

## Performance, kinetics and equilibrium in biosorption of anionic dye Acid Red 14 by the waste biomass of *Saccharomyces cerevisiae* as a low-cost biosorbent

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**Abstract:** Equilibrium, kinetics and thermodynamic studies on the removal of Acid Red 14 (AR14) anionic dye by biosorption onto dried waste biomass of *Saccharomyces cerevisiae* have been investigated. In batch experiments, the parameters studied included the effect of the dye concentration, temperature, contact time, adsorbent dosage, agitation speed, pH, and salt concentration. The pseudo-first-order and pseudo-second-order kinetic models were applied to the experimental kinetic data. High correlation coefficients with low standard deviations favor the pseudo-second-order model for the present systems. The biosorption process was found to be chemical adsorption and it has an endothermic nature. The entropy ( $\Delta S^\circ$ ), enthalpy ( $\Delta H^\circ$ ), and activation energy ( $E_a$ ) were estimated as 49.51 J/mol K, 16.36 kJ/mol, and 10.44 kJ/mol, respectively. The positive values of standard Gibbs free energy change ( $\Delta G^\circ$ ) indicate feasible and nonspontaneous adsorption of AR14 on *S. cerevisiae*. Langmuir, Freundlich, Temkin, and Halsey adsorption models were used for the mathematical description of the batch biosorption equilibrium data and model constants were evaluated. The Langmuir model gives the best agreement with obtained experimental isotherms data. A design for a batch adsorption unit using data from isotherm studies was made.

**Key words:** Biosorption, Acid Red 14, *Saccharomyces cerevisiae*, kinetics, thermodynamics, isotherm models, process design

### 1. Introduction

Synthetic dyes are extensively used in the textile, paper, leather, and other industries. Dyes include several structural varieties such as acidic, reactive, basic, disperse, azo, diazo, anthraquinone-based and metal complex dyes (Padmesh et al., 2005).

Even a small amount of dye in water (10–50 mg/L) affects the aesthetic value, water transparency, and gas solubility in water bodies (Gulnaz et al., 2004). In addition to their visual effects and their adverse impacts in terms of chemical oxygen demand, many synthetic dyes are toxic, mutagenic, and carcinogenic. Moreover, they affect human beings by damaging their liver, kidneys, and central nervous and reproductive systems (Kiran et al., 2006; Ehrampoush et al., 2011).

Removal of dyes from wastewater is still of major environmental concern because they are difficult to remove by conventional wastewater treatment systems since they are designed to be resistant to many chemicals, oxidizing agents, light, and heat and are biologically nondegradable (Kargi and Ozmihci, 2004). Existing colored wastewater treatment methods involve combination of physical and chemical processes including adsorption,

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precipitation, sedimentation, ultrafiltration, reverse osmosis, flotation, color irradiation, oxidation, ozonation, and coagulation. However, the use of these technologies in color removal are restricted due to technical and economic reasons ranging from little applicability to a wide range of dye wastewaters to high operating costs (Kiran et al., 2006; Farah et al., 2007). This led to a search directed at developing low-cost and locally available adsorbing materials with maximum adsorption capacity.

The use of biomaterials as biosorbents for wastewater treatment has been found as a potential and cost-effective alternate to the conventional treatment methods. A wide variety of dead bacteria, yeast, fungi and algae have been used for the purpose of decolorizing dye-containing wastewaters, owing to their special surface properties, high selectivity, cost-effectiveness, abundant availability, and environmental acceptability (Aksu, 2005; Padmesh et al., 2005; Kiran et al., 2006; Won et al., 2006; Farah and El-Gendy, 2007; Wang et al., 2008; Yu et al., 2009; Yu et al., 2010).

In Egypt, the ability of *Saccharomyces cerevisiae* as an inexpensive, safe, easily grown, high-yielding, readily and locally available biosorbent for heavy metals has been recognized (Zaied et al., 2008; Gad et al., 2010; Hamza et al., 2010; Abd-Elsalam, 2011; Abdelaty et al., 2011). However, there have been few Egyptian studies on biosorption of dyes by *S. cerevisiae* (Farah et al., 2007; Farah and El-Gendy, 2007).

For industrial waste management in Egypt, the objective of this research was to evaluate the feasibility of dried waste biomass of *S. cerevisiae* taken from solid state fermentation processing of bagasse for production of bioethanol, for Acid Red 14 (AR14) dye removal from aqueous solution and determination of adsorption equilibrium and kinetics.

## 2. Materials and methods

### 2.1. Biosorbent

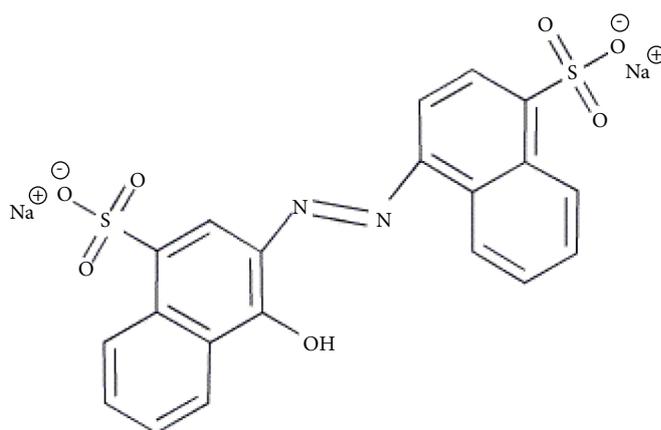
Spent biomass of *S. cerevisiae* taken from the solid state fermentation process of bagasse for production of bioethanol, undertaken in the Petroleum Biotechnology Laboratory of the Egyptian Petroleum Research Institute, was used in this study.

The biomass was washed with distilled water many times and dried at 60 °C for 24 h. The dried yeast biomass was ground in a mortar sieved to constant sizes (0.315–0.4 mm) and stored for further use.

