


Synthesis of composite sorbent for the treatment of aqueous solutions contaminated with methylene blue dye

Maad F. Al Juboury, Musa H. Alshammari, Mohammed R. Al-Juhaishi, Laith A. Najji, Ayad A. H. Faisal, Mu. Naushad  and Eder C. Lima

ABSTRACT

To apply the principles of sustainability, this study aims to prepare the composite sorbent from mixing of solid wastes that resulted from activities of treatment plants for wastewater and water supply. The manufacturing process depends on the mixing of sewage sludge with waterworks sludge at different proportions and the best mixture is modified by ferric nitrate solution. The prepared composite sorbent was evaluated as permeable reactive barrier (PRB) in the capturing of methylene blue (MB) dye presented in the simulated groundwater. Results proved that the suitable mixture of composite sorbent consisting of 0.25 g sewage sludge with 0.75 g waterworks sludge coated with aqueous solution of 2 g of $\text{Fe}(\text{NO}_3)_2$ achieved the maximum sorption capacity. In comparison with Freundlich model, Langmuir expression described the sorption measurements in a well manner; so, the chemisorption is governed by the removal of MB with maximum adsorption capacity reached to 268.98 mg/g. Kinetic measurements could be more representative by pseudo-first-order model and this means that the sorption process is supported by physical forces. Finally, the effects of inlet concentrations and bed thickness on the migration of MB front were simulated in an efficient manner by COMSOL Multiphysics 3.5a package with root mean squared errors not in excess of 0.152.


Key words | composite, COMSOL multiphysics, methylene blue, sewage sludge, sustainability, waterworks sludge

Maad F. Al Juboury
Musa H. Alshammari
College of Engineering,
University of Kerbala,
Kerbala, Iraq

Mohammed R. Al-Juhaishi
Department of Water Resources Engineering,
College of Engineering,
University of Baghdad,
Baghdad, Iraq

Laith A. Najji
Technical Instructors Training Institute,
Middle Technical University,
Baghdad, Iraq

Ayad A. H. Faisal
Department of Environmental Engineering,
College of Engineering,
University of Baghdad,
Baghdad, Iraq

Mu. Naushad  (corresponding author)
Department of Chemistry, College of Science,
King Saud University,
Bld#5, Riyadh, Saudi Arabia
E-mail: mnaushad@ksu.edu.sa

Eder C. Lima
Institute of Chemistry,
Federal University of Rio Grande do Sul (UFRGS),
Porto Alegre, RS, Brazil

HIGHLIGHTS

- Composite prepared from mixing of solid wastes resulted from water treatment plants.
- Composite was evaluated as permeable reactive barrier (PRB) in capturing of MB dye.
- Chemisorption is governed the removal of MB with qm reached to 268.98 mg/g.

INTRODUCTION

Disposal of chemical compounds within the wastewater can result from different industries and this is considered a major environmental problem for aquatic ecosystem (Khan *et al.* 2018; Znad *et al.* 2018). Effluents from cosmetics, leather, plastics, paper, pharmaceuticals and textiles industries contain broad types of highly toxic and carcinogenic contaminants (Sonal *et al.* 2018; Faisal & Najji 2019; Alshammari *et al.* 2020). Dyes are aromatic compounds and they have hazardous effects on several microorganisms as well as the cause of serious destruction for their catalyst

properties. The dyes can cause acute and chronic problems to the ecological system due to their toxic nature (Arslan-Alaton *et al.* 2009; Duan *et al.* 2010). Also, these compounds have a high ability to reflect/absorb sunlight reaching to the surface water system and this may cause a drastic influence on the growth of micro-organisms. Many biological/chemical changes can occur on the dyes in the wastewater disposed to the water resources and this will be accompanied with depletion of the dissolved oxygen required for healthy aquatic life. Methylene blue (MB) is

considered an essential substance for dyeing cotton, silk and wood. Its use is responsible for many diseases in the eyes of human and animals. There are many symptoms which refer to the diseases like vomiting, profuse sweating, mental confusion and methemoglobinemia (Kwok & Howes 2006; Kang *et al.* 2018). There is also unsystematic breathing through ingestion in the mouth which produces a burning sensation with nausea. Therefore, it must treat the effluent holding such dye as a result of its significant impact on the quality of receiving waters (Shah *et al.* 2020).

Coagulation and flocculation, ultra-chemical filtration, biological degradation, adsorption, and membrane filtration are familiar techniques applied for removal of dyes and other pollutants from aqueous medium (Naushad *et al.* 2019; Faisal *et al.* 2020). Adsorption is the efficient technique that proved its efficacy in comparison with other wastewater treatment methods (Naushad & ALOthman 2015) because it has a number of advantages such as: (i) it can be applied to the toxic compounds; (ii) it is efficient in the elimination of the organic contaminants; (iii) its flexibility in the design and operation; and (iv) the required area is less than that occupied by the biological system. Because the cost of activated carbon and its regeneration is very expensive, cheaper and economically available sorbents have been extensively tested in the past decades. Clay minerals, bark wastes, fly ash, peat, industrial byproducts, coffee grounds, wood powder, metal hydroxide sludge, and agricultural waste are utilized to treat the wastewater contaminated with different types of dyes (Sonal *et al.* 2018). In addition, non-conventional sorbents have also been tested to find its ability in the remediation of aqueous solutions polluted with MB such as clay, diatomite, activated sludge biomass, algae gelidium, rice husk, banana peel, sewage sludge from an urban wastewater and others.

Sewage sludge is the solid, semisolid, or slurry residual material that contains phosphorus, nitrogen and organic substances in its composition. According to EPA records focused on biosolids generated by publicly owned treatment works and the subsequent management practices, approximately 7.7×10^6 and 6.8×10^6 tons of dry sewage sludge resulted from municipal wastewater treatment plants in the USA through 1997 and 1998, respectively (US EPA 1999). The growth rate of this sludge was predicted as 10×10^6 tons per year in European countries for the year 2006 (Martínez *et al.* 2007). Together with residues of coagulants, the sewage sludge also contains humic and mineral matters precipitated from stream of raw water. Available literature estimated that 10,000 tons of waterworks sludge are produced daily on the global scale (Babatunde & Zhao 2007).

