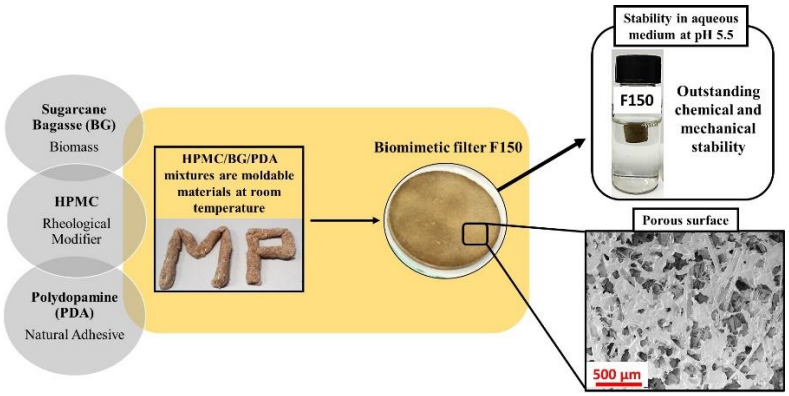
Graphical Abstract



Schematic representation of moldable HPMC/BG/PDA mixtures and F150 biomimetic filter composition with SEM image of F150 filter and photographs of F150 filter in MilliQ water at pH 5.5, after 24 h under stirring.

BIOMIMETIC FILTER FOR REMOVAL OF ORGANIC POLLUTANTS AND OIL/WATER SEPARATION

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Abstract: Oil spill and water contamination resulting from human activities are potentially harmful to human health and aquatic organisms. Adsorbents based on sustainable materials, with low cost and high efficiency might mitigate the contamination problem. In this study, a biomimetic filter was obtained by combining sugarcane bagasse (BG) microparticles with hydroxypropyl methylcellulose (HPMC), and polydopamine (PDA), which conferred adherence between the components, chemical and mechanical stability for the adsorbents. The adsorbents were prepared from mixtures of HPMC (30 g/L), PDA (6 g/L) and BG at 100 g/L (F100), 150 g/L (F150) or 200 g/L (F200). SEM images showed that the filters have a porous and cohesive structure. The F150 biomimetic filter was stable for 24 h in aqueous medium at pH 5.5 and 25 ± 1 °C, without loss of material or shape. In the absence of PDA the filters dissolved after 30 min in water. The F150 filter showed 70% and 100% removal efficiency towards bisphenol-A (BPA) and methylene blue (MB), respectively, and oil retention of 100% from a mixture of 1:4, sunflower oil : water.

Keywords: sugarcane bagasse; polydopamine; hydroxypropyl methylcellulose; oil and water separation; adsorption

INTRODUCTION

The control of substances released into the environment through industrial effluents, agricultural activities, domestic sewage, and wastewater from Sewage Treatment Plants has become a matter of great environmental concern in recent decades. Oil spills and water contamination by molecules resulting from human activities, such as endocrine disruptors, compounds potentially harmful to human health and aquatic organisms, demands new adsorbents based on sustainable materials, with low cost and high efficiency. Materials developed for pollutants adsorption from water must be

mechanically stable, insoluble in water and recyclable. According to the National Supply Company (Conab), Brazil is the world's largest producer of sugarcane, having great importance for Brazilian agribusiness. The estimate for the harvest in 2020/21 was 630.7 million tons.[1] Sugarcane bagasse (BG) is the residue obtained after sugarcane processing, representing 30% of the initial biomass, corresponding to approximately 200 million tons in 2020/21.[2] The contents of holocellulose, lignin, and ash in the BG amounted to 79.0%, 20.5% and 0.2%.[3] BG has great potential for removing heavy metals from effluents.[4] Hydroxypropyl methylcellulose (HPMC) is a cellulose ether; the degree of substitution (DS) is related to substitution of hydroxyl groups by methyl groups, and the molar substitution (MS) is related to the insertion of hydroxypropyl groups.[5] HPMC has been applied as rheological modifier, food additive, emulsion stabilizer and excipient in controlled release of drugs.[6] Polydopamine (PDA) is a mussel-inspired adhesive, which has attracted the attention of researchers due to its simplicity, low cost and interesting coating properties. PDA coatings occur due to the autooxidation of dopamine under alkaline medium.[7] Favorable interactions between PDA and cellulose esters allowed the development of adsorbents to remove caffeine.[8] Therefore, in this work, the optimized combination of aqueous dispersions of BG microparticles, HPMC, and PDA led to a moldable material at room temperature. After water evaporation by heating, the material presented a highly cohesive porous structure with outstanding mechanical and chemical stability in water. Biomimetic filters showed high efficiency to separate oil from oil/water mixtures and to remove organic contaminants in water.

