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Ultrasound-assisted synthesis of polyacrylamide-grafted sodium alginate and its application in dye removal

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Abstract: A polymeric adsorbent based on sodium alginate (SAG) grafted with polyacrylamide (PAM) (SAG-*g*-PAM) was synthesized using an ultrasound-assisted method. The addition polymerization was carried out with ammonium persulfate as the initiator, at different acrylamide (AM) concentrations. The SAG-*g*-PAM copolymers were evaluated by FTIR and ¹³C NMR spectroscopies, thermogravimetric analysis, grafting efficiency (%GE) and intrinsic viscosity in NaCl solution at 25 °C. Graft copolymers could be obtained in reaction lasting until 10 min by using ultrasound energy with grafting efficiency above 75%. The decolorization efficiency and adsorption capacity of the SAG-*g*-PAM copolymers were investigated in the adsorption of methylene blue (MB). The dye adsorption was pH dependent, and adsorption capacity (69.13 mg/g) maxima was at pH 10. All the graft copolymers have shown the same decolorization efficiency (99%), and the best one for MB removing is the SAG-*g*-PAM⁶ (%GE = 75%), since lower acrylamide content is required in the synthesis.

Keywords: graft copolymer, alginate, acrylamide, ultrasound, adsorbents, methylene blue.

1. Introduction

Polysaccharides derivatives have many potential applications such as hydrogel, tissue engineering, cell immobilization, food applications and have also been used extensively as adsorbents for contaminants removal from polluted water^[1,2]. The solubility, hydrophobicity, physicochemical properties, and biological characteristics of the polysaccharides can be modified by reacting the hydroxyl and carboxyl groups with suitable compounds through derivatization of the functional groups^[3-5], grafting^[6,7], oxidative reactions^[8], and/or hydrolytic degradation^[9].

A convenient method to produce polysaccharide derivatives is the grafting of synthetic polymers onto the polysaccharide backbone^[6,7,10,11]. Alginate grafted with acrylamide obtained by conventional, gamma rays and microwaves methods has frequently been used as polyelectrolyte in drug delivery^[1,12,13], flocculant^[14-16] and adsorbent in dyes removal^[17]. Ultrasound-assisted method was used to produce

polysaccharides modified with acrylamide, and it promoted shorter graft copolymerization time and higher grafting efficiency^[18]. Ultrasound has been used to enhance the performance of a wide range of chemical reactions by cavitation process within a liquid, in which energy is introduced in a short period of time producing large number of microbubbles that collapse in few microseconds, providing extra energy to the system^[19-24]. High-intensity ultrasound is also used to accelerate mass transport in mixing, drying, and extraction processes and other applications^[25].

Environmental regulations are becoming stricter in what concerns the discharge and removal of dyes from aqueous effluents^[26], since dyes are widely used in the textile, leather tanning, paper, plastic, food, cosmetic, and printing industries, for the coloration of their respective products^[27]. The dyes are commonly synthetic and based on complex aromatic structures highly stable not biodegradable^[28] that pollute water if not treated properly before discharge into the environment^[29]. Methylene blue (MB), a common dye used in colouring cotton, silk, and wool, has adverse effects on human health such as eye irritations, breathing problems, diarrhea, etc. Not only photosynthetic activity but also aquatic biota^[27,30,31] is affected by MB, and 15% of this is discharged into rivers by the textile industry^[32]. It is well known that polyacrylamide homopolymer is used as an efficient adsorbent^[2,7,11] or flocculant^[7,14-16,18]. However, the high cost in addition the presence of unreacted acrylamide, which is toxic and carcinogenic, limits its application in water treatment. The new regulations and the growing of environmental awareness around the world have triggered the search for more environmentally friendly materials and processes. Low cost adsorbents based on agricultural wastes (industrial solid wastes and biomass versus clays minerals and zeolites) have being highly efficient, a renewable biomass to be exploited for MB remediation. It is estimated that over 7×10^5 tonnes of coloured wastewater are produced annually for the more than 100,000 commercially available dyes^[33].