Therefore, efforts have been made to reuse these materials in beneficial methods like adsorbents in wastewater treatment in line with the prevailing legislative and economic drives. Hence, this study aims to manufacture a composite sorbent prepared from (sewage sludge + waterworks sludge) coated with nanoparticles material resulted from adding ferric nitrate, where waterworks sludge represents the alkaline agent for enhancement of the coating process. The ability of composite material in the wastewater treatment was evaluated by using MB dye as the target contaminant.

EXPERIMENTAL WORK

Materials

Al-Rustumia's wastewater treatment plant, Baghdad, Iraq was the source of sewage sludge utilized in this work. Five days was the duration adopted for drying this sludge at ambient temperature ($\approx 25^\circ\text{C}$). Thereafter, the sewage sludge was washed with distilled water and the particles in size from 1 to 0.063 mm can be separated through the sieving process which dried for 6 h at 70°C .

The use of waterworks sludge that contains alum salts in its composition was specified and, accordingly, this sludge was collected from Al-Weihooda water treatment plant, Baghdad, Iraq because it purifies the raw water by adding these salts. Three days was the period applied to dry the collected sludge at atmospheric temperature ($\approx 25^\circ\text{C}$) and, then, grinding must be achieved to obtain the same range of particles size for sewage sludge with d_{50} of 0.25 mm.

At room temperature, the contaminated water was prepared by dissolution of a certain quantity of MB dye in 1 L of distilled water to obtain 1,000 mg/L. The prepared water can be diluted to achieve any required concentration of MB dye and 0.1 M of sodium hydroxide or hydrochloric acid can be applied to change the pH of the solution for required value.

Manufacturing of composite sorbent

The different proportions of sewage sludge and waterworks sludge were mixed in 50 mL of water that contains 2 g of $\text{Fe}(\text{NO}_3)_2$. The mixture was agitated for 3 h and thereafter dried for 4 h at 105°C . However, the solid particles resulted from the mentioned process were also dried at 105°C for 24 h and, finally, it can be stored for batch and continuous experiments (Phuengprasop *et al.* 2011). The ability of

prepared composite material in the treatment of wastewater streams was evaluated by calculating the adsorption capacity of MB dye onto composite sorbent under different preparation conditions. Surface morphology for both pristine waterworks sludge and sewage sludge with prepared composite sorbent coated with ferric nitrate nanoparticles was investigated by scanning electron microscopy (SEM) equipped with energy-dispersive X-ray spectroscopy (EDS) (XFlash 5010; Bruker AXS Microanalysis, Berlin, Germany).

Adsorption study

A set of 250 mL conical-flasks were employed and each flask was filled with 50 mL of methylene blue dye solution with different initial concentration (C_o) of 10, 20, 80, 100, 200 and 300 mg/L. Different dosages of composite sorbent (0.05–0.5 g/50 mL) were added to the solutions of the flasks and they must be agitated at 200 rpm for 3 h using shaker type (Edmund Buhler SM25, Germany). Filter paper type (JIAO JIE 102) was used to separate solid particles from liquid phase after ending the agitation process and 10 mL of clear liquid was analyzed by ultraviolet-visible (UV) spectrophotometer at absorption wavelength of 666 nm to identify the MB dye final concentration (C_e) (Senthilkumar et al. 2005). For specifying the best agitation time, the batch tests were required to take the periodic samples with durations ranged from 5 to 180 min. Also, investigation into the effect of initial pH on the removal efficiency of MB was required, changing it from 3 to 11. Equation (1) can be used to determine the removal efficiency for chemical compound under consideration as below:

$$R = \frac{(C_o - C_e)}{C_o} \times 100 \quad (1)$$

The mass of solute retained in the unit mass of sorbent (q_e , mg/g) for a certain volume of water sample (V , L) and sorbent mass (m , g) is determined by:

$$q_e = (C_o - C_e) \frac{V}{m} \quad (2)$$

The outputs of the equilibrium isotherm and kinetic tests resulted from the experimental procedure described previously are subject to a set of isotherm and kinetic models. Freundlich and Langmuir equilibrium models are applied to characterize the relation between the quantity of solute captured within the solid matrix per unit mass of sorbent

(q_e , mg/g) and (C_e) at a constant temperature. Also, the design of suitable sorption process requires to find the rate of solute removal from aqueous solution and this can be found by applying the kinetic models like pseudo-first-order and pseudo-second-order for description of the relation between (q_e) and (t). The mathematical expressions for the equilibrium and kinetic models used in this study with definition of all parameters can be written as below:

$$\text{Freundlich: } q_e = K_F C_e^{\frac{1}{n}} \quad (3)$$

$$\text{Langmuir: } q_e = \frac{q_{max} b C_e}{1 + b C_e} \quad (4)$$

$$\text{Pseudo-first-order: } q_t = q_e [1 - \exp(-k_1 t)] \quad (5)$$

$$\text{Pseudo-second-order: } q_t = k_2 q_e^2 t / (1 + k_2 q_e t) \quad (6)$$

where K_F is the Freundlich and n is the sorption intensity; q_{max} is the maximum adsorption capacity (mg/g) and b is the affinity constant (L/mg); k_1 is the first-order rate constant (1/min), k_2 is the second-order rate constant (g/mg min), and q_t is the quantity of sorbed contaminant at time t (mg/g).

Continuous study

Perspex column with diameter of 2.5 cm and height of 100 cm (Figure 1) was manufactured to represent the interaction between packed composite sorbent and flowed stream of water contaminated with MB dye. Three ports designated as P1, P2 and P3 at distances of 10, 20, and 30 cm, respectively, were equipped from the bottom of the column to monitor the propagation of dye plume with the time by taking periodic samples of effluent water. Viton stoppers were utilized for blockage of these ports and syringes can be inserted to the center axis of the column to withdraw the required samples.

