

Chitosan-g-poly(acrylamide)/Diatomite superabsorbent composites: synthesis and investigation of swelling properties

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Abstract — A series of intelligent superabsorbent polymers composites was prepared through free radical graft-copolymerization of acrylamide (AAM) onto chitosan backbone and crosslinking in absence and in presence of diatomaceous Earth (DE) as inorganic additive at different compositions in aqueous medium using potassium persulfate (KPS) and N,N'-methylenebisacrylamide (MBA) as initiator and crosslinker, respectively. These materials were also hydrolyzed to achieve superabsorbents with ampholytic properties. The structural characterization was realized by Fourier Transform Infrared Spectroscopy (FTIR) and the porous morphology was observed by scanning Electron Microscopy (SEM). The application of such superabsorbents as hygienic products has been prospected by studying the effect of DE content on the load-free swelling absorbency in deionized water and 0.9% saline solution, the Centrifuge Retention Capacity (CRC), and the Absorbency Under Load (AUL). The results have revealed that the optimized values of free-swelling and CRC were reached at 15 wt. % DE loading. Also, the presence of the inorganic additive within the network has improved the AUL values.

Keywords: superabsorbent composite, chitosan, free swelling capacity, CRC, AUL

I. Introduction

Superabsorbent polymers (SAPs) or hydrogels are crosslinked highly hydrophilic bicomponent systems that can hold a large amount of water and/or biological fluids [1]. They have large field of applications such as disposable diapers, and agriculture [2,3]. The hydrogels are commonly manufactured from synthetic polymers, but due to their superior price-to-efficiency balance and environmental protection, many researchers have supported the green approach to replace partially or totally the synthetic by natural polymers. The vinyl Graft-polymerization onto polysaccharide is well-known method for synthesis of natural-based superabsorbent hydrogels [4, 5].

Chitosan (CTS) is an amino polysaccharide produced from chitin, the most abundant biomass in the world. It has potential applications [6]. However natural-based SAPs have low gel strength that has restricted their applications. To overcome this limitation, low cost inorganic fillers were used such as montmorillonite, vermiculite, and attapulgite [7-9]. Diatomaceous Earth (DE) known as diatomite and kieselgur is a siliceous rock. DE is composed of the fossilized skeletal remains of microscopic single-celled aquatic plants called diatoms. DE has many applications such as absorbent, and filler and catalyst carrier [10] due to its unique properties, i.e. micronized porous structure, light weight, and chemical inertness. Following our previous report on SAPs composites [11-13], this paper is aimed to synthesize superabsorbent composites via radical copolymerization-grafting based on CTS and AAM at various DE contents. The effect of DE on swelling properties was

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examined. The commercial SAP (BASF) was used for comparison study.

II. Experimental section

II.1. Materials

Chitosan (Cs, 75 % degree of deacetylation, medium molecular weight, viscosity 200-800 cps). Acrylamide (AAm), potassium persulfate (KPS), N,N'-methylenebisacrylamide (MBA) were used as received. The diatomite (DE), from Algerian type Roussel in Sig, was supplied by ENOF chemical Ltd, algeria. Deionized water was used for synthesis and swelling studies.

II.2. Synthesis of superabsorbent composites

CTS-g-PAAm/DE superabsorbent composites were prepared at various DE contents (10, 15 and 20 wt.%) via graft-copolymerization of AAm monomer onto CTS and crosslinking in aqueous solution at 60 °C, as the procedure described in our earlier study [11]. An required amount of CTS (20 wt.%) was dissolved in 30 mL 1% (v/v) acetic acid solution in three-neck flask, equipped with reflux condenser and nitrogen line. After flask was placed in bath at 60 °C for 30 min under N₂ flux, and then KPS (2 wt.%) was added and the mixture was stirred for 15 min. The DE suspension was ultrasonically pre-treated for 30 min and was added to aqueous mixed solution of AAm (5g) and MBA (1wt %) and stirred for 30 min. Next, this suspension, previously purged with inert was added to the flask and stirred for another 3 h. The resulting gel was neutralized, washed repeatedly, dehydrated with methanol and dried in oven at 60 °C. Then, the dry hydrogel composite was hydrolyzed at 95 °C in alkaline solution, dewatered and dried in oven. Finally, the product was ground at particles size 30-50 mesh (300-600 μm) and stored away from moisture. Free-DE hydrogel was also prepared.