### 2.2. Adsorbate

The adsorbate AR14 dye was purchased from Sigma-Aldrich. It is used for dyeing all natural fibers like cotton, silk, and wool, as well as synthetics like polyesters, acrylic, and rayon. It is also used for leather and plastics, and in making paints, coating and inks [C.I. number: 14720, C.I. name: Acid Red B, chemical formula:  $C_{20}H_{12}N_2Na_2O_7S_2$ , molecular weight: 502.42, formal chemical name (IUPAC): disodium(E)-4-hydroxy-3-((4-sulfonatophthalen-1-yl)diazonyl)naphthalene-1-sulfonate, commercial name: carmoisine or azorubine; it is a synthetic acid dye containing NN and CC chromophore groups; pyrazolone dye]. The structure of AR14 is given in Figure 1.

An accurately weighed quantity of AR14 was dissolved in distilled water to prepare stock solution of 4000 mg/L. Experimental solutions of the desired concentrations were prepared by dilution of stock solution with distilled water.



**Figure 1.** Chemical structure of Acid Red 14 dye.

### 2.3. Batch adsorption experiments

Each batch adsorption experiment was conducted by contacting 50 mL of a known concentration of AR14 dye (adsorbate) with an appropriate amount of dried biomass of *S. cerevisiae* (adsorbent) in a 250-mL Erlenmeyer flask closed with Parafilm M to prevent evaporative loss and placed in an orbital shaking incubator set at the required agitation speed at different temperatures (Table 1). Adsorbent was separated from the solution at predetermined time intervals by centrifugation at 4000 rpm for 15 min. The absorbance of the supernatant solution at 519 nm was measured to determine the residual dye concentration and to calculate the percentage of dye removal. Negative controls (with no sorbent) were carried out to ensure that sorption was by dried biomass only and that any sorption effect of dye onto the wall of the conical flasks could be ruled out. The dye concentration of the control was used as the initial concentration for calculating the quantity of dye removed from the dye solution. Adsorption capacity and percentage of dye removal were determined at prescribed time intervals with different environmental parameters. The initial pH of the solution was adjusted using 0.1 M HCl or 10% NaOH. Table 1 illustrates all the process factors used for adsorption experiments. All experiments were carried out in duplicate.

**Table 1.** Different process conditions used for biosorption of AR14.

Process factors	Other conditions
Different dye concentrations and contact times (60–520 mg/L)	Temperature: 25 °C; biomass dosage: 0.4% w/v; agitation: 150 rpm; initial pH: 7; different contact time intervals (0–300 min)
Different temperatures and contact times (15, 25, 35, and 45 °C)	Biomass dosage: 0.4% w/v; agitation: 150 rpm; initial dye concentration: 120 mg/L; initial pH: 7; different contact time intervals (0–300 min)
Different biomass dosages (0.2, 0.4, 0.6, and 0.8 % w/v)	Temperature: 25 °C; agitation: 150 rpm; initial dye concentration: 120 mg/L; initial pH: 7; contact time: 300 min
Agitation speed (50, 100, 150, and 200 rpm)	Temperature: 25 °C; biomass dosage: 0.4% w/v; initial dye concentration: 120 mg/L; initial pH: 7; contact time: 300 min
Initial pH (3, 5, 7, 9, 11)	Temperature: 25 °C; agitation: 150 rpm; biomass dosage: 0.4% w/v; initial dye concentration: 120 mg/L; contact time: 300 min
Effect of ionic strength (0, 0.05, 0.1, 0.2, 0.3 M NaCl)	Temperature: 25 °C; biomass dosage: 0.4% w/v; agitation: 150 rpm; initial dye concentration: 120 mg/L; initial pH: 7; contact time: 300 min
Isotherm studies	Temperature: 25 °C; biomass dosage: 0.4% w/v; agitation: 150 rpm; initial pH: 7; contact time: 300 min; different dye concentrations (30–4000 mg/L)

Amount of dye adsorbed,  $q_e$  (mg/g) was calculated as follows:

$$q_e = \frac{(C_o - C_e)V}{M} \tag{1}$$

where  $C_o$  and  $C_e$  are the initial and final concentrations (mg/L), respectively, and  $M$  is the adsorbent dosage (g) and  $V$  is the volume of solution (L).

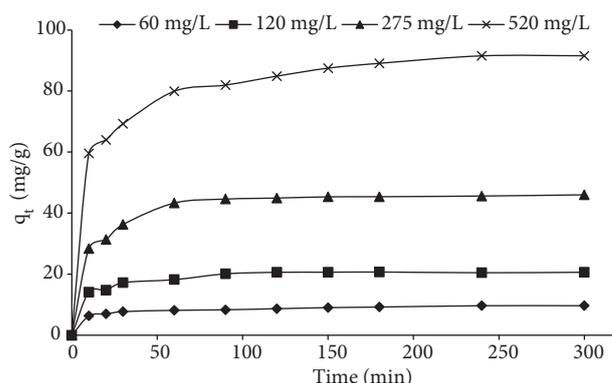
### 2.4. Analysis of dye

The  $\lambda_{max}$  of AR14 was determined on a JASCO UV/Vis/NIR spectrophotometer model V-570. The observed  $\lambda_{max}$  was found to be 519 nm. The standard curve for different concentrations of the dye solution was established.

## 3. Results and discussion

### 3.1. Effect of initial dye concentration and contact time

Biosorption of AR14 at different initial concentrations ( $C_o$  60, 120, 275, and 520 mg/L) was studied as a function of contact time (Figure 2). It was noticed that the adsorption curves (Figure 2) were smooth and continuous leading to saturation at various concentrations of AR14 on the outer interface of the biomass. This shows the possibility of mono-layer coverage of AR14 on the outer interface of the biosorbent (Dogan et al., 2004; Farah et al., 2007).



**Figure 2.** Effect of initial dye concentration on biosorption process.

The process was found to be initially very rapid, with about 45% of the total amount of dye removed within approximately 10 min; thereafter the dye uptake process tended to proceed at a slow rate, recording percentage removal of about 55% after 30 min. The dye removal then increased with time, until equilibrium was attained after nearly 60–150 min from the increase of the initial dye concentration. Therefore, the equilibrium time was set conservatively at 300 min for further experiments.

