BETA-CYCLODEXTRIN FUNCTIONALIZED CELLULOSE NANOFIBER FOR THE REMOVAL OF PALMITIC ACID

NURUL AQILAH BINTI MOHD SHAH

A dissertation submitted in partial fulfilment of the
requirements for the award of the degree of
Master of Engineering

School of Chemical and Energy Engineering
Faculty of Engineering
Universiti Teknologi Malaysia

APRIL 2020

ACKNOWLEDGEMENT

In the name of Allah, the most Beneficient, the most Merciful. Peace and blessing be upon the Prophet Muhammad SAW.

My research project entitled *Beta-Cyclodextrin Functionalized Cellulose Nanofiber For The Removal of Palmitic Acid* had finally come to an end. There were numerous of challenges, hardship, obstacles and the ups and down in completing this research but behind all of the struggles, I was blessed with beautiful souls that always pour their endless support to me.

First and foremost, I would like to express my special thanks of gratitude to my supervisor, Dr Nor Hasmaliana Binti Abdul Manas who had expertly guided me throughout my research project, shared the opinions, valuable knowledge and encouragement to complete this project. Their personal generosity help make my time at UTM enjoyable.

Next, my special appreciation also extends to my laboratory colleagues and roomate, for the moral support and also helped sustained a positive atmosphere in doing this research. I also acknowledge UTM Skudai for the facilities offered, laboratory staffs and technician of SCEE, who helped me a lot in technical problems. Lastly, this thesis is especially dedicated to my beloved parents who paved the path before me upon whose shoulders I stand.

ABSTRACT

Functionalization of cellulose nanofibers with beta-cyclodextrin (CNF/ β-CD) were performed. β-CD functionalization onto CNF was achieved by polymerization between β-CD and citric acid as crosslinker. β-CD coating was permanently adhered onto the surface of CNF. Fabrication of CNF with 15% concentration of cellulose acetate had produced average fiber diameter of 312 nm and 177 nm for CNF and CNF/ β-CD, respectively when characterized by using SEM analysis and revealed that functionalization of CNF with β-CD did not deform the original nanofibrous structure of CNF mats. The Fourier Transfer Infrared (FTIR) spectrum that showed adsorption band of carbonyl group due to high intensity peak at 1740 cm−1 of CNF/ β-CD confirmed the chemical linkages between CNF and citric acid via ester bonds. Thermal decomposition of CNF/ β-CD was higher than CNF when characterized by using thermogravimetric analyser (TGA) and onset degradation temperature of CNF/ β-CD was 20 oC higher than CNF which suggested the successful functionalization of the CNF/ β-CD. The highest removal of palmitic acid by 33% at 60 minutes of contact time was recorded by CNF/ β-CD that were functionalized with 7% of β-CD concentration and 8% of citric acid concentration during crosslinking process. It was recorded that rate of absorption of CNF/ β-CD was 17% higher compared to CNF. Reusability of CNF and CNF/ β-CD were also investigated and CNF/ β-CD was found to have similar removal percentage (±30%) even after four attempts compared to CNF which can only reused for two times. The adsorption process of the modified CNF on the removal of palmitic acid concentration was best-explained by Langmuir isotherm model and the adsorption kinetics for the palmitic acid was found to follow pseudo second order kinetic model. These findings suggested that β-CD-functionalized CNF can be a very good candidate as an adsorbent for removal of palmitic acid from wastewater or for wastewater treatment owing to their very large surface area as well as inclusion complexation capability of surface associated β-CD.

ABSTRAK

Selulosa nanofibers (CNF) yang telah difungsikan dengan beta-cyclodextrin (CNF/ β-CD) telah dihasilkan. Pembentukan β-CD ke CNF dicapai melalui pempolimeran antara β-CD dan asid sitrik sebagai agen penghubung silang. Analisis menggunakan pengimbasan mikroskop elektron (SEM), fabrikasi CNF dengan 15% konsentrasi selulosa asetat telah menghasilkan CNF yang mempunyai 177 nm purata diameter serat manakala CNF/ β-CD yang terhasil selepas proses hubung silang mempunyai purata diameter serat yang lebih besar iaitu 312 nm. Seterusnya, analisis spektrum menggunakan transformasi fourier inframerah (FTIR) membuktikan bahawa wujud hubungan kimia antara CNF dan asid sitrik melalui ikatan ester kerana terdapat puncak intensiti yang tinggi pada 1740 cm-1 yang mewakili penjerapan ikatan kumpulan karboksil. Penguraian termal CNF / β-CD adalah lebih tinggi daripada CNF yang tidak diubah suai apabila dicirikan dengan menggunakan penganalisis termogravimetrik (TGA) dan suhu kemerosotan permulaan CNF / β-CD sebanyak 20 oC lebih tinggi daripada CNF mencadangkan CNF/ β-CD berjaya dihasilkan. Penyingkiran asid palmitik yang paling tinggi sebanyak 33% pada kadar masa 60 minit tindak balas telah direkodkan bagi CNF/ β-CD yang diubahsuai dengan kepekatan optimum β-CD sebanyak 7% dan kepekatan optimum asid sitrik sebanyak 8%. Proses penjerapan bagi CNF/ β-CD untuk mengurangkan kepekatan asid palmitik dapat dijelaskan oleh Langmuir isotherm model dan penjerapan kinetik untuk asid palmitik didapati mengikuti model kinetik urutan pseudo kedua. Penemuan dalam kajian ini turut mencadangkan bahawa CNF/ β-CD boleh menjadi calon yang sangat baik sebagai merawat asid palmitik dari air kumbahan atau untuk rawatan air buangan berikutan kawasan permukaannya yang sangat besar serta keupayaan β-CD yang mampu membentuk komplek inklusif di permukaan CNF/ β-CD.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

