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ON THE USE OF POLYELECTROLYTES IN WATER AND WASTEWATER TREATMENT.

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تطبيقات البوليمرات الالكتروليتية فى تنقية المياه ومعالجة مياه الصرف الصحى والصناعى

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خلاصــــة

تلعب البوليمرات الإلكتروليتية - الطبيعية والتخليقية - دوراً هاماً فى تنقية المياه وفى معالجة مياه الصرف الصحى والصناعى .

وفى هذه المقالة تم عمل مسح فى المراجع والدوريات العلمية الحديثة من الإستخدامات المختلفة لهذه المركبات فى مجال تنقية مياه الشرب والمياه المستخدمة للأغراض الصناعية المختلفة وكذلك إستخداماتها فى معالجة مياه الصرف الصحى والصناعى المختلفة . ولقد وجد ان إستخدام هذه المركبات أحدث ثورة هائلة فى هذه المجالات وزادت كفاءة العمليات الطبيعية والكيميائية المختلفة المستخدمة فى تنقية المياه ومعالجة مياه الصرف إلى مستوى لم يكن نحلم به من قبل ، حيث إنخفضت التكاليف كما قل حجم الحمأة الناتجة عن العمليات المختلفة .

ABSTRACT

Synthetic or natural polyelectrolytes have an important role to play in the treatment of water and wastewater. In this article, a comperhensive review on the different uses of polyelectrolytes in the fields of potable and industrial water supply and industrial and municipal effluent treatment have been discussed.

Polyelectrolytes have been used for different purposes in the field of potable water supply such as : removal of organic matter, suspended solids, bacteria, algae, trihalomethane precursors, colour and turbidity, water softening, desalination, improvement of mass transfer zone of ozone used for disinfection and it improve the process of direct filtration and the management of water treatment sludge. In the field of industrial effluent treatment polyelectrolytes have been applied in : trace metal removal, dissolved air flotation process, radioactive effluent treatment, conditioning anaerobically digested sludge, treating oil-contaminated industrial wastewater,treatment of tannery effluents, removal of suspended solids from lime-sulfied unhairing effluents, detoxification and decolorization of kraft pulp mill effluents, ore enrichment plant wastewater containing sprucewood tannins.

Polyelectrolytes, generally, have revolutionised the treatment processes, increasing the efficiency of the processes to a level which could not be dreamt of in the past, reducing the cost of chemicals required, producing compact relatively smaller quantities of compact sludge that can drained and disposed of easily and simplifying handling and dosing of the chemicals.

1. INTRODUCTION :

The colloids usually found in water and wastewater vary in size from approximately 10 nm to 10 µm and are characterized by a zeta potential of - 15 to - 20 mv. Colloide are stable due to repulsive forces induced by a high zeta potential or due to adsorption of a relatively small lyophilic protective colloid on a larger hydrophilic colloid or adsorption of a nonionic polymer. Most microscopic and colloidal particles are stabilized by the formation of layers of ions, which tend to collect around the particle and form a protective barrier for stabilization. These ionic layers act as a part of the particle and travel with it through solution inhibiting the close approach of respective particles to each other [1].

The zeta potential is a measure of the stability of a particle and indicates the potential that would be required to penetrate the layer of ions surrounding the particle for destabilization. The higher the zeta potential the more stable the particle. The purpose of coagulation is to reduce the zeta potential by adding a specific ions and then induce motion for the destabilized particles to agglomerate [2]. Coagulation may be accomplished by one of the following:

1. Lowering the zeta potential by the addition of a strong cationic electrolyte such as $Al_2(SO_4)_3$. This reduces the repulsive forces, permitting the van der Waals attractive forces become effective, resulting in agglomeration. The dosage of cationic electrolyte is dependent on the concentration of colloid.

   The addition of a cationic electrolyte and an alkali resulting in the formation of a charged hydrous oxides, $Me_x(OH)_y^z$. These cations become adsorbed on the colloid, resulting in a coating or sheathing the colloidal particles .

