



Adsorption of toxic crystal violet dye using coffee husks: Equilibrium, kinetics and thermodynamics study

Gilbert K. Cheruiyot^a, Wycliffe C. Wanyonyi^{a,*}, Joyce J. Kiplimo^a, Esther N. Maina^b

^a Department of Physical Sciences, School of Science and Technology, University of Kabianga, P.O. Box 2030, 20200 Kericho, Kenya

^b Department of Biochemistry, University of Nairobi, P.O. Box 30197, 00100 Nairobi, Kenya

ARTICLE INFO

Article history:

Received 10 January 2019

Revised 6 June 2019

Accepted 19 July 2019

Keywords:

Adsorption
Crystal violet dye
Waste coffee husk
Isotherms
Kinetics
Equilibrium

ABSTRACT

Crystal violet (CV) dye is a water-soluble, toxic, recalcitrant organic dye that causes severe health problems and environment pollution. The current study assesses the potential of Waste Coffee Husks (WCH) in adsorption of crystal violet (CV) dye. Batch experiments were designed to determine the effect of pH, dye concentration, adsorbent dose, and contact time in dye removal. Result revealed that removal of CV was highly favored by lower temperatures and acidic medium. Dye removal per unit mass of WCH increased with increase in contact time, dye concentration and surface area. At ambient temperature, the maximum adsorption efficiency of up to 94% was achieved within 10 min at pH 3. Adsorption capacity of Waste Coffee Husks was found to be 12.0360 mg/l for initial dye concentration of 12.2394 mg/l at 25 °C. The experimental data followed pseudo-second-order kinetic models indicating that dye adsorption was controlled by chemical process involving valence forces through sharing or exchange of electrons between CV dye and WCH. Adsorption equilibrium data followed Freundlich and Langmuir isotherm models. Gibbs free energy (ΔG°) of the system showed increasing spontaneity with temperatures while positive entropy value (ΔS°) implied random disorder of molecules featured at solution/solid interface. Negative enthalpy value (ΔH°) confirmed exothermic nature of this adsorption process. These results demonstrate that Waste Coffee Husk are cost-effective, eco-friendly and low-cost bio renewable material for dye removal in industrial effluents.

© 2019 The Authors. Published by Elsevier B.V. on behalf of African Institute of Mathematical Sciences / Next Einstein Initiative.
This is an open access article under the CC BY license. (<http://creativecommons.org/licenses/by/4.0/>)

1. Introduction

Synthetic dyes are enormously used to impart colour to the substrates in the textile, plastics, pharmaceutical, paper, printing, rubber, leather, paint, cosmetic, food, pulp and paper industries [1–3]. Increased demand and applications of synthetic dyes in chemical based industries has led to discharge of highly polluted wastewater resulting in health problems and environmental pollution. It is approximated that about 10–15% of the dyes utilised in textile dying process do not bind with the fibres and are discharged into the environment [1]. As a result, more than 50,000 tons of organic dyes are disposed in

* Corresponding author.

E-mail address: wwanyonyi@kabianga.ac.ke (W.C. Wanyonyi).

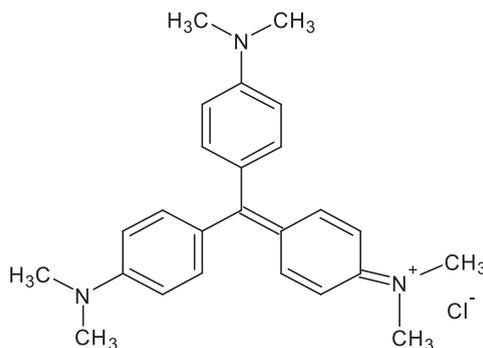


Fig. 1. Chemical structure of crystal violet (CV) dye.

the environment yearly from dyeing processes globally. Dyes are noxious, carcinogenic and mutagenic which makes them hazardous flora and fauna. Furthermore, presence of the dyes in aqueous ecosystems even at low concentrations diminishes photosynthetic phenomena by preventing light penetration thereby deteriorating the water quality, gas solubility and destroying aesthetic value of water [1].

Crystal violet dye (Fig. 1) is a tri-phenylmethane dye (IUPAC name: N-[4-[bis [4-dimethyl-amino)-phenyl]-methylene]-2,5-cyclohexadien-1-ylidene]-N-methyl-methanaminium chloride) is known to be carcinogenic, mutagenic but still extensively used in commercial textile operations, biological staining and as a dermatological agent [4]. The dye can be absorbed in harmful amounts through the skin and cause skin irritation and digestive tract irritation. Exposure to the dye may induce moderate eye irritation and painful sensitization to light [4]. In extreme cases, it may lead to respiratory complication, kidney failure and permanent blindness [5].

Treatment of azo dyes in wastewaters is a great challenge because these dyes are believed to be electron deficient xenobiotic compounds with complex structure which make them resistant to degradation. Conventional treatment methods such as biological degradation, precipitation, photocatalytic, adsorption, membrane filtration, chemical oxidation, coagulation, flocculation, ion exchange, ozonation, irradiation and solvent extraction have been investigated with varying degree of success in dye removal [6,7]. They have certain disadvantages, including high investment and operating costs, inefficiency in dye removal and the need for appropriate treatment residual dye sludge [8]. Adsorption remains one of the most widespread treatment technique because of its simplicity, low cost and efficacy [9]. The commonly used adsorbent is activated carbon, but its high cost of activation make it less economically viable as an adsorbent [10]. This has led many researchers to search for cost effective alternative materials such as $\text{Fe}_2\text{O}_3/\text{CeO}_2\text{-ZrO}_2$ /palygorskite composite catalyst [11], smectite rich natural clays [12] graphene based nanomaterials [13], modified tea leaves [14], biochar chitin [15], poplar sawdust [16], macadamia nutshell [17] and root of *Eichhornia crassipes* [18].

Agricultural bio-wastes are continuously being explored for removal of dye from wastewaters due to their abundance, high carbonaceous contents (cellulose, lignin and hemicelluloses) and high affinity towards sequestering organic molecules. In addition agro-materials possess favorable chemical and physical qualities for dye adsorption, require few or no processing before use [19]. Waste Coffee Husk (WCH) belongs to this category of agricultural by-products. WCH residue is the main by-product obtained from a coffee scrub, a cash crop that is cultivated in over 80 countries across the world. During processing of coffee beans, huge amounts of coffee husks are generated. It is estimated that 0.18 ton of the husks are generated per every ton of harvested coffee fruits [20]. The waste husk residue has limited uses and their accumulation at milling sites poses negative impact on environment. Efforts to find an alternative technology to exploit Coffee husk in solving environmental mess is gainful given its abundance across the globe. In this study, the efficacy Coffee husk in the removal of CV dye was investigated and factors affecting batch adsorption process optimized.

