JOURNAL of THE TURKISH CHEMICAL SOCIETY
SECTION: A
CHEMISTRY
TURKISH CHEMICAL SOCIETY

Effective Removal of Heavy Metal Ions Using Glycerol and Starch Xanthate

Aliyu Danmusa Mohammed[1]*, Johan Hendriks[2]

[1]Research Focus Area for Chemical Resource Beneficiation, Catalysis and Synthesis Research Group, North-West University, Private Bag X6001, Potchefstroom 2520, South Africa
[2] Centre for Water Sciences and Management, North-West University, Private Bag X6001, Potchefstroom 2520, South Africa

Abstract: Glycerol and insoluble starch xanthates were synthesised and effectively used in the removal of Pb, Cd, and Cu from aqueous solutions. The insoluble metal complex formed between the sulphur atoms in the xanthates and the heavy metals were easily separated. Lower dosage of glycerol xanthate was required in each case, with the optimum molar ratio of metal ions to glycerol xanthate (M^{2+}/GX) of 2. Moreover, the use of glycerol xanthate requiring no pH adjustments gave a 100 % heavy metal removal within the range of the detection limit. As for the insoluble starch xanthate, there was a remarkable metal scavenging activity when the xanthate contained high amount of sulphur per molecule (10.12% S) and when the pH was adjusted to 6. Butyl xanthate was also synthesised to make a good comparison with the glycerol and insoluble starch xanthate. The xanthates from these two sustainable materials (Starch and glycerol) are proven to be more effective in metal scavenging activity. Fourier transform infrared and CHNS elemental analyses were used to prove the evidence of xanthation, in addition, carbon-13 nuclear magnetic resonance spectroscopy was used to characterise the glycerol xanthate.

Keywords: Glycerol, heavy metals, starch, sulphur, xanthates.

Submitted: May 11, 2017. **Accepted:** September 29, 2017.

Cite this: Mohammed A, Hendriks J. Effective Removal of Heavy Metal Ions Using Glycerol and Starch Xanthate. JOTCSA. 2017;4(3):1031–44.

DOI: to be assigned.

***Corresponding author. E-mail:** aly27moh27@gmail.com; Tel: +2348032334889.

INTRODUCTION

Heavy metals such as lead, cadmium, and copper pose serious environmental hazards. The expansion of the human population, human activities, scientific and technological advancement are responsible for the introduction of lethal substances to our ecosystem. Water is one of the greatest media through which pollution gets its way into the whole planet. Many ways are considered in limiting the effects of these hazardous materials to the environment. One of these techniques is the treatment of wastewater from either domestic or industrial effluent. The strategy involves the ultimate treatment of the wastewater to make it fit for drinking, or in some cases the removal of deadly contaminants present in the wastewater that might be directly hazardous to the environment (1).

Since the dawn of modern technology, several techniques have been employed in the removal of heavy metals from wastewater, these include precipitation, flotation, solvent extraction, adsorption, membrane processing, and electrolytic methods (2). All these techniques are met with some limitations which range from the high cost of the materials to operational costs. Patterson (3) reported that one of the widely used techniques is the precipitation using hydroxides to form heavy metal hydroxide precipitates. Due to the safety concern of this technique, its application is followed by the processes of solidification and stabilisation that are needed for the released metal hydroxide in the environment. Another technique, a heavy metal scavenging process using xanthates, is considered a promising technique (4) and requires a low-cost of operation. The efficiency of the technique depends on the formation of insoluble complexes with the heavy metal ions, and unlike the sulphide precipitation technique, the use of xanthates is not associated with the problem of residual sulphide in the treated water (5).

In this study, insoluble starch xanthate (ISX) and fully substituted glycerol xanthates (GX) were synthesised and used in the removal of Cu, Cd and Pb from wastewater. The efficiency of each xanthate at different conditions was investigated. The use of starch xanthate has been reported to have an impressive efficiency in metal scavenging activity (2-6). A good comparison in efficiency with alkyl xanthate, in this case butyl xanthate, was studied in this work. Glycerol polyhydroxysodium xanthate has been used as a depressing agent in the separation of minerals due to its structural features (7).The aim was to study the effect of a many xanthate group per molecule of starch and glycerol on the metal scavenging activity. Apart from what earlier works emphasised the efficiency of xanthates is not only based on the number of sulphur atoms per molecules of the compound, but also on the structural feature of GX. Unlike in starch xanthates whereby the sulphur groups are attached to the bulky polymeric structure of the glucose units, GX is a small molecular organic compound containing a more exposed sulphide groups at spatial positions and without molecular hindrance that could be expected in starch xanthates. In the case of ISX in this study, there was further exploration of experimental conditions to maximise the effectiveness of the heavy metal removal. The increase in the amount of sulphur per average glucose unit and the suitable adjustment of pH of the mixture were investigated.