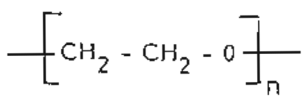
3. Agglomeration by the addition of sufficient cationic polyelectrolyte to lower the zeta potential to zero. Attractive forces are then operative and mechanical briding is achieved by the polymer. The larger the chain length, the more effective the bridging .
4. Mutual coagulation of anionic and cationic polyelectrolytes in a system.
5. Agglomeration of a negative colloid with an anionic or nonionic polyelectrolyte.

Polyelectrolytes are water-soluble polymers with many adsorption sites which are available on adsorption on the colloid particles [3]. They may be synthetic or natural and are high molecular weight polymers [1]. One polymer molecule can therefore become adsorbed onto several colloid particles thus forming a bridge between particles and producing a stable floce. Such polymers may be anionic (negatively charged) or cationic (positively charged) or even nonionic. This article reviews the different uses of polyelectrolytes in water and wastewater treatment.

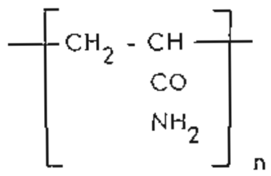
2. Examples of Polyelectrolytes Used in Water and Wastewater Treatment :

Polyelectrolytes are being sold by many companies and are used extensively for different purposes to control solids in potable water, municipal wastewaters and different industrial wastewaters. Some typical examples are [3] :

Nonionic :

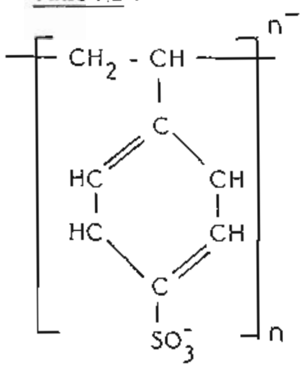


Polyethylene oxide

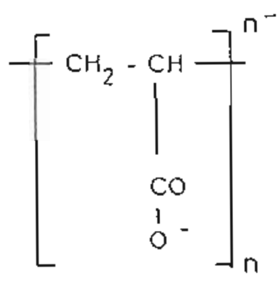


Polyacrylamide

Anionic :

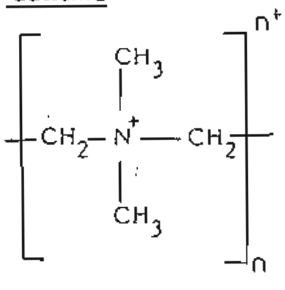


Polystyrene sulphonate

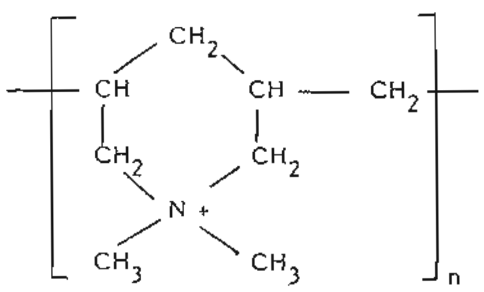


Poly acrylic acid

Cationic :



Quaternary polyamide



Polydiallyldimethyl-ammonium

Other compounds have been cited in literature that function as polyelectrolyt, from these are :

- Acetamide derivatives of polydiallylamine [4]. These derivatives displayed a typical polyelectrolyte behavior caused by residual amine units .
- Vaidya and Bulusu [5] used CA-14 which is a synthetic organic polyelectrolyte based on polyacrylamide. It has a weak anionic properties and gives a good performance in the improvement of coagulation process for turbidity removal in water treatment.
- Polyethyleneimine which is a cationic polyelectrolyte was applied as a flocculant for Escherichia coli suspension [6] as well as it was used as a flocculant for purification of industrial effluent containing petroleum impurities [7] .
- Poly-4-vinyl-N-benzyl-3-methylammonium chloride and poly-2-methyl-5-vinyl-N-ethyl-pyridinium bromide were also used as a flocculant for purification of industrial efluents containing petroleum impurities [7] .

Pilipenko et al [8] reported the optimal conditions for the use of poly-N, N-dimethyl-N, N-diallylammonium chloride for flocculation process.

The extract of Nirmali seeds (strychnos potatorum)—a tree grows in India and South East Asia—was found to be an anionic polyelectrolyte proved by IR spectral and other studies [9]. It was found that it is very efficient in the coagulation-flocculation of hydrophopic colloids (such as clay turbidity) but a poor flocculant in the case of hydrophilic colloids such as bacteria.

