Adsorption of methylene blue from aqueous solutions using water treatment sludge modified with sodium alginate as a low cost adsorbent

Hamid Poormand, Mostafa Leili and Marzieh Khazaei

ABSTRACT

In this research, aluminum-based drinking water treatment sludge is used as a starting material and immobilized by sodium alginate to develop low cost adsorbent for the removal of methylene blue (MB) from aqueous solutions. The studied variables included pH, adsorbent dose, initial MB concentration and contact time. Characteristics of the adsorbent were also studied using scanning electron microscopy and Fourier transform infrared spectroscopy (FTIR). It was revealed from kinetic tests that removal efficiency of MB was 88.5% under the optimum conditions of pH 8, initial MB concentration of 50 mg/L, contact time of 60 min, and adsorbent dose of 0.3 g/L. The oxygen functional groups such as –OH, C–O–C and C=O were found on the surface of developed adsorbent by FTIR. In addition, the adsorption data fitted well the Langmuir adsorption model with the maximum sorption capacity of 909.1 mg/g, and followed the pseudo-second-order kinetics. Findings of this study indicate that the prepared adsorbent is promising for further development of an effective and economical adsorbent material in the near future.

Key words | adsorption kinetics, equilibrium isotherm, methylene blue, sodium alginate, water treatment sludge

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INTRODUCTION

The presence of industrial effluents in the environment is associated with many harmful effects and currently considered to be one of the world's major environmental problems (Méndez-Paz et al. 2005). Dyes are an important class of pollutants which may exist in the industry effluent and can even be identified by the naked eye. Industries such as textile, painting, rubber, leather, cosmetics, pharmaceutical, food, paper, and plastics are some of the sources for dye effluents (Gupta 2009; Moghaddam et al. 2011). Various dyes such as radioactive, azo, cationic, and basic dyes are used in these industries (dos Santos et al. 2007). The discharges of organic dyes in aquatic environments can reduce light penetration and photosynthesis (Khataee et al. 2013). Furthermore, disposal of highly colored effluents from these industries poses significant environmental risks and can be harmful to aquatic life and human beings due to their toxicity and non-biodegradability properties (Modirshahla et al. 2012). In addition, some dyes and their metabolites have also mutagenic and carcinogenic effects, hence posing a potential health hazard to all forms of life (Modirshahla et al. 2011). Methylene blue (MB) is one of the most commonly used dyes in industrial applications. Nevertheless, it has various dangerous effects on humans and the environment. For example, it can cause high pulse rate, nausea and vomiting (Pavan et al. 2008; El-Mekkawi et al. 2016; Li et al. 2016). Therefore, the discharge of dyes in precious water resources must be avoided. A variety of treatment technologies, including biological (Hayat et al. 2015), adsorption process using several adsorbents (Madrakian et al. 2012; Hassani et al. 2014), coagulation and flocculation (Mahmoud et al. 2013), chemical oxidation (Modirshahla et al. 2011), and membrane processes (Wu et al. 1998), have been used or are in use for the removal of various dyes from wastewater or aquatic environments (Gupta 2009). Notwithstanding, there are a few drawbacks encountered in some of these methods, which could limit their applications. For example, although biological methods are environmentally friendly techniques (Moussavi

et al. 2009), they have some inhibitory effects on microbial metabolism particularly at high concentrations because of low biodegradability of some dyes (Ghoreishi & Haghighi 2003). Chemical techniques impose some operational costs such as electric power and materials shipment. Furthermore, some chemicals (e.g. ozone) which are used in advanced oxidation processes are highly corrosive and toxic (US EPA 1999). Membrane processes have also undesirable effectiveness in the removal of dyes because of membrane fouling issues and vulnerability of the membranes to organic solvents of effluents (Zazouli et al. 2010).

Adsorption, the most popular and effective economical alternative, has attracted considerable attention compared to other techniques because of the advantages in terms of cost, the recovery of pollutant from waste streams, ease of operation, flexibility and simplicity of design, production of a high quality effluent, etc. (Liu et al. 2011). Accordingly, a variety of natural and synthetic materials, as adsorbents, have been used to treat colored wastewaters.

Activated carbon is an adsorbent which is widely used for removal of different contaminants from aqueous solutions and wastewater (Ramakrishna & Viraraghavan 1997; Babel & Kurniawan 2003). Nonetheless, it has a few downsides and shortcomings such as high cost, difficulties in regeneration, non-selectivity properties, and unsuitable for dispersed dyes. Thus, nowadays a huge range of different substances have been used by a number of researchers to develop highly efficient and low cost alternative adsorbent to treat contaminated environments. Large quantities of drinking water treatment sludge (DWTS), as an inevitable water industrial waste, are produced every day all over the world. DWTS mainly consists of removed solids (both dissolved and suspended), coagulants and other chemicals that have been used to separate water impurities. This waste has been disposed mainly by landfilling, incineration and even discharge to ocean. Because of the increases of sludge disposal cost, environmental effects consideration and reduction in landfill capacity, the reuse of DWTS has received more interest in recent decades (Yang et al. 2015). The use of DWTS has been studied extensively as a low cost adsorbent for removing some pollutants from the aqueous solutions or wastewater. For instance, Changhui Wang used water treatment residuals to remedy soil contaminated with multiple metals in China (Wang et al. 2012) and found that the treatment of soil containing heavy metals with water treatment residuals resulted in its transformation into more stable forms. Chiang et al. (2012) showed that at the highest DWTS dosage of 250 mg/L, concentrations of the cationic contaminants (heavy metals) decreased by at least 80%. The use of adsorbent derived from DWTS was also investigated by other researchers to remove cadmium (Siswoyo et al. 2014), ammonium (Yang et al. 2015) and chromium(VI) (Shams Khorramabadi et al. 2012) from the polluted environments. The corresponding removal efficiencies were 70–90%, 80–90% and about 55%, respectively. Adsorption of MB using chemically and physically treated adsorbents from DWTS (alum sludge and mud sludge) has also been reported in the recently published work (Rashed et al. 2016). Based on the study, the optimum adsorption conditions for the adsorption are initial MB concentration of 100 ppm, contact time of 1 hour, solution temperature of 250 °C, solution pH of 7 and adsorbent dosage of 0.25 g/L. Given the better fitness of experimental data with the Langmuir model, the maximum adsorption capacity of alum and mud sludge was 70.4 and 65.79 mg/g, respectively.
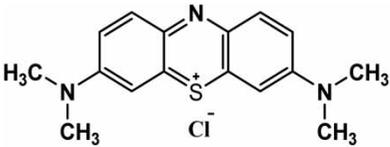
Therefore, the aim of the present research was to study the possibility of employing modified sludge from a water treatment plant as a low cost adsorbent for removal of MB. The modification was conducted using sodium alginate (SA) and adsorption experiments were carried out under different concentrations of adsorbent, adsorbate, pH and contact time. Alginate (as calcium and sodium salts) has been applied as one of the most effective biological agents for the immobilization of various fine adsorbents due to its special properties such as biodegradability, water solubility, low cost and non-toxicity towards aqueous environment (Martinsen et al. 1989; Hassan et al. 2014). The obtained data were also applied to find out the kinetic and isotherm of MB adsorption from solutions. Furthermore, the role of functional groups was also discussed. To the best of our knowledge, the adsorption of MB on DWTS modified by SA has not been previously reported.

