



Synthesis of grafted copolymer alginate-g-poly(1-carboxylic 4-acrylamidobenzenesulfonamide) and its application in water treatment

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ABSTRACT

NaAlg-g-PNa-C4ABS grafted copolymer was synthesized to be used in water treatment to remove heavy metal ions and dyes. Sodium salt of 1-carboxylic 4-acrylamidobenzenesulfonamide (Na-C4ABS) was grafted onto sodium alginate (NaAlg-g-PNa-C4ABS) through free-radical polymerization technique using potassium persulfate ($K_2S_2O_8$) as initiator in aqueous solution. The grafting parameters of Na-C4ABS from sodium alginate were studied. The homopolymer PNa-C4ABS was prepared using same technique. The homopolymer and grafted copolymer NaAlg-g-PNa-C4ABS were considered using Fourier-transform infrared spectroscopy and X-ray diffraction. The maximum grafting yield was achieved at $[Na-C4ABS] = 0.5 \text{ mol L}^{-1}$, $[K_2S_2O_8] = 6 \times 10^{-2} \text{ mol L}^{-1}$ and reaction temperature = 60°C for 2 h. The change in the morphology of alginate occurred due to grafting process was proved using a scanning electron microscopy. Grafted copolymers enable alginate to be used in water treatment and showed high ability for basic dyes and heavy metal ions uptake especially chromium ion (Cr^{6+}). Adsorption of the cationic dyes is highly improved by increasing the percentage graft of poly(sodium salt of 1-carboxylic 4-acrylamidobenzenesulfonamide).

Keywords: Sodium alginate; Grafting; Homopolymer; Poly(Na-C4ABS); Heavy metals; Dyes; Removal; Characterization

1. Introduction

Sodium alginate (NaAlg) has acidic character, a biodegradable and renewable biopolymer that has got big attention recently. It is a linear polymer that consists of poly- β -1,4-d-mannuronic acid (M units) and α -1,4-l-glucuronic acid (G units) in different quantity by 1–4 linkages. Alginate has been widely used in different industrial applications such as cosmetic, food and pharmaceuticals [1]. The solubility, stability and adsorbing capacity of natural polymers can be utilized via grafting [2]. Researchers have appeared interest in the field of polymer nanocomposites to take control of the drawbacks of traditional chemically grafted polymer because they give large surface area, excellent mechanical resistance, recommendable porosity

and higher hydrodynamic radius [3–7]. Most dyes and their transitional products have been known to be toxic, carcinogenic or mutagenic [8,9]. Dye molecules extend into surface water, groundwater system, drinking water and collect along the food group. Dyes can be remaining within the aqua environment for a long time after introduction because they do not degrade biologically due to their complex aromatic structures [10]. Full removal of toxic dyes from industrial waste water is turning more important due to their poisonous effect on living organism. Azo dye is the main class of synthetic dye which renders about 90% of all organic colorants [11]. Congo red (CR) is one of the best examples for azo dye and is chemically known as sodium salt of 3,3'-([1,1'-biphenyl]-4,4'-diyl)bis(4-aminonaphthalene-1-sulfonic acid) [12]. It is widely used in

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wood, pigment, textile, dyeing, plastic and printing industries [13–17]. It is toxic in nature and leads to danger both humans and animals. It causes a lot of health problems in humans such as anorexia, weakness and gastrointestinal irritation [18,19]. As it is a benzidine based dye, it is suspected to have carcinogenic and mutagenic property [20,21]. Congo red is an anionic azo dye. It enters the water bodies through various industrial emissions. Because of its high structural stability, it is quite resistant towards biodegradation and thus Congo red continues as contaminant to water environment for a long period of time. Bismark brown is a cationic azo dye widely used in textiles, paper, rubber, and plastic industries. Expel of wastewater containing these dyes are harmful to the receiving ecological system [22]. So, there is a serious need to initiate economical technique to remove the Bismark brown dye from wastewaters. Last few decades, different processes are used for Bismarck brown dye removal usually include physical, chemical, and biological methods [23]. Some processes such as electrochemical techniques and ion-pair extractions are also used for dye waste water treatment, while others have been used in the industry for a long time [24]. Adsorption has been found to be higher than other techniques for water quality in conditions of initial cost, simple design, use of operation, and insensitivity to toxic substances [25]. The removal of dye from industrial wastewater is computed as an important application of adsorption processes. Heavy metals are those metals that have density more than 5 g mL⁻¹. Water pollution with heavy metals is an important trouble at the current time worldwide [26]. In literature, poly(4-acrylamidobenzene-sulfonamide) was grafted onto chitosan and bioactivity application was tested [27]. The aim of this research is to find a decent adsorbent for the removal of Congo red from water [28]. Work was done on dyes removal (such as Congo red and Bismark brown) and heavy metal ions removal from water using grafted polymer NaAlg-g-PNa-C4ABS. NaAlg-g-PNa-C4ABS grafted copolymer has chelating groups for heavy metal ions as carboxylic groups onto alginate and sulfonamide on the grafted polymer chains [29]. Therefore, this copolymer is interesting candidate for water purification of heavy metals ions. NaAlg-g-PNa-C4ABS was prepared using potassium persulfate (K₂S₂O₈, KPS) via grafting onto sodium alginate in aqueous solution.

