International Journal of Technology (2018) 6: 1112-1120
ISSN 2086-9614

FABRICATION OF CHITOSAN NANOPARTICLES CONTAINING SAMARIUM ION POTENTIALLY APPLICABLE FOR FLUORESCENCE DETECTION AND ENERGY TRANSFER

Anwar Usman[1*], Eny Kusrini[2**], Andikaputra Brahma Widiantoro[2], Esza Hardiya[2], Nurul Aliah Abdullah[1], Yoki Yulizar[3]

[1]*Department of Chemistry, Faculty of Science, Universiti Brunei Darussalam,*
Jalan Tungku Link, Gadong BE1410, Brunei Darussalam
[2]*Department of Chemical Engineering, Faculty of Engineering, Universitas Indonesia, Kampus UI Depok, Depok 16424, Indonesia*
[3]*Department of Chemistry, Faculty of Mathematics and Natural Sciences, Universitas Indonesia, Kampus UI Depok, Depok 16424, Indonesia*

(Received: June 2018 / Revised: October 2018 / Accepted: November 2018)

ABSTRACT

Chitosan is a natural polysaccharide that has ideal properties as a polymer nanoparticle for drug delivery applications because it is easy to synthesize, inexpensive, biocompatible, biodegradable, non-immunogenic, and non-toxic. In this study, chitosan nanoparticles were fabricated in an acidic solution in the presence of potassium persulfate using a microwave technique. The effects of the reaction time, temperature, and weight ratio of potassium persulfate/chitosan on the yield and particle size were evaluated. It was found that the yield increased non-linearly, whereas the size of chitosan nanoparticles was 3 nm in the absence of potassium persulfate, which tended to increase with an increase in the potassium persulfate concentration. The chitosan nanoparticles were also treated with samarium for fluorescence detection. The fluorescence intensity at 590 nm of samarium-treated chitosan nanoparticles increased by a factor of more than 20 when compared with the samarium ion itself and was significantly higher than that of the untreated chitosan nanoparticles. It is indicated that chitosan nanoparticles are not only useful for drug carriers, where the drug delivery can be traced by monitoring fluorescence emission, but with the photoemissive properties of chitosan nanoparticles treated with samarium, they could also be applicable as environmentally friendly photocatalysts for the photodegradation of discharged pollutants as well as efficient photosensitizers that participate in energy transfer.

Keywords: Chitosan; Microwave technique; Nanoparticles; Potassium persufate; Samarium

1. INTRODUCTION

Nanotechnology is a promising field because the materials in nanometer scales (Moura et al., 2008) can be manipulated due to their large surface area, large surface reactivity, and unique physicochemical properties for novel applications (Sonia & Sharma, 2011). The reactivity of the nanometer-sized materials is determined by the atoms on their surface (Abdullah et al., 2008). Though most efforts have been devoted to fabrications and applications of semiconductor nanoparticles, those for biomaterials have also attracted attention due to their biocompatible and biodegradable properties (Moura et al., 2008). For instance, natural polysaccharides, such as

---

[*] Corresponding author's email: anwar.usman@ubd.edu.bn (AN), Tel: +673-2-463001 Ext.1349, Fax: +673-2-461003
[**] Corresponding author's email: ekusrini@che.ui.ac.id (EK), Tel: +62-21-7863516 ext. 204, Fax. 62-21-7863515
Permalink/DOI: https://doi.org/10.14716/ijtech.v9i6.2576

chitosan, are ideal biomaterials and have become important due to their availability in large quantities, their low cost (Lee et al., 2009), and their non-immunogenic and non-toxic properties (Tiyaboonchai, 2003), which allow them to be applied as drug carriers (Kocak et al., 2011; Kusrini et al., 2014). For this drug carrier application, chitosan is strongly considered due to its antimicrobial activity (Dutta et al., 2009). The use of composites of chitosan with clay, which can be applied for packaging materials, has also been widely studied (Haerudin et al., 2010). In particular, the chitosan particles and composites can be fabricated to be within a few hundreds of nanometers.

