

IB Chemistry SL

Internal Assessment

Title

An investigation into the effect of pH of wastewater on the adsorption of copper (II) ions.

Personal code



1 Introduction

During my Geography lessons, I learnt under the influence of consumerism, the demand for goods and services around the globe has risen exponentially over time. As a result, the number of heavy-duty industries operating have been increasing, such as manufacturing, mining, and metallurgy. I was saddened to understand that an unfortunate by-product of such industries are massive amounts of toxic wastewater. According to Ouyang et al., wastewater includes large amounts of heavy metals such as Cu^{2+} , Zn^{2+} , and Fe^{3+} , of which possesses many carcinogenic effects to organisms. When wastewater is untreated, it can severely disrupt the aquatic ecological system, and can also percolate through rocks and intoxicate our groundwater table, indirectly causing anaemia, kidney failure and even death for humans.

Because these heavy industries are predominantly located in less economically developed countries, companies do not have the financial incentive to process their wastewater. It has therefore piqued my interest about whether there is a cost-efficient method of removing heavy metals from wastewater. Upon further research, out of the different methods of removing heavy metals, such as adsorption, precipitation, reverse osmosis and membrane processes, adsorption is the most economically affordable (Demiral and Güngör). As it is important to secure resources and ensure healthiness for the future generations, it has greatly inspired me to investigate on the different parameters that can maximise the efficiency of copper ion removal from wastewater via adsorption.

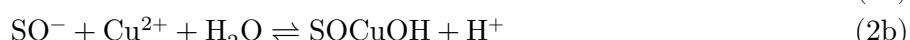
PE: Personal interest showing independent thinking

1.1 Background *Ex: You should have your research question clearly stated*

Adsorption is the process of adsorbates adhering to the surface of an adsorbent, which happens mainly due to chemisorption, the attraction due to bonds formed from chemical reactions, and physisorption, the attraction due to intermolecular van der Waals forces (Schaefer et al.). A commonly used adsorbent is activated carbon, which is made by repeatedly carbonising charcoal to create many microscopic pores, so to increase the surface area of the sorption sites. According to Mopoung et al., the surface sorption sites are predominantly composed of hydroxyl groups (SOH) that possess amphoteric properties, allowing it to chemiadsorb Cu^{2+} ions. Yu and Kaewsarn suggested that adsorption first begins with the dissociation of the hydroxyl group:



, which follows by reactions between the SO^- ion and Cu^{2+} ion:



However, when the pH of the sorption site is low, the high concentration of H^+ ions undergo the following reaction with the sorption site:

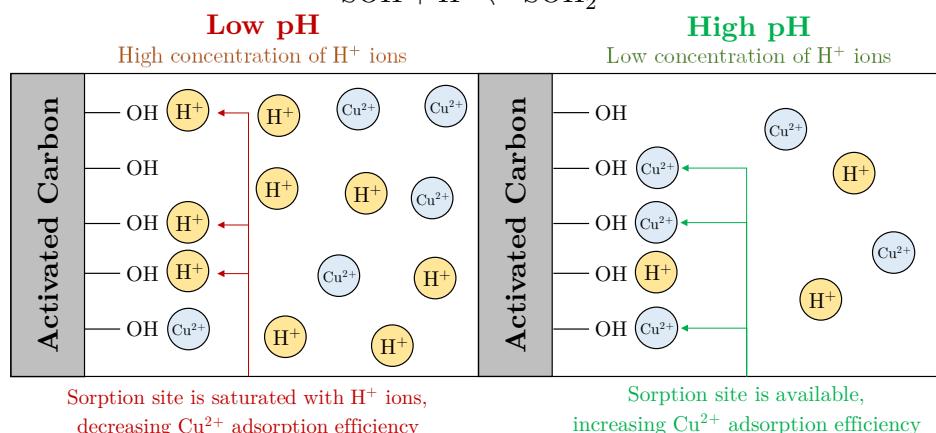


Figure 1. Demonstration of the general effect of pH on the adsorption capacity of Cu^{2+} . (Bratt; Diniz et al.)

As shown in Figure 1, the H^+ ions compete with Cu^{2+} ions, effectively reducing the sorption efficiency. In order to determine the performance of an adsorbent, the conventional Langmuir isotherm is first used, which theorises that the amount of copper ions adsorbed (q) logarithmically increases as the concentration of copper ions (C) increases (Langmuir):

$$q = q_{max} \left(\frac{bC}{1 + bC} \right) \quad (4)$$

, where q_{max} is the maximum adsorption capacity of the adsorbent, b is some constant that characterises the adsorption efficiency, which is affected by the type of activated carbon used. Since the adsorption efficiency is heavily governed by the surface charge of the adsorbent, Yu and Kaewsarn suggested that the maximum adsorption capacity (q_{max}) accounted for effects of pH is:

$$q_{max} = \frac{q_{max_1} + q_{max_2} 10^{\text{pH}-\text{p}K_a}}{1 + 10^{\text{pH}-\text{p}K_a}} \quad (5)$$

Where q_{max_1} , q_{max_2} are constants to be found, and $\text{p}K_a = -\log K_a$ is the adsorbent dissociation constant in (1). By substituting (5) into (4), the amount of copper ions adsorbed (q) is:

$$q = \frac{q_{max_1} + q_{max_2} 10^{\text{pH}-\text{p}K_a}}{1 + 10^{\text{pH}-\text{p}K_a}} \left(\frac{bC}{1 + bC} \right) \quad (6)$$

The percentage of copper ions adsorbed, or the adsorption efficiency is:

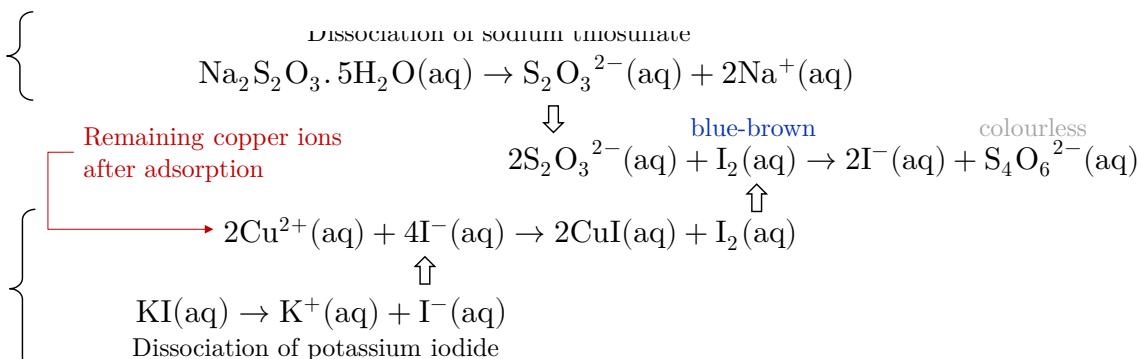
$$P = \frac{q}{q_0} \quad (7)$$

where q_0 is the initial amount of copper ions. Since this investigation is only concerned of the effect of pH on the adsorption efficiency P , other variables (q_0 , b , C) are assumed to be constant and hence be combined to one unknown constant. By substituting (6) into (7) and rewriting:

$$P = \frac{\alpha + \beta 10^{\text{pH}-\text{p}K_a}}{1 + 10^{\text{pH}-\text{p}K_a}} \quad (8)$$

where α , β and $\text{p}K_a$ are unknown constants to be found from the experiment.

