

Sorption model for the removal of M-Anisidine dye from solution using baker's yeast (*Saccharomyces cerevisiae*)

ABSTRACT

This study investigates the potential of baker's yeast in the removal of M – Anisidine dye in solution. The dependence of some experimental variables like pH, dye concentration, contact time, temperature and the adsorbent dosage on the sorption of M – Anisidine (dye) from aqueous solution by baker's yeast was investigated so as to evaluate the optimum condition for the adsorption process. The results obtained were further fitted into the Freundlich and Langmuir Models and also into adsorption kinetics of the Pseudo – First Order and Pseudo – Second Order so as to determine the adsorption rate and mechanism. Similarly, some thermodynamic quantities that affect the process were also determined. The results obtained showed that increase in contact time increased adsorption rate. Over 88.8% of the dye was removed at 100 minutes of contact time. The 30°C was obtained as the optimum temperature for the adsorption process. The adsorbent dosage decreased adsorption. Also, 2g of adsorbent dosage was recorded as optimum dye removal (86%). Increase in dye ion concentration increased adsorption tendency. S_f value of 0.629mg/g was obtained. K_f was 0.041 while R^2 was obtained as 0.999, which produced linear plot, indicating that pseudo – second order favourably described the sorption process. The ΔG , ΔS and ΔH , obtained, revealed that the process was not a spontaneous one.

Keywords: Adsorption, isotherms, sorption, kinetics, thermodynamics.

Introduction

The discharge of colored substances into the environment is a source of esthetic pollution of aquatic systems. Some types of azo dyes and their degradation products like aromatic amines are very carcinogenic (Mohammed, 2004). Proper treatment and management of the dye effluent is therefore an issue of concern. This has given rise to an intensive search for the best available technology that can be utilized for the clean-up of dye substances in aqueous systems (Yamin *et al.*,

2007). Various biological, chemical and physical techniques have been employed for the treatments of dye containing waste water. Some chemical oxidation by Fenton reagent ozone, UV plus H_2O_2 or NaOCl resulted in the aromatic ring cleavage and also generated chemical sludge or by products that may be more toxic (Robinson, 2000). Methods like aerobic biological treatment is known to be ineffective for dye removal, however, aerobic techniques like, bioremediation

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enables water soluble dyes to be decolourized (Carliell, 1996; Laowansiri, 2008).

Many studies have been carried out to evaluate the potentials of low – cost sorbents which include bentonite, silica, fly ash, maize cob, china clay, wood shaving and peat. However, only few of these listed could be used effectively to remove coloured materials (dyes) from the waste water (Singh and Srivastava, 2001; Safariket *et al.*, 2002; Mishra *et al.*, 2009).

In this present study, the potentials of baker's yeast *Saccharomyces Cerevisiae* in the sorption of M-anisidine dye from aqueous streams was investigated under varying conditions such as temperature, absorbent dosage, contact time and concentration. These were carried out so as to determine the appropriate condition that favours the dye removal process.

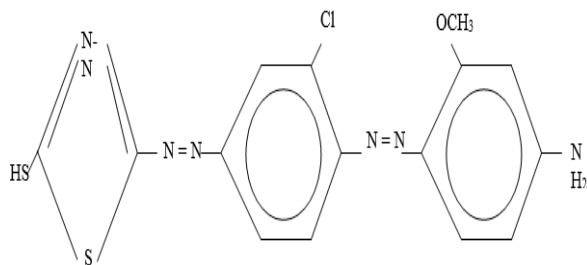


Figure 1: The typical structure of M – Anisidine
Source: (Otutu, 2011).

Materials and Methods

Preparation of M-anisidine dye solution

The dye used in this work was a standard commercial dye (made by willicom industries). The dye solution was prepared by dissolving 100g weighed dye in 1000cm³ of distilled water. This was used for all the parameters investigated.

Preparation of adsorbent

The adsorbent (baker's yeast) used in this work was obtained from a commercial market but produced by zinco Ltd. The adsorbent was

preserved in a plastic container without any other purification no activation.