Different methods have been investigated for the removal of dyes from water and wastewaters including biological, physical (membrane filtration, adsorption, coagulation, flocculation, precipitation, reverse osmosis, ion exchange, etc.), and chemical (oxidation, ozonation, etc.) processes^[32]. Adsorption is one of the most efficient methods to remove pollutants from effluents because of its simplicity of design, ease of operation, and insensitivity to toxic substances^[34]. Acrylamide-grafted polysaccharides as a polymeric adsorbent or flocculant instead of polyacrylamide can be attributed to its biodegradability, less-toxic characteristic, abundance in nature, and its economic attractiveness. Alginate grafted with acrylamide has been used as adsorbents and flocculants in dye removal due to its superior performance compared with other grafted polymers^[16,17].

In this paper, sodium alginate (SAG) modified with acrylamide (AM) was obtained by an ultrasound-assisted method aiming to get an improved route of synthesis, and evaluate the effect of the ultrasound energy on the grafting reaction and efficiency of the copolymers SAG-g-PAM. The graft copolymers were synthesized at different monomer concentrations, and evaluated as methylene blue adsorbent in a MB 2.2×10^{-6} mmolL⁻¹ aqueous solution.

2. Materials and Methods

2.1 Materials

SAG (viscosity, 15-20 cP) and AM (99%) were purchased from Sigma-Aldrich. Ammonium persulfate PA (APS, 98.6%) and MB were purchased from NEON. Glacial acetic acid PA (99.7%), and acetone PA (99.5%) were purchased from ACS. Formamide PA (99.5%) was purchased from Vetec Chemical Industries (Brazil). All the chemicals were used without further purification.

2.2 Synthesis of the graft copolymer by ultrasound-assisted method (SAG-g-PAM)

The graft copolymers of sodium alginate and acrylamide were synthesized following previous work on modification of polysaccharide by using ultrasound carried out in our lab^[18]. One gram of SAG (0.0062 mol of anhydroglucose unit) was dissolved in 40 mL of distilled water, specific concentrations of AM from 6 to 23 mol were diluted in 10 mL of water, and 1.75×10^{-3} mol of APS was dissolved in 5 mL of water. The three solutions were poured into a 100 mL three-neck round-bottom flask fitted with an ultrasound 13 mm stainless steel sonic wave emission probe, and the reactional mixture was sonicated using an ultrasonic generator (VCX 750, Sonics & Materials) operating at an output power of 750 W and 20 kHz frequency, under N₂. The dissipation power of the probe was determined to be 19.6 W at 30% amplitude, using a calorimetric method reported by Margulis & Margulis^[35]. The sonication has lasted between 7 and 10 min when the solution reached the gel point, and thus, the reaction time was dependent on the acrylamide concentration. In meanwhile, the reaction temperature increased from room temperature to 65 ± 5 °C since the reaction is exothermic and due to ultrasound energy. At the end of the reaction, the flask was cooled by immersing in ice water, and the gel was precipitated by adding 50 to 100 mL of acetone into the flask. The resulting precipitate, graft copolymer and polyacrylamide as sub-product, was filtered and washed with 50-100 mL of acetone, dried in an oven at 60 °C, and pulverized. The pulverized product was purified with a formamide/acetic acid mixture (1:1 v/v) to remove the homopolymer^[36],

and then washed with acetone^[37]. The grafting efficiency (%GE)^[38] of the SAG-*g*-PAM copolymers was evaluated according to Equation (1) :

$$\%GE = \frac{Wt. \text{ copolymer} - Wt. \text{ polysaccharide}}{Wt. \text{ monomer}} \times 100_{(1)}$$

2.3 Polymer characterization

2.3.1 Fourier transform infrared (FTIR) spectroscopy

FTIR spectra of SAG, PAM, and SAG-*g*-PAM were recorded on a spectrometer (Perkin Elmer, Spectrum 1000) in the 4000 to 400 cm⁻¹ region, using a KBr disk.

2.3.2 ¹³C NMR spectroscopy

The ¹³C NMR spectra of the SAG, AM, PAM, and SAG-*g*-PAM were recorded at 125 MHz in an NMR spectrometer (Agilent 500-MHz) with standard pulse programs in deuterated water at 50 °C.

