Continuous flow biosorptive removal of methylene blue and crystal violet dyes using alginate–water hyacinth beads

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Abstract: The effectiveness of continuous flow biosorption of methylene blue and crystal violet dyes from aqueous solution was investigated using water hyacinth immobilized in sodium alginate. Characterization of the biosorbent was carried out using Fourier Transform Infrared Spectrometer (FTIR) and scanning electron microscopy (SEM). The adsorption process was optimized for adsorbate flow rate, initial dye concentration, and bed depth at fixed pH 8 under room conditions. The SEM showed the presence of a macroporous structure, whilst FTIR confirmed the presence of amine and hydroxyl groups. Increasing linear flow rate and initial dye concentration reduced breakthrough time ($t_b$) and exhaustion time ($t_e$), whilst the adsorption capacity at breakthrough point ($q_b$) increased with initial dye concentration and column bed depth. The adsorption data fitted both the Bed Depth Service Time (BDST) and the Yoon–Nelson models, with a BDST model adsorption capacity per unit volume ($N_o$) value of 14.2 mg/L and a critical bed depth ($X_o$) of 2.23 cm obtained. Regeneration and reuse of adsorbent gave an adsorption efficiency above 80% for both dyes in the binary solution phase for 3-sorption–desorption cycles. Water hyacinth showed great potential as a low-cost, efficient and effective biosorbent for the purification of dye-contaminated wastewater.

ABOUT THE AUTHORS
Prof Courtie Mahamadi holds a Doctor of Philosophy Degree from the University of Zimbabwe, whereas Mr Epias Mawere is a collaborating researcher. The authors’ research interests are on studying alternative technologies for the removal of metals and organic pollutants from water through use of low-cost adsorbents. The authors’ work contributes to knowledge on production of adsorbents using renewable materials such as abundant agricultural wastes and aquatic macrophytes. Emphasis is placed on the characterization of the adsorbents in terms of their physico-chemical properties and determination of their effectiveness in the removal of pollutants from water. Specifically, this study examines the removal of Methylene blue and Crystal Violet dyes from water using water hyacinth beads in continuous flow systems.

PUBLIC INTEREST STATEMENT
The environmental problems arising from high levels of dyes in aquatic systems are well documented. On the other hand, there are challenges associated with the rapid growth of water hyacinth weed, which has attracted significant attention as the world's worst invasive aquatic plant due to its extremely rapid proliferation and congests growth. Attempts to control the weed have been ineffective and have attracted high costs and labour requirements. The authors therefore found it of much interest to study ways of turning water hyacinth into an adsorbent for pollutants, therefore unlocking value in the otherwise troublesome aquatic weed. The authors show that beads produced using water hyacinth can easily be used in continuous flow adsorption and have potential for scaling-up for application in the removal of dyes such as methylene blue and crystal violet dyes from aqueous solution.
1. Introduction
Discharge of industrial effluents containing high levels of synthetic dyes into public aquatic systems has emerged as a major environmental pollution concern (Elemen, Kumbasar, & Yaper, 2012; Ma et al., 2018). Over 100,000 different varieties of dyes are in existence and the annual global production of synthetic dyes stands at over $7 \times 10^5$ metric tons (Soni, Sharma, Srivastava, & Yadav, 2012; Zhou, Lu, & Luo, 2017). These dyes cause serious environmental pollution due to their chemical composition and structure consisting of carcinogenic substances such as chromium and aromatics (Lazar, 2005; Yagub, Sen, Afroze, & Ang, 2014). Furthermore, some dyes have been found to adversely affect microbiological organisms and some fish species through mutagenic, or teratogenic mechanisms (Yagub et al., 2014). Additionally, for human beings, dyes can result in dysfunctional key organs such as kidney, liver, brain and central nervous system (Kadirvelu et al., 2003). Challenges caused by the presence of dyes in aquatic systems is exacerbated by their chemical stability which makes them relatively non-biodegradable. Therefore, it is imperative that dye-bearing waste waters are treated to remove residual dyes before the effluents are discharged into the environment.

Research into development of possible adsorbent materials for removal of dyes has yielded significant results over the decades. Particular attention has been drawn to activated carbon due to its effectiveness (Dimitrios, George, Antonis, & Nikolaos, 2016; Hao, Wanga, Wang, & He, 2019; Ramakrishna & Viraraghavan, 1997). However, the use of activated carbon has been limited by its high cost, non-selectivity, and regeneration challenges (Babel & Kurniawan, 2003). It has therefore been attractive for many workers to research on potential low-cost materials to be applied as adsorbents. Such materials would typically be abundant in nature, require minimum processing or would be wastes from other industrial processes. These include activated carbon based on biomass solid waste-precursor, industrial by-products such as waste slurry, biosolids, red mud, and fly ash; inorganic materials such as clay minerals, siliceous materials, zeolites and metal oxides (Yagub et al., 2014).

