SORPTION MODEL FOR THE REMOVAL OF M-ANISIDINE DYE FROM AQUEOUS SOLUTION USING BEAKER'S YEAST (*SACCHAROMYCES CEREVISIAE)*

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ABSTRACT

Sorption Model for the removal of M – Anisidine dye from aqueous solution, using baker's yeast has been investigated. The effect of contact time, pH, temperature, adsorbent dosage and dye concentration on the removal of M – Anisidine (dye) from aqueous solution, using baker's yeast was undertaken so as to determine the optimum condition for the sorption process. The results generated were fitted into the adsorption isotherms (Freundlich and Longmuir Models) and further into adsorption kinetics of the Pseudo – First Order and Pseudo – Second Order so as to predict adsorption rate and mechanism. The thermodynamic properties of the sorption process were also examined. The result shows that increase in contact time increased adsorption rate. 88.8% of dye was removed at 100 minutes of contact time. 30^0C was the optimum temperature for the sorption process. Adsorbent dosage decreased adsorption. 2g adsorbent dosage recorded optimum dye removal of 86%. Increase in dye ion concentration increased adsorption tendency. 50mg/L, produced optimum recondition of 82%. S_F value of 0.629mg/g was obtained. K_F as 0.041. R^2 was obtained as 0.999, which produced linear plot, indicating that pseudo – second order favourably described the adsorption process. ΔG, ΔS and ΔH, obtained shows that the process is not a spontaneous one.

Keywords: *Sorption kinetics, adsorption isotherms and thermodynamics of sorption.*

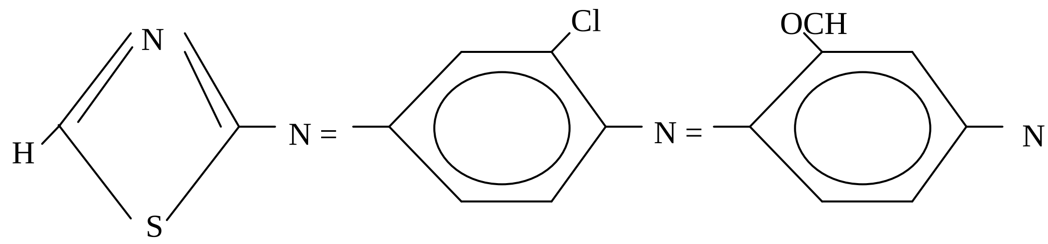
1. INTRODUCTION

The release of colored dye into the ecosystem is a dramatic source of esthetic pollution of eutrophication and of perturbation in aquatic life. Some azo dyes and their degradation products such as aromatic amines are highly carcinogenic[1]. Proper treatment of the dye effluent is thus, a matter of concern before discharge. This has led to an intensive search for the best available technology which can be used for the removal and remediation of dyes[2]. In addition, it makes the treatment of industrial effluent to be an important target for industry and environment protection. Various physical, chemical and biological methods have been used for the treatments of dye containing waste water. Some chemical oxidation by Fenton reagent ozone, UVplus H_2O_2 or NaOCl results in aromatic ring cleavage and generate chemical sludge or by products that are likely to be more toxin[3]. Aerobic biological treatment is know to be ineffective for dye removal but aerobic bioremediation enables water soluble dyes to be decolorized[4, 5].

Physical adsorption technology, i.e. by activated carbons has gained favour recently because it is favorable for high stable dyes and it is economically feasible when compared to other methods (3, 4 & 5). However, activated carbons are expensive and not easily regenerated[3]. Many studies have been undertaken to find low – cost sorbents which include peat, bentonite, fly ash, china clay, maize cob, wood shaving and silica. Only few of them could be employed effectively to remove dyes from the waste stream[6,7,8].

