CH 3522: Unit Operations Lab
Adsorption Kinetics

Batch - R, Group - 05
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1. Objective

- To determine the mass transfer coefficient K_c for batch adsorption of dye on activated charcoal.

- To compare the mass transfer coefficients with correlation-derived estimates for similar systems.

2. Introduction

Adsorption kinetics is a fundamental aspect of chemical engineering, playing a crucial role in processes such as catalysis, water treatment, and separation technologies. Understanding the rate at which adsorbates adhere to solid surfaces enables engineers to design and optimize systems for efficient contaminant removal and resource recovery.
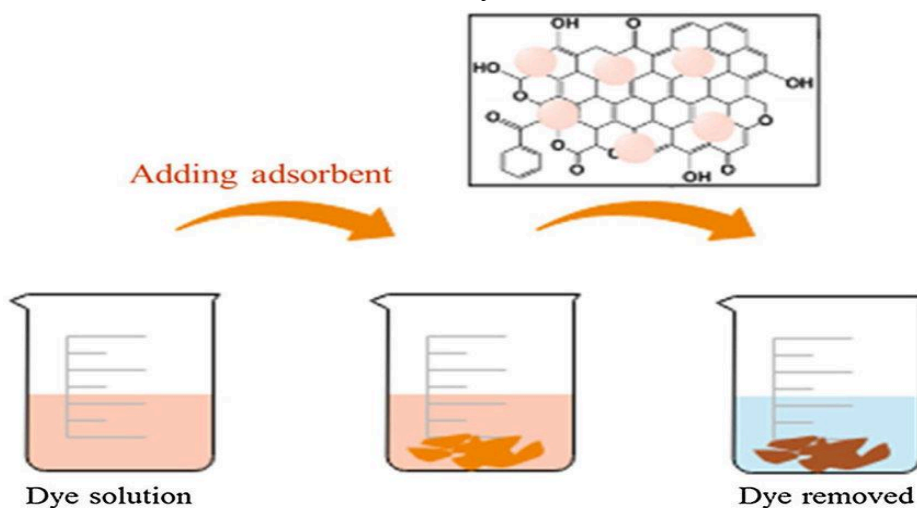

Figure 1: Adsorption Phenomenon

In this experiment, we investigate the adsorption kinetics of methylene blue dye onto activated charcoal. By monitoring the concentration of the dye over time, we aim to determine key parameters such as the rate constant and equilibrium adsorption capacity. These parameters are essential for modeling adsorption processes and scaling them for industrial applications.

Through this study, we will apply kinetic models to experimental data, enhancing our understanding of the mechanisms governing adsorption. This knowledge is vital for the development of effective adsorption-based systems in various chemical engineering fields.

3. Theory

Few of the important theoretical aspects behind the current experiments are explained below.

Adsorption

Adsorption is a surface phenomenon where molecules or particles (adsorbates) adhere to the surface of a solid or liquid material (adsorbent). This process is distinct from absorption, where substances are taken up into the bulk of the material. The adhesion occurs due to intermolecular forces between the adsorbate and the surface of the adsorbent.

Adsorption can be classified into two types based on the nature of the interaction between the adsorbate and adsorbent:

- **Physisorption (Physical Adsorption)**:
    a. Involves weak van der Waals forces.
    b. It is a reversible process that occurs at lower temperatures.
    c. There is no significant electron transfer or chemical bonding involved.
    d. <u>Example</u>: Adsorption of gases like oxygen or nitrogen on activated carbon.
- **Chemisorption (Chemical Adsorption)**:
    a. Involves strong chemical bonds, either covalent or ionic.
    b. This process is irreversible and occurs at higher temperatures.
    c. It is specific to certain adsorbent-adsorbate pairs.
    d. <u>Example</u>: Adsorption of oxygen on metal surfaces during catalysis.

In a batch adsorption experiment, commonly used to study adsorption in liquids, a known amount of dye is introduced into a liquid with an initial concentration. The system is then stirred or agitated, and at intervals, samples are taken to measure the concentration of the dye as it decreases due to adsorption until it reaches a constant value, signifying equilibrium.

