

Adsorption and Enhanced Electrochemical Adsorption for the Treatment of Pharmaceutical Wastewater

Low Jeen Liang (3S3, 15), Yiu Yi Hin Kinsey (3S1, 32), Tan Wei An (3S3, 26)

Group 1-44

ABSTRACT

Organic pharmaceutical wastewater effluent causes bioaccumulation which is harmful to the ecosystem. Activated carbon fibers (ACF) is often used to treat industrial wastewaters. However, it is not effective in adsorbing polar organics. In such a case, an attractive treatment method is the electrochemical enhancement of ACF. In this study, pharmaceutical wastewater was analysed and the major organics present were determined to be acetone and tetrahydrofuran (THF). The adsorption capacity of both activated carbon fibers (ACF) and granular activated carbon (GAC) on acetone and THF were compared. Both ACF and GAC were comparable in the adsorption of acetone across a range of adsorbent mass (0.5g - 2g). However, 0.5g and 1.0g of ACF were significantly better than GAC in adsorption of THF. The maximum adsorption capacity of ACF as derived from the Langmuir and Freundlich isotherms was then compared with the adsorption capacity of other organic compounds by ACF in other studies. The adsorption of THF was consistent with the usual performance of ACF for adsorption of organic compounds but not acetone: ACF was only able to adsorb a limited amount of acetone. Electrochemical polarization of ACF at an electrolyte concentration of 0.001 M and at -1.0 V was able to remove 1.39 times the amount of acetone than unenhanced ACF. This could be attributed to the polarization induced inelastic deformation of the surface of ACF, hence increasing the density of its surface mesopores. As such, the electrochemically enhanced ACF shows tremendous promise in the treatment of pharmaceutical effluents.

1. INTRODUCTION

Pharmaceutical manufacturing is a batch process in which organic pollutants with different chemical properties are discharged. Such effluents hold different compositions of pharmaceutical organics, which possess numerous hazards such as environmental bioaccumulation (Gadipelly, et al, 2014) and air pollution as they contain volatile organic compounds (VOCs).

A key challenge faced by the pharmaceutical industry is “Recycling and Waste Minimization”. According to Heberer (2002), approximately half of pharmaceutical

wastewater is improperly discharged as waste due to the high costs of treatment. Such treatments include reverse osmosis and electrochemical oxidation which are energy intensive (Foo & Hameed, 2009). Adsorption by activated carbon fiber (ACF) is commonly used to pretreat wastewater, reducing the intensity of subsequent treatment. ACF is able to adsorb organic and inorganic compounds due to its large porous surface area, thermal-stability and fibril structure (Li, Zhang, Peng, Li, & Zhu, 2008). However, despite its potential for adsorption, industries tend to use granular activated carbon (GAC) due to greater understanding of its adsorption capabilities and mechanisms. Hence there is a need to cast more light on the performance of ACF for the adsorption of different pollutants.

Additionally, treatment of pharmaceutical wastewater by adsorption is expensive. Pharmaceutical wastewater produced from different geographical locations has a variety of molecular weights and polarities, which play a large role in determining the overall adsorption performance of the ACF, which directly affects treatment costs. ACF has been demonstrated to be less efficient in its adsorption of polar organics with low molecular weights (Han, Quan, Ruan & Zhang, 2008).

An attractive method that can effectively increase the adsorption capacity of ACF, with the possibility of increased economic feasibility, is the use of electrosorptive techniques employing high area electrodes such as ACF. Upon passing a low voltage current through electrically conductive adsorbents, adsorption capacity was shown to be exponentially increased (Han et al, 2008). However, no study has yet examined the feasibility of electrochemically enhanced ACF for the treatment of pharmaceutical wastewater. Presently, primary applications of electrochemically enhanced adsorbents lie in the desalination of seawater (Foo & Hameed, 2009) and the adsorption of organic dyes from textile wastewater. According to Han et al (2008), the maximum adsorption capacity of ACF for acid-orange 7, an organic dye, was increased by 115%. ACF, unlike other industrial adsorbents is also highly suitable for electrochemical enhancement due to its electrical conductivity and structural integrity (Ziati *et al*, 2017).

This study will first compare the adsorption performance of ACF with GAC in the adsorption of pharmaceutical organics to shed light on the adsorption process. Subsequently, it will evaluate the adsorption performance of electrochemically enhanced ACF and its suitability for pharmaceutical wastewater treatment.

OBJECTIVES

1. Analyse pharmaceutical wastewater to determine the major pharmaceutical organics (Section 3.1: found to be acetone and THF) within the samples.
2. Compare the adsorption capacity of activated carbon fibers (ACF) and granular activated carbon (GAC) on acetone and THF.
3. Evaluate and compare the maximum adsorption capacity of acetone/THF by ACF against other studies.
4. Compare the adsorption performance of electrochemically enhanced ACF against the adsorption performance of unenhanced ACF in the adsorption of acetone.

HYPOTHESIS

1. The adsorption capacity of unenhanced ACF for adsorption of pharmaceutical organics will be comparable to that of GAC.
2. The maximum adsorption capacity of acetone will be lower than that of other organic compounds by ACF, thus highlighting a need to enhance the adsorption of acetone.
3. Electrosorption will enhance ACF's adsorption of acetone/THF.

2. MATERIALS AND METHODS

2.1 Materials

Granular activated carbon (GAC), tetrahydrofuran (THF), acetone, sodium sulfate, potassium dichromate(VI) and silver nitrate were procured from Sigma Aldrich. Activated carbon fiber (ACF) was purchased from Shenzhen, China. All pharmaceutical wastewater samples, instruments and apparatus were supplied by the National University of Singapore (NUS).

