



NATURAL POLYMER GRAFTED WITH SYNTETHIC MONOMER BY MICROWAVE FOR WATER TREATMENT - A REVIEW

POLÍMERO NATURAL INJERTADO CON MONÓMERO SINTÉTICO, SÍNTESIS ASISTIDA POR MICROONDAS, CON APLICACIONES PARA TRATAMIENTO DE AGUA - UN ANÁLISIS

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Recepción 13/03/2012
Evaluación 15/05/2012
Aprobado 11/06/2012

Abstract

In this study, the use of natural polymers grafted with synthetic monomers to obtain copolymers for specific applications is revised. This review highlights current uses of microwave heating, in the grafting modifications of natural polymers, with other synthetic monomers and explores methodology of this technique. Microwave assisted and microwave initiated synthesized graft copolymers show superior flocculation characteristics when compared with graft copolymers produced by conventional methods. Synthesis, mechanism and characterization of these materials by different analytical techniques such as spectroscopic analysis and others are reviewed. We explore information concerning the development and characterization of grafting polymers, which have been receiving enlarged attention in recent years as flocculants for water treatment. The effectiveness of flocculation for applications in reduction of pollutants in wastewater is also evaluated.

Keywords: Copolymer, Flocculant, Grafting, Microwave, Wastewater

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Resumen

En este estudio se revisa la literatura sobre el uso de los polímeros naturales injertados con monómeros sintéticos, para obtener copolímeros de aplicaciones específicas. Esta revisión destaca los usos actuales de la irradiación por microondas, en las modificaciones de injerto de los polímeros naturales con otros monómeros sintéticos, y explora la metodología de esta técnica. Copolímeros de injerto obtenidos por las técnicas asistida o iniciada por microondas, muestran características superiores de floculación cuando se comparan con copolímeros de injerto sintetizados por métodos convencionales. Se examina la síntesis, caracterización y mecanismo de estos materiales por diferentes técnicas analíticas, como el análisis espectroscópico, entre otras. Se explora la información relativa al desarrollo y la caracterización de los polímeros de injerto, que han estado recibiendo amplia atención en los últimos años como floculantes para el tratamiento del agua. Se evalúa la eficacia de la floculación en la reducción de los contaminantes en las aguas residuales.

Palabras clave: Aguas residuales, copolímero, floculante, injerto, microondas.

Introduction

An intensive research effort is being made worldwide to find environmentally acceptable replacements for current synthetic flocculants used for different industries. Chemical grafting is one of the most effective methods for modifying structure and properties of biopolymers. Graft copolymerization of natural polysaccharides is becoming an important resource for developing new flocculants as it can improve the functional properties of these materials [1-3]

Various traditional and advanced technologies have been utilized for the removal of these colloidal particles from water, such as ion exchange, precipitation, flotation, solvent extraction, adsorption, flocculation and electrolytic methods. Among these techniques, flocculation is generally preferred for the removal of colloidal particles as well as heavy-metal ions because of its high efficiency, easy handling, and availability of various kinds of flocculants. So, the search for cost-effective flocculants and economic



method of removing toxic heavy metal ions as well as suspended particles, has also become the focus of many studies [1, - 4].

Most of the suspended particles carry charge in neutral aqueous medium. To destabilize the system, inorganic coagulants such as alum, polyaluminium chloride, ferric chloride, ferrous sulfate, magnesium chloride, have been used for decades. However, this process is strongly pH dependent and decreases the alkalinity of the water. Moreover, the inorganic coagulants are required in large amount to achieve effective settling rate. As a consequence, a large volume of metal hydroxide sludge is produced. This again creates disposal problem. Apart from this disposal problem, the uses of inorganic salts such as alum derivatives, are now very much controversial due to the possible impact of residual aluminium in the recycled water on Alzheimer disease [1].

In this review, we discuss the results reported in the literature. We require better understanding of methods of microwave synthesis more reproducibility than those of conventional methods and suitability to improve synthesis, select the highest method of graft copolymer synthesis by use of microwave radiation to generate the free radical sites on the backbone polymer or combination with chemical radical initiator.

The present review provides an outline of recent information concerning the development and characterization of grafting polymers, which have been receiving enlarged attention in recent years as flocculants for water treatment. Their preparation methods by microwave and relatively unique properties of hybrid materials have become an essential area to be reviewed in this paper, considering there is no systematic compilation available for these materials for flocculation of water. A particular emphasis is given to the application of natural polymer grafted with synthetic in treating water, through flocculation method.