Chitosan nanoparticles with sizes between 100–600 nm, for instance, have been fabricated by various methods, including coacervation from suspension (Aloys et al., 2016), ionotropic gelation (Calvo et al., 1997), emulsion cross-linking (Riegger et al., 2018), emulsion-droplet coalescence (Balcerzak et al., 2013), reverse micellar process (Zhao, 2011), and sieving (Agnihotri, 2004). All these methods involve surfactants and cross-linking agents, such as glutaraldehyde, making the fabrication of chitosan nanoparticles complicated and non-environmentally friendly. To overcome this issue, a simple method using potassium persulfate in formic acid without involving any organic solvents, surfactants, or precipitation agents to produce 50–110 nm-sized chitosan nanoparticles has been proposed (Kusrini et al., 2015). Persulfate ions are able to cut the biopolymeric chains of chitosan (Hsu et al., 2002). The use of an acid as a solvent has been exhibited to have strong effects on the size and morphology of the resulting chitosan nanoparticles (Soltani et al., 2012). The effect of potassium persulfate in an acidic solvent, including acrylic acid, methyl methacrylic acid, and methacrylic acid, has been explored (Hsu et al., 2002; Moura et al., 2008). The size of the chitosan nanoparticles is within the range of 60–300 nm. Compared with conventional heating, the chemical process using a microwave has also received considerable attention due to the higher conversion and shorter reaction times required to form chitosan nanoparticles by the ionic gelation method with acetic acid as the solvent (Kocak et al., 2011).

In this study, chitosan nanoparticles were fabricated from chitosan using potassium persulfate in formic acid. The microwave technique was used to accelerate the bond breaking reaction of chitosan. Using this technique, chitosan nanoparticles with different sizes and morphologies were fabricated. The size of the chitosan nanoparticles was as small as 3 nm. The chitosan nanoparticles were then treated with samarium to enhance their fluorescence intensity so that they could potentially be used for light-electricity conversion as well as for drug carrier applications. For the former, the chitosan nanoparticles containing samarium or dyes might be capable of electron and energy transfers, while the latter is promising for tracing drug delivery by monitoring the emission of chitosan nanoparticles.

2. METHODS

2.1. Materials

Chitosan, which had a degree of deacetylation of 85% and a molecular weight of 200 kDa, extracted from shrimp shells was obtained from Cirebon, Indonesia. The formic acid solution (98-100%) and potassium persulfate ($K_2S_2O_8$) in analytical grade were purchased from Merck, Singapore, and $Sm(NO_3)_3.6H_2O$ was obtained from Aldrich Chemical Co. (Milwaukee, USA). All the chemicals were used as received without any further purification.

2.2. Fabrication of Chitosan Nanoparticles

First, the solution of chitosan in formic acid was prepared by dissolving 3% wt chitosan and 2% wt formic acid in water, and the pH of the mixture was set at pH 4. The mixture was continuously stirred, and potassium persulfate with different concentrations (1.0, 1.5, and 2.0 mmol) was then added to the mixture. The homogenous solution was then subjected to a low power microwave for 5 min, and it was repeated twice. The mixture was then cooled at room temperature, and the mixture became clear. The colloidal suspension was then dried in an oven. The functional groups of the chitosan nanoparticles were characterized using Fourier transform infrared spectroscopy (FTIR, Shimadzu). The morphology was monitored by field emission scanning electron microscopy (FESEM, JEOL), and their particle sizes were measured using a Zetasizer Nano ZEN 1600 (Malvern Instruments). The measurements were performed on freshly prepared nanoparticles.

