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REVIEW AND PROSPECTS OF XANTHAN APPLICATION IN WATER CONTAMINANTS REMOVAL

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ABSTRACT

This review explores the novel perspectives and application of xanthan in the removal of emerging water contaminants. Xanthan is a nontoxic, biocompatible, and biodegradable biopolymer of microbial origin. Industrial production of xanthan is usually conducted by aerobic submerged batch cultivation of the bacterium *Xanthomonas campestris* ATCC 13951 on the medium containing glucose or sucrose under optimal conditions, and findings of researchers worldwide indicate that xanthan can be successfully biosynthesized on media containing different waste streams, using various *Xanthomonas* strains. Common application of xanthan is in the food industry as a stabilizer, thickener, and emulsifier because of its high viscosity at lower concentrations and excellent solubility in hot and cold water. The application of xanthan is not only limited to the food and other branches of industry, but also to medicine, biomedical engineering, agriculture, and wastewater treatment. Recent studies have confirmed the excellent photocatalytic activity and emulsifying capacity of xanthan biosynthesized on waste-based media, which offers promising potential for its application in the decontamination of environment. Moreover, the xanthan-based hydrogel has great selectivity for the cationic dye and on the other side, chemically modified xanthan has a great potential as an adsorbent for the removal of metal ions.

Keywords: biopolymer, xanthan, environmental application, water contaminants removal

1. INTRODUCTION

Biopolymers are constantly finding novel applications in the food, cosmetic, and pharmaceutical industries, drug delivery systems, biomedicine, tissue engineering, and environmental protection owing to their outstanding structural and rheological characteristics, non-toxicity, biodegradability, biocompatibility, and abundance [1-3]. Among them, microbial biopolymers represent a promising alternative to existing polymers. Scientists have focused on the development of the production and application of microbial biopolymers because their production does not depend on the geographical area, climatic conditions, or season, which is the case with plant biopolymers.

Xanthan is a microbial biopolymer of great commercial significance. It is produced by the aerobic submerged batch cultivation of pure bacterial culture from the genus *Xanthomonas* on appropriately formulated media and under optimal conditions [4]. This biopolymer is frequently used as a rheological modifier, thickener, stabilizer, and emulsifier in various industries [5, 6]. The European List of Permitted Food Additives has classified xanthan as a food additive E 415. Moreover, the United States Food and Drug Administration gave the GRAS status (Generally Recognized as Safe) to the ethanol precipitate of xanthan [7].

Various *Xanthomonas* species such as *X. malvacearum*, *X. phaseoli*, *X. axonopodis* and *X. euvesicatoria* possess the ability to successfully produce xanthan, but *X. campestris* is commonly used for its industrial production [8, 9]. Commercially, production of xanthan is mainly performed by reference strain *X. campestris* ATCC 13951. The success of industrial xanthan production is influenced mainly by the composition of the cultivation medium and bioprocess parameters [10]. Sugars such as sucrose and glucose are generally used as carbon sources in the media for xanthan production [11]. Considering that the cost of the substrate is an important factor for commercial xanthan production and that the price of the

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aforementioned sugars is rising, it is clear that there is a need to exploit more economical carbon sources to reduce the overall production costs [12].
Results from several studies have confirmed that various alternative substrates of lower market value may be used as carbon source in cultivation medium for successful xanthan production [13-16]. Research related to the xanthan biosynthesis on alternative substrates is still in initial stages and there is a need for more detail examination regarding isolation of new *Xanthomonas* strains, defining the composition of the cultivation medium, optimization of process parameters values, as well as finding a novel application of biopolymers synthesised in these conditions.
Although xanthan is a relatively inexpensive renewable natural resource, little attention has been paid to its application in environmental protection. Hence, the aim of the present study is to review current xanthan applications and explore new prospects for xanthan applications in the removal of emerging contaminants from water.

