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# NMR characterization and kinetic performance of polysiloxane immobilized thiosalicylic ligand system on Cr (III) ion from tannery wastewater

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## ABSTRACT

Tannery wastewater hurts the ecosystem with the chemical components used to convert this raw hides and skins into a stable collagen matrix with attendant limitations of various treatment methods was employed. This necessitated the synthesis of Polysiloxane Immobilized Thiosalicylic Ligand System (PITSLS), was characterised and employed for the adsorption of Cr (III) Ion from Tannery Wastewater. The product was characterized using a Nuclear Magnetic Resonance Spectrometer (NMR). <sup>1</sup>H-NMR spectrum showed chemical shifts (ppm) at 2.2 assigned to (2H, S); <sup>13</sup>C signals at 169.093 assigned to (C=N, C=O) and 124.948 to 139.008 assigned to aromatic carbon respectively for PITSLS which was soluble in deuterated dimethyl sulfoxide. The adsorption percentage of Cr <sup>3+</sup> in tannery wastewater using PITSLS (20 mg), was 97.443 % and 30 mg gave 98.430 % at pH 6.00 respectively. For contact time the results showed a significant adsorption in the first minute of contact time and consequently reduced with an increase in time to 120 min respectively due to the unavailability of reactive sites for adsorption. PITSLS has proven to be a promising adsorbent in the adsorption/detoxification of Cr (III) ions in tannery wastewater.

**Keywords:** Adsorption, immobilized, polysiloxane, tannery, thiosalicylic, wastewater

## 1. INTRODUCTION

Removal of heavy metals in wastewater and industrial waste have become a critical environmental issue. The complete removal of toxic heavy metal ions using methods incompatible with biological systems requires expensive treatment to produce water that is again useful for domestic use (Monteagudo and Ortiz, 2002). Hence, the application of some classical techniques for heavy metal removal from solutions:

solvent extraction (Shukla and Rao, 2002); precipitation and co-precipitation (Kagaya et al., 2000); chemical and bio-sorption (Chang et al., 2002); pre-concentration, reverse osmosis (Gibert et al., 2010); and ion exchange (Nabi and Naushad, 2008). Extraction of metal ions by adsorption process involving chelating resins or polymers has several advantages over conventional methods (Zougagh et al., 2005): (i) Selective determination of metal ions is made possible by using a polymeric resin having a functional group with specified atoms possessing high selectivity to the targeted metal ion, (ii) economical method since polymeric resin has high adsorption capacity and easily regenerated, (iii) trace metal ions even at low concentrations (ppb) can be determined due to stabilization of the targeted ion occurs through bond formation with polymeric matrix, and (iv) Use of carcinogenic organic solvents is avoided making the technique eco-friendly. Hence, polysiloxane immobilized thiosalicylic ligand matrix in form of a sol-gel was employed for the detoxification of heavy metals in tannery wastewater.

Sol-gel is a highly flexible route for synthesizing inorganic, organic-inorganic networks (Milea et al., 2011). According to Hossain et al., (2024); Sol-gel is a word that consists of two syllables; the first is (sol) and it means the suspension or dispersion of colloidal particles in solution, where the particles range from 1-100 nm in size. Over time, the particles continue to grow until they finally link in three dimensions, forming a rigid gel network that encompasses pores of trapped fluid (Liu, 2008; Zhang et al., 2023); which allows to creation of composite nano-structure in situ during the process of synthesis (Iryna et al., 2014). Hence, the chemical modification of the pre-prepared functionalized polysiloxane appears as an interesting alternative mainly on account of the substitution of organo-functionalized groups when appropriate chelating silane agents are difficult to prepare (El-Ashgar and Saadeh, 2006; El-Nahhal et al., 2003). These functionalized compounds help in the detoxification of heavy metals in wastewater, like in the case of tannery. The characteristics of tannery wastewater vary considerably from one tannery to another, depending on the size of the tannery and the chemicals used, amount of water used, and, the final products produced.

