

Investigating the efficiency of sawdust and sawdust ash in the removal of crystal violet dye in aqueous media using ultrasound

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Abstract

Industrial wastewater discharge contains high amounts of heavy metal ions and dyes, which poses a serious threat to the environment, and to those who depend on such water bodies. While there are methods of removing such pollutants such as using activated carbon as an adsorbent, such methods are costly and uneconomical. An alternative would be sawdust, which is a common waste product of furniture making, and is widely regarded as an active ingredient in water purification of metal ions and textile dyes. This study aims to investigate the effectiveness of using *Tectona Grandis* (teak) sawdust as an adsorbent for crystal violet (CV) dye, a common yet carcinogenic and mutagenic textile dye found in factory wastewater. By varying adsorbent dosage, initial dye concentration and sonication time, optimization can be conducted to obtain optimal parameters for the adsorption of CV using teak. After which carbonisation of the sawdust can be carried out. Results of this investigation show that sonication had limited effect on the ability of treated sawdust to remove CV. Data fitted the Langmuir isotherm model better, indicating that the adsorption of CV is monolayer with a high percentage removal of CV at 99.6% after only 24 h of contact time, rendering it an affordable but effective adsorbent for initial purification.

1. Introduction

According to a recent study, it is estimated that nearly 790 million people lack access to clean water (WHO & UNICEF, 2019). Clean water is vital to good health as consuming water contaminated by organic pollutants is shown to bring about adverse health effects (Mashkoo et al., 2018). Dyes are often from a synthetic origin such as originating from waste products of factories such as those in the textile industry. Crystal violet (CV) is an example of such dye. It is a common dye in many common day objects such as various types of ink and textiles. This dye may be present in wastewater and, when exposed to it, may cause numerous health problems in

humans such as skin irritation, respiratory diseases, and mental disorders, and in some cases may even be carcinogenic and mutagenic (Mashkoo et al., 2018). Being cationic in nature (Fig 1.1), it is more toxic than anionic dyes as it can easily form interactions with negatively charged membrane surfaces and can enter cells (Rehman et. al., 2017), making it more toxic than anionic dyes. As such, it is vital that it be removed from wastewater to improve and maintain the health of people and the marine life dependent on the water body. However, most dyes have high thermal and photostability and thus are hard to decompose because of their stable structure and synthetic origin (Forgacs et al., 2004).

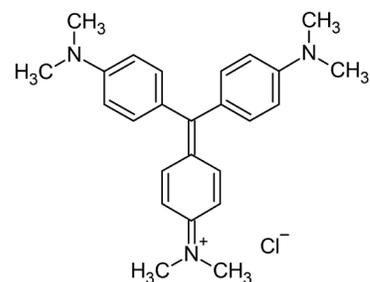


Figure 1.1. Molecular structure of CV

While traditional adsorbents such as silica gel or activated carbon are plausible tools for purifying the water, it may not necessarily be the most economically viable option due to their high costs and regeneration issues. Sawdust are viable alternatives to that of commercial clean-up tools due to its cheap prices and its characteristics. Sawdust has lignocellulosic material that is associated with its ability to act as an adsorbent. The adsorption of organic pollutants can be attributed to intraparticle diffusion interactions between the cationic dyes and the negatively charged surfaces of the sawdust (Sahmoune et al., 2015). Furthermore, 52% of wood used in factories for carpentry and furniture-making is disposed of as sawdust, as there are no practical uses for them (U.S. Department of Agriculture, 1969; Zafar, 2021). As such, sawdust is an extremely suitable material for the adsorption of dyes and pollutants due to its economic viability and the fact that by doing so it is recycling waste materials.

One possible type of sawdust for the removal of the CV dye is by using *Tectona grandis* (teak). Teak may be considered as an adsorbent due to its unique weather resistant qualities and ease of obtainment as it is the waste product of extraction activities (Palanisamy et al, 2009). *Tectona Grandis* sawdust (TGSD) is put forth as being viable as it is biodegradable and has an affinity for water (Can et al., 2015). According to Mashkoo et al. (2018), another reason why teak is such an effective medium for water purification is due to the abundant amounts of lignin, cellulose, hemicellulose, and functional groups such as polar hydroxyl, carboxyl, and amine

groups. The cationic dyes are attracted to the negatively charged functional groups such as deprotonated $-OH$ ($-O^-$) and deprotonated $-CO_2H$ ($-COO^-$). This results in strong electrostatic forces of attraction between these oppositely charged ions between ions of CV and those present in sawdust. It is even hypothesized that there may be strong hydrogen bonds present between polar groups (O^- and COO^-) in sawdust and charged centres CV that are responsible for its adsorption capacity (Fig 1.2) (Mashkoo et al., 2018). As such, teak is a great adsorbent as it contains useful functional groups that contribute to adsorption of pollutants.

