

Treatment of Pulp and Paper Mill Effluents using Novel Biodegradable Polymeric Flocculants based on Anionic Polysaccharides: a New Way to Treat the Waste Water

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Abstract

Wastewater and industrial effluent treatment require removal of suspended solids for purification and possible re-usage. Despite the impact of the industry on the environment, the world of pulp and paper industry continues to expand at alarming rates and so more and more paper mills are booming up in the newly industrialized countries. Pulp and paper mill produces large number of highly heterogeneous waste waters containing sulphur based compounds, nitrogen oxide, chlorinated based and many other toxic pollutants. All these lead to very high chemical oxygen demand (COD) values of effluent water. Although there are many cheapest processes available for treatment of various organic effluents, but present need is to use a process which is efficient in reducing pollution and also eco- friendly. Available industrial waste treatment processes are expensive and pose a major threat to the environment. Several methods have been attempted by various researchers throughout the world for the reduction in COD of pulp and paper mill effluents. So this paper is a comprehensive review of various literature sources for adaptation in pollutants and chemical oxygen demand by biodegradable anionic polymers. These anionic polymers are more frequently employed in industrial water clarification plants because of improved flocculation. Also they frequently permit appreciable dosage reduction in primary coagulants. They are exposed to a greater number of separate particles when added to the water because of their strong bridging action. Hence this paper comprises the potential of various biodegradable anionic polymers in purifying the effluent water and to reduce the dose of COD and biological oxygen demand (BOD).

Key Words: Biodegradable, Anionic polysaccharides, Flocculants, Polymer, Pulp, Paper, Effluent, Environment, Pollutants, Coagulants.

[1] Introduction

The pulp and paper industry has been facing more stringent limitations on its discharges during the

last few decades and the same trend will continue in the future. Pulp and paper mill is a major industrial sector utilizing a huge amount of lignocellulose materials and water during the manufacturing process and release chlorinated lignosulphonic acids, chlorinated resin acids, chlorinated phenols and chlorinated hydrocarbon in the effluent [1].

The highly toxic and recalcitrant compounds, dibenzo-p-dioxin and dibenzofuran are formed unintentionally in the effluent of pulp and paper mill [2, 3]. The untreated effluents from pulp and paper mills that are discharged into water bodies, damages the water quality. The undiluted effluents are toxic for aquatic organisms and exhibit a strong mutagenic effect. In spite of the major process investments in environmental protection, the supplementary treatment of wastewater will become ever-more important in the future due to the large quantities of wastewater that are generated. The de-colorization of effluents, at least, should be performed. Conventional biological treatment processes have little or no effect on wastewater de-colorization. The brownish color is mainly due to lignin and its derivatives which are difficult to degrade naturally. Biological treatment removes most of the wood extractives and the effluent is highly diluted in the receiving water system. However, wood extractives (e.g. resin acids and sterols) can get transformed to other toxic compounds during biological treatment. Furthermore, there is no guarantee that biological

treatment will always work properly and serious toxicity breakthroughs may occasionally occur. However, the biological color removal process is particularly attractive since in addition to color and COD, it also reduces BOD and low molecular weight chloro-lignins [4,5]. Intensive water recirculation in pulp mills leads to an accumulation of wood extractives in the water cycles, as well as other harmful substances such as non-process elements. Non-process elements, which are unintended components of the pulping and bleaching chemicals, enter the process as trace elements in wood and impurities in process chemicals and raw water. Among other things, these elements cause corrosion (mainly Chlorine), deposits on equipment (Aluminum, Barium, Calcium, and Silicon) increase the consumption of bleaching chemicals (Manganese, Iron and Copper) and have a negative impact on the environment (Nitrogen, Phosphorus and heavy metals) [6,7]. The principle of biodegradation technologies is an optimization of nutrient ratios and an application of suitably selected isolated microorganism strains with relevant degradation abilities [8]. Although the physical and chemical methods are on the track of treatment, they are not on par with biological treatment because of cost ineffectiveness and residual effects. The biological treatment is known to be effective in reducing the organic load and toxic effects of krafts mill effluents [9]. The microorganism treats the effluents mainly by two process; action of enzymes and biosorption [10]. The various enzymes involved in the treatment of pulp and paper mill effluent are lignin peroxidase, manganese peroxidase and laccase [11]. Microorganisms showing good production of these enzymes have the potency to treat the effluent. The efficient removal of toxic substances from process waters will make it possible to close the water circuits. This supplementary treatment of wastewater would, in turn lower the amount of detrimental compounds and their access to the