In the study, the potentials of baker's yeast (Saccharomyces Cerevisiae) in the removal of M-anisidine dye from aqueous solution have been investigated. It has a very low cost and it is common everywhere. Experimental parameters affecting the absorption process such as concentration, absorbent dosage, contact time and temperature were studied. The equilibriums adsorption data were fitted in Langmuir and Freundlich, isotherm, pseudo-first order and pseudo-second order were considered. Thermodynamics parameters were also estimated in order to study the nature of the system.

Structure of *(M-Anisidine*)



MATERIALS AND METHODS

Dye Solution Preparation

The dye used in this study was a standard commercial dye. The dye stock solution was prepared by dissolving accurately weighed dye in distilled water to the required concentration for each of the experimental parameter been considered.

COLLECTION AND PREPARATION OF THE ADSORBENT

The adsorbent (baker's yeast) in this was obtained from a commercial market without further purification. The adsorbent obtained was preserved in a plastic container for further studies.

EXPERIMENTAL PROCEDURES

a. EFFECT OF CONTACT TIME ON ADSORPTION

The experiment on the effect of contact time on the adsorption of the dye ion by the baker's yeast adsorbent was performed according to the previous works of Sumanjit et al,[9]. 2g of the adsorbents was weighed into five different conical flasks. Concentration of 10mg/L of the dye was prepared using distilled water and 50ml of the dye solution was measured into the five flasks. The flasks were then labelled for time intervals of 20, 40, 50, 60, 80 and 100 minutes. The flasks were tightly covered and agitated at the appropriate time intervals. At the end of each time interval, the suspensions were filtered using Whatman No. 45 filter paper and then centrifuged. The dye ion concentration was determined using DR 2010 spectrophotometer.

b. EFFECT OF ADSORBENT DOSAGE ON ADSORPTION

The experiment on the effect of adsorbent dosage in the adsorption of dye ion by the baker's yeast adsorbent was performed according to the previous works of Sumanjit et al, [9]. 2, 3, 4, 5 and 6g of the adsorbent were weighed into five different conical flasks. The flasks were then labeled for dosages differences of 2, 3, 4, 5 and 6g. The flasks were tightly covered and agitated for 20 minutes and thereafter the suspensions were filtered using Whatman No. 45 filter paper, and then centrifuged. The dye ion concentration was determined using DR 2010 spectrophotometer.

c. EFFECT OF DYE ION CONCENTRATION ON ADSORPTION

The experiment on the effect of dye concentration on adsorption was performed according to the previous works of Sumanjit et al, [9]. Several standard dye solutions of 10, 20, 30, 40 and 50mg/L were prepared. 50ml of each dye solution was added to accurately weighed 2 ± 0.01mg adsorbent in five different flasks and agitated for 20 minute. At the end of the time, the suspension was filtered using Whatman No. 45 filter paper and centrifuged. The dyes ion concentration was determined using Dr 2010 spectrophotometer.

d. EFFECT OF TEMPERATURE ON ADSORPTION

The experiment on the effect of temperature on adsorption was performed according to the previous work of Mishra, S. et al., [8]. 2g of the adsorbent was weighed into five different conical flasks and 50ml of the dye solution (10mg/L) was measured into the five flasks. The flasks were tightly covered and heated at the appropriate temperature using thermostatic water bath, at 20 minutes each. At the end of the time, each of the flasks were brought out and agitated for about 5 minutes. Then the suspensions were filtered using Whatman No. 45 filter paper and centrifuged. The dye ion concentration was determined using DR 2010 spectrophotometer.

DATA EVALUATION

1. CALCULATION OF THE DEGREE OF DYE REMOVAL

The amounts of dye removal by the adsorbent during the series of the batch experiments were determined using a mass equation expressed as shown below.

$$qe = (Co - Ce) \frac{V}{M}$$

Where qe – dye concentration on the biomass (mg/g) at equilibrium.
Ce = dye concentration in solution (mg/L) at equilibrium
Co = initial dye concentration in solution (mg/L)
V = volume of dye solution used (ml)
M = mass of adsorbent used (g)

