

INTRODUCTION

- The oil sands industry has resulted in the formation of oil sands process-affected water (OSPW). These waters contain high concentrations of naphthenic acids (NAs) that are toxic to the environment and must be removed through appropriate means, such as adsorption. (Ajaero, 2016)
- Adsorption is a process in which molecules from a dissolved solid, liquid or gas are held on the surface of a solid or liquid by adhesion. This method is often utilized in water treatment processes to remove pollutant molecules effectively. (Worch, 2012)
- Granular activated carbon (GAC) is a commonly used adsorbent in water treatment. Its large surface area and pore size allow it to remove large quantities of adsorbate for a small cost. (Trussell, 2012)
- The GAC used in this experiment had hydrophobic properties due to the carbon molecules on its surface. The hydrophobicity of NAs should affect their ability to adsorb as well as many other factors such as molecular size, chemistry structures, and functional groups. (Wypych, 2001)
- The specific NA's tested in this experiment were dicyclohexylacetic acid (DCHA), 1-adamantaneacetic acid (AAA), heptonic acid (HPA), and 5-Phenylvaleric acid (PVA).

Table 1 Model Naphthenic acids

Model Compound	Abbrev.	Formula	Structure	Log P Value
Dicyclohexylacetic acid	DCHA	C ₁₄ H ₂₄ O ₂		4.71
1-Adamantaneacetic acid	AAA	C ₁₂ H ₁₈ O ₂		3.13
Heptanoic acid	HPA	C ₇ H ₁₄ O ₂		2.37
5-Phenylvaleric acid	PVA	C ₁₁ H ₁₄ O ₂		2.70

PURPOSE

The purpose of this study was to determine the most effective concentration of GAC on various NAs over a 48 hour period and assess the effectiveness of reused GAC. This study was also conducted to observe how the hydrophobicity of the acids affects their adsorption rate.

METHOD

- Potassium phosphate buffer solutions with a pH of 8 for every model NA stock solution were prepared using potassium dibasic monohydrogen phosphate and potassium monobasic dihydrogen phosphate. These solutions were assembled to be used in the experiment to mimic oil sands processed water.
- 50 mg/L NA stock solution was transferred to an Erlenmeyer flask for each model. 0.25 g/L of GAC was added to each solution, and then placed on a platform shaker at 210 RPM.
- After 0.5, 1, 2.5, 4, 22, 24, 25, 27, and 29 hours samples were taken from the solutions and filtered to ensure adsorbent particles were removed.
- This was repeated for 0.5 g/L, 1 g/L, 1.5 g/L, and 2.0 g/L of GAC. Although for concentrations of 0.5 g/L, 1.0 g/L, 1.5 g/L, and 2.0 g/L GAC samples were only taken up to 24 hours.
- A liquid chromatography - mass spectrometry (LC-MS) was used to determine the concentration of NAs remaining in the solution after the adsorption experiment.
- The GAC from each concentration used was filtered out of the solution and stored. The concentration of GAC that was found to be optimal in the first trial (1 g/L) was then reused to test the stability of the GAC in a second trial.