EXPERIMENTAL

Materials and methods

Glycerol, potato starch, epichlorohydrin (99 %) and carbon disulphide (Sigma-Aldrich) were used as received. The instrument used is Agilent 7500CE ICP-MS and it was run at the following experimental conditions: RF Power: 1550 W, Sample depth: 8 mm, Carrier gas: 1 L/min, Makeup Gas: 0.17 L/min, S/C Temp: 2 °C.

The FTIR analysis of the samples was carried out using a Bruker VERTEX 80 FTIR spectrometer. The infrared spectra of the samples were recorded in absorbance mode, at a frequency range of 550–4000 cm^{-1}, at room temperature, with a resolution of 4 cm^{-1} based on 32 scans and using an ATR Bruker Platinum-Diamond accessory.

The NMR analyses was carried out by dissolving a sample of GX (25 mg) in deuterium oxide (D_2O), and the ^1H and ^{13}C NMR spectra were recorded at room temperature on a 600 SB Ultra Shield^{TM} Plus NMR spectrometer equipped with an Oxford magnet (14.09 T), operating at 600 MHz.

Preparation of GX

Glycerol (7.3 mL), mixed with NaOH (12 g), were stirred in a three-necked round-bottomed flask for 30 min at a temperature of 35 °C. CS_2 (18 mL) was added to the mixture and stirred for 14 h at 10 °C. The yellow solid was precipitated with methanol, washed with acetone and ether and dried in a vacuum oven. Scheme 1 shows how a fully substituted glycerol xanthate is synthesised.

Selected IR, *v* (cm^{-1}):1430 (O-CS), 1068 (C=S), 820 (C-S), 2976 (C-H). ^{13}C NMR (D_2O) δ= 61 (CH), 72 (-CH_2-glycerol), 167 (CS).

Insoluble starch xanthate (ISX).

The procedure reported by Wing *et al.*(6) was used. Dried starch (20 g) was slurried in water (150 mL) containing NaCl (0.3 g) and epichlorohydrin (EPI) (1.1 mL), at a temperature of 50 °C. KOH (1.2 g) was slowly added to the reaction mixture over a period of 30 min. The reaction mixture was allowed to cool to 30 °C followed by the addition of water (5 mL) containing EPI (0.4 mL) and stirred for 16 h. NaOH (9.6–15 g) in water (50 mL) was added to the flask containing the cross-linked starch and stirred. CS_2 (3.0–5.0 mL) was added and stirred for another 16 h. The product was washed with water and acetone and dried in vacuum oven to constant weight. Scheme 2 shows the synthesis of starch xanthate.

Selected IR, *v* (cm^{-1}):1436 (O-CS), 1079 (C=S), 816 (C-S), 3241 (O-H)

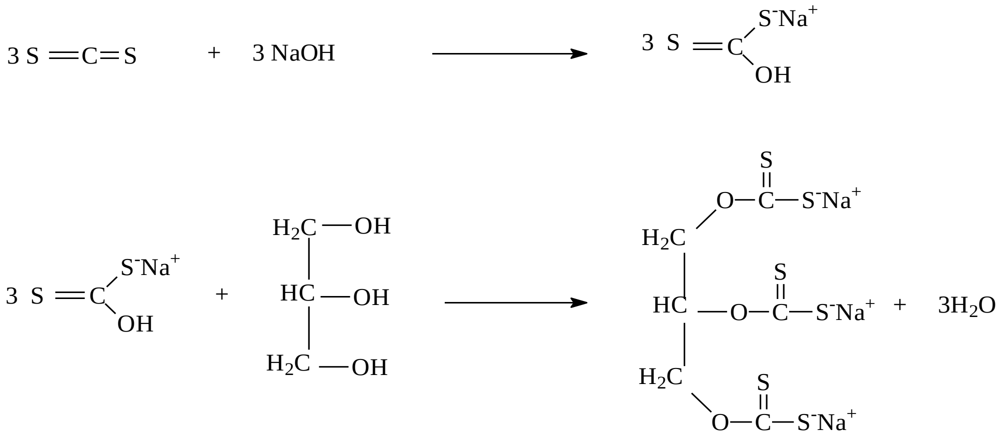
Potassium butyl xanthate (KBX).

The procedure reported by Mohammed *et al*. (8) was used. A flask containing n-butanol (50 mL) was purged with nitrogen gas to maintain an inert atmosphere, KOH (1.12 g) was added and the mixture was vigorously stirred. CS_2 (1.2 mL) was slowly added over a period of 30 min. The cloudy yellow solution was allowed to stir for 2 h until a yellow precipitate was formed. The mixture was filtered and washed with n-butanol and stored in a vacuum oven overnight.