2. KINETIC TREATMENT OF EXPERIMENTAL DATA

In order to comprehensively investigate the adsorption, the equations of pseudo-first order and pseudo-second order mechanisms were applied to experimental data.
The linear form of pseudo-first-order model is given as:
In(qe-qt) = Inqe-kt
Where qe = mass of dye adsorbed at equilibrium (mg/g)
Qt = mass of dye adsorbed at time t (mg/g)
K = equilibrium constant
The linear plot of In(qe-qt) versus t confirms the model. The linear form of pseudo-second-order model is given below as:

$$\frac{I}{qt} = \frac{I}{ho} + \frac{It}{qe}$$

Where qt = amount of dye ions on the adsorbent surface (mg/g) at anytime t.
qe = the amount of dye ions adsorbed at equilibrium (mg/g)
ho = the initial adsorption capacity (mg/g min)
The initial adsorption rate, ho is defined as:
$ho = K_2qe^2$
Where K_2 is the pseudo-second order rate constant (g/mg min)

RESULTS AND DISCUSSION

1. EFFECTS OF CONTACT TIME

The effect of stay time for the adsorption of the dye was studied between the interval of 20 minutes and was varied from 20 to 100 minutes. Figure I illustrates the adsorption of dye at different time duration. The contact time was increased from 20 to 100minutes, the amount of dye ions increased from 0.212mg/g to 0.222mg/g.
From figure I below, the amount of dye removed increased with increase in time, as well as the percentage of dye removed in which maximum percent (88.8%) was obtained at 100minutes. This may be due to the fact that as the dye solution-adsorbent, system is being agitated at longer time, more of the molecules or atoms of the dye tend to accumulate on the surface of the adsorbate until equilibrium is reacted. However, similar trends have been observed by some other researchers [8, 9, 10].

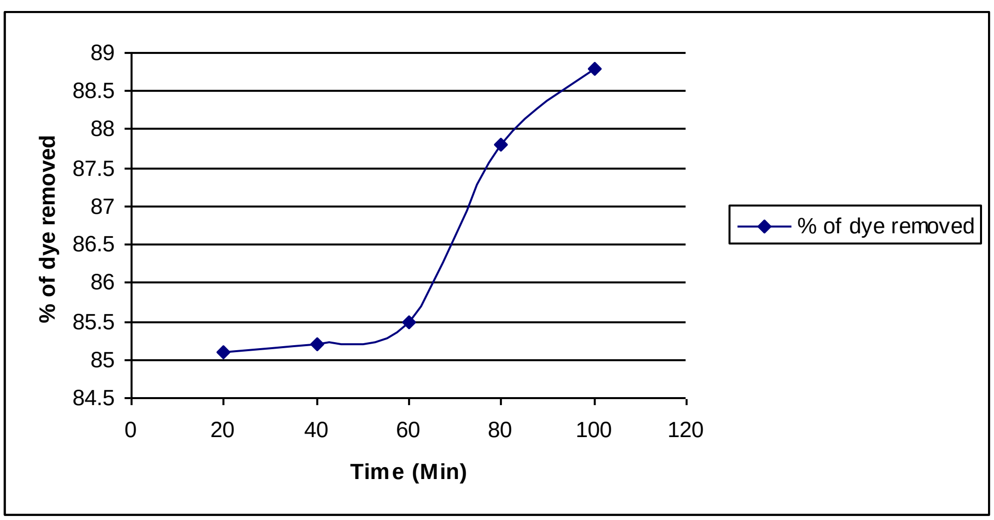


Figure I: Effect of contact time on the adsorption of dye by baker's yeast adsorbent.

2. EFFECT OF TEMPERATURE

The dependence of dye adsorption on temperature was studied within the range of temperatures 30^oc-70^oc at the interval of 10^0c. The effect of temperature on the adsorption of dye is shown in figure II in which the amount of dye adsorbed decreased from 30 to 70^oc.

Though the decrease in the amount of dye removed as the temperature increased is not much significant, the lower removal due to increasing temperature may be attributed to stronger bends being formed at lower temperature supporting the fact that adsorption is exothermic.