After packing the column with composite sorbent, the bed must be saturated with distilled water by applying up-flow mode; then, contaminated water was injected through the bed with a flow rate of 5 mL/min. This flow rate was achieved by constant head tank, flow meter, and two valves (1 with 2, 3 or 4). The continuous tests were implemented by selection of different inlet concentrations with values of 10, 50, and 100 mg/L implemented in three columns as in Figure 1 and monitoring of MB from ports was extended for 10 days. The flow rate of contaminated water was measured periodically by dividing the cumulative volume of effluent water on the elapsed time and the results

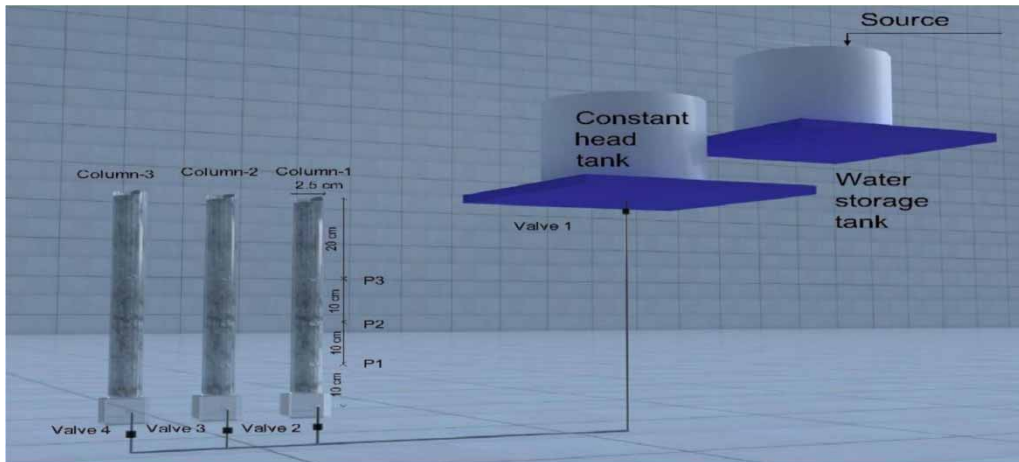


Figure 1 | Schematic diagram of the laboratory-scale column.

proved that this rate remained constant; so, the cross sectional area prepared for flow was not changed with the time. The outputs of continuous study are very important in the evaluation of prepared sorbent performance for elimination of MB contamination.

RESULTS AND DISCUSSION

Manufacturing of composite sorbent

The manufacturing of composite sorbent consisted of sewage sludge and waterworks sludge was investigated by

adding 2 g of ferric nitrate to the different proportions of these materials such as 0/1, 0.25/0.75, 0.5/0.5, 0.75/0.25 and 1/0 g/g, respectively. The aim of coating using ferric nitrate is to generate new reactive sites on these materials by the planting process. The criterion utilized to specify the best proportion is the highest value of adsorption capacity for composite sorbent to remove MB from contaminated water. [Figure 2](#) draws the variation of adsorption capacity versus the mass proportions of sewage sludge and waterworks sludge for C_o of 10 mg/L, time of 3 h, speed of 200 rpm and pH of 11. This figure certifies that the pure sludge coated with iron oxide has a good ability in the elimination of this dye where q_e reached to 1.3 and 2 mg/g for

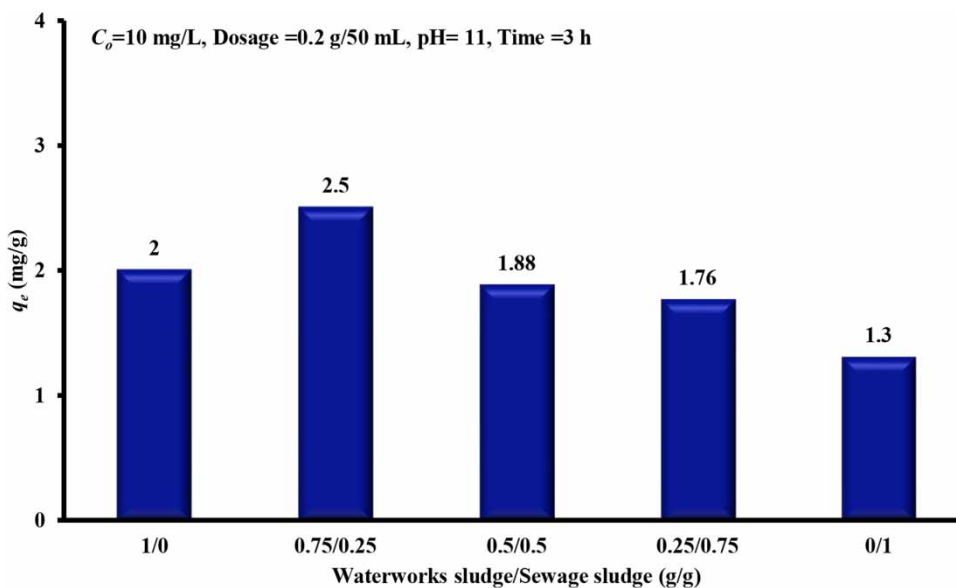


Figure 2 | Variation of MB sorption capacity onto composite sorbent prepared from coating of different proportions of waterworks sludge and sewage sludge with solution of ferric nitrate.