Synthesis of graft copolymers

Graft copolymers, by definition, consists of a long sequence of one polymer (backbone polymer) with one or more branches (grafts) of another (chemically different) polymer [5]. The process of graft copolymer synthesis starts with a natural polymer in this case; an external agent is used to

create free radical sites on this preformed polymer. The agent should be effective enough to create the required free radical sites, once the free radical sites are formed on the polymer backbone, the monomer (i.e. acrylamide compound) can get added up through the chain propagation step, leading to the formation of grafted chains. The properties of natural polymers can be modified by hybridization with synthetic polymers. The chemical combination of natural and synthetic polymers yields new materials which could have desirable properties [6].

Recent studies on grafting of polymer chains, usually monomer, to the backbone polymer. It is one of the methods to increase the compatibility between synthetic polymers and cellulose [7]. Graft copolymerization of chitosan with synthetic monomers can introduce desired properties and extend the field of potential application of them by choosing various types of side chains, and research on the graft copolymerization of vinyl monomers such as acrylic acid, methyl methacrylate, acrylonitrile, vinyl acetate onto chitosan using free radical initiation has been reported. On the other hand, rosin and its derivatives have degradability, excellent solubility, biocompatibility, and lower polarity compared to chitosan [8].

The synthesis of glycogen-g-polyacrylamide (Gly-g-PAM) was carried out by a ceric ion-induced solution polymerization technique. Anionic starch derivatives bearing carboxyl groups were prepared by reacting maize starch and hydrolyzed maize starch with a previously synthesized citric acid adduct (2-hydroxy-3-chloropropylcitric acid) using the dry process. [9]. Graft copolymers of carboxymethylcellulose and polyacrylamide synthesized by a ceric-ion-induced solution polymerization technique. By the variation of the monomer and catalyst concentrations, six grades of graft copolymers were synthesized [10].

The synthesis of cashew gum-g-polyacrylamide was carried out at 60°C by a radical polymerization using potassium persulphate as the redox initiator under N₂ atmosphere. A series of graft copolymers, varying in acrylamide concentration and keeping the concentration of the initiator and polysaccharide constant, was prepared [2]. A high performance anionic flocculant was synthesized by partial alkaline hydrolysis of polyacrylamide



grafted tamarind kernel polysaccharide. [11]. Low-molecular-weight high-charge-density cationic poly diallyldimethyl ammonium chloride (polyDADMAC) was grafted onto nonionic polyacrylamide (PAM) using organic peroxide initiators in the molten state carried out in a batch mixer. The graft copolymer can be used as a high performance flocculant. [12].

Graft copolymerization of acrylic acid (AA) onto starch was carried out with ceric ammonium nitrate as initiator under nitrogen atmosphere. The grafting percentages (GP %) of starch-graft-acrylic acid (St-g-AA) copolymers were determined. The effect of GP% of St-g-AA copolymers on the competitive removal of Co^{2+} , Ni^{2+} , Zn^{2+} ions from aqueous solution was investigated at different pH (2, 4, 6) [13]. A synergetically acting new flocculant on the basis of starch-graft-poly (acrylamide)-co-sodium xanthate (CSAX) was synthesized by grafting copolymerization of crosslinked corn starch, acrylamide (AM), and sodium xanthate, using epichlorohydrin (EPI) as cross-linking agent and ceric ammonium nitrate (CAN) as polymerization initiator in aqueous solution. The effects of some factors, such as crosslinker, initiator, AM, NaOH, on the %Tr (turbidity removal rate) [14].

Microwave radiation

Microwaves comprise electromagnetic radiation in the frequency range of 300 MHz to 300 GHz. On exposure to microwaves, the charged or polar particles tend to align themselves with electric field component of the microwaves which rapidly reverses its direction e.g. at the rate of $2.4 \times 10^9/\text{s}$ at 2.45 GHz microwave frequency. As the polar or charged particles in a reaction medium fail to align themselves as fast as the direction of the electric field of microwaves changes, friction is created to heat the medium [15]. Microwave irradiation, as efficient thermal energy, constitutes a very original procedure of heating materials, different from the classical ones. Main advantage is that it results into almost instantaneous 'in core' heating of materials in a homogeneous and selective manner. Microwave heating can result rapid transfer of the energy into bulk of the reaction mixture, and the depth of the materials is of the same order of magnitude of the wavelength and, therefore, can interact with substances of appreciable thickness (about 10 cm) [16].

