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# Silica gel matrix immobilized *Chlorophyta hydrodictyon africanum* for the removal of methylene blue from aqueous solutions: Equilibrium and kinetic studies

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***Chlorophyta hydrodictyon africanum* was immobilized on a silica gel matrix to improve its mechanical properties. The algae-silica gel adsorbent was used for batch sorption studies of a cationic dye, methylene blue (MB). Optimum adsorption was obtained with a dosage of 0.8 g bio sorbent. Results from sorption studies show that 124.11 mg·g$^{-1}$ of MB could be adsorbed at an optimum pH of 8 and immobilization of 300 mg per gram silica. Maximum immobilization was 400 mg biomass per gram silica. Sorption capacity increased with an increase in initial dye concentration and reached equilibrium within 30 min. Three models were used to simulate kinetic data and the pseudo–second order model gave a better fit with $R^2$ greater than 0.98 in all cases. Equilibrium studies revealed that the adsorption of MB followed Freundlich isotherm ($R^2$=1.00).**

**Key words:** Adsorbent, algae, Langmuir model, Freundlich isotherm.

## INTRODUCTION

The ever growing population and industrialization has led to environmental disorder as large numbers of xenobiotic compounds are being accumulated (Khataee et al., 2013). Dye effluent from the textile, pulp and paper industries is one of the major environmental concerns from a toxicological perspective (Ahmaruzzaman, 2009). The industries use dyes and pigments to color their products. Mane et al. (2007) reported that the colored effluent from these industries is a dramatic source of aesthetic pollution and perturbation of aquatic life. According to Namasivayam et al. (2001) and Waranusantigul et al. (2003), dye effluents in receiving streams interfere with transmission of light into streams and reduce photosynthesis. Many dye compounds and their metabolites are either, toxic, carcinogenic or teratogenic (Gong et al., 2007).

Removal of low concentrations of organic and inorganic substances from industrial effluent has encountered both technical and economic challenges. Although there are traditional methods of treating industrial effluent, these methods have challenges of their own and hence there has been a continual research in to more economic and environmentally friendly methods (Srinivasan et al., 2010; Gupta et al., 2009; Kyzas and Matis, 2013). One of the approaches that have attracted a lot of research interest has been the development of bio-adsorbents based on

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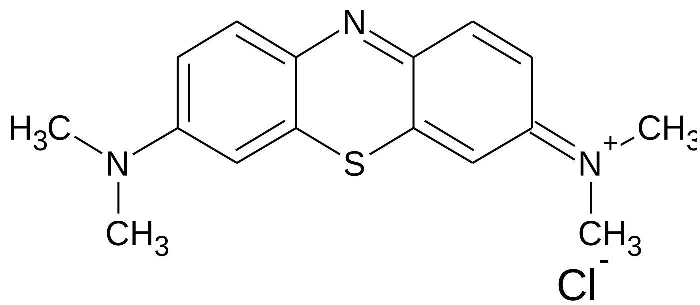

**Figure 1.** Chemical structure of methylene blue.

**Table 1.** Methylene Blue biosorption using selected alga species.

| Algal species | Maximum adsorption ($mg \cdot g^{-1}$) | References |
|---|---|---|
| Brown alga *cystoseira barbatula* Kützing | 38.61 $mg \cdot g^{-1}$ at 35°C | Caparkaya and Cavas, 2008 |
| *Chaetophora elegans* algae | 333 $mg \cdot g^{-1}$ at 30°C | El Jamal and Ncibi, 2012 |
| *Carolina* | 55 $mg \cdot g^{-1}$ at 19°C | Hammud et al., 2011 |
| Green alga *Uva latuca* | 40.2 $mg \cdot g^{-1}$ | El Sikaily et al., 2006 |
| *Chlorophyta hydrodictyon africanum* | 124.11 $mg \cdot g^{-1}$ at 25°C | Current study |
| *Scollymus Hispanics L.* | 263.92 $mg \cdot g^{-1}$ | Barka et al., 2011 |

