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Introduction

- For each barrel of bitumen produced, nearly three barrels of freshwater are used. A harmful effect of Canada's oil sands industry is the release of naphthenic acids (NAs) into this oil sands process-affected water (OSPW). NAs are toxic to living organisms and can damage equipment over time. (Quinlan, P.J., Tam K.C. 2015)
- Adsorption is a method used to remove NAs from OSPW. During this process, the NAs will act as adsorbates and will hold to the surface of an adsorbent with the help of hydrophobic and electrostatic forces. (Nam, s. et al 2014)
- Granular Activated Carbon (GAC) is an effective adsorbent that can be used for the removal of NAs. (Islam, MD.S. et al 2015)

Purpose

The purpose of this experiment was to determine which concentration of GAC is most efficient and whether or not it is reusable. This study was also formulated to understand how the hydrophobicity of the substances used affects the amount of NAs adsorbed.

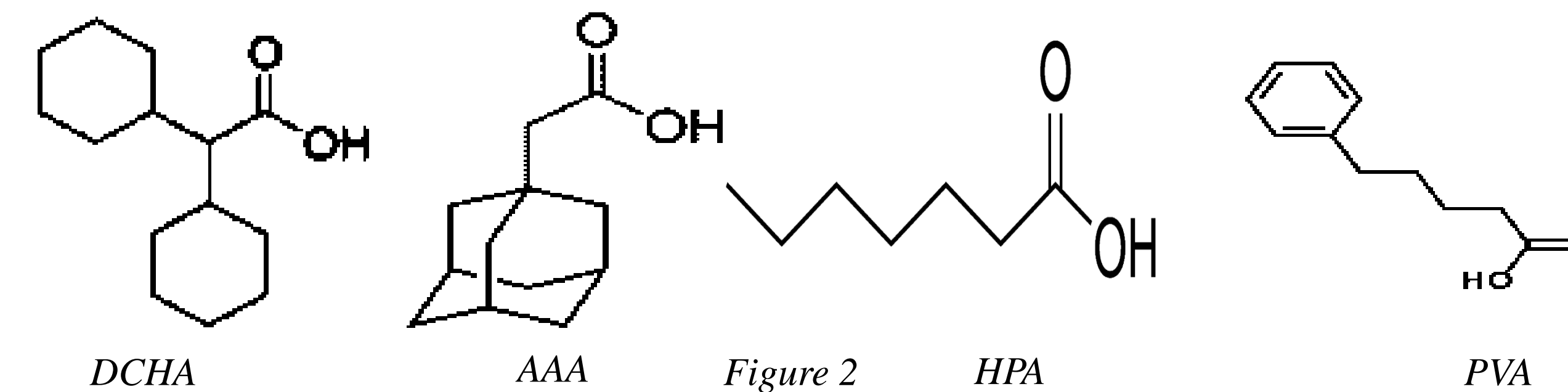
Methods

- To mimic OSPW, a Phosphate buffer solution with a concentration of 50 mM was made and we experimented with four different NAs all of which have a concentration of 50 mg/L: Dicyclohexylacetic acid (DCHA), Adamantaneacetic acid (AAA), Heptanoic acid (HPA) and Phenylvaleric acid (PVA).
- For each NA, GAC concentrations of 0.5 g/L, 1.0 g/L, 1.5 g/L and 2.0 g/L as well as a control experiment with no GAC were used. Our reactors were placed on a New Brunswick™ Innova® 2100 platform shaker (Eppendorf Inc., USA) that operated at 210 RPM (Figure 1). We took samples at 0.5 hours, 1 hour, 2.5 hours, 4 hours, 22 hours and 24 hours. The samples all passed through a filter as to ensure no GAC could pass into the vials and that the adsorption process would come to an end.
- We tested each NA with 0.25 g/L and 0.5 g/L over a 29 hour period to observe the saturation of GAC.
- The remaining NA concentration was quantified by Liquid Chromatography – Mass Spectrometry (LC-MS) Analysis. Standard concentrations of 5 mg/L, 10 mg/L, 20 mg/L, 40 mg/L and 50 mg/L were produced to set a calibration curve. AAA, HPA and DCHA could be analyzed directly, however, PVA had to be diluted 10 times.
- After determining which concentration of GAC is most efficient a stability test was conducted to see if the GAC is reusable.