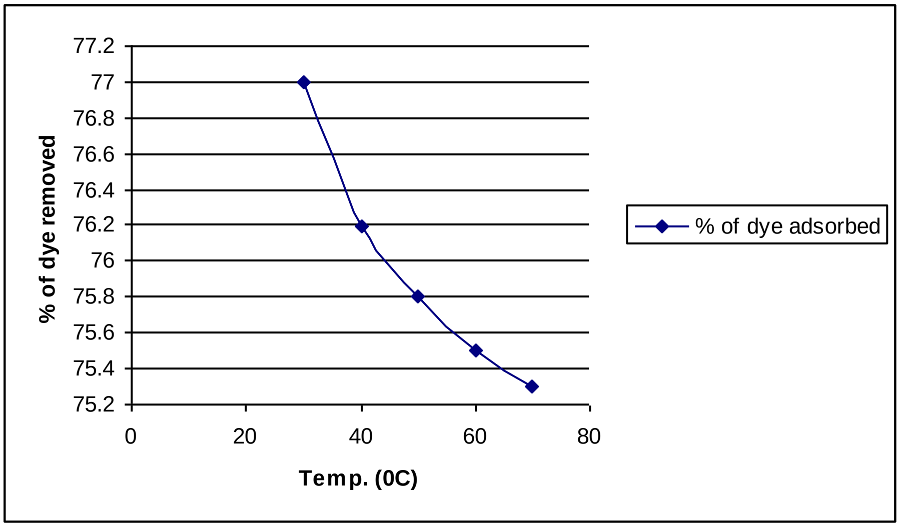


Figure II: Effect of temperature

3. EFFECT OF ADSORBENT DOSAGE

The effect of amount of adsorbent (baker's yeast) or the adsorption of dye was studied in which the amount of adsorption was varied from 2 to 6g.

Figure III shows that the dye decreased from 0.215 to 0.210mg/g as the adsorbent dosage was increased from 2-6g. It was observed that the maximum percentage (86%) of dye adsorbed is obtained at dosage (2g).

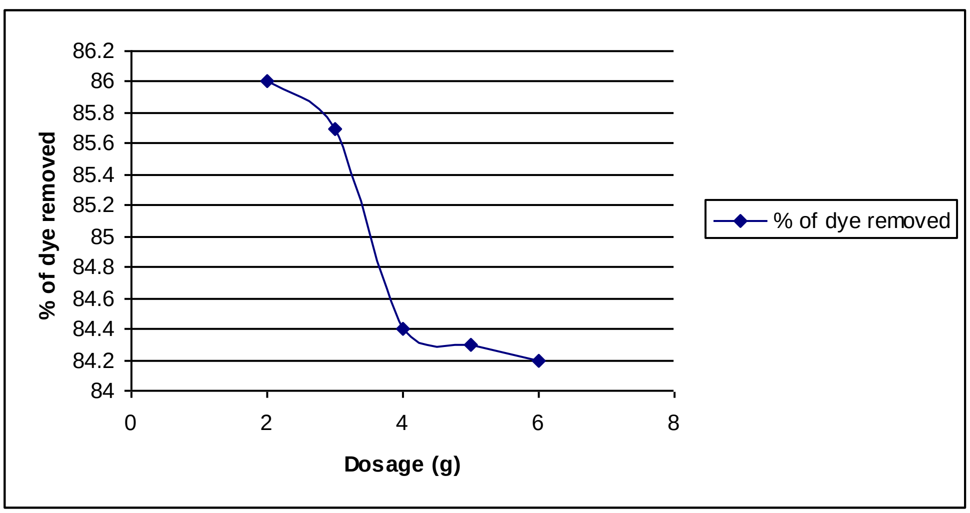


Figure III: Effect of adsorbent dosage on the adsorption of dye

However, the decrease in dye uptake could be attributed to certain reasons [11, 12]. It was observed that as particle size decrease the adsorption of the dye increase and hence the removal of the dye increases with smaller particles.

