Fixed-bed column studies for the removal of hazardous malachite green dye from aqueous solution using novel nano zerovalent iron algal biocomposite

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Abstract *Sargassum swartzii*, a marine alga was used as precursor for the synthesis of novel nano zerovalent iron *S. swartzii* (nZVI-SS) biocomposite for the removal of malachite green (MG) from simulated wastewater in a fixed-bed column. The performance of the biocomposite was evaluated in the fixed-bed column at various operating conditions such as bed height (3–9 cm), flow rate (5–15 mL/min) and initial MG concentration (5–15 mg/L). The lowest bed height (3 cm), lowest flow rate (5 mL/min) and highest inlet MG concentration (15 mg/L) resulted in highest MG uptake of 0.56 mg/g, compared to other experimental conditions. The column experimental data obtained at different conditions were analyzed using three different models, viz., Adam–Bohart model, Thomas model and Yoon–Nelson model. All three models provided a good breakthrough curve prediction; however, the results obtained from Thomas model and Yoon–Nelson model were more satisfactory. The well-recognized BDST model was also used for describing the effect of bed height on the breakthrough curve. The various characteristics of the biocomposite were studied using SEM, DLS, XRD, XRF and XANES. The nZVI-SS biocomposite fixed-bed column proved to be the potential biosorbent for the removal of MG from aqueous phase.

Keywords Biosorption · Dye · Algae · Zerovalent iron · Wastewater · Fixed-bed column

List of symbols

A	Cross-sectional area of the bed (cm^2)
C_{ad}	Concentration of dye removal (mg/L)
C_0	Influent dye concentration (mg/L)
C_t	Effluent dye concentration (mg/L)
k_{AB}	Kinetic constant (L/mg min)
k_{Th}	Thomas model constant (mL/min mg)
k_{YN}	Rate constant (min^{-1})
m_{total}	Amount of adsorbate sent to column (g)
N_0	Saturation concentration (mg/L)
q_0	Adsorption capacity (mg/g)
q_{eq}	Equilibrium dye uptake (mg/g)
q_{total}	Total mass of dye adsorbed (mg)
Q	Volumetric flow rate (cm^3/min)
t	Total flow time (min)
t_{total}	Total flow time (min)
U_0	Superficial velocity (cm/min)
V_{eff}	Effluent volume (mL)
Z	Bed depth of the fixed-bed column (cm)
Y	Percentage of MG removal (%)

Greek symbol

τ Time required for 50 % adsorbate breakthrough (min)

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Introduction

Dyes and pigments are extensively used in most of the processing industries to color their products. Dyes and their metabolites are one among the severe pollutants of our environment. Perhaps, some of the dyes are known to have

toxic as well as carcinogenic, mutagenic and teratogenic effects on aquatic life and humans. Malachite green (MG) or basic green 4, a triphenylmethane is widely used in aquaculture as a parasiticide and in food, health, textile and other industries for various applications. In aquaculture industry, MG is used as biocide against parasitic treatment and for fungal and bacterial infections in fish and fish eggs due to its potent anti-parasitic effect [1]. It is also widely used in various industries like silk, wool, jute, leather and paper to color their products [2].

Several methods have been investigated for the removal of dyes from wastewater. Chemical precipitation is a common conventional treatment where a large quantity of chemical is necessary for the dye treatment which in turn generates a large volume of sludge [3]. Other treatment methods are ion exchange, activated carbon, filtration, electrolysis and reverse osmosis which requires high capital investment and operational costs [4]. Interestingly, biosorption was known to be a low-cost method for the treatment for dye-containing wastewater [5]. Of course, this technique has attracted most of the researchers because of its low initial cost, flexibility and simplicity of design, ease of operation, reusability of biosorbent and high efficiency. Various biosorbent materials such as bacteria, yeast, algae and other agricultural waste have been used to remove dyes from wastewater [5, 6]. However, the constituents of biosorbents are mainly responsible for the removal of any particular pollutants from wastewater [7]. *Sargassum*, a marine brown alga was found to have various functional groups over the surface of the cell wall serves as excellent ligand for the sorption of ions from the aqueous solution [8, 9]. However, to enhance the biosorption capacity, there is a need for the modification of the biosorbent. Nowadays, zerovalent iron gaining much importance in the treatment of hazardous and toxic wastes [10]. Interestingly, development of biomaterials and composites in nanoscale is gaining attention for adsorption of dyes and heavy metal ions [11]. Zerovalent iron (ZVI) composites are eco-friendly cost-effective reducing agent and are reliable biosorbent for dye and heavy metals removal from wastewater.

