**Preparation, characterisation and application of sorbent envelopes with Carica papaya seeds and Citrus grandis rind for cationic dyes removal**

M. Q. Hoa and S. F. Y. Lia,b\*

aDepartment of Chemistry, National University of Singapore, 3 Science Drive 3, Singapore 117543. Singapore; bNational Environment Research Institute (NERI), #02-01 T-Lab Building (TL), 5A Engineering Drive 1, Singapore 117411, Singapore.

Correspondence: chmlifys@nus.edu.sg

**Supplementary Information S1**

**Solid-state Nuclear Magnetic Resonance Characterisation**

MAS NMR (Magic Angle Spinning Nuclear Magnetic Resonance) scans were obtained using Bruker 400 with Xwinnmr 2.6 software and signal processing with TopSpin 1.3 software.

13C CP-MAS NMR

Fig. S1 (a) showed the 13C CP-MAS NMR (Cross Polarization-Magic Angle Spinning-Nuclear Magnetic Resonance) of fresh pristine *Citrus grandis* rind using different spin rates. It was found that 8 kHz spin rate was sufficient to obtain the characteristic NMR trace of the rind sample. Hence, further 13C CP-MAS NMR on the rind sample prior and post sorption of MB dye were performed at 8 kHz spin rate and the respective NMR were illustrated in Fig. S1 (b) where MP = decayed rind, MPMB = decayed rind post MB dye sorption, OP = fresh pristine rind and OPMB = fresh pristine rind post MB dye sorption.

|  |  |
| --- | --- |
|  |  |
| 1. 13C CP-MAS NMR of pomelo rind (75 - 150μm particle size) OP75 at different spin rates
 | 1. 13C CP-MAS NMR of fresh and decayed pristine pomelo rind and rind samples sorbed with Methylene Blue (MB) dye
 |

Figure S1 - 13C CP-MAS NMR of Pomelo Rind (POM) prior and post MB dye sorption

1H HR-MAS NMR

The 1H HR-MAS NMR (High Resolution Magic Angle Spining Nuclear Magnetic Resonance) spectrum of fresh pomelo rind was shown in Figure 3(a), compared to fresh pomelo rind sorbed with MB dye in Fig. S 2(b), the trace showed a change in profile in the region δ 3.0 ~ 4.5 ppm. When the 1H HR-MAS-NMR spectra was compare between the fresh pomelo rind and decayed pomelo rind in Fig. S2 (c), a similar change was also found in the region δ 3.0 ~ 4.5 ppm.

1H HR MAS-NMR had been applied in quality control and classification of food and agricultural produce it was found here to be more discerning between fresh and decayed rind, pristine rind and rind sorbed with methylene blue dye.

|  |  |
| --- | --- |
|  |  |
| (a)1H HR-MAS NMR on fresh rind (75 – 150 μm) | (b)1H HR-MAS NMR on fresh rind (75 – 150 μm) sorbed with MB |
|  |  |
| (c)1H HR-MAS NMR on decayed rind (75 – 150 μm) | (d)1H HR-MAS NMR on decayed rind (75 – 150 μm) sorbed with MB |

Figure S2 - 1H HR-MAS NMR of fresh pomelo rind prior and post sorption with Methylene Blue (MB) dye

**Sorbent Characterisation**

Traditional techniques of solid sorbent characterization included elemental analysis, particle size and surface area analysis and FTIR (Fourier Transform Infra Red) spectroscopy. These had been reported in biosorption studies involving both organic and inorganic sorbates. To our knowledge, solid-state NMR (Nuclear Magnetic Resonance) had not been extensively explored in sorption studies. It has been shown that 1H HR-MAS NMR could differentiate the different sorbent more distinctively than FTIR techniques.

Since methylene blue had three N-sites and is relatively planar compared to brilliant green dye with two N-sites and trigonal about the central C to which the three aromatic rings were directly attached, methylene blue could potentially stick onto surfaces like a plaster. Both methylene blue and brilliant green are cationic dyes expected to have affinity for negatively charged surfaces or surfaces possessing electron-donating groups or of Lewis base character.

As highlighted by Simpson et al (2012), further work is still needed in industrial applications to enhance understanding structural correlation with waste treatment process. On the other hand, it had been critiqued that such expensive instrumental analysis may not surpass in value to the use of traditional wet chemistry techniques in laboratory evaluation of the interaction of cationic sorbates like metals with natural biosorbents.

**Future Work and Implications**

MAS NMR has been a possible tool to probe the molecular interactions involved in biosorption and could be further harnessed to profiling the vast variety of agricultural waste for environmental remediation through sorption. This tool has also been used for sorption of humic substances by soil particles (Francioso et al 2007) and thus the potential of its applicability in sorption or “sorption-omics” to develop predictive sorbent-sorbate models.

**References**

Simpson, A.J., Simpson, M.J., Soong, R., 2012. Nuclear Magnetic Resonance Spectroscopy and Its Key Role in Environmental Research. Environ. Sci. Technol. 46, 11488–11496. https://doi.org/10.1021/es302154w

Francioso, O., Ferrari, E., Saladini, M., Montecchio, D., Gioacchini, P., Ciavatta, C., 2007. TG-DTA, DRIFT and NMR characterisation of humic-like fractions from olive wastes and amended soil. J. Hazard. Mater. 149, 408–417. https://doi.org/10.1016/j.jhazmat.2007.04.002