algae (El-Batal et al., 2012). Different algae species have been tested of their capability to adsorb dyes (Daneshvar et al., 2012; Akar et al., 2009; Igbal and Saeed, 2007; Padmesh et al., 2005). Moreno-Garrido (2008), described current micro algae immobilization techniques and applications. The techniques, according to Moreno-Garido (2008) include passive immobilization, chemical attachment, active immobilization, silica gel entrapment, use of synthetic polymers etc. Entrapment of biosorbents improves mechanical properties and reduces problems associated with clogging (de-Bashan and Bashan, 2010; Kanchana et al., 2014).

In this study, we report a potentially viable approach for the removal of methylene blue (MB) from aqueous solutions using silica gel immobilized *Chlorophyta hydrodictyon africunum*, an algae species that widely thrives in the Zimbabwean summer weather. The chemical structure of methylene blue is shown in Figure 1. Studies carried out by other researchers have demonstrated that alga based adsorbents can be used for the removal of methylene blue with varying success. Table 1 lists some of the examples of methylene blue removal using various alga species.

## MATERIALS AND METHODS

### Instruments

A Genesys 10S UV/Vis spectrophotometer was used to determine concentrations of dye solutions. An orbital shaker was used to shake adsorbents suspended in dye solutions. pH measurements were taken using a pH meter and Hanna Instruments.

### Reagents

Chemicals used in this research were of reagent grade unless otherwise specified. The dye MB was purchased from Saarchem (Pvt) Ltd, (South Africa). Sodium hydroxide and hydrochloric acid were purchased from Skylabs (Pvt) Ltd. (South Africa). Sodium silicate was of technical grade purchased from a local supplier, Zimbabwe Phosphate Industries. All experiments were conducted in distilled water.

### Sample preparation

*C. hydrodictyon africanum*, an algae species that blooms in summer weather, was harvested from Mwenje Dam in Mashonaland Central Province (Zimbabwe), washed with distilled water before being dried at room temperature over a period of 30 days. The dried algae was ground and sieved through a 53-µm sieve. The fine particulate powder was used for immobilization experiments.

### Preparation of adsorbent

The immobilization of algae into silica gel matrix was carried out using a method previously reported (Rangasayatorn et al., 2004). 200 to 1000 mg of dry algae biomass was mixed with 25 mL of 6% sodium silicate solution (v/v) and 25 mL of distilled water. With continual stirring, the pH of the solution was reduced to 7.3 by gradual addition of 18% HCl solution (v/v) by which gelling will have started embedding the algae in the process. The gel was aged for 3 days at 40°C. The gel was washed with distilled water and dried at 80°C overnight. The gel was cut into smaller pieces and sieved to remove smaller than 150 µm ones. The immobilization of the algae ranged from 100 to 400 $mg \cdot g^{-1}$ depending on the algae added to a fixed volume of sodium silicate solution. A flow diagram for the general preparation of the immobilized bio sorbent is shown in Figure 2 and a picture for the immobilization step in Figure 3.