UV-Vis Spectroscopy for Dye Concentration Measurement

UV-Vis spectroscopy is a powerful technique to analyze the concentration of substances, particularly dyes, in a solution. A double-beam UV-Vis spectrophotometer is typically used, where

one beam passes through a reference solution and the other through the sample solution. The intensity of light transmitted through the sample is measured and compared to the reference solution. The absorbance (A) is calculated using the relation,

$$A = log_{10}(\frac{I_0}{I})$$

(1)

Where I_0 is the intensity of light passing through the reference solution which is assumed to undergo minimal particle scattering, meaning that maximum light intensity passes through it. , and I is the intensity of light transmitted through the sample.

And Beer-Lambert's law proposes that the concentration (C) of the dye in the sample is proportional to the absorbance.

$$C \propto A$$

(2)

Adsorption Kinetics

The adsorption kinetics model is more complex and requires the use of differential equations. The *pseudo-first-order model*, in which k_l is the rate constant and q_t is the amount of dye adsorbed at time t, is one that is frequently used

$$\frac{dq_t}{dt} = k_l(q_e - q_t)$$

(3)

Assuming a linear model for equilibrium, i.e.

$$q = kC_e$$

(4)

Mass balance gives

$$V(C_0 - C) = m(q - q_0) = m \times q \qquad [\,since,\ q_0 = 0\,]$$

(5)

where,

- q_t is the amount of dye adsorbed at time t,
- q_e is the equilibrium amount of dye adsorbed,
- V is the volume of the system.

If K_c is the mass transfer coefficient & a is this is the area available for mass transfer per unit volume, we can write

$$\frac{dC}{dt} = K_c a\,(C_e - C)$$

(6)

Making the assumptions of first order kinetics,

$$\frac{dC}{dt} = K_c a \left(\frac{q}{k} - C\right) \tag{7}$$

$$\Rightarrow \frac{dC}{dt} = K_c a \left(\frac{V(C_0 - C)}{k} - C\right)$$

$$\Rightarrow \frac{dC}{[(1 + \frac{V}{mk})C - (\frac{V}{mk})C_0]} = -(K_c a) \, dt$$

Integrating both the sides we get the final expression of the model we will be the our experimentally obtained data against,

$$ln\left[(1 + \frac{V}{mk})\frac{C}{C_0} - (\frac{V}{mk})\right] = (1 + \frac{V}{mk}) \times (-K_c at)$$

$$\Rightarrow C = \left[exp\{(1 + \frac{V}{mk}) \times (-K_c at)\} + \frac{V}{mk}\right]\frac{C_0 mk}{(V + mk)} \tag{8}$$

Figure 2: UV-Vis Spectrophotometer

4. Apparatus Required

- Methylene Blue Dye
- Pipettes, Microbalance
- Activated Charcoal, Distilled water
- UV-Vis Spectrophotometer (shown in figure 2)
- Heating plate, beakers and test tubes
- Magnetic stirrer (operated at low rpm, around 300)

5. Schematic of Experimental Setup

Experimental setup includes the following components:

- **Adsorbent** – Activated charcoal used for dye adsorption.
- **Dye Solution** – Prepared solution of the target dye for adsorption studies.
- **Agitation System** – Magnetic stirrer as orbital shaker ensuring uniform mixing of adsorbent and dye solution.
- **Spectrophotometer** – Measures the absorbance of the supernatant to determine dye concentration.
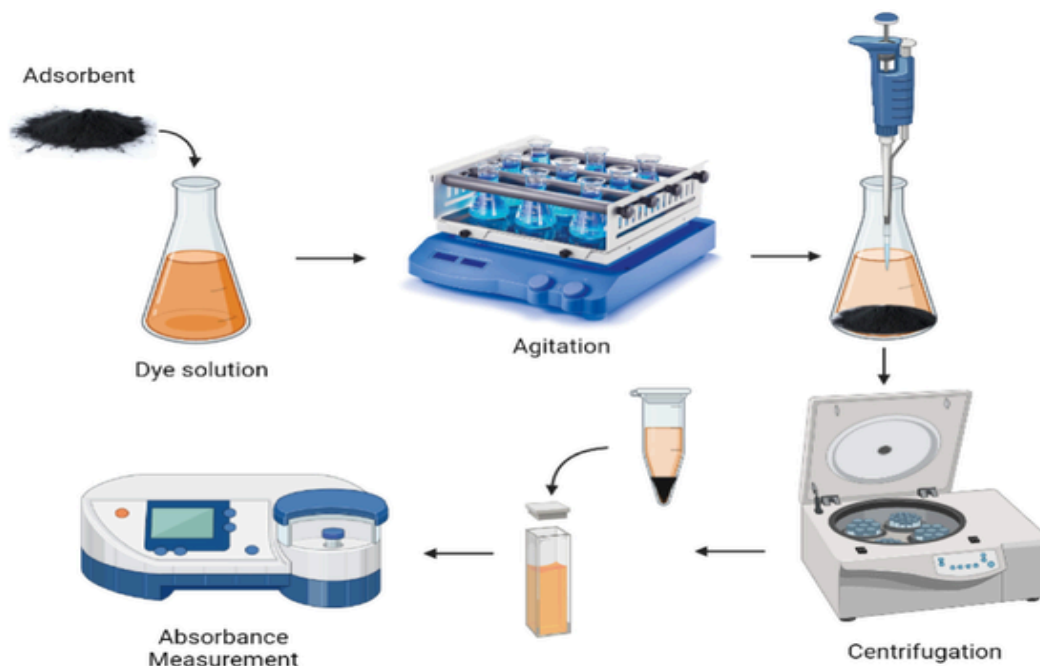- **Cuvettes and Pipettes** – For sample handling and preparation before absorbance measurement.

