International Journal on Science and Technology (IJSAT)
E-ISSN: 2229-7677 ● Website: www.ijsat.org ● Email: editor@ijsat.org

Monosaccharides Xanthates and Their Application in the Removal of Toxic Metal Ions from Contaminated Water: A Review

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Abstract

The regular increase of pollutants with toxic metal ions in water reservoir that show a substantial world-wide issue because of their persistence, non-biodegradable behaviour and it easily accumulate in living organism. Their minimum concentrations caused adverse effect on livening being. A suitable emerging materials monosaccharide xanthate an organic compound which was synthesised by using simple sugar and carbon disulfides under basic medium which acts as an effective biosorbents for removal of toxic metal ions. Due to presence of significant amounts of hydroxyl groups, biodegradable and non-toxic nature it has much affinity toward metal ions, xanthates formed from glucose, fructose, and mannose a monosaccharide that reveal outstanding chelating and adsorption potential. This review illustrated about the synthetic routes, structure and functional process of the xanthates that focused on its important for removal of Pb^{2+}, Cd^{2+}, Cu^{2+} and Hg^{2+} form aqueous medium. There are also discussed on the experimental parameters that effects the removal of toxic metal ions. At the end it also focused on it limitation and future guidelines for emerging economical and eco friendly adsorbent of xanthates for commercially applicable for wastewater treatment.

Keywords: Monosaccharide xanthates; heavy metal, metal ions removal; biosorption; green adsorbents; carbon disulfide modification; sustainable remediation.

1. Introduction

There are contaminated fresh water with toxic heavy widely distributed on the earths, the presence of metals ions in above permissible concentration cause are harmful effects to the living being [1-3]. Some metals as cadmium caused adverse effect on kidney, skeleton and lungs [4], chromium caused cancer, respiratory issues, damaged skin it also affects the metabolic system [5], mercury that damaged neurological and renal systems and also damaged skin [6], copper generates a Wilkinson disease and nickel caused allergy [7-8] are caused adverse effect to the health of environment and living being [8-9]. The metallic pollutants primarily produced by the activity of mining, electroplating, tanning, paint production, and battery industries [10]. The metallic pollutants are non-biodegradable in nature and it easily involved in biological cell by food chain and triggered the effect of carcinogenic, mutagenic and neurotoxic in human [1] and other living organisms while organic contaminants are easily degradable in nature and shows eco-friendly nature.

The physicochemical mechanism as precipitation [11], ion exchange [12], reverse osmosis [13] and filtration with membrane [14] are commonly used in previous era in which mostly inorganic substances are used for the removal of toxic metal ions from contaminated water. These techniques are not economical and produced secondary pollutants. To overcome the above shortcoming essential requirement of substance that have eco-friendly, cost effective, and competent adsorbent for metal appropriation. The sorbents materials which are synthesized by polysaccharide, cellulose, chitin, and starch [15] have widely discovered, monosaccharides having simple structural network, easily tailorable in their functional groups that shows extra advantage in their fine-tuning adsorption potential.

Monosaccharides xanthates an emerging material which are chemically derived by introducing xanthates ($-OCS_2-$) functional groups with the sugar hydroxyl group sites with carbon disulfide (CS_2) in alkaline medium [7], [16]. The nature of sulfur is basic nature that behaves as soft base while heavy metals have soft acidic nature [7], these behaviour of the sulfur shows effective removal of toxic metal ions from contaminated water. This process signifies a pioneering and supportable approach for purification wastewater, joining green chemistry with active impurity removal.

2. Synthesis of Monosaccharide Xanthates

The monosaccharide xanthates were synthesized by using suitable reducing sugar like glucose or fructose and carbon disulfide in basic medium which maintained sodium hydroxide, resulting product sodium salt of monosaccharide xanthates was obtained. The common reactions are illustrated as:[7][16]

$$R\text{–}OH + CS_2 + NaOH \rightarrow R\text{–}OCS_2Na + H_2O$$

Here R-OH represents the hydroxyl group present in monosaccharides, the reactions are influence in the substitution behaviour and binding potential to the metal ions with the influence of temperature, pH, carbon disulfide and time.

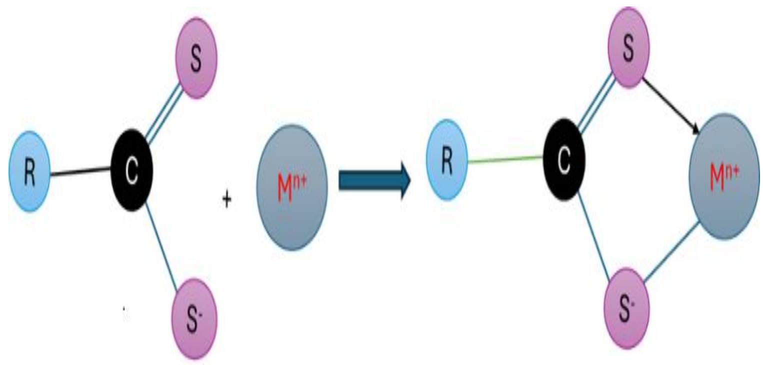
Synthesized products were isolated by precipitation or gently evaporation of solvents, a sulfur rich compounds were isolated which are freely soluble in water which act as a good bio-sorbents. Obtained compounds were confirmed by using FTIR and NMR which shows the presence of C=S and C-O-C [7-8] stretching frequency that indicate the xanthation is successful and gets desired xanthates.