In our previous work, nano zerovalent *Sargassum swartzii* (nZVI-SS) was employed as biosorbent in batch mode of operation and the results showed that nZVI-SS was promising biosorbent. Thus, present objective of the research is to investigate the practical applicability of the biosorbent in a continuous column operation. The influence of several operational parameters such as bed depth, feed flow rate and inlet dye concentration has been analyzed. Further, the fit of the experimental data to various models such as Thomas, bed depth service time (BDST), Adams–Bohart and Yoon–Nelson was subjected to describe the breakthrough curves.

Materials and methods

Reagents and chemicals

Dye (malachite green) was purchased from Nice Chemicals, India. Dye used in the present study is of commercial grade with 70 % purity (oxalate form). Sodium borohydride (NaBH_4 , 98 %, Alfa Aesar), iron (III) chloride (FeCl_3 , 98 %, Alfa Aesar) were purchased and used without further purification. All other chemicals were purchased locally with at least 98 % purity and used without any further purifications.

Preparation of biosorbent and dye solution

Raw *S. swartzii* was collected locally from Mandapam, Tamil Nadu, India. The collected seaweed was washed with distilled water for five times and subsequently dried in hot air oven at 60 °C for 24 h. The dried biomass was chopped using mechanical grinder and sieved to a particle size of 0.5–1.0 mm (B.S.S Mesh No. 25). The processed biomass was protonated using 0.1 M HCl. The biomass was then washed several times with distilled water to remove the excess of acid adhering onto the surface, and the protonated biomass was dried overnight at 60 °C. Malachite green (MG) was selected as the model dye for the present investigation. The stock solution was prepared by dissolving 1 g of dye in 1000 mL of distilled water. Working solutions were prepared by diluting the stock solution. The maximum absorbance of malachite green is 617 nm and at this absorbance, dye decolorization was monitored.

Synthesis and characterization of nZVI-*Sargassum swartzii* biocomposite

The nanoscale zerovalent iron (nZVI)-*S. swartzii* biocomposite material was prepared by borohydride reduction method using FeCl_3 and macroalgae (*S. swartzii*) in the ratio 1:1 (mass basis). The protonated biomass was added to the solution containing 0.05 M FeCl_3 in a beaker and stirred using a magnetic stirrer for 2 h. After a thorough mixing, 10 mL of 0.53 M NaBH_4 solution was added into the above mixture and further stirred well for another 30 min to form precipitates. The precipitates formed were washed several times with ethanol and filtered using 0.45- μm Millipore filter paper and dried at 50 °C overnight [12].

The formation of iron precipitates was observed using scanning electron microscopy (JSM – 6390LV, JEOL, USA). Dynamic light scattering (DLS) analysis was performed to determine the diameter of nZVI particles. To investigate the material structure of iron nanoparticles, the