water system. Pre-treatment before biological wastewater treatment could have a positive impact on the performance of the biological process. Effluent disposal is a major problem around the world. Growing along with the population growth, industries create environmental problems and health hazards for the population. The effluents are highly undesirable and unsafe to use. Wastewater contains solid particles with a wide variety of shapes, sizes, densities and composition. Specific properties of these particles affect their behaviour in liquid phases and thus the removal capabilities. Many chemical and microbiological contaminants found in wastewater are adsorbed on or incorporated in the solid particles and is thus essential for purification and recycling of both wastewater and industrial effluents is the removal of solid particles. Hence environmental concerns and progressing depletion of raw material resources behave scientists and engineers to develop materials from renewable agricultural and plant resources to lower the extent of environmental pollution. These polymeric materials already play an important role as alternatives to fossil raw materials due to both their non-toxic nature and the constantly rising global demand for energy and raw materials. Depending upon the source these contain various impurities and also exhibit a variety of molecular characteristics. However, by purification, grafting and anionization, useful products can be made usable as flocculating, drag reducing and viscosity enhancing [12]. Also comprehensive and appropriate information about the characteristics of effluent is essential for optimizing existing treatment methods and for developing new ones. Hence we discuss biodegradable anionic based polymers since they provide both stability and bridging action and anionic polymers are perhaps the most reliable coagulant aids inasmuch as drastic overdoses have little or no effect on zeta potential. However, over treatment is still possible since good

flocculation does not occur if more than 50% of the particle surface is covered by polymer.

[2] Pulp and Paper Mill

The pulp and paper industries use three types of raw materials namely hard wood, soft wood, and non-wood fiber sources (straw, bagasse, bamboo, kenaf, and so on). Hard woods (oaks, maples, and birches) are derived from deciduous trees. Soft woods (spruces, firs, hemlocks, pines, cedar) are obtained from evergreen coniferous trees. In the pulp mills the potential of the pulp is much greater than the paper making units. The utilization of plant fiber for paper production is one of the oldest manufacturing industries and is built upon age-old technologies. It was not until this became mechanized and the scale of production escalated in the early part of last century and many of today's environmental problems associated with the pulp and paper industry emerged. For example, in the industrial manufacture of paper from wood fiber, it was known that natural compounds were released during processing that caused harm to the aquatic population [12]. Pulp and paper are manufactured from raw materials containing cellulose fibers, generally wood, recycled paper and agricultural residues. In developing countries, about 60% of cellulose fibers originate from non-wood raw materials such as bagasse (sugar cane fibers), cereal straw, bamboo, reeds, esparto grass, jute, flax and sisal. In World Bank studies [13], pulp and paper manufacturing units have production capacities greater than 100 metric tons per day. As per the Ministry of Environment and Forest (MoEF), Government of India, the pulp and paper sector is in the Red Category list of 17 industries having a high polluting potential. Pulp and paper production is a major industry in India with a total capacity of over 3 million tons per annum [14]. The pulp and paper industry usually produce high volume of waste amounting to 225 to 320 m³/tons of the paper produced. The pulp and paper waste have high

color with high COD mainly because of lignin derivatives derived from cellulosic raw material. Lignin is not easily degraded by microorganisms; hence the BOD remains much lower than COD values. The pH of waste remains in the alkaline range with high amount of total suspended solids. The paper and pulp industrial procedure flow chart was given in **Figure-1**.