3. Heavy Metal Ion Removal Mechanism

Monosaccharide xanthates involved a number of routes for the metal ions pollutants removal.

3.1. Chelation

compounds, in this process xanthates act as bidentate ligand and formed chelate compounds represented in figure 1. The coordination compounds are in soluble in water and easily settled down which can be removed by easy filtration methods. The xanthate compounds contain sulfur donor atoms which acts as a soft base. Most of the heavy or toxic metal ions have soft basic or border line basic and cationic properties [7-8][17]. During the treatment of water both sulfur of xanthates donates their lone pair of electrons formed coordinate bonds and it precipitate in form of coordination compounds which can easily removed by simple filtration methods.



Where R= long chain of monosaccharide, M^{n+} = metal ions present in water.

Figure 1: Chelation of Sulfur of xanthates with metal ions

3.2. Ion exchange

This mechanism generally employed in the treatment of wastewater treatment in which metals ions are available in form of pollutants. This method is handy to used and cost effective. There is a desired column used in which xanthates are filled with help of unreactive resin or other resin or other neutral substances, availability of sulfur in xanthates makes anionic atmosphere of within the column. The wastewater passing

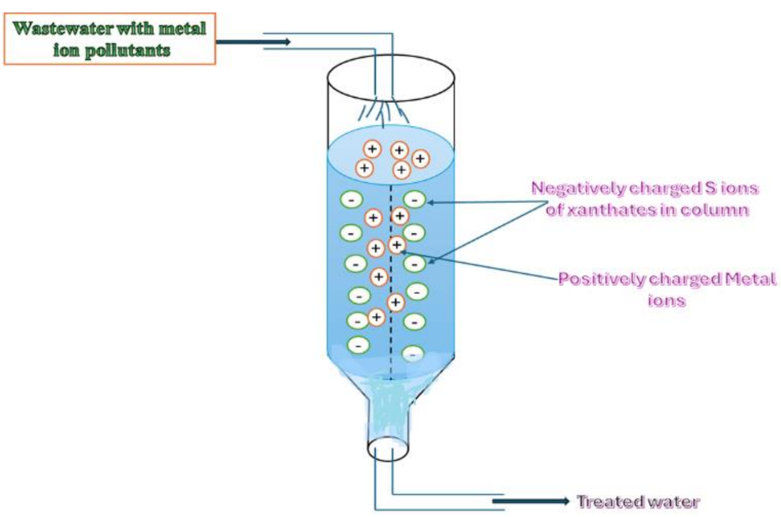


Figure 2: Ion exchange of metal ions with xanthates.

through the column in which cationic metal ions as Cu^{2+}, Pb^{2+}, Ni^{2+} etc. are present, the positively charged metal ions trapped into the column by anionic sulfur of xanthates and treated water free from metal ion obtained shown in figure2. The used column further used after the removing of trapped metal ions using suitable solvents. This process also helped for recovering of metal ions [12][18].

3.3. Surface adsorption

The presents of xanthates groups that contains sulfur atoms, it revealed more attraction towards metal ions as Pb^{2+}, Cu^{2+}, Cd^{2+}, Hg^{2+} etc which are behaves as soft and lying at the border line of the soft and hard acids. It forms strong complexes with such metal ions trough coordination linkage. In these systems the adsorbates as metal ions adsorbed on the surface of adsorbents (xanthates) surface, thought it involved physical and chemical forces and it attached on adsorbents therefore this method is highly active, tuneable and economical which is given in figure3[19].

The xanthates groups of monosaccharides have durable complexation capability, shows excellently restraining metal ions from aqueous medium. The availability of hydroxyl groups in xanthates produced electrostatic attraction and hydrogen bonding that facilitate toward the sorption ability. The removal of metal ions from contaminated water with the monosaccharide's xanthates are depend on various experimental parameters.