2. Materials and methods

2.1. Preparation of the adsorbents

Waste Coffee Husks were collected from Roret coffee factory, Kericho County, Kenya. Suspended impurities were removed through extensive washing with tap water then sun dried for four days. Dried husks were crushed into fine powder using Lab Ball mill before washing several times with distilled water. Clean powder was dried in an oven at 60°C until it attained constant weight. The adsorbent material was sieved through standard sieves to obtain particle sizes between 0.15 - 0.3; 0.3 - 0.6; 0.6 - 1.118; 1.118 - 2.36 and 2.36 - 4.75 mm in diameter for adsorption studies.

2.2. Adsorbate solution

Crystal violet, ($\text{C}_{25}\text{H}_{30}\text{N}_3\text{Cl}$) (CI Classification number: 42,555; CAS number: 548-62-9) was purchase from Ranbaxy Fine Chemicals Limited, Nairobi, Kenya and used without further purification. Stock solutions of the dye containing 1.0 g/l were

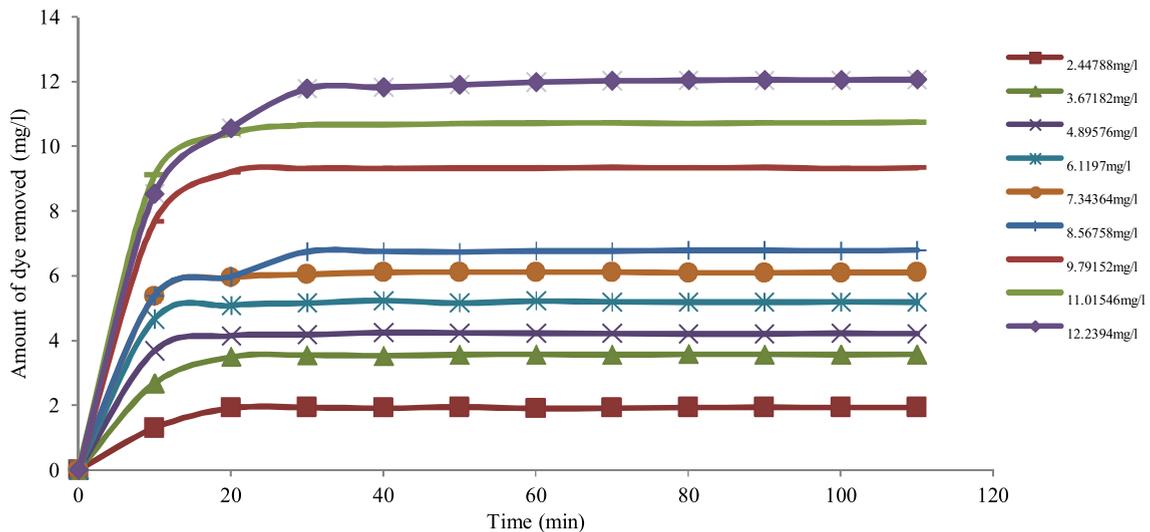


Fig. 2. Effect of initial dye concentration on adsorption of CV dye (WCH: 0.25 g, 50 ml; Temp: 25 °C, pH 4).

prepared by dissolving appropriate weight of the dye into double distilled water. Dye solutions for batch experiments were prepared from the stock solution by suitable dilution. Initial pH was adjusted using either 0.1 NaOH or 0.1 M HCl.

2.3. Adsorption experiments

Batch experiments were conducted in 250 mL Erlenmeyer flask placed on a mechanical shakers agitation at 140 r.p.m until the equilibrium was reached at 25°C. All the experiments were done in duplicate and average value reported. Fixed amount of adsorbent was mixed with 50 ml of aqueous dye. After different time intervals, aliquots were drawn from reaction mixture and remaining CV dye concentrations determined using UV/Visible spectrophotometer at maximum wavelength ($\lambda_{\max} = 580 \text{ nm}$). Effect of contact time was determined using 0.5 g WCH, and 50 mL CV dye solution mixed in 250 mL flask placed on a mechanical shaker. Samples were drawn from the flask at various intervals and analysed for residual CV concentration. The adsorbent dose was investigated using 12.2394 mg/l initial CV dye concentration with sorbent masses of 0.1, 0.25, 0.5, 0.75, 1.0, 1.25 and 1.5 g. Dye adsorbed per unit mass of the adsorbent q_e (mg/g) and the extent of adsorption (%) was calculated using Eq. (1).

$$q_e = \frac{V(C_o - C_e)}{W} \quad (1)$$

Where C_o and C_e are the initial and the equilibrium CV dye concentrations (mg/l), V is the volume of solution (L) and W is the amount of WCH used (g). Percentage dye removal (%) was calculated using Eq. (2);

$$\% \text{Removed} = \frac{(C_o - C_e)}{C_o} \times 100 \quad (2)$$

Adsorption kinetics was determined using different initial CV dye concentrations at 25 °C by altering the contact time. 0.5 g of WCH of particle size 0.15–0.3 mm was mixed with 50 mL CV dye in a 250 mL conical flask agitation at 140 rpm. After 10 min time interval, 3 mL were withdrawn, from the conical flask, residual CV concentration determined and then returned back in the conical flask to restore the initial volume.

3. Results and discussion

3.1. Effect of contact time and initial dye concentration

The period of contact between the biosorbent and biosorbate is crucial in costing when designing a biosorption system for large scale application in an industry. The impact of contact time on the adsorption of CV dye by WCH was examined at different initial dye concentrations ranging from 2.448 to 12.239 mg/l at 25 °C and pH 4. Generally, dye uptake increased with increase in time. The rate of dye removal for the studied concentration was rapid in the first 10 min before attaining equilibrium at about 30 min (Fig. 2). As time progressed, adsorbent's surface was occupied by dye molecules, became saturated and could not take up any amount of dye [21]. High initial rate of CV removal was due to availability of more vacant binding sites on the adsorbent during the first few minutes. The results shows that the time needed to attain equilibrium

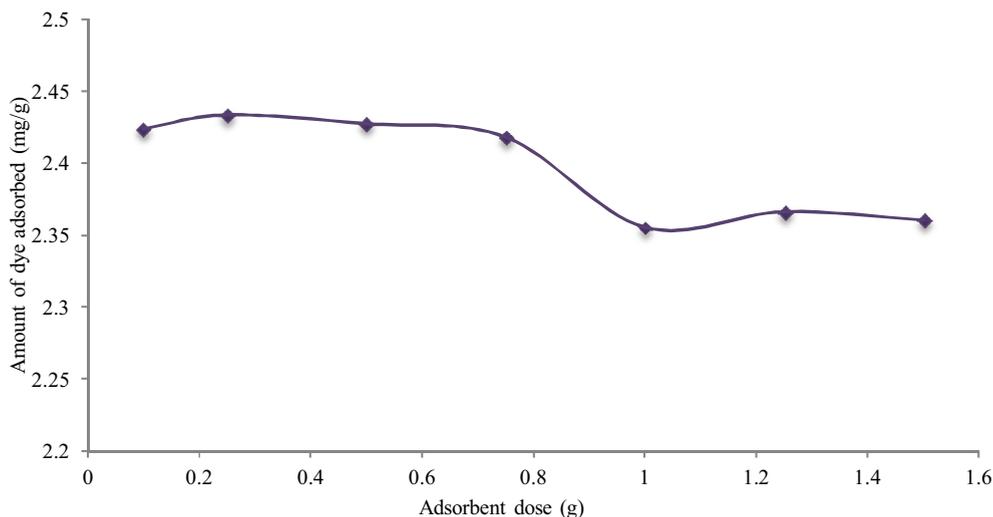


Fig. 3. Effect of adsorbent dose on CV dye removal (dye conc: 12.2394 mg/l; 50 ml, Temp: 25 °C, pH 4).

ranged between 20 and 40 min. Adsorption efficiency of 98% was achieved at equilibrium when 12.239 mg/l CV dye concentration was used. These findings agreed with related studies on CV dye removal from aqueous solution using pineapple (*Ananas comosus*) leaf powder [22] where dye removal increased with increase in contact time.