1.2 Iodometric titration



To measure the sorption efficiency of each trial, a copper solution adjusted to a specific pH will be adsorbed by activated carbon through agitation. I^- solution (prepared by dissolving KI into distilled water in Equation 12) will be added to the Cu^{2+} solution, which will then be back titrated against $\text{S}_2\text{O}_3^{2-}$ solution (prepared by dissolving $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ into distilled water in Equation 9).

1.3 Hypothesis

As demonstrated above, with decreasing pH, the sorption sites are increasingly saturated by H^+ , decreasing the effective sorption surface area and efficiency. Therefore, the adsorption efficiency is expected to increase exponentially from zero as pH increases, before levelling off to a plateau, the maximum adsorption capacity, as shown in Figure 2 on the right.

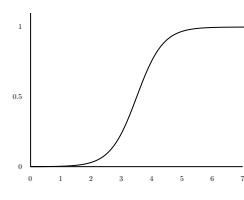


Figure 2

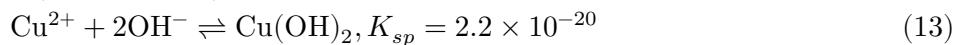
Ex: Provided relevant and appropriate background info. Clear hypothesis is stated.

2 Experimental Design

2.1 Variables

2.1.1 Independent Variable

The independent variable is the initial pH of the solution, which will be collected at regular intervals of 2.00, 2.90, 3.80, 4.70 and 5.60. The reason for the upper bound of the pH is because Cu^{2+} precipitates to $\text{Cu}(\text{OH})_2$ when $\text{pH} > 6.07$ (Candal et al.):



, which will reduce the concentration of the Cu^{2+} ions and ultimately decrease the adsorption efficiency. Furthermore, since values of $\text{pH} < 2.00$ require adding large amounts of concentrated acid which will pose significant safety risks, the range of the pH is controlled to be between 2.00 and 5.60.

Ex:
**Justified
the range
of IV**

2.1.2 Dependent Variable

The dependent variable is the percentage of copper ions adsorbed, P . This will be plotted against the pH and the curve in (6) will be fitted according to this data.

2.1.3 Controlled Variables

To reduce the impact of random errors on the accuracy of the experiment, a set of variables are kept constant, listed below:

Controlled variable	Explanation
Type of activated carbon used	According to Shahrokh-Shahraki et al., the adsorption efficiency is heavily influenced by the activated carbon's pore size, surface area and presence of different types of functional groups. To ensure that the macroscopic characteristics are the same across trials, the same type of industrially manufactured charcoal-based solid activated carbon is used across all trials. The size of the activated carbon is also ensured to be constant by crushing it using a pestle and mortar for ten minutes and further filtered through a sieve to reduce the inconsistencies in the size and surface area.
Concentration of copper ions	According to (3), the concentration of copper ions is a major factor of the Langmuir isotherm, where an increased concentration has a positive effect on the adsorption capacity up to a plateau. As Bouhamed et al. suggests, many researchers use an adsorbate concentration ranging between $10-500 \text{ mg dm}^{-3}$. While lower concentrations are generally more representative of the adsorption efficiency, they require high precision equipment such as atomic adsorption spectroscopy (AAS). Therefore, under the precision constraints of traditional titration equipment, the initial copper ion concentration of 100 mg dm^{-3} has been selected across all trials and maintained constant by using the same stock solution.
Dose of activated carbon	Similar to the concentration of copper ions, the dose of activated carbon is also a major factor in the Langmuir isotherm. Therefore, to ensure that the number of potential adsorption sites is equal across all trials, the activated carbon is added to the stock solution and further equally separated.
Time of agitation	Since chemical processes require time to progress, the amount of time the adsorbate and adsorbent are allowed to interact has a large impact on the final adsorption performance. According to Demiral and Güngör, the time required for the reaction to reach equilibrium ranges from 8-24h. Therefore,

	it has been decided that the copper ion solution should be agitated for the same period, for 24h.
Temperature of surrounding during agitation	According to Ding et al., adsorption is an exothermic process, hence the sorption process is accelerated at greater temperatures. It has therefore been decided that the experiments shall be conducted simultaneously at the same temperature.
Evaporation during agitation	As evaporation can change the concentration of the solution and hence yield inaccurate results, to reduce the probability of water molecules escaping the system, the convection is minimised by putting a lid on top of the glass bottles that hold the mixture.
Deionised water	To reduce the possibility of ion contamination, which can induce ion-ion competition during adsorption, the same grade of deionised water that is free of copper ions are used in all trials.
Rate of titrant flow	To reduce the possibility of misjudging the endpoint during the titration, the titrant is dispensed slowly drop-by-drop, to avoid the overestimation in the volume of titrant required for the colour change.

Ex: Described CV in detail with reasoning

2.2 Apparatus and Chemicals

0.500 \pm 0.001g Activated Carbon	50.00 \pm 0.05 cm ³ burette	5 Magnetic stirrers
0.196 \pm 0.001g CuSO ₄ .5H ₂ O	25.00 \pm 0.03 cm ³ pipette	1 pH meter
0.250 \pm 0.001g Na ₂ S ₂ O ₃ .5H ₂ O	100.0 \pm 0.5 cm ³ measuring cylinder	1 White tile
0.262 \pm 0.001g KI	500 \pm 50 cm ³ beakers	1 Clamp and stand
0.1M NaOH	25 \pm 10 cm ³ conical flasks	Filter paper
0.1M HCl	200 \pm 25 cm ³ glass bottles	Deionised water
Starch solution	Spatula and plastic dishes	Electronic scale
Pestle and mortar		Sieve with grain size 0.25 mm

2.3 Procedure

2.3.1 Adsorption

1. Prepare 2 0.5000 \pm 0.0025 dm³ 0.001570 \pm 0.000016 M Cu²⁺ solution by dissolving 0.196 \pm 0.001 g CuSO₄.5H₂O into 0.5000 \pm 0.0025 dm³ of deionised water in the beaker.
2. Crush the activated carbon using a pestle and mortar for 10 minutes until it has reduced to fine particles and filter it through the sieve.
3. Add 0.500 \pm 0.001 g of activated carbon to the Cu²⁺ solution.
4. Separate 0.12500 \pm 0.00015 dm³ of the solution into 5 200 \pm 25 cm³ glass bottles.
5. For each glass bottle, adjust the pH to the required intervals by slowly adding small drops of 0.1M HCl and 0.1M NaOH using a pipette, magnetic stirrer, and pH meter.
6. Agitate the mixtures for 24h using a magnetic stirrer and allow them to settle for 1h.
7. Remove the activated carbon by decanting the mixture through a filter paper.

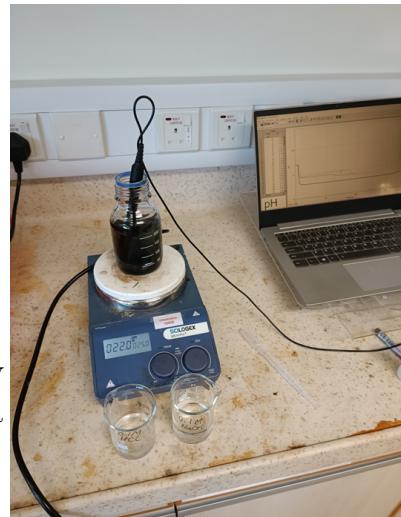


Figure 3. The experimental setup for Step 5.