[3] Waste source and characterization

Pulp and paper mills are categorized as a core sector industry and are the fifth largest contributor to industrial water pollution. Pulp and paper industry is one of the most water and energy consuming industry in the world. It uses the fifth largest energy consumer processes, approximately 4% of total energy that is used worldwide. Also during pulp and paper process, important amount of waste is produced. It has been estimated that 500 million tons of paper and etc. per year will be produced in 2020. Waste and wastewaters are generated from both of pulp and bleaching processes. Additionally, 100 million kg of toxic pollutants are released every year from this industry [15].

[4] Composition of spent pulping liquors

Agro-residue mills typically employ a soda or alkaline sulfite pulping. Typical composition of the spent liquors generated from the small-scale agro-residue utilizing pulp and paper mills are shown in **Table- 1**. It is evident from the table that 45–50% of the total solids were represented by lignin. Most of the lignin present in the black liquor was high molecular weight fraction, a key factor contributing to low BOD/COD ratio.

[5] Pulp bleaching process

About 5–10% of the original lignin cannot be removed from the pulp without substantial damage to the cellulosic fraction. Removal of the residual lignin which are responsible for imparting dark color to the pulp and the production of white pulp, requires a series of steps employing bleaching chemicals. Pulp bleaching is normally accomplished by sequential treatments with elemental chlorine, alkali, chlorine dioxide, and alkali and chlorine dioxide. The stage chlorination (C) consists of charging slurry of the pulp (at 3–4% consistency) with elemental chlorine (60–70 kg/ton of pulp) at 15–308⁰C at pH 1.5–2.0 [16]. The largest quantity of pulp is dissolved during the Chlorine and alkali stages. Alternate pulp bleaching

techniques such as the elemental chlorine free (ECF), total chlorine free (TCF). Compounds responsible for imparting toxicity to the spent bleach effluents originate during the chlorination (C) stage and caustic extraction (E) stages. The major classes of toxic compounds are resin acids, fatty acids, and adsorbable organic halide (AOX). Fatty and resin acids in bleach liquors often originate from the washing of unbleached pulps. Adsorbable organic halides are the products of lignin degradation formed exclusively during the C stage of pulp bleaching and get dissolved into the bleaching liquors during the E stage. About 1–3% of the AOX fraction is extractable into non-polar organic solvents and is referred to as extractable

Table -1: Characteristics of Agro-Residue Based Spent Black Liquors.

Parameter	Mill 1 (bagasse, wheat straw, and lake reed used as raw material)	Mill 2 (wheat straw used as the raw material)	Mill 3 (rice straw used as the raw material)
pH	9.7	10.2	8.8
Total solids (g/L)	44	42	38
Silica % (w/w) as SiO ₂	2.4	3.2	12.0
Total organics % (w/w)	74.4	74.0	76.7
Lignin (g/L)	16.0	13.2	14.4
COD (mg/L)	48,700	45,600	40,000
BOD (mg/L)	15,500	13,800	16,500
COD/BOD	3.4	3.3	2.4

fraction poses greater environmental risks than the remaining 99% of the AOX and comprises compounds that are lipophilic with the ability to penetrate cell membranes and potential to bioaccumulate in the fatty tissues of higher organisms.

[6] Characteristics of Pulp and Paper Mill Effluents

The pulp and paper industry produces effluents with large BODs and CODs. One of the specific

problems that have yet not been solved properly is the strong black brown colour of the effluent, which is primarily due to lignin and its derivatives released from the substrate and discharged in the effluents, mainly from pulping, bleaching and chemical recovery stages. The brown colour of the effluent may increase water temperature and decrease photosynthesis, both of which may lead to decreased concentration of dissolved oxygen [17]. The generation of waste water and characteristics of pulp and paper mill effluent depends upon the type

of manufacturing process adopted and the extent of reuse of water employed in plant. Effluents depend upon type of manufacturing process adopted and the extent of reuse of water employed in plant. Effluent of Kraft pulping is highly polluted and characterized by parameters unique to such wastes such as colour, AOX and related organic compound. The alkaline extraction stage of bleach plant effluent is the major source of colour and is mainly due to lignin and derivatives of lignin [18]. Lignin wastewater is discharged from the pulping, bleaching and chemical recovery sections. Lignin is a heterogeneous, three dimensional polymer,

composed of oxyphenylpropanoid units. The high chlorine content of bleached plant reacts with lignin and its derivatives formed to form highly toxic and recalcitrant compounds and are responsible for high biological and chemical oxygen demand. Trichlorophenol, trichloroguicol, tetrachloroguicol, dichlorophenol, dichoroguicol and pentachlorophenol are major contaminates formed in the effluent of pulp and paper mill [19].