AFD	-	Average fiber diameter
CTR	-	Citric acid
CD	-	Cyclodextrin
CNF	-	Cellulose nanofiber
DMAc	-	Dimethylacetamide
HPLC	-	High performance liquid chromatography
SEM	-	Scanning electron microscope
SHPI	-	Sodium hydrophosphite hydrate
TGA	-	Thermogravimetric analyser
β- CD	-	Beta- cyclodetxrin

LIST OF SYMBOLS

C_o	-	Initial concentration
C_e	-	Concentration at equilibrium
L	-	Litre
mg	-	miligram
nm	-	nanometer
q_e	-	Amount of adsorbate adsorbed

LIST OF APPENDICES

CHAPTER 1

INTRODUCTION

1.1 Research Background

Excessive releases of pollutants from industrial activities have created a global major concern. As the world now are undergoing rapid industrialization and development eras, it caught the attention of scientist, researchers and engineers all around the world to design an effective wastewater treatment technology in order to keep the environment healthy and to ensure all humankind are continuously feed with safe water. There are a lot of components contain in wastewater including chemical, biological and physical pollutants resulted from various sources such as from communities and industrial activities (Silva-Bedoya *et al*, 2016). A lot of studies are conducted today to ensure that the water pollution is still under control and researchers are intended to help the world to face this challenge by designing new technologies that can be implemented in treating the wastewater effluent before it is released to the natural water sources.

An efficient and low-cost materials for the removal of highly toxic organic compounds from wastewater had given a highlight to the effort of all the scientist in finding the best wastewater treatment. Cost of raw materials in developing the method of new invention will always become a debatable issue and it is one of the critical factors need to be considered. Nowadays, the utilization of all such potential materials as low-cost adsorbents for the treatment of wastewater make the study toward this issue more interesting (Gupta *et al*., 2009). Besides of searching for the potential low-cost method that can be implemented in designing a better wastewater treatment, effective techniques for removal of the pollutants have also drawn significant interest. There are a lot of techniques can be used for wastewater treatment including coagulation, filtration, precipitation, ozonation, adsorption, ion

exchange, reverse osmosis and advanced oxidation processes. However, adsorption technique by solid adsorbents draws possible potential as one of the most efficient method due to its advantages over the other methods as it has simple design and involves low investment in term of both initial cost and land required (Nageeb, 2013). In Malaysia, a strong development of oleochemical industry was supported by a continuous supply of palm oil as the feedstock. However, it has had contributed to the effluent discharged that may contain high amount of fatty acids and glycerol. Recently, as the number of oleochemical industry keep increasing, finding the best method to treat the contaminants from wastewater always become a global challenge.

Cellulose is inexpensive and comes as the most abundant natural bio polymer could be considered in developing a cost-effective wastewater treatment technology. Cellulose offers a lot of promising advantages to be used as wastetwater treatment agent due to its biodegradability, renewability, recyclability, high stiffness with low density, safe (non-toxic) and cheaper (Kabsch *et al*., 2010). In adition to the expanding of nanotechnology for fabricating polymer-based materials, cellulose nanofiber (CNF) manufactured by electrospinning technique seem to have promising method to be used in wastewater treatment. As reported by Wang *et al*., (2016) nanofibrous materials hold excellent potential for various environmental applications including in the treatment of wastewater such as the separation of oily wastewater due to it has high porosity, bigger surface area, better connectivity and various types of materials can be used like polymer, ceramic and carbon thus make the scalable synthesis of it much easier. The key success of nanofibrous materials was due to it voids among fibers which led to a better selectivity. Nanofibrous materials were said to have higher sorption capacity compared to non-nanofibrous or non-porous materials. Zhu *et al*., (2011) had proved that the sorption capacities of electrospun polyvinyl chloride (PVC)/ polystyrene (PS) fibers worked 5- 9 times greater compared to commercial polypropylene (PP) sorbent (non- nanofibrous) for oil spill cleanup. Other than that, Lin *et al*., (2012) had synthesized the nanofibrous sorbents for oily subtances by using nanoporous polystyrene (PS) fibers and it showed that the sorbent exihibit a relatively high sorption capacity for edible oils (bean and sunflower seed oil) approximately 3- 4 times greater than nonporous materials.

On the other hand, CNF usually have a main drawback where it have high hydrophilicity in nature due to a high concentration of hydroxyl group which may lead to unsatisfactory performance. In order to enhance or expand its properties, it is essential to modified CNF by increasing its surface roughness (Ravi *et al*., 2018). Beta-cyclodextrin (β-CD) functionalized electrospun polyacrylic acid (PAA) nanofiber had been synthesized by Zhao *et al*., (2015) and it had drawn a positive result in improving the adsorption and separation of contaminated methylene blue dye in wastewater. Besides that, surface modification of cellulose acetate (CA) nanofiber with β-CD as reported by Celebioglu *et al*., (2014) had recorded that 64% of removal efficiency was achieved in treating phenanthrene from aqueous solution. Another remarkable example of surface modification with β-CD was also proved by Kayaci *et al*., (2013) where cyclodextrins functionalized electropsun polyethylene terepthalate (PET) could successfully removed 83% of penanthrene from aqueous solution. However, study on β-CD functionalized CNF for removal of fatty acids has not been performed before.