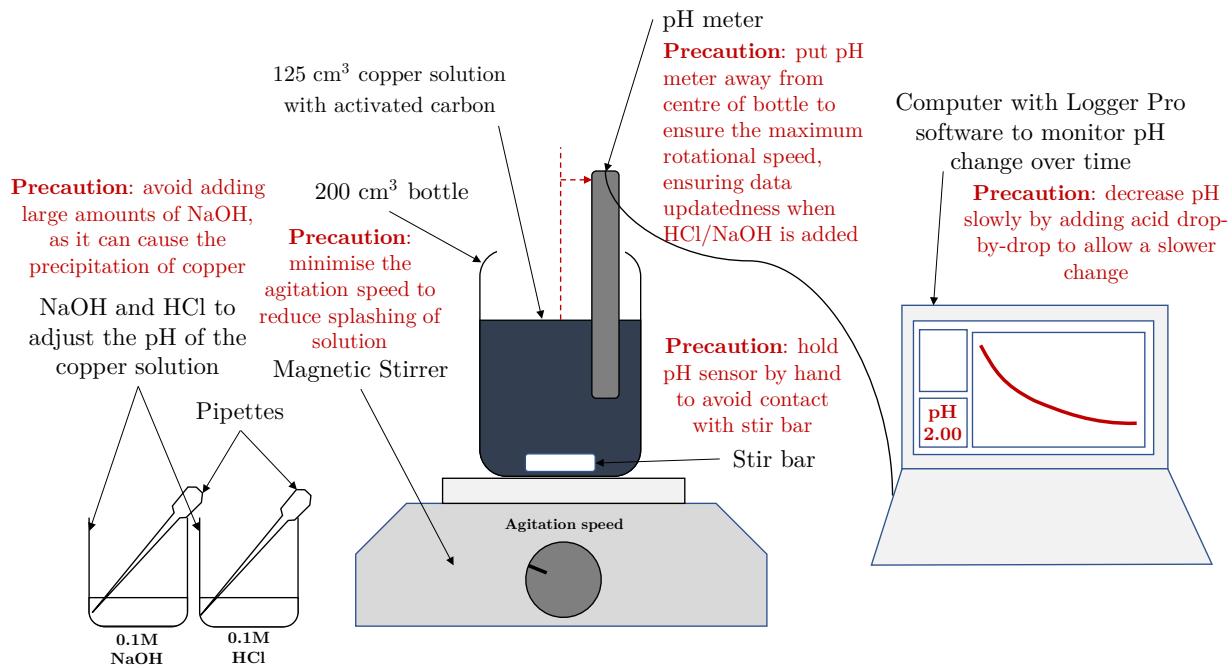
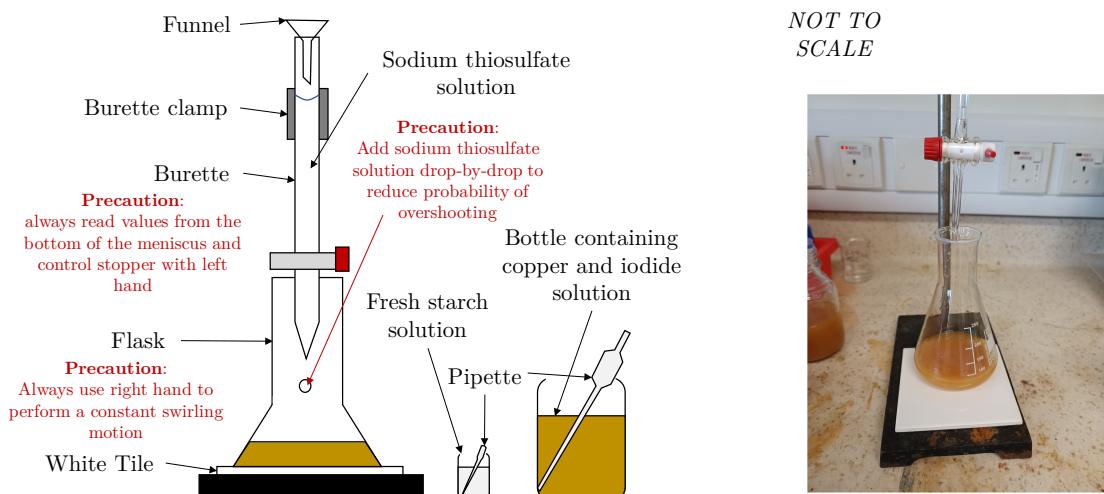


Figure 4. The experimental setup for Step 5 and its associated precautions.

2.3.2 Iodometry

1. Prepare $0.5000 \pm 0.0025 \text{ dm}^3$ $0.001571 \pm 0.000016 \text{ M}$ $\text{S}_2\text{O}_3^{2-}$ solution by dissolving $0.195 \pm 0.001 \text{ g}$ $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ into $0.5000 \pm 0.0025 \text{ dm}^3$ of deionised water.
2. Transfer the $\text{S}_2\text{O}_3^{2-}$ solution to the burette as the titrant.
3. Transfer $0.02500 \pm 0.00003 \text{ dm}^3$ of the mixture into the conical flask using a pipette.
4. Add an excess of KI (exceeding 0.014 g) to the mixture.
5. Add 5mL of starch solution to the mixture and perform the titration. Note down the value when the titrate changes from blue-black to colourless.
6. Repeat Steps 3-4 and perform the titration without the starch solution. When the amount of titrant added approaches, the value obtained in Step 5, add 5mL of starch solution to the titrate and continue the titration¹. Record the value when the titrate changes from blue-black to colourless.
7. Repeat Step 6 for a total of 3 trials.
8. Repeat Steps 3-7 for the remaining intervals.



¹ This is done because starch will react with the I_2 in (8), affecting the amount of $\text{S}_2\text{O}_3^{2-}$ required for the colour change in (9). It is therefore necessary to add the starch as close as the endpoint to minimise the reaction between starch and I_2 .

2.4 Ethical, safety and environmental concerns

Chemicals involved	Type	Explanation and Prevention
CuSO ₄ · 5H ₂ O, Na ₂ S ₂ O ₃ · 5H ₂ O and KI	Safety	These chemicals are irritant especially to the eyes. It is therefore ensured that protective eye goggles are used throughout the experiment.
	Environmental	These chemicals are carcinogenic (Ouyang et al.), and when being flushed directly into the ocean, it can harm the aquatic ecosystem. It is therefore important to dispose the chemical waste carefully.
NaOH and HCl	Safety and Environmental	These chemicals are corrosive to the skin and harmful to aquatic life. It is therefore important to wear a lab coat and protective gloves at all times, as well as disposing the chemical waste carefully.
N/A	Ethical	Since the chemical waste is properly treated and disposed of, there are minimal ethical concerns.

Ex: Aware of the the safety, ethical and environmental issues.