2.2 Analysis of pharmaceutical wastewater

Real pharmaceutical wastewater samples were characterized by Gas Chromatography Mass Spectrometry (GC-MS) with abundant pharmaceutical organics being identified and studied.

2.3 Comparing the adsorption capacity of ACF and GAC for the adsorption of pharmaceutical compounds

Differing masses (0.5 g, 1.0 g, 2.0g) of adsorbent (GAC or ACF) was added to 1600 ppm of acetone/THF (100ml) and shaken at 150rpm for 24 hours. There were 5 replicates.

Consequently, the samples were filtered through a 0.45 micron glass filter using a Buchner funnel and analysed. The final concentration of acetone was assessed via UV-Vis Spectroscopy at a wavelength of 267 nm. Gas Chromatography Mass Spectrometry (GC-MS), which identifies individual compounds based on their unique retention times, was used to determine the final concentration of THF solutions.

2.4 Evaluating the maximum adsorption capacity of ACF

Different masses of ACF (0.5 g, 1.0g, 2.0g, 3.0g and 4.0g) were added to an identical setup as section 2.3. Adsorption capacity (Q_e) was calculated by the following formula:

$$Q_e \text{ (mg/g)} = ((C_i - C_e) \times V) / m$$

where C_i is the initial concentration, C_e is the final concentration, V is the volume in dm^3 and m is the mass in g.

The equilibrium concentration data were then fitted into the Langmuir and Freundlich isotherms to derive the maximum adsorption capacity of ACF and GAC on acetone and THF (Appendix, Pg 12-16).

2.5 Comparing Electrochemically Enhanced ACF with unenhanced ACF

The electrosorption set up for the electrochemical enhancement of ACF is shown in Figure 1.

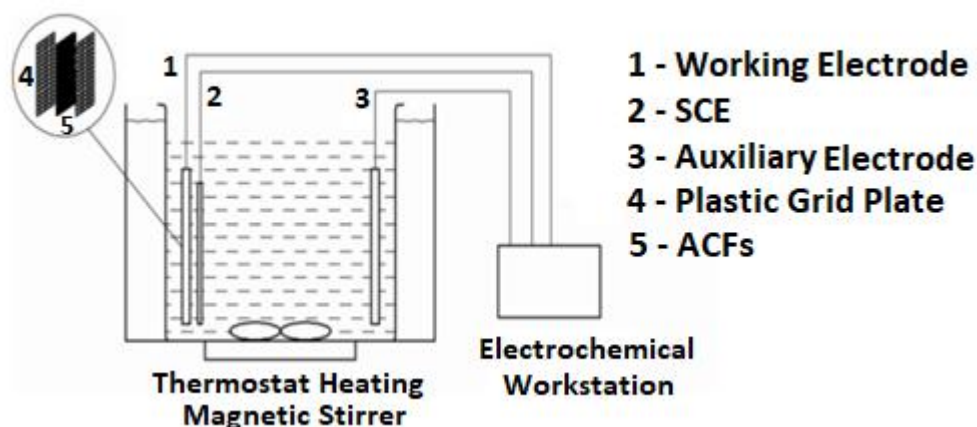


Figure 1: Schematic diagram for electrosorption setup

1.25 g of ACF was added to 2000 ppm of 250 ml acetone and shaken at 150rpm for 24 hours with 3 replicates. The samples were filtered through a 0.45 micron glass filter. The electrochemical enhancement of ACF was performed at -1.0 V, meaning that it is cathodic in nature. An explanation of the specific experimental conditions can be found in appendix (page 16). A saturated calomel electrode served as the reference electrode and a titanium-

ruthenium alloy acted as the auxiliary electrode. An identical setup with ACF but with no voltage applied (0V) served as the control. Lastly, a setup without ACF and voltage applied was used to account for the volatilization of the organics.

In addition to percentage removal of acetone, Chemical Oxygen Demand (COD) and Total Organic Carbon (TOC), were also measured. COD represents the amount of oxidizable organic matter in a sample. A higher COD means a greater consumption of the dissolved oxygen of water bodies in which the wastewater is discharged thus having negative environmental impacts. A lower COD is hence desirable. COD was analysed via reaction with acidified potassium dichromate(VI), followed by incubation and analysis using the COD function on the UV-Vis Spectrometer. In order to support the trend by COD, TOC, which directly measures the amount of carbon in a wastewater sample and hence its toxicity was determined with the use of a TOC Analyser.

