, thiosalicylic 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 controlled using 0.1 Mol/dm^3 HCl and NaOH (Carson 2000pH Model) respectively.

2.2 Synthesis of Polysiloxane Immobilized Thiosalicylic / Mercaptoethanol Bi-Ligand System

Immobilization of thiosalicylic/mercaptoethanol ligand was carried out with respect to the methods of El- Nahhal *et al.,* (2002); Salman and Nizam (2006) and Nizam, (2008), with modifications. The functionalized product, was measured (3.200g) and added to (0.05 mol; density 1.49 g/cm^3; 7.959 g and 0.05 mol; density 1.114 g/cm^3; volume 3.50 cm^3) thiosalicylic and mercaptoethanol respectively in ethyl-chloroacetate (0.244 mol; density 1.145 g/cm^3; volume 26.20 cm^3) and 5cm^3 of triethylamine in a round-bottomed flask (250cm^3) and refluxed for 12 h at 110^{o}C the product formed was filtered, washed successively with 50cm^3 portions of de-ionized water, methanol and diethyl ether, dried at 110^{o}C in an oven for 10 h, labelled and dried over $CaCl_2$.

2.3 Digestion of Tannery Wastewater

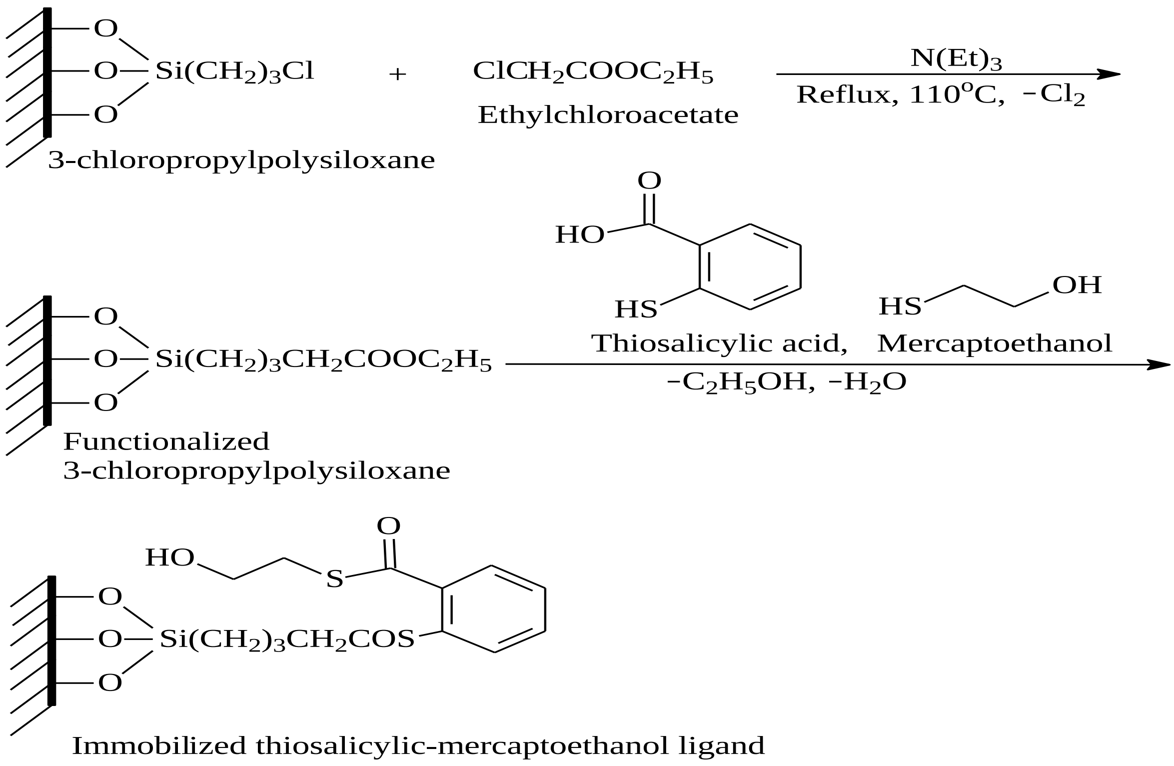
Tannery wastewater sample of 1000 cm^3 was transferred into a conical flask and evaporated till dried. The dried sample was digested in 10:1 HNO_3:$HClO_4$ (v/v). White crystals were found in the digested samples and were dissolved in 150 ml de-ionized water. The supernatants were filtered using Whatman No.41 filter paper and were read directly with Agilent MPAES-4200 (Shahida *et al.,* 2017).