3 Results

3.1 Raw and processed data table

pH ± 0.01	Volume of S ₂ O ₃ ²⁻ added / cm ³						Com: Better separate the two tables and give individual title	
	Trial 1		Trial 2		Trial 3			
	Initial V_{1_i}	Final V_{1_f} $\Delta V_{1_i} = 0.05 \text{ cm}^3$	Initial V_{2_i}	Final V_{2_f} $\Delta V_{2_i} = 0.05 \text{ cm}^3$	Initial V_{3_i}	Final V_{3_f} $\Delta V_{3_i} = 0.05 \text{ cm}^3$		
2.01	17.75	34.20	2.32	20.43	20.43	37.40		
2.89	16.54	32.85	3.45	19.13	19.13	36.32		
3.77	14.49	26.94	1.56	13.65	13.65	25.03		
4.64	10.51	19.85	19.85	29.82	29.82	41.13		
5.62	15.98	25.54	25.54	34.11	34.11	42.86		
pH ± 0.01	Volume of S ₂ O ₃ ²⁻ added / cm ³							
	Trial 1		Trial 2		Trial 3		Percentage adsorbed	
	Initial V_1 $\pm \Delta V_1 = 0.10 \text{ cm}^3$	Final V_2 $\pm \Delta V_2 = 0.10 \text{ cm}^3$	Initial V_3 $\pm \Delta V_3 = 0.10 \text{ cm}^3$	Average V $\pm \Delta V$			P $\pm \Delta P$	
2.01	16.45	18.11	16.97	17.18 ± 0.93			31 ± 5	
2.89	16.31	15.68	17.19	16.39 ± 0.86			35 ± 4	
3.77	12.45	12.09	11.38	11.97 ± 0.63			53 ± 3	
4.64	9.34	9.97	11.31	10.21 ± 1.09			59 ± 5	
5.62	9.56	8.57	8.75	8.96 ± 0.60			64 ± 3	

3.2 Qualitative Observation

As shown in Figure 6 below, after the agitation, the samples are observed to change from a faint blue colour to a colourless solution, indicating that the blue coloured Cu²⁺ ions have in fact been adsorbed by the activated carbon. It has also been observed that the magnitude of colour change is greater for a larger pH, suggesting that the adsorption efficiency increases with pH. Similarly, when an excess of KI is added to the mixture, the colour change from colourless to brown is observed to be more

A: Qualitative data has shown

significant for lower pH. When $S_2O_3^{2-}$ is titrated against the mixture, there is an observable change of colour from blue-black to colourless as it reaches the endpoint.

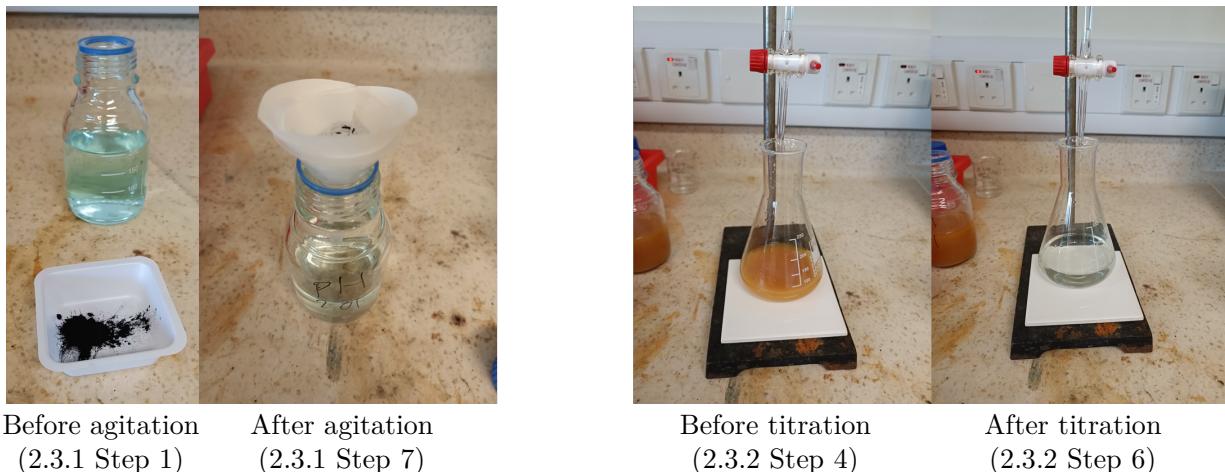


Figure 6. An image showing the in colour for the sample pH = 2.00.

3.3 Sample Calculation for pH = 2.01 ± 0.01

Let $V_k = \{V_1, V_2, V_3\}$, the average volume of $S_2O_3^{2-}$ solution required for the titration (V) can be calculated by the average of the three trials, while the uncertainty is calculated by the sum of the half-range between the maximum and minimum volumes of V_k and the instrumental uncertainty ΔV_k :

$$V = \frac{V_1 + V_2 + V_3}{3} \pm \frac{(\max(V_k) + \Delta V_k) - (\min(V_k) - \Delta V_k)}{2} \quad (14)$$

The average amount of $S_2O_3^{2-}$ required for the titration to reach the endpoint can be calculated by the product of the concentration of $S_2O_3^{2-}$ (c) and its volume from above (V):

$$n(S_2O_3^{2-} \text{ titrated}) = c(\text{stock } S_2O_3^{2-}) \times V \quad (15)$$

Since $c = \frac{n}{V}$, $n = \frac{m}{M_r}$, and that the mole ratio of $\frac{\text{Na}_2S_2O_3 \cdot 5\text{H}_2\text{O}}{S_2O_3^{2-}}$ is 1:1 in (9), the concentration of the stock $S_2O_3^{2-}$ solution is:

$$c(\text{stock } S_2O_3^{2-}) = \frac{n(S_2O_3^{2-})}{V(\text{H}_2\text{O of } S_2O_3^{2-} \text{ solution})} = \frac{\frac{m(\text{Na}_2S_2O_3 \cdot 5\text{H}_2\text{O added})}{M_r(\text{Na}_2S_2O_3 \cdot 5\text{H}_2\text{O})}}{V(\text{H}_2\text{O of } S_2O_3^{2-} \text{ solution})} \quad (16)$$

Because the mole ratio of $\frac{S_2O_3^{2-}}{I_2}$ is 2:1 in (10), the average concentration of I_2 in the flask is:

$$c(I_2 \text{ in flask}) = \frac{n(I_2)}{V(\text{flask})} = \frac{\frac{1}{2}n(S_2O_3^{2-} \text{ titrated})}{V(\text{flask})} \quad (17)$$

The average amount of I_2 in the bottle can be calculated by:

$$n(I_2 \text{ in bottle}) = c(I_2 \text{ in flask})V(\text{bottle}) \quad (18)$$

In (11), since the mole ratio between $\frac{Cu^{2+}}{I_2}$ is 2:1, the average amount of Cu^{2+} in the bottle is:

$$n(Cu^{2+} \text{ in bottle after agitation}) = 2n(I_2 \text{ in bottle}) \quad (19)$$

Substituting (16) → (15) and (15) → (17) → (18) → (19), (19) can be simplified to:

$$n(Cu^{2+} \text{ in bottle after agitation}) = \frac{m(\text{Na}_2S_2O_3 \cdot 5\text{H}_2\text{O added})V(\text{bottle})}{M_r(\text{Na}_2S_2O_3 \cdot 5\text{H}_2\text{O})V(\text{H}_2\text{O of } S_2O_3^{2-} \text{ solution})V(\text{flask})} \quad (20)$$

