Modifications of Chitosan Films with Anhydrous Clay and Silane Treated Anhydrous Clay

Souparnika *,S. Anbudyanidhi ** Neetha John[1]**, K.A Rajesh**
*PSGR Krishnammal College for Women, Coimbatore, Tamilnadu , India
**CIPET: IPT -Kochi, HIL Colony, Edayar Road, Udyogamandal. P.O
Eloor, Kochi , Kerala , India683501

Abstract:- Chitosan due to its potential to replace traditional petrochemical based polymers gains a great attention among the researchers in the recent years. Some of its properties such as barrier properties, heat resistance etc need to be modified for various applications. One of the methods to modify Chitosan is adding clay as filler to Chitosan. In the current work the study of specially modified Silane treated anhydrous clay on various physical and chemical properties of Chitosan films. Characterization methods were conducted like FTIR (Fourier Transform Infrared Spectroscopy), OTR (Oxygen transmission).

Keywords:- *Treated Clay, Chitosan , Hydrous Clay Etc.*

I. INTRODUCTION

In recent times, research interest into the development of biodegradable, cost-effective and environmental friendly adsorbents with favourable properties for adsorption of pollutants is a challenge. Chitosan is a natural polycationic polysaccharide obtained commercially from the deacetylation of chitin [1] functions as a hemostatic and bacteriostatic agent, leading to reduced blood loss and promoted tissue healing [2,3]. It has a multifunctional material with excellent biocompatibility and is nonirritating and nonimmunogenic and [4]. Chitosan is having positively charged free amino ions can induce red blood cell aggregation around wound sites through electrostatic interaction with negatively charged neuraminic acid residues on the surface of the RBC membrane, thus causing blood coagulation [5].

Chitosan is inexpensive as well as nontoxic and exhibits high mechanical strength, hydrophilic character, good adhesion, etc. Thus chitosan has been usually applied as a food additive, a supporting material for chromatography and a chelating polymer for heavy metals removal [6-9]. In bio-related applications chitosan has been used for immobilization of biomolecules on solid substrates [10] and biomedicines as a anticoagulant or a wound-healing accelerator due to its biocompatibility [11]. Chitosan is also employed as a coagulant in water treatment to remove colloidal particles, similar to other polysaccharides, due to a known aggregation effect of organic matters in soils [12].

Modification of chitosan via different physical and chemical methods has gained attention as a promising approach for removing organic and inorganic pollutants from aqueous medium. In this regard, researchers have reported grafting and cross-linking approach among others as a potentially useful method for chitosan's modification for improved adsorption efficiency with respect to pollutant uptake [13]. Recently, chitosan–clay nanocomposites have emerged because of their high abundance, ease of fabrication, and efficacy as adsorbents. Quantitatively, this particular class of composites is capable of removing 99% of dyes, metals, and harmful negative ions from various solutions[14]. Clay is a layered silicate composed of silicon-oxygen tetrahedron and aluminum-oxygen octahedron. According to the ratio of tetrahedral lamella to octahedral lamella, clays are mainly divided into two types: 1:1 clay (kaolin) [15] and 2:1 clay (montmorillonite) [16]. Kaolin and montmorillonite can induce the human blood coagulation cascade reaction by rapidly absorbing the water of the wound blood, enriching platelets and clotting factors, and forming a clay layer that seals the wound to stop the bleeding.

The objective of this work is therefore to determine the effects of chitosan and clay concentrations on the barrier, mechanical, optical and thermal properties of chitosan films containing clay micro/nanoparticles in view of their possible use in the food and medical industries. This kind of applications will increase the added value of the products.

II. EXPERIMENTAL

- *Materials*

Chitosan powder (>80% DA) is purchased from Marine hydro colloids Kochi, Kerala, all other chemicals of laboratory grade purchased from Nice Chemicals (P) Ltd. Hydrous untreated clay and silane treated metal clay purchased from English India clay , Kerala

- *Methods*
- *Preparation of Pure Chitosan Film*

Chitosan solution was prepared by dissolving 1 g of chitosan powder in 100 ml of aqueous acetic acid solution (1%, v/v), under continuous stirring at room temperature for 2 h followed by vacuum filtering to remove the insoluble residue. This solution was cast into Petri dishes and dried at 50°C for 20 h to evaporate the solvent and form the films. The dried films were soaked with an aqueous solution of 0.05 M NaOH to remove residual acetic acid, followed by rinsing with distilled water to neutralize, and then dried at room temperature.

