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Performance and kinetic studies on biosorption of Astrazon blue dye by dried biomass of Baker's yeast as a low cost biosorbent

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ABSTRACT

The effects of adsorbent dosage, agitation speed, and initial dye concentration on adsorption of Astrazone Blue (F2RL 200%) basic dye onto dried biomass of Baker's yeast have been investigated in this study. The specific uptake capacity of dye decreases with the increase of sorbent dosage. The maximum dye uptake has been obtained at moderate agitation speed of 150 rpm. The amount of dye adsorbed per gram biomass increases with increasing initial dye concentration and contact time. The kinetic experimental data of the effect of initial dye concentration were analyzed using four kinetic equations including pseudo-second-order model, intraparticle diffusion model, Elovich model and the modified Freundlich model. The best fit equation was identified by four error functions; residual root mean square error, chi-square test, sum of the squares of the errors and average relative error. Modified Freundlich model gave the lowest error function values and consequently best fitting the adsorption data. A design for a batch adsorption unit using data from previous isotherm studies has been done in this study. Comparative study for the cost of Astrazone Blue dye removal with dried biomass of Baker's yeast and commercial activated carbon (NORTI) illustrated that the expected cost of removing dye with dried biomass of Baker's yeast is about 18.79% of that of commercial activated carbon.

Key words: Biosorption, Astrazone Blue, Baker's yeast, Kinetics, Error analysis, Process design, Comparative cost.

INTRODUCTION

Most of the synthetic dyes are extensively used in paper, textile, rubber, plastics, printing, cosmetics, pharmaceutical, food and mineral processing industries because of their ease of use, inexpensive cost of synthesis, stability and variety of colors compared with natural dyes. They have complex aromatic structures which possibly come from coal-tar based hydrocarbons such as benzene, naphthalene, anthracene, toluene and xylene (Gong *et al.,* 2007) which make them more stable and more difficult to degrade (Kiran *et al.,* 2006). Today there are more than 10,000 types of dyes commercially available (Aksu and Cagatay, 2006). Over 7 X 10^5 tones of these dyes are produced annually worldwide and it was estimated that 10-15% of these chemical compounds are discharged into waste streams (Nicibi *et al.,* 2007). This often poses pollution problems in the form of; coloration of the water bodies, damaging the aesthetic nature of water, toxicity to the aquatic life, reduction of light penetration through water's surface and also reduction in the photosynthetic activity of aquatic organisms. They are also carcinogenic and mutagenic (Kumar *et al.,* 2006). Moreover, they affect severely human beings by damaging the liver, kidneys, brain, central and reproductive systems (Iscen *et al.,* 2007). Therefore, decolration of dye-containing effluents is becoming an obligation both environmentally and for water re-use.

Dyes are classified into three categories (Mishra and Tripathy, 1993): anionic (direct, acid and reactive dyes), cationic (basic dyes) and non-ionic (disperse dyes). In particular, due to the presence

of metals in their structure, basic dyes are considered one of the most toxic substances (US EPA, 1996).

Various physical, chemical and biological methods have been used for the treatment of dye-containing wastewater. Some chemical oxidation by Fenton reagent, ozone, UV plus H_2O_2 or NaOCl results in aromatic ring cleavage and may generate chemical sludge or by-products that are likely to be more toxic (Robinson *et al.,* 2001). Aerobic biological treatment is known to be ineffective for dye removal but anaerobic bioremediation enables water-soluble dyes to be decolorized (Carliell *et al.,* 1995). Adsorption technology using activated carbons, has gained favor recently because it has a high efficiency in the removal of highly stable dyes. However, this process proved to be uneconomic due to the high cost of activated carbon and also the additional cost involved in regeneration (Kumar and Porkodi, 2007). This led to directing research towards developing low cost and locally available adsorbing materials with high adsorption capacity (El-Khaiary, 2007). Microbial methods like biosorption have found utility in this context and they are applied not only to the biosorption of organic effluents such as dyes (Aksu, 2005) and phenols (Denizili *et al.,* 2005) but also to the recovery or removal of heavy metal ions such as lead, chromium and gold from industrial effluents (Paravathi *et al.,* 2007).

The key parameters controlling sorption of Astrazone Blue F2RL 200%, cationic (basic) dye from an aqueous solution onto dried biomass of Baker's yeast, *Saccharomyces cerevisiae* are expected to be biomass concentration, initial dye concentration and agitation speed thus they were the focus of study in this work. The biosorption kinetics were also investigated and the results have been analyzed by applying conventional theoretical models to fit the experimental data. Baker's yeast was selected as the biosorbent as it can be easily obtained in considerably substantial quantities at low costs.