MATERIALS AND METHODS

Materials

The characteristics and molecular structure of the MB as a typical organic dye are shown in Table 1. SA (BDH, UK) and MB (Merck, Germany) were of analytical grade. All solutions were made with double distilled water. The sludge existing in the drying bed of a water treatment plant was used as starting materials to prepare adsorbent. The pH of the solutions was adjusted with hydrochloric acid (HCl) and sodium hydroxide (NaOH) (0.1 N). The stock MB solution was prepared by dissolving the appropriate amount of MB of purity 97% in a solution containing distilled water and then it was stored in a glass container at room

Table 1 | Characteristics of MB dye (Reddy et al. 2016)

Trade name	Chemical structure	Molecular formula	Molecular weight (g/mol)	λ_{max}
MB		$C_{16}H_{18}ClN_3S$	319.85	664

temperature. Required working concentrations of MB standards were instantaneously prepared through appropriate dilution of this stock solution for each experiment series.

Preparation of adsorbent and its stabilization on SA

The starting material was taken from Shahid Beheshti drinking water treatment plant (DWTP) in Hamadan city, Iran. The sludge was collected from a sludge drying bed, which is a part of the process unit in the DWTP to dry the sludge generated from the sedimentation tank. Aluminum sulfate (alum) is used as the most common coagulant in this water treatment plant. The main characteristics of collected sludge are shown in Table 2. The collected sludge was firstly washed with distilled water and then dried at a temperature of 105 °C for 24 hours (Asilian et al. 2010). Then, the sludge was cooled down at room temperature and stabilized with SA. To do this, about 10 g of SA was dissolved in 500 mL of double distilled water and stirred for 2 hours to make a gelatinous mixture. After that, about 20 g of the adsorbent was added to the gelatinous mixture at the ratio of 1:2. The resulting mixture was stirred for 2 hours and then put

on a table to vent the bubbles out. For stabilization of sludge adsorbent, this mixture was added drop by drop to 0.5 M calcium chloride solution in order to let the alginate and adsorbent particles take shape. These particles were kept in calcium chloride solution for 24 hours. Finally, these particles were separated from the solution and again washed with distilled water (Hassani et al. 2015). The prepared adsorbent was dried, crushed into a powder form and sifted with a 1 mm sieve. The powdery sludge was used as the adsorbent to adsorb MB from aqueous solution (Figure 1).

Characterization of surface properties and chemical compositions

A scanning electron microscope (SEM) equipped with an energy dispersive X-ray microanalysis (LEO-1430 VP) was used to determine the surface morphology and the porous structure of the adsorbent. The surface functional groups of prepared adsorbent were determined using Fourier transform infrared spectroscopy (FTIR) at wavenumbers ranging from 400 to 4,000 cm^{-1}.

Determination of the point of zero charge

The pH at point of zero charge (pzc) (pH$_{pzc}$) can be used to determine the quality of the relationship between pH and cephalexin adsorption. The pzc was determined using 0.01 molar NaCl as an electrolyte by adding 0.1 N NaOH or 0.1 N HCl solutions. For this matter, 50 mL of the electrolyte was introduced into eight beakers and then the pH was adjusted to the required value in the range 2–12. After that, 0.3 g of adsorbent was added into each beaker and the beakers were shaken for 2 h. Then, the adsorbent was filtered and the final pH of the filtrate was measured. By plotting the initial pH vs. the pH after 2 h, the pzc of developed adsorbent was determined from the intersection of these curves (Kalhori et al. 2013).

Table 2 | The main characteristics of the sludge from Shahid Beheshti DWTP

Parameters	Mean (unit)	Parameters	Mean (unit)
pH	6.8 (–)	Mn	522 (mg/kg.dry solids)
N	1.28 (%w/w)	Cd	1.6 (mg/kg.dry solids)
H	3.15 (%w/w)	TS	21,052 (mg/L)
O	32.15 (%w/w)	TDS	1,040 (mg/L)
C	23.5 (%w/w)	TSS	20,012 (mg/L)
Al	1,240 (mg/kg. dry solids)	Volatile solids/ fixed solids	0.17
Fe	853 (mg/kg.dry solids)	Moisture content	98.65 (%)

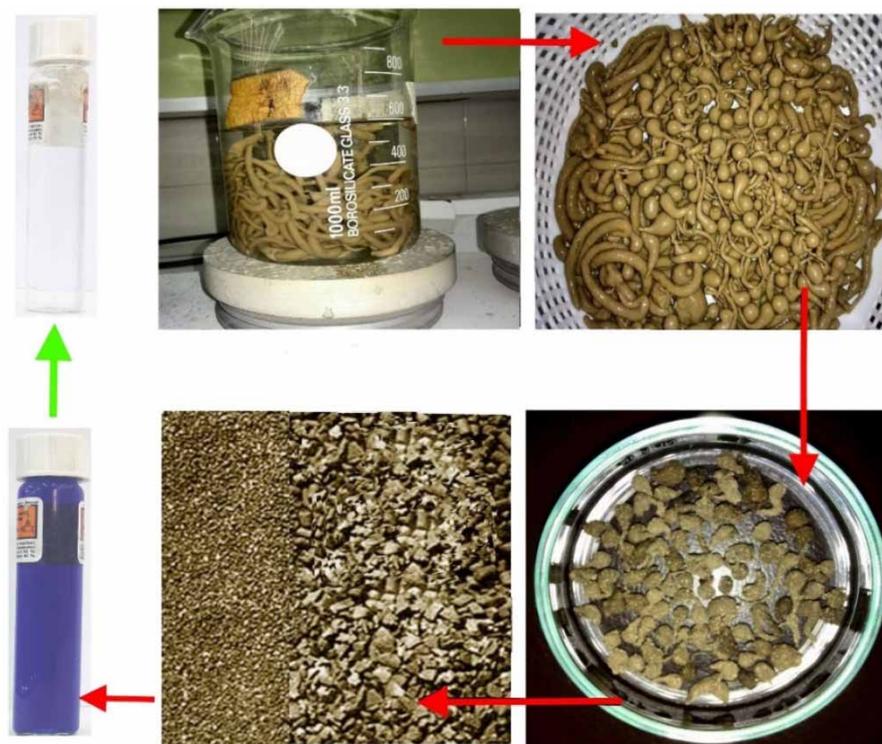TS, total solids; TDS, total dissolved solids; TSS, total suspended solids.

Figure 1 │ The stabilization of sludge with SA and prepared granular and powdered adsorbent for MB removal.