Figure 1

Islam, MD.S., Zhang, Y., McPhedran, K.N., Gamal El-Din, M. (2015) Granular activated carbon for simultaneous adsorption and biodegradation of toxic oil sands process-affected water organic compounds. *Journal of Environmental Management*, 152, 49-57
 Quinlan, P.J., Tam, K.C. (2015) Water treatment technologies for the remediation of naphthenic acids in oil sands process-affected water. *Chemical Engineering Journal*, 279, 696-714
 Nam, S., Choi, D., Kim, S., Her, N., Zoh, K. (2014) Adsorption characteristics of selected hydrophilic and hydrophobic micropollutants in water using activated carbon. *Journal of Hazardous Materials*, 270, 144-152



- We researched the structure and hydrophobicity of the substances used. The specific GAC we used has hydrophobic properties therefore it was adept at adsorbing non-polar substances. (Kilduff, J.E., Karanfil, T. 1999)
- The NAs we used (figure 2) were all hydrophobic meaning non-polar or not attracted to water. Because of this they adsorbed to GAC as it is also non-polar.
- Log P, where P is the Partition Coefficient, is used to express the hydrophobicity of a substance. The greater the Log P value is, the more hydrophobic a substance is and the better it should be adsorbed as they are directly related. (Cambridge MedChem Consulting [CMC] 2017)
- The Log P of DCHA = 4.71, AAA= 3.13, HPA = 2.37, PVA= 2.70.