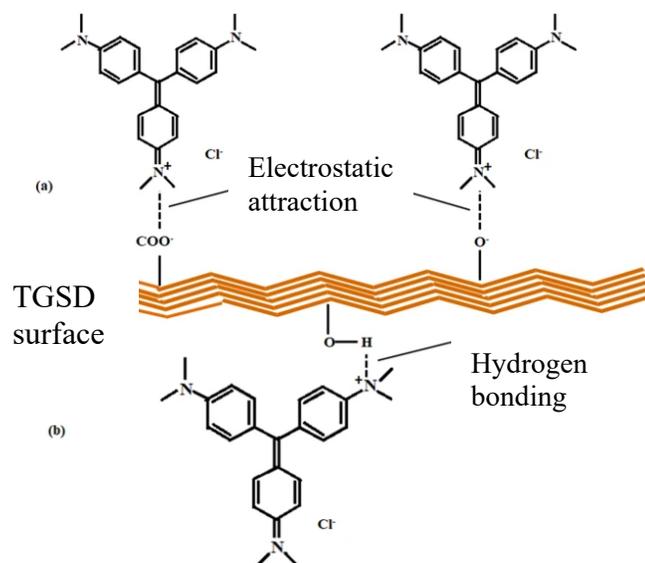


Figure 1.2. Theorised mechanism for the adsorption of CV onto the surface of sawdust

There are a few factors that influence the adsorption of CV onto TGSD, including pH level and sonication. The pH of the solution also has a significant effect on the adsorption efficiency of the TGSD. When the pH of the solution increased from 3 to 7, there was a significant increase in the adsorption efficiency of the sawdust. This is because the increase in the pH of the solution resulted in stronger electrostatic forces of attraction between the CV dye and the TGSD surface (Mashkoo et al., 2018). The increase in pH has resulted in the TGSD surface becoming more negatively charged due to the deprotonating of the functional group present on the adsorbent. The deprotonated functional group allowed for more binding sites for the cationic CV dyes, which increased the adsorption efficiency of TGSD. Results showed that the optimal pH level is 7.5, and this will be used in the experiments.

According to Potrich et al. (2017), ultrasound is a viable method for purifying wastewater containing CV dyes. When an ultrasound of the right frequency is used, bubbles of high pressure are created which may burst at high temperatures, allowing organic contaminants such as CV to degrade, therefore being removed effectively (Fig 1.3).

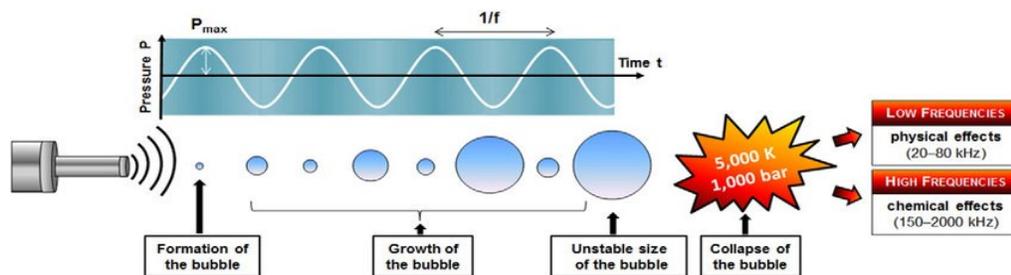


Figure 1.3. How sonication works (Chatel et al., 2015)

Up to date, there are no studies researching the effect of sonication on the adsorption capacity of TGSD. As such, this study aims to investigate and determine the optimal sonication time for adsorption of CV using TGSD as an adsorbent, and to experiment with different concentrations of initial CV dyes to find the optimal ratio of TGSD to CV dye. Further, this study also aims to determine whether carbonisation of the sawdust had any impact on the adsorption capacity of TGSD.

1.1 Objectives

1. Determine the optimal parameters for TGSD to be used in an experiment to adsorb CV
2. Determine the efficiency of ultrasound in removing CV dyes by oxidation and the degradation of CV
3. Compare and contrast the difference between the efficacy of carbonised and raw sawdust in the removal of CV

1.2 Hypothesis

Modification of the teak sawdust will lead to an increase in the adsorption of CV dye

2. Materials and Methods

2.1 Materials

Teak sawdust was obtained from sawing planks of teak wood bought on Amazon and collecting the sawdust. Crystal violet ($C_{25}N_3H_{30}Cl$) was obtained from Sigma Aldrich. Other miscellaneous chemicals used in the experiments were obtained from Hwa Chong Institution's Science Research Centre.

2.2 Methods

2.2.1 Preparation and Treatment of sawdust

Teak flooring planks purchased on Amazon were sawed and the sawdust was obtained. After several washings of the sawdust with deionised water to remove impurities, it was then left to dry in an oven at 373 K for 24 hours. For carbonisation of the sawdust, 50 g of raw teak sawdust was calcined in a furnace at 573 K for 30 minutes to carbonize the raw sawdust to increase the amount of carbon present in sawdust.

2.2.2 Degradation studies

2.2.2.1 Calibration curve for CV dye

Calibration curve of dye was prepared by diluting 50 ppm of stock dye solution to solutions of different concentrations. The absorbance of each concentration was measured at wavelength 590 nm (Fig 2.1) (Rehman et. al., 2017) with a UV-VIS spectrophotometer (Shimadzu UV 1800). Graphs of absorbance against concentration were plotted. The calibration curves (Appendix A) were used to determine the concentration of CV dye in all subsequent experiments.