Synthesis by microwave

Microwave reactions have been done both in solution as well as in dry medium, in homogeneous electric field of microwaves is created to produce localized superheating zones called hotspots measuring about 900–1000 m and having temperatures higher (~100–200 K) than the bulk temperature. These hot spots accelerate the solid supported reactions and make them more productive than solution phase reactions. New microwave ovens were made over the past decade [15]. Though the special advantages (Figure 1) of carrying out grafting reactions under microwaves can be explained mostly by the heating effect of microwaves, the involvement of non-thermal microwave effects cannot be completely denied. More investigations are required for resolving this issue and may be a point for future research. But advantages of carrying out grafting reactions under microwaves are attractive enough to reap long term benefit for the commercial exploitation of microwave technology in developing macromolecular materials from polysaccharides [15].

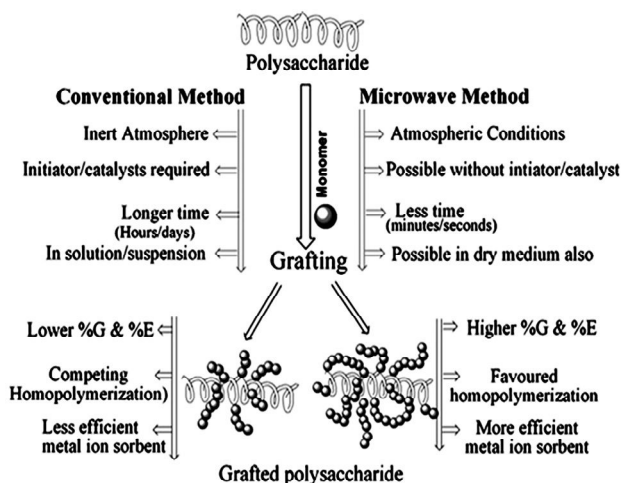
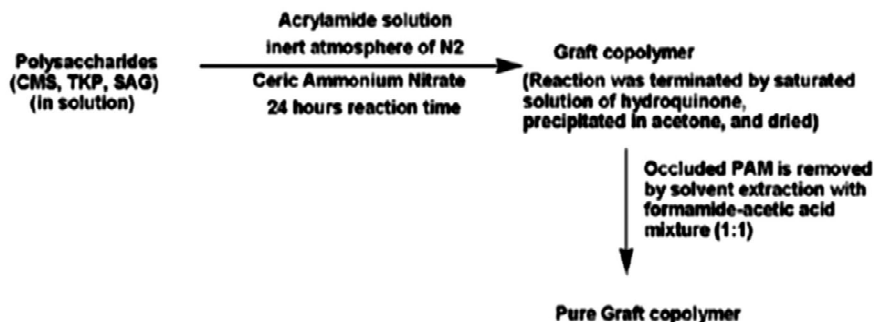


Figure 1. Schematic diagram of microwave induced grafting of the polysaccharides [15].

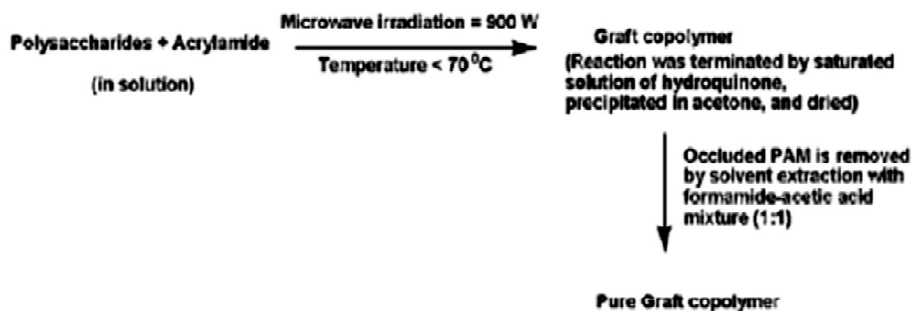
The various methods of graft copolymer (Scheme 1) synthesis actually differ in the ways of generation of the free radical sites on this preformed polymer. Conventionally, chemical free radical initiators (e.g. ceric ammonium nitrate (CAN)) [17].



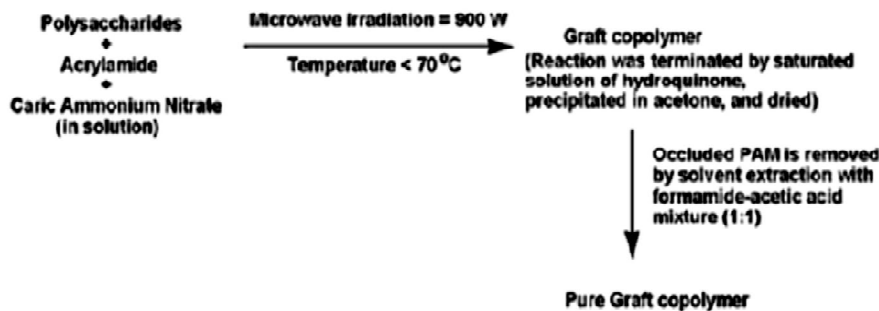
Conventional method of synthesis of Graft copolymer



Microwave initiated method of synthesis of Graft copolymer



Microwave assisted method of synthesis of Graft copolymer



Scheme 1. Representation for the synthesis of graft copolymer using conventional, microwave initiated and microwave assisted methods [17].