2.3. Synthesis Nanochitosan-Samarium Complex

Chitosan nanoparticles (2 g) were added to 100 mL of a nitrate solution (3000 ppm) in water. The suspension was continuously stirred for 6 h at 500 rpm. The precipitated nanochitosan-samarium complex was then filtered using filter paper (Whatman No. 42) and was washed with distilled water. The nanochitosan-samarium complex was then dried at 60°C and ground, and they were characterized using FTIR spectroscopy. The morphology and trace elements in the complex were monitored by scanning electron microscopy (SEM-EDX), and their fluorescence spectra were measured using a spectrofluorometer (Perkin Elmer).

3. RESULTS AND DISCUSSION

3.1. The Formation of Chitosan Nanoparticles

Table 1 shows the yield of chitosan nanoparticle formation fabricated using a microwave technique with potassium persulfate in formic acid. It was clearly observed that the yield of chitosan nanoparticles increased nonlinearly with the concentration of potassium persulfate, indicating that potassium persulfate efficiently cuts the polymer chains of chitosan; however, at higher concentrations of potassium persulfate, the increase in the yield of chitosan nanoparticles was less pronounced.

Table 1 Results of the preparation of chitosan with potassium persulfate

Initial Chitosan (g)	Potassium Persulfate (mmol)	Chitosan Nanoparticles (g)	Yield (%)
2	1.0	0.12	6
2	1.5	0.31	15.5
2	2.0	0.33	16.3
3	1.0	0.22	7.3
3	1.5	0.36	12
3	2.0	0.42	14

3.2. Particle Size

The particle size distribution of chitosan nanoparticles fabricated in different concentrations of potassium persulfate is summarized Table 2. In the absence of potassium persulfate, the formation of chitosan nanoparticles was only caused by formic acid. In this case, it was found that the sizes of the chitosan nanoparticles were in the range of 3–17 nm, which is much smaller than those in the presence of potassium persulfate (480–5590 nm). This suggests that formic acid efficiently cuts the biopolymer chains of chitosan into small-sized nanoparticles and forms new protonated chitosan structures with particle sizes in nanometer scales. For comparison, chitosan nanoparticles derived from their natural polymers using a microwave technique have particle sizes generally in the range of 10–1000 nm (Hsu et al., 2002; Moura et al., 2008; Kocak et al., 2011). In this regard, the addition of potassium persulfate to formic acid dissociates into persulfate ions, which become sulfate ion radicals. These radicals will attack the C–O–C bond on the chitosan chain length, generating chitosan radicals and disconnecting the monomers from the natural polysaccharide. In other words, potassium persulfate induces the depolymerization of chitosan.

The oligomer radical ions then interact with each other via their carbonyl groups, deactivating the radical ions and forming new polymer structures with shorter molecular chains (Hsu et al., 2002), which then form globular chitosan oligomers. Therefore, the particle size distribution of chitosan nanoparticles varies depending on the potassium persulfate concentration. For a specific ratio of chitosan/potassium persulfate, i.e. 2 g/1.5 mmol, the particle size distributions of the chitosan nanoparticles were quite narrow, suggesting the homogeneity of particle size. This nanoparticle has potential for drug delivery because the drug loading yield performance is more efficient (Fan et al., 2012). The other advantage of these nanoparticles is their potential capability as matrices to encapsulate electron-accepting or -donating dyes. With the electron accepting or donating ability, the chitosan nanoparticles containing dyes are applicable for bulk heterojunction solar cells, and an optimized photoactive layer can be expected (Eita et al., 2015).

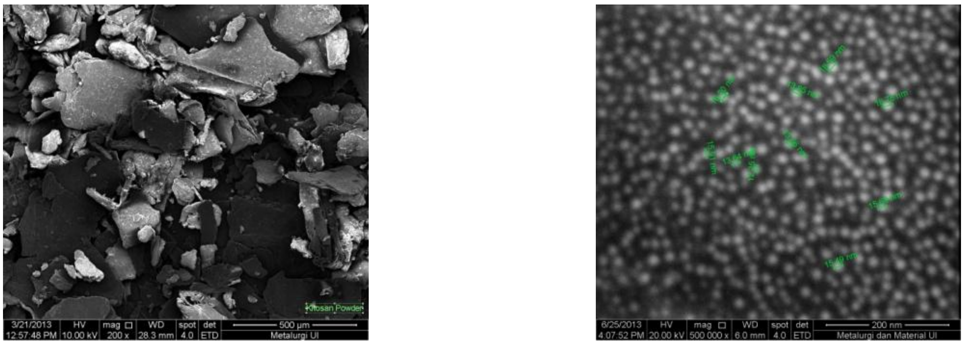
Table 2 Particle sizes of chitosan nanoparticles depending on potassium persulfate

