

***Casuarina equisetifolia* cone as sustainable adsorbent for removal of Malachite green dye from aqueous solution using batch experiment method**

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Abstract

Various methods have been devised in order to treat the wastewaters before they are disposed into water bodies such as the rivers and the seas. One of the methods used is adsorption as it has the advantages of cheap, environmentally friendly and wide range of materials can be used. In this study *Casuarina equisetifolia* cone (CEC) was used to remove malachite green (MG) from aqueous solution and the adsorption process was investigated through contact time, pH, temperature, ionic strength and dye concentration. The experimental results indicated that CEC can operate well in high ionic strength solution and was not significantly affected by temperature. The adsorption process followed the pseudo-2nd order and can be described using the Langmuir model where the maximum adsorption capacity was determined as 58 mg g⁻¹.

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1. Introduction

Synthetic dyes play an important role in human society as they are used in textile, ink, cosmetics and food. However, most of them are toxic and even carcinogenic [1]. Water pollution due to direct discharge of synthetic dye is commonly found where textile industries are thriving. This will greatly affect the ecology of the water bodies where the discharged dyes could reduce the photosynthetic activity of the water plants and are toxic to the microorganisms. Small amount of dye in water could also change the colour of the water body causing unaesthetic view. The Fenton's method, reverse osmosis, ozonation, destruction of chromophore by addition of oxidising and reducing agents, phytoremediation and adsorption methods are few of the common methods for remediation of dye wastewater [2-5]. Adsorption is one of the simplest methods to remove a wide range of organic and inorganic pollutants from water. It uses simple concept of adhering the pollutants onto the adsorbent's surface through chemical and/or physical interactions which is an advantage as no secondary pollution is produced from the process. Activated carbon and resin are efficient as adsorbents but due to their high costs and complex preparations, their use in wastewater treatment is therefore limited [6]. Another advantage of adsorption method is that a wide range of materials can be used as adsorbents, as discussed in the literatures [7,8]. *Casuarina equisetifolia* tree grows in tropical and subtropical areas such as in Southeast Asia and Australia. It can thrive in dry climate and nutrient deficient soils as it forms symbiosis relationship with phosphate mobilising mycorrhizae and nitrogen-fixing *Frankia* in root nodules [9]. The tree has been used for several purposes such as timber production, mulching, landscaping, fuel, and as wind breaker at coastal areas while its needle like leaves can be used as mulch. Malachite green (MG) is a cationic dye that belongs to triphenylmethane dye. It is used as a colouring agent for textile and is also widely used as an antifungal agent in aquaculture to treat adult fish, fish eggs and fry, due to its effectiveness and low-cost of treatment [10]. However, MG is known to accumulate in fish's tissues as a nonpolar leuco form known as leucomalachite green [10]. This poses a major concern for human exposure as MG can transfer through food chain. Moreover, animal testing on rodents revealed the mutagenic and carcinogenic properties of MG where tumour formation in the rodent's liver and lungs adenomas were reported [11]. The aim of this research is to explore the potential use of *Casuarina equisetifolia* cone (CEC) as an adsorbent to remove MG from aqueous solution. Recent studies showed the applicability of *Casuarina equisetifolia* as an adsorbent to remove heavy metals [12-14] and dyes [15-17]. Recently, CEC was used to remove rhodamine b [18] dye and this suggests the possibility of CEC having potential to remove other basic dyes and thus, it was chosen as an adsorbent for this study to remove MG dye.

2. Materials and method

2.1 Sample and stock solution preparation

CEC were collected from campus ground; washed using distilled water and dried in an oven at 70 °C overnight. The dried cones were then blended and sieved to obtain particle size of < 355 µm. Stock solution of MG (90% purity, Sigma-Aldrich) was prepared by dissolving an appropriate amount of the dye in distilled water. Serial dilution was used to obtain lower MG concentrations. Distilled water was used throughout the experiment and all reagents were used without further purification.