Fe mixture was subjected to XRD analysis (AXS D8, Bruker Kappa, USA) at 45 kV and 30 mA and the scanning angle was set between 20° to 60° because at this scanning range the iron and iron species were covered. The scanning rate of 2.0°/min was maintained throughout the analysis. The synthesized nZVI particles were subjected to XRD analysis to validate the ferrous ion in the nZVI-SS biocomposite. The X-ray fluorescence (XRF) analysis which confirms the presence of Fe in the nZVI-SS biocomposite. The reverse bias of 800 V was applied across the semiconductor junction of Si(Li) detector, and the resolution of the detector was 150 eV at 5.9 keV. The nZVI-powder was placed in front of an XRF spectrometer. For the excitation of the samples, Cd¹⁰⁹ radioactive source was employed in annular geometry to prevent the direct exposure of the excitation source to the detector and minimize backscatter interference. The Cd¹⁰⁹ emits Ag K X-ray (energy 22.25 keV). The X-ray spectra were recorded for a counting time of 2000 s and stored in a PC based multi-channel analyzer for further offline analysis. Further, to understand the valency of the iron, the X-ray absorption near edge structure (XANES) spectra of iron samples including metallic Fe, FeO, Fe₂O₃ and Fe₃O₄ were obtained from INDUS-II synchrotron source Raja Ramanna Centre for Advanced Technology (RRCAT), Indore, India. It gives spectra of iron samples including metallic Fe, FeO, Fe₂O₃ and Fe₃O₄. XANES uses synchrotron radiation to photo-ionize the core electrons of Fe atom and provides useful information on the valance of iron. The electron storage ring was operated with energy of 1.3 GeV and a current of 100–200 mA. The data were collected in transmission mode with a Lytle detector in the region of Fe-K edge (7112 eV) at room temperature.

Operation of fixed-bed column

The fixed-bed column studies were performed using a laboratory-scale glass column with an internal diameter of 1.5 cm and a length of 20 cm. Glass wool was supported, and the column was closed to maintain good liquid distribution. Column was packed with 1.5, 3.0 and 4.5 g of nZVI-SS to obtain a particular bed height of 3, 6, 9 cm, respectively, keeping flow rate and influent MG concentration constant at 10 ml/min and 10 mg/L, respectively. The MG solution of known concentrations (5, 10 and 15 mg/L) at natural pH 10 was pumped using peristaltic pump (Rivotek-50171 002; Rivieria, India) through the column at a desired flow rate (5, 10 and 15 mL/min). The pH was adjusted using 0.1 N HCl/NaOH solution in multiparameter portable meter (Model H19829, Hanna Instruments, USA). Effluent samples were collected at

regular time intervals to determine the residual dye concentration in the effluent solutions using double beam U–V spectrophotometer (2201; Systronics, India) at 617 nm. The influent to the column was continued until there was no further adsorption, i.e., the operation was stopped when the effluent concentration exceeded a value of ~99.5 mg/L or higher.

Column data analysis

The performance of the fixed-bed column is predicted based on the breakthrough curves. For determining the operation and dynamic response of a sorption column, the time for breakthrough appearance and shape of the breakthrough curve are essential characteristics. The breakthrough point is nothing but when the effluent concentration (C_t) from the column that reaches about 0.1 % of the influent concentration (C_0). Similarly, the point where the effluent concentration reaches ~99 % is called the “point of column exhaustion”. The breakthrough curve for a given bed depth is generally expressed in terms of the ratio C_t/C_0 as a function of time or volume of the effluent. The volume of the effluent, V_{eff} (mL), can be calculated from the following equation:

$$V_{\text{eff}} = Q t_{\text{total}} \quad (1)$$

where Q is the volumetric flow rate (mL/min) and t_{total} is the total flow time (min).

The total mass of dye adsorbed, q_{total} (mg), can be calculated from the area under the breakthrough curve:

$$q_{\text{total}} = \frac{Q}{1000} \int_{t=0}^{t=\text{total}} C_{\text{ad}} dt \quad (2)$$

where C_{ad} is the concentration of dye removal (mg/L).

Equilibrium metal uptake or maximum capacity of the column, $q_{\text{e,exp}}$ (mg/g), in the column is calculated as follows:

$$q_{\text{e,exp}} = \frac{q_{\text{total}}}{m} \quad (3)$$

where m is the dry weight of adsorbent in the column (g).