The initial rapid uptake of the dye indicates that the sorption process could be ionic in nature where the acidic (anionic) dye molecules bind to the various positively charged organic functional groups present on the surface of the biomass (Gulnaz et al., 2004). The rapid kinetics has significant practical importance as it will facilitate smaller reactor volumes ensuring efficiency and economy (Aksu, 2001).

The percentage of dye removal increases with increase in initial dye concentration, recording  $\approx$  64%, 70%, and 75%, at  $C_o$  60, 120, and 275 mg/L, respectively after 300 min. Percentage removal then decreases

with further increase in the initial dye concentration, recording  $\approx 70\%$  removal at  $C_o$  520 mg/L after 300 min. Similar observations were reported by Padmesh et al. (2006) and Jaikumar and Ramamurthi (2009). At lower dye concentrations the ratio of sorbet concentration to biosorbent sites is high, which causes an increase in color removal; subsequently the fractional sorption becomes independent of initial concentration. At higher dye concentration the removal decreases due to the saturation of the sorption sites on the biosorbent. However, the actual amounts of dye adsorbed (mg/g) increase with increasing of the initial dye concentration (Figure 2). This may be due to the increase in the driving force of the concentration gradient for mass transfer with the increase in initial dye concentration. Similar observations were reported by other investigators (Aksu, 2003; Gulnaz et al., 2004; Farah et al., 2007; Farah and El-Gendy, 2007; Ehrampoush, 2011). According to Mane et al. (2007), as the adsorption process proceeds, the driving force decreases with time.

### 3.2. Effect of temperature on the adsorption process

Biosorption of AR14 at different temperatures (15, 25, 35, and 45 °C) was studied as a function of contact time (Figure 3). The increase of temperature led to slight increase in dye uptake, recording percentage removals of  $\approx 61\%$ , 70%, 73%, and 74%, respectively. This indicates that the adsorption of the AR14 by waste dried biomass of *S. cerevisiae* is endothermic in nature. When the temperature was increased, the mobility of the dye molecules increased and the retarding forces on the diffusing ions decreased, thereby increasing the sorption capacity of the adsorbent. The enhancement of adsorption capacity of the adsorbent at high temperatures may be also attributed to the enlargement of pore size and activation of the adsorbent surface (Ho and McKay, 2003; Farah et al., 2007; El-Aila et al., 2011). The slight increase of the maximum adsorption capacity from  $\approx 18$  to 23 mg/g with increase in temperature from 15 °C to 45 °C indicates that the temperature has little effect on the adsorption process.

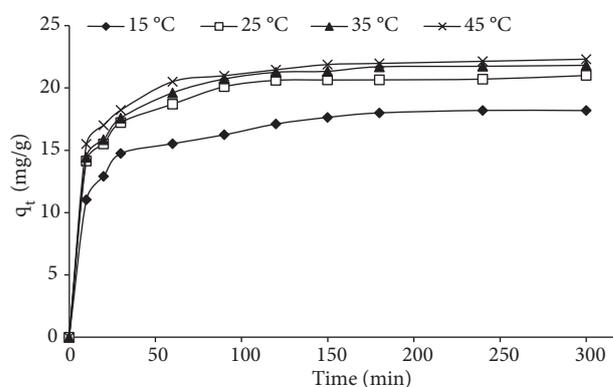


Figure 3. Effect of temperature on biosorption process.

Thermodynamic equilibrium parameters such as change in Gibbs free energy ( $\Delta G^\circ$ , J/mol), enthalpy ( $\Delta H^\circ$ , J/mol), and entropy ( $\Delta S^\circ$ , J/mol K) can be evaluated by:

$$\Delta G^\circ = -RT \ln K_c \quad (2)$$

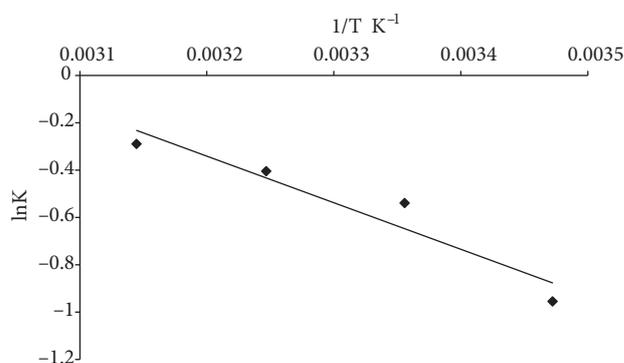
Here, R is the universal gas constant (8.314 J/mol K) and T is the absolute temperature (K). The apparent equilibrium constant  $K_c$  (L/g) of the adsorption is defined as follows.

$$K_c = \frac{q_e}{C_e} \quad (3)$$

$$\ln K_c = -\frac{\Delta G^\circ}{RT} = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (4)$$

The  $\Delta H^\circ$  and  $\Delta S^\circ$  values can be obtained from the slope and intercept of the van't Hoff plots of  $\ln K_c$  versus  $1/T$  (El-Aila et al., 2011; Piccin et al., 2011).

The van't Hoff plot shown in Figure 4 was considered satisfactory due to the coefficient of correlation value,  $R^2 = 0.96$ . Positive values of  $\Delta G^\circ$  (2.29, 1.34, 1.04, and 0.77 kJ/mol) indicated the nonspontaneous nature of adsorption for AR14 at 15, 25, 35, and 45 °C, respectively. The decrease of  $\Delta G^\circ$  with increasing temperatures indicates that a better adsorption is actually obtained at higher temperatures. The positive value of  $\Delta H^\circ$  (16.36 kJ/mol) shows the endothermic nature of the adsorption, which is an indication of the existence of a strong interaction between biomass and AR14 (Shahryari et al., 2010). The positive enthalpy of adsorption obtained indicates chemical adsorption. This suggests that the chemical bonds between the yeast surface and the dye molecules are strong enough and the dye molecules cannot be easily desorbed by physical means such as simple shaking or heating (Farah et al., 2007). The positive value of  $\Delta S^\circ$  (49.51 J/mol K) shows the increased randomness at the solid/solution interface during the adsorption of AR14 on biomass, reflecting the affinity of waste dried biomass of *S. cerevisiae* for AR14 (Shahryari et al., 2010; Salman et al., 2011).



