

Experimental evaluation of the stability of chitosan based biocomposites under various environmental conditions

*Wondalem Misganaw Golie and M.A. Azaz Ahmed

Department of Chemical Engineering, College of Engineering, Ethiopian Defence University, Bishoftu, Ethiopia

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ABSTRACT

Chitosan is naturally derived polysaccharide and has various engineering applications. However, chitosan in its original form is not suitable for practical use due to its sensitivity to wide range of pH and has poor morphological properties and low mechanical stability. The properties and performance of chitosan could be improved by crosslinking and formation of composites using appropriate additives. In this study, an eco-friendly chitosan based crosslinked organic-inorganic hybrid biocomposites, such as chitosan/bentonite(ChBT), chitosan/titanium oxide (ChTi), and chitosan/alumina (ChAl); were prepared and the stabilities of the prepared biocomposites were evaluated under acidic and aqueous environments. The stabilities of the prepared biocomposites were evaluated under acidic and aqueous environments. Stability of ChBT, ChTi, and ChAl in acidic solution increased with increase in crosslinker and inorganic doses. Similarly, the stability of the prepared biocomposites increased in aqueous environment. ChAl has shown the highest stability in both conditions.

Key words: Biocomposites, Chitosan, Crosslinking, Hybrid, Stability evaluation

Introduction

Many of the well-established materials, such as metals, ceramics or plastics cannot fulfill all technological desires for the various new applications. Scientists and engineers realized early on that mixtures of materials can show superior properties compared with their pure counterparts. One of the most successful examples is the group of composites which are formed by the incorporation of a basic structural material into a second substance, the matrix. A major attraction of such research activities is to combine these desired advanced properties in the organic/inorganic hybrid materials, which can even be improved in comparison with the intrinsic properties

of each component. Hybrid materials have wide range of applications in environmental engineering, such as air pollution control, water and wastewater treatment, removal of organic contaminants from water, removal of inorganic pollutants (cations and anions), and recovery of precious metals from water and wastewater, recovery of nutrients from water and wastewater (Michalak *et al.*, 2013), (Perju and Dragan, 2010).

The interest in natural polymers has increased substantially over the last three decades. Recently, great attention has been driven towards the natural materials and their derivative products, such as cellulose, lignin, starch, alginate, gelatin, chitin, and chitosan for various environmental engineering ap-

plications (Gadd, 2009), (Fomina and Gadd, 2014), (Kuyucak and Volesky, 1988). Among these biomaterials, chitosan has received wide attention in the environmental engineering field as effective biosorbents for the removal of various aquatic pollutants. Chitosan is a natural amino polysaccharide produced from N-deacetylation of chitin. The primary source of raw materials to produce chitin and its N-deacetylated derivatives are wastes of the fishing industry. Exoskeletons of marine organisms, including shrimp, crab, crayfish, krill, squid, are widely used for this purpose. The process of chitin extraction and its transformation into chitosan includes three major steps: demineralization, deproteinization, and deacetylation. Demineralization step is used to remove the calcium carbonate and calcium chloride, which are the main inorganic constituents of the exoskeletons of crustaceans. Currently, there are two well-known methods of chitosan preparation. The first approach is to extract chitosan directly from cell walls of molds. The second approach utilizes thermo-chemical or enzymatic methods of chitin deacetylation to remove the N-acetyl groups from chitin (Rinaudo, 2006); (Rocha *et al.*, 2016); (Ravi Kumar, 2000); (Wan Ngah *et al.*, 2011); (Bhatnagar and Sillanpää, 2009). The unique features of chitosan include, being readily available, low cost, non-toxic, biodegradability, biocompatibility, and reactive as well as adsorptive properties, resulting from the presence of high contents amino and hydroxyl functional groups in the polymer chain (Wan Ngah *et al.*, 2011); (Bhatnagar and Sillanpää, 2009); (Kyzas and Bikiaris, 2015).

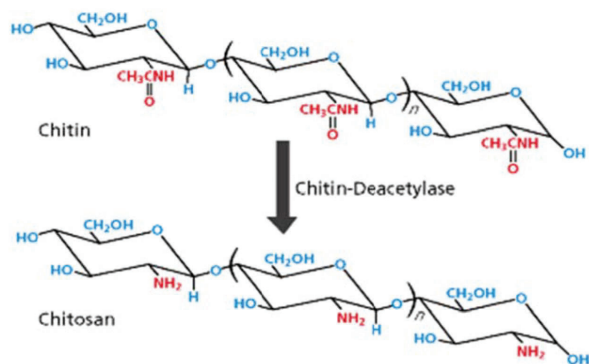


Fig. 1. Preparation of chitosan by N-deacetylation of chitin [6]

However, chitosan in its original form is not suitable for practical use due to its sensitivity to wide range of pH and relatively low sorption perfor-

mance. Moreover, chitosan has poor morphological properties and low mechanical stability, which cause a significant pressure drop which would affect filtration, possible obstruction, and is difficult to regenerate in the packed column operation, and finally, these properties restrict its field applications (Rangel-mendez *et al.*, 2010).