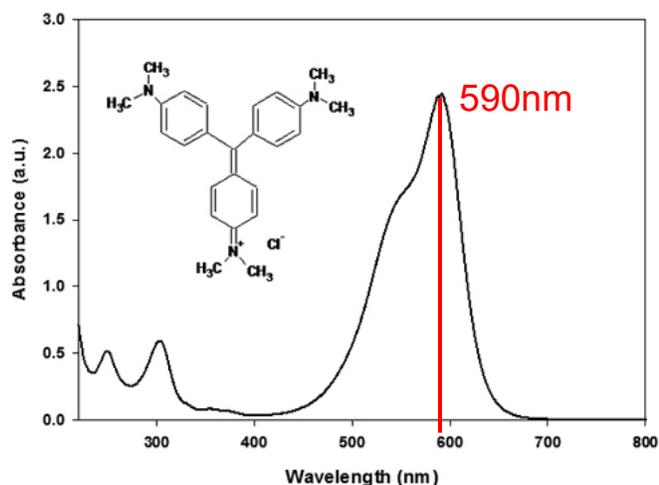


Figure 2.1. UV absorption spectrum of CV solution

2.2.2.2 Adsorption of CV dye

Varying masses of untreated and treated sawdust was separately added to 50ml of CV dye with concentrations varying from 25ppm to 150ppm. The mixture was then sonicated for 5 minutes to 15 minutes, before the supernatant was retrieved and analysed using a UV-Vis spectrophotometer. The percentage of CV dye removed was calculated using the following formula:

$$\text{Percentage removed} = \frac{\text{Initial concentration} - \text{Final concentration}}{\text{Initial concentration}} \times 100\%$$

2.2.3 Optimization studies

2.2.3.1 Varying mass of untreated and treated sawdust

The mass of untreated and treated sawdust ranged from 0.30 g L⁻¹ to 87.5 g L⁻¹ at a constant temperature. Adsorption studies listed in 2.2.2.2 were then conducted with a fixed concentration of CV dye and sonication duration.

2.2.3.2 Varying sonication duration

The duration of sonication was varied from 5 minutes to 15 minutes at a constant temperature. Adsorption studies listed in **2.2.2.2** were then conducted with a fixed concentration of CV dye and mass of untreated sawdust and treated sawdust.

2.2.3.4 Varying concentration of CV dye

The concentration of CV dye added varied from 25 ppm to 150 ppm at a constant temperature. Adsorption studies listed in **2.2.2.2** were then conducted with a fixed mass of untreated and treated sawdust and sonication duration.

2.2.4 Adsorption isotherm

Adsorption isotherms were determined by carrying out **2.2.3.4** at a constant pH, equal sonication time and adsorbent dosage. Equilibrium concentrations were then fitted into Langmuir and Freundlich isotherms (Appendix **B**).

2.2.5 Adsorption kinetics

The kinetics behind the adsorption of CV onto TGSD were determined by making time the independent variable, while keeping initial concentration of CV at 25 ppm, sonication time at 0 min, and adsorbent dosage at 7.00 g/L. Concentrations at intervals of 20 min were calculated and the results were fitted to the three most used kinetic models, namely pseudo-first order, pseudo-second order, and intraparticle diffusion (Appendix **C**).

3. Results and Discussions

3.1 Optimization studies

Results collected from this study was plotted in MATLAB to obtain Fig 3.1 and for optimisation as stated in 1.1. Through optimisation services provided by MATLAB, optimal parameters for the adsorption of CV were found as such:

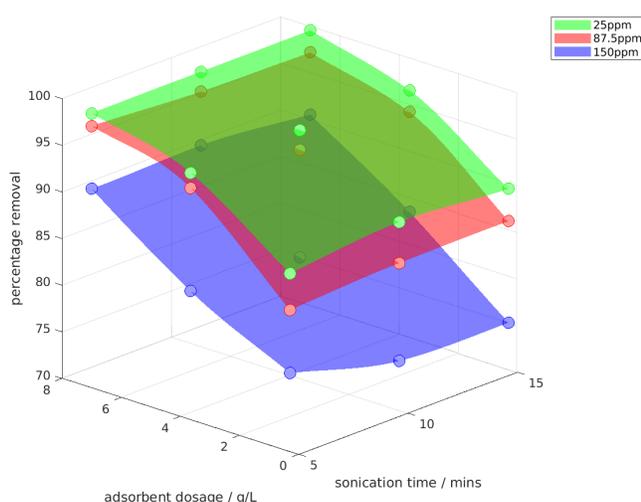


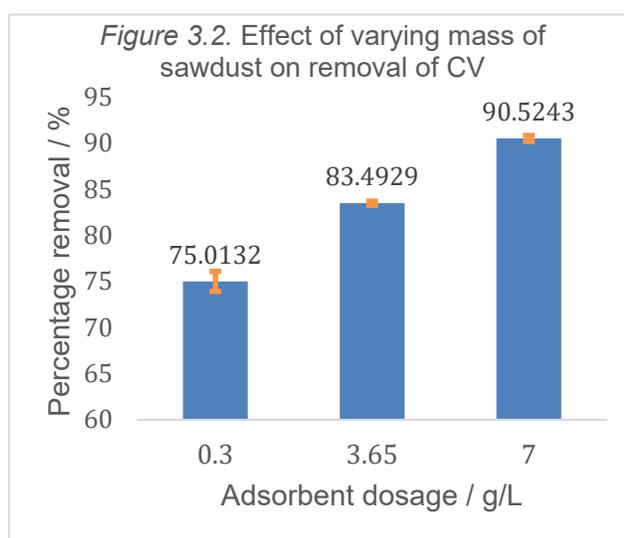
Figure 3.1. Overall results for optimization studies

Adsorbent dosage (g/L)	Sonication time / min	Initial concentration (ppm)
4.90	5.00	54.1

This result will be used in a subsequent experiment involving the efficiency of carbonised sawdust on the adsorption of CV.