Microwave irradiation exhibits the most potential to synthesize the grafted polymers. This is because in microwave irradiation based synthesis, the percentage grafting depends on monomer concentration, power and exposure time of the irradiation; these factors are electronically controlled. Moreover, microwave irradiation as efficient thermal energy constitutes a very original method of heating materials, different from the classical ones [15, 18-23]. The main advantage is that it results in almost instantaneous homogeneous heating of materials in a selective manner. Another reason that microwave irradiation reveals is due to a fact that the free radicals are generated by means of microwave photons, the chain opening of polysaccharide backbones does not take place hence rigidity of the polysaccharide chain is maintained giving higher percentage of grafting [16, 19, 23-26]. Grafting of polyaniline onto gum acacia and grafting of acrylic acid onto chitosan have involved the use of MW irradiation. Polyacrylamide was graft copolymerized onto chitosan using MWR [27]. Synthesis of *Cassia marginata* seed gum-graft-polyacrylamide (MWS-GP). No initiator or catalyst was required in this synthesis, and the conditions for the grafting were optimized by variation of the acrylamide concentration, MW power, and exposure time. [28]

Guar gum was grafted with polymethylmethacrylate (PMMA) by microwave initiated method. The synthesis was optimized for highest percentage grafting, by varying the microwave irradiation time and monomer (methyl methacrylate) concentration [29].

Literature reported a novel microwave initiated method for synthesis of polyacrylamide grafted Psyllium (Psy-g-PAM). Psyllium was modified through grafting of polyacrylamide (PAM) chains on it using microwave radiations only, in absence of any other free radical initiator [22]. Microwave-initiated synthesis of polyacrylamide-grafted sodium alginate, a graft copolymer with wide variety of applications, has been reported. The effect of reaction parameters (i.e., irradiation time and monomer concentration) onto the percentage grafting has been investigated [30].

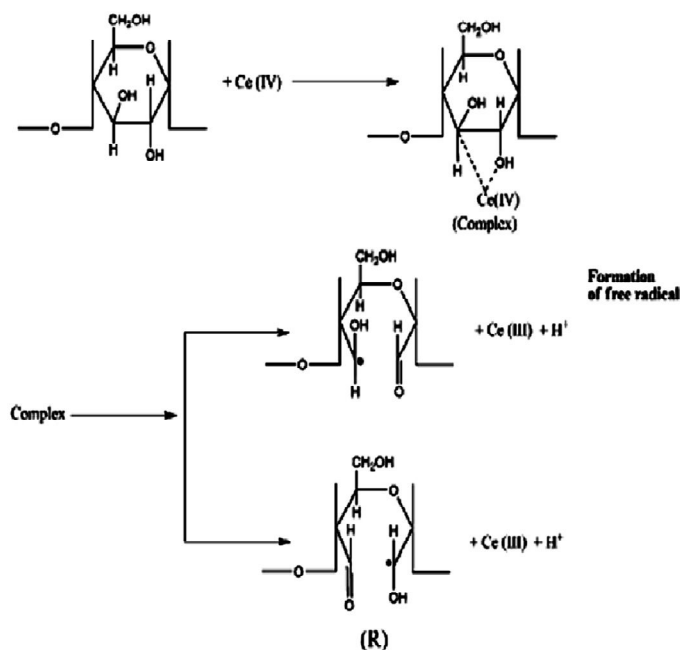
An environmentally benign and efficient route of synthesis of polyacrylic acid grafted carboxymethyl cellulose (CMC-g-PAA) was developed using microwave radiation alone to initiate the grafting reaction [31]. Polyacrylamide chains (PAM) were grafted onto the backbone of gum by