Chitosan needs certain modifications to overcome the above mentioned limitations to increase the stability of the material in acid media (good mechanical properties, etc.), and to enhance the sorption performance, including sorption capacity, selectivity, good diffusion and hydrodynamic behaviour (Bhatnagar and Sillanpää, 2011), (Liu and Zhang, 2015), (Arora *et al.*, 2010); (Wang and Chen, 2014). The easy separation from real effluent after treatment and the cost effectiveness of the sorbents preparation are also important. Thus, chitosan modification by introducing the desired properties in physical, chemical, and mechanic properties is key issues in order to enhance its contaminant sorption capacity, to improve its affinity for the specific ions, to change the selectivity series for ion sorption, and to alter the optimum pH range. Modification of chitosan molecule by grafting, cross-linking, or functionalization for forming composites leads to the formation of chitosan derivatives with superior properties, (Loganathan *et al.*, 2013); (Loganathan *et al.*, 2013), (Viswanathan and Meenakshi, 2010), (Samatya *et al.*, 2007).

Particularly, in the environmental engineering field, chitosan has been applied for the removal of innumerable noxious contaminants (Sulak and Yatmaz, 2012). However, instability in acidic conditions, easy agglomeration, poor mechanical strength, and low density of chitosan limits its field application (Rangel-mendez *et al.*, 2010). The applicability and effectiveness of chitosan in a wide pH range and its mechanical strength can be enhanced by producing crosslinked chitosan biocomposites (Kyzas and Bikiaris, 2015). Moreover; cross-linking may improve the reusability of the biosorbent, (Hu *et al.*, 2015). Sorption capacity of chitosan can be enhanced by chemical modifications, like protonation of the amino groups in the chitosan molecules (Loganathan *et al.*, 2013). In recent years, there has been considerable interest in chitosan based composites composed of polymer matrix and inorganic particles for its application in the removal of different pollutants from aquatic environment (Golie and Upadhyayula, 2016); (Rajiv Gandhi *et al.*, 2010),

(Zhang *et al.*, 2012). A major attraction of such research activities is to combine these desired advanced properties in the organic/inorganic hybrid materials, which can even be improved in comparison with the intrinsic properties of each component (Golje and Upadhyayula, 2017). Bentonite, titanium oxide, and alumina are attractive immobilization materials for chitosan due to their low cost as well as chemical and mechanical stability. On the other hand, polymer component of the composites offers structural flexibility, convenient processing, and binding of nanoparticles of an inorganic component. Furthermore, chitosan composites exhibit high adsorption capacity and resistance to acidic environment (Dinu and Dragan, 2010).

The main objectives of this work is to prepare an eco-friendly chitosan based organic-inorganic hybrid biocomposites, such as chitosan/bentonite, chitosan/titanium oxide, and chitosan/alumina; and to evaluate the stability of the prepared biocomposites in acidic and aqueous environments.

Methodology

Materials

For the preparation of chitosan based organic-inorganic biocomposites, chitosan pure (85% deacetylated and M.W 193400 g/mol) and potassium nitrate were purchased from Sisco Research Laboratory (SRL), New Delhi (India). Alumina, bentonite powder, titanium oxide, and glutaraldehyde solution (25%) were purchased from Central Drug House (CDH), New Delhi (India). Glacial acetic acid and sodium hydroxide were purchased from Fisher Scientific, New Delhi (India). Hydrochloric acid (GR, 35%) was purchased from Merck, New Delhi (India).

Preparation of organic-inorganic hybrid biocomposites

The chitosan based crosslinked organic-inorganic hybrid biocomposites were prepared by dispersing different selected inorganics, such as bentonite, titanium oxide, or alumina powder into chitosan solution at different organic to inorganic ratio with modifications of the procedure of previous report (Golje and Upadhyayula, 2016), (Golje and Upadhyayula, 2017). Protocols for preparation of chitosan based crosslinked organic-inorganic hybrid biocomposites is shown in the following Figure.

