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Biosorption of methylene blue by activated sludge

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ABSTRACT

The ability of the use of dried activated sludge for removing methylene blue (MB) was investigated. The dye binding capacity of biosorbent was shown as a function of initial dye concentration, initial pH, and temperature at agitation rate 700 rpm. The experimental results indicated that the equilibrium between the dye and the adsorbent in the solution was established within 30 min and the maximum % removal value was found as 96.54% at pH 7.5. The uptake biosorption increased with increasing initial MB concentration. The maximum MB adsorption capacities were obtained at the temperature of 30˚C. The equilibrium data fitted very well to the both Freundlich and Redlich–Peterson adsorption models with high correlation coefficient ($R^2 > 0.99$). The pseudo-first-order and pseudo-second-order kinetic models were applied to test the experimental data, consequently; the results showed that the dyes uptake processes followed the pseudo-second-order rate expression. So, it can be concluded that dried activated sludge could be a potential low-cost biosorbent for the MB removal from aqueous solutions.

Keywords: Biosorption; Methylene blue (MB); Dried activated sludge

1. Introduction

Water pollution is a very persistent problem. Industrialization use of hazardous chemical products both in domestic and industrial activities has led to the release of various substances—the so-called "emerging pollutants"—in the environment. Removal of hazardous compounds from industrial effluents is one of the growing needs of the present time.

Several industries, mostly textile industry, propagate colored effluents containing dyes and pigments. It has been estimated that 10–15% of the dye is lost in the dye effluent [1]. The discharge of dyes in the environment is a matter of concern for both toxicological and esthetical reasons, causing serious water pollution problems to aquatic life due to the reduced light penetration. There are more than 100,000 dyes available commercially, most of which are difficult to decolorize due to their complex structure and synthetic origin [2]. The presence of even very small amounts of dyes

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in water—less than 1 mg/L for some dyes—is highly visible and undesirable [3,4].

Various techniques like coagulation, adsorption, chemical oxidation, and froth floatation have been used for the removal of organics as well as inorganics from wastewaters. Among these techniques, adsorption is considered to be the most potential one due to its high efficiency and ability to separate a wide range of chemical compounds [5–10]. Adsorption is a well established and powerful technique for treating domestic and industrial effluents. Where the activated carbon is the most widely used adsorbent for removal of dyes and treatment of textile effluents but due to its high price it is not used on a great scale [11,12]. Recently, the use of less expensive and efficient biosorbents for the removal of dyes and pigments to replace activated carbon is of significant interest.

Using micro-organisms as adsorbents for dyes also offers a potential alternative to existing methods for detoxification. The cell wall of micro-organisms essentially consisting of various organic compounds such as chitin, lipids, amino acids, and other cellular components could provide a passive uptake of reactive dyes [12–14].

These dyes are typically azo-based chromophores combined with different types of reactive groups which interact with the active groups on the cell surface in a manner of surface adsorption, ion exchange, complexation, chelation, and micro-precipitation [12,15].

Recent studies have shown that different biomasses possess impressive adsorption capacities for a range of heavy metal ions, organics, and dyes [16–21]. Probably, the most abundant source of mixed microbial biomass is the activated sludge wastewater treatment process.

In the present work, the attention is focused on methylene blue (MB), the most commonly used substance for dying cotton, wood, and silk. It can cause eye burns which may be responsible for permanent injury to the eyes of humans and animals [11,22]. Therefore, the treatment of effluent containing such dye is of interest due to its harmful impacts on receiving waters.

The ability of activated sludge biomass to remove methylene blue MB from aqueous solution is studied. The influence of some essential parameters, namely contact time, initial MB concentration, temperature, and initial pH, on the static adsorption of MB on this dried activated sludge is investigated.

The modeling of the experimental data at equilibrium was performed with Langmuir, Freundlich, and Redlich–Peterson models. Batch biosorption models, based on the assumption of the pseudo-first-order and pseudo-second-order mechanisms, are applied to study the kinetics of the adsorption.

2. Materials and methods

2.1. Preparation of biosorbent

Aerobic activated sludge was collected from the wastewater treatment system STEP of Oued Lahrèche, Médéa, Algeria. The cells of that waste activated sludge was centrifuged at 5,000 rpm for 5 min and washed thoroughly with sterile distilled water, and then dried at 60℃ for 24 h before use (Fig. 1).

Scanning electron microscopy (SEM) analysis was carried out for the waste activated sludge to study the surface morphology. The analysis was carried out using a scanning electron microscope (QUANTA 2000). The surface functional groups of the waste activated sludge were detected by Fourier transform infrared (FT-IR) spectroscope (SHIMADZU FT-IR-8400). The spectra were recorded from 4,000 to 400 cm^{-1}.

2.2. Chemicals

Methylene blue (99.9% from Aldrich) was used as model adsorbate. A stock solution of 1,000 mg/L was prepared by dissolving an appropriate quantity of MB in a liter of distilled water. The working solutions were prepared by diluting that stock solution (1,000 mg/L) with distilled water to give the appropriate concentration of the working solutions. The pH of each solution was adjusted to the required value with diluted or concentrated HCl and NaOH solutions before mixing the biosorbant with solution. The ranges of concentrations of these solutions vary between the values of 50 and 500 mg/L.

Fig. 1. Flocks of waste activated sludge.