Figure 1: NA stock solutions with GAC on platform shaker

RESULTS

The Effectiveness of Different Concentrations of GAC on Various NAs

Percent Removal of NAs with 0.5 g/L GAC

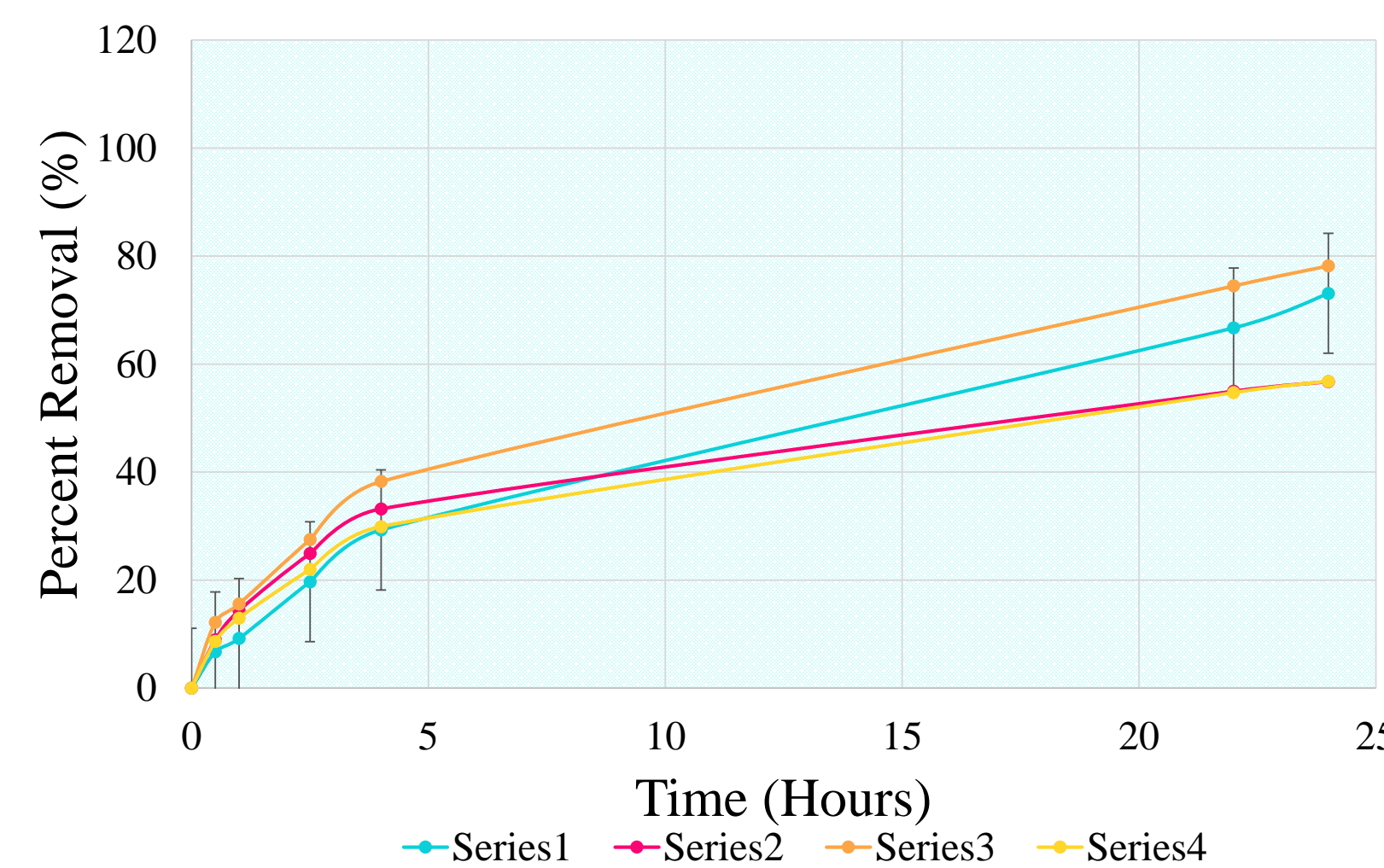


Figure 2: The effect of 0.5 g/L GAC on various NAs over a 24 hour period