Determination of MB content and adsorption–desorption experiments

Concentration of MB in supernatant solution was measured by a spectrophotometer at a wavelength of 662 nm (Mahmoud *et al.* 2013). Other parameters were measured according to the methods well described in the *Standard Methods* (APHA 2005). The effect of pH, adsorbent dosage, reaction time, and MB concentration was examined in the range of 2–12, 0.1–2 g/L, 0–120 min, and 50–500 mg/L, respectively.

This study was investigated in batch mode and adsorption experiments were performed in 250 mL Erlenmeyer flasks. The contents of all Erlenmeyer flasks were mixed thoroughly using magnetic stirrers with a fixed setting to achieve a constant speed. For every experiment, 250 mL of samples with a given concentration was added into the Erlenmeyer flask. The desired level of pH for each experiment was adjusted using 0.1 N HCl or NaOH. Then, a determinate dose of adsorbent was added into the Erlenmeyer flask and was shaken immediately at a regulated speed of 150 rpm by shaker. After the desired contact time, to separate adsorbents from aqueous solution, the samples were filtered through Whatman filter paper (0.45 µm) and then centrifuged at 5,000 rpm (5810 R,

Eppendorf Biotech Company) for 15 minutes to determine residual MB concentration. All the experiments were carried out at room temperature in triplicate and mean values of data were reported to ensure the reproducibility of the results. Since standard deviations never exceeded ±1.5%, the error bars are not shown in the figures.

In all kinetic experiments, pH of the solution was kept at optimum condition ($\approx$8), which was predetermined by studying the pH effects on the removal efficiency. For equilibrium studies, various concentrations of MB ranging from 50 to 200 mg/L were contacted and shaken in several 250 mL flasks with a constant 0.3 g/L dose of adsorbent at room temperature. The flasks were sealed and the contents were stirred for 2 h.

The MB adsorption capacities at equilibrium, q_e (mg MB/g adsorbents), were determined using Equation (1):

$$q_e = \frac{(C_0 - C_e) \times V}{m} \tag{1}$$

where C_0 and C_e are initial and final concentrations of MB (mg/L), respectively, V is the volume of solution (L), and m is the adsorbent mass (g) as dry.

The kinetics of MB adsorption were analyzed by fitting data from the experiment of this step with pseudo-first-order

and pseudo-second-order models as shown in Table 3. In this table, k_1 and k_2 are constants of adsorption rate, q_t is adsorption capacity at time t, and q_e is adsorption capacity at equilibrium condition. Regarding the adsorption isotherm analysis, it is crucial to understand the interaction between an adsorbate and the adsorbent or to describe the nature of the adsorption (Samarghandi et al. 2015). Thus, to provide quantitative information, these data were fitted by the Langmuir, Redlich–Peterson and Freundlich isotherm models by using the equations presented in Table 3. The q_m parameter is the maximum adsorption capacity (mg/g), b is a constant related to the energy of adsorption (L/mg), k_f is a constant related to the adsorption capacity (mg/g) and can be defined as the distribution coefficient, where, with the increases of k_f values, the adsorption capacity of the adsorbent was also increased, A and B are the Redlich–Peterson isotherm constants, and g is an exponent which lies between 0 and 1. The parameters of the Redlich–Peterson isotherm can be evaluated from the plot between $\log(AC_e/q_e - 1)$ and $\log C_e$. As this model contains three parameters, the iteration method was used to estimate the parameter A (L/g) with the maximum R^2 value. To perform the iteration, Solver add-in of Microsoft Excel was used.

To assess and compare the performance of kinetic and isotherm models, the predicted versus experimental values were evaluated by comparing the chi-square statistic (χ^2), which can be described by the following equation and is recommended as an appropriate statistic to compare models with two parameters (McKay et al. 2011):

$$\chi^2 = \frac{(q_{e,exp} - q_{e,cal})^2}{q_{e,cal}} \qquad (2)$$

where $q_{e,exp}$ and $q_{e,cal}$ (mg/g) are the experimental and model estimated adsorption capacities, respectively. Small numerical value of χ^2 in combination with high R^2 values means that data calculated from the model are similar to the experimental value, while a large χ^2 indicates the difference between them.

RESULTS AND DISCUSSION

Analysis of infrared spectra and SEM

Figure 2 shows the FTIR analysis of both sludge of drinking water and SA/sludge composite beads to specify the presence of functional groups on the surface of adsorbent. The spectra were recorded at wavenumber ranging from 400 to 4,000 cm^{-1}. As it is evident in the figure, the FTIR spectrum showed some absorption peaks. It was clear that the adsorbents have strong bands at about 3,400 cm^{-1} indicating stretching vibrations of the OH group. Alginate presents asymmetric and symmetric stretching vibrations at 1,634 and 1,444 cm^{-1} due to carboxyl anions. Peaks located around 1,028 cm^{-1} could be related to C–O–C cyclic ether groups. Furthermore, the morphological structure of both sludge of drinking water and SA/sludge composite beads was studied through SEM analysis (Figure 3). As shown, both materials were porous and had uneven structure and non-uniform size distribution, since activated carbon was used in the treatment process (Siswoyo et al. 2014), which is requisite for effective removal of MB ions in aqueous solutions. Moreover, the SA modified sludge (Figure 3(b)) has nonporous and irregular morphology and there are many spherical aggregates, indicating a smooth surface with scattered cavities and bumps, unlike the morphology of the raw sludge (Figure 3(a)). The variety of the bump sizes on the surface of the adsorbents makes them well-supported material due to the fact that the presence of these structures

Table 3 | The name and equations of the studied isotherm and kinetic models

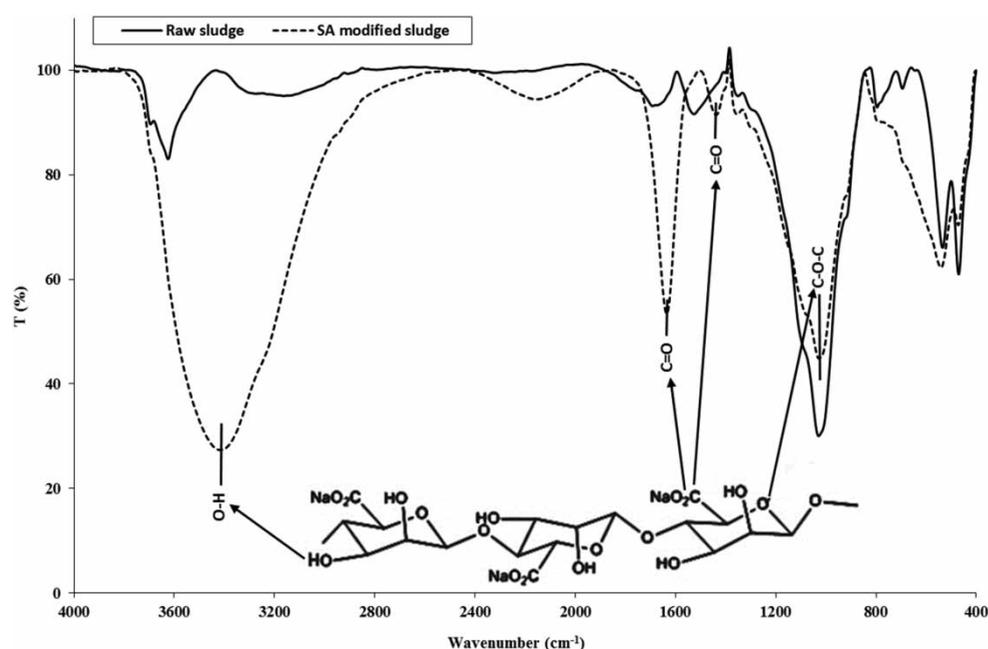| Model types	Name	Equation	Ref.
Isotherm models	Langmuir	$\dfrac{C_e}{q_e} = \dfrac{C_e}{q_m} + \dfrac{1}{q_m b}$	Tarlani Azar et al. (2016)
	Freundlich	$\log q_e = \log k_f + \dfrac{1}{n}\log C_e$	Tarlani Azar et al. (2016)
	Redlich–Peterson	$\ln\left(A\dfrac{C_e}{q_e} - 1\right) = g\ln(C_e) - \ln(B)$	Kumar (2007)
Kinetic models	Pseudo-first-order	$\ln(q_e - q_t) = \ln q_e - k_1 t$	Lagergren (1898)
	Pseudo-second-order	$\dfrac{t}{q_t} = \dfrac{1}{k_2 q_e^2} + \dfrac{t}{q_e}$	Ho & McKay (1999)