Experimental procedures

The effect of contact time on the adsorption of M-anisidine dye

The effect of contact time on the removal of M-anisidine dye by the baker's yeast (adsorbent) was carried out in line with the previous works of Sumanjitet *et al.* (2007). A 2g of the baker yeast was weighed into five different conical flasks. The 10mg/L of the M-anisidine dye was prepared by dissolving 100mg/L dye stock into 50 mL of distilled water and measured out into five separate flasks. The flasks were then labeled for the different time intervals of 20, 40, 60, 80 and 100 minutes. Furthermore, the flasks were well covered and agitated at different time intervals. Towards the end of every contact time, the resulting suspensions were then filtered with the aid of a Whatman No. 45 filter paper and centrifuged. The dye ion contents were determined using DR 2010 spectrophotometer.

Variation of adsorbent dosage on the adsorption of M-anisidine dye

The variation of adsorbent dosage on the adsorption of M-anisidine dye ion by the baker's yeast was conducted following the recommendation of Sumanjitet *et al.* (2007). 2, 3, 4, 5 and 6g of the adsorbent were measured into five separate conical flasks. These conical flasks were labeled for the dosage differences (2, 3, 4, 5 and 6g). The five flasks were fully covered and then agitated for an interval of 20 minutes; thereafter the accompanying suspensions were then filtered using Whatman No. 45 filter paper before centrifuging. The M-anisidine dye ion concentrations were obtained using DR 2010 spectrophotometer.

The effect of m-anisidine dye ion concentration on adsorption process

The study on the influence of dye concentration on adsorption was conducted following the previous

study of Sumanjit *et al.* (2007). The different standard dye solutions (10, 20, 30, 40 and 50 mg/L) were prepared. 50ml of each of the M-anisidine dye solution was added to a weighed 2 ± 0.01 mg baker's yeast into five different flasks and then agitated for 20 minutes. Towards the end of the study time, the resulting suspensions were filtered by Whatman No. 45 filter paper and then centrifuged. The dyes ion contents were then determined by DR 2010 spectrophotometer scientific equipment.

Temperature dependence on adsorption

The influence of temperature on adsorption was carried out following the method described by Mishra *et al.* (2009). 2g of the baker's yeast was weighed into five distinct flasks and a 50ml of M-anisidine dye solution (10mg/L) was measured into the five conical flasks. The flasks were fully covered and further heated at the varying temperature (30, 40, 50, 60, and 70°C) by a thermostatic water bath, at 20 minutes time interval. Towards the end of the experiment, each of the conical flasks were brought out and then agitated for another 5 minutes. The resulting suspensions were then filtered with a Whatman No. 45 filter paper and centrifuged. The dye (M-anisidine) ion contents were obtained using the DR 2010 spectrophotometer.

Evaluation of data

Estimation of the degree of M-anisidine (dye) removed

The contents of the dye removed by the baker's yeast during the several batches of experiments were estimated by the mass balance equation expressed as follows:

$$q_e = (C_o - C_e) \frac{V}{M}$$

Where:

q_e = dye concentration on the baker's yeast (mg/g) at equilibrium.

C_e = concentration of dye in solution (mg/L) at equilibrium

C_o = initial M-anisidine dye concentration in the solution (mg/L)

V = volume of M-anisidine dye solution used (mL)

M = mass of baker's yeast used (g)

Kinetic treatment of sorption data

To investigate the adsorption comprehensively, the equations of the pseudo-first order and pseudo-second order mechanisms were used to treat the experimental data.

The linear nature of pseudo-first-order model is denoted by:

$$\ln(q_e - q_t) = \ln q_e - kt$$

Where q_e = The mass of M-anisidine dye adsorbed at equilibrium point (mg/g)

q_t = The mass of M-anisidine dye adsorbed at a given time t (mg/g)

K = equilibrium constant

The linear graph of $\ln(q_e - q_t)$ versus t confirms the model. However, the linear nature of pseudo-second-order model is given below as:

$$\frac{t}{q_t} = I + \frac{It}{h_o q_e}$$

Where:

q_t = Quantity M-anisidine ions on the baker's yeast surface (mg/g) at any given time interval.

q_e = Quantity of the dye ions removed at equilibrium (mg/g)

h_o = The initial adsorption capacity measured in mg/g min

The initial rate of adsorption (h_o) is described by the equation:

$$h_o = K_2 q_e^2$$

Note: K_2 represents the pseudo-second order rate constant (g/mg min)

Results and Discussion

Influence of contact time on adsorption

The influence of time on the adsorption of M – anisidine dye was investigated within the interval of 20 minutes and was further varied from 20 to 100 minutes. The observation is illustrated in Figure I below. From the plot, it was evident that when the contact time was increased from 20 to 100 minutes, the amount of dye ions adsorbed also increased from 85 – 89%.