Therefore in this study, CNF from cellulose acetate fabricated by electrospinnning process was functionalized with β-CD to enhance its adsorption properties. The effect of functionalization of CNF were studied by analyzing its morphological characteristics and investigating the removal efficiency of the CNF on the uptake of palmitic acid that act as a model of fatty acids from the industrial oleochemical wastewater that were using palm oil as their feedstock.

1.2 Problem Statement

Safe and healthy water is very essential to mankind. Therefore, water sources must be free from any form of environmental pollutions including the contaminated wastewater discharged from industries. Oleochemicals industry is one of the largest sector in Malaysia due to constant supply of palm oil and palm kernel oil. Wastewater from oleochemical effluent which may contained fatty acids and glycerol can be considered as a current challenge for environmentally acceptable disposal because improper treatment could eventually contributes serious and

long lasting consequences to human and life. The treatment for oleochemicals wastewater are including physical, chemical and biological treatment which reported to consume high hydraulic retention time and requires huge space. Furthermore, activated sludge and activated carbon system are the conventional oleochemical wastewater treatment methods for oleochemicals wastewater. However, activated sludge system in conventional oleochemical wastewater treatment plant has higher operating costs while the activated carbon method method seem to be time consuming as it cannot attract contaminant particles efficiently and it was also said to require high intensity heat treatment to reactivate its water cleaning properties. Among the other possible treatment process, adsorption by solid adsorbents shows as one of the most efficient methods for the treatment and removal of organic contaminants in wastewater treatment. An improvement towards adsorption method in treating the wastewater discharged from the oleochemical industry had become an interesting topic to be discovered and explored.

Due to the expanding usage of nanotechnoly-based materrial such as electrospun nanofiber, it seem to have a better and promising adsorption performance as its porous or fibrous structure may offers large surface area for adsorption process. Moreover, combining the nanotechnology technique with low-cost adsorbent material such as cellulose-based polymer could definitely makes this approach more interesting. Cellulose nanofibers has been used for wastewater treatment including removal of dyes, heavy metals, organic compounds and others but there was still no study performed for its application on removal of fatty acid from oily wastewater. However, CNF was reported to have high hydrophilicity that contributes to low adsorption performance for oily pollutants. Thus, to improve its adsorption, CNF needs to undergo surface modification. In response to this concern, this study was carried out to synthesize β-CD functionalized cellulose CNF for treatment of palmitic acid as model of fatty acids wastewater. The effectiveness of using β-CD functionalized CNF in reducing the concentration of palmitic acid was the problem considered in this study.

1.3 Research Objectives

a) To synthesize and characterize the synthesized CNF with and without functionalization with β-CD.

b) To optimize the factors affecting functionalization of β- cyclodextrin (β-CD) with cellulose nanofiber (CNF) for treatment of fatty acids.

c) To evaluate the adsorption performance of β-CD functionalized CNF for removal of fatty acids compounds from industrial oleochemical wastewater.

1.4 Research Scopes

a) Synthesis of CNF by using cellulose acetate as polymer via electrospinning technique. Citric acid act as the crosslinking agent and sodium hydrophosphite hydrate as catalyst to produce β-CD functionalized CNF (CNF/ β-CD).

b) Optimize on the functionalization of β-CD with CNF by manipulating the concentration of β-CD and citric acid during crosslinking process.

c) Characterization of the CNF and CNF/ β-CD by using scanning electron microscope (SEM) and thermogravimetric analysis (TGA). Fourier-transform infrared spectroscopy (FTIR) is also used to analyse the functional group of CNF and CNF/ β-CD.

d) Adsorption of palmitic acid as the model of fatty acids by using CNF and CNF/ β-CD were carried out at different contact time. The reduction of palmitic acid content in the aqueous solution was measured by using high performance liquid chromatography (HPLC) at 210 nm. The reusability of the modified and unmodified CNF were also investigated.

1.5 Significance of Study

This study offers an alternative treatment for removal of fatty acids from industrial oleochemical wastewater especially in Malaysia. By tailoring the cellulose nanofiber via electrospinning process and functionalized with β- CD, it is believed that the modified adsorbent could suit to the target adsorbate. Hence, the study would provide a low-cost and environmental friendly solution as well as high adsorption performance of fatty acids for the treatment of oleochemical wastewater. In addition, the adsorption isotherms and kinetics deduced from this study will provide an important knowledge on nature of the adsorption reaction phenomenon. Last but not least, the analysis of this study will serve as future reference for researchers on using β-cyclodextrin to take up fatty acids compounds.

REFERENCES

Abdel-Halim, M.M.G. Fouda, I. Hamdy, F.A. Abdel-Mohdy, S.M. El-Sawy (2010), Incorporation of chlorohexidin diacetate into cotton fabrics grafted with glycidyl methacrylate and cyclodextrin, *Carbohydrate Polymers* 79 47– 55, 3.

Ademola Rabiu, Samya Elias and Oluwaseun Oyekola (2018). Oleochemicals from Palm Oil for the Petroleum Industry, Palm Oil, Viduranga Waisundara, IntechOpen, DOI: 10.5772/intechopen.76771.

Ahmad, W. R. (2006). The Changing World of Oleochemical. Palm Oil Developments 44, 15- 28.

