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Polyacrylamide polymers for the removal of heavy metals: A review

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ABSTRACT

Polyacrylamide (PAM) polymers are organic polymers that have found varied application in almost all major industrial processes. In the petroleum industry, they help to formulate surfactants that help flood underground crude oil reservoirs towards ensuring maximum production of oil. In wastewater treatment processes, PAMs are used as copolymers of polymer composites in the recovery of heavy metals such as Cr^{2+} and Cu^{2+} which would have otherwise been produced as effluents into the natural environment. This is in addition to its long-standing use in this sector as flocculants in the dewatering of sludge from sewage and paper industries. Their excellent functionality is due to their surface enhanced hydrophilicity which aids their electrostatic interactions in aqueous media. Furthermore, these materials possess tunable viscosity and excellent co-blending with different polymers and composites. Recent approaches have made use of various nanocomposite-based PAMs with materials such as nanozirconia, silver, clay and starch towards corrosion prevention, catalytic, biomedical, and electronic use. Increasing adoption of this class of polymeric materials must be corroborated with toxicity and contaminant studies to help continue these sustained industrial applications.

Keywords:polyacrylamide (PAM), composites, hydrophilicity, nanocomposite, toxicity

I. BACKGROUND

Polyacrylamide (PAM) is an organic polymer that was first synthesized in the year 1893 by Charles Moreau through a low-temperature reaction between acryloyl chloride and ammonia. The International Union of Pure and Applied Chemistry (IUPAC) allows for two naming conventions for this synthetic group of macromolecular polymers; poly(2-propenamide) or poly(1-carbamoylethylene) based on its molecular formula [(C3H5NO)n]. PAM has found varied areas of application following the commencement of its commercial production in United States by 1954, ranging from wastewater treatment to sludge flocculation to crude oil enhanced oil recovery and heavy metal recovery. Suitable properties of PAM include its high solubility in water, weight-dependent viscosity and being able to promote diverse reaction mechanisms (such as hydrolysis, methylation and sulfonation) (Swift, 2021). As a result of this versatility, it is possible to synthesize PAM polymers with different ionic behaviors. Non-ionic or neutral PAM are resonant polymers in which the vacant electron pair present in the amide group couples with carbonyl group double bond to produce high hydrophilic properties in the polymers. Anionic PAM are an important group of flocculants formed from the alkaline hydrolysis of non-ionic PAM to produce a generally electronegative molecule containing acidic functional groups within their structure. Cationic PAM are positively charged polymers which are generally considered dispersion polymerization products formed from dispersing PAM in an acrylated ammonium chloride solution. The figure below presents the structure of the repeating units of PAM in its basic form. Apart from these three major forms of PAM, there also exists the amphoteric and zwitterionic types which are of high purity and expended application.

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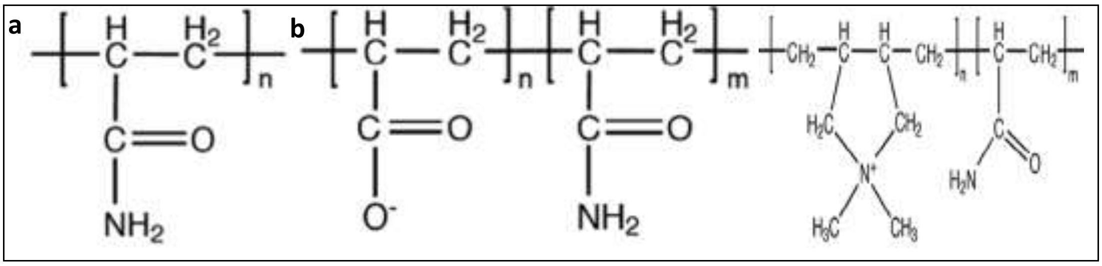

Figure 1 PAM repeating groups in its non-ionic (a), anionic (b) and cationic (c) form. (Xiong et al., 2018)

From the structure shown, it can be seen that the amide group present in these polymers are not within the material backbone, hence why they are not referred to as polyamides but rather as polyolefins or polyethylenes with amide additives (Pei et al., 2016). PAM is also capable of being used as a copolymer in the production of polymer blends with inferential properties in various areas of application. Umoren and Obot (2008) discovered that blending PAM with polyvinyl pyrrolidone (PVP) could help inhibit corrosion in aluminum-based materials in acidic mediums in temperature ranges of 30 – 60℃.

Higher volumes of acrylamide monomers remaining after the formation of the polymeric form is a source of increasing concern in industrial applications, with concentrations as high as 600ppm having been reported, even in nanotoxic NMC-materials (Andersen, 2005; Soneye et al., 2022). Drinking water concentrations of 5mg/kgday have also been documented, which is also significantly higher than the no-adverse effect level of 0.5mg/kgday thereby requiring updated review of intake effects. This review presents updated information on novel synthesis techniques associated with the fabrication of PAM, properties of the polymer in aqueous media which help promote various reaction mechanisms, environmental applications of PAM especially in the recovery of heavy metals, as well as ongoing toxicity concerns and present solutions.

