

Adsorption of surfactant-rich stickies onto mineral surfaces

Authors

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Supplementary Information

Table S1 Classification of stickies.

Sticky formation method	Microstickies	Macrostickies
Introduced by pulping chemically or mechanically at start of recycling process.	Primary microstickies smaller than 100 or 150 μm , not removed by screening through 100 or 150 μm screen.	Primary macrostickies, larger than 100 or 150 μm , removed by screening during recycling.
Introduced by changing physical or chemical conditions during recycling process.	Secondary microstickies smaller than 100 or 150 μm , formed by aggregation of colloidal particles, or breakup of larger particles.	Secondary macrostickies, formed by aggregation of microstickies. Sometimes removed by screening, dependent on paper recycling stage when formed.

Mineral Preparation and Information

Mondo Minerals Oy, Finland, supplied undispersed talc (Finntalc PO5), i.e. as a powder without surfactant. The feedstock for Finntalc PO5 was separately processed via comminution to give an additional delaminated talc grade, with increased surface area as measured by nitrogen adsorption on a Micromeritics Gemini 2360 (Micromeritics Instrument Corp. USA) [1]. The PO5 talc is referred to as low surface area (LSA) talc and the processed

talc is referred to as high surface area (HSA) talc. The talcs exhibit different aspect ratios – the HSA talc having a significantly higher aspect ratio than LSA talc. The assessment of particle size distribution was made in aqueous suspension using static light scattering performed in a Malvern Mastersizer 2000 (Malvern Instruments Ltd, UK.). The talc (refractive index (RI): 1.59, absorption value: 0.01) was dispersed into suspension in water (RI: 1.33) for the size measurement using polyacrylate (RI: 1.49) and a wetting agent (sodium dodecyl sulphate). The results were then interpreted with Mie theory [2] to obtain the weight proportion particle size distribution. The d_{10} , d_{50} and d_{90} represent values where 10 %, 50 % or 90 % of the material weight, respectively, is found to be finer than this particle size.

The modified calcium carbonate samples (MCC: RI: 1.59, absorption value: 0.1), LSA MCC and HSA MCC, were obtained from Omya Development AG, Switzerland. HSA MCC is a natural calcium carbonate marble treated with 20 % phosphoric acid and 5 % citric acid, which creates a surface rugosity with no significant internal pore volume. It is supplied as a dispersed product, where the dispersant once again is polyacrylate, rendering the surface on average anionic. The LSA MCC is a natural calcium carbonate chalk treated with phosphoric acid to give micro- and macro-porosity coupled with some surface rugosity. When in a dry packed bed, the substance acts as a porous system, with fine intra-particle and coarser inter-particle porosity. However, when in suspension, as in this study, the effect of the inter-particle porosity disappears and the substance acts as a system of porous suspended particles. The LSA MCC is supplied as an undispersed product.

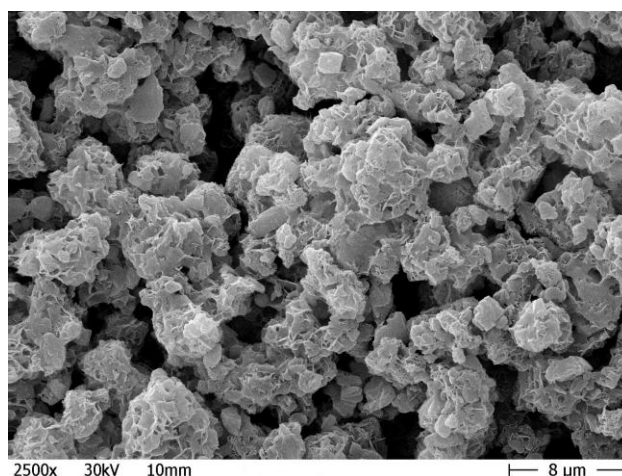


Figure S1 SEM image of LSA MCC.

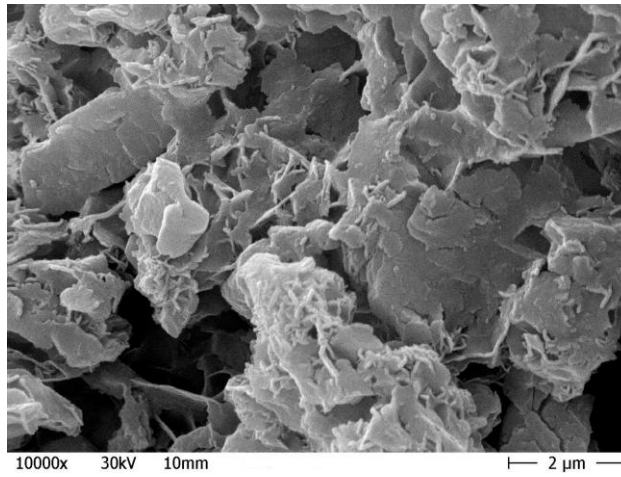


Figure S2 SEM image of LSA MCC.