MATERIAL AND METHODS

Biosorbent preparation

Baker's yeast (product of Three Pyramids Company, Egypt, with 70% moisture by weight) was dried in a hot air oven at 60°C overnight, then powdered using mortar and sieved to select the particle size (0.63-0.8 mm) for use as a biosorbent.

Batch biosorption experiments

A known weight of biosorbent was suspended in 50mL of known concentration of Astrazone Blue F2RL 200% dye solution of approximately pH7 in 250mL Erlenmeyer flasks and agitated at predetermined rpm in a rotary shaking incubator at 30°C for six hours.

Samples were withdrawn at prescribed time intervals to determine the remaining dye concentration using JASCO UV/Vis/NIR spectrophotometer model V-570 at 574nm, after the separation of adsorbent by centrifugation at 4000rpm for 15 minutes using distilled water as a blank, as previously described (Farah *et al.,* 2007). Negative controls (with no biosorbent) subjected to all experimental conditions were used as the initial dye concentrations for calculating the quantity of dye removal after biosorption experiments.

To study the effect of biosorbent dosage, dry biomass of Baker's yeast was added to 100ppm dye solution to yield concentrations (w/v) of (0.2, 0.4, 0.6, 0.8, 1, 1.2, 1.4, 1.6, 1.8 and 2%), at agitation speed of 150 rpm.

Effect of agitation speed was conducted on biosorption mixtures of 100ppm dye concentration at (100, 150, 300, 500 and 700 rpm), maintaining the biosorbent concentration constant at 0.4%.

Effect of different initial dye concentration was conducted at concentrations of (100, 500 and 1000ppm), maintaining the biosorbent concentration constant at 0.4%, at agitation speed of 150 rpm.

RESULTS AND DISCUSSION

Effect of biosorbent dosage

Fig. (1). shows the plot of equilibrium uptake capacity, q_e(mg/g) and % dye removal against the biosorbent concentration (%, w/v). It was observed that the maximum percentage removal obtained ($\approx$ 72%) at biosorbent concentration of 0.4% (w/v) which was the same as that obtained at

0.6% (w/v) and then decreased as the biosorbent concentration increased. Based on these results, 0.4% (w/v) of biosorbent concentration was used for further experiments. On the other hand, the adsorbed dye quantity per gram of dried biomass was maximum at biosorbent concentration of 0.2% (w/v) which was then decreased with the increase of biosorbent concentration. Similar effect was previously reported (Han *et al.,* 2006). The primary factor explaining this performance is that at biosorbent concentration of 0.2% (w/v), adsorption sites remain unsaturated during the adsorption reaction, whereas the number of sites available for adsorption increases by increasing the adsorbent concentration to 0.6% (w/v) due to the increase of surface area. The presence of relatively higher concentration of biosorbent in the solution resulting in reduced distances between the biosorbent particles, thus making many binding sites unoccupied (Bohel *et al.,* 2004). Also the inter-particles interactions such as aggregation, overlapping and overcrowding occur at high biosorbent concentration and lead to decrease in total surface area (Iscen *et al.,* 2007). Another reason could be due to the splitting effect of concentration gradient between dye molecules and biomass concentration causing a decrease in the amount of dye biosorbed onto unit weight of biomass (Malik, 2004).

