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Kinetics and Recyclability of Polymer-Modified Beads for Removal of Organics from Contaminated Water

Peter P. Gennaro
Clemson University

Rachel E. Perry
Clemson University

Kara Jolly
Clemson University

Clayton Little
Clemson University

Rhett C. Smith

Kinetics and Recyclability of Polymer-Modified Beads for Removal of Organics from Contaminated Water

Peter P. Gennaro, Rachel E. Perry, Kara Jolly, Clayton Little, Rhett C. Smith*

Department of Chemistry and Laboratory for Creative Inquiry in Chemistry,
Clemson University, Clemson, SC 29634

I. Introduction

Solid supports have been exploited extensively in materials chemistry and organic synthesis as convenient supports for the selective absorption/reaction with solution-phase species followed by facile removal of the solid-supported material from the solution. In the current contribution we report the modification of silica-coated magnetic microspheres with a variety of phosphonium polyelectrolytes. These silica-coated microspheres were selected because they are easily removed from a fluid such as drinking water that has been purified by the modified particles. Once prepared, the phosphonium-support constructs were examined for uptake of organic materials from aqueous solution. The kinetics of organic material uptake and the recyclability over at least ten cycles are discussed. Possible applications of these materials would be as bioremediation or therapeutic agents. The analytical techniques discussed in this contribution from the Laboratory for Creative Inquiry in Chemistry include UV-vis spectroscopy and scanning electron microscopy.

II. Polymer Synthesis and Application

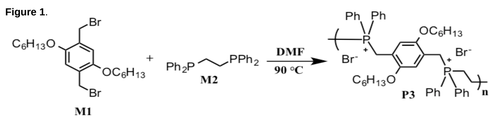


Figure 1. Reaction of M1 and M2 to form P3

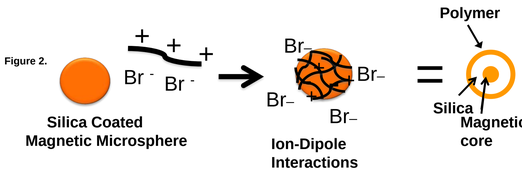


Figure 2. Silica has a very polar surface which creates strong adhesion of ionic compounds

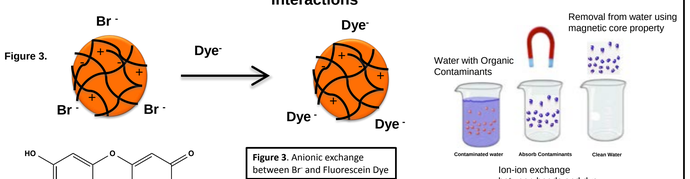


Figure 3. Anionic exchange between Br^- and Fluorescein Dye

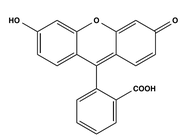


Figure 4. Fluorescein Dye Molecular structure

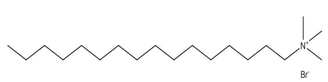


Figure 5. Cetyltrimethyammonium bromide (CTAB) Molecular Structure

III. Scanning Electron Microscopy (SEM)

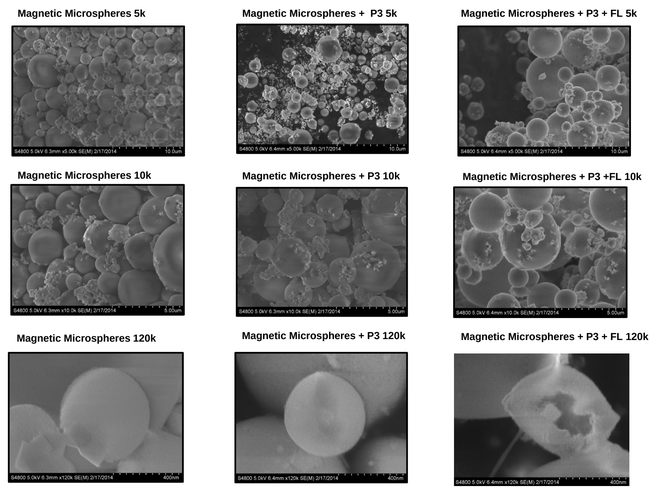


Figure 6. Fragments can be seen at 5k times magnification, these are little bits of silica broken off due to aggregation, stirring and shipment. These images show that the structural integrity of the beads has been preserved and no damage has been done to the surface due to the exposure of the polymer or Fluorescein dye. Magnification shows the faint glow around the spheres providing evidence of polymer's adhesion to the surface of the beads.

IV. Absorption Kinetics & Recyclability

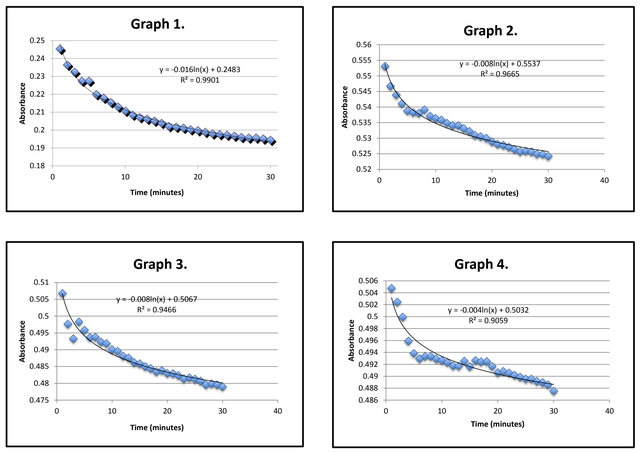


Figure 7. Representative demonstration of how UV-vis spectra change as fluorescein is removed from water by the microspheres