Figure 2 | FTIR spectra of adsorbent.

on the surface increases the chance of MB molecules being trapped and adsorbed onto the surface of the adsorbent. The obtained images showed that the immobilization of sludge by alginate has been performed favorably. The Brunauer–Emmett–Teller (BET) surface area and total pore volume of the modified DWTS was measured by a BET instrument (BELSORP-mini, BEL Japan Inc., Osaka Japan) and were found to be about 225 m^2/g and 0.291 cm^3/g, respectively. As said, the relatively large surface area may be related to activated carbon addition in the treatment process.

Effect of operating variables on the MB adsorption

Effects of the solution pH

The pH of the solution is considered as one of the most important factors affecting the adsorption processes. Because of this immense importance, the MB removal efficiency as a function of pH changes was assessed for a series of initial pH values of 2–12 (Figure 4). The adsorption experiments at each pH were carried out in triplicate and the average values together with their corresponding standard deviations (shown by error bars) are presented in the figure. As demonstrated, with the increase of pH from to 2 to 8, MB removal efficiency was also increased from 33.10% to 84.72% for SA modified sludge and from 15.55% to 34.22% for raw sludge. When the solution pH was raised further, the removal efficiency did not show significant changes and the enhancement of

the removal efficiency was only about 6% within the pH range 8–12 for SA modified sludge. As a result and from the operational point of view, pH 8 was selected as the optimal pH for the next experiments. The effects of only adjusting the pH on the MB concentration in the absence of adsorbent (i.e. blank or control samples) were also tested. The results showed that in acidic pH (pH <4), single agitation has little effect on MB initial concentration reduction (<1%). Basic pHs, however, appear to have more effect than the acidic pHs on MB initial concentration reduction (initial concentration decreased ≈3.5%, on average; 4.42% concentration reduction for pH = 10, and 8.64% concentration reduction for pH = 12). The standard deviations could somewhat justify the effects. These blank samples were considered for all experiments in the study; however, provided that the differences were more than 2%, the control test results have been considered for the net removal efficiency calculation, otherwise they were ignored.

A similar result was found in a study conducted by Kush-waha *et al.* (2014), where cationic MB and malachite green dyes in aqueous solution were removed by waste materials of *Daucus carota*. In another research conducted by Pavan *et al.* (2008), it was observed that efficiency rose to 96% by increasing the solution pH to 12. Rashed *et al.* (2016) also found that the removal efficiency of MB increases when solution pH rises from 3 to 7 but further enhancement of pH resulted in the decline of removal efficiency. Hameed *et al.* (2007) investigated the adsorption of AG25 dye on activated
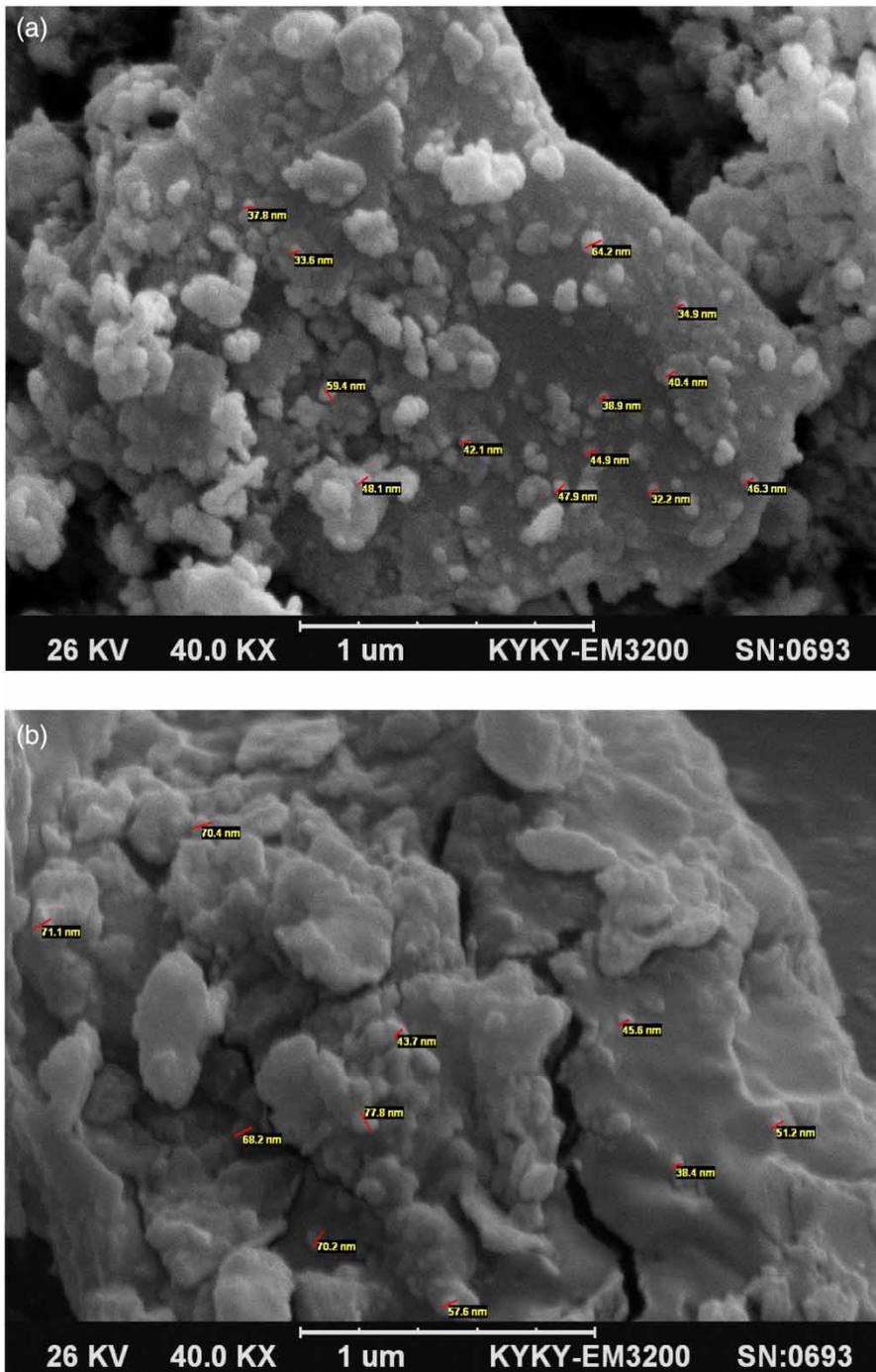
Figure 3 | SEM micrograph of (a) fresh (raw) and (b) SA modified sludge.