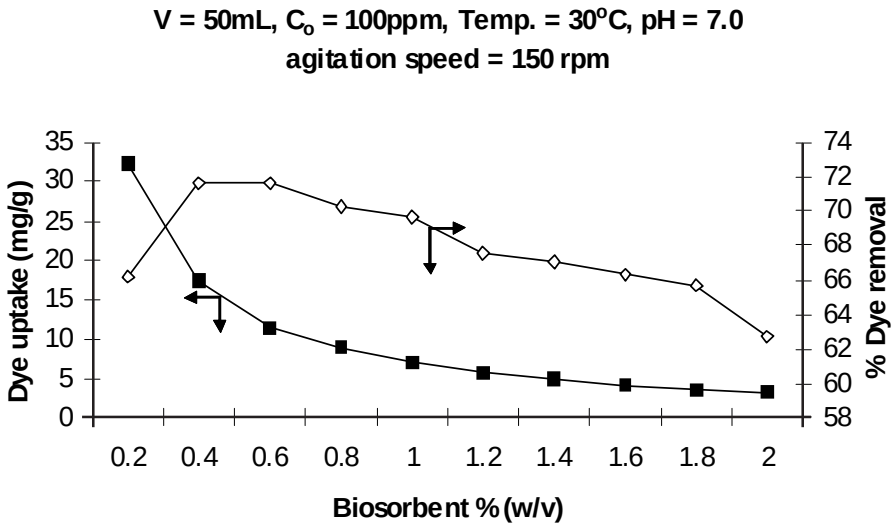

Fig. 1: Effect of biosorbent concentration on dye biosorption

Effect of agitation speed

Fig. (2). shows the effect of agitation speed on dye uptake, which increased from ≈ 18mg/g at 100 rpm, with % removal of ≈ 72% to 21 mg/g with dye removal of ≈ 84% at 150 rpm. Then decreased at higher shaking rates (300, 500 and 700 rpm) where the dye uptake were ≈17, 16 and 15.5 mg/g, respectively with dye removal of ≈ 68%, 64% and 62%, respectively. These results indicate that the contact between biomass and dye solution is more effective at moderate agitation speed (150 rpm) this speed was thus selected for further experiments. The observed lower dye uptake at relatively lower agitation speed (100 rpm) might be due to the agglomeration of biomass particles. Increase in agitation speed up to 150 rpm might have facilitated proper contact between dye solution and biomass binding sites and thereby promoted effective transfer of sorbate ions to the sorbent sites (Asma *et al.,* 2006). The observed decrease in dye removal beyond 150 rpm might be attributed to the increased turbulence promoted desorption of the adsorbates in the solution and hence the residual concentration of dyes were increased (Alam, 2004).

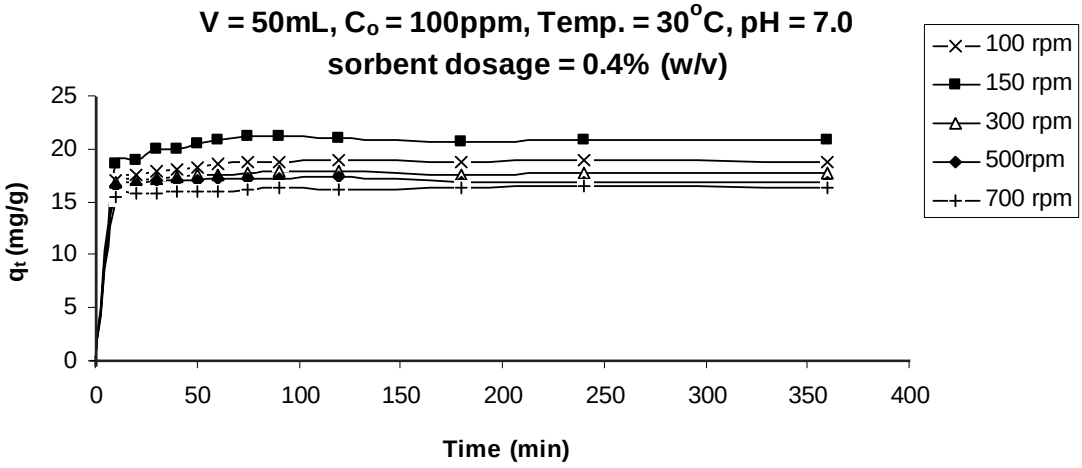

Fig. 2: Effect of agitation speed on dye biosorption

Effect of initial dye concentration

The effect of initial dye concentration on the rate of dye uptake is shown in Fig. (3). It was observed that the amount of dye adsorbed per gram biomass increased with increasing initial dye concentration and contact time. The rate of dye uptake was observed to be very rapid for the initial period of 10 min and thereafter the dye uptake process tends to proceed at a very slow rate and finally reached equilibrium within two hours. The rapid kinetics has significant practical importance as it will facilitate smaller reactor volumes ensuring efficiency and economy (Asku, 2001). The dye removal decreased from 75.44% to 47.66% with the increase in initial dye concentration (C_o, 100-1000ppm). C_o provides the necessary driving force to overcome the resistances against the mass transfer of dye between the aqueous and the solid phases. The increase in the C_o also enhances the