2.3. Analysis

The methylene blue concentration in the supernatant solution was analyzed using a UV spectrophotometer (Shimadzu UV Mini-1240) by monitoring the absorbance changes at a wavelength of maximum absorbance of 665 nm [11,23].

2.4 Process of adsorption

The method retained for the establishment of the adsorption isotherm consists in putting in a thermostatic bath a series of bottles that were continuously stirred at 700 rpm. Each bottle contains a volume (*V*) of MB solution of known concentration and a mass (m) of biosorbent. After a fixed time of contact, the filtrate of the solution is recovered to be analyzed by UV/visible spectrophotometer.

The adsorbed quantity of aqueous solution (*q*) per unit mass of the solid support is calculated by the following formula:

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

where q is the adsorbed quantity of MB per gram of biomass at time t (mg/g); q_e is the adsorbed quantity of MB per gram of biomass at equilibrium (mg/g); C_e is the concentration of the solution at equilibrium (mg/L); C_0 is the initial MB concentration (mg/L); V is the volume of MB solution (L); m is the mass of biosorbants (g).

Thus, the curve of the isotherms of adsorption is: q (mg) = f (C_e (mg/L)).

3. Results and discussion

3.1. Textural characterization of prepared waste activated sludge

The surface morphology of aerobic activated sludge is exemplified by the scanning electron micrograph in Fig. 2. As shown in the SEM micrograph, the dead biomass particle surface was irregular with rough and highly heterogeneous structures. Various sorption mechanisms may be involved in the sorption process.

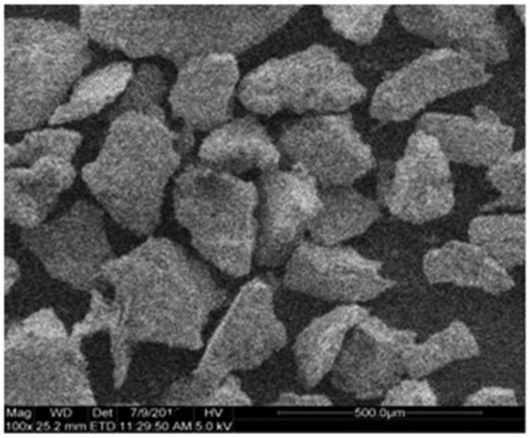

Fig. 2. Shows the SEM image of waste activated sludge.

The FT-IR spectrum of biomass (Fig. 3) shows distinct peaks between 3,753.6 and 3,440.9 cm^{-1}, indicating the presence of OH, NH, and NH_2 groups. At 2,926.11 cm^{-1} asymmetric vibration of CH and 2,860.53 cm^{-1} symmetric vibration of CH. 2,382.17 vibration of carboxylic acids is indicated. 1,641.48 and 1,552.75 cm^{-1} stretching vibration of C=O and NH peptidic bond of proteins. 1,433.16 cm^{-1} of phenolic OH and CO stretching. The 1,037.74 cm^{-1} band is vibration of C–O–C polysaccharides. The <1,000 cm^{-1} is fingerprint zone which is phosphate and alkyl halides groups [24]. So, it can be concluded that the waste activated sludge has different functional groups of proteins, lipids, polymeric compounds and carboxylic, amine, and amide groups may be responsible for biosorption process.

Biosorption data for the uptake of MB onto dried activated sludge were investigated at various initial concentrations, temperatures, and pH. The results are given as the units of adsorbed dyes quantity per gram of biomass at time t (q, mg/g) and at equilibrium (q_e, mg/g), unadsorbed dyes concentration in solution at time t (C, mg/L) and at equilibrium (C_e, mg/L). Adsorption yield is given as:

$$\text{Adsorp.}\,\% = \frac{C_0 - C_e}{C_0} \times 100 \tag{2}$$

where C_0 (mg/L) is the initial dye concentration.

3.2. Effect of contact time

In order to determine the time of contact necessary for the establishment of adsorption equilibrium, the absorbed quantity of aqueous solution on dried activated sludge is measured as a function of the time of contact corresponding to adsorption equilibrium. The variation of the quantity adsorbed versus the time of contact is shown in Fig. 4.

Adsorption experiments were carried out at temperature of 20°C ± 02 with an initial concentration 500 mg/L and for a contact period of 90 min at