Total amount of metal ion entering to the column (m_{total}) is calculated from the following equation

$$m_{\text{total}} = \frac{C_0 Q t_{\text{total}}}{1000}, \quad (4)$$

and the removal percentage of MG can be obtained using the following equation

$$Y (\%) = \frac{q_{\text{total}}}{m_{\text{total}}} \times 100 \quad (5)$$

Result and discussion

Characterization of nZVI-SS biocomposite

The formation of iron pellets can be observed in scanning electron micrograph as shown in Fig. 1. The average diameter of iron nanoparticles observed in dynamic light scattering (DLS) is about 1734 nm as shown in Fig. 2. The XRD analysis report reveals the presence of zerovalent iron in the mixture of nZVI-SS biocomposite as shown in Fig. 3. In the XRD spectra between 20° to 50° as shown in Fig. 3, peaks obtained were sharper. This peak represents the various state of Fe particle. The larger peak at 2-Theta ° of $\sim 45^\circ$ denotes the excessive occurrence of ZVI in the nZVI-SS biocomposite. The other shorter peaks represent the presence of FeO, Fe_2O_3 and Fe_3O_4 [13].

The X-ray spectrum Fig. 4 shows the counts with respect to channels, and the peaks of Fe-K α and Fe-K β are

Fig. 1 Scanning electron microscopy image of nZVI

Fig. 2 Dynamic light scattering of nZVI

seen with high counts. Also there are no other elements present as seen from the spectrum. Hence, it is concluded that there are only Fe particles present in the nZVI-SS biocomposite. The XANES spectrum of iron particles present in the nZVI-SS biocomposite is shown in Fig. 5. An elevation in the photon energy level from 7120 to 7180 eV indicates the presence of both FeO and zerovalent iron (Fe^0). Though, the shell is largely made of iron oxides (i.e., FeO), the iron nanoparticles likely to have a core of main zerovalent iron particles [14].

Effect of different bed depths on breakthrough curve

Bed height is one of the essential parameter in the column biosorption influencing the breakthrough curve packed bed column. The breakthrough curves at different bed depth are shown in Fig. 6. The retention time of MG depends on the bed depth of the nZVI-SS biocomposite. From Fig. 6, it is clear that as the bed depth increased, the retention time and the effluent volume (V_{eff}) increased. The removal efficiency had increased trend as the mass of the biosorbent increased Table 1. This result specifies that smaller bed get saturated faster than the larger bed [15]. In the present study, maximum exhaustion time of 24 min was recorded for a highest bed depth of 9 cm. Meanwhile, as the bed depth decreased, the axial dispersion of MG increased along the depth of fixed-bed column which resulted in the formation of steeper breakthrough curve. Further, the slope of the breakthrough curve decreased, as the bed depth increased, which resulted in a broadened mass transfer zone. The sorption column data were evaluated and presented in Table 1. As shown in Table 1, the bed depth has strongly influenced the biosorption capacity of MG 0.48, 0.37 and 0.33 mg/g which was recorded at 3, 6, 9 cm. Percentage of MG removal was found to increase from 60 to 62.5 % as the bed height increased from 3 to 9 cm. The decrease in MG uptake with increasing bed depth in fixed-bed column may be due to the increase in the surface area of the biosorbent, and contact time was less in the case of continuous experiment [16].

Effect of flow rate on breakthrough curve

Flow rate is also another factor which influences the breakthrough. Figure 7 shows the various breakthrough curves at different flow rate of MG solution in the packed bed column. From Fig. 7, significant shrinkage of breakthrough curves was observed when the flow rate was increased from 5 to 15 mL/min. An increase in flow rate has reduced the external film mass resistance over the surface of the biosorbent which tends to decrease the residence time. Therefore, the saturation time decreased,

Fig. 3 XRD spectra of nZVI **Fig. 4** X-ray fluorescence spectra of nZVI

which in turn lead to the diminution in the removal efficiency. Conversely, at lower flow rate, the period of mass transfer inside the pores of the biosorbent would be increased which in turn allows the accession of more binding sites [17]. Thus, the percentage removal would be increased. As discussed, the breakthrough became steeper Fig. 7 as the flow rate increased. The biosorption capacity was strongly influenced by influent flow rate. Lower the flow rate greater the biosorption capacity and vice versa. In particular, at higher flow rate, a poor binding capacity between the functional groups of the biosorbent and the MG ions [18]. Thus, attainment of biosorption equilibrium

was tragic; hence, the biosorption capacity was also limited.