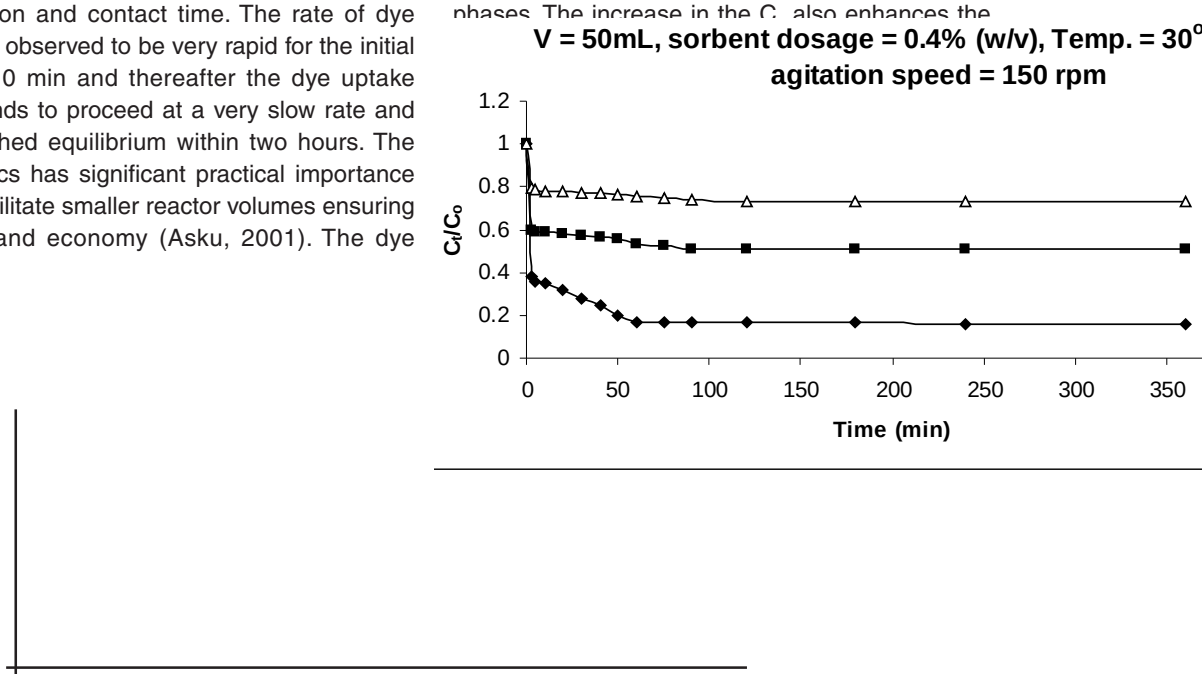

Fig. 3: Effect of initial dye concentration on biosorption rate

Adsorption kinetic study

In order to investigate the adsorption processes of Astrazone Blue F2RL 200% onto dried biomass of Baker's yeast, various kinetic models were tested for the obtained data to elucidate the adsorption mechanism.

Pseudo- second- order model

This model can be represented in the following form (Ho and Mckay, 1999):

...(1)

Where q_e and q_t are the amount of dye sorbed at equilibrium and at time t (mg/g) respectively, k_s is the pseudo- second- order rate constant (g/mg min) and t is the time (min).Values of q_e, k_s are calculated from the plot of t/q_t against t as illustrated in Fig. (4).

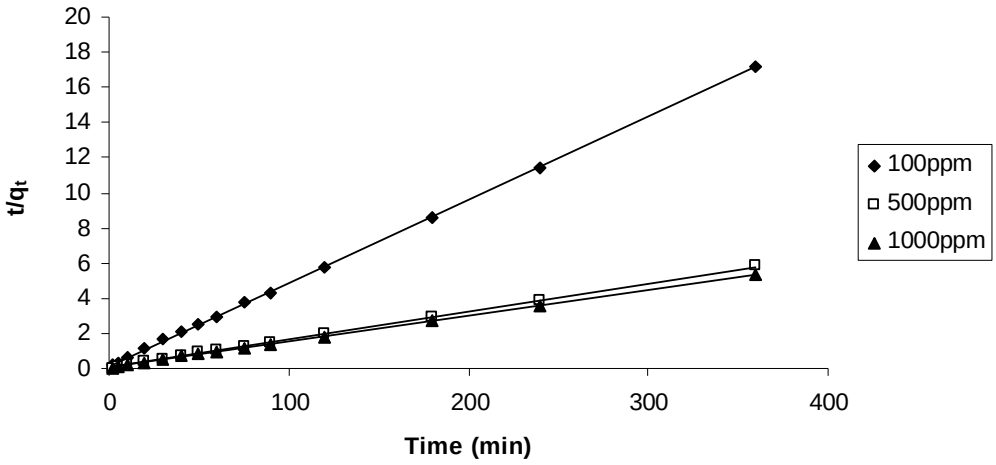

Fig. 4: Pseudo- second- order kinetic plots

The intraparticle diffusion model

Based on the theory proposed by Weber and Morris (1963), the interaparticle diffusion model can b expressed as follows:

$$q_t = k_p t^{1/2} + c \qquad ...(2)$$

Where k_p is the intraparticle diffusion rate constant (mg/g $min^{1/2}$) and c (mg/g) is a constant that gives idea about the thickness of the boundary layer, i.e. the larger the value of c the greater is the boundary layer effect (Kannan and Sundaram, 2001). According to this model, the plot of uptake, q_t, versus the square root of time, $t^{½}$, should be linear if particle diffusion is involved in the biosorption process and if these lines pass through the origin so the intraparticle diffusion is the rate controlling step (Chen *et al.,* 2003). When the plots do not pass through the origin, this is indicative that the intraparticle diffusion is not the only rate limiting step (Poots *et al.,* 1978). The plot of the intraparticle diffusion model at different initial concentration is shown in Fig. (5). which showed that the plots of the obtained data didn't pass through the origin indicating that the intraparticle diffusion is not the sole rate limiting step.

