

CEE 4530 Final Report Experiments with Coffee Grounds Group 2:

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Introduction and Objectives

Caffeine is now one of the most widely detected organic chemicals in drinking waters all over the world. Since caffeine passes through the human body and wastewater treatment plants relatively untransformed, studies have shown that caffeine can actually be used as an indicator of fecal contamination in drinking water treatment plants. However, caffeine is also detected in watersheds without known wastewater contamination sources but known coffee production, suggesting that runoff from coffee farming actually contains high concentrations of caffeine. For this project we were initially interested in developing a simple way to monitor the removal of caffeine from water, with the idea that this could serve as a tracer for other organic chemicals, and thus by measuring caffeine removal we could make assumptions about the removal of more toxic but harder to detect organic chemicals. The first part of this project was to see if we could monitor caffeine concentrations with pH. Unfortunately, this experiment failed and we decided that within the constraints of our lab, we would not be able to measure caffeine concentrations.

After this conclusion, we shifted our focus to see if coffee grounds could actually be used as an adsorbent to remove other chemicals from water. We conducted a series of experiments with red dye 40 to try to develop a simple method to activate coffee grounds so that they could be used to remove chemicals from water.

Procedures Part 1: We had initially hoped to be able to monitor caffeine concentrations in water by using pH. Using the pHa of caffeine, we modeled an expected calibration curve:

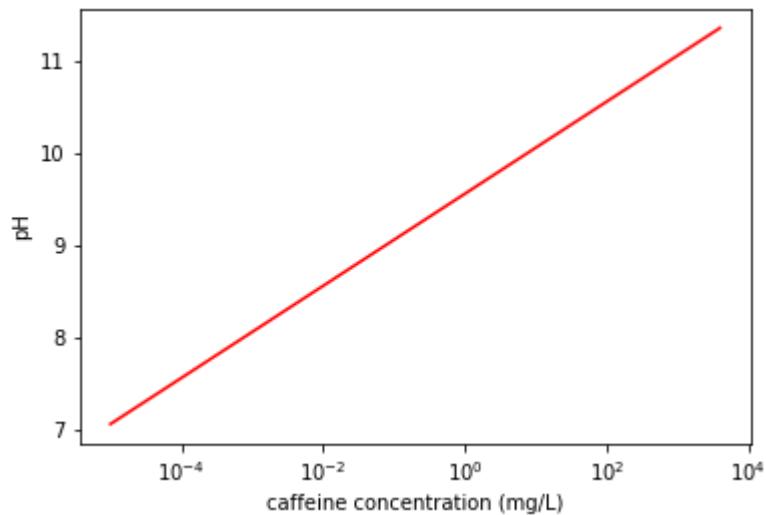


Figure 1. pH vs Caffeine concentration (logscale)

Before continuing our experiments, we first attempted to verify this calibration curve. We created standards by dissolving caffeine pills with known caffeine content (200mg) in 1L of distilled water.

However, even though well below the reported solubility limit of caffeine ($2 * 10^6$ mg/L), the caffeine pills would not fully dissolve. We tried stirring and boiling the water to increase the solubility, but this resulted in losing some water and still did not achieve complete dissolution. We hypothesize that this was due to the calcium present in the caffeine pills as a binding agent.

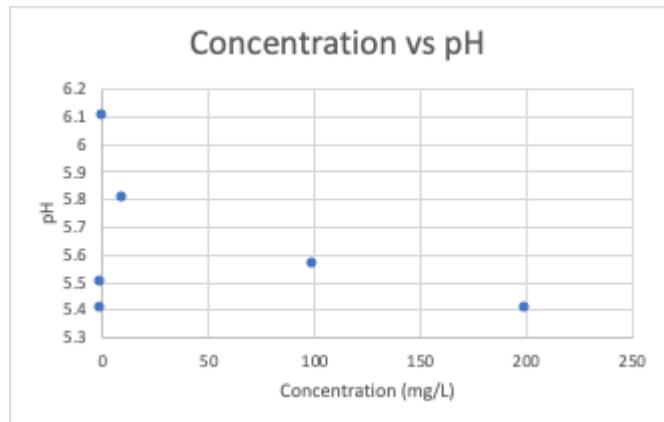


Figure 1: Caffeine pill in boiling water.