In recent times, biosorption, has emerged as an attractive technique with potential to offer a more efficient and cost-effective approach to removal of synthetic dyes from contaminated solutions (Fontana et al., 2016; Rangabhashiyam & Balasubramanian, 2018). The technique is increasingly gaining ground as a competitive, effective and low-cost approach that is more selective than traditional ion-exchange resins and commercial activated carbons (Rafatullah, Sulaiman, Hashim, & Ahmad, 2010). A wide range of materials have been studied for their potential as biosorbents, and these include biological materials, such as peat, chitin, rice straw, rice husk, chitosan, yeasts, fungi or bacterial biomass, and aquatic macrophytes (Sanghi & Verma, 2013). Water hyacinth, which is a wild fern belonging to the family pontederiaceae found abundantly in various tropical and sub-tropical countries of Latin America and the Caribbean, Africa, Southeast Asia and the Pacific, has shown promising potential for removal of heavy metals and dyes (Mahamadi & Nharingo, 2010). In related studies, Mahamadi and Majwere (2014) reported high adsorption capacities for batch removal of methylene blue and crystal violet (CV) dyes using water hyacinth fixed on alginate. However, literature search does not indicate that the adsorbent has been studied for removal of the dyes in continuous flow systems.

The current study therefore sought to establish the potential of water hyacinth immobilized in alginate for the removal of methylene blue and CV dyes from monocomponent and binary component aqueous solutions using continuous flow systems.
2. Materials and methods

2.1. Instruments
Micro-tube MP-3 peristaltic pump (Eyela, Japan); Genesys 10S (Thermo Scientific) UV/VIS spectrophotometer; magnetic stirrer (Stuart Scientific), Checker pH meter (Hanna Instruments, UK), scanning electron microscopy and FT-IR (done at University of Cape Town, South Africa).

2.2. Chemicals and reagents
The following chemicals were used: CaCl$_2$ (Saarchem Limited, South Africa); methylene blue dye (C.I. 5205) (Thomas Baker Chemicals Limited, India); CV dye (C.I. 42555) (Saarchem Limited, South Africa); and sodium alginate (Sigma Aldrich, Germany).

2.3. Sampling and preparation of water hyacinth biomass
The sampling procedure followed was adapted from Mahamadi and Nharingo (2010). Young water hyacinth plants were carefully selected from Pote river, Bindura, and washed thoroughly with river water on site before they were translocated to a water pond at the Bindura University of Science Education. The water hyacinth plants were then further washed with tape water before being introduced into the water pond. This was done to reduce the risk of heavy metal contamination on the plants. The water hyacinth was allowed to propagate in the pond for a 30 day period, at the end of which the parent plants were removed and daughter plants allowed to grow for a further 30-day period before harvesting. The stems were separated from the roots and discarded. The roots were thoroughly washed with tape water to remove grit, followed by rinsing with distilled water. The washed roots were then taken to the laboratory, spread on paper and left to air dry for 14 days. The dried roots were then ground into powder using mortar and pestle and the powder produced was sieved through a 75 µm aperture laboratory test sieve. The sieved powder, with particles size ranging between 50–75 µm was used for the experiments. In order to remove any residual, previously adsorbed inorganic materials and heavy metals, the biomass powder, in the ratio 20 g powder per 100 mL of acid solution was soaked in 0.1 M HNO$_3$ for 12 h at room temperature. The powder was then washed with distilled water until a pH range of 6–7 was obtained. The biomass powder was finally oven dried for 24 h at 60°C, and stored in a previously cleaned glass bottle.

2.4. Preparation of alginate–water hyacinth beads
The extrusion method previously reported by Samuel et al. (2013) was used for bead fabrication.

