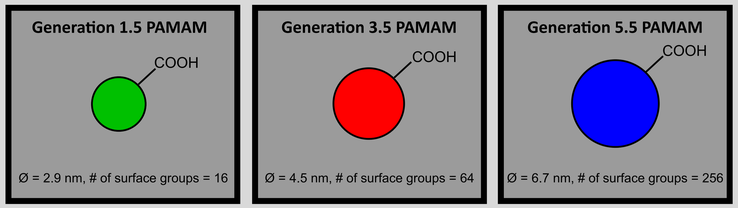
Dendrimeric organic nanomaterials at the Fe(III)-oxide-water interface: Size effects on dynamics of binding

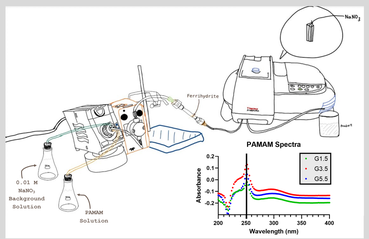
Brooke Newell
Faculty Advisor: Dr. Omar R. Harvey
Department of Geological Sciences, Texas Christian University

Introduction

- Synthetic nanomaterials revolutionize how we do things industrially, medically, and domestically
- Increased use means an inevitable entrance into the environment
- It is important to concurrently develop of an understanding of environmental interactions to support sustainable use
- Polyamidoamine (PAMAM) dendrimers are commonly used in the biomedical field (with important applications in drug and gene delivery) and vary in both size and functionality
- This research investigates the effect of PAMAM size on interactions with ferrihydrite (FFH) while holding functionality constant (PAMAM-COOH)

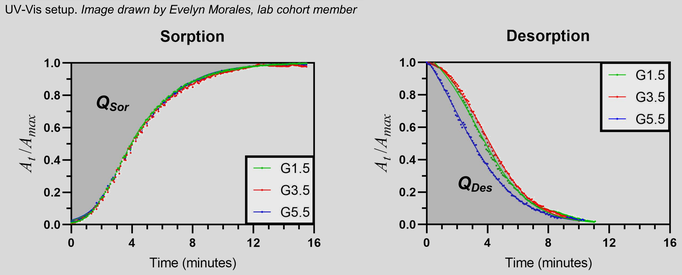


Methods



UV-Vis setup. *Image drawn by Evelyn Morales, lab cohort member*

- Number of carboxylic groups was held constant
- All experiments were run at pH 5 and in triplicates
- Effluent absorbance was monitored using UV-Vis at a wavelength of 250 nm



Data output for sorption and desorption, where quantity sorbed and quantity desorbed are the shaded areas represented by Q_{Sor} and $Q_{Des,}$ respectively.

Results

Effect of Size on Quantity

	Quantity	
	Q_{Sor}	f_{Des}
G1.5	29.6 ± 1.1%	94.7 ± 3.9%
G3.5	30.1 ± 0.6%	95.9 ± 2.5%
G5.5	29.9 ± 1.2%	76.2 ± 11.6%

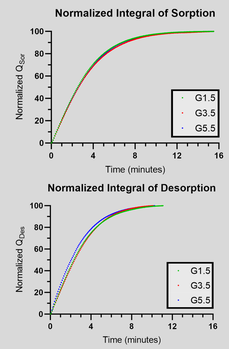
Where,

Q_{Sor} is the quantity sorbed, or percentage of the total amount of PAMAM passed through the column that attached to FFH

f_{Des} is the fraction desorbed, or amount of PAMAM removed from FFH divided by the amount of PAMAM sorbed (Q_{Des}/Q_{Sor})

- Quantity sorbed was similar for all three sizes of PAMAM, ranging from 29.6% to 30.1%
- **G1.5 Q_{Sor} = G3.5 Q_{Sor} = G5.5 Q_{Sor}**
- Fraction desorbed ranged from 76.2% to 95.9%
- G1.5 and G3.5 both desorbed around 95% of what was originally sorbed onto FFH, where-as G5.5 was significantly less at 76.2%
- **G1.5 f_{Des} = G3.5 f_{Des} >> G5.5 f_{Des}**

Effect of Size on Kinetics and Dynamics



In order to analyze the rate and dynamics of each PAMAM size, the normalized integral of both sorption and desorption are fitted to:

$$y = \frac{S_1}{1+e^{k_1'(t-t_{1/2,1})}} + \frac{S_2}{1+e^{k_2'(t-t_{1/2,2})}}$$

where,

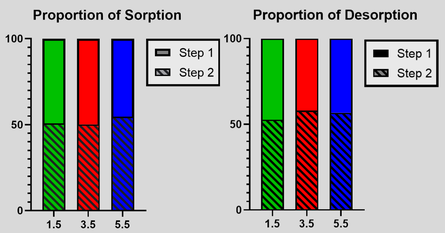
S_1 **and** S_2 are the fractional sorption/desorption accounted for by stage 1 and 2, respectively
k_1' **and** k_2' are the rate constants for stage 1 and 2, respectively
$t_{1/2,1}$ **and** $t_{1/2,2}$ are the half-life for stage 1 and 2, respectively
t is the overall reaction time