2.3.3 Thermogravimetric analysis (TGA)

The thermal stability of SAG, PAM, and SAG-*g*-PAM (~20 mg) was evaluated in a thermogravimetric analyzer TGA 2050 (TA Instrument), at a heating rate of 20 °C/min from 20 °C to 600 °C, under nitrogen flux (100 mL/min).

2.3.4 Intrinsic viscosity measurement

Viscosity measurements of the polymer solutions were carried out with an Ubbelohde viscometer (viscosity constant: 0.004925 mm²/s²; capillary diameter: 0.46 mm) at 25±0.1 °C in a 0.1 M NaCl aqueous solution. The flow time of duplicate solutions was taken at four different concentrations (0.1, 0.05, 0.025, and 0.0125 g/dL). The relative viscosity (η_{rel} = τ/τ₀) was obtained using the flow time of the polymer solutions (τ) and that of the solvent (τ₀). Specific viscosity (η_{sp} = η_{rel} - 1), reduced viscosity (η_{red} = η_{sp}/C), and inherent viscosity (η_{inh} = ln η_{rel}/C) (C = polymer concentration in g/dL) were mathematically calculated, and η_{red} and η_{inh} were simultaneously plotted against concentration. The intrinsic viscosity was obtained from the point of intersection after the extrapolation of the two plots (i.e., η_{red} versus C and η_{inh} versus C) to zero concentration.

2.4 Dye removal from aqueous media using copolymer adsorbent

The removal of MB dye by adsorption on the SAG-*g*-PAM copolymer was performed in a batch system. In a 250 mL vessel filled with 50 mL of dye solution (2.2×10^{-6} mmol/L) was added 500 mg of SAG-*g*-PAM copolymer, and the mixture agitated at 130 rpm for 8 h at 25 ± 2 °C. The mixture pH has varied from 4.0 to 10 by adding the required amounts of 1.0 M HCl or NaOH solutions. The adsorbed dye was separated from the leftover dye in solution by centrifugation at 6000 rpm for 40 min. Dye concentration in solution before and after centrifugation process was analyzed using a UV-visible spectrophotometer (PG Instruments, T80+), at a wavelength of 650 nm. A linear relationship between absorbance and dye concentration was determined at this wavelength and used as the calibration curve to determine the dye concentration at each equilibrium. Deionized water was used as reference and the percentage of decolorization efficiency (%DE) was calculated according to Equation (2):

$$\%DE = \frac{C_0 - C}{C_0} \times 100 \quad (2)$$

Where C_0 and C are the concentrations of the dye solution, respectively, before and after treatment with the adsorbent polymer. The amount of dye adsorbed by mass unit of the copolymer (mg/g) was calculated according to Equation (3):

$$q(\text{mg/g}) = \frac{(C_0 - C) \times V}{m} \quad (3)$$

where C_0 and C are the concentrations of the dye solution (mg/L), respectively; before and after treatment with the adsorbent polymer; V is the volume of the aqueous phase (L); and m is the amount of dry adsorbent (g).

3. Results and Discussions

The SAG-*g*-PAM copolymers were synthesized by changing the AM concentration and keeping constant the initiator (APS) concentration and the US power. The chemical modification of sodium alginate with acrylamide occurs at the hydroxyl groups of the D-glucopyranosyl unit, and grafting reaction mechanism of PAM into SAG backbone is depicted in Figure 1. According to Wang and Wang^[39], the free radicals of the APS decomposition attack the D-glucopyranosyl hydroxyl groups and generated macro-radicals (SAG#O•) that attack the acrylamide producing PAM grafts into SAG backbone. Chain termination occurs as in a typical radical polymerization reaction. The ultrasound cavitation