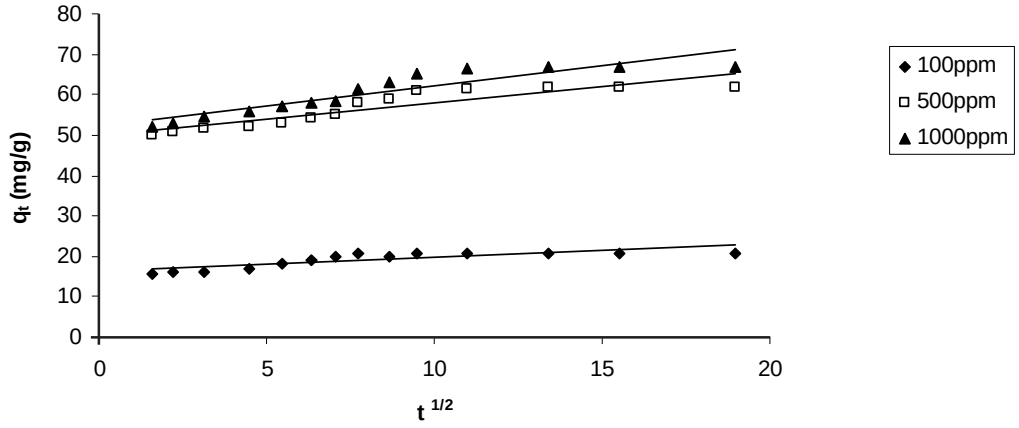

Fig. 5: Intraparticle diffusion model plots

Elovich model

Elovich equation is also very often used to interpret the kinetics of adsorption (Cheung *et al.,* 2000). The linear form of Elovich equation is represented as follows:

...(3)

Where α (mg/g min) and β(g/mg) are the Elovich constants where α and β are related to the initial sorption rate and the extent of surface coverage and activation energy for chemisorptions, respectively. Therefore, the plots of q_t versus lnt as shown in Fig. (6), enable the model parameters to

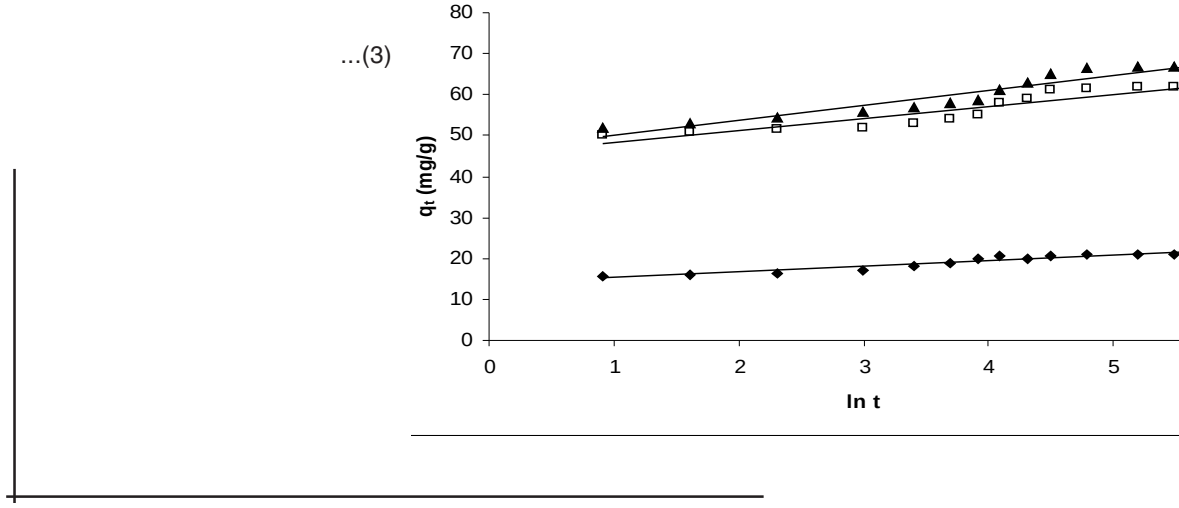

Fig. 6: Elovich model plots

The modified Freundlich model

Modified Freundlich equation was originally developed by Kuo and Lotse (1973). The linear form of modified Freundlich equation is given as:

$$\ln q_t = \ln(k_{mf} C_o) + \frac{1}{m} \ln t \qquad ...(4)$$

Where q_t is the amount of adsorbed dye (mg/g) at time t, k_{mf} the apparent adsorption rate

constant (L/g min), C_o the initial dye concentration (mg/L), t the contact time (min) and m is the Kuo–Lotse constant. The plots of the modified Freundlich model are illustrated in Fig. (7).