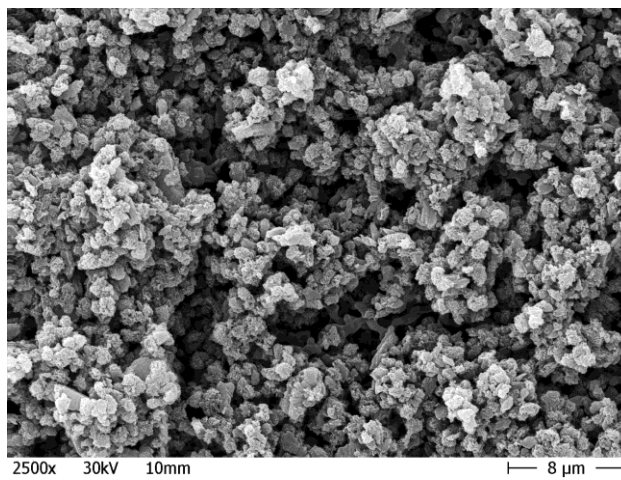


Figure S3 SEM image of HSA MCC.

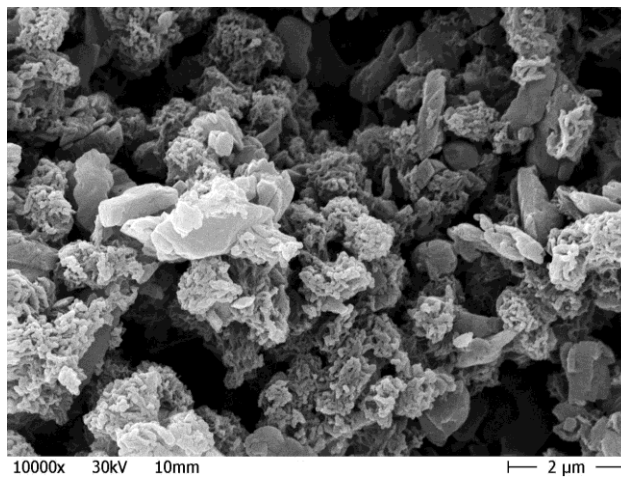


Figure S4 SEM image of HSA MCC.

Dissolved organic carbon analysis

A glass filter apparatus was acid washed and heated to 450 °C prior to use. Supernatants were then filtered through 0.7 µm glass fibre filters, which had been previously heated to 450 °C for four hours to remove organic residues. Filtrates were acidified with 10 µl of 50 % v/v phosphoric acid per 10 cm³ of sample and sparged with high purity oxygen to remove inorganic carbon.

Organic carbon standards (up to 600 µmol dm⁻³) were prepared from analytical grade glycine and potassium hydrogen phthalate sourced from Thermo Fisher Scientific UK. Accuracy was checked against a certified reference material (CRM) which reflected this instrument's normal use for marine applications; namely sea water collected at a depth of 700 m from the Florida Strait from Hansell Laboratory, University of Miami. Analysis of the CRM gave results within the acceptable error range of the CRM (± 2 standard deviations).

Elemental Analysis

Approximately 2 – 4 mg of sample was weighed into a tin cup, which was then combusted with 10 cm³ of high purity oxygen. The carbon dioxide concentration was measured using a thermal conductivity detector at 65 °C. Analysis of a reference marine sediment, PACS-1 (NRC, Canada), certified for carbon, was also analysed and revealed results that were within the acceptable error range.

Langmuir Isotherm values

Table S2 Comparison of regression coefficient R^2 and significance p values of the gradient for fatty acid ester defoamer (FAED) and acrylic acid ester copolymer (AAEC) isotherms.

Mineral	Adsorbate	Single isotherm		Stage I		Stage II		Stage III	
		R^2	p	R^2	p	R^2	p	R^2	p
LSA Talc	FAED	0.221	0.0119	0.795	<0.0001	0.686	0.0260	0.618	0.0015
HSA Talc	FAED	0.300	0.0033	0.710	0.0009	0.892	0.0029	0.896	<0.0001
LSA MCC	FAED	0.698	<0.0001						
HSA MCC	FAED	0.527	<0.0001	0.988	<0.0001	0.661	0.0047		
LSA Talc	AAEC	0.854	<0.0001	0.970	<0.0001	0.993	0.0001		
HSA Talc	AAEC	0.324	0.0022	0.818	<0.0001	0.985	<0.0001	0.695	0.024
LSA MCC	AAEC	0.663	<0.0001						
HSA MCC	AAEC	0.681	<0.0001	0.584	0.0001	0.809	0.0093		

The statistical justification for the multi-stage fits is shown in Table S2. It can be seen that the regression coefficient R^2 , increases considerably when multiple stages are fitted. The confidence level of the fit is always better than 95 % (i.e. $p < 0.05$) and in most cases better than 99 %. The first stage is arbitrarily defined as linear when three stages are fitted, as there are insufficient low concentration data to fit a Langmuir isotherm with confidence, and stages II and III are both Langmuir.