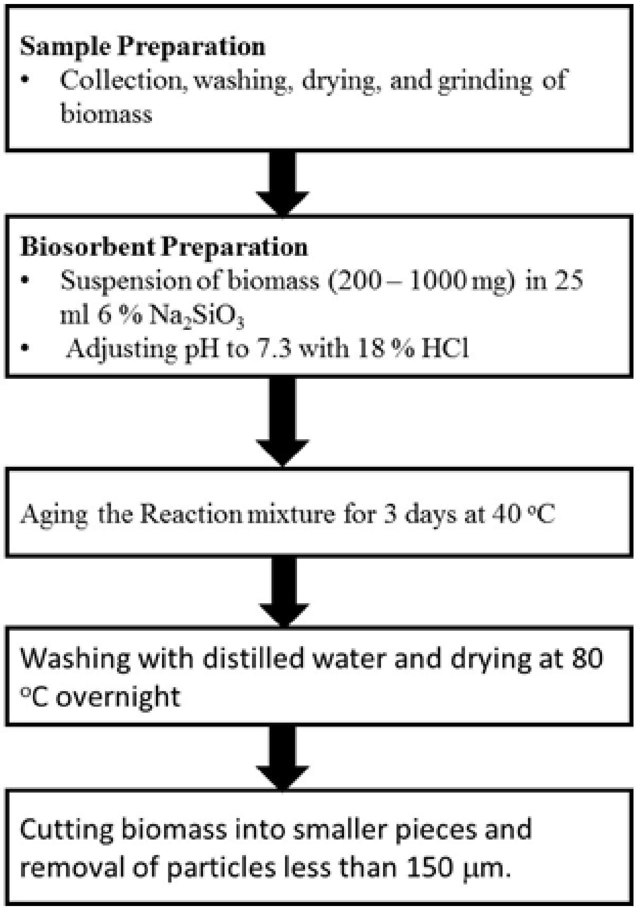


**Figure 2.** Flow diagram for the preparation of immobilized biosorbent.

**Figure 3.** Picture of immobilization of *Chlorophyta hydrodictyon africanum* in silica gel matrix.

#### Characterization of the adsorbent

Adsorption experiments were carried out to determine the effect of pH, algae loading capacity and contact time on the adsorption properties of silica gel immobilized *C. hydrodictyon africanum* adsorbent. This was achieved by mixing 50 mL of 25, 50, 100 and 200 mg·L$^{-1}$ dye solutions with known mass of silica gel embedded algae. The mixture was equilibrated by shaking with an orbital shaker. The initial and final dye concentrations were measured on a Genesys 10S UV/Vis spectrophotometer.

## RESULTS AND DISCUSSION

### Effect of pH

The effect of pH for the pH range 2-8 at an initial dye concentration of 200 mg·L$^{-1}$ and an adsorbent dosage of 0.8 g·L$^{-1}$ was investigated. At pH>8 the silica begins to dissolve releasing algae. The adsorption capacity of silica gel-immobilized alga was determined from the concentration difference of the solution, at the beginning and at equilibrium using equation (1).

$$q_e = \frac{V(c_i - c_e)}{100 \times m_{ads}} \quad (1)$$

Where, $c_i$ and $c_e$ are initial and equilibrium dye concentration, V the volume of the solution and $m_{ads}$ mass of adsorbent. The results are illustrated in Figure 4. From the diagram, it can be observed that there was a general increase in adsorption capacity with increase in pH for MB. It can be assumed that at lower pH, the surface of algae is positively charged prompting repulsion between the surface and dye molecules. This trend has also been observed by Fernandes et al. (2012) and Rubin et al. (2005) and was attributed to competition between the $H^+$ and dye cations at lower pH for sorption sites on the immobilized adsorbent resulting in low sorption capacity.

### Effect of dosage levels

The effect of adsorbent dosage levels was investigated for the dosage range 100 to 400 mg biomass per g silica. The results illustrated in Figure 5, shows an increase in adsorption up to a dosage of 300 mg biomass per gram silica. No significant increase was observed for dosage levels above 300 mg biomass per g silica. A maximum adsorption of 124.11 mg·g$^{-1}$ was obtained for MB. A high adsorption capacity for basic dyes was also observed by Khataee et al. (2013) on the biosorption of acid orange 7, basic red 46 and basic blue 3.

### Effect of initial dye concentration

The effect of initial dye concentration at maximum biosorbent loading capacity was investigated within the 25 to 200 mg·L$^{-1}$ dye concentration range. Figure 6 shows a general increase in adsorption capacity with