Ahmed, F. E., Lalia, B. S., & Hashaikeh, R. (2015). A review on electrospinning for membrane fabrication: Challenges and applications. *Desalination*, 356, 15–30.

Alemdar, A.; Sain, M. (2008). Biocomposites from wheat straw nanofibers: Morphology, thermal and mechanical properties. *Composites Science and Technology*, 68 (2), 557-565.

Ali, I., Asim, M., & Khan, T. A. (2012). Low cost adsorbents for the removal of organic pollutants from wastewater. *Journal of Environmental Management*. 113, 170–183.

Anbia, M., & Amirmahmoodi, S. (2011). Adsorption of phenolic compounds from aqueous solutions using functionalized SBA-15 as a nano-sorbent. *Scientia Iranica*, 18(3), 446–452.

Bashar, M. M., Zhu, H., Yamamoto, S., & Mitsuishi, M. (2017). Superhydrophobic surfaces with fluorinated cellulose nanofiber assemblies for oil–water separation. *RSC Advances*, 7(59), 37168–37174.

Bhardwaj, N., & Kundu, S. C. (2010). Electrospinning: A fascinating fiber fabrication technique. *Biotechnology Advances*, 28(3), 325–347.

Celebioglu, A., Demirci, S., & Uyar, T. (2014). Cyclodextrin-grafted electrospun cellulose acetate nanofibers via “Click” reaction for removal of phenanthrene. *Applied Surface Science*, 305, 581–588.

Celebioglu, A., Yildiz, Z. I., & Uyar, T. (2017). Electrospun crosslinked poly-cyclodextrin nanofibers: Highly efficient molecular filtration thru host-guest inclusion complexation. *Scientific Reports*, 7(1).

Ceramic Ultrafiltration Membranes For Separation Of Natural Organic Matter From Water. *Environment Protection Engineering*, 36(01), 125-135.

Chen, G., Shah, K. J., Shi, L., & Chiang, P.-C. (2017). Removal of Cd(II) and Pb(II) ions from aqueous solutions by synthetic mineral adsorbent: Performance and mechanisms. *Applied Surface Science*, 409, 296–305.

Chen, Zhu, P., Liang, H.-W., Lv, X.-H., H.-Z., Yao, H.-B., & Yu, S.-H. (2011). Carbonaceous Nanofiber Membrane Functionalized by beta-Cyclodextrins for Molecular Filtration. *ACS Nano*, 5(7), 5928–5935.

Chitpong, N., & Husson, S. M. (2017). Polyacid functionalized cellulose nanofiber membranes for removal of heavy metals from impaired waters. *Journal of Membrane Science*, 523, 418–429.

Choudhury, A. K. (2017). Cellulose cross- linker. In Principle of Textile Finishing (pp. 245-284). United Kingdom: Woodhead Publishing.

Chronakis, I. S. (2010). Micro-/Nano-Fibers by Electrospinning Technology. *Micro-Manufacturing Engineering and Technology*, 264–286

Coma, V., Sebti, I., Pardon, P., Pichavant, F. ., & Deschamps, A. (2003). Film properties from crosslinking of cellulosic derivatives with a polyfunctional carboxylic acid. *Carbohydrate Polymers*, 51(3), 265–271.

Connors, K. A. (1997). The Stability of Cyclodextrin Complexes in Solution. *Chemical Reviews*, 97(5), 1325–1358.

Crini G. (2003). Studies on adsorption of dyes on beta-cyclodextrin polymer. *Bioresource Technology*, 90,193-198.

Crini, G. (2005). Recent developments in polysaccharide-based materials used as adsorbents in wastewater treatment. *Polymer Science*, 38-70.

Crini, G., Peindy, H., Gimbert, F., & Robert, C. (2007). Removal of C.I. Basic Green 4 (Malachite Green) from aqueous solutions by adsorption using cyclodextrin-based adsorbent: Kinetic and equilibrium studies. *Separation and Purification Technology*, 53(1), 97–110.

De Gisi, S., Lofrano, G., Grassi, M., & Notarnicola, M. (2016). Characteristics and adsorption capacities of low-cost sorbents for wastewater treatment: A review. *Sustainable Materials and Technologies*, 9, 10–40.

Deitzel, J. ., Kleinmeyer, J., Harris, D., & Beck Tan, N. (2001). The effect of processing variables on the morphology of electrospun nanofibers and textiles. *Polymer*, 42(1), 261–272.

Demitri C, Del Sole R, Scalera F, Sannino A, Vasapollo G, Maffezzoli A, et al. (2008) Novel superabsorbent cellulose-based hydrogels crosslinked with citric acid. *J Appl Polym Sci*;110(4):2453-60.

Demitri, C., Del Sole, R., Scalera, F., Sannino, A., Vasapollo, G., Maffezzoli, A., Nicolais, L. (2008). Novel superabsorbent cellulose-based hydrogels crosslinked with citric acid. *Journal of Applied Polymer Science*, 110(4), 2453–2460.

Dichtel, Alzate-Sánchez, D. M., Smith, B. J., Alsbaiee, A., Hinestroza, J. P., W. R. (2016). Cotton Fabric Functionalized with a β-Cyclodextrin Polymer Captures Organic Pollutants from Contaminated Air and Water. *Chemistry of Materials*, 28(22), 8340– 8346.