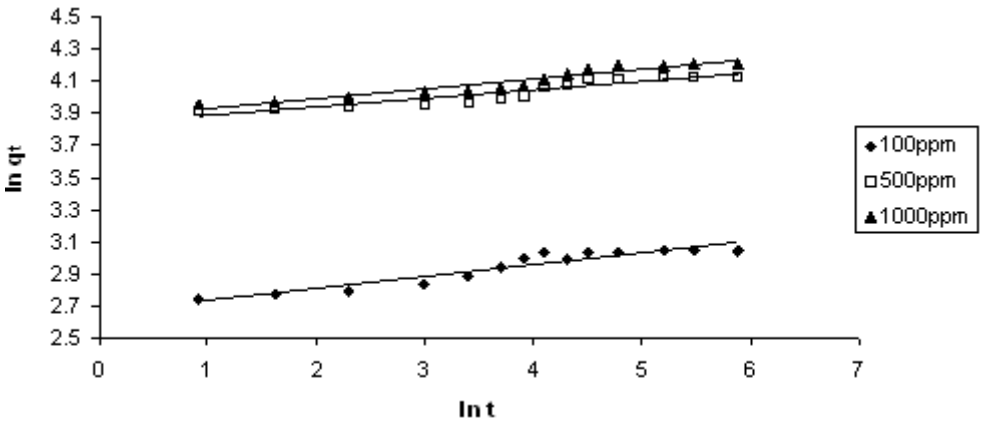

Fig. 7: Modified Freundlich model plots

All parameters of each of the used models are summarized in Table (1). The correlation coefficients, R, for the pseudo second order kinetic model were greater than that of the intraparticle diffusion coefficients, strongly suggesting a chemisorption mechanism (Ho and Mckay, 1998), which was in agreement with the results reported in our previous study (Farah *et al.,* 2007).

Table 1: Kinetic parameters for the biosorption of Astrazone blue F2RL 200% on dried biomass of Baker's yeast

	100 ppm	500 ppm	1000 ppm
Pseudo- second- order model			
k_s x 10^3 (g/mg min)	16.07	4.5	3.5
R (-)	0.999	0.999	0.999
Intraparticle diffusion model			
k_p (mg/g $min^{1/2}$)	0.345	0.824	0.997
C (mg/g)	16.219	49.75	52.18
R (-)	0.841	0.91	0.926
Elovich model			
α x 10^4 (mg/g min)	3.5	121.5	139.2
β (g/mg)	0.732	0.336	0.276
R (-)	0.943	0.932	0.956
Modified Freundlich model			
k_{mf} (L/gmin)	0.143	0.092	0.047
m (-)	13.40	18.83	16.42
R (-)	0.945	0.936	0.961

Validity of kinetic models

The adsorption kinetics of Astrazone Blue F2RL 200% onto the dried biomass of Baker's yeast was verified at different initial dye concentrations. The classical method to find out the most suitable kinetic model to represent the experimental data was the use of the correlation coefficient (R), which measures the difference between the experimental and theoretical data in linear plots only, but not the errors in kinetics curves.

Due to the inherent bias resulting from linearization, the validity of each model was determined by error function. Explanations of various error functions used in the present study are given in Table (2).

Table 2: Explanation of different error functions

Error function	Definition/ Expression	References
The residual root mean square error RMSE		Tsai and Juang, (2000)
The chi-square test X^2	$\sum_{i=1}^{N} \frac{(q_{t,\exp.} - q_{t,cal.})^2}{q_{t,cal.}}$	Ho *et al.,* (2005)
The sum of the squares of the errors SSE	$\sum_{i=1}^{N} (q_{t,cal.} - q_{t,\exp})^2$	Wong *et al.,* (2004)
The average relative error ARE	$\frac{100}{N} \sum_{i=1}^{N} \left[\frac{(q_{t,cal} - q_{t,\exp})}{q_{t,\exp}} \right]$	Kapoor and Yang, (1989)
	$\sqrt{\frac{1}{N-2} \sum_{i=1}^{N} (q_{t,\exp.} - q_{t,cal.})^2}$	

Where $q_{t,exp.}$ is the experimental data of the adsorption capacity (mg/g), $q_{t,cal.}$ is the capacity obtained by calculations from the used models (mg/g) and N is the number of data points.