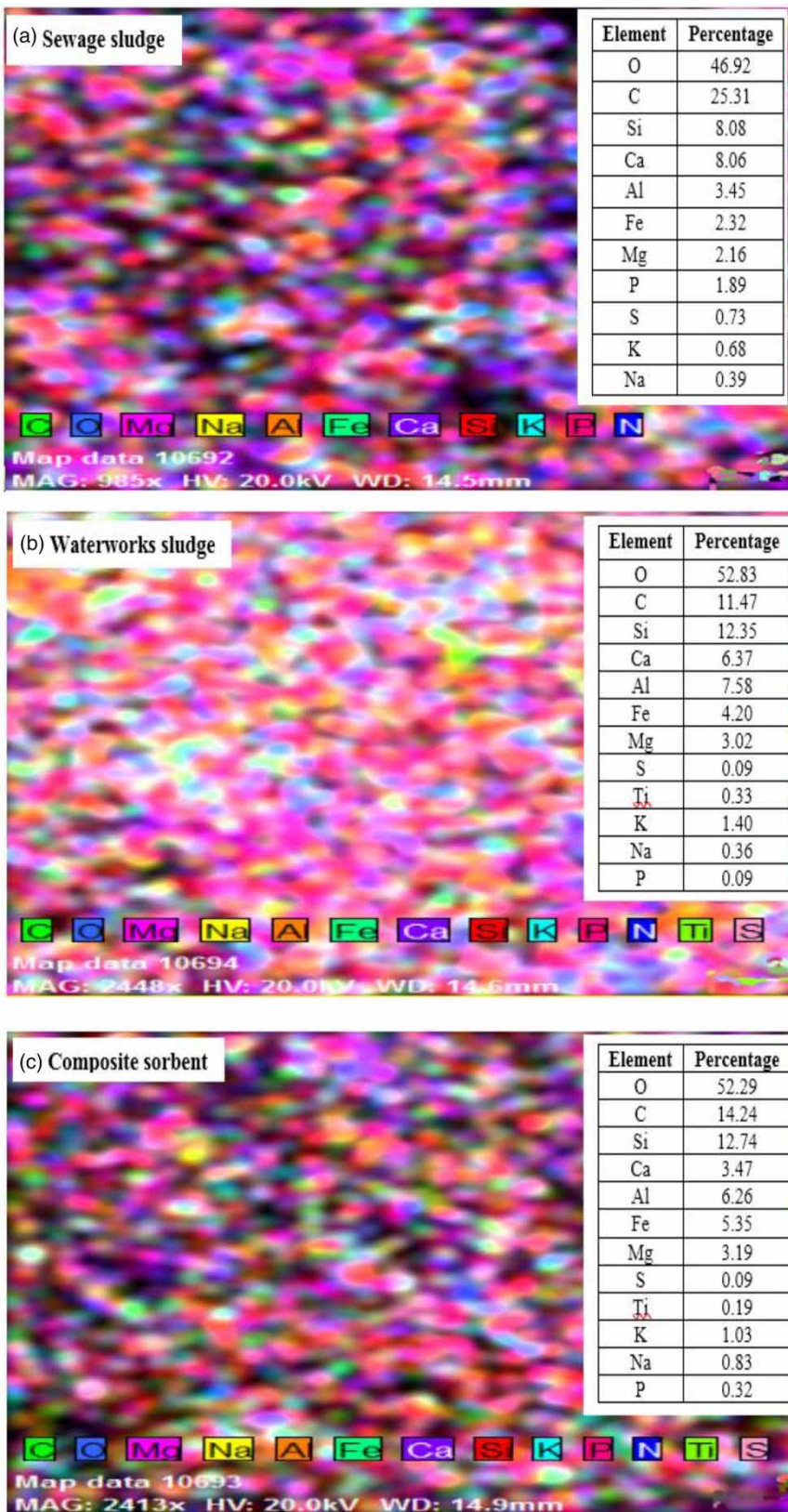


Figure 3 | EDS mapping images for sorbents utilized in this study.