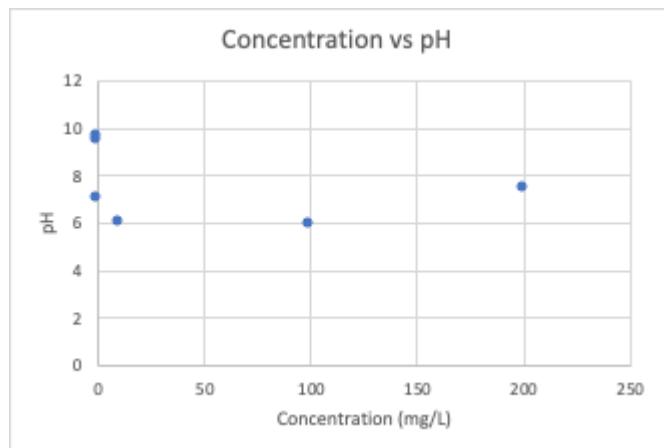
The accuracy of our first series of dilutions was admittedly low, since we had lost water in the boiling process and still not achieved full dissolution. We attempted to improve accuracy in a second trial by keeping the glass beaker covered and boiling for longer.

We created dilutions based on our two 200 mg/L standard When we measured the pH of all of the dilutions, we saw no trend in pH:

Trial 1:



Trial 2:



After these experiments, we concluded that we would be unable to use pH to monitor caffeine concentrations in water.

Part 2:

Our second experiment was to see if we could use coffee grounds as a sorbent for organic chemicals. We decided to experiment with a column setup similar to that from the Adsorption lab, using red dye 40 as our model "organic contaminant."

Our column setup was to pump water up into the bottom of our column filled with coffee grounds, and then from the top of the column through a photometer which was connected to ProCoDa. The water then discharged the system.



Figure 1: Coffee grounds adsorption set up

As a preliminary experiment, we filled the column with 24g of plain untreated coffee grounds. When we pumped DI water through the column, it discharged brown. In order to be able to measure red dye, we needed to let DI water run through the column for several minutes until it came out clear and our photometer reading was close to zero. Then we began running 5mg/L red dye solution in water through the column. We saw a pretty quick breakthrough time of 0.001 day fractions.

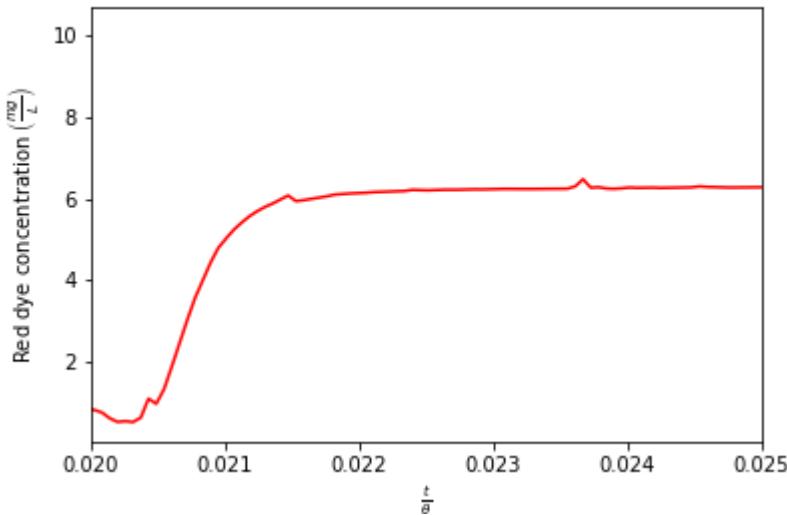


Figure 2: Breakthrough curve for untreated coffee grounds.