The lower the values of error function the better the fit is. Table (3) lists the values of the used error functions obtained for the studied four kinetic models. By comparing the results of the obtained

Table 3: The values of different error analyses of kinetic models

	RMSE	X^2	SSE	ARE
100 ppm				
Second order model	2.01	4.65	48.72	-2.64
Intraparticle diffusion model	1.18	0.86	16.56	0.33
Elovich model	0.72	0.32	6.91	0.10
Modified Freundlich	0.75	0.35	6.88	0.06
500 ppm				
Second order model	8.47	29.69	860.31	-4.86
Intraparticle diffusion model	1.98	0.80	47.24	0.11
Elovich model	1.74	0.66	36.46	0.07
Modified Freundlich	1.67	0.60	33.71	0.03
1000 ppm				
Second order model	9.38	36.48	1054.7	-4.99
Intraparticle diffusion model	3.91	0.87	55.39	0.11
Elovich model	1.68	0.57	33.84	0.05
Modified Freundlich	1.59	0.49	30.36	0.02

values of error functions, it was found that the modified Freundlich model gave the lowest error function values and consequently best fitting the adsorption data.

Design batch adsorption from isotherm studies

Equilibrium data, commonly known as adsorption isotherms, are basic requirements for the design of adsorption systems and provide information on the capacity of the adsorbent or the amount required to remove a unit mass of pollutant under the system conditions. Assuming the batch adsorption to be a single-stage equilibrium operation, the separation process can be defined mathematically using these isotherm constants to estimate the residual concentration of dye or amount of adsorbent for desired purification (Aksu and Tezer, 2000). Based on the best fit isotherm (Farah *et al.,* 2007), a single stage adsorber as shown in Fig. (8). is designed for different solution volumes. The solution to be treated contains V solvent (L), and the initial concentration is reduced from C_0 to C_1 (mg/L). The amount of adsorbent is M and the solute concentration increases from q_0 to q_1 (mg/g). If fresh adsorbent is used, $q_0 = 0$. The mass balance equates the solute removed from liquid to that picked up by the adsorbent. The mass balance equation for the sorption system can be written according to Alkan *et al.,* (2005) as:

$$V(C_o - C_1) = M(q_o - q_1) \qquad ...(5)$$

Under equilibrium conditions

$C_1 \rightarrow C_e$ and $q_1 \rightarrow q_e$

Since the previous study (Farah *et al.,* 2007) confirmed that the equilibrium isotherm data for Astrazone Blue (F2RL 200 %) onto dried biomass of Baker's yeast best fitted by Langmuir isotherm equation so Langmuir isotherm is used for batch adsorber design. The Eq. (5) can be rearranged as

$$\frac{M}{V} = \frac{C_o - C_1}{q_o - q_1} = \frac{C_o - C_e}{q_e} = \frac{C_o - C_e}{(K_L C_e / 1 + a_L C_e)} \qquad ...(6)$$

Where K_L (L/mg) and a_L (L/g) are Langmuir constants. Equation (6) can be used to design the Astrazone Blue / dried biomass of Baker's yeast sorption system at different conditions of; dye percentage removal, initial dye concentrations, solution pH and volumes.

Fig. 9: Shows a series of plots (90%, 80%, 70% and 60% color removal) at different initial dye concentrations (50 – 250ppm) for 1 L of dye solution at 30°C and pH=7, where K_L=1.72 L/g and a_L=2.29 L/mg.

Fig. 10: Shows the required amount of yeast needed for the desired percentage removal (80%) of Astrazone Blue for different initial dye concentrations (25-200ppm) and solution volumes (1-10 L) at 30°C and pH=7, where K_L=1.72 L/g and a_L=2.29 L/mg.

Fig. 11: Shows the required amount of dried biomass to treat 1 L of dye solution at different initial dye concentrations (50-250ppm) to reach 90% dye removal at 30°C and different pH values 4, 6, 8 and 9, where K_L=1.62, 2.09, 1.85 and 2.74 L/g, respectively and a_L=3.62, 3.13, 1.09 and 1.29 L/mg, respectively.