2. XANTHAN STRUCTURE AND PROPERTIES

Xanthan represents heteroextracellular polysaccharide that consists of pentasaccharide repeating units formed by D-glucose, D-mannose, and D-glucuronic acid with a molar ratio of 2:2:1, as shown in Fig. 1 [17]. The backbone of xanthan consists of linear (1 → 4)-linked β-D-glucose, and the side chains are composed of glucuronic acid residues linked to a terminal D-mannose unit with (1 → 4) and (1 → 2) to an inner mannose unit, which is linked to the backbone. As it can be seen from Fig. 1, C-4 of the terminal D-mannose unit contains a pyruvate group, and C-6 of the inner D-mannose unit is replaced by an acetyl group [17]. The pyruvic acid content is highly influenced by the bioprocess conditions and on the *Xanthomonas* strains used. Side chains provide approximately 65% of the xanthan molecular weight and are of great importance for the molecular conformation [18]. Xanthan can interact synergistically with other polysaccharides such as cellulose and its derivatives to enhance the viscosity of aqueous solutions [8, 18]. This biopolymer can build a complex network by conforming to a multiple helix or random coil conformations (single, double, and triple) with strong intermolecular associations. The synergism of xanthan with other polysaccharides can be disrupted by external effects like temperature, and shear rate, leading to order-disorder transition within helix [19, 20].

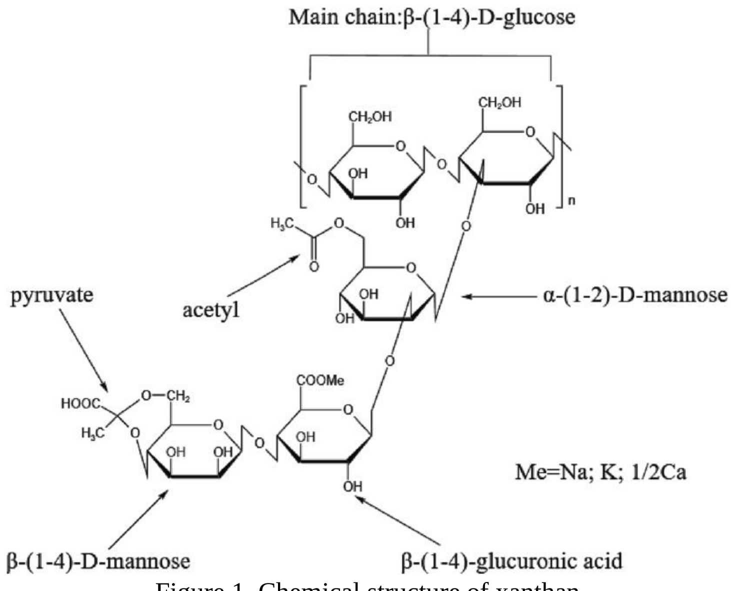

Figure 1. Chemical structure of xanthan

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The molecular formula of xanthan is $(C_{35}H_{49}O_{29})_n$. The molecular weight of xanthan depends on the association between structural chains and usually varies from around $2 \cdot 10^5$ g/mol to $2 \cdot 10^7$ g/mol [13]. Due to its high molecular weight, unique chemical structure, biocompatibility, biodegradability, and non-toxic nature, xanthan exhibits outstanding pseudoplasticity, thickening, and emulsifying properties. This biopolymer has good solubility in both cold and hot water. The hydroxyl groups that are present within the xanthan chain have the possibility of forming hydrogen bonds with water. Moreover, the glycosidic oxygen atoms which are connecting one monosaccharide to another have also the ability to form hydrogen bonds in aqueous solution [18]. Xanthan solutions are highly viscous even at low polymer concentrations and it is believed that the thickening ability of xanthan solutions is related with viscosity. Xanthan solutions are pseudoplastic, and the viscosity decreases with increasing shear rate. Viscosity of xanthan solutions is greatly influenced by the biopolymer concentration, and is quite stabile during changes in temperature and pH value in a wider range. Considering that xanthan solution has outstanding properties such as good salt resistance, high viscosity even at low concentrations of biopolymer, and great tolerance to acid, alkali, and enzymatic hydrolyses, it can be used in wide range of industrial applications [21].