ISSN No:-2456-2165

- *Preparation of chitosan/ clay films*

Chitosan/Hydrous Untreated clay (Super shine) films were prepared using the casting/solvent evaporation technique. 1% chitosan solutions were prepared by dissolving 1 g of chitosan powder in 100 ml of aqueous acetic acid solution (1%, v/v), under continuous stirring at room temperature for 2 h followed by vacuum filtering to remove the insoluble residue. Nanocomposite samples were obtained by dispersing selected amounts of filler in aqueous solution and stirred at 50°C until swelling was completed. After, the dispersion was slowly added to the CS solution to reach a final clay concentration of 0.5, 1, 1.5, 2, and 2.5 wt% followed by stirring at room temperature for 5 h and then for 30 min at 25°C in ultrasonic bath. Similar process is done for silane treated metal clay (Amfine). A blend of both types of clays was also studied by blending in 50/50 ratio.

The nanocomposite solutions were then poured into Petri dishes and dried at 50°C for 20 h to evaporate the solvent and form the films. Free chitosan and nanocomposite films plasticized with glycerol were obtained by adding glycerol (30% (wt/wt) on solid CS) to the CS solution while stirring for 20 min at room temperature. Following the same procedure used for chitosan films, the dried films were soaked with an aqueous solution of 0.05 M NaOH to remove residual acetic acid, followed by rinsing with distilled water to neutralize, and then dried at room temperature.

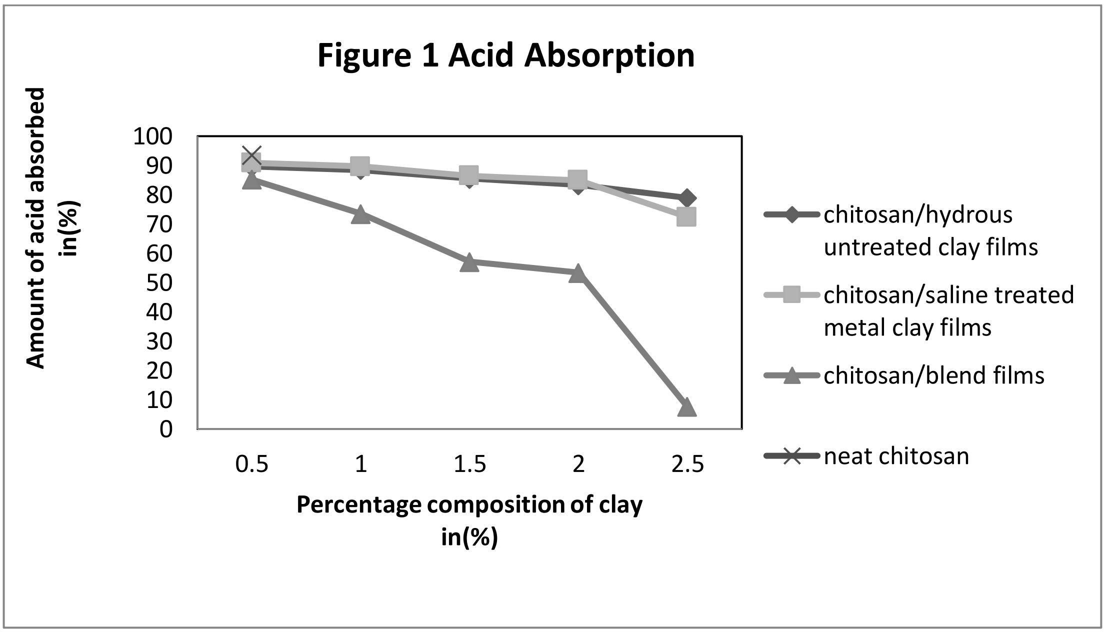
- *Characterisation*

A small piece of chitosan film from each composition of hydrous untreated clay, silane treated metal clay and blend of these two clays were exposed to dilute acids, alkalies and water. The films were also characterized by DSC, FTIR , water and gas transmission etc.