3.1.1 Effect of varying mass of untreated sawdust

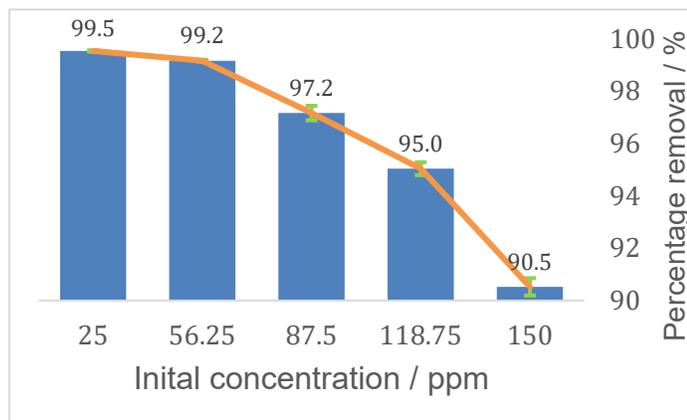
Results from this study indicated that percentage removal varied linearly to the amount of adsorbent present during the adsorption. This suggests that it would fit the Langmuir isotherm better as it assumes adsorption is monolayer which is confirmed in Appendix B. However, this might be limited as the same might not be said to higher adsorbent dosage.



Sonication time = 15 min, initial concentration = 150 ppm

3.1.2 Effect of varying initial concentration

Adsorption studies of CV onto TGSD showed how initial concentration affected the percentage removal of CV (Fig 3.3). As expected, when the initial concentration increases, the percentage absorbed decreases. However, the relationship is not linear, which means the change in percentage removal increases, which could be due to the TGSD still having available adsorption sites for CV to interact with and be adsorbed.

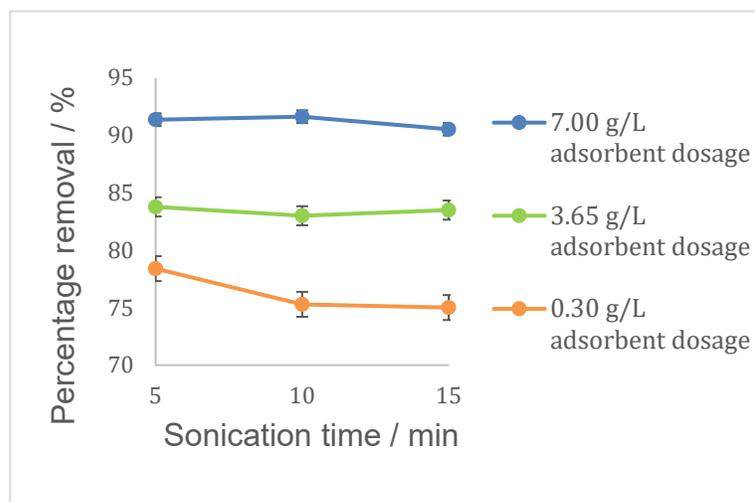


Sonication time = 15 min, adsorbent dosage = 7.00 g/L

Figure 3.3. Effect of initial concentration on removal of CV

3.1.3 Effect of sonication time

Overall, sonication showed no improvement to the adsorption capacity of TGSD as seen in Fig 3.4. This could have been due to the frequency of the sonication being too low to agitate the CV molecules to induce adsorption, or the sonication time being too short to see any significant impact, suggesting that there is a threshold to cross for frequency and time before sonication has an impact on the adsorption of CV.



Initial concentration = 150 ppm

Figure 3.4. Effect of sonication time on removal of CV

3.1.4 Effect of carbonisation

Results clearly show that carbonising the sawdust had negative impact on adsorption capacity. A possibility could be that calcining reduced the amount of negatively charged functional groups responsible for interacting with CV. Another possibility could be due to the absence an activating agent during the process, like $ZnCl_2$ listed in some literature review. This resulted in the wood just being in a burnt state, where actual carbonisation and activation did not occur.

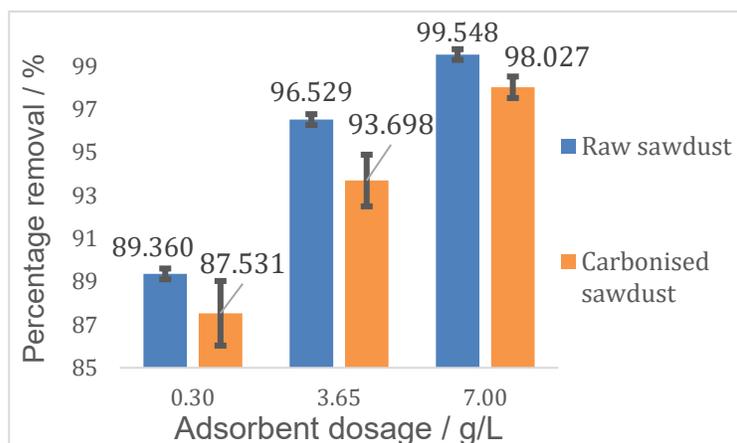


Figure 3.5. Effect of sonication time on removal of CV

3.2 Adsorption studies

The equilibrium concentration obtained from this study was fitted into the Langmuir and Freundlich isotherms (Appendix B). Langmuir isotherm was a better fit, suggesting that the adsorption of CV onto TGSD is monolayer. The maximum adsorption capacity was calculated from the plots which came out to be around 16.5 mg/g for TGSD, and 16.2 mg/g for carbonised TGSD for an adsorbent dosage of 7.00 g/L. Comparing both values, it shows that carbonising had little impact on the adsorption of CV, or the carbonisation process was flawed.

3.3 Adsorption kinetics

The concentration at intervals of 20 min obtained from this study were fitted into pseudo-first order, pseudo-second order and intraparticle diffusion models (Appendix C). The R^2 value obtained for the pseudo-second order kinetics was significantly higher than that of pseudo-first order and intraparticle diffusion, indicating that the adsorption of CV followed a pseudo-second order kinetics, where the rate limiting step is chemisorption.

