



Waste Coffee Ground-derived Bioelastomeric Foam as Organic Dye-Adsorbing Agent

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Abstract: This study focused on the utilization of waste coffee ground-derived bioelastomeric foam for the removal of methyl violet and methylene blue, two commercially available yet highly polluting organic dyes, from water. Waste coffee grounds (WCG), a major by-product from the production of coffee, was mixed and cured with a silicon elastomer and surfactant mixture to create a bioelastomeric foam with a solid, porous structure, which allowed it to extract the dyes from the solutions without the need for post-processing. Characterization of the WCG-derived bioelastomeric foam using FTIR revealed that the WCGs are only physically bonded to the silicone elastomer and chemically unaltered. UV-Vis spectrometry was used to analyze the post-adsorption concentration of the dye solutions and the removal efficiency of the foam under varying conditions: contact time, adsorbent dosage, and initial concentration. High removal efficiency was achieved for conditions with higher contact time and higher adsorbent dosage, whereas minimal changes were observed between changes in initial concentration.

Key Words: waste coffee grounds, bioelastomer, organic dye removal, adsorption

1. INTRODUCTION

Textile dyes are among the largest contributors to water pollution, with 700,000 metric tons of 10,000 types of dyestuff being commercially available worldwide (Zaharia & Suteu, 2012). The presence of contaminants in these dyes cause

negative physical changes in bodies of water along with various carcinogenic and/or mutagenic effects to humans and other life forms (Suteu et al, 2009).

One known method of removing pollutant dyes from water is through the use of adsorptive agents, which are materials that allow contaminants to separate from the contaminated solution and adhere to the surface of porous surfaces due to



differences in molecular weight, shape, or polarity (Seniūnaitė, Vaiškūnaitė, & Bolutienė, 2014).

Waste coffee grounds (WCGs), by-products of mass (1.5 billion cups per day) coffee consumption (Luttinger & Dicum, 1999), contain properties that allow it to be an adsorptive agent for contaminants such as heavy metals (Naga Babu et al., 2018) and organic dyes (Franca, Oliveira, & Ferreira, 2009; Phatai, Utara, & Hatthapanit, 2013), an important component in textile dyestuff.

However, these grounds are most commonly used in a powdered form, which requires solutions post-adsorption to be filtered, making the general use of this material as an adsorbent difficult and inefficient.

Recent studies, however, have focused on the efficient utilization of waste coffee grounds in water remediation. Chavan, et al. (2016) explored the use of the grounds as fillers for an adsorbent bioelastomeric foam. In this form, the waste coffee grounds simply need to be taken out of the water as compared to the post-adsorption processes of the powdered form.

Given the aforementioned, this study explores the usage of a waste coffee ground-derived bioelastomeric foam for the removal of two industrial dyes from water: methyl violet ($C_{24}H_{28}N_3Cl$), a carcinogen and mitotic poison for certain marine organisms (Mani & Bharagava, 2016); and methylene blue ($C_{16}H_{18}ClN_3S$), which causes tremors and other negative effects to the central nervous system of humans (Vutskits, et al., 2008).

2. METHODOLOGY

2.1 Materials

Waste coffee grounds were collected from local Starbucks branches (Manila, Philippines). Elastosil E43 (acetoxypolysiloxane) was purchased from Siliconesandmore (Geleen, Netherlands), while silicone emulsion (polydimethylsiloxane) was purchased from Dalkem Corporation. Hexane was procured from RCI Labscan Limited. Methyl violet (Sigma-Aldrich) and methylene blue (HiMedia) stock solutions were prepared in distilled water, while test solutions (10 - 40 μM) were obtained by diluting portions of the stock solutions with distilled water.

2.2 Pre-treatment of Coffee Grounds

Upon collection, the coffee grounds were washed with tap water and rinsed with distilled water in cheesecloth until the filtrate turned clear. The washed grounds were then oven-dried at 110°C for 24 hours. After drying, the grounds were sieved to obtain a particle size ranging from 150 μm – 420 μm .

2.3 Preparation of the Bioelastomeric Foam

To produce the foam, 4 g of acetoxypolysiloxane, 0.04 g polydimethylsiloxane, and 3 mL hexane were mixed. 6 g of coffee grounds and 8 g of granulated sugar (particle size < 420 μm) were then incorporated while the mixture was stirred until all components were completely mixed. The resulting mixture was left to cure in a silicone mold with dimensions 1 cm x 1 cm x 1 cm (per cube) for 24 hours at room temperature.

The cured composite was placed under sonication for 2 hours at 60°C to dissolve the sugar in the polymer, which resulted in the formation of pores on the surface of the now-obtained WCG-derived bioelastomeric foam.