2. Experimental section

2.1. Materials

Sodium alginate with viscosity of 1,000–1,200 cPs was purchased from (Nice Chemicals Private Limited). Sulfanilamide and maleic anhydride were purchased from via Loba Chemie Pvt. Ltd. Potassium persulfate (KPS) was obtained from (Sigma-Aldrich, USA). No further purification was needed for the other reagents and solvents used in the current study as they were bought with the standard analytical grades.

2.2. Characterization techniques

Native sodium alginate and grafted copolymer alginate-g-PNa-C4ABS were characterized by Fourier-transform

infrared spectroscopy (FT-IR) spectroscopy, over range of wave number from 600 to 4,000 at 25°C using TENSOR Testcan Shimadzu Infrared-Spectrophotometer (model 8000, KBr pellets). In addition, the morphology of sodium alginate and grafted copolymer alginate-g-PNa-C4ABS were investigated by Quanta 250 FEG Microanalyzer at 30KV scanning electron microscopy (SEM, JOEL S150A) (with field emission gun). Dry samples were covered with gold (Au) layer with thickness about 100 μm via ion sputter coating unit. The heavy metal ions (Cr⁶⁺, Cu²⁺, Ni²⁺ or Cd²⁺) removal by grafted copolymer was determined using atomic ion adsorption. The metal ions removal was done by soaking the grafted copolymer in metal chloride solutions with known concentrations (2 M) (G%) and kept undisturbed till equilibrium. The concentration of unadsorbed metal chloride solutions was determined by atomic absorption technique. The cationic and acidic dyes uptake via grafted copolymer was studied by colorimetric spectrophotometry (UNICO 1200 spectrophotometer). Different concentrations of the cationic and anionic dyes were prepared. Same weight of the grafted copolymer was soaked in each one until equilibrium. The initial and remaining concentrations of dyes were determined colorimetric ally as a function of the absorbance. The measured wavelength for Bismark brown and Congo red was adjusted at λ_{max} 580 and 480, respectively. The calculation of equilibrium adsorption amount was done according to the following equation [30].

$$Q = \frac{(N_a - N_s)}{W} \quad (1)$$

where Q : quantity of adsorbed dye at equilibrium (mg)/weight of the substrate (g), N_a amount of initial dye (mg), N_s amount of remaining dye in the solution (mg), and W mass of the grafted copolymer (g).

2.3. Preparation of sodium salt of 1-carboxy-4-acrylamidobenzene-sulfonamide (Na-C4ABS)

Synthesis of 1-carboxy-4-acrylamidobenzenesulfonamide was performed via following the procedure reported for aniline [31]. This method is preferred to synthesis monomer with carboxylic group using safe materials. Synthesis was done by adding (0.1 mol) solution of maleic anhydride in diethyl ether dropwisly to (0.1 mol) sulfanilamide solution in acetone with equimolar ratio. The mixture was stirred for 1 h in ice bath at 0 to -5°C. The precipitate was washed by acetone and Et₂O to remove unreacted materials and dried using air oven at 40°C. The obtained 1-carboxy-4-acrylamidobenzenesulfonamide was treated with Na₂CO₃ solution to convert to its sodium salt to be grafted onto sodium alginate in aqueous solution. Finally, sodium salt of 1-carboxy-4-acrylamidobenzenesulfonamide was collected by lyophilization.

2.3.1. Polymerization of sodium salt of 1-carboxylic 4-acrylamidobenzenesulfonamide (Na-C4ABS)

Thermal polymerization of Na-C4ABS in aqueous solution was done using potassium persulfate and sodium

bisulfate as initiator at 60°C. The PNa-C4ABS was precipitated in methanol, dried and characterized using FT-IR, X-ray diffraction and its solubility was tested in different solvents.

2.3.2. General procedures of (Na-C4ABS) grafting onto sodium alginate

The effect of grafting parameters (such as Na-C4ABS and initiator concentration, time and temperature of the reaction) onto grafting process was studied. Define weight (W_{NaAlg}) of sodium alginate was dissolved in distilled water in three-necked bottom flask with stirring under N_2 flow. Then, ($W_{\text{Na-C4ABS}}$) of Na-C4ABS and solution of potassium persulfate

(KPS) were added to the sodium alginate solution under the nitrogen with constant temperature for definite time (Fig. 1). The homogeneous alginate-g-PNa-C4ABS copolymer mixture was precipitated from cold acetone, dried and weighted (W_{total}). For extraction of homopolymer ethanol was used through Soxhlet device for 8 h. The alginate-g-PNa-C4ABS copolymer was dried until constant weight ($W_{\text{NaAlg-g-PNa-C4ABS}}$). Finally, the grafting % (%G) and grafting efficiency (%GE) were estimated using the following Eqs. (2) and (3).

$$\text{Graft Yield (\%G)} = \frac{W_{\text{NaAlg-g-PNa-C4ABS}} - W_{\text{NaAlg}}}{W_{\text{NaAlg}}} \times 100 \quad (2)$$