4. Conclusions and Future Work

4.1 Conclusions to objectives

TGSD was successful in removing CV from a CV solution. A short sonication time had little to no impact on the adsorption capacity of TGSD. It was observed that the adsorption capacity of TGSD was directly influenced by a few factors including initial concentration, adsorbent dose, and contact time. The adsorption of CV was proved to be monolayer on a homogenous adsorbent surface, and follows a pseudo-second-order kinetics, where maximum adsorption is reached at around 140 min. Carbonisation failed to improve the adsorption capacity of TGSD due to the removal of negatively charged functional groups responsible for the removal of cationic dyes like CV.

4.2 Limitations

While the experiment sought to find out if carbonisation had any effect on the adsorption capacity of TGSD, other forms of modifications such as magnetisation was not investigated due to time constraints from COVID-19 and shipment of the wood. Given that the species of sawdust used may affect its percentage of CV adsorbed, there is uncertainty pertaining to whether the ideal parameters found by this experiment can be replicated by other species of sawdust. Furthermore, certain constant variables such as pH and contact time were decided on by literature reviews and thus their impact on the adsorption capacity was not confirmed in this study.

4.3 Future work

In the future, different species of sawdust could be used to determine if the ideal parameters found could hold true amongst them. Investigations about the effect of sonication could also be extended to other species of sawdust. Other variables such as pH of the solution and contact time between TGSD and the solution could be investigated independently to determine its impact on the percentage of CV dye adsorbed by the sawdust. Characterisation of raw sawdust, carbonised sawdust and sawdust loaded with CV can also be done through Fourier Transform Infrared (FTIR), X-ray Diffraction (XRD) and Scanning Electron Microscopy (SEM). Finally, thermodynamics studies could also be conducted to gain more insight to the adsorption mechanism of CV onto TGSD.

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Appendix A: Calibration curve

The absorbance of varying concentrations of CV ranging from 0.25 ppm to 3 ppm were used to plot a calibration curve (Fig A.1), which was subsequently used for the remainder of the project to determine the concentrations of the solutions after the experiments. Results of the data collection are reflected in Table A.1.

Concentration / ppm	Absorbance / Au
0.25	0.169
0.5	0.220
0.75	0.302
1	0.397
1.25	0.535
1.5	0.629
1.75	0.693
2	0.761
3	1.1

Table A.1. Values used to create calibration curve

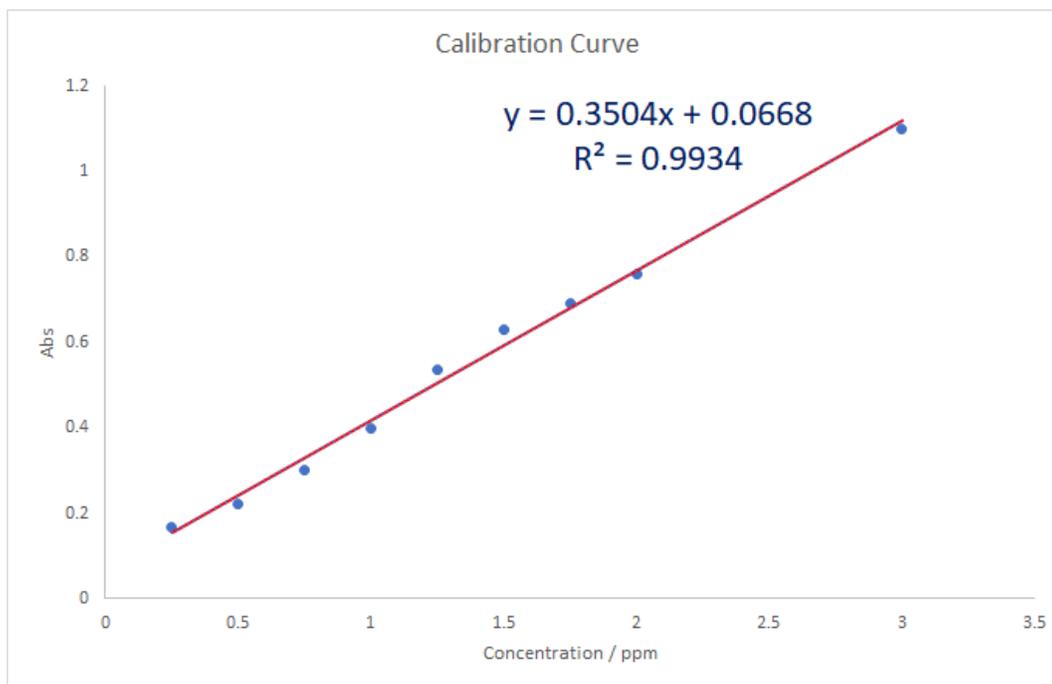


Figure A.1. Calibration curve

Appendix B: Adsorption isotherms

The equilibrium concentration data obtained from adsorption isotherm studies of the adsorption of CV were fitted onto Langmuir and Freundlich's isotherms.

Langmuir isotherm assumes that the adsorbate is adsorbed over a uniform layer on the adsorbent at a constant temperature, or simply the adsorption is monolayer. The linear form used for this study is given by

$$\frac{1}{q_e} = \frac{1}{q_m b} \cdot \frac{1}{C_e} + \frac{1}{q_m}$$

where q_e is the equilibrium adsorption capacity of TGSD (mg/g), q_m is the maximum adsorption capacity (mg/g), C_e is the equilibrium concentration of CV, and b is the Langmuir constant, which indicates the extent of interaction between adsorbate and the surface.