2.4 Thermodynamic Studies and Effect of Adsorbent

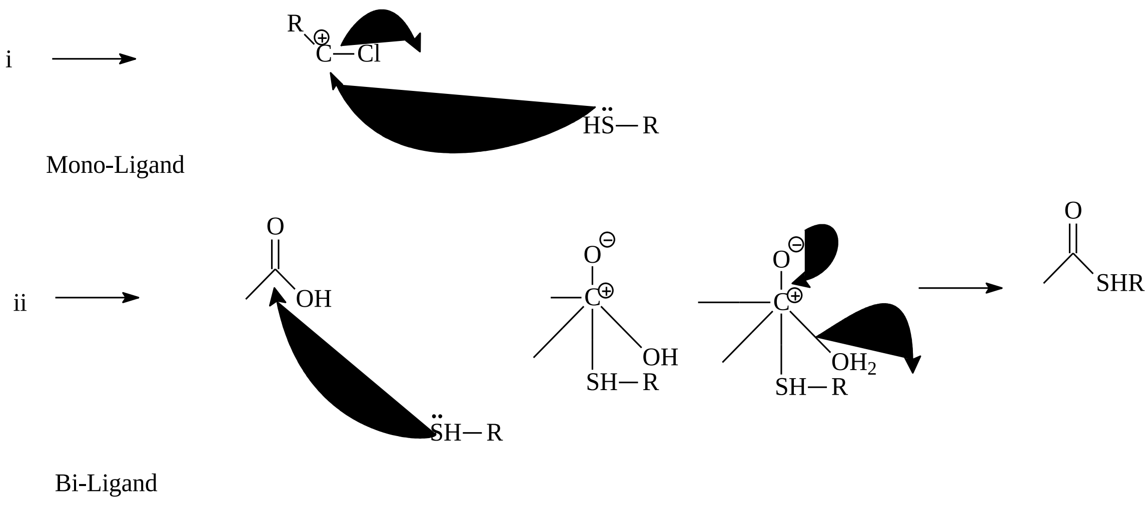
A volume of 60 cm^3 solution of the tannery wastewater adjusted at pH 6 (optimum) was transferred into 150 cm^3 conical flask and 10 mg of the PITSMCBLS was added and adjusted in a thermostatic multi-shaker at 100 rpm for 2 h at 30 ^oC. The resultant solutions were filtered using Whatman No.41 and the residual metal concentrations analysed (Cr^{3+} and Fe^{3+}) using Agilent MPAES-4200 (Bernard and Jimoh 2013; Senthil and Kirthika, 2009; Horsfall *et al.,* 2006) This procedure was repeated for 20 and 30 mg of PITSMCBLS respectively and at temperatures of 35 and 40 ^oC respectively.

3. Results and Discussion

The leather industry contributes immensely in the generation of wastewater without proper treatment thereby contaminating or polluting the eco-system (Okoduwa, *et al.*, 2019). Hence the use of PITSMCBLS was employed to adsorbed heavy metals (Cr^{3+} and Fe^{3+}) present in the wastewater. This was made possible due to the availability of reactive sites in the polysiloxane matrix in Scheme 1 and the mechanism of the reaction in Scheme 2. The mechanism could be surface adsorption or chemisorption. 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.



Scheme 1: Synthesis of polysiloxane immobilized thiosalicylic-mercaptoethanol bi-ligand system.



Scheme 2: Reaction mechanism for polysiloxane immobilized thiosalicylic/mercaptoethanol bi-ligand system.