Sodium alginate (2 g) was dissolved in 100 mL of distilled water at 60 °C to give a 2 % alginate gelling solution. The mixture was continuously agitated for 4 h using a magnetic stirrer (Stuart Scientific) to obtain a polymer solution of homogenous viscosity. After cooling to room temperature, water hyacinth root powder (6 g) was introduced into 100 mL of the sodium alginate solution to make adsorbent of 6% biomass loading (Previous batch studies by Mahamadi and Mawere (2014) had shown that the 6% adsorbent dosage had a dye adsorption capacity greater than 90%). The Water hyacinth biomass powder–alginate solution mixture was stirred for a further 4 h at room temperature to ensure thorough mixing. Spherical beads were prepared by extruding this biomass polymer mixture into 100 mL of 0.1 M CaCl$_2$ solution through a glass funnel tip. The beads were left in the supernatant solution for 2 h to ensure adequate contact time for effective cross-linking, before being cured by placing them in 2 M CaCl$_2$ solution for a further 12 h at room temperature. Any beads that floated on top of the solution were removed and discarded. The remaining beads were then washed to remove excess CaCl$_2$ solution by agitating approximately 20 g of the beads (wet weight) in 100 mL of distilled water in 250 mL conical flasks on a horizontal shaker at 125 rpm for 30 min, the solution discarded and the process repeated five times. The beads were allowed to air dry at room temperature for 7 days, and then stored in a dry place for use in biosorption experiments.
2.5. Preparation of dye solutions
The single component simulated dye waste water solution was prepared by dissolving 1.0 g of methylene blue in a standard 1 L volumetric flask and diluting to 1000 cm$^3$ using distilled water to make a stock solution of 1000 mg/L. Solutions for adsorption experiments were then prepared from the stock solutions by serial dilution. The 1:1 binary dye stock solution was also prepared as described, but with 1.0 g of each dye being dissolved in the same volumetric flask. The two basic dyes were specifically chosen because their absorption peaks are well separated in binary solution. Methylene blue has a maximum wavelength of absorption of 663 nm in the UV/Vis region (Fernandez, Nunell, Bonelli, & Cukierman, 2012). CV has an absorption peak of 590 nm wavelength in the UV/Vis region (Eren, Cubuk, Cifti, Eren, & Caglar, 2010).

2.6. Column preparation
A cylindrical glass column of internal diameter 12 mm and length 300 mm was used throughout the investigations. The column was packed dry with varying quantities of the alginate–water hyacinth beads up to a predetermined depth. Prior to the start of biosorption experiments, the column was conditioned by pumping distilled water through the column at a flow rate of 1.5 mL/min using a peristaltic pump. This was done until the first few drops of water began to appear at the exit point. Thereafter the column was left standing for 4 h to allow close biomass packing. This process was repeated for each of the column biosorption experiments.

2.7. Biosorption studies
For all experiments, the dye solution pH was initially adjusted to pH 8 using 0.1 M HNO$_3$ and 0.1 M Na$_2$CO$_3$. This was decided after preliminary batch studies (Mahamadi & Mawere, 2014) showed this to be optimum pH. The column was operated in the down-flow mode throughout all the experiments. The effluent samples were collected at the exit point at specific time intervals and the dye concentrations analysed using a UV/Vis spectrophotometer at the maximum wavelength of absorption of each dye specified above.

2.8. Effect of flow rate
The effect of feed flow rate on the uptake the dyes was investigated using methylene blue at flow rates of 1.5 mL/min and 3 mL/min. The initial dye concentration and bed depth were fixed at 20 mg/L and 2.5 cm, respectively, throughout the sorption experiments. Dye solutions were collected at the column exit points and analysed for residual dye concentration at predetermined time intervals using a UV/Vis spectrophotometer.

2.9. Effect of bed depth
The dependence of dye uptake on bed depth was investigated by setting column height at 2.5, 5 and 8.5 cm, respectively. The inlet dye concentration was kept constant at 20 mg/L, whilst a fixed flow rate of 1.5 mL/min was used throughout. Dye solutions collected at the exit point were analysed for residual dye concentration using a UV/Vis spectrometer at regular time intervals.

2.10. Effect of initial dye concentration
The effect of initial dye concentration was investigated for the concentration ranging from 5 to 20 mg/L, with bed depth and linear flow rate fixed at 2.5 cm and 1.5 mL/min, respectively. Residual dye concentration was determined at fixed time intervals from solutions collected at the outlet point using a UV/Vis spectrophotometer.

2.11. Binary dye solution system column study
The biosorption experiments for the binary dye solution were carried out at a bed depth of 2.5 cm and inlet concentration of 20 mg/L. The flow rate was maintained at 1.5 mL/min. The solution collected at the column exit point was periodically collected and analysed for remaining dye concentration in the composite mixture using a UV/Vis spectrophotometer.
2.12. Biosorbent regeneration and re-use
Biosorbent desorption and re-use studies were investigated under batch conditions (Salleh, Mahmoud, Karim, & Idris, 2011). Alginate–water hyacinth beads (0.1 g) were shaken together with 50 mL of 20 mg/L of the 1:1 binary dye solution at 125 rpm for 120 min in an Erlenmeyer flask. At the end of this period, the beads were filtered from the solution and the residual dye concentration determined using a UV/Vis spectrophotometer. The dye saturated beads were then shaken with 50 mL of 0.1 M HNO$_3$ in 250 mL Erlenmeyer flasks at 125 rpm for another 120 min to desorb the dyes. The desorbed beads were washed with distilled water until a pH in the range 6–7 was obtained. The beads were then washed once with 10 mL of 0.01 M NaOH to recondition them, then with distilled water until excess NaOH was removed. The beads were then shaken for the second time with a fresh solution of 50 mL of 20 mg/L, 1:1 binary mixture of the dyes, and the procedure was repeated for three sorption-desorption cycles, and dye removal efficiency calculated.

