

Biosorption of Astrazone Blue basic dye from an aqueous solution using dried biomass of Baker's yeast

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Abstract

In this study dried biomass of Baker's yeast, *Saccharomyces cerevisiae*, is used as a sorbent for Astrazone Blue basic dye aqueous solution.

Factors affecting the adsorption process: dye concentration, contact time, temperature and pH were investigated. The equilibrium concentration and the adsorption capacity at equilibrium were determined using three different sorption models namely: Langmuir, Freundlich and Temkin isotherms. It was found that increasing temperature and pH result in higher dye loadings per unit weight of the sorbent. The results gained from this study were described by Langmuir isotherm model better than Freundlich and Temkin isotherm models. The calculated heat of adsorption of the dye–yeast system indicates that the bio-sorption process is taking place by chemical adsorption and has an endothermic nature. The maximum adsorption capacity at 30 °C and pH 7 was calculated as 70 mg/g for dried biomass of Baker's yeast compared to 18.5 mg/g for commercial granular activated carbon, indicating that dried biomass of Baker's yeast can be considered as a good sorbent material for Astrazone Blue solution.

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1. Introduction

Controlling pollution is the main concern of society today. Large amounts of dyes are annually produced and used in textile, cosmetics, paper, leather, pharmaceutical, food and other industries. The textile industry accounts for two-thirds of the total dyestuff market [1]. Even a very small amount of dye in water (10–50 mg/L) affects the aesthetic value, water transparency and gas solubility in water bodies [2]. Moreover, it may also affect photochemical activities in aquatic systems by reducing light penetration [3]. It has been also reported that several commonly used dyes are carcinogenic and mutagenic for aquatic organisms [4].

Removal of textile dyes from waste water is still of a major environmental concern because they are difficult to be removed by the conventional waste water treatment systems since they are designed to be resistant to degradation or fading by oxidizing agents and light. They must also be resistant to both high temper-

atures and enzyme degradation resulting from detergent washing. For these reasons, methods based on photo-degradation, aerobic and anaerobic biodegradation are slow and complete mineralization of most dyes is rather difficult. Degradation products are toxic to aquatic organisms [5]. The presence of such compounds in waste water is offensive and their removal is difficult.

Many physical and chemical methods including coagulation, flocculation, precipitation, filtration, adsorption, chemical degradation, ozonation and oxidation have been used for the treatment of dye-containing effluents [6]. Coagulation and flocculation using polyelectrolytes, lime, alum or ferrous salts produce huge amounts of toxic sludge that pose handling and disposal problems in addition to materials cost [7]. Alternatively, various adsorbents such as activated carbon and silica gel have been tested and used for the removal of dyes from polluted water. Activated carbon is the most widely used adsorbent for the removal of color and the treatment of textile effluents, but it is expensive [2]. This led many workers to search for the use of cheap and efficient alternative materials such as bagasse pith, carbonized bark, natural clay, peat, soil, wood chips, rice husk ash, fly ash, living or dead microbial biomass and algae, etc. [8–10].

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Nomenclature

a_L	Langmuir isotherm constant (L/mg)
A	Temkin constant (L/g)
A_c	Clausius–Clapeyron constant
B	Temkin constant
C_o	initial liquid-phase concentration (mg/L)
C_e	equilibrium liquid-phase concentration (mg/L)
ΔH	heat of adsorption (cal/mol)
K_f	Freundlich isotherm constant (L/g)
K_L	Langmuir isotherm constant (L/g)
M	mass of adsorbent (g)
n	Freundlich isotherm constant
N	number of isotherm parameters
P	number of data points
q_e	equilibrium solid-phase concentration (mg/g)
q_{ecal}	calculated equilibrium solid-phase concentration (mg/g)
$q_{max\ exp}$	experimental maximum adsorption capacity (mg/g)
$q_{max\ theo}$	theoretical maximum adsorption capacity (mg/g)
R	universal gas constant (cal/mol K)
R_L	dimensionless constant separation factor
T	absolute temperature (K)
V	liquid-phase volume (L)

Biologically based adsorption (biosorptions) uses low cost biological materials, namely living or dead microorganisms. Removal of organic colors using biosorption process stems from the work on the removal of metals in biological waste water treatment systems. The interactions between microorganisms (yeast, bacteria and/or fungi) and dyes depend on the chemical properties of all the reaction partners. Each dye has certain affinity to various microorganisms and on the other side one microorganism is able to bind or degrade more types of dyes [11].