Similarly, the Figure I below also showed that the amount of dye adsorbed increased with corresponding increase in time. The percentage of dye recovered was maximum at (88.8%) with contact time of observation at 100 minutes. This may be attributed to the fact that when the dye solution-adsorbent system is agitated at longer time, more of the atoms or molecules of the dye tends to accumulate on the surface of the adsorbate pending when equilibrium is obtained. Similar observations have been made by other researchers (Ndiokwere and Ukhun, 2006; Sumanjitet *al.*, 2007; Mishra *et al.*, 2009).

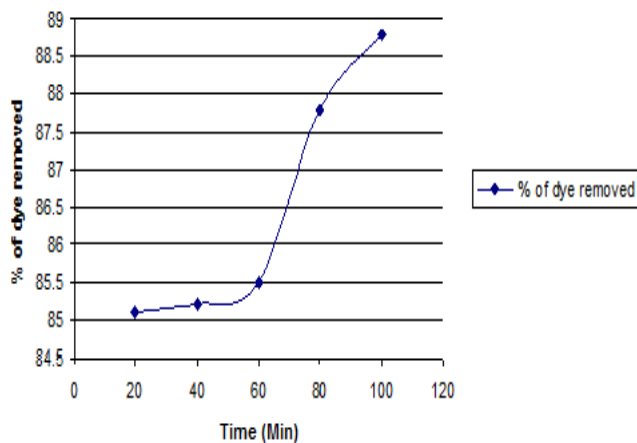


Figure 2: Effect of contact time on the adsorption of dye by baker's yeast adsorbent

The effect of temperature on the removal of M – anisidine dye

The results showed that the amount of M – anisidine dye adsorbed decreased from (77.0 – 75.3%) as represented in the Figure 2. However, this observation may be linked to the fact that stronger bonds are formed at lower temperature, indicating that the adsorption process was exothermic.

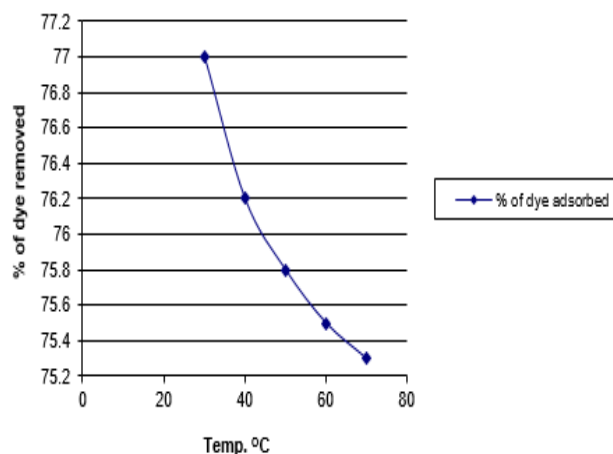


Figure 3: Effect of temperature on the removal of M – Anisidine dye

The effects of adsorbent dosage on the removal of M – anisidine dye from aqueous solution

The result of the effects of adsorbent (baker's yeast) dosage or the adsorption of M-anisidine dye is represented in Figure 3. The results showed that the amount of dye adsorbed decreased from 86.0 – 84.2% as adsorbent dosage was varied from 2-6 g. It was also observed that the maximum percentage of dye removed was 86.0% at 2g of adsorbent dosage.

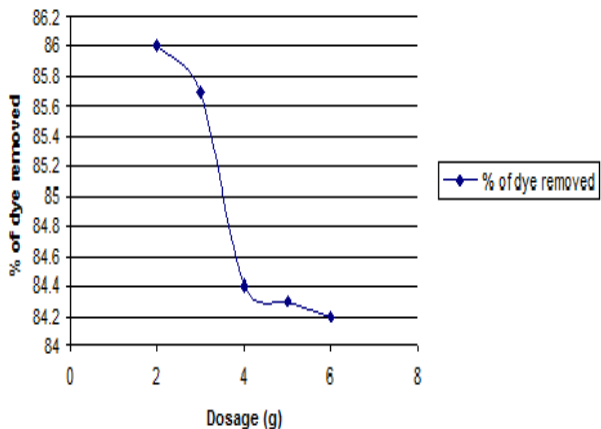


Figure 4: Effect of adsorbent dosage on the removal of M – anisidine dye

Effect of dye ion concentration on the removal of M – anisidine dye by baker’s yeast