Dubinin-Radushkevich characteristic energies

Table S3 Table of Dubinin-Radushkevich characteristic energies

	Fatty acid ester defoamer	Acrylic acid ester copolymer
LSA Talc	36.1 J mol ⁻¹	162 J mol ⁻¹
HSA Talc	32.4 J mol ⁻¹	64.8 J mol ⁻¹
LSA MCC	71.6 J mol ⁻¹	50.8 J mol ⁻¹
HSA MCC	71.2 J mol ⁻¹	46.2 J mol ⁻¹

Zeta Potential

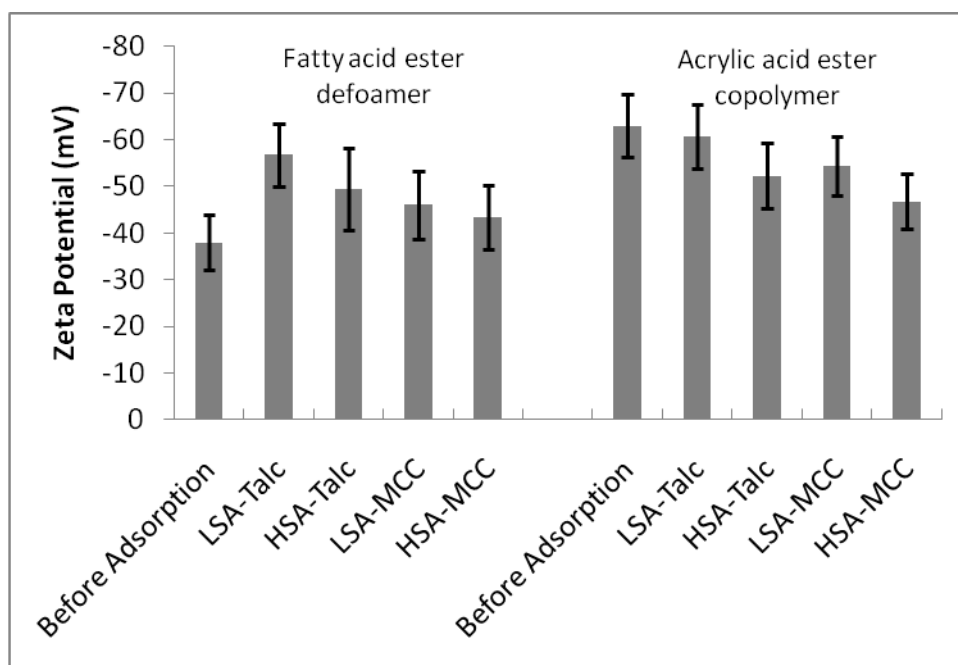


Figure S5 Mean zeta potentials of the supernatant suspensions before adsorption of a fatty acid ester defoamer and acrylic acid ester copolymer, and after adsorption onto the minerals shown and deposition

of the mineral / adsorbate species by centrifuging. The sticky suspension concentration being adsorbed was 0.5 g dm⁻³, which saturates the mineral. The error bars indicate the standard deviation of the zeta potential distribution at 50 % of the maximum height of the distribution.

ARIAN isotherm equation fits of experimental data

The Arian bilayer equation, Equation 4 found in the main text, and low bilayer, Equation S 1, and monolayer isotherm, Equation S 2 shown below, were fitted to the experimental data. The fits are shown below.

$$q_e = c_e \left(\frac{q_{\text{mon}} K_{\text{sa}}}{1} + \frac{q_{\text{mon}}}{c_e} + \frac{q_{\text{mon}}}{x c_e^2} \right) \quad (\text{S1})$$

$$q_e = c_e \left(\frac{q_{\text{mon}} K_{\text{sa}}}{1} + \frac{q_{\text{mon}}}{c_e} \right) \quad (\text{S2})$$