3. Results and discussion

3.1. Characterisation of alginate–water hyacinth beads by SEM and FTIR
The surface characterisation of the immobilised Water hyacinth was carried out by SEM, whilst the identification of the essential biosorbent surface functional groups was done using FTIR. Figure 1 is an FTIR spectrum for the immobilised beads, whilst Figure 2(a–d) shows the scanning electron micrographs.

An intense FTIR peak at 3560 cm$^{-1}$ is indicative of the presence of hydroxyl (O-H) group. The peak at 1600.85 cm$^{-1}$ is due to the bending vibrations of an amine (N-H) group or aromatic C = C. Weak bands occurring at 1365.45; 1316.75; 1288.34; 1251.81; 1227.46; 1190.93 cm$^{-1}$ are attributed to a C–O stretch and suggests the presence of an acyl C–O, phenol C–O, or alkoxy C-O. The band centred at around 773 cm$^{-1}$ is associated with out-of-plane bending vibrations of C–H or O–H group. This suggests that functional groups, particularly hydroxyl and amine groups, potentially act as the active sites for the binding of cationic dyes and metal ions on alginate–water hyacinths beads. Mahamadi and Mawere (2014) showed that the alginate beads had the highest binding capacity at pH of 8, indicating the presence of negatively charged groups that were able to attract the positively charged ionic dyes from the solution. This deduction is supported by Soni et al. (2012) and Witek-Krowiak (2011), who reported that adsorbents of plant origin commonly have carboxyl,
hydroxyl and amino functional groups, and increase their adsorption capacity with pH. The surface structure of the beads shown in Figure 2, indicates that the adsorbent has a highly porous structure consisting of a network of organized fibres.

3.2 Optimization of factors that affect the biosorption of methylene blue and crystal violet by Alginate–Water hyacinth beads

3.2.1. Effect of flow rate
Figure 3 shows the effect of flow rate on the uptake of methylene blue at 1.5 mL/min and 3 mL/min flow rates with bed depth and initial dye concentration fixed at 8.5 cm and 20 mg/L, respectively. From these results, it can be observed that as the flow rate was increased from 1.5 mL/min to 3 mL/min, the breakthrough curve shifted towards the left and became steeper. The consequence of this increase in flow rate was that the breakthrough time ($t_b$) decreased from 240 to 120 min, whilst the exhaustion time ($t_e$) also decreased from 510 to 330 min (Table 1). It can be observed as well from Table 1 that increasing the flow rate, whilst maintaining other parameters constant, led to a reduction in the uptake capacity of the column, $q_b$, from 68.0 to 34.5 mg/g at breakthrough time. These findings are in agreement with the general trend observed for column biosorption studies reported by other workers (Aksu, Cagatay, & Gonen, 2007; Vinodhini & Das, 2010). A possible explanation for this trend is that an increase in flow rate reduces the dye residence time in the column, implying that the dye molecules
in the solution have less contact time with biosorbent. Aguayo-Villarreal et al. (2013) suggested that inadequate interaction time between the adsorbent and sorbate molecules in the column reduces the mass transfer time and therefore reduces sorbate diffusion time. This then transmits into shorter breakthrough and exhaustion times, as well as decreased adsorption capacity. It can be concluded from these results that higher flow rates do not make efficient utilization of the biosorbent and the column, as a higher adsorption capacity was recorded at a lower flow rate compared to higher flow rate. In addition, since for fixed bed column biosorption the volume of effluent treated can be determined as $V_{eff} = \text{flow rate} \times t_b$, it can further be concluded that a significant decrease in the time to reach breakthrough point may mean a large decrease in the volume of wastewater that may be treated, and the whole process may then become inefficient.