II.3. Morphological characterization

ATR-FTIR spectra were performed on Bio-Rad spectrometer model FTS-162. Morphology surface was observed with a Scanning Electron Microscope (SEM) HITACHI S-4800.

II.4. Free swelling study by Tea Bag Method

Tea bag (100 mesh nylon screen) containing an accurately weighed sample was dipped in deionized water or 0.9 % saline solution and allowed to soak for a desired interval time. Then, tea bag was hung up for 10 min. Finally, the

loaded tea bag is weighed and the free swelling capacity (Q) at t and t equilibrium was calculated by Eq. (1).

$$Q(\text{g/g}) = \frac{W_2 - W_0 - W_1}{W_1} \quad (1)$$

Where Q is water absorbency of xerogel sample, W₀ the weight of the tea bag alone (tare), W₁ the weight of dried sample, and W₂ the weight of both the tea bag and swollen sample.

II.5. Centrifuge retention capacity (CRC)

The sample (W₁) contained in bag was dipped in deionized water or saline solution and was allowed to equilibrate and then taken out. The excess fluid is removed with a centrifugation for 3 min at 1400 rpm/min. Then, the weight of filled bag (W₂) is measured. The same stages are carried out with an empty bag (W₀), and the The CRC is then calculated using Eq. 1.

II.6. Absorbency Under Load (AUL)

A macro-porous sintered glass filter plate (porosity # 0, d = 120 mm, and h = 7 mm) was placed in a Petri dish and a dried sample (0.9 ± 0.001 g) was uniformly placed on the surface of a polyester gauze located on the sintered glass. A cylindrical solid load (0.7 psi), which could slip freely in a glass cylinder, was applied to the dry sample particles. Then, a 0.9 % NaCl solution was added to the Petri disk. After interval time in hours, the swollen particles were weighed again, and the AUL was calculated using the Eq. (2).

$$\text{AUL}(\text{g/g}) = \frac{W_2 - W_1}{W_1} \quad (2)$$

Where, W₁ and W₂ are the weights of each sample in dried and swollen states, respectively.

III. Results and discussion

III.1. Structural study by FTIR-ATR

The superabsorbent composites are prepared by radical-graft polymerization and crosslinking of AAm onto CTS in presence of diatomite as filler. The formation pathway of the hydrolyzed network [11] and its DE-loaded composites is schematically outlined in Fig.1. The persulfate ions S₂O₈²⁻ decompose under heating, generate sulfate anion-radicals SO₄^{•-}, remove the hydrogen from OH groups of CTS and produce alkoxy radicals that initiate the AAm polymerization. The growth of PAAm led to the grafted network. Concurrently, the DE particles incorporate within the network to form the composite. As well,

during the hydrolysis, the ammonia evolves and carboxamide groups of PAAm are converted to carboxylate ions COO^- . Thus, the hydrolyzed CTS-g-PAAm comprises a CTS backbone with side chains having functional groups amine, carboxamide, and carboxylate, ensuing in grafted superabsorbent with ampholytic properties.