III. RESULTS AND DISCUSSION

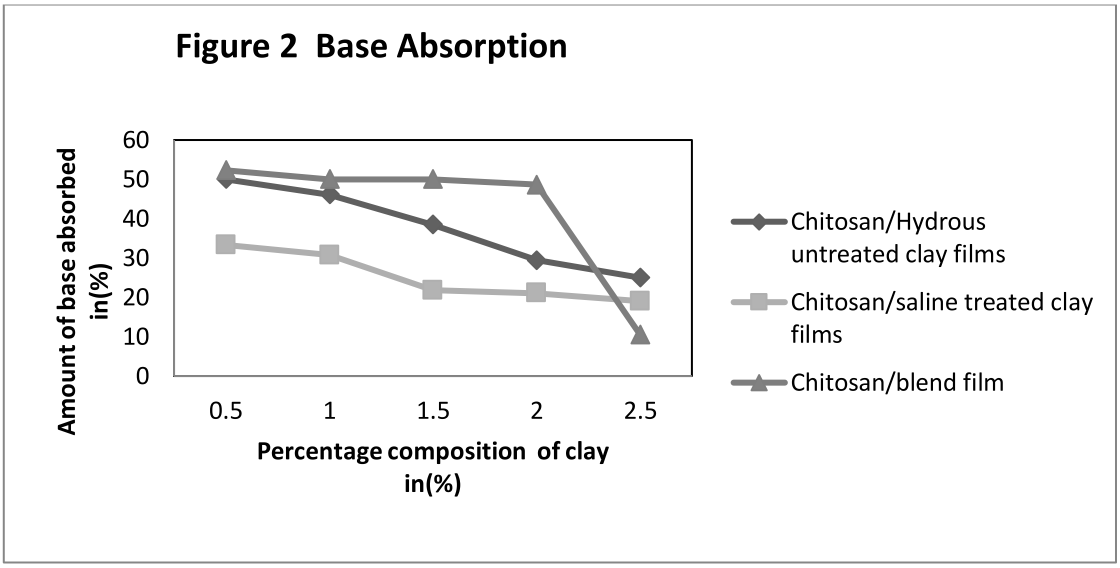
➢ *Acid resistance*

The acid absorption of neat chitosan film with chitosan/ hydrous untreated clay, chitosan/saline treated clay, chitosan/blend were expressed in Figure 1. From figure 1 the chitosan/hydrous untreated clay and chitosan/saline treated clay do not have much differences. Whereas the chitosan/blend film with 2.5% composition shows highest acid absorption. Neat chitosan film shows around 93% acid absorption. Chitosan/ hydrous untreated clay, chitosan/saline treated with 2.5 % composition shows 78.94 and 72.41 percentage acid absorption. Chitosan/blend with 2.5 % composition shows only 7% acid absorption. From the above data it is clear that chitosan/blend film with 2.5 % composition is much better for acid resistance.