Figure 3: Schematic representation of the experimental set-up

The schematic (figure 3) illustrates the adsorption experiment workflow, beginning with the preparation of a dye solution and the introduction of an adsorbent. The mixture undergoes agitation to facilitate adsorption. The supernatant is then collected and analyzed using a spectrophotometer to measure absorbance, providing insights into the adsorption efficiency.

We also show the samples taken in test-tubes & the microbalance used while performing the experiment in the laboratory in the following figures.
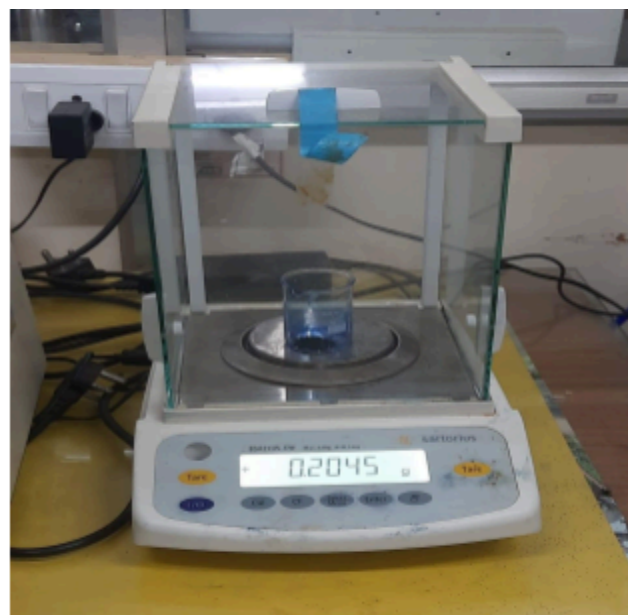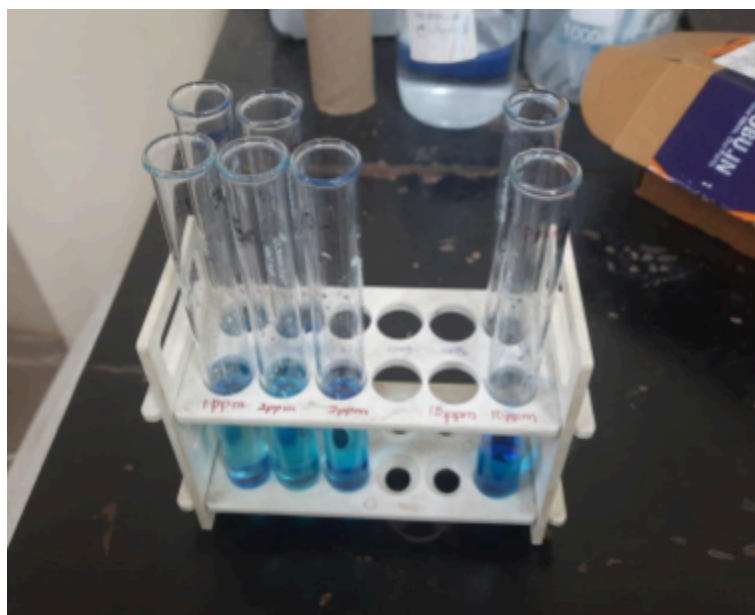

Figure 4: Samples in test-tubes & Microbalance for accurate weight measurements

6. Procedure

Dye solution preparation:
- Weigh 0.1g of methylene blue dye on a microbalance and transfer to the beaker.
- Make 1L of the dye solution using distilled water.