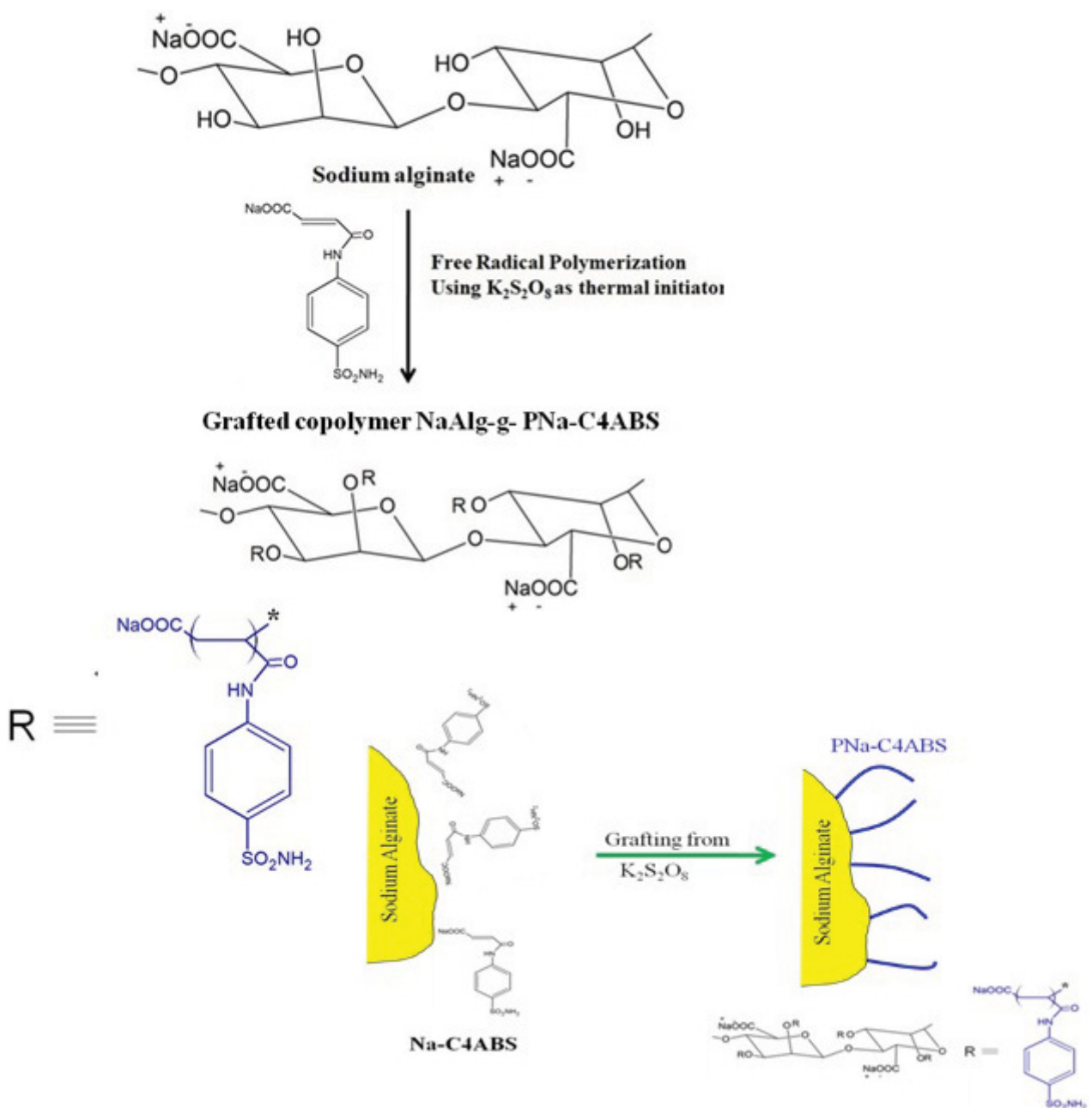


Fig. 1. Grafting process of Na-C4ABS from sodium alginate using free-radical polymerization.

Grafting efficiency (%GE)

$$= \left(\frac{(W_{\text{NaAlg-g-PNa-C4ABS}} - W_{\text{NaAlg}})}{(W_{\text{total}} - W_{\text{NaAlg}})} \right) \times 100 \quad (3)$$

where $W_{\text{NaAlg-g-PNa-C4ABS}}$ = weight of grafted copolymer NaAlg-g-PNa-C4ABS after Soxhlet; W_{NaAlg} = initial weight of sodium alginate (NaAlg); W_{total} = total weight of product before Soxhlet.

3. Results and discussion

Parameters affecting the grafting process of C4ABS onto sodium alginate were examined. These different parameters are: the concentrations of C4ABS and concentration of $\text{K}_2\text{S}_2\text{O}_8$, time, and temperature of the reaction.

3.1. Temperature effect

The effect of change in the temperature of grafting process was estimated using concentrations of Na-C4ABS and KPS equal to 0.5 and $8 \times 10^{-2} \text{ mol L}^{-1}$, respectively. These used concentrations achieved highest G% and GE%. The change in temperature was from 50°C to 70°C as shown in Fig. 2.

3.2. Time effect

The grafting process of Na-C4ABS on sodium alginate was conducted for different time intervals as 1, 2, 3 and 4 h at constant conditions which lead to the highest %G and %GE are Na-C4ABS and KPS equal to 0.5 and $8 \times 10^{-2} \text{ mol L}^{-1}$, respectively at 60°C as shown in Fig. 3. The highest grafting yield percent and efficiency were achieved

around 2 h. After this time, the grafting percent was decreased that could be explained as no more monomer and initiator were present and consequently, the grafted chain started to depolymerize.