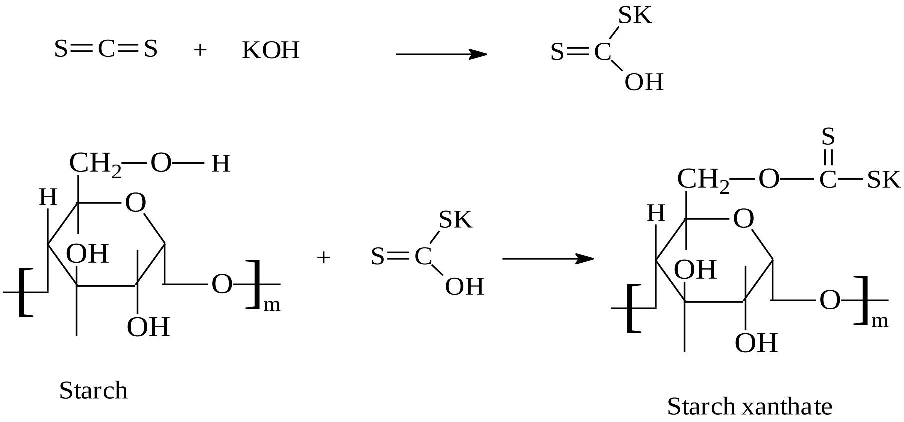
Removal of heavy metal

Three different samples of synthetic wastewater containing $Pb(NO_3)_2$, $Cd(NO_3)_2 \cdot 4H_2O$, and $Cu(NO_3)_2 \cdot 3H_2O$ (5–1000 ppm), respectively, were tested to determine the metal removal efficiency using a fully-substituted glycerol xanthate at different molar ratios of 0.3–3 (0.3, 0.5, 0.7, 1.0, 1.5, 2.0 and 3.0 for M^{2+} and the xanthate, respectively). Starch xanthate was also used in the wastewater samples containing the same concentration of the metals at different doses. The mixture was centrifuged at a speed of 200 rpm in a centrifuge for 30 minutes at room temperature and then increased to 2000 rpm for another 30 min. The insoluble complex of M^{2+} was obtained after decantation and oven-dried at 25 °C for 24 h. The solution was filtered again and the filtrate was analysed to detect the presence of metal ions using ICP-MS. There was no pH adjustment in the use of glycerol xanthates throughout the experiment. In the use of starch xanthate, however, the pH was adjusted to 6 as has been reported by Rao and Leja to be the appropriate pH for the application of starch xanthate in metal removal, as at lower pH possible decomposition of the xanthates could occur (5).

The same experiment was repeated using 100 ppm of $Pb^{2+}$to optimise the stoichiometric ratio. The stoichiometric ratio obtained was used to determine the removal of Pb^{2+}, Cd^{2+}, and Cu^{2+} at 1000, 500, 100, 50 and 5 ppm for each of the metals from aqueous medium.



Scheme 1: Synthesis of GX.



Scheme 2: Synthesis of starch xanthate.

RESULTS AND DISCUSSION

FTIR analyses

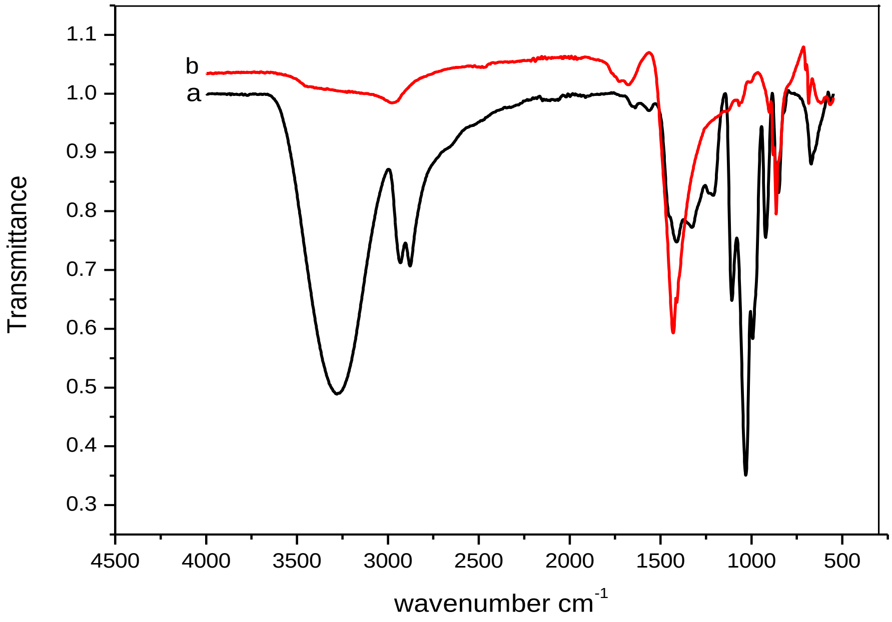


Figure 1: FTIR Spectra of glycerol (a) and GX (b).