**Figure 4.** van't Hoff plot of  $\ln K_c$  versus  $1/T$ .

### 3.3. Effect of adsorbent dosage on the adsorption process

The effect of biosorbent dosage on the removal of AR14 is shown in Figure 5a. It can be seen that dye removal increased by up to 0.4% (w/v), recording  $\approx 70\%$  removal, and then slightly decreased at higher adsorbent dosages, recording  $\approx 68\%$  removal at an adsorbent dosage of 0.8% (w/v). Higher percentage of adsorption with the increase of adsorbent concentration up to 0.4 % (w/v) may be due to the availability of more surface area, after which equilibrium is achieved. However, the biosorption capacity (mg/g) decreased with increase in biosorbent dosage, due to the agglomeration of the adsorbent particles. Similar observations were reported by Farah and El-Gendy (2007) and Jaikumar and Ramamurthi (2009).

### 3.4. Effect of agitation speed on the adsorption process

Agitation is an important parameter in adsorption phenomena influencing the distribution of the solute in the bulk solution and formation of the external boundary film. The effect of agitation speed on the removal of AR14 is shown in Figure 5b. Dye uptake slightly increased from  $\approx 17.53$  mg/g at 50 rpm, with removal of  $\approx 58\%$  to 21 mg/g with dye removal of  $\approx 70\%$  at 150 rpm. It then remained nearly constant at higher agitation speeds,

where the dye uptake was  $\approx 20$  mg/g with dye removal of  $\approx 67\%$  at an agitation speed of 200 rpm. Increasing the speed of agitation causes the thickness of the adsorbent boundary layer to decrease, which decreases the resistance for transfer of AR14 to the surface of adsorbent. The observed relatively lower dye uptake at lower agitation speeds (50 rpm) might be due to the agglomeration of biomass particles (Asma et al., 2006). These results also indicate that the contact between biomass and dye solution is more effective at a moderate agitation speed (150 rpm), and this speed was thus selected for further experiments. It can be also assumed that the film diffusion does not dominantly control the overall adsorption process (Kundu and Gupta, 2006).

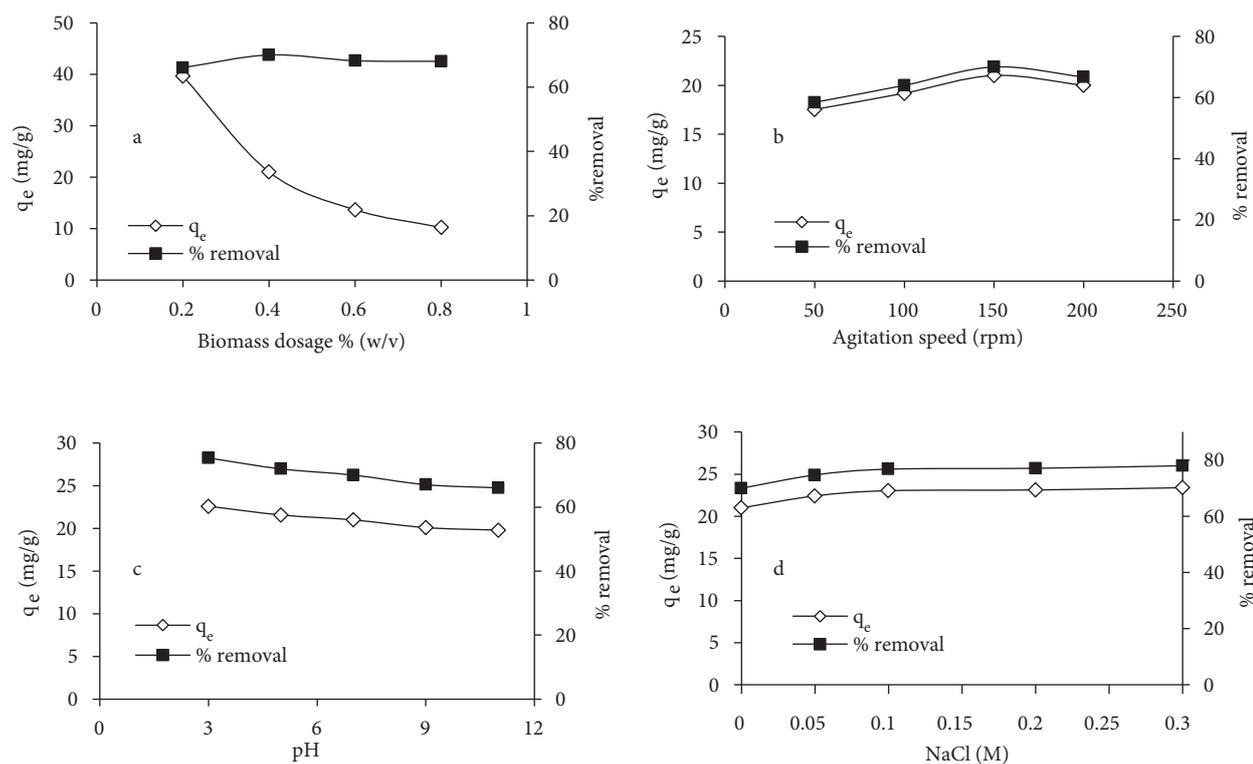


Figure 5. Effect of different parameters on biosorption of AR14.