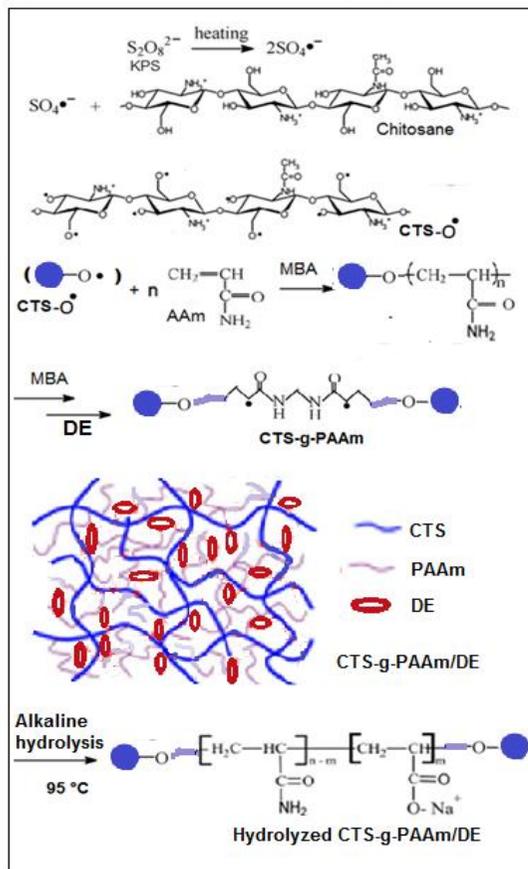


Fig. 1 Synthesis pathway of the hydrolyzed grafted CTS-g-PAAm/DE superabsorbent composites

Fig. 2 regroups the ATR-FTIR spectra of diatomite, grafted CTS-g-PAAm superabsorbent and its typical DE-loaded composite. The main chemical composition of the natural or calcinated diatomite contain Si and Al oxides ($\text{SiO}_2 \sim 76\%$, $\text{Al}_2\text{O}_3 \sim 15\%$). So, the spectrum of DE exhibits a large band centered at 3420 cm^{-1} due to $\nu_{\text{O-H}}$ of moisture, intense band at 1080 cm^{-1} ascribed to $\nu_{\text{Si-O}}$ of siloxane group, and a pick of low intensity at 798 cm^{-1} related to $\nu_{\text{Al-O}}$ in Al_2O_3 . In the other hand, it is obvious from the spectral comparison of the free network and its composite that all the bands are pronominally attributed to the grafted CTS-g-PAAm that overlapped those of the DE. These include mainly: the broad band

centered at 3370 cm^{-1} due to $\nu_{\text{N-H}}$ from amide and amine groups as well as $\nu_{\text{O-H}}$. The band at 1674 cm^{-1} ascribes to $\nu_{\text{C=O}}$ from acetyl and amide groups, and the bands at 1560 and 1406 cm^{-1} due to $\nu_{\text{C=O}}$ asymmetric and symmetric respectively, of carboxylate. [12]. The addition of DE causes an enhancement in the intensity ratio for the bands of carboxylate $\nu_{\text{C=O}}$ and $\nu_{\text{N-H}}$ and $\nu_{\text{O-H}}$. So, it is suggest that the entrapped DE particles within network develop interactions such as hydrogen bond with the network groups.

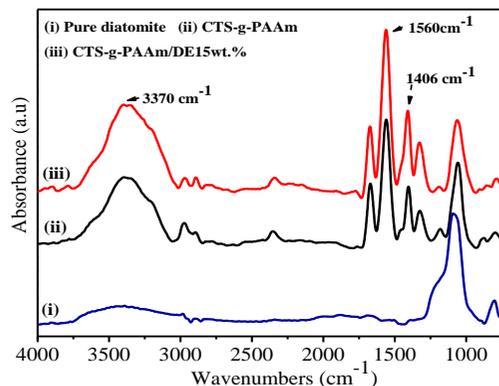


Fig. 2 FTIR-ATR spectra of diatomite, the hydrolyzed CTS-g-PAAm hydrogel, and its composite

III.2. Morphology study by SEM

SEM micrographs of CTS-g-PAAm and its composites with 15 and 20 wt. % DE contents were observed and are shown in Fig. 3. CTS-g-PAAm network displays a smooth and dense surface, whereas its composites exhibit relatively loose and coarse surfaces and some pores and gaps can be noticed. Higher pores are visibly observed in composite with 15 wt.% DE. It should be mention that the diatomite, used as received, has been calcinated at $900\text{ }^\circ\text{C}$ to obtain clean and clear porous structure. So, the presence of DE improves the porous morphology of the grafted network that is suitable for fluid uptake. Also, no phase separation is observed, which reaffirms the homogeneity of our composites.