The result of the removal of dye by baker’s yeast at various initial dye ion concentrations is represented in Figure 4. The actual percent removal of the M – anisidine dye was observed to increase with increase in the initial dye concentration, (Figure 4). The observation could be linked to the fact that when the dye concentration is increasing, more of the dyes are made available for adsorption on the baker’s yeast. In other words, this observation could be linked to the effect of concentration gradient which is the principal driving force for most adsorption process (Mishra *et al.*, 2009). Similarly, this trend has been observed by other researchers (Sumanjitet *al.*, 2007; Hajiraet *al.*, 2008; Mishra *et al.*, 2009).

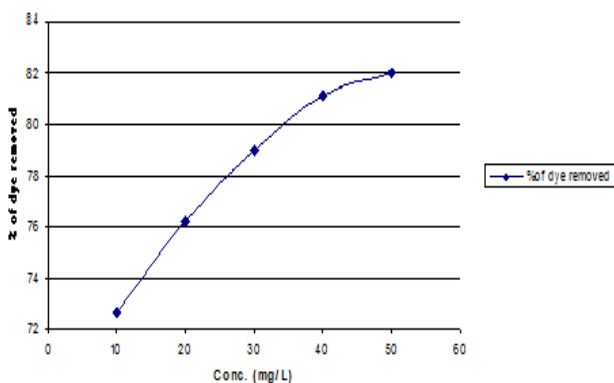


Figure 5: Effect of concentration on dye removal

Langmuir isotherm investigation on the adsorption process

Langmuir isotherm model was adopted for the evaluation of the maximum adsorption capacity which describes completely the monolayer coverage on the biomass surface. The graphs of specific adsorption (ce/qe) to the equilibrium concentration (ce) are represented in Figure 5. The linear isotherm parameters qm_kL and the coefficient of determinations R^2 are shown in Table 1.

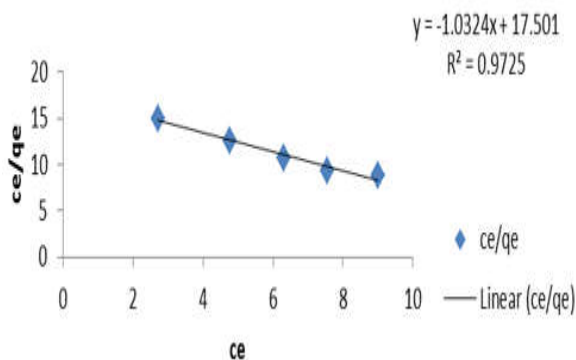


Figure 6: Langmuir equilibrium

Table 1: Linear isotherm Parameters

Dye ion	qm (mg ⁻¹)	K _L (L _g ⁻¹)	R ²	S _F
M-anisidine	-0.969	0.059	0.97	0.629

The coefficient of determination (R^2) value suggested that the Langmuir isotherm provides a good model to describe the adsorption process. The Langmuir isotherm model is described in terms of a dimensionless constant referred to as the separation factor, S_f . The separation factor S_f is represented by the following relationship.

$$S_f = \frac{1}{1 + K_L C_0}$$

Where: K_L = Langmuir isotherm constant C_0 = initial dye ion concentration of 10 mg/L. The

parameter determines the shape of the isotherm as shown below:

$S_f = 1$ linear isotherm

$S_f = 0$ irreversible isotherm

$0 < S_f < 1$ favorable isotherm

$S_f > 1$ unfavorable isotherm

From the data shown in Table 1, the separation parameter of the dye is less than one indicating that baker's yeast is an excellent adsorbent for M-anisidine dye.

Freundlich isotherm evaluation of the sorption process

In this investigation, the Freundlich model was employed to estimate the adsorption intensity of the adsorbate on the baker's yeast surface. The linear plot of the Freundlich isotherms for the adsorption of the M – anisidine dye ion onto baker's yeast biomass is presented in Figure 6. Critical examination of the graph revealed that the model is also appropriate to describe the adsorption process under investigation. Table 2 also showed that the linear Freundlich sorption isotherm constant and the coefficient of determination (R^2). The R^2 value obtained in this study, the Freundlich isotherm seems to produce a reasonable model for the interpretation of the adsorption process under investigation. The linear form of the Freundlich isotherm produced a reasonable model for the adsorption of baker's yeast.