3. RESULTS & DISCUSSION

3.1 Characterization of Pharmaceutical Wastewaters

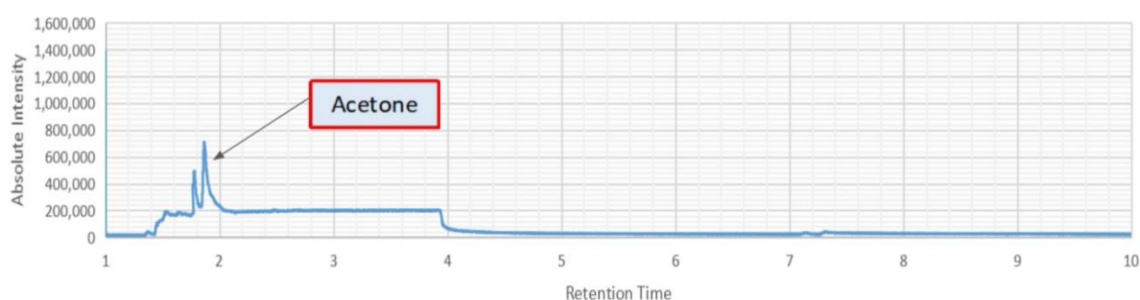


Figure 2: GC-MS of wastewater sample 1

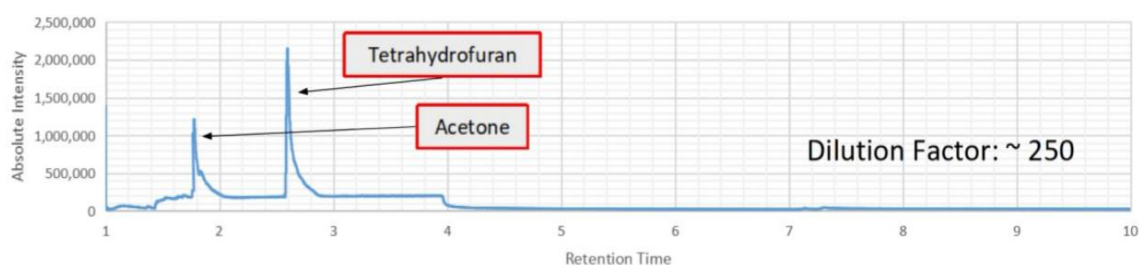


Figure 3: GC-MS of wastewater sample 2

Identification of peaks by GC-MS showed that the most abundant pharmaceutical organics within the wastewater samples were acetone and tetrahydrofuran (THF). This was in agreement with similar studies which identified them as common solvents used in the manufacturing of pharmaceuticals (Gadipelly et al, 2014). Hence, in order to model the

treatment of pharmaceutical wastewater, the adsorption of acetone and THF and electrosorption of acetone were studied.

3.2 Comparing the adsorption capacity of ACF and GAC

Figures 4 and 5 show the adsorption of acetone and THF by various mass of ACF and GAC (0.5g - 2.0g). This range of masses was used to compare percentage removal of acetone and THF of ACF to that of GAC which is a prevalent adsorbent in wastewater treatment. Hence the relative potential of ACF for industrial application could be determined.

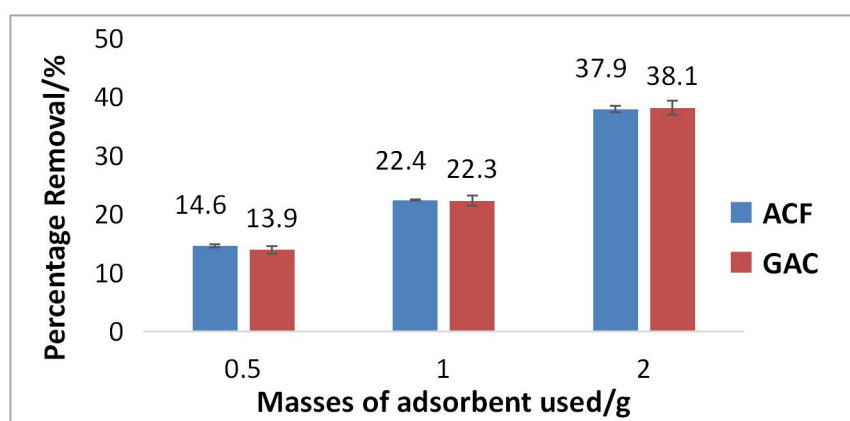


Figure 4: Removal of acetone by varying masses of GAC and ACF

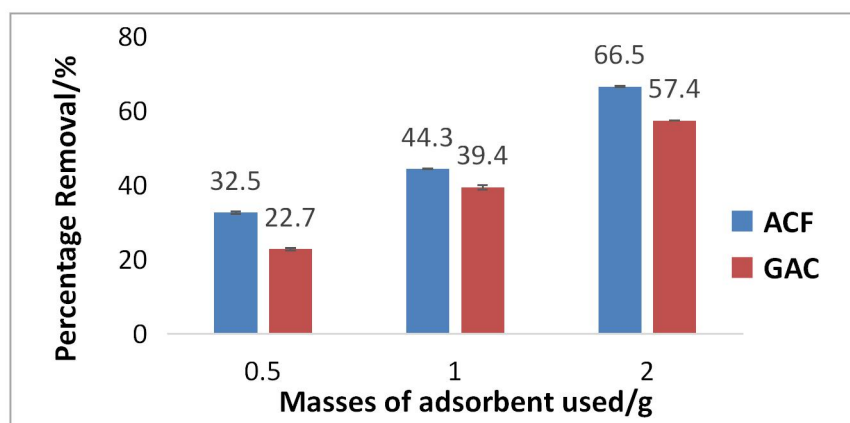


Figure 5: Removal of THF by varying masses of GAC and ACF

ACF at 0.5 g and 1.0 g adsorbed a greater amount of acetone, while ACF adsorbed THF than GAC at all masses. To determine whether the adsorption of acetone and THF by GAC and ACF is significantly different, Mann Whitney U test was carried out for all three masses of ACF and GAC.

Table 1: P-values of Mann Whitney Test (ACF Vs GAC)

Mass of Adsorbent/g	P-value (Acetone)	P-value (THF)
0.5	0.69	0.004
1.0	0.50	0.007
2.0	0.43	0.053

As evident from Table 1, the P-values for adsorption of acetone with different mass of adsorbents used were all more than 0.05, suggesting that there was no significant difference between GAC and ACF. However, when 0.5 g and 1.0 g of adsorbents were used in the adsorption of THF, there is a significant difference in the percentage of THF adsorbed between ACF and GAC. ACF was thus shown to be a more suitable adsorbent for the treatment of pharmaceutical wastewater.

