CSCE Annual Conference
Growing with youth – Croître avec les jeunes

Laval (Greater Montreal)
June 12 - 15, 2019

FABRICATION OF NANO PARTICLES MODIFIED CELLULOSE BIOMASS FOR OIL-WATER SEPARATION

Yunqiu Liu[1], Gordon Huang[1, 2*], Chunjiang An[3], and Xiujuan Chen [1]
[1] Faculty of Engineering and Applied Science, University of Regina, Regina, S4S 0A2, Canada
[2] Institute for Energy, Environment and Sustainable Communities, University of Regina, Regina, S4S 0A2, Canada
[3] Department of Building, Civil and Environmental Engineering, Concordia University, Montreal, H3G 1M8, Canada

Abstract: Attention has been paid to the problem of oily water contamination. In order to meet the strict discharging requirement and obtain a high product quality, efficient separation is required. Cellulose biomass can be used in separation processes due to its good performance and low cost. Although cellulose biomass has been fabricated into hydrophobic or even superhydrophobic filter through various methods in some previous studies, the techniques about producing hydrophilic and underwater oleophobic materials are limited. The hydrophilic filter based on such natural material is also featured energy saving and anti-fouling. Coating hydrophilic nanoparticles onto cellulose biomass surface has the potential for developing novel filter. Therefore, this study aims to modify cellulose biomass through attaching nanoparticles on the biomass surface. The hydrophilic characteristics of modified biomass were analysed through the measurement of contact angle. The optimum modification conditions were determined based on factorial analysis. The modified biomass were also characterized by scanning electron microscope (SEM) and Fourier-transform infrared spectroscopy (FTIR) analyses. The modified biomass was used in oil-water separation. After modification, it was found the restriction of oil was enhanced. The modified biomass filter was proved to be suitable in defencing oil from immiscible oil/water. This innovative green separation technique filter can be widely applied in future water recovery.

Keywords: Nano particles; Cellulose biomass; Oil-water separation

1. PROJECT OVERVIEW

Marine spillages of oil caused by petroleum platform and transportation are widespread water pollutants and can be transported by wind and current, which has become a leading global risk factor for environment and human health (Ivshina et al. 2015). Traditional separation methods such as combustion, gravity separation, centrifugation, and etc. require complicated operation and may cause potential secondary pollutants (Stack et al. 2005, Grimes 2012, Naghdi and Peer 2016). Therefore, it is urgent to find a kind of material with special wettability surface to separate oil-water (Xue et al. 2014). Both synthetic and natural materials with special wettability have been fabricated into oil barrier. Compared with the synthetic material, biomass material takes advantage in biological degradability, resource abundance and low cost (Wang et al. 2018). Therefore, studies related to modify nature materials performing as oil barrier are increasing. For instance, Jin et al 2015. created polydimethylsiloxane (PDMS)-coated cotton to absorb oil taking advantage of its superhydrophobic and superoleophilic characteristic. Adsorption method was used to remove amounts of oil by hydrophobic kapok fiber (Hori et al. 2000). Yuan et al. 2018 created superhydrophobic biomass carbon@SiO_2@MnO_2 aerogel derived from environmentally friendly sisal cellulose. Previous studies mentioned before mainly focused on fabricating hydrophobic or superhydrophobic filter. Methods about forming a hydrophilic surface of natural biomass were limited (Wang et al. 2015). The hydrophilic filter based on such natural material was featured energy saving and anti-fouling (Rohrbach et al. 2014). Coating hydrophilic nanoparticles onto cellulose biomass surface has the potential for developing novel filter. Therefore, this study aims to modify cellulose biomass through attaching hydrophilic nanoparticles on the biomass surface. Organizations and clients such as Department of Fisheries and Oceans (DFO), Suncor and Husky and Chevron may benefit from the project.

2. CASE STUDY METHODS:

There were mainly three steps in the process of fabrication. The fabrication method was put forward by You et al. 2012. Plasma was first induced to curve the surface of biomass, contributing to an activated surface cover by oxidized free radicals. It was found that although nanoparticles might exist in cracks and be absorbed in biomass, the surface of biomass could not attach nanoparticles firmly and stably. The oxidation groups such as hydroxyl generated by plasma could react with carboxyl. So in the next step, the plasma-treated biomass was immersed into acrylic acid. Finally, the polymer acrylic acid (PAA) layered biomass was immersed into TiO_2 nanoparticles solution. The PAA layer formed on biomass surface played an important role in catching hydrophilic TiO_2 nanoparticles by electrostatic interaction, ion coordination or hydrogen bonding.