EXPERIMENTAL

Preparation of biomimetic filter

HPMC E4M (DS = 1.9 and MS = 0.25, M_w = 2.5 x 10^5 , g/mol), kindly supplied by Dow Chemical Company was dissolved in MilliQ® water at 30 g/ L, volume (V) of 20 mL. Then, BG (supplied by local market) microparticles were incorporated under vigorous stirring into the polymer matrix at 100 g/L, 150 g/L or 200 g/L; the systems were coded as F100, F150 and F200, respectively. Then 10 mL of a dopamine (Sigma-Aldrich H60255, 189.64 g/mol) solution at 6.0 g/L, prepared in Tris-HCl buffer (10 mM, pH 8.5), was added to the HPMC/BG mixtures. The oxidation reaction of dopamine into polydopamine took 4 h. **Figure 1a** shows the darker color of the mixtures evidencing the formation of PDA. For contaminant removal tests, the HPMC/BG/PDA mixtures were molded into a plastic Petri dish (diameter = 5.7 cm and thickness = 3 mm), as shown in **Figure 1b**. For sunflower oil separation from water/oil mixtures, HPMC/BG/PDA mixtures were molded in acrylic mold, with diameter = 10 mm and thickness = 6 mm. After this step, the materials were placed in oven at 60 °C for drying, during 4 h. Afterwards, the materials were placed in a glass Petri dish for pre-crosslinking on a heating plate at ~ 90 °C and slowly bathed with a crosslinking solution containing 10 g/L citric acid (crosslinker, Labsynth, Brazil), 6.2 g/L succinic acid (crosslinker, Sigma-Aldrich) and 5.5 g/L sodium hypophosphite (catalyst, Labsynth, Brazil). For the crosslinking bath, it was fixed a ratio of 0.077 between the mass of the material being crosslinked and the volume of crosslinking solution incorporated (m_{filter} (g) / $V_{solution}$ (mL)). The dried filters were taken to oven at 172 °C for 10 min for crosslinking (esterification reaction) (**Figure 1c**). Finally, the materials were washed to remove unreacted molecules, after drying the F100, F150 and F200 biomimetic filters were characterized. F150 filter was chosen for the adsorption of organic pollutants and oil retention.

Characterization of biomimetic filters

Scanning electron microscopy (SEM) analyses were performed for F100, F150 and F200 coated with gold (~ 10 nm) in Jeol Neoscope JCM-5000 microscope operating at 10 kV. The chemical stability of the F100, F150 and F200 filters were evaluated at pH 5.5 (MilliQ water) for 24 h.

Removal capacity of methylene bule (MB) and bisphenol A (BPA)

Adsorption of methylene blue (MB, M9140 Sigma Aldrich, 319.85 g/mol) and bisphenol A (BPA, 133027 Sigma, 228.29 g/mol) was performed with F150 filter. The experiment was carried out in reduced pressure filtration system (~ 600 mbar), which the filter was placed directly into a Büchner funnel. The solutions of MB (V = 45 ml) and BPA (V = 25 ml) were prepared at initial concentration (C_0) 5 mg/L and 388 mg/L, respectively. Separately, the solutions were pumped through the filter and the samples were quantified by spectrophotometer in the UV-Vis region (Beckman-Coulter DU640) for AM (λmax = 662 nm) and BPA (λmax = 276 nm). The removal capacity (%) of MB and BPA by F150 biomimetic filter was determined by:

$$Removal\ (\%) = \frac{C_0 - C_t}{C_0} \times 100 \qquad (1)$$

where C_0 is initial concentration and C_t is concentration after a given contact time.

Oil and water separation

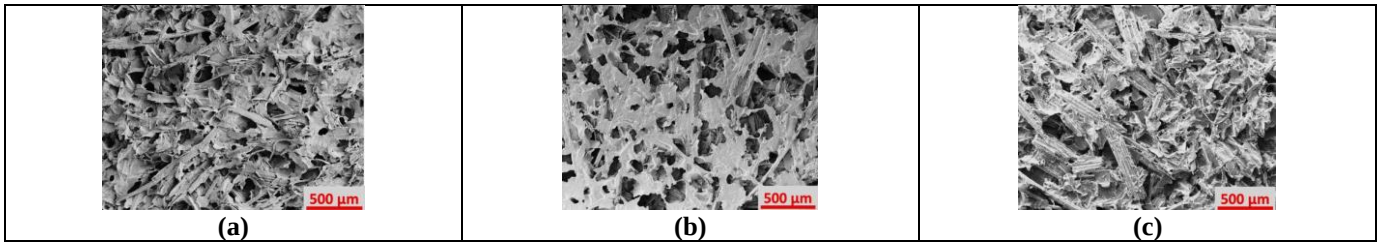
Sunflower oil and water mixture was prepared at a ratio of 1:4, sunflower oil: water (V = 5 mL), this mixture was poured over the filter in a static column system and the volume of water after oil retention was measured by graduated cylinder.

