# Electronic Supplemental Information for:

## Valorization of shoe sole waste into high-performance cationic dye sorbents via sulfonation

*Mark Robertson [a], Andrew Barbour [a], Zhe Qiang[a,*]*

[a]School of Polymer Science and Engineering, The University of Southern Mississippi, Hattiesburg, Mississippi, 39406, USA

Corresponding author: Zhe Qiang (Email: zhe.qiang@usm.edu)

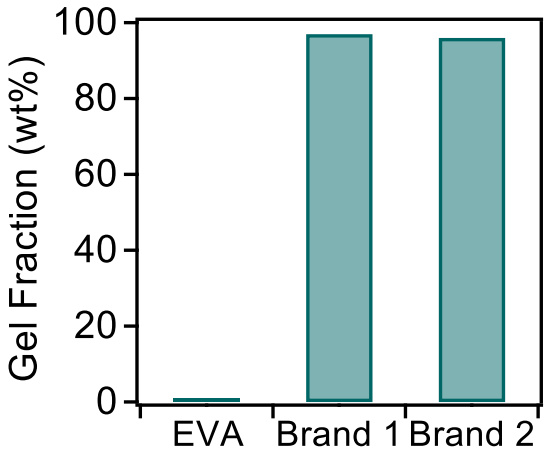


Figure S1. Gel fraction results for virgin EVA and both post-consumer waste foams in dichloromethane for 12 h.

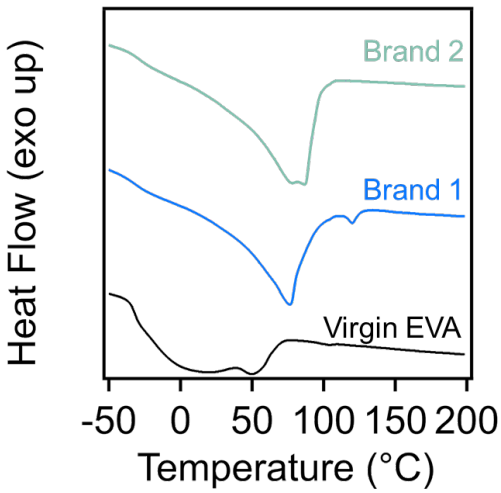


Figure S2. Differential scanning calorimetry thermograms of virgin EVA and the post-consumer waste foams.

The virgin EVA exhibits a broad endothermic transition with a distinct peak at 51 °C. This broad transition is common in EVA copolymers with large vinyl acetate contents and has been reported in multiple works. The two post-consumer waste foams exhibit a more distinct melting transition at elevated temperatures of 75 °C and 79 °C, respectively. This increase in melting temperature compared to the virgin material is characteristic of EVA copolymers with reduced vinyl acetate content.

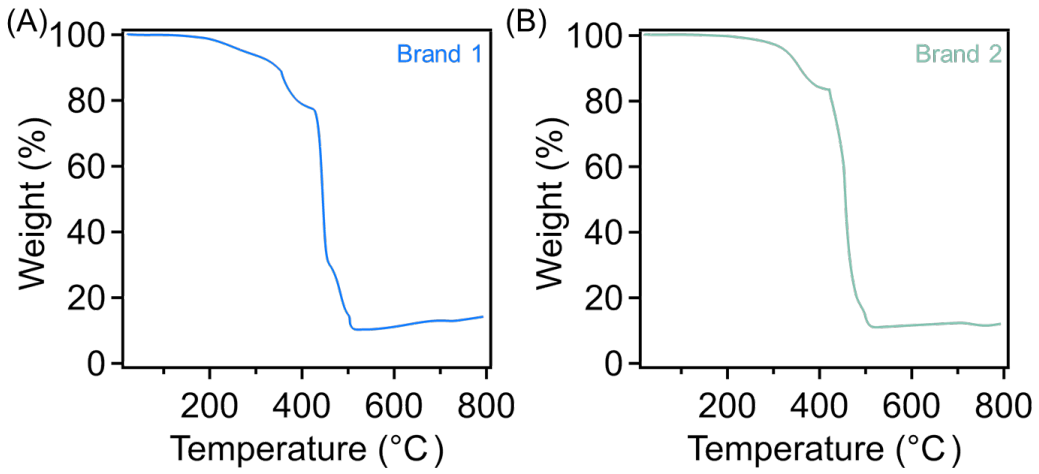


Figure S3. TGA thermograms performed in air of the post-consumer waste foams.

To further confirm the presence of inorganics in the shoe wastes, TGA experiments were also conducted under air to completely decompose the organic components of the waste foams. The resulting residual masses after degradation above 800 °C are 10.2 wt% and 11.2 wt% for Brand 1 and Brand 2, respectively; the increased residual mass compared to the experiments performed under nitrogen are increased which is likely a result of oxidation of the inorganic components.

