

SYNTHESIS OF NOVEL SUGAR BASED XANTHATES FOR THE REMOVAL OF COPPER AND NICKEL HARMFUL HEAVY METALS FROM WATER

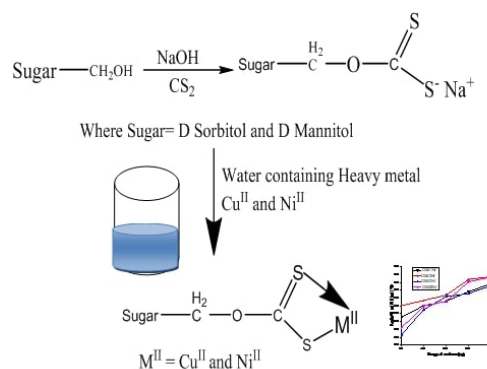
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Received March 20, 2020

Sugar based xanthates viz *D*-sorbitol xanthate and *D*-mannitol xanthate (DSX1, DSX2, DMX1 and DMX2) have been synthesized by the reaction of *D*-sorbitol (DS)/ *D*-mannitol (DM) with carbon disulfide (CS₂) in basic medium at room temperature by varying carbon disulphide and base ratio with respect to sugars. The synthesized xanthates were extracted with ether, and dried in air. The xanthates were characterized by micro analytical data, Elemental analysis (C, H, O, S), Fourier transform infrared (FTIR) spectroscopy, and ¹H nuclear magnetic resonance (1HNMR) spectroscopy. The synthesized xanthates were used for the removal of Cu²⁺ and Ni²⁺ from aqueous solutions. The metal complexes formed during the process of removal of metal ions were confirmed with FTIR spectroscopy. The removal of copper and nickel metal from water was quantitatively determined by UV-visible absorption spectroscopy.



INTRODUCTION

Today humanity is facing the serious problem of water pollution caused by heavy metals like copper and nickel.¹⁻³ Due to the rapid growth of industrial technology, a huge quantity of untreated wastewater is released into the environment which represents severe universal environmental problems.⁴⁻⁵ It is essential to remove the toxic heavy metals from wastewater before draining it into the environment.⁶⁻⁷ Although a number of heavy metals are essential for the human body in trace amount, after certain concentration level these metals cause adverse effect on human, plants and other living being. Nickel and Copper are essential elements in living beings which are involved in various metabolic processes, but these elements become hazardous above the maximum permissible limits. Ni is not a cumulative toxin, but

exposure at higher concentration makes it toxic and even carcinogenic.⁸ Higher concentration of Cu²⁺ ion causes Alzheimer's disease.⁹ Several methods have been used for the removal of heavy metals from wastewater, like precipitation, complexation, flotation, solvent extraction, adsorption, membrane processing and electrolysis.¹⁰ A variety of chemicals have been utilized in the treatment of wastewater like activated carbon,^{11,12} polyacrylamide¹³ lignin and its derivatives¹⁴⁻¹⁶ branched polyethylenimine (PEI), sodium dodecyl sulfate (SDS)¹⁷⁻¹⁹ etc. Low-cost and environment friendly inorganic-organic composite membranes have been used for aquatic dyes removal²⁰. CS₂-modified alkaline lignin²¹ carboxymethyl cellulose-immobilized Fe₃O₄ nanoparticles,^{22,23} poly(acrylic acid-co-acrylamide)-sawdust composite,²⁴ Chitosan solution,²⁵ polysaccharides and other coagulant/flocculants^{26,27} have also been used in

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wastewater treatment, but these have some limitations. Generally, natural and synthetic flocculants are used alone in wastewater treatment which generates flocs and heavy metals are co-precipitated with flocculants, however this process has low capability towards removal of heavy metal ions.²⁸ Therefore, other methods *viz.* chemical precipitation, electrolysis, ion exchange, reverse osmosis must be used for the removal of heavy metal ions from industrial effluents. These methods are not cost effective and may cause undesirable changes in the property of treated water.