Duan, Z., Song, M., Li, T., Liu, S., Xu, X., Qin, R. Zhang, M. (2018). Characterization and adsorption properties of cross-linked yeast/β-cyclodextrin polymers for Pb(II) and Cd(II) adsorption. *RSC Advances*, 8(55), 31542–31554.

Elanchezhiyan, S. S. D., & Meenakshi, S. (2017). Facile Fabrication of Metal Ions-Incorporated Chitosan/β-Cyclodextrin Composites for Effective Removal of Oil from Oily Wastewater. *Chemistry Select*, 2(35), 11393–11401.

Fenlin Huang, Qufu Wei, Yibing Cai & Ning Wu. (2008). Surface Structures and Contact Angles of Electrospun Poly(vinylidene fluoride) Nanofiber Membranes. *International Journal of Polymer Analysis and Characterization*, 13(4), 292-301.

Fourmentin S, Outirite M, Blach P, Landy D, Ponchel A, Monflier E, Surpateanu G (2007). Solubilisation of chlorinated solvents by cyclodextrin derivatives. A study by static headspace gas chromatography and molecular modelling. *J Hazard Mater* 141(1):92–97.

Gawish, S. M., Ramadan, A. M., Abo El-Ola, S. M., & Abou El-Kheir, A. A. (2009). Citric Acid Used as a Cross-Linking Agent for Grafting β-Cyclodextrin onto Wool Fabric. *Polymer-Plastics Technology and Engineering*, 48(7), 701-710.

Gawish, S. M., Ramadan, A. M., Mosleh, S., Morcellet, M., & Martel, B. (2005). Synthesis and characterization of novel biocidal cyclodextrin inclusion complexes grafted onto polyamide-6 fabric by a redox method. *Journal of Applied Polymer Science*, 99(5), 2586–2593.

Ghorpade, V. S., Yadav, A. V., & Dias, R. J. (2016). Citric acid crosslinked cyclodextrin/hydroxypropylmethylcellulose hydrogel films for hydrophobic drug delivery. *International Journal of Biological Macromolecules,* 93, 75–86.

Gopakumar, D. A., Pasquini, D., Henrique, M. A., de Morais, L. C., Grohens, Y., & Thomas, S. (2017). Meldrum's Acid Modified Cellulose Nanofiber-Based Polyvinylidene Fluoride Microfiltration Membrane for Dye Water Treatment and Nanoparticle Removal. *ACS Sustainable Chemistry & Engineering,* 5(2), 2026–2033.

Gupta, V. K., Carrott, P. J. M., Ribeiro Carrott, M. M. L., & Suhas. (2009). Low-Cost Adsorbents: Growing Approach to Wastewater Treatment—a Review. *Critical Reviews in Environmental Science and Technology*, 39(10), 783–842.

Haimhoffer, Rusznyak, Reti-Nagy, Vasvari, Varadi, Vecsernyes, Fenyvesi. (2019). Cyclodextrins in Drug Delivery Systems and their Effects on Biological Barriers. *Scientia Pharmaceutica*, 87(4), 33-53.

Hohman, M. M., Shin, M., Rutledge, G., & Brenner, M. P. (2001). Electrospinning and electrically forced jets. I. Stability theory. *Physics of Fluids*, 13(8), 2201–2220.

Huang, H., Fan, Y., Wang, J., Gao, H., & Tao, S. (2013). Adsorption kinetics and thermodynamics of water-insoluble crosslinked β-cyclodextrin polymer for phenol in aqueous solution. *Macromolecular Research*, 21(7), 726–731.

Huang, X., Liu, Y., Liu, S., Tan, X., Ding, Y., Zeng, G., Zheng, B. (2016). Effective removal of Cr(vi) using β-cyclodextrin–chitosan modified biochars with adsorption/reduction bifunctional roles. *RSC Advances*, 6(1), 94–104.

Huang, Z.-M.; Zhang, Y.Z.; Kotaki, M.; Ramakrishna, S. A (2003) Review on Polymer Nanofibers by Electrospinning and Their Applications In Nanocomposites. *Compos. Sci. Technol.* 63, 2223–2253.

Ifuku, S.; Nogi, M.; Abe, K.; Handa, K.; Nakatsubo, F.; Yano, H. (2007). Surface modification of bacterial cellulose nanofibers for property enhancement of

optically transparent composites: dependence on acetyl-group DS. B*iomacromolecules*, 8 (6), 1973-1978.

Ismail, Z., Mahmood, N. A. N., Ghafar, U. S. A., Umor, N. A., & Muhammad, S. A. F. (2017). Preliminary Studies on Oleochemical Wastewater Treatment using Submerged Bed Biofilm Reactor (SBBR). *IOP Conference Series: Materials Science and Engineering*, 206, 012087.

K M, Ravi & Hiremath, Lingayya & Gupta, Praveen Kumar & Srivastava, Ajeet. (2018). Functionalized Cellulose Nanofiber–Composite Membranes for Waste Water Treatment -a Review. *Journal of Nanotechnology and Materials Science*, 5(1), 35-43.

Kafy, A., Kim, H. C., Zhai, L., Kim, J. W., Hai, L. V., Kang, T. J., & kim, J. (2017). Cellulose long fibers fabricated from cellulose nanofibers and its strong and tough characteristic. *Scientific Reports*, 7(1).

Kang, Y., Choi, Y. K., Kim, H. J., Song, Y., & Kim, H. (2015). Preparation of anti-bacterial cellulose fiber via electrospinning and crosslinking with β-cyclodextrin. *Fashion and Textiles*, 2(1), 1-10.