3.3. Potassium persulphate concentration effect

Initiator concentration ($\text{K}_2\text{S}_2\text{O}_8$) effect on the grafting reaction of C4ABS on sodium alginate was studied at constant temperature equal to 60°C and C4ABS concentration equals to 1.5 mol L^{-1} . We observed the optimum concentration of KPS is $4 \times 10^{-2} \text{ mol L}^{-1}$ that gives the highest graft yield (G%) and graft efficiency (GE%) obtained with initiator concentration is $8 \times 10^{-2} \text{ mol L}^{-1}$ (Fig. 4). Above this initiator concentration, graft yield (G%) decreases due to competition between initiation and termination process of initiator.

3.4. Sodium salt of 1-carboxy-4-acrylamidobenzenesulfonamide (Na-C4ABS) concentration effect

The effect of change in the concentration of sodium salt of 1-carboxylic 4-acrylamidobenzenesulfonamide on its grafting process on sodium alginate was studied at constant temperature at 60°C and the concentration of KPS is $8 \times 10^{-2} \text{ mol L}^{-1}$ which achieved highest %G and %GE. The highest graft yield percent (G%) was obtained at Na-C4ABS concentration equals 0.5 mol L^{-1} as shown in Fig. 5.

3.5. Characterization of the synthesized grafted copolymers

3.5.1. Fourier-transform infrared spectroscopy

As shown in Fig. 6, FT-IR-spectra of sodium alginate, PNa-C4ABS and grafted copolymer were shown. The

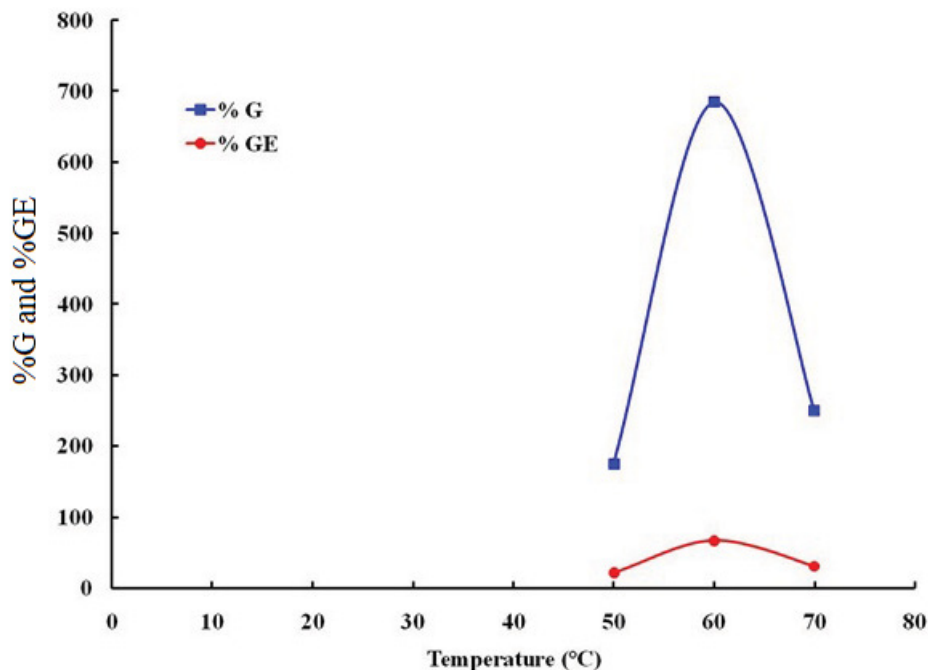


Fig. 2. The relation between temperature of the reaction, graft yield (G%) and graft efficiency (GE%) ([Na-C4ABS] = 0.5 mol L^{-1} , $[\text{K}_2\text{S}_2\text{O}_8]$ = $6 \times 10^{-2} \text{ mol L}^{-1}$ and reaction time = 2 h).