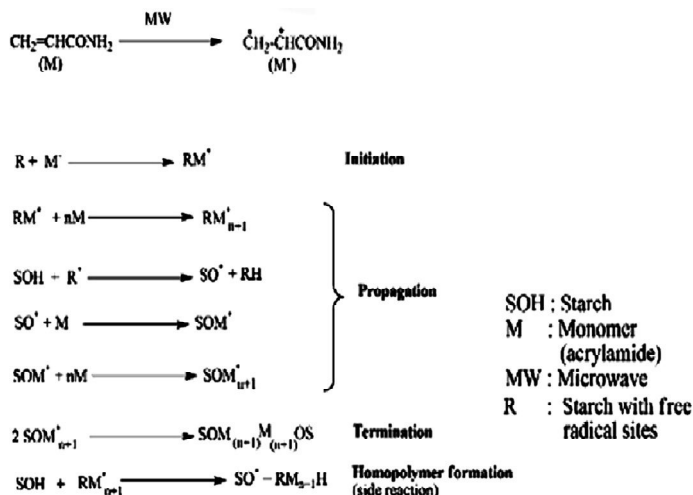
microwave assisted method [32]. In another investigation, sago starch was modified through microwave assisted chemical synthesis using acrylamide as grafting monomer [33]. Polyacrylamide grafted dextrin (Dxt-g-PAM) was synthesized by microwave assisted method (using microwave energy as well as potassium persulphate as initiator to generate free radical sites). Various grades of graft copolymers were synthesized by varying the reaction parameters [19].

Polyacrylamide grafted starch (St-g-PAM) was made by a novel method of synthesis, involving combination of microwave radiation and a chemical free radical initiator (ceric ammonium nitrate) to initiate grafting reaction. This method (microwave assisted synthesis) is quick, highly reliable, reproducible and yields high quality product as compared to the conventional method (which uses a chemical free radical initiator alone to initiate the grafting reaction) [34].

The reaction will follow the mechanistic pathway as shown in Scheme 2.



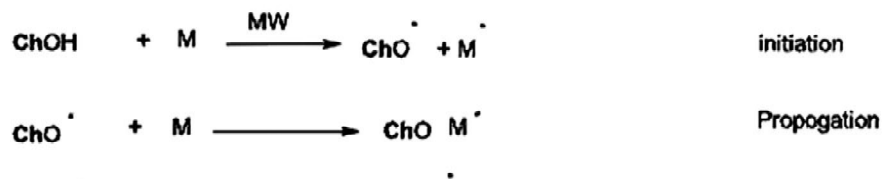
Scheme 2. Schematic representation for microwave assisted synthesis of St-g-PAM [34].



Chitosan molecule is quite a large molecule with pendent -OH and -NH₂ groups. These groups attached to the large chitosan molecule may behave as if anchored to an immobile raft and its localized rotations [16], therefore, will be observed in the microwave region and resulting dielectric heating of the chitosan molecule may result in an enhancement of reaction rates specifically at these groups. The dielectric heating will involve rapid energy transfer from these groups to neighboring molecules (acrylamide and water), since it is not possible to store the energy in a specific part of the molecule. In the chitosan molecules there are a large numbers of pendent groups and, therefore, this energy amount is expected to be enormous that results O-H and N-H bond breaking, creating radical sites at oxygen and/or nitrogen atoms. More grafting is expected at N-H sites, as bond energy of the O-H bond is higher as compared to N-H bond (Scheme 3).

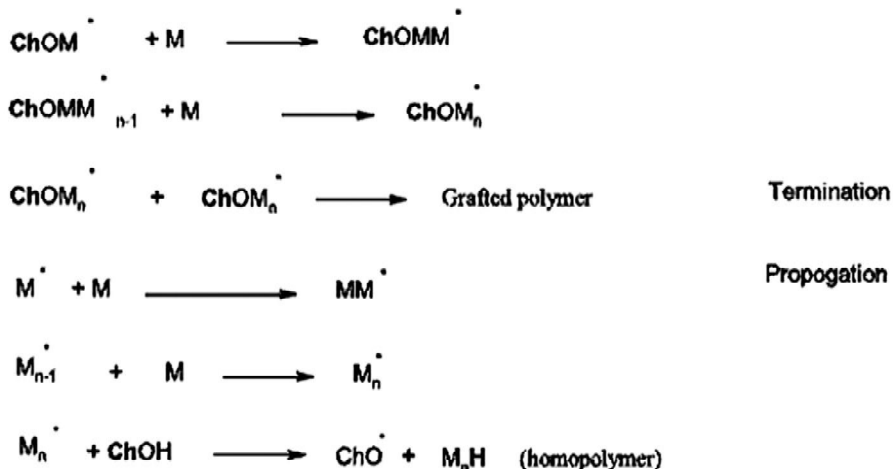
Scheme 3. Grafting mechanism of chitosan with acrylamide under microwave irradiation [16].