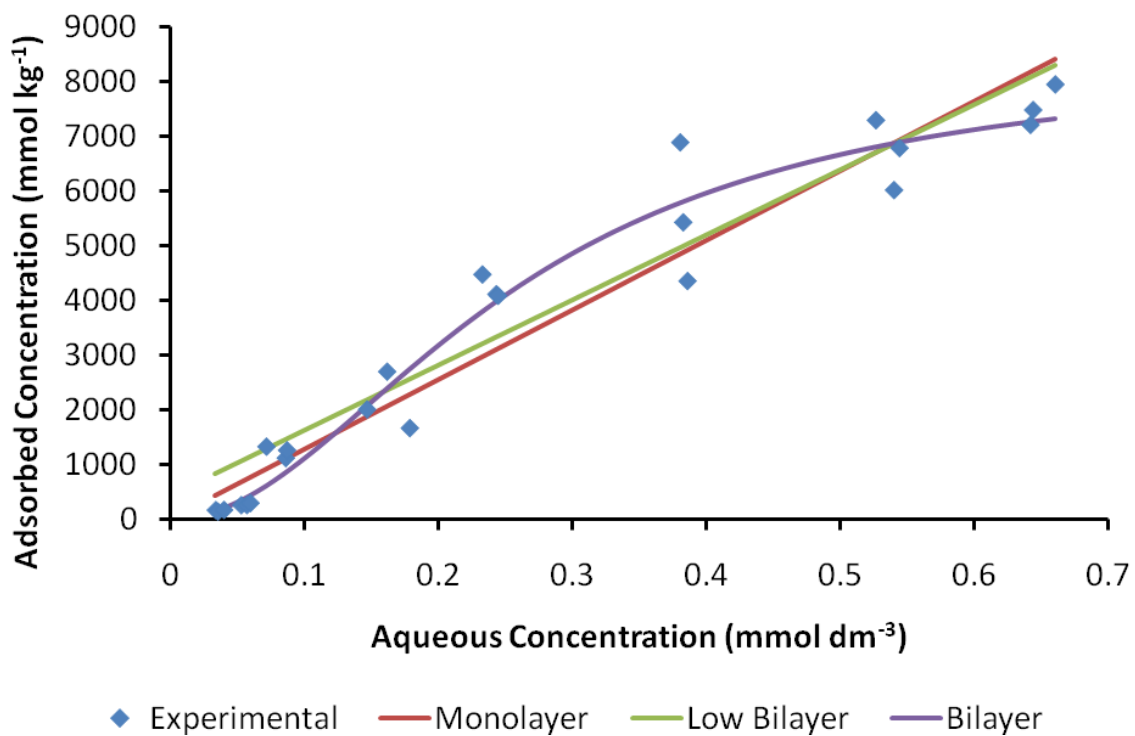


Figure S6 Graph of ARIAN isotherms for LSA Talc adsorbing fatty acid ester defoamer