process also promotes the grafting reaction by generating extra energy and heat in the medium. We believe that the ultrasound energy favors instantly the production of both radicals, since the monomer incorporation occur in its totality at a very short period compared to conventional process reaction time. In the absence of initiator in the reaction medium the gel point was not reached, and thus no product. Table 1 shows the reaction yield, %GE, and intrinsic viscosity (η) of the SAG-*g*-PAM copolymers synthesized as a function of the monomer (AM) concentrations. The intrinsic viscosity of the pristine alginate (SAG) and of the sonicated alginate with (SAG-US-APS) and without (SAG-US) the initiator was comparatively determined. The reaction yield, the grafting efficiency and intrinsic viscosity of the SAG-*g*-PAM copolymers increased as a function of the AM/SAG molar ratio. On the other hand, reaction time decreased with the monomer concentration's increasing, since the gel point occurred faster due to the high acrylamide incorporation into alginate backbone, with consequent increasing of the polymer molecular weight. Under the reactional conditions, the reaction yield has changed from 83% to 99% and was of the same order of those reported using conventional method^[18,40]. The great advantage of using ultrasound or sonication process is the time reduction, which was much short (< 10 min) in comparison to 24 h needed in the conventional grafting reaction process; in addition, same yield and grafting efficiency were obtained. As the AM/SAG molar ratio increased from 6 to 23 mol, %GE increased reaching almost 100%. A high molar ratio provides more monomer molecules per polysaccharide macro-radical in the reaction medium, leading to a high acrylamide incorporation in the polysaccharide backbone or higher %GE^[41].

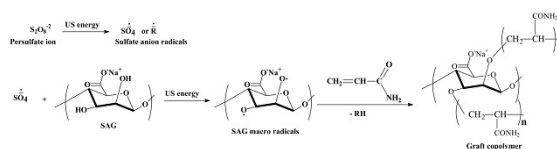


Figure 1.

Grafting reaction mechanism of SAG D-glucopyranosyl units with acrylamide.

Table 1.

Reaction yield (%), grafting efficiency (GE) and intrinsic viscosity of the SAG- *g*-PAM copolymers as functions of acrylamide concentration *.

| Run | [SAG] (mol/L) | [AM] (mol/L) | [APS] (mol/L) | Time (min) | Yield (%) | GE (%) | η (dL/g) |
|-----|---------------|--------------|---------------|------------|-----------|--------|---------------|
| 1 | 0.01 | 0.06 | 0.005 | 10 | 83 | 10 | 2.2 |
| 2 | 0.01 | 0.12 | 0.005 | 10 | 99 | 90 | 5.9 |
| 3 | 0.01 | 0.23 | 0.005 | 10 | 99 | 99 | 5.9 |
| 4 | 0.01 | 0.06 | 0.005 | 10 | 99 | 90 | 5.9 |
| 5 | 0.01 | 0.12 | 0.005 | 10 | 99 | 90 | 5.9 |
| 6 | 0.01 | 0.23 | 0.005 | 10 | 99 | 99 | 5.9 |

The graft copolymers showed intrinsic viscosity between 2.2 and 5.9 dL/g due to the acrylamide concentration, since the initiator concentration was constant. The alginate sonicated only with the initiator, or in the absence of the monomer (SAG-US-APS), undergoes chain cleavage and thus a molecular weight reduction, since the intrinsic viscosity decreased dramatically to 1.0 dL/g, if compared with viscosities of both alginate sonicated (SAG-US) and pristine polymer (SAG). The degradation of a polymer in a solution depends on the ultrasound

power generated in the medium^[24]. This is in agreement with works by Iida et al.^[42] and Hosseini et al.^[43] that observed a decreasing of intrinsic viscosity of starch and sodium alginate solutions after sonication. The same intrinsic viscosity values for the alginate sonicated and non-sonicated shows that the ultrasound energy does not degrade the polysaccharide molecules under the conditions used in this work. On the other hand, the low viscosity of the alginate sonicated with the APS, shows that the initiator radicals attack the alginate molecules producing polysaccharide macro-radicals that in the absence of monomer molecules degrade easily other alginate macromolecules. Thus, the viscosity of the graft copolymer depends on the monomer concentration, and there is a synergic effect between the ultrasound energy and the initiator. The highest intrinsic viscosity of the SAG-*g*-PAM²³ copolymer is because there is high concentration of PAM short chain branches into the alginate backbone, or instead it a low concentration of longer chain branches.