4. EFFECT OF DYE ION CONCENTRATION

The experimental result of the removal of dye by baker's yeast at various initial dye in concentrations are shown in figure IV. The adsorption capacity increased from 0.182 to 1.025mg/l, having maximum adsorption of 1.025mg/l at 50mg/l. However, the actual percent removal of the dye was found to increase with increase in initial dye concentration, (figure IV). This may be due to the fact that as the dye concentration is increasing, more dye is available for adsorption on the adsorbent. This is due to the effect of concentration gradient which is the main driving force for the adsorption process[8]. Similarly, this trend has been observed by other workers [8, 9, 11]

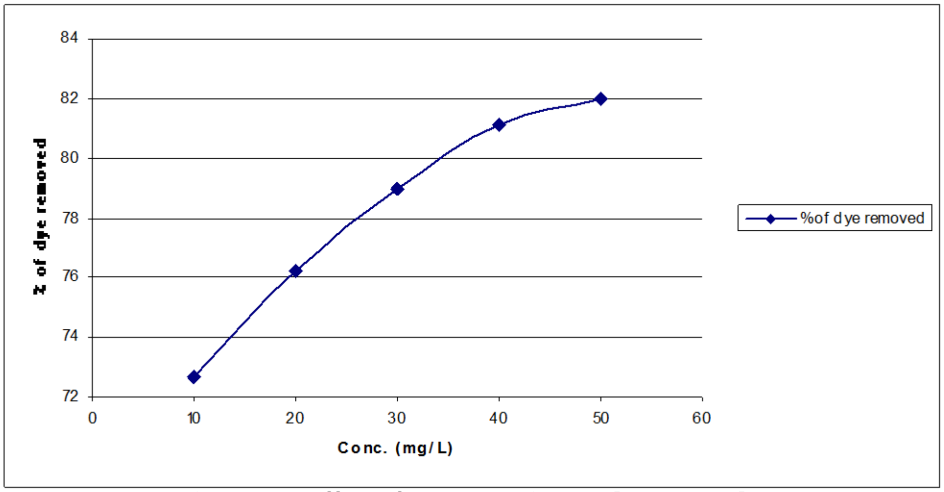


Figure IV: Effect of concentration on dye removal

LANGMUIR ISOTHERM

The Langmuir isotherm model was chosen for the estimation of maximum adsorption capacity corresponding to complete monolayer coverage on the biomass surface. The plots of specific adsorption (ce/qe) against the equilibrium concentration (ce) are shown in figure V and the linear isotherm parameters. qm k_L and the coefficient of determinations are presented in table I.

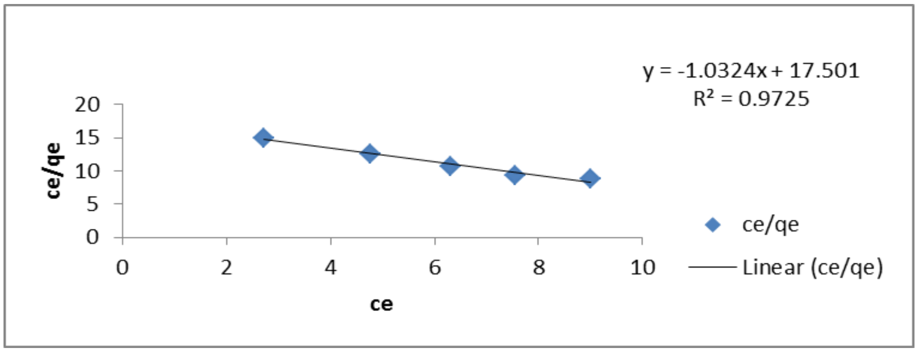


Figure V: Langmuir Equilibrium

The R^2 value suggested that the Langmuir isotherm provides a good model of the adsorption. The favorability of adsorption of the dyes ions on the baker's yeast. The Langmuir isotherm model is expressed in terms of a dimensionless constant called separation factor, S_F. The separation factor S_F is defined by the following relationship.