Adsorption of solutes (adsorbates) from solutions or suspensions onto solid materials (adsorbents) occurs mainly through one of the following mechanisms: exchange of molecules from solution to the adsorbent, physical adsorption due to van der Waals forces and chemisorption [12].

Ability of Baker's yeast (*Saccharomyces cerevisiae*) as biosorbent for heavy metals has been recognized [13–16]. However, there have been few researches on biosorption of textile dyes by *S. cerevisiae* which is inexpensive, safe, easily grown, readily available and produces high yields of biomass [1,17], that is why it was selected as adsorbent material for the present study. Aim of this study is to investigate the sorption of a basic dye, Astrazone Blue, from an aqueous solution using dried biomass of Baker's yeast *S. cerevisiae*. Effect of some system variables including; dye concentration, contact time, temperature and pH were studied. Different published adsorption isotherm models were examined in order to choose the best fitting one to the obtained experimental data.

2. Equilibrium isotherms

Isotherms are the equilibrium relations between the concentration of the adsorbate on the solid phase and its concentration in the liquid phase. From the isotherms the maximum adsorption capacity ($q_{max\ exp}$) can be obtained.

Analysis of such isotherms is important in order to develop an equation which accurately represents the results and could be used for design purposes. Langmuir, Freundlich and Temkin models are among the most common isotherms describing solid–liquid sorption systems.

2.1. Langmuir isotherm

Langmuir isotherm [18] is often used to describe sorption of solutes from liquid solutions and expressed by the following equation:

$$q_e = \frac{K_L C_e}{1 + a_L C_e} \quad (1)$$

Characteristic constants of Langmuir equation; K_L , a_L can be determined from the linearized form of Eq. (1):

$$\frac{C_e}{q_e} = \frac{1}{K_L} + \frac{a_L}{K_L} C_e \quad (2)$$

They can be calculated by plotting of C_e/q_e versus C_e . Slope and intercept of the line are a_L/K_L and $1/K_L$, respectively. The theoretical maximum adsorption capacity ($q_{max\ theo}$) corresponding to Langmuir constants is numerically equal to K_L/a_L [19].

The essential features of Langmuir can be expressed in terms of dimensionless constant separation factor R_L which was defined by Weber and Chakravorti [20] as:

$$R_L = \frac{1}{1 + a_L C_o} \quad (3)$$

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 ($R_L = 0$).

The constant K_L can be used to determine the enthalpy of adsorption, ΔH , using Clausius–Clapeyron equation [21]:

$$K_L = A_c \exp \left(\frac{-\Delta H}{RT} \right) \quad (4)$$

where A_c is the constant containing the entropy term, ΔH (cal/mol) the heat of adsorption, R the universal gas constant (1.987 cal/mol K) and T is the absolute temperature (K). Hence a plot of $\ln K_L$ versus $1/T$ yields a line with a slope = $-\Delta H/R$ from which ΔH can be calculated.

2.2. Freundlich isotherm

Freundlich isotherm [22] is the earliest known relationship describing the sorption equation. This fairly satisfactory empirical isotherm can be used for non-ideal sorption that involves heterogeneous sorption and is expressed by the following

equation:

$$q_e = K_f C_e^{1/n} \quad (5)$$

K_f and n are the characteristic constants of the system. The equation may be linearized by taking the logarithm of both sides:

$$\log q_e = \frac{1}{n} \log C_e + \log K_f \quad (6)$$

When plotting $\log q_e$ against $\log C_e$, this will form a straight line with a slope of $1/n$ and an intercept of $\log K_f$. The magnitude of exponent n indicates the favorability of the adsorbent/adsorbate system where value of $n > 1$ represents favorable adsorption [23].