It was noticed that the amount of dye adsorbed increased from 1.924 to 12.0611 mg/l when the initial dye concentration increased from 2.448 to 12.239 mg/l respectively. This may be ascribed to the increased concentration gradient acting as an increasing driving force to overpower all mass transfer resistances of the dye molecules between the solid and aqueous phases, leading to an increase in equilibrium sorption till attainment of saturation [23]. However, the efficiency declined with increase CV dye concentration. Faster saturation of active adsorption sites on the surface of WCH when high dye concentration is used could rationalize this observation.

3.2. Effect adsorbent dose

Adsorbent efficiency in treatment of polluted wastewaters mainly depends on the number of active adsorption sites available on adsorbent. The quantity of adsorbent applied in the adsorption process is crucial because it dictates the sorbent-sorbate ratio in the process and also in cost forecasting [23,24]. The influence of WCH dose on adsorption of CV dyes was investigated using dye concentrations of 12.239 mg/l and WCH dose ranging from 0.1 g to 1.5 g. The results revealed that the percentage of CV dye adsorbed increased with increase in WCH dose and also the time needed to attain equilibrium decreased when high doses were employed. Increase in dye removal with increase in WCH dose can be attributed to increased adsorbent surface and accessibility of more adsorption sites [25]. However, when adsorption capacity of CV was expressed in mg adsorbed per gram of WCH, the capacity decreased with the increasing amount of sorbent (Fig. 3). This may be attributed to overlapping or aggregation of adsorption sites resulting in a decrease in the total adsorption surface area available to the dye and an increase in the diffusion path length [26]. The result shows that available surface sites for small dosages were sufficiently covered by dye molecules in solution. Similar findings have also been proposed by Etim et al. in his studies of removal of cationic dye from aqueous solution using Coconut coir dust as a low cost adsorbent [26].

3.3. Effect of particle size

Dye removal from aqueous solution is proportional to the surface area available on adsorbent. The impact of particle size on removal of CV was studied using initial dye concentration of 12.2394 mg/l and different particle sizes of the WCH. The results depicted in Fig. 4 indicate that the percentage dye adsorbed reduced with increase in particle size. The highest sorption percentage of (96.082%) was realized at equilibrium for the finest powder (0.15–0.3 mm) as compared to 89.854% for biggest particle size (2.36–4.75 mm). The large surface area on small particles sizes was responsible for higher dye removal as compared to small surface area in large particles sizes.

3.4. Effects of initial pH of solution

pH plays a critical role in controlling the charge on adsorbent surface, the magnitude of adsorbate ionization and dissociation of different functional groups on the adsorbent [27]. The effect of Initial pH effect on CV adsorption in was evaluated results presented in Fig. 5. The optimum removal from the aqueous solution was achieved at pH 3. The amount of dye

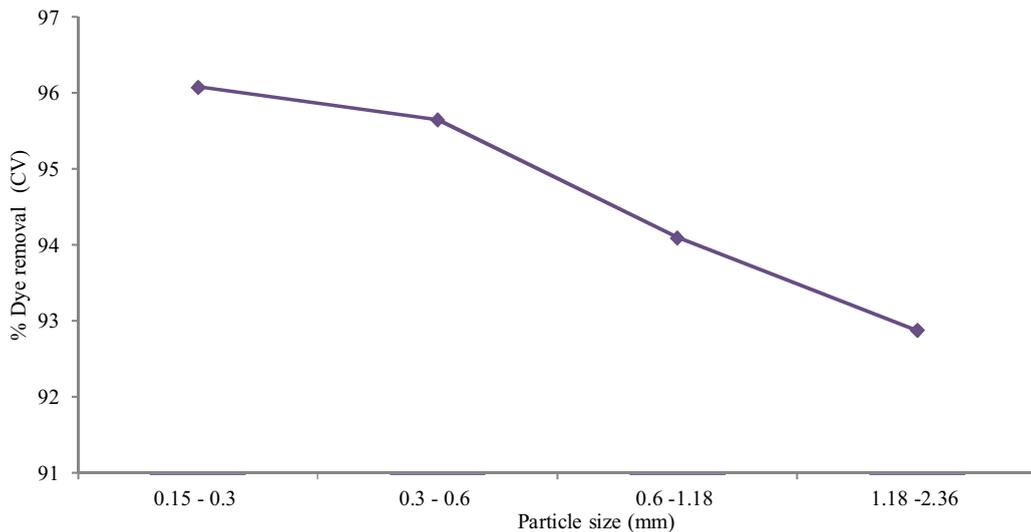


Fig. 4. Effect of particle size on the removal of CV dye (WCH: 0.25 g; 50 ml, dye conc: 12.239 mg/l, temp: 25 °C, pH: 4).

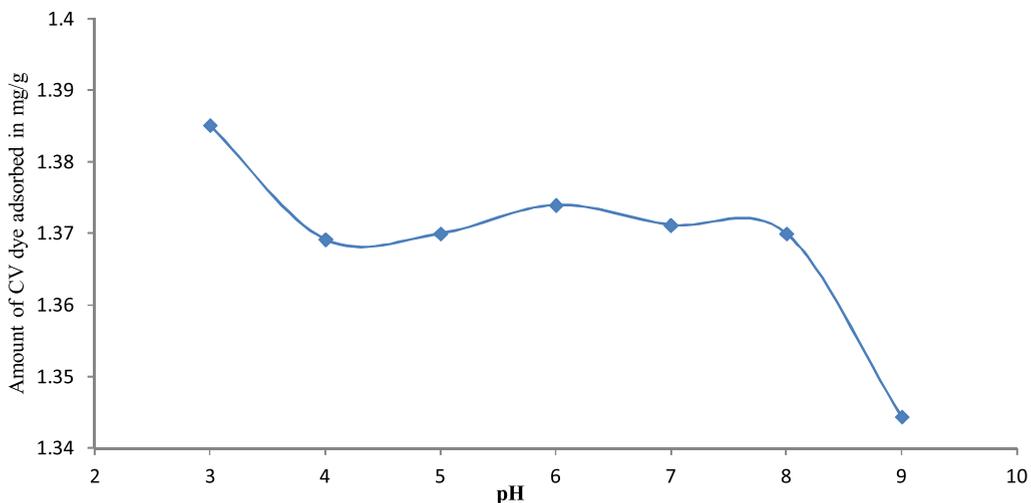


Fig. 5. Influence of pH on the removal of CV dye. (WCH: 0.25 g; 50 ml; dye conc: 12.2394 mg/l temp: 25 °C).

adsorbed by WCH reduced gradually with increase in pH till pH 8.0, after which there was a slight decrease in adsorption. This trend can be attributed to increased negative charge density on adsorbent surface in acidic pH media [28], resulting in attraction between the positively charged CV dye molecule and WCH. As the pH increased, the surfaces charge density on the adsorbent declined, resulting in electrostatic repulsion from the positive charge of the dye molecule [29].