### 3.5. Effect of initial pH on the adsorption process

The pH value of the dye solution is an important controlling parameter in the adsorption process and particularly on the biosorption capacity, and the initial pH value of the solution has more influence than the final pH, which influences both the cell surface dye binding sites and the dye chemistry in water (Padmesh et al., 2005; Wang et al., 2008). The variation in the biosorption of AR14 was studied in the range of pH 3–11, and the results are shown in Figure 5c. The uptake slightly decreased in a range from 22.6 to 19.8 mg/g with an increase in pH from 3 to 11, indicating that pH has little effect on the biosorption of AR14. This may give more potential to dried waste biomass of *S. cerevisiae* in practical applications. The maximum percentage removal of  $\approx 75\%$  occurred at pH 3, decreasing thereafter and reaching 66% at pH 11. Two sulfonate groups of AR14 are easily dissociated and have negative charges in the aquatic environment. The surface of *S. cerevisiae* has 3 functional groups: carboxyl, phosphonate, and amine. Therefore, the negative sites of biomass such as the carboxyl and phosphonate groups do not favor the biosorption of dye anions due to electrostatic repulsion, whereas the amine group ( $-\text{NH}_2$ ) mainly found in protein molecules in the biomass can be protonated as a form of  $-\text{NH}_3^+$  (Won

et al., 2006). Such positively charged groups are likely to be the binding sites for negatively charged AR14. In general, acidic dye uptake is higher in acidic solutions than in neutral and alkaline conditions (Jaikumar and Ramamurthi, 2009).

### 3.6. Effect of ionic strength on the adsorption process

Dyes are applied to fabric in a high salt concentration in order to lower the dye solubility. NaCl is mainly used as a salt to enhance the bath dye exhaustion. Therefore, unfixed dye in wastewater is accompanied by a high concentration of salts that are likely to interfere with dye biosorption (Won et al., 2006). It is important to investigate the effect of these ions on the adsorption process. In order to investigate the effect of ionic strength, NaCl concentrations ranging from 0 to 0.3 M were used. The results illustrated in Figure 5d reveal that the effect of the salt concentration on the dye uptake was negligible, ranging from 21 to 23.4 mg/g while the percentage removal increased from 70% to 78% at NaCl concentrations of 0 and 0.3 M, respectively. This indicates that Cl ions do not compete with the sulfonate group of AR14 molecules to bind the biomass. In addition, it can be noted that an elevated ionic strength with NaCl does not electrostatically interfere with the binding of AR14 to the biomass significantly, confirming that the biomass has good selectivity to AR14. From a practical point of view, this result implies that the waste biomass of *S. cerevisiae* can be used for the removal of AR14 from salt-containing wastewaters.

### 3.7. Adsorption kinetics

Adsorption is a physiochemical process that involves the mass transfer of a solute (adsorbate) from the liquid phase to the adsorbent surface. A study of kinetics of adsorption is desirable as it provides information about the mechanism of adsorption, which is important for efficiency of the process. The applicability of the pseudo-first-order and pseudo-second-order model was tested for the adsorption of different initial dye concentrations onto waste dried biomass of *S. cerevisiae* and was also tested on the effect of temperature at initial dye concentration of 120 mg/L while all other parameters were fixed: pH 7, sorbent dosage 0.4% wt, 150 rpm, and 0 M NaCl.

The best fit model was selected based on the linear regression correlation coefficient,  $R^2$  values, and the standard deviation (S.D.), using the following equation:

$$SD = \sqrt{\frac{\sum \left[ \frac{q_{e,exp} - q_{e,cal}}{q_{e,exp}} \right]^2}{(n - 1)}} \quad (5)$$

where  $q_{e,exp}$  and  $q_{e,cal}$  (mg/g) are the experimental and theoretical adsorbed amounts at equilibrium, respectively, while  $n$  is the number of data points.

The pseudo-first-order reaction equation of Lagergren (1898) is widely used for the adsorption of liquid/solid systems on the basis of solid capacity. Its linear form is generally expressed as follows:

$$\log(q_e - q_t) = \log q_e - \frac{K_1}{2.303} t \quad (6)$$

where  $q_e$  (mg/g) and  $q_t$  (mg/g) are the adsorbed amount at equilibrium and time  $t$  (min), respectively.  $K_1$  ( $\text{min}^{-1}$ ) is the rate constant in the pseudo-first-order adsorption process. The constants were determined experimentally by the plotting of  $\log(q_e - q_t)$  versus  $t$  and are listed in Table 2. The plots have  $R^2$  values of

0.777–0.977, but the theoretical values of ( $q_{e,cal}$  mg/g) are far lower than those of experimental data,  $q_{e,exp}$  (Table 2) with high S.D., implying that the adsorption process does not follow fully the pseudo-first-order adsorption rate expression, although it has high  $R^2$ .

**Table 2.** Pseudo-first-order kinetic parameters for AR14 adsorption on dried waste biomass of *Saccharomyces cerevisiae*.

Effect of initial dye concentration					
$C_o$ mg/L	$K_1 \times 10^{-3}$ min <sup>-1</sup>	$q_{e,exp}$ mg/g	$q_{e,cal}$ mg/g	$R^2$	S.D.
60	25	9.66	5.82	0.777	0.5753
120	15.3	21	5.38	0.824	0.8876
275	5	51.56	24.48	0.826	0.7237
520	2.5	91.55	65.60	0.815	0.4585
Effect of temperature					
Temperature °C	$K_1 \times 10^{-3}$ min <sup>-1</sup>	$q_{e,exp}$ mg/g	$q_{e,cal}$ mg/g	$R^2$	S.D.
15	24.8	18.21	11.81	0.951	0.8472
25	15.3	21	5.38	0.824	0.8876
35	20.7	21.82	6.84	0.977	0.7678
45	16.2	22.51	8.02	0.970	0.8454

The pseudo-second-order model proposed by Ho and McKay (1999) is based on the assumption that the adsorption follows second-order chemisorption. The linear form can be written as follows:

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} t \tag{7}$$

where  $K_2$  is the pseudo-second-order rate constant (g/mg min). By plotting  $t/q_t$  against  $t$ ,  $q_e$ , and  $K_2$  can be evaluated. The initial adsorption rate,  $h_0$  (mg/g min) is defined as (Yao et al. 2010):

$$h_0 = K_2 q_e^2 \tag{8}$$

The values of  $q_{e,cal}$ ,  $K_2$ ,  $h_0$ , and  $R^2$  are listed in Table 3. The dependence of  $t/q_t$  versus  $t$  gives an excellent straight-line relation for all the experimental concentrations and all the  $R^2$  values are close to 1. There is only a little difference between  $q_{e,exp}$  and  $q_{e,cal}$ , with low S.D. values. This suggests that the overall rate of the dye adsorption process appears to be controlled by chemisorption process (Slimani et al., 2011). It can also be seen in Table 3 that, with an increase in initial dye concentration, the initial adsorption rate ( $h_0$ ) increased, and the rate constant of adsorption  $K_2$  decreased. Meanwhile, with the increase in temperature  $K_2$  and  $h_0$  increased.