Chitosan (g)	Potassium Persulfate (mmol)	Particle Size (nm)
2	0.0	3
2	1.0	1112–5386
2	1.5	480
2	2.0	ND*
3	0.0	17
3	1.0	1079
3	1.5	1616
3	2.0	513–5590

*ND = Not Detected, possibly because the particles were too large (> 10µ)

3.2.1. Surface morphology

Figure 1 shows SEM images of chitosan nanoparticles together with those of commercially available chitosan. It can be clearly observed that the chitosan nanoparticles are spherical and monodispersed with a size distribution within 12–18 nm, whereas the commercially available chitosan has irregular blocks in shape with a size of approximately 1-100 µm.



(a) (b)

Figure 1 SEM images of: (a) Commercially available chitosan; and (b) Chitosan nanoparticles

The particle size distribution of chitosan nanoparticles is slightly smaller than that measured using a particle size analyzer. This is due to the different natures of the measurements. SEM imaging is recorded on dried nanoparticles, whereas a particle size analyzer is based on light scattering from the nanoparticles suspended in distilled water. It is well-known that chitosan nanoparticles in water at pH 7 can undergo aggregation and swelling. The particle aggregation is facilitated by the change in the ionic state of the chitosan group in a basic environment; thus, there is no electrostatic repulsion between the particles to avoid their aggregation.

3.2.2. Functional groups

Figure 2 shows the FTIR spectra of chitosan nanoparticles fabricated at different concentrations of potassium persulfate (0–2.0 mmol). It can be clearly observed that chitosan nanoparticles contained O–H and N–H groups, which appeared as a broad band with a peak at 3354 cm^{-1}. This functional group was slightly downshifted to 3338 cm^{-1} for chitosan nanoparticles fabricated in the presence of potassium persulfate. Similarly, the vibrational band of amine N–H was 1585 cm^{-1} for chitosan nanoparticles fabricated without potassium persulfate, and it was downshifted to 1507 cm^{-1} for those prepared in the presence of potassium persulfate. This indicates that the interactions of chitosan are via its primary amine group with a sulfate anion from potassium persulfate. A new S–O bond is formed. The different concentrations of potassium persulfate also modify the relative intensity of the vibrational spectrum as well as the peak broadening of the O–H group. A similar observation has been reported by Negrea et al. (2015).

The infrared spectra of chitosan nanoparticles and those modified with samarium are shown in Figure 3. Some spectral shifts were observed upon treatment due to chemical binding between samarium and hydroxyl and the amine groups of chitosan. For instance, the vibrational bands of chitosan amide and amine N–H groups at 1631 and 1533 cm^{-1} were downshifted to 1585 and 1531 cm^{-1}, respectively. This indicates that samarium is chemically bound to chitosan, involving these functional groups. Therefore, upon treatment with samarium, the vibrational bands of the C–H, C–O, and C–N groups were also slightly downshifted.