The pollutants at various stages of the pulping and paper making process are presented in **Figure–2**[20].

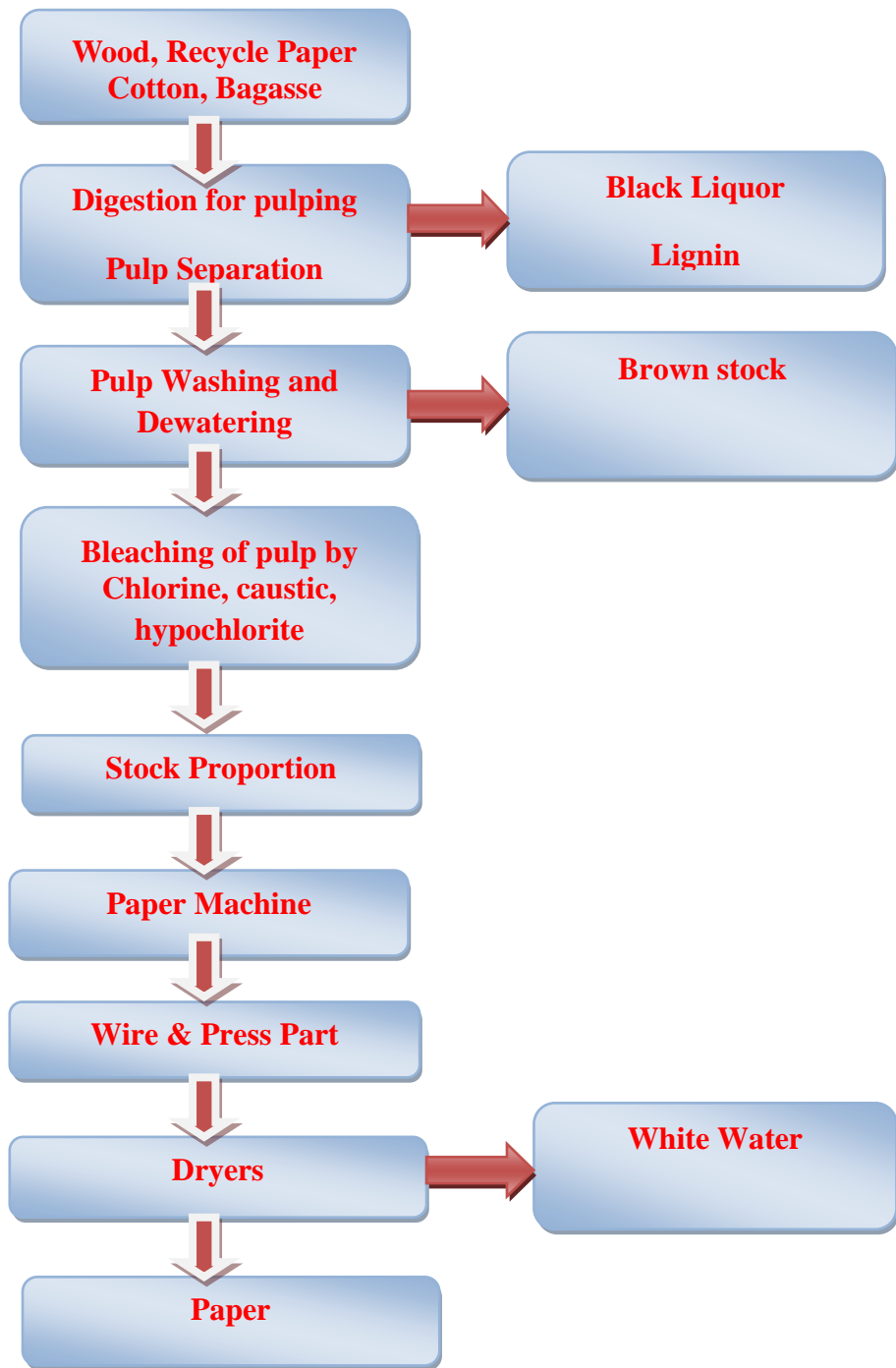


Figure-1: Pulp and paper industrial procedure flow chart.