Results

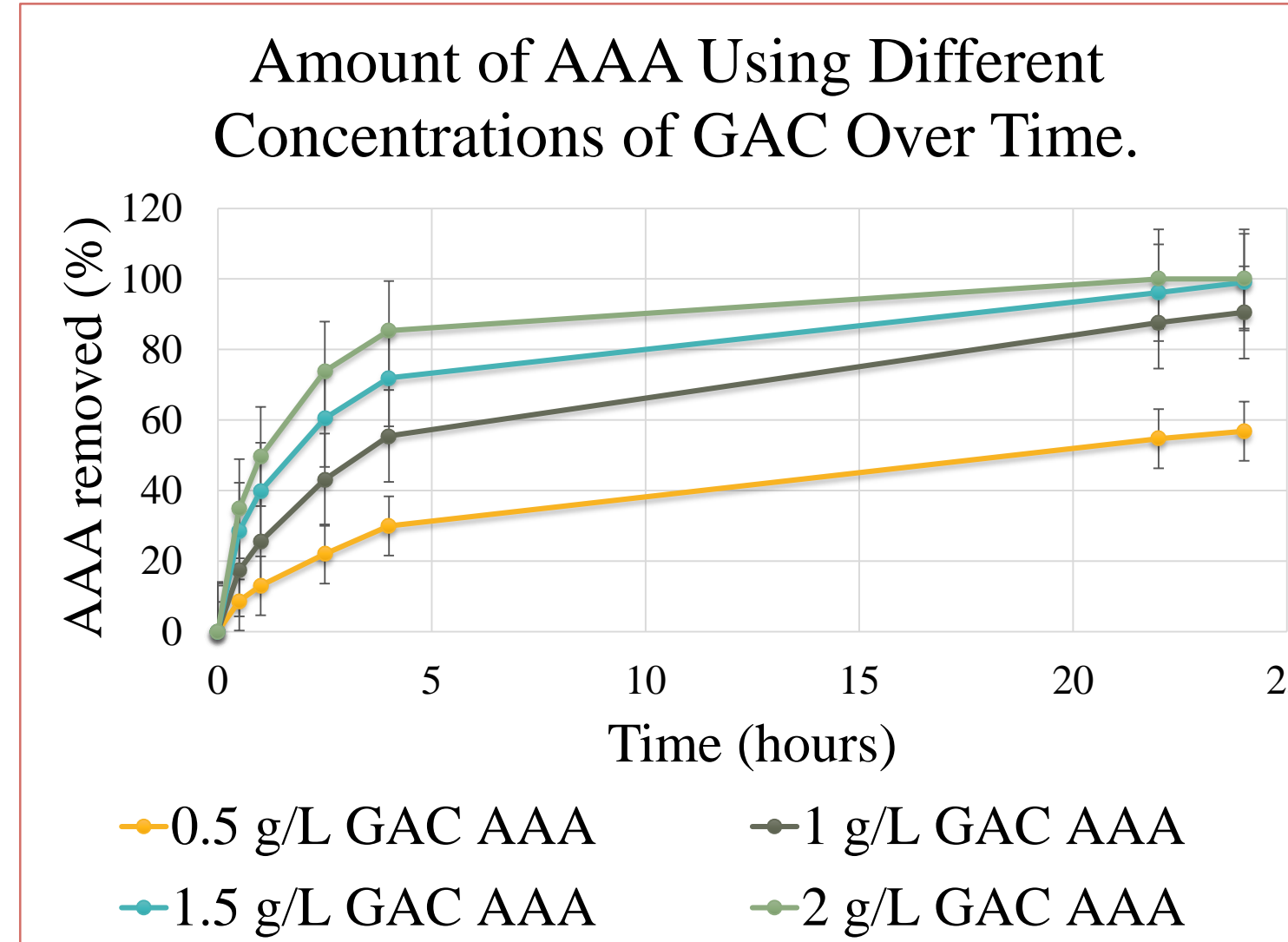