Wastewater is characterized mainly by the measurement of pH (Song, 2000; Kurt et al., 2007; Mandal et al., 2010), biochemical oxygen demand (BOD), (Ogabiela et al., 2007); chemical oxygen demand (COD), (Richard and Walter, 2013; Islam et al., 2014), suspended solids (SS) and total dissolved solids (TDS), (Jahan et al., 2014; Islam et al., 2014), chromium and sulphides (Nandy et al., 1999). These effluents are basic, dark brown or greenish (Kongjao et al., 2008). These wastes encroach on rivers and agricultural lands (Sreeram and Ramasami, 2003; Stoop, 2003; Bienkiewicz, 1983). The release of these materials into the environment causes serious health problems (Ukoha et al., 2018; Luter et al., 2012); due to their toxicity, non-biodegradable nature and bio-accumulating tendency (Igwe and Abia, 2007; Mohammad and Nwaedozie, 2011; Igwe and Abia, 2006); to the terrestrial, aquatic and aerial environments.

## 2. METHODOLOGY

### 2.1. Synthesis of Polysiloxane Immobilized Thiosalicylic Acid Ligand System (PITSLS)

The methods of El-Nahhal et al., (2003), Salman and Nizam, (2006), and Nizam, (2008), were adopted. The functionalized product was measured (3.200 g) and modified using (0.05 mol; density 1.49 g/cm<sup>3</sup>; 7.959 g) thiosalicylic acid in ethyl chloroacetate (0.244 mol; density 1.145 g/cm<sup>3</sup>; volume 26.20 cm<sup>3</sup>) and 5cm<sup>3</sup> of triethylamine in a round-bottomed flask (250 cm<sup>3</sup>) and refluxed for 12 h (hour) at 383 K the product was filtered, washed successively with 50 cm<sup>3</sup> portions of de-ionized water, methanol, and diethyl ether, dried at 383 K in an oven for 10 h, and dried over CaCl<sub>2</sub> as presented in Scheme 1.

### 2.2. Nuclear Magnetic Resonance Spectroscopy (NMR)

The Nuclear Magnetic Resonance Spectroscopy analysis was conducted at the Ahmadu Bello University (Chemistry Multi-User Laboratory in Zaria). Exactly 5 mg of PITSLS was dissolved in 0.5 cm<sup>3</sup> of deuterated dimethyl sulfoxide (DMSO-d<sub>6</sub>) solvent in a syringe-like tube and inserted into a chamber. <sup>1</sup>H and <sup>13</sup>C-NMR were recorded on Agilent 400 MHZ, NMR spectrometer. The <sup>1</sup>H NMR was observed at 400 MHZ, at a pulse sequence of 31 degrees with a chemical shift range of 0-14 ppm. The <sup>13</sup>C-NMR was observed at 400 MHZ at a pulse sequence of 31 degrees with a chemical shift range of 0-220 ppm.

### 2.3. Kinetic Studies on Simulated Chromium Solution

Batch kinetic studies according to Bernard and Jimoh (2013), Zaid and Mohammed (2008), Onyeji and Aboje (2011), Horsfall et al., (2006), and Vasanth and Kumar, (2006) methods were adopted. Six conical flasks containing 50 cm<sup>3</sup> of simulated solutions (Cr<sup>3+</sup>) were buffered at pH 2, 4, 6, 7, and 9. Furthermore, 20 mg (125-150 µm) of PITSLS were dispensed into the buffered solutions separately and

loaded into the orbital shaker (SI-300R) adjusted for 100 oscillations at 303 K. Aliquots of 7 cm<sup>3</sup> were withdrawn from the solution after 1, 5, 10, 20, 30, 60 and 120 min (minutes), respectively, filtered using Whatman No.41 and the residual Cr<sup>3+</sup>, metal concentrations analysed using Agilent MPAES-4200.

#### 2.4. Tannery Effluent Sample Collection and Preservation

Samples were collected three times at one-day intervals (7:00 am daily) at a point where three effluent channels confluence before mixing with Challawa River. The samples were filtered using Whatman filter paper and preserved using 1.0 mol dm<sup>-3</sup> of nitric acid.