1. Pam Polymer Synthesis Techniques

The adopted technique in the synthesis of PAM depends majorly on the form of polymer that is being produced. Non-ionic is principally synthesized using a radical polymerization followed by a hydrolysis process. This is a redox type of reaction that starts with the catalytic hydration of acrylonitrile using potassium persulfate ($K_2S_2O_8$) and sodium hydrogen sulfate ($NaHSO_4$) or similar chemicals as initiators (Giz et al., 2001; Shatat et al., 2018). This is then followed by free radical polymerization of the acrylamide monomer at various conditions of temperature, pH, and reaction time to form PAM that can be precipitated out as crystals. The final step involves the purification of produced polymer using either methanol, ethanol, or acetone. Studies have also shown the possibility of controlling the molecular weight of the produced polymer by use of additives such as isopropanol or sulfonic compounds, and novel methods that do not required insulated hydrolysis have been proposed (Cai et al., 1999, Sonker et al., 2019).

Cationic PAMs are generally produced using two techniques. The first approach is a free radical copolymerization reaction between nonionic PAM and suitable cationic monomers such as acryloyloxyethyltrimethyl ammonium chloride (AETAC) and methaacryloxyethyltrimethyl ammonium chloride (DMC) (Jiang and Junren, 2014). The second method are termed "Mannich" reactions in which the amide groups present in PAM are reacted with a formaldehyde and a second amine containing compound to produce cationic derivatives and Mannich bases at moderate temperatures and acidic pH conditions (Shatat et al., 2019). Anionic PAMs are synthesized in a somewhat similar approach to the above mentioned, with the only difference being the use of anionic monomers as opposed to cationic ones.

PAM polymer and solvent

The density of PAM is 1.302 g/cm3 at room temperature, a refractive index of 1.452, glass transition and softening temperatures of 153℃ and 210℃ respectively thereby indicating wonderful thermal stability (Visakh and Artem, 2018). PAM exhibits excellent solubility in water even under stirring conditions, and these are considered better than other water-soluble polymers. The solubility of PAM is more responsive to polymer molecular weight than to the mixing temperature in low molecular weight types, with higher molecular weight PAMs requiring additional heating due to higher intermolecular bonds in place. In other solvents however, the solubility is very poor with characteristics behavior in these mediums ranging from no solubility to swelling without dissolution (Wu and Shanks, 2004; Wang et al., 2017). Due to PAM being able to exist in 3 different forms (powder, aqueous and emulsion), it can exhibit some hygroscopic properties. The powdery form can be stored for elongated periods without absorbing water molecules while low concentration solutions (lesser than 17%) could exhibit changes in viscosity (Visakh and Artem, 2018).

Operating conditions

PAM synthesizing reactions are basically low temperature (room temperature to 35℃) and are generally exothermic. The reaction pH is also around 4-5.5 with about 5-7 hours reaction time (Visakh and Artem, 2018). Thus, they can generally be termed mild reaction processes. As nonionic PAMs are the most vital of all the polymers in that other forms are synthesized from them, care must be taken in their production. Temperature is the most vital parameter to nonionic PAMs, as temperatures above 60℃ have been found to promote hydrolysis reactions which favor the formation of anionic PAMs.

2. Application Of Pam-Based Polymers In Water Treatment

Water treatment (solids and heavy metal removal) represents the most important field of PAM polymer application. This is due to their outstanding ability to flocculate these materials thereby aiding their separation from the aqueous media, while also forming a type of barrier (bridge) to aid the material aggregation. The occurrence of PAM in different forms consequently affect their structure and hence their ability to facilitate coagulation in various ways, both as copolymeric or composite forms.