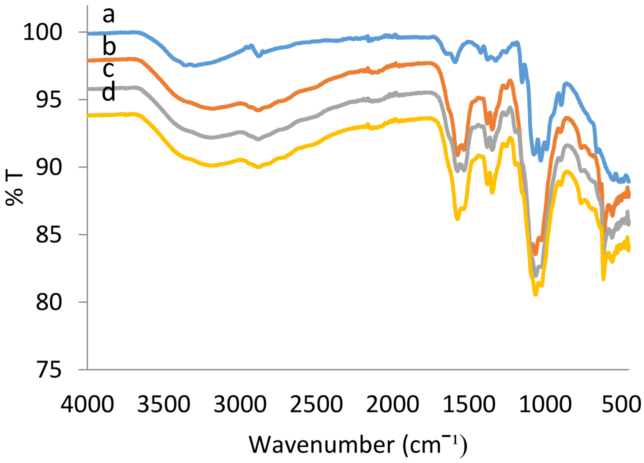


Figure 2 FTIR spectra of: (a) Chitosan nanoparticles fabricated without potassium persulfate, and those with potassium persulfate; (b) 1; (c) 1.5; and (d) 2 mmol

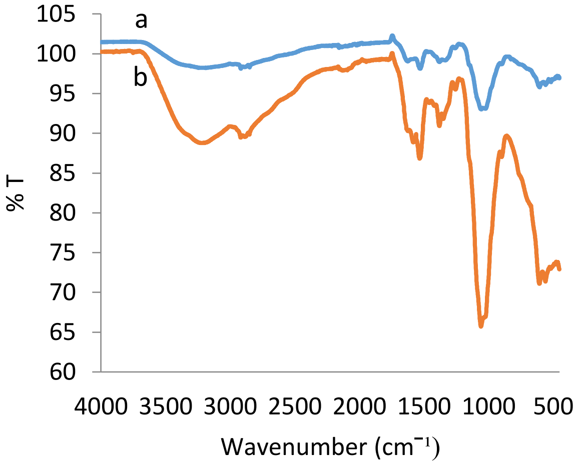
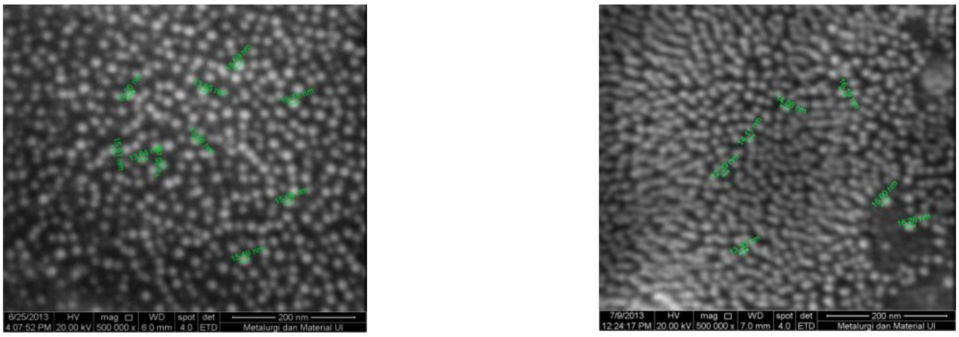


Figure 3 FTIR Spectra of: (a) Chitosan nanoparticles; and (b) Those treated with samarium

3.3. The Effect of Samarium on Surface Morphology

The SEM images of chitosan nanoparticles and those treated with samarium are shown in Figure 4. The morphology of chitosan nanoparticles was not very clear, though they tend to be spherical in shape. Upon treatment with samarium, the particle size distribution was unchanged, but the nanoparticles became more solid and clear-cut. The EDX results suggest the presence of samarium (1.10%) in the chitosan nanoparticles after treatment. This finding further proves that the samarium ions are chelated with chitosan oligomers and form chitosan-samarium complexes in the nanoparticles.