2.3. Temkin isotherm

Temkin and Pyzhev [24] considered the effect of some indirect sorbate/adsorbate interactions on the adsorption isotherm. This isotherm assumes that; the heat of adsorption of all the molecules in a layer decreases linearly with surface coverage of adsorbent due to sorbate–adsorbate interactions. This adsorption is characterized by a uniform distribution of binding energies. The Temkin isotherm has the following form:

$$q_e = \frac{RT}{b} [\ln(AC_e)] \quad (7)$$

Eq. (7) can be expressed in its linear form as:

$$q_e = B \ln A + B \ln C_e \quad (8)$$

where $B = RT/b$, T is the absolute temperature in K , R the universal gas constant, A the equilibrium binding constant and the constant B is related to the heat of adsorption. According to Eq. (8), a plot of q_e versus $\ln C_e$ enables the determination of the isotherm constants A and B .

3. Materials and methods

3.1. Preparation of the microorganism

Baker's yeast employed in this study is the commercial strain of *S. cerevisiae* (product of the Three Pyramids Company, Egypt). It was supplied in the form of compressed blocks with 70% moisture by weight. It was dried at 60 °C until a constant weight of dead biomass was obtained. For the biosorption studies, the dried yeast biomass was grounded in a mortar to powder and sieved through standard sieves to constant sizes (0.63–0.8 mm).

3.2. Batch adsorption experiments

Each batch adsorption experiment was conducted by contacting 50 mL of known concentration of basic dye (adsorbate) with 200 mg of dried biomass of Baker's yeast as an adsorbent in a 250 mL Erlenmeyer flask closed with PARAFILM 'M' to prevent evaporative loss and placed in a rotary shaking incubator of 150 rpm 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 574 nm was measured to determine the residual dye concentration and to calculate the percentage of dye removal. A stock solution of basic dye with a concentration of 1000 mg/L was prepared, which was further diluted according to the experimental conditions. Negative controls (with no sorbent) were carried out to ensure that sorption is by dried biomass of Baker's yeast only and any sorption effect of dye onto the wall of the conical flasks can 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 different contact times with different initial dye concentrations to know the equilibrium contact time. Effect of temperature, and initial pH were also studied. The initial pH of the solution was adjusted using 0.1 M HCl or 10% NaOH. The adsorption capacity of Astrazone Blue on commercial granular activated carbon supplied by NORIT Netherlands was also studied for comparison. Table 1 illustrates all the process factors used for adsorption experiments. All the experiments were carried out in duplicates.

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

$$q_e = \frac{(C_o - C_e)V}{M} \quad (9)$$

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

3.3. Analysis of dye

λ_{\max} of Astrazone Blue (F2RL 200%), a basic blue dye supplied by Dyestar was determined on a JASCO UV/Vis/NIR spectrophotometer model V-570. The observed λ_{\max} was found to be 574 nm. Standard curve for different concentrations of the dye solution (10–1000 mg/L) was established.

Table 1
Different process conditions used for biosorption of Astrazone Blue

Process factors	Other conditions
Contact time 0, 0.5, 1, 1.5, 2, 3, 4, 6 (h)	Temperature: 30 °C; agitation 150 rpm; adsorbent dose: 0.2 g; initial pH 7; different dye concentrations: 100, 500 and 1000 mg/L
Temperature 20, 30, 50 (°C)	Contact time: 4 h; agitation 150 rpm; adsorbent dose: 0.2 g; initial pH: 7; different dye concentrations: 100–1000 mg/L
Effect of initial pH 4, 6, 8, 9	Contact time: 4 h; temperature: 30 °C; agitation 150 rpm; adsorbent dose: 0.2 g; different dye concentrations: 100–1000 mg/L
Commercial granular activated carbon (GAC)	Contact time: 4 h; temperature: 30 °C; agitation 150 rpm; adsorbent dose: 0.2 g; initial pH: 7; different dye concentrations: 100–1000 mg/L