3.3 Comparison of maximum adsorption capacity to other studies

The Langmuir and Freundlich isotherms were plotted (Appendix, Pg 12 to 16). R^2 of both plots were obtained for each adsorbent. R^2 , the coefficient of determination, is a statistical measure of how close the data are to the fitted regression line. The larger the R^2 , the better the data fits the isotherm. R^2 value of the Freundlich isotherm was a better fit for the adsorption of THF by GAC as well as the adsorption of acetone and THF by ACF, indicating multilayer and heterogeneous adsorption. In contrast, the adsorption of acetone by GAC fits Langmuir isotherm better, where adsorption was inferred to be homogenous and single-layer.

Table 2: R^2 values of Langmuir and Freundlich isotherm

Adsorbent	Compound	Langmuir R^2	Freundlich R^2
Granular Activated Carbon (GAC)	Acetone	0.9897	0.9861
	THF	0.9081	0.9729
Activated Carbon Fibres (ACF)	Acetone	0.366	0.83
	THF	0.836	0.9599

The maximum adsorption capacity of each adsorbent on acetone and THF was derived from the inverse of the gradients of Langmuir plots, while K_f which is proportional to adsorption capacity was derived from the Freundlich plots (Appendix, Pg 12 to 16). The constants (K_f and Q_{max}) were then compared with other studies, where the results are shown in table 3.

Table 3: Comparison of maximum adsorption capacity of ACF for pharmaceutical organics with other organic compounds

Adsorbent	Compound	K_f	Q_{max} (mg/g)	Source
ACF	Acetone	0.24	93	This study
ACF	THF	1.51	139	This study
ACF	m-cresol	1.08	246	Han <i>et al.</i> , 2007
ACF	Aniline	1.33	132	Han <i>et al.</i> , 2006

Q_{max} and K_f of acetone are observed to be lower than the rest of organic pollutants, suggesting that ACF is not effective in adsorbing acetone. To account for this observation, the properties of acetone was compared with THF (Table 4).

Table 4: Chemical properties of Acetone and THF

Organic Compound	Dielectric Constant	Miscibility with water	Molecular Weight
Acetone	20.7	Miscible	58.08
THF	7.58	Less Soluble	72.11

The limited adsorption of acetone by ACF could be due to the unfavourable interactions between the non-polar surface of ACF and the highly polar acetone (Table 4: dielectric constant) which forms stronger hydrogen bonds with water molecules (Table 4: Miscibility in water). Acetone also has a low molecular weight, meaning it has few electrons. Hence it could only interact with ACF via weak dispersion forces, further reducing its tendency to be adsorbed onto the surface of ACF.

3.4 Comparing Electrochemically Enhanced ACF with unenhanced ACF

Due to the limited adsorption of acetone, electrochemically enhanced adsorption of acetone was selected as a target substance to model the electrosorption of pharmaceutical organics. Figure 6 reveals that electrosorption enhances the adsorption of acetone by 9.7%. The removal of COD and TOC increases by 6.6% and 3.8% respectively when the ACF is electrochemically enhanced. This represented an adsorption enhancement of 1.39 times the initial removal of acetone by ACF and lowered COD and TOC by 1.26 and 1.22 times as compared to unenhanced ACF, as seen from Figure 7.

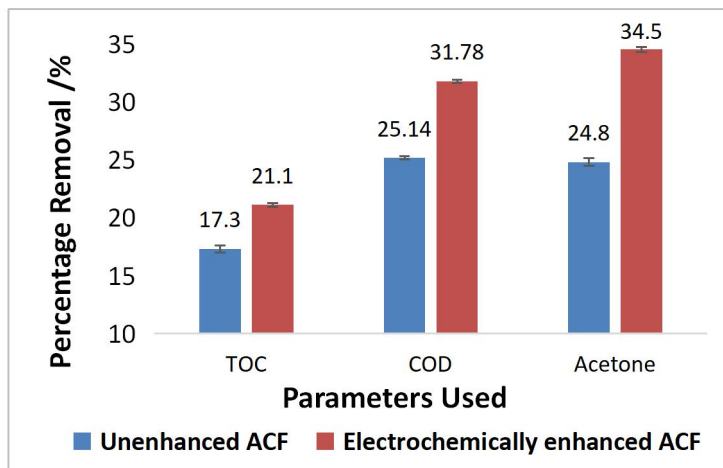


Figure 6: Removal of acetone, COD and TOC by electrosorption and unenhanced ACF

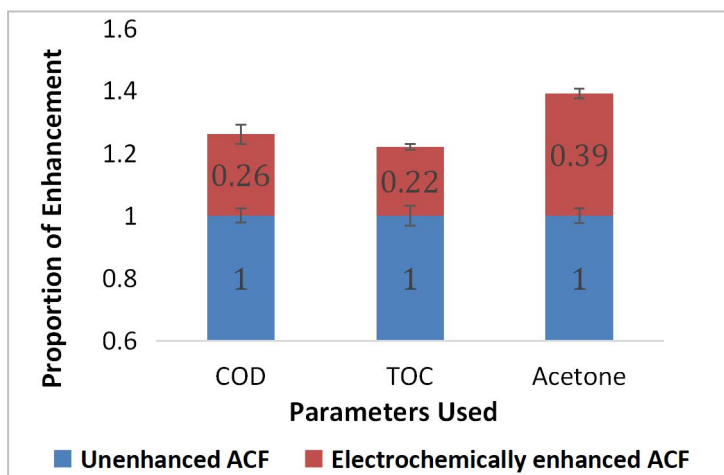


Figure 7: Proportion of enhancement by electrosorption and unenhanced ACF

Figures 8 and 9 show the Scanning Electron Micrographs (SEM) of ACF and electrochemically enhanced ACF respectively. Upon electrical polarization, ACF displayed a higher density of mesopores under the same magnification as compared to its unenhanced counterpart. The formation of mesopores - pores of width between 2nm and 50nm - is an important factor affecting monolayer adsorption capacity due to the increase in specific surface area (Vathyam et al, 2011). As evident from Figure 8 and 9, electrochemical polarization was able to induce inelastic deformation of the surface of ACF, which is

attributed to electrostatic repulsion between surface functional groups (Su & Hatton, 2017). The enhancement of adsorption capacity for acetone may mainly be due to the increased mesopore distribution as well as pore density, enhanced by the polarization of the -1.0 V electric field. This low voltage suggests high cost-efficiency.