The sulfides of heavy metals have very low solubility products, a fact which has attracted the attention of researchers towards the use of these compounds for the removal of heavy metals through the formation of metal sulfide complexes.²⁹ Similarly, xanthates, which belong to the sulfur containing organic species, have also attracted the attention of researchers for the removal of heavy metals. Because of the ability of formation of coordination complex, xanthates have been used as a reagent in the analytical determination and separation of a number of metal ions.^{30,31} A number of polymeric xanthates have been synthesized and used for the wastewater treatment, however only a few monosaccharide based xanthates such as xanthates of the 2-deoxy – *D*-Ribose and *D*-xylose have been synthesized.³² In this paper we report the synthesis and characterization of the xanthates of *D*-sorbitol and *D*-mannitol and also their use for the removal of copper and nickel ions from wastewater.

EXPERIMENTAL

1. General

D-Sorbitol, *D*-Mannitol, Carbondisulphide, Sodium hydroxide, Nickel Sulphate and copper sulphate (analytical grade 99.9% pure) were obtained from S. D. Fine- Chem. Ltd, and used as received. The solvents used were of analytical grade. The synthesized compounds were identified by micro analytical data. Elemental analyses of C, H, O and S were performed using elemental analyzers Euro-E 3000 instruments. FTIR spectra (KBr discs) were recorded on a Bruker FT-IR spectrophotometer within 400-4000 cm⁻¹ range. ¹HNMR spectra were recorded on Bruker 400MHz NMR, Advanced III spectrometer. The products formed during the removal of metal ion from water were confirmed by the IR spectra (KBr discs) and amount of metal ion determined by the UV-visible absorption, Microprocessor UV-visible double beam spectrophotometer L1-2700 using wavelength range 200-800 nm.

2. Synthesis of *D* - sorbitol and *D*- mannitol xanthates

D-Sorbitol and *D*-Mannitol xanthates (DSX and DMX) (Scheme 2 and 3) were synthesized by mixing equimolar amount of sugar 3.64g (20 mmole) and Sodium hydroxide 0.8 g (20 mmole) dissolved in 25 mL distilled water and put into two neck 100 mL round flask with constant stirring for 1.5 h at 80°C, after that reaction mixture cooled at room temperature, then 31.6 g (20 mmole) carbon disulphide was added into the reaction mixture with constant stirring at room temperature for about 12 h, and an orange color turbid solution was obtained. The resulting product was extracted with ether and dried in air. The synthetic and elemental analysis detail of various grades of xanthates are given in Table 1.

3. Removal of Cu^{II} and Ni^{II} by DSX and DMX experiments

The removal of metal ions by the complexation methods has been performed in 100 mL glass beakers using 100mg, 80 mg, 60 mg, 40 mg and 20 mg quantity of the xanthates DSX1, DSX2, DMX1 and DMX2 as complexing agents and 50 mL (1 mg/mL) stock solutions of metal ion. The stock solution of Cu^{II} and Ni^{II} were prepared by dissolving appropriate amount 0.329 mg (1000 mg/L) of CuSO₄·5H₂O and 0.5125 mg (1000 mg/L) of NiSO₄ in 100 mL distilled water. The solution with xanthates of each beaker was stirred for about 8 h at room temperature. After 2 hours the precipitates of metal xanthates settle down at the bottom of the beaker and are separated easily by filtration. The blackish and greenish precipitate of copper xanthate, and nickel xanthate were obtained respectively. The concentration of the metal ion present in the solution after complexation reaction was determined by UV-visible spectroscopy. The wavelength used for the determination of Cu²⁺ was 380 nm and for Ni²⁺ was 590 nm. The total percentage removal of metal ion was calculated by the equation 1.

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

where Q = Percentage removal of metal ion after 8 h.