All graft copolymers evaluated by FTIR, NMR and thermogravimetry have shown the same curve profiles. To follow the chemical modification in the graft copolymer, only the spectra and thermogram of the SAG-*g*-PAM¹¹ copolymer, obtained with the medium acrylamide concentration, have been discussed compared with those of the neat polymers SAG and PAM.

3.1 FTIR spectroscopy

The FTIR spectra of the neat polymers SAG and PAM, and the SAG-*g*-PAM¹¹ copolymer are shown comparatively in Figure 2. The SAG spectrum at wavenumber of 818 cm⁻¹ shows the characteristic absorption bands of Na-O stretching, at 3442 cm⁻¹ shows a broad peak due to the stretching frequency of the -OH group, at 1610 and 1416 cm⁻¹ two absorption peaks relative to COO⁻ group, and at 1031 cm⁻¹ one sharp peak due to the C-O group^[44]. Meanwhile, the PAM FTIR spectrum exhibits broad absorption bands at 3400 and 3180 cm⁻¹ assigned to the stretching vibrations of N-H, at 1664 cm⁻¹ band attributed to C=O stretching, and at 1612 cm⁻¹ band of the N-H bending. In the SAG-*g*-PAM¹¹ spectrum, all the absorption peaks mentioned above have shifted indicating that some interaction among the functional groups of sodium alginate and polyacrylamide has occurred. Accordingly, the double N-H stretching vibration peak of polyacrylamide at 3400 cm⁻¹ (Figure 2 PAM) and the OH stretching vibration peak of sodium alginate at 3442 cm⁻¹ (Figure 2 SAG) is overlapped in SAG-*g*-PAM¹¹ copolymer at 3410 cm⁻¹. Some additional peaks in the copolymer spectrum are the peaks at 1682 and 1615 cm⁻¹ that correspond, respectively, to the carbonyl amide and N-H stretching vibrations, and the peak at 1402 cm⁻¹ due to C-N stretching vibrations. This last peak signifies grafted PAM chains in

the copolymer and confirms the intended grafting. This result is in good agreement with the results reported in the literature^[45].

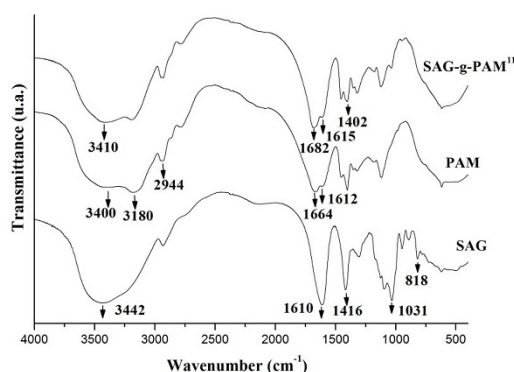


Figure 2.
FTIR spectra of (SAG), (PAM), and SAG-*g*-PAM¹¹ copolymer.

3.2 ¹³C NMR spectroscopy

The ¹³C NMR spectra of SAG, AM, PAM, and SAG-*g*-PAM¹¹ copolymer are shown in Figure 3. The ¹³C NMR spectrum of SAG (Figure 3 a) shows three distinct resonance signals. The chemical shift (δ) at 102.3 ppm is referenced to the anomeric carbon atom (C-1) of the oxygen linkage. The resonance peak at δ 177.9 ppm is assigned to the carbon of the $\text{#COO}^- \text{Na}^+$ group, located at C-6. The overlapping resonance peaks in the range 60-85 ppm are assigned to the carbon atoms (C-2, C-3, C-4, and C-5) of the glucopyranosyl units. The ¹³C NMR spectrum of acrylamide (Figure 3 b) has three distinct resonance peaks. The peak at δ 171.19 ppm is due to the amide carbonyl carbon (C=O), and the peaks at δ 128.01 and δ 129.03 ppm signs the two sp^2 hybridized carbon atoms (i.e. $\text{CH}_2=\text{CH}$). In ¹³C NMR spectrum of the polyacrylamide (Figure 3 C), the peaks at δ 179.6, 35.1 and 42.1 ppm corresponding to the carbonyl group of its amide (CONH_2) and sp^3 hybridized carbon atoms, respectively. The ¹³C NMR spectrum of the SAG-*g*-PAM¹¹ copolymer (Figure 3 d) shows three additional resonance signals, compared to SAG. The stronger peak at δ 179.6 ppm is due to the amide carbonyl groups. The presence of the two additional peaks at δ 35.1 ppm and 42.1 ppm with sp^3 hybridized carbon atoms, due to the presence of groups CH and CH_2 , respectively, confirm that the PAM chains ($-\text{[CH}_2\text{-CH]}_n-$) are grafted onto the SAG backbone. The chemical shifts shown in Figure 3 are comparable with those reported in the literature^[45]. The peaks at δ 175, 166.9 and 20.9 ppm are due to solvents trace (formamide and acetic acid) used in the purification of the graft copolymer.