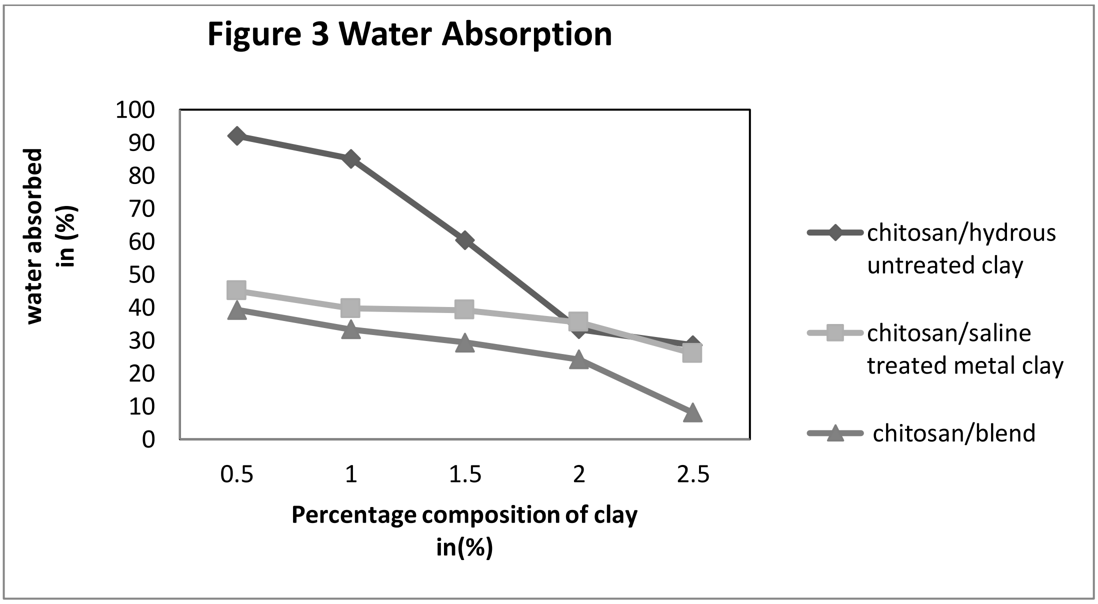
➢ *Alkali resistance*

Figure 2 shows alkali resistance , on comparison with the base absorption of neat chitosan film with chitosan/ hydrous untreated clay, chitosan/saline treated clay, chitosan/blend; the base absorption is found less for all the films except neat chitosan film. For the chitosan/ blend film with composition 2.5 % shows least base absorption among them. From the graph it is clear that when the addition of clay its base adsorption decreases, that is its base resistant property increasing by the addition of these modified clay particles.



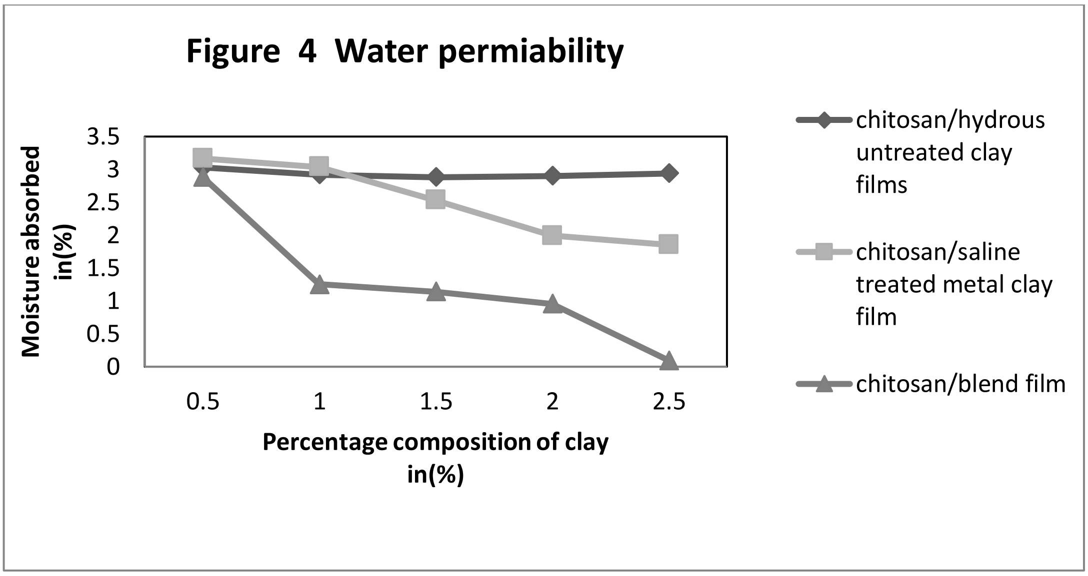
- *Water resistance*

Figure 3 compares the water absorption of neat chitosan film with chitosan/ hydrous untreated clay, chitosan/saline treated clay, chitosan/blend; the water absorption is lesser for all the films except neat chitosan film. For the chitosan/ blend film with composition 2.5 % shows least water absorption among them. From the graph it is clear that when the addition of clay its water adsorption decreases. Saline treated metal clay and blend shows the better property in water absorption i.e. their water absorption percentage is less. So, they can use very well used as packing materials.



