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Preparation and characterization of water-absorbing composite membrane for medical applications

Taher A. Salah El-Din[1], Ahmed A. Elzatahry[2,4]*,Sultan S. Aldeyab[3] and Elbadawy A. Kamoun[4]

[1]Regional Center for Food and Feed, Agricultural Research Center, 9 El Gamaa Street, Giza, Egypt.
[2]Petrochemical Research Chair , Department of Chemistry, Faculty of Science, King Saud University, Riyadh, Kingdom of Saudi Arabia.
[3]King Abdulaziz Medical City, Riyadh, Kingdom of Saudi Arabia.
[4]Polymer Materials Research Department, Advanced Technology & New Materials Research Institute (ATNMRI), City of Scientific Research and Technological Applications (SRTA-City), New Borg Al-Arab City 21934, Alexandria, Egypt.

The present work introduces a novel method for the formation of water absorbing composite membrane. The prepared composite is based on chitosan, carboxymethyl cellulose (CMC), and Montmorillonite. Prepared composite membrane exhibits high water absorbing and holding capacity with increasing clay content. The water absorbency was studied as a function of the hydrogel composition and the medium pH. Structure and morphologies of the prepared composite have been characterized by X-ray diffraction (XRD), and transmission electron microscope (TEM). TEM study showed that the formed membrane is homogenous and prepared uniformly.

Key words: Composite, clay, superabsorber, chitosan, carboxymethyl cellulose, composite membranes.

INTRODUCTION

Polymers have been extensively used as superabsorbent due to its hydrophilic network structure resulting from the different degree of crosslinking (Yu et al., 2009; Omidian 2005). It can absorb and retain high amounts of aqueous fluids up to 100 times of their dry weight. These materials have been used as hygienic products (Zamani et al., 2010; Li et al., 2007; Kabiri et al., 2003; Zhang et al., 2006), drug-delivery systems (Sadeghi and Hossein zadeh, 2008), and agriculture applications (Liang et al., 2009). Several polymers have been used as superabsorbent, such as synthetic polymers (Li et al., 2007; Doorkosh et al., 2000), and natural polymers (Yu et al., 2009; Doorkosh et al., 2000; Raju et al., 2003). Chitosan (CHI), a polysaccharide natural polymer, derived chemically from chitin, has been used as an effective hydrogel due to the presence of amino and hydroxyl groups in its backbone chain. It shows interesting chemical and biological properties such as

chelation ability, low toxicity, biocompatibility, and biodegradability. Superabsorbent with antibacterial activity has been made from chitosan and used in different products (Wang et al., 2010). Cellulose, the most abundant natural polymer, is a biodegradable and bio-compatible polymer that has many drawbacks, such as poor solubility in water and poor activity. These draw backs have been overcome by modification of cellulose to produce different derivatives. One of these derivatives is carboxymethyl cellulose (CMC), which is prepared by an alkali catalyzed reaction of cellulose backbone. The high reactivity and the hydrophilic nature make the carboxymethyl cellulose a good candidate for super-absorbent applications (Wang et al., 2010). In the meantime, clay has been used to improve the mechanical properties and to enhance the physicochemical pro-perties of many superabsorbents (Pang et al., 2007; Zhang et al., 2007; Lee and Chen, 2005; Neaman et al., 2004; Lin et al., 2001). Most of the super-absorbent materials are based on synthetic petroleum-based materials, which have dangerous environmental impact and high-cost production. Therefore, there is an urgent need to develop new superabsorbent materials based on

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*Corresponding author. E-mail: aelzatahry@ksu.edu.sa. Tel: +966 544 20 30 28. Fax: +966 1 4675992.

natural resources, which will be able to absorb and hold body fluids such as urine, menses, or blood, under pressure exerted by the user.