Dye sample preparation for calibration:
- 10 mL of the dye solution is pipetted out and transferred to sample vials and diluted with appropriate amounts of distilled water.
- Samples of varying concentrations (1, 2, 3 , 4 and 5 ppm) made for preparing the calibration data set of concentration-absorbance using a UV-Vis spectrophotometer.

Batch Adsorption:
- 4g of activated charcoal of known quality is added to the dye solution.
- The activated charcoal is kept suspended by mild stirring of the slurry using a magnetic stirrer (keep a moderate stirring rate).

Sampling for UV-Vis Analysis:
- At periodic intervals of time, stop the stirring, wait for the suspension to settle down, and draw 5 mL of particle free liquid sample for analysis of the concentration using the UV-Vis spectrophotometer.
- Sufficient quantity of the sample is transferred to the cuvette for analysis.

Concentration analysis of sample:
- After turning on the spectrophotometer and the computer, run the spectrum analysis and measurement software.
- Adjust the measurement parameters, including the wavelength range and scan rate.
- Prior to measuring the samples, make reference measurements with distilled water.
- Insert the sample into the allotted slot, making sure its transparent side is facing the laser beam.
- Ensure that the sample slot is clean to prevent fingerprint marks interference. Store purified water in the designated reference slot.
- Start the process of gathering data. After the data is collected, find the absorbance values and peak position.

7. Experimental Observations

The RPM was set to 290-310 throughout. All the experimental observations that were tabulated during the laboratory session are included in order at the end.

In the following two tables, we include the calibration data along with the experimental values of the absorbance obtained from the specific solution samples of concern after specific time intervals. The wavelength at which the calibration data was taken is 663 nm.

Concentration of Solution (ppm)	Absorbance
0	0.0001
1	0.1582
2	0.3242
3	0.5281
4	0.7360
5	0.9034

Table 1: Calibration Table

Now the absorbance data obtained from each of the samples after certain amount of dilution is,

Sampling Time (min)	Absorbance	Dilution Level
5	0.1727	100 (times diluted)
10	0.1331	100
15	0.5568	20
20	0.5492	20
25	0.4509	20
35	0.2783	20
45	0.2439	20
55	0.2680	20
65	0.1412	20
75	0.1629	20
90	0.1200	20

Table 2: Experimentally obtained absorbance values for each sample

8. Sample Calculations

At the very first, we used the calibration data to come up with the calibration model given as equation (14) in the "*Results & Discussions*" section. This model is used in the later step where we have the absorbance values of several samples at different time-stamps in order to find their concentrations. For example at time-step 10 minutes, the sample we obtained has an absorbance value of 0.1331. Now using the model (eq 14) we get,

$$conc\,(ppm) \;=\; (5.422739) \,*\, (0.1331) \;+\; 0.104957 \;=\; 0.826724\,ppm$$

Then using the known dilution value from table 2 we get the original / corrected concentration of the undiluted sample which contains the information of the amount of dye being adsorbed after 10 minutes the experiment commenced. So the actual concentration is 82.6724 ppm. The values of the corrected concentrations estimated from this model are tabulated in table 3 in the "*Results & Discussions*" section.

Then these concentration values are used to fit a non-linear model provided as equation 8 in the "*Theory*" section. The equation 8 can simply simply be written as follows

$$C = A \exp(-Bt) + D \tag{9}$$

And the parameters A, B & D are estimated using a non-linear optimization in MATLAB using in-built function *lsqnonlin.* The estimates are as follows

$A = 97.4965; \quad B = -0.000590; \quad D = 10.8756$

These values used to extract out the unknown quantities in the equation 8 which are k & $K_c a$ & the results are discussed in the following section and a plot of the fitted model is also given in figure 6. The known quantities are,

$C_0 = 100 \, ppm$ (the initial concentration of the solution, the adsorption experiment started with),

the mass of the adsorbent (activated charcoal) is 4g or 4000 mg and the volume of the beaker is 1 L which is nothing but the initial volume of the solution.