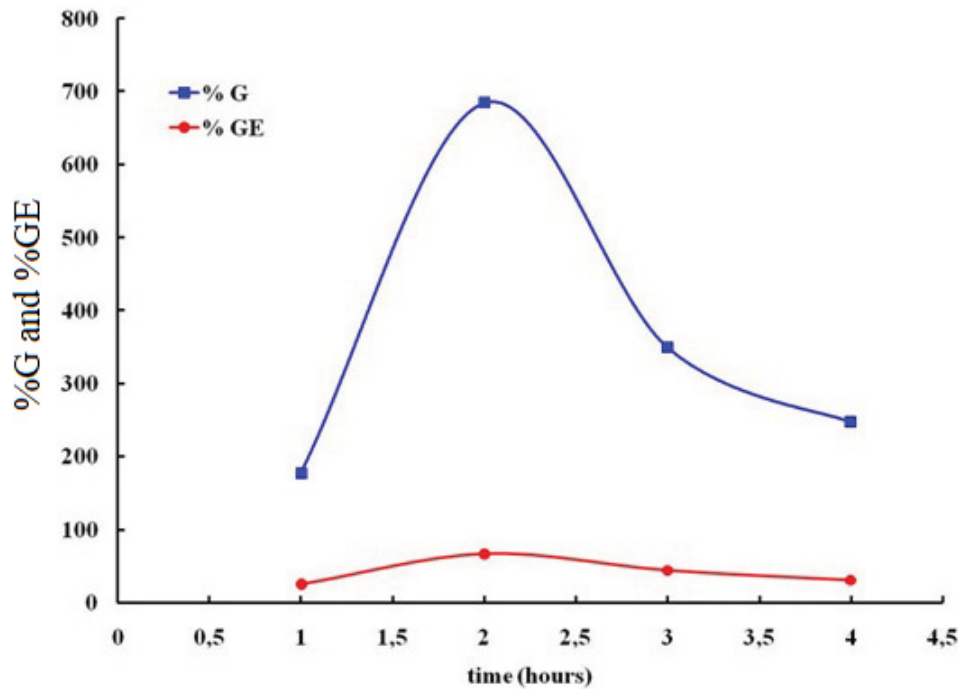


Fig. 3. The relation between time of the reaction, graft yield (G%) and graft efficiency (GE%) ($[\text{Na-C4ABS}] = 0.5 \text{ mol L}^{-1}$, $[\text{K}_2\text{S}_2\text{O}_8] = 6 \times 10^{-2} \text{ mol L}^{-1}$ and reaction temperature = 60°C).

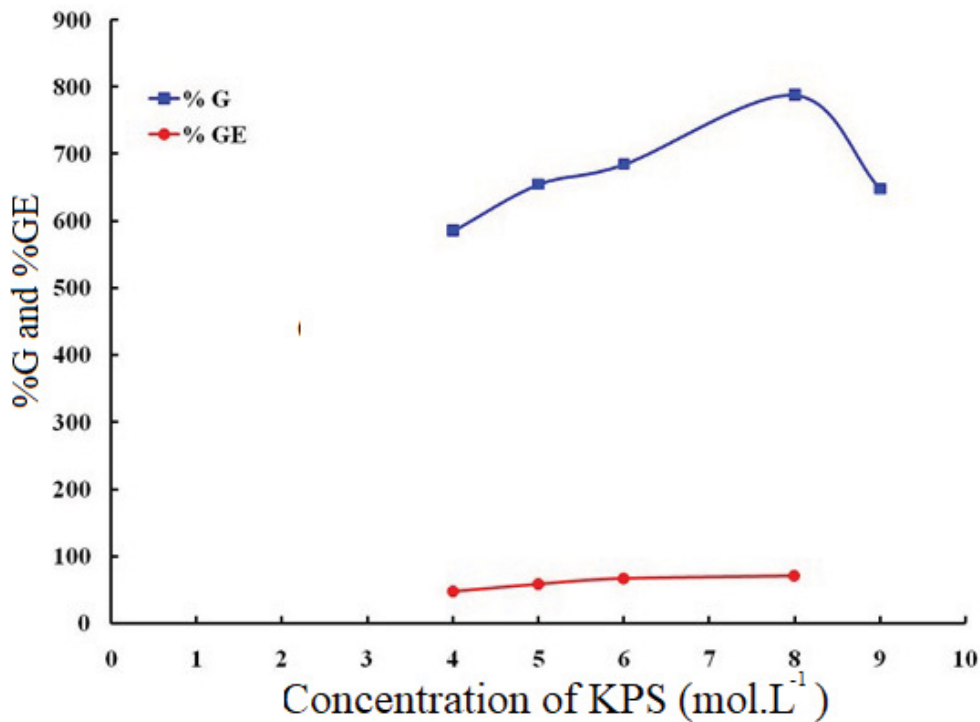


Fig. 4. The relation between $\text{K}_2\text{S}_2\text{O}_8$ concentration, graft yield (G%) and graft efficiency (GE%) where ($[\text{Na-C4ABS}] = 1.5 \text{ mol L}^{-1}$, reaction time = 2 h and reaction temperature = 60°C).

characteristic absorption bands were observed of the polysaccharide structure in FT-IR spectrum of sodium alginate at 1,100; 1,017 and 800 cm^{-1} Fig. 6. FT-IR spectrum of PNa-C4ABS showed bands at 3,349 and $3,263 \text{ cm}^{-1}$ that are

characteristic for stretching of amino group. The absorption bands at 1,625 and $1,698 \text{ cm}^{-1}$ indicate carbonyl groups of amide and carboxylic groups presence, respectively. SO_2NH_2 has absorption bands at 1,265 and $1,160 \text{ cm}^{-1}$ and