The FTIR spectrum of glycerol is shown in Fig. 1(a). The absorption band at 3280 and 2930–2877 cm^{-1} is assigned to the OH and C-H stretching vibrations, respectively. In Figure 1 (b), in addition to the existing peaks in glycerol, the GX showed other important peaks at around 1674 cm^{-1} due to the stretching of SP^2 carbon skeleton nature, 1430 cm^{-1} due to O-CS stretching vibration, 1068 and 820 cm^{-1} due to C=S and C-S stretching modes respectively. The C-H stretching mode was confined to 2976 cm^{-1} in GX. The disappearance of any OH stretching in the final product confirms that complete xanthation of the glycerol has been successfully achieved. In starch xanthate, see Figure 2, important peaks appeared at 3241 cm^{-1} due to OH stretching, 1589 and 1436 cm^{-1} were due to O-CH and O-CS stretching vibrations. The C=S stretching mode of the xanthated starch was assigned to 1079 cm^{-1}.

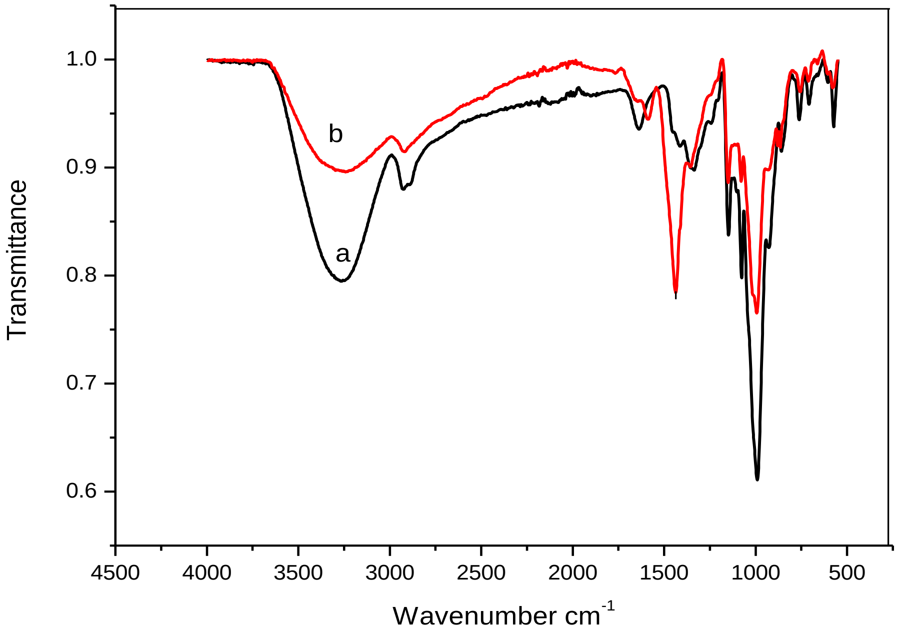


Figure 2: FTIR Spectra of starch (a) and starch xanthate (b).

CHNS analysis and heavy metal removal of the xanthates

The elemental analysis showed the amount of carbon, hydrogen, and sulphur present in the xanthate molecules as shown in Table 1. The CHNS analysis confirmed that xanthation of all the chemical substrates did take place, moreover, the percentage S present in each xanthate determined the level of efficiency in the heavy metal removal. GX has the highest %S, hence the most effective heavy-metal scavenging activity. The %S determined the number of xanthate groups that were chemically bound to the chemical substrates. The more the number of xanthate groups present in a molecule, the more its ability to chemically-interact with the heavy metals ions to form the insoluble complex.