- *Water permeability*

As percentage of water absorption decreases its advantage to use as a best packing material is increasing. Here the chitosan/ hydrous untreated clay shows high water absorption when compare to other two types of films. And we can see from the graph as well as the table 16 the chitosan/blend film with 2.5 % shows very less percentage of water absorption. So its best as packing material.



➢ *FTIR*

The two similar peak at 1026 cm-^{1,} 1060 cm^{-1} indicating the presence of Si-O stretching vibration, strong absorption. Chitosan FTIR spectra showed sharp peak at 564cm^{-1} (out-of-plane bending NH, out-of-plane bending C-O) here we can't see any sharp peak at this region. a peak at 1555.72 cm^{-1} due to C=O stretching. 1151.1 cm^{-1} due to C-O-C stretching.

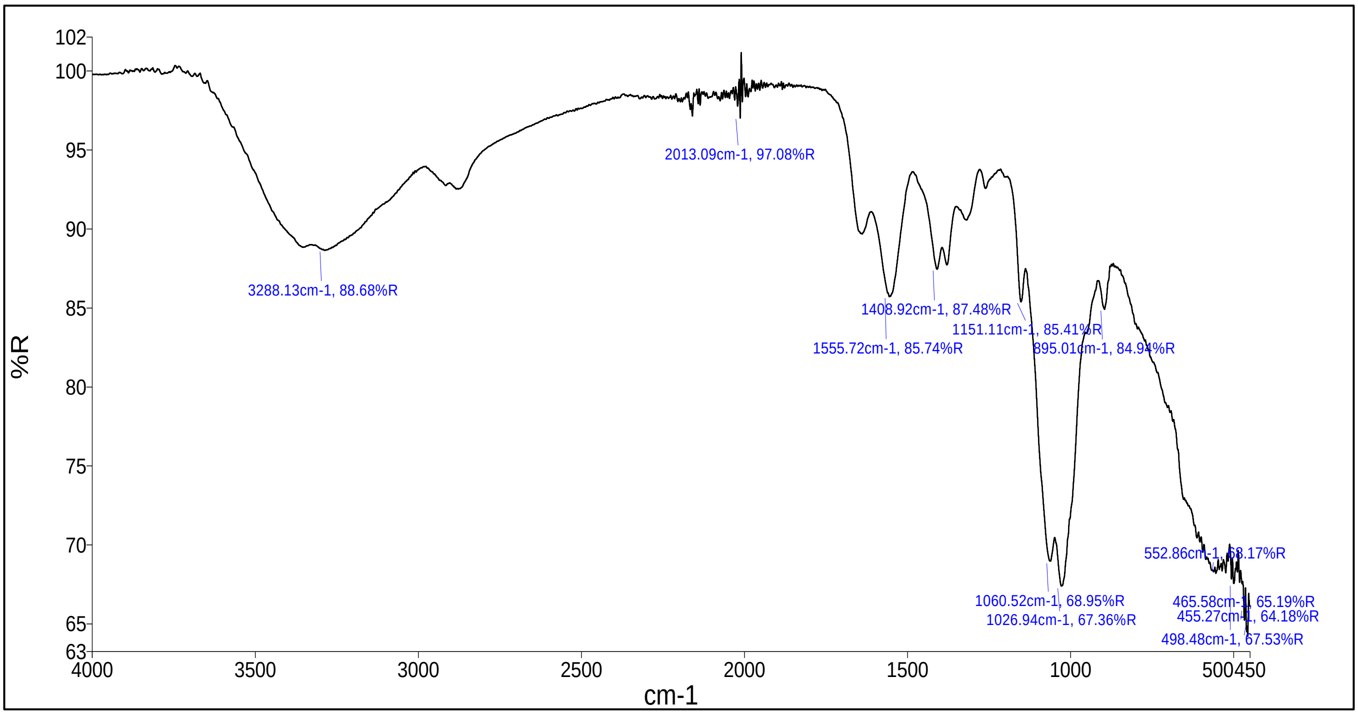


Fig 5:- FTIR of composite

➢ *DSC*

DSC is a thermal analysis technique in which the heat flow into or out of a sample is monitored as a function of temperature or time while the sample is exposed to a controlled temperature program. Based on through DSC and MA measurements, the glass transition temperature of chitosan which had previously been unknown, was established to be 203°C. The melting point of chitosan films were 214.77.