3. Applications of polyelectrolytes in Potable Water Supply :

Polyelectrolytes offer many advantages as filtration aids or as primary flocculants. Different uses of polyelectrolytes in potable water supply are given below :

Udaya and Gupta [10] prepared five anionic polyelectrolytes, with different molar ratios of acrylamide and acrylic acid monomers, which have a removal efficiency of 65% of the organic refractory material in raw water measured as the chemical oxygen demand, (COD). Edzwald et al [11] reported that direct filtration with a cationic polymers is a feasible method of treatment for waters containing 5 mg/lit total organic carbon (TOC) or less with an efficiency of 40% .

Robinson in his study [12] discussed that, for seven years, a cationic polyelectrolyte pretreatment process has successfully been used at the Topeka, Kansas, Water Department, to remove organic mater from raw water and reduce the amount of chemicals needed for conventional water treatment .

Magnetite particles can be used to remove turbidity and colour from water supplies. The impurity-laden iron oxide particles are rapidly separated from the product water by magnetic techniques. Turbidity removal by this process is greatly enhanced if soluble cationic polyelectrolyte is employed in the clarification step [13].

Prasad's[14] investigation describes bench scale experiments for removing high rbidity from river water using polyacrylamide as a coagulant aid in conjunction with alum. It is claimed that relatively small concentrations of polyacrylamide could remove high turbidity to acceptable limits and reduce half of the original amount of alum dose without essentially any difference in achievement of steady state .

The removal of colour from water supplies using alum, polymers and alum-polymer combinations was discribed by Edzwald et al [15], where humic acid was used as the natural colour colloid and their results indicate that :

(1) Alum alone requires relatively high dosages .
(2) Low molecular weight cationic polyelectrolytes used alone chemically interact with humic acid .

(3) Alum combined with high molecular weight polymers is an effective coagulation process.

Edzwald [16] examined the stoichiometry between the initial concentration of humic material and the optimum coagulant dosage. He examined the degree of chemical interaction between humic substances and cationic polyelectrolytes. Flocculation of humic and fluvic acids has been investigated by Narkis and Rehhun [17] to show that the sodium salts of these acids, which are anionic polyelectrolytes, react chemically with the flocculants such as cationic polyelectrolytes and aluminum sulfate through carboxylate and phenolate groups. They found [17] a stoichiometric relationship between humic and fulvic acids content in solution and the cationic polyelectrolyte or alum dose required for effective flocculation of the humic substances .

Udaya [10] prepared five anionic polyelectrolytes with different molar ratios of acrylamide and acrylic acid monomers. He tested these polymers for coli form bacteria removal with 98% efficiency. Fomchenkov et al [18] studied the effect of cationic, nonionic and anionic water-soluble polymers on the frequency of the electro-orientation and electrophoretic mobility of rod-shaped bacteria, where Treweek and Morgan [6] found that the extent of flocculation of Escherichia coli suspension produced by the addition of cationic polyelectrolyte polyethyleneimine was a function of polyelectrolyte polyethyleneimine molecular weight and dose and of reactor-chamber-mixing intensity and time.

Malek et al [19] focused their study on the effect of various doses of alum and cationic polyelectrolytes on the virus removal in low turbidity water of approximately 14 NTU. Polyelectrolytes help to produce water of low turbidities (less than 0.2 NTU) that complete inactivation of virus can be ensured, which is not possible to achieve if the turbidity of water is higher [20]. Most filtered water, without the help of polyelectrolyte, achieve a turbidity of around 1 NTU under the optimum conditions. The reliance on chlorination for removal of virus proves ineffective. This is why that viral diseases are epidemic in developing countries. The removal of viral diseases from developing countries can be of monumental importance in the crusade against disease and disability, in which polyelectrolytes have a great role to play [20].

Algae could not be removed by the conventional unit processes of water treatment such as microscreening, rapid sand filtration, aeration, or slow sand filtration. Klute and Neis [21] applied polymerized aluminum chloride and cationic and anionic polyelectrolytes as coagulant and they found the efficiency of algae aggregation and the subsequent removal by rapid sand filtration or dissolved air floatation was acceptable.