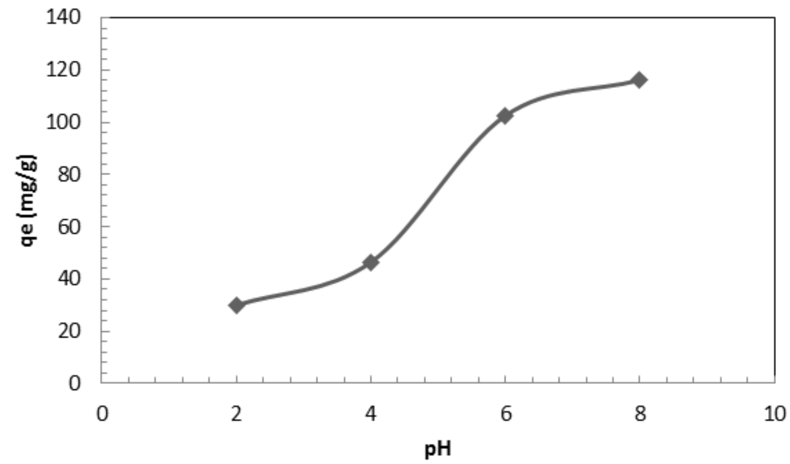


**Figure 4.** Effect of pH on the adsorption capacity of MB onto *Chlorophyta hydrodictyon africanum* ($c_0$=200 mg·L$^{-1}$, *t*=90 min, agitation speed= 135 rpm).

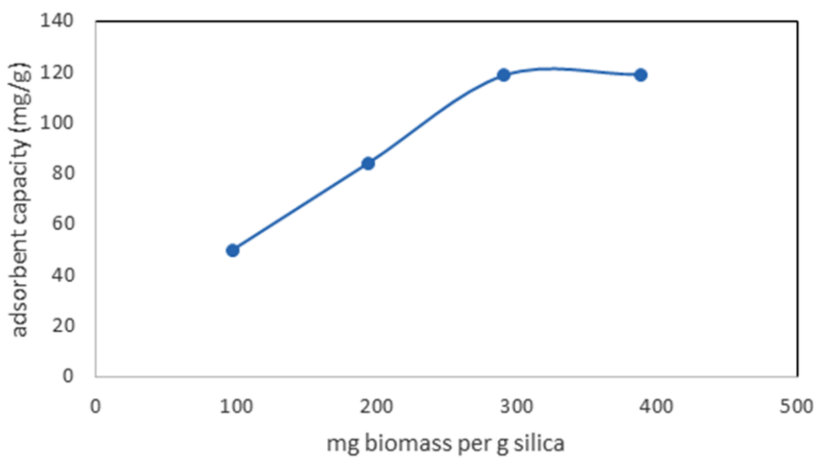


**Figure 5.** Effect of dosage level on maximum adsorption capacity of MB onto *Chlorophyta hydrodictyon africanum* encapsulated on to silica gel (pH8, t=90 min, T=25°C, agitation speed = 135 rpm).

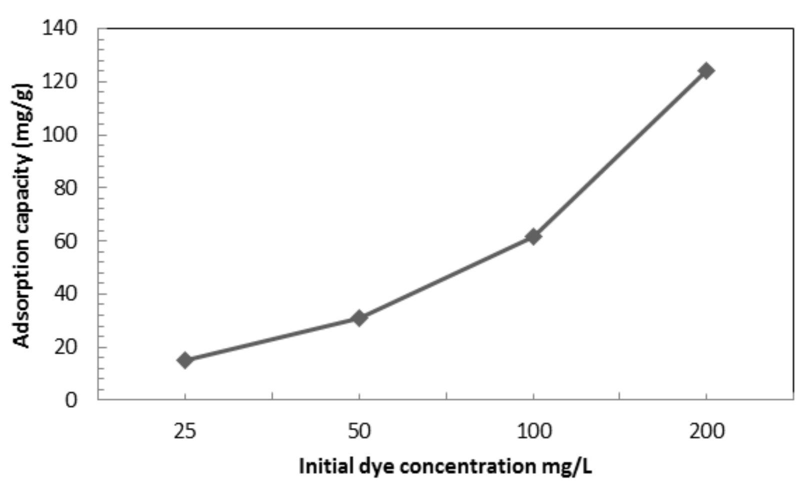


**Figure 6.** Effect of initial concentration on the adsorption capacity of MB at an adsorbent dosage of 0.8 g·L$^{-1}$ and pH8.