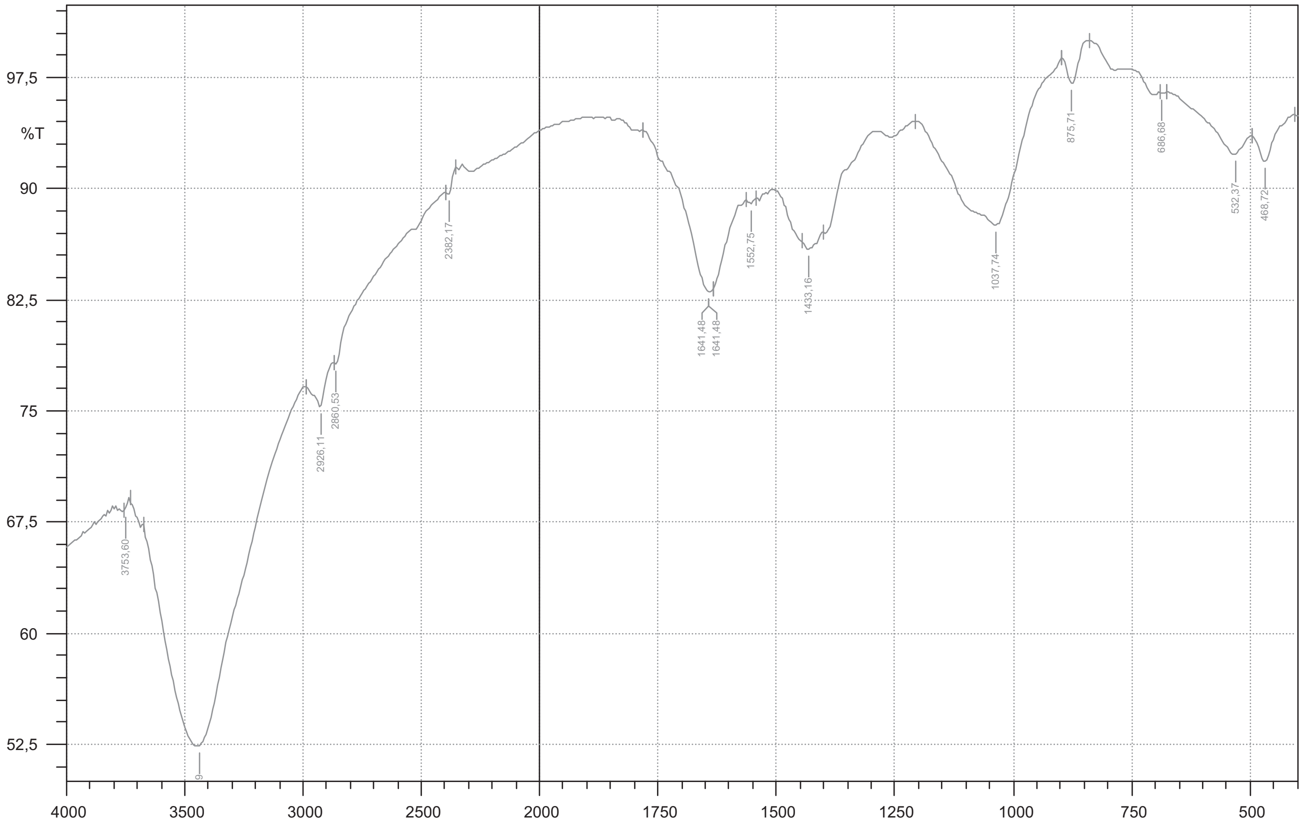

Fig. 3. FT-IR spectra of waste activated sludge.

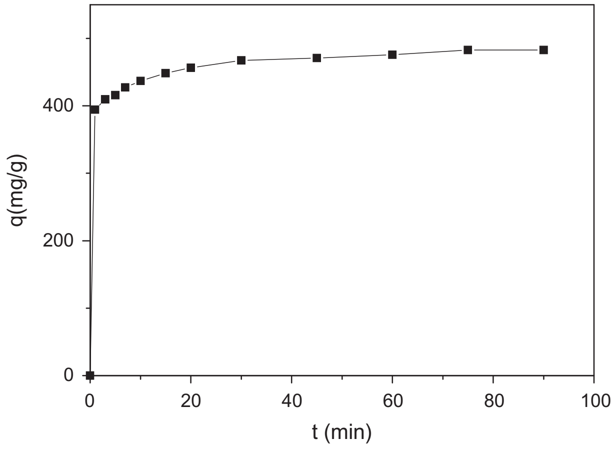

Fig. 4. Effect of contact time on adsorption at given condition: $C_0 = 500$ mg/L, pH 7.5, $m_s = 0.1$ g, $V = 100$ ml, $T = 20$°C, and stirring velocity = 700 rpm.

pH 7.5. The results show that adsorption process is clearly time dependent. As can be observed, a large fraction of the total amount of MB was removed from solution within the first few minutes and the equilibrium was established after approximately a contact period of 30 min. The reason for this can be explained from the fact that at this stage biosorbent molecules are being sorbed onto the surface where there are no other such molecules and consequently the sorbate–sorbate interactions are negligible [23,25]. This rapid initial phase is then followed by a much slower uptake, which is due to saturation of sorption sites.

3.3. Effect of the initial concentration of MB

The initial concentration provides an important driving force to overcome all mass transfer resistance of all molecules between the aqueous and solid phases [26]. To determine the impact of the initial concentration on the adsorption of MB in aqueous solution in contact with dried activated sludge, different initial concentrations C_0 (50, 70, and 100 mg/L) have been examined. The results of these experiments are displayed in Fig. 5, which shows that the sorption capacity of the sorbent increases from 45.5 to 94.8 mg/g with increasing initial MB concentration from 50 to 100 mg/L, respectively. The increase in loading capacity of dried activated sludge with increasing initial MB concentration may also be due to higher

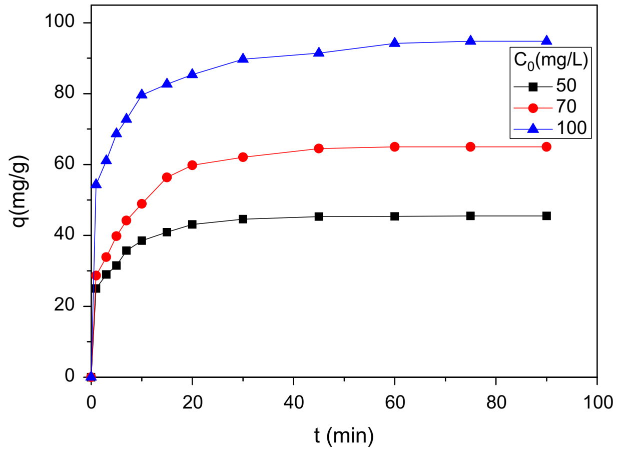

Fig. 5. Effect of MB concentration on the kinetics of MB removal at 20˚C.

interactions between MB and the biosorbent. As dried activated sludge offered a limited number of binding sites, MB sorption showed a saturation trend at higher initial MB concentration.