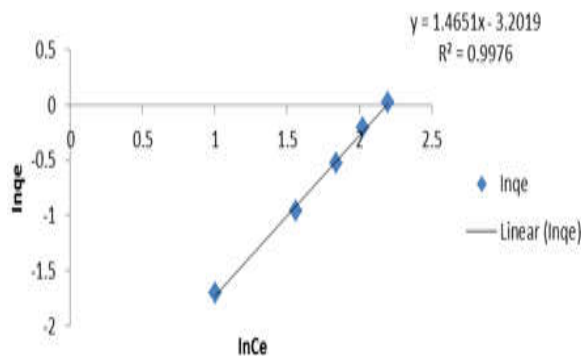


Figure 7: Freundlich Equilibrium Isotherm Model

Table 2: Freundlich Equilibrium Isotherm

Dye ion	1/n	K_F	R^2
M-anisidine	1.465	0.041	0.997

Adsorption kinetics

Pseudo – First Order Kinetics

The kinetics of sorption is one of the most vital quantities utilized in evaluating the rate at which adsorption occurs for a chosen system. The graph of $\ln(q_e - q_t)$ against t as shown in Figure 7, produced the pseudo- first order kinetics. From the flow, it is evident that the relationship between the dye ion diffusivity, $\ln(q_e - q_t)$ and the time is linear, therefore confirming the model. Table 3 presents the value of the coefficient of determination R^2 . The result of the R^2 value obtained indicated that pseudo-first order model provide a fairly good interpretation for the adsorption of M-anisidine on baker's yeast biomass.

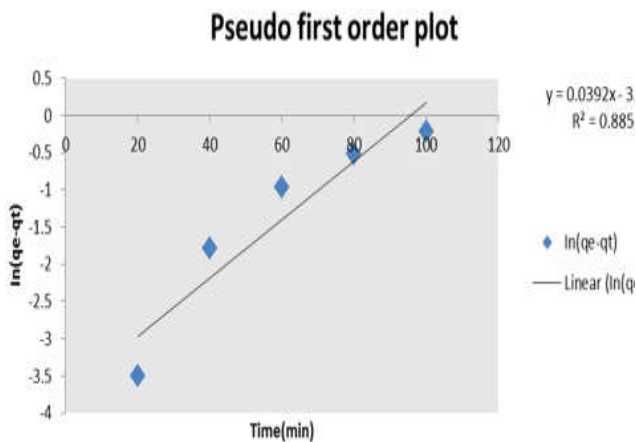


Figure 8: Pseudo First Order to evaluate the behaviour of the sorption process

Table 3: values of pseudo-first order kinetic parameters

Dye ion	K ₁	q _e (mgg ⁻¹)	R ²
M-anisidine	0.0392	0.024	0.885

While confirming suitability and the linearity of the Pseudo-first order model, this finding was compared with other works. It was reported that similar observation has been reported by Gunusamy (2002) for the adsorption of basic dye on the strongly chelating polymer.

Pseudo - Second Order Model

A graph of t/qt against t as presented in figure 8 produced the pseudo-second order kinetics. From the flow, it was observed that the relationship between t/qt and t is linear which confirms the model. Similarly, the pseudo-second order rate constant (K₂), the initial sorption rate (h₀), the coefficient of determination (R²) and the equilibrium adsorption capacity (q_e) are shown in table 4. On the basis of the value of coefficient of determination (R²), it was concluded that the pseudo-second order model gave a better description for the adsorption process relative to the pseudo-first order model. Similar observation has been recorded by Che (2004) while studying

the adsorption of acid dye, direct dye and basic blue using activated carbon and clay-based adsorbent.