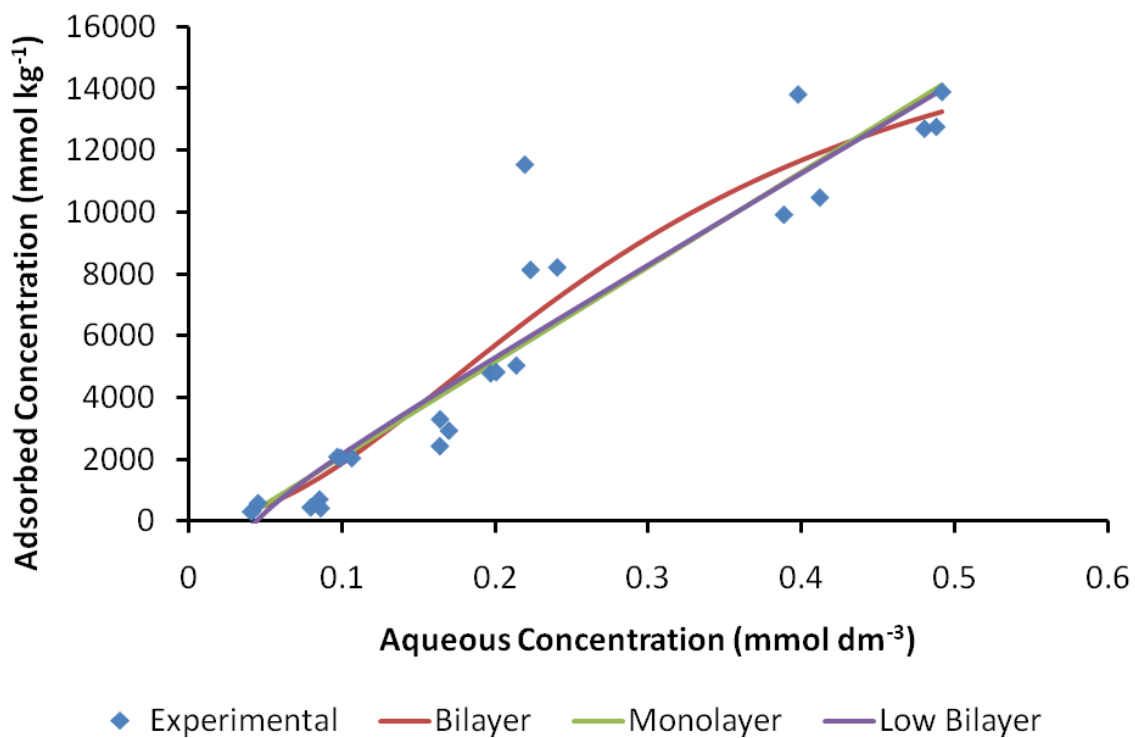


Figure S7 Graph of ARIAN isotherms for HSA Talc adsorbing fatty acid ester defoamer

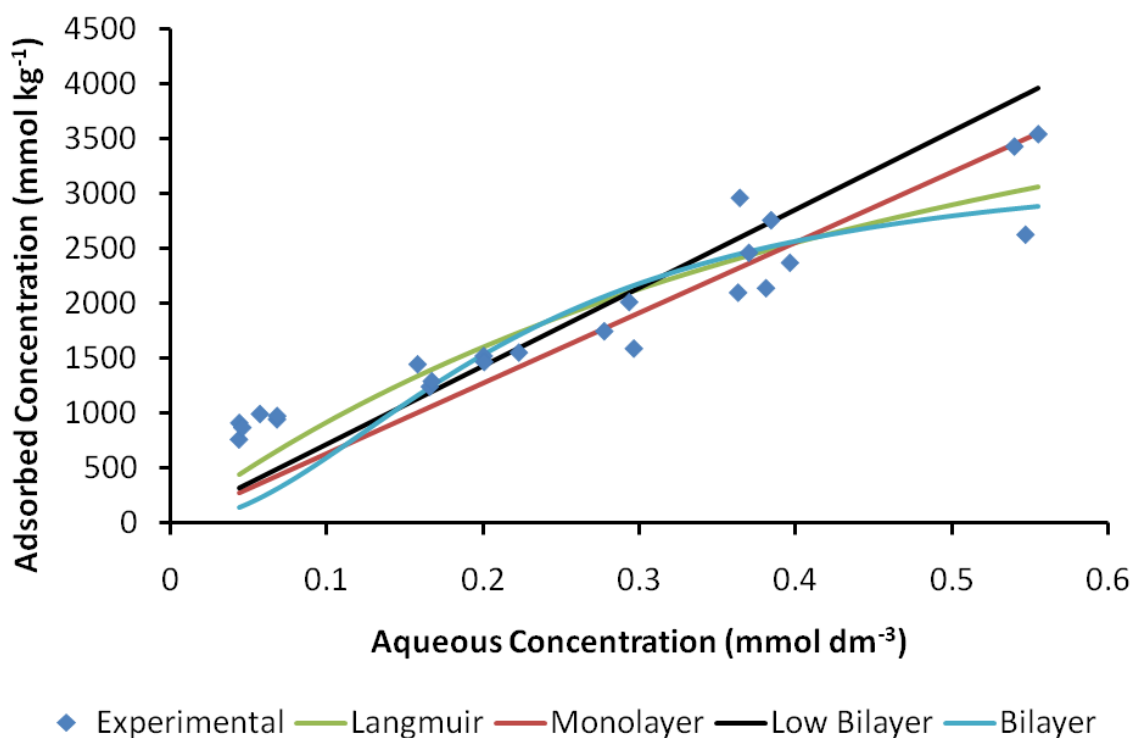


Figure S8 Graph of Langmuir and ARIAN isotherms for LSA MCC adsorbing fatty acid ester defoamer