### 3.2.2. Effect of bed depth

Results for the effect of bed depth on the breakthrough curves for the column biosorption of methylene blue dye are shown in Figure 4. It can be observed that at a constant flow rate of 1.5 mL/min and fixed initial dye concentration of 20 mg/L, increasing column bed depth had a net effect of increasing both the time to reach breakthrough point ($t_b$), and the exhaustion time ($t_e$). The dye adsorption capacities also increased from 31 mg/g for a column depth of 2.5 cm, to 44 mg/g at 5 cm bed depth and finally 68 mg/g for 8.5 cm bed depth (Table 1). The results agree with those reported by Uddin, Rukanuzzaman, Khan, and Islam (2009), for the fixed bed removal of methylene blue by jackfruit. At lower bed depth, the amount of adsorbent present in the column is reduced, therefore there is a decreased number of biosorbent active sites. This leads to reduced dye adsorption capacities at lower bed depth, and the breakthrough times are shorter as well since the few active sites available would become quickly saturated. Therefore as bed depth is increased, a corresponding increase in breakthrough times, exhaustion times and adsorption capacities is observed.
3.2.3. Effect of initial dye concentration

The fixed bed biosorption of methylene blue in the mono-component solution was investigated for initial dye concentrations ranging from 5 to 20 mg/L. At all initial dye concentration values, the solution exiting the column at first contained negligible concentration of the dye. However, with time, the concentration of dye in the effluent began to rise, with a faster increase in residual dye concentration in the effluent being observed at the highest initial dye concentration of 20 mg/L. The breakthrough curves for the effect of initial dye concentration are shown in Figure 5 and results are summarized in Table 1. It can be seen from both Figure 5 and Table 1 that increasing the inlet concentration reduced both the breakthrough time and exhaustion time. However, higher concentrations resulted in improved adsorption capacities, possibly due to increasing concentration gradients. Aksu et al. (2007), made the same observations and also emphasised that concentration gradient plays a significant role in determining the time to reach saturation and breakthrough point. The longer breakthrough times observed at lower dye concentrations can be due to the fact that the reduced numbers of dye molecules in the solution require more time to completely saturate all the biosorbent active sites. Thus at low concentration, larger volume of waste water would be expected to be treated before the breakthrough point is reached. The increase in dye adsorption capacity at higher concentration can be attributed to a higher driving force that quickly saturates biosorbent adsorption sites as more dye molecules are present per unit of volume of dye solution passing through the column per given time.
3.2.4. Binary column adsorption of methylene blue and crystal violet
The efficacy of alginate–water hyacinth beads for the removal of dyes from binary systems was studied using a 1:1 dye mixture of methylene blue and CV, and the breakthrough curves are shown in Figure 6. The results demonstrate that the biosorbent can be effective in removal of dyes in binary dye systems, though the breakthrough time for methylene blue is shorter than that of CV. Initially, the two dyes bind simultaneously, with almost similar binding capacities, but the breakthrough curves eventually separate as the methylene blue adsorption reaches breakthrough faster than CV. A similar trend in results was reported by Aksu et al. (2007) for the biosorption of reactive dyes, and the authors suggested that the differences in the rate of binding could be explained by differences in molecular structure of the dyes and the mechanism of interaction of dye functional groups with the biosorbent functional groups, which are primarily the hydroxyl, the carboxyl and the amine groups.

3.2.5. Biosorbent regeneration
The potential for biosorbent reuse was investigated under batch sorption conditions and the results of three sorption-desorption cycles are presented in Figure 7. Initially three different solutions, 0.1 M NaCl, 0.1 M NaOH and 0.1 M HNO₃ were investigated for their potential to desorb the dyes. The amount of dye desorbed by 50 mL of each reagent after shaking for 120 min at 125 rpm was determined using UV/Vis spectrophotometer. The initial results showed very high desorbed concentration using HNO₃. NaCl showed a very low amount of desorbed dye in solution, whilst the beads began to destabilise and break up using NaOH. Therefore HNO₃ was selected as the desorbing agent. The results clearly indicate that although dye uptake capacity was over 80% for the three sorption-desorption cycles investigated, there was a significant decrease in removal efficiency for both dyes as the regeneration cycles increased, from 96 to 81% for methylene blue, and 92 to 81 for CV for the three cycles. This could probably be due to a less than 100% desorption as some of the active sites buried inside the inert immobilizing agent could not readily release the adsorbed dyes and remained saturated. The results also showed that the removal efficiency for methylene blue dye was consistently higher than that of CV, which suggests a preference for methylene blue over CV. Mahamadi and Mawere (2014) observed a similar trend in the biosorption of the two dyes, and suggested an antagonistic competitive interaction for the two dyes in binary solution.
3.3. Kinetic modelling of column sorption data

3.3.1. Bed-depth service time model

The BDST model describes the linear relationship between the service time of the column and the packed bed column depth, and produces data that can be used to predict column behaviour without the need for further experimental runs. According to the BDST model, the whole adsorption process is described by (Vijayaraghavan & Prabu, 2006)

\[ t = \frac{N_o}{C_o Q} Z \frac{1}{kC_o} \ln \left( \frac{C_o}{C_b} - 1 \right) \]  

(1)

where \( N_o \) is the adsorption capacity (mg/g), \( Z \) is the column bed depth (cm), and \( t \) is the service time linearly related to the bed depth.

