CELLULAR POLYMERS FOR OIL/WATER MIXTURES SEPARATION – EVALUATION OF PROCESS CONDITIONS

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Abstract

This study investigates the usage of cellular polymers for large scale oil/water separation. The model polyester polyurethane foam was characterized for sustainability and oil adsorption efficacy in a batch system. The temporal mass uptake and its efficacy were experimentally optimized at various temperatures and stirring speeds. With favorable surface, morphology, and bulk properties in conjunction with process conditions, and a mass uptake of 21 g/g of foam, this polymer lends itself as a very promising material for oil adsorption.

Introduction

Petroleum is a critical component of our energy and economic infrastructure. In recent years, due to decline in conventional fossil fuel reserves, extraction of oil from unconventional bitumen oil sands has been actively explored. For Canada, the economic impact is enormous, as it is home to the world’s largest oil sands reserves, estimated at 1.7 trillion barrels of bitumen [1]. Unfortunately, the unconventional oil extraction processes produce 1 billion m\(^3\) of oily wastewater, referred to as oil sands tailings, causing many environmental impacts [2]. One of the challenges in treating tailings is removal of residual organic compounds of droplet size less than 10 \(\mu\)m. Thus, effective, low-cost, and sustainable treatment methods are required to treat rapidly growing oily wastewater effluents, such as oil sands tailings, produced water, petrochemical effluents and oil spills.

Current treatment technologies are limited by either effectiveness, cost, or sustainability factors. For example, the pressure-driven membrane technology relies on size exclusion to remove oil droplets. However, the expensive membrane pores clog easily and polymeric membranes degrade due to high pressures causing decline in permeation and flux [3]. Therefore, it is an energy and cost intensive technology. Secondly, the biological treatment methods are very slow, require large amount of land, and require chemical dispersants to accelerate the process [2]. Therefore, it is not an environmental friendly process. Finally, adsorption technology is considered as the most effective, simple to operate, and low-cost technology. The best adsorbent material to date is activated carbon. However, it has low attrition, low selectivity, low mass uptakes, and is expensive to regenerate [4]. Natural adsorbents, such as cotton, kapok, and wood are readily available. Yet, they have poor mass uptake and selectivity [2]. Recently, superwetting cellular polymers with multifunctional properties have found pervasive usage in oil spill remediation owing to their enhanced mass uptake, self-cleaning properties, and reusability [4-8]. However, only a few superwetting foams exhibited effectiveness towards emulsified organic compounds [9]. Furthermore, these materials are fabricated with expensive materials, such as carbon nanotubes, graphene, metal oxides that are have a negative impact on the environment [10,11].

Alternatively, we applied a hydrophilic polyester polyurethane foam to remove dissolved and emulsified oil droplets from stable oil/water emulsions [12-14]. Even though the foam is hydrophilic, due to its basic functional groups, it has an affinity towards acidic oil droplets via acid-base and other molecular interactions [15-17]. Furthermore, the adsorption capacity could be enhanced with process conditions temperature and stirring speed. The temperature may increase the adsorption due to the reduction in oil/water interfacial tension, and the endothermic process of adsorption [9,18]. Similarly, hydrodynamic forces influence droplets adsorption onto the solid surface due to faster drainage of interfacial film between oil droplets and solid surface [18-21]. In this work, the influence of temperature and stirring speeds were explored to determine the minimum temperature and stirring speed required for maximum adsorption of oil droplets at various concentrations of oil in the surrogate oily wastewater (model crude oil/water emulsions). We have also characterized the foam for its thermal stability and elasticity strength towards long-term, sustainable usage. Preliminary results show polyester polyurethane foam has the potential to employ as the adsorbent for dissolved and emulsified organics removal at minimum operating conditions determined in this study.
Materials and Methods

Commercial polyester polyurethane (PESPU) open cell polymer foam with a density of 28.8-35.2 kg/m$^3$, thermal conductivity of approximately 0.038 W/m K, porosity of 96.8%, and an average pore size of approximately 700 μm was selected as the adsorbent material for the study. Texas raw crude, which is a mixture of various hydrocarbons, surfactants, and impurities, was used as a model organic pollutant in model oil/water emulsions, to employ as a surrogate for tailings water, in order to achieve consistency in results. The emulsions were prepared using a high-speed mixer at desired oil concentrations. Detailed characterization of oil/water emulsions is provided elsewhere [14].