#### 2.5. Digestion of Tannery Wastewater

The method of Radojevic and Bashkin, (1999) was adopted. Composite samples were acidified at pH 2. A wastewater sample of 5000 cm<sup>3</sup> was transferred into a beaker and evaporated till almost dried and digested in 10:1 HNO<sub>3</sub> : HClO<sub>4</sub> (v/v) in a Kjhedahl apparatus. White crystals in the digested sample were dissolved in 1000 cm<sup>3</sup> distilled water. The supernatant was filtered (0.45 μm pore size), filter paper and dissolved concentrations (Aklilu, 2014); of heavy metals in the samples were determined using Microwave Plasma Atomic Emission Spectrophotometer Agilent MPAES-4200. A blank sample was digested to allow for blank correction.

#### 2.6. Performances of Various pHs on Digested Tannery Wastewater

The methods of Onyeji and Aboje (2011), Horsfall et al., (2006), and Vasanth and Kumar, (2006), were adopted. Five conical flasks containing 50 cm<sup>3</sup> of digested tannery wastewater solutions were buffered each to pH 2, 4, 6, 7, and 9 respectively and modified using 20 mg (125-150 μm) PITSLS and adjusted in an orbital shaker (SI-300R) at 100 oscillations for two hours respectively at 303 K. The resultant solutions were filtered using Whatman filter paper No.41 and the residual metal (Cr<sup>3+</sup>) ion concentrations analysed using Agilent MPAES-4200.

#### 2.7. Performance of Adsorbent on Digested Tannery Wastewater

The methods of Bernard and Jimoh, (2013), Senthil and Kirthika, (2009), Horsfall et al., (2006), were adopted. A volume of 60 cm<sup>3</sup> solution of the tannery wastewater adjusted at pH 6 (optimum) was transferred into six conical flasks, 150 cm<sup>3</sup> each and modified using 10 mg (125-150 μm) of the PITSLS were added separately in a thermostatic multi-shaker (Gallenkamp) at 100 oscillations for two hours at 303 K. The resultant solutions were filtered using Whatman No.41 filter paper and the residual metal (Cr<sup>3+</sup>) concentrations analysed using Agilent MPAES-4200. This procedure was repeated for polysiloxane immobilized ligand systems at 20 and 30 mg.

#### 2.8. Detoxification Potentials of PITSLS on Raw Tannery Wastewater Buffered to pH 6

The methods of Onyeji and Aboje (2011), Horsfall et al., (2006), and Vasanth and Kumar (2006), were adopted. A volume of 50 cm<sup>3</sup> solution buffered to pH 6.000, was collected into six (150 cm<sup>3</sup>) conical flasks and modified using 30 mg (125-150 μm) of PITSLS in an Orbital shaker (SI-300R) at 100 oscillations for two hours at 303 K. The resultant solutions were filtered using Whatman No.41, and the residual metal (Cr<sup>3+</sup>) concentrations and analysed using Agilent MPAES-4200.

### 3. RESULTS AND DISCUSSION

#### 3.1. Results

The results are presented as follows: scheme 1, the equation for the synthesis of polysiloxane immobilized thiosalicylic ligand system; Figures 1 and 2 represent the proton and carbon NMR spectrum for PITSLS; Table 1 shows some physical properties of the synthesized polysiloxane; Table 2 shows some standard stock solutions and various buffer solutions respectively. Table 3 shows Simulated Solution of Cr (III) at various pHs; Table 4 shows the Effect of pH on the Adsorption of Cr (III) in Simulated Water at PITSLS 20 % Adsorbent and Table 5 shows the Effect of pH on the Adsorption of Cr (III) in Tannery Wastewater at PITSLS 20 % Adsorbent respectively. Figures 1 and 2 represent proton and carbon NMR spectra of the Polysiloxane Immobilized Thiosalicylic Ligand System.