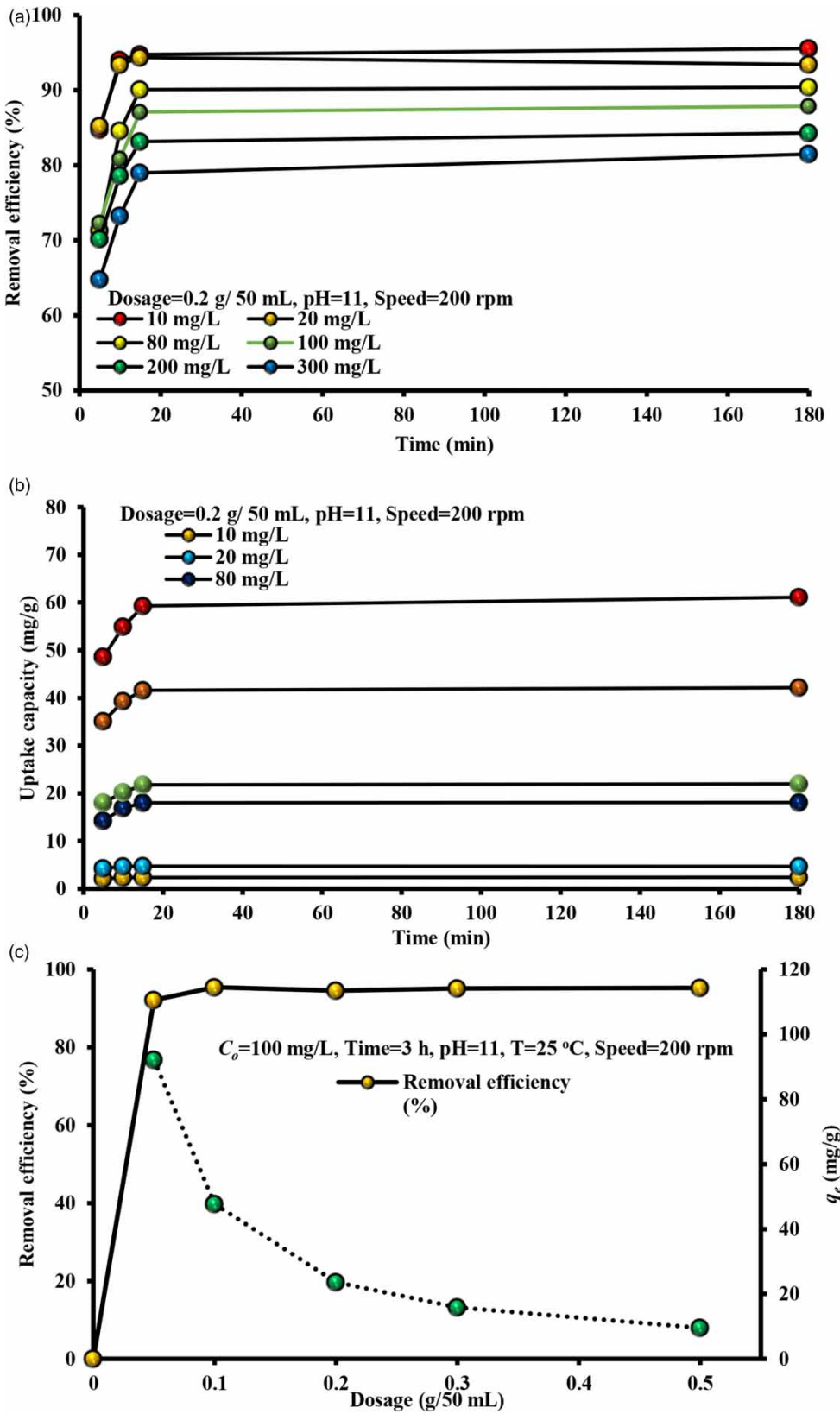


Figure 4 | The effects of operational conditions on the sorption of MB dye from contaminated water composite sorbent.

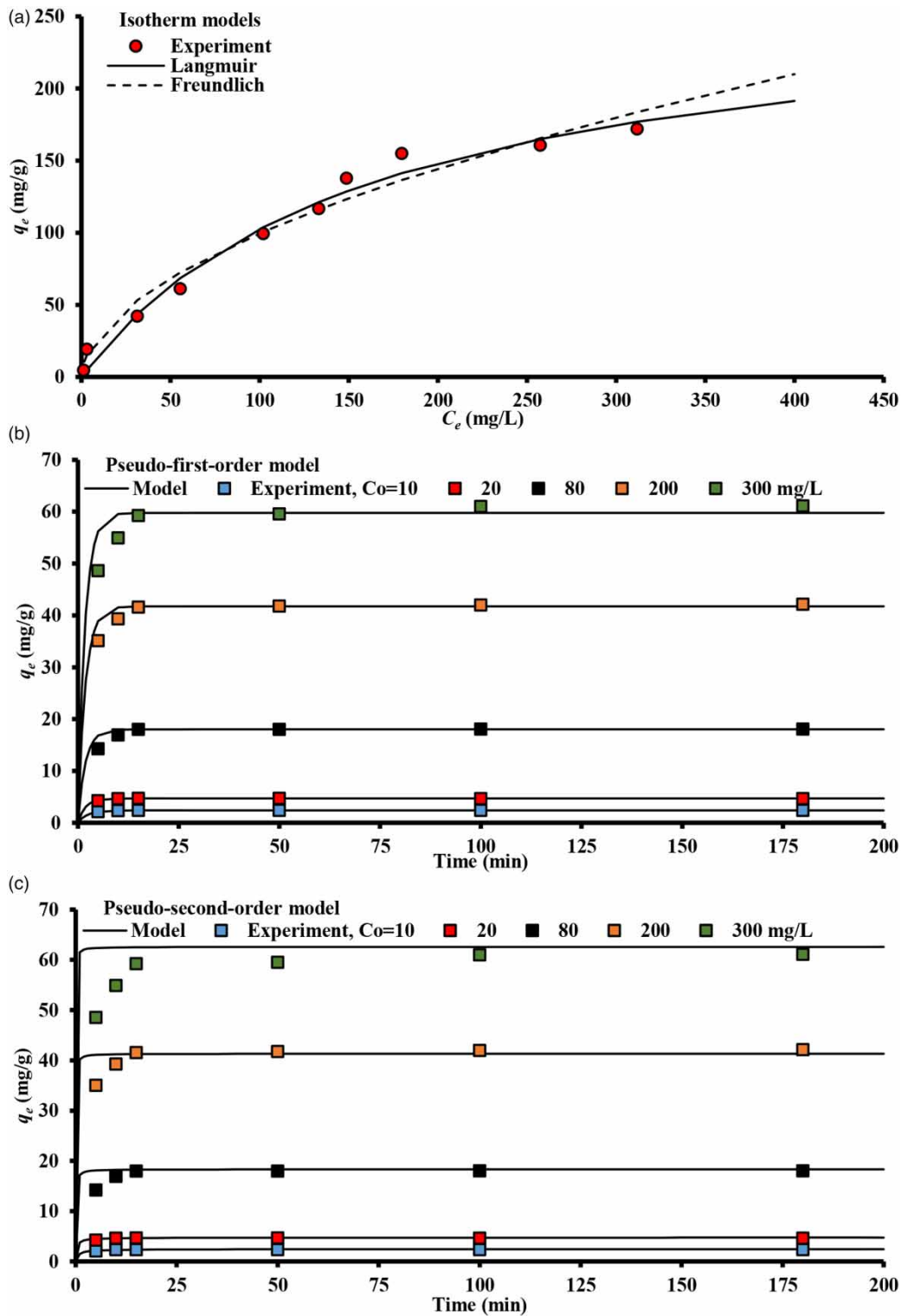


Figure 5 | Sorption isotherm and kinetic models used for description of sorption measurements.

pure coated sewage sludge and waterworks sludge respectively. Results revealed that the mixing of these materials will enhance the adsorption capacity to reach the maximum

value of 2.5 mg/g when 0.25 g of pure coated sewage sludge is mixed with 0.75 g of pure coated waterworks sludge. Accordingly, this proportion is adopted as the best value

Table 1 | Constants of isotherm models with statistical measure for sorption of MB onto composite sorbent

Isotherm model	Parameter	Value
Freundlich	K_F (mg/g)(L/mg) ^{1/n}	8.331
	n	1.857
	R^2	0.969
Langmuir	b (L/mg)	0.00617
	q_{max} (mg/g)	268.98
	R^2	0.976

for manufacturing composite sorbent that is used for removal of dye under consideration from contaminated solutions.