Material characterization

Thermogravimetric analysis experiments were performed using a TA instrument (TGA Q50 V20.13 Build 39). Aluminum pans, each containing 5-10 mg of PESPU samples in a nitrogen atmosphere of 1 atm, were heated from 25 °C to 700 °C at a heating rate of 10 °C/min. The foam’s compressive strength was determined by subjecting it to a cyclic compression test in an Instron 5848 microtester 50 N load cell. The test was done at a compression rate of 1 mm/min. and a maximum strain of 90% for 10 cycles. The foam was then compressed to a maximum strain of 90% at a very low stress level of 0.32 kPa.

Adsorption experiments

To determine the influence of the process conditions on the mass uptake, batch adsorption experiments were carried out using a hot plate and stirrer (CORNING, PC-420D) at room temperature and 40 °C and at 0 rpm and 500 rpm. In the batch experiments, the volume of the model emulsion was typically 100 mL, and approximately 0.75 g of PESPU foam sample was used in each adsorption experiment. The procedure was employed as follows: 100 mL of crude oil/water emulsion at the desired concentration was placed in a beaker, heated to the required temperature, and stirred at a constant speed. The foam sample was then submerged in the emulsion and was weighed at predefined intervals to determine the change in the mass uptake. The amount of emulsion adsorbed per unit weight of the foam was calculated from the measured change in the mass uptake and the initial weight of the foam, $M_i$, according to the equation:

$$\text{Fractional mass uptake}, \frac{M_f - M_i}{M_i}. \quad (1)$$

where, $M_i$ is the instantaneous adsorbent weight (g), and $M_o$ is the initial weight of the adsorbent (g).

Typically, fine and dilute emulsions show noticeable turbidity. The initial and residual turbidity of the model emulsions were measured using a LaMotte turbidity meter (LTC-3000we). The bulk oil contamination removal was estimated as change in turbidity using the following equation:

$$\text{Turbidity removal}, \eta\% = \left(1 - \frac{C}{C_0}\right) \times 100. \quad (2)$$

where, $C_0$ and $C$ are the initial and final turbidity of the emulsion (NTU), respectively.

Results and Discussion

The material thermal stability and decomposition temperature were obtained using thermal gravimetric analysis (TGA). The TGA curve in Fig. 1 shows the weight loss versus the temperature up to 500 °C, at which the foam had completely decomposed. The TGA results suggested the foam was thermally stable up to 220 °C. As the oil/water emulsions adsorption/desorption process temperatures were well below 220 °C, the foam could be considered as sustainable. Furthermore, to improve the rate of oil/water separation, the foam could be operated anywhere below this temperature, such as in the off-shore production line or on-shore oil spill cleanup soon after the incident.

The crosslinked structure of the polymer provides mechanical stability to the foam and therefore it can be compressible. To determine the compressive strength necessary for the foam’s reusability via mechanical compression, the samples were subjected to a cyclic compression test in a controlled environment according to ASTM D-395. To determine the compressive strength, cyclic compression test was performed using an Instron 5848 microtester 50 N load cell. The test was done at a compression rate of 1 mm/min at a maximum strain of 90% for ten cycles. The foam was compressed to a maximum strain of 90% at a very low stress level of 0.32 kPa. The adsorbent exhibited permanent shape changes of less than 1% after ten cyclic compressions indicating excellent compressive strength. This suggested that the foam could be regenerated by mechanical compression. The adsorbed oil can also be extracted by rinsing the foam with aqueous surfactant solution. Compared with rinsing, mechanical compression is advantageous because it results in higher oil recovery and foam reusability without the need of chemicals. To limit the environmental impact and the material costs, the highly compressible PESPU foam can be reused multiple time after the adsorbed oil has been extracted.

The small droplets, because of interfacial repulsive forces, remain in random Brownian motion resulting in
limited transport to and deposition onto the foam. Through adjusting process parameters, such as temperature and agitation, these interfacial repulsive forces can be reduced to enhance adsorption onto the solid surface.