3.4. Effect of temperature on adsorption equilibrium

Effect of temperature on the equilibrium MB sorption capacity of waste activated sludge was investigated in the temperature range of 20–40˚C at different initial MB concentrations of 50, 100, and 500 mg/L.

As seen from Fig. 6, at all MB concentrations, the effect of temperature on the adsorption equilibrium was not significant in the interval of 20–40˚C. So, temperature did not importantly effect the dye removal. However, the maximum adsorption capacities were found at 30˚C with different initial MB concentrations. Above and under this point, biosorption of MB on dried activated sludge tends slightly to decrease. This result can be attributed to change in surface characteristics and activity of dried activated sludge [27,28].

3.5. Effect of pH on MB uptake

pH is an important parameter affecting the biosorption process. The effect of initial pH on the % removal of MB is given in Fig. 7, at 500 mg/L initial dye concentration and 0.1 g of biosorbent.

The % removal of MB increased with pH up to 7.5 and then declined with further increase in pH. The maximum % removal value was found as 96.54% at pH 7.5. Several reasons may be attributed to MB adsorption behavior of the sorbent relative to solution pH. The surface of biomass may contain a large number of active sites and the solute (MB ions) uptake can be related to the active sites and also to the chemistry of the solute in the solution [2]. When the pH of the solution increases, the positive charge on the interface of the solution decreases and the adsorbing surface appeared to be negatively charged. A similar trend was observed for the biosorption of MB on other low-cost biosorbents such as Breadnut peel [32], *Artocarpus camansi* Blanco (Breadnut) core [33], and *Artocarpus odoratissumus* [34].

However, the level of influence of the solution pH on the adsorption capacity might vary, depending on the adsorbent–adsorbate system [29].

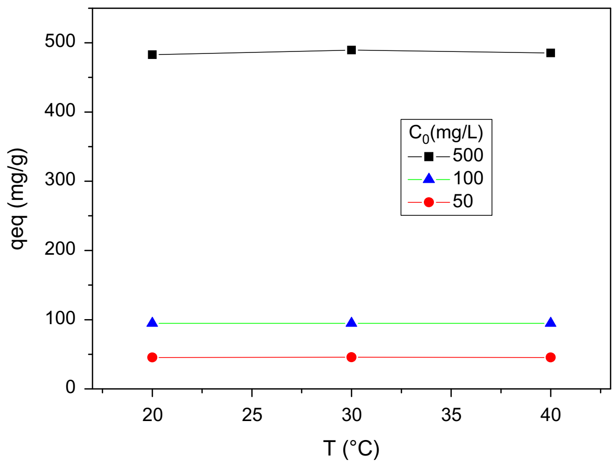

Fig. 6. Effect of temperature on adsorption equilibrium at various initial MB concentrations.

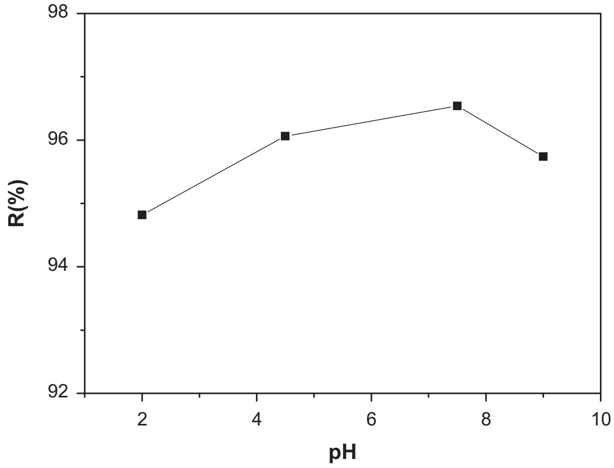

Fig. 7. Effect of solution pH on the removal of MB after 80 min.

3.6. Adsorption isotherms

An adsorption isotherm is characterized by some constant values, which express the surface properties and affinity of the adsorbent and can also be used to compare the adsorptive capacities of the adsorbent for different pollutants. This kind of adsorption isotherm generally fits the Langmuir or Freundlich models [33,34].

In order to describe the interactions between MB and waste activated sludge, the experimental data points were fitted to the Langmuir (Eq. (3)), Freundlich (Eq. (4)), and Redlich–Peterson (Eq. (5)) equations which are applicable to sorption process.

3.6.1. The Langmuir model

The Langmuir model assumes the presence of a finite number of binding sites, homogeneously distributed over the adsorbent surface, presenting the same affinity for sorption of a single layer, and having no interaction between adsorbed species. The well-known Langmuir expression [38] is presented as follows:

$$q_e = \frac{Q_0 k C_e}{1 + k C_e} \tag{3}$$

where q_e is the amount of MB bound per gram of biomass at equilibrium (mg/g), C_e (mg/L) is the residual MB concentration in solution after binding, Q_0 (mg/g) is the maximum amount of MB per unit weight of biomass to form a complete monolayer on the surface bound at high C_e, and k (L/mg) is a constant related to the affinity of the binding sites.