Effect of influent dye concentration of breakthrough curve

In biosorption of MG to nZVI-SS biocomposite in a fixed-bed column, the change in influent dye concentration seems to influence the various column parameters like breakthrough time, uptake of dye and removal efficiency. Figure 8 shows the effect of influent MG concentration on the breakthrough curves. From Fig. 8, it was noted that due to

Fig. 5 XANES spectra of iron particles of nZVI **Fig. 6** Breakthrough curves for MG biosorption onto nZVI-SS biocomposite at different bed depth (flow rate: 10 mL/min, C_0 : 10 mg/L and pH 10.0) **Fig. 7** Breakthrough curves for MG biosorption onto nZVI-SS biocomposite at different flow rate (bed depth: 3 cm; 10 mL/min, C_0 : 10 mg/L and pH 10.0)**Table 1** Parameters in packed bed column for MG biosorption by nZVI-SS biocomposite

C_0 (mg/L)	Q (mL/min)	Z (cm)	t_{total} (min)	m_{total} (mg)	q_{total} (mg)	$q_{\text{e,exp}}$ (mg/g)	V_{eff} (mL)	Y (%)
10	10	3	12	1.2	0.72	0.48	120	60
10	10	6	20	2.0	1.11	0.37	200	55.5
10	10	9	24	2.4	1.50	0.33	240	62.5
10	5	3	20	1.0	0.60	0.4	100	60
10	10	3	15	1.5	0.84	0.56	150	56
10	15	3	10	1.5	0.74	0.49	150	49.33
5	10	3	15	0.75	0.50	0.33	150	66.67
10	10	3	12	1.2	0.73	0.48	120	60.83
15	10	3	9	1.35	0.76	0.56	90	33.33

Fig. 8 Breakthrough curves for MG biosorption onto nZVI-SS biocomposite at different influent dye concentration (flow rate: 10 mL/min; bed depth: 3 cm; 10 mL/min and pH 10.0)

an increase in the MG concentration, the biosorbent gets saturated faster which resulted in the decrease in the breakthrough time. Likewise, as the MG feeding concentration was low, the breakthrough curve and the effluent volume collected were increased. From the above discussion, obviously the biosorption capacity was also greater at higher MG concentration. This is due to the higher mass transfer rate due to an increased diffusion coefficient or mass transfer coefficient at higher influent dye concentration [19]. When the initial MG concentration is increased from 5 to 15 mg/L, the biosorption capacity elevated from 0.33 to 0.56 mg/g. Of course, at higher influent dye concentration, the driving force reached maximum. Therefore, it helps to overcome the mass transfer resistance [20, 21]. Meanwhile, the exhaustion time tends to decrease from min to min as the influent dye concentration increased from 5 to 15 mg/L. These results demonstrated that higher inlet MG concentration allowed the biosorbent material to get saturated faster. Therefore, it is concluded that higher influent MG concentration offered an ambient driving force, relatively smaller mass transfer zone and increased sorption capacity [22].

Breakthrough curve modeling

The performance and successful design of a fixed-bed column are described through the modeling of the breakthrough curve. In a fixed-bed biosorption column, the two important characteristics determining the operation and the dynamic response from adsorption column are breakthrough time and the shape of the breakthrough curve. For the past years, several mathematical models have been proposed for describing and analyzing the experimental values, in order to develop an industrial scale adsorption column [23]. In the present investigation, four different

mathematical models were proposed to predict the breakthrough curves obtained at various experimental parameters. The four models are Adams–Bohart, Thomas–Yoon models, Yoon–Nelson Model and BDST model.