The goal of this work is to develop a new composite in a membrane form, that have a high-water absorbency and holding capacity for low cost disposable personal-care and medical applications. The prepared membrane should be able to absorb and hold body fluids such as menses, urine, and blood. Also, the antibacterial nature of chitosan, the main component of the prepared membrane, may extend for wound dressing applications. This has been achieved by preparing chitosan, carboxymethyl cellulose and clay in a uniform matrix. Nanobentonite with different weight percentages has been added to the composite structure. Furthermore, the effect of pH on the formed composite has been studied to find the optimum applicable conditions for the formed materials.

MATERIALS AND METHODS

Chitosan with a medium molecular weight and a degree of deacetylation of 85%, and sodium carboxymethyl cellulose, with an average molecular weight of 90000 g were purchased from Sigma-Aldrich (Germany). Clay was obtained from Egypt Nano Technologies Company (Alexandria, Egypt). All other reagents used in the experiments shown here were of analytical grade.

Preparation of composite hydrogel

1 wt% chitosan solution was prepared by dissolving chitosan in 1% acetic acid solution at an ambient temperature, with stirring for overnight to produce 2% wt/v chitosan solution. Different amounts of clay corresponding to 0, 2.5, 5 and 10 wt% was added slowly to a chitosan solution, as prepared before, with vigorous stirring for 24 h and casted in a Petri-dish at an ambient temperature for 24 h, and heating at 40°C for 4 h. After that, membranes were soaked in 1 wt% Na carboxymethyl cellulose solution for 24 h. Next, the membranes were removed, washed with distilled water several times and dried in a vacuum oven at 40°C.

Transmission electron microscope (TEM)/x-ray diffraction (XRD) characterization

TEM analysis was done using a Philips EM 400 at an acceleration voltage of 200 kV. All images were taken at a magnification of 130000. On the other hand, powder XRD data were collected on PANalytical: X'Pert PRO diffractometer using Cu Kα radiation source for the investigation of structure and phases with a scanning rate of $0.07° s^{-1}$ in a 2θ range from 20 to 80°.

Water absorbency

The water absorbing capacity of the prepared composite membranes was determined by using a gravimetric method according to method described by Liuyun et al. (2009). In a typical experiment, 0.05 g of composite membrane with $3 \times 3 cm^2$ in size was dried in a vacuum oven at 40°C to a constant weight (noted as W_0), then immersed in excess distilled water (1000 ml) for 24 h until the membranes adsorbed water to equilibration, and the samples were removed from the fluid, cleaned with filter paper to get rid of water on the surface and weighed again (noted as W_1). The water

absorbency of the prepared composite membranes (Qeq) is calculated based on the formula; Qeq (%) = $(W_1 − W_0) / W_0 \times 100\%$. Five specimens were measured for each membrane to obtain an average value.

Effect of various pH solutions on water absorbency

Water absorbency at different pH solutions is determined similar to that of above measurement, and pH values of the external solution were adjusted by addition of 0.1 mol L^{-1} HCl and 0.1 mol L^{-1} NaOH solutions.

Dehydration (stability test)

0.05 g of each composite membrane with $3 \times 3 cm^2$ in size were dried in a vacuum oven at 40°C and after that, immersed in excess distilled water (1000 ml) for 24 h until the membranes adsorbed water to equilibration, and the samples were removed out from the fluid, cleaned with filter paper to get rid of water on the surface and weighed again (noted as W_0), which is proportional to 100% hydration. Same sample was centrifuged at 2000 rpm for pre-scheduled time intervals between 5 and 20 min, then samples were removed out from the centrifuge, cleaned with filter paper to get rid of water on the surface and weighed again (noted as W_1), where it is proportional to different samples' weight at different interval times. The rate of water loss or dehydration percentage (D) is calculated based on the formula of $D = (W_0 − W_1) / W_0 \times 100\%$, where W_0 and W_1 denote the weights of sample before and after centrifuging, respectively. Five specimens were measured for each membrane to obtain an average value.

