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

Bulus Habila, Pius Onyeoziri Ukoha, Stanley I.R. Okoduwa, Ahmed Salim, Muazu B. Babangida, Adamu Simon

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

4

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13

14**Abstract**

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35wastewater. The Thermodynamic values indicate spontaneous, endothermic reactions and
36high degree of disorderliness with respect to metal ion binding capacity to the ligand system.
37This development would improve tannery wastewater treatment.

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

411. Introduction

42Leather industries play very significant role in the economy of many countries, but also
43generate harmful wastes into water bodies (Bulus *et al.*, 2018; Igiri *et al.*, 2018; Evangelo and
44Ebel, 2007). The harmful wastes are generated from cleaning, fleshing, splitting, tanning,
45shaving and buffing of raw hides or skins (Onukak *et al.*, 2017). These waste materials in
46water bodies' results in environmental risks associated with health hazard (Okoduwa *et al.*,
472017, 2019). Several living organisms in ecosystem including human have suffered severe
48toxicity threat emanating from untreated discharged of tanning chemicals in the environment
49(Okoduwa, et al 2019; Igiri *et al.*, 2018; Okolo *et al.*, 2016). During tanning alone about 300
50kg of chemicals are added per ton of hides or skins (Durai and Rajasimman 2001).
51Additionally, large volume of water, 35 L is consumed per kilogram of raw hide or skin

52processed and an average of 35,000 L of wastewater is produced per ton of raw hide or skin
53(Islam *et al.*, 2014). Not more than 20% of the chemicals used are absorbed by leather; the
54remainder flows out with the effluent causing environmental pollution when discharged
55untreated or partially treated (Muthukkauppan and Parthiban, 2018). These resultant
56wastewaters that are discharged contain toxic metallic components such as Cr^{6+} , Fe^{3+} , Cd^{2+} ,
57 Cu^{2+} (Machado *et al.*, 2009). Some of these toxic heavy metals are difficult to detoxify (Islam
58*et al.*, 2014). Conventional methods used in the tannery wastewater treatments include
59electrochemical treatment, coagulation/flocculation, activated sludge process and sequential
60batch reactor (Ayoub *et al.*, 2011; Ganesh *et al.*, 2006). All these technologies have
61limitations such as production of toxic sludge (Jahan *et al.*, 2014) and inability to remove
62heavy metals at trace level. It is therefore imperative to develop innovative technologies
63which require low maintenance, high energy efficiency, low cost and better operational
64techniques than the conventional methods. This prompted the use of polymeric modified
65surfaces with excellent thermal, mechanical and chemical stability properties such as
66polysiloxane functionalized or immobilized with ligands (El- Ashgar, 2009). Although they
67have been employed as a recyclable extractant for heavy metals and in stationary phases in
68chromatographic techniques using simulated water but have not been used nor investigated
69on tannery wastewater. The immobilized ligand system could be synthesized directly by sol
70gel or by chemical modification of prepared functionalized polysiloxane (El- Ashgar, 2009;
712012). A variety of spectroscopic techniques such as Fourier Transform Infra-red (FTIR) (Issa
72*et al.*, 2002; Nizam and Salman, 2006), Nuclear Magnetic Resonance (NMR), Scanning
73Electron Microscopy (SEM) (Abdussalam *et al.*, 2012; Piotr *et al.*, 2016) and Energy
74Dispersive X-ray Analysis (EDX) (Abdussalam *et al.*, 2012; Piotr *et al.*, 2016), have been
75employed to study the ligand modified polysiloxane systems. This study therefore described

76the synthesis and characterization of polysiloxane-Immobilized thiosalicylic acid ligand
77system and its potential in the detoxification of tannery wastewater.

782. **Materials and Methods**

792.1 *Reagents and Chemicals*

80Tetraethylorthosilicate, 3-chloropropyltrimethoxysilane, thiosalicylic acid and methanol,
81where purchased from Sigma-Aldrich Chemical Company and used without further
82purification. Triethylamine, ethylchloroacetate, sodium hydroxide (LOBA Chemie). Diethyl
83ether (spectroscopic grade). Different pH values in the range of 2.0 – 9.0 were controlled
84using 0.1 Mol/dm³ HCl and NaOH (Carson 2000pH Model) respectively.