Grafting at O-H groups of Chitosan

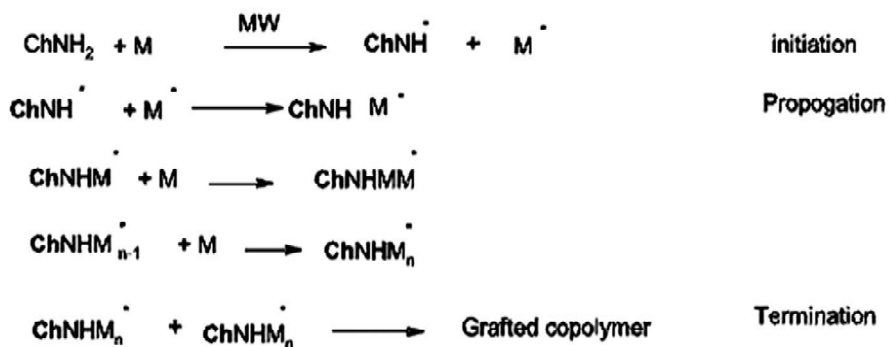




Natural Polymer Grafted with Synthetic
Monomer by Microwave for Water Treatment
- A Review



Grafting at NH₂ groups of chitosan



Where Ch stands for Chitosan
M stands for acrylamide
MW stands for microwave

Grafting ratio (%), efficiency, and conversion (%) were all found to depend on the content of potassium persulfate and AGA as well as on reaction temperature and time [35]. The percentage grafting of the microwave initiated synthesized copolymer [3, 29, 31, 34, 36] was generally evaluated by Equation 1:

Equation 1. Percentage of grafting microwave assisted synthesis [3, 29, 31, 34, 36].

$$\% \text{ grafting} = \frac{\text{wt. of graft copolymer} - \text{wt. of polysaccharide}}{\text{wt. of polysaccharide}} \times 100$$

Characterization

Most of the graft copolymers were characterized by intrinsic viscosity measurements [2] and FTIR spectroscopy. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) measurements were carried out under N₂ flow [2, 35, 37, 38]. The structure of the cationic copolymer was identified by FTIR [2, 35, 37-39] and [40-43] NMR spectroscopy, differential scanning calorimetric (DSC) studies, thermal gravimetric analysis (TGA) studies and scanning electron micrographs (SEMs), and X-ray diffraction techniques. Grafting of polyacrylonitrile (PAN) onto XG was confirmed by instrumental techniques mentioned above, techniques that have been used to study the thermal and morphological changes in the materials [44]. Evidence of grafting was obtained by FTIR, ¹³C NMR spectra, differential scanning calorimetry, X-ray diffraction, and scanning electron microscopy [35].

Flocculation

Today, water pollution has become a serious problem that is threatening the survival of human beings, plants, and animals. Flocculation is one of the most important processes in the primary treatment for water, natural polymer-based flocculants have received much more attention in water treatment, since they are believed to be highly efficient, relatively inexpensive, biodegradable, and environmentally friendly materials [32, 45]. Flocculation is aggregation of suspended particles with polyelectrolytes (cationic, anionic, or ampholytic) mainly by either a bridging or a patch mechanism.

Thus, flocculation is a process whereby finely divided or dispersed particles are aggregated together to form large particles of such a size so as to cause their settling or it is the agglomeration of tiny particles to form flocs



which settle and cause clarification of the system. Flocculation makes the suspension non-homogenous on a macroscopic scale [46]. Flocculants are the materials, which are used in fast solid-liquid separations. They act on a molecular level on the surfaces of the particles to reduce repulsive forces and increase attractive forces. By the addition of flocculant (in ppm) finely divided or dispersed particles are aggregated together to form flocs of such a size so as to make them settle speedily and to clear the system [46].

Their flocculation efficiency was studied in a clay suspension as a function of the grafted chains content and length as well as of some flocculation parameters: the polycation dose, the settling time, the parent solution concentration of polycation. All the polysaccharide samples showed flocculation ability: the higher the grafted cationic chain content and length, the lower the amount of pullulan derivative was required for reaching the maximum clarity degree (of about 100%).

Various processes occur simultaneously during flocculation: adsorption of polymer molecules at the particles surface; rearrangement (or re-conformation) of adsorbed polymeric chains; collisions between destabilized particles to form aggregates (flocs); and break-up of flocs. The importance of each process depends on the flocculant characteristics, like structure, molecular weight, charge density and concentration; on the characteristics of the suspended particles, like size and charge density; on the characteristics of the suspending medium, like pH, conductivity and ionic charge; and, finally, on the contact time and turbulence intensity, among others the contact [47].