RESULTS AND DISCUSSION

Transmission electron microscope (TEM)/x-ray diffraction (XRD) characterization

Clay exhibits a random distribution within the composite membrane with an average size of 260 nm, which can be confirmed by TEM in Figure 1. As can be seen from Figure 1, the formed membrane is homogenous and prepared uniformly. Figure 2 shows the XRD patterns corresponding to the used clay, the pure composite membrane (chitosan/carboxymethyl cellulose), and the final composite membrane (chitosan/carboxymethyl cellulose/clay). On another hand, it can be seen that the clay patterns showed that the used clay is mont-morillonite. The sum of reflection intensities at 2θ of 6.297, 19.819, and 36.022°, are corresponding to (0 0 1), (0 0 3), and (2 0 0) planes of a monoclinic crystal system, which was confirmed by comparing the standard data for montmorillonite (ref: 00-060-0318). Also, it can be seen that the characteristic peaks of montmorillonite in the (Chitosan/CMC/Clay) composite disappeared due to the incorporation of used clay within the polymer composite layers. This could be explained as a result of different stages of the preparation process, where first stage involved the formation of a homogenous mixture of chitosan/clay, which has been casted in a membrane form, followed by coating with CMC solution as final stage of composite formation as shown in Figure 3.
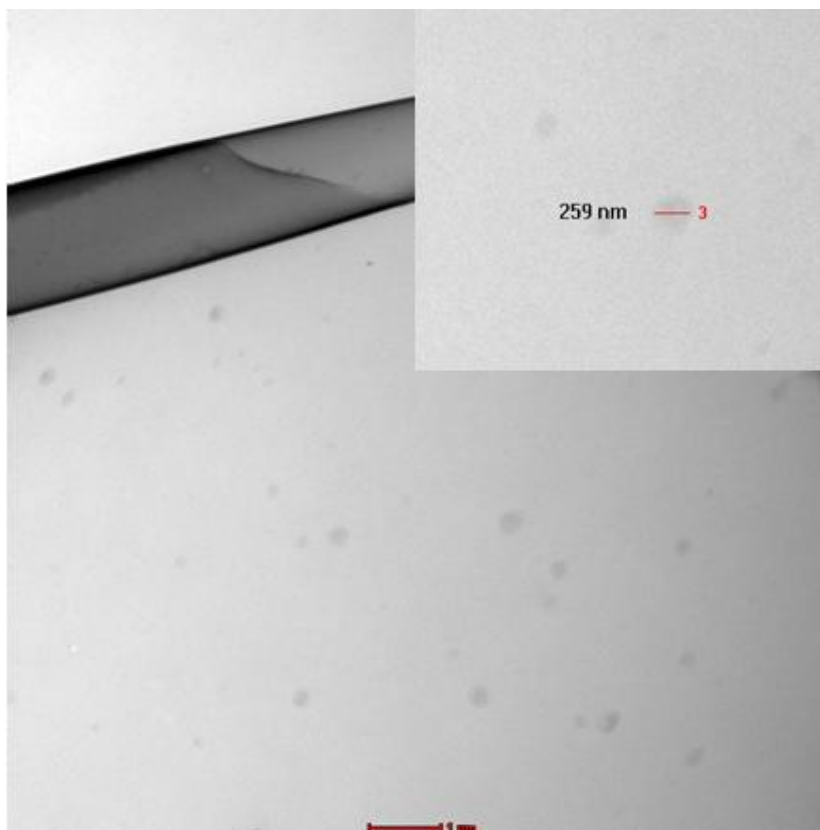
Figure 1. TEM images of chitosan/CMC/clay composite membrane, 5 wt% clay.
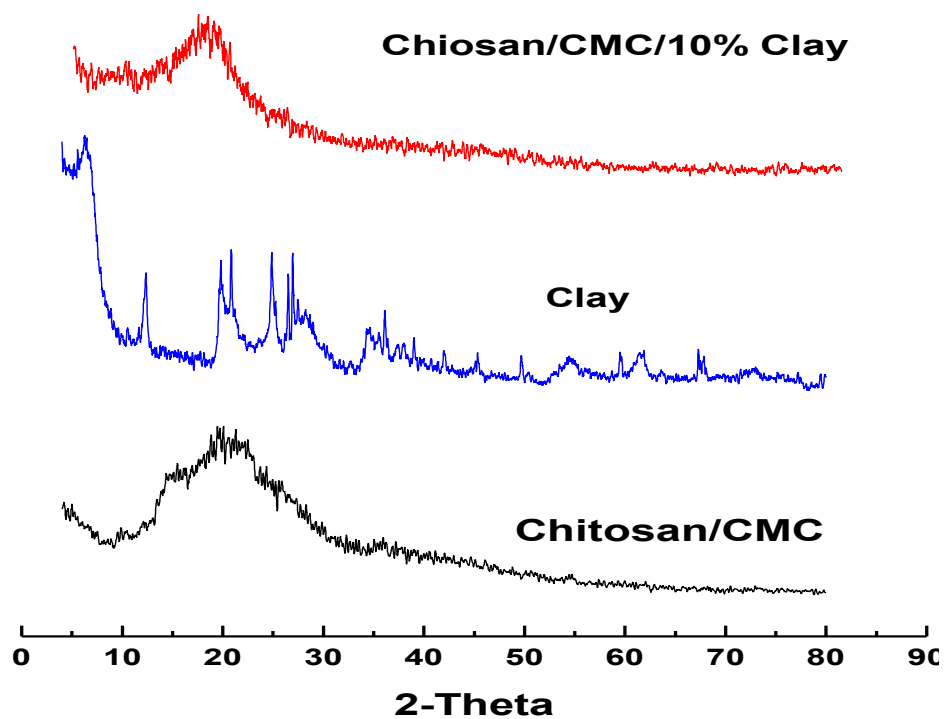