From the Langmuir constant b , an equilibrium parameter, R_L , can be determined using the following equation

$$R_L = \frac{1}{1 + bC_0}$$

where C_0 is the highest concentration used for fitting the isotherms (mg/L). The value of R_L determines how favourable the adsorption is, as follow:

$R_L = 0$	Adsorption is irreversible
$0 < R_L < 1$	Adsorption is favourable
$R_L > 1$	Adsorption is unfavourable

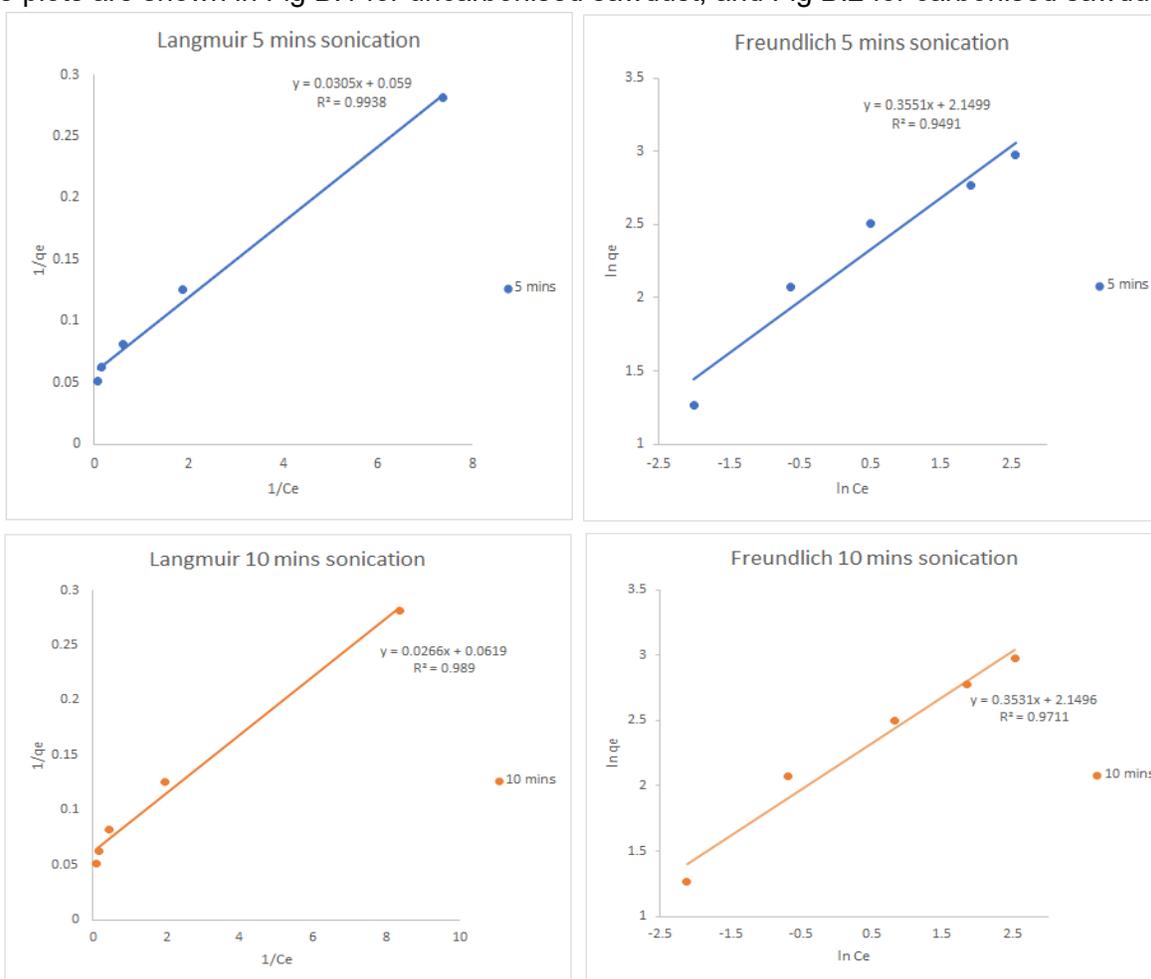
Freundlich isotherm is the opposite of Langmuir, where it assumes that the adsorbate is adsorbed on a heterogeneous surface at constant temperature, or simply the adsorption is multi-layer. The linear form used for this study is given by

$$\ln q_e = \frac{1}{n} \ln C_e + \ln K_F$$

where q_e is the equilibrium adsorption capacity of TGSD (mg/g), C_e is the equilibrium concentration of CV, K_F is the Freundlich constant, and n describes the linearity of the adsorption and adsorption intensity as follows:

$n < 1$	Adsorption is a chemical process
$n = 1$	Adsorption is linear
$n > 1$	Adsorption is a physical process
$n < 1$	Unfavourable sorption
$1 < n < 10$	Favourable sorption

The plots are shown in Fig B.1 for uncarbonised sawdust, and Fig B.2 for carbonised sawdust.



