A Green Chemistry Experiment: Magnetic Citrate Alginate Hydrogels Remove Methylene Blue from Water.

Katelynn R. Setters and Dr. Elizabeth M. Thomas,

Department of Biology and Chemistry, Morehead State University, Morehead, KY 40351

Introduction

The objective of this research was to design a green chemistry experiment that synthesizes magnetic citrate alginate hydrogels (Fig. 1) and test their effectiveness for the removal of methylene blue (MB) dye. Methylene blue dye is a common water pollutant that is toxic, carcinogenic, and nonbiodegradable; thus, can cause a severe threat to human health and environmental safety (Fig. 1.)[1] Hence, there is a need to develop an environmentally friendly, efficient technology for removing MB from wastewater.

Green chemistry is a growing field that continues to get more attention around the world at universities and institutions each year. It is the design of chemical products and processes to reduce the use and generation of hazardous substances.[2] The twelve principles of green chemistry include rules to help chemists achieve the goal of sustainability at the molecular level. The twelve principles include: prevention, atom economy, less hazardous chemical synthesis, designing safer chemicals, safer solvents and auxiliaries, design for energy efficiency, use of renewable feedstocks, reduce derivatives, catalysis, design for degradation, real-time analysis for pollution prevention, and inherently safer chemistry for accident prevention (Fig. 1).

In this experiment, our lab used alginic acid to synthesize the magnetic nanoparticles that were used to remove the MB from the samples (Scheme 2). Alginic acid is derived from marine brown algae and continues to get more recognition as a renewable feedstock.[4] The blue color of MB was monitored using the color imager app "Colorimeter" which is easily applicable to high school and undergraduate research experiments.

The magnetic nanoparticles were synthesized first (Scheme 1), and then incorporated into alginate hydrogels. To test the effectiveness of MB removal, the magnetic citrate alginate hydrogels were dispersed evenly into three separate beakers containing the same concentration of methylene blue for varying times. To test the results, the app "Colorimeter" was used, obtaining the absorbance value of the solution in each of the three beakers to generate a graph and correlation value, R^2, to evaluate the effectiveness of the experiment.

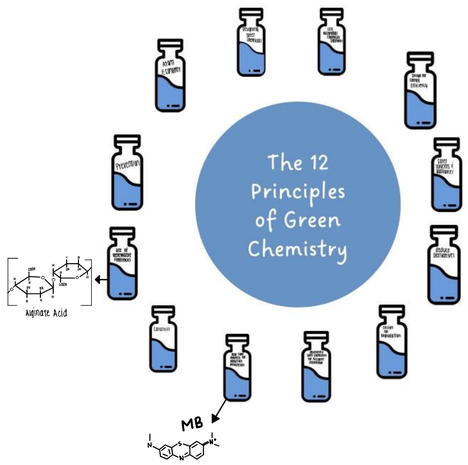
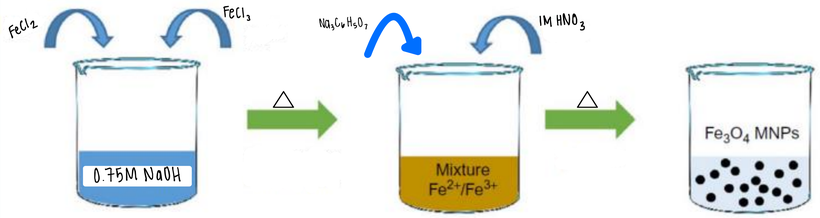
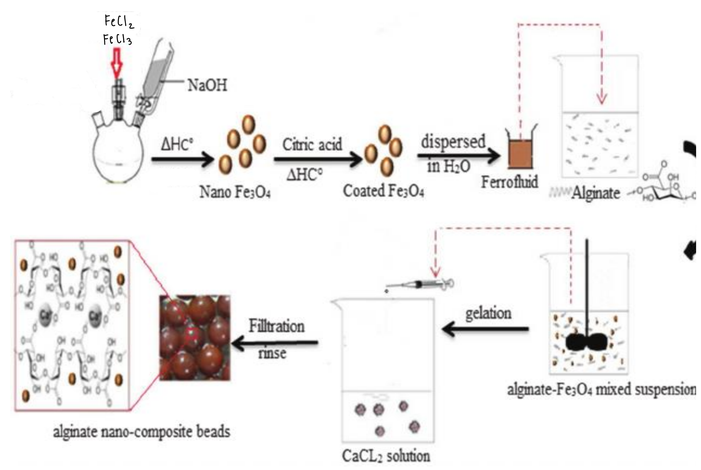


Figure 1: The 12 Principles of Green Chemistry including structures of MB & alginate acid

Method



Scheme 1. Synthesis of MNPs coated in sodium citrate.