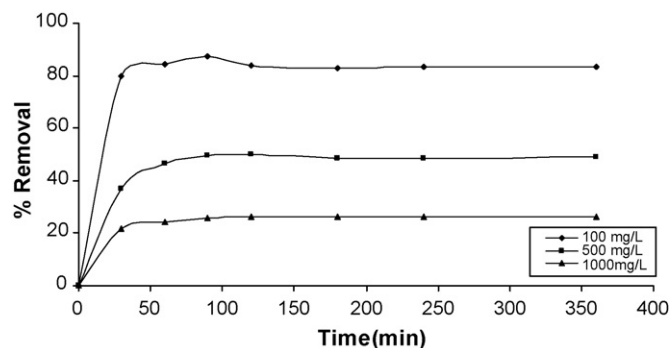


Fig. 1. Effect of contact time at different initial dye concentrations on its percent removal by dried biomass of Baker's yeast.

4. Results and discussion

4.1. Effect of initial dye concentration and contact time

Adsorption of Astrazone Blue at different initial concentrations (100, 500, 1000 mg/L) on Baker's yeast was studied as a function of contact time (Figs. 1 and 2). Removal of Astrazone Blue (F2RL 200%) from aqueous solutions by adsorption on dried biomass of Baker's yeast increases with time, till equilibrium is attained, nearly after 2 h. Therefore, equilibrium time was set conservatively at 4 h for further experiments. It was found by Marungrueng and Pavasant that *Macroalga Caulepra lentilifera* have adsorption capacity for basic dye, Astrazone Blue FGRL for the whole range of concentrations employed in that work (20–1280 ppm) and adsorption reached equilibrium within the first hour [25].

It is noticed that the adsorption curves (Fig. 2) are smooth and continuous leading to saturation at various concentrations of Astrazone Blue (F2RL 200%) on the outer interface of the biomass. This shows the possibility of mono-layer coverage of Astrazone Blue (F2RL 200%) on the outer interface of the dried biomass of Baker's yeast [26].

Process was found to be initially very rapid, and a large fraction of the total amount of dye was removed within approximately 30 min. The rapid uptake of the dye indicates that the sorption process could be ionic in nature where the basic (cationic) dye molecules bind to the various negatively charged

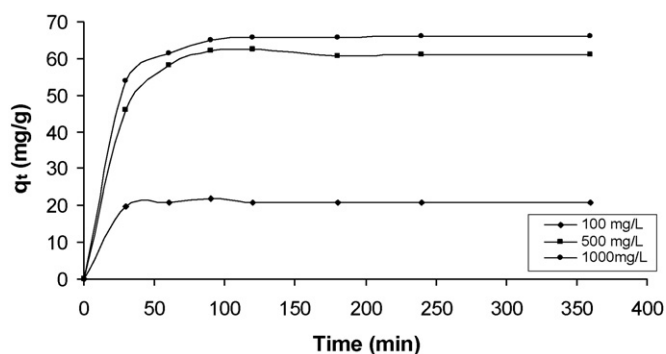


Fig. 2. Effect of contact time at different initial dye concentrations on its total removal by dried biomass of Baker's yeast.

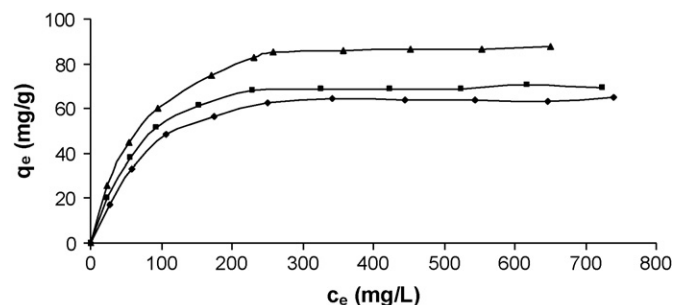


Fig. 3. Adsorption of dye on dried biomass of Baker's yeast at different temperatures (♦) 20 °C; (■) 30 °C; (▲) 50 °C.

organic functional groups present on the surface of the biomass [2].

The percentage of dye removal decreases with the increase in the initial dye concentration (Fig. 1). This may be due to the saturation of the sorption sites on the biosorbent as the concentration of the dye increases. The actual amounts of dye adsorbed increase with increasing of the initial dye concentration, i.e., the increase in adsorption is limited with biosorbent dose (Fig. 2). This was confirmed by other investigators [2,27] and they attributed this phenomenon to the increase in the driving force of the concentration gradient, with the increase of the initial dye concentration. Hence a higher initial concentration of dye will enhance the adsorption process [17].