Equation (1) can be simplified to:

\[ t = aZ + b \]  

(2)

where \( a \) is the slope and \( b \) is the intercept of the BDST line. It follows therefore that the quantities: \( \frac{N_o}{C_o} \) and \( \frac{1}{kC_o} \ln \left( \frac{C_o}{C_b} - 1 \right) \) can be evaluated from the slope and intercept of a linear plot of \( t \) at specific saturation point (10% of the inlet concentration for the current study) against bed depth, \( Z \).

According to Kumar and Bandyopadhyay (2006), it is possible to determine the critical depth from the BDST model equation, which is the minimum column depth required to produce an effluent concentration of \( C_b \) by setting time to \( t = 0 \) and solving for \( X_o \). This yields:

\[ X_o = \frac{Q}{kN_o} \ln \left( \frac{C_o}{C_b} - 1 \right) \]  

(3)

BDST evaluation of the biosorption data were performed at a flow rate fixed at 1.5 mL/min and initial dye concentration of 20 mg/L for methylene blue dye in the single dye aqueous system. From the results shown in Figure 8, a strong correlation between the service time and the bed depth \( (R^2 = 0.9963) \), demonstrated that the BDST model described the experimental data adequately. The BDST kinetic parameters: adsorption capacity \( N_o \) and the rate constant \( k \) derived from the plot of service time against bed depth at constant inlet dye concentration of 20 mg/L and feed flow velocity of 1.5 mL/min are presented in Table 2. The value of \( N_o \) at 14.2 mg/g was relatively
high, showing high effectiveness of the water hyacinth beads in removing methylene blue from solution. A low value of the rate constant $k$ was obtained (0.104 L/mg h), which further demonstrates the potential of the adsorbent in remediating dye waste water (Vinodhini and Das 2010).

The larger the value of $k$, the greater the likelihood of the column to avoid breakthrough, but as $k$ decreases, then a progressively longer bed is required to avoid breakthrough. The critical bed depth, $X_o$, which is the minimum column depth required to produce breakthrough concentration, was determined to be 2.23 cm for the experimental data.

### 3.3.2. Yoon–Nelson kinetic constants

The linear form of the Yoon–Nelson adsorption equation is given by (Bulgariu & Bulgariu, 2013)

$$\ln\left(\frac{C}{C_o - C}\right) = k_{YN}t - \tau k_{YN}$$  \hspace{1cm} (4)

where $k_{YN}$ is the Yoon–Nelson rate constant, $\tau$ is the time required to reach 50% breakthrough, and $t$ is the breakthrough time.

The adsorption parameters $k_{YN}$ and $\tau$ are determined from the slope and intercept of plot of $\ln\left(\frac{C}{C_o - C}\right)$ versus time ($t$).

Aksu et al. (2007), pointed out that since 50% breakthrough occurs at time $t = \tau$, then complete bed saturation should occur at $t = 2\tau$. Thus the determination of the time required to reach 50% saturation from the linear plot of $\ln\left(\frac{C}{C_o - C}\right)$ versus time ($t$) enables the prediction of complete bed saturation time.

Additionally, to predict the adsorption capacity of the column as a function of inlet dye concentration ($C_o$), feed flow rate ($Q$), biomass quantity in the column ($X$) and 50% breakthrough time ($\tau$) using the Yoon–Nelson model, the following equation can be used:
where \( q_{oYN} \) is the column adsorption capacity and the other parameters in the equation are as described above.

The experimental data were fitted to the Yoon–Nelson model as shown in Figure 9. It is evident that the model generally provided a good fit for the data throughout the concentration range under investigation (\( R^2 \) ranged from 0.9419 to 0.9916), with best fitting being observed at the higher initial dye concentration. This observation may suggest that the biosorption process is mass transfer-diffusion controlled. The results shown in Table 3 indicate that at a constant flow rate, the rate constant \( k_{YN} \) and the column adsorption capacity, \( q_{oYN} \) increased as the inlet dye concentration increased, whilst \( \tau \), the time to reach 50% breakthrough point increased with increase in initial dye concentration. These results are supported by those reported by Aksu et al. (2007), who investigated the removal of reactive dyes using dried \( Rhizopus arrhizus \) and also concluded that the time to reach 50% breakthrough time decreased with increasing inlet concentration.