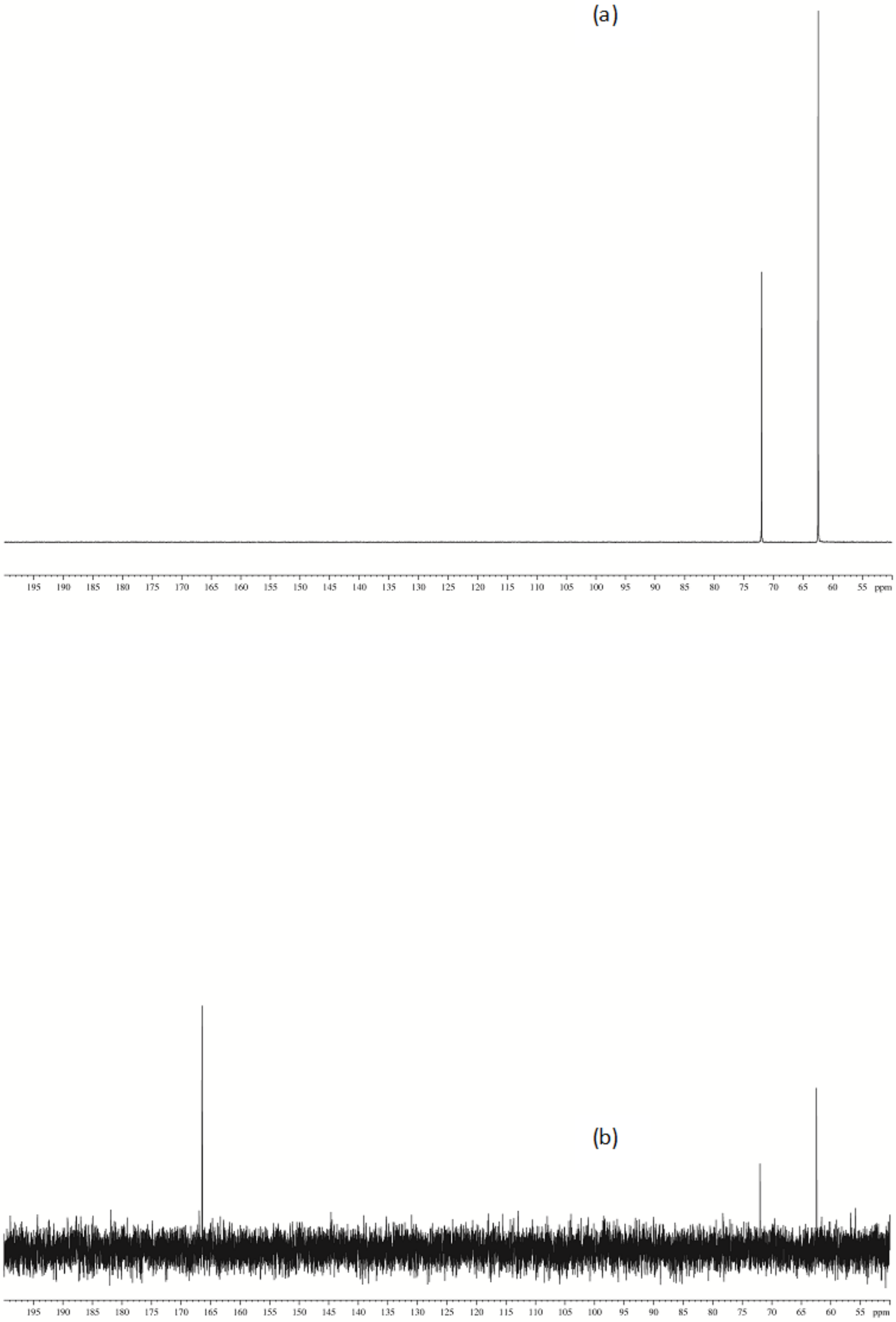


Figure 3: ^{13}C NMR spectra of (a) Glycerol and (b) GX.

^{13}C NMR of GX

Figure 3(a) is the ^{13}C NMR spectrum of glycerol. The signals shown at 61 and 72 ppm are assigned to CH and CH_2 carbon-hydrogen bond in the glycerol; while in the xanthated glycerol, Fig. 3(b), a new signal at 167 ppm is due to sulphur-carbon bond (CS) from the xanthate (9,10). This indicated a successful xanthation of the glycerol.

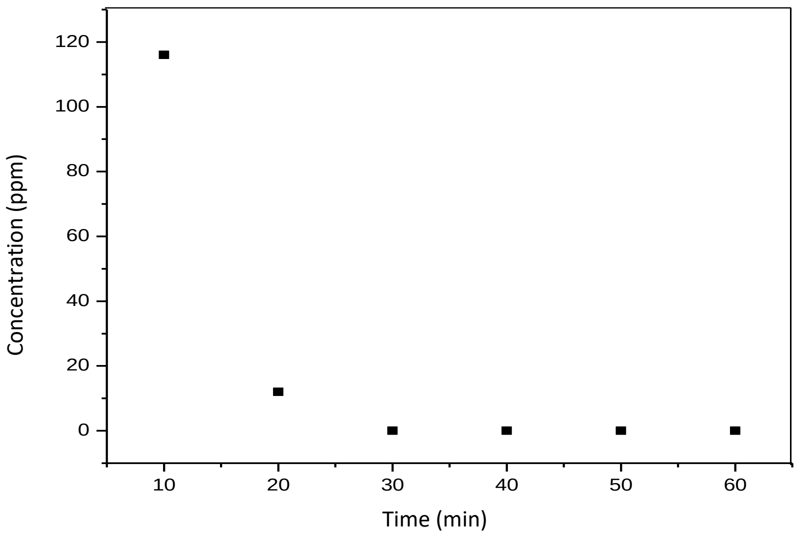


Figure 4: Removal of lead by GX at different contact time; 2.0 S/M^{2+}; 1000ppm of Pb.