3.1 SEM/EDX Analysis for polysiloxane Immobilized Thiosalicylic/Mercaptoethanol Bi-ligand System

The SEM (EVO/LS10 ZEISS) showed irregular particle sizes of the following polysiloxane matrices at various magnifications (µm): 3- chloropropylpolysiloxane (500); functionalized 3-chloropropylpolysiloxane (500 µm) and PITSMCBLS (200 µm) in Plate I, with the EDX (EVO/LS10 ZEISS) elemental composition in that order (wt %); 3-CPP; Si (50.45), O (25.02) and Cl (24.57); F-3-CPP; O (58.68), Si (41.32) (Abdussalam *et al.*, 2012) the ligand was introduced after polymerization by nucleophilic displacement of a halide anion (Brad *et al.*, 2009) and the % weight (Sulphur) of PITSMCBLS gave 11.93in Plate I. The value was obtained because of the availability of reactive sites in nano sizes which is shown in Table 1, which assisted in the immobilization process, with mean and standard deviation of4.4294 ± 1.7187 nm for immobilized PITSMCBLS. This is in agreement with the nano particle sizes of silica at the range of 2-5 nm (El-Nahhal and El-Ashgar, 2007) with an extraordinary surface-to-volume ratio. Pore volume of 100.1614 ± 101.3491 $nm^3$was obtained, which played a vital role in adsorption of heavy metals in the tannery wastewater. The Sulphur in PITSMCBLS which was not present originally in the synthesized 3-CPP and the Functionalized 3-CPP confirmed its immobilization to the matrix. The wt %: 11.94 was above the range of 6.1-10.4 reported by Issa *et al.*, (2010); 8.0, El-Ashgar (2009); 4.30-11.30 (Issa *et al.*, 2015); 3.90-6.80 (Mona *et al.*, 2016) for similar synthesis. The presence of Sulphur in the matrix is in consonant with the FTIR (C 620 Agilent Technology) results with vibrational frequencies (cm^{-1}) as shown in Figure 1: alcohol (O-H, 3339), alkane (C-H, 2928) thiol (SH, 2685); silane (Si-H, 2497), carbonyl (C=O, 1587.8 – 1707) and siloxane (Si-O, 1028) respectively.

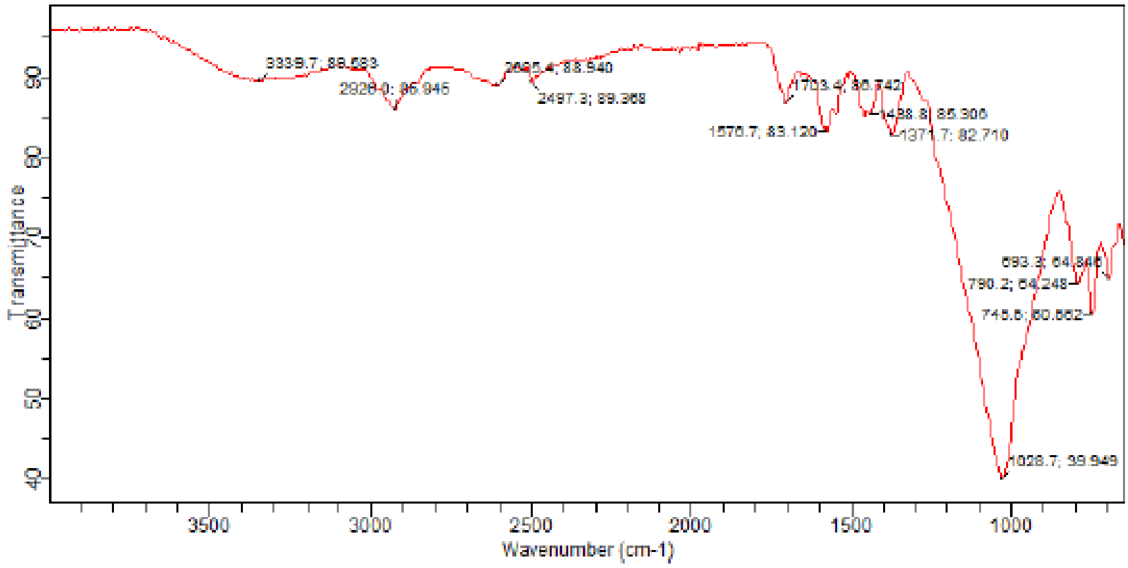
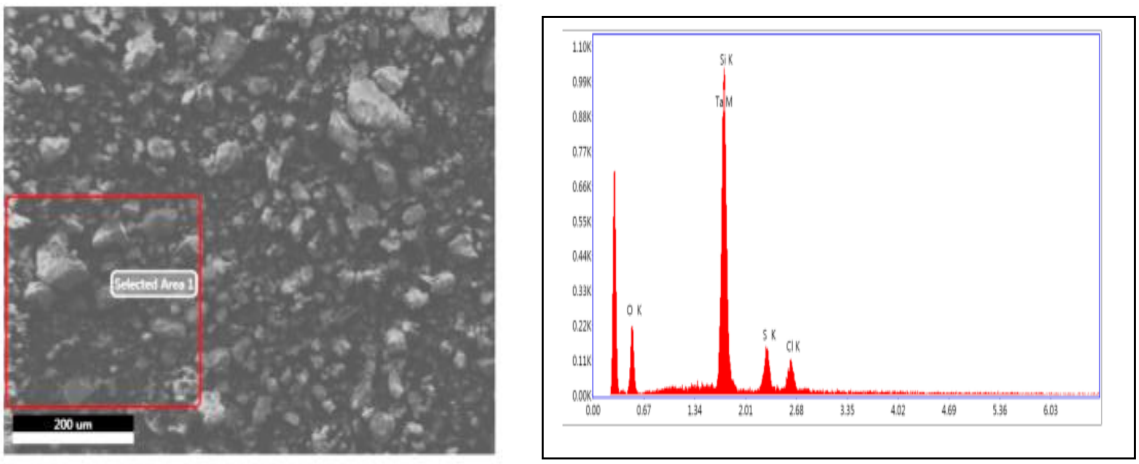