Figure 2. XRD patterns of pure composite (chitosan/carboxymethyl cellulose), clay and composite (chitosan/carboxymethyl cellulose/clay).
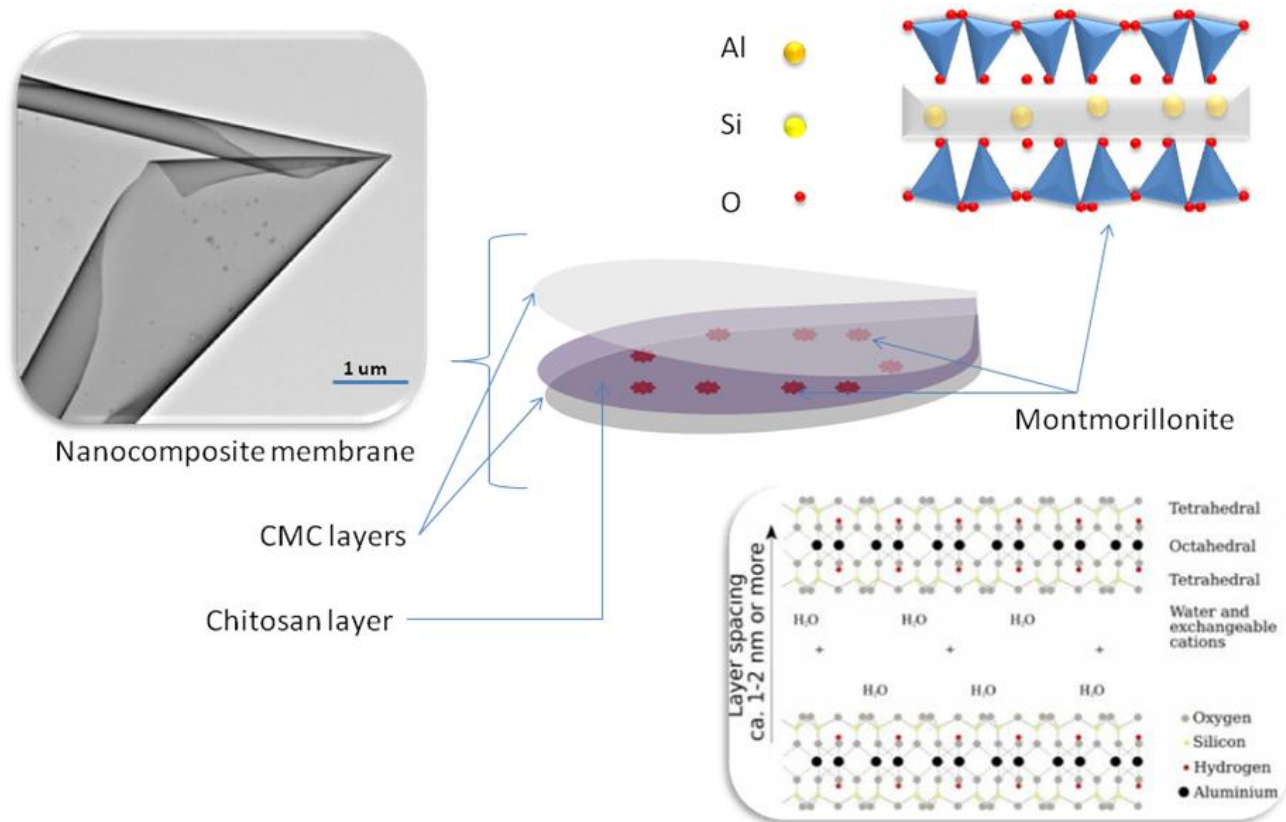
Figure 3. Proposed structure of the prepared composite membrane (chitosan/CMC/clay).