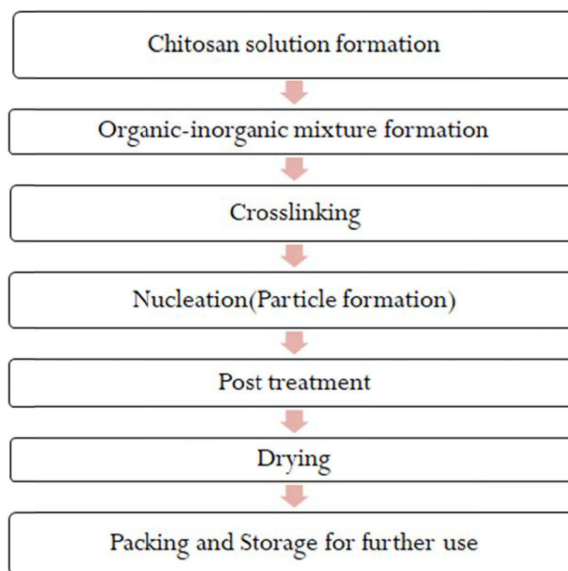


Fig. 2. Flow diagram of chitosan based crosslinked organic-inorganic hybrid biocomposites preparation

The prepared biocomposites were denoted as follows.

1. Chitosan/bentonite referred to as ChBT
2. Chitosan/titanium oxide referred to as ChTi
3. Chitosan/alumina referred to as ChAl.

Stability evaluation

The main drawback of chitosan is its low stability under various environments and poor performance. To improve the stability and performance of chitosan, the original material was modified by crosslinking and composite formation. The stability of the modified chitosan was investigated under various environmental conditions.

The stability of the biocomposites in acidic environment was studied based on weight loss after treatment with HCL solution. In this study, known quantity of biocomposite was immersed in 1 M HCL solution and magnetically stirred at 323 K for 1 h. After acid treatment, the samples were collected, dried at 333 K for 24 h and weighed. The stability of the biocomposite was evaluated on the basis of weight loss (%) of using the following expression.

$$\text{Weight loss (\%)} = \left(\frac{W_i - W_f}{W_i} \right) \times 100 \quad \dots (1)$$

Where W_i and W_f are initial weight of dry biocomposite and final weight of dried biosorbent after acid treatment, respectively.

To investigate stability of biocomposites in aqueous solution, 0.4 g of completely dried sample was immersed in 200 mL deionized water and kept at room temperature for a period of 24 h under static condition. Swollen sample was then separated from unabsorbed water by vacuum filtration through Whatman TM filter paper. After weighing the swollen sample, swelling ratio (%) of the biocomposite was derived from the mass change before and after swelling, and calculated using the following equation.

$$\text{Swelling ratio (\%)} = \frac{(W_s - W_d)}{W_d} \times 100 \quad \dots (2)$$

where W_d and W_s are the weights of the dry sample and the swollen sample (g), respectively.

Results and Discussion

Stability evaluation in acidic environment

The effects of crosslinker and inorganic dosages on the stability of ChBT, ChTi, and ChAl biocomposites in acidic solution are illustrated in Figure 3 and 4. The results show the weight loss of chitosan based organic-inorganic hybrid biocomposites decreased drastically as the crosslinker dose is increased. This indicates that the stability of the biocomposites in acidic solution increased with increase in crosslinker (Figure 3). Similarly, the weight loss of the three biocomposites decreased with an increase of inorganic dosages (Figure 4). In both cases, ChAl has shown the highest stability among the three biocomposites. From the results, it can be concluded

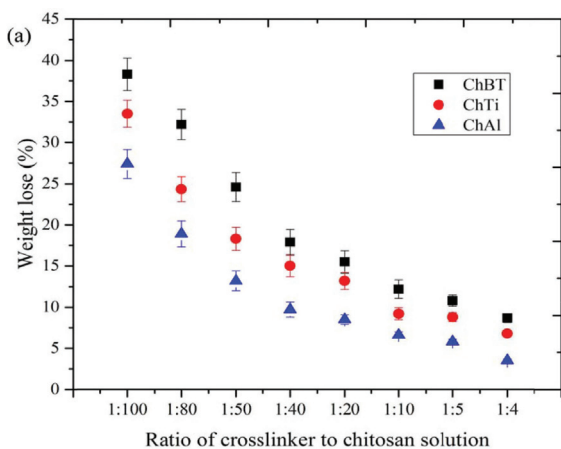


Fig. 3. Effect of crosslinker dose on the stability of ChBT, ChTi, and ChTi biocomposites in acidic environment

that the stability of chitosan under acidic environment can be modified and improved by using appropriate crosslinking and composite formation.