Kaur, S., Kotaki, M., Ma, Z., Gopal, R., Ramakrishna, S., & Ng, S. C. (2006). Oligosaccharide Functionalized Nanofibrous Membrane. *International Journal of Nanoscience*, 05(01), 1–11.

Kayaci, F., Aytac, Z., & Uyar, T. (2013). Surface modification of electrospun polyester nanofibers with cyclodextrin polymer for the removal of phenanthrene from aqueous solution. *Journal of Hazardous Materials*, 261, 286–294.

Kecili, R., & Hussain, C. M. (2018). Mechanism of Adsorption on Nanomaterials.*Nanomaterials in Chromatography*. New Jersey: Elsevier Publisher, pp 89 -115.

Koo, C. H., Mohammad, A. W., & Suja', F. (2011). Recycling of oleochemical wastewater for boiler feed water using reverse osmosis membranes — A case study. *Desalination*, 271(1-3), 178–186.

Korhonen, J. T., Kettunen, M., Ras, R. H. A., & Ikkala, O. (2011). Hydrophobic Nanocellulose Aerogels as Floating, Sustainable, Reusable, and Recyclable Oil Absorbents. *ACS Applied Materials & Interfaces*, 3(6), 1813–1816.

Kwak, H. S., Kim, S. H., Kim, J. H., Choi, H. J., & Kang, J. (2004). Immobilized β-cyclodextrin as a simple and recyclable method for cholesterol removal in milk. *Pharmacal Research*, 27(8), 873–877.

Lee, C.-W. K.-J. (2010). Preparation of bitter taste masked cetirizine dihydrochloride/β-cyclodextrin inclusion complex by supercritical antisolvent (SAS) process. *J. Supercrit. Fluids*. 55, 348–357.

Lin, J., Shang, Y., Ding, B., Yang, J., Yu, J., & Al-Deyab, S. S. (2012). Nanoporous polystyrene fibers for oil spill cleanup. *Marine Pollution Bulletin*, 64(2), 347–352.

Lin, T., Wang, H., Wang, H., & Wang, X. (2004). The charge effect of cationic surfactants on the elimination of fibre beads in the electrospinning of polystyrene. *Nanotechnology*, 15(9), 1375–1381.

Liu H. & Hsieh Y. (2002). Ultrafine Fibrous Cellulose membranes from Electrospinning of cellulose Acetate. *Journal of Polymer Science.* 40, 2119-2129.

Loftsson T, Hreinsdottir D, Masson M. (2005). Evaluation of cyclodextrin solubilization of drugs. *Int J Pharm* 302:18–28.

Lyons, J.; Ko, F.K. Nanofibers. Encycl. Nanosci. Nanotechnol. (2004), 6, 727–738.

M. Gou, F. C. (2004). 'Chemical Modification of Cellulose in Orderto Increase the Wettability and Adhesionin Composites', *Afinidad* 61 (513), 393-395.

M. Kabsch-Korbutowicz & Agnieszka Urbanowska. (2010).Encapsulation of triclosan within 2-hydroxypropyl–β–cyclodextrin cavity and its application in the chemisorption of rhodamine B dye. *Journal of Molecular Liquids*. 282, 235-243.

Md. Akhratul Islam, M. M. (2004). Adsorption Equilibrium and Adsorption Kinetics: A Unified Approach, *Chemical Engineering Technology*, 1095-1098.

Meghan Mc Coy. (2018). Types of Waste Water. *Sciencing.*

Missoum, K., Belgacem, M., & Bras, J. (2013). Nanofibrillated Cellulose Surface Modification: A Review, *Materials*, 6(5), 1745–1766.

Mittal, A. (2011). Biological Wastewater Treatment. *Water Today* , 32-44. Morin-Crini, N., Winterton, P., Fourmentin, S., Wilson, L. D., Fenyvesi, E. & Crini, G. (2018). Water-insoluble β-cyclodextrin–epichlorohydrin polymers for removal of pollutants from aqueous solutions by sorption processes using

batch studies: A review of inclusion mechanisms, *Polymer Science*, 78, 1–23.

Morozov, V. N. (2009) '*Electrospray Deposition of Biomolecules'*, in Advanced Biomedical engineering/ Biotechnology. Berlin, Heidelberg (pp. 115- 162)

Murcia-Salvador, A., Pellicer, J. A., Fortea, M. I., Gomez-Lopez, V. M., Rodríguez-Lopez, M. I., Núñez-Delicado, E., & Gabaldón, J. A. (2019). Adsorption of Direct Blue 78 Using Chitosan and Cyclodextrins as Adsorbents. *Polymers*, 11(6), 1003.

N. Blanchemain, S. Haulon, E. Marcon-Bachari, M. Traisnel, C. Neut, J. Kirkpatrick, M. Morcellet, H. Hildebrand, B. Martel, (2007) Vascular prostheses with controlled release of antibiotics. Part 1. Surface modification with cyclodextrins of PET prostheses. *Biomolecular Engineering* 24 149–153.

Nageeb, M. (2013). Adsorption Technique for the Removal of Organic Pollutants from Water and Wastewater. Organic Pollutants - Monitoring, Risk and Treatment.

Neha Sharma & Ashish Baldi (2016) Exploring versatile applications of cyclodextrins: an overview. *Drug Delivery*, 23:3, 729-747.