852.2 *Synthesis of Polysiloxane Immobilized Thiosalicylic / Mercaptoethanol Bi-Ligand System*

86Immobilization of thiosalicylic/mercaptoethanol ligand was carried out with respect to the
87methods of El- Nahhal *et al.*, (2002); Salman and Nizam (2006) and Nizam, (2008), with
88modifications. The functionalized product, was measured (3.200g) and added to (0.05 mol;
89density 1.49 g/cm³; 7.959 g and 0.05 mol; density 1.114 g/cm³; volume 3.50 cm³)
90thiosalicylic and mercaptoethanol respectively in ethyl-chloroacetate (0.244 mol; density
911.145 g/cm³; volume 26.20 cm³) and 5cm³ of triethylamine in a round-bottomed flask
92(250cm³) and refluxed for 12 h at 110°C the product formed was filtered, washed
93successively with 50cm³ portions of de-ionized water, methanol and diethyl ether, dried at
94110°C in an oven for 10 h, labelled and dried over CaCl₂.

952.3 *Digestion of Tannery Wastewater*

96Tannery wastewater sample of 1000 cm³ was transferred into a conical flask and evaporated
97till dried. The dried sample was digested in 10:1 HNO₃:HClO₄ (v/v). White crystals were
98found in the digested samples and were dissolved in 150 ml de-ionized water. The

99supernatants were filtered using Whatman No.41 filter paper and were read directly with
100Agilent MPAES-4200 (Shahida *et al.*, 2017).

101

1022.4 *Thermodynamic Studies and Effect of Adsorbent*

103A volume of 60 cm³ solution of the tannery wastewater adjusted at pH 6 (optimum) was
104transferred into 150 cm³ conical flask and 10 mg of the PITSMCBLS was added and adjusted
105in a thermostatic multi-shaker at 100 rpm for 2 h at 30 °C. The resultant solutions were
106filtered using Whatman No.41 and the residual metal concentrations analysed (Cr³⁺ and Fe³⁺)
107using Agilent MPAES-4200 (Bernard and Jimoh 2013; Senthil and Kirthika, 2009; Horsfall
108*et al.*, 2006) This procedure was repeated for 20 and 30 mg of PITSMCBLS respectively and
109at temperatures of 35 and 40 °C respectively.

1103. **Results and Discussion**

111The leather industry contributes immensely in the generation of wastewater without proper
112treatment thereby contaminating or polluting the eco-system (Okoduwa, *et al.*, 2019). Hence
113the use of PITSMCBLS was employed to adsorbed heavy metals (Cr³⁺ and Fe³⁺) present in
114the wastewater. This was made possible due to the availability of reactive sites in the
115polysiloxane matrix in Scheme 1 and the mechanism of the reaction in Scheme 2. The
116mechanism could be surface adsorption or chemisorption. The protonation of COOH to COO⁻
117by triethylamine, SH to S⁻, and the presence of oxy ions contributes to the adsorption of these
118heavy metals.

119

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

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

130

1313.1 *SEM/EDX Analysis for polysiloxane Immobilized Thiosalicylic/Mercaptoethanol Bi-*
132 *ligand System*