The magnitude of activation energy  $E_a$  may give an idea about the type of adsorption. According to Slimani et al. (2011), activated chemical adsorption means that the rate varies with temperature according to  $E_a$  comprising 8.4–83.7 kJ/mol in the Arrhenius equation. According to El-Aila et al. (2011), the values of rate constant obtained according to the pseudo-second-order can be used to calculate the  $E_a$  of the adsorption process.

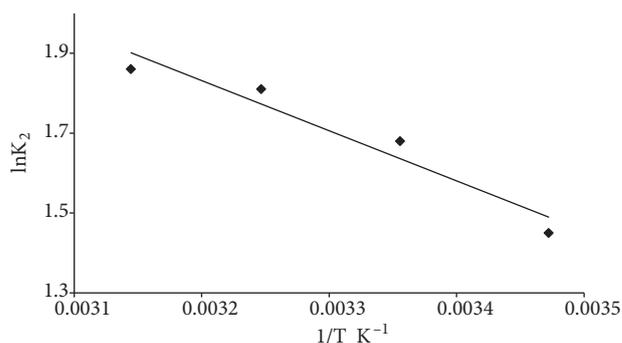
**Table 3.** Pseudo-second-order kinetic parameters for AR14 adsorption on dried waste biomass of *Saccharomyces cerevisiae*.

Effect of initial dye concentration						
$C_o$ mg/L	$K_2 \times 10^{-3}$ g/mg min	$q_{e,exp}$ mg/g	$q_{e,cal}$ mg/g	$h_0$ mg/g min	$R^2$	S.D.
60	8.87	9.66	9.93	0.88	0.998	0.1004
120	5.35	21	21.41	2.45	0.999	0.0603
275	1.27	51.56	52.36	3.48	0.995	0.0963
520	1.02	91.55	94.34	9.08	0.999	0.0771
Effect of temperature						
$C_o$ mg/L	$K_2 \times 10^{-3}$ g/mg min	$q_{e,exp}$ mg/g	$q_{e,cal}$ mg/g	$h_0$ mg/g min	$R^2$	S.D.
15	4.28	18.21	18.83	1.52	0.998	0.0885
25	5.35	21	21.41	2.45	0.999	0.0603
35	6.10	21.82	22.42	3.07	0.999	0.0383
45	6.43	22.51	22.78	3.34	0.999	0.0460

The  $E_a$  for AR14 adsorption was calculated with the Arrhenius equation as is defined by the following relationship:

$$\ln K_2 = \ln A - \frac{E_a}{RT} \tag{9}$$

The Arrhenius plot shown in Figure 6 was considered satisfactory due to the coefficient of correlation value,  $R^2 = 0.94$ . The  $E_a$  was determined from the slope of  $\ln K_2$  versus  $(1/T)$  and was found to be 10.44 kJ/mol, which is in the range of chemical adsorption. This shows that AR14 adsorption is of a chemical nature.



**Figure 6.** Relationship of  $\ln K_2$  versus  $1/T$  to verify Arrhenius equation.

### 3.8. Sorption equilibrium and process design

Adsorption isotherm models are fundamental in describing the interactive behavior between the adsorbate and adsorbents, and are important for investigating mechanisms of adsorption. Analysis of equilibrium data is important to develop an equation that accurately represents the results and could be used for design purposes.

Langmuir, Freundlich, Temkin (Farah et al., 2007), and Halsey (Samarghandi et al., 2009) models were used for the equilibrium modeling of the studied biosorption system. Isotherm constants and the correlation coefficient,  $R^2$ , with the experimental data are listed in Table 4.

**Table 4.** Adsorption isotherm constants, correlation coefficients, and standard deviation for AR14 adsorption on dried waste biomass of *Saccharomyces cerevisiae*.

Isotherm models	Isotherm constants	$R^2$	S.D.
Langmuir	$K_L$ 0.799 L/g, $a_L$ $1.6 \times 10^{-3}$ L/mg, $R_L$ 0.135	0.989	0.0993
Freundlich	$K_f$ 0.939 L/g, $1/n$ 0.855	0.899	0.3982
Temkin	$K_t$ 0.04 L/mg, $B_t$ 30.09 J/mol	0.966	0.3054
Halsey	$K_h$ 0.843 L/g, $n_h$ 1.1699	0.899	0.7344

The initial dye concentrations ranging from 30 mg/L to 4000 mg/L with equilibrium dye concentrations in the range of 13.71–2506 mg/L were used to investigate the equilibrium of biosorption. The biosorption capacity increased with increasing dye concentrations. The biosorption capacity was 2.44 mg/g and 374 mg/g at an initial dye concentration of 30 mg/L and 4000 mg/L, respectively. The isotherm curve became smooth and approached the plateau value at higher dye concentrations. The plateau region of the isotherm represents well-packed dye molecules covering the total surface of the biosorbent (Sankar et al., 1999).