Sorption Fitted Model Parameters

	S_1	$k_1'(min^{-1})$	$t_{1/2,1}(min)$	S_2	$k_2'(min^{-1})$	$t_{1/2,2}(min)$
G1.5	49.2	1.59	1.57	50.8	0.656	4.37
G3.5	49.9	1.53	1.63	50.1	0.628	4.60
G5.5	45.4	1.64	1.55	54.6	0.661	4.29

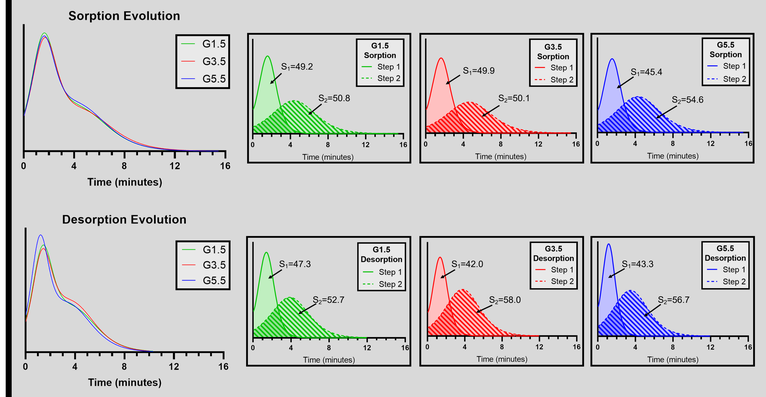
Desorption Fitted Model Parameters

	S_1	$k_1'(min^{-1})$	$t_{1/2,1}(min)$	S_2	$k_2'(min^{-1})$	$t_{1/2,2}(min)$
G1.5	47.3	1.80	1.40	52.7	0.767	3.88
G3.5	42.0	1.91	1.35	58.0	0.816	3.75
G5.5	43.30	2.16	1.16	56.7	0.816	3.47



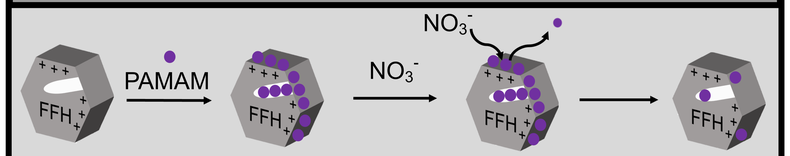
- All three sizes of PAMAM sorb/ desorb onto/off of FFH in two distinct steps: a faster first step and a slower second step
- For both sorption and desorption, close to half of the reaction took place in step 1 and half of the reaction took place in step 2 for all three sizes of PAMAM

Results



- The sorption rates were similar for all three sizes of PAMAM
- **G1.5 $k_1'_{Sor}$ = G3.5 $k_1'_{Sor}$ = G5.5 $k_1'_{Sor}$ & G1.5 $k_2'_{Sor}$ = G3.5 $k_2'_{Sor}$ = G5.5 $k_2'_{Sor}$**
- The desorption rates for step 1 were similar for G1.5 and G3.5 but faster for G5.5
- The desorption rates for step 2 were similar for all three sizes of PAMAM
- **G1.5 $k_1'_{Sor}$ = G3.5 $k_1'_{Sor}$ < G5.5 $k_1'_{Sor}$ & G1.5 $k_2'_{Sor}$ = G3.5 $k_2'_{Sor}$ = G5.5 $k_2'_{Sor}$**

Conclusion



Size has no effect on how PAMAM sorbs onto ferrihydrite. During desorption, less G5.5 is removed but at a faster rate than G1.5 and G3.5, both of which behave similarly during desorption. The interaction between PAMAM and FFH occurs in two steps. It is believed that the first faster step takes place on the ferrihydrite surface, whereas the second slower step is diffusion into micropore spaces within the ferrihydrite.

References and Acknowledgements

Araújo, R., Santos, S., Igne Ferreira, E., & Giarolla, J. (2018). New Advances in General Biomedical Applications of PAMAM Dendrimers. Molecules, 23(11), 2849. https://doi.org/10.3390/molecules23112849

Fatemi, S. M., Fatemi, S. J., & Abbasi, Z. (2020). PAMAM dendrimer-based macromolecules and their potential applications: recent advances in theoretical studies. Polymer Bulletin, 77(12), 6671-6691. https://doi.org/10.1007/s00289-019-03076-4

This research is supported by the TCU Science & Engineering Research Center Grant, the John V. Roach Honors Undergraduate Research Grant, and the Dr. Arthur J. Ehlmann Scholarship for Research Excellence.