3. INDUSTRIAL APPLICATION OF XANTHAN

The main industrial applications of xanthan are related to its aforementioned characteristics which are a consequence of the unique structure. The food industry is the major field of application for xanthan. Thus, xanthan is used in a variety of food products along with dressings, sauces, baked goods, dairy products, desserts, beverages, and frozen products [21]. Compared to other hydrocolloids, xanthan appears to be the best for improving gluten-free bread. Xanthan improves the texture, viscosity, appearance, flavour release-like properties of food, and rheology of the final products. In food formulations, the content of xanthan usually varies from 0.05 to 0.7 wt% and it is generally used in combination with guar or locust beans to increase the desired properties and reduce the production cost [22].

In addition to the food industry, xanthan is also used as a thickening agent in toothpaste, shampoos, creams, and lotions products to enhance their flow behaviour and to give them the right thickness and stable creamy foam [22]. Xanthan is widely used in other cosmetics and cleaning products as well as in coatings and paints. The leading application of xanthan gum is in controlled drug delivery systems in the pharmaceutical industries [23]. This biopolymer is used as a cohesive agent in solid drug products and drug delivery systems, and as a thickening, suspending, or stabilizing agent in liquid oral formulations [24]. Its application in the agricultural sector is reflected in the improvement of flow behaviour of fungicides, herbicides, and insecticides.

Because of its ability to disperse and hydrate rapidly, as well as its non-polluting nature and good colour yield, xanthan is suitable for application in jet injection and printing. In the petroleum industry, xanthan is primarily used in oil drilling, fracturing, and pipeline cleaning [22]. Another important application of xanthan is enhanced oil recovery, owing to its water control and suspension stabilization under extreme conditions of temperature and high salt concentrations. In addition, xanthan can be used in oil drilling, pipe cleaning, and fracturing [25]

4. WATER PURIFICATION AND WASTEWATER TREATMENT APPLICATION OF XANTHAN

Water pollution is becoming increasingly serious worldwide. The release of domestic, industrial, pharmaceutical, and medical wastes into groundwater and rivers disrupts the ecological equilibrium of aquatic systems. A large population lacks access to drinking water. Water contamination has emerged as a significant issue in industrialized areas. The food and pharmaceutical industries play a significant role in the pollution of water resources [22].

In this section, water purification and wastewater treatment applications of different xanthan samples proposed in the literature are discussed. Accordingly, findings regarding xanthan application in the removal of food oils, organic solvents, pharmaceuticals, heavy metals, and dye pollutants are considered (Fig. 2).

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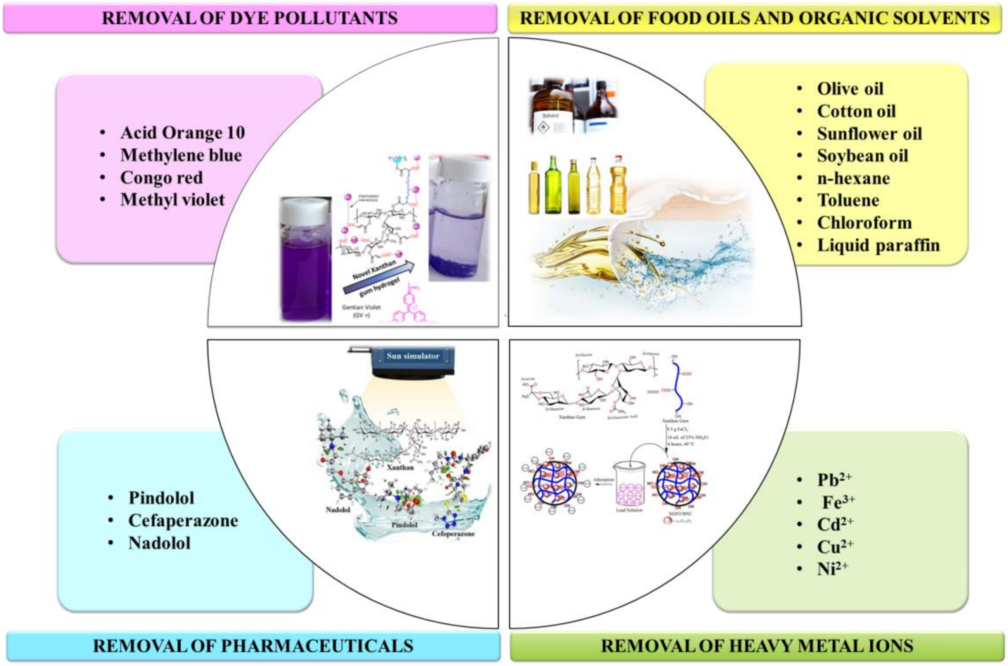