Adam–Bohart Model

Bohart and Adams [24] proposed a fundamental equation based on the surface reaction theory describing the relationship between C_t/C_0 and t in a continuous system. This model assumes that equilibrium is not instantaneous. It is used for the description of the initial part of the breakthrough curve. The expression is as follows:

$$\ln\left(\frac{C_t}{C_0}\right) = k_{AB}C_0t - k_{AB}N_0\left(\frac{Z}{U_0}\right) \quad (6)$$

where C_0 and C_t are the influent and effluent concentration (mg/L), respectively; k_{AB} is the kinetic constant (L/mg min), N_0 is the saturation concentration (mg/L), Z is the bed depth of the fixed-bed column (cm), and U_0 is the superficial velocity (cm/min) defined as the ratio of the volumetric flow rate Q (cm³/min) to the cross-sectional area of the bed A (cm²). The range of t was taken into consideration from the beginning to the end of breakthrough. A linear plot of $\ln(C_t/C_0)$ against t gives the values of the parameters k_{AB} and N_0 . The corresponding values of k_{AB} and N_0 were calculated and presented in Table 2. From Table 2, it is observed that kinetic constant (k_{AB}) increased with increase in influent flow rate, but decreased with increasing bed depth and influent MG concentration. This indicates at initial stage overall system kinetics may be influenced by external mass transfer in the column adsorption [25].

Thomas model

Thomas model is one of the most widely used models to describe the packed bed column adsorption data [26]. This model assumes plug flow behavior in the bed. Basically, the rate driving force obeys the second-order reversible reaction kinetics. Therefore, it assumes Langmuir kinetics of adsorption–desorption and negligible axial dispersion in the column adsorption [27]. The linearized form of this model can be described by the following expression,

$$\ln\left(\frac{C_0}{C_t} - 1\right) = \frac{k_{Th}q_0M}{Q} - k_{Th}C_0t \quad (7)$$

where C_0 is the initial metal ion concentration in the liquid phase (mg/L); C_t is the metal concentration at time t in the solution (mg/L); k_{Th} is the Thomas model constant (mL/min mg); q_0 is the adsorption capacity (mg/g); M is the amount of adsorbent in the packed bed column (g); and

Table 2 Parameters of Adam–Bohart model at different experimental conditions

C_0 (mg/L)	Q (mL/min)	Z (cm)	Adams–Bohart parameter		R^2
			k_{AB} (L/mg min)	N_0 (mg/L)	
10	10	3	0.0658	47.54	0.908
10	10	6	0.0396	38.46	0.887
10	10	9	0.0343	32.16	0.914
10	5	3	0.0363	39.61	0.924
10	10	3	0.0532	57.11	0.853
10	15	3	0.0507	57.32	0.804
5	10	3	0.1	31.22	0.939
10	10	3	0.0734	47.99	0.896
15	10	3	0.0572	51.85	0.764

Table 3 Parameters of Thomas model at different experimental conditions

C_0 (mg/L)	Q (mL/min)	Z (cm)	Thomas model parameter		R^2
			k_{TH} (mL/min mg)	q_0 (mg/g)	
10	10	3	0.122	471.42	0.982
10	10	6	0.077	364.71	0.974
10	10	9	0.056	334.47	0.952
10	5	3	0.069	383.96	0.963
10	10	3	0.097	565.09	0.996
10	15	3	0.114	503.93	0.992
5	10	3	0.163	328.26	0.955
10	10	3	0.131	486.25	0.968
15	10	3	0.102	528.03	0.969

Q is the flow rate (mL/min). A plot of $\ln[(C_0/C_t) - 1]$ against t gives the values of k_{TH} and q_0 . The R^2 values along with the relative constants are tabulated in Table 3. From Table 3, it was noted, as the flow rate increased, the value of k_{TH} also increased; however, the q_0 value tends to decrease. Also, from Table 3, it can be seen that the bed depth increased as the k_{TH} values decreased. The value of k_{TH} decreased with increasing initial influent MG concentration. It was attributed to the driving force for adsorption in the concentration difference. Thus, lower flow rate, higher influent concentration and higher bed depth would increase the adsorption of MG onto nZVI-SS biocomposite packed column.

Yoon–Nelson model

A simple theoretical model developed by Yoon–Nelson [28] was applied to investigate the breakthrough behavior of MG on nZVI-SS biocomposite. This is based on the assumption that the rate of decrease in the probability of biosorption of each adsorbate molecule is proportional to the probability of the adsorbate adsorption and the adsorbate breakthrough on the adsorbent [20, 22]. The linearized

Yoon–Nelson model for a single component system can be expressed as:

$$\ln\left(\frac{C_t}{C_0 - C_t}\right) = k_{YN}t - \tau k_{YN} \quad (8)$$

where k_{YN} is the rate constant (min^{-1}) and τ is the time required for 50 % adsorbate breakthrough (min). The parameter values are determined from the linear plot of $\ln[C_t/(C_0 - C_t)]$ against t .