palm ash in the pH range of 2–13 and reported that dye removal declines with the increase in pH, due to increase of OH anion and the change in surface charge of the adsorbent (Hameed *et al.* 2007). In addition, the effects of solution pH on the removal efficiency can be explained by considering both pH dependency of the adsorbents and the dissociation constant (pK$_a$) of MB. The variation in the solution pH can lead to change in surface charge as well as the functional group chemistry of the adsorbent surface (Crini *et al.* 2007). Since the pH$_{pzc}$ of modified sludge was 7.55 (Figure 5), positive charges developed on adsorbent surfaces at pH below pH$_{pzc}$ which, in turn, results in high density of H$^+$ on the
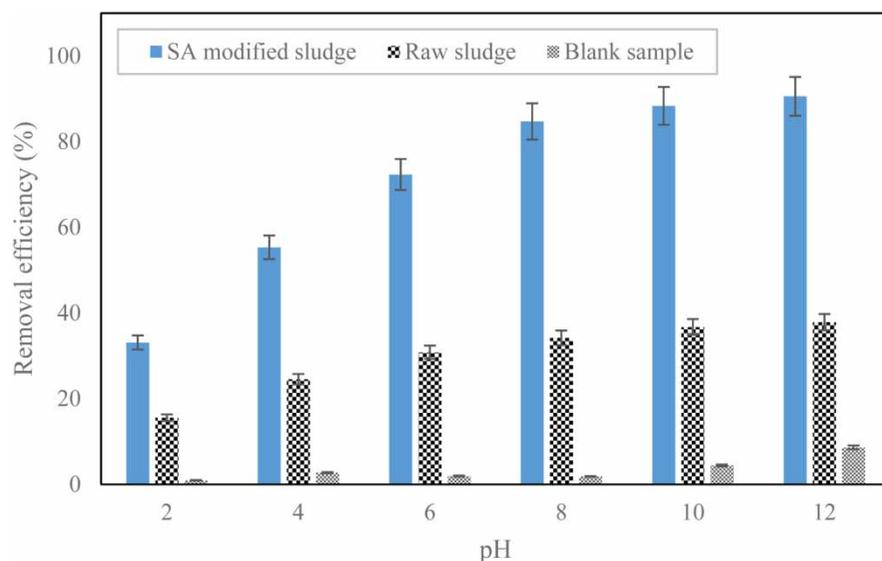
Figure 4 │ Effect of solution pH on removal of MB from aqueous solutions (initial MB concentration: 50 mg/L, adsorbent dose: 0.2 g/L, reaction time: 60 minutes).
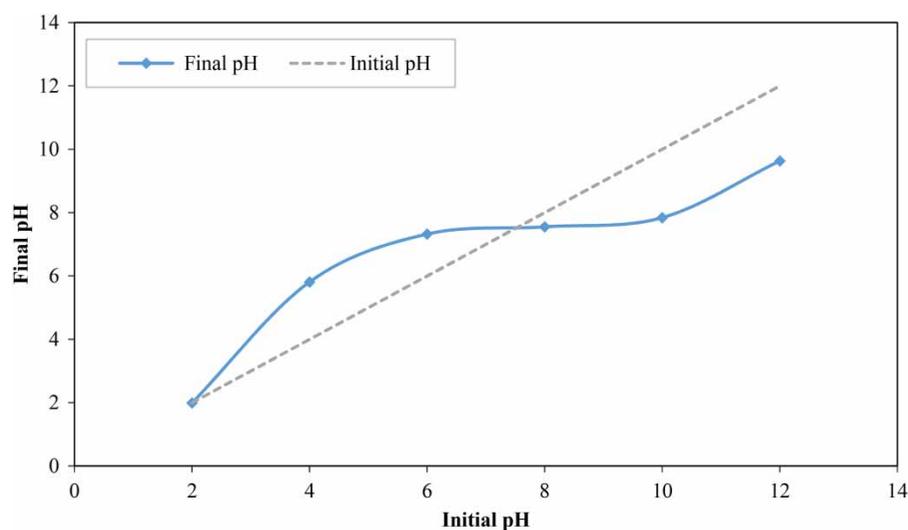

Figure 5 │ Determination of the point of zero charge (pH_{pzc}).

surface of adsorbent. This brings about a competition between H^+ and MB cation on getting access to the adsorption sites (Hamdaoui 2006; Almeida *et al.* 2009) and thereby removal efficiency is lowered. But when the solution pH goes above 7.55, the negatively charged surface of the adsorbent elevates the adsorption of MB cation (El Haddad *et al.* 2016).

Effect of the adsorbent dosages

To determine the effect of adsorbent dose on the MB removal, doses of 0.1–2 g/L of the adsorbent, for both SA modified and raw sludge, were used. Initial concentration

of dye, reaction time, and optimum pH for experiments were 50 mg/L, 60 minutes, and 8, respectively. According to Figure 6, the removal efficiency and dosages of adsorbent have linear relationships. For example, with the increase of adsorbent dose of SA modified sludge from 0.1 to 0.3 g/L, the removal efficiency was also increased from 64.48 to 86.93%. At doses higher than 0.3 g/L, the further increase in removal efficiency was negligible. Therefore, 0.3 g/L was chosen as the best dose for further investigation. This enhancement could be due to increased available surface area for adsorption and reaction sites (Leili *et al.* 2013) and the reduction of inter-particle emission (Vimonses *et al.*
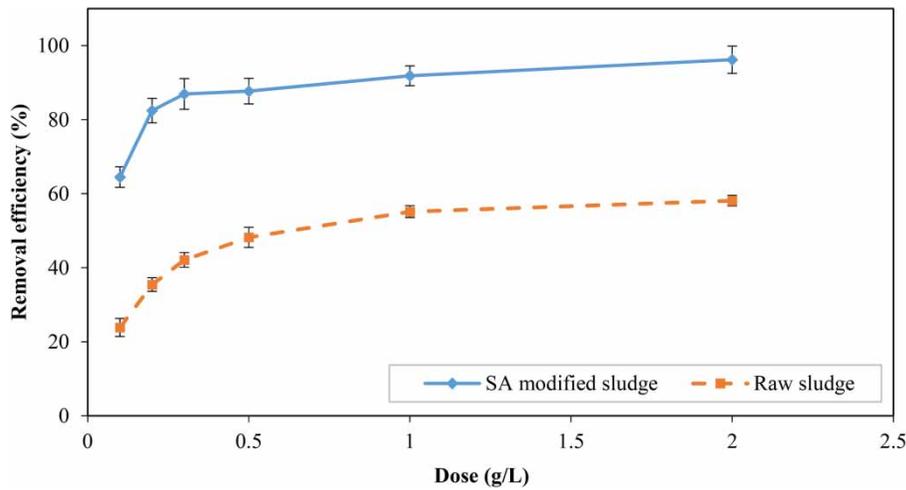
Figure 6 │ Effect of adsorbent dose on removal of MB from aqueous solutions (pH: 8, initial MB concentration: 50 mg/L, reaction time: 60 minutes).