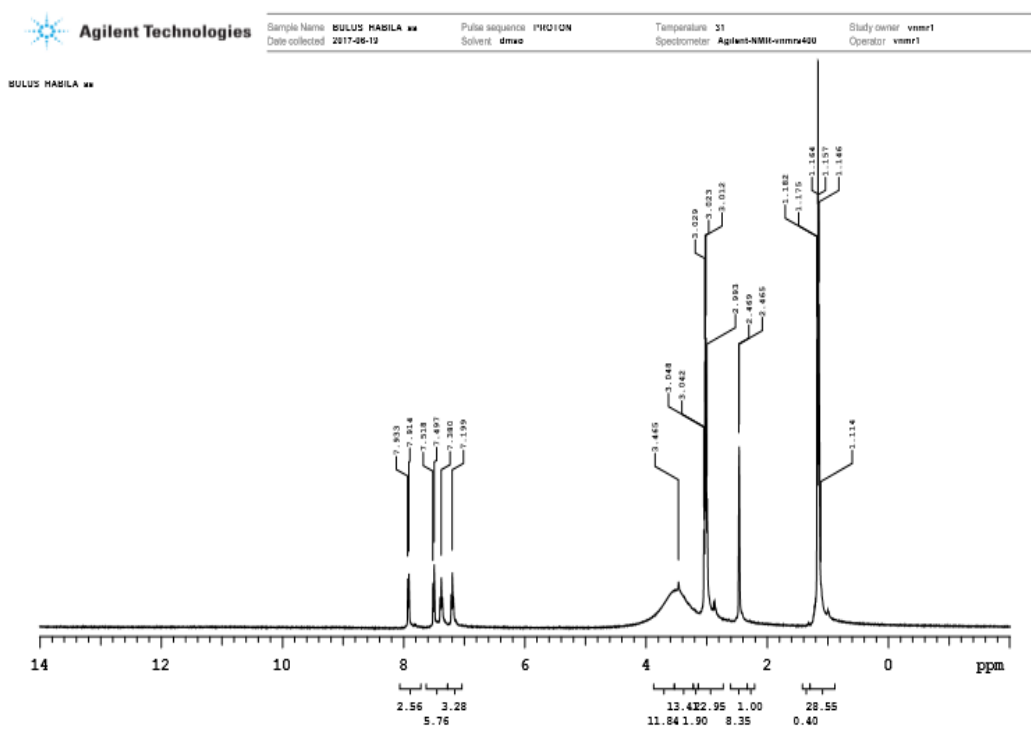
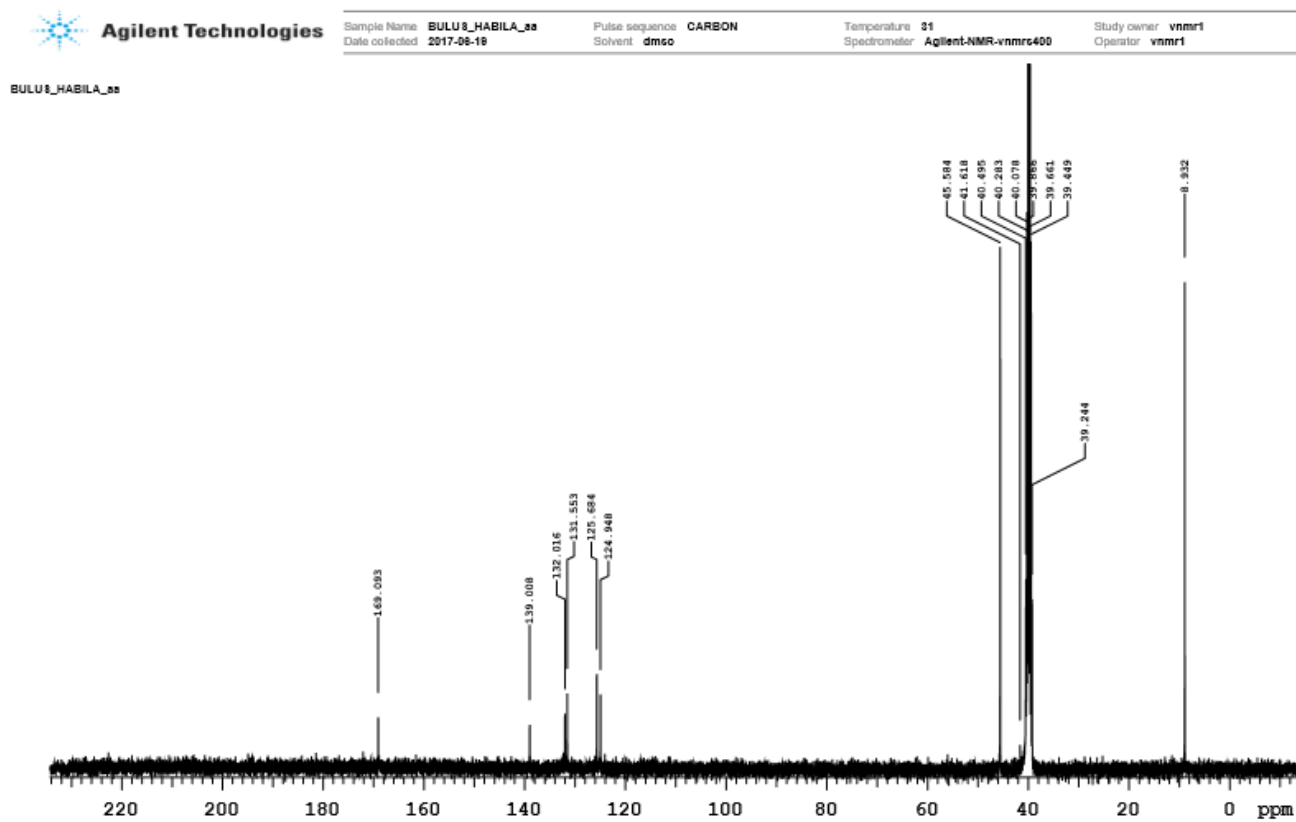