133The SEM (EVO/LS10 ZEISS) showed irregular particle sizes of the following polysiloxane
134matrices at various magnifications (μm): 3- chloropropylpolysiloxane (500); functionalized
1353-chloropropylpolysiloxane (500 μm) and PITSMCBLS (200 μm) in Plate I, with the EDX
136(EVO/LS10 ZEISS) elemental composition in that order (wt %); 3-CPP; Si (50.45), O
137(25.02) and Cl (24.57); F-3-CPP; O (58.68), Si (41.32) (Abdussalam *et al.*, 2012) the ligand
138was introduced after polymerization by nucleophilic displacement of a halide anion (Brad *et*
139*al.*, 2009) and the % weight (Sulphur) of PITSMCBLS gave 11.93 in Plate I. The value was
140obtained because of the availability of reactive sites in nano sizes which is shown in Table 1,
141which assisted in the immobilization process, with mean and standard deviation of $4.4294 \pm$
142 1.7187 nm for immobilized PITSMCBLS. This is in agreement with the nano particle sizes of
143silica at the range of 2-5 nm (El-Nahhal and El-Ashgar, 2007) with an extraordinary surface-
144to-volume ratio. Pore volume of 100.1614 ± 101.3491 nm³ was obtained, which played a vital
145role in adsorption of heavy metals in the tannery wastewater. The Sulphur in PITSMCBLS
146which was not present originally in the synthesized 3-CPP and the Functionalized 3-CPP
147confirmed its immobilization to the matrix. The wt %: 11.94 was above the range of 6.1-10.4
148reported by Issa *et al.*, (2010); 8.0, El-Ashgar (2009); 4.30-11.30 (Issa *et al.*, 2015); 3.90-
1496.80 (Mona *et al.*, 2016) for similar synthesis. The presence of Sulphur in the matrix is in
150consonant with the FTIR (C 620 Agilent Technology) results with vibrational frequencies
151(cm^{-1}) as shown in Figure 1: alcohol (O-H, 3339), alkane (C-H, 2928) thiol (SH, 2685);
152silane (Si-H, 2497), carbonyl (C=O, 1587.8 – 1707) and siloxane (Si-O, 1028) respectively.

153

154

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

157

1583.2 *Effect of Polysiloxane Immobilized Thiosalicylic/Mercaptoethanol Bi-Ligand Dose on*
159
160 *the Adsorption of Heavy Metals*

161 The adsorption effects of various weights of the adsorbent from 10 to 30 mg/60 cm³ were
162 used for the extraction of metal ion in Table 1. All the mass showed significant extraction of
163 the metal ions. The Cr³⁺ percentage adsorption decreases with increase in the amount of
164 adsorbent while Fe³⁺ showed no significant increase with increased in the amount of
165 adsorbent in the treated tannery wastewater.

166

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

169

170**Table 1:** Polysiloxane Immobilized Thiosalicylic/Mercaptoethanol Ligand Particle Size
 171 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

172r = radius, d = particle size, v = pore volume

173

174**Table 2:** Effect of Immobilized Thiosalicylic/Mercaptoethanol Bi-Ligand Dose on the
 175 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
	Tb		Cib	10.952	10.952
			Cfa	0.304	0.328
			Cfb	0.304	0.328
			%ADS	97.224	97.005
Fe (ppm)	A	-52.477			
	B	-61.983	Cia	0.328	0.328
	Tb		Cib	0.328	0.328
			Cfa	-0.190	-0.327
			Cfb	0.000	0.000
			%ADS	100.000	100.000

176A = de-ionized water; B = sample blank; rC_{oi} = relative initial concentration; rC_{ef} = relative final concentration; %ADS =
 177percentage adsorption

17

18

1793.3 *Thermodynamic Study of Polysiloxane Immobilized Thiosalicylic/Mercaptoethanol Bi-* 180 *Ligand System*