2.4 Characterization of the Bioelastomeric Foam

The WCG-derived bioelastomeric foams were viewed under a scanning electron microscope (SEM; JEOL JSM 5310) and subjected to FTIR (Thermo Scientific Nicolet 6700) for surface and composition analysis, respectively.

2.5 Adsorption Tests

To determine the removal efficiency of the foam in the organic dye solutions, several tests were performed by soaking individual pieces of a 1 cm x 1 cm x 1 cm cube-shaped foam (~0.7 g mass) into 20mL dye solutions of methyl violet (MV) and methylene blue (MB) in still conditions at room temperature.

UV-vis spectrophotometry (Hitachi U-2900 Spectrophotometer) was then performed to compare the concentration before and after the foam was applied to the solutions. Triplicate measurements were carried out for all the tests.



The removal efficiency of the foam was determined by equation 1:

$$\%RE = \frac{(C_0 - C_t)}{C_0} \quad (\text{Eq. 1})$$

where:

C_0 = initial concentration (μM)

C_t = (μM) concentration after a certain period

The removal efficiency of the foam was determined in various conditions: contact time, adsorbent dosage, and initial concentration of the dye solutions. For the initial concentration tests, the foams were dipped in MV and MB samples with fixed contact time (24 hours), and varying concentration (10 μM – 30 μM for MV, 20 μM – 40 μM for MB). For contact time tests, the foams were dipped in the MV and MB solutions (30 μM & 40 μM respectively) at two contact times (1 hour and 24 hours). For adsorbent dosage, varying amounts of foam (1, 2, or 3 pieces, ~0.7 g each) were dipped in the MV and MB solutions with fixed concentrations (30 μM & 40 μM respectively). All samples were tested at 1 hour and 24 hour-contact time points.

3. RESULTS AND DISCUSSION

3.1 SEM Microscopy & FTIR Analysis

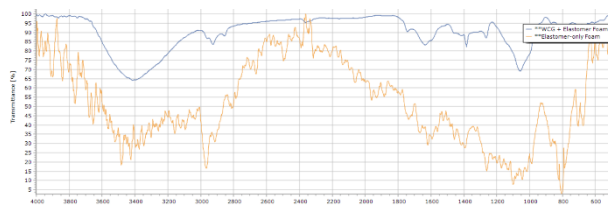


Fig. 1. FTIR spectra for the elastomer-only foam and the WCG-derived bioelastomeric foam.

The obtained FTIR spectra (Fig. 1) was used to examine the composition of the WCG-derived bioelastomeric foam in comparison to its elastomeric

base, which is comprised of acetoxy polysiloxane (acetoxy-functional silicone) and polydimethyl-siloxane ($\text{C}_2\text{H}_6\text{OSi}$) to determine the interaction of the coffee grounds and the elastomeric base.

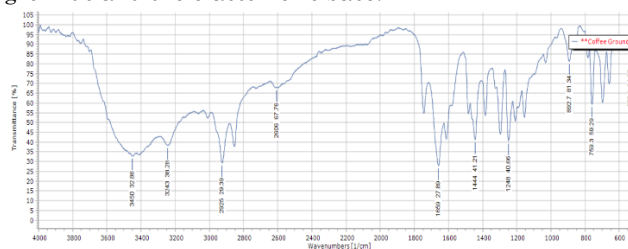


Fig. 2. FTIR spectra of the waste coffee grounds (WCGs).

The peaks at wavenumbers 1107 cm^{-1} and 1100 cm^{-1} (for WCG-derived bioelastomeric foam and elastomeric base spectra, respectively) correspond to the presence of Si-O-Si asymmetric stretching. However, a broad peak at wavenumber 3428 cm^{-1} in the WCG-derived bioelastomeric foam spectra denotes the presence of an alcohol group (particularly O-H stretching), which is present in the IR spectra of the coffee grounds (Fig. 2.) This implies that the WCG-derived bioelastomeric foam retains the chemical structure of its elastomeric base (Si-O-Si being the main repeating chain in siloxanes) and that the interaction between the coffee grounds and the elastomer is only physical.



Further evidence of the physical interaction between the coffee grounds and the elastomeric base could be seen in the SEM images (Figs. 3 & 4). In Fig. 3, active sorption sites (encircled in yellow) of the WCGs show a porous structure, which is easily distinguishable from the elastomer (as shown in Fig. 4, which shows a portion without WCGs present). These features indicate that the elastomer only holds the WCGs in a compact, yet heterogeneous structure.