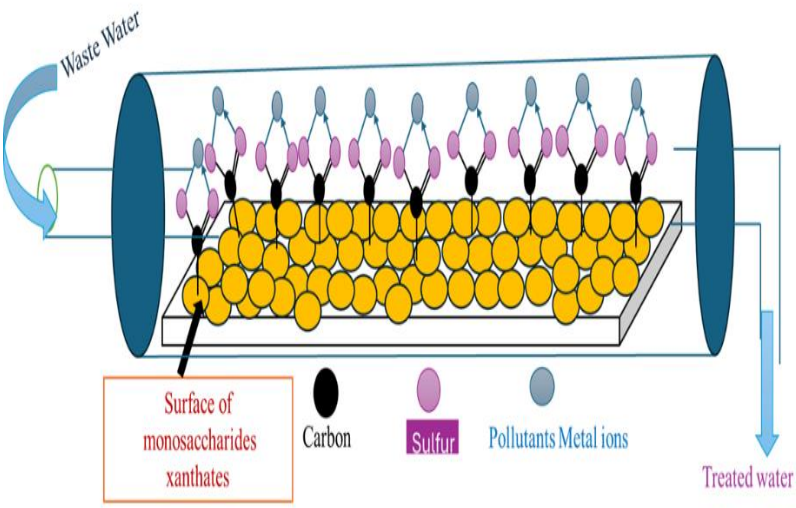


Figure3: Surface adsorption metal ions with xanthates

Maximum adsorption of xanthates obtained at pH 5-7 because of metal ions are freely soluble and negative charged of xanthates are free at pH 5-7.Because of lower pH 5 xanthates ions ($ROCS_2^-$) become protonated and convert into xanthic acid ($ROCS_2H$), it is unstable in water solution and easily break into carbon disulphide (CS_2) and constituent alcohol (ROH), which reduced the active site of xanthates that leads to decrease of adsorption potential hence retort the efficiency towards the metal ion removal given in flowing reactions[7-8].

$ROCS_2^- \quad + \quad H^+ \quad \rightarrow \quad ROCS_2H$

Xanthate ion   Acid   Xanthic acid

$ROCS_2H \quad \rightarrow \quad CS_2 \quad + \quad ROH$

Xanthic acid   Carbon disulphide   Alcohol

In the basic medium pH above than 7 adsorption competition in between xanthates and hydroxide ions (OH^-)for adsorption on the site. The hydroxide ion more potential of adsorption as compared to xanthate on the surface of minerals, in basic medium more concentration hydroxide ions are occurred which hindered the adsorption.

Generally, adsorption processes are exothermic reaction so that lower temperature facilitate the xanthate binding capacity to metal ions and enhanced removal of metal ions from waste water.

4. Applications of xanthates in Removal of Heavy Metal

Numbers of monosaccharides xanthates have efficient potential for elimination of several toxic metal ions from polluted water given in table 1.

Table1: Adsorbents and their efficiency for metal ions removal

Adsorbent	Metal ions	Adsorption (mg/g)	References
Powder Chitosan	Cd^{2+}	420	[20]
Beads form of Chitosan	Cd^{2+}	518	[20]
Brown algae seaweed	Cd^{2+}	67	[21]
Starch based xanthate	Cd^{2+}	33.3	[22-23]
	Cr^{2+}	17.6	,,
	Hg^{2+}	1.15	,,
Cellulose based xanthate	Cd^{2+}	19.9	[22]
	Cr^{2+}	19.7	,,
	Hg^{2+}	0.64	,,
Dust of xanthates	Cd^{2+}	21.4	[23]
	Hg^{2+}	30.1	,,

5. Merits and Limitations

5.1. Merits

a. These xanthates are synthesized from monosaccharide that obtained by the natural source with biodegradable and renewable character.

b. There are various xanthates site are available that facilitate the binding capacity with metal ions present as pollutants in water.

c. There synthesis routes are caring of environment and also show non- toxic behaviour.

d. It has effective capability for the removal metal ions even its present low concentrations.

e. It potentially regenerate and reuse as adsorbate after washing with low amount of acid.

5.2. Limitations

a. The monosaccharides have instable nature to chemicals because the xanthates groups hydrolysed with strong acid.
b. Their wide applications are limited because of its solubility problems in various solvents.
c. The easily degradation of carbon disulfide occurs that affects the security and cost.
d. There are partially loss of active site occurs during regeneration of xanthates.

6. Future Scope:

The monosaccharide xanthates having low molecular weight their fore it has limitation in stability, reusability and selectivity capability. In future improving the these by grafting, cross-linking and nanocomposite with merging from cellulose or chitosan natural polymer, after that hybrid materials are obtained, that have more mechanical strength and adsorption capability. Further to develop the ecofriendly synthetic process by using economical carbon disulfide or their alternatives as biogenic sulfur donor which may enhanced the safety towards atmosphere.

7. Conclusion

The monosaccharide xanthates signified a gifted grade of supportable adsorbents that eliminate the toxic metal ions from polluted water. Their effective capacity to binding with metal ions, favourable to environment and economically favourable materials that produce them as an appropriate aspirant for development of recent technologies in wastewater treatment. Thought more optimization in mechanical strength and wide applicability is mandatory that formerly used on commercial scale.

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