After researching activation methods that have been relatively successful at creating sorbents with other carbon sources, we decided to try several processes to activate our coffee grounds and increase their sorption capacity. We first burnt half of our coffee grounds in an anaerobic environment (a pot with a lid on it) over a charcoal fire for 4 hours and 40 minutes. The goal of this process was to burn off the other elements in caffeine molecules by pyrolysis, and to thus create a pure carbon source. We then attempted to increase the pore size of our carbon by using two activation methods. Typically, a strong acid, a strong base, or a salt can all increase pore size. We tried using HCl (a strong acid) and NaCl(a salt). For the salt treatment, we created a 300 g/L NaCl solution using table salt and distilled water. We broke up our coffee grounds for four separate trials. In order to mimic our initial experiment as closely as possible, we measured out approximately 24g of grounds for each trial:

1. 24.156 g Coffee
2. 23.996g coffee
3. 22.5 g burnt coffee
4. 25.802 g burnt coffee

We then combined 1 and 3 with 85 mL of .05N HCl and stirred the samples for 50 minutes.

We combined 2 and 4 with 300mL salt solution, and stirred for 1 hour.

To remove residual salt or acid from each of the samples, we put them in our column and rinsed DI water through the column for 10 minutes each.

We then repeated our initial experiment that used untreated coffee grounds for each of the four prepared samples.

Results and Discussion

Our breakthrough curves are as follows:

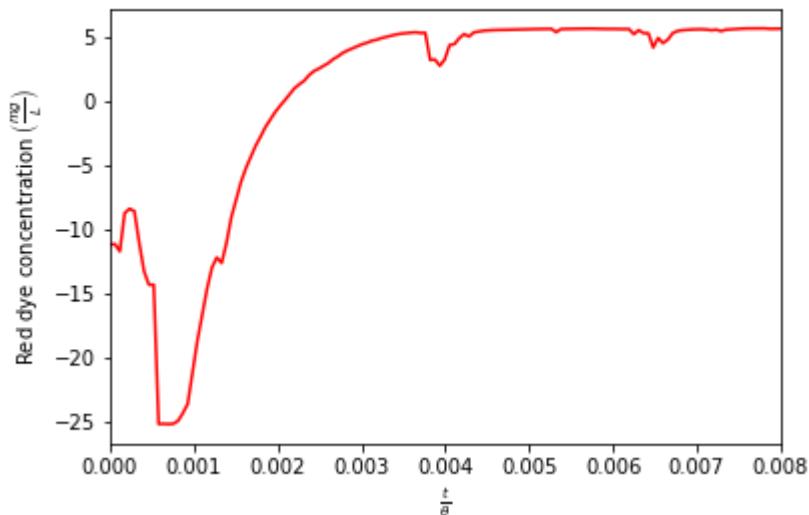


Figure 3: Breakthrough curve for unburnt coffee grounds treated with HCl

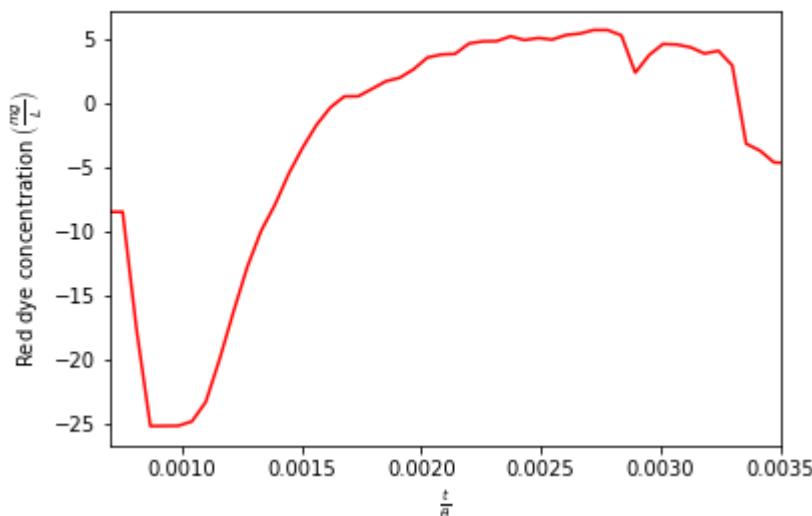


Figure 4: Breakthrough curve for burnt coffee grounds treated with HCl

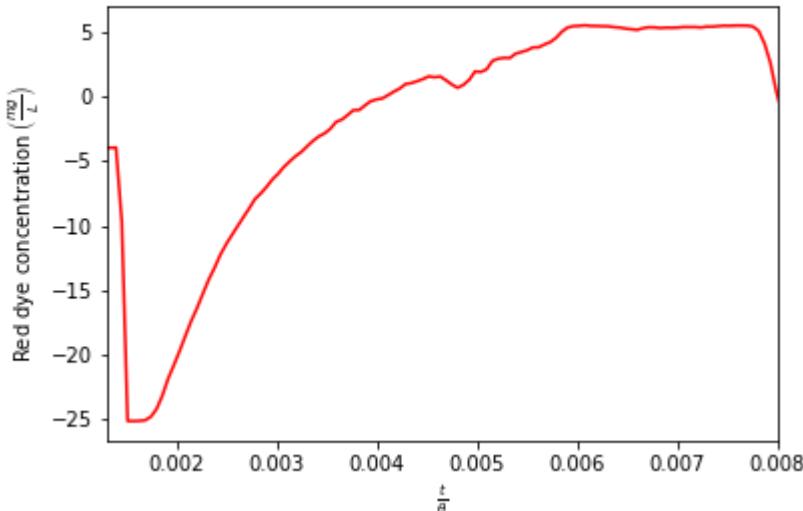


Figure 5: Breakthrough curve for burnt coffee grounds treated with NaCl.

Unfortunately, during our experiment with 2 (unburnt, NaCl treated), the coffee grounds clogged up the column filter and prevented water from getting through. We had a noticeable pressure buildup in our column (see image below), and had to stop that run so we have no data.

We also had problems with ProCoDA and measuring the concentration. We only realized after our experiment ended that the actual concentrations were not recorded in some trials, so we had to correct for those in our Python analysis. This can be seen in our appendix at the end.

The breakthrough curves for the burnt coffee grounds were slightly better than those of the unburnt coffee grounds. In addition, these breakthrough curves are all better than the breakthrough curve for the unburnt, untreated coffee grounds we ran at the beginning of the experiment. Although the curves are steeper than we anticipated and hoped for, they are still promising. There were many things we could have improved in this experiment if we were to do it again.

First, we could have burned the coffee grounds more consistently and using a burning method more robust than Anya's charcoal grill. We had to check the fire every 20-40 minutes, and sometimes when we would check the fire, we realized that it had run out. Next time, we would add new charcoal bits more consistently over the course of the 5 hours. In addition, we would measure the same amount of coffee grounds in the four samples we used. Because the mass of coffee grounds was different across the four setups, we could not get very consistent data. Next time, to be more consistent, we would measure the same mass of coffee and rinse each one for the same amount of time with the NaCl and HCl.

As mentioned earlier, we experienced problems with pressure buildup in the adsorption column. We hypothesize that this pressure build-up was due to a buildup in coffee grounds in the exit of the column. The coffee grounds from Wegmans were already ground and also very fine. Some of the fine coffee grounds escaped through the filter in the column, and at one point in the experiment, when we loosened the adsorption column to take out, the entire top part popped off due to air pressure build-up.



Figure 6: Pressure build up in adsorption column

Another interesting finding from our experiment was that the coffee grounds actually float in the water, as seen below.



Figure 7: Coffee grounds inside adsorption column

We also note that the adsorption column was not completely full during all of the experiments, as seen in the photo above. It was hard to keep a consistent mass of coffee that we put in the column, because we put it in directly after the HCl/NaCl rinses, so it was very hard to tell how much actual coffee was in the column until we ran water through it. This may have affected our results and curves, because there would be less coffee and therefore a faster breakthrough curve because there is less adsorbent.

Overall, our results showed somewhat of a trend with a less steep breakthrough curve and longer retention times for red dye in the treated coffee grounds compared to the untreated coffee grounds. There are many improvements that could be made to this experiment if we had more time during the semester to continue. Coffee grounds show some promising adsorbent qualities as "DIY activated carbon," and we recommend more analysis in this area before making any final conclusions.

References

Edwards, Quincy A., Sergei M. Kulikov, and Leah D. Garner-O'Neale. "Caffeine in surface and wastewaters in Barbados, West Indies." SpringerPlus 4.1 (2015): 57. Rosal, Roberto, et al. "Degradation of caffeine and identification of the transformation products generated by ozonation." Chemosphere 74.6 (2009): 825-831.