Characterization of composite sorbent

Multi-elemental EDS mapping images for some sorbents before interaction with MB dye are elucidated in Figure 3 and it is clear the presence of the following elements; C, O, Mg, Na, Al, Fe, N, Ca, Si, Ti, N, S and P in the composition of these sorbents. Apparently, the corresponding C, O, Mg, Na, Al, Fe, N, Ca, Si, Ti, N, S and P maps evidenced bright spots corresponding to the calcified area and illustrated a heterogeneous distribution of the elements in the field of view of the cross-section. EDS digital images of C, O, Mg, Na, Al, Fe, N, Ca, Si, Ti, N, S and P corresponding to the micrographs of coated composite adsorbent showed the increased intensities of Fe as appeared in the green dotted areas which the modification surface of the coated sorbent.

Operational conditions

(1) Equilibrium time and initial concentration: The equilibrium time should be determined to achieve the equilibrium concentrations; Figure 4(a) elucidates the influence of time on removal of MB dye with initial

concentration of 10, 20, 80, 100, 200, and 300 mg/L and sorbent dosage of 0.2 g/50 mL at room temperature. It seems that the removal percentages are increased in the dramatic trend during the first 15 minutes for all initial concentrations and then slowed decrease in the sorption rate can be recognized. This behavior depends on the sufficient vacant sites in the initial stages of sorption process which may decrease with the time. Results proved that the maximum removal efficiency was equal to 94% at 15 min for 10 mg/L of dye and no change can be observed beyond this time. At 15 min, this figure certified that the increase of dye concentration from 10 to 300 mg/L can cause significant decrease in the removal efficiency to reach the value of 79%. Finally, Figure 4(b) illustrates that the adsorption capacity is changed in the same trend of removal efficiency versus contact time and initial concentration of the dye where the highest capacity has value of 61.12 mg/g at 3 h for 300 mg/L of dye concentration.

- (2) Initial pH: The results proved that the values of initial pH have slight effects on the removal efficiency of MB dye which changed from 94 to 96.6% due to increase of pH from 2 to 11 and this satisfied with previous literature like Badeenezhad *et al.* (2019); Garg (2004). However, the pH of 11 was adopted as best value because it leads to the highest adsorption capacity and the maximum removal efficiency.
- (3) Adsorbent dosage: It is significantly influenced on the removal of MB dye due to change of dosage from 0.05 to 0.5 g/50 mL with initial concentration of 100 mg/L at initial pH 11 for contact time of 3 h. Figure 4(c) elucidates the increase of removal efficiency due to increase of sorbent dosage (i.e. vacant binding sites) until stabilized at approximately 95% beyond 1 g/50 mL; however, this behavior will be associated with significant decrease in the sorbent adsorption capacity from 92.15 to 9.53 mg/g for the mentioned range of dosage (Faisal & Naji 2019).

Table 2 | Kinetic parameters for the adsorption of MB onto composite sorbent

Kinetic model	Parameter	C_0 (mg/L)				
		10	20	80	200	300
Pseudo-first-order	k_1 (min ⁻¹)	0.4302	0.5359	0.5434	0.5394	0.5659
	q_e (mg/g)	2.3817	4.6941	18.0267	41.7417	59.7719
	R^2	0.997	0.971	0.994	0.952	0.999
Pseudo-second-order	k_2 (g/mg min)	0.6299	0.7892	0.8417	0.8799	0.9118
	q_e (mg/g)	2.4422	4.7422	18.3300	41.3188	62.5813
	R^2	0.834	0.705	0.861	0.946	0.807