The relative constant and statistical parameters of Yoon–Nelson model obtained at various operating conditions are tabulated in Table 4. From Table 4, it was noted that the coefficient of determination was higher and shows a better goodness of fit with the experimental data. Also, from Table 4, the rate constant k_{YN} increased and the 50 % breakthrough time (τ) decreased with increasing both flow rate and influent MG concentration. However, when the bed depth is increased, the τ values increased, while the values of k_{YN} decreased [29]. Perhaps, it was due to the rapid saturation of nZVI-SS biocomposite in the column. Likewise, due to an increase in the bed depth both τ and k_{YN} values decreased.

Table 4 Parameters of Yoon–Nelson at different experimental conditions

C_0 (mg/L)	Q (mL/min)	Z (cm)	Parameters		R^2
			k_{YN} (min^{-1})	τ (min)	
10	10	3	1.220	7.07	0.982
10	10	6	0.770	10.94	0.974
10	10	9	0.566	15.05	0.952
10	5	3	0.692	11.51	0.963
10	10	3	0.976	8.47	0.996
10	15	3	1.144	5.03	0.992
5	10	3	0.817	9.82	0.955
10	10	3	1.318	7.24	0.968
15	10	3	1.531	5.27	0.969

BDST model

BDST is a model for predicting the relationship between depths and service time at different values of breakthrough. This model was proposed based on the assumption of forces like intra particle diffusion and external mass transfer resistance negligible and that the adsorbate is adsorbed onto the adsorbent surface directly [30]. The main objective of the BDST model is the estimation of column characteristics such as biosorption capacity and kinetic constant. The linearized BDST model is expressed as follows:

$$t_s = \left(\frac{N_0 Z}{C_0 U_0} \right) - \left(\frac{1}{C_0 k_a} \right) \ln \left(\frac{C_0}{C_b} - 1 \right) \quad (9)$$

where t_s is the service time (min), u is the influent linear velocity of the MG solution passed through the bed (cm/min), N_0 is the saturation concentration of bed (mg/L), Z is the bed depth (cm), and k_a is the rate constant in BDST model (L/mg min). A plot of t_s against bed depth Z derived from BDST equation is used to determine the constant values N_0 and k_a from the slope and intercept, respectively.

The experimental results obtained from MG biosorption in a column by nZVI-SS biocomposite were fitted to the BDST model to determine the biosorption capacity and kinetic constant. The R^2 value was found to be 0.964 which indicates the validity of BDST model for the packed bed biosorption using nZVI-SS biocomposite. The rate constant k_a computed from the intercept of the BDST plot characterizes the rate of solute transfer from the liquid phase to the solid phase [27]. The calculated N_0 and k_a were 16.67 mg/L and -9.6514 L/(mg min), respectively, at 10 ml/min and 10 mg/L. If k_a is large, even a short bed will avoid breakthrough, but as k_a decreases, progressively longer bed is required to avoid breakthrough [31].

Conclusions

This study demonstrated that the nZVI-SS biocomposite could be used as an effective biosorbent for the treatment of MG-containing wastewater. The novel nZVI-SS biocomposite synthesized was characterized using SEM, XRD, DLS XRF and XANES. The packed bed investigation on the biosorption of MG onto nZVI-SS biocomposite revealed the importance of bed height, flow rate and inlet solute concentration on MG biosorption. The column performance was better at higher inlet concentration, while the lowest flow rate and bed depth favored the column biosorption. The increase in bed height resulted in the extension of the breakthrough time, whereas increase in flow rate down-regulated the breakthrough time. The column data were well described using Thomas and Yoon–Nelson models. In addition, BDST model was successfully used to predict the breakthrough curves at different flow rates and inlet MG concentrations.

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