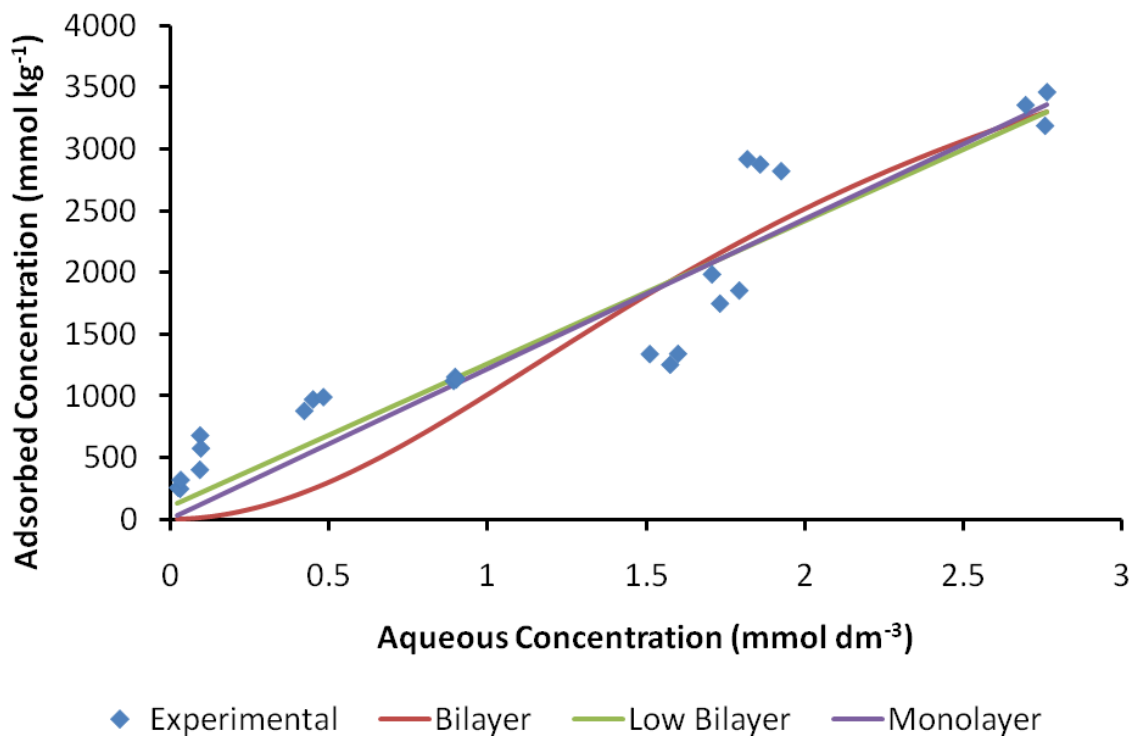


Figure S9 Graph of ARIAN isotherms for HSA MCC adsorbing fatty acid ester defoamer

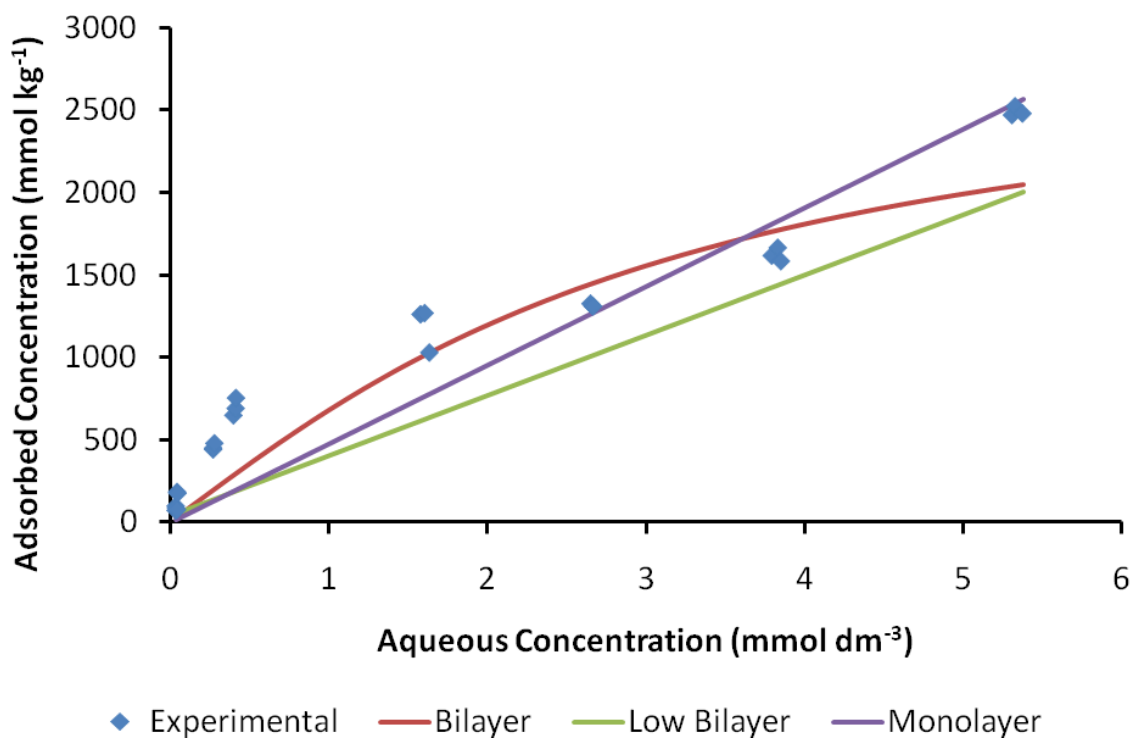


Figure S10 Graph of ARIAN isotherms for LSA Talc adsorbing acrylic acid ester copolymer