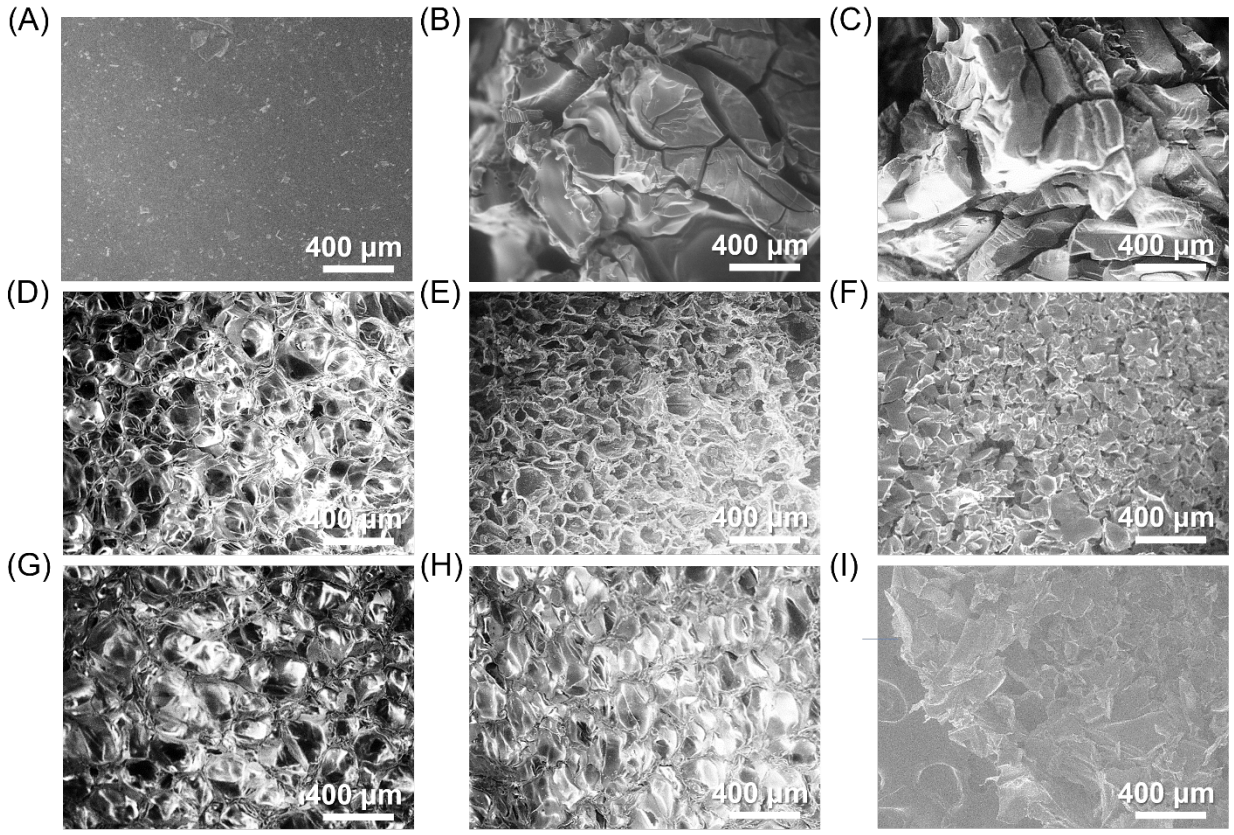


Figure S4. SEM micrographs of (A) virgin EVA pellet cross-section, virgin EVA particle after sulfonation at 150 °C for (B) 5 min and (C) 15 min. Post-consumer waste Brand 1 structure (D) prior to reaction and after (E) 5 min and (F) 15 min of the sulfonation process. Post-consumer waste Brand 2 structure (G) prior to reaction and after (H) 5 min and (I) 15 min of the sulfonation process.

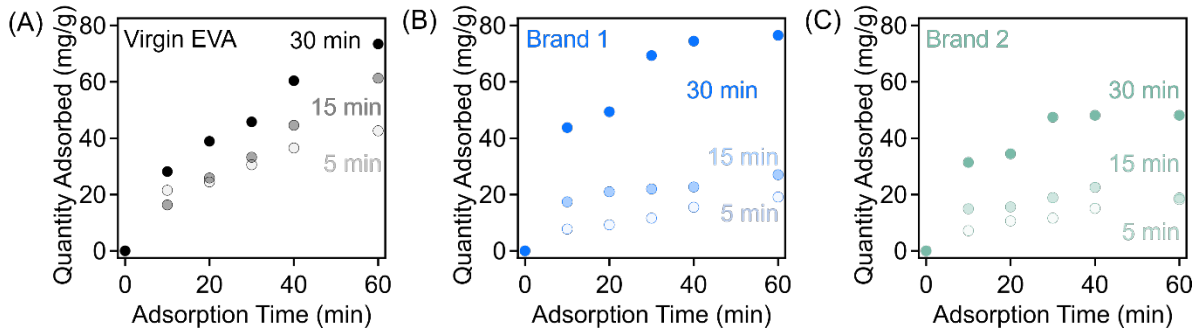


Figure S5. Adsorption of crystal violet by sulfonated polymer sorbents derived from (A) virgin EVA, (B) Brand 1, and (C) Brand 2.