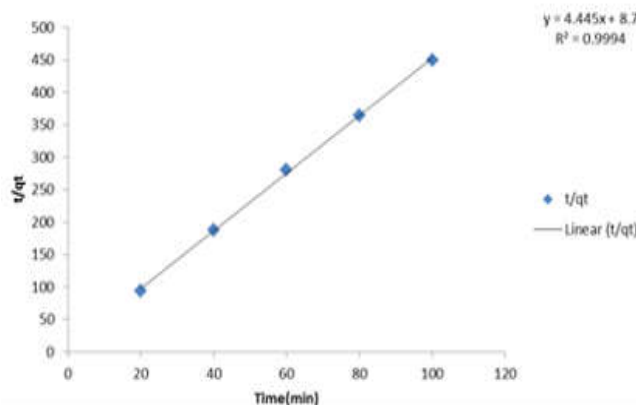


Figure 9: Pseudo Second Order Plot to evaluate the behaviour of the sorption process.

Table 4: Values of Pseudo-Second Order Kinetic Parameters

Dye ion	K ₂	q _e	h ₀	R ²
M-anisidine	0.53	0.225	0.12	0.999

Thermodynamic parameters

The values of the thermodynamic quantities like enthalpy (Δ^oH), free energy (Δ^oG), and entropy (Δ^oS) of the adsorption process was calculated from the Langmuir constant K using the equations presented below:

$$lnk = \frac{\Delta S}{R} - \frac{\Delta H}{RT}$$

$$\Delta G = \Delta H - T\Delta S$$

$$\Delta G = -RT lnk_L$$

The value of ΔS^o and ΔH^o were calculated from the slope of the graph and intercept of the linear variation of lnk with the reciprocal of temperature (1/T) are shown in the Table 5 and Figure 9.

The table and the values of ΔG^o obtained at different temperatures are positive, which shows

that the process is not spontaneous. Similarly, the values of enthalpy obtained were positive, indicating the endothermic nature of the adsorption process. The entropy values were positive. Similar observation has been recorded in respect to the endothermic nature of adsorption process by Hajiraet *al.* (2008) for the removal of basic dye methylene blue by bio-adsorbents ulvalactuca and sargassum.

Table 5: Thermodynamic parameters of the adsorption process

Temp. (°C)	ΔH° (KJ/mole)	ΔG° (KJ/mole)	ΔS° (J/K)
30	1263.42	1187.22	0.254
40	1263.42	1183.92	0.254
50	1263.42	1181.38	0.254
60	1263.42	1178.84	0.254
70	1263.42	1176.29	0.254

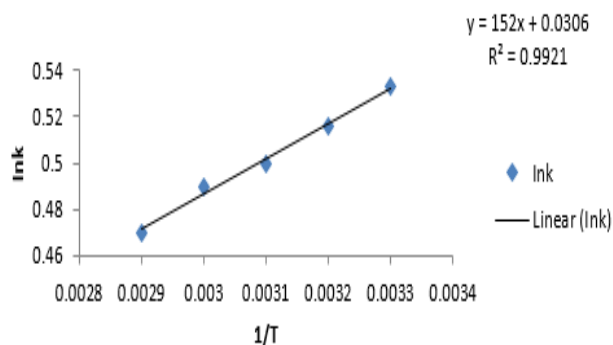


Figure 10: Plot of Ink against 1/T

Conclusion

The effects of M-anisidine dye ion concentration on adsorption capacities indicated that the baker's yeast (*Saccharomyces cerevisiae*) biomass really adsorbed the dye ions from aqueous solution, with an increase in the adsorption capacity of the

biomass and with increased dye ion concentration. The overall percentage removal of dye ions from aqueous solutions also increased with corresponding increase in the initial dye ion concentration. It was also observed, that increase in adsorbent dosage also increased the actual percent dye removal. Similarly, contact time increase also increased the amount of dye ion adsorbed and the actual percent of dye removal. The equilibrium data actually fitted the Langmuir and the Freundlich isotherms adequately. The separation factor of the equilibrium parameter obtained from Langmuir isotherm showed that the adsorption of the M-anisidine dye ions onto the baker's yeast biomass was indeed favourable.

The kinetic quantities clearly established that the pseudo-second order model provide a more appropriate description of the adsorption process. Consequently, the thermodynamic variables showed that the adsorption process was endothermic. The data obtained from this study revealed that baker's yeast biomass was a useful adsorbent for removing coloured substances from wastewater and may also serve as good alternative adsorbent to other conventional, means. *Saccharomyces cerevisiae* is not only inexpensive and readily available, but it also has the potential for dye removal from wastewaters or contaminated waters.

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