C_o = Initial concentration of metal ion

C_e = Concentration of metal ion after 8 h.

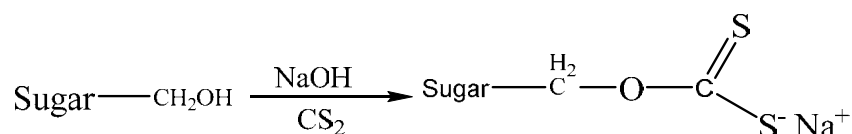
RESULTS AND DISCUSSION

1. Preface

The two new sugar xanthates DSX and DMX were synthesized by the reaction of carbon disulphide with *D* sorbitol and *D* mannitol respectively in basic medium. The formation of the xanthates was confirmed by their elemental analysis, ¹HNMR and FTIR spectra. The preparation of sugar based xanthates by changing the ratio of sugar, sodium hydroxide and carbon disulphide (1:1:1 and 1:2:2) are shown in Scheme 1 and 2.

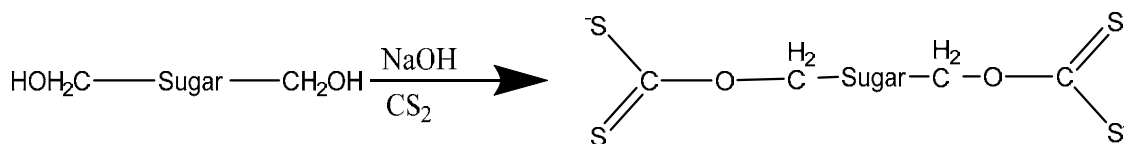
Table 1
Synthetic ratio, molecular weight, C, H, N, O, S percentage

Sugar	NaOH	CS ₂	Symbol and Molecular formula	Yield %	Molecular weight	Elemental analysis (Calc.) Found %			
						C	H	O	S
DS 1	1	1	DSX1 C ₇ H ₁₃ O ₆ S ₂	85	257	(32.68) 32.66	(5.06) 5.05	(37.35) 37.33	(24.90) 24.88
DS 1	2	2	DSX2 C ₈ H ₁₂ O ₈ S ₄	87	332	(28.92) 28.89	(3.61) 3.59	(28.92) 28.91	(38.55) 38.53
DM 1	1	1	DMX1 C ₇ H ₁₃ O ₆ S ₂	86	257	(32.68) 32.67	(5.06) 5.04	(37.35) 37.34	(24.90) 24.89
DM 1	2	2	DSX2 C ₈ H ₁₂ O ₈ S ₄	87.9	332	(28.92) 28.89	(3.61) 3.60	(28.92) 28.91	(38.55) 38.54



Where Sugar = *D*-Sorbitol or *D*-Mannitol

Scheme 1 – Synthetic route for sugar based xanthates of sugar, NaOH and CS₂ ratio (1:1:1).



Sugar = *D*-Sorbitol or *D*-Mannitol

Scheme 2 – Synthetic route for sugar based xanthates of sugar, NaOH and CS₂ ratio (1:2:2).

2. FTIR study

In the Table 1 FT-IR spectra of xanthates, (DSX1, DSX2, DMX1 and DMX2) have been recorded before and after M^{II} ion (M^{II}=Cu^{II} and Ni^{II}) complexation. There are a series of characteristic bands for xanthates. A broad absorption peak in between 3368- 3393cm⁻¹ that indicates -OH group stretching, 1632-1639cm⁻¹ -OH bending, presence of absorption peaks in between 1206-1230cm⁻¹ characteristics peaks of -O-C(=S)-S⁻³³ which indicates that CS₂ molecule attached with the sugar compounds and 1015-1018cm⁻¹ peaks illustrate the -C-O-C- group present in xanthates compounds. FT-IR spectra analyzed after xanthates metal ion