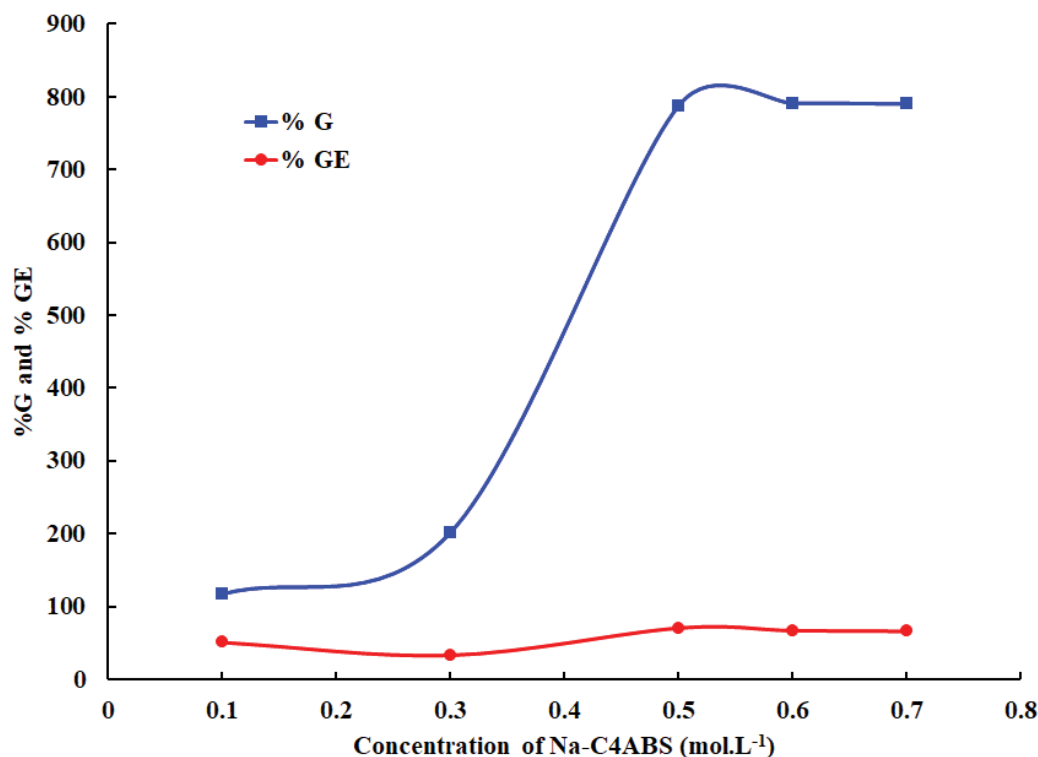


Fig. 5. The relation between the Na-C4ABS concentration and graft yield (G%) and graft efficiency (GE%) ($[K_2S_2O_8] = 8 \times 10^{-2} \text{ mol L}^{-1}$, reaction time = 2 h and reaction temperature = 60°C).

furthermore, two additional peaks at 846 and 625 cm^{-1} . IR spectrum of the grafted copolymer PNa-C4ABS-g-NaAlg (Fig. 6) shows also an overlapped broad band at $3,400\text{--}3,600 \text{ cm}^{-1}$ due to the existence of --OH stretching. For the NaAlg-g-PNa-C4ABS, the absorption bands at $3,675$ and $3,438 \text{ cm}^{-1}$ were referring to the stretching vibration of the NH_2 group in PNa-C4ABS incorporated with OH group of sodium alginate. At $1,019$ and 671 cm^{-1} , the peaks appear due to the presence of the bending vibration of the SO_2NH_2 group. The absorption bands at $1,431$ and $1,625 \text{ cm}^{-1}$ were assigned to the stretching vibration of aromatic ring in PNa-C4ABS. The distinctive peaks of PNa-C4ABS revealed in the FT-IR spectrum of graft copolymer spectrum NaAlg-g-PNa-C4ABS proved the successful grafting of Na-C4ABS onto sodium alginate.

3.6. Microstructure detection of the prepared grafted copolymers

Scanning electron microscope images of sodium alginate and grafted copolymers NaAlg-g-PNa-C4ABS (%G = 176% and 250%) are shown in Fig. 7a–c. Native surface of sodium alginate was observed to be smooth which changed as compared with the surface of the grafted samples as illustrated in Fig. 7a. In images of the grafted copolymers, it was found that PNa-C4ABS grafted chain has partially and completely covered the surface of sodium alginate with grafting percentage 176% and 250%, respectively (Fig. 7b and c). The crystals structure of graft polymer PNa-C4ABS onto sodium alginate surface resulting in surface porosity. This new surface structure gives the copolymer alginate-g-PNa-C4ABS its efficiency in water treatment.

4. Performance of grafted copolymers for application in water treatment

4.1. Dyes removal

The uptake capacity of grafted copolymers based on alginate and PC4ABS were investigated using Bismark brown and Congo red dyes as models of basic and acidic dyes, respectively. Concerning the uptake of basic dye which is Bismark brown, (Fig. 8), the data revealed the adsorption capacity for Bismark brown increases with increasing grafting percent of PC4ABS. That could be explained by increasing the percentage of PC4ABS leading to increase the number of free carboxylic groups which enables to form H-bond with amino groups on the Bismark brown. On the other hand, acidic dye which is Congo red, (Fig. 8), the dye uptake was not improved by increasing the acidic graft chains PC4ABS content onto alginate.

4.2. Heavy metal ions removal

The data reveals that grafted copolymers based on alginate and PC4ABS showed good efficiency for heavy metal ions uptake, as shown in Table 1. By comparing the adsorption of all the metal ions via grafted copolymers irrespective to the percentage of graft, it was found to be the highest metal ion is Cr^{6+} . The results showed that chromium has the highest percentage of removal which could be explained by the higher stability of the formed complexes between chromium metal ions and grafted copolymers.