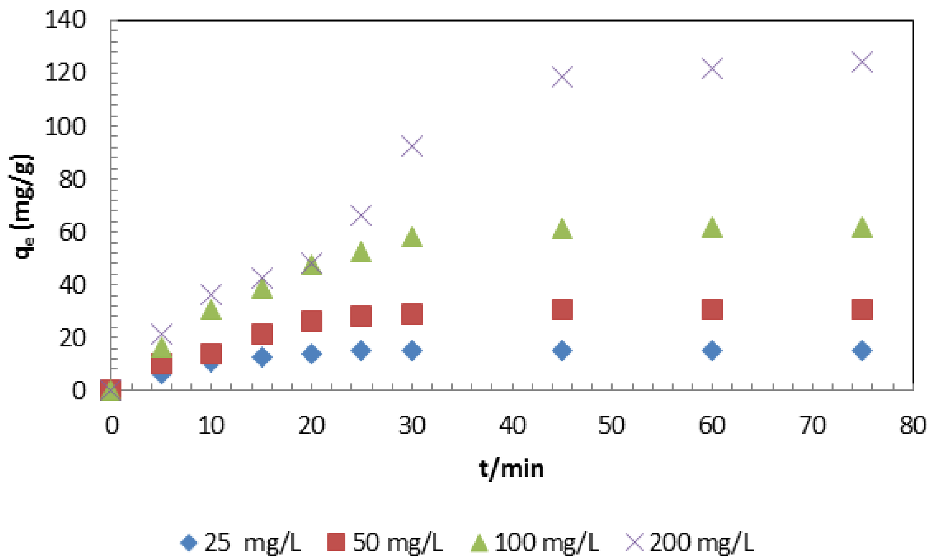


**Figure 7.** Effect of contact time on adsorption capacity of MB onto silica gel immobilized *Chlorophyta hydrodictyon africanum* for different initial dye concentrations (pH8, T=25°C, agitation speed =135 rpm, adsorbent dosage = 0.8 $g \cdot L^{-1}$).

increase in initial dye concentration up to a maximum adsorption of 124.11 $mg \cdot g^{-1}$. Adsorption of MB using *Spirodela polyrrhiza* (Waranusantigul et al., 2003) and *Ulothrix sp*. (Doğar et al., 2010) yielded comparable results.

## Effect of Contact time

Contact time determines the adsorbent's sorption capacity. Shorter equilibration times are most desirable for the application of adsorbents. The removal efficiency as function of time and initial dye concentration was investigated for equilibration times of up to 80 min. The result is graphically presented in Figure 7. From the graph, it can be observed that equilibrium was quickly reached in 30 min for initial concentrations of less than maximum adsorption capacity. At higher initial concentrations, equilibrium was reached after 45 min. The results are similar to adsorption experiments with acid dye, acid orange 7 and two basic dyes; Basic Red 46 and Basic Blue 3 carried out by Khataee et al. (2013). Doğar et al. (2010) who carried out similar experiments with MB using the green algae *Ulothrix sp.* biosorbent attributed their observations to concentration gradient between bulk and sorbent surface.

## Kinetic studies

### *Pseudo-first and second order kinetics*

Kinetic data were fitted into three models namely the pseudo-first order, pseudo-second and the intra-particle diffusion. Adsorption experiments were carried out using 0.8 g adsorbent which was added to 50 mL of MB. Equilibrium was attained by shaking with an orbital shaker for 90 min at 25°C and an agitation speed of 135 rpm.

The pseudo-first order model is expressed as:

$$\frac{dq}{dt} = k_1(q_e - q) \quad (2)$$

Where, $k_1$ is the pseudo-first order constant, $q_e$ and q are the amounts adsorbed at equilibrium and after a certain time t, respectively. Assuming that when $t$=0 and $q$=0 and integrating the Equation (2) gives:

$$\log(q_e - q) = \log q_e - \frac{k_1}{2.303} t \quad (3)$$

The value of $k_1$ can be obtained from the slope of a plot of *log* $(q_e\text{-}q)$ against *t*. The results are illustrated in Figure 8.