$$S_F = \frac{1}{I+K_L C0}$$

Where K_L = Langmuir isotherm constant Co = initial dye ion concentration of l0rng/L. The parameter indicates the shape of the isotherm as follows:

$S_F > 1$ unfavorable isotherm
$S_F = 1$ linear isotherm
$S_F = 0$ irreversible isotherm

$O<S_F<l$ favorable isotherm

The separation parameter of the dye is less than unity indicating that baker's yeast biomass is an excellent adsorbent for m-anisidine. The separations parameter and other Langmuir isotherm parameters are shown in table I below:

Table I: 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

FREUNDLICH ISOTHERM

The Freundlich model was chosen to estimate the adsorption intensity of the adsorbate on the adsorbent surface. The linear Freundlich isotherms for the adsorption of the dye ion onto baker's yeast biomass are presented in figure VI. Examination of the plot reveals that the Freundlich isotherm is also an appropriate model for the adsorption process under consideration. Table II shows the linear Freundlich sorption isotherm constant and the coefficient of determination (R^2). However, based on the value of R^2, the linear form of the Freundlich isotherm appears to produce a reasonable model for the adsorption process under consideration. The linear form of the Freundlich isotherm appears to produce a reasonable model for the adsorption of baker's yeast.

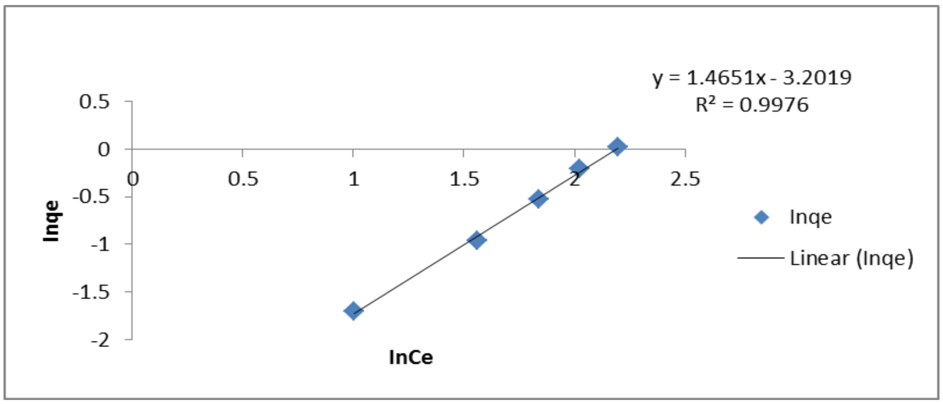


Figure VI: Freundlich Equilibrium Isotherm Model

Table II: Freundlich Equilibrium Isotherm

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

ADSORPTION KINETICS

a. Pseudo – First Order Kinetics

The kinetic of adsorption is probably the most important factor in predicting the rate at which adsorption takes place for a given system. A plot of ln(qe-qt) against t as shown in figure VII gave the pseudo- first order kinetics. From the plot it is observed that the relationship between dye ion diffusivity, In(qe-qt) and time is linear which confirm the model. n table III. The value of coefficient of determination R^2 is shown and the value indicates that pseudo-first order mode provide a good description for the adsorption of M-anisidine on the baker's yeast biomass.