The metal removal ability at different experimental conditions of ISX and GX are shown in Figures 4 and 5 and Tables 2 and 3. The overall efficiency of each xanthate was carefully studied and monitored at different conditions on different metal ions. From previous works, Pb and Cu were reported to have poorer sorption ability to the scavengers when compared to Hg and Cd. The poor sorption is attributed to the following: Relative atomic size, ability of the metal ion to react with the scavenging agent, charge density of the metal ion, and reactivity of the metal ion (11). The heavy metal removal ability of GX was impressively higher than ISX. The use of ISX in the removal of Pb, Cd and Cu using different molar ratios is shown in Table 2. The ease of complexation (with the xanthate group) and the removal of the insoluble product determined the scavenging efficiency in each case. At higher amount of xanthate:metal ratio there was a complete removal of all the metals. Conversely, at lower amount (< 3.0) and at excessive amount (> 3.0) of xanthate:metal ratio, there was a partial removal of all the metals, with copper being the most in solution.

Table 1 : % element by mass from the elemental analysis of different xanthates**.**

Samples	C (%)	H (%)	S (%)
Starch	40.8	7.61	0.00
ISX (1)	28.33	6.06	5.30
ISX (2)	19.89	4.32	10.12
BuX	31.12	4.43	34.01
GX	18.02	1.26	49.32

On the other hand, lower dosage of GX was found to be effective in the complete removal of all the metals (within the detection limits) on different concentrations of the heavy metals. GX, though soluble in water, immediately formed an insoluble complex with the metal ion present in the water sample. The mixture was centrifuged and the solution decanted out. The solution was filtered and the filtrate was analysed.

Table 2: Removal of Pb, Cd, and Cu at different doses of ISX; 1000 ppm solution of each metal ion; 60 min contact time; room temperature. Detection limit: 0.1 ppb.

ISX : M^{2+} ratio	Concentration of Pb (ppm) left	Concentration of Cd (ppm) left	Concentration of Cu (ppm) left
2.0	43	27	320
3.0	< 0.1 ppb	< 0.1 ppb	< 0.1 ppb
4.0	< 0.1 ppb	< 0.1 ppb	93
5.0	12	4.0	97

Effect of treatment time on the removal of heavy metals

The rate of metal removal increased with an increase in time at the beginning until all the available metal ions were bound with the active groups in the xanthates. In Figure 4, the rate of metal ion removal levelled off after 20 minutes which showed that from that time all the available metal ions were taken off by the active groups of the xanthates. It, moreover, indicated that all the processes involved, from the release of mobile metal ions in the solution to the complex formation with the sulphur donor atoms of the xanthates, took a short period of time. Thus, the technique could effectively be employed in industrial application for wastewater treatment.

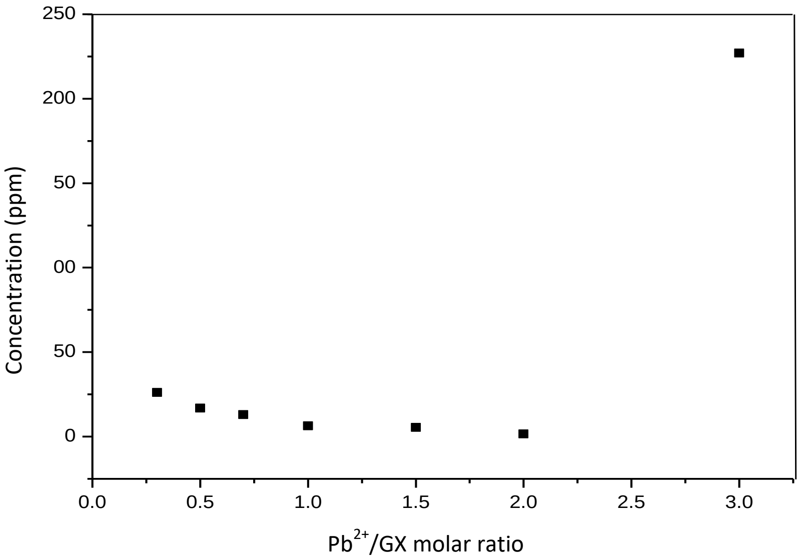


Figure 5: Removal of lead by GX at different molar ratios; at 60 min contact time; room temperature. Detection limit: 0.1 ppb.