(a) (b)

Figure 4 SEM Images of: (a) Chitosan nanoparticles; and (b) Chitosan-Sm nanoparticles

3.4. Florescence Properties of Chitosan Nanoparticles

Figure 5 shows the fluorescence properties of chitosan nanoparticles, samarium nitrate, and chitosan nanoparticles treated with samarium. The fluorescence of the samarium ions shows a peak at its hypersensitive $^4G_{5/2} \rightarrow {}^6H_{7/2}$ transition with an emission wavelength of 590 nm. This is consistent with the finding proposed by Lunstroot et al. (2009), where the Sm^{3+} ion can emit orange photoluminescence. The emission intensity at 590 nm was measured to be 6.96, 38.75, and 585 a.u. for chitosan nanoparticles, samarium nitrate, and chitosan nanoparticles treated with samarium, respectively. This indicates an extreme increase in the fluorescence intensity of chitosan nanoparticles upon treatment with samarium, supporting the notion that samarium is chelated to the chitosan nanoparticles. These results suggest that chitosan nanoparticles are not only useful for drug carriers, where drug delivery can be traced by monitoring the fluorescence emission, but with the photoemissive properties chitosan nanoparticles treated with samarium developed herein, they could also be applicable as environmentally friendly photocatalysts for the photodegradation of discharged pollutive dyes. Most importantly, the chitosan nanoparticles treated with samarium can be efficient photosensitizers and can participate in energy transfers (Wu et al., 2005). It can be expected that the chitosan nanoparticles absorb light in the UV−Vis spectral region and emit an intense light at 590 nm to excite the surrounding electron-donor dyes in bulk heterojunction solar cells.

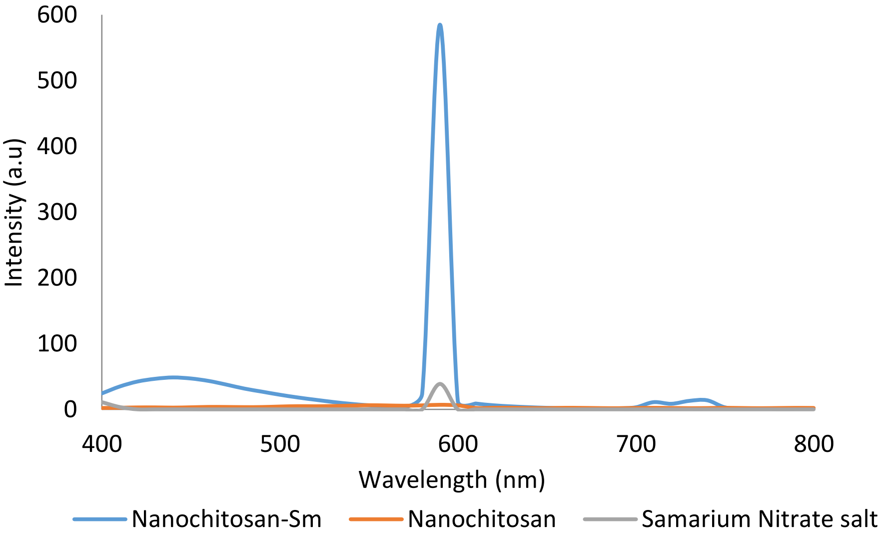


Figure 5 Fluorescence spectra of chitosan nanoparticles with and without samarium treatment (blue and red spectra) and samarium nitrate salt (green spectrum)

4. CONCLUSION

Chitosan nanoparticles have been fabricated through a depolymerization process of chitosan utilizing potassium persulfate and formic acid and a microwave technique. The potassium persulfate is a depolymerization agent, and formic acid acts as a proton donor. The yield of chitosan nanoparticles increased non-linearly with the presence of potassium persulfate, and similarly, the size increased with increasing potassium persulfate concentration. The chitosan nanoparticles fabricated at a specific ratio of potassium persulfate/chitosan were found to be monodispersed. The infrared vibrational spectrum of chitosan nanoparticles is similar to that of chitosan, indicating that the chitosan nanoparticles still contained O–H and N–H groups. With these functional groups, the chitosan nanoparticles are potentially capable of acting as matrices to encapsulate electron-accepting or -donating dyes for bulk heterojunction solar cells, optimizing the photoactive layer. The chitosan nanoparticles were then treated with samarium for fluorescence detection. It was found that samarium was chelated by chitosan oligomers via the hydroxyl and amine groups of chitosan, and the composition of samarium in the complex was 1.10%. The fluorescence intensity at 590 nm of chitosan nanoparticles containing samarium was 585 a.u., which increased by a factor of more than 20 when compared with samarium ion itself (38.75 a.u.) and was significantly higher than that of the untreated chitosan nanoparticles (6.96 a.u.). These results suggest that when chitosan nanoparticles are applied to drug carriers, drug delivery can be traced by monitoring the fluorescence emission. With their photoemissive properties, chitosan nanoparticles treated with samarium developed herein could also be applicable as environmentally friendly photocatalysts for the photodegradation of discharged pollutive dyes. The chitosan nanoparticles treated with samarium can also be efficient photosensitizers and can participate in energy transfers.

