Removal of Nickel^{II} and Copper^{II} ion from Water by novel compound Pentaerythritolxanthate

Nath A.[1*] and Pande P.P.[2]
1. B.R.D. P.G. College, Deoria, 274001, INDIA
2. M.M.M. University of Technology, Gorakhpur, 273010, INDIA
*a.nath76.brdpg@gmail.com

Abstract
Pentaerythritol xanthate (PEX) has been synthesized by the reaction of pentaerythritol (PE) and carbon disulphide (CS_2) by condensation reaction. In this reaction water is used as solvent and product PEX is soluble in water. The xanthate was extracted by ether and purified by re-crystallization from methanol.

The yield of synthesized PEX is about 80%. PEX was characterized by using micro-analytical data, Elemental analysis of C, H, N, S and O, spectral data as Fourier – Transform Infrared (FT-IR), Nuclear Magnetic Resonance (NMR). The PEX is used in removal of metal ion (Cu^{II} and Ni^{II}) from water by complexation a method which was studied using by Ultra Violet (UV-visible) absorption spectra.

Keywords: Pentaerythritol xanthates, metal ions, complexation, drinking water.

Introduction

Currently human society is baffled with the extensive environmental pollution present in every part of earth. Among this water pollution is one of the major serious problems from which more than 8 lac people die every year by consuming polluted drinking water[1]. Many of the harmful effects of polluted water are caused by different metal ions such as nickel, copper, lead, cadmium, mercury etc. which go into the aquatic ecosystem by direct draining of toxic wastewater into the natural water bodies. Some metal ions enter into the body of living being by the use of contaminated water and gradually get accumulated into the cells.

Therefore, the concentration of metal ions continuously increases into living cells. After reaching a certain concentration level, these metal ions not only affect the human health[2-4] but also change the genetic character of the living organism[5]. These metals come into the water system from various industries likes mining, galvanoplastics, pipe corrosion etc. The removal of metal ions is essential for the human health, for this purpose various types of chemical and polymeric materials such as polyacylamide[6] activated carbon, silica gel, aluminium silicates[7]and metal solvent extraction [8]have been used.

An important class of organic compounds is xanthates which show a variety of applications as in industries, analytical and coordination chemistry[9]. On the basis of their coordination behavior, xanthates are used as reagent in analytical chemistry and also used in separation of metal ions from water[10-12]. Copper xanthates adducts with derivatives of pyridine[13] attracted the attention of researchers for removal of metal ions from the water by complexation process for this purpose. Diphenylmethyl xanthates are used as ligands for complexation with divalent metal ions (Fe^{II}, Co^{II}, Ni^{II}, Cu^{II} etc.)[9].

Pentaerythritol with their derivatives has a variety of applications viz. recovery of exhaust of heat[14], retardation of flame[15], oil based lubricant[16], supramolecular gelator[17], energetic materials[18] and some azo oxetane derivatives used as energy binder as in rocket propellent[19].

In this study, the synthesis and characterization of pentaerythritol xanthates have been discussed and the use of this compound is investigated as novel compound which is used for the removal of Ni^{II} and Cu^{II} ions from the drinking water by the complexation process.

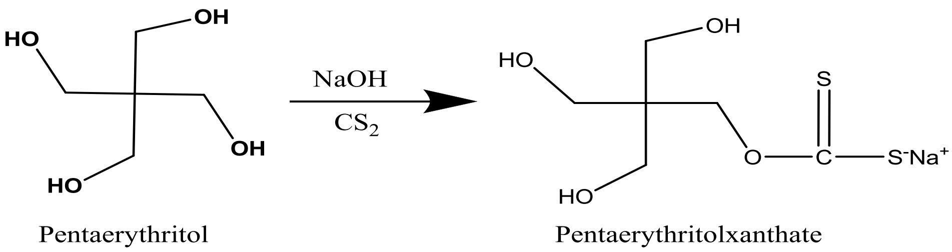
Material and Methods

Materials: Pentaerythritol, carbon disulphides, sodium hydroxide, ether, alcohol, nickel and copper metal ions as sulphates salts are of synthetic grade (99.9% pure) commercially obtained by S.D. Fine Chem. Ltd. and used without further purifications.

Synthesis of Pentaerythritol Xanthates: 5.44 g (40mmole) pentaerythritol was dissolved in 25mL of deionized water in two neck 250 mL round bottom flask and stirred for 30 minutes, then 1.6g (40mmole) NaOH was dissolved in 25mL deionized water, mixed into the pentaerythritol solution, stirred for 1.5h at 80^oC and then 2.50g (40mmole) carbon disulphide was added into the solution and stirred for 24h at room temperature, orange color turbid solution was obtained.