Figure 1: FTIR Spectrum for Polysiloxane Immobilized Thiosalicylic-Mercaptoethanol Bi-Ligand System

3.2 Effect of Polysiloxane Immobilized Thiosalicylic/Mercaptoethanol Bi-Ligand Dose on the Adsorption of Heavy Metals

The adsorption effects of various weights of the adsorbent from 10 to 30 mg/60 cm^3 were used for the extraction of metal ion in Table 1. All the mass showed significant extraction of the metal ions. The Cr^{3+} percentage adsorption decreases with increase in the amount of adsorbent while Fe^{3+} showed no significant increase with increased in the amount of adsorbent in the treated tannery wastewater.



Plates 1: SEM/EDX, Morphology and Elemental Composition for Poliysiloxane Immobilized Thiosalicylic/Mercaptoethanol Bi-Ligand System.

Table 1: Polysiloxane Immobilized Thiosalicylic/Mercaptoethanol Ligand Particle Size Results.

	Area(nm)	**Mean**	**Min**	**Max**	**r^2**	**r (nm)**	**d (nm)**	**v (nm^3)**
Mean	17.7193	255	255	255	5.6402	2.2147	4.4294	100.1614
Standard Error	0.8505	0	0	0	0.2707	0.0569	0.1138	6.7120
Median	16	255	255	255	5.0929	2.2567	4.5135	72.2162
Mode	4	255	255	255	1.2732	1.1283	2.2567	9.0270
Standard Deviation	12.8423	0	0	0	4.0878	0.8593	1.7187	101.3491
Sample Variance	164.9253	0	0	0	16.7104	0.7385	2.9541	10271.64
Range	44	0	0	0	14.0056	2.7804	5.5608	366.2197
Minimum	4	255	255	255	1.2732	1.1283	2.2567	9.0270
Maximum	48	255	255	255	15.2788	3.9088	7.8176	375.2467
Sum	4040	58140	58140	58140	1285.9719	504.954	1009.9079	22836.8
Count	228	228	228	228	228	228	228	228
Confidence Level (95.0%)	1.6758	0	0	0	0.5334	0.1121	0.2242	13.2258

r = radius, d = particle size, v = pore volume

Table 2: Effect of Immobilized Thiosalicylic/Mercaptoethanol Bi-Ligand Dose on the Adsorption of Heavy Metals

METAL	**BLANKS**		**Conc.**	**Adsorbent (mg)**		
	A	-0.014		**10**	**20**	**30**
Cr (ppm)	**B**	-0.034	**Cia**	10.952	10.952	10.952
	Tb		**Cib**	10.952	10.952	10.952
			Cfa	0.304	0.328	0.127
			Cfb	0.304	0.328	0.127
			%ADS	97.224	97.005	98.840
Fe (ppm)	**A**	-52.477				
	B	-61.983	**Cia**	0.328	0.328	0.328

Tb	**Cib**	0.328	0.328	0.328
	Cfa	-0.190	-0.327	-1.354
	Cfb	0.000	0.000	0.000
	%ADS	100.000	100.000	100.000