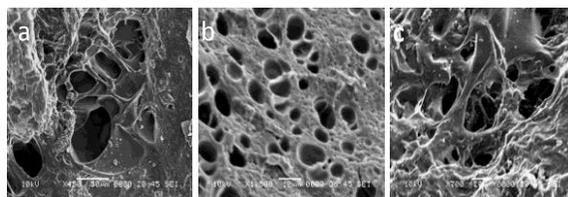


Fig. 3 SEM micrographs of (a) CTS-g-PAAm and its composites (b) 15 and (c) 20 wt.% of DE

III.3. Swelling properties

Fig. 4 (a,b) displays the effects of diatomite content on free-swelling capacities of CTS-g-PAAm network and its composites, together with commercial (BASF) SAP, in deionized water and 0.9 wt. % NaCl solution.

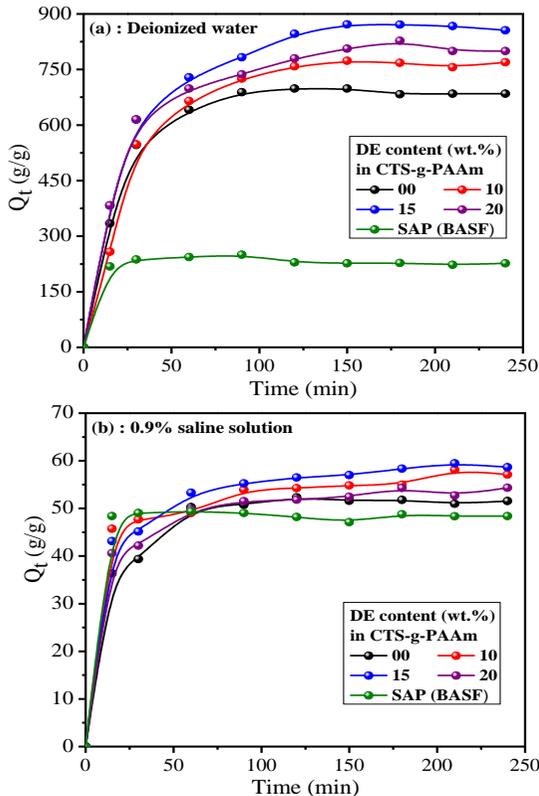


Fig. 4 Free-swelling kinetics of CTS-g-PAAm superabsorbent and its composites together marketed SAP in (a) deionized water and (b) NaCl solution

The free swelling of all increases with time contact until the equilibrium is reached (Fig.4a). Also, the water absorbency values are notably higher than those of free network and commercial SAP. The optimal value of Q is obtained for composite with 15 wt. % of DE content. Also, as the content of DE increase, the affinity for water is enhanced. However, at higher DE content, these particles may act as cross-linkers agents that generate more cross-linking density. The higher crosslinked structure cannot expand and led to low free-absorbency. Similar swelling behavior was reported for other inorganic clays [11,14]. Fig.4b shows similar trend in free swelling in 0.9 wt. % NaCl solution. Even if the absorbency values are close among

them, they still less than those obtained in water. This undesired swelling-loss in saline solution, which is often observed in ionic hydrogels, is due to the charge screening effect of the mobile Na^+ cations in the swelling medium, which shield the COO^- anions and reduce the anion-anion electrostatic repulsions. Thus, the osmotic pressure between the network and external solution decreases, and the absorbed water is driven out of network. It is, also, noticed that the swelling values of SAP (BASF) are still less than our elaborated materials.