Figure 2. Xanthan application in in water contaminants removal

4.1 REMOVAL OF FOOD OILS AND ORGANIC SOLVENTS

Industrial wastewaters containing oils and organic solvents represent a notable environmental threat and hence, there is a need for effective and environmentally friendly wastewater treatment techniques for the removal of these pollutants. To achieve this, successful separation of the oil/water mixture before releasing wastewater into the environment should be performed [26]. As mentioned earlier, the viscosity of xanthan solutions is stable over a wide range of temperatures and pH values, which is why it is widely used to control the rheological properties of emulsions by contributing to their stability. However, the ability of xanthan to increase both the viscosity and stability of emulsions greatly depends on the concentration and structure of the biopolymer [21]. The emulsification properties of xanthan produced on media containing waste streams and by-products from different industries have been poorly explored, and there are a few studies exploring the emulsification index for newly synthesized biopolymers [26, 27]. Emulsification activity of xanthan has been confirmed within study conducted in Brazil [27], where the emulsifying properties of biopolymers produced by *X. campestris* pv. *campestris* 1866 and 1867 from lignocellulosic agroindustrial wastes were examined in four different vegetable oils (cotton, olive oil, corn, and soybean). Xanthan produced by *X. campestris* pv. *campestris* 1866 strain exhibited higher emulsification activity in olive oil, while biopolymers produced by *X. campestris* pv. *campestris* 1867 strain showed better emulsification activity in cotton oil, both after 24 of resting.

Findings from research conducted in Serbia, where the emulsifying activity of xanthan produced by reference strain *X. campestris* ATCC 13951 on medium containing crude glycerol generated in domestic biodiesel factory was examined in the presence of n-hexane, toluene, chloroform, liquid paraffin, sunflower oil, olive oil, and soybean oil, also confirmed great ability of this biopolymer to form and stabilize emulsions [26].

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According to the obtained results, the emulsification activity of xanthan varies with the xanthan sample and oil/organic solvent used indicating that emulsification properties of xanthan mainly depend of producing strain, cultivation medium composition and process conditions. Xanthan produced within this research showed great ability to form and stabilize emulsions with all hydrocarbons/oils tested but somewhat better activity was achieved when using food oils.

Aforementioned findings are very important from an ecological aspect as they suggest prospects for application of xanthan produced by different producing strains and in different cultivation conditions, in emulsification bioremediation of environmental contaminants and oil recovery processes.

4.2 REMOVAL OF PHARMACEUTICALS

Pharmaceuticals represent a distinctive category of emerging environmental pollutants because of their ability to trigger physiological responses in humans even at low doses. Intensive scientific investigations have consistently identified the presence of various pharmaceuticals in various environmental domains. This increasing awareness raises significant concerns regarding potential adverse impacts on human health and wildlife [28]. The inadequate availability of practical techniques for the removal of pharmaceutical contaminants from water necessitates the discovery of a new suitable solution for their removal. Findings from recent study indicate a new prospect for removal of pharmaceutical contaminants by microbial biopolymer [26]. Despite the fact that biopolymers have been recognized for their impressive adsorption abilities and the application of biopolymer-supported TiO_2 in photocatalysis, their potential as substitutes for metal-based nanomaterial has not been extensively investigated. However, scientists from Serbia [26] reported photocatalytic activity of xanthan produced by reference strain *X. campestris* ATCC 13951 on medium containing crude glycerol from biodiesel production. In this study, under the influence of a simulated solar light source, xanthan exhibited significant degradation rates for pindolol (77%) and cefoperazone (91%) while, nadolol's degradation efficiency was notably lower (10%). These findings suggest that the molecular structure can substantially influence the efficiency of the purification process. The obtained results represent unique report on photocatalytic application of xanthan and may provide a great background for examination of novel xanthan application and pave the way for further investigations to harness the unique properties of xanthan for efficient and sustainable environmental remediation and related applications.