Water absorbance capacity

The influence of the different clay content on water absorbency of prepared composite membranes was exhibited in Figure 4. The water absorbency increases with increasing clay content from 0 to 10%. This can be explained according to the nature of the used clay, montmorillonite, which has a structure composed of a layer of octahedral sheet of alumina sandwiched between two layers of fused silica tetrahedral sheets, and it was previously reported that water molecules can easily penetrate between these layers due to the weak intermolecular force between the layered sheets which leads to an expansion of the whole lattice, and the occupation of water (Dalaran et al., 2011) (Figure 3). Also, it is noticeable that the membrane composite with 0% clay content had water absorbency of 60% since both of chitosan and carboxymethyl cellulose are hydrophilic polymer.

Effect of pH

Figure 5 shows the behavior of the prepared composite for water-holding capacity at different solutions' pH values. The interaction between carboxymethyl cellulose and chitosane is formed through ionic interaction between the positively charged nitrogen atoms on chitosan and the negatively charged carbonyl groups on carboxymethyl cellulose, considering that pKa values of the carboxyl groups in carboxymethyl cellulose and the amino groups in chitosan are 3.9 and 6.5, respectively. It was reported that "viscosity measurements dramatically increased between pH 4.0 and 4.5, indicating that polymer chains stretched above pH 4.0 due to the dissociation of carboxyl moieties. Also, same results were reported for chitosan below pH 6.5 due to complete dissociation of amino groups (Kaihara et al., 2011). However, the presence of clay will moderate and enhance, to a certain limit, the ability of water-holding capacity. On another hand, going above a pH value of 6, and due to the electrostatic repulsion of protonated amino groups of chitosan within polymer layers, less compact polymeric structure, and possible presence of voids will be presented, which eventually enhance the swelling and water absorption capability.