To this study's knowledge, the electrosorption of acetone has not been discussed within the present literature.

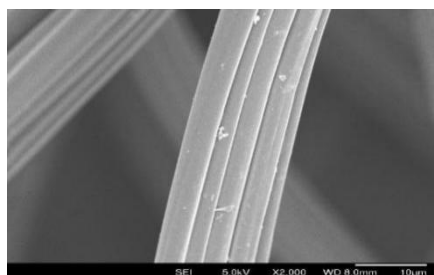


Figure 8: SEM of ACF

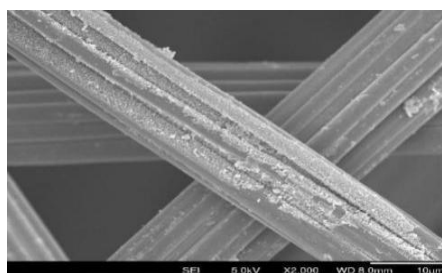


Figure 9: SEM of ACF after electrosorption

4. CONCLUSION AND FUTURE WORK

Acetone and THF were found to be common organic pollutants present in pharmaceutical wastewater. ACF displayed a similar effectiveness for adsorption of acetone as compared to GAC. However, adsorption of THF by 0.5 and 1.0 grams of ACF was greater than that by GAC, which is widely hailed as a prevailing choice of adsorbent due to its high adsorption capacity. ACF is thus a promising adsorbent for application within the pharmaceutical industry. The adsorption of acetone onto ACF was limited due to its polar property and small number of electrons. Subsequently, upon electrochemical polarization, electrochemical enhancement of ACF at a low voltage was able to remove 1.39 times more acetone and lowered COD by 1.26 times and TOC by 1.22 times as compared to unenhanced ACF. As evident from the comparison to industrially employed GAC, the attractive combination of the already formidable ACF and electrochemically enhanced ACF for the removal of THF and acetone indicate great promise to be applied in the treatment of pharmaceutical wastewater.

In Singapore, there is increased demand for pharmaceutical products due to its aging population. This leads to greater amounts of waste being discharged each year. Increasingly sustainable and efficient treatments of pharmaceutical waste are pertinent. Hence the current study could be extended to investigate the regeneration of electrochemically enhanced ACF to render the electrosorption process more sustainable. The effect of surface doping on the adsorption capacity of ACF could also be explored.

REFERENCES

- De Hemptinne, X., & Schunck, K. (1969). Electrochemical reduction of acetone. Electrocatalytic activity of platinized platinum. *Transactions of the Faraday Society*, 65, 591-597.
- Foo, K., & Hameed, B. (2009). A short review of activated carbon assisted electrosorption process: An overview, current stage and future prospects. *Journal of Hazardous Materials*, 170(2-3), 552-559. doi:10.1016/j.jhazmat.2009.05.057
- Gadipelly, C., Pérez-González, A., Yadav, G. D., Ortiz, I., Ibáñez, R., Rathod, V. K., & Marathe, K. V. (2014). Pharmaceutical Industry Wastewater: Review of the Technologies for Water Treatment and Reuse. *Industrial & Engineering Chemistry Research*, 53(29), 11571-11592. doi:10.1021/ie501210j
- Han, Y., Quan, X., Chen, S., Wang, S., & Zhang, Y. (2007). Electrochemical enhancement of adsorption capacity of activated carbon fibers and their surface physicochemical characterizations. *Electrochimica Acta*, 52(9), 3075-3081. doi:10.1016/j.electacta.2006.09.059
- Han, Y., Quan, X., Chen, S., Zhao, H., Cui, C., & Zhao, Y. (2006). Electrochemically enhanced adsorption of aniline on activated carbon fibers. *Separation and Purification Technology*, 50(3), 365-372. doi:10.1016/j.seppur.2005.12.011
- Han, Y., Quan, X., Ruan, X., & Zhang, W. (2008). Integrated electrochemically enhanced adsorption with electrochemical regeneration for removal of acid orange 7 using activated carbon fibers. *Separation and Purification Technology*, 59(1), 43-49. doi:10.1016/j.seppur.2007.05.026
- Heberer, T. (2002). Occurrence, fate, and removal of pharmaceutical residues in the aquatic environment: A review of recent research data. *Toxicology Letters*, 131(1-2), 5-17. doi:10.1016/s0378-4274(02)00041-3
- Li, W., Zhang, L., Peng, J., Li, N., & Zhu, X. (2008). Preparation of high surface area activated carbons from tobacco stems with K₂CO₃ activation using microwave radiation. *Industrial Crops And Products*, 27(3), 341-347. doi: 10.1016/j.indcrop.2007.11.011

Su, X., & Hatton, T. A. (2017). Electrosorption at functional interfaces: From molecular-level interactions to electrochemical cell design. *Physical Chemistry Chemical Physics*, 19(35), 23570-23584. doi:10.1039/c7cp02822a

Vathyam, R., Wondimu, E., Das, S., Zhang, C., Hayes, S., Tao, Z., & Asefa, T. (2011). Improving the Adsorption and Release Capacity of Organic-Functionalized Mesoporous Materials to Drug Molecules with Temperature and Synthetic Methods. *The Journal of Physical Chemistry C*, 115(27), 13135-13150. doi:10.1021/jp1108587