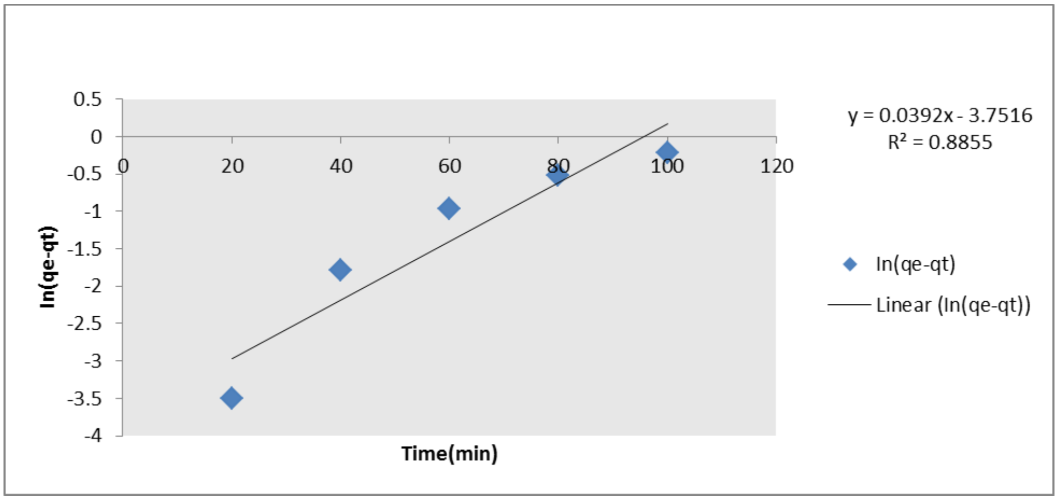


Figure VII: Pseudo First Order Plot

Table III: values of pseudo-first order kinetic parameters

Dye ion	**K_1**	**qe (mgg^{-1})**	**R^2**
M-anisidine	0.0392	0.024	0.885

However, in confirming the linearity of the pseuso-first order model, the same observation has been reported by Gunusamy[14] for the adsorption of basic dye on strongly chelating polymer.

PSEUDO - SECOND ORDER MODEL

A plot of t/qt against t as shown in figure VIII gave the pseudo-second order kinetics. From the plot, it is observed that the relationship between t/qt and t is linear which confirms the model. Also, the initial sorption rate ho, the equilibrium adsorption capacity qe, the pseudo-second order rate constant K_2 and the coefficient of determination R^2 are presented in table IV. Based on the value of coefficient of determination, R^2 it indicates that pseudo-second order model provide a better description for the adsorption process batter than pseudo-first order model. This observation has been reported by Che[15] for the adsorption of basic blue, acid blue and direct red dyes using clay-based and activated carbon adsorbent.

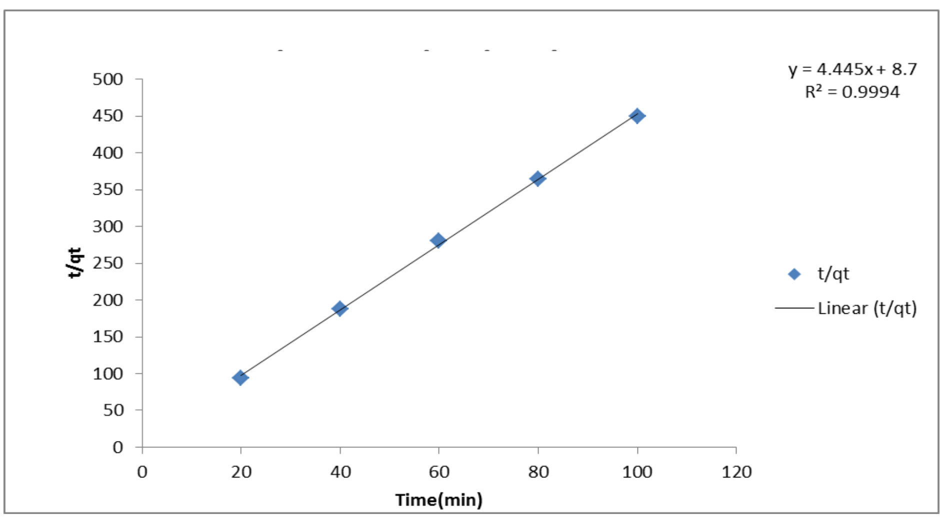


Figure VIII: Pseudo Second Order Plot

Table IV Values of Pseudo-Second Order Kinetic Parameters

Dye ion	**K_2**	**qe**	**Ho**	**R^2**
M-anisidine	0.53	0.225	0.12	0.999

THERMODYNAMIC PARAMETERS

The values of thermodynamic parameters like free energy (Δ°G), enthalpy (Δ°H) and entropy (Δ°S) of the adsorption process were calculated from the Langmuir constant K using the following equations.