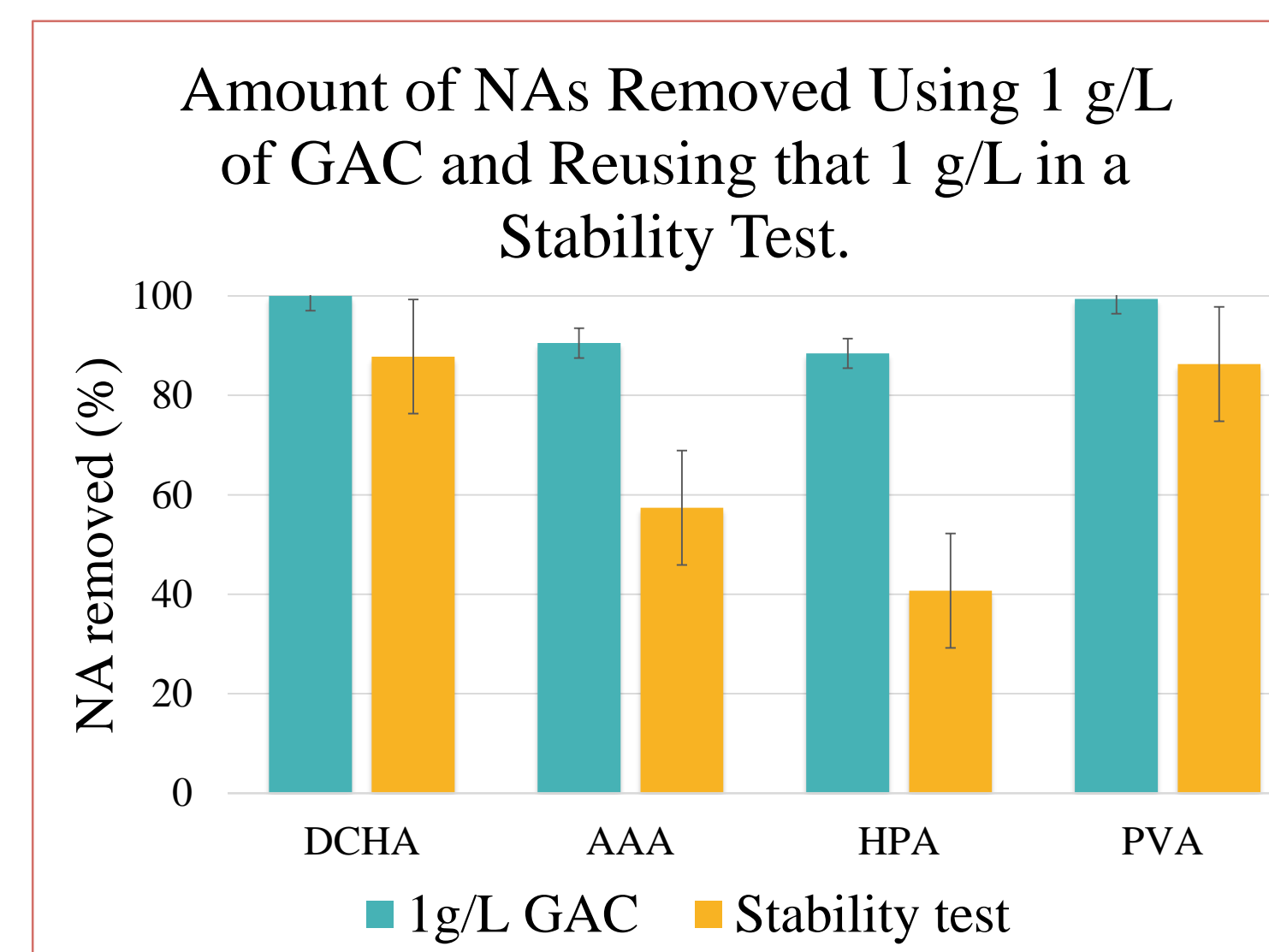