3.6.2. The Freundlich model

The Freundlich model is an empirical equation based on adsorption on a heterogeneous surface suggesting that binding sites are not equivalent and/or independent [39].

$$q_e = k_f C_e^{\frac{1}{n_f}} \tag{4}$$

where k_f and n_f are Freundlich parameters related to the adsorption capacity and adsorption intensity, respectively.

3.6.3. Redlich–Peterson model

The three-parameter Redlich–Peterson equation, which has a linear dependence on concentration in the numerator and an exponential function in the denominator, has been proposed to improve the fit by the Langmuir or Freundlich equation [37,38] and is given by Eq. (5):

$$q_e = \left(\frac{k_{RP} \times C_e}{1 + a_{RP} \times C_e^{\beta}} \right) \tag{5}$$

where K_{RP}, $a_{RP,}$ and β are the Redlich–Peterson parameters. β lies between 0 and 1. For $\beta = 1$, Eq. (5) converts to the Langmuir form [39].

For each isotherm, initial MB concentrations were varied while the adsorbent weight in each sample was held constant. The parameters for each model were estimated by nonlinear regression using STATISTICA version 6 and EXCEL 2007 software. All parameters with correlation coefficient are summarized in Table 1.

From Table 1, the magnitude of K_f and $1/n_f$, the Freundlich constants, showed easy uptake of the dye from wastewater with high adsorptive capacity of biosorbent. Table 1 also indicates that $1/n_f$ is below one, indicating that the dye is favorably adsorbed by waste activated sludge [12].

Values of Q_0 and K for MB are also tabulated in Table 1. The maximum capacity Q_0 determined from the Langmuir isotherm defines the total capacity of the biosorbent as 243.9 mg/g with correlation coefficient $R^2 > 0.8$ for 30°C at pH 7.5.

Redlich–Peterson adsorption parameters calculated according to the three-parameter isotherm of Redlich–Peterson are also tabulated in Table 1 at three different temperatures. Redlich–Peterson constant K_{RP} indicated that the adsorption capacity of waste activated sludge increased with increasing temperature up to 30°C. The exponent β was close to 1 for 20°C, showing the closeness of the model to the Langmuir isotherm. It should be noted that β normally lying between 0 and 1, indicated a favorable adsorption for waste activated sludge.

So, the experimental data yielded excellent fits within the following isotherms order: Redlich−Peterson > Freundlich > Langmuir, based on its R^2 values.

3.7. Adsorption kinetics

Two simplified kinetic models were adopted to examine the mechanism of the adsorption process. First, the kinetics of adsorption was analyzed by the pseudo-first-order equation given by Lagergren and Svenska [37] as:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \tag{6}$$

Table 1
Langmuir, Freundlich, and Redlich–Peterson isotherm model constants and correlation coefficients for adsorption of MB onto waste activated sludge

Isotherm model		20°C	30°C	40°C
Freundlich	R^2	0.997	0.998	0.997
	K_f (mg/g(l/mg)$^{1/n}$)	5.927	1.404	3.891
	n_f	0.648	0.402	0.557
Langmuir	R^2	0.950	0.810	0.910
	Q_0 (mg/g)	134.956	243.948	52.406
	K (L/mg)	0.002	0.001	0.005
Redlich–Peterson	R^2	0.997	0.998	0.998
	k_{RP} (L/g)	2.857	3.610	0.149
	a_{RP} (l/mg)$^{\beta}$	0.006	0.005	0.004
	B	0.936	0.258	0.150

where q_e and q_t are the amounts of MB adsorbed (mg/g) at equilibrium and at time t (min), respectively, and k_1 (min^{-1}) is the rate constant of adsorption. Values of k_1 at 20°C were calculated from the plots of $\log(q_e - q_t)$ vs. t for different initial concentrations of MB.

The k_1, $q_{e,cal}$ and correlation coefficients R^2 are listed in Table 2. The correlation coefficient R^2 for the first-order kinetic model was $R^2 \geq 0.735$ for adsorption of MB onto the dried activated sludge.

On the other hand, the pseudo-second-order equation based on equilibrium adsorption [25] is expressed as:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \qquad (7)$$

where k_2 (g/mg min) is the rate constant of second-order adsorption. The linear plot of t/q_t vs. t at 20°C, as shown in Fig. 8, yielded R^2 values that were greater than 0.999 for all MB concentrations. It also showed a good agreement between the experimental and the calculated q_e values (Table 2), the model can be applied for the entire data.

3.7.1. Validity of kinetic models

The adsorption kinetics of MB onto the prepared waste activated sludge was verified at different initial concentrations. The validity of each model was determined by the sum of squared errors (SSE, %) given by:

$$\text{SSE} = \sqrt{\frac{\sum (q_{e,\,exp} - q_{e,cal})^2}{N}} \qquad (8)$$

where N is the number of data points.