4.3 REMOVAL OF HEAVY METAL IONS

Along with the rapid development of metal plating facilities, mining operations, fertilizer industries, tanneries, batteries, paper industries, etc., heavy metals containing wastewaters are directly or indirectly discharged into the environment increasingly. In contrast to organic contaminants, heavy metals are not biodegradable and tend to accumulate in living organisms. Heavy metals of particular concern in treatment of industrial wastewaters include zinc, copper, nickel, mercury, cadmium, lead and chromium, and many of them are known to be toxic or carcinogenic [29]. Removal of heavy metals from water has been generally carried out by chemical precipitation for its simplicity process and inexpensive capital cost. However, chemical precipitation is usually adapted to treat high concentration of heavy metal ions and it is ineffective when treating wastewater with low concentration of this pollutants. On the other side, chemical precipitation is not economical and can produce large amount of sludge to be treated with great difficulties. Biosorption is considered as very effective technique for the treatment of wastewaters that contain heavy metals. Recent studies have confirmed that various biogenic products, including native and functionalized biopolymers, have been successfully employed in technologies aiming for the environmentally sustainable immobilization and removal of heavy metals at contaminated sites, including commercially available heteropolysaccharide - xanthan [30-32].

Xanthan-based adsorbents have a great potential in the removal of heavy metal ions from water due to their negatively charged nature, which can attract positively charged metal ions [33]. Study conducted in Serbia resulted in successful crosslinking of xanthan produced on winery wastewater-based medium by

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X. campestris ATCC 13951 with Pb^{2+} and Fe^{3+} ions, indicating a promising potential of this biopolymer in heavy metal removal from aqueous solutions [34]. Results from another study conducted in China indicate that xanthan complexes Pb^{2+} with a fast rate and xanthate could improve the complexation ability of xanthan to Pb^{2+} [31].

The modification of xanthan with functional groups, or by using nanofillers can additionally enhance its adsorption capacity and selectivity towards specific metal ions. An example is a green functional nanocomposite material which was synthesized by immobilizing α-Fe_2O_3 nanoparticles with xanthan to produce an adsorbent for the removal of Pb^{2+} ions from wastewater [35]. The synthesized material exhibited significant binding capability due to the presence of key functional groups such as –COOH and –OH, through an endothermic and spontaneous reaction. The regeneration studies suggested that aforementioned material is highly effective towards Pb^{2+} ions removal, can be effectively reused by using 0.2 M HCl solution, and therefore can be utilized as an efficient adsorbent material for the treatment of contaminated wastewater.

In another study conducted in Iran, xanthan and chitosan are physically crosslinked (self-assembled) into a biodegradable hydrogel film and adsorption of Cd^{2+}, Cu^{2+} and Ni^{2+} by the obtained biofilm in aqueous solution was examined [32]. It is reported that maximum amount of Cd^{2+}, Ni^{2+}, and Cu^{2+} ions was adsorbable with 50 mg of the adsorbent at pH 6.0 for an initial metal concentration of 50 mg/L and that the biofilm was capable of regenerating, allowing metal ions to adsorb and desorb for five consecutive cycles. Considering this and all the aforementioned findings it can be concluded that xanthan offers the promising potential for removal of specified metal ions.