### 4. Conclusion

The ability of alginate–water hyacinth beads to remove two cationic dyes from single and binary aqueous solution was evaluated under fixed bed column studies. The effect of process parameters, namely feed flow rate, bed depth and initial dye concentration on the breakthrough curves was investigated. Breakthrough times were observed to decrease with increasing dye concentration and flow rate, whilst overall dye uptake increased as inlet concentration increased. These results showed that the alginate–Water hyacinth beads can act as effective biosorbents for the column remediation of dye contaminated waste water. Evaluation of breakthrough data using the BDST and Yoon–Nelson models showed that both models could effectively describe the biosorption data,

### Table 3. Yoon–Nelson parameters for methylene blue dye

| \( C_0 \) (mg/L) | \( Q \) (mL/min) | \( k_{YN} \) (L/min) | \( \tau \) (min) | \( q_{oYN} \) (mg/g) | \( R^2 \)  |
|-----------------|-----------------|------------------|--------------|-------------------|--------|
| 5               | 1.5             | 0.0061           | 552.95       | 9.215             | 0.9419 |
| 10              | 1.5             | 0.0079           | 343.72       | 11.457            | 0.9854 |
| 20              | 1.5             | 0.0145           | 174.63       | 11.642            | 0.9916 |
and these results can be used to predict and design adsorption columns at a larger scale. Immobilization of water hyacinth in alginate beads allowed effective recycling of the biomass. The results show water hyacinth fixed in alginate beads to be an effective biosorbent for the continuous flow decontamination of industrial waste waters polluted by dyes.

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Competing Interests
The authors declares no competing interests.