Orelma, H., Virtanen, T., Spoljaric, S., Lehmonen, J., Seppälä, J., Rojas, O. J., & Harlin, A. (2018). Cyclodextrin-Functionalized Fiber Yarns Spun from Deep EutecticCellulose Solutions for Nonspecific Hormone Capture in Aqueous Matrices. *Biomacromolecules*, 19(2), 652–661.

Ottewell, S. (2018). Scientists Eye Cheaper Adsorbent. Large.

Panesar, D., Leung, R., Sain, M., & Panthapulakkal, S. (2017). 'The effect of sodium hydroxide surface treatment on the tensile strength and elastic modulus of cellulose nanofiber. *Sustainable and Nonconventional Construction Materials Using Inorganic Bonded Fiber Composites, 17–26.*

Paulino, A. T., Belfiore, L. A., Kubota, L. T., Muniz, E. C., & Tambourgi, E. B. (2011). Efficiency of hydrogels based on natural polysaccharides in the removal of Cd^{2+} ions from aqueous solutions. *Chemical Engineering Journal.* 168(1), 68–76

Pellicer, J., Rodríguez-López, M., Fortea, M., Lucas-Abellán, C., Mercader-Ros, M., Lopez-Miranda, S., Gabaldón, J. (2019). Adsorption Properties of β- and Hydroxypropyl-β-Cyclodextrins Cross-Linked with Epichlorohydrin in

Aqueous Solution. A Sustainable Recycling Strategy in Textile Dyeing Process. *Polymers,* 11(2), 252-261.

Perlman, H. (2 December, 2016). USGS. Retrieved from Wastewater Treatment: https://water.usgs.gov/edu/wuww.html

Quellmalz, A., & Mihranyan, A. (2015). Citric Acid Cross-Linked Nanocellulose-Based Paper for Size-Exclusion Nanofiltration. *ACS Biomaterials Science & Engineering,* 1(4), 271–276.

Raucci, M. G., Alvarez-Perez, M. A., Demitri, C., Giugliano, D., De Benedictis, V., Sannino, A., & Ambrosio, L. (2014). Effect of citric acid crosslinking cellulose-based hydrogels on osteogenic differentiation. *Journal of Biomedical Materials Research Part A,* 103(6), 2045–2056.

Reneker, D. H., & Yarin, 'A. L. (2008). Electrospinning jets and polymer nanofibers', *Polymer*, 49 (10), 2387- 2425

Reneker, D.H.; Hou, H. Electrospinning. Encycl. Biomater. Biomed. Eng. (2004), 1, 543–550.

Rodrigo Ortega-Toro, A. J. (2014). Properties of starch–hydroxypropyl methylcellulose based films obtained by compression molding. *Carbohydrate Polymer*, 155-165.

Saha, D., & Grappe, H. A. (2017). Adsorption properties of activated carbon fibers, *Activated Carbon Fiber and Textiles*, 143–165.

Sanderson, H., Fricker, C., Brown, R. S., Majury, A., & Liss, S. N. (2016). Antibiotic resistance genes as an emerging environmental contaminant. *Environmental Reviews*, 24(2), 205–218.

Sehaqui, H., de Larraya, U. P., Liu, P., Pfenninger, N., Mathew, A. P., Zimmermann, T., & Tingaut, P. (2014). Enhancing adsorption of heavy metal ions onto biobased nanofibers from waste pulp residues for application in wastewater treatment, *Cellulose*, 21(4), 2831–2844.

Seligra, P. G., Medina Jaramillo, C., Famá, L., & Goyanes, S. (2016). Biodegradable and non- retrogradable eco-films based on starch–glycerol with citric acid as crosslinking agent. *Carbohydrate Polymers,* 138, 66–74.

Semeraro P, Fini P, D'Addabbo M, Rizzi V, Cosma P. (2017). Removal from wastewater and recycling of azo textile dyes by alginate-chitosan beads. *International Journal of Environmental, Agriculture and Biotechnology*, 2, 1835-1850.

Semeraro, P., Rizzi, V., Fini, P., Matera, S., Cosma, P., Franco, E., Ferrándiz, M. (2015). Interaction between industrial textile dyes and cyclodextrins. *Dyes and Pigments*, 119, 84–94.

Shen, H.-M., Zhu, G.-Y., Yu, W.-B., Wu, H.-K., Ji, H.-B., Shi, H.-X. She, Y.-B. (2015). Surface immobilization of β-cyclodextrin on hybrid silica and its fast adsorption performance of p-nitrophenol from the aqueous phase. *RSC Advances*, 5(103), 84410–84422.

Sikder, M. T., Kikuchi, T., Suzuki, J., Hosokawa, T., Saito, T., & Kurasaki, M. (2013). Removal of Cadmium and Chromium Ions Using Modified α, β, and γ- Cyclodextrin Polymers. *Separation Science and Technology*, 48(4), 587–597.

Silva-Bedoya, L. M., Sánchez-Pinzón, M. S., Cadavid-Restrepo, G. E., & Moreno-Herrera, C. X. (2016). Bacterial community analysis of an industrial wastewater treatment plant in Colombia with screening for lipid-degrading microorganisms. *Microbiological Research*, 192, 313–325.

Smith LA, Ma PX. (2004). Nanofibrous scaffolds for tissue engineering. *Biointerfaces*, 39:125–31.

Snyder, A., Bo, Z., Moon, R., Rochet, J.-C., & Stanciu, L. (2013). Reusable photocatalytic titanium dioxide–cellulose nanofiber films. *Journal of Colloid and Interface Science*, 399, 92–98.