The lower the value of SSE indicates the better a fit is. Table 2 lists the SSE values obtained for the two kinetic models studied. It was found that the pseudo-second-order kinetic model yielded the lowest SSE

Table 2
Comparison of the pseudo-first-order and pseudo-second-order adsorption rate constants, and calculated and experimental q_e values for different initial MB concentrations

		Pseudo-first-order kinetic model				Pseudo-second-order kinetic model				Intraparticle diffusion model	
C_0 (mg/L)	$q_{e,exp}$ (mg/g)	k_1 (1/min)	$q_{e,cal}$ (mg/g)	R^2	SSE (%)	k_2 (g/mg min)	$q_{e,cal}$ (mg/g)	R^2	SSE (%)	k_{diff} (mg/g min$^{1/2}$)	R^2
50	45.5	0.0986	22.4238	0.9701	23.0762	0.0122	46.5766	0.9997	1.0766	5.398	0.973
70	65.0	0.0992	44.3057	0.9833	20.6943	0.0052	67.5219	0.9994	2.5219	9.343	0.993
100	94.8	0.0683	42.7828	0.9291	52.0172	0.0050	96.8999	0.9996	2.0999	9.399	0.955
500	482.7	0.0513	103.0078	0.7359	379.6922	0.0022	485.4369	0.9998	2.7369	18.206	0.991

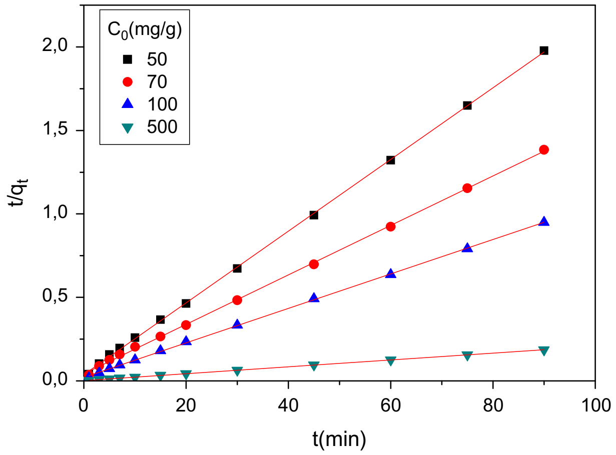

Fig. 8. Pseudo-second-order kinetic for adsorption of MB on waste activated sludge.

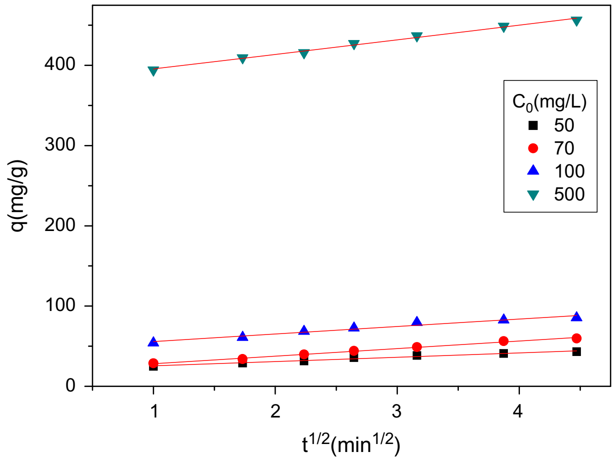

Fig. 9. Intraparticle diffusion plot for adsorption of MB on waste activated sludge or different initial MB concentrations.

values. This proves that the adsorption of MB onto the dried activated sludge could be best described by the pseudo-second-order kinetic model.

3.7.2. Intraparticle diffusion study

In order to investigate the mechanism of the MB biosorption onto waste activated sludge, intraparticle diffusion-based mechanism was studied. The most commonly used technique for identifying the mechanism involved in the adsorption process is by fitting an intraparticle diffusion plot. It is an empirically found functional relationship, common to most adsorption processes, where uptake varies almost proportionally with $t^{1/2}$ rather than with the contact time t. According to the theory proposed by Weber and Morris [38]:

$$q = k_{\text{diff}} t^{1/2} \tag{9}$$

where K_{diff} is the intraparticle diffusion rate constant (mg/(g min$^{1/2}$)). If intraparticle diffusion occurs, then q vs. $t^{1/2}$ will be linear and if the plot passes through the origin, then the rate limiting process is only due to the intraparticle diffusion.

The first sharper portion is the instantaneous adsorption or external surface adsorption. As can be seen from Fig. 9, the linear lines did not pass through the origin indicating that the mechanism of MB removal on waste activated sludge is complex and both the surface adsorption as well as intraparticle diffusion contributes to the actual adsorption process [2]. And this deviation from the origin or near saturation might be due to the difference in the mass transfer rate in the initial and final stages of adsorption [39,11].

Equilibrium sorption capacities of some biosorbents for MB are shown in Table 3. One may observe

Table 3
Comparison of adsorption capacity on various biosorbents for MB

Type of biosorbents	Adsorption capacity (mg g^{-1})	Refs.
Dried activated sludge	243.9	Present study
Artocarpus camasi (Breadnut) peel	409.0	[29]
Breadnut core	369.0	[30]
Water hyacinth root	185.0	[43]
Artocarpus odoratissimus	184.6	[31]
Giant duckweed	119.0	[44]
Dried sewage sludge (Urban)	114.9	[22]
Dried *Pleurotus mutilus* biomass	111.0	[15]
Dried sewage sludge (agrofood industry)	86.957	[22]
Phoenix tree leaves	80.9	[28]
Modified sawdust	32.3	[45]

that the dried activated sludge reported the highest adsorption capacity with 243.9 mg/g than most other biomasses reported (Table 3). As consequence, the dried activated sludge may be used as low-cost, natural, and plentiful source for the removal of dyes as an alternative to more high-priced materials such as activated carbon.