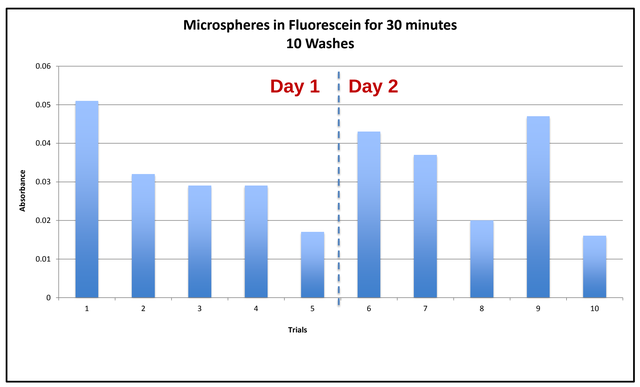
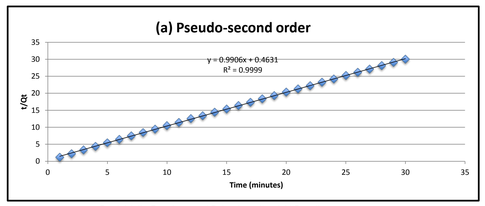


Figure 8. In this chart, absorbance on the y-axis is plotted against trial number on the x-axis. With an additional non-consecutive five trials, the change in absorbance remains relatively small and generally consistent with the first five trials with the exception of trial 9.

V. Adsorption Kinetics



Graph (a), the Pseudo-second Order shows the plot t/Q_t on the y-axis versus time on the x-axis.

$$Q_e = \frac{(C_0 - C_e)V}{W}$$

where C_0 and C_e are the initial and final concentrations (mg L^{-1}) of the dye solution, respectively, and V and W are the solution volume (L) and absorbent weight (g) respectively.[1]

Table 1. Absorption kinetics parameters	
Pseudo – first order	
k_1 (min^{-1})	0.13
R^2	0.98517
Q_e,cal (mg g^{-1})	0. 9984
Pseudo – second order	
k_2 (min^{-1})	0.9906
R^2	0.99986
Q_e,cal (mg g^{-1})	0.9978

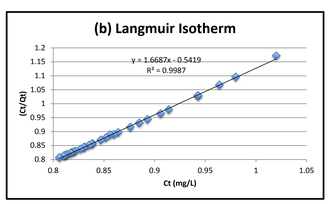
Pseudo-first Order kinetic Model of Lagergren

$$\ln(Q_e - Q_t) = \ln(Q_e) - k_1 t$$

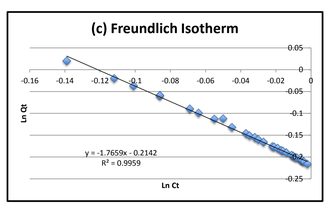
Pseudo-second Order kinetic model of Ho

$$\frac{t}{Q_t} = \frac{1}{k_2 Q_e^2} + \frac{t}{Q_e}$$

where Q_t and Q_e (mg g^{-1}) are the amounts of absorption on the polymer at time t and equilibrium, respectively, and k_1 (min^{-1}) and k_2 (g mg^{-1} min^{-1}) are the rate constants for the pseudo-first-order and the pseudo-second order models respectively.[1]



Graph (c), the Langmuir Isotherm shows the plot C_t/Q_t on the y-axis versus C_t on the x-axis



Graph (d), the Freundlich Isotherm shows the plot Ln Q_t on the y-axis versus C_t on the x-axis.

Table 3.
Kinetic parameters of the absorption of Fluorescein by AccuBead™Silica Magnetic Beads for application of Langmuir and Freundlich isotherm models

Langmuir isotherm constants			Freundlich isotherm constants		
Q_0 (mg g^{-1})	b (L mg^{-1})	R^2	K_F (mg g^{-1})	n (L mg^{-1})	R^2
0.417	0.887	.99868	.807	-0.56	.99588

Langmuir isotherm:

$$\frac{C_e}{Q_e} = \frac{1}{Q_o b} + \frac{C_e}{Q_0}$$

where Q_e is the amount of solute absorbed per unit weight of absorbent (mg g^{-1}), C_e the equilibrium concentration (mg L^{-1}), Q_0 the monolayer absorption capacity (mg g^{-1}) and b a constant. The model parameters (Q_0 and b) can be determined for a linear plot of C_e/Q_e against C_e.[1]

Freundlich equation model (for absorption kinetics on a heterogeneous surface):

$$\ln(Q_e) = \ln(K_F) + \frac{1}{n}\ln(C_e)$$

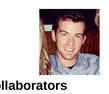
where K_F and n are Freundlich constants, which absorption capacity and absorption intensity, respectively. K_F and n can be calculated from a linear plot of ln Q_e against ln C_e.[1]

VI. Conclusions

Polymer-modified silica magnetic microspheres were prepared and absorption and adsorption properties were investigated to examine the uptake of Fluorescein dye from aqueous solution. The surfactant CTAB displayed a consistent trend in its ability to remove the dye from the surface of the polymer to allow for recyclability. In solution the polymer-modified spheres efficiently separated absorbent from the contaminated media. Removal of organic contaminants in this way can be used as a green solution for the bioremediation of organic pollutants from contaminated water.

VII. Acknowledgements and References

Research Team



Peter Gennaro
Peter Gennaro is a junior Chemistry major and has been working with the Smith Group for the past two years.

Collaborators

Kara M. Jolly
Kara Jolly is a junior biological sciences major with a minor in chemistry at Clemson University. She has been researching with the Smith Group for two years.

Clayton Little
Clayton Little is a junior Chemistry major and has been working with the Smith Group for the past two years.

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