Since purification (desalination) of water relies on electrostatic mechanisms for the removal of soluble ionic and dispersed colloidal impurities, charged polymers, whether in insoluble resin or dissolved polyelectrolyte form, play a major part as desalinating reagents. Bolto [22] reported a recent developments in desalination of water by means of special polymers. A key item in the processes, he discussed, is that the insoluble reagents are recoverable, and can be regenerated and recycled.

Hendrix [23] reported that the use of polyelectrolytes in recent experiments (at the Murfreesboro Tennessee, Stone River Water Treatment and Softening Plant) yielded reductions in chemical costs and in the amount of sludge produced.

Modern theory of filtration has shown that the important mechanisms involved in the removal of fine particles by filteration are (a) transport and (b) attachment of particles to the sand grains [24]. The attachment mechanism is the most important major factor in filtration in case of biological flock [25]. The coagulants form a fine film around the sand grains to which the colloids adhere. Attachment forces provided by alum film are quite effective for conventional sand filters but are relatively inadequate in resisting the shear force encountered in high rate filter [26].

Cationic polymers used for water treatment have proved to be very effective either as filter aids or as primary coagulants [27]. However, which polymer works best seems to depend upon several variables including mixing conditions and polymer molcular weights. Stump and Novak [27] evaluated the performance of several different commercial polymers in direct filtration applications.

Results of laboratory and pilot-plant studies designed to define the optimum conditions for direct filtration at the Brasilia, (Braszil), water treatment plant showed that for the raw waters studied , the use of cationinc polyelectrolytes to reduce the metal coagulant dosage was not feasible [28]. On the other hand Edzwald et al [11] reported that direct filtration with cationic polymers is a feasible method of treatment for waters containing 5 mg/lit total organic carbon or less. The use of polyelectrolyte is an important important factor which determine the choice of an acceptable filtration rate [29].

Polyelectrolytes with nonionic, anionic or cationic character have very special effects on suspended solids or colloids, depending on their molecular weights or degree of polymerization [30]. Low-molecular weight types act as dispersing agents, high-molecular weight types flocculate the suspended solids. The flocculation polyelectrolytes are used as sedimentation accelerators in clarification and thickening processes and as dewatering agents in filtration and centrifugation technology. Tanka and Pirbazari [31] investigated the important parameters influencing the degree of particulate removal from low turbidity water in a configuration that include rapid mixing followed by filtration. The varied parameters were rapid-mixing velocity gradient, cationic polyelectrolyte type, and polyeletrolyte dosage. Statistical analysis demonstrted that the choice of polyelectrolyte was the only significant factor.

The removal of trihalomethane precursors by coagulation was studied by Hubel and Edzwald [32], for low turbidity and low alkalinity waters containing high levels of aquatic humic matter. Jar tests were conducted with synthetic and natural waters using alum, high molecular weight polymers, cationic polymers and various combinations of these coagulants. Cationic polymers alone were found to be less effective than alum in the coagulation of humic substances. High-molecular weight polymers used. aid with alum improved turbidity removal but not precursor removal, whereas high-charge-density cationic polymers with alum as a coagulant aid provided good precursor removals at low alum dosages. Edzwald et al [11] reported that cationic polymers can remove approximately 40% of trihalomethane precursors. Amy and Chadik [33] reported an insight into the use of cationic polyelectrolytes as a sole coagulants for removing trihalomethane precursors from a broad spectrum of natural waters.

For potable water treatment, the intent of disinfection is to provide absolute safety in terms of pathogenic microorganisms or viruses. Ozone is one of the famous disinfectants used in water treatment plants. Richard and Conan [34] reported that certain polyelectrolytes have an effect on the mass tranfer of ozone. That effect seems to be present both on bubble-water mass transfer and on disinfection. So the addition of polyelectrolyte before ozonation is able to reduce the applied ozone dose required. In this way a substantial cost savings can be achieved.