3.5. Effects of temperature

Temperature plays key role in adsorption process because it influences mobility and solubility of dye molecules in aqueous solution and surface properties of adsorbent. In addition, increase in temperature result in an increased rate of diffusion of the adsorbate molecules across the external boundary layer of the adsorbent particles and inside their internal pores, accompanied with reduced solution viscosity [30]. Effect of temperature on the adsorption of CV dye was investigated and the results displayed in Fig. 6. The result shows that the adsorption of CV dye onto WCH was an exothermic process where rise in temperature prompted diminished adsorption. For example, at 25 °C, 2.0238 mg/g of dye was adsorbed as compared to 1.3235 mg/g at 85 °C. This observation may be due to weakening of binding forces which helps in detachment of dye molecules from the surface of adsorbent causing in reduced adsorption at elevated temperatures [31]. This observation is similar to the results obtained when CV was adsorbed on to mango stone bio-composite [32] and on palm fiber [29] where the adsorption process was found to be exothermic.

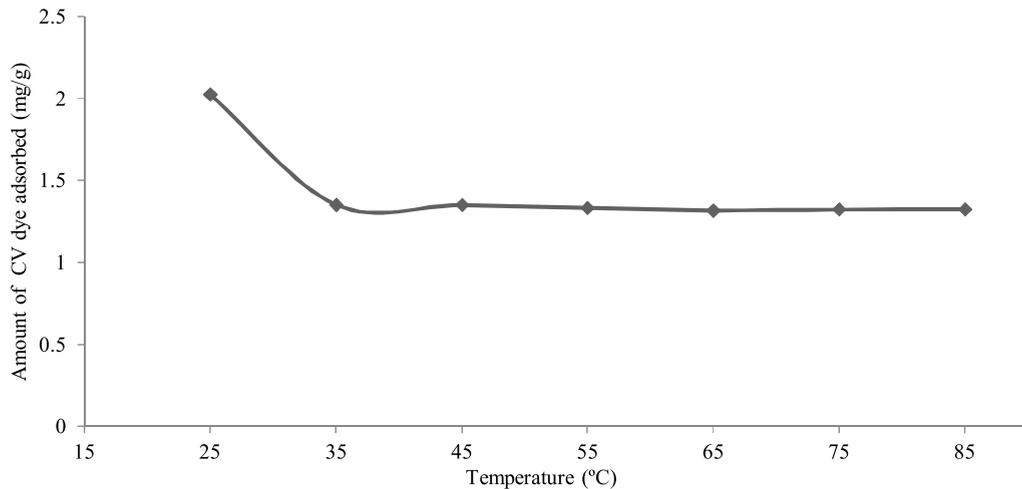


Fig. 6. Effect of temperature on the adsorption of crystal violet. (WCH: 0.25 g/50 ml, dye conc: 12.2394 mg/l, particles size: 0.15–3.0 mm).

Table 1

Kinetic modelling data for the removal of crystal violet dye by Waste Coffee Husks biomass.

Crystal violet dye concentration (mg/l)	Pseudo-first-order kinetic parameters				Pseudo-second-order kinetic parameters		
	$q_{e,exp}$ (mg g ⁻¹)	$q_{e,cal}$ (mg g ⁻¹)	k_1 (g mg ⁻¹ min ⁻¹)	R^2	$q_{e,cal}$ (mg g ⁻¹)	k_2 (g mg ⁻¹ min ⁻¹)	R^2
1.224	0.030	0.023	0.004	0.005	0.030	0.0001	0.992
3.672	0.406	6.761	0.048	0.768	0.410	0.155	0.999
6.120	0.589	9.099	0.030	0.013	0.591	2.520	0.999
11.016	1.220	5.848	0.048	0.771	1.227	2.962	0.999
12.239	1.368	4.406	0.037	0.299	1.397	0.495	0.999

3.6. Kinetic studies

A cost-efficient adsorbent for removing of contaminants in waste water should not only have massive adsorbate capacity but also a rapid in sorption. The cost and performance of an adsorbent and the mode of application are always key factors in controlling process efficacy [4]. The experimental adsorption kinetic data was modelled using pseudo-first order [33] and pseudo-second order [34]. These two models are broadly employed in adsorption processes to examine controlling mechanism of adsorption process such as adsorption surface, chemical reaction and/or diffusion mechanisms [35]. The integral form of pseudo-first order kinetic model can be presented by Eq. (3).

$$\text{Log}(q_e - q_t) = \text{log } q_e - \frac{tk_1}{2.303} \quad (3)$$

where k_1 is the rate constant of pseudo-first-order adsorption, q_e and q_t are the amounts of CV adsorbed by WCH at equilibrium and at time, t , respectively. Plot of $\text{log}(q_e - q_t)$ against time (t) resulted in curves with lower correlation coefficients ($R^2 < 0.77$) as summarised in Table 1. First order mechanism is unsuitable since the values obtained for q_e from the graph showed a huge deviation with the experimental data. Experimental data were further subjected to pseudo-second-order kinetic model to evaluate adsorption kinetics of CV dye on WCH. The pseudo second-order model is given by the Eq. (4).

$$\frac{t}{q_t} = \frac{1}{k_2} \cdot \frac{1}{q_e^2} + \frac{t}{q_e} \quad (4)$$

where k_2 is the rate constant for pseudo-second-order adsorption (gmg⁻¹min⁻¹), q_e and q_t are the quantity of CV adsorbed (mg/g) at equilibrium and at time t (min) respectively. The plot of t/q_t vs t of Eq. (4) gives a linear line, from which, q_e and k_2 can be calculated from the slope and intercept of the plot. Fig. 7 displays pseudo second - order kinetics graph for the adsorption of CV dye by WCH at different initial dye concentrations.

The graph shows that experimental had a good fit to Pseudo-second-order kinetics model with higher values of correlation coefficient ($R^2 > 0.99$). The rate constants, anticipated equilibrium uptakes and the corresponding correlation coefficients for the tested concentrations were determined and presented in Table 1. The high concurrence between calculated and experimental values proves that the adsorption of CV onto WCH perfectly followed pseudo second order kinetic model. The result suggest that the overall rate adsorption process was controlled by chemical process involving valence forces through sharing or exchange of electrons between dye and adsorbent [23]. Similar adsorption kinetic behaviour for pineapple leaf powder adsorbent [36], mango stone biocomposite [32] and formosa papaya seed powder [37] for crystal violet has been reported.