Owing to its serious pollution threat, it is mandatory for pulp and paper mills to take appropriate measures to comply with the discharge standards set by the Central Pollution Control Board (CPCB) [21], which is the national agency responsible for environmental compliance. The minimum national standards for pulp and paper mills wastewater discharge according to CBCP are shown in **Table-2**.

Table: 2. Minimum national Standards for pulp and paper mills wastewater discharge (CPCB, 2000)

PARAMETER	LARGE PAPER MILLS	SMALL PAPER MILLS
pH	6.5-8.5	5.5-9.0
Suspended Solids (mg/l)	100	100
BOD AT 27 ⁰ C(mg/l)	30	Inland: 30 Land: 100
COD (mg/l)	350	-
Total Organic Chlorine (TOCL) (kg/ton paper 1992 onwards)	2.0	-
Sodium Absorption Ratio (SAR)	-	26

[7] Treatment of pulp and paper wastewater

Pulp and paper effluents contain a number of compounds which are harmful in receiving alters and are inhibitory or recalcitrant to biological treatment. Commonly used physical and chemical

treatment methods are electro coagulation [22], ultrasound [23], reverse osmosis [24], photo catalytic systems using titanium dioxide (TiO₂) and zinc oxide (ZnO) under UV/solar irradiation [25], hydrogen peroxide, Fenton's reagent (H₂O₂/Fe²⁺), UV,UV/ H₂O₂, photo-Fenton (UV/ H₂O₂/Fe²⁺),

ozonation and peroxon (ozone/ H₂O₂) [24].Some of these studies have optimized the operating