Stability

To investigate the water-holding stability of the composite membrane, monitoring the water-loss of the composite
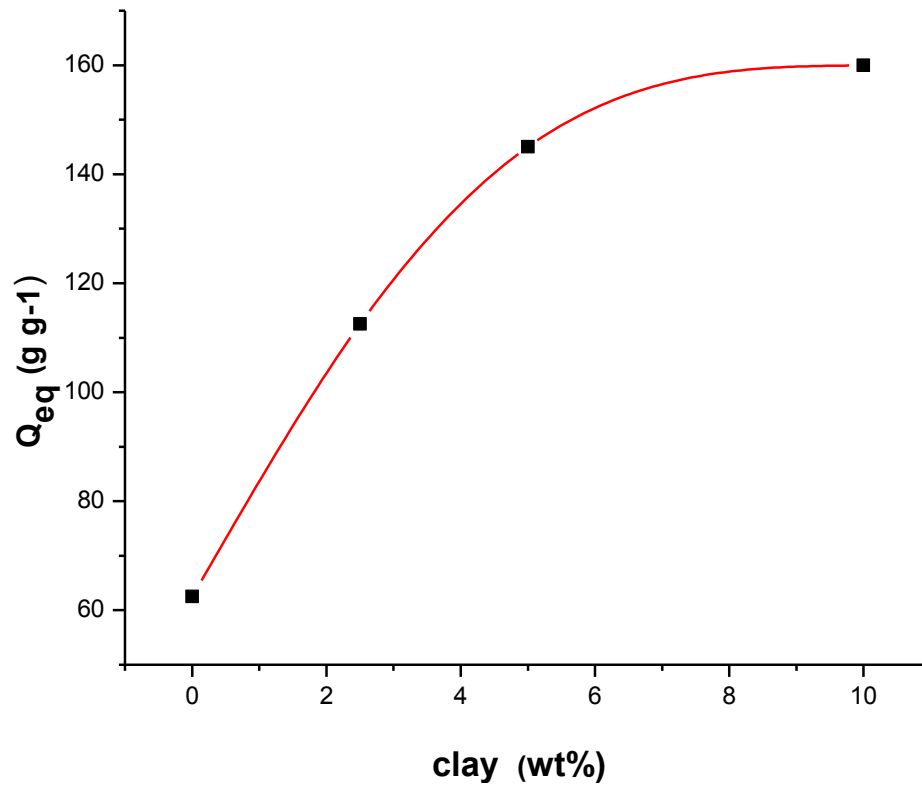
Figure 4. Variation of water absorbency for the membrane composites with different treatment clay content.
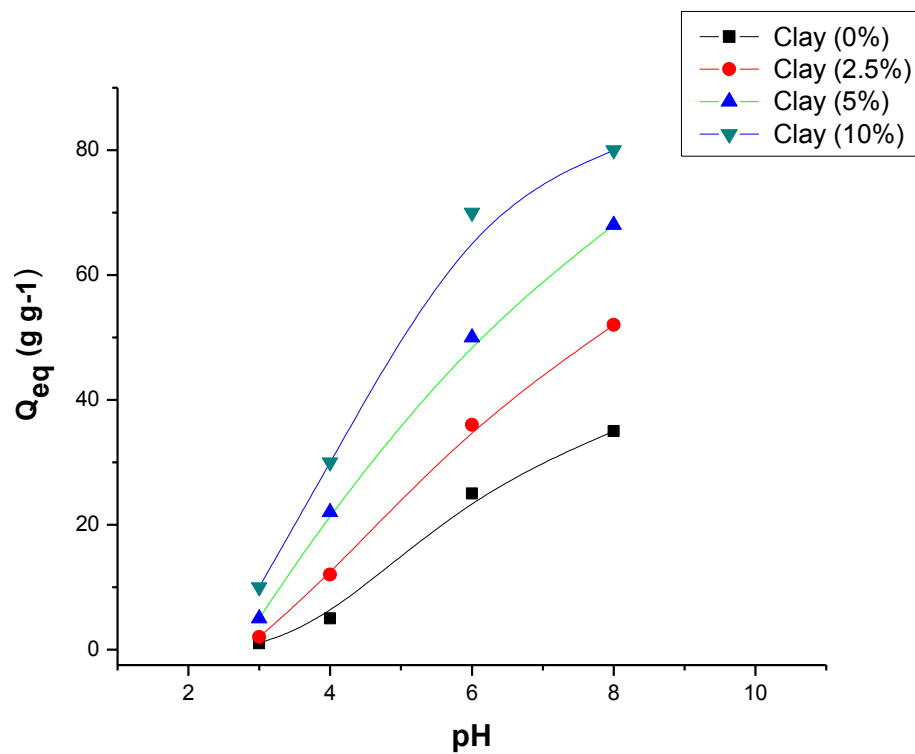