Figure 1: Proton NMR Spectrum of PITLSL

Figure 2: <sup>13</sup>C-NMR Spectrum of PITLSL

**Table 1:** Some physical properties of synthesized 3-chloropropylpolysiloxane and other immobilized ligand matrices

Compounds	water	Solubility Methanol	Diethyl Ether	Colour	Texture
3-CPP	Insoluble	Insoluble	Insoluble	White	Amorphous
F 3-CPP	Insoluble	Insoluble	Insoluble	White	Amorphous
PITSLS	Insoluble	Insoluble	Insoluble	White	Amorphous

**Table 2:** Preparation of buffer solutions at various pHs

0.5 mol/dm <sup>3</sup> Solutions							Total Vol of Buffer
pH	KPH	HCl	NaOH	Na <sub>2</sub> HPO <sub>3</sub>	KH <sub>2</sub> PO <sub>3</sub>	Vol of solution	
2	250	247.5				500	2500
4	250	0.5				500	2500
6			28		250	500	2500
7		122		378		500	2500
9		22.5		477.5		500	2500

**Preparation of Standard Stock Simulated Chromium Solution**

Metal salt	Metal salt (g/mol)	Metal	Metal g/mol	g	Volume cm <sup>3</sup>	Conc PPM
K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub>	294.18	Cr	103.992	0.3395	1000	61.135

**Table 3:** Simulated solution of Cr (III) at various pHs

Metal	Stock Initial conc	Theoretical Stock Final conc	Stock Vol	Final Buffer Vol	pH	Final Volume achieved
	(C <sub>1</sub> ) ppm	(C <sub>2</sub> ) Ppm	(V <sub>1</sub> ) cm <sup>3</sup>	(V <sub>2</sub> ) cm <sup>3</sup>		cm <sup>3</sup>
Cr	61.135	10	81.7862	418.214	2	500
	61.135	10	81.7862	418.214	4	500
	61.135	10	81.7862	418.214	6	500
	61.135	10	81.7862	418.214	7	500
	61.135	10	81.7862	418.214	9	500