Figure 3

The percent removal for AAA using different amount of GAC over a 24 hour period. All NAs showed the same trend.

Figure 4

Comparing the original trial and the stability test to determine if GAC is reusable. The Percent Removal from both trials after 24 hours.



Kilduff, J.E., Karanfil, T. (1999) Role of Granular Activated Carbon Surface Chemistry on the Adsorption of Organic Compounds. 1. Priority Pollutants *Environmental Science and Technology* 33, 3217-3224.
 Cambridge MedChem Consulting (2017, March 2). Lipophilicity. Retrieved from <http://www.cambridgemedchemconsulting.com/resources/physiochem/logD.html>

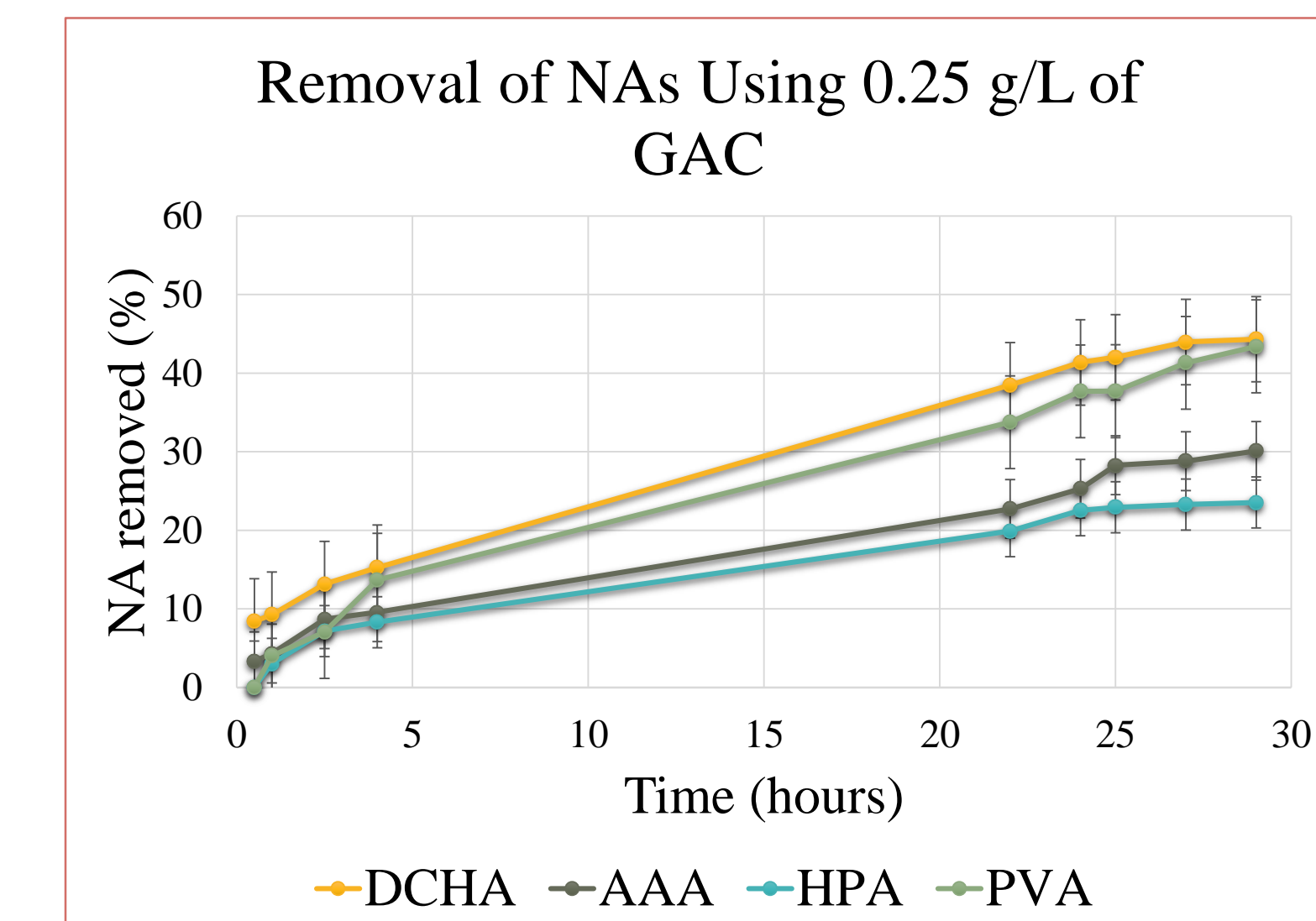
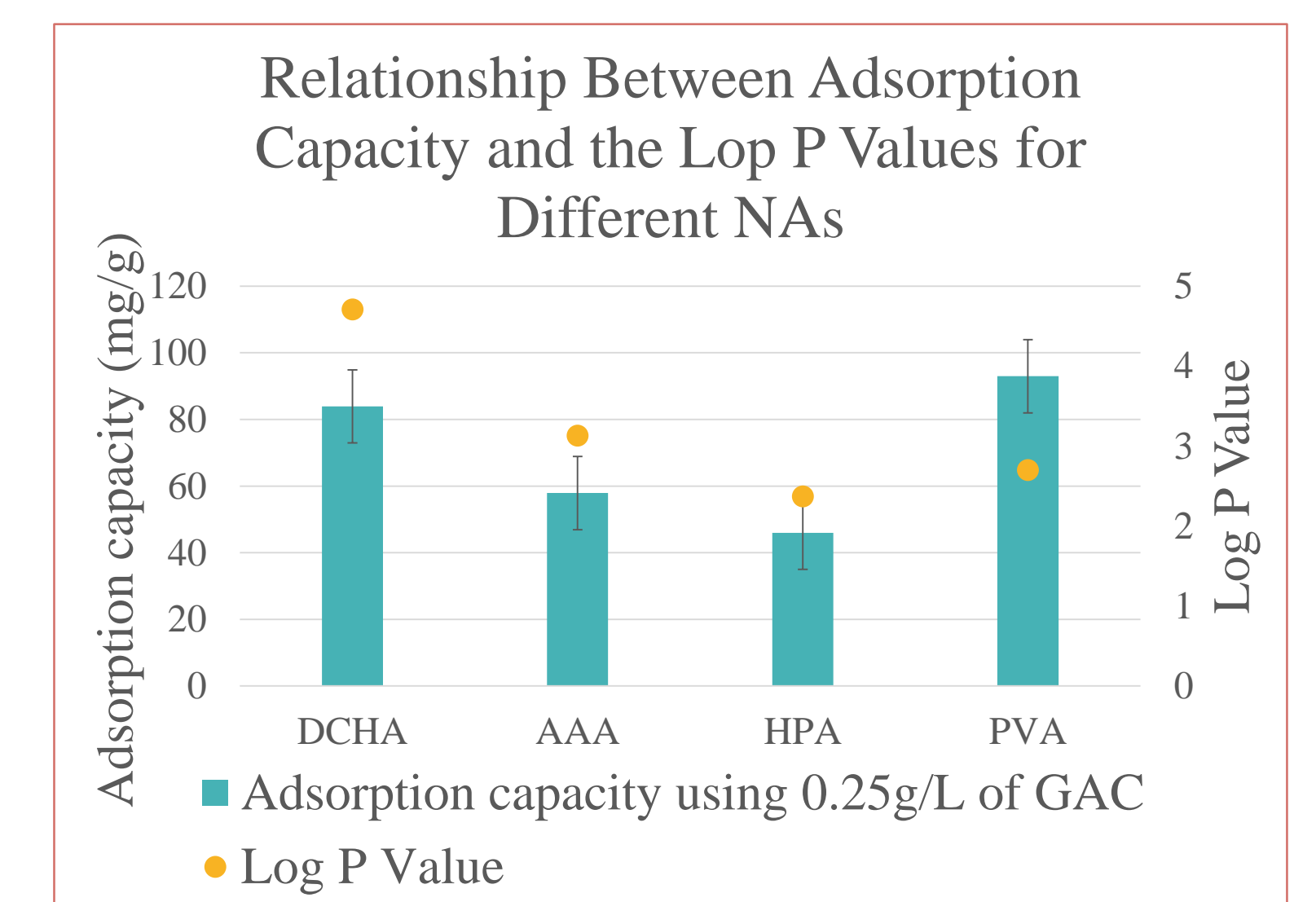


Figure 5

Using 0.25 g/L of GAC over a longer period of 29 hours to test the saturation of GAC for different NAs.

Figure 6

The adsorption capacity of 0.25 g/L of GAC with different NAs after 29 hours in relation with the Log P value of the NA.



Conclusions

- After evaluating the results and considering the retail price of GAC we have concluded that it is most efficient to use 1 g/L of GAC. While using larger amounts of GAC adsorbs NAs more quickly, there is not as big of a difference between 1 and 1.5 g/L of 1 and 2 g/L to justify the extra cost.
- From our stability test we have found that GAC is reusable for DCHA and PVA as more than 80% of the NA is adsorbed. For AAA and HPA it is not reusable because the adsorbent is over saturated at this point. We can conclude that AAA and HPA are less attracted to GAC than the others NAs.
- The hydrophobicity did have an effect on the rate of adsorption. DCHA had the highest Log P value and it was adsorbed at a higher rate than the other NAs. PVA, although possessing a lower Log P value than AAA, adsorbed very well due to the other factors involved such as the NAs structure and size. HPA had the lowest Log P value and thus performed the poorest.

Acknowledgments

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