2.2 Characterisation of CEC

Fourier transform infrared (FTIR) spectra of CEC, before and after treatment with MG, were recorded between 400 and 4000 cm⁻¹ with Shimadzu Model IR Prestige-21 spectrophotometer using KBr disc method. CEC was gold coated using SPI-MODULE™ Sputter Coater at plasma current of 8 mA for 60 seconds before its surface was studied using scanning electron microscope (SEM) (Tescan Vega XMU). CEC's point of zero charge (pH_{pzc}) was carried out using

salt addition method [19]. Briefly, the pH of 0.1 M KNO₃ (20 mL) solutions were adjusted using 0.1 M NaOH and HNO₃ to pH range of 2 – 10. CEC (0.04 g) was then added to each solution and the mixtures were agitated for 24 h at 250 rpm. The final pH of the mixtures was measured and the plot of ΔpH (final pH - initial pH) vs initial pH was used in order to determine the pH_{pzc}.

2.3 Batch experiment procedures

The batch experiment method involves changing one parameter at a time while other parameters are kept constant in order to investigate the effect of each parameter on the adsorption process. The parameters that were being investigated were contact time (5 – 240 min), dosage (0.01 – 0.06 g), pH (3 – 7), temperature (25 – 55 °C), ionic strength (0.1 – 0.8 M KNO₃) and dye concentration (20 – 500 mg L⁻¹). Generally, CEC (0.04 g) and MG of specific concentration (20 mL) were mixed in conical flasks and agitated at 250 rpm for a predetermined period of time. The dye content after the agitation was analysed using UV–visible spectrophotometer (Shimadzu UV-1601PC) at wavelength 618 nm. Equations (1) and (2) show the calculation used to determine the adsorption capacity (q_e) and the percentage removal (%), respectively.

$$\text{Adsorption capacity, } q_e \text{ (mg g}^{-1}\text{)} = \frac{(C_i - C_e)V}{m} \quad (1)$$

$$\text{Percentage removal} = \frac{(C_i - C_e) \times 100 \%}{C_i} \quad (2)$$

where C_i is the initial MG concentration (mg L⁻¹), C_e is the MG concentration at equilibrium (mg L⁻¹), V is the volume of MG used (L) and m is the mass of CEC used (g).

2.4 Error analyses

Two error functions were used namely the sum of absolute error (EABS) and chi-square test (χ^2) in order to gauge the suitability of a model in describing the experimental data. Low error function values indicate that the model and experimental data are in close agreement [20]. The equations of the two error functions are as follows:

$$\text{Sum of absolute error (EABS): } \sum_{i=1}^n |q_{e,exp} - q_{e,cal}| \quad (3)$$

$$\text{Chi - square test } (\chi^2): \sum_{i=1}^n \frac{(q_{e,exp} - q_{e,cal})^2}{q_{e,exp}} \quad (4)$$

where $q_{e,exp}$ is the q_e value obtained from the experiment while $q_{e,cal}$ is the calculated value from the theoretical models, n is the number of data points in the experiment and p is the number of parameters of the model.

2.5 Regeneration study

Distilled water and 0.1 M NaOH were used as the washing solutions in order to desorb MG from CEC and restore CEC's adsorption capability. The spent CEC was collected from the mixing of fresh CEC with 50 mg L⁻¹ MG and was washed thoroughly with distilled water in order to get rid of excess MG on the CEC. The sample was then divided into two portions where one portion was agitated with distilled water while the other with 0.1 M NaOH for 1 h followed by repeated rinsing using distilled water until the pH is neutral. Both portions were then dried in an oven at 70 °C overnight and the process was repeated for two times.

3. Results and discussions

3.1 Characterisations of CEC

Figure 1A shows the FTIR spectrum displaying the peaks corresponding to different types of functional groups on the CEC's surface. Hydroxyl (OH) and/or amino (NH) stretching can be found at 3431 cm⁻¹. This band underwent shift to 3417 cm⁻¹ as seen in Figure 1B after treatment with MG. Peak at 1736 cm⁻¹ belongs to carbonyl (C=O) group shifted

to 1741 cm^{-1} after treatment with the dye. Aromatic CO^- and phenolic OH stretching can be found at 1244 cm^{-1} while alcoholic OH is found at 1033 cm^{-1} . The shifts observed at these peaks may suggest the interactions between these functional groups on CEC with MG. Surface morphology of CEC is shown in Figure 2 where it can be seen that its surface is irregular and lack of any identifiable structures. CEC's pH_{pzc} is determined to be 4.22. This parameter is used to determine the pH at which the adsorbent has zero net charge i.e. neutral. When the medium $\text{pH} > \text{pH}_{\text{pzc}}$, the functional groups such as COOH will get deprotonated resulting in the increase of negative charge on the surface. While when the $\text{pH} < \text{pH}_{\text{pzc}}$, protonation of the functional groups such as NH will cause an increase of the surface's positive charge.