2009). For dosages larger than the optimum point, it can be stated that with the increase in the adsorbent concentration under the same conditions, the number of active and available sites for interactions between the adsorbent and dye molecules also goes up, successively reducing the adsorptive capacity of the modified sludge (Gong *et al.* 2005; Mahmoud *et al.* 2013).

Effect of the initial MB concentration

To assess the effect of initial MB concentration on the removal efficiency, the operating parameters of adsorbent dose, reaction time, and pH were set to 0.3 g/L, 60 minutes, and 8, respectively. According to Figure 7, removal efficiency dwindles as initial MB concentration increases. For

instance, the removal efficiency of 84% was achieved when the initial MB concentration was 50 mg/L, but with the increase of initial concentration to 500 mg/L, removal efficiency goes down to approximately 45%. This observation was inconsistent with the Rashed *et al.* (2016) study, which found an inverse relation between initial MB concentration and its removal percent, but is consistent with Reddy *et al.* (2016), who reported that the amount of MB removal onto bio-waste-derived adsorbent material went down with the increment of initial MB concentration. This observation may be explained by the fact that a fixed number of sites are available on a certain amount of adsorbent. In other words, the number of available adsorption sites are relatively high at lower concentrations; therefore, the adsorbate molecules were easily adsorbed. At higher initial concentrations, on
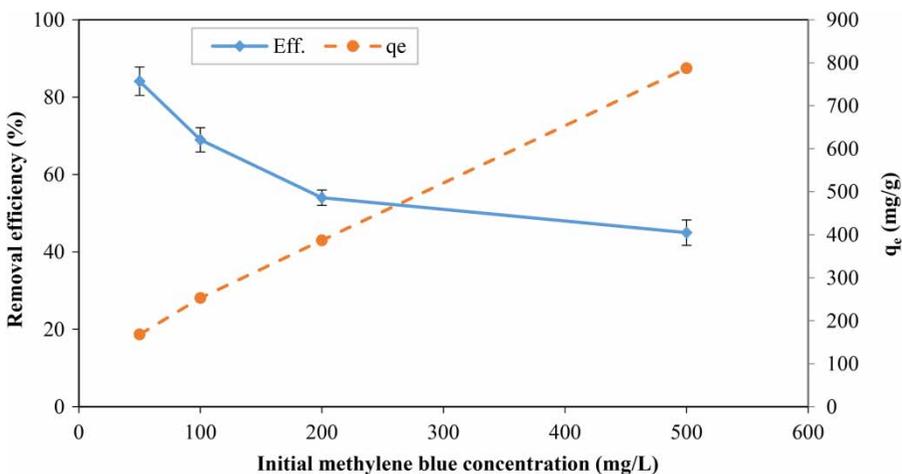

Figure 7 │ Effect of initial MB concentration on removal efficiency (pH: 8, adsorbent dose: 0.3 g/L, reaction time: 60 minutes).

the other hand, there are be a limited number of the adsorption sites, which would consequently cut the removal efficiencies (Tarlani Azar *et al.* 2016). Despite that, as the initial concentration increased, the MB uptake from aqueous solution was also increased because the initial concentration provides an important driving force to overcome all mass transfer resistances of MB between the aqueous and solid phases (Wu *et al.* 2012). Therefore, in the present study, 50 mg/L was considered as the optimal dye concentration and used for further experiments.

Effect of contact time

In order to determine the equilibration time for maximum adsorption of adsorbate and to study the kinetics of the adsorption process, the adsorption of MB on the raw and SA modified sludge was studied as a function of contact time, and the results of three assessed MB concentrations, namely, 50, 100, and 200 mg/L, are shown in Figure 8(a)–(c). As seen, the MB adsorption onto adsorbent increased with time at all concentrations. For instance, the removal efficiency of 49% was reached in 5 min reaction time increased to 88% after 60 min, and the equilibrium was achieved in ca. 60 min for the initial MB concentration of 50 mg/L and SA modified sludge. Regarding 100 mg/L initial MB concentration, the removal efficiency of 39% in 5 min reaction time increased to 83% after 60 min contact time. Although a similar trend was observed for initial MB concentration of 200 mg/L, $\approx$10% removal efficiency reduction was achieved. Based on the aforementioned observation and taking into account material cost and the potential environmental damage, 50 mg/L was selected as optimal initial MB concentration. However, to ensure equilibrium, the samples were shaken for 2 h. It was found that during the initial stage of reaction, many vacant surface sites were available for the adsorption and the adsorption rate was rapid, so most of the solutes were adsorbed within the first 60 min, but with the lapse of time, an equilibrium was achieved as most of the available sites were occupied by the MB (Zolfaghari *et al.* 2011). A similar observation and the same optimal contact time of 60 min were also reported in the study conducted by Rashed *et al.* (2016). Accordingly, the optimum conditions in this study were determined as follows: pH = 8, adsorbent dosage = 0.3 g/L, C_0 = 50 mg/L and contact time = 60 min. The removal efficiency of MB in this condition was 88.5%, while it was 39% for raw sludge. Accordingly, kinetic and adsorption studies were only conducted for SA modified sludge.
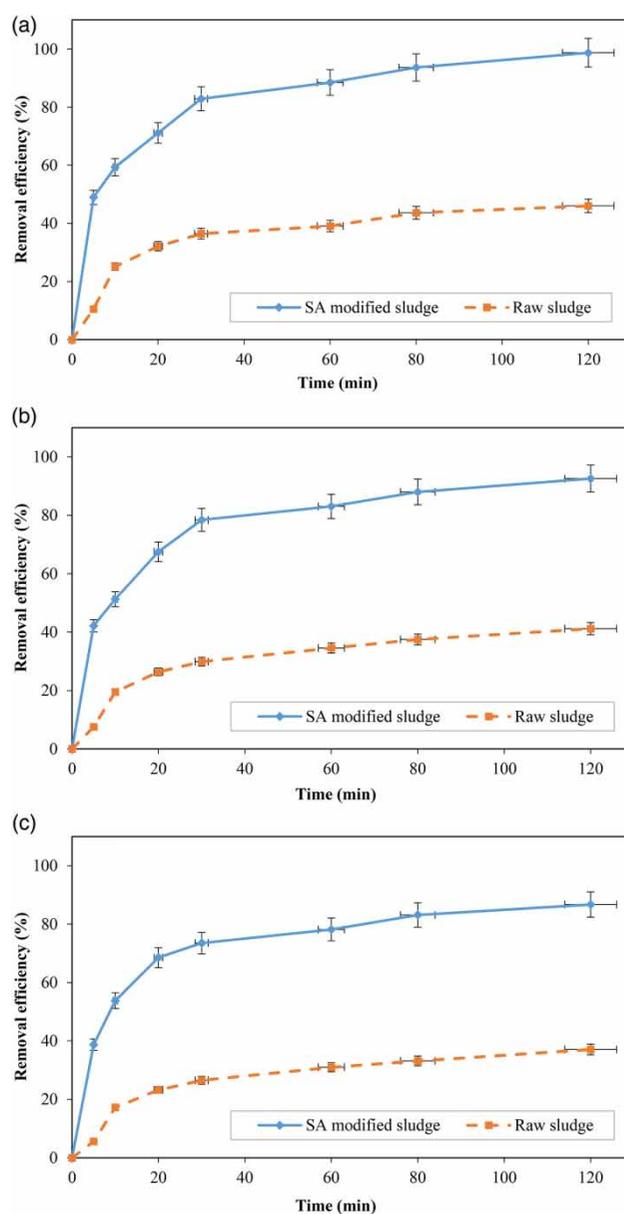