Snyder, A., Bo, Z., Moon, R., Rochet, J.-C., & Stanciu, L. (2013). Reusable photocatalytic titanium dioxide–cellulose nanofiber films. *Journal of Colloid and Interface Science*, 399, 92–98.

Song, C., Ding, L., Yao, F., Deng, J., & Yang, W. (2013). β-Cyclodextrin-based oil-absorbent microspheres: Preparation and high oil absorbency, *Carbohydrate Polymers*, 91(1), 217–223.

Stephen R. (2015). Treatment of Industrial Oleochemical Wastewater Using Electrocoagulation Method. *Chemical & Natural Resources.* 46-58.

Szejtli, J. (1998). Introduction and general overview of cyclodextrin chemistry. *Chemistry Review*. 743-1753.

T. Uyar, R. Havelund, J. Hacaloglu, F. Besenbacher, P. Kingshott, Functional (2010) Electrospun Polystyrene Nanofibers Incorporating α-, β-, and γ-cyclodextrins: Comparison of Molecular Filter Performance, *ACS Nano* 4 5121–5130.

Taha, A. A., Wu, Y., Wang, H., & Li, F. (2012). Preparation and application of functionalized cellulose acetate/silica composite nanofibrous membrane via electrospinning for Cr (VI) ion removal from aqueous solution, *Journal of Environmental Management*, 112, 10–16.

Valle, E. D. (2004) Cyclodextrins and their uses: a review. Process Biochemistry. 39(9): 1033-1046

Vidhathri, B.S., V.R. Ramakrishna Parama, C.T. Subbarayappa, T.K. Narayanaswamy, R. Muthuraju, D.S. Mahesh and Vidyashree, D.N. (2017). Isolation and Detection of Alpha Linolenic Acid from Silkworm Pupal Residue Oil using HPLC. Int.J.Curr.Microbiol.App.Sci. 6(7): 2202-2206.

Voisin, H., Bergström, L., Liu, P., & Mathew, A. (2017). Nanocellulose-Based Materials for Water Purification, *Nanomaterials*, 7(3), 57-65.

Wang X., Yeh T.-M., Wang Z., Yang R., Wang R., Ma H., Hsiao B.S., Chu B. (2014). Nanofiltration membranes prepared by interfacial polymerization on thin-film nanofibrous composite scaffold, *Polymer Science*, 55, 1358–1366.

Wang, C.-C., & Chen, C.-C. (2005). Physical properties of the crosslinked cellulose catalyzed with nanotitanium dioxide under UV irradiation and electronic field, *Applied Catalysis A: General*, 293, 171–179.

Wei, Y., Van Houten, R. T., Borger, A. R., Eikelboom, D. H., & Fan, Y. (2003). Minimization of excess sludge production for biological wastewater treatment. *Water Research*, 37(18), 4453–4467.

Wilpiszewska, K., Antosik, A.K. & Zdanowicz, M. J Polym Environ (2019) 27: 1379.

Xie X, Liu Q. (2004) Development and physic-chemical characterization of new resistant citrate starch from different corn starches. *Starch*, 56(8):364-70.

Xie, X. (Sherry), Liu, Q., & Cui, S. W. (2006). Studies on the granular structure of resistant starches (type 4) from normal, high amylose and waxy corn starch citrates, *Food Research International*, 39(3), 332–341.

Yilmaz, E., Memon, S., & Yilmaz, M. (2010). Removal of direct azo dyes and aromatic amines from aqueous solutions using two β-cyclodextrin-based polymer. *Journal of Hazardous Materials*. 174(1-3), 592–597.

Yin, C., Cui, Z., Jiang, Y., van der Spoel, D., & Zhang, H. (2019). Role of Host−Guest Charge Transfer in Cyclodextrin Complexation: A Computational Study. *Journal of Physical Chemistry*. 123 (29), 17745-17756.

Yoon, K., Hsiao, B. S., & Chu, B. (2008). Functional nanofibers for environmental applications. *Journal of Materials Chemistry*, 18(44), 5326-5334.

Youn-Mook Lim, Hui-Jeong Gwon, Joon Pyo Jeun, and Young-Chang Nho (2010). Preparation of Cellulose-based Nanofibers Using Electrospinning, Nanofibers, Ashok Kumar, IntechOpen, doi: 10.5772/8153

Yuan, G., Prabakaran, M., Qilong, S., Lee, J. S., Chung, I.-M., Gopiraman, M. Kim, I. S. (2017). Cyclodextrin functionalized cellulose nanofiber composites for the faster a dsorption of toluene from aqueous solution. *Journal of the Taiwan Institute of Chemical Engineers*, 70, 352–358.

Zhang Z., Sèbe G., Rentsch D., Zimmermann T., Tingaut P. (2014). Ultralightweight and flexible silylated nanocellulose sponges for the selective removal of oil from water, *Chem. Mater*, 26, 2659–2668.

Zhao, R., Wang, Y., Li, X., Sun, B., & Wang, C. (2015). 'Synthesis of β-Cyclodextrin- Based Electrospun Nanofiber Membranes for Highly Efficient Adsorption and Separation of Methylene Blue', *ACS Applied Materials & Interfaces*, 7(48), 26649–26657.

Zhou YJ, Luner P, Caluwe P. Mechanism of crosslinking of papers with polyfunctional carboxylic acids. *J Appl Polym Sci* 1995;58(9):1523-34. 39.