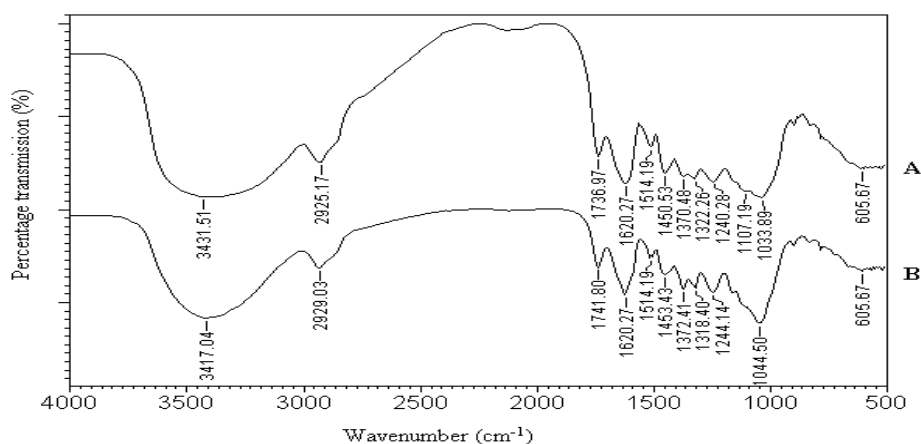


Figure 1. FTIR spectra of A) untreated CEC and B) CEC-MG

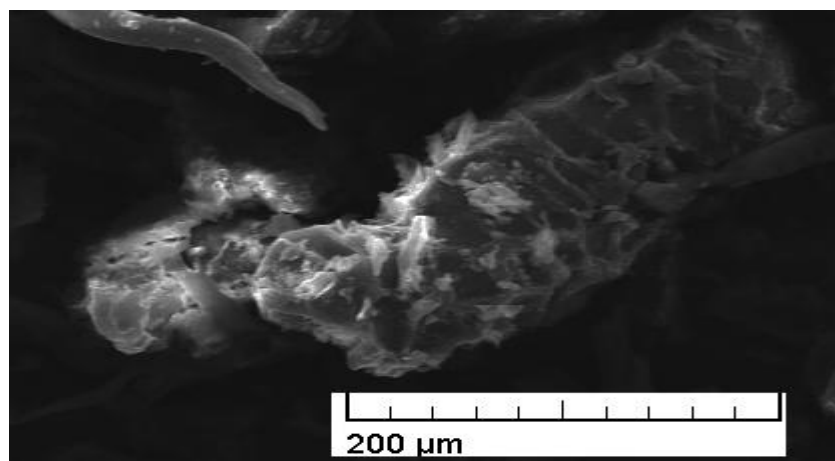


Figure 2. SEM image of untreated CEC

3.2 Effect of dosage

As seen in Figure 3, the percentage removal increases as the amount of CEC increases and this is contributed to the increasing amount of active sites for the MG molecules to interact with. The percentage removal reached a plateau beyond 0.04 g of CEC and thus, 0.04 g of CEC was chosen as the optimum amount to be used for the rest of the experiment.