Ziati, M., Khemmari, F., Kecir, M., & Hazourli, S. (2017). Removal of chromium from tannery wastewater by electrosorption on carbon prepared from peach stones: Effect of applied potential. *Carbon Letters*, 21, 81-85, doi:10.5714/cl.2017.081

Appendix

Adsorption Isotherms of Acetone and Tetrahydrofuran (THF)

The final concentration data (C_e) from adsorption isotherm studies on acetone and THF with ACF and GAC was used to calculate Q_e , and both were fitted into the Freundlich and Langmuir isotherms. The maximum adsorption capacity q_0 , favourability of adsorption $1/n$, and K_f , related to maximum sorption capacity were then derived.

First, the adsorption capacity at equilibrium (Q_e) was calculated with the following formula:

$$Q_e = \frac{(C_i - C_f)V}{m}$$

Q_e was varied by varying the mass of adsorbent used.

The Langmuir isotherm assumes monolayer adsorption onto a homogenous surface. The linearized form of the langmuir isotherm is given by:

$$\frac{C_e}{Q_e} = \frac{1}{bq_0} + \frac{C_e}{q_0}$$

Where C_e is the final concentration of organics at equilibrium (mg/L), Q_e is the amount adsorbed at equilibrium (mg/g), q_0 is the maximum adsorption capacity (mg/g), and b is a dimensionless constant. From the langmuir isotherm, the inverse of the gradient may be calculated to find q_0 , the maximum adsorption capacity.

The Freundlich isotherm assumes multilayer adsorption onto a heterogeneous surface. Its linearized form is given by:

$$\log Q_e = \log K_f + 1/n \log C_e$$

C_e is the final concentration of organics at equilibrium (mg/L), Q_e is the amount adsorbed at equilibrium (mg/g), K_f is a dimensionless constant proportional to sorption capacity and $1/n$ determines whether the adsorption of acetone or THF is favourable.

If $n=1$, then adsorption is linear; if $n<1$, then adsorption is a chemical process; if $n>1$, then adsorption is a physical process. If $1/n < 1$, the adsorption is favourable. Generally, the higher the n value, the more favourable the adsorption.

The Langmuir and Freundlich isotherms are shown below:

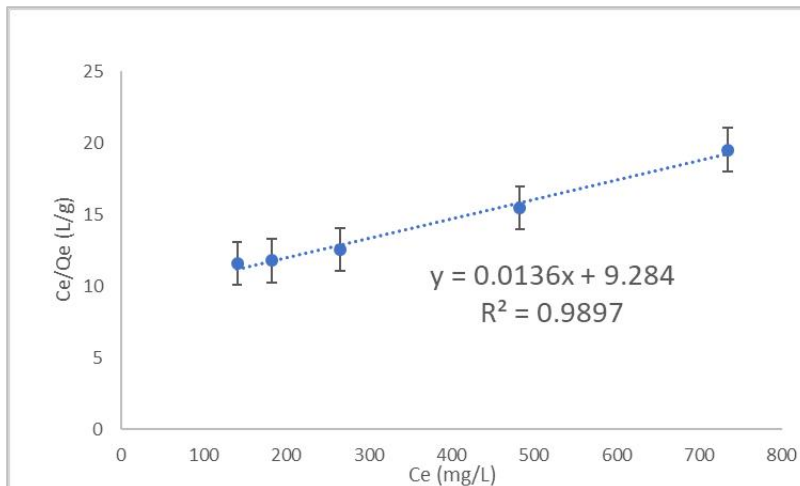


Figure 10: Langmuir Isotherm for adsorption of acetone by GAC

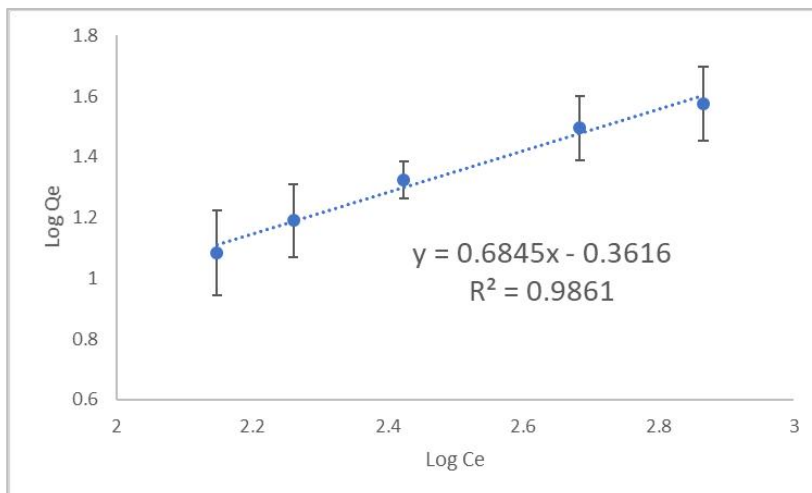


Figure 11: Freundlich isotherm for adsorption of acetone by GAC

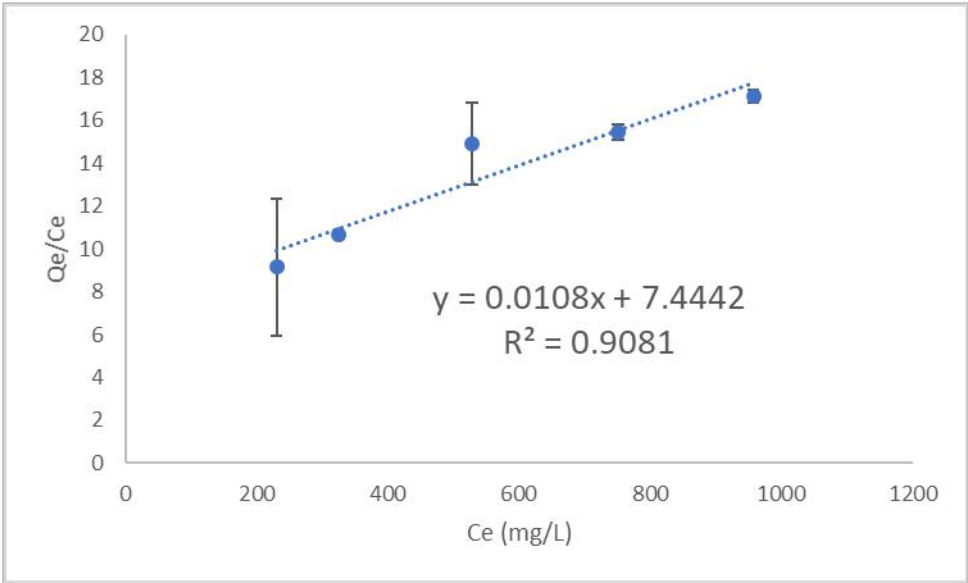


Figure 12: Langmuir isotherm for adsorption of THF by GAC

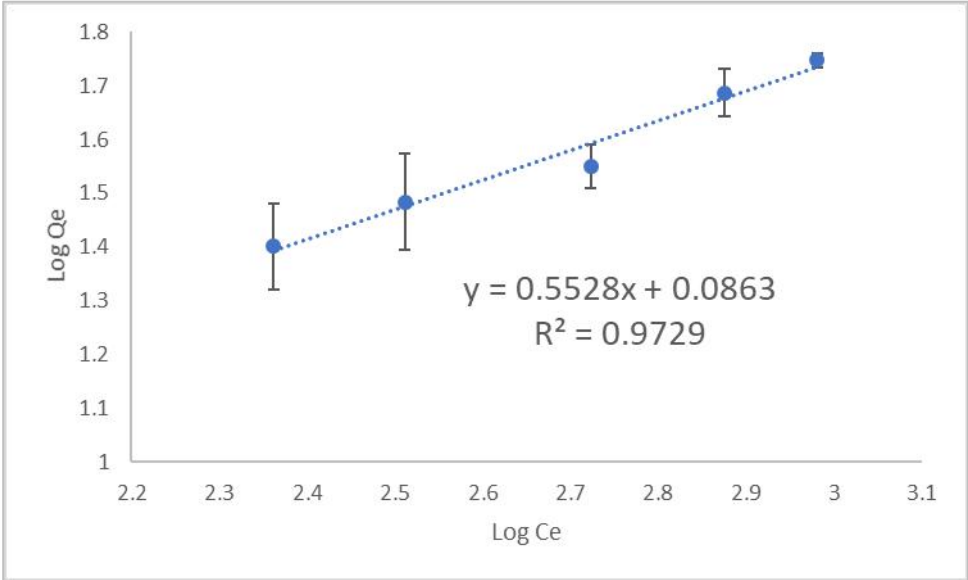


Figure 13: Freundlich isotherm for adsorption of THF by GAC

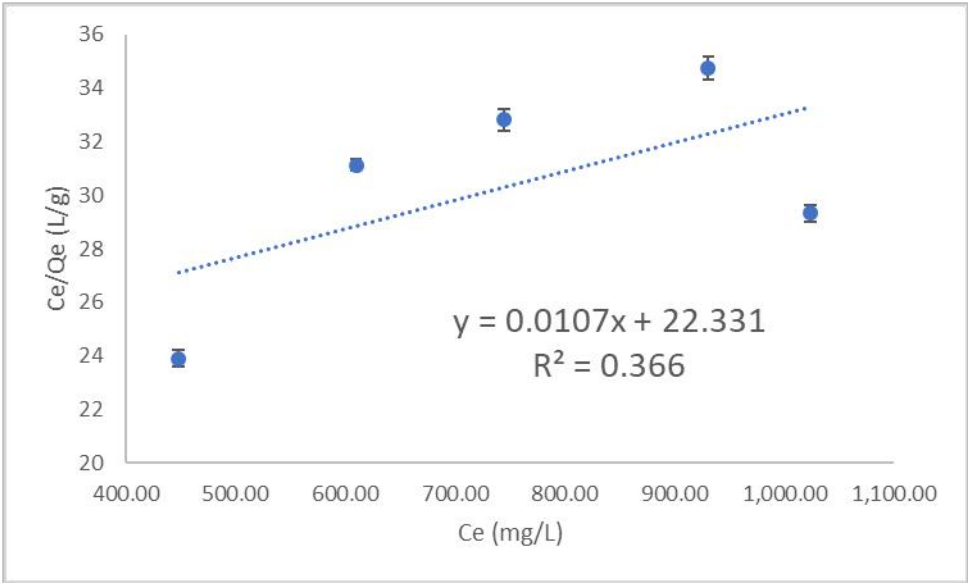


Figure 14: Langmuir isotherm for ACF adsorption of acetone

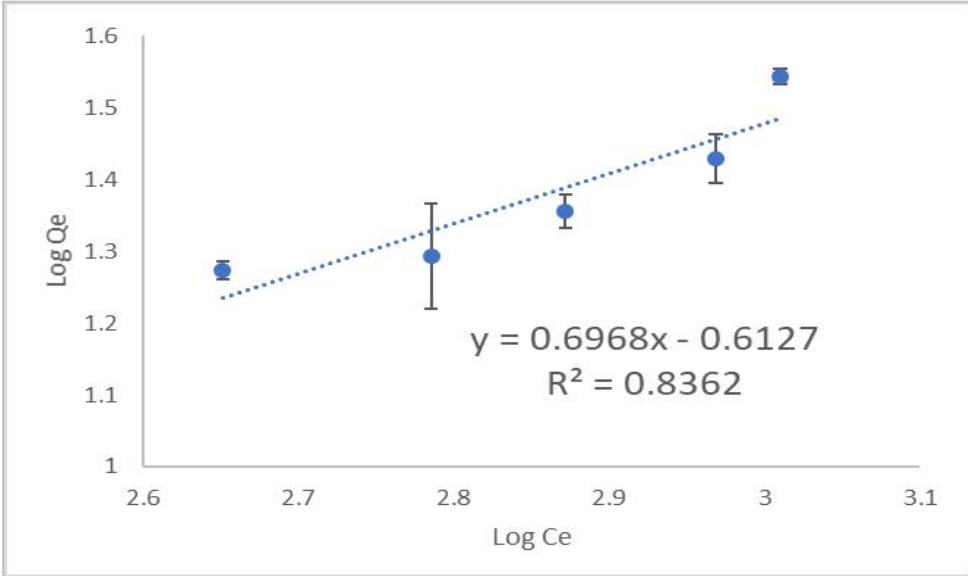


Figure 15: Freundlich isotherm for ACF adsorption of acetone

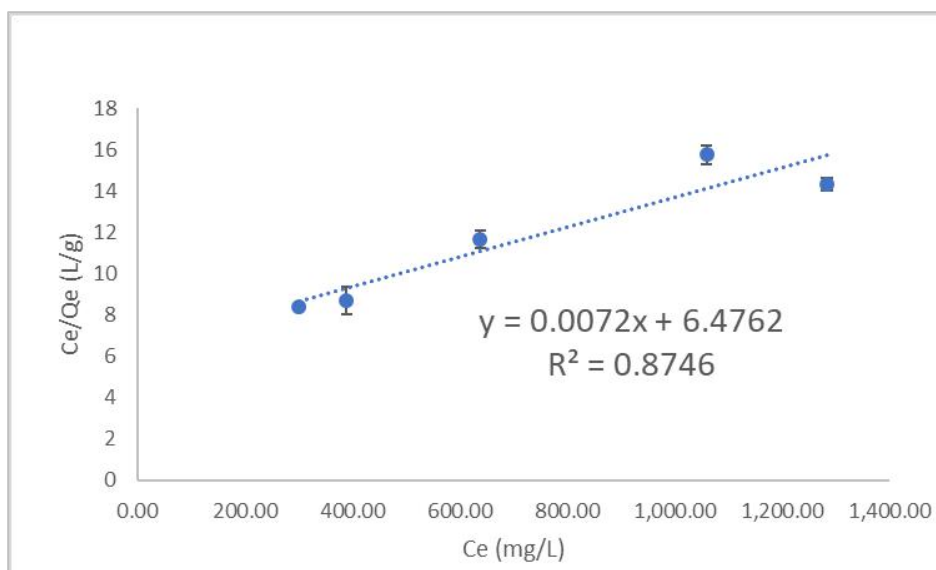