**Table 4:** Effect of pH on the adsorption of Cr(III) in simulated water at PITSLS 20 % adsorbent

Adsorbents	Adsorbents Dose (mg)	Initial Concentration (ppm)	Final Conc (ppm)	pH	Amount Adsorbed (ppm)	% Adsorbed
PITSLS	20	11.13	0.24	2	10.89	97.84
			0.14	4	10.99	98.74
			0.09	6	11.04	99.19
			0.15	7	10.98	98.65
			0.08	9	11.05	99.28

**Table 5:** Effect of pH on the adsorption of Cr(III) in tannery wastewater at PITSLS 20 % adsorbent

Metal	Blanks	Conc.	pH					
			2.000	4.000	6.000	7.000	9.000	
Cr (ppm)	A	0.000						
	B	0.000	Cia	17.112	14.854	10.952	5.897	3.693
	Tb		Cib	17.112	14.854	10.952	5.897	3.693
			Cfa	15.368	11.999	0.280	0.514	1.136
			Cfb	15.368	11.999	0.280	0.514	1.136
		%ADS		10.192	19.220	97.443	91.284	69.239

Note: A and B= Blanks, Tb=Total blank, 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.

**Table 6:** Effect of adsorbent dosage (PITSLS) at pH 6 on the adsorption of heavy metals in tannery wastewater

Metal	Blanks	Conc.	Adsorbent (mg)			
			10	20	30	
Cr (ppm)	A	-0.014				
	B	-0.034	Cia	10.952	10.952	10.952
	Tb		Cib	10.952	10.952	10.952
			Cfa	0.280	0.198	0.172
			Cfb	0.280	0.198	0.172
		%ADS		97.443	98.192	98.430

Note: A and B= Blanks, Tb=Total blank, 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

**Table 7:** The effect of contact time on the adsorption of Cr<sup>3+</sup> using PITSLS on simulated wastewater

Ligand	Time (t)	Cr <sup>3+</sup> = 11.14 ppm					Intercept	k <sub>2</sub>	q <sub>e</sub>	C <sub>e</sub>
		C <sub>t</sub>	q <sub>t</sub>	t/q <sub>t</sub>	slope					
PITSLS	1	2.763	20.933	0.048						
	5	1.810	23.316	0.214						
	10	1.440	24.241	0.413						
	20	0.745	25.978	0.770	0.038	0.018	0.083	26.247	0.638	
	30	0.733	26.008	1.153						
	60	0.706	26.076	2.301						
	120	0.671	26.163	4.587						

### 3.2. Discussion

#### 3.2.1. Nuclear Magnetic Resonance Analysis of PITSLS

The <sup>1</sup>H NMR spectrum of PITSLS presented in Figure 1 shows signals at (ppm): 1.16 (methyl proton); 2.4 (DMSO); 3.02 (residual peak due to DMSO) and 3.04 (proton adjacent to carbonyl group); 7.38 and 7.19 (aromatic proton); 7.933, d, J=7.6 Hz and 7.518, d, J= 8.4Hz (aromatic proton).

The <sup>13</sup>C NMR spectrum of PITSLS presented in Figure 2, which shows signals at (ppm): 169.09 (carbonyl group); 139.00 – 124.94 (aromatic carbon atoms); 45.58 (carbon adjacent to carbonyl group); 41 – 39.44 (solvent peak for DMSO) and 8.93 (alkyl or methyl carbon atoms).

<sup>29</sup>Si NMR was not obtained because DMSO could not dissolve the polysiloxane matrix completely but this could be resolved using Solid State Nuclear Magnetic Resonance (Issa *et al.*, 2015).

**3.2.2. Optimization of Adsorption Parameters:** Parameters such as pH, contact time and adsorbent dosage have been studied to evaluate their effects on the heavy metal removal efficiency of an adsorbent and were optimized, keeping other parameters constant as presented in Tables 5, 6 and 7 respectively.