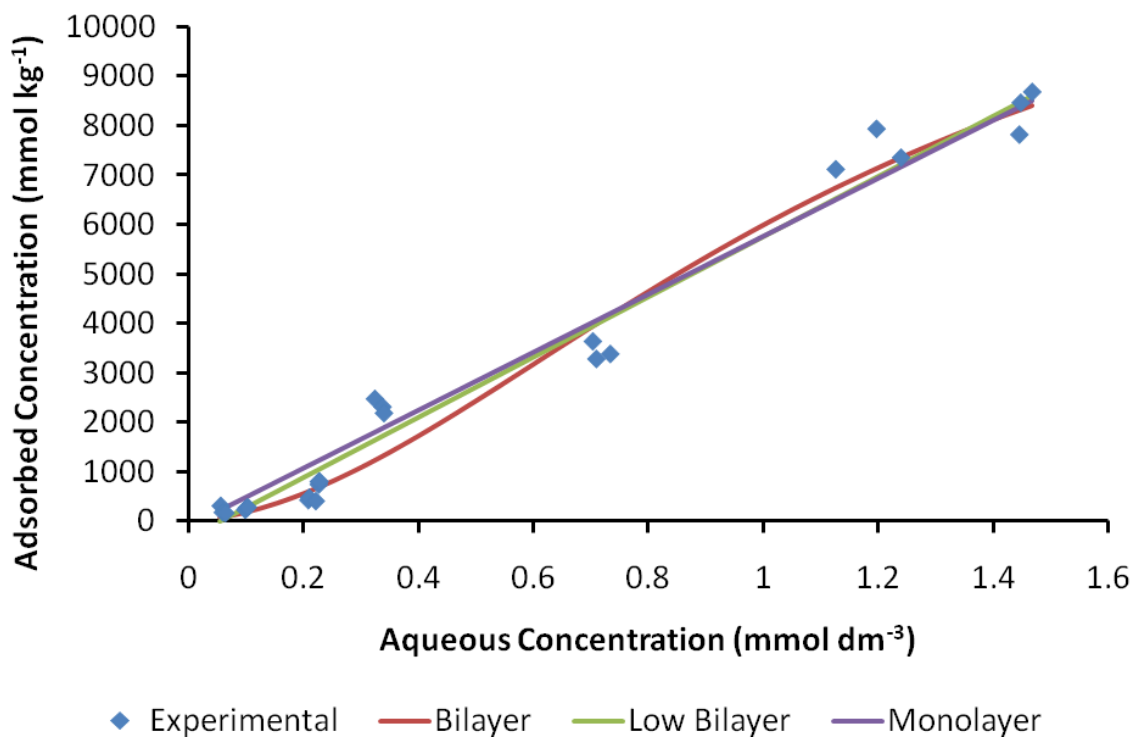


Figure S11 Graph of ARIAN isotherms for HSA talc adsorbing acrylic acid ester copolymer