conditions for effluent treatment [26-27]. The

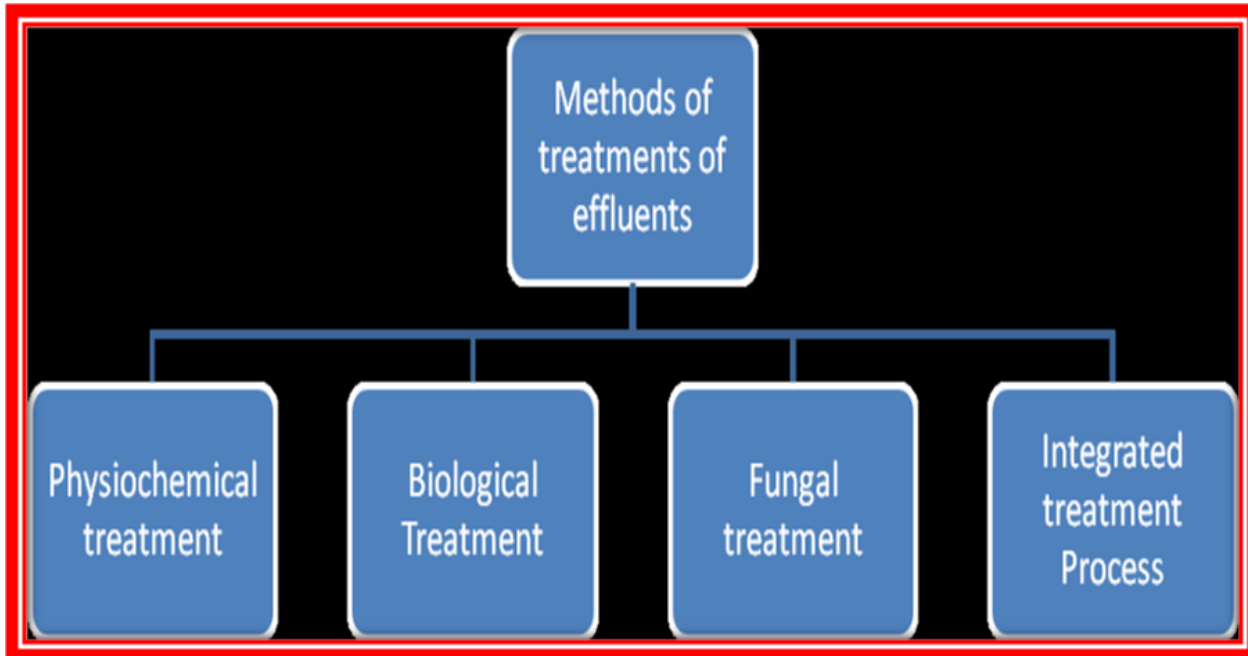


Figure-2.showing different techniques used in the treatment of pulp and paper mill effluents.

biological treatment studies have also confined themselves to the evaluation of microorganism, basic mechanism behind treatment and changes in the effluent after treatment. Not even a single study has optimized the process of effluent treatment. The conventional treatment processes like chemical pre-treatment, lagooning, and activated sludge process (ASP) are not adequate to meet the regulatory effluent standards for being discharged into sewers.

Therefore, the pulp and paper industry has to use tertiary polishing stage to meet the effluent discharge standards. The anionic polymers technique uses the action of bridging action. This treatment will make the secondary treatment cost effective as well as efficient in the removal of residual toxic organic compounds and colour. When anionic biodegradable polymers are used as coagulant aids with inorganic coagulants, dosages in the range of 0.1 to 0.5 ppm are most frequently employed. Dosages from 0.1 to 0.2 are usually sufficient for most waters. Like most coagulant aids, these polymers are usually most effective when fed shortly after the primary coagulant or at the point of initial floc formation [41]. Different techniques used in the treatment of pulp and paper mill effluents are shown in the Figure-2.

[8] Bridging mechanism

Long chain polymers [42,43] when added in small dosage to a suspension of colloidal particles, adsorb onto them in such a manner that an individual chain can become attached to two or more particles thus “Bridging” [42] them together. Interestingly this phenomenon is observed up to a particular optimum polymer dosage beyond which flocculation diminishes, known as Steric stabilization. The essential requirements for polymer bridging are that there should be sufficient unoccupied particle surface for attachment of polymer segments from chains attached to other particles and the polymer bridges should be of such an extent that they span the distance over which inter-particle repulsion prevails. Thus at lower dosages, there is insufficient polymer to form adequate bridging links between the particles. With excess polymer, there is no longer enough bare particle surface available for attachment of segments and the particles become destabilized, which may also involve some steric repulsion. On average, bridging flocculation gives aggregates (flocs) which are much stronger than those produced by the addition of salts (i.e., by reduction in electrical repulsion). However, such stronger floccs produced by the bridging mechanism

[28] may not reform once broken at high shear rates. The schematic illustration of Bridging action (a) and re-stabilization by adsorbed polymers (b) is shown in the Figure-3.

[9] Environmental Impact of Paper and Pulp Mills

The environmental impact of paper and pulp mills is of particular concern since these units generate 150-200 m³ effluent/ton paper with a high pollution loading of 90-240 kg suspended solids /ton paper, 85-370 kg biochemical oxygen demand (BOD)/ton paper and 500-1100 kg chemical oxygen demand (COD)/ton paper [29]. Apart from the pollution, there is a growing water scarcity and deterioration in water quality in many parts of India [30].]. Thus, in the context of reduced freshwater availability, declining water quality and environment pollution from inadequately treated effluent, there is an urgent need for efficient water management in pulp and paper mills. About 500 different chlorinated organic compounds have been identified in paper mill effluents [31]. The high chemical diversity of these pollutants causes a variety of clastogenic, carcinogenic, endocrinic and mutagenic effects on fishes and other aquatic communities in recipient water bodies [32-33].



Figure-3. Schematic illustration of bridging action (a) and re-stabilization by adsorbed polymers (b).