At the end, the experimentally found mass transfer coefficient is compared with the theoretical correlation of finding mass transfer coefficient. Thus this "*Sample Calculation*" section not only provides the individual computation of a result of a subpart of the whole flow but also provides the complete flow of calculation methodology that is being followed to obtain the required results.

Calculation of Theoretical K_c from correlations:

The adsorption in the setup can be related to single spherical particle adsorption to calculate the mass transfer coefficient. The correlation for the same is

$$Sh = Sh_0 + 0.74 \times Sc^{1/3} \times Re^{0.5} \tag{10}$$

Here $Sh_0 = 2$. To calculate the Reynold's number, velocity is averaged across the beaker.

Considering beaker diameter as 13 cm and from the expression of Reynold's number we get

$$Re = v d_p / \mu \tag{11}$$

Similarly, the Schmidt number can be calculated as

$$Sc = v/D_L \tag{12}$$

which is coming out to be 1.0503×10^7, where D_L is the molecular diffusion coefficient. Thus the Sherwood number is coming out to be 8457.7165. Now using, the definition of Sherwood number,

$$Sh = K_c d_p / D_L \tag{13}$$

Here, the characteristic length considered is the average length of adsorbent particles, we get the mass transfer coefficient as $K_c = 2.6337 \times 10^{-7} \, m/s$.

9. Results & Discussions

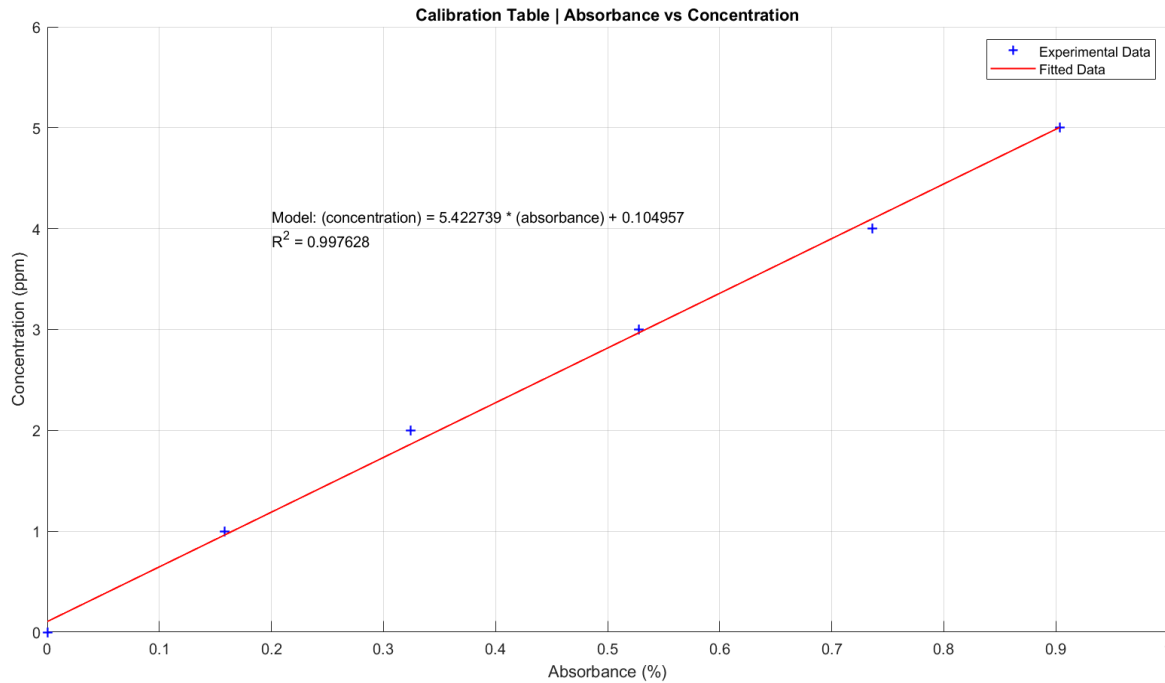At first we have used the calibration data to obtain a model and using TLS objective we have got the

Figure 5: Calibration curve

following model,

$$conc\ (ppm)\ =\ (5.422739)\ *\ absorbance\ +\ 0.104957 \tag{14}$$

And the coefficient of determination (R^2) value of this model comes out to be 0.997628, which is a quite good model for calibration purposes since this gives the result of the following parts of the flow of the calculation described in the "*Sample Calculation*" section. The plot of the fitted model is given in the above figure (figure 5).