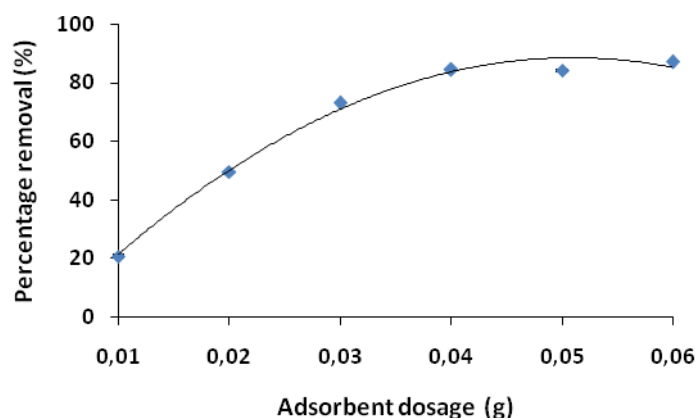


Figure 3. The effect of varying the amount of CEC on the adsorption process

3.3 Contact time and kinetics study

For practical purposes, it is important to determine the time taken for the adsorption process to reach equilibrium. Figure 4A shows the effect of contact time on the adsorption of 50, 100 and 200 mg L⁻¹ MG onto CEC. Aside from 50 mg L⁻¹, a common trend could be observed whereby the adsorption capacity increased rapidly within the first 30 min due to the initial availability of CEC's active sites and followed by a gradual increase as the active sites are gradually being filled until they become saturated with the dye molecules reaching a plateau. Kinetics models are used to investigate the mechanisms of the adsorption process and in this study, three widely used models are employed i.e. the pseudo-1st-order (equation 5) [21], pseudo-2nd-order (equation 6) [22] and Weber-Morris intraparticle diffusion (equation 7) [23]. The models' linear equations are as follow:

$$\log (q_e - q_t) = \log q_{e(cal)} - \frac{t}{2.303} k_1 \quad (5)$$

$$\frac{t}{q_t} = \frac{1}{q_{e(cal)}^2 k_2} + \frac{t}{q_{e(cal)}} \quad (6)$$

$$q_t = k_3 t^{1/2} + C \quad (7)$$

where t is the time (min), q_t is the adsorption capacity at given time (mg g⁻¹), $q_{e(cal)}$ is the calculated adsorption capacity (mg g⁻¹) and C is the intercept. k_1 (min⁻¹), k_2 (g mg⁻¹ min⁻¹) and k_3 (mg g⁻¹ min^{-1/2}) are rate constants for pseudo-1st-order, pseudo-2nd-order and Weber-Morris intraparticle diffusion model, respectively. Table 1 summarises the parameters for the three kinetics models. The pseudo-1st-order model yielded good correlation of determination (R^2) values of >0.9 for all the three dye concentrations. However, there are large deviations between the $q_{e(cal)}$ and $q_{e(expt)}$ values as well as large error functions values. This clearly indicates that this model does not fit well into the experimental data. The pseudo-2nd-order, on the other hand, has high R^2 values with good agreement between $q_{e(cal)}$ and $q_{e(expt)}$ values and small error functions values, indicating that the model is best fitted into the experimental data.

The Weber-Morris model is also applied to further understand the adsorption process mechanism whereby intraparticle diffusion is considered as rate limiting step when the linear Weber-Morris plot passes through the origin [22]. In some cases, the Weber-Morris plot will display multi linear lines, suggesting more than one mechanism is involved. Generally, three linear lines could be seen and they are represented as the film diffusion (1st linear line), intraparticle diffusion (2nd linear line) and equilibrium phase (3rd linear line). In Figure 4B, only two linear lines were seen; this is because the film diffusion is a very fast process which occurs for a short time during the agitation. From Table 1, the y-intercepts (represented as C) for all concentrations are non-zero values indicating that intraparticle diffusion is not the rate limiting step in the adsorption process.