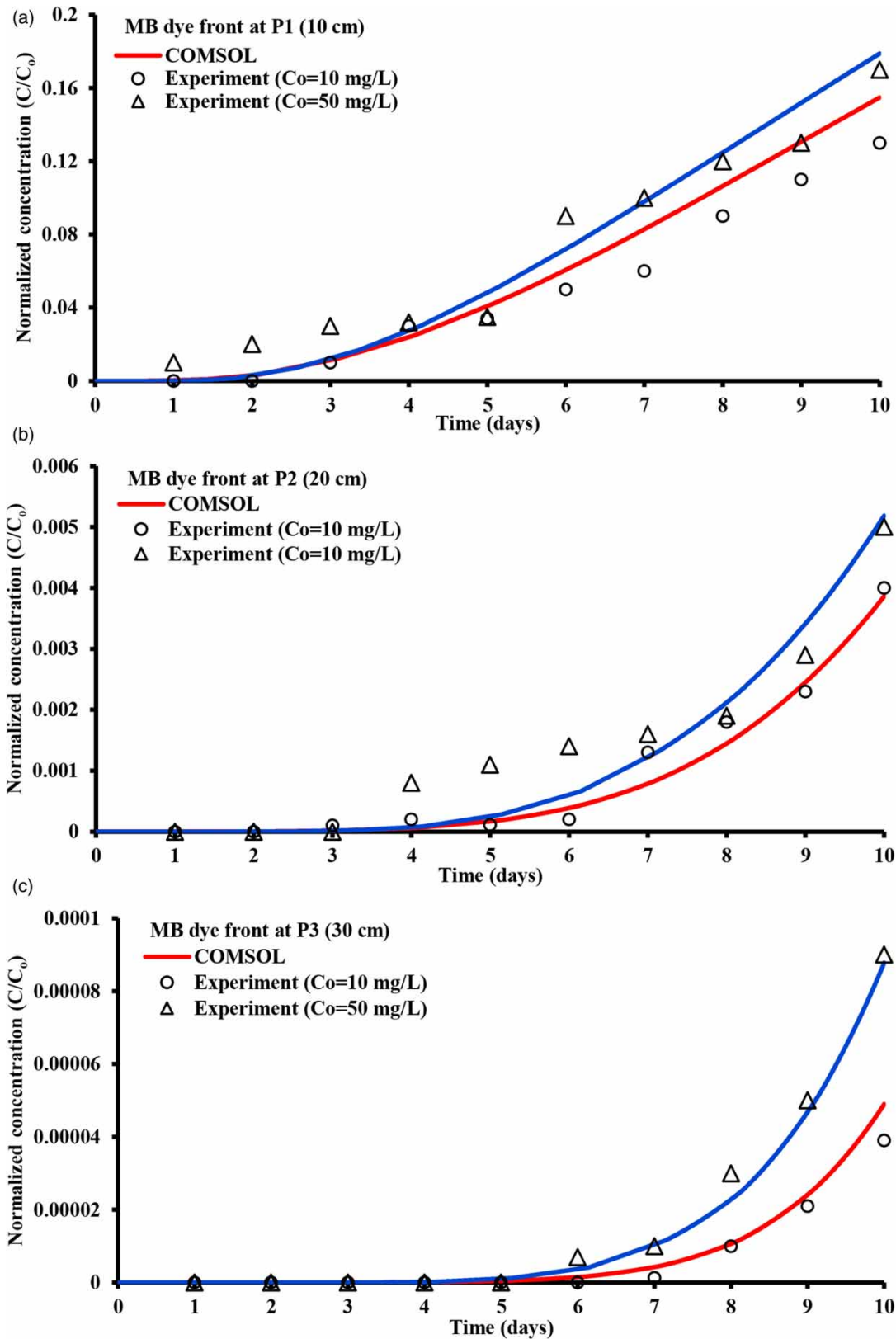


Figure 6 | Comparison between measured MB dye concentrations and predictions of COMSOL package for different values of inlet concentration at different depths.

Isotherm and kinetics and models

Sorption tests are carried out under conditions of pH = 11, dosage = 0.2 g/50 mL, speed = 200 rpm and contact time = 3 h for different dye concentrations of 20, 80, 200, 300, 500, 600, 700, 800, 900 and 1,000 mg/L. The Freundlich and Langmuir isotherms are shown graphically in Figure 5(a) and Table 1 lists their constants calculated by using nonlinear fitting of these models with sorption measurements through the application of ‘Solver’ option in the Microsoft Excel 2016 (Ahmed *et al.* 2020). Based on this figure and coefficient of determination (R^2) in Table 1, Langmuir isotherm is better than Freundlich model in the description of sorption measurements; so, this means that the chemisorption may be the predominant mechanism in the removal of this dye with uniform surface distribution of active sites on this sorbent (Bulut & Aydin 2006). This table proved that the maximum adsorption capacity for composite sorbent with MB dye as calculated from Langmuir model has reached 268.98 mg/g and this value reflects the high ability of present sorbent in the remediation of contaminated water.

The same fitting method was applied to fit the pseudo-first and pseudo-second-order models with kinetic measurements as plotted in Figure 5(b) and 5(c). Based on the calculated values of determination coefficients (R^2) inserted in Table 2, the pseudo-first-order kinetic model was more representative for kinetic sorption measurements than the pseudo-second-order model where R^2 was ≥ 0.952 . Also, it seems that the pseudo-first-order rate constant (k_1) increased with the increase of the initial concentration. This confirmed that the initial concentration is the driving force that enhances the incorporation of MB dye with the interlayer structure of the sorbent. If the adsorption kinetics obey the pseudo-first-

order model then a linear relation can be expected between the rate constant and the solution concentration. Adsorption process can be limited by pore diffusion when the rate of adsorption is related to the initial concentration through nonlinear relationship (Sepehr *et al.* 2014). In this study, the adsorption of MB dye onto composite sorbent was not limited by the pore diffusion process when the relation was observed to be linear. In addition, the application of first-order model means that the sorption process was due to interaction of MB dye with composite sorbent which can be supported by physical forces.

Breakthrough curves

The measured breakthrough curves for propagation of MB dye along the column packed with composite sorbent at ports P1, P2 and P3 under different values of initial concentration are plotted in Figure 6. For 5 mL/min, the higher initial influent concentrations of contaminant can cause a higher increase in the mass transfer driving force and, hence, MB concentration will saturate the packed bed more quickly which results in a significant decrease in the exhaust time. Also, the increase of concentration can generate sharper (i.e. steeper) breakthrough curves and these findings are consistent with previous studies (Khan *et al.* 2012; Al-baidhany 2016). In addition, this figure certified that there is a remarkable decrease in the effluent normalized concentration of pollutant for a certain value of influent concentration due to the increase of thickness from 10 to 30 cm. The remaining contaminated water for a long period of time within the longer bed may be the major cause for improvement of the sorption process. It seems that the MB concentration is increased with the time due to saturation of sorbent with sorbed pollutant and, consequently, the decrease of retardation factor (i.e. functionality) of the bed.

To represent the experimental measurements mathematically, an advection–dispersion equation (Equation (7)) can be solved numerically by finite element method through the application of COMSOL Multiphysics 3.5a (2008). This equation is used for finding the contaminant concentration (C) in the one dimensional column packed with composite sorbent as follows:

$$D_z \frac{\partial^2 C}{\partial z^2} - V_z \frac{\partial C}{\partial z} = R \frac{\partial C}{\partial t} \quad (7)$$

Table 3 | Constants, boundary and initial conditions used in the modeling of MB dye transport in 1D column

Item	Parameter	Value
Composite sorbent	Depth (cm)	30
	Porosity (n)	0.35
	Dispersivity (α , cm)	18.9
	Bulk density (ρ_b , g/cm ³)	1.052
Initial condition	Initial concentration (mg/L)	zero
Boundary conditions	Concentration @ $z = 0$ (mg/L)	10
	Advective flux @ $z = 30$ cm	zero