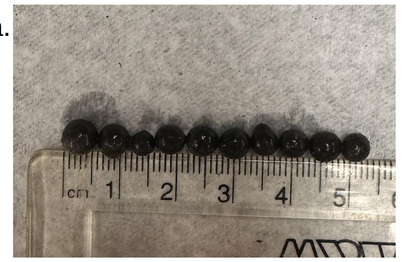
Scheme 2: Schematic diagram for the synthesis of magnetic citrate alginate hydrogels.

Synthesis of Magnetic Nanoparticles (MNP). A mixture of .300 g ferrous chloride ($FeCl_2$) and 0.600 g ferric chloride ($FeCl_3$) were mixed with 50 mL of 0.75 M NaOH, and then heated at 100°C until a black precipitate formed. The remaining precipitate was washed with 1 mL of HNO_3 and heated to 90°C. Then 150 mL of 5 mg/mL sodium citrate was added and heated for 20 minutes at 90°C, cooled to room temperature, and stirred for 1 hour. The product was then isolated using magnetic decantation, washed with deionized water, and dried with rotovap (Scheme 1).

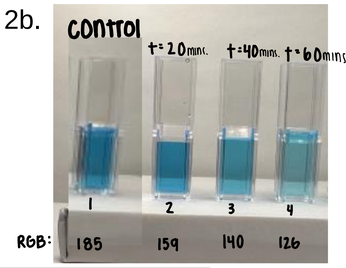
Synthesis of Magnetic Citrate Alginate Hydrogels. A 2 % sodium alginate solution was made and mixed with the MNPs. The solution was then added to the 1.5 % calcium chloride solution. The beads hardened for 45 minutes. Another batch of alginate hydrogels was prepared following the same procedure, not including the MNPs. Once the beads finished hardening, the diameter of 10 beads was measured to find the average individual width per bead. Then, 9 MNP beads were placed into 3 separate cuvettes all containing equal concentration of 1 % MB. The control contained alginate bead with no MNPs, cuvettes 2, 3, and 4 incubated with MNP beads for 20, 40, and 60 minutes, respectively. The resultant MB concentration was measured by absorbance (RGB value) using app "Colorimeter" available on most smartphones.

Results

2a.



2b.



2c.

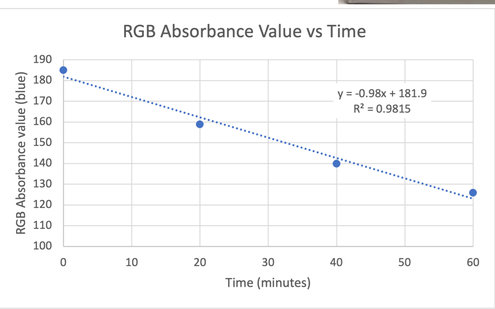


Figure 2. a) Average size of a MNP bead b) Concentration of MB incubated with MNP beads over time c) RGB Absorption value of MB using app "Colorimeter" vs Time

The RGB value was recorded using the app "Colorimeter" and gave the following values: 185, 159, 140, and 126. A linear correlation between the amount of time and the concentration of MB was observed, generating a linear trendline and r^2 value of 0.9815.

Discussion

The objective of this research was to design a green chemistry experiment to remove MB from a sample using synthesized MNP citrate alginate beads. This experiment was successful in removing MB. Samples containing 1% MB incubated at different times with MNP citrate alginate beads showed a decreasing linear correlation (y= -0.98x + 181.9, R^2= 0.9815) indicating the removal of MB from the sample solution by the MNP beads.

Acknowledgements

We would like to thank the Morehead State, Research and Creative Productions, and the Biology and Chemistry Department for the opportunity to work on this research.

Literature Cited

1. Khan, I.; et.al. *Water* **2022**, *14* (2), 242.
2. Anastas, P.; Eghbali, N. *Chem. Soc. Rev.* **2009**, *39* (1), 301–312.
3. Paredes JuÃ¡rez, G. A.; Spasojevic, M.; Faas, M. M.; de Vos, P. *Frontiers in Bioengineering and Biotechnology* **2014**, *2*.
4. Lee, K. Y.; Mooney, D. J. *Progress in Polymer Science* **2012**, *37* (1), 106–126.
5. Rocher, V.; et.al. *ElSevier* **2007**, 1290–1298.
6. Jiang, Y.-J.; Yu, X.-Y.; Luo, T.; Jia, Y.; Liu, J.-H.; Huang, X.-J. *Journal of Chemical & Engineering Data* **2013**, *58* (11), 3142–3149.