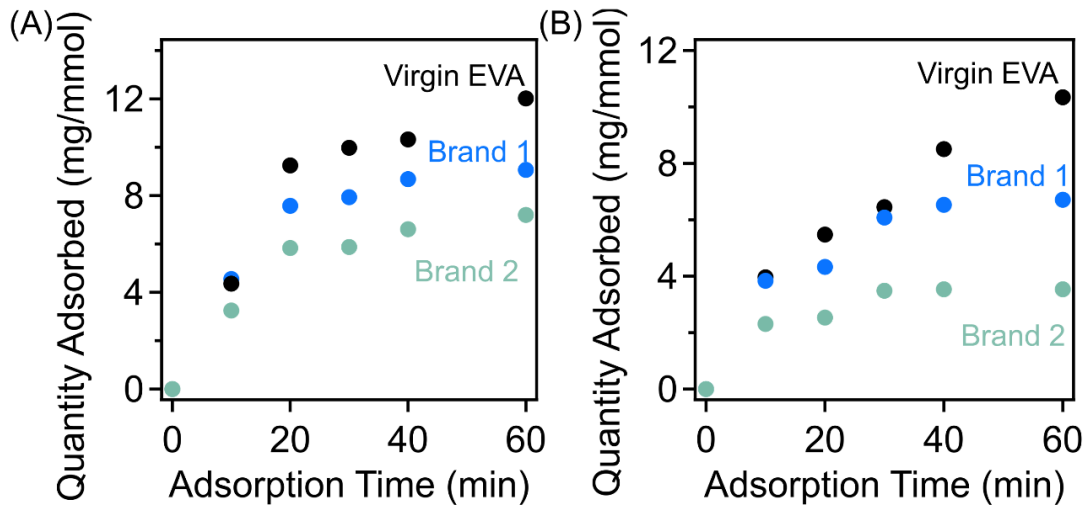


Figure S6. Quantity of (A) methylene blue and (B) crystal violet adsorbed as function of time normalized by the acid content of the sorbents.

Table S1. Fitting parameters from adsorption experiments to a pseudo-second order kinetic model.

| | Methylene Blue | | | Crystal Violet | | |
|---|---|---|---|---|---|---|
| Material | $Q_e$ mg/g | K g/mg*min | $R^2$ | $Q_e$ mg/g | K g/mg*min | $R^2$ |
| Virgin EVA | 94.4 | 0.0011 | 0.912 | 61.5 | 0.0023 | 0.874 |
| Brand 1 | 110.6 | 0.0017 | 0.972 | 82.6 | 0.0019 | 0.957 |
| Brand 2 | 105.3 | 0.0014 | 0.956 | 38.3 | 0.0060 | 0.961 |

Table S2. Fitting parameters for multiple materials in the literature to pseudo-second order adsorption kinetics for methylene blue.

| $k_2$ g/mg*min | $Q_e$ mg/g | Reference |
|---|---|---|
| 0.00167 | 49.2 | 41 |
| 0.09429 | 50.25 | 40 |
| 0.03595 | 5.015 | 39 |
| 0.001595 | 120.5 | 38 |
| 0.01391 | 54.05 | 37 |
| 0.000425 | 23.91 | 36 |
| 0.0067 | 74.85 | 34 |
| 0.001 | 99.6 | 33 |
| 0.00098 | 295.85 | 32 |
| 0.002 | 166 | 31 |
| 0.00138 | 47.6 | 30 |
| 0.0078 | 10.657 | 29 |
| 0.0033 | 45.41 | 28 |
| 0.0096 | 20.8 | 27 |
| 0.0653 | 2.94 | 26 |
| 0.0169 | 3.3553 | 25 |

Table S3. Fitting parameters for multiple materials in the literature to pseudo-second order adsorption kinetics for crystal violet.

| $k_2$ g/mg*min | $Q_e$ mg/g | Reference |
|---|---|---|
| 0.0102 | 9.59 | 53 |
| 0.00016 | 23.35 | 54 |
| 0.00035 | 27.62 | 55 |
| 0.00234 | 42.053 | 56 |
| 0.0107 | 2.28 | 57 |
| 0.004 | 10.309 | 58 |
| 0.0202 | 26.45 | 59 |
| 0.000086 | 121.95 | 60 |
| 0.005 | 24.31 | 61 |
| 0.007 | 18.501 | 62 |
| 0.0000684 | 27.62 | 63 |
| 0.0047 | 18.34 | 64 |

Table S4. Fitting parameters for Langmuir and Freundlich models for the adsorption of crystal violet

| | Langmuir | | | Freundlich | | |
|---|---|---|---|---|---|---|
| Material | Qe | k | $X^2$ | k | n | $X^2$ |
| Virgin EVA | 183.0 | 0.0509 | 1255 | 62.8 | 5.59 | 2443 |
| Brand 1 | 215.1 | 0.0323 | 986 | 35.5 | 3.23 | 258 |
| Brand 2 | 296.9 | 0.0066 | 606 | 9.7 | 1.89 | 1509 |