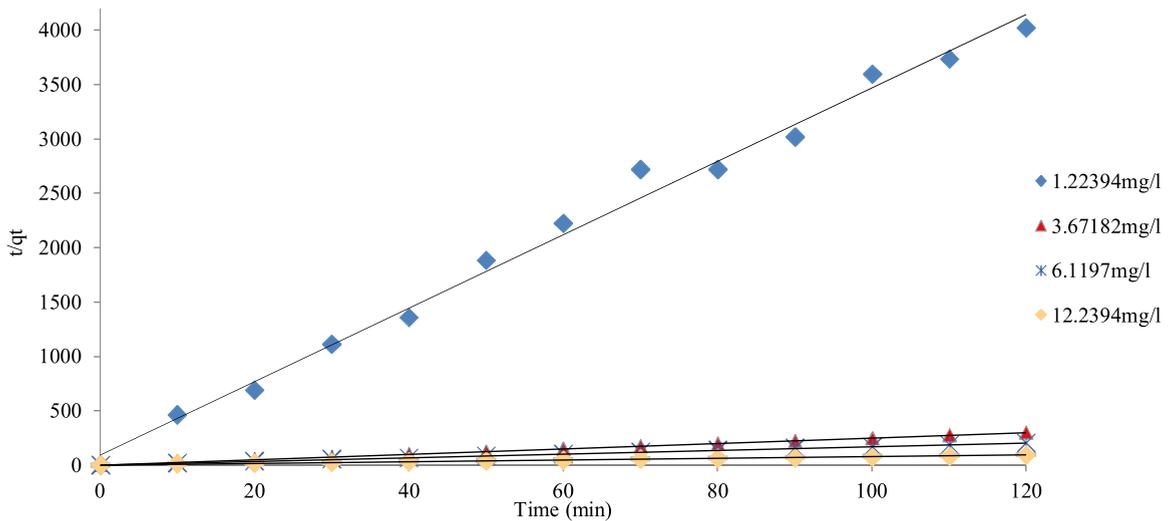


Fig. 7. Pseudo-second-order kinetics plot for the adsorption of CV dye on WCH.

Table 2
Langmuir and Freundlich isotherm constants for adsorption of CV dye on WCH.

Langmuir adsorption isotherm				Freundlich adsorption isotherm		
q_0	b	R^2	R_L	K_F	n	R^2
0	0	1	1	4.998	1	1

3.7. Equilibrium studies

Adsorption properties and equilibrium data, frequently referred to as adsorption isotherms, outline how adsorbate molecules interact with adsorbent and so, are important in optimizing the use of adsorbents [35]. Isotherm models express the distribution of dye molecule between the solid phase and liquid phases thus providing qualitative information on the position of equilibrium in the adsorption process. Experimental adsorption data were subjected to Langmuir [38] and the Freundlich [39] adsorption isotherms to evaluate adsorption of CV on WCH. Langmuir isotherm model infers that the adsorptions occur at specific homogeneous sites on the adsorbent and is used successfully in many monolayer adsorption processes. The linearized forms of Langmuir isotherm is given in Eq. (5):

$$\frac{1}{q_e} = \frac{1}{bC_e q_0} + \frac{1}{q_0} \quad (5)$$

where c_e (mg/l) is the dye concentration in the solution at equilibrium, q_e (mg/g) is the amount of dye adsorbed per unit mass of adsorbent at equilibrium time, q_0 (mg/g) and b (l/mg) are the Langmuir constants related to maximum monolayer adsorption capacity and energy of adsorption that is affinity of binding sites respectively. These values are determined from the slope and intercept, respectively, of the plots of $1/q_e$ versus $1/c_e$. Further, separation factor which is defined below was also applied to get insights of the isotherm.

$$R_L = \frac{1}{1 + bC_0} \quad (6)$$

where c_0 (mg/l) is the initial dye concentration and b (l/mg) is the Langmuir constant. Four R_L scenarios are possible for any adsorption: $R_L > 1$ (unfavourable), $R_L = 1$ (linear), $R_L = 0$ (irreversible) and $0 < R_L < 1$ (favourable) [40]. Fig. 8 represent a plot of $1/q_e$ versus $1/C_e$ for the adsorption of CV onto WCH and the correspondent Langmuir isotherm constants are tabulated in Table 2. The experimental data showed a good fit to Langmuir model with high correlation coefficient ($R^2 = 1$) indicating that the model was appropriate to describe the adsorption process of CV onto WCH. Langmuir constant associated with adsorption energy of the system was at minimal suggesting spontaneous nature of the process while linearity was confirmed by separation factor, $R_L = 1$.

Experimental adsorption data were also analysed by Freundlich isotherm model. The model assumes multilayer adsorptions on heterogeneous adsorbent surface. The linearized form of the equation is give as:

$$\ln q_e = \ln k_f + \frac{1}{n} \ln c_e \quad (7)$$

where q_e (mg/g) is the amount sorbate per unit weight of adsorbent used, c_e (mg/l) is the equilibrium concentration of dye in the solution, k_f (l/g) is Freundlich constant, representing the adsorption capacity and n is the Freundlich exponent that

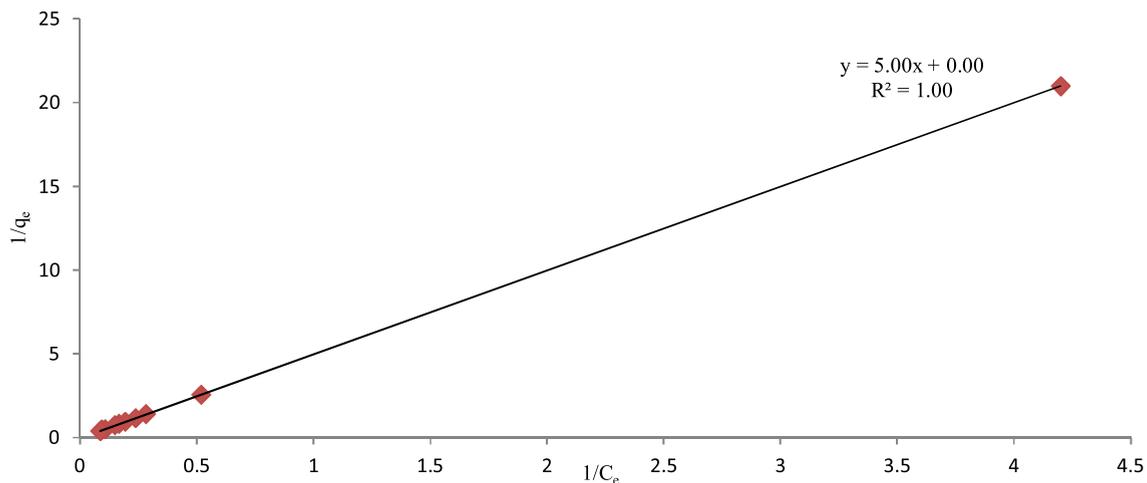


Fig. 8. Langmuir isotherm plot for CV adsorption on WCH.