Comparative cost of dye removal

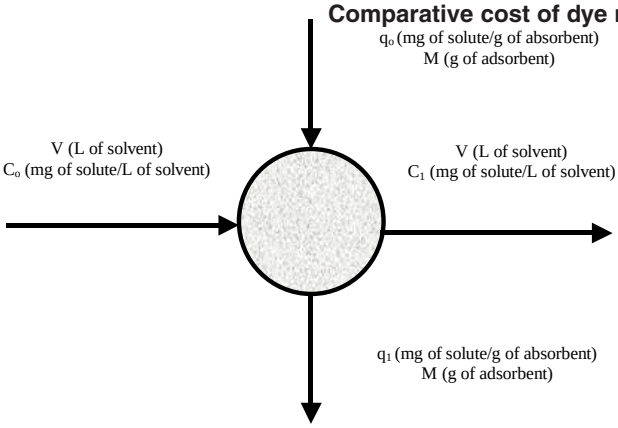

Fig. 8: Single stage batch adsorber design

Fig. 9: Initial dye concentration against adsorbent mass for different % removal

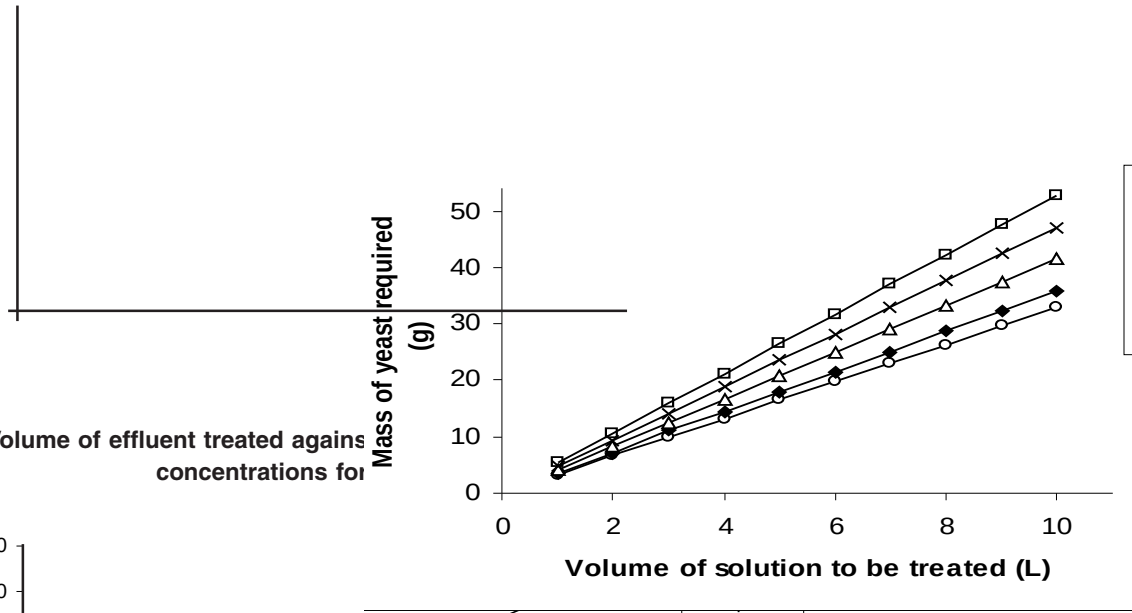

Fig. 10: Volume of effluent treated agains
concentrations for

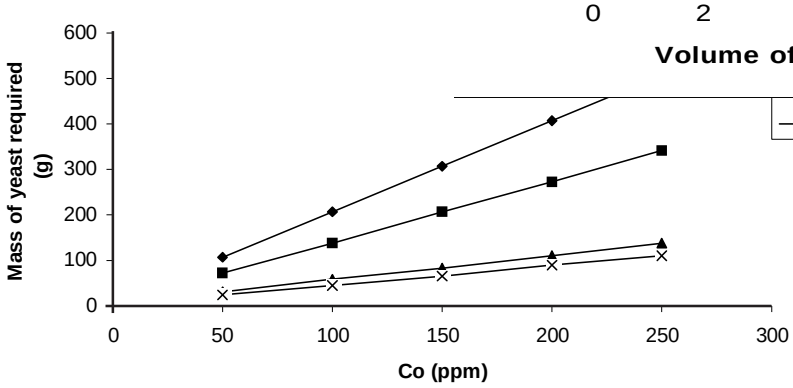

Fig. 11: Initial dye concentration against adsorbent mass at different pH values for 90% dye removal

Farah *et al.,* (2007) studied the uptake capacity of dried biomass of Baker's yeast and commercial activated carbon (NORTI) for Astrazone Blue F2RL 200% at 30°C and pH 7 with initial dye concentration range of 100-1000ppm. The maximum obtained values for adsorption capacity were used in this study to assess the quantity of adsorbent required to remove 1 kg of dye. The adsorbent quantities have been used as a basis for estimating the expected cost for the adsorption process.

The economic data recorded in Table (5) illustrate that, the expected cost of removing dye with dried biomass of Baker's yeast is about 18.79% of that when commercial activated carbon is used.

Table 5: The expected relative cost for dye removal

Adsorbent	Adsorption capacity (mg/g)	Adsorbent needed to remove 1kg dye(kg)	Unit price (L.E)*	Cost to remove 1 kg dye(L.E)	Relative cost to remove 1 kg dye(%)
Activated carbon (NORTI)	18.5	54.05	15	810.75	100
Dried Baker's yeast	70	14.29	10.66	152.33	18.79

* L.E. = Egyptian pound = 1/5.70 $

Conclusion

The rapid uptake, high capacity in addition to the relative low cost in removing Astrazone Blue dye using dried biomass Baker's yeast which was found to be 18.79 % of that of commercial activated carbon, proved that the dried biomass of Baker's yeast is a very attractive alternative sorbent material for conventional used sorbents.

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