The product was extracted by using excess amount of ether and separated by filtration. The product was dried at 40^oC temperature in hot air oven and purified by re-crystallization in methanol (reaction shown in scheme 1). The synthesized compound PEX is ($C_6H_{11}O_4S_2$) M.W. 211, Yield: 80%. Elemental anal.: (Calc) Found %: C (34.12) 34.01, H (5.21) 5.20, O (30.33) 30.31 and S (30.33) 30.32.

PEX metal ion (Cu^{II} and Ni^{II}) reaction in water: Cu^{II}(Cu1000mg/L) and Ni^{II}(Ni 1000mg/L) solution were prepared by dissolving 1.9645 g $CuSO_4.5H_2O$ and 1.3119g $NiSO_4$ in 500mL distilled water.



Scheme 1: Synthetic diagram of pentaerythritolxanthate.

Table 1
Spectral data of PEX and Metal complex of PEX

Compounds	Absorption Range (cm^{-1})	Type of Vibration
PEX	3329	O-H Stretching[20]
	1633	O-H Bending[20]
	1041	-C=S and C-S group[9]
	1129	,,
	1015	–C-O- group[9]
Cu-PEX	3318	O-H Stretching
	1623	O-H Bending
	1022	-C=S and C-S group coordinated with metal ion[9]
	1080	,,
Ni-PEX	3334	O-H Stretching
	1635	O-H Bending
	1025	-C=S and C-S group coordinated with metal ion
	1085	,,

100, 80, 60, 40 and 20 mg of PEX were mixed into 50mL of prepared metal ion solution and stirred for 12h at room temperature, a blackish and greenish precipitate were obtained in Cu^{II} and Ni^{II}ion solution respectively. The reaction mixture left for 2h and the settled down precipitate was separated by filtration of solution. Precipitates were dried in hot air oven and confirmed by IR spectroscopy as PEXM (M^{II}= Cu^{II} and Ni^{II}) complex compounds (shown in figure 1) and percentages removal of metal ion obtained by the UV-visible spectra and percentage removal of metal ion as calculated by the equation 1.

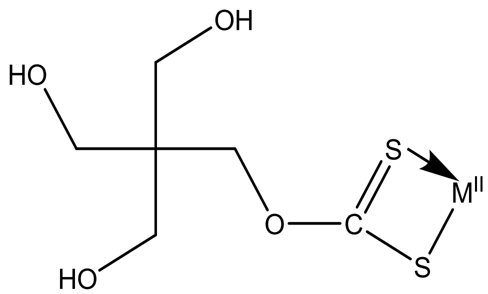


Figure 1: PEX metal complex.
where M^{II} = Cu^{II} and Ni^{II} ion

$$Q = \frac{C_o - C_e}{C_o} X\ 100 \quad (1)$$

where Q = Percentage removal of metal ion after 12h, Co = Initial concentration of metal ion and Ce = Concentration of metal ion after 12h.

Spectroscopic Characterization: Elemental analyses of C, H, N, S and O percentage were obtained by using an elemental analyzers Euro-E 3000 instrument, Fourier – Transform Infrared(FT-IR) spectra recorded on a Parkin Elmer spectrum version 10.03.06., 1_HNMR spectra recorded by Burker, 400MHz NMR, Advanced III and UV-visible absorption were recorded Microprocessor UV-visible double beam spectrophotometer L1-2700.

Results and Discussion

IR Spectral: Table 1 shows the spectral data of pentaerythitolxanthate and their complex with metal ion observed. The absorption peak 3329cm^{-1} and 1633cm^{-1} confirmed O-H stretching bending which confirmed the presence of hydroxyl (–OH) group that means all the hydroxy (–OH) groups of pentaerythritol were not replaced by carbondisulphides. The CS_2 group (C=S and C-S) attached with the pentaerythritol shows the presence of –C-O- group in xanthates. The reduction of absorption peak from1129cm^{-1} to 1080 cm^{-1} and 1041cm^{-1} to 1022cm^{-1} frequencies indicate that-C=S of –O-C(=S)-S- participates in complexation with transition metal.

NMR Spectroscopy:1H NMR spectra were recorded in duterated acetone. The doublet peak at δ3.5 ppm indicates the 8H in form of –CH_2-group and δ3.6 to δ37ppm shows the presence of 3H of –OH group in triplet.