Knee, Karen L., et al. "Caffeine and agricultural pesticide concentrations in surface water and groundwater on the north shore of Kauai (Hawaii, USA)." Marine Pollution Bulletin 60.8 (2010): 1376-1382.

Thomas, Paul M., and Gregory D. Foster. "Tracking acidic pharmaceuticals, caffeine, and triclosan through the wastewater treatment process." Environmental Toxicology and Chemistry: An International Journal 24.1 (2005): 25-30.

Appendix

```

from aguaclara.core.units import unit_registry as u
import aguaclara.research.environmental_processes_analysis as epa
import aguaclara.core.physchem as pc
import aguaclara.core.utility as ut
import numpy as np
import matplotlib.pyplot as plt
import collections
import os
from pathlib import Path
import pandas as pd

#Beginning of caffeine pill calculations
#one pill
Ca=75*u.mg
Caffeine=200*u.mg
L=1*u.L
C=Caffeine/L

pKa = 10.4
pKb = 14-pKa
pKb
Kb = 10**(-pKb)
Kb
molweight = 194.19*u.g/u.mol

caff_init=C

caff_added=()
def molperL(caff):
    """convert mg/L of caffeine to mol/L
    :param caff: concentration of caffeine in mg/L
    :type caff: float

    :return: concentration of caffeine in mol/L
    :rtype: float
    """
    return (caff/molweight).to(u.mol/u.L)
molperL(200*u.mg/u.L)

def pH(caff):
    """calculate the pH of solution based on concentration of caffeine added in moles/Liter
    :param caff: initial concentration of caffeine in solution
    :type caff: float

    :return: pH of solution
    :rtype: float
    """
    return 14+np.log10(np.sqrt(((Kb*u.mol/u.L)*(caff))).magnitude)

pH(C)
pH(C/2)

```

```
pH(C/4)
```

```
pH(C/20)
```

```
def dilute(C1, C2, V2):
    """Return instructions on how much of the original sample and how much DI water to add to achieve the desired concentration.
    :param C1: concentration of sample being used for Dilutions
    :type C1: float
    :param C2: concentration desired
    :type C2: float
    :param V2: volume desired
    :type V2: float

    :return: volume of
    :rtype: string
    """
    V1 = C2*V2/C1
    return ('Add {0:.2f} of concentration {1:.2f} solution to {2:.2f} of DI water'.format(V1, C1, V2))

dilute(200*u.mg/u.L, 100*u.mg/u.L, 100*u.mL)
dilute(100*u.mg/u.L, 10*u.mg/u.L, 100*u.mL)
dilute(10*u.mg/u.L, .1*u.mg/u.L, 100*u.mL )
dilute(10*u.mg/u.L, .01*u.mg/u.L, 100*u.mL)
dilute(.01*u.mg/u.L, .0001*u.mg/u.L, 100*u.mL)

#Dilutions:
full=200*u.mg/u.L
#calculating mass of precipitated solids
m_papertowel+holder=6.049*u.g
#to measure when it is dry (thursday)
```

```
#Graphing our data
```

```
def adsorption_data(C_column, dirpath):
    """This function extracts the data from folder containing tab delimited files of adsorption data. The file must be the original tab delimited file.
```

```
Parameters
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```
C_column : int
```

```
    index of the column that contains the dissolved oxygen concentration data.
```

```
dirpath : string
```

```
    path to the directory containing aeration data you want to analyze
```

```
Returns
```

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```

```
filepaths : string list
```

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    all file paths in the directory sorted by flow rate
```

```
time_data : numpy array list
```

```
    sorted list of numpy arrays containing the times with units of seconds
```

```
Examples
```

```

-----
"""