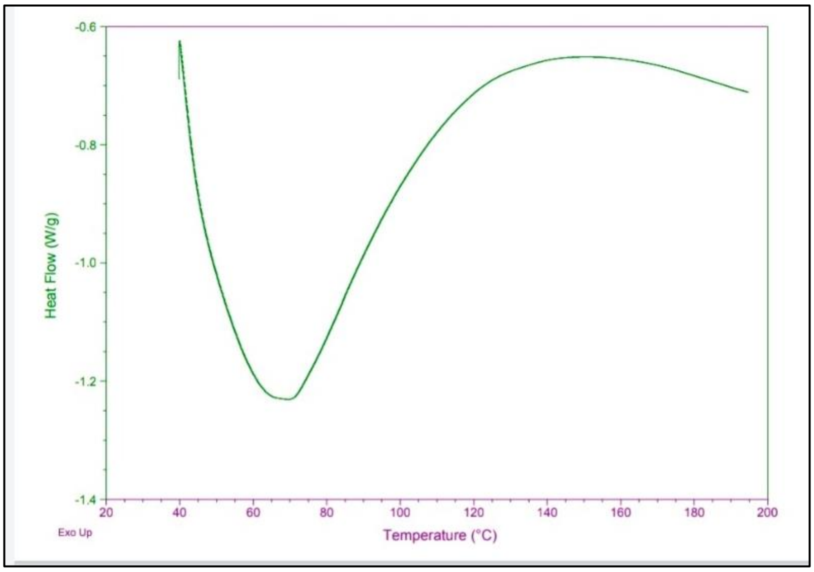


Fig 6:- DSC for the composite

➢ *OTR*

The gas permeability results are shown in Table 1. The oxygen transfer rate is the rate at which oxygen is delivered from a gas into a liquid, such as a bioprocess vessel's agitated suspension culture. The OTR value of chitosan films was found to be 2.2cc/m^2. Here we chosen chitosan film with silane treated metal clay, which decreased the OTR rate as 1.151cc/m^2. So its show good barrier property and therefore best for packing applications.

Test	**Chitosan/ hydrous untreated clay films, gm/cc**	**Chitosan/ silane treated metal clay gm/cc**	**Chitosan/blend gm/cc**
Gas permeability	1.15 x10^{-3} cm^3/m^2.d Pa	1.25 x10^{-3} cm^3/m^2.d Pa	1.35 x10^{-3} cm^3/m^2.d Pa
Permeability Coefficient	2.398 x10^{-14} cm^3 cm/cm^2 .s.Pa	2. 8 x10^{-14} cm^3 cm/cm^2 .s.Pa	2.9 x10^{-14} cm^3 cm/cm^2 .s.Pa

Table 1:- Gas permeability

Percentage Composition of Film			
	Chitosan/ hydrous untreated clay films, gm/cc	**Chitosan/ silane treated metal clay gm/cc**	**Chitosan/blend gm/cc**
0.5	1.347	1.414	1.3755
1.0	1.375	1.572	1.469
1.5	1.397	1.703	1.572
2	1.408	1.807	1.965
2.5	1.572	1.965	2.161
Neat chitosan	1.31		

Table 2:- Density

The density of chitosan film found to be 1.31gm/cm^3. By the addition of clay particles with different composition we can see that the density is increasing. This is because of the clay particles are bulky and heavier. Hence by the addition of clay particles increases the density of the films.

➢ *Thickness*

Thickness of the chitosan/hydrous untreated clay, chitosan/silane treated metal clay, chitosan/ blend films were noted by taking average value and it is given in the table 3 below. The thickness increases as percentage filler increaser and then decreases after an optimum level.