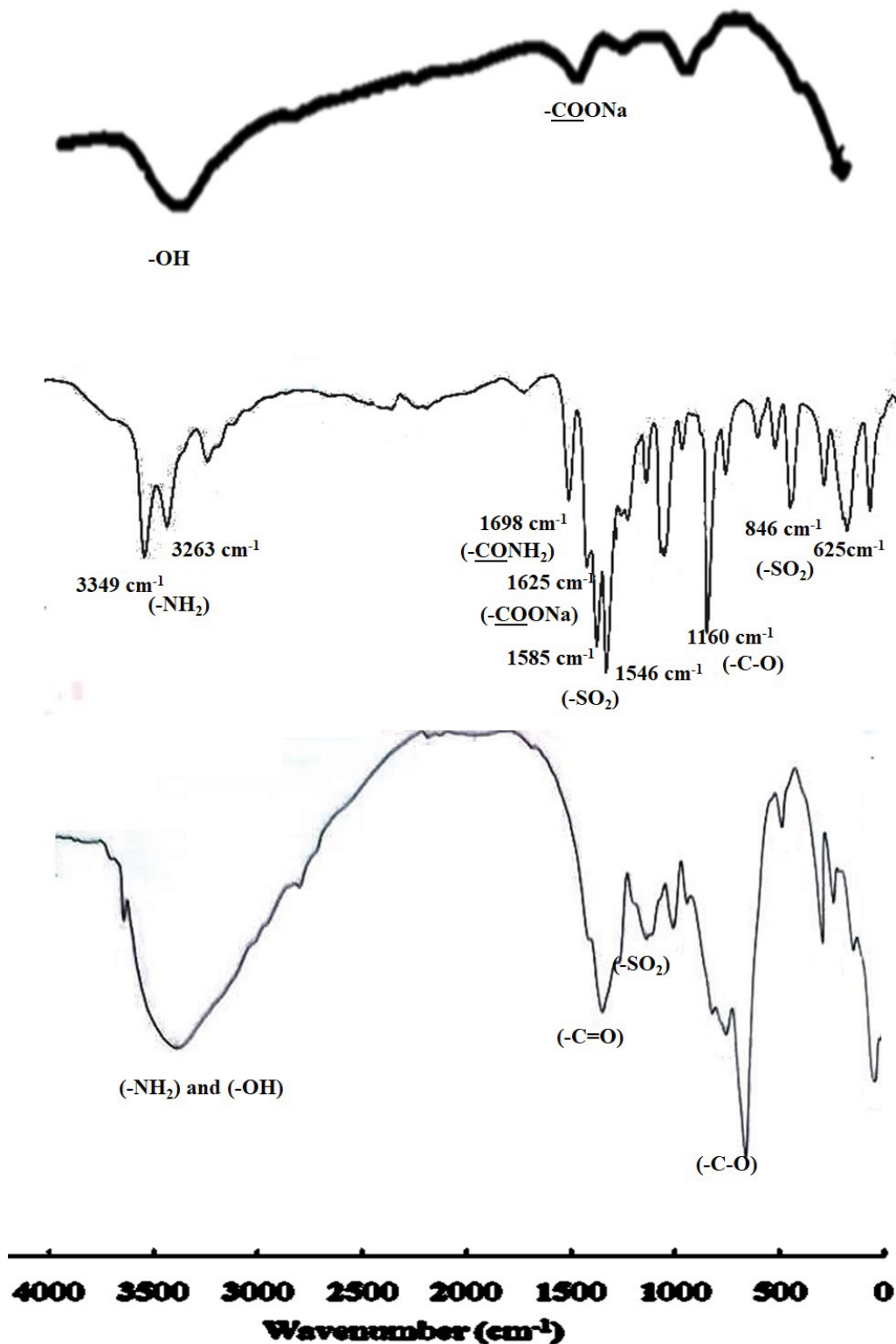


Fig. 6. FT-IR of sodium alginate, PNa-C4ABS and its grafted copolymer NaAlg-g-PNa-C4ABS.

5. Conclusion

Sodium alginate was modified using grafting technique. The prepared homopolymer (PNa-C4ABS) and grafted

alginate copolymer (NaAlg-g-PNa-C4ABS) were characterized using FT-IR. The effect of grafting parameters onto grafting process of the grafting was reported as monomer and initiator concentration, time and temperature.