Effect of xanthate dose on the heavy metal removal.

The effect of GX dose is shown in Fig. 5. The various M:GX molar ratios showed a varying role in the removal of Pb^{2+} from aqueous solution.

The efficiency in Pb^{2+} removal initially increased with increase in the M:GX ratio. In Figure 5 the highest amount of heavy metal removal was observed at a molar ratio of Pb^{2+}/GX of 2, with about 100 % removal. Also, the optimum molar ratio is not affected by the pH of the mixture. The M:GX molar ratio can best be explained on the basis of chemical interaction between the xanthate functional group (CS_2^-) in the substrate and the metal ions which resulted in the complexation reaction to form an insoluble metal complex compound. At lower amount of M:GX ratio (< 2.0), there was insufficient sulphur atoms in the substrate for the metal ions needed for complexation. Hence, there was incomplete removal of the metal ions. On the other hand, excess amount of GX in the mixture (> 2.0 M:GX) in the metal ion solution could be attributed to the possible interaction of the xanthate molecules with each other. The flocculation behaviour of heavy metals and xanthate system is similar to the colloid-cationic system in water treatment. The positively charged metal species are considered as colloids and anionic xanthate as polyelectrolyte. Thus, in higher amount of xanthate dose, the residual charges from the unreacted xanthates prevailing on the metal-xanthate complex could hinder the particles aggregation (3).

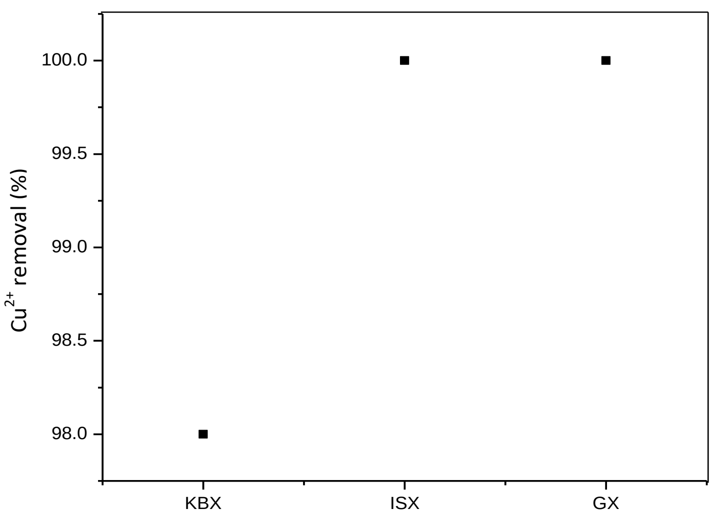


Figure 6: Removal of copper by different xanthates; 1000 ppm of Cu; 60 mins contact time.

Each sample of xanthate was used at its optimum conditions to allow a good comparison in the scavenging ability. Aqueous solution containing copper (II) ions was selected due to the difficulty usually encountered in its removal when compared to other metals as explained earlier. Complete removal (100 %) of copper by ISX and GX (compared to 98 % removal by KBX (Figure 6) showed that xanthates from these two sustainable products (starch and glycerol) were quite efficient in the metal scavenging activity. Generally, GX required a straightforward and simple chemical technique of synthesis, while the insoluble starch xanthate containing >5% S required much more chemical procedures of synthesis.

All what has been mentioned above could not be unconnected with the structural features of glycerol and starch. The simple molecular structure of glycerol compared with the polymeric molecular structure of starch played a fundamental role in the effective and easy complexation with the metal ions in an aqueous mixture. This property coupled with its greater reduction ability (than from sugars) facilitated its simple xanthation and other chemical reactions that could be used in the production at higher yields of ethanol, xylitol, propionate and succinate (12).

Table 3: Removal of different concentration of Pb, Cu and Cd using a ratio of 3:0 S/M^{2+} of two different samples of ISX; at 60 min contact time; pH 6, room temperature and under detection limits of 0.1, 0.2 and 0.1ppb for Pb, Cu and Cd respectively.

Conc. (ppm)	% sulphur	Conc. of Pb (ppm) left	Conc. of Cd (ppm) left	Conc. of Cu (ppm) left
1000	5.3	113	93	202
500	5.3	94	67	171
100	5.3	47	41	62
50	5.3	20	11	34
5	5.3	2	2	3
1000	10.12	<0.1 ppb	<0.1 ppb	<0.1 ppb
500	10.12	<0.1 ppb	<0.1 ppb	<0.1 ppb
100	10.12	<0.1 ppb	<0.1 ppb	<0.1 ppb
50	10.12	<0.1 ppb	<0.1 ppb	<0.1 ppb
5	10.12	<0.1 ppb	<0.1 ppb	<0.1 ppb

The GX in this experiment contained three xanthate groups per molecule, which probably acted as a bidentate ligand in the complex formation with the metal ions. At a higher amount of M:GX molar ratio, the free metal ion remained in solution as unreacted species when all the available xanthate groups were used up, hence, the metal removal efficiency became low. On the other hand, a low molar ratio of M:GX (excess GX) also results in a relatively poor removal efficiency, as colloidal solution was formed which became difficult to separate.