With the help of polyelectrolytes, the sludge can be dewatered to an extent, which is impossible to achieve otherwise. This can be done quickly and economically, making easier to dry and dispose of the sludge [24 , 35]

4. Applications of Polyelectrolytes in Industrial Water Supply :

Producing high quality water for various inplant usages reliably and cost efficiently is of prime concern. Raw water contains a variety of impurities which need to be removed before it is suitable for industerial use. The water will contain suspended and colloidal particles of quartz, calcite, clay minerals, various plant and animal detritus, algae and bacteria. The other problem which can be of great concern to certain industries, for example paper production, is natural colour. Green [36] reported that the ideal solution would be for a polyelectrolyte to be used both a primary coagulant and coagulant aid. It should also be capable of effecting the removal of organic colour (soluble humic substances) as well as particular impurities, without imparting any undesirable dissolved solide which could foul resins.

The production of ammonia, aniline, acrylonitril, methanol, tetraethyl lead, and various proprietary products requires high quality water for boiler makeup, cooling tower makeup, and various process systems. Du Pont's Beaumont Works (Tex, USA) produces these products and has successfully meet these demands using synthetic organic polyelectrolytes instead of the traditional inorganic coagulants [37]. Coal preparation plants need large volume of recycled water. The dirty water can be recycled after flocculation with organic polyelectrolyte [38] .

5. Applications of Polyelectrolytes in Industrial Effluent Treatment :

Polyelectrolytes improve the process performance in waste treatment plants. Due to the increase in efficiency of coagulation by polymers, many industrial wastewaters may require no other treatment except coagulation-sedimentation for their disposal [24]. This can greatly help in the abatement of water pollution by industry by eliminating the need for additional capital investments in order to meet effluent quality criteria [39]. The following is an illustration of some important applications of polyelectrolytes in indutrial effluent treatment.

The formamide polymer synthesized by Mathias et al [4] displayed typical polyelectrolyte behavior caused by residual amine units. Complexation of this polymer with iodine and transition metal cations was strong as shown by UV, IR and NMR evidence indicating the potential of these polymers for trace metal recovery and waste treatment. Anionic polyelectrolytes are an effective aid for copper removal from both synthetic and actual industrial effluent. Wing et al [40] showed that treatment of solutions of copper complexes (such as EDTA, citrate, or gluconate) with calcium hydroxide, calcium oxide (lime), calcium chloride or calcium sulfate at pH 11.6-12.5 effectively removes copper from the solution as copper hydroxide, then flocculation of the copper hydroxide with anionic polyelectrolytes accelerate settling of the sludge.

Wastewater discharges from pharmaceutical manufacturing facilities must meet stringent requirements for removal of biochemical oxygen demand (BOD), suspended solids, and various nutrients. Feric chloride and polyelectrolyte flocculants can be added to oxidation ponds and effluents to precipitate soluble phosphorus and agglomerate suspended algal cells prior to removal of suspended solids by dissolved air flotation [41]. Also, dissloved air flotation was evaluated as a technique for the removal of colar bodies from kraft mill effluent [42]. Best results were obtained with alum and selected cationic-synthetic-high molecular weight polyelectrolytes. Unflocculated suspensions, in dissolved air flotation, are generally destabilized with coagulants and the attachment of bubbles to floc particles may be enhanced by the introduction of chemicals such as polyelectrolytes [43].

The treatment of radioactive effluents can lead to problems because of the presence of detergents. The principal radioactive pollutants are in general Cs^{134} and Cs^{137}. A treatment is recommended which includes the addition of a copper hexacyanoferrate to the wastewater, precipitation with 100 ppm $FeCl_3$, the addition of 1 ppm polyelectrolyte, the establishment of pH 8 with caustic Soda, settling of the sludge and filtration. This treatment leads to activity concentration under $5x10^{-5}$ curie/m^3 [44]

In wastewater treatment, widespread use is made of physicochemical methods employing mineral coagulant, polyelectrolytes, and sorbents. Physicochemical methods have a number of advantages over biochemical treating methods. Polyelectrolytes, mainly of cationic type, used as flocculant for purification of industrial effluents containing petroleum impurities [7]. The polyelectrolytes used are polyethyleneimine, poly-4-vinyl-N-benzyl-3-methylammonium chloride, and poly-2methyl-5-vinyl-N-ethylpyridinium bromide. These polyelectrolytes were used with model emulsions of the oil-in-water type, then checked on wastewaters from several refineries, stream samples having been taken after the oil trap in the second system of industrial waste collection, as representing the most contaminated streams.