(Cu^{II} and Ni^{II}) complexation the observed peaks of DSX1M^{II}, DSX2M^{II}, DMX1^{II} and DMX2M^{II} (Cu^{II} and Ni^{II}) are 3350-3354 cm⁻¹, 3365-3367 cm⁻¹, 3344-3348 cm⁻¹ and 3352-3355 cm⁻¹ clearly indicate that -OH group is present in all metal xanthates. The shifting of absorption peaks of 1296-1230 cm⁻¹ into 1142-1189 cm⁻¹ and 1142-1189 cm⁻¹ to 1027-1045 cm⁻¹ point toward the involvement of -C(=S)-S group into complex formation with metal ion. But the presence of weak absorption peaks 1224-1226 cm⁻¹ and 1072-1085 cm⁻¹ in DSX2Cu^{II}, DSX2Ni^{II}, DMX2Cu^{II} and DMX2Ni^{II} complexes obviously explained that only one -C(=S)-S group participate in complex formation shown in Figure 1.

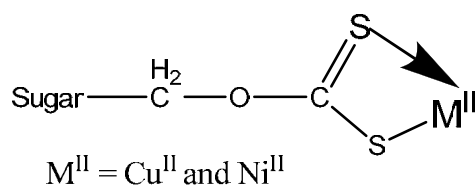


Fig. 1 – Xanthates metal complexes.

3. ¹HNMR study

¹HNMR data δ3.58 (4H of secondary -OH), δ 3.65(1H of primary -OH), δ 3.37 and 3.38 m (4H of -CH-), δ 3.81 and δ 3.356 m (4H of 2-CH₂ group) of the DSX1, δ3.56 (4H of secondary -OH), δ 3.35 and 3.37 m (4H of -CH-), δ 3.79 and δ 3.354 m (4H of 2-CH₂ groups) of xanthates DSX2, and nearly same spectral data were obtained xanthates DMX1 and DMX2 respectively which confirmed that only one CS₂ molecule attached with primary -CH₂OH group of sugar in sugar, base and carbon disulphide ratio 1:1:1 and formed DSX1 and DMX1 compounds, while the above ratio changed as 1:2:2, DSX2 and DMX2 compounds were obtained in which two CS₂ molecule attached with both -CH₂OH groups of sugar.

4. UV-visible absorption study

The performance of xanthates in the removal of CuII and NiII ion from water was evaluated by complexation process are described above in experimental. The results of UV-visible absorption

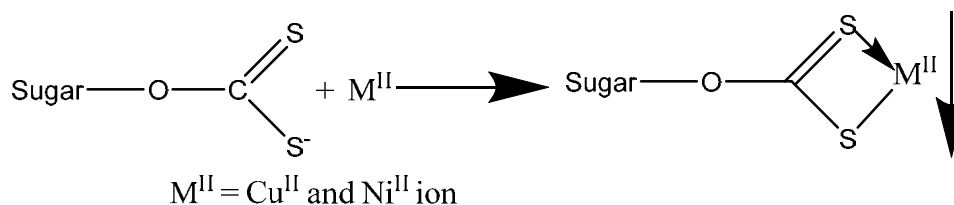
and percentage removal of metal ion are discussed as follows:

4.1. The effect of xanthates dosage of UV-visible absorption of Cu^{II} and Ni^{II} ion solution

The xanthates dosages are of more significant to identify UV-visible absorption. The results are shown in Figure 2 and 3. It shows that the UV-visible absorption of metal ions is decreasing with increasing dosage of xanthates. It seems to be a stoichiometric relationship between metal ions and xanthates can be explained as: (Scheme 3).

4.2. Effect of xanthates dosage on percentage removal of Cu^{II} and Ni^{II} from water

With the help of UV-visible absorption and equation 1, percentage removals of Cu^{II} and Ni^{II} ions are calculated and results are illustrated in figure 4 and 5. The Results shows that 100 mg of xanthates DSX1 and DMX1 have optimum removal metal ion removal capacity while at same experimental environment xanthates grades DSX2 and DMX2 required only 80mg for optimum removal capacity.