$$\Delta G = -RT\ Ink_L$$

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

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

The value of ΔH° and ΔS° were calculated from the slope and intercept of the linear variation of ink with the reciprocal of temperature (l/T) and are given in table V and in figure IX.

Table IX: Thermodynamics parameters of the adsorption process.

Temp. (^{0}C)	ΔH^0(KJ/mole)	ΔG^0(KJ/mole)	ΔS^0(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

From the table, the values of ΔG° at different temperatures are positive, which shows that the adsorption process is not spontaneous. The values of enthalpy are also positive, which reveals the endothermic nature of the process. The values of entropy are positive. Meanwhile, the same observation has been reported in regards to the endothermic nature of the process by Hajira et al (11) for the removal of basic dye methylene blue by using bio-adsorbents ulva lactuca and sargassum.

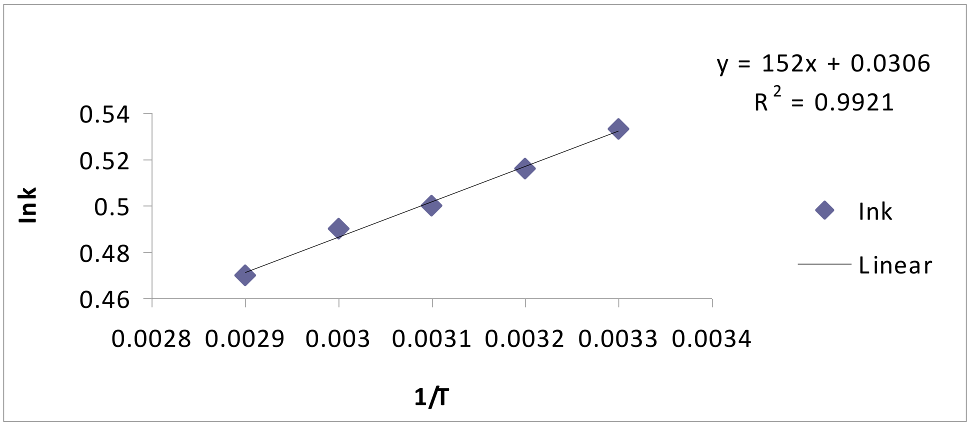


Figure IX: Plot of Ink against 1/T

CONCLUSION

The effects of M-anisidine ion concentration on adsorption capacities show that baker's yeast *(Saccharomyces Cerevisiae)* biomass adsorbed the dye ions from solution, with an increase in adsorption capacity of the biomass with increased dye ion concentration. The actual percentage removal of the dye ions from solution also increased with increase initial dye ion concentration. On the effect of adsorbent dosage on the adsorption of M-anisidine by the baker's yeast biomass there is also observed decrease in the actual percent removal. The effect of contact time increase on the amount of dye ion adsorbed and the actual percent removal. The effect of temperature on the adsorption of M-anisidine by baker's yeast decrease in the actual percent removal. However, the equilibrium data fitted the Langmuir and Freundlich isotherms very well, and the separation factor or equilibrium parameter obtained from the Langmuir isotherm showed that adsorption of the dye ions onto the baker's yeast biomass is favorable.

The kinetic data clearly established that pseudo-second order model provide a more appropriate description of the dye ions adsorption process of M-anisidine. Moreso, the thermodynamic parameters showed that the adsorption process was endothermic. On the whole, the data showed that baker's yeast biomass was successful as adsorbent for removing dyes from wastewater and may serve as an alternative adsorbent to conventional, means. Hence 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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