The flocculation characteristics of all the hydrolyzed graft copolymers and the unhydrolyzed xanthan gum-g-polyacrylamide were determined in 5 wt % iron ore and kaolin suspensions by P. Adhikary, R.P. Singh [48]. Application of the cationized products as well as their parent materials in textile sizing was also undertaken. Moreover, hybrids of starch-Quat 188 and CMC-Quat 188 were used as flocculants; flocculation was carried at pH 6 using different flocculant dose. Results obtained indicate that the cationic-based hybrids – under investigation display characteristics, which qualify them to function as an excellent sizing and flocculating agents [49].

Mechanism of flocculation

Numerous authors and coworkers [10, 50, 51] developed a bridging theory that provides a useful description of the ability of polymers with high molecular weights to destabilize colloidal dispersion. Destabilization by bridging occurs when segments of a polymer chain adsorb on more than one particle, thereby linking the particles together. When a polymer molecule comes into contact with a colloidal particle, some of the reactive groups on the polymer adsorb at the particle surface, leaving other portions of the molecule extending into the solution. The polymer will adsorb on the surface in a series of loops (segments extending into the solution) and trains (segments adsorbed on the surface). If a second particle with some vacant adsorption sites, contacts these extended loops and tails, attachment can occur. A particle–polymer–particle aggregate is formed in which the polymer serve as a bridge [46].

The configuration of an adsorbed polymer chain can be very different from the random coil in solution. A widely accepted model of an adsorbed polymer chain [52] is shown in Figure 1. In this model, three distinct categories of segment are assumed: attached to the surface in trains, projecting into the solution as tails, and in the form of loops, between trains.

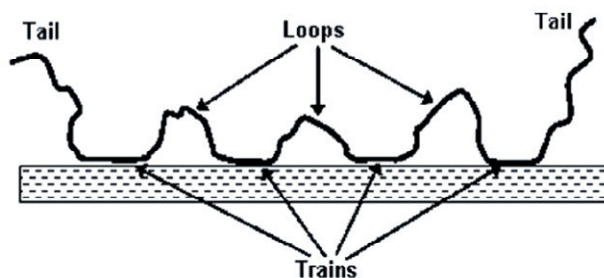


Figure 1. Model of an adsorbed polymer chain [53] .

The flocculating effect increased with the increase of grafting ratio until reaching a maximum, and then it was decreased. It may be due to the cooperative effects of the bridging flocculating and charge neutralization mechanisms of polymer flocculants. Based on the bridging flocculating

mechanism, higher grafting ratio was beneficial to increase the molecular weight of flocculants, and improve its actual flocculating capacity. On the other hand, longer and more PAM branch chains would also efficiently shield the cationic groups of $-NH_3^+$ on the chitosan backbone, as shown in Figure 2 [54].

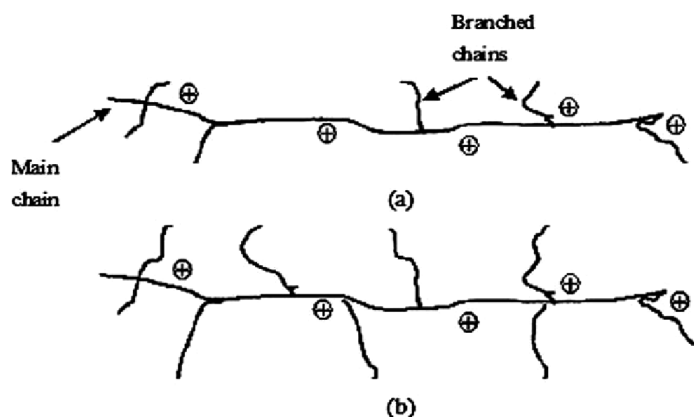


Figure 2. The available structures of chitosan-g-PAM samples, with low (a) and high (b) grafting ratio, dissolved in acidic media [54].

Mechanisms of flocculation of particles by polymers can be described under the following directions: polymer bridging, charge neutralization, depletion flocculation (free, unadsorbed polymer) [53]. Long-chain polymers adsorbed on particles can have loops and tails extending some way into solution. This gives the possibility of attachment of these polymer segments to other particles, thus 'bridging' particles together. Such a mechanism has been recognized since the 50s of last century [55] and is extremely important in practice. A schematic picture of particles bridged by adsorbed polymer is given in Figure 3.1. An essential requirement for bridging flocculation is that there should be sufficient unoccupied surface on a particle for attachment of segments of polymer chains adsorbed on other particles. It follows that the adsorbed amount should not be too high, otherwise the particle surfaces will become so highly covered that there are insufficient adsorption sites available. Here the particles are said to be destabilized (Figure 3.2) [53].