Scheme 3 – Formation of metal- xanthate complexes.

Table 2

Frequency of IR spectra of sugar xanthates and its metal complexes

Compound	IR frequency (cm-1)	Assignment	Compound	IR frequency (cm-1)	Assignment
DSX1	3373 1637 1216 1098 1016	O-H Stretching ²⁰ O-H Bending ²⁰ -C=S and C-S group ⁹ " -C-O- group ⁹	DMX1	3368 1632 1206 1078 1015	O-H Stretching ³⁴ O-H Bending ³⁴ -C=S and C-S group ³⁵ " -C-O- group ³⁵
DSX1 Cu	3354 1633 1149 1038 1014	O-H Stretching ²⁰ O-H Bending ²⁰ -C=S and C-S group ⁹ "coordinate to Cu ^{II} -C-O- group ⁹	DMX1Cu	3350 1630 1143 1027 1013	O-H Stretching ³⁴ O-H Bending ³⁴ -C=S and C-S group ³⁵ "coordinate to Cu ^{II} -C-O- group ³⁵

Table 2 (continued)

DSX1 Ni	3348	O-H Stretching ²⁰	DMX1 Ni	3344	O-H Stretching ³⁴
	1636	O-H Bending ²⁰		1634	O-H Bending ³⁴
	1145	-C=S and C-S group ⁹		1142	-C=S and C-Sgroup ³⁵
	1038	"coordinate to Ni ^{II}		1028	"coordinate to Ni ^{II}
	1013	-C-O- group ⁹		1012	-C-O- group ³⁵
DSX2	3393	O-H Stretching ²⁰	DMX2	3383	O-H Stretching ³⁴
	1639	O-H Bending ²⁰		1637	O-H Bending ³⁴
	1230	-C=S and C-S group ⁹		1229	-C=S and C-Sgroup ³⁵
	1087	"		1076	"
	1017	-C-O- group ⁹		1018	-C-O- group ³⁵
DSX2 Cu	3365	O-H Stretching ²⁰	DMX2 Cu	3367	O-H Stretching ³⁴
	1633	O-H Bending ²⁰		1628	O-H Bending ³⁴
	1228	-C=S and C-S group ⁹		1226	-C=S and C-Sgroup ³⁵
	1085	"		1073	"
	1189	-C=S and C-S group ⁹		1183	-C=S and C-Sgroup ³⁵
	1045	"coordinate to Cu ^{II}		1024	"coordinate to Cu ^{II}
	1012	-C-O- group ⁹		1011	-C-O- group ³⁵
DSX2 Ni	3355	O-H Stretching ²⁰	DMX2Ni	3364	O-H Stretching ³⁴
	1629	O-H Bending ²⁰		1624	O-H Bending ³⁴
	1227	-C=S and C-S group ⁹		1224	-C=S and C-S group ³⁵
	1083	"		1072	"
	1186	-C=S and C-S group ⁹		1181	-C=S and C-S group ³⁵
	1043	"coordinate to Ni ^{II}		1022	"coordinate to Ni ^{II}
	1011	-C-O- group ⁹		1012	-C-O- group ³⁵

CONCLUSIONS

Xanthates DSX1, DSX2, DMX1 and DMX2 were synthesized by the chemical addition of CS₂ with D- sorbitol and D-mannitol in basic medium using different ratio of sugar, a base and CS₂. Although change the above ratio in chemical reaction, but isolated xanthates have the same properties as above xanthates. These xanthates have good ability to form complexes with metal ion M^{II} (M^{II}= Cu^{II} and Ni^{II}) The FT-IR spectral data

revealed that the removal mechanism of Cu and Ni ion involves complexation. The sugars used are also obtained from natural sources; therefore the synthesized xanthates are inexpensive and eco-friendly. The synthetic procedure and isolation are easy to carry out. The experimental findings indicate that the newly synthesized xanthates are promising candidates, which could be used as complexing agents for the removal of Cu^{II} and Ni^{II} ion from wastewater.