Percent Removal of NAs with 1.0 g/L GAC First Trial and Stability Test

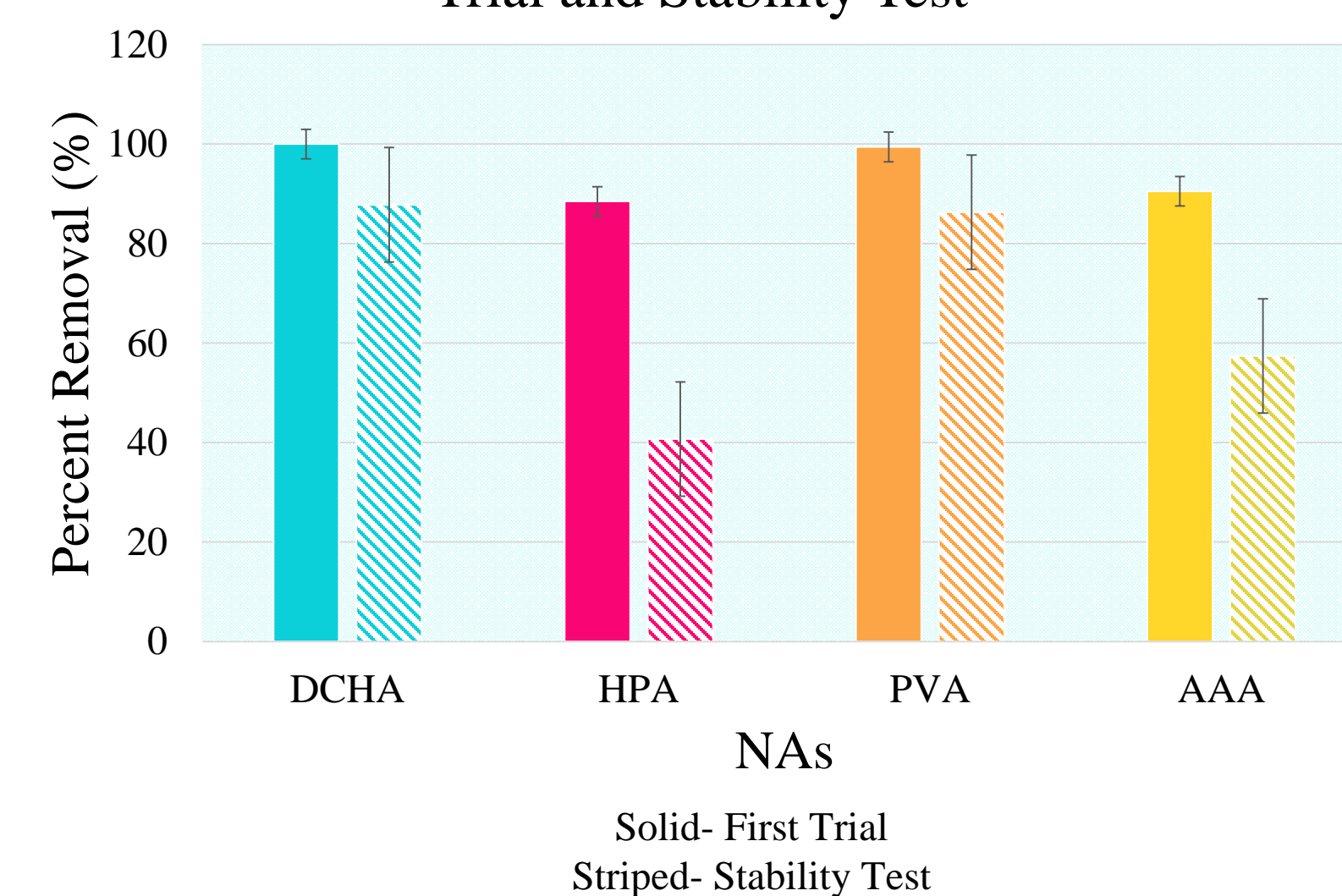


Figure 3: The effect of 1.0 g/L GAC on various NAs during the first trial and stability test over 24 hours