4.4 REMOVAL OF DYE POLLUTANTS

Dyes represent another category of chemical substances that can contaminate water. Industries such as textiles, leather, paper, and plastics repeatedly use synthetic or natural compounds, known as dyes [36]. During the dyeing process, considerable volumes of water are utilized to rinse and wash products, resulting in the production of a significant amount of wastewater that is then released into water sources. Dyes can also end up in water through improper disposal of household and commercial products containing dyes [33]. The negative effects of dyes on water bodies are reflected by the reduction in oxygen levels, disruption of aquatic ecosystems, and harm to aquatic life. They also cause skin irritation, respiratory problems, and allergic reactions in humans [32]. Hence, the removal of dyes from industrial waste is very important because of their toxic effects on both humans and aquatic life. Therefore, cost-effective treatment of industrial wastewater for dye removal has recently gained significant importance.

Scientists from Egypt [37] investigated the removal efficiency of Acid Orange 10 dye (AO-10) and Cr^{4+} from aqueous solutions using carboxymethyl xanthan gum-g-poly (4-vinyl pyridine), CMX-g-P (4VP). It was reported that the adsorption capacity of AO-10 and Cr^{4+} was pH-dependent and the highest at pH 2.5. Moreover, the adsorbent was found to be efficiently reusable for up to five cycles according to desorption studies. Overall, the results showed that the used adsorbent is a promising material for removing toxic organic dyes.

Xanthan based hydrogels were synthesized and used as potent adsorbents for the removal of dye pollutants from waste water effluents in research conducted in Germany [38]. The adsorbents were synthesized by esterification of xanthan with maleic anhydride, followed by thiolene cross-linking chemistry with 2,2′-(ethylenedioxy) diethanethiol. Methylene blue was used as model cationic dye to mimic dye polluted water. Findings from this study confirmed efficient uptake of methylene blue dye by xanthan-based hydrogel adsorbents with a maximum adsorption capacity at pH 11, and that the hydrogel showed a potential to be re-used for at least for twenty times after regeneration and maintaining over 95% efficiency dye removal as well as recovery.

Another study was conducted in India where removal of Congo red (80%) dye from aqueous solution by eco-friendly novel bionanocomposite was examined [39]. The results obtained within this study suggest that novel xanthan-glutathione/zeolite bionanocomposite have been proved to be an excellent and feasible adsorbent that can be explored for the removal of heavy metals and dyes from wastewater.

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In another study, the superporous hydrogels of acrylic acid and acrylamide with xanthan were synthesized using glass blowing and foaming technique and tested the feasibility of synthesized hydrogels to removal of methyl violet dye by the process of adsorption from aqueous solution [40]. It was observed that SPH-4 hydrogel can be utilized successfully for five successive adsorption and desorption cycles of methyl violet dye removal. Based on these findings SPH-4 has all the desired properties to be used as an adsorbent for cationic impurities for several large-scale industrial applications.

5. FUTURE OUTLOOK

Currently, water contamination with hazardous and toxic substances, including oils, organic solvents, pharmaceuticals, metal ions, and dyes, is a primary concern worldwide. Therefore, efficient removal of these contaminants, at least to the levels established by regulations, has become increasingly essential. Different chemical, physical, and biological processing methods have been employed for the treatment of water contaminants, including adsorption, which is cost-effective, simple, yet efficient, and the applied adsorbent can be selected from a wide array of natural materials.

This review aims to provide an overall perspective of recent advances that have been done in water purification and wastewater treatment. Accordingly, this review presents findings from recent studies that have exploited raw or modified xanthan for the decontamination of water, such as the removal of food oils, organic solvents, pharmaceuticals, heavy metals, and dyes.

Research on the application of xanthan in water purification and wastewater treatment is still in the initial stages and comprises the development of new and more effective xanthan-based adsorbents and their testing under optimized laboratory conditions. Despite this, experiments should be performed at a larger scale to evaluate the viability and cost-effectiveness of xanthan employment in remediation technologies. This review will certainly be helpful for further research and exploration of new materials for intended purposes.

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