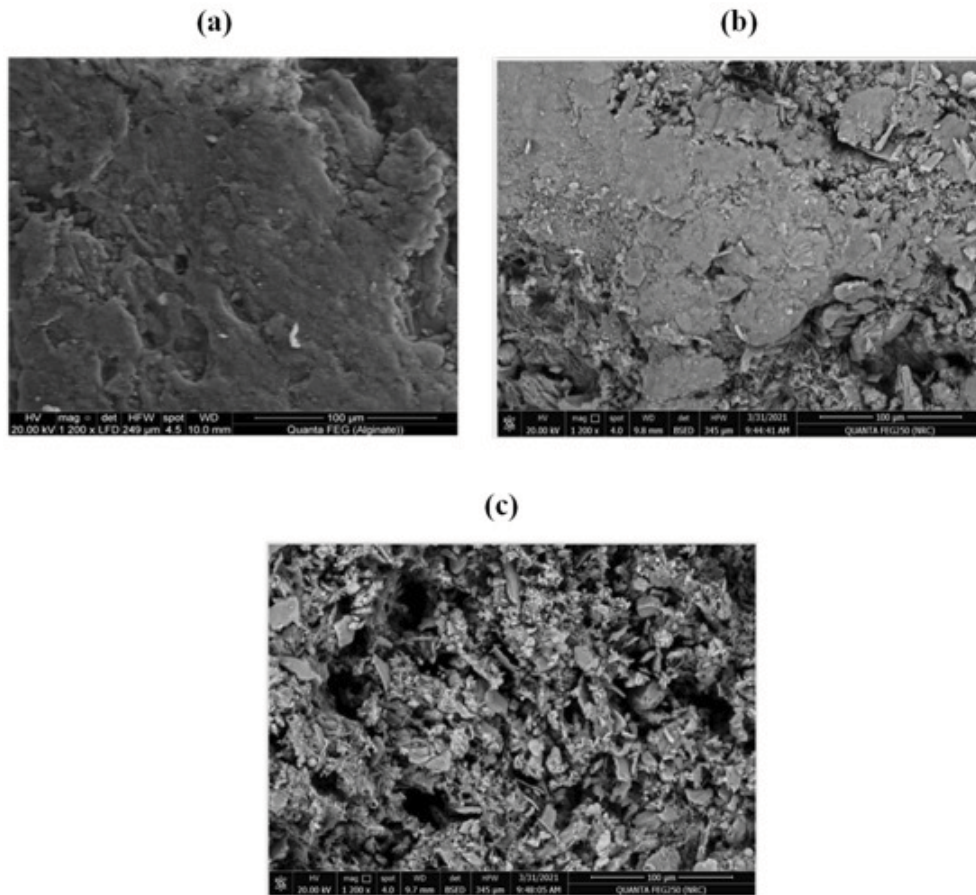


Fig. 7. SEM pictures of (a) sodium alginate and its grafted copolymers NaAlg-g-PNa-C4ABS with graft percent 176% (b) and 250% (c).

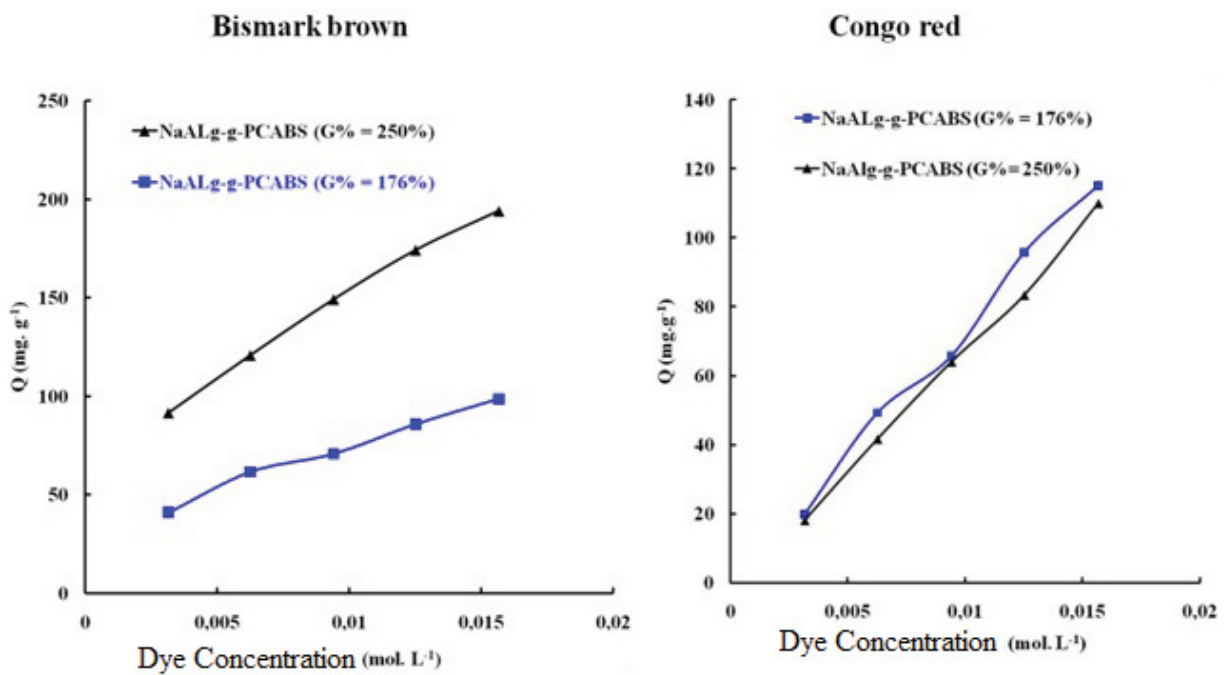


Fig. 8. Variation of the concentration of adsorbed dyes by grafted copolymers NaAlg-g-PNa-C4ABS with graft percent (b) 176% and (c) 250%.

Table 1
The removal of heavy metal ions by grafted copolymers NaAlg-g-PNa-C4ABS

NaAlg-g-PNa-C4ABS	Cu ²⁺	Ni ²⁺	Cr ⁶⁺	Co ²⁺
	Removal %			
176%	75	79	87	78
250%	73	78	85	76

SEM showed a change in the morphology of sodium alginate surface by grafting of Na-C4ABS. The original sodium alginate and grafted copolymer NaAlg-g-PNa-C4ABS have been examined for their application in water treatment.

The results were concluded as follows:

- Good absorption ability for Cu²⁺, Ni²⁺, Co²⁺, and Cr⁶⁺ ions. The grafted copolymer shows adsorption for both anionic and cationic dyes.
- A significant increase observed for cationic dye absorption with increasing grafting percentage.

The heavy metal ions removal and dye uptake tests revealed that the efficiency of sodium alginate to metal and dye removal was improved by Na-C4ABS grafting on its backbone.

Conflicts of interest

The authors declare no conflict of interest.

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