Figure 5. Variation of water absorbency for the membrane composites with different pH of external solution.
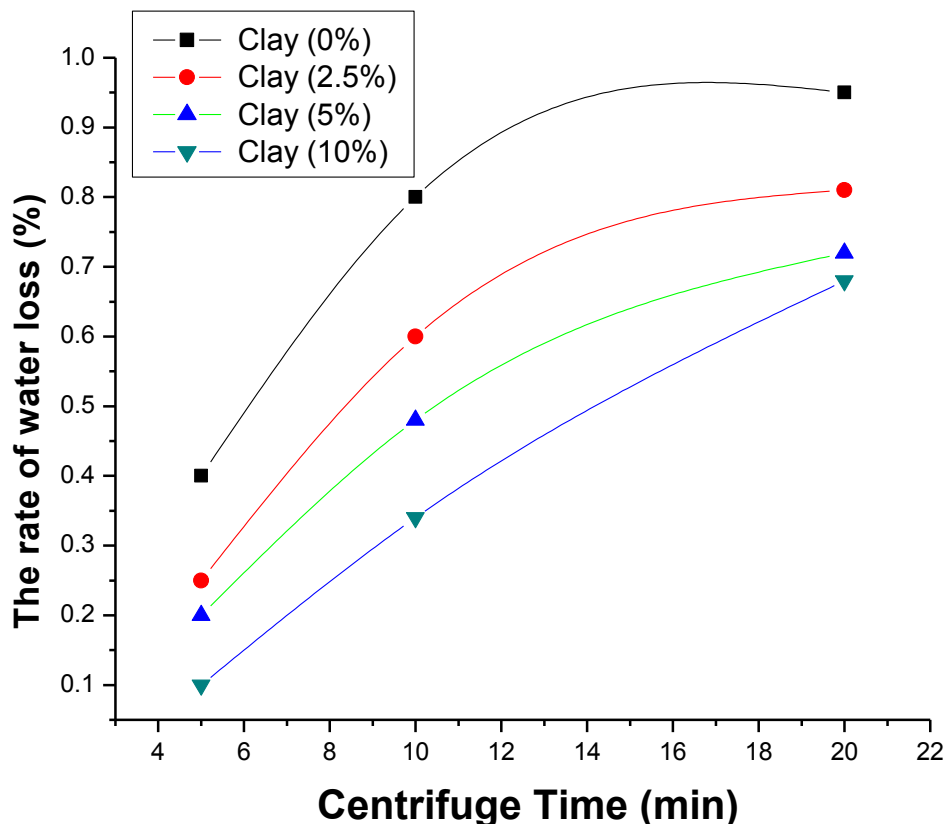
Figure 6. The effect of centrifuge time on the dehydration of composite membrane.

membrane is a reliable method. In this study, a significant amount of water was expelled, and shrinking of the prepared samples has been observed when the hydrated membrane samples have been subjected to 2000 rpm centrifugal force. Figure 6 shows the effect of centrifuging time on the ability of prepared composite membrane to hold and reserve water. The rate of water dehydration increases with increasing the centrifuge time as a result of the gradual increase of the centrifuge squeezing force. At the same time, resistivity of water samples for dehydration has been observed with increasing the amount of clay percentage that is, the presence of clay material, not only enhances the absorption of water but also resists losing water easily due to its presence in between polymeric chain network, which narrows the polymeric network windows, and not facilitate the release of water from the composite polymeric matrix.

Conclusion

Composite membranes (Chitosan/CMC/Clay) have been prepared by a simple chemical route. They showed a high holding and absorbing water capacity, their sensitivity for pH medium and absorbing efficiency varies according to the clay loading percentage. The prepared

composite membranes give an example of a super biodegradable absorber for medical applications such as medical spills and human fluids.

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