Synthetic organic polyelectrolytes can be used to condition sludges to enhance their dewaterability. When conditioning biological sludges, the charge on the polymer has a significant impact on the effectiveness of the polymer as a conditioner. Cationic polymers with molecular weights in excess of 10^6 appear to be effective in conditioning anaerobically digested sludge prior to dewatering [45]. Three polyacrylamides under trade names Magnofolc R 140, Magnafolc R 155 and Polyfloc LP have been investigated on a laboratory and plant scale as sludge conditioners and found to be effective [46].

Treating tannery effluents with polyelectrolytes to precipitate the suspended solids is very difficult and requires a different type and amount of polyelectrolyte for each tannery stream and it is expensive [47].

Polyelectrlytes were investigated as a possible solution to the problem of overloaded clarifiers [48]. The addition of polyelectrolytes drastically increased floc sizes, and the permissible overflow rates rose from 300 to 1600 gpd/ft^2 with the addition of 0.3 mg/lit or less of moderately hydrolyzed high molecular weight anionic polyacrylamides.

Seven new polyelectrolytes were evaluated as flocculants and coagulants for removing suspended solids from highly alkaline, lime-sulfide, hair-pulping effluents from a hide processor [49]. Six of these are chemical derivatives of starch with acrylic acid or acrylamide. Four of these polyelectrolytes were effective at levels of 5 to 25 ppm, without pH adjustment of the effluent, and reduced the suspended solids about 95%. No auxiliary agents were required to assist in the coagulation of the suspended solids.

A novel sequential method of using activated carbon for the detoxification and decolorization of pulp mill effluents has been developed by the Pulp and Paper Research Institute of Canada [50]. This improved method involves the addition of powdered activated carbon, aeration in the presence of carbon, addition of settling aids, namely, alum and polyelectrolyte, and clarification of the treated effluent by conventional means. Bench scale tests using softwood bleached kraft pulp mill effluents showed that the toxicity can be reduced effectively to levels which could meet current Canadian government regulations. Typically, 70 to 85% of the color was simultaneously removed. The BOD and COD reductions were in the range of 20 to 40% .

Complex reagents (including a complex coagulant and polyelectrolytes) have been found to be efficient on the treatment of the recycled flotation water from ore enrichment plants to remove the solid phase and sprucewood tannins [8]. When the system contains 30-70 ppm polyelectrolytes, (polyethyleneimine or poly-N, N-dimethyl-N, N-diallyl-ammonium chloride), the quantity of sprucewood tannins decreases from 350 to 50-70 ppm.

6. Application of Polyelectrolytes in Municipal Sewage Treatment:

Elimination of turbidity from municipal sewage plant effluents by coagulation with ferric chloride and flocculation with polyelectrolytes ($FeCl_3$ of about 40 ppm and 1 ppm polyelectrolyte) have been found to reduce turbidity with about 10% [51].

7. Application of Polyelectrolytes as Scale Inhibitors:

For sea water desalination plants, polyelectrolytes were evaluated as antiscalants

[52]. Field tests showed that corrosion rate decreased significantly without causing excessive fouling. Maintenance costs and outage time were considerably reduced, with a saving of energy and decrease of the cost of the product water. Polyelectrolytes were used as a scale inhibitor in the vapor compression distillation process [53].

Conclusions :

Synthetic and natural polyelectrolytes are being extensively used in treatment of water and wastewater in the technically advanced countries of the world. Their use increases the efficiency of different processes in water and wastewater treatment, reducing the cost of chemicals required, producing smaller quantities of compact sludge that can be drained and disposed off easily. Full benefits that can be achieved by the use of polyelectrolytes, are not derived-specifically in the developing countries-due to ignorance about certain practical considerations regarding their use.

Polyelectrolytes are used either alone or in compination with inorganic coagulant, like alum or ferric chloride. It is also used as scale inhibitors.

Poly electrolytes help in flocculation and filtration, to produce water of low turbidities and thus enable complete inactivation of virus by chlorination. They help in maintaining residual aluminium within permissible limits, and remove trihalomethanes (which are carcinogenic). Hence polyelectrolytes hav a positive role to play in ensuring public health by providing high quality water.

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