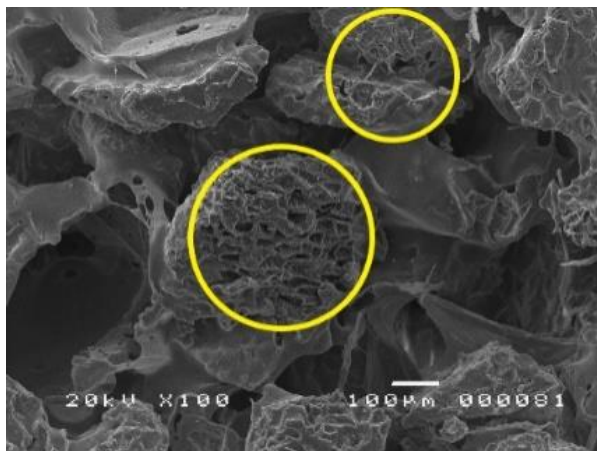


Fig. 3. 100x SEM image of the WCG-derived bioelastomeric foam.

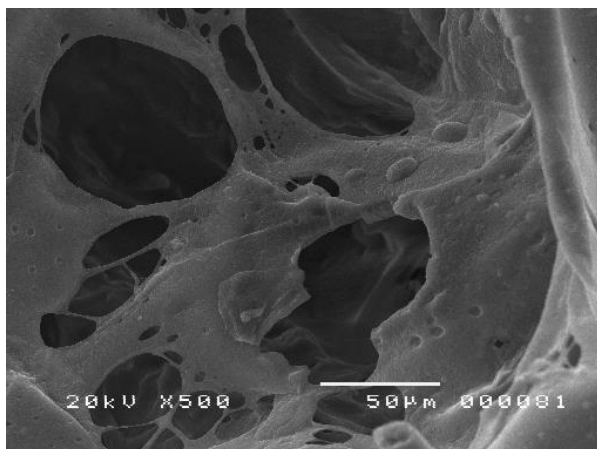


Fig. 4. 500x SEM image of the WCG-derived bioelastomeric foam.



Fig. 5. Cube-shaped sample of the WCG-derived bioelastomeric foam.

Based on Figs. 3 & 4, the pore diameters range from sub-100 μm – 500 μm . These pores were created mostly by the sonicated sugar particles (~150 μm – 420 μm particle size), while larger pores (those beyond the particle size range of the sugar) were likely created during the foam formation and curing process. Fig. 5 shows that these pores (as well as some of the elastomeric base) are still visible to the naked eye.



3.3 Adsorption Tests

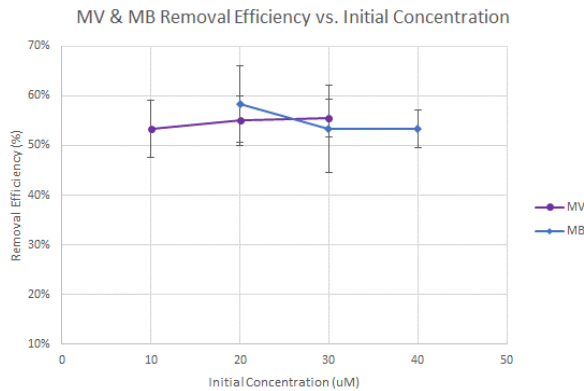


Fig. 6. The initial concentration-dependent removal efficiency of the foam in MV and MB solutions.

The effect of the initial MV and MB concentrations on the removal efficiency of the foams was first examined (Fig. 6). For MV, higher initial concentration resulted in slightly higher removal efficiency whereas the opposite was observed for MB. Both plots have been observed to stay within similar values, thus no significant changes in removal efficiency were observed for the different initial concentrations and all values were within the standard error (represented by the error bars).

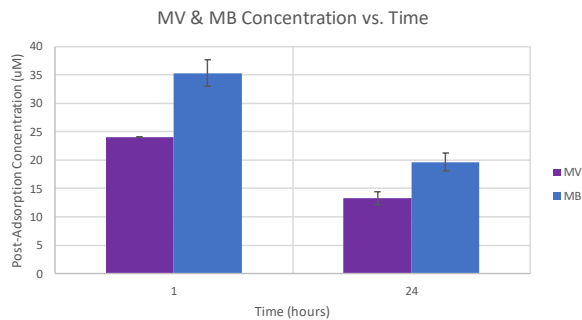


Fig. 7. Contact time-dependent post-adsorption concentration of the MV & MB solutions.

As demonstrated by Fig. 7, both MV and MB solution concentrations decreased as contact time between the foam and the solutions increased. This resulted in an increase in removal efficiency from 20% to 56% for MV and 12% to 51% for MB between 1 and 24 hours. (Table 1).