Percent removal of NAs with 1.5 g/L GAC

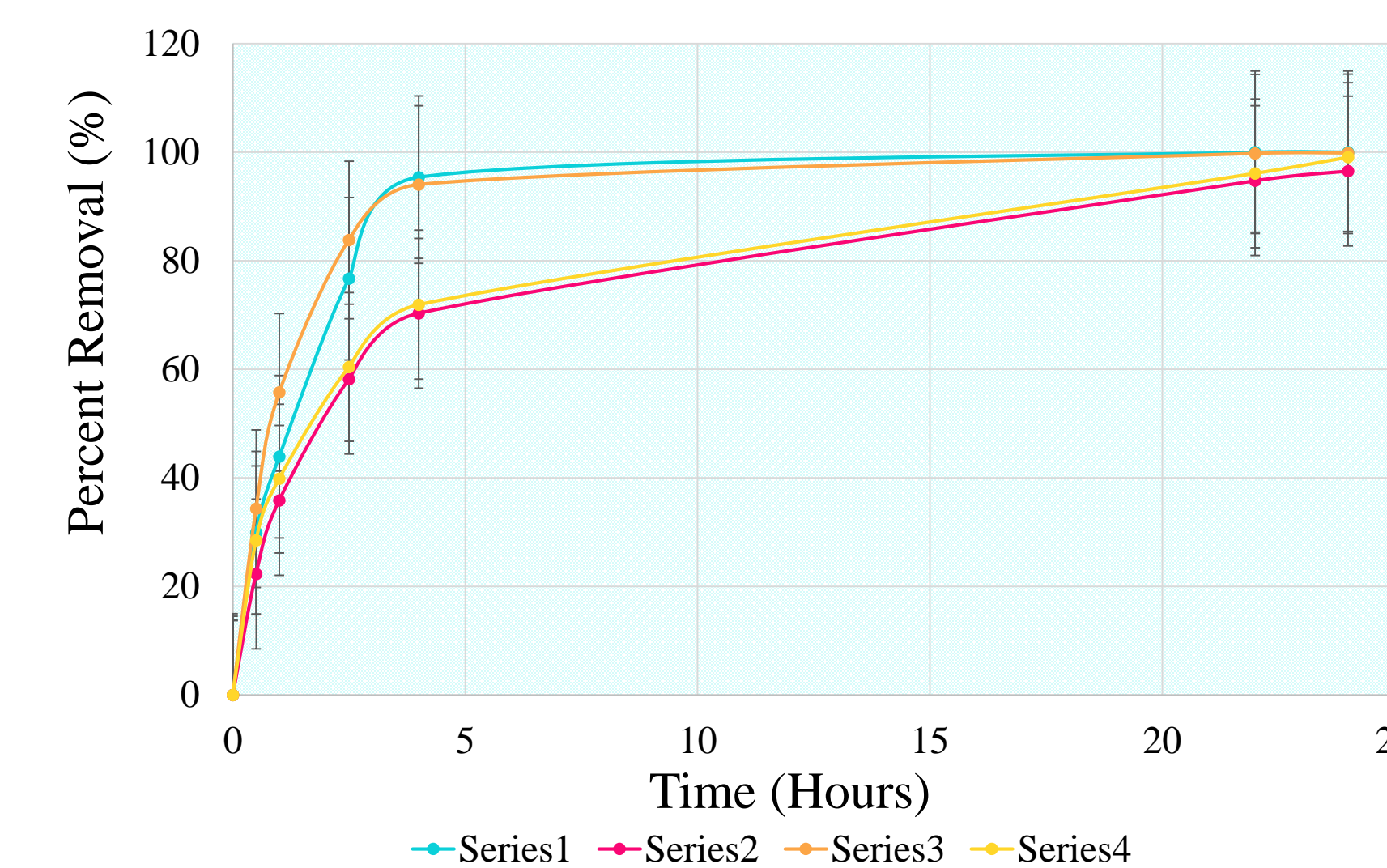


Figure 4: The effect of 1.5 g/L GAC on various NAs over a 24 hour period

Percent Removal of NAs with 2.0 g/L GAC