4.2. Effect of temperature on the adsorption process

Increasing the temperature is known to increase the diffusion rate of the adsorbate molecules across the external boundary layer and in the internal pores of the adsorbent particles, owing to the decrease in the viscosity of the solution. In addition, the change temperature affects the equilibrium capacity of the adsorbent for a particular adsorbate [25,26]. Fig. 3 shows the results of the effect of temperature on the sorption of Astrazone Blue (F2RL 200%) on dried Baker's yeast biomass. The sorption of Astrazone Blue (F2RL 200%) increases by increasing the temperature of the solution from 20 to 50 °C, therefore this system is endothermic [27]. In addition, the creation of some new active sites for additional sorption on the surface of the sorbent also is endothermic [28,29]. It is a chemisorption mechanism where there is an increase in the number of molecules acquiring sufficient energy to undergo chemical reaction with increasing temperature.

4.3. Effect of initial pH on adsorption process

pH is one of the most important factors controlling the adsorption of a dye onto suspended particles. Fig. 4 shows that as the pH increases the removal of Astrazone Blue (F2RL 200%) increases. This can be explained by the electrostatic interaction of the basic dye cationic species with the negatively charged surface of the biosorbent. The electrostatic attraction force of the dye compound with biosorbent surface is likely to be raised when the pH value increases [25,30]. This can be also explained that at lower pH, the hydrogen protons would compete effec-

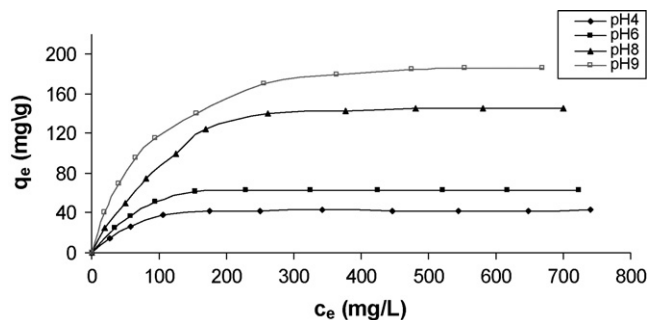


Fig. 4. Adsorption of dye on dried biomass of Baker's yeast at different initial pH values.

tively with the dye cations thus leaving it in the solution. At higher pH, negative charges of the biomass leading to electrostatic attraction of the dye cations. This confirms that there is a clear competition between hydrogen protons and dye cations for the sorption sites in the biomass. As pH of the system decreases, the number of free negatively charged adsorbent sites decreases. This does not favor the adsorption of the positively charged dye cations [26,31].

4.4. Analysis of isotherm data

Analysis of equilibrium data is important to develop an equation which accurately represents the results and could be used for design purposes.

Langmuir, Freundlich and Temkin models have been used for the equilibrium modeling of biosorption system.

Langmuir constants a_L and K_L can be determined from the linear plots of C_e/q_e versus C_e at different temperatures and pH values. The maximum adsorption capacity (q_{max}) and dimensionless constant separation factor R_L have been calculated at initial dye concentration C_0 of 1000 ppm. Results are listed in Table 2. It can be observed that the calculated values of R_L at different conditions (temperatures and pH) are ranging between 0 and 1 which means that the systems at different conditions have favorable isotherm.

Heat of adsorption can be calculated using Clausius–Clapeyron equation. Fig. 5 shows a plot of $\ln K_L$ against $1/T$, from the gradient of the straight line ΔH have been calculated. The positive enthalpy of adsorption obtained indicates chemical adsorption. This suggests that the chemical bonds between the

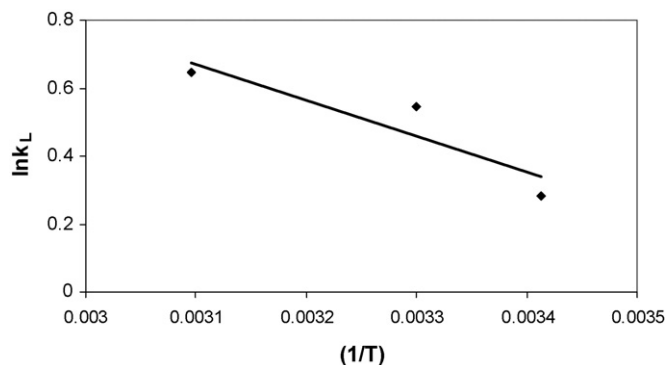


Fig. 5. Clausius–Clapeyron plot for adsorption of dye on dried biomass of Baker's yeast.