Effect of PEX amount on absorption: The effects of amount of PEX (mg) on the absorbency were investigated after 12h constant stirring of PEX and metal ion solutions as shown in table 2. The graph shown in figure 2 (Cu^{II} ion) and in figure 3 (Ni^{II} ion) shows that UV-visible absorption decreases with increase of PEX doses. The metal ions were combined with PEX to form precipitate of PEX-metal complex easily removed by the filtration.

Table 2
Amount of PEX and UV absorption of Cu^{II} ion and Ni^{II} ion solution after 12h.

Amount of PEX (mg)	**100**	**80**	**60**	**40**	**20**
Absorption of Cu^{II} (%)	0.169	0.178	0.192	0.202	0.226
Absorption of Ni^{II} (%)	0.043	0.047	0.049	0.054	0.057

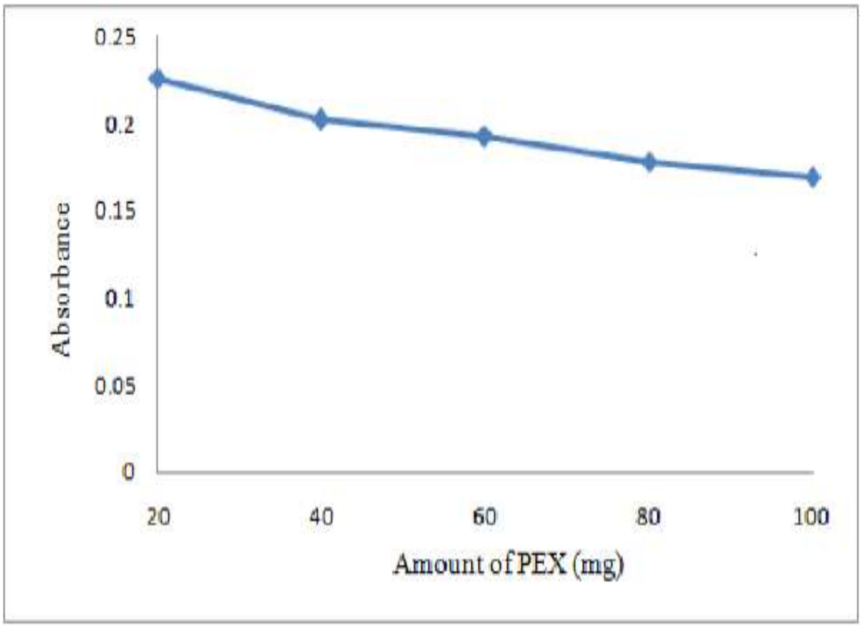


Figure 2: Graph for UV absorption of Cu^{II} ion solution *v/s* PEX amount (mg)

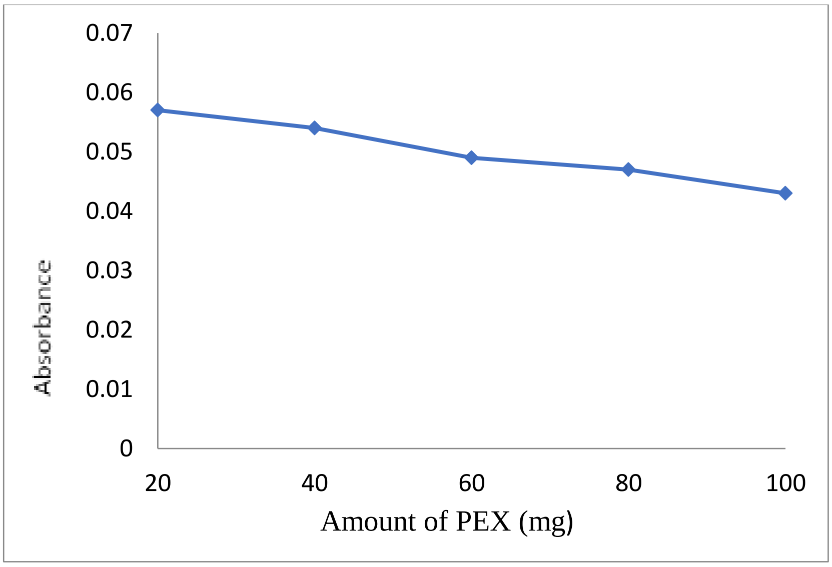


Figure 3: Graph for UV absorption of Ni^{II} ion solution *v/s* PEX amount (mg)