#return the list of files in the directory
metadata = pd.read_csv(dirpath + '/metadata.txt', delimiter='\t')
filenames = metadata['file name']
#extract the flowrates from the filenames and apply units
#sort airflows and filenames so that they are in ascending order of flow rates

filepaths = [dirpath + '/' + i for i in filenames]
#C_data is a list of numpy arrays. Thus each of the numpy data arrays can have different lengths
# cycle through all of the files and extract the column of data with oxygen concentrations and
C_data=[concfromsample(epa.column_of_data(i,epa.notes(i).last_valid_index() + 1,C_column,-1,'n
time_data=[(epa.column_of_time(i,epa.notes(i).last_valid_index() + 1,-1)).to(u.s) for i in fi]

adsorption_collection = collections.namedtuple('adsorption_results','metadata filenames C_data
adsorption_results = adsorption_collection(metadata, filenames, C_data, time_data)
return adsorption_results

b=.019*u.m
epsilon=2508*u.m**2/u.g
Blank_Volts = 3.49727 * u.V
Dark_Volts = -1.3065 * u.V

def concfromsample(Vsample):
    """return concentration given a sample voltage
    :param Vsample: sample voltage in V
    :type Vsample: float

    :param Vdark: dark voltage in V
    :type Vdark: float

    :param Vblank: blank voltage in V
    :type Vblank: float

    :param epsilon: extinction coefficient
    :type epsilon: float

    :param b: path length in m
    :type b: float

    :return: concentration of sample in mol/L
    :rtype: float

    """
    C=-np.log10(((Vsample-Dark_Volts)/(Blank_Volts-Dark_Volts)))/(epsilon*b)
    return C.to(u.mg/u.L)

dirpath_untreated="https://raw.githubusercontent.com/cc2394/CEE4530/master/april24%20round%202.xls"
dirpath_untreated[0]

```

```

C_column=2
dirpath_untreated[0]

C_data_untreated=concfromsample(epa.column_of_data(dirpath_untreated,1,2)*u.V)*-500
time_data=(epa.column_of_time(dirpath_untreated,1))

plt.plot(time_data.magnitude, C_data_untreated.magnitude,'r');
plt.xlabel(r'$\frac{t}{\theta}$');
plt.ylabel(r'Red dye concentration $\left( \frac{mg}{L} \right)$');
plt.xlim(.02,.025)
plt.savefig('unburnt coffee')
plt.show()

dirpath_unburnt_HCl="https://raw.githubusercontent.com/cc2394/CEE4530/master/1.unburnt%20HCl%20act"
C_data_unburnt_HCl=concfromsample(epa.column_of_data(dirpath_unburnt_HCl,1,1)*u.V)*1000
time_data_unburntHCl=(epa.column_of_time(dirpath_unburnt_HCl,1))

plt.plot(time_data_unburntHCl.magnitude, C_data_unburnt_HCl.magnitude,'r');
plt.xlabel(r'$\frac{t}{\theta}$');
plt.ylabel(r'Red dye concentration $\left( \frac{mg}{L} \right)$');
plt.xlim(0,0.008)
plt.savefig('unburnt_HCl')
plt.show()

dirpath_burnt_HCl="https://raw.githubusercontent.com/cc2394/CEE4530/master/2.%20burnt%20grounds%26"
C_data_burnt_HCl=concfromsample(epa.column_of_data(dirpath_burnt_HCl,1,1)*u.V)*1000
time_data_burntHCl=(epa.column_of_time(dirpath_burnt_HCl,1))

plt.plot(time_data_burntHCl.magnitude, C_data_burnt_HCl.magnitude,'r');
plt.xlabel(r'$\frac{t}{\theta}$');
plt.ylabel(r'Red dye concentration $\left( \frac{mg}{L} \right)$');
plt.xlim(0.0007,0.0035)
plt.savefig('burnt_HCl')
plt.show()

dirpath_burnt_NaCl="https://raw.githubusercontent.com/cc2394/CEE4530/master/4.%20burnt%20nacl.xls"
C_data_burnt_NaCl=concfromsample(epa.column_of_data(dirpath_burnt_NaCl,1,1)*u.V)*1000
time_data_burntNaCl=(epa.column_of_time(dirpath_burnt_NaCl,1))

plt.plot(time_data_burntNaCl.magnitude, C_data_burnt_NaCl.magnitude,'r');
plt.xlabel(r'$\frac{t}{\theta}$');
plt.ylabel(r'Red dye concentration $\left( \frac{mg}{L} \right)$');
plt.xlim(0.0013,0.008)

```

```
plt.savefig('burnt_NaCl')  
plt.show()
```