Figure 8 | Effect of reaction time on removal of MB from aqueous solutions: (a) 50 mg/L, (b) 100 mg/L, and (c) 200 mg/L MB concentration (pH: 8, adsorbent dose: 0.3 g/L).

Adsorption kinetics

Adsorption kinetics can explain the solution uptake rate and show the adsorption efficiency of the adsorbents (Zhua *et al.* 2010). Kinetics experiments were conducted in Erlenmeyer flasks containing 250 mL of MB solution with initial MB concentrations of 50, 100, and 200 mg/L, pH = 8 and 0.3 g of adsorbent, which were agitated at room temperature. After regular time intervals, 5 mL of solution was sampled from the mixtures and MB concentration was analyzed until the reaction reached equilibrium. Two of the most
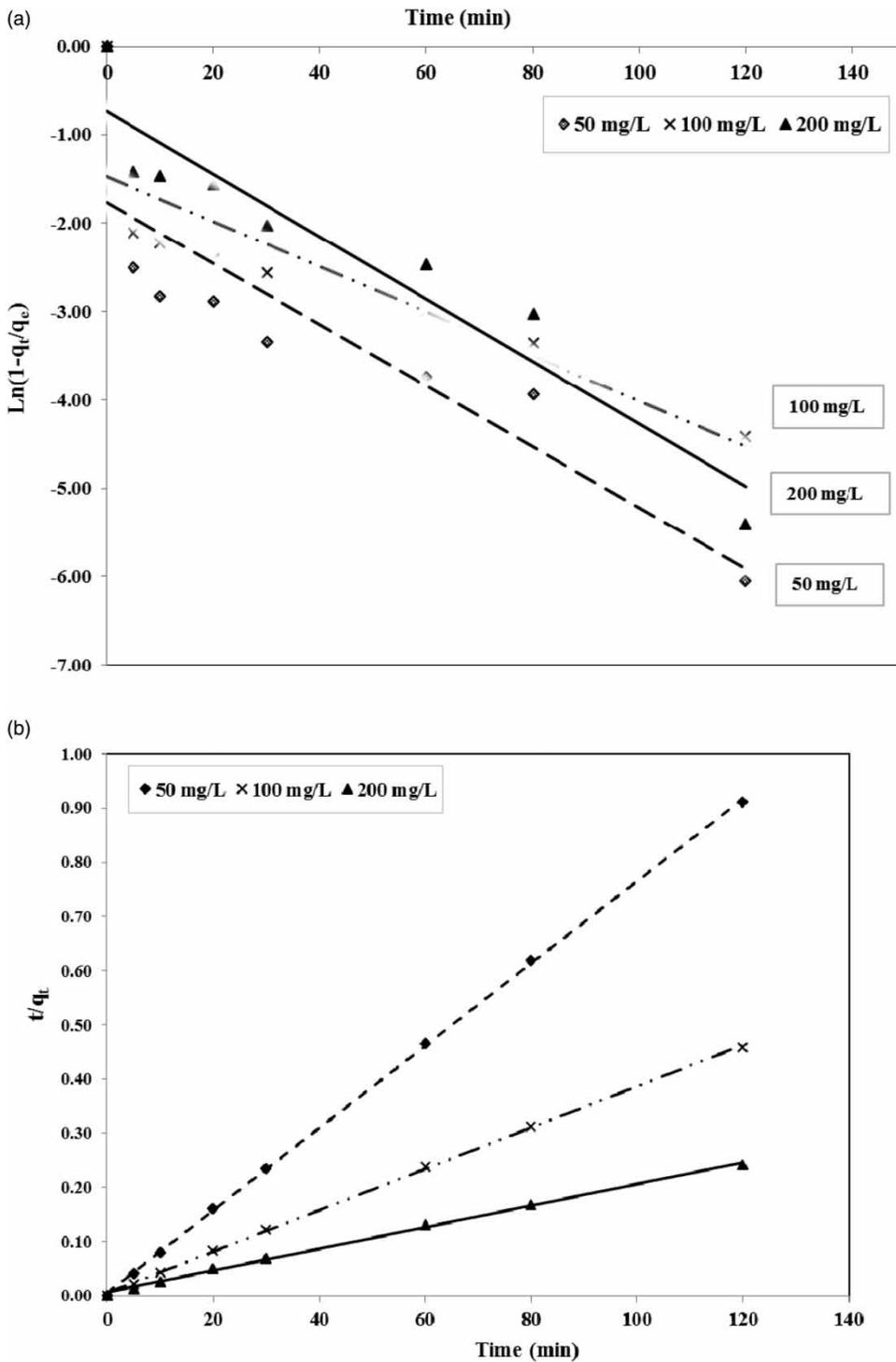
Figure 9 | Linearization of MB adsorption kinetics on adsorbent: (a) pseudo-first-order model and (b) pseudo-second-order model (pH: 8, adsorbent dose: 0.3 g/L).

widely used kinetic models, namely, Lagergren first-order kinetic model and pseudo-second-order model (Table 3), were applied to understand the adsorption kinetic behavior of MB onto SA modified sludge adsorbent.