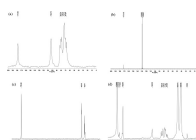


Figure 3.

(a) ^{13}C NMR spectra of SAG; (b) AM; (c) PAM; (d) SAG-*g*-PAM¹¹ copolymer.

3.3 Thermal stability of the graft copolymers

Figure 4 shows the mass loss (a) and derivative (b) TGA curves of the neat polymers SAG and PAM, and of the SAG-*g*-PAM¹¹ copolymer. The sodium alginate decomposition (Figure 4 a) showed three distinct stages of mass loss. The initial event at 25-125 °C is due to the moisture desorption from the polysaccharide, with a mass loss of approximately 11%. The second and third events from 170 °C to 300 °C result of the decomposition of the carbohydrate backbone, followed by a mass loss of approximately 40%. The mass loss with maximum degradation rate at 221 °C (T_{max}) (Figure 4 b) is due to groups COO^- decomposition, with a subsequent decarboxylation of CO_2 . The mass loss at T_{max} of 239 °C (Figure 4 b) is due to the SAG backbone decomposition^[46] with a subsequent chain cyclization. Above 330 °C the organic material undergoes carbonization remaining at 575 °C a residue of 37%. The PAM degradation shows two distinct stages of mass loss with T_{max} at 300 °C and at 411 °C (Figure 4 b). The continuous mass loss until 150 °C is due to the moisture desorption from the sample. Above 230 °C, the polyacrylamide first undergoes oxidation with 25% of mass loss due to ammonia by imidization (intra- and intermolecular) and water by dehydration. The second event with T_{max} of 411 °C is due to the chains cyclization process with mass loss approximately of 46%^[47], remaining at 600 °C a residue equivalent to 24%.