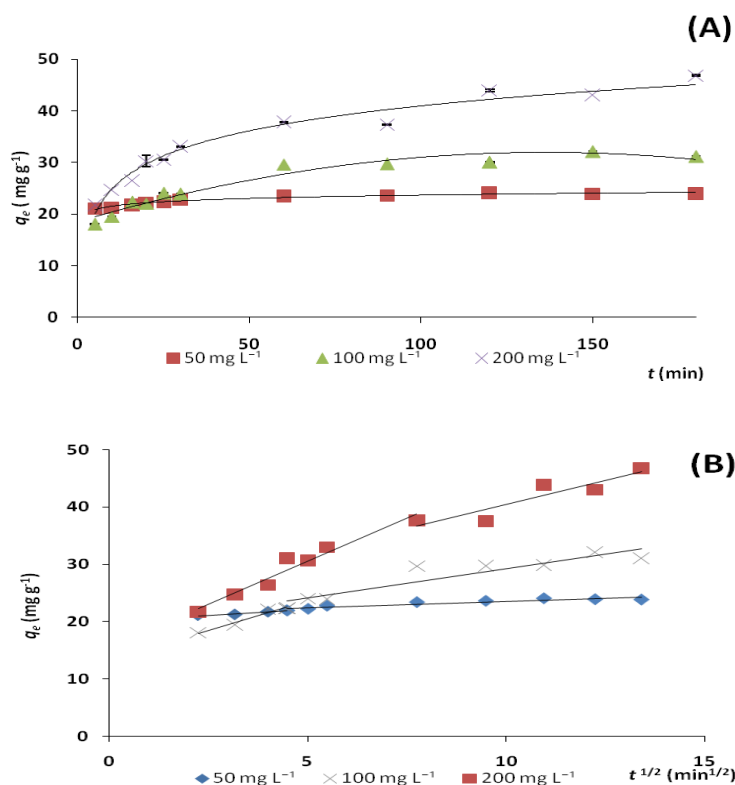


Figure 4. A) Effect of contact time and B) Weber-Morris plots on the adsorption of various MG concentrations onto CEC

Table 1. Calculated parameters of pseudo-1st-order, pseudo-2nd-order and Weber-Morris intraparticle models

Pseudo-1 st -order model			
C_i (mg L^{-1})	50	100	200
$q_{e,cal}$ (mg g^{-1})	2.660	12.107	23.435
$q_{e,exp}$ (mg g^{-1})	24.078	32.134	46.734
k_1	0.017	0.015	0.014
R^2	0.926	0.903	0.912
χ^2	221.202	170.789	181.127
EABS	235.038	217.661	255.884
Pseudo-2 nd -order model			
$q_{e,cal}$ (mg g^{-1})	24.146	32.674	47.629
$q_{e,exp}$ (mg g^{-1})	24.078	32.134	46.734
k_2	0.026	0.004	0.002
R^2	1.000	0.998	0.992
χ^2	1.129	12.387	22.306
EABS	13.478	47.903	78.524
Weber-Morris intraparticle diffusion model			
k_3	0.403	2.076	2.977
C	20.116	13.323	15.669
R^2	0.935	0.954	0.953

3.4 Effects of pH and ionic strength

The interactions between the adsorbent and adsorbate such as hydrogen bonding, electrostatic interaction and hydrophobic interactions can be affected by both pH and the ionic strength of the solution [24,25]. Therefore, it is imperative for these two parameters to be investigated as the real wastewater often involve in various range of pH and ionic strength. Figure 5A shows the effect of pH on the adsorption process. The q_e value, without any pH alteration, is 32 mg g^{-1} which increased to 37 mg g^{-1} when the pH was raised to pH 4. Beyond pH 4, the q_e values decreased drastically with each increasing pH. Usually, adsorptions of basic dyes are favourable at higher pH [26,27] but in this study high pH yielded low MG uptake by CEC. MG is known to be used as pH indicator [28] and thus the dye's intensity would change at certain pH. This change of intensity could be observed even without the addition of adsorbent and this might be the reason for the deviation from the literatures. Therefore, for the rest of the experiments, no pH alteration was done in order to avoid the decolorisation of MG. The adsorption of 50 mg L^{-1} MG onto CEC in various ionic strengths is shown in Figure 5B. It can be seen that the q_e values across the increasing ionic strength did not change significantly i.e. 20 mg g^{-1} for the mixture without addition of NaCl and 21 mg g^{-1} for the mixture with 0.8 M NaCl. This is another deviation found in this study whereby the adsorption of basic dyes would decrease with the increasing ionic strength due to electrostatic repulsion as well as the competition between the dye molecules and the salt's cation [24]. This suggests that electrostatic interaction might not play a major role in the adsorption of MG onto CEC. The removal of methylene blue and MG by *Casuarina equisetifolia* needle also showed similar result where the dyes uptakes were not severely affected by the increase in the ionic strength [16]. This can be considered as an advantage in the use of CEC in wastewater with high ionic strength.