The amount of Cu^{2+} in the bottle before the agitation is calculated by the product of the concentration of Cu^{2+} (c) and the volume of the bottle:

$$n(Cu^{2+} \text{ in bottle before agitation}) = c(Cu^{2+} \text{ solution})V(\text{bottle}) \quad (21)$$

Cu^{2+} solution is prepared by the dissociation of $CuSO_4 \cdot 5\text{H}_2\text{O}$:



Since $c = \frac{n}{V}$, $n = \frac{m}{M_r}$ and that the mole ratio of $\frac{\text{CuSO}_4 \cdot 5\text{H}_2\text{O}}{\text{Cu}^{2+}}$ is 1:1 in (i), the concentration of the Cu^{2+} solution is:

$$c(\text{Cu}^{2+} \text{ solution}) = \frac{n(\text{Cu}^{2+})}{V(\text{H}_2\text{O} \text{ in beaker})} = \frac{\frac{m(\text{CuSO}_4 \cdot 5\text{H}_2\text{O added})}{M_r(\text{CuSO}_4 \cdot 5\text{H}_2\text{O})}}{V(\text{H}_2\text{O} \text{ in beaker})} \quad (23)$$

Finally, the percentage of Cu^{2+} adsorbed P can be calculated by:

$$P = 1 - \frac{n(\text{Cu}^{2+} \text{ in bottle after agitation})}{n(\text{Cu}^{2+} \text{ in bottle before agitation})} \quad (24)$$

Substituting in (23) \rightarrow (21) \rightarrow (24) and (20) \rightarrow (24) yields:

$$P = 1 - \frac{\frac{m(\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O added})V(\text{bottle})}{M_r(\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O})V(\text{H}_2\text{O of S}_2\text{O}_3^{2-} \text{ solution})V(\text{flask})}V}{\frac{m(\text{CuSO}_4 \cdot 5\text{H}_2\text{O added})V(\text{bottle})}{M_r(\text{CuSO}_4 \cdot 5\text{H}_2\text{O})V(\text{H}_2\text{O in beaker})}} \quad (25)$$

The total absolute uncertainty in the percentage of Cu^{2+} adsorbed is therefore²:

$$\Delta P = (1 - P) \left(\frac{\Delta m(\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O added})}{m(\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O added})} + \frac{\Delta V(\text{bottle})}{V(\text{bottle})} + \frac{\Delta V}{V} + \frac{\Delta V(\text{H}_2\text{O of S}_2\text{O}_3^{2-} \text{ solution})}{V(\text{H}_2\text{O of S}_2\text{O}_3^{2-} \text{ solution})} + \frac{\Delta V(\text{flask})}{V(\text{flask})} + \frac{\Delta m(\text{CuSO}_4 \cdot 5\text{H}_2\text{O added})}{m(\text{CuSO}_4 \cdot 5\text{H}_2\text{O added})} + \frac{\Delta V(\text{H}_2\text{O in beaker})}{V(\text{H}_2\text{O in beaker})} \right) \quad (26)$$

Substituting in the values for $\text{pH} = 2.01 \pm 0.01$:

A:Detailed example calculations provided but the steps can be simplified

$$P = 1 - \frac{\frac{0.195 \text{ g} \times 0.12500 \text{ dm}^3}{248.19 \text{ g mol}^{-1} \times 0.5000 \text{ dm}^3 \times 0.02500 \text{ dm}^3} \times \left(\frac{0.01645 + 0.01811 + 0.01697}{3} \text{ dm}^3 \right)}{\frac{0.196 \text{ g} \times 0.12500 \text{ dm}^3}{249.69 \text{ g mol}^{-1} \times 0.5000 \text{ dm}^3}} = 0.3123074977120068... = 31\% \quad (27)$$

$$\Delta P = (1 - 0.312...) \left(\frac{0.001 \text{ g}}{0.195 \text{ g}} + \frac{0.00015 \text{ dm}^3}{0.12500 \text{ dm}^3} + \frac{\frac{(0.1811 + 0.01) - (0.01645 - 0.01)}{2} \text{ dm}^3}{\frac{0.01645 + 0.01811 + 0.01697}{3} \text{ dm}^3} + \frac{0.00003 \text{ dm}^3}{0.02500 \text{ dm}^3} + \frac{0.001 \text{ g}}{0.196 \text{ g}} + \frac{0.0025 \text{ dm}^3}{0.5000 \text{ dm}^3} \right)$$

$$\Delta P = 0.052796535215179526... = 5\% \quad (28)$$

3.4 Graph

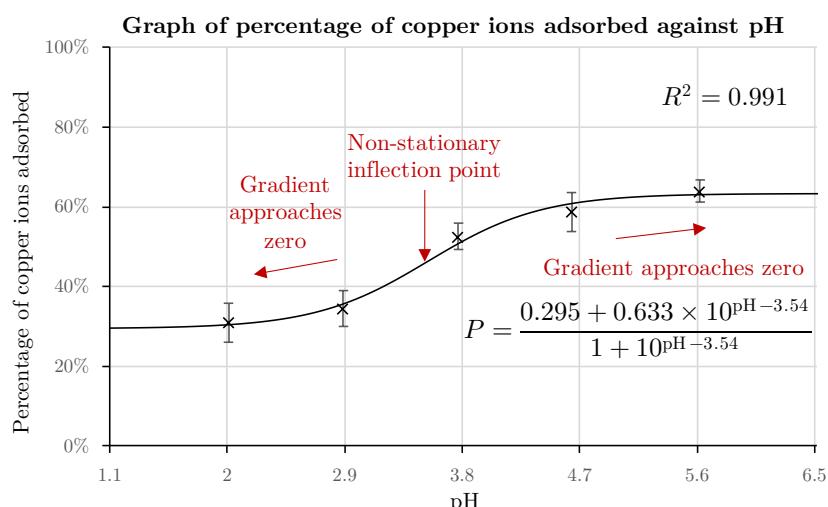


Figure 7. A scatter plot showing the relationship between the percentage of copper ions adsorbed and the pH, with a trendline fitted accordingly to Equation 6.³

² Note that the percentage uncertainty in the molar mass (M_r) in $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ and $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ is assumed to be zero. The uncertainty in the volume of the bottle ($V(\text{bottle})$) is added once only because the same bottle is used before and after the agitation.

³ The trendline fitting is performed using the `scipy` module in Python, a programming language. The code could be found in the Appendix.

4 Analysis

As shown in Figure 7, since the correlation coefficient of the trendline ($R^2 = 0.991$) is very high, there is a very strong positive logistic correlation between the adsorption efficiency and the pH. Regarding the choice of the trendline, because the data points are observed to have a decreasing gradient on both sides of the x -axis (both $\text{pH} \rightarrow -\infty$ and $\text{pH} \rightarrow \infty$), it is not suitable to fit a linear or polynomial trendline. Additionally, because it is observed that there is a non-stationary inflection point at $\text{pH} = 3.54$, or that $\frac{d^2P}{d(\text{pH})^2} = 0$, the use of the logistic trendline is justified. **A: Justified the best fit line**

Since all data points are located within close proximity to the trendline, and that the trendline also passes through the windows of all error bars, the random error can be said to be statistically insignificant.