Table 3

Isotherm constants in Freundlich model at different temperatures and pH

Parameters	K_f (L/g)	n	Correlation coefficient
Temperature (°C)			
20	7.32	2.80	0.91
30	9.65	3.06	0.91
50	10.28	2.86	0.94
pH			
4	8.47	3.73	0.87
6	13.25	3.87	0.86
8	7.90	2.07	0.94
9	14.99	2.41	0.96

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 [25]. Also the positive value of ΔH implies that the adsorption reaction of Astrazone Blue (F2RL 200%) onto Baker's yeast is endothermic [32]. The increase in adsorption of dye with temperature may be due to dissolution of the adsorbing species, changes in the pores sizes of adsorbents and enhanced rate of intra-particle diffusion. Positive value of enthalpy also suggests some structural changes in adsorbate and adsorbent [33].

Plots of $\log q_e$ against $\log C_e$ at different temperatures and pH values enable the determination of Freundlich constants n and K_f . Results are summarized in Table 3. Values of the Freundlich exponent $n > 1$ indicate that the systems are favorable.

Table 2

Isotherm constants in Langmuir model at different temperatures and pH

Parameters	K_L (L/mg)	a_L (L/mg)	$q_{max\ theo}$ (mg/g)	R_L	Correlation coefficient
Temperature (°C)					
20	1.33	1.89×10^{-2}	69.93	5.03×10^{-2}	0.99
30	1.72	2.29×10^{-2}	75.19	4.18×10^{-2}	0.99
50	1.91	1.99×10^{-2}	96.16	4.79×10^{-2}	0.99
pH					
4	1.62	3.62	44.64	2.68×10^{-2}	0.99
6	2.09	3.13	66.67	3.10×10^{-2}	0.99
8	1.85	1.09	169.50	8.4×10^{-2}	0.99
9	2.74	1.29	212.77	7.19×10^{-2}	0.99

Table 4
Isotherm constants in Temkin model at different temperatures and pH

Parameters	A (L/mg)	B	Correlation coefficient
Temperature (°C)			
20	0.21	14.01	0.94
30	0.29	14.30	0.94
50	0.22	19.23	0.96
pH			
4	0.63	7.61	0.94
6	0.57	11.45	0.95
8	0.10	37.54	0.97
9	0.13	44.40	0.98

Experimental equilibrium data have been also analyzed using Temkin isotherm and the constants were determined from the plots of q_e versus $\ln C_e$ at different values of temperature and pH. Results are listed in Table 4. Constant B which is related to the heat of adsorption increases with the increase in temperature, proving endothermic adsorption.

By comparing results listed in Tables 2–4, it is clear that equilibrium data fit Langmuir, Freundlich and Temkin models. Correlation coefficient of Langmuir model is higher than that of Freundlich and Temkin, which means that Langmuir sorption isotherm more accurately describe the sorption of Astrazone Blue (F2RL 200%) onto Baker's yeast.

The use of correlation coefficients is limited for representing linear form of different isotherms equations. Error analysis method is employed to enable the optimization process and to evaluate the fitting of different isotherms equations to experimental data. In this study hybrid fraction error function (HYBIRD) developed by Porter et al. [34] is used, as shown in the following equation:

$$\text{HYBIRD error function} = \frac{100}{P - N} \sum_{i=1}^P \left(\frac{(q_e - q_{ecal})^2}{q_e} \right)_i \quad (10)$$

By comparing the results listed in Table 5; it is clear that Langmuir results represent the lowest values which means that Langmuir model gives the best agreement with experimental isotherms data obtained.