Table 3
Amount PEX and percentage removal of M^{II}after 12h. (M= Cu^{II} and Ni^{II})

Amount of PEX (mg)	**20**	**40**	**60**	**80**	**100**
Removal of Cu^{II} (%)	56	63	69	72	78
Removal of Ni^{II} (%)	58	61	69	74	86

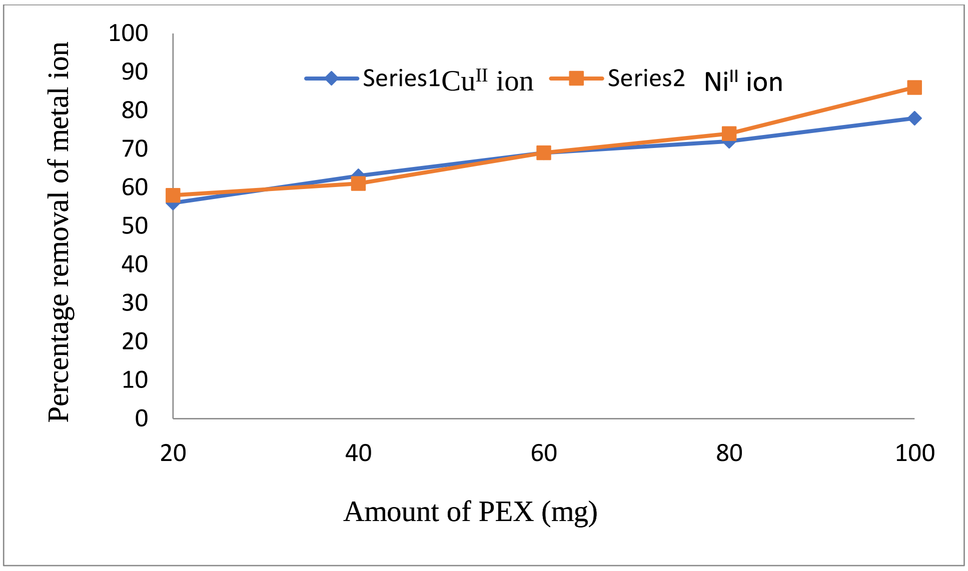


Figure 4: Graph for percentage removal of $Cu^{II}$and Ni^{II} ion from solution v/s PEX amount (mg)

Effect of PEX doses on percentage removal of metal ion: The percentage removal of Cu^{II} and Ni^{II} was calculated by the equation 1 (shown in table 3) and graph shown in figure 4 shows that the percentage removal of Cu^{II} increases from 56-78% and Ni^{II} from 58 to 86% with increasing of PEX doses.

Conclusion

Analysis of IR and NMR data clearly shows that the only one CS_2 molecule reacts with pentaerythritol and also IR data indicate that the -(C=S)-S group acts as ligand during the complexation with metal ion forming precipitate which is easily separable. The UV data shows results of removal of metal ion form the water.

Acknowledgement

We acknowledge thanks to Principal, B.R.D.P.G. College for providing permission for research and we also thank to Vice Chancellor, M.M.M.U.T. for providing research facilities.

References

1. Goel R., Khan I.A., Kori J.A., Mahar R.B., Tariq H. and Vistro M.R., Metagenomic analysis of drinking water samples collected from treatment plants of Hyderabad City and Mehran University Employees Cooperative Housing Society, *Environ. Sci. Pollut. Res.*, **26**, 29052–29064 **(2019)**

2. Guo L., Ju B.Z., Quan X., Yang J.Z. and Zhang S.F., Removal of Pb(II) from aqueous solution by cross-linked starch phosphate carbamate, *Journal of Polymer Research*, **13(3)**, 213–217 **(2006)**

3. Ali H., Ilahi I. and Khan E., Environmental chemistry and ecotoxicology of hazardous heavy metals Environmental persistence, toxicity and bioaccumulation, *J. Chem.*, https://doi.org/10.1155/2019/6730305 **(2019)**

4. Ayeshamariam A., Jayachandran M., Karunanithy Kaviyarasu K.M., Nivetha P.P., Prabhavathi G., Rafi K.M. and Sekar N., Removal of heavy metals from waste water treatment using composite nanomaterials–A Review, *J. Nanosci. Nanoeng. Appl.*, **9**, 27–44 **(2019)**

5. Bhattacharjee M., Sarma M.P. and Barbhuyan R., Nickel hyperaccumulation associated genetic changes in Cataranthus roseus (L.) G. Don, *Res. J. Chem. Environ.*, **23(11)**, 103-112 **(2019)**