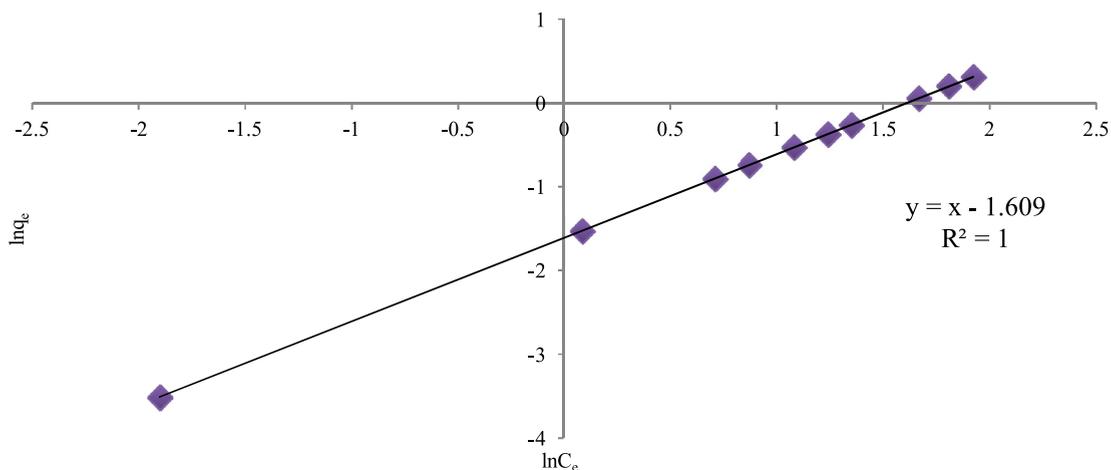


Fig. 9. Freundlich Isotherm plot for CV adsorption on WCH.

depicts the adsorption intensity (dimensionless). The magnitude of the exponent, $1/n$, gives an indication of the favourability of adsorption. Values of $n > 1$ represent favourable adsorption conditions [40]. Values of k_f and n are calculated from the intercept and slope of the plot of $\ln q_e$ against $\ln C_e$. Fig. 9 shows a plot of $\ln q_e$ versus $\ln C_e$ for the adsorption of CV onto WCH and the corresponding Freundlich isotherm constants summarized in Table 2. The results suggest that CV dye was favourably adsorbed by WCH with high values of the correlation coefficient ($R^2 = 1$) indicate that the Freundlich isotherm has been best fitted for the adsorption of CV dye on WCH. It is noteworthy to point out that experimental data fitted well both Langmuir and the Freundlich adsorption isotherms models indicating that both models are suitable for describing the adsorption equilibrium of both the dyes in the studied concentration ranges. Similar patterns has been reported in the biosorption of reactive dyes by dried activated sludge [41].

3.8. Thermodynamic analysis

The thermodynamic behaviours for adsorption of CV on WCH was investigated. Thermodynamic parameters such as Gibbs free energy, ΔG° , (kJ/mol), enthalpy change, ΔH° , (kJ/mol) and entropy change, ΔS° , (J/K/mol) were calculated using the following equations

$$\Delta G^\circ = -RT \ln k_d, \quad (8)$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (9)$$

$$\ln k_d = -[\Delta H^\circ/RT] + [\Delta S^\circ/R] \quad (10)$$

where k_d is the distribution coefficient for adsorption expressed as $k_d = C_{\text{solid}}/C_{\text{liquid}}$; C_{solid} and C_{liquid} (mg/l) are the concentrations of solid and liquid phase respectively at equilibrium. T is the absolute temperature in Kelvin and R is the gas

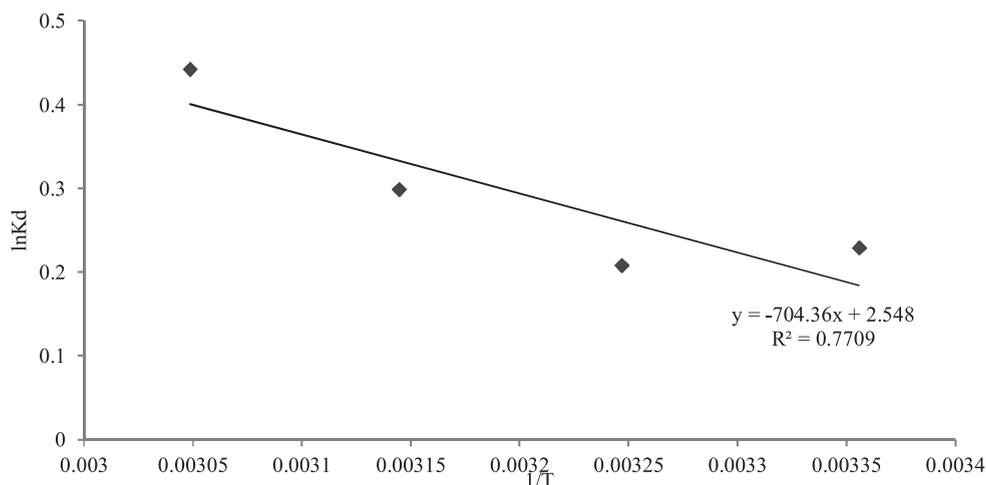


Fig. 10. Plot of $\ln K_d$ versus $1/T$ (K^{-1}) for CV adsorption onto WCH (Dose: 0.25 g/50 ml, dye conc: 12.239 mg/l).

Table 3
Thermodynamic parameters for CV adsorption onto WCH.

R^2	ΔG° (kJ/mol)						ΔH° (kJ/mol)	ΔS° (J/K/mol)
0.770	25 °C	35 °C	45 °C	55 °C	65 °C	65 °C	-5.856	21.184
	-0.002	-0.002	-0.003	-0.003	-0.004	-0.004		

constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$) Experimental data, after 10 min which was considered time of active adsorption was used for this study. Values of ΔH° and ΔS° from slope and intercept, respectively, on Van't Hoff equation plot of $\ln k_d$ against $1/T$ (Fig. 10) were calculated, and then ΔG° obtained. Table 3 summarizes the variations of the thermodynamic parameters for the adsorption of CV on the WCH. ΔG° values were all negative as implying adsorption was favourable and spontaneous. Negative value of ΔH° (slope) further confirmed the process was exothermic. Magnitude of enthalpy value is also indicative of adsorption mechanism. It suggests adsorption mechanism by physisorption through van der Waals if less 20 kJ mol^{-1} or electrostatic type of forces between dye and adsorbent if it falls between 20 and 80 kJ mol^{-1} [42]. This also inferred others mechanisms such as van der Waals played some part during CV removal by WCH. Positive value of ΔS° showed some disorder and randomness associated to the sorption process at sorbent/sorbate interface. Similar results have been reported on the adsorption of CV dye onto date palm fiber [29].