4. Conclusion

In this study, the batch biosorption of MB—the most commonly used substance for dying cotton, wood, and silk—on *dried activated sludge* was investigated as a function of temperature, initial MB concentration, and pH. The results show first that the adsorption equilibrium was reached within 30 min, adsorption augmented as initial MB concentration which increased up to 50 mg/L; after that, the maximum adsorption was obtained at the initial solution pH of 7.5 with initial concentration 500 mg/L and at temperature of 30°C.

The equilibrium data obtained at three different temperatures fitted well with the Freundlich model and Redlich–Peterson. The suitability of the first- and second-order kinetic models for the sorption of dye onto biomass is also discussed. So, it was decided that the biosorption kinetics of MB to dried activated sludge obeyed the second-order adsorption kinetics. According to Weber–Morris model, the mechanism of MB removal on waste activated sludge is complex and both the surface adsorption as well as intraparticle diffusion contribute to the actual adsorption process.

In general, waste activated sludge represents a remarkable affinity and potential for the removal of MB from aqueous solutions. It may be concluded that the waste activated sludge may be used as low-cost plentiful source for the removal of dyes as an alternative to more high-priced materials such as activated carbon.

References

[1] A.N. Fernandes, C.A. Almeida, N.A. Debacher, M.M. Souza Sierra, Isotherm and thermodynamic data of adsorption of methylene blue from aqueous solution onto peat, J. Mol. Struct. 982 (2010) 62–65.

[2] A. Özer, G. Akkaya, M. Turabik, Biosorption of Acid Red 274 (AR 274) on Enteromorpha prolifera in a batch system, J. Hazard Mater. 126 (2005) 119–127.

[3] M. Rafatullah, O. Sulaiman, R. Hashim, A. Ahmad, Adsorption of methylene blue on low-cost adsorbents: A review, J. Hazard. Mater. 177 (2010) 70–80.

[4] T. Robinson, G. McMullan, R. Marchant, P. Nigam, Remediation of dyes in textiles effluent: A critical review on current treatment technologies with a proposed alternative, Bioresour. Technol. 77 (2001) 247–255.

[5] A. Mittal, L. Krishnan, V.K. Gupta, Use of waste materials—Bottom Ash and De-Oiled Soya, as potential adsorbents for the removal of Amaranth from aqueous solutions, J. Hazard. Mater. 117 (2005) 171–178.

[6] I.A.W. Tan, B.H. Hameed, A.L. Ahmad, Equilibrium and kinetic studies on basic dye adsorption by oil palm fibre activated carbon, Chem. Eng. J. 127 (2007) 111–119.

[7] G. Dursun, H. Çiçek, Y.A. Dursun, Adsorption of phenol from aqueous solution by using carbonised beet pulp, J. Hazard. Mater. 125 (2005) 175–182.

[8] W.S. Adriano, V. Veredas, C.C. Santana, L.R.B. Goncalves, Adsorption of amoxicillin on chitosan beads: Kinetics, equilibrium and validation of finite bath models, Biochem. Eng. J. 27 (2005) 132–137.

[9] H. Cherifi, S. Hanini, F. Bentahar, Biosorption of phenol by dried biomass, Desalin. Water Treat. 52 (2014) 1699–1704.

[10] B. Armagan, F. Toprak, Using pistachio shell for Remazol Red removal from aqueous solutions: Equilibrium, kinetics and thermodynamics, Desalin. Water Treat. 56 (2015) 136–145.

[11] H. Cherifi, S. Hanini, F. Bentahar, Kinetic studies on the adsorption of methylene blue onto vegetal fiber activated carbons, Appl. Surf. Sci. 282 (2013) 52–59.

[12] Z. Aksu, Biosorption of reactive dyes by dried activated sludge: Equilibrium and kinetic modeling, Biochem. Eng. J. 7 (2001) 79–84.

[13] N.S. Maurya, A.K. Mittal, P. Cornel, E. Rother, Biosorption of dyes using dead macro fungi: Effect of dye structure, ionic strength and pH, Bioresour. Technol. 97 (2006) 512–521.

[14] T-L. Hu, Removal of reactive dyes from aqueous solution by different bacterial genera, Water Sci. Technol. 34 (1996) 89–95.

[15] N. Yeddou-Mezenner, Kinetics and mechanism of dye biosorption onto an untreated antibiotic waste, Desalination 262 (2010) 251–259.

[16] N. Ertugay, Y.K. Bayhan, Biosorption of Cr(VI) from aqueous solutions by biomass of Agaricus bisporus, J. Hazard. Mater. 154 (2008) 432–439.

[17] S.T. Akar, A. Gorgulu, Z. Kaynak, B. Anilan, T. Akar, Biosorption of Reactive Blue 49 dye under batch and continuous mode using a mixed biosorbent of macro-fungus Agaricus bisporus and Thuja orientalis cones, Chem. Eng. J. 148 (2009) 26–34.

[18] Z. Aksu, T. Kutsal, S. Gün, N. Haciosmanoglu, M. Gholaminejad, Investigation of biosorption of Cu(II), Ni(II) and Cr(VI) ions to activated sludge bacteria, Environ. Technol. 12 (1991) 915–921.

[19] Z. Aksu, J. Yener, Investigation of the biosorption of phenol and monochlorinated phenols on the dried activated sludge, Process Biochem. 33 (1998) 649–655.

[20] M. Tsezos, J.P. Bell, Comparison of the biosorption and desorption of hazardous organic pollutants by live and dead biomass, Water Res. 23 (1989) 561–568.