The pseudo-second order rate equation is expressed as

$$\frac{dq}{dt} = k_2(q_e - q)^2 \quad (4)$$

Where, $k_2$ is the rate constant of the second-order sorption. The linearized integrated form of Equation 4

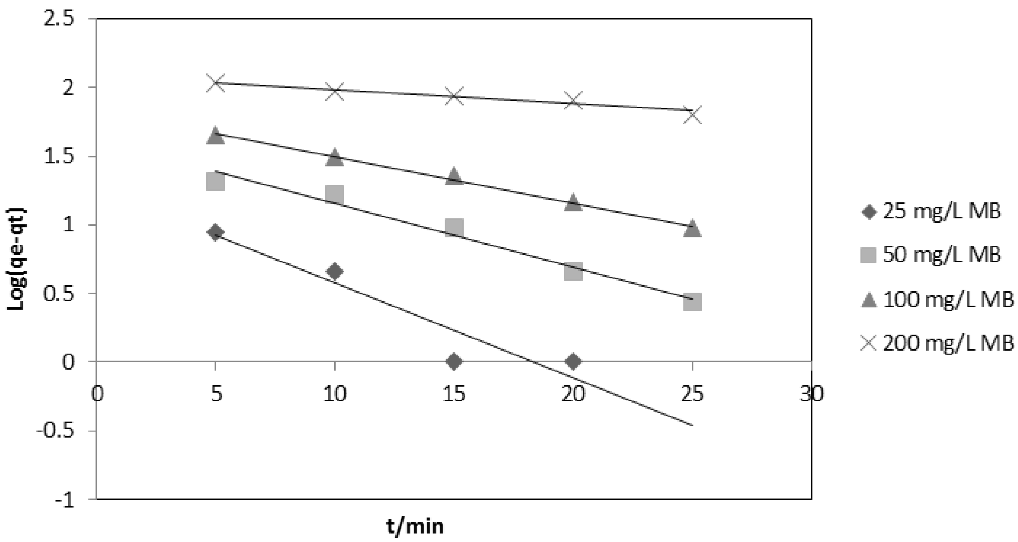


**Figure 8.** Pseudo first order kinetic modelling for the adsorption of MB on to silica gel immobilized *Chlorophyta hydrodictyon africanum* (pH=8, agitation speed = 135 rpm, T=25°C).

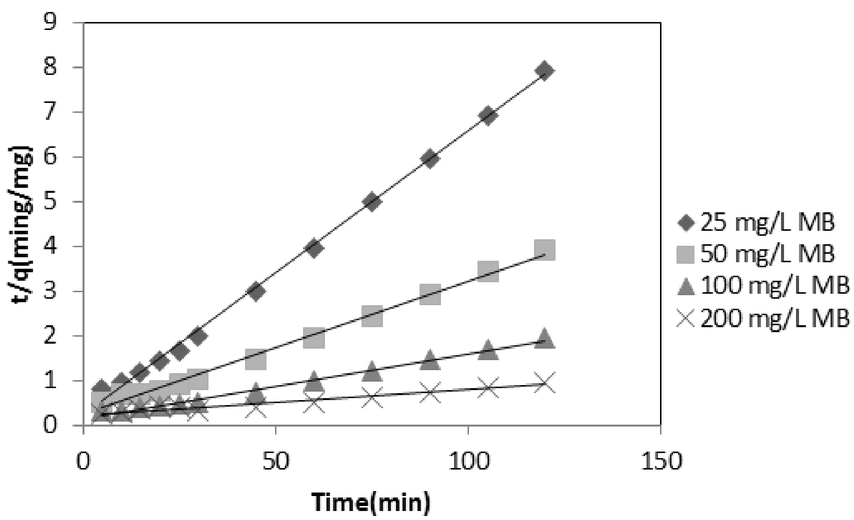


**Figure 9.** Pseudo second order kinetic modelling of adsorption of MB onto silica gel immobilized C*hlorophyta hydrodictyon africanum (*pH=8, agitation speed = 135 rpm, T=25°C).