El-Sweify et al., 2019 functionalized multiwalled carbon nanotubes (MWCNTs) on PAM by refluxing a mixture of nitric (70%) and sulfuric (98%) acids at 160℃ for 90mins. The oven-dried sample was then used in the adsorption of Co(II) and Eu(II) radioisotopes, and this was found to be strongly enhanced compared to just using the PAM polymer. Optimization of operating conditions also showed the possibility of completely isolating these contaminants, and even separating them from each other. Amidoxime functionalization of PAN-based composite was also found to be effective in the removal of Cu2+ and Ni2+ in a spontaneous adsorption process, with efficiencies above 90% reported up to five cycles of use (He et al., 2021). Heavy metal recovery was also performed on drinking water sources using Zn-MOF-74/PAN composite for the removal of As(III) (Ploychompoo et al., 2021). The Zn-MOF-74 nanoparticle synthesized by room temperature precipitation approach was immobilized on PAM synthesized through radical polymerization, and this proved an effective method in removing up to 99.8% of As(III) from an 0.2ppm drinking water source thereby achieving drinking water levels in just 15 minutes of adsorption. Mechanistic study of this approach revealed a combination of both chemical and physical adsorptive processes in play, while also following a pseudo-second-order kinetic model and Langmuir isotherm, while structural study using FTIR and XPS spectroscopies revealed the domination of the adsorption process by amine (-NH2) and hydroxyl (-OH) groups. Comparable studies were also documented in the removal of Co2+ and Pb2+ using other suitable co-materials (Abou El-Reash et al., 2017; Moreno-Sader et al., 2019). The table below also presents results comparing adsorption efficiencies of Cu^{2+} and Ni^{2+} from different polymer composites.

Table 1 Heavy metal removal levels using different operating parameters

Adsorbent	Adsorption Capacity (mg/L) Cu2+, Ni2+		Condition	Ref
Bifunctionalized chitosan derivative with zwitterionic	71.4	42.6	pH= 4.5 and 7.5	Rezende De Almeida et al., 2016
Chitosan/poly vinyl alcohol membrane	86.1	75.5	T = 25℃ pH = 6.0	Sahebjamee et al., 2019
Aryl cross-linked chitosan hydrogels	84.0	78.0	T = 25℃ pH = 6.0	Timur and Pasa, 2018
Chitosan functionalized with 2[-bis-(pyridylmethyl) aminomethyl]-4-methyl-6-formylphenol	109.0	9.6	T = 25℃ pH = 3.0 and 5.5	Justi et al., 2005
Cross-linked magnetic	124.2	67.3	T = 25℃	Monier et al., 2012

chitosan-2-aminopyridine glyoxal Schiff's base			pH = 5.0	
Amidoximated grafted cellulose	101.7	49.3	T = 30℃ pH = 5.5	El-Khouly et al., 2011
Amidoxime chelating resin	146.2	113.9	T = 30℃ pH = 5.4 and 6.0 T =25℃	Shaaban et al. 2014
Amidoxime-functionalized polyacrylamide-modified chitosan	190.7	128.9	pH = 5.0 T = 25℃	He et al., 2021

3. Perspectives

PAMs have found renewed used in multiple industrial applications. High molecular weight PAMs in particular, are common wastewater flocculants, soil conditioners and crude enhanced recovery materials. The high flow rate and pressures associated with some of these processes have been shown to result in the degradation of these materials in the natural environment. These degraded PAMs have been shown to permeate into agricultural land through wastewater treatment effluents due to their hydrophilicity and seemingly low concentration (Xiong et al., 2018). Exposure of humans to low concentrations of PAM have been deemed nontoxic to humans, although long periods of exposures (up to 15 weeks) have been shown to cause nerve alterations. Proposed options to help reduce these impacts include Fenton reactions, reverse osmosis,and coagulation, which add to the overall cost of the entire process. As a consequence, there is a need for more integrative and cost-effective approaches to ensure continued feasibility of PAM-based polymer use. Algae biofilm approaches stand out as one of the preferred options for multiple reasons; because these PAM polymers occur principally in aqueous wastewater media, algae can benefit from the presence of supporting nutrients (such as carbon and nitrogen) to grow and simultaneously secrete bacteria (such as cyanobacteria and acinetobacter) which help cleave the main carbon backbone in PAM thereby aiding its conversion to smaller molecules such as acrylamide or acrylic acid (Zhang et al., 2021). Therefore, chain reactions can be initiated which further promote the degradation to elemental components such as those observed in quantum materials (Soneye and Sadiku, 2022).

II. CONCLUSION

PAM-based polymers are an important group of polymers in industrial applications. The ability to synthesize these polymers in different forms (nonionic, cationic, anionic, zwitterionic, amphoteric, etc) is a major reason for its widespread use, as these various forms can help catalyze various processes. One of its very significant uses is in the recovery of heavy metals from water and wastewater bodies, which is possible as polymer blends or as composites. When used with nanomaterials such as multiwalled carbon nanotubes (MWCNTs), zinc-based Zn-MOF-74 and silica, it is possible to recover heavy metals such as Cr(VI)ions, Co(II), Eu(II) and As(III). These studies show comparable adsorption kinetics which followed pseudo-second order-kinetic models and Langmuir isotherms, with adsorbents demonstrating high stability in pH regions of 4-10 with high reusability (up to 4 times reported). The constantly growing demand of polymers of this nature clearly show the need for more investigations into novel synthesis methods as well as updated toxicity measurement approaches.

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