[21] F. Deniz, Potential use of shell biomass (Juglans regia L.) for dye removal: Relationships between pseudo-second-order kinetic model parameters and biosorption efficiency, Desalin. Water Treat. 52 (2014) 219–226.

[22] M. Otero, F. Rozada, L.F. Calvo, A.I. García, A. Morán, Kinetic and equilibrium modelling of the methylene blue removal from solution by adsorbent materials produced from sewage sludges, Biochem. Eng. J. 15 (2003) 59–68.

[23] E.A. Ofomaja, Sorptive removal of Methylene blue from aqueous solution using palm kernel fibre: Effect of fibre dose, Biochem. Eng. J. 40 (2008) 8–18.

[24] A.H. Sulaymon, D.W. Abbood, A.H. Ali, A comparative adsorption/biosorption for the removal of phenol and lead onto granular activated carbon and dried anaerobic sludge, Desalin. Water Treat. 51 (2013) 2055–2067.

[25] Y.S. Ho, G. McKay, Sorption of dye from aqueous solution by peat, Chem. Eng. J. 70 (1998) 115–124.

[26] Z. Aksu, O. Tunç, Application of biosorption for penicillin G removal: Comparison with activated carbon, Process Biochem. 40 (2005) 831–847.

[27] G. Bayramoğlu, M. Yakup Arıca, Biosorption of benzidine based textile dyes "Direct Blue 1 and Direct Red 128" using native and heat-treated biomass of Trametes versicolor, J. Hazard. Mater. 143 (2007) 135–143.

[28] R. Han, W. Zou, W. Yu, S. Cheng, Y. Wang, J. Shi, Biosorption of methylene blue from aqueous solution by fallen phoenix tree's leaves, J. Hazard. Mater. 141 (2007) 156–162.

[29] L.B.L. Lim, N. Priyantha, D.T.B. Tennakoon, H.I. Chieng, M.K. Dahri, M. Suklueng, Breadnut peel as a highly effective low-cost biosorbent for methylene blue: Equilibrium, thermodynamic and kinetic studies, Arabian J. Chem. (in press), doi: 10.1016/j.arabjc.2013.12.018.

[30] L.B.L. Lim, N. Priyantha, H.I. Chieng, M.K. Dahri, Artocarpus camansi Blanco (Breadnut) core as low-cost adsorbent for the removal of methylene blue: Equilibrium, thermodynamics and kinetics studies, Desalin. Water Treat. 57(12) (2016) 56735685.

[31] L.B.L. Lim, N. Priyantha, D.T.B. Tennakoon, M.K. Dahri, H.I. Chieng, T. Zehra, M. Sukleung, Artocarpus odoratissumus skin as potential low-cost biosorbent for the removal of methylene blue and methyl violet 2B, Desalin. Water Treat. 53 (2015) 964–975.

[32] B.H. Hameed, Grass waste: A novel sorbent for the removal of basic dye from aqueous solution, J. Hazard. Mater. 166 (2009) 233–238.

[33] S.F. Montanher, E.A. Oliveira, M.C. Rollemberg, Removal of metal ions from aqueous solutions by sorption onto rice bran, J. Hazard. Mater. 117 (2005) 207–211.

[34] J.M. Smith, Chemical Engineering Kinetics, third ed., McGraw-Hill, Singapore, 1981.

[35] I. Langmuir, The adsorption of gases on plane surfaces of glass, mica and platinum, J. Am. Chem. Soc. 40 (1918) 1361–1403.

[36] H. Freundlich, Adsorption in solution, J. Phys. Chem. 40 (1906) 1361–1368.

[37] O. Redlich, D.L. Peterson, A useful adsorption isotherm, J. Phys. Chem. 63 (1959) 1024–1027.

[38] M. Autaa, B.H. Hameed, Chitosan–clay composite as highly effective and low-cost adsorbent for batch and fixed-bed adsorption of methylene blue, Chem. Eng. J. 237 (2014) 352–361.

[39] C. Namasivayam, D. Kavitha, Removal of Congo Red from water by adsorption onto activated carbon prepared from coir pith, an agricultural solid waste, Dyes Pigm. 54 (2002) 47–58.

[40] S. Langergren, Zur theorie der sogenannten adsorption geloester stoffe, Veternskapsakad Handlingar. 24 (1898) 1–39.

[41] W.J. Weber, J.C. Morris, Kinetics of adsorption on carbon from solution, J. Sanitary Eng. Div. Proc. Am. Soc. Civil Eng. 89 (1963) 31–60.

[42] K. Mohanty, D. Das, M.N. Biswas, Adsorption of phenol from aqueous solutions using activated carbons prepared from *Tectona grandis* sawdust by $ZnCl_2$ activation, Chem. Eng. J. 115 (2005) 121–131.

[43] K.S. Low, C.K. Lee, K.K. Tan, Biosorption of basic dyes by water hyacinth roots, Bioresour. Technol. 52 (1995) 79–83.

[44] P. Waranusantigul, P. Pokethitiyook, M. Kruatrachue, E.S. Upatham, Kinetics of basic dye (methylene blue) biosorption by giant duckweed (Spirodela polyrrhiza), Environ. Pollut. 125 (2003) 385–392.

[45] D.S. De, J.K. Basu, Adsorption of methylene blue onto a low cost adsorbent developed from sawdust, Indian J. Environ. Prot. 19 (1998) 416–421.