is given as

$$\frac{t}{q} = \frac{1}{k_2 {q_e}^2} + \frac{1}{q_e} t \quad (5)$$

The rate parameters $k_2$ and $q_e$ can be obtained directly from the intercept and slope of the plot of *t/q* versus t. The results for the plot are illustrated in Figure 9. Parameters for both pseudo-first order and pseudo second order kinetics are shown in Table 2. The results show that adsorption processes for MB are better described by a pseudo-second order kinetics with $R^2$>0.99 in most cases.

## Intra-particle diffusion

The intra-particle diffusion or the Weber and Morris model describes processes involved in the sorption of the sorbate by sorbent (Wang et al., 2008; Qui et al., 2009). These include transport of the solute molecules from the aqueous phase to surface of sorbent particles and diffusion of the solute molecules into the pores of

**Table 2.** Pseudo-first and second order parameters for adsorption of MB on silica immobilized *Chlorophyta hydrodictyon africanum.*

| Concentration ($mg \cdot L^{-1}$) | Pseudo first order parameters | | | Pseudo second order parameters | | |
|---|---|---|---|---|---|---|
| | $K_1$ | $q_e$ | $R^2$ | $K_1$ | $q_e$ | $R^2$ |
| 25 | 0.1601 | 18.797 | 0.8913 | 4.7824 | 15.6986 | 0.9979 |
| 50 | 0.1069 | 41.5528 | 0.9772 | 4.3309 | 33.4448 | 0.9938 |
| 100 | 0.0783 | 69.0558 | 0.9957 | 7.1327 | 68.4932 | 0.9933 |
| 200 | 0.0241 | 123.2537 | 0.9363 | 4.761 | 172.4138 | 0.9430 |

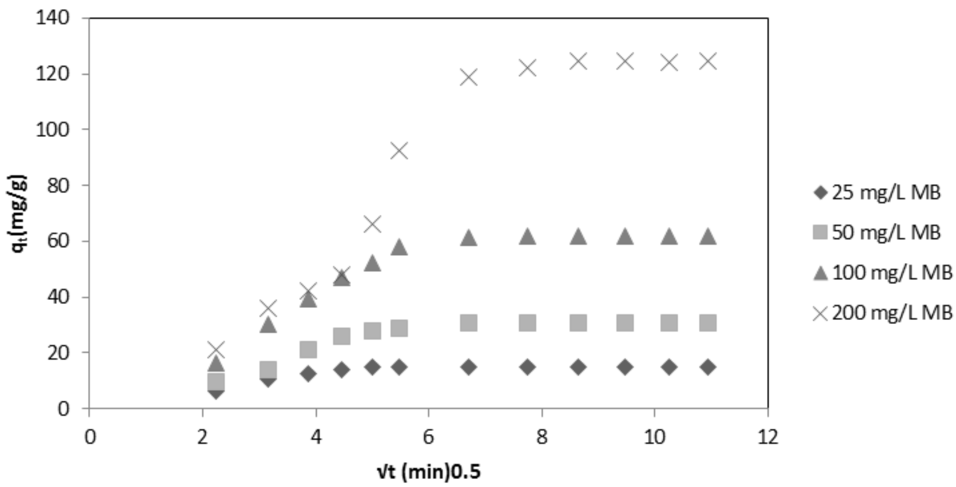


**Figure 10.** Intra-particle diffusion plot for the adsorption of MB using immobilized *Chlorophyta hydrodictyon africanum* (pH 8, adsorbent dosage = 1.6 $g \cdot L^{-1}$ at 25°C).