6. Nath A. and Pande P.P., Polyacrylamide based polymers: smart materialsused in wastewater treatment, *Adv. Sci, Engg. and Medi*, **12**, 105–107 **(2020)**

7. Anamica Nath A., Pande P.P. and Yadav M., Materials used for coagulation and flocculation in wastewater treatment, International Conference on Energy, Environment & Material Sciences (ICE2M) **(2019)**

8. Mohammad K., Zinc Solvent extraction from wastewater liquor of a lead and zinc plant, *Res. J. of Chem. and Environ.*, **23(12)**, 81-86 **(2019)**

9. Aeed S.A.F. and Emam I.A., Synthesis and characterization of $Iron^{II}$, $Cobalt^{II}$, $Nickel^{II}$, $Copper^{II}$ and $Zinc^{II}$ complex using diphenylmethyl xanthates ligand, *A Scientific J. of Koya Univ.*, **6**, 33-37 **(2018)**

10. Exarchos G., Robinson S. and Steed J., The synthesis of new bimetallic complex salts by halide/sulfur chelate cross transfer: X-ray crystal structures of the salts $[Ni(S_2CNEt_2)(dppe)]_2[HgBr_4]$, $[Pt(S_2CNEt_2)(dppe)]_2[CdCl_4]$, $[Co(S_2CNEt_2)_2(dppe)]_2[Cl_3ZnO:(Ph)_2PCH_2CH_2P(Ph)_2:OZnCl_3]$ and $[Pd(S_2CN^nBu_2)(bipy)]_2[CdCl_4]$, *Polyhedron*, **20,** 2951-2963 **(2001)**

11. Cox M.J. and Tiekink E.R.T., Stnthises and characterization of aryl xanthates of group 12th elements, *Kristallog*, **211**, 111-113 **(1996)**

12. Vastag S., Marko L. and Rheingold A.L., Mononuclear cobalt carbonyls containing monodentate thiolate or xanthate groups, The structures of $PhSCo(CO)_2(PPh_2OMe)_2$ and $MeOCS_2Co(CO)_2(PPh_2{}^iBu)_2$, *J. of Organometa. Chem.*, **397**, 231-238 **(1990)**

13. Gurpreet K., Inderjeet K. and Renu S., Synthesis and characterization of the adducts of bis(O-ethyldithiocarbonato)

copper(II) with substituted pyridines, *International Journal of Inorganic Chemistry*, https://doi.org/10.1155/2013/502856 **(2013)**

14. Praveen B., Suresh S. and Venkitaraj K.P., Energy storage performance of pentaerythritol blended with indium in exhaust heat recovery application, *Thermochimica Acta*, https://doi.o/10.1016/j.tca.2019.178343 **(2019)**

15. Ding Y., Liu P., Tang H.,Wang F.,Wang Y., Xie M.,Yang M. and Zhang S., Synthesis of a heat-resistant DOPO derivative and its application as flame-retardant in engineering plastics, *J. Appl. Polym. Sci.*, https://doi.org/10.1002/app.44892 **(2017)**

16. Suresh S. and Venkitaraj K.P., Experimental thermal degradation analysis of pentaerythritol with alumina nano additives for thermal energy storage application, *Journal of Energy Storage*, **22**, 8-16 **(2019)**

17. Bietsch J., Chen A., Wang D. and Wang G., Synthesis and characterization of pentaerythritol derived glycoconjugates as supramolecular gelators, *Org. Biomol. Chem.*, **17**, 6043-6056 **(2019)**

18. Hao J., Lou W., Wang X., Xu Z., Zhao G. and Zhang M., Pentaerythritol rosin ester as an environmentally friendly multifunctional additive in vegetable oil-based lubricant, *Tribology International*, **135**, 213-218 **(2019)**

19. Kasztankiewicz A.B., Kopacz W. and Maksimowski P., 3,3-Bis(azidomethyl)oxetane (BAMO) Synthesis via Pentaerythritol Tosyl Derivates, *Propellants Explos. Pyrotech*., **42**, 1–8 **(2017)**

20. Patel Z.J., Patel M.C., Chaturbhuji P.M., Patel V.A. and Patel D.R., Preparation and characterization of penta allyl sucrose, *Res. J. Chem. Environ*., **24(1)**, 73-77 **(2020)**.

(Received 13th February 2020, accepted 12th April 2020)