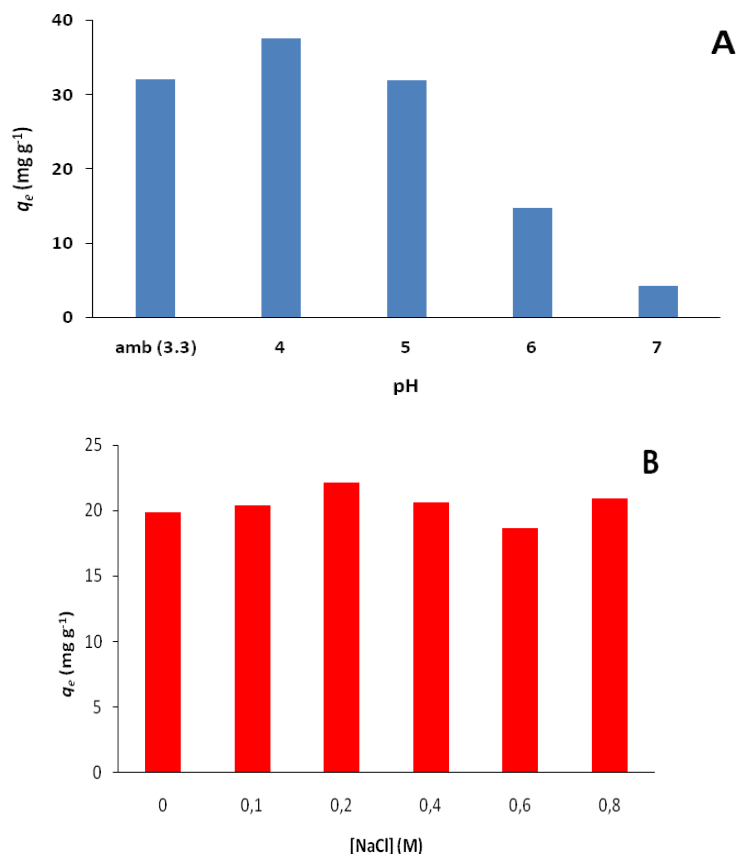


Figure 5. The effects of A) pH and B) ionic strength on the adsorption of MG onto CEC

3.5 Effect of temperature and thermodynamics study

As seen in Table 2, temperature has little effect on the adsorption of MG onto CEC. There is only slight increase of q_e values from 25 °C (20 mg g⁻¹) to 55 °C (22 mg g⁻¹). Adsorption thermodynamics provides information on the energy change in adsorption process by using the Van't Hoff equation. Gibbs free energy (ΔG°), enthalpy change (ΔH°) and entropy change (ΔS°) are obtained in order to further understand adsorption process. From Table 2, the adsorption is thermodynamically feasible and spontaneous throughout the temperature range as seen from the negative ΔG° values. Positive values of ΔH° and ΔS° indicate the endothermic nature and the increase in the system's randomness (favourable), respectively. The equations are shown as follows:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (8)$$

$$\Delta G^\circ = -RT\ln K \quad (9)$$

$$K = \frac{C_s}{C_e} \quad (10)$$

By inserting eq (8) into eq (9), the following equation is obtained:

$$\ln K = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (11)$$

where T is the temperature (K), R is the gas constant, K is the distribution coefficient for adsorption, C_s is the equilibrium dye concentration adsorbed on CEC (mg L⁻¹).

Table 2. The thermodynamics parameters and q_e values at different temperatures

T (°C)	ΔG° (kJ mol ⁻¹)	ΔH° (kJ mol ⁻¹)	ΔS° (J mol ⁻¹ K ⁻¹)	q_e (mg g ⁻¹)
25	-3.45	14.24	59.89	19.86
35	-4.69			21.16
45	-5.12			21.95
55	-5.43			21.60

3.6 Effect of concentration and isotherm modeling

Figure 6 shows the effect of increasing MG concentration on the adsorption capacity of CEC. It can be seen that increasing the dye concentration, the q_e values also increases. This might be caused by the increase in the mass transfer driving force as the concentration increases and thus, forcing more dyes to move towards the adsorbent.

Adsorption isotherm models are theoretical models that can be fitted with the experimental data in adsorption study in order to understand the adsorption process. Three isotherm models are used in this study and they are the Langmuir [29], Freundlich [30] and Sips [31] models. Their theories and applications have been discussed greatly in literature [20] and their expressions are shown in equations 12, 13 and 14. Table 3 depicts the adsorption isotherm parameters of each model as well as their error functions values. Comparing the three models' R^2 , EABS and χ^2 values, it can be said that Langmuir has the highest R^2 value (0.98) as well as the lowest error functions values amongst the three isotherm models. This therefore suggests that the experimental data can be described using the Langmuir model which assumes that the dye molecules will adsorb onto the adsorbent's surface at single layer. The R_L and n_F values indicate that the adsorption of MG onto CEC is favourable. The maximum adsorption capacity, q_m , value is determined as 58 mg g⁻¹ which is comparable to rattan sawdust (63 mg g⁻¹) [32], rice husk carbonised using NaOH (57 mg g⁻¹) [33], *Azolla pinnata* (87 mg g⁻¹) [34], walnut shell (91 mg g⁻¹) [35] and clay (40 mg g⁻¹) [36].