**Table 3.** Intra-particle diffusion parameters for the adsorption of MB on *Chlorophyta hydrodictyon africanum* immobilized of silica gel.

| Dye concentration ($mg \cdot L^{-1}$) | $k_{id1}$ | $R^2$ value | $k_{id2}$ | $R^2$ value |
|---|---|---|---|---|
| 25 | 3.1602 | 0.9718 | 0.198 | 0.3685 |
| 50 | 7.0371 | 0.9788 | 0.3872 | 0.6043 |
| 100 | 13.044 | 0.9961 | 0.5174 | 0.5100 |
| 200 | 14.728 | 0.9423 | 1.1918 | 0.7030 |

sorbent. The later step is a very slow process. Intra-particle diffusion processes can be described by equation (6).

$$q = k_{id}\sqrt{t} + c_{id} \quad (6)$$

Where, $k_{id}$ ($mg \cdot g^{-1} min^{-0.5}$) is the intra-particle diffusion rate constant and $c_{id}$ is the intercept. In the intra-particle diffusion model, the intercept helps to predict the effect of the boundary layer on the sorption process. The larger the intercept, the greater the boundary layer effect. These parameters can determined from a plot of q against $\sqrt{t}$. A plot of intra-particle diffusion is illustrated in Figure 10. The diagram shows two distinct zones. The first portion of the plot can be attributed to bulk diffusion and the other portion to intra-particle diffusion. The $k_{id1}$ and $k_{id2}$ values are shown in Table 3. The $k_{id1}$ values are as expected greater than $k_{id2}$ values.

## Equilibrium studies

Adsorption isotherms were used for the design of adsorption systems and study of surface properties of sorbents. Isotherms that were used are the Langmuir and

**Table 4.** Isotherm parameters for the decolorization of MB using *Chlorophyta hydrodictyon africanum* fixed on to silica gel.

| Dye | Langmuir constant | | | Freundlich | | |
|---|---|---|---|---|---|---|
| | $mg \cdot g^{-1}$ | $K_L$ ($L \cdot mg^{-1}$) | $R^2$ | $K_F(mg^{1-1/n}L^{1/n}g^{-1})$ | *n* | $R^2$ |
| MB | 227.27 | 0.2990 | 0.9898 | 0.5810 | 1.9870 | 1.00 |

$R^2$ values show that MB adsorption can accurately be described by the Freundlich model than the Langmuir model although both models could be used as evidenced by $R^2$ values of 1.00 and 0.9898, respectively.

Freundlich. The Langmuir assumes a monolayer homogeneous sorption site while the Freundlich assumes a heterogeneous sight. Table 4 shows isotherm parameters for the removal of MB from synthetic wastewaters. It can be seen that the data fits well to the Freundlich isotherm with $R^2$ approaching a unit value for MB. The $R^2$ values for Langmuir isotherms of MB 0.9898. The Freundlich constants $K_F$ and *n* indicate the affinity of the adsorbent towards the biomass. When *n* is greater than 1, there is positive binding and a heterogeneous nature of adsorption. The *n* values of 1.987 indicated a favorable biosorption of MB.

## Conclusion

The present study investigated the adsorption of MB from aqueous solutions using silica gel immobilized *C. hydrodictyon africanum.* This adsorbent has been demonstrated to be a highly effective material for the adsorption of MB from aqueous solutions. The adsorption capacity was found to be strongly pH dependent; adsorption capacity increased from about 30 $mg.g^{-1}$(pH=2) to about 124 $mg.g^{-1}$ (pH=8) at the biosorbent immobilization of 300 g biomass per gram silica. Adsorption kinetics studies revealed that the adsorption process followed the Pseudo-second order kinetic model. The equilibrium data were described by the Freundlich and the Langmuir isotherm models, but the Freundlich fit the experimental data well, with an $R^2$ value of 1.00. Value of *n* was greater than 1 confirming that the prepared adsorbent is favorable for adsorption of MB dye. This research showed that the adsorbent, silica gel immobilized *C. hydrodictyon africanum,* could be applied as a possible adsorbent for the removal of MB dye from wastewaters.

## Conflict of interests

The authors did not declare any conflict of interest.

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