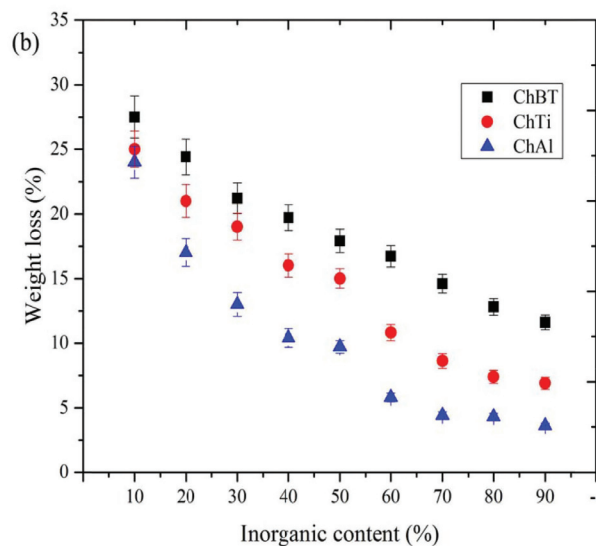


Fig. 4. Effect of inorganic content on the stability of ChBT, ChTi, and ChTi biocomposites in acidic environment

Stability evaluation in aqueous environment

The influence of crosslinker and inorganic dose ratio on water uptake by chitosan biocomposites are shown in Figure 5 and 6. It is evident that the stability of ChTB, ChTi, and ChAl biocomposites in water is influenced by crosslinker and inorganic dose. Water uptake of ChTB, ChTi, and ChAl biocomposites decreased with increase in crosslinker dose (Figure 5). The sharp decrease in swelling ratio by chitosan biocomposites with increased in crosslinker dose can be attributed to the formation more crosslinked polymeric network, and then decreases the elasticity of the polymer chains. Consequently, the swelling tendency of the chitosan biocomposites decreases. Similarly, water uptake by ChBT, ChTi, and ChAl biocomposites decreased with increase in inorganic content dose (Figure 6). This can be attributed to the intensive interaction of inorganic with chitosan which the lowers the hydrophilicity of the biocomposites is with a higher inorganic content, and also restricts its swelling. On the other hand, it was found that the swelling ratio of biocomposites are in the order of ChBT>ChTi>ChAl. This may be due to that the -OH of bentonite in ChBT enhances the water absorbency. In conclu-

sion, low swelling ratio indicate the stability of ChB, ChTi, and ChAl biocomposites in deionized water and the higher stability of biocomposites may be attributed to both the crosslinking of chitosan with glutaraldehyde and interaction of inorganics with chitosan.

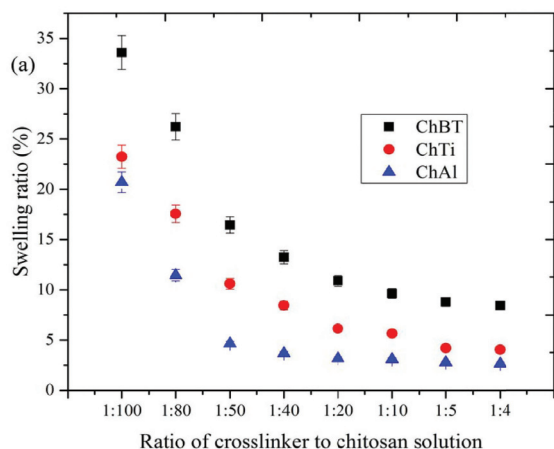


Fig. 5. Effect of crosslinker dose on water uptake by chitosan biocomposites in deionized water

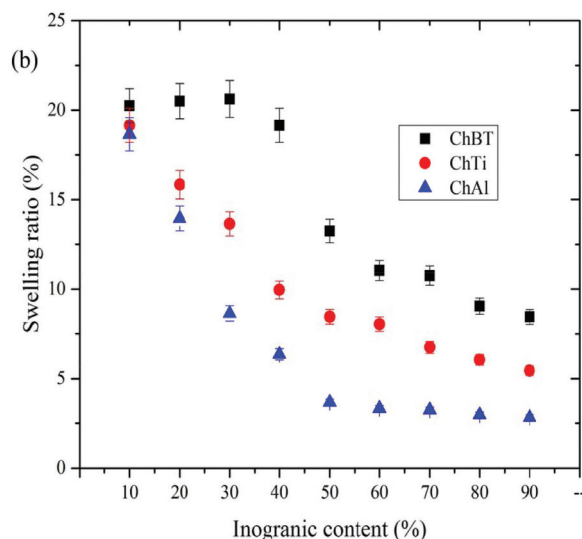


Fig. 6. Effect of inorganic content on water uptake by chitosan biocomposites in deionized water

Conclusion

In this study, an eco-friendly chitosan based organic-inorganic hybrid biocomposites, such as chitosan/bentonite (ChBT), chitosan/titanium oxide (ChTi), and chitosan/alumina (ChAl) were prepared. The stabilities of the prepared biocomposites were evaluated under acidic and aqueous environ-

ments. Stability of ChBT, ChTi, and ChAl in acidic solution increased with increase in crosslinker and inorganic doses. Similarly, the stability of the prepared biocomposites increased in aqueous environment. ChAl has shown the highest stability in both conditions. It can be concluded that mixtures of materials have shown superior properties compared with their pure counterparts. A major attraction of such research activities is to combine these desired advanced properties in the organic/inorganic hybrid materials, which can even be improved in comparison with the intrinsic properties of each component.

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