Table 1. Contact time-dependent removal efficiency of the WCG-derived bioelastomeric foams.

Contact Time (hours)	MV Removal Efficiency	MB Removal Efficiency
1	20%	12%
24	56%	51%

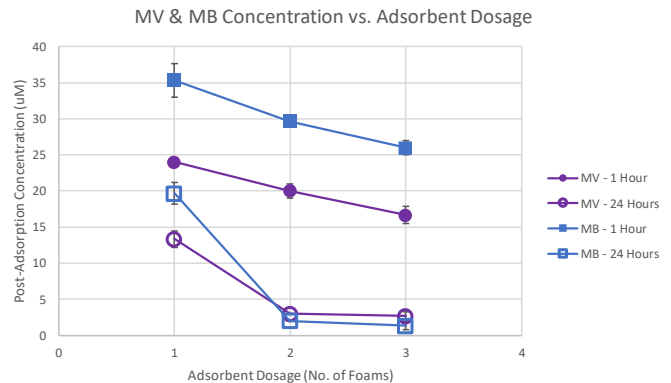


Fig. 8. Adsorbent dosage-dependent post-adsorption concentration of the MV & MB solutions.

Adsorbent dosage, defined here as the amount of adsorbent placed in the solution, has also been shown to affect the post-adsorption concentration of the MV and MB solutions and the removal efficiency of the foams. For the 24-hour trials, the post-adsorption concentration of both dye solutions decreased significantly (Fig. 8) as the adsorbent dosage was increased from 1 foam to 2 foams and plateaued between tests for 2 and 3 administered foams. However, for the 1-hour trials, the same pattern was not observed where the decrease was observed to be linear with respect to the number of foams used.



The removal efficiency of the foams increased as more foams were applied to the dye solutions. Peak removal efficiency for both dyes was attained with 3 foams dipped for 24 hours: 91% for MV, 97% for MB (Table 2).

Table 2. The adsorbent dosage-dependent removal efficiency of the WCG-derived bioelastomeric foams.

Adsorbent Dosage (No. of Foams)	MV Removal Efficiency		MB Removal Efficiency	
	1 hr.	24 hrs.	1 hr.	24 hrs.
1	20%	56%	12%	51%
2	33%	90%	26%	95%
3	44%	91%	35%	97%

Since the removal efficiencies were virtually the same for 2 and 3 foams, the adsorption of the dyes may have already achieved saturation. A previous adsorption study on the WCG-derived bioelastomeric foam (Chavan et al., 2016) shows that the adsorption mechanism of the foam starts to approach equilibrium after 9 hours under continuous stirring; however, since the adsorption tests of this study were performed under still conditions, the solutions and the foam may have approached equilibrium later (i.e. ~24 hours, as indicated by the tests).

In a previous study, Lafi, ben Fradj, Hafiane, & Hameed (2014) obtained a maximum removal efficiency of 97% for crystal violet (structurally similar to MV) using coffee waste with 10g/L adsorbent dosage applied for 24 hours. In contrast, the equivalent g/L WCG adsorbent dosage for 3 foams (wherein the maximum MV removal efficiency was obtained) is 63g/L. Similarly, for MB, Franca et al. (2009) it has been shown to obtain a 99% removal efficiency at 30g/L adsorbent dosage after 12 hours with spent coffee grounds while the WCG-derived bioelastomeric foam obtained a 97% removal efficiency at 63g/L after 24 hours.

However, the disparity between the results can be attributed to the method used by Lafi, et al. (2014) & Franca, et al. (2009), in which both studies utilized powdered/granulated WCGs in dye solutions placed under constant agitation. This method effectively creates a surface area greater than that of the foam (which means the active sorption sites on the granules are much more exposed to the dye particles).

The WCG-derived bioelastomeric foam, aside from being able to remove most of the dye particles even in still solutions, has the added advantage of having a single, solid structure which makes it easier to extract from the dye solutions at the cost of higher WCG adsorbent dosage and time.

4. CONCLUSIONS

This study presents the successful use of waste coffee ground-derived foams as an adsorptive agent for methyl violet and methylene blue. The waste coffee grounds, which is an adsorptive material, are simply aggregated into a compact, porous configuration with no changes made to their chemical structure. The foams have shown high removal efficiencies for both dye solutions despite being performed without agitation; $\geq 90\%$ removal efficiency was achieved in both dyes for a ~1.4g adsorbent (or higher):20mL dye solution ratio. These results show that the WCG-derived bioelastomeric foams retain their adsorptive capabilities during application when compared to powdered waste coffee ground adsorbents whilst demonstrating improved versatility and convenience as an WCG-based adsorbent.

5. ACKNOWLEDGMENTS

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