4.1 Mathematical Interpretation

Recalling from the equation of the relationship between P and pH:

$$P = \frac{\alpha + \beta 10^{\text{pH}-\text{p}K_a}}{1 + 10^{\text{pH}-\text{p}K_a}} \quad (8)$$

As $\text{pH} \rightarrow -\infty$, the sorption sites are fully saturated by H^+ ions, meaning a theoretical **zero** adsorption efficiency. Because $\lim_{\text{pH} \rightarrow -\infty} P = \alpha$, minimum adsorption capacity of the activated carbon α is 29.5%.

As $\text{pH} \rightarrow \infty$, there are no H^+ ions in the solution, meaning a theoretical maximum adsorption efficiency. Because $\lim_{\text{pH} \rightarrow \infty} P = \beta$, maximum adsorption capacity of the activated carbon β is 63.3%.

The $\text{p}K_a$ of the activated carbon is 3.54.

A: Valid conclusion was drawn based on the graphical analysis and mathematical interpretation

4.2 Calculation of the uncertainty in parameters

Because (8) is a nonlinear equation, to calculate the uncertainty in the trendline's parameters ($\Delta\alpha$, $\Delta\beta$, $\Delta\text{p}K_a$), 1,000,000 Monte Carlo simulations have been performed. This process involves⁴:

1. Each data point is uniformly randomly translated by $\text{pH} \in [-\Delta\text{pH}, \Delta\text{pH}]$ and $P \in [-\Delta P, \Delta P]$.
2. Equation (8) is fitted according to the translated data points.
3. Steps 1-2 are repeated for 1,000,000 times, outputting a list of parameters within the windows of errors of the inputs.

As such, the below shows the distribution of the trendlines generated from the simulations (Liu et al):

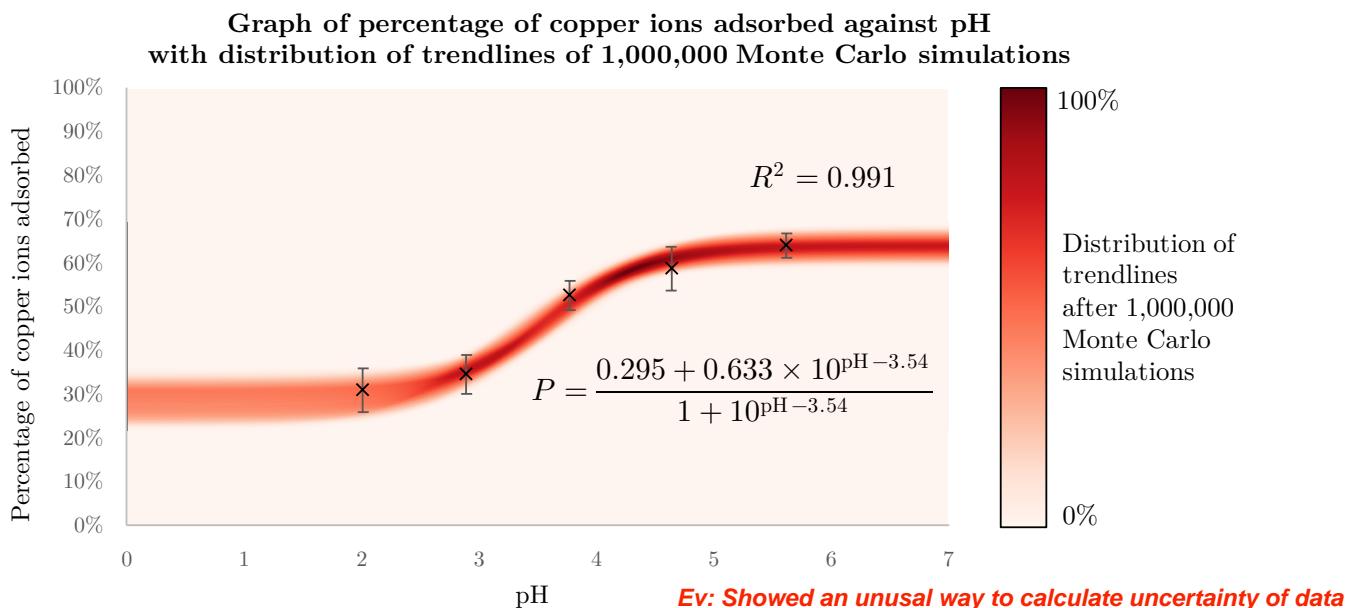


Figure 8. Graph of the distribution of trendlines after 1,000,000 Monte Carlo simulations.

⁴ The code used to perform the Monte Carlo simulations can be found in the Appendix.

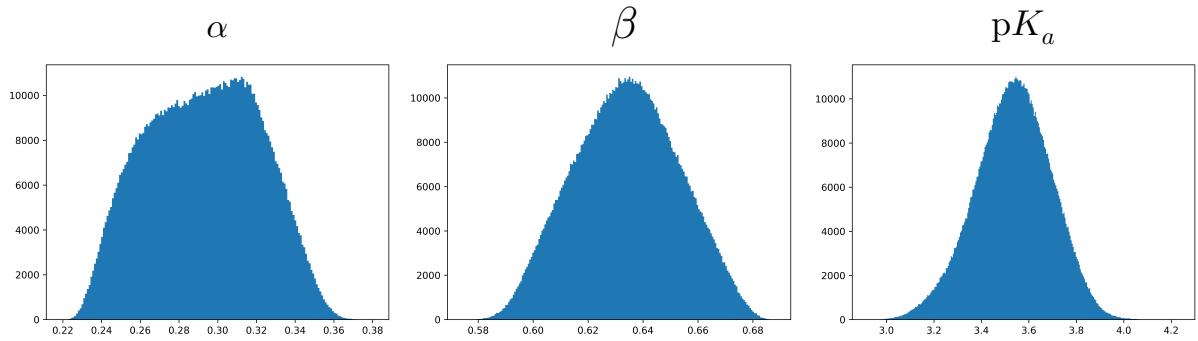


Figure 9. A histogram of the parameters (α , β , pK_a) after 1,000,000 Monte Carlo simulations. From Figure 9, it can be derived that the parameters with uncertainties up to their 95% confidence level is:

α	β	pK_a
$(29.2 \pm 4.7)\%$	$(63.4 \pm 3.1)\%$	3.53 ± 0.27

4.3 Comparison with literature

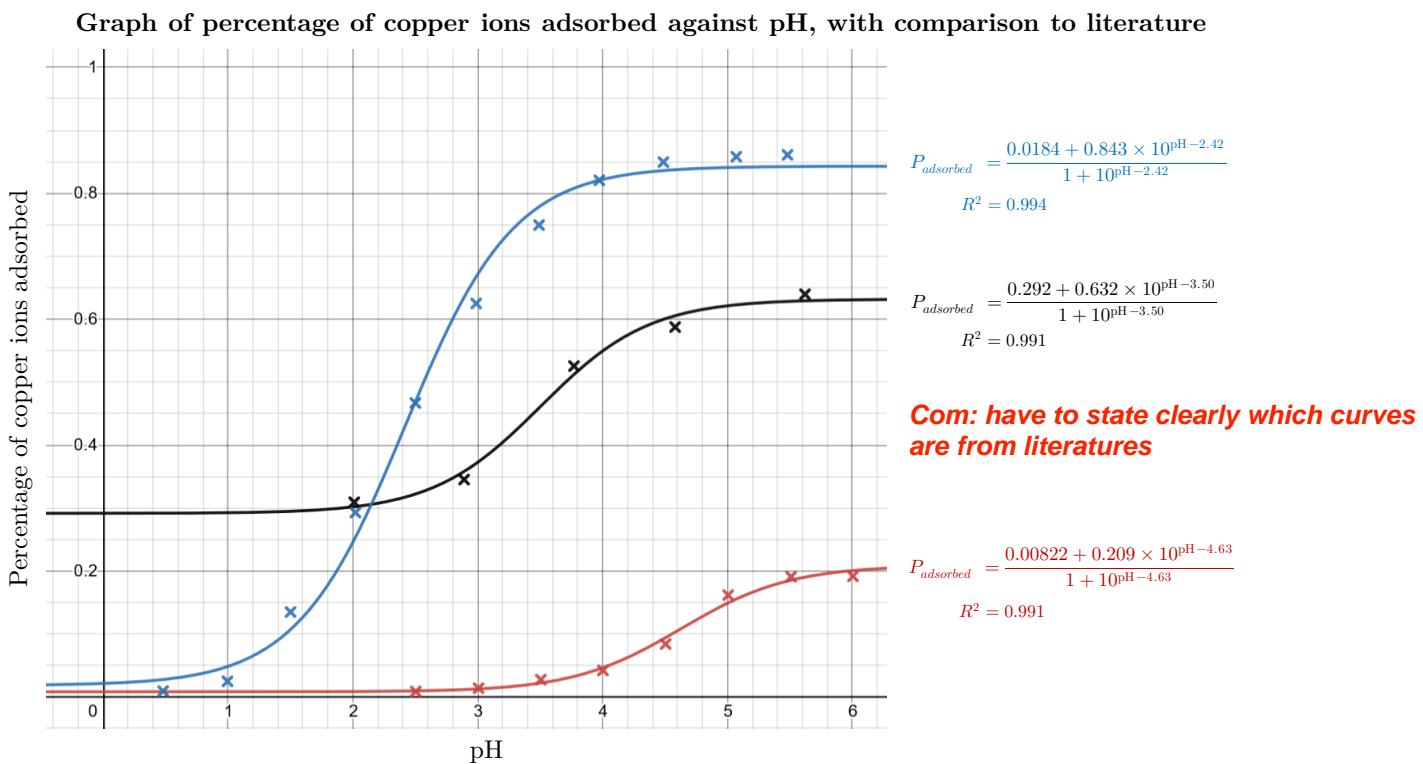


Figure 10. The results of this study compared to the literature (Kim et al., Yu and Kaewsarn). Yu and Kaewsarn investigated the effect of pH on the adsorption characteristics of dried kelp, while Kim et al. also obtained adsorption characteristics of dried biomass. Since both materials are often used as cheap substitutes for activated carbon, they are used to compare with the values of this study. As seen in Figure 2, both literature values appear to have the lower y -asymptote at 0, meaning that the adsorption efficiency is expected to be zero. However, in this study, α is 0.292, indicating that the adsorption capacity at $pH = 0$ is approximately 29.2%. Since this value does not agree with the literature, it is evident that there is a systematic error, showing a constant overestimation in adsorption capacity of $(29.2 \pm 4.7)\%$. Accounting for this systematic error, below is a comparison of the parameters of this study and the literature:

	Maximum Adsorption Efficiency ($\beta - \alpha$)	pK_a	R^2
This Study	(34.2 ± 7.8)%	3.53 ± 0.27	0.991
Kim et al. (2004)	82.5%	2.42	0.994
Yu and Kaewsarn (1999)	20.1%	4.63	0.991
Liu et al. (2010)	44.4%	2.47	0.696
Crist et al. (1990)	--	3.38-3.65	--
Buffle (1988)	--	2.6-4.7	--

Table 1. The literature values for adsorbent dosage 1g/L, initial Cu^{2+} concentration 100mg/L and time of agitation 24 hours.

As seen from above, because the maximum adsorption efficiency (34.2 ± 7.8)% does not fall within any of the literature values (20.1%, 44.4%, 82.5%), the results are unreliable. Similarly, because the pK_a of this study (3.50 ± 0.27) only falls within the range of one literature (Crist et al.), it appears that the reliability of this experiment is low.

5 Conclusion

In conclusion, as seen from Figure 2 and the analysis, there is a very strong positive relationship between the adsorption efficiency and pH, strongly suggesting the initial hypothesis. This can be explained by the fact that at low pH, the high concentration of H^+ causes sorption sites to be protonated, therefore decreasing the ability for Cu^{2+} to bind to the sorption site, and therefore hampering adsorption performance (Schiewer and Volesky, Kuyucak and Volesky).

Since the trendline passes through all error bars, the magnitude of random error is negligible. However, it has been observed that there is a significant systematic error that overestimates the adsorption capacity, which potentially affects the reliability of the final maximum adsorption efficiency. Additionally, since the parameters generally do not fall between the observed literature values, the final results are overall unreliable. The following section will attempt to explain the possible sources of error and offer solutions to the problems and further extensions.

6 Evaluation

Ev: A conclusion is correctly described and justified through relevant comparison to the accepted scientific investigation

Throughout the experimental procedure, multiple precautions have been made such that controlled variables stay constant, for example, the kinetics of the reactions are kept the same by maintaining the same time of agitation, temperature. The procedure has also been done slowly with great care, for example, ensuring that solutions are properly and fully transferred and measuring substances with much attention. However, despite efforts at employing good experimental techniques during all stages, the results still show a significant systematic error, indicating that there is a major flaw in the experimental design.

Source of error	Significance of error	Solutions to the error
Reaction between KI and the air causes the loss of iodide. During the experiment, for a short period of time, the stock solution of KI has been exposed to the air, of which oxidation could happen	Slightly significant in affecting the systematic error, because this reduces the amount of $\text{S}_2\text{O}_3^{2-}$ required to titrate the remaining copper	Adding Na_2CO_3 into the solution releases heavy CO_2 gas, reducing the magnitude of oxidation from occurring (Hammock and Swift)

When preparing the KI solution, only 10% excess of KI has been added., and	Considering that iodine is highly volatile and can evaporate in the air, it reduces the amount of $S_2O_3^{2-}$ required for the titration, hence slightly increases the systematic error.	Add a significant excess amount of iodine and perform the experiment as quick as possible.	Ev: <i>Sources of error listed. Better to evaluate the impact of each to your final results. Some of them seemed minor.</i>
Starch solution is slightly milky.	This may have affected the quality and endpoint determination of the titration, causing a slight systematic error.	In order for the colour change to be accurate and stark, fresh starch solution should be prepared.	
Speed of agitation is not the same, as the knobs on the magnetic stirrer did not have an absolute scale or system to ensure a constant rotational speed	This slightly amplifies the random error but the effect is rather negligible because the speed is already turned to the maximum, which can be perceived as the same.	Use a magnetic stirrer with a specific rpm toggle.	
Conical flask used throughout the experiment is observed to be stained with iodine which is hard to be washed away	This may cause random fluctuations in the true iodine titrated, but because the volume of the stain is insignificant, the random error is negligible.	Wash the conical flask after every trial.	