#### 3.2.3. pH Studies of Simulated Water and Tannery Wastewater

Solution pH is a key parameter that influences the adsorption process, particularly the adsorption capacity. The pH of the solution can affect the surface charge of the adsorbent, the degree of ionization of the adsorbent molecule, and the extent of dissociation of functional groups on the adsorbent's active sites.

The effect of pH on adsorption of heavy metals in simulated water is presented in Table 4 and 5, due to the recurrent appearance and performance to adsorption, pH six was selected and used for kinetic studies which is in agreement with the works reported by Hayel *et al.*, (2005); El-Ashgar (2009); Issa *et al.*, (2015) and consequently employed in the detoxification of tannery digested wastewater.

#### 3.2.4. Effect of Adsorbent Dosage (PITSLS) on the Adsorption of Heavy Metals

After Treatment of Tannery Wastewater, as presented in Table 6, from the batch experiment, the results showed a significant increase in the adsorption percentage when 10 and 20 mg of adsorbents were used. This increase in the adsorbent dosage is effective in breaking the resistance originating from mass transfer per unit weight, resulting in increased adsorption. Still, the adsorption was higher when 30 mg was used, with a 98.430 percent adsorption, which could account for additional reactive sites for this adsorption, which are in agreement with the work as reported by Ejikeme *et al.*, (2011).

#### 3.2.5. Effect of Contact Time on Heavy Metals in Simulated Water

The kinetic results obtained are presented in Table 7 from the batch experiments. The results show that adsorption was significantly high in the first minute, with total adsorption for PITSLS, and subsequently reduced with an increase in time to 120 minutes, which is

in agreement with the work reported by Ejikeme et al., (2011). This trend can be explained by the fact that within the first 30 minutes, the adsorbent still had a vast number of unoccupied sites onto which the adsorbate particles could adsorb. As a result, there was a high probability of adsorption for every migrating/diffusing molecule of adsorbate. As so many adsorbent particles were adsorbed, and within this time, the number of unoccupied sites decreased and the adsorbent surface started approaching saturation.

#### 4. CONCLUSION

The product was characterised using a Nuclear Magnetic Resonance Spectrometer (NMR). <sup>1</sup>H-NMR spectrum showed chemical shifts (ppm) at 2.2 assigned to (2H, S); <sup>13</sup>C signals at 169.093 assigned to (C=N, C=O) and 124.948 to 139.008 assigned to aromatic carbon, respectively, for the thiosalicylic acid ligand system, which was soluble in DMSO. The adsorption percentage of immobilized Thiosalicylic acid ligand system gave 97.443 % at pH 6.00 with an adsorbent dose of 30 mg, resulting in an adsorption percentage of 98.430 % for chromium in tannery wastewater. The results showed significant adsorption within the first minute of contact time, followed by a gradual reduction with an increase in time to 120 minutes, respectively, due to the unavailability of reactive sites for adsorption. PITSLS has proven to be a promising adsorbent in detoxifying tannery wastewater.

#### Authors contribution:

*Habila Bulus*: Gathered and organized data. Created the manuscript's first draft, which included the ligand preparation, NMR analysis and interpretation of the results. Revised and edited the manuscript to improve clarity, quality, and accuracy.

*Emmanuel. C. Ezeh*: Gathered and organized data, carried out analysis and interpretation of the results. Revised and edited the manuscript to improve clarity, quality, and accuracy.

*Ezendaba Joy Okwuchukwu*: statistical analysis and type setting

*Agbo, Ndidiamaka Justina*: Collection of samples for analysis and preparations

*Simon. S. Moses*: Collection of samples for analysis and preparations

#### Informed consent

Not applicable.

#### Conflicts of interests

The authors declare that there are no conflicts of interests.

#### Ethical approval & declaration

Not applicable.

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The study has not received any external funding.

#### Data and materials availability

All data associated with this study are present in the paper.

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