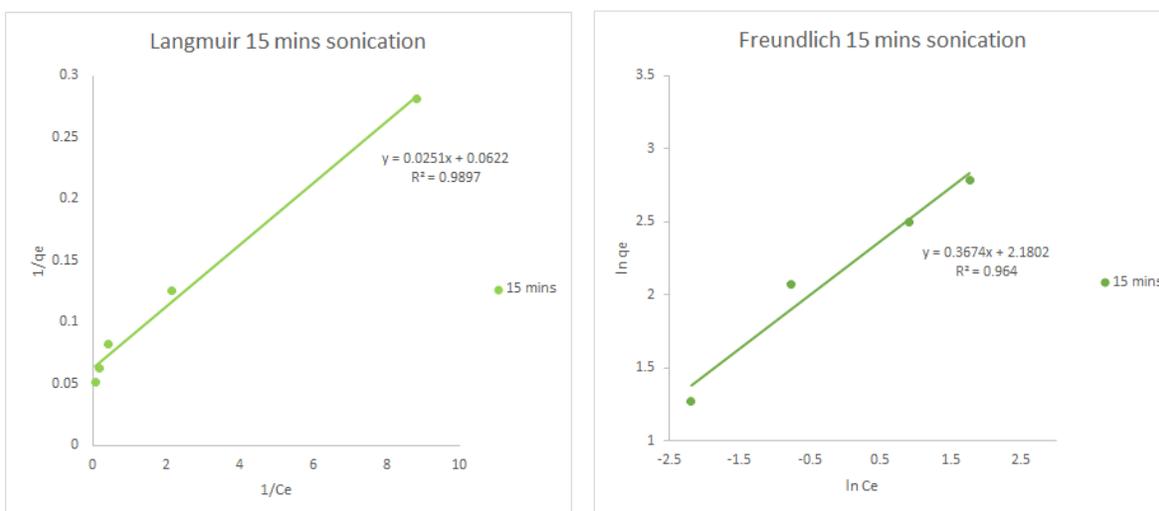


Figure B.1. Langmuir and Freundlich isotherm models for 7.00 g/L adsorbent dosage

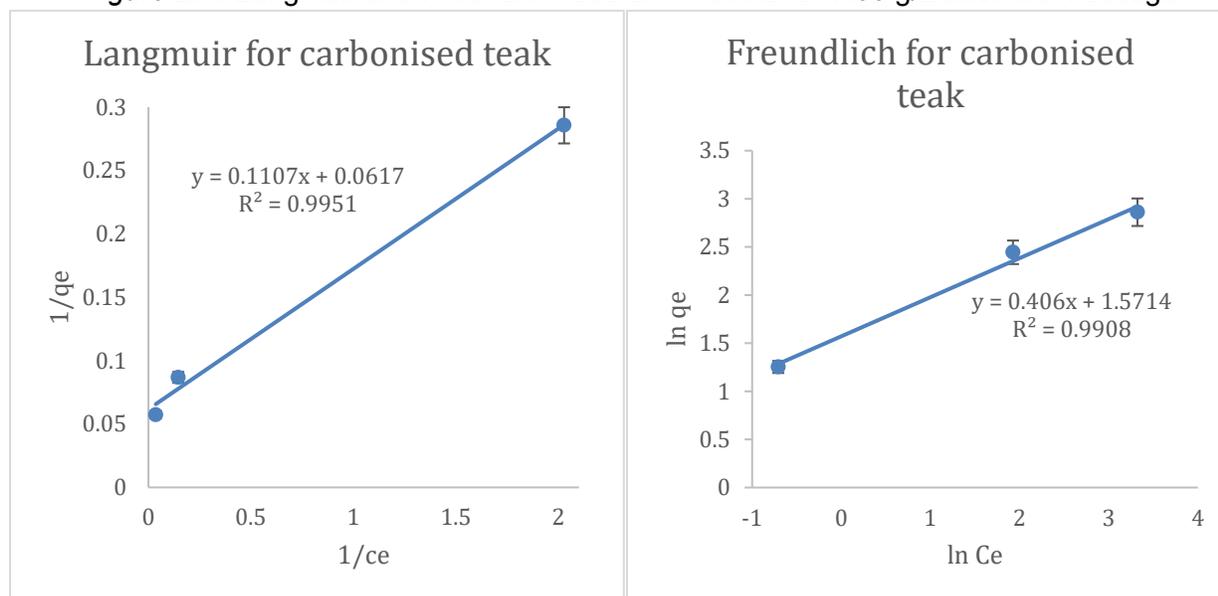


Figure B.2. Langmuir and Freundlich isotherm models for carbonised sawdust, 7.00 g/L adsorbent dosage

Type	Sonication time / min	Langmuir				Freundlich		
		q_m (mg/g)	b (L/mg)	$R_L = \frac{1}{1+bC_0}$	R^2	n	K_F	R^2
Uncarbonised sawdust	5	16.9	1.93	0.00343	0.994	2.82	8.58	0.949
	10	16.2	1.69	0.00393	0.989	2.83	8.58	0.971
	15	16.1	2.48	0.00268	0.990	2.72	8.85	0.964
Carbonised sawdust	15	16.2	2.02	0.00328	0.995	2.46	4.81	0.991

Table B.1. Parameters for the adsorption of CV onto TGSD

Comparison of the R^2 values for both isotherms indicates that the Langmuir isotherm was a better fit for the adsorption of CV onto TGSD for both carbonised and uncarbonised sawdust, as confirmed by Mashkoo et. al. (2018). Furthermore, the R_L value is between 0 and 1, i.e., $0 < R_L < 1$, indicating that the Langmuir adsorption isotherm was favourable. In addition, the value of n of the Freundlich isotherm is greater than 1, suggesting that the mechanism of the adsorption of CV is likely to be a physical process, possibly through hydrogen bonding or electrostatic interactions between ions.

Appendix C: Adsorption kinetics

The equilibrium concentration data obtained from adsorption kinetics studies of the adsorption of CV were fitted onto pseudo-first order, pseudo-second order and intraparticle diffusion models.