5. ACKNOWLEDGEMENT

This research was financially supported by Universitas Indonesia through the grant PITTA No. 2430/UN2.R3.1/HKP.05.00/2018.

6. REFERENCES

Abdullah, M., Virgus, Y., Nirmin, Khairurrijal, 2008. Review: Sintesis Nanomaterial (A Review: Nanomaterial Synthesis). *Jurnal Nanosains & Nanoteknologi,* Volume 1(2), pp. 33–57

Agnihotri, S.A., Mallikarjuna, N.N., Aminabhavi, T.M., 2004. Recent Advances on Chitosan-Based Micro- and Nanoparticles in Drug Delivery. *Journal of Controlled Release,* Volume 100(1), pp. 5–28

Ahmed, T.A., Aljaeid, B.M., 2016. Preparation, Characterization, and Potential Application of Chitosan, Chitosan derivatives, and Chitosan Metal Nanoparticles in Pharmaceutical Drug Delivery. *Drug Design, Development and Therapy,* Volume 10, pp. 483–507

Aloys, H., Korma, S.A., Alice, T.A., Chantal, N., Ali, A.H., Abed, S.M., Ildephonse, H., 2016. Microencapsulation by Complex Coacervation: Methods, Techniques, Benefits, and Applications - A Review. *American Journal of Food Science and Nutrition Research,* Volume 3(6), pp. 188–192

Balcerzak, J., Kucharska, M., Gruchała, B., 2013. Preparation of Micro and Nanostructures of Chitosan by Ultrasonic Coalescence of W/O Emulsion. *Progress on Chemistry and Application of Chitin and Its Derivatives,* Volume XVIII, pp. 13–20

Calvo, P., Remuñan-Lopez, C., Vila-Jato, J.L., Alonso, M.J., 1997. Novel Hydrophilic Chitosan-Polyethylene Oxide Nanoparticles as Protein Carriers, *Journal of Applied Polymer Science,* Volume 63(1), pp. 125–132

Dutta, P.K., Tripathi, S., Mehrotra, G.K., Dutta, J., 2009. Perspectives for Chitosan Based Antimicrobial Films in Food Applications. *Food Chemistry*, Volume 114(4), pp. 1173–1182

Eita, M., El Labban, A., Cruciani, F., Usman, A., Beaujuge, P.M., Mohammed, O.F., 2015. Ambient Layer-by-Layer ZnO Assembly for Highly Efficient Polymer Bulk Heterojunction Solar Cells. *Advanced Functional Materials*, Volume 25(10), pp. 1558–1564

Fan, W., Yan, W., Xu, Z., Ni, H., 2012. Formation Mechanism of Monodisperse, Low Molecular Weight Chitosan Nanoparticles by Ionic Gelation Technique. *Colloids and Surfaces B: Biointerfaces*, Volume 90, pp. 21–27

Haerudin, H., Pramono, A.W., Kusuma, D.S., Jenie, A., Voelcker, N.H., Gibson, C., 2010. Preparation and Characterization of Chitosan/Montmorillonite (MMT) Nanocomposite Systems. *International Journal of Technology*, Volume 1(1), pp. 65–73