To establish the baseline, the adsorption experiments were conducted at crude oil concentrations of 1 vol% and 3 vol% at the ambient room temperature (Fig. 2). At 1 vol% oil concentration, the polymer mass uptake was 18.3 g/g of adsorbent and turbidity removal was 96.1%. At 3 vol% oil concentration, 18.8 g/g of adsorbent and turbidity removal was 96.6%. Although there is difference in concentration, there is no significant difference between the mass uptake trends of 1 vol% and 3 vol% oil concentrations, indicating that the driving force for oil adsorption is the concentration gradient. When the temperature was increased from the room temperature to 40 °C at 1 vol% oil concentration, the turbidity removal improved from 96.1% to 97.3%, while the treatment time is reduced from 24 hrs to 18 hrs. Similarly, at 3 vol% oil concentration, the turbidity removal improved from 96.6% to 97.4%, while the treatment time is reduced from 24 hrs to 18 hrs. The improvement in separation efficacy and reduction in time are attributed to endothermic nature of the adsorption. As the temperature increases, the surface chemistry of the droplets changes causing reduction in the oil/water interfacial tension. Thus, the droplets agglomerate and/or coalescence [9]. Furthermore, in the case of solid-droplet attachment, the increase in the temperature causes improvement in endothermic adsorption due to enhanced intermolecular forces [18].

Emulsions agitation also aids the adsorption process through pressure exerted by the dynamic pressure oil droplets onto the solid surface. The higher the pressure, the faster the water film depletes between the oil droplets and the solid surface, resulting in adhesion of oil droplets onto the foam surface [19]. To quantify these effects, adsorption experiments were performed at agitation rates of 0 rpm and 500 rpm at room temperature. The mass uptakes were improved when subjected to a constant agitation rate of 500 rpm. At 1 vol% oil concentration, there was a change turbidity 96.1% to 99.9%. In addition, the treatment time is reduced from 24 hrs to 2 hrs. Similarly, at 3 vol% oil concentration, the turbidity improved from 96.6% to 99.9%, while the treatment time is reduced from 24 hrs to 8 hrs. The improvement in oil removal rate indicates that there is a faster film drainage between the droplets and solid surface due to hydrodynamic forces [20,21].

The synergic effect of temperature and agitation on the turbidity removal and treatment times was also experimentally characterized. The experimental results are listed in Table 1. As shown, after 4 hrs treatment time at 40 °C, and 500 rpm, turbidity removal of 98.1% was achieved with 1 vol% oil while, 98.7% of oil removal was achieved with 3 vol% oil removal within 2 hrs. The treated emulsified water before and after treatment is shown in Fig. 3. These results show that there are tradeoffs to be considered when choosing the operational droplets that need to be transported/adsorbed. A larger force is required to overcome the interfacial forces, which is provided by both temperature and agitation. It is worth noting that for both oil concentrations, when subject to temperature and agitation demulsification, 95% of turbidity removal is achieved within the initial 0.5-1 hrs of treatment due to faster physisorption, while for the remaining oil, the treatments times are prolonged most likely due to chemisorption or lower number of active functional groups.

Conclusions

The polyester polyurethane foam is a good adsorbent to remove dissolved and emulsified organic compounds. Its acid-base surface composition allows oil uptake by adsorption, which improves with increase in temperature and stirring may be by enhanced acid-base interactions and interfacial film depletion. The foam also possesses temperature stability below 220 °C and high compressive strength. Future experiments will be performed at higher temperatures and flow rates using a lab scale filtration system.

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References

Figures and Tables

Figure 1. Thermogravimetric analysis of the polyester polyurethane foam showing thermal stability up to 200 °C.

Figure 2. Adsorbent isotherms showing the effect of initial oil concentration at room temperature on the adsorption rate, mass uptake, and treatment times.

Figure 3. Model crude oil/water emulsions A) before and B) after cleaning with PESPU foam at 40 °C and 500 rpm. Three samples of cleaned water show the foam consistent with oil removal.
Table 1. Mass uptake and turbidity removal efficiency at examined process conditions.

<table>
<thead>
<tr>
<th>Process conditions</th>
<th>Turbidity removal (%)</th>
<th>Mass uptake (g/g of foam)</th>
<th>Treatment time (hrs)</th>
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<tbody>
<tr>
<td><strong>At 1 vol% crude oil concentration</strong></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Room temp and 0 rpm</td>
<td>96.1</td>
<td>18.3</td>
<td>24</td>
</tr>
<tr>
<td>40 °C and 0 rpm</td>
<td>97.3</td>
<td>18.3</td>
<td>18</td>
</tr>
<tr>
<td>Room temp and 500 rpm</td>
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<td>16.1</td>
<td>2</td>
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<tr>
<td>40 °C and 500 rpm</td>
<td>98.1</td>
<td>17.5</td>
<td>4</td>
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<tr>
<td><strong>At 3 vol% crude oil concentration</strong></td>
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<tr>
<td>Room temp and 0 rpm</td>
<td>96.6</td>
<td>18.8</td>
<td>24</td>
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<tr>
<td>40 °C and 500 rpm</td>
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