Table 5
Values of error analysis (HYBIRD) of different used models at different parameters

Parameters	Models		
	Langmuir	Freundlich	Temkin
Temperature (°C)			
20	43.78	163.45	78.17
30	40.24	158.47	79.03
50	22.71	138.79	51.06
pH			
4	54.59	105.04	73.34
6	74.25	135.89	100.96
8	85.60	452.35	122.42
9	13.41	276.41	43.25

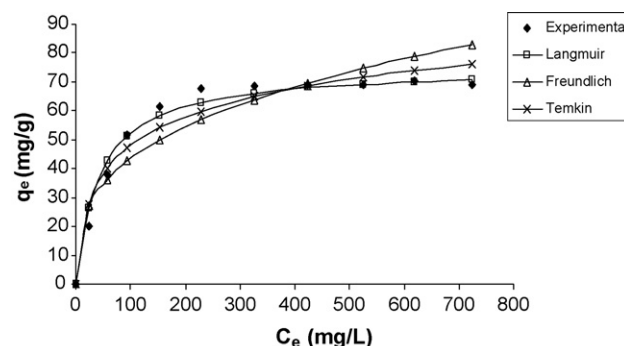


Fig. 6. Comparison of theoretical isotherm plots with experimental results for Astrazone Blue (F2RL 200%) onto Baker's yeast at 30 °C and pH 7.

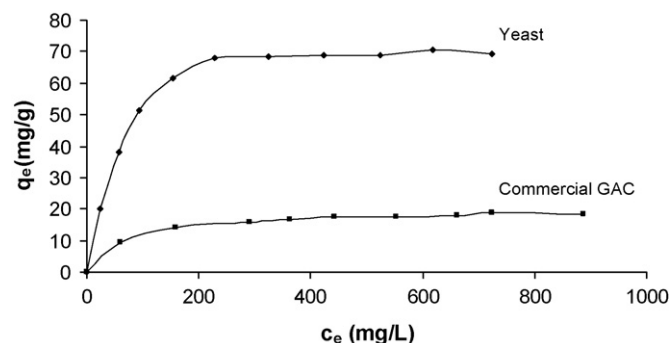


Fig. 7. Comparison for the adsorption capacity of dye on dried biomass of Baker's yeast and commercial activated carbon at 30 °C and pH 7.

Fig. 6 represents plots, as an example, for comparing the theoretical Langmuir, Freundlich and Temkin isotherms with experimental data at 30 °C and pH 7.

4.5. Adsorption of Astrazone Blue (F2RL 200%) on commercial activated carbon

A comparison for the adsorption capacity for Astrazone Blue (F2RL 200%) on dried biomass of Baker's yeast and the most widely used adsorbent; commercial granular activated carbon (GAC) supplied by NORIT Netherlands, has been done at 30 °C and pH 7 for the whole range of dye concentrations employed in this work (100–1000 ppm). Results are illustrated in Fig. 7. The experimental maximum adsorption capacities have been calculated, it was about 18.5 and 70 mg/g for commercial activated carbon and dried yeast, respectively. This indicates that the affinity of the dried biomass of Baker's yeast to adsorb Astrazone Blue (F2RL 200%) is higher than that of commercial activated carbon and the adsorption capacity of the commercial activated carbon is 26.4 % that of the yeast.

5. Conclusion

It is evident that dried biomass of commercial Baker's yeast is a good sorbent for Astrazone Blue (F2RL 200%) basic dye.

The increase in temperature results in a higher dye loadings per unit weight of the sorbent.

Increase in pH of the dye solution results in a higher dye loadings per unit weight of the sorbent.

Results obtained from this study are well described by Langmuir isotherm model and to a lower degree by Freundlich and Temkin isotherm models.

Calculated heat of adsorption of the dye–yeast system indicates that the bio-sorption process takes place by chemical adsorption and has an endothermic nature.

It has been also concluded that dried biomass of Baker's yeast has a higher adsorption capacity for Astrazone Blue (F2RL 200%); 70 mg/g as compared to that of commercial activated carbon; 18.5 mg/g at 30 °C and pH 7.

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