$$\text{Langmuir: } \frac{C_s}{q_e} = \frac{1}{K_L q_m} + \frac{C_s}{q_m} \quad (12)$$

$$\text{Freundlich: } \ln q_e = \frac{1}{n_F} \ln C_s + \ln K_F \quad (13)$$

$$\text{Sips: } \ln\left(\frac{q_e}{q_m - q_e}\right) = K_{LF} \ln C_e + \ln K_S \quad (14)$$

where q_m (mg g^{-1}) is the maximum monolayer adsorption capacity, K_L (L mg^{-1}) is the Langmuir constant, K_F ($\text{mg g}^{-1} (\text{L mg}^{-1})^{1/n}$) is the adsorption capacity of the adsorbent, n_F value (between 1 and 10) indicates favorability of the adsorption process, K_S (L g^{-1}) is Sips constant and K_{LF} is the exponent. The dimensionless parameter, R_L , is a characteristic of the Langmuir model which can be used to gauge the favourability of the adsorption process [37].

$$R_L = \frac{1}{(1 + K_L C_i)} \quad (15)$$

when $R_L = 0$ is considered as irreversible reaction; unfavorable when $R_L > 1$; linear when $R_L = 1$; and favourable when $0 < R_L < 1$ [38].

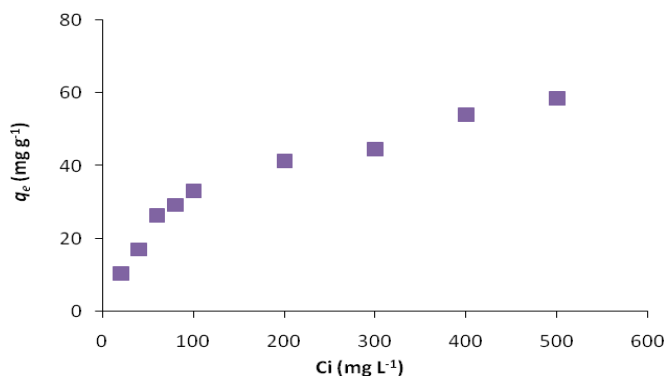


Figure 6. The effect of various concentrations of MG on the adsorption process

Table 3. The adsorption isotherm models' calculated parameters

Langmuir isotherm	
q_m (mg g^{-1})	58.14
K_L (L mg^{-1})	0.04
R_L	0.05
R^2	0.98
χ^2	3.10
EABS	22.40
Freundlich isotherm	
K_F ($\text{mg g}^{-1} (\text{L mg}^{-1})^{1/n}$)	9.74
n	3.30
R^2	0.91
χ^2	5.20
EABS	30.49
Sips	
q_m (mg g^{-1})	80.00
K_s (L mg^{-1})	0.10
K_{LF}	1.93
R^2	0.95
χ^2	3.17
EABS	23.99

3.6 Regeneration study

The reusability of an adsorbent can be gauged through various means and one of the methods is through chemical leaching of the pollutant from the adsorbent's surface. In this study, water and 0.1 M NaOH were used as washing solutions in order to investigate CEC's reusability. Initially, the removal of 50 mg L⁻¹ MG by CEC was 64 % which increased to 67% and 86% after first washing with water and the base, respectively. Upon second washing, the percentage removal increased again to 74% (water) and 86% (base). This shows that CEC's adsorption capability can be easily regenerated using these two solutions, particularly water which is an advantage as it is an inexpensive method of regenerating the adsorbent.

4. Conclusions

The results from this study showed the effectiveness of using CEC in removing MG from aqueous solution and its maximum adsorption capacity (58 mg g⁻¹) is comparable to other adsorbents in other works. The experimental data can be fitted into the pseudo-2nd-order kinetics and the Langmuir isotherm models. Thermodynamically, the adsorption process is feasible, endothermic and favourable. The advantages of using CEC, aside from its abundance and easy access, it that the adsorbent can operate well in water bodies with high ionic strength, can be easily regenerated and not significantly affected by the change in temperatures.

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