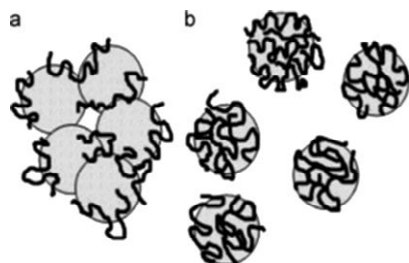


Figure 3.1 Schematic picture of (a) bridging flocculation and (b) restabilization by adsorbed polymer chains [53].

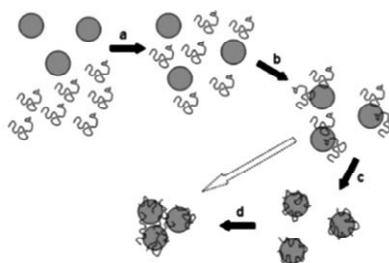


Figure 3.2 Steps involved in the flocculation of particles by adsorbing polymer [53].

Based on the experimental facts from in situ size and fractal dimension measurements, different flocculation mechanisms play key roles at various pH levels, resulting in substantially varied flocculation kinetic processes under three pH conditions. In acidic condition, patching was the main mechanism involved in the opposite zeta potential between CMC-g-PAM and the kaolin suspension. A flat configuration was favored when the polymeric flocculant was adsorbed onto the particle surface, leading to a slower initial floc growth rate, but larger and denser flocs. Bridging was the dominant mechanism in neutral and alkaline conditions. A faster initial rate of bridging resulted in smaller and more open floc structures. A rearrangement process in neutral pH subsequently led to more compact flocs, whereas no restructuring of flocs occurred in alkaline conditions because of the electrostatic repulsion of the same negative charges on the flocculant and particles [56].

Flocculant evaluation

Most of the grafted copolymers obtained by microwave irradiation, follow a similar pattern for assessment or evaluation, as shown in the literature, most of them perform “jar test” procedures [20-22, 29, 36, 37, 57]. The flocculation efficiency of the grafting acrylamide to tamarind kernel polysaccharide (TKP) products, were evaluated in kaolin suspension, municipal sewage wastewater and textile industry wastewater, was primarily dependent on the length of the grafted polyacrylamide chain. The flocculant obtained by microwave-assisted grafting method was superior to



TKP and polyacrylamide-based commercial flocculant (Rishfloc 226 LV) in flocculation tests [57].

Applications of Polymethylmethacrylate grafted guar (GG-g-PMMA), synthesis initiated by microwave was studied by standard 'Jar test' procedure in 0.5% kaolin suspension, to assess its application as flocculating agent for wastewater treatment and mineral ore beneficiation. Correlation between percentage grafting and intrinsic viscosity was also studied for the possibility of using it as a tool to control the intrinsic viscosity in the final product. This leads to the possibility of application of the grafted product as superior viscosifier than guar gum [29].

Polyacrylamide grafted agar (Ag-g-PAM) and its application as flocculant for wastewater treatment Flocculation efficacy of the synthesized graft copolymers was studied in kaolin suspension, through 'Jar test' procedure. Further, flocculation efficacy of the 'best grade' in wastewater was studied for possible application in reduction of pollutant load of wastewater [36]. The flocculation characteristics of these cationic guar gums have been evaluated in silica suspension by jar test. It has been found that among the various grades of cationic guar gums, the one with longer N- (3- Chloro-2-hydroxypropyl) trimethyl ammonium chloride (CHPTAC) chains shows better performance [58].

Conclusions

It is very important to approach and review the literature on the methodology for the microwave synthesis of natural polymer grafted with synthetic monomers, in order to obtain superior copolymers. The grafting/crosslinking methodology as a tool to manipulate natural polymers, with the precise control over the graft polymer, under microwave irradiation can be a powerful approach for the development of valuable derivatives with modifies properties. The properties of microwave synthesized graft polysaccharides are higher to the derivatives synthesized conventionally. Special attention through literature is given to natural polymer derivatives, as they are economically attractive materials. However, greater effort is needed to bring many more of grafted polymers from the experimental level to the pilot scale production and extend their practical applications. Further studies are needed on

coadjuvant properties, to flocculation dosing, studies e.g., zeta potential, particle size, aggregated flocs formation, stability and degradability among other characteristics. We need to have access to better microwave equipment such as monowave, we have severely limiting the usage of this technology. One possible difficulty with the commercialization of microwave-assisted synthesis of polymers could be the scale-up, as higher energy input is required for larger quantities. More research is needed in this area, to derive maximum benefits of microwave technology, which is gaining popularity worldwide.

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