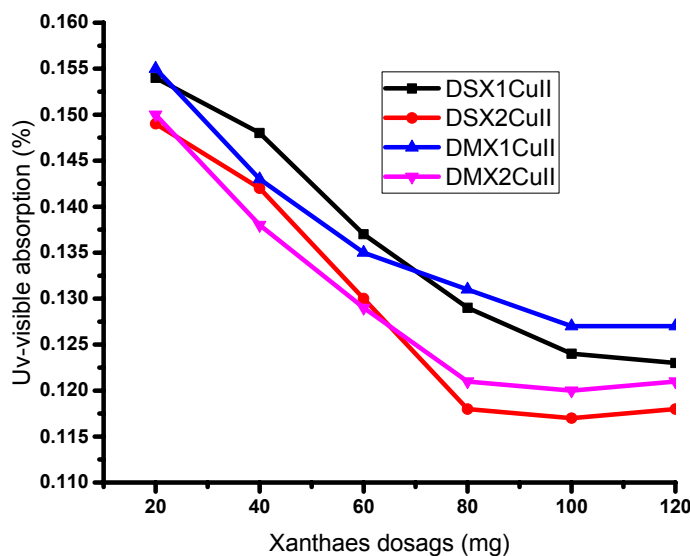


Fig. 2 – UV-visible absorption v/s xanthaes dosage for Cu^{II} ion solution.

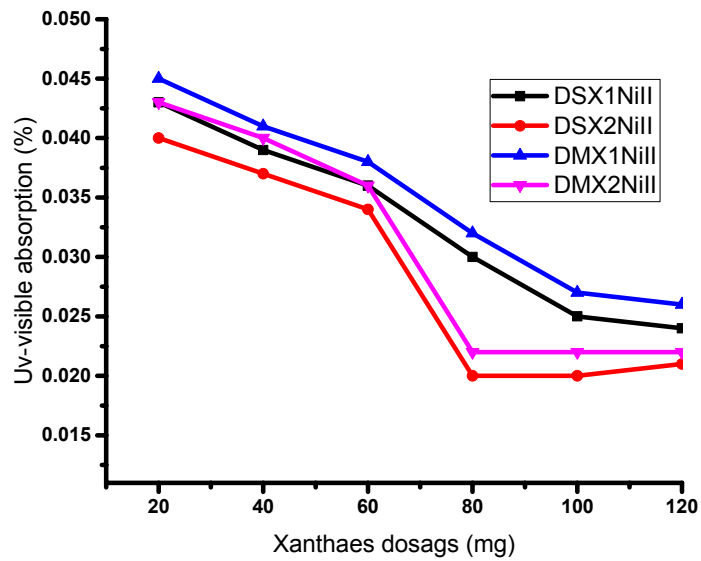


Fig. 3 – UV-visible absorption v/s xanthaes dosage for Ni^{II} ion solution.

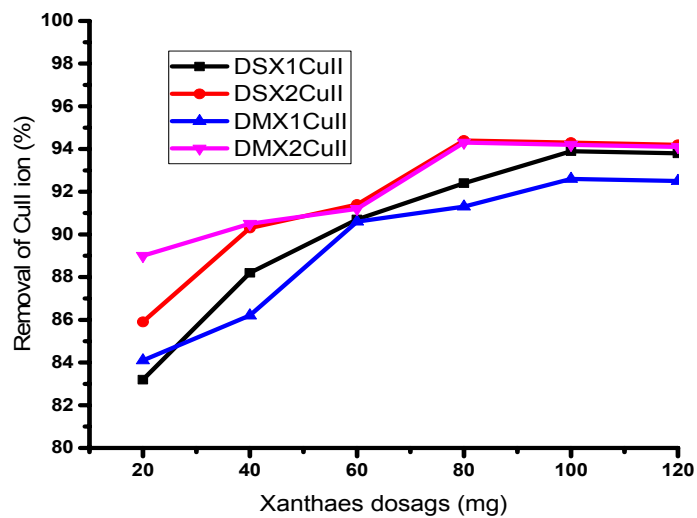


Fig. 4 – Effect of xanthaes dosage on percentage removal of Cu^{II} ion solution.