	F100	**F150**	**F200**
(a)			
(b)			
(c)			

Figure 1*. (a) HPMC/BG/PDA mixtures of F100 (left), F150 (center) and F200 (right) after 4 h of DOPA oxidation packaged and stored in a refrigerator for later use/molding. (b) Mixtures of F100, F150 and F200 molded in cylindrical shape (c) Biomimetic filters after the steps of pre-crosslinking and crosslinking*

RESULTS AND DICUSSION

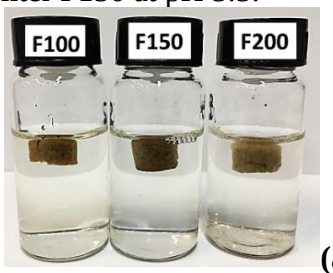
SEM images in **Figures 2a**, **2b** and **2c** shows the porous and cohesive structure of filters F100, F150 and F200, respectively; the presence of PDA did not affect the filters morphology. BG microparticles dominate the surface structure, because BG is the main component of these materials.



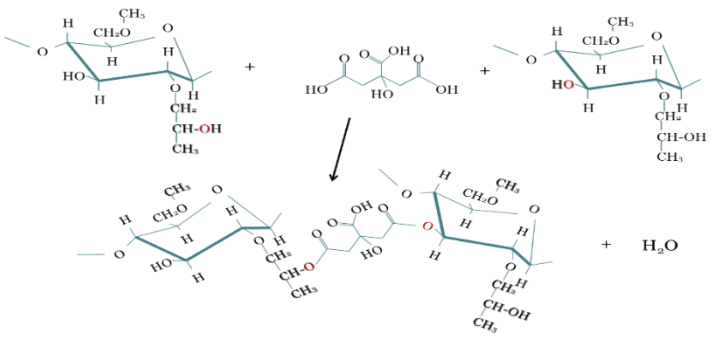
(a) **(b)** **(c)**

Figure 2*. SEM images of biomimetic filter (a) F100, (b) F150 and (c) F200*

Figure 3a demonstrates the stability of F100, F150 and F200 filters at pH 5.5 after 24 h under stirring. The F100 filter was not chemically stable, the medium became yellowish because PDA was released to the aqueous medium, and F200 filter had loss of material after 24 h. On the other hand, F150 filter showed excellent chemical and mechanical stability at pH 5.5. Meanwhile, the material without PDA dissolved completely after 30 min under stirring in water. Confirming that for materials with high content of BG, the esterification reaction (**Figure 3b**) was not efficient. Probably, the hydroxyl groups on BG particles were not available for crosslinking with citric acid molecules due to the strong intermolecular H bonds. Therefore, the combination of PDA and citric acid favored the adhesive properties of PDA in the system with high amount of BG, providing chemical stability for biomimetic filter F150 at pH 5.5.



(a)



(b)

Figure 3*. (a) Photographs of F100, F150 and F200 filters in MilliQ water at pH 5.5 after 24 h under stirring. (b) Schematic representation of the esterification reaction between citric acid and HPMC hydroxyl groups*

MB and BPA adsorption was performed with F150 filter in a reduced pressure filtration system. After pumping 45 mL of MB solution (C_0 = 5.0 mg/L) through F150, the removal capacity yielded 100% (**Figure 4a**). The time required to treat 45 mL of solution was 30 seconds. This result indicated that this material has a high affinity for MB. The interactions between MB and the adsorbent might be driven by MB methyl groups and methyl groups on the polymer surface, and ion-dipole interactions with hydroxyl groups in BG. After adsorption, the filter was placed under sunlight for one week to promote the filter recovery by photooxidation of MB molecules.[9] **Figure 4b** shows that the adsorbent could be recovered for a next filtration process. The same filtration system was used for adsorption of BPA, after pumping 25 mL of BPA solution (C_0 = 388 mg/L) the removal capacity was 70%. Probably, the adsorption of BPA occurred through the interactions of the methyl and aromatic groups of BPA and HPMC methyl groups, and H bonds between BPA and HPMC hydroxyl groups. The time required for filtering 25 mL was 15 seconds. Another potential application for the F150 filter was

presented with the 100% oil retention from a 1:4 mixture of sunflower oil: water (V = 5 mL). The time required to collect 4 mL of water was 10 min, in a static column.

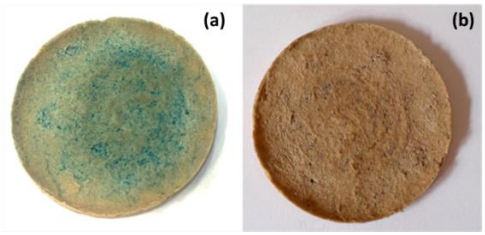


Figure 4. *Photographs of F150 filter (a) after MB adsorption and (b) after filter recovery through photooxidation with sunlight*

CONCLUSIONS

The HPMC/BG/PDA mixtures are moldable into filters that presented dimensional and chemical stability. The combination of PDA and crosslinking reaction with citric acid provided chemical and mechanical stability in aqueous media at pH 5.5 for the F150 filter. This filter showed great potential for adsorption of organic pollutants achieving removal of 100 % and 70 % for MB and BPA, respectively, and oil retention. Not less important, the cost to produce HPMC/BG/PDA filters at lab scale was estimated as US$ 0.025/g, considering the local prices for HPMC, citric acid, DOPA, water, and energy.

ACKNOWLEDGMENT

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