The Langmuir adsorption is based on the assumption of monolayer adsorption on a structurally homogeneous adsorbent, where all the sorption sites are identical and energetically equivalent. The linear form of Langmuir equation can be expressed as follows:

$$\frac{C_e}{q_e} = \frac{a_L C_e}{K_L} + \frac{1}{K_L} \tag{10}$$

where  $C_e$  is the concentration of AR14 at equilibrium (mg/L),  $q_e$  is the amount of AR14 adsorbed per unit mass of dried waste biomass of *S. cerevisiae* at equilibrium (mg/g), and  $a_L$  (L/mg) and  $K_L$  (L/g) are the Langmuir isotherm constants. The essential features of Langmuir can be expressed in terms of dimensionless constant separation factor  $R_L$ , which was defined by Weber and Chakravorti (1974) as:

$$R_L = \frac{1}{1 + a_L C_o} \tag{11}$$

Values of  $R_L$  indicate the shapes of isotherms to be either unfavorable ( $R_L > 1$ ), linear ( $R_L = 1$ ), favorable ( $0 < R_L < 1$ ), or irreversible ( $R_L = 0$ ), where  $C_o$  (4000 mg/L) is the maximum initial concentration used in isotherm studies. Langmuir constants determined from the plots of  $C_e/q_e$  versus  $C_e$  were found to be linear over the whole studied concentrations range, with  $R^2 = 0.970$  and  $R_L = 0.1354$ , indicating favorable isotherms.

The Freundlich isotherm model is an empirical expression that encompasses the heterogeneity of the surface and the exponential distribution of sites and their energies. The linear form of Freundlich equation can be expressed as follows:

$$\log q_e = \frac{1}{n} \log C_e + \log K_f \tag{12}$$

$K_f$  (L/g) and  $n$  (-) are the characteristic constants of the system. The magnitude of dimensionless exponent  $n$  is related to the intensity of biosorption, where a value of  $1/n < 1$  represents favorable adsorption (Wang et

al., 2008). When plotting  $\log q_e$  against  $\log C_e$ , a straight line was obtained with  $R^2 = 0.899$  and  $n = 1.17$ , indicating that AR14 was favorably adsorbed by dried waste biomass of *S. cerevisiae*.

The Temkin isotherm assumes that the heat of adsorption of all the molecules in a layer decreases linearly with surface coverage of the adsorbent due to sorbate-adsorbate interactions. This adsorption is characterized by a uniform distribution of binding energies. The linear form of the Temkin isotherm can be expressed as follows:

$$q_e = \frac{RT}{B_t} \ln C_e + \frac{RT}{B_t} \ln K_t \quad (13)$$

where  $K_t$  (L/mg) is the Temkin isotherm constant  $B_t$  is a constant related to the heat of adsorption (J/mol),  $R$  is the universal gas constant (8.314 J/kmol), and  $T$  is the absolute temperature (K). By plotting  $q_e$  against  $\ln C_e$  a straight line was obtained, with  $R^2 = 0.966$  and  $B_t = 30$  J/mol. The value of  $B_t$  is greater than 8 J/mol, indicating strong interaction between dye and biomass and considered as chemisorption of an adsorbate onto the adsorbent (Anwar et al. 2010; Boparai et al., 2011).

The Halsey model describes multilayer sorption at relatively large distances from a nonuniform surface. The model is mostly based on the assumption of nonuniform distribution of the adsorption sites. The linear form of the Halsey isotherm can be expressed as follows:

$$\ln q_e = \frac{1}{n_h} \ln C_e + \frac{1}{n_h} \ln K_h \quad (14)$$

$K_h$  (L/g) and  $n_h$  (-) are Halsey constants. By plotting  $\ln q_e$  against  $\ln C_e$ , a straight line was obtained, with  $R^2 = 0.899$ .

In order to quantitatively compare the applicability of each isotherm model for the sorption system, the S.D. was calculated using Eq. (5).

By comparing the results listed in Table 4, it is clear that the Langmuir model represents the highest  $R^2$  and lowest S.D. values, which means that the Langmuir model gives the best agreement with the experimental isotherm data obtained. These results also show that the sorption of AR14 onto dried waste biomass of *S. cerevisiae* cannot be explained by assumption of multilayer adsorption phenomena.

Based on the best fit isotherm, a single-stage absorber as shown in Figure 7 was designed. Consider an effluent containing volume  $V$  (L) of solution and the dye concentration reduced from  $C_o$  to  $C_1$  (mg/L). The amount of adsorbent is  $M$  (g) and the solute loading changes from  $q_o$  to  $q_1$  mg dye/g adsorbent. When fresh adsorbent is used,  $q_o = 0$  mg/g and the mass balance equates the dye removed from the liquid to that picked up by the solid. The mass balance equation for the sorption system in Figure 7 can be written as:

$$V(C_o - C_1) = M(q_1 - q_o) = Mq_1 \quad (15)$$

At equilibrium conditions,  $C_1 \rightarrow C_e$  and  $q_1 \rightarrow q_e$ .

In the case of the adsorption of AR14 on dried waste biomass of *S. cerevisiae*, the Langmuir isotherm gives the best fit to experimental data. Consequently, the Langmuir equation can be best substituted for  $q_e$  in the rearranged form of Eq (15) as follows:

$$\frac{M}{V} = \frac{C_o - C_e}{q_e} = \frac{C_o - C_e}{(K_L C_e / (1 + a_L C_e))} = \frac{C_o - C_e}{(0.799 C_e / (1 + 0.0016 C_e))} \quad (16)$$

Eq. (16) can be used to design the AR14/dried waste biomass of *S. cerevisiae* sorption system at different conditions of batch volume, initial dye concentration, and adsorbent dosage, as shown in Figure 8.

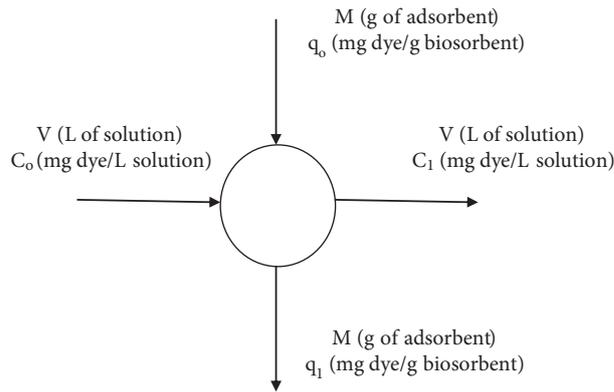


Figure 7. Schematic for a single-stage batch adsorption process.