To further extend on this topic, a wider range of pH should be used to increase data representativeness. Since adsorption is also a thermodynamic and temporal process, by testing the adsorption efficiency against other independent variables such as metal concentration, dosage and agitation time, a full isotherm and profile of the activated carbon can be constructed, of which can be used by companies to accelerate the development of sewage systems around the world. **Ev: Showed extension of the investigation**

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8 Appendix

8.1 Code used to process raw data and perform Monte Carlo simulations

Language: Python 3.8.10

External modules used: numpy 1.19.5, rich 9.10.0, scipy 1.6.0, pandas 1.1.2

```
import numpy as np
from rich import print, inspect
from rich.progress import Progress
from scipy.optimize import curve_fit
import pandas
from timeit import default_timer as timer

m_na2s2o3, Δm_na2s2o3 = 0.195, 0.001 # g
mr_na2s2o3, Δmr_na2s2o3 = 248.19, 0 # g mol⁻¹
v_s2o3_sol, Δv_s2o3_sol = 0.5000, 0.0025 # dm³
v_flask, Δv_flask = 0.02500, 0.00003 # dm³
v_bottle, Δv_bottle = 0.12500, 0.00015 # dm³
m_cuso4, Δm_cuso4 = 0.196, 0.001 # g
mr_cuso4, Δmr_cuso4 = 249.69, 0 # g mol⁻¹
v_beaker, Δv_beaker = 0.5000, 0.0025 # dm³

class SampleSet:
    def __init__(self) -> None:
        exp = [(pH, (e0+e1+e2)/3e3, ((max(e0,e1,e2)+0.1)-(min(e0,e1,e2)-0.1))/2e3) for pH, (e0, e1, e2) in (
            (2.01, (16.45, 18.11, 16.97)),
            (2.89, (16.31, 15.68, 17.19)),
            (3.77, (12.45, 12.09, 11.38)),
            (4.64, (9.34, 9.97, 11.31)),
            (5.62, (9.56, 8.57, 8.75)),
        )]
        self.pH = [] # dimensionless
        self.V_s2o3 = [] # dm³
        self.dV_s2o3 = [] # dm³
        self.pctAgitated = []
        self.pctAgitatedError = []

        print('[green]Processing raw data...!')
        for e in exp:
            self.pH.append(e[0])
            self.V_s2o3.append(e[1])
            self.dV_s2o3.append(e[2])
            pctAgitated = self.calculate_pctAgitated(e[1])
            self.pctAgitated.append(pctAgitated)
            self.pctAgitatedError.append(self.calculate_pctAgitated_error(e[1], e[2], pctAgitated))

    def calculate_pctAgitated(self, v:float) -> float:
        n_cu_postAgitation = (m_na2s2o3*v_bottle*v)/(mr_na2s2o3*v_s2o3_sol*v_flask)
        n_cu_preAgitation = (m_cuso4*v_bottle)/(mr_cuso4*v_beaker)

        return 1 - n_cu_postAgitation/n_cu_preAgitation

    def calculate_pctAgitated_error(self, v:float, Δv:float, pctAgitated:float) -> float:
```

```

    return sum([
        # post agitation
        Δm_na2s2o3 / m_na2s2o3,
        # Δmr_na2s2o3 / mr_na2s2o3,
        Δv_s2o3_sol / v_s2o3_sol,
        Δv_flask / v_flask,
        Δv_bottle / v_bottle,
        Δv / v,

        # pre agitation
        Δm_cuso4 / m_cuso4,
        # Δv_bottle / v_bottle, # removed because the initial and final volume of the beaker are the same.
        # Δmr_cuso4 / mr_cuso4,
        Δv_beaker / v_beaker,
    ]) * (1 - pctAgitated)

def regression_function(self, pH:float, a:float, b:float, c:float) -> float:
    e = 10***(pH-c)
    return (a+b*e)/(1+e)

def run_montecarlo(self, iterations:int) -> list:
    paramMatrix = []
    regression_function = self.regression_function

    xVals, xValLen = np.array(self.pH), len(self.pH)
    yVals = np.array(self.pctAgitated)
    yError = np.array(self.pctAgitatedError)

    with Progress() as progress:
        task = progress.add_task(f'[green]Running {iterations} simulations...', total=iterations)

        start = timer()
        for iterCount in range(iterations):
            rng = np.random.default_rng()
            x_randomShift = xVals + rng.uniform(-0.01, 0.01, xValLen)
            y_randomShift = yVals + rng.uniform(-yError, yError)

            try:
                a, b, c = curve_fit(
                    f=regression_function,
                    xdata=x_randomShift,
                    ydata=y_randomShift,
                    p0=(0.288889522729405, 0.630477731089562, 3.490845036064320) # initial guesses for a, b, c
                )[0]
                paramMatrix.append((a, b, c, regression_function(0, a, b, c)))
            except RuntimeError:
                print('[red]failed!')

            if iterCount % 1000 == 0:
                progress.update(task, advance=1000)

        end = timer()
        print(f'[green]Completed {iterations} MC simulations in {end-start} seconds.')

    self.paramMatrix = paramMatrix

if __name__ == '__main__':
    ss = SampleSet()
    ss.run_montecarlo(iterations=1000000)
    print('Writing to file...')
    df = pandas.DataFrame(ss.paramMatrix, columns=['a', 'b', 'c', 'yint'])
    df.to_csv('out/main.csv', index=False)

```

8.2 Code used to generate histograms

Language: Python 3.8.10

External modules used: numpy 1.19.5, rich 9.10.0, scipy 1.6.0, pandas 1.1.2, matplotlib 3.3.4, pydlc 0.2

```
import pandas as pd
from rich import print, inspect
from rich.progress import Progress
from matplotlib import pyplot as plt
import numpy as np
from scipy import stats
from pydlc import dense_lines
from montecarlo import SampleSet

def freedman_diaconis(d):
    data = np.array(d, dtype=np.float64)
    binwidth = 2*stats.iqr(data, rng=(25, 75))/np.power(data.size, 1/3)
    bincount = int(((data.max() - data.min()) / binwidth)) or 1
    return bincount

if __name__ == '__main__':
    main = pd.read_csv('out/main.csv')
    ss = SampleSet()
    print('[green]Finished reading MC simulations.')
    for col in main:
        data = main[col]
        lower, upper = np.quantile(data, 0.05), np.quantile(data, 0.95)
        print(col, lower, upper)

        plt.hist(data, bins=freedman_diaconis(data))
        plt.savefig(f'out/{col}_histogram.png', dpi=600)
        plt.clf()

    x = np.arange(0,7,0.01, dtype=np.float32)
    with Progress() as progress:
        iterations = 1000000 # to conserve RAM
        task = progress.add_task('[green]Drawing lines from MC simulations', total=iterations)
        ys = []
        for idx, (a, b, c, _yint) in main.iterrows():
            ys.append(ss.regression_function(x, a, b, c))
            if idx % 1000 == 0:
                progress.update(task, advance=1000)
            if idx > iterations:
                break

    print('[green]Drawing line density plot')
    im = dense_lines(ys, x, cmap='Reds', ny=600)
    plt.colorbar(im)
    plt.savefig('out/density.png', dpi=600)
```