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References
Aguayo-Villarreal, T. A., Ramirez-Montoya, L. A., Hernandez-Montoya, V., Bonilla-Petriciolet, A., Montes-Moran, M. A., & Ramirez-Lopez, E. M. (2013). Sorption mechanism of anionic dyes on pecan nut shells (Carya illinoinensis) using batch and continuous systems. Industrial Crops and Products, 48, 89–97. doi:10.1016/j.indcrop.2013.04.009
Aksu, Z., Cagatay, S. S., & Gonen, F. (2007). Continuous fixed bed biosorption of reactive dyes on dried Rhizopus oryzae: Determination of column capacity. Journal of Hazardous Materials, 143, 362–371. doi:10.1016/j.jhazmat.2006.09.039
Babel, S., & Kurniawan, T. A. (2003). Low-cost adsorbents for heavy metals uptake from contaminated water: A review. Journal of Hazardous Materials, 97(1), 219–243.
Bulgariu, D., & Bulgariu, L. (2013). Sorption of Pb(II) onto a mixture of olive waste biomass and anion exchanger in a packed-bed column. Bioresource Technology, 129, 374–380. doi:10.1016/j.biortech.2012.10.142
Dimitrios, A. G., George, Z. K., Antonis, A., & Nikolaos, K. L. (2015). Multi-parametric adsorption effects of the reactive dye removal with commercial activated carbons. Journal of Molecular Liquids, 213, 381–389. doi:10.1016/j.molliq.2015.07.010
Elemen, S., Kumbasar, E. P. A., & Yaper, S. (2012). Modelling the adsorption of textile dyes onto organoclays using an artificial neural network. Dyes and Pigments, 95, 102–111. doi:10.1016/j.dyepig.2012.03.001
Eren, E., Cubuk, O., Cifti, B., Eren, B., & Caglar, B. (2010). Adsorption of basic dye from aqueous solutions by modified sepiolite: Equilibrium, kinetics and thermodynamic study. Desalination, 252, 88–96. doi:10.1016/j.desal.2009.10.020
Fernandez, M. E., Nunell, G. V., Bonelli, P. R., & Cukierman, A. L. (2012). Batch biosorption of basic dyes from binary solutions by alkaline-treated cypress cone chips. Bioresource Technology, 106, 55–62. doi:10.1016/j.biortech.2011.12.003
Fontana, K. B., Chaves, E. S., Sanchez, J. D. S., Watonobe, E. R. L. R., Pietrobelli, J. M. T. A., & Lenzi, G. G. (2016). Textile dye removal from aqueous solutions by malt bagasse: Isotherm, kinetic and thermodynamic studies. Ecotoxicology and Environmental Safety, 124, 329–336. doi:10.1016/j.ecoenv.2015.11.012
Hao, Y., Wang, Z., Wang, Z., & He, Y. (2019). Preparation of hierarchically porous carbon from cellulose as highly efficient adsorbent for the removal of organic dyes from aqueous solutions. Ecotoxicology and Environmental Safety, 168, 298–303. doi:10.1016/j.ecoenv.2018.10.076
Kadirvelu, K., Kaviyipri, M., Karthika, C., Radhika, M., Vennilaminai, K., & Pattabhi, S. (2003). Utilization of various agricultural wastes for activated carbon preparation and application for the removal of dyes and metal ions from aqueous solutions. Bioresource Technology, 87(1), 129–132.
Kumar, U., & Bandypadhyay, M. (2006). Sorption of cadmium from aqueous solution using pretreated rice husk. Bioresource Technology, 97, 104–109. doi:10.1016/j.biortech.2005.02.027
Lazar, T. (2005). Color chemistry: Synthesis, properties, and applications of organic dyes and pigments. Color Research and Application, 30(4), 313–314. doi:10.1002/cral.20132
Ma, H., Kang, A., Ji, Y., He, B., Song, Y., & Li, J. (2018). Ultrahigh adsorption capacities for anionic and cationic dyes from wastewater using only chitosan. Journal of Cleaner Production. doi:10.1016/j.jclepro.2018.12.217
Mahamadi, C., & Mawere, E. (2014). High adsorption of dyes by water hyacinth fixed on alginate. Environmental Chemistry Letters, 12(2), 313–320. doi:10.1007/s10311-013-0465-z
Mahamadi, C., & Nharingo, T. (2010). Competitive adsorption of Pb(II), Cd(II) and Zn(II) ions onto Eichhornia crassipes in binary and ternary systems. Bioresource Technology, 101, 859–864. doi:10.1016/j.biortech.2009.08.097
Rafatullah, M., Sulaeman, O., Hashim, R., & Ahmad, A. (2010). Adsorption of Methylene Blue on low-cost adsorbents: A review. Journal of Hazardous Materials, 177(1–3), 70–80. doi:10.1016/j.jhazmat.2009.12.047
Ramakrishna, K. R., & Viraraghavan, T. (1997). Dye removal using low cost adsorbents. Water Science and Technology, 36(2), 189–196. doi:10.2166/wst.1997.0516
Rangabhashiyam, S., & Balasubramanian, P. (2018). Biosorption of hexavalent chromium and malachite green from aqueous effluents, using Cladophora Sp. Chemistry and Ecology, 34(4), 371–390. doi:10.1002/chee.20181627232
Salleh, M. A. M., Mahmoud, P. K., Karim, A. V. A., & Idris, A. (2011). Cationic and anionic adsorption by agricultural solid wastes: A comprehensive review. Desalination, 280, 1–13. doi:10.1016/j.desal.2011.07.019
Samuel, J., Pulini, M., Paul, M. L., Mauya, A., Chandrasekaran, N., & Mukherjee, A. (2013). Batch and continuous flow studies of adsorption of adsorptive removal of Cr(III) by adapted bacteria.
consortia immobilised in alginate beads. Bioresource Technology, 128, 423–430. doi:10.1016/j.biortech.2012.10.116
Sanghi, R., & Verma, P. (2013). Decolorisation of aqueous dye solutions by low-cost adsorbents: A review. Coloration Technology, 129, 85–108. doi:10.1111/cote.2013.129.issue-2
Soni, M., Sharma, A. K., Srivastava, J. K., & Yadav, J. S. (2012). Adsorptive removal of Methylene Blue dye from an aqueous solution using water hyacinth root powder as a low cost adsorbent. International Journal of Chemical Sciences and Applications, 3(3), 338–345.
Uddin, M. T., Rukanuzzaman, M., Khan, M. K. R., & Islam, M. A. (2009). Adsorption of Methylene Blue from aqueous solution by jackfruit (Artocarpus heterophyllus) leaf powder: A fixed bed column study. Journal of Environmental Management, 90, 3443–3450. doi:10.1016/j.jenvman.2009.05.030
Vijayaraghavan, K., & Prabu, D. (2006). Potential of Sargassum wightii biomass for copper(II) removal from aqueous solutions: Application of different mathematical models to batch and continuous biosorption data. Journal of Hazardous Materials, 137, 558–564. doi:10.1016/j.jhazmat.2006.02.030
Witek-Krowiak, A. (2011). Analysis of influence of process conditions on kinetics of adsorption of malachite green biosorption onto beech sawdust. Chemical Engineering Journal, 171, 976–985. doi:10.1016/j.cej.2011.04.048
Yagub, M. T., Sen, T. K., Afroz, S., & Ang, H. M. (2014). Dye and its removal from aqueous solution by adsorption: A review. Advances in Colloid and Interface Science, 209, 172–184. doi:10.1016/j.cis.2014.04.002
Zhou, J., Lu, Q.-F., & Luo, -J.-J. (2017). Efficient removal of organic dyes from aqueous solution by rapid adsorption onto polypyrrole-based composites. Journal of Cleaner Production, 167, 739–748. doi:10.1016/j.jclepro.2017.08.196