The pseudo-first order model assumes that the rate of change of CV uptake with time is directly proportional to difference in saturation concentration and the amount of CV uptake. The linear form of the Lagergren pseudo-first order model used for this study is

$$\ln(q_e - q_t) = \ln q_e - k_1 t$$

where q_e and q_t are the amounts of the amount adsorbed at equilibrium and at time t respectively, k_1 is the rate equilibrium rate constant for the pseudo-first order model.

The pseudo-second order model assumes that the rate-limiting step is chemical sorption or chemisorption and predicts the behaviour over the whole range of adsorption. The linear form of the pseudo-second order model used for this study is

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t$$

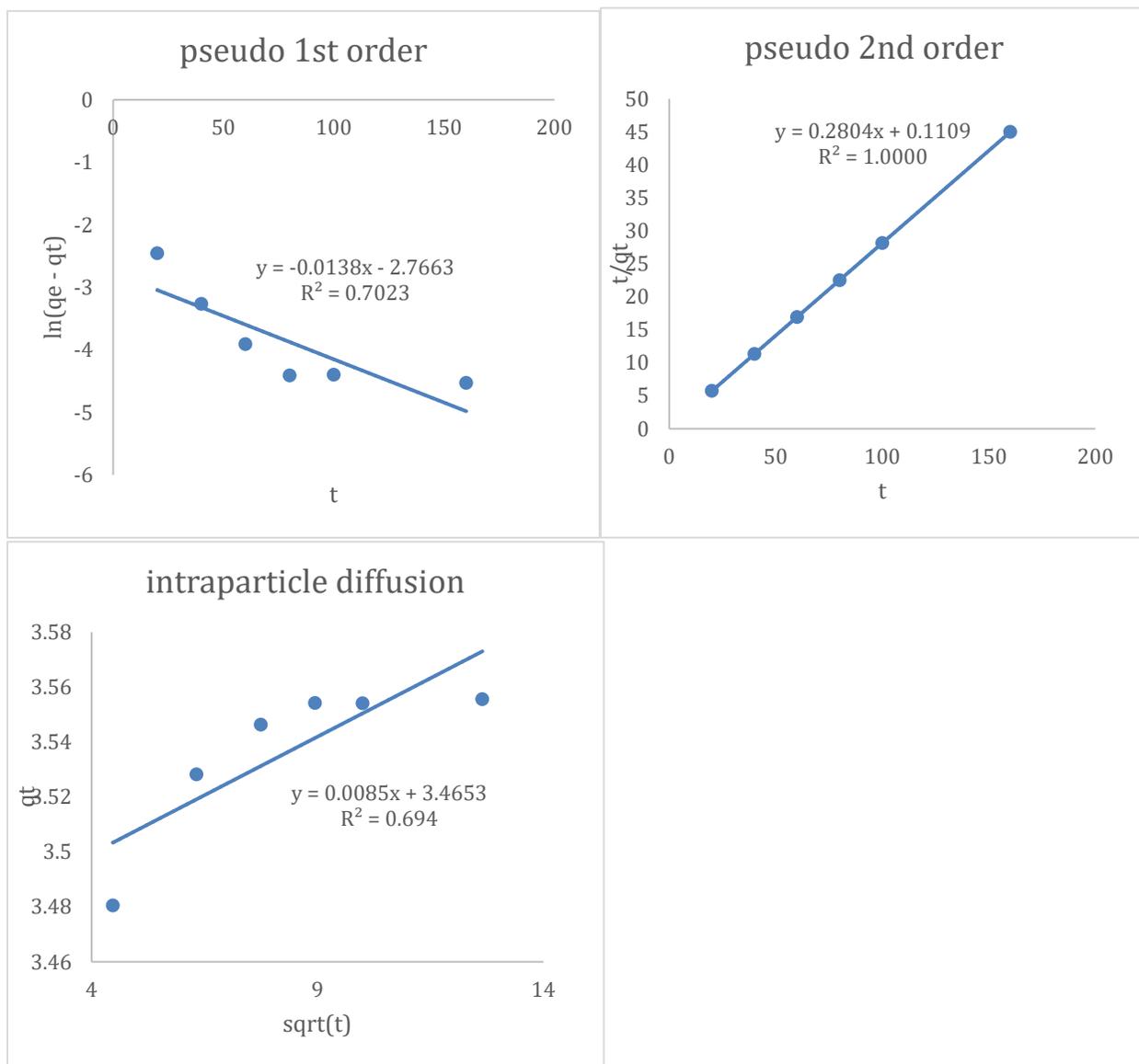
where k_2 is the equilibrium rate constant for the pseudo-second order model.

The intraparticle diffusion model reveals whether intraparticle diffusion is involved in the adsorption process and identifies the diffusion mechanism of the adsorption. The linear form of the intraparticle diffusion model used for this study is

$$q_t = k_i \sqrt{t} + c_i$$

where k_i is the intraparticle diffusion rate, and c_i gives information about the thickness of the boundary layer.

The plots are as shown



Model	Parameters	Values	R^2
Pseudo-first order	k_1 (1/min)	0.0138	0.702
	$q_{e, \text{cal}}$ (mg/g)	15.9	
Pseudo-second order	k_2 (g/min mg)	0.709	1.00
	$q_{e, \text{cal}}$ (mg/g)	3.57	
Intraparticle diffusion	k_i (mg min ^{-1/2} /g)	0.00852	0.694
	c_i (mg/g)	3.47	

The R^2 value for the pseudo-second order model is significantly higher than the one of pseudo-first order and intraparticle diffusion, which is in accordance with Mashkoo et. al. (2018).