Now we provide the table containing the corrected concentrations of the samples taken in the specified time-steps (table 2) which are further used in building the adsorption kinetics model.

The fitted model on the concentration data is given in the following figure (figure 6). The parameters give the resulting mass transfer coefficient & equilibrium constant values which are coming out to be

$k\ =\ 0.002049\ L/mg\ =\ 0.002049\ ppm^{-1}$;

$K_c \times a\ =\ 0.0005259775\ s^{-1}$ and these are obtained from a model which has a R^2 value of 0.967.

Sampling Time (min)	Absorbance	Corrected Concentration (ppm)
5	0.1727	104.14641
10	0.1331	82.6724
15	0.5568	62.4868
20	0.5492	61.6625
25	0.4509	51.0014
35	0.2783	32.2821
45	0.2439	28.5513
55	0.2680	31.1650
65	0.1412	17.4129
75	0.1629	19.7664
90	0.1200	15.1137

Table 3: Corrected Concentrations of the Solution Samples

Considering the radius of the adsorbent particles to be 1mm, the value of the liquid mass transfer coefficient is coming out to be,

$K_c = 0.0005259775 / a = 0.0005259775 \times 0.001 \times (1/3) = 1.75326 \times 10^{-7} m/s.$

From the trend found in figure 6, we can represent the equation 8 as follows,

$$C = (C_0 - C_\infty) exp(- 0.0005259775 \times t) + C_\infty \qquad (15)$$

And using the estimates of the model parameters (A, B & D), we can extract the values of initial and saturated concentration values, which are

$C_\infty = 10.8756 \, ppm$ and $C_0 = 108.372144 \, ppm$ respectively.

10. Conclusions
- As expected, the absorbance vs concentration plot demonstrated conformity to the linear model (used as calibration model here).
- The concentration vs time graph exhibited an anticipated exponential decay trend.
- Both the calibration data and the concentration data are fitted to the obtained models really well, confirmed from the value of the coefficient of determination which implies that the
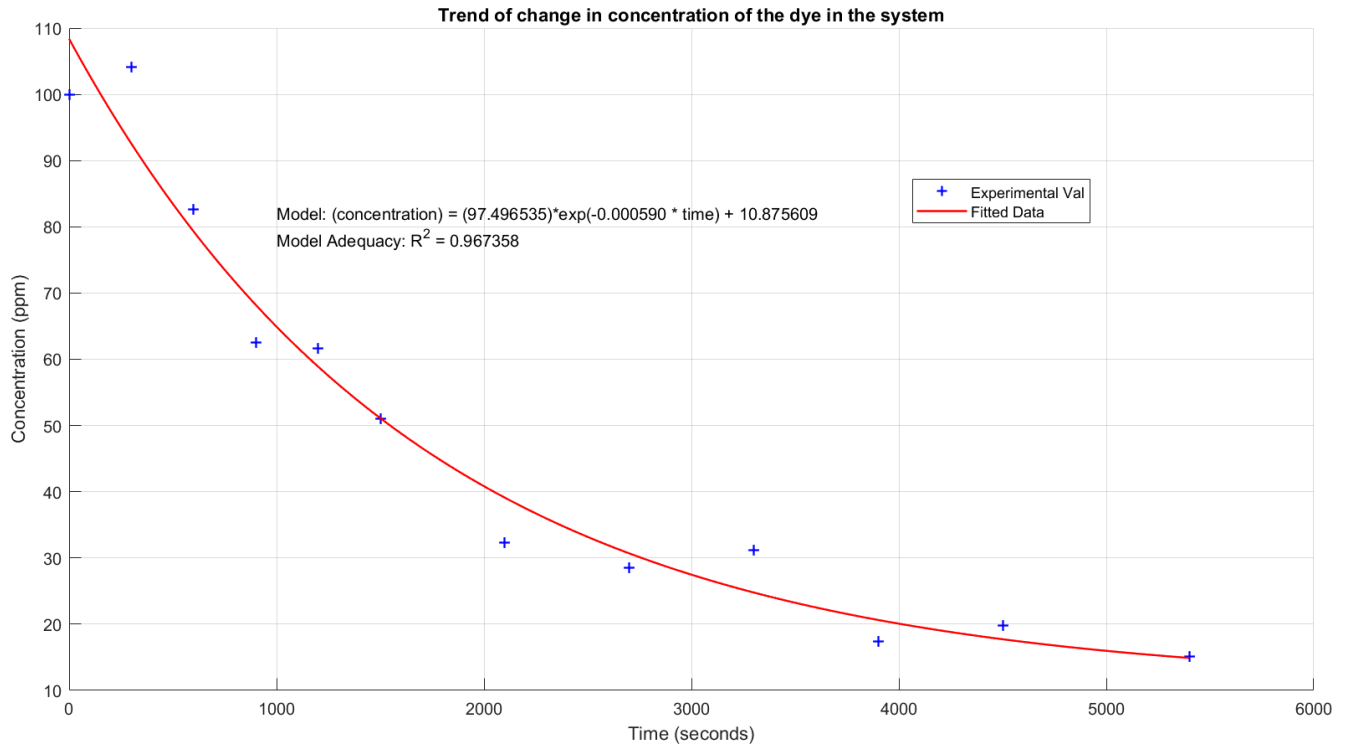
Figure 6: The change in concentration of dye due to adsorption on activated charcoal