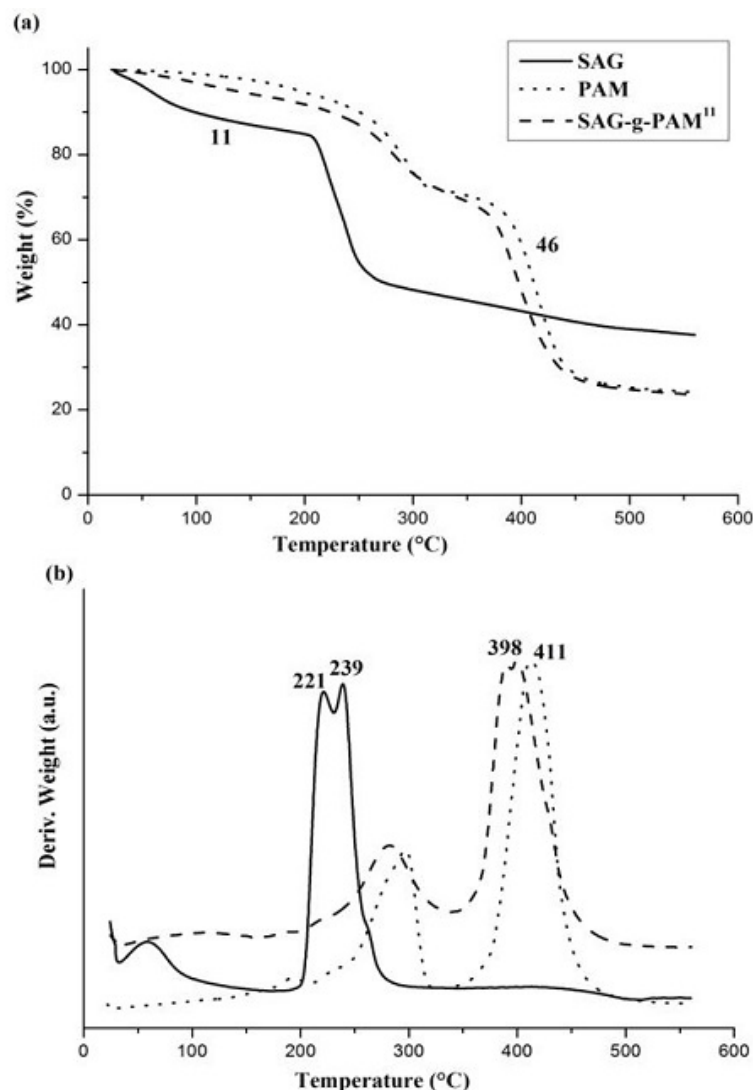


Figure 4.

(a) Mass loss and (b) derivative TGA curves of the neat polymers (SAG) and (PAM), and SAG-*g*-PAM¹¹ copolymer.

The degradation profile of the SAG-*g*-PAM¹¹ copolymer was lightly different of that presented by PAM, but also shows two mass loss event with T_{\max} at 280 °C and at 398 °C (Figure 4 b). This little difference is consequence of the alginate chains modification by the PAM long chain branching. The mass loss from 200 °C to 350 °C is due to SAG decomposition and as well PAM oxidation. In the graft copolymer thermogram, there is an overlap of the mass loss of the SAG (200-270 °C) with the first mass loss of the PAM (200-320 °C), occurring an unique mass loss in the range of 200 °C to 350 °C. Before 200 °C, the SAG-*g*-PAM¹¹ copolymer presents better thermal resistance than SAG because it losses lower water content due to the functional groups chemical modification, and there is also a new type of chemical interaction between both polymers. According to the literature^[48], hydrogel grafted with acrylamide, instead of acrylic acid, also presented better thermal

stability, probably due to different types of covalent bonds in the grafting copolymer backbone.

3.4 Decolorization efficiency of methylene blue solution

Figure 5 shows the absorption capacity (q mg/g) of methylene blue dye, by the SAG-*g*-PAM¹¹ copolymer, as a function of the pH, at an initial fixed concentration of dye 2.2×10^{-6} mmolL⁻¹ and SAG-*g*-PAM¹¹ of 500 mgL⁻¹. The adsorption capacity of the SAG-*g*-PAM¹¹ copolymer was higher as the pH of the methylene blue solution increased. The maximum absorption capacity was at pH 10 (69 mg/g), since the alkaline medium favors stronger electrostatic force of attraction between the anionic groups of graft copolymer and the polar groups of the dye MB.

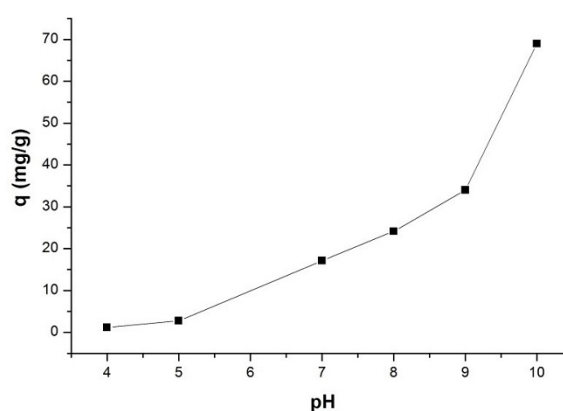


Figure 5.

Absorption capacity of MB, by the SAG-*g*-PAM¹¹ copolymer, as a function of the pH.

This result indicates that the adsorption process is controlled by a charge neutralization mechanism, where the cationic groups of MB are electrostatically attracted by the anionic carboxylate groups ($\text{COO}^- \text{Na}^+$) of the SAG and the free electrons of the NH_2 groups of the acrylamide of the grafting. Figure 6 illustrates the adsorption process of the cationic dye molecules by the anionic groups of SAG-*g*-PAM copolymer. When the carboxylate groups completely neutralize the cationic charges of MB, the decolorization efficiency reached the maximum value. However, when the molar ratio is exceeded, destabilization can take place by electrostatic repulsion between the cationic dye molecules that are already bound by the copolymer^[49].