4. Conclusion

The study revealed that WCH is indeed viable, affordable adsorbent for the adsorptive removal of CV dye from contaminated wastewater with over 98% dye removal. Batch studies consideration of operating conditions such as contact time, biosorbent dose, particle size, initial concentration, pH and temperature showed varied influence on adsorption process. Highest CV dye removal was recorded at 25 °C and pH 3 using smallest particle sizes of 0.15–0.3 mm and adsorbent dose of 1.5 g. By examining correlation coefficients, excellent linear fits was observed for Langmuir and Freundlich isotherm models applied and this explained CV removal by WCH, assumed both monolayer and multilayer adsorption WCH surface. Further information derived from kinetic studies revealed pseudo-second order kinetic model was in better agreement compared to pseudo-first order kinetic model. Thermodynamically, CV adsorption onto WCH displayed spontaneity and feasibility basing on the value (negative) of ΔG° . It was also exothermic in nature. These findings demonstrated that WCH is suitable and efficient adsorbent for removing CV from contaminated dye wastewater. Thus, the present study concludes that WCH could be employed as a low-cost and eco-friendly adsorbent as an alternative to the current expensive methods of removing dyes from wastewaters.

Declaration of Competing Interest

None.

Acknowledgements

The authors wish to thank the Department of Physical Sciences, University of Kabanga (UoK) and Department of Chemistry, University of Nairobi are for the provision of research facilities and space to undertake this study.