Figure 9(a) and (b) show the adsorption kinetics of MB on adsorbent, and the results of fitting adsorption data with pseudo-first-order and pseudo-second-order kinetics models and respective parameters are listed in Table 4. As can be

Table 4 | Parameters of adsorption kinetic models for the MB adsorption onto adsorbent

C$_0$ (mg/L)	Pseudo-first-order				Pseudo-second-order			
	k$_1$ (min^{-1})	q$_e$ (mg/g)	R^2	χ^2	k$_2$ (g/mg-min)	q$_e$ (mg/g)	R^2	χ^2
50	0.035	5.79	0.759	2751.1	0.011	131.57	0.999	145.4
100	0.025	4.37	0.732	15544.3	0.003	263.15	0.999	1330.5
200	0.035	2.08	0.906	119194.7	0.0006	500	0.997	2008.6

seen in the aforementioned figures, the pseudo-second-order model has the highest values of the coefficient of determination (R^2 > 0.99) and lowest χ^2 for all concentrations, suggesting that the pseudo-second-order kinetic model describes this adsorption process better than the Lagergren first-order model (El-Mekkawi et al. 2016; Li et al. 2016).

Adsorption isotherms

The plots of solid-phase MB concentration against liquid-phase MB concentration are shown in Figure 10. The parameters of the three assessed isotherm models and the calculated adsorption isotherm parameters for MB adsorption onto the adsorbent are given in Table 5. Taking into consideration the values of the correlation coefficient (R^2) and chi-square statistic (χ^2) as criteria for goodness of fit for the system, the adsorption isotherm is better described by the Langmuir and the Redlich–Peterson models. The lowest R^2 and highest χ^2 values for the Freundlich isotherm signifies that, at least comparatively, this isotherm is not in an appropriate agreement with the equilibrium sorption mechanism. The reason may be the homogeneous distribution of identical active sites on the surface of prepared adsorbent and the monolayer adsorbing mechanism assumption of the Langmuir model, which confirms physisorption followed by chemisorption (Langmuir 1918). Accordingly, the adsorption capacity (q$_m$) of adsorbent was found to be 909.1 mg/g, which was considerably high compared to other studies (El-Mekkawi et al. 2016; Li et al. 2016; Rashed et al. 2016).

To determine the characteristic of the adsorption process and to examine whether adsorption is favorable in terms of R$_L$, a dimensionless constant commonly known as the separation factor, R$_L$ is calculated using Equation (3) (Weber & Chakravorti 1974):

$$R_L = \frac{1}{(1 + K_L C_0)} \tag{3}$$

The value of R$_L$ indicates the adsorption nature to be either unfavorable (R$_L$ > 1), linear (R$_L$ = 1), favorable
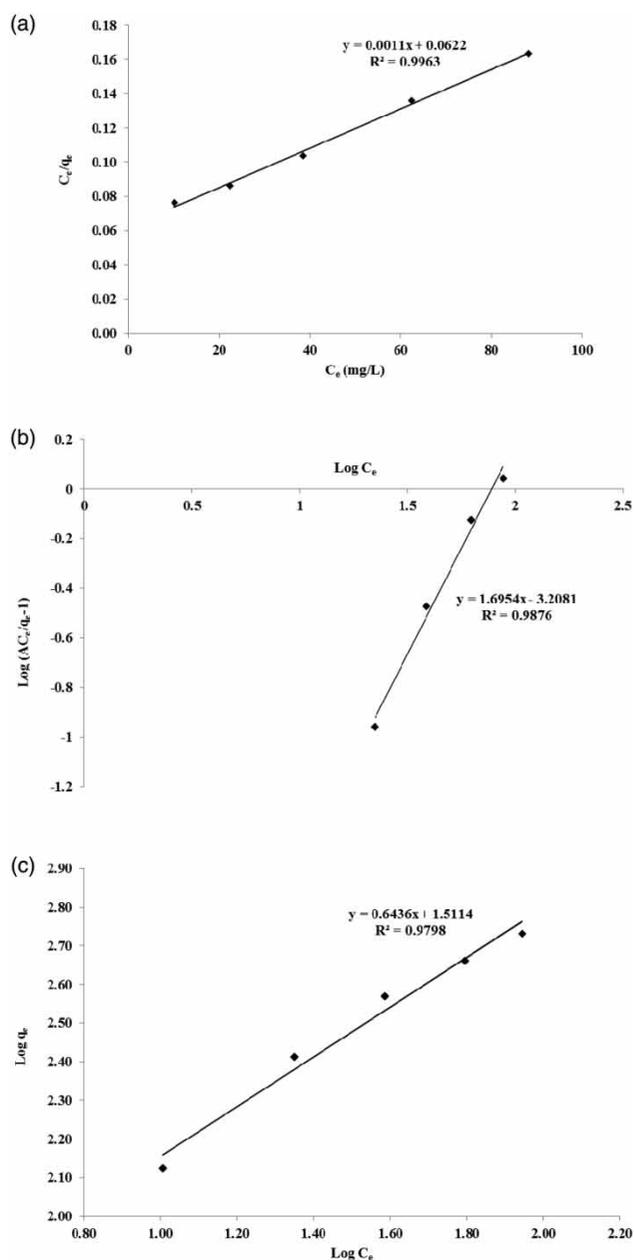

Figure 10 | Adsorption isotherms of MB on adsorbent. (a) Langmuir model, (b) Redlich–Peterson model and (c) Freundlich model (pH: 8, adsorbent dose: 0.3 g/L, concentration range: 50–250 mg/L).

Table 5 | Isotherm parameters for MB adsorption onto adsorbent

Isotherm	Parameter values
Langmuir	
q_m (mg/g)	909.1
K_L (L/mg)	0.018
R_L	0.18–0.53
R^2	0.996
χ^2	403.5
Redlich–Peterson	
A	12.87
B	0.006
g	0.93
R^2	0.988
χ^2	543.67
Freundlich	
n	1.55
k_f	32.46
R^2	0.980
χ^2	886.8

$(0 < R_L < 1)$ or irreversible $(R_L = 0)$. The Langmuir constant K_L was found to be 0.018. This value also means that a higher affinity of MB for sorbent is expected. Moreover, the value of R_L obtained for MB was 0.18 to 0.53, indicating favorable adsorption of MB onto sorbent as it lay between 0 and 1 for the prepared adsorbent.

CONCLUSION

In this study, the sludge stabilized by SA was used for removal of MB from aqueous solutions. The highest removal efficiency was observed at initial concentration of 50 mg/L, adsorbent dose of 0.3 g/L, reaction time of 60 minutes, pH 8, and room temperature. The results showed that removal efficiency has a direct relationship with adsorbent dose, reaction time, and pH, and an inverse relationship with initial concentration of dye. The study of the kinetics and isotherms of the adsorption showed that the MB removal capacity of sorbent is substantially and significantly high. Based on the isotherm analyses, the monolayer sorption capacity for MB by adsorbent was found to be 909.1 mg/g. The sorption kinetics of MB on adsorbent could also be explained by the pseudo-second-order model. From the experimental results we can conclude that the developed low-cost sorbent from DWTS has a considerable potential for removal of MB and could be considered as a promising material for the removal of dyes and probably other organic pollutants from aqueous solutions.

CONFLICTS OF INTEREST

The authors declare no conflict of interest.

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