Figure 16: Langmuir isotherm for adsorption of THF by ACF

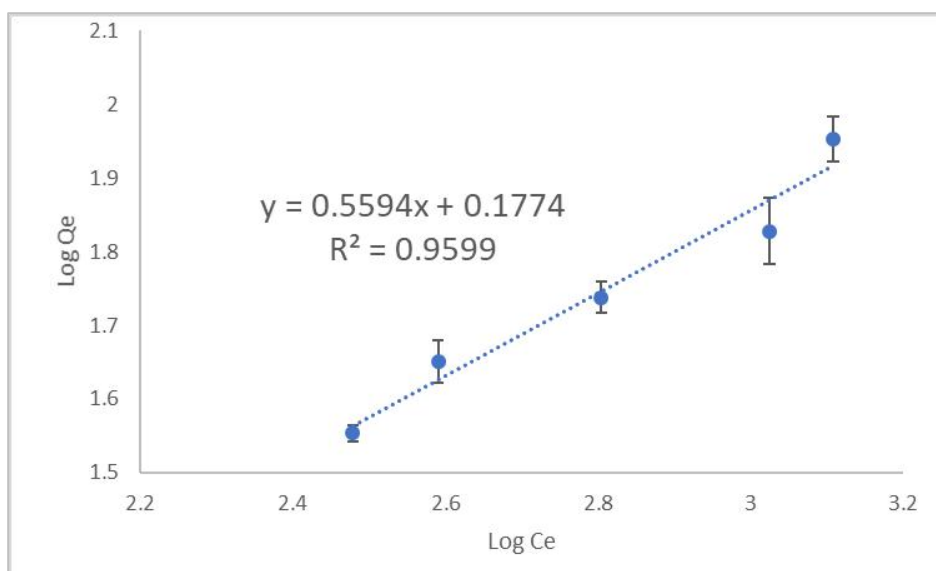


Figure 17: Freundlich isotherm for adsorption of THF by ACF

Rationale for Cathodic Electrosorption:

Anode: Electrode in an electrochemical cell where oxidation reactions occurs. It is marked as positive.

Cathode: Electrode in an electrochemical cell where reduction reaction occurs. It is marked as negative.

Should adsorption of acetone be carried out at a positive voltage, it may be reduced to form either propane or isopropanol which are outside our field of study. In order to eliminate this, cathodic electrosorption was performed (De Hemptinne & Shunck, 1969).