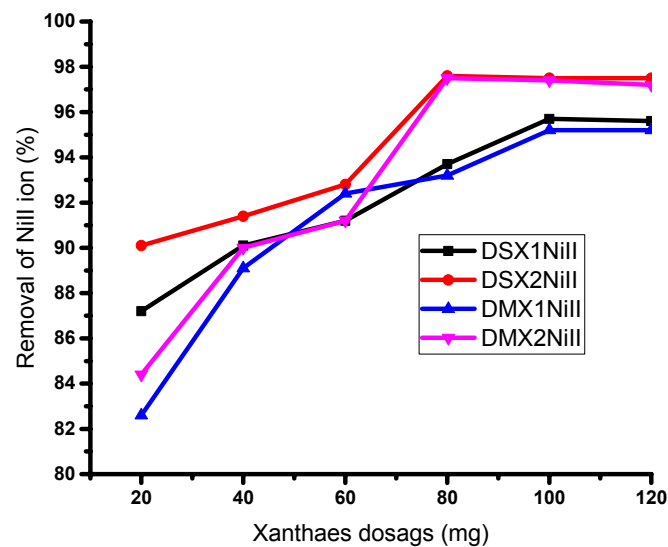


Fig. 5 – Effect of xanthaes dosage on percentage removal of Ni^{II} ion solution.

Acknowledgements. We gratefully thanks to authority of B. R.D. P. G. College, Deoria, to provide me doing research opportunity and also thanks to, Hon.Vice chancellor M. M. M. U. T. for providing research facilities.