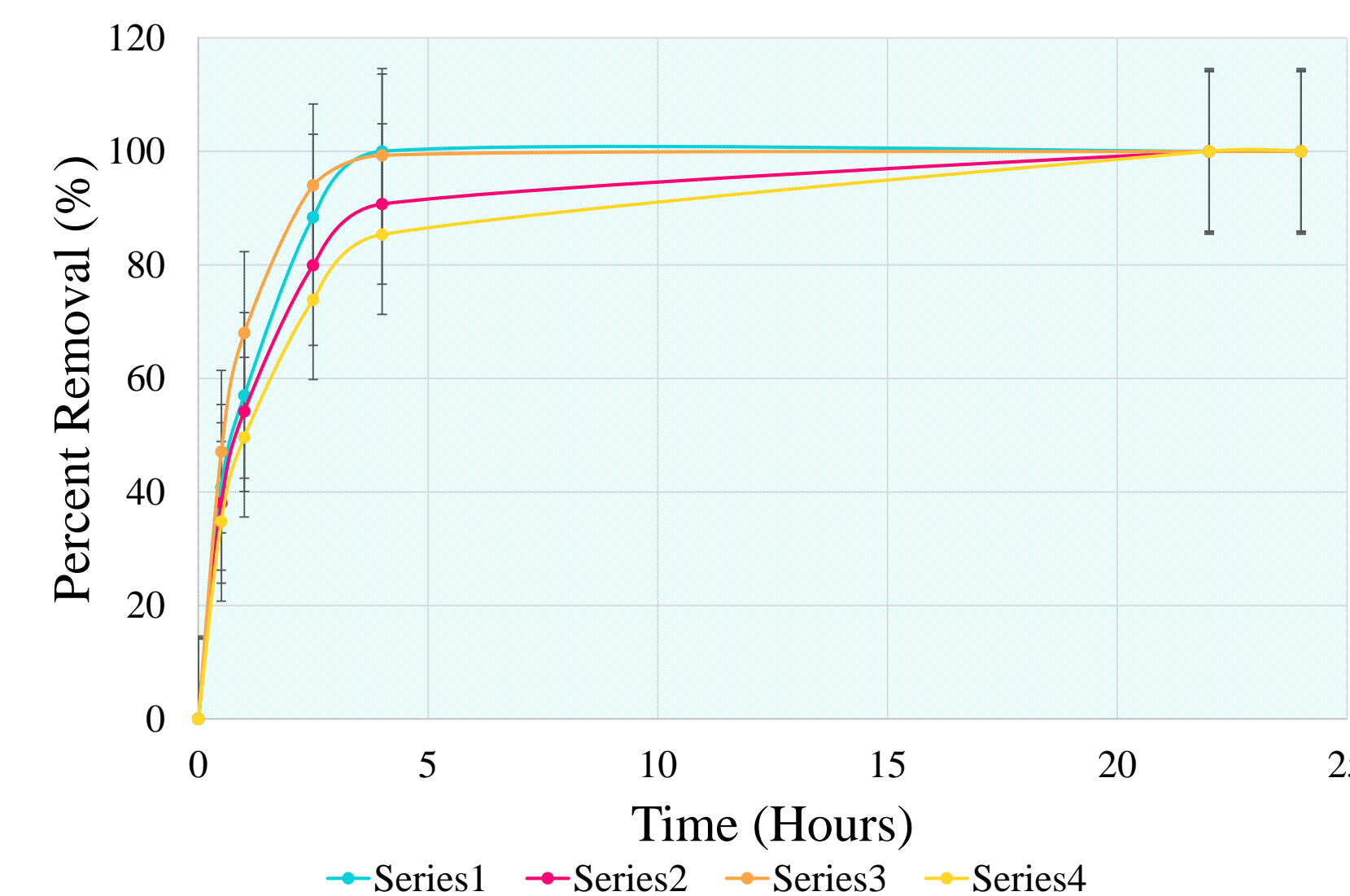


Figure 5: The effect of 2.0 g/L GAC on various NAs over a 24 hour period

Relationship Between Adsorption Capacity with 0.25 g/L GAC and Log P Value of Various NAs