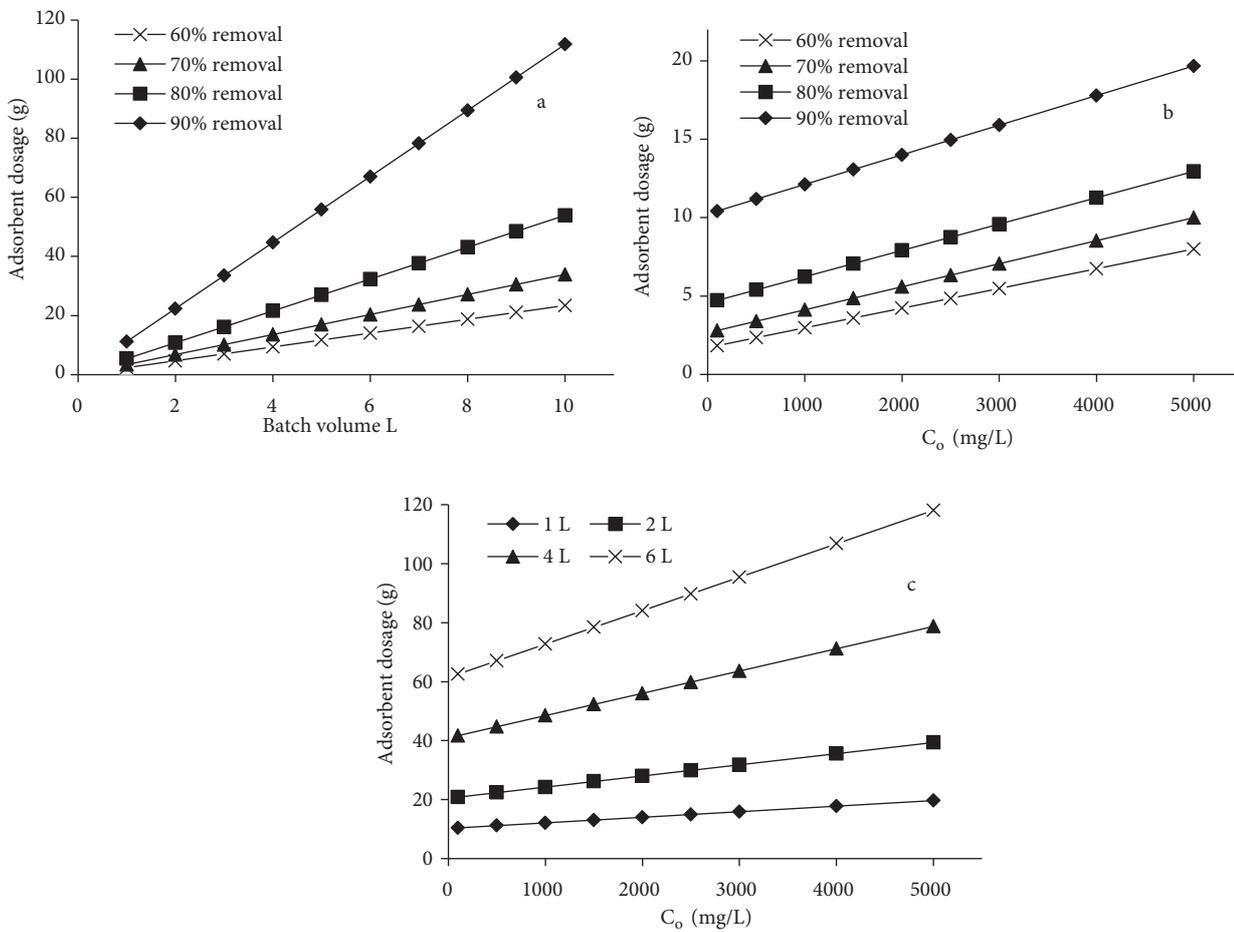


Figure 8. Plots representing required biosorbent dosage in different batch systems.

Figure 8a shows a series of plots for 60%–90% color removal in different batch volumes with fixed initial dye concentration  $C_0$  500 mg/L, 150 rpm, 30 °C, and pH 7. This means, for example, that when the batch to be treated is 8 L with  $C_0$  500 mg/L to reach 90% dye removal within 300 min, 11.18 g biomass/L is required.

Figure 8b shows the amount of biosorbent required to reduce the color content by 60%–90% at different initial dye concentrations  $C_0$  50–5000 mg/L with batch volume of 1 L, 150 rpm, 30 °C, and pH 7. This means,

for example, that when the batch to be treated is 1 L with  $C_o$  2000 or 5000 mg/L to reach 90% dye removal within 300 min, 14 and 20 g biomass/L are required, respectively.

Figure 8c shows the amount of biosorbent required to remove 90% of AR14 in different batch volumes of 1–6 L with different initial dye concentrations (100–5000 mg/L), 150 rpm, 30 °C, and pH 7. This means to treat a batch of 2 L with  $C_o$  3000 and a batch of 6 L with  $C_o$  5000 mg/L within 300 min, 32 and 118 g biomass/batch are required, respectively.

#### 4. Conclusions

Biosorption capacity (mg/g) increased with increase of initial dye concentration and time but decreased with increase in biosorbent dosage. The maximum dye uptake (mg/g) was obtained at a moderate agitation speed of 150 rpm. The effect of salt concentration on the dye uptake was negligible. It was also found that increasing temperature and decreasing pH resulted in higher dye loadings per unit weight of the sorbent (mg/g). The adsorption process follows fully the pseudo-second-order adsorption rate expression. The dye adsorption process is a feasible, nonspontaneous chemisorption process and is endothermic in nature. The Langmuir model gives the best agreement with the experimental isotherms data obtained. The obtained results also show that the sorption of AR14 onto dried waste biomass of *S. cerevisiae* cannot be explained by assumption of multilayer adsorption phenomena. This study proved that dried waste biomass of *S. cerevisiae* can be an attractive candidate for removal of acid dyes from wastewater.

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