[10] Future Prospect and Affects of Pulp and Paper Mill Effluents

Various studies have reported detrimental effects of pulp and paper mill effluent on animals living in water bodies receiving the effluent. The effects are in form of respiratory stress, liver damage and geno-toxicity [34-36]. A study reported health impacts such as vomiting, headaches, nausea and diarrhoea and eye irritation on children and workers due to the pulp and paper mill wastewater discharge to the environment [37]. The effluent has high chemical diversity of organic chemicals present in it. Many of them are carcinogenic, mutagenic and endocrinic disrupters. Exposure to the effluent adversely affects diversity and abundance of phytoplankton, zooplankton and zoobenthos, disrupting benthic algal and invertebrate communities [35]. Therefore it is obligatory to treat the effluent before disposal.

[11] Polymer coagulants over physio-chemical and cationic coagulants

The main aim of this study is demonstrating the use of anionic polymers (Starch, Carboxymethyl-chitin (Chitosan), Cellulose gum etc.) as a bio-coagulant for uptake of chemical coagulant for paper and pulp effluent. Chemical coagulants have the demerits to produce chemical sludge and non biodegradable, whereas Starch, Carboxymethyl-chitin (Chitosan), Cellulose gum, Chitosan are biodegradable and the sludge produced is also biodegradable and eco-friendly. The overall treatment cost of effluent water varies, depending on the process employed and the local conditions. In general, the technical applicability, plant simplicity, ready availability and inexpensiveness are the key factors for selecting this anionic polymers treatment for the effluent.

[12] Anionic Polysaccharides

Native starch is one of the most abundant biopolymers available on earth and is present in living plants as energy storage material. Starches are mixtures of two polyglucans, amylopectin and amylose, but they contain only a single type of carbohydrate, glucose. Chitin is a naturally abundant mucopolysaccharide extracted from crustacean shells, which are wastes products of seafood processing industries. Chitin is the second biopolymer in nature, after cellulose, in terms of abundance, but it is the most abundant amino polysaccharide. The polymer contains 2-acetamido-2-deoxy-b-D-glucose through a β (1/4) linkage. It may be regarded as cellulose with hydroxyl at position C-2 replaced by an acetamido group. Since such wastes (shrimp, lobster and crab shells) are abundantly available, chitosan may be produced commercially at low cost. Starch and chitin are biologically inert, safe for humans and natural environment. They possess several other advantages and characteristics that make them excellent materials for industrial use [38,39]. There are also some more anionic polysaccharide like Pectin, Hyaluronic Acid, Chondroitin Sulfate. Pectin also called Pectin polysaccharide is used as thickening and stabilizing agent. Chondroitin sulfate is also major component among anionic polysaccharides which is primarily used in moisturizer based on their great water-binding capacity in effluent water. Hence it can also be used for coagulating agent for effluent treatment. Chemical structure of Starch, Chitosan, Pectin, Chondroitin sulfate is given below in **Figure-4**.

[13] Application of Anionic Polysaccharides other than flocculants

Apart from the use of these polymers in the field of effluent treatment, they also play a significant role as thickening agent [40] in the cosmetic industry,

mineral processing industry, film-formers or nail polishers, suspending agents, hair conditioners, moisturizers, emulsifiers, emollients and even as wound-healing agents.