References

- [1] S. Asad, M.A. Amoozegar, A.A. Pourbabaee, M.N. Sarbolouki, S.M.M. Dastgheib, Decolorization of textile azo dyes by newly isolated halophilic and halotolerant bacteria, *Bioresour. Technol.* 98 (2007) 2082–2088, doi:10.1016/j.biortech.2006.08.020.
- [2] R.L. Singh, P.K. Singh, R.P. Singh, Enzymatic decolorization and degradation of azo dyes – a review, *Int. Biodeterior. Biodegrad.* 104 (2015) 21–31, doi:10.1016/j.ibiod.2015.04.027.
- [3] C. Srikanth, G.K. Suriaishkumar, S. Srivastava, Effect of light on the kinetics and equilibrium of the textile dye (Reactive red 120) adsorption by *Helianthus annuus* hairy roots, *Bioresour. Technol.* 257 (2018) 84–91, doi:10.1016/j.biortech.2018.02.075.
- [4] G.K. Sarma, S. Sen Gupta, K.G. Bhattacharyya, Adsorption of crystal violet on raw and acid-treated montmorillonite, K10, in aqueous suspension, *J. Environ. Manag.* 171 (2016) 1–10, doi:10.1016/j.jenvman.2016.01.038.
- [5] A. Mittal, J. Mittal, A. Malviya, D. Kaur, V.K. Gupta, Adsorption of hazardous dye crystal violet from wastewater by waste materials, *J. Colloid Interface Sci.* 343 (2010) 463–473, doi:10.1016/j.jcis.2009.11.060.
- [6] Z. Noorimotlagh, S.A. Mirzaee, S.S. Martinez, S. Alavi, M. Ahmadi, N. Jaafarzadeh, Adsorption of textile dye in activated carbons prepared from DVD and CD wastes modified with multi-wall carbon nanotubes: equilibrium isotherms, kinetics and thermodynamic study, *Chem. Eng. Res. Des.* 141 (2019) 290–301, doi:10.1016/j.cherd.2018.11.007.
- [7] W.C. Wanyonyi, J.M. Onyari, P.M. Shiundu, F.J. Mulaa, Effective biotransformation of reactive black 5 dye using crude protease from *Bacillus cereus* strain KM201428, *Energy Procedia* 157 (2019) 815–824, doi:10.1016/j.egypro.2018.11.247.
- [8] M. Abbas, S. Kaddour, M. Trari, Kinetic and equilibrium studies of cobalt adsorption on apricot stone activated carbon, *J. Ind. Eng. Chem.* 20 (2014) 745–751, doi:10.1016/j.jiec.2013.06.030.
- [9] Z. Harrache, M. Abbas, T. Aksil, M. Trari, Thermodynamic and kinetics studies on adsorption of indigo carmine from aqueous solution by activated carbon, *Microchem. J.* 144 (2019) 180–189, doi:10.1016/j.microc.2018.09.004.
- [10] P.R. Pawar, S.M. Bhosale, Heavy Metal Toxicity, Health hazards and their removal technique by natural adsorbents: a short overview, *IJCET* (2018) 8, doi:10.14741/ijcet/v.8.2.35.
- [11] J. Ouyang, Z. Zhao, S.L. Suib, H. Yang, Degradation of congo red dye by a Fe₂O₃/CeO₂-ZrO₂/Palygorskite composite catalyst: synergetic effects of Fe₂O₃, *J. Colloid Interface Sci.* 539 (2019) 135–145, doi:10.1016/j.jcis.2018.12.052.
- [12] I. Chaari, E. Fakhfakh, M. Medhioub, F. Jamoussi, Comparative study on adsorption of cationic and anionic dyes by smectite rich natural clays, *J. Mol. Struct.* 1179 (2019) 672–677, doi:10.1016/j.molstruc.2018.11.039.
- [13] A. Carmalin Sophia, T. Arfin, E.C. Lima, Recent developments in adsorption of dyes using graphene based nanomaterials, in: Mu. Naushad (Ed.), *A New Generation Material Graphene: Applications in Water Technology*, Springer International Publishing, Cham, 2019, pp. 439–471, doi:10.1007/978-3-319-75484-0_18.
- [14] S. Wong, H.H. Tumari, N. Ngadi, N.B. Mohamed, O. Hassan, R. Mat, N.A. Saidina Amin, Adsorption of anionic dyes on spent tea leaves modified with polyethyleneimine (PEI-STL), *J. Clean Prod.* 206 (2019) 394–406, doi:10.1016/j.jclepro.2018.09.201.
- [15] M.A. Zazycki, P.A. Borba, R.N.F. Silva, E.C. Peres, D. Perondi, G.C. Collazzo, G.L. Dotto, Chitin derived biochar as an alternative adsorbent to treat colored effluents containing methyl violet dye, *Adv. Powder Technol.* (2019) S0921883119301165, doi:10.1016/j.apt.2019.04.026.
- [16] U. Tezcan Un, F. Ates, Low-cost adsorbent prepared from poplar sawdust for removal of disperse orange 30 dye from aqueous solutions, *Int. J. Environ. Sci. Technol.* 16 (2019) 899–908, doi:10.1007/s13762-018-1716-9.
- [17] M.J. Phele, I.P. Ejidike, F.M. Mtunzi, Adsorption efficiency of activated macadamia nutshell for the removal organochlorine pesticides: endrin and 4,4-DDT from aqueous solution, *J. Pharm. Sci.* 11 (2019) 5.
- [18] L. Liu, S. Hu, G. Shen, U. Farooq, W. Zhang, S. Lin, K. Lin, Adsorption dynamics and mechanism of aqueous sulfachloropyridazine and analogues using the root powder of recyclable long-root eichhornia crassipes, *Chemosphere* 196 (2018) 409–417, doi:10.1016/j.chemosphere.2018.01.003.
- [19] S. Rangabhashiyam, N. Anu, N. Selvaraju, Sequestration of dye from textile industry wastewater using agricultural waste products as adsorbents, *J. Environ. Chem. Eng.* 1 (2013) 629–641, doi:10.1016/j.jece.2013.07.014.
- [20] P.S. Murthy, M.M. Naidu, Recovery of phenolic antioxidants and functional compounds from coffee industry by-products, *Food Bioproc Tech* 5 (2012) 897–903, doi:10.1007/s11947-010-0363-z.
- [21] A. Khasri, M.A. Ahmad, Adsorption of basic and reactive dyes from aqueous solution onto intsia bijuga sawdust-based activated carbon: batch and column study, *Environ. Sci. Pollut. Res.* 25 (2018) 31508–31519, doi:10.1007/s11356-018-3046-3.
- [22] S. Neupane, S.T. Ramesh, R. Gandhimathi, P.V. Nidheesh, Pineapple leaf (*Ananas comosus*) powder as a biosorbent for the removal of crystal violet from aqueous solution, *Desalin. Water Treat.* 54 (2015) 2041–2054, doi:10.1080/19443994.2014.903867.
- [23] W.C. Wanyonyi, J.M. Onyari, P.M. Shiundu, Adsorption of congo red dye from aqueous solutions using roots of eichhornia crassipes: kinetic and equilibrium studies, *Energy Procedia* 50 (2014) 862–869, doi:10.1016/j.egypro.2014.06.105.
- [24] G.B. Oguntimein, Biosorption of dye from textile wastewater effluent onto alkali treated dried sunflower seed hull and design of a batch adsorber, *J. Environ. Chem. Eng.* 3 (2015) 2647–2661, doi:10.1016/j.jece.2015.09.028.
- [25] G. Crini, H. Peindy, F. Gimbert, C. Robert, Removal of C.I. basic green 4 (Malachite Green) from aqueous solutions by adsorption using cyclodextrin-based adsorbent: kinetic and equilibrium studies, *Sep. Purif. Technol.* 53 (2007) 97–110, doi:10.1016/j.seppur.2006.06.018.
- [26] U.J. Etim, S.A. Umoren, U.M. Eduok, Coconut coir dust as a low cost adsorbent for the removal of cationic dye from aqueous solution, *J. Saudi Chem. Soc.* 20 (2016) S67–S76, doi:10.1016/j.jscs.2012.09.014.
- [27] S. Banerjee, M.C. Chattopadhyaya, Adsorption characteristics for the removal of a toxic dye, tartrazine from aqueous solutions by a low cost agricultural by-product, *Arab. J. Chem.* 10 (2017) S1629–S1638, doi:10.1016/j.arabjc.2013.06.005.
- [28] G.K. Ramesha, A. Vijaya Kumara, H.B. Muralidhara, S. Sampath, Graphene and graphene oxide as effective adsorbents toward anionic and cationic dyes, *J. Colloid Interface Sci.* 361 (2011) 270–277, doi:10.1016/j.jcis.2011.05.050.
- [29] M. Alshabanat, G. Alsenani, R. Almufarji, Removal of crystal violet dye from aqueous solutions onto date palm fiber by adsorption technique, *J. Chem.* 2013 (2013) 1–6, doi:10.1155/2013/210239.
- [30] F. Bouaziz, M. Koubaa, F. Kallel, R.E. Ghorbel, S.E. Chaabouni, Adsorptive removal of malachite green from aqueous solutions by almond gum: kinetic study and equilibrium isotherms, *Int. J. Biol. Macromol.* 105 (2017) 56–65, doi:10.1016/j.ijbiomac.2017.06.106.
- [31] Y.-S. Ho, T.-H. Chiang, Y.-M. Hsueh, Removal of basic dye from aqueous solution using tree fern as a biosorbent, *Process Biochem.* 40 (2005) 119–124, doi:10.1016/j.procbio.2003.11.035.
- [32] S. Shoukat, H.N. Bhatti, M. Iqbal, S. Noreen, Mango stone biocomposite preparation and application for crystal violet adsorption: a mechanistic study, *Microporous Mesoporous Mater.* 239 (2017) 180–189, doi:10.1016/j.micromeso.2016.10.004.
- [33] S. Langergren, B.K. Svenska, Zur theorie der sogenannten adsorption gelöster stoffe, *Veternskapskad Handlingar* 24 (1898) 1–39.
- [34] Y.S. Ho, G. McKay, Kinetic models for the sorption of dye from aqueous solution by wood, *Process Saf. Environ. Prot.* 76 (1998) 183–191, doi:10.1205/095758298529326.
- [35] G. Crini, P.-M. Badot, Application of chitosan, a natural aminopolysaccharide, for dye removal from aqueous solutions by adsorption processes using batch studies: a review of recent literature, *Prog. Polym. Sci.* 33 (2008) 399–447, doi:10.1016/j.progpolymsci.2007.11.001.
- [36] S. Neupane, S.T. Ramesh, R. Gandhimathi, P.V. Nidheesh, Pineapple leaf (*Ananas comosus*) powder as a biosorbent for the removal of crystal violet from aqueous solution, *Desalin. Water Treat.* 54 (2015) 2041–2054, doi:10.1080/19443994.2014.903867.
- [37] F.A. Pavan, E.S. Camacho, E.C. Lima, G.L. Dotto, V.T.A. Branco, S.L.P. Dias, Formosa papaya seed powder (FPSP): preparation, characterization and application as an alternative adsorbent for the removal of crystal violet from aqueous phase, *J. Environ. Chem. Eng.* 2 (2014) 230–238, doi:10.1016/j.jece.2013.12.017.
- [38] I. Langmuir, The adsorption of gases on plane surfaces of glass, mica and platinum, *J. Am. Chem. Soc.* 40 (1918) 1361–1403, doi:10.1021/ja02242a004.

- [39] H.M.F. Freundlich, Over the adsorption in solution, *J. Phys. Chem.* 57 (1906) 385–470.
- [40] V.J.P. Poots, G. McKay, J.J. Healy, Removal of basic dye from effluent using wood as an adsorbent, *J. Water Pollut. Control Feder.* (1978) 926–935.
- [41] Z. Aksu, Biosorption of reactive dyes by dried activated sludge: equilibrium and kinetic modelling, *Biochem. Eng. J.* 7 (2001) 79–84, doi:[10.1016/S1369-703X\(00\)00098-X](https://doi.org/10.1016/S1369-703X(00)00098-X).
- [42] G.R. Mahdavinia, F. Bazmizyynabad, B. Seyyedi, *kappa* -carrageenan beads as new adsorbent to remove crystal violet dye from water: adsorption kinetics and isotherm, *Desalin. Water Treat.* 53 (2015) 2529–2539, doi:[10.1080/19443994.2013.870741](https://doi.org/10.1080/19443994.2013.870741).