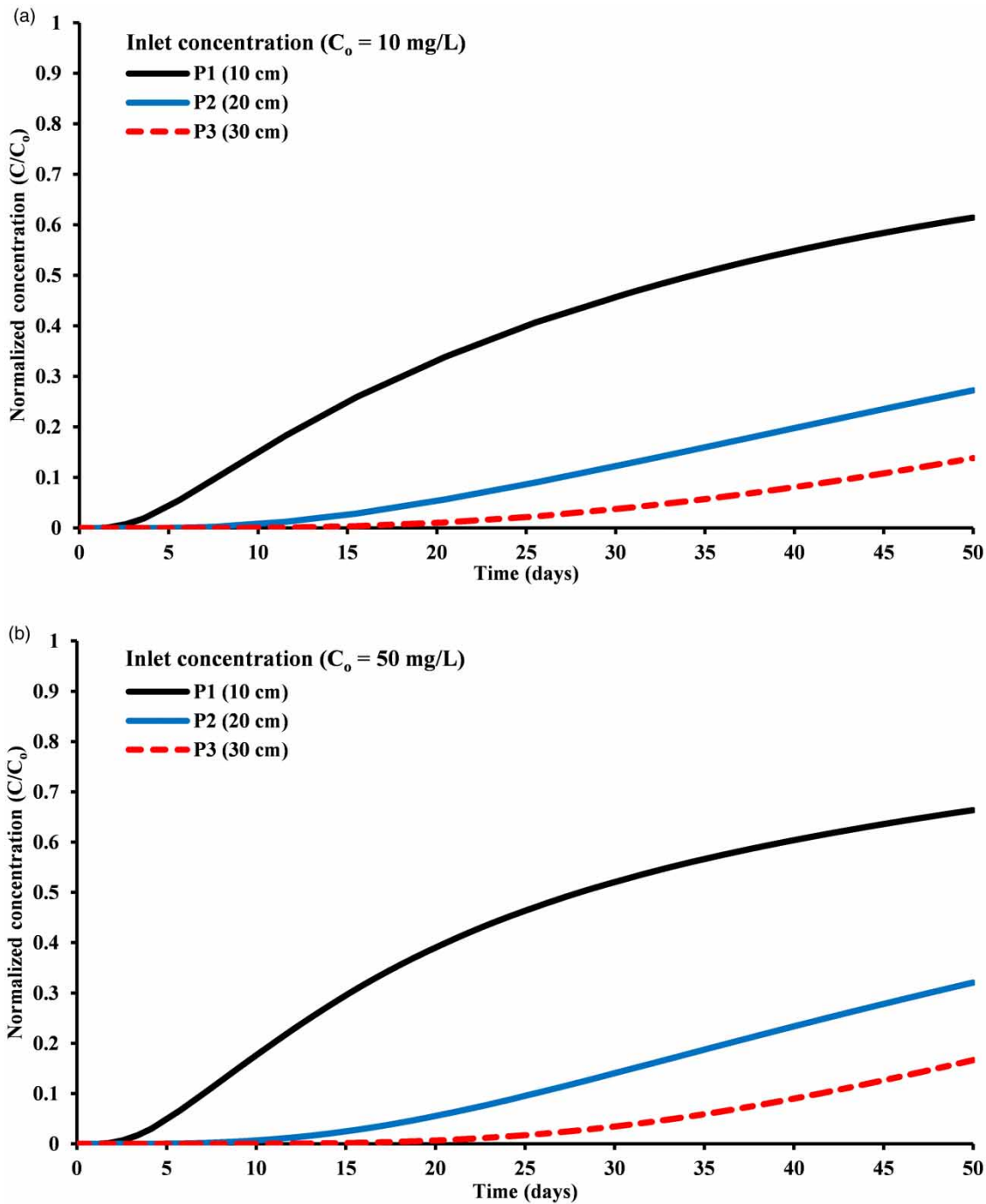


Figure 7 | Breakthrough curves as predicted by COMSOL package for MB dye propagation at different depths and inlet concentrations.

where V_z is the water velocity, D_z is the dispersion coefficient, and R is the retardation factor. The value of R must be greater than 1 for reactive medium as for composite sorbent used in the present tests. Because the sorption of MB onto composite sorbent is more represented by the Langmuir model, the

retardation factor is expressed as follows:

$$R = 1 + \frac{\rho_b}{n} \left(\frac{268.98 \cdot 0.00617}{(1 + 0.00617C)^2} \right) \quad (8)$$

where n is the porosity and ρ_b is the bulk density.

To complete the modeling process, the dispersivity must be calculated for bed under consideration from experimental results described by the following relationship:

$$D_L = 18.9V + 0.64 \quad R^2 = 0.9792 \quad (9)$$

This equation is similar to the following expression:

$$D_L = D_{mech} + D^* \quad (10)$$

The outputs of solution for physical problem illustrated in Figure 1 by applying of COMSOL on the Equations (7)–(9) are plotted together with the experimental measurements in Figure 6. All information related to the composite sorbent with boundary and initial conditions required for the solution is mentioned in Table 3. The predicted concentrations of MB dye for different magnitudes of inlet concentrations and bed depth showed that the contaminant plume is hindered by composite sorbent and the effluent concentration may be low in the initial times and then increased with the time as observed from Figure 7. Reasonable matching between the predicted values and experimental results can be recognized for MB dye concentrations with root mean squared errors <0.152.

CONCLUSIONS

The composite sorbents manufactured from mixing wastes resulted from wastewater and water supply treatment plants with coating of the mixture by ferric nitrate have a good ability for remediating water contaminated with MB dye based on batch and continuous tests. The best mixture of the prepared sorbent consisted of 0.25 g sewage sludge and 0.75 g waterworks sludge with coating by using aqueous solution of 2 g iron nitrate. The maximum adsorption capacity of this mixture reached 268.98 mg/g as calculated from Langmuir model which proved its ability in the description of sorption data; however, the pseudo-first-order model was able to represent the kinetic data. The application of these models means that the removal process was governed by chemisorption and physical forces played a significant role in supporting the removal process. Finally, a mathematical model solved by COMSOL package was able to simulate the breakthrough curves under the effects of different inlet concentrations and bed depths with root mean squared errors not in excess of 0.152.

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