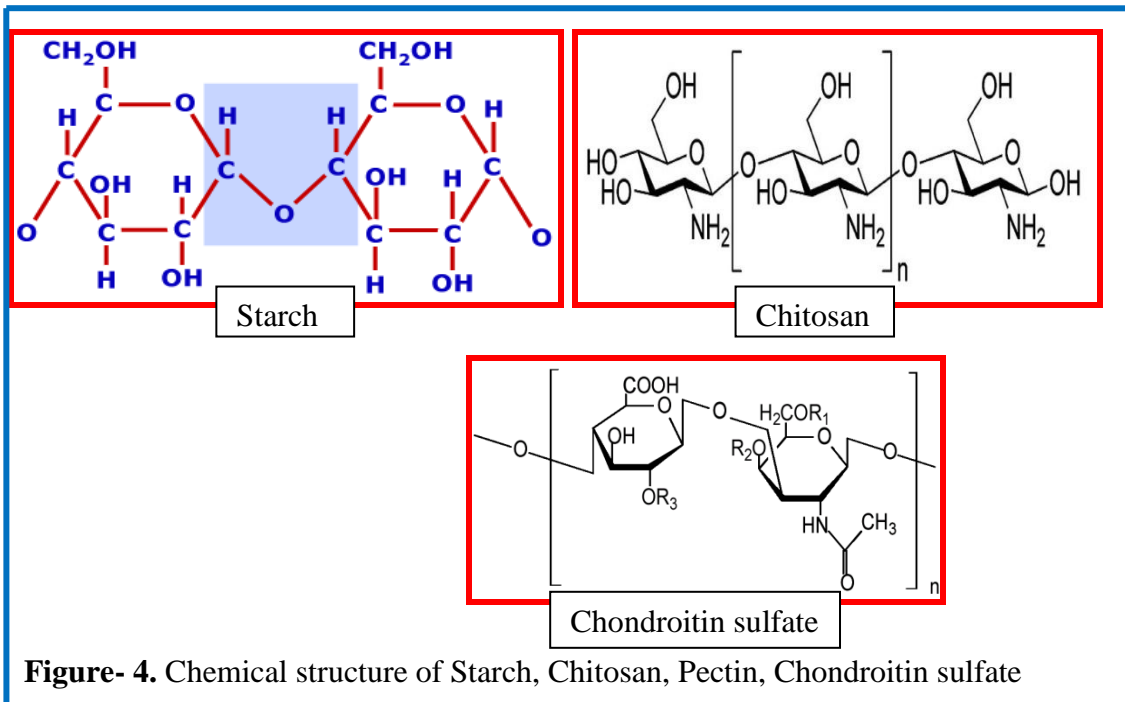


Figure- 4. Chemical structure of Starch, Chitosan, Pectin, Chondroitin sulfate

[14] Concluding remarks

This review article may therefore serve as a challenge to researchers to continue developing better methods to degrade the effluents. These anionic polymers are highly efficient flocculants for industrial effluent treatment, municipal sewage wastewater treatment and removal of color from simulated reactive dye. Environmental problems caused by the industrial effluents are mainly due to accumulation of pollutants having toxic compounds. There is a quick need to degrade these toxic compounds in an eco-friendly way out of various anionic polymers, starch, chitosan, pectin, chondroitin sulfate, that are found to provide the best performance in various wastewaters. This literature survey suggests that this polymeric technique gives the best and fast bridging action because their polymer chains are more uncoiled and are therefore exposed to a greater number of separate particles when added to the water. Anionic polymers may function as primary coagulants when

the colloidal particles are positively charged. One major advantage is that they have little or no effect in neutralizing the negative particle charges, but instead function by improving the bridging action of the primary coagulants. Due to improved flocculation with these polymers, they frequently permit appreciable dosage reduction of other primary coagulants than cationic polymers. However, over treatment is still possible since good flocculation does not occur if more than 50% of the particle surface is covered by polymer. However this treatment can also be used as an effective primary treatment method to remove much of the toxicity, color, COD and BOD. This treatment will make the secondary treatment cost effective as well as efficient in the removal of residual toxic organic compounds and color which in turn will have better approachability to the contaminants in the effluent in accordance. On the whole anionic polymeric polymers were found to cover wide range of recalcitrant degradation and are known to be a best choice because of its nature of degradation and less

toxicity. The objective of this study was to introduce such flocculants which forms

Acknowledgement

The author would like to offer his sincere thanks to co-authors for providing their valuable support which were very useful in interpreting the inferences to this article. We also appreciate every contributions made by everyone to this work.

Conflict Of Interest

Author declares no conflict of interest.

Financial Disclosure

The work is not supported by any grant.

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biodegradable sludge and eco-friendly. These anionic polymers fulfill this basic objective.

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