Percentage composition of film(%)	Thickness(micrometer)		
	Chitosan/ Hydrous untreated clay composite films	**Chitosan/ silane treated metal clay composite films**	**Chitosan/Blend clay composite films**
0.5	175	179	169
1.0	202	174.66	184
1.5	193	192.33	193
2.0	206.66	169.33	206.66
2.5	189.66	164.33	189.66
Neat Chitosan	150		

Table 3:- Thickness of the films

IV. CONCLUSIONS

The properties of modified chitosan were studied which are modified with clay particles like hydrous untreated clay and silane treated metal clay. The properties are compared of neat chitosan films with chitosan/ hydrous untreated clay films, chitosan/ silane treated clay films, chitosan/blend films the modified chitosan films with modified clay shows better properties in acid resistance, base resistance, water absorption, membrane property, heat resistance etc. the clay particles increased its chemical as well as physical properties.

The results of OTR the silane treated metal clay decreases the gas transition rate which improves its packing qualities. Not any change in its Tg and melting point. The clay particles are heavier and bulky which increases the density of films that by the addition of clay particles the density of films increasing. From the studies it can be concluded that the clay particle can improve the properties of chitosan film even in a small percentage of addition.

REFERENCES

[1]. Cao J., Li D., Liang W., Wang Y., Wul D. Glutaraldehyde Cross-Linked Chitosan Nanofibers: Preparation, Characterization and Application in Adsorption of Cu (II) *J. Nanosci. Nanotechnol.* 2016;16:2922–2928.

[2]. Matica M.A., Aachmann F.L., Tøndervik A., Sletta H., Ostafe V. Chitosan as a Wound Dressing Starting Material: Antimicrobial Properties and Mode of Action. *Int. J. Mol. Sci.* 2019;20:5889

[3]. Dowling M.B., Smith W., Balogh P., Duggan M.J., MacIntire I.C., Harris E., Mesar T., Raghavan S.R., King D.R. Hydrophobically-modified chitosan foam: Description and hemostatic efficacy. *J. Surg. Res.* 2015;193:316–323.

[4]. Ong S.Y., Wu J., Moochhala S.M., Tan M.H., Lu J. Development of a chitosan-based wound dressing with improved hemostatic and antimicrobial properties. *Biomaterials.* 2008;29:4323–4332.

[5]. Bennett B.L., Littlejohn L. Review of new topical hemostatic dressings for combat casualty care. *Mil Med.* 2014;179:497–514.

[6]. J.W. Park, M.-O. Park, K.K. Park, Bull. Kor. Chem. Soc. 5 (1984) 108–112.

[7]. C. Peniche-Covas, L.W. Alvarez, W. Arguelles-Monal, J. Appl. Polym. Sci. 46(1992) 1147–1150

[8]. E. Guibal, C. Milot, O. Eterradossi, C. Gauffier, A. Domard, Int. J. Biol.Macromol. 24 (1999) 49–59.

[9]. T. Tianwei, H. Xiaojing, D. Weixia, J. Chem. Technol. Biotechnol. 76 (2001)191–195.

[10]. X. Wei, J. Cruz, W. Goroski, Anal. Chem. 74 (2002) 5039–5046.

[11]. L.L. Balassa, J.F. Prudden, Proceedings of the First International Conference onchitin/chitosan, MIT, Boston, 1978, pp. 335354.

[12]. J.R. Pan, C. Huang, S. Chen, Y.-C. Chung, Colloids Surf. A 147 (1999) 359–364.

[13]. Ismaila Olalekan Saheed, Wen Da Oh Faiz Bukhari mohd Suah, Chitosan modifications for adsorption of pollutants – A review, Journal of Hazardous Materials ,volume 408, 15 April 2021.

[14]. Shanta Biswas**,** Jannatun Fatema, Tonmoy Debnath and Taslim Ur Rashid, Chitosan–Clay Composites for Wastewater Treatment: A State-of-the-Art Review, *CS EST Water* 2021, 1, 5, 1055–1085, March 24, 2021.

[15]. Detellier C. Functional Kaolinite. *Chem. Rec.* 2018;18:868–877.

[16]. Liu C., Liu C., Yu S., Wang N., Yao W., Liu X., Sun G., Song Q., Qiao W. Efficient antibacterial dextran-montmorillonite composite sponge for rapid hemostasis with wound healing. *Int. J. Biol. Macromol.* 2020;160:1130–1143.