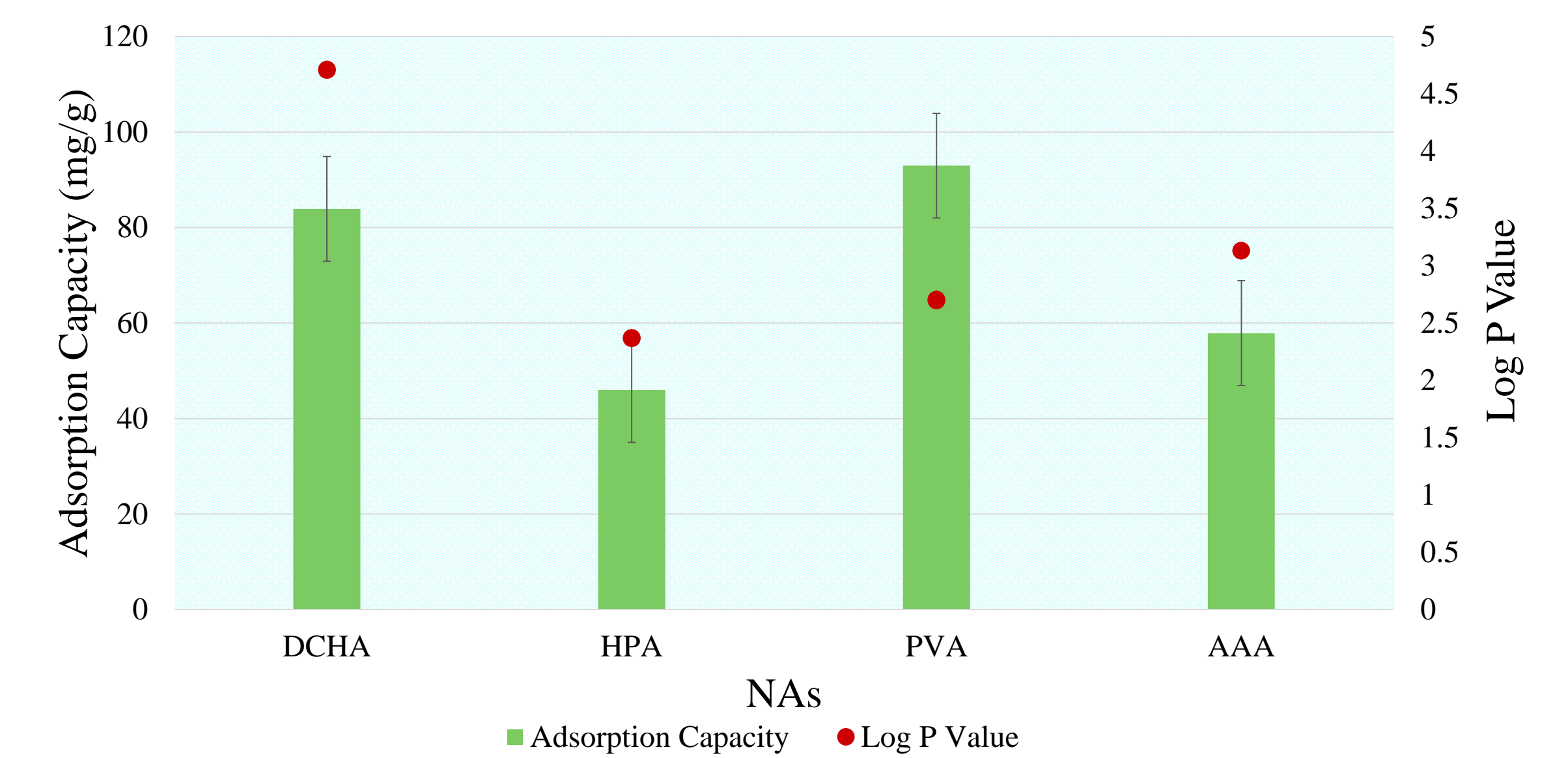


Figure 6: Adsorption capacity with 0.25 g/L GAC and Log P value of various NAs over 24 hours

CONCLUSIONS

- The results indicate that for all of NA models tested, over time the amount of NAs remaining in the solutions significantly decreased when GAC was added. When the concentration of GAC added to the solution was increased, it was evident that a greater amount of NA were adsorbed from the solution.
- Primarily, results reveal that the hydrophobicity of the NAs tested did affect their ability to adsorb along with many other factors. From this experiment we can conclude that AAA and HPA are less attracted to the GAC than DCHA and PVA because they had lower adsorption capacities.
- All of the NA models were saturated around the 25 hour mark with 0.25 g/L GAC. This suggests a small concentration of GAC is not as effective considering high amounts of NAs were still present in the solutions. By determining the saturation point of the NAs we were able to display the relationship between their adsorption capacities and Log P values. As the Log P value increased, adsorption capacity increased, except for the PVA model. This may be caused by molecular shape.
- 1 g/L GAC is the most effective concentration when considering cost and efficiency because it removed the most amount of NA with the least amount of GAC in the first trial. Although, when the GAC from the 1 g/L test was reused in the stability test, it showed that the GAC was less effective. For the model compounds DCHA and PVA, the stability test displayed that the GAC can be reused due to the fact that it still removed over 80% of the NAs, while the reused GAC is not as effective for AAA and HPA. This may be caused by the reused GAC already being partially saturated from the first trial for AAA and HPA.
- From these results we can consider the effectiveness of the various concentrations of GAC on each NA model to help determine appropriate GAC concentrations to be used on OSPW.

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LITERATURE CITED

- Ajaero, C., Headley, J. V., Peru, K. M., McMartin, D. W., & Barrow, M. P. (2016). Forensic studies of naphthenic acids fraction compounds in oil sands environmental samples and crude oil. *Standard Handbook Oil Spill Environmental Forensics*, 343-397. doi:10.1016/b978-0-12-803832-1.00007-6
- Worch, E. (2012). Adsorption Technology in Water Treatment. doi:10.1515/9783110240238
- John C. Trussell, R. Rhodes Hand, David W. Howe, Kerry J. Tchobanoglous, George (2012). Adsorption. *MWHs Water Treatment*, 1117-1262. doi:10.1002/9781118131473.ch15
- Wypych, G. (2001). Solvent Recycling, Removal and Degradation. *Handbook of Solvents*.