REFERENCES

- J. Li, B. Jiang, Y. Liu, C. Qiu, J. Hu, G. Qian, W. Guo and H. H. Ngo, *J. Clean. Produ.*, **2017**, *158*,51-58.
- Y. Chen, W. Zhang, S. Yang, A. Hobiny, A. Alsaedi and X. Wang, *Sci. China Chem.*, **2016**, *59*, 412-419.
- V. Zarezade, M. Behbahani, F. Omid, H. S. Abandansari and G. Hesam, *Rsc. Advan.*, **2016**, *6*, 103499-103507.
- B. A. Lajayer, M. Ghorbanpour and S. Nikabadi, *Ecotox. Environ. Safe.*, **2017**, *145*, 377-390.
- A. Ahmed, M. A. A.Abdel, S. A. A. Abdulraheem and S. R. Moamen, *Rev. Roum. Chim.*, **2019**, *64*, 817-828.
- K. Feng and G. We, *Intern. J. Polym. Sci.*, **2017**, *2017*, 1-9.
- L. Guo, S. F. Zhang, B. Z. Ju, J. Z. Yang and X. Quan, *J. Polym. Res.*, **2006**, *13*, 213–217.
- B. Shahzad, M. Tanveer , A. Rehman, S. A. Cheema, S. Fahad, and A. Sharma, *Plant Physio. Biochem.*, **2018**, *132*, 641-651.
- A. Pourkhabbaz and H. Pourkhabbaz, *Iran. J. Basic Med. Sci.*, **2012**, *15*, 636–644.
- Z. Li, J. Chen, H. Guo, X. Fan, Z. Wen, M. H. Yeh, C. Yu, X. Cao and Z. L. Wang, *Adv. Mater.*, **2016**, *28*, 2983-2991.
- I. A. Aguayo-Villarreal, A. Bonilla-Petriciolet and R. MuñozValencia, *J. Mol. Liq.*, **2017**, *230*, 686-695.
- H. Xiyili, S. Çetintaş and D. Bingöl, *Proc. Env. Prot.*, **2017**, *109*, 288-300.
- A. Nath, P. P. Pande, *Adv. Sci. Eng. Medi.*, **2020**, *12*, 105–107.
- Y. Ge and Z. Li, *ACS Sust. Chem. Eng.*, **2018**, *6*, 7181-7192.
- N. Ponomarev, O. Pastushok, E. Repo, B. Doshi and M. Sillanpää, *ACS Appl. Nano Mater.*, **2019**, *2*, 5492-5503.
- X. O. H. Zhang, S. L. Lai, J. Gao and L. Gao, *React. Funct. Polym.*, **2020**, *149*, 104502; DOI 10.1016/j.reactfunctpolym.2020.104502.
- M. Chen and N. P. Hankins., *J. Water Proc. Eng.*, **2020**, *34*, 101170.
- A. Olga, C. Ramirez, M. A. Omar, P. Arivalagan and R. R. Eldon, *Curr. Pollu. Rep.*, **2020**, *6*, 8-27.
- M. Hassan, R. Naidu, J. Du, Y. Liu and F. Qi, *Sci. of The Total Env.*, **2020**, *702*, 134893.
- J. Zhang, Y. Ge, Z. Li and Y. Wang, *J. Environ. Manag.*, **2020**, *256*, 109969.
- Q. Wang, C. Zheng, W. Cui, F. He, J. Zhang, T. C. Zhang and C. He, *Chemic. Eng. J.*, **2019**, 123581.
- H. Fan, X. Ma, S. Zhou, J. Huang, Y. Liu and Y. Liu, *Carbohydrate Polym.*, **2019**, *213*, 39-49.
- S. Zhang, H. Chen, S. Zhang, C. Kai, M. Jiang, Q. Wang and Z. Zhou, *Cellulose*, **2019**, *26*, 3437-3453.
- A. Q. Khan, A. U. Rahman, M. Yaseen, H. U. Rashid, M. Iqbal and M. U. Rehman, *Rev. Roum. Chim.*, **2019**, *64*, 949-963.
- A. Kong, Y. Ji, H. Ma, Y. Song, B. He and J. Li, *J. Clean. Produ.*, **2018**, *192*, 801–808.
- A. Nath and P. P. Pande, *Progressive Research – An International, J.*, **2018**, *13*, 600-603.
- A. Nath, Anamica, M. Yadav, R. Kumar and P. P. Pande, 2019 IEEE Uttar Pradesh Section International Conference on Energy, Environment & Material Sciences (ICEEM) Accepted.
- J. R. Pledge, T. S. Young and G. S. Wu, *J. Macromol. Sci. Chem.*, **1986**, *42*, 415-426.
- Q. Chang, X. Hao and L. Duan, *J. Hazar. Mater.*, **2008**, *159*, 548-553.
- G. Exarches and S. Robinson, *J. Steed, Polyh.*, **2001**, *20*, 2951.
- M. J. Co and E. R. T. Tiekink, *Kristallog*, **1996**, *211*, 111-113.
- E. M. L. Vidal, G. L. Gregory, G. K. Khon and A. Buchaed, *Polym. Chem.*, **2018**, 1577-1582.
- N. Wang, X. Xu, H. Li, J. Zhai, L. Yuan, K. Zang and H. Yu, *Ind. Eng. Chem. Res.*, **2016**, *55*, 4960-4968.
- Z. J. Patel, M. C. Pate, P. M. Chaturbhujji, V. A. Patel and D. R. Patel, *Res. J. Chem. Env.*, **2020**, *24*, 73-77.
- S. A. F. Aeed and I. A. Emam , *A Sci. J. Koya Univ.*, **2018**, *6*, 33-37.