181The distribution coefficients, K_D for the extraction of Cr^{3+} and Fe^{3+} metal ions from solutions
182of tannery wastewater by PITSMCBLS was studied at different temperatures of 30, 35 and 40
183°C (Table 3). The results for Cr^{3+} showed that the distribution coefficients K_D increased with
184increase in temperature because the rate of adsorbate diffusion across the external boundary
185layer and in the internal pores of the adsorbate particles increases with increase in
186temperature with a resultant decrease in liquid viscosity while Fe^{3+} showed no significant
187change with increase in temperature. In order to determine the thermodynamic feasibility and
188the thermal effects of sorption, the thermodynamic parameters were evaluated using $\Delta G^\circ =$
189 $-RT \ln K_D$ and $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$, where ΔG° , ΔH° , ΔS° and T are Gibbs free energy,
190enthalpy, entropy and absolute temperature respectively (El-Ashgar, 2009; Parimalam *et al.*,
1912011). R is the gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$) and K_D is the equilibrium constant. Plots of $\ln K_D$
192against $1/T$ gave the numerical values of ΔH° and ΔS° from slope and intercept respectively
193(Rajashree *et al.*, 2012). The values of ΔG° , ΔH° and ΔS° are given for Cr^{3+} and Fe^{3+} in Table
1942. The negative values of the Gibbs free energy ΔG° for all temperatures with appreciable
195affinity for PITSMCBLS towards Cr^{3+} and Fe^{3+} , suggests spontaneity of the adsorption
196process which does not require an external energy source for the system. ΔG° (Cr^{3+} -14.187 to
197-14.832 and Fe^{3+} - 14.369 to -14.843 kJ mol^{-1}). Consequently, ΔG° of -15 kJ/mol are connected
198with physical interaction between adsorption site and metal ions which was observed in this
199study to be less, whereas -30 KJ/mol involves charge transfer from adsorbent surface to the
200metal ion to form a coordination bond. This is a total deviation from the results obtained in
201this work. The positive values: ΔH° (Cr^{3+} 5.345 and Fe^{3+} 0.000 KJ mol^{-1}), suggest variation of
202enthalpies accompanying sorption of metal ions on the PITSMCBLS (indicating an
203endothermic process) which is facilitated by higher temperatures. The positive entropy

204changes: ΔS° (Cr^{3+} 64.459 and Fe^{3+} 47.421 $\text{Jmol}^{-1}\text{K}^{-1}$) is characterised by irregular increase in the
 205randomness at the composite material-solution interface during adsorption procedure of the
 206system (Zhiguang *et al.*, 2011). The results above were characterised by chemisorption
 207process, favoured at higher temperatures. The thermodynamic parameters considered are in
 208harmony with the work of Nizam and Zeyad (2009).

209

210**Table 3: Adsorption Thermodynamics for polysiloxane Immobilized**
 211**Thiosalicylic/Mercaptoethanol**
 212**Bi- Ligand System**

METAL		K_D			ΔG°	ΔH°	ΔS°	Rel.C _i	Rel.C _f	%	
ION	T (K)	q_e (mgg ⁻¹)	(Lg ⁻¹)	lnK _D	(KJmol ⁻¹)	(KJmol ⁻¹)	(Jmol ⁻¹ K ⁻¹)	(ppm)	(ppm)	Cd	ADS
Cr^{3+}	303.000	3057.600	279.182	5.632	-14.187			10.952	0.760	10.192	93
	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
Fe^{3+}	303.000	98.400	300.000	5.704	-14.369			0.328	0.000	0.328	100
	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

213

2144. Conclusion

215The PITSMCBLS has been prepared by hydrolytic polycondensation of
 216tetraethylorthosilicate with a mixture of 3- chloropropyltrimethoxysilane, methanol and
 217sodium hydroxide as a catalyst. The instrumental analysis of FTIR, SEM and EDX
 218confirmed that the ligands were chemically immobilized to the polysiloxane network. The
 219PITSMCBLS showed high potential for the extraction of Cr^{3+} and Fe^{3+} at an optimum pH of
 2206.0 in the tannery wastewater. Extraction of metal ion increased with increase in the
 221adsorbent dose and temperature respectively. The thermodynamic parameters suggest a
 222spontaneous 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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- Polysiloxane-Immobilized thiosalicylic-mercaptoethanol ligand system was prepared.
- Scanning Electron Microscopy of the ligand system gave mesopore particle size.
- A negative ΔG° and positive values for ΔH° and ΔS° were obtained.
- High extraction potential of Cr^{3+} and Fe^{3+} in tannery wastewater was exhibited.
- This method would be more effective in detoxifying Cr^{3+} and Fe^{3+} from wastewater.

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