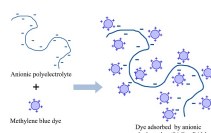


Figure 6.

Schematic illustration of the MB dye adsorption by SAG-*g*-PAM copolymer.

At alkaline pH, the number of positively charged sites decreases and the number of negatively charged sites increases that favors the removal

of MB. The results are in accordance with literature reports on the adsorption of cationic dyes by other polymeric adsorbents; similar trends were observed for the adsorption of Basic Violet 7 on sodium alginate modified with acrylamide^[17], and for cationic dye removal by natural adsorbents^[50].

Table 2 shows the %DE and adsorption capacity (q mg/g) of methylene blue dye by the SAG-g-PAM copolymers evaluated in pH 10. After 8h, the decolourization efficiency and adsorption capacity of methylene blue dye was of the same order for all graft copolymers, independent on the percentage grafting efficiency. Since the SAG-g-PAM⁶ copolymer with lower grafting efficiency (%GE =75%) showed the same performance that the others, this must be preferentially used in MB removing, because lower acrylamide content is used in the synthesis, and fewer polyacrylamide residue will be present in wastewater, reducing environmental contamination. An extra time or higher concentration of SAG-g-PAM copolymers seems to be useless in our experiments, since decolouring efficiency was almost hundred per cent, thus 69 q mg/g must be the adsorption capacity of the grafting copolymers produced. However, larger amounts of adsorbent would imply in greater surface area and a higher number of available sites for dye adsorption^[17].

Table 2.

Decolourization efficiency (%DE) and adsorption capacity (q) of the SAG-g-PAM copolymers in solution of MB pH 10.

| Copolymer | %GE | %DE | q (mg/g) |
|------------------------|-----|-----|----------|
| SAG-g-PAM ¹ | 100 | 100 | 69 |
| SAG-g-PAM ² | 100 | 100 | 69 |
| SAG-g-PAM ³ | 100 | 100 | 69 |
| SAG-g-PAM ⁴ | 100 | 100 | 69 |
| SAG-g-PAM ⁵ | 100 | 100 | 69 |
| SAG-g-PAM ⁶ | 75 | 100 | 69 |

In both conditions, solution acid and basic, the adsorption of MB by the SAG was not observed, since no chemical interaction is facilitated or favoured. In neutral solution (pH 7), the neat alginate salt will be dissociated, and the ions COO⁻ and Na⁺ will be solvated by water molecules. In a neutral solution, the cationic groups of MB and the sodium ions will compete by the carboxylic ions, and the system will reach an equilibrium. By lowering the solution pH with HCl, the salt NaCl is produced and the carboxylic acid is regenerated. By increasing the solution pH with NaOH, harder will be the SAG salt dissociation and free dissociated species in solution.

4. Conclusion

In this work was shown that graft copolymer of sodium alginate and with different concentrations of acrylamide (SAG-g-PAM) could be synthesized in a short period of time by using ultrasound energy at low frequency. An improvement of grafting reaction was reached by using ultrasound or sonication process, since the time reaction was significantly reduced (< 10 min) in comparison to 24 h needed in the conventional grafting reaction process reported in the literature^[18,40]. The grafting efficiency %GE was dependent on the

acrylamide monomer concentrations and the SAG-g-PAM copolymers were obtained with %GE higher than 75%. All the graft copolymers obtained by ultrasound-assisted method showed high decolorization efficiency (99%) independent of grafting efficiency, and the maximum amount of methylene blue adsorbed was 69.13 mg/g. The efficiency of dye adsorption was dependent on the pH of the methylene blue solution. The best SAG-g-PAM copolymer to be used as adsorbent was the one with lower content of incorporated acrylamide (%GE = 75%), because lower amount of acrylamide is used in the synthesis, and there will be lesser wastewater contamination by polyacrylamide, attenuating environmental contamination.

5. Acknowledgements

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