A = de-ionized water; B = sample blank; rC_{oi} = relative initial concentration; rC_{ef} = relative final concentration; %ADS = percentage adsorption

3.3 Thermodynamic Study of Polysiloxane Immobilized Thiosalicylic/Mercaptoethanol Bi-Ligand System

The distribution coefficients, K_D for the extraction of Cr^{3+} and Fe^{3+} metal ions from solutions of tannery wastewater by PITSMCBLS was studied at different temperatures of 30, 35 and 40 ^{0}C (Table 3). The results for Cr^{3+} showed that the distribution coefficients K_D 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+} 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 $\Delta G^o = -RT\ \text{In}K_D$ 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 (El-Ashgar, 2009; Parimalam *et al.*, 2011). R is the gas constant (8.314$Jmol^{-1}K^{-1}$) and K_D is the equilibrium constant. Plots of $\text{In}K_D$ against 1/T gave the numerical values of ΔH^o and ΔS^o from slope and intercept respectively (Rajashree *et al.*, 2012). The values of ΔG^o, ΔH^o and ΔS^o are given for Cr^{3+} and Fe^{3+} in Table 2. The negative values of the Gibbs free energy ΔG^o for all temperatures with appreciable affinity for PITSMCBLS towards Cr^{3+} and Fe^{3+}, suggests spontaneity of the adsorption process which does not require an external energy source for the system. ΔG^o (Cr^{3+} -14.187 to -14.832 and Fe^{3+} - 14.369 to -14.843 $kJmol^{-1}$). Consequently, ΔG^o of -15 kJ/mol are connected with physical interaction between adsorption site and metal ions which was observed in this study to be less, whereas -30KJ/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+}5.345 and Fe^{3+}0.000KJmol^{-1}), suggest variation of enthalpies accompanying sorption of metal ions on the PITSMCBLS (indicating an endothermic process) which is facilitated by higher temperatures. The positive entropy changes: ΔS^o (Cr^{3+}64.459and Fe^{3+}47.421Jmol^{1}K^{1}) is characterised by irregular increase in the randomness at the composite material-solution interface during adsorption procedure of the system (Zhiguang *et al.,* 2011). The results above were characterised by chemisorption process, favoured at higher temperatures. The thermodynamic parameters considered are in harmony with the work of Nizam and Zeyad (2009).

Table 3: Adsorption Thermodynamics for polysiloxane Immobilized Thiosalicylic/Mercaptoethanol Bi- Ligand System

METAL ION	**T (K)**	**q_e (mgg^{-1})**	**K_D (Lg^{-1})**	**lnK_D**	**ΔG^O (KJmol^{-1})**	**ΔH^O (KJmol^{-1})**	**ΔS^O (Jmol^{-1}K^{-1})**	**Rel.C_i (ppm)**	**Rel.C_f (ppm)**	**Cd**	**% ADS**
	303.000	3057.600	279.182	5.632	-14.187			10.952	0.760	10.192	93
Cr^{3+}	308.000	3160.200	288.550	5.665	-14.506	5.345	64.459	10.952	0.418	10.534	96
	313.000	3272.100	298.767	5.700	-14.832			10.952	0.045	10.907	100
	303.000	98.400	300.000	5.704	-14.369			0.328	0.000	0.328	100
Fe^{3+}	308.000	98.400	300.000	5.704	-14.606	0.000	47.421	0.328	0.000	0.328	100
	313.000	98.400	300.000	5.704	-14.843			0.328	0.000	0.328	100

4. Conclusion

The PITSMCBLS 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 ligands were chemically immobilized to the polysiloxane network. The PITSMCBLS showed high potential for the extraction of Cr^{3+} and Fe^{3+} at an optimum pH of

6.0 in the tannery wastewater. Extraction of metal ion increased with increase in the adsorbent dose and temperature respectively. The thermodynamic parameters suggest a spontaneous and an endothermic affinity of the chelating ligand.

Authors' Contributions: This study was conducted between all the authors (BH, POU, SIRO, ASa, MBB and ASi). Author POU and BH got the concept and design of the study. The laboratory investigation, analysis and manuscript draft was done by BH and SIRO. The statistical analysis was done by ASi and POU. ASa and MBB participated in the laboratory work. The final version was written by BH and SIRO. SIRO and POU critically reviewed the manuscript for important intellectual content. All the authors gave final approval of the revised version for publication.

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