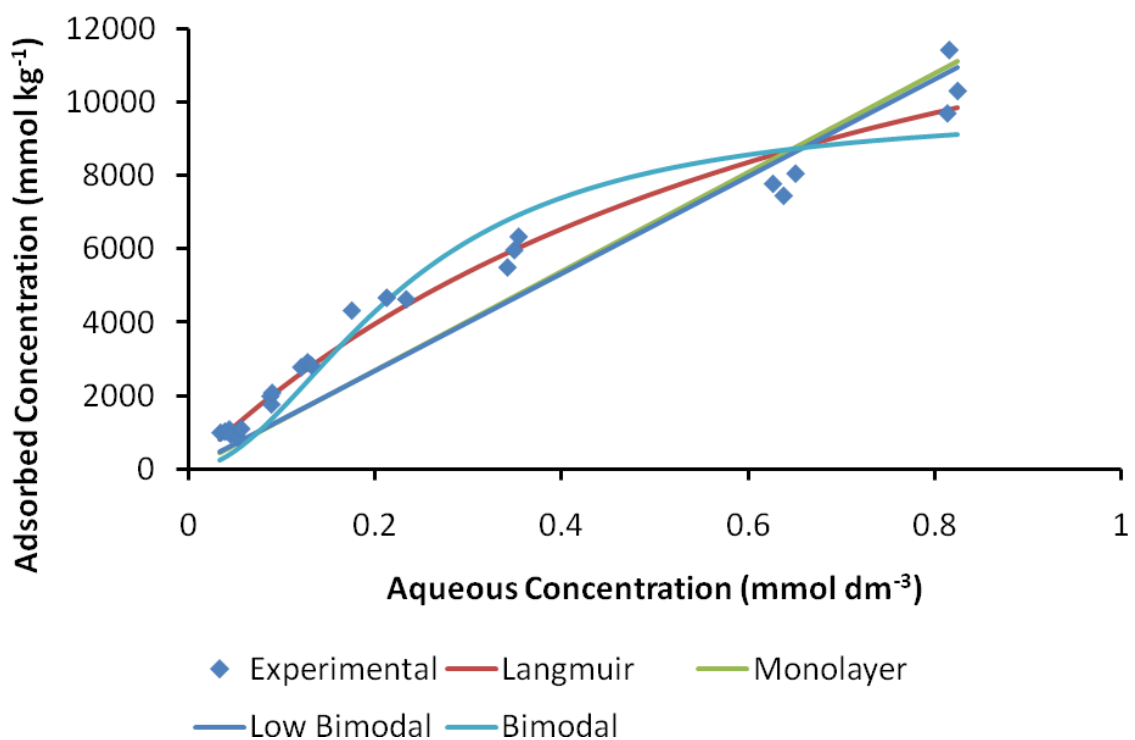


Figure S12 Graph of Langmuir and ARIAN isotherms for LSA MCC adsorbing acrylic acid ester copolymer

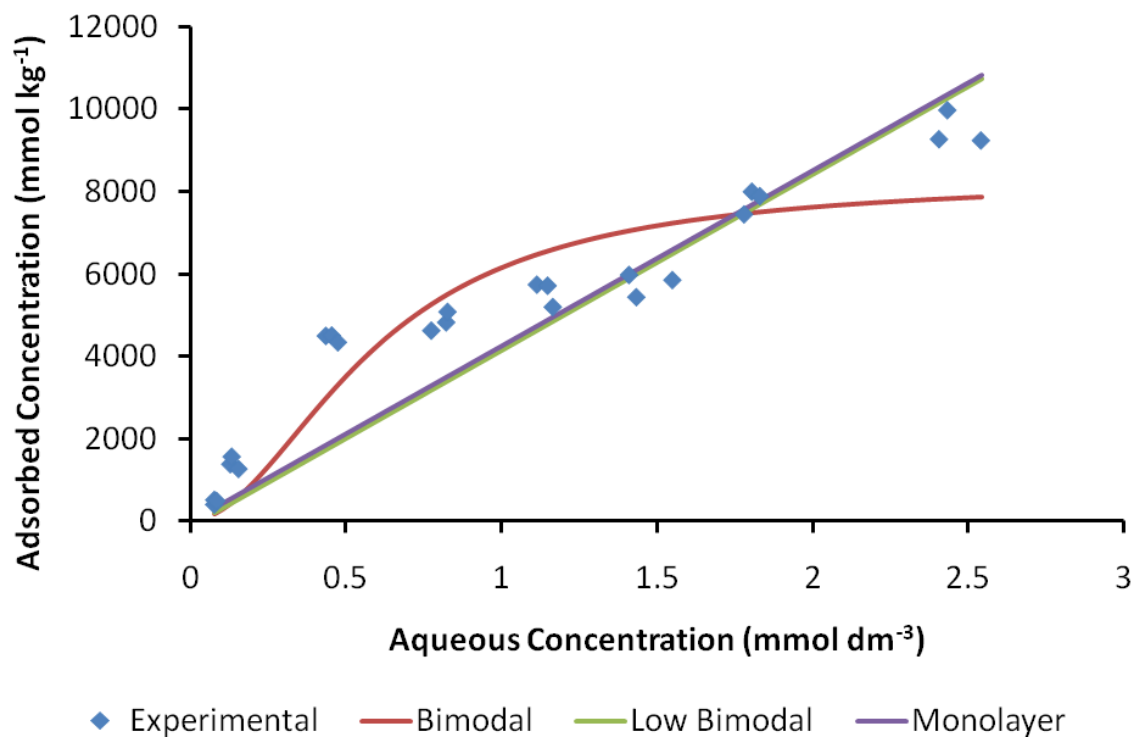


Figure S13 Graph of ARIAN isotherms for HSA MCC adsorbing acrylic acid ester copolymer

- 1 S. Brunauer, P. H. Emmett and E. Teller, J. Am. Chem. Soc. 60 (1938) 309-319.
- 2 G. Mie, Ann Phys-Leipzig 330 (1908) 377-445.