In the ISX, similarly, the efficiency was enhanced with more %S in the starch molecules. The more %S the greater the availability of active groups (xanthate) ready for complexation reaction with the metal ions. Table 3 shows the partial removal of the metals when the % sulphur was 5.3 in the ISX. There was, however, an excellent metal scavenging activity of ISX when the xanthation parameters were adjusted to produce a high sulphur % of 10.12 in the product. Even Cu^{2+} which could not precipitate out easily from an aqueous mixture at a lower percentage of sulphur was completely removed (within the detection limit). This could be explained based on what has been stated above. The amount of sulphur in xanthates determined the bonding and complexation power with the heavy metal ion. Moreover, both the GX and ISX have structural features that could accommodate more xanthate groups as can been seen in Schemes 1 & 2.

CONCLUSIONS

Xanthates from starch and glycerol are proven to be reliable and efficient metal scavengers in aqueous media. An easy and fast complexation reaction between the heavy metal ions and the sulphur atoms in the xanthate, followed by precipitation of the insoluble metal complex showed how effective and reliable these xanthates are. The structural features of xanthates from these sustainable substances could allow more xanthate groups to be synthesised in their structures. This explained why they are more efficient in metal scavenging activity than common alkyl xanthates, like butyl xanthate. In this study, moreover, glycerol xanthate was found to be the most effective, as lower dosage was required and not dependent on pH, like the insoluble starch xanthate and the alkyl xanthates.

ACKNOWLEDGEMENT

The authors are grateful to the North-West University, Sasol Technology and the South African National Research Foundation (NRF) for financial support.

REFERENCES

1. Brostow W, Pal S, Sing R. P., A Model of Flocculation. Materials Letters, 2007;February:61(22):4381–4.

2. Guo L., S. Zhang S., Ben-Zhi Ju B., Yang J., Quan X., Removal of Pb(II) from Aqueous Solution by Cross-linked Starch Phosphate Carbamate. Journal of Polymer Research. 2006 September;13(3):213–7.

3. Chaudhari S., Tare V., Heavy Metal–Soluble Starch Xanthate Interactions in Aqueous Environments. Journal of Applied Polymer Science. 1999 Feb 22;71(8):1325–32.

4. Patterson J. W., Effect of carbonate ion on precipitation treatment of cadmium, copper and lead. Proceeding 36th annual industrial waste conference, Purdue University, West Lafayette, Indiana 1981;579-602

5. Chang YK., Shih PH., Chiang LC., Chen TC., Lu HC., Chang JE., Removal of heavy metal by insoluble starch xanthate. Environmental Informatics Archive. 2007;5:684-9.

6. Wing R.E., Doane W. M., Russel C. R., Insoluble starch xanthate: Use in heavy metal removal. Journal of Applied Polymer Science. 1975 Mar;19(3):847–54.

7. Dao-ling X., Yue-hua H., Wen-qin Q., Ming-fei H., Synthesis of glycerine-xanthate and its depressing mechanism in separation of marmatite from arsenopyrite. Journal of Central South University of Technology. 2006 Dec;13(6):678–82.

8. Mohamed A. A, Kani I., Ramirez A. O., Fackler J. P., Synthesis, Characterization, and Luminescent Properties of Dinuclear Gold(I) Xanthate Complexes: X-ray Structure of [Au2(nBu-xanthate)2. Inorganic Chemistry. 2004 Jun;43(13):3833–9.

9. Gorgulu A. O., Celikkan H., Arslana M., The Synthesis, Characterization and Electrochemical Behaviour of Transition Metal Complexes Containing Nitrogen Heterocyclic Sulphur Donor Ligand. Acta Chimica Slovenica. 2009 Jul;56:334-9.

10. Tan R., Datong Song D., C−H and C−S Activations of Quinoline-Functionalized Thiophenes by Platinum Complexes. Organometallics. 2011 Mar; 30:1637–45.

11. Mostafa, KM., Samarkandy M., El-Sanabary AA. Graft Copolymers and their Application in Waste Water Treatment. Journal of Applied Polymer Science. 2009 Nov;112:2838-46.

12. Dharmadi Y., Murarka A, Gonzalez R., Anaerobic Fermentation of Glycerol by E. Coli. Biotechnology and Bioengineering. 2006 Aug;94:821-9.