As three steps were mentioned in the fabrication process, there were a variety of factors that might have effect on the assembly of hydrophilic nanoparticles on biomass. In order to investigate the significance of each operation factor and find the optimal operation condition, factorial experiment design was performed. The modified biomass under the optimal parameters was applied to filtrate water while repel oil. To test whether the modified biomass could be used in real cases, biomass was tested to separate immiscible oil/water. 5 mL oil dyed by Red oil-O and 5 mL distilled water were mixed and poured into the funnel with compressed biomass at the bottom. The distilled water used was in neutral pH and conductivity was 0.06 mS/cm. Analytical methods included tests in contact angle and oil rejection efficiency. Comprehensive characterizations of modified biomass were also studied by scanning electron microscope (SEM) and Fourier-transform infrared spectroscopy (FTIR).

3. RESULTS:

After nanoparticles binding, the cellulose biomass was found to be hydrophilic. Figure 1 showed the hydrophilic nanoparticles were successfully bonded with biomass. Water contact angle under different operation parameters was recorded and the best combination was put forward at plasma power at 200 W, AA concentration at 80 % and hydrophilic nanoparticles concentration at 1%. When applied in separating oil-water, the modified biomass showed good performance with rejection rate at 92.4%. Figure 2 showed the separation performance of the modified biomass. The water was filtrated while oil was defenced at the top. This innovative green separation technique filter can be widely applied in future oil defence and separation cases.

4. INNOVATION:

For one thing, most of studies fabricated hydrophobic or superhydrophobic natural materials, but this study found a novel method to modify hydrophilic biomass. For another, the experiment design referred to factorial design. The modification influencing parameters and their combinations were investigated and the optimal levels were selected via relatively less experiments and less labour. In addition, nanoparticles were found difficult to be attached on biomass surface and are unstable, in this study, a plasma induced PAA layer was able to catch nanoparticles firmly.

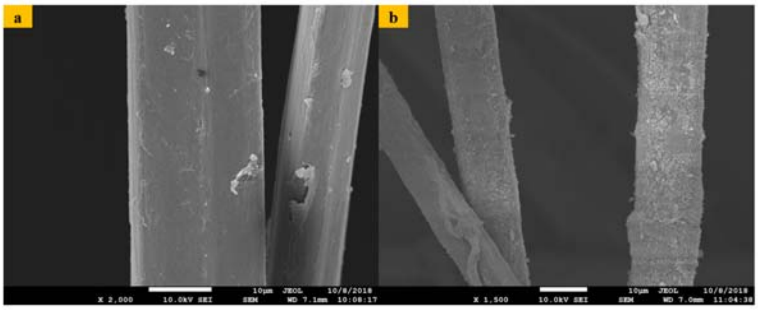

Figure 1: SEM image of biomass: (a) untreated biomass; (b) hydrophilic nanoparticles modified biomass