raw data collection process has been done significantly well.

- The experimental & theoretical liquid mass transfer coefficient values are 1.75326×10^{-7} m/s & 2.6337×10^{-7} m/s, which are pretty close. Though one might use more complex correlation of Sherwood number such as given in equation 16 to obtain even more accurate results to correlate with the experimental result.

$$Sh = \frac{K_c d_p}{D_L} = Sh_0 + (0.47)(Re)^{0.62}(Sc)^{0.36}(d_{impeller}/d_{beaker})^{0.17} \qquad (16)$$

The above correlation is given by Levins & Glastonbury and was also used in the paper "*Liquid-to-Particle Mass-Transfer in a Stirred Batch Adsorption Tank with non-linear Isotherm*".

- Though from the model (equation 9 & 15) the value of C_0 is coming out to be 108.372144 ppm, but according to the experiment conditions, the initial concentration of the solution was 100 ppm. This erroneous estimation has come because the raw data collected might have issues with the values of dilution or absorbance.
- We might control some factors while taking the raw data to avoid further possibilities of human and machine errors.

- Some experimental sources of error include inadequate amount of solution was sampled, even during decantation, instrument errors cause erroneous amounts. Besides inaccuracies in UV spectrometer measurements and errors brought on by sample weight loss during solution preparation.

11. References

I. CH 2014 : Heat & Mass Transfer Course Notes.

II. Application note on *Theory of Absorbance* by Trilogy Laboratory.

III. *Liquid-to-Particle Mass-Transfer in a Stirred Batch Adsorption Tank with non-linear Isotherm,* 1982 paper to obtain the theoretical correlation & kinetic model for adsorption.

IV. *Liquid-Solid Mass Transfer in Adsorption systems - An Overlooked Resistance*, 2020 paper to obtain more inference on adsorption theory.

V. *Determination of Mass Transfer Coefficients for Adsorption of Pb and Cd Onto Coir Pith and Statistical Analysis*, 2020 paper to get the derivation of the frequently used kinetic model to capture the adsorption phenomenon.

VI. The Engineering Toolbox to find the kinematic viscosity of water at $30^{\circ}C$ used in the computation of Sherwood number.

VII. Valves Instruments Plus Ltd. provided list to obtain density of water at $30^{\circ}C$.

VIII. *Diffusion Coefficient* article by Thermopedia.

IX. The GitHub repository contains all the related data and coded scripts used for calculations.

CH3522-UNIT OPERATIONS LAB

Data Sheet

Experiment: ADSORPTION KINETICS   Date: 29/1/2025

Batch: R

Group No: 5

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$\lambda = 663$ nm   RPM $-$ 290 to 310.

C (ppm)	absorbance
1	0.1582
2	0.3242
3	0.5281
4	0.7360
5	0.9034

Calibration table

5	0.1727	100X
10	0.1331	100X
15	0.5568	20X
20	0.5492	20X
25	0.4509	20X
35	0.2783	20X
45	0.2439	20X
55	0.2680	20X
65	0.1412	20X
75	0.1629	20X
90	0.1200	20X

0.1g methylene blue dye in 1L water. (100ppm)

Amount of activated charcoal = 4g.