Fig.5 presents centrifugal retention capacity of CTS-g-PAAm superabsorbent with varying DE loadings. Analogous retention trend is noticed in both media, while the resulted values are less in saline solution than in water. It is concluded that DE is an efficient additive that led to more porous structure, which promotes water diffusion through network, and thus improve the retention capacity of the grafted CTS-g-PAAm. The optimum CRC values are in presence of 15 wt.% of DE, Overall, the retention capacities of our materials are really higher than that the SAP.

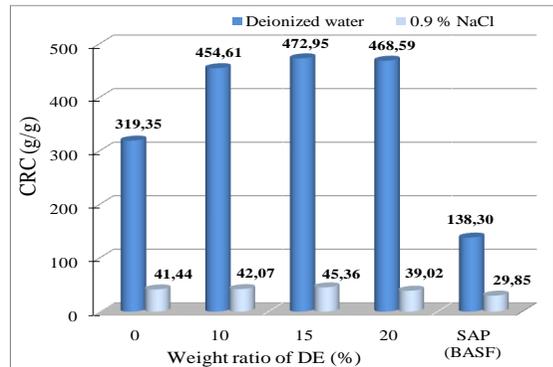


Fig. 5 Effect of diatomite content on CRC of CTS-g-PAAm superabsorbent hydrogel in deionized water and 0.9 wt. % NaCl solution

Fig.6 shows the AUL behavior of CTS-g-PAAm network and its composites, together with the commercial (BASF) SAP. A simple AUL tester (0.7 psi) is used to study the AUL that was monitored for 22 h. The saline swelling capacity under load of SAP is achieved during 1 h, whereas the grafted network and its loaded-DE composites display unlike behavior. Indeed, the related AUL values still increase gradually with time contact until the equilibrium is reached for 6h and they approximate the AUL of SAP. Also, these values increase with the DE content. Indeed, high AUL value is strongly related to

high value of saline load-free absorbency or with high mechanical strength [15]. So, at relatively higher content (20 wt.% of DE), these particles give rise to a higher cross-linking density, and in turn strengthen the swollen gels. This may lead to uppermost AUL values and lowest saline free-swelling and CRC values. As well, the AUL at lower content of DE is higher than the free network owing to its greater saline free swelling.

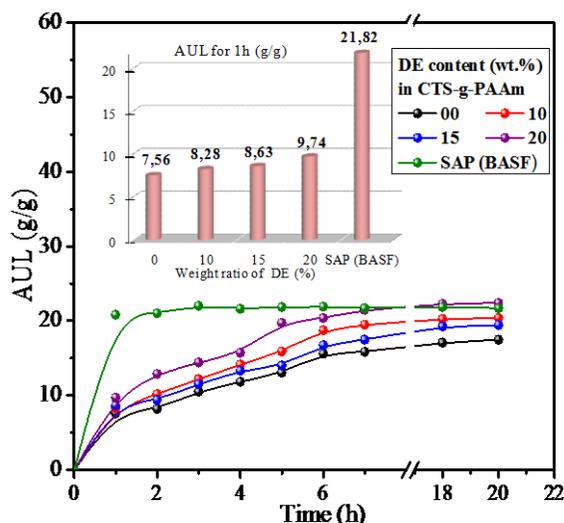


Fig.6 Effect of diatomite content on AUL of CTS-g-PAAm superabsorbent in deionized water and 0.9 wt. % NaCl solution

IV. Conclusions

Superabsorbent composites were successfully prepared via graft-copolymerization of AAm onto CTS in presence of diatomite. The addition of diatomite has provided an increase of both free-swelling in water and in 0.9 % NaCl solution and centrifugal retention capacity CRC. These values were decreased when the content of diatomite was over than 15 wt. %. The data of AUL have indicated that the inorganic content led to an increase in saline-absorbency load. However, the synthesis of a superabsorbent with high AUL value is still challengeable.

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