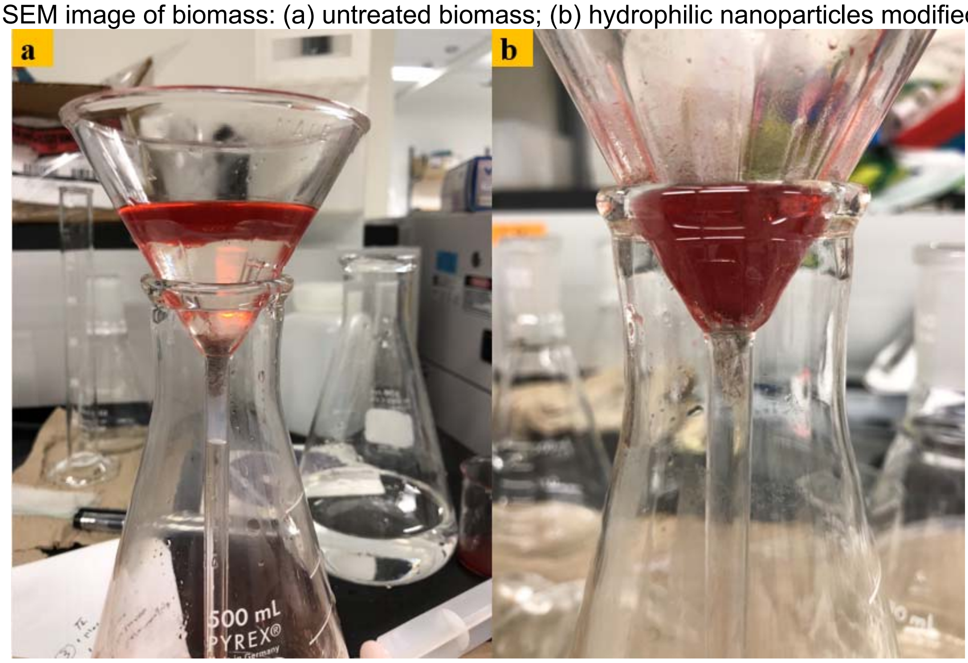

Figure 2: Application in oil-water separation: (a) initial immiscible oil-water; (b) separation after 15 min

5. LESSONS LEARNED:

Firstly, factorial design was found to be a useful tool to analyze single parameter and their interactions and thus the optimal operation parameter could be selected. Compared to “one factor at a time” design, it featured in less labor and the potential interactions between factors could be found. Secondly, the modified hydrophilic biomass could filtrate water while repel oil automatically by gravity, saving much energy. Therefore, the modified biomass is promising since it is recyclable, sustainable and biodegradable and may be further used as oil defence or oil barrier in separating oil-water. However, limitations still exist in the chemical valence between nanoparticles and biomass being unknown. Another problem is how to build a connected and strong oil barrier when used in real case. The individual biomass should be connected together in order to build oil barrier due to the short length of biomass. However, the network within biomass is complicated so its structure is stable and is difficult to be broken.

References:

Grimes, B.A. 2012. Population balance model for batch gravity separation of crude oil and water emulsions. Part I: model formulation. *Journal of Dispersion Science and Technology*, **33**(4): 578-590.
Hori, K., et al. 2000. Excellent oil absorbent kapok [Ceiba pentandra (L.) Gaertn.] fiber: fiber structure, chemical characteristics, and application. *Journal of wood science*, **46**(5): 401-404.
Ivshina, I.B., et al. 2015. Oil spill problems and sustainable response strategies through new technologies. Environmental Science: Processes & Impacts, 17(7): 1201-1219.
Jin, Y., et al. 2015. Superhydrophobic and superoleophilic polydimethylsiloxane-coated cotton for oil–water separation process: An evidence of the relationship between its loading capacity and oil absorption ability. Journal of hazardous materials, 300: 175-181.
Naghdi, Forough Ghasemi, and Peer M. Schenk. 2016. Dissolved air flotation and centrifugation as methods for oil recovery from ruptured microalgal cells. Bioresource technology, 218: 428-435.
Rohrbach, K., et al. 2014. A cellulose based hydrophilic, oleophobic hydrated filter for water/oil separation. Chemical Communications, 50(87): 13296-13299.
Stack, L.J., et al. 2005. Factors influencing the ultrasonic separation of oil-in-water emulsions. Ultrasonics sonochemistry, 12(3): 153-160.
Wang, B., et al. 2015. Biomimetic super-lyophobic and super-lyophilic materials applied for oil/water separation: a new strategy beyond nature. Chemical Society Reviews, 44(1): 336-361.
Wang, W., et al. 2018. Adsorption of anionic azo dyes from aqueous solution on cationic gemini surfactant-modified flax shives: synchrotron infrared, optimization and modeling studies. Journal of cleaner production, 172: 1986-1997.
Xue, Z., et al. 2014. Special wettable materials for oil/water separation. Journal of Materials Chemistry A, 2(8): 2445-2460.
Yuan, D., et al. 2018. Recyclable biomass carbon@ SiO2@ MnO2 aerogel with hierarchical structures for fast and selective oil-water separation. Chemical Engineering Journal, 351: 622-630.

You, S.J., et al. 2012. Evaluation of the antifouling and photocatalytic properties of poly (vinylidene fluoride) plasma-grafted poly (acrylic acid) membrane with self-assembled TiO2. Journal of Hazardous materials, 237: 10-19.