Hsu, S.C., Don, T.M., Chiu, W.Y., 2002. Free Radical Degradation of Chitosan with Potassium Persulfate. *Polymer Degradation and Stability*, Volume 75(1), pp. 73–83

Kocak, N., Sahin, M., Akin, I., Kus, M., Yilmaz, M., 2011. Microwave Assisted Synthesis of Chitosan Nanoparticles. *Journal of Macromolecular Science, Part A: Pure and Applied Chemistry*, Volume 48(10), pp. 776–779

Kusrini, E., Arbianti, R., Sofyan, N., Abdullah, M.A.A., Andriani, F., 2014. Modification of Chitosan by using Samarium for Potential Use in Drug Delivery System. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, Volume 120, pp. 77–83

Kusrini, E., Shiong, N.S., Harahap, Y., Yulizar, Y., Dianursanti, Arbianti, R., Pudjiastuti, A.R., 2015. Effect of Monocarboxylic Acids and Potassium Persulfate on Preparation of Chitosan Nanoparticles. *International Journal of Technology*, Volume 6(1), pp. 11–21

Lee, D.W., Lim, H., Chong, H.N., Shim, W.S., 2009. Advances in Chitosan Material and Its Hybrid Derivatives: A Review. *The Open Biomaterials Journal*, Volume 1, pp. 10–20

Lunstroot, K., Nockemann, P., Van Hecke, K., Van Meervelt, L., Görller-Walrand, C., Binnemans, K., Driesen, K., 2009. Visible and Near-Infrared Emission by Samarium(III)-Containing Ionic Liquid Mixtures. *Inorganic Chemistry*, Volume 48, pp. 3018–3026

Moura, M.R., Aouada, F.A., Mattoso, L.H.C., 2008. Preparation of Chitosan Nanoparticles using Methacrylic Acid. *Journal of Colloid and Interface Science*, Volume 321(2), pp. 477–483

Negrea, P., Caunii, A., Sarac, I., Butnariu, M., 2015. The Study of Infrared Spectrum of Chitin and Chitosan Extract as Potential Sources of Biomass, *Digest Journal of Nanomaterials and Biostructures*, Volume 10(4), pp. 1129 –1138

Rieggera, B.R., Bäurera, B., Mirzayevaa, A., Tovara, G.E.M., Bach, M., 2018. A Systematic Approach of Chitosan Nanoparticle Preparation via Emulsion Crosslinking as Potential Adsorbent in Wastewater Treatment. *Carbohydrate Polymers*, Volume 180, pp. 46–54

Soltani, N., Saion, E., Hussein, M.Z., Bahrami, A., Naghavi, K., Yunus, R.B., 2012. Microwave Irradiation Effect on Hydrothermal and Polyol Synthesis of ZnS Nanoparticles. *Chalcogenide Letters*, Volume 9(6), pp. 265–274

Sonia, T.A., Sharma, C.P., 2011. Chitosan and Its Derivatives for Drug Delivery Perspective. *In:* Chitosan for Biomaterials I, Part of the Advances in Polymer Science Book Series, Jayakumar, R., Prabaharan, M., Muzzarelli, R., (eds.), Volume 243, pp. 23–53, Springer, Berlin, Heidelberg

Tiyaboonchai, W., 2003. Chitosan Nanoparticles: A Promising System for Drug Delivery. *Naresuan University Journal*, Volume 11(3), pp. 51–66

Wu, S., Zeng, F., Zhu, H., Tong, Z., 2005. Energy and Electron Transfers in Photosensitive Chitosan. *Journal of the American Chemical Society*, Volume 127(7), pp 2048–2049

Zhao, L.-M., Shi, L-E, Zhang, Z.-L., Chen, J.-M., Shi, D.-D., Yang, J., Tang, Z.-X., 2011. Preparation and Application of Chitosan Nanoparticles and Nanofibers, *Brazilian Journal of Chemical Engineering*, Volume 28(3), pp. 353 – 362