



SORPTION STUDIES FOR THE REMOVAL OF 1-NAPHTHYL AMINE DYE FROM AQUEOUS SOLUTION USING ORANGE PEEL BIOSORBENT



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Abstract: This study presents the sorption model for the removal of 1-naphthyl amine dye from waste water using orange peels as the adsorbent. The responses of the various experimental quantities such as contact time, adsorbent dosage, temperature and concentration were investigated. Results showed that as the adsorbent dosage was increased from 2 to 6 g the amount of dye adsorbed increased from 0.098 to 0.219 mg/g. Similarly, increase in the time interval from 20 to 100 min results in increase in the amount of dye removed from 0.110 to 0.215 mg/g. The effect of dye concentration on adsorption showed that maximum adsorption of 1.093 mg/g at 50 mg/l. For an increase in temperature from 30 to 70°C showed that the amount of dye adsorbed increased from 0.13 to 0.144 mg/g. The equilibrium values were fitted into the Langmuir and the Freundlich adsorption isotherms. A separation factor of 0.478 was obtained from the Langmuir equation representing a favourable adsorption. The coefficient of determination for both isotherms (R^2) were 0.788 and 0.970, respectively. Pseudo First order and Pseudo Second order kinetics were employed to analyze the experimental quantities in which the rate constants K_1 and K_2 were obtained as 0.029 and 0.119 g/mg/min, respectively. Thermodynamic parameters like enthalpy (ΔH), entropy (ΔS) free energy (ΔG) were also accessed, which revealed that the process is endothermic.

Keywords: Sorption isotherm, dye removal, sorption kinetics, adsorption factors

Introduction

Most coloured substances are usually synthetic in origin and made from complex molecular structure which make them more stable but more difficult to biodegrade (Mishra *et al.*, 2009). In recent times, there are 10,000 dyes commercially available. Dyes are most widely employed in rubber, leather, textiles, food, plastics, cosmetics, pharmaceutical and paper industries. The widespread use of dyes of ten results to serious pollution problems in the form of colored wastewater discharge into environmental water bodies (Hajira *et al.*, 2008). Dyes not only affect the aesthetic merit but hinder light penetration and the rate photosynthesis in the water bodies by green plants.

Consequently, the removal of coloured substances from the wastes discharged by industries, especially the textile

industries has become an issue of urgent attention so as to safeguard our environment and preserve public health. In line with efforts to reduce pollution by coloured materials, a number of conventional methods are available for the sorption of dyes from wastewaters including adsorption, coagulation, ion exchange and membrane technology (Yamin, 2007).

In this investigation, the capability of modified orange peels in the removal of 1-naphthyl amine dye from solutions was carried out. The biomass is a low cost plant waste that is common in the southern region of Nigeria. The experimental variables that affect the adsorption process such as contact time, concentration, temperature and adsorbent dosage were studied. While the thermodynamic quantities were considered in order to understand the nature of the process.

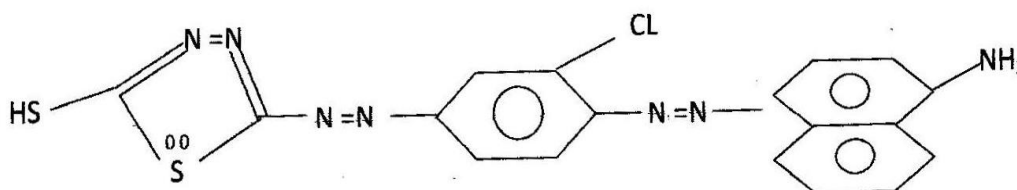


Fig. 1: The structure of 1-Naphthyl amine dye

Materials and Methods

Collection of samples and preparation of the adsorbent

The adsorbent (Orange peels) of about 2.0 kg were collected from the deposits at selling points of the Abraka main market in Etiope East Local Government Area, Delta State, Nigeria. They were washed to remove dust and other particles before it was sun dried for eight days. The orange peels were sun-dried was then ground and sieved using 450 μm sieves. The sieved adsorbent (orange peels) was preserved for further analysis.

Dye solution preparation

The dye stock solution was prepared by using 10 g of dye and dissolved in 1000 cm^3 of distilled water. This was repeated for the different sets of experimental analysis conducted.

Experimental

Effect of contact time

The influence of contact time on the removal of 1-Naphthyl amine dye by orange peel adsorbent was conducted according to the earlier studies by Yamin *et al.* (2007). A 2 g of the modified orange peels (adsorbents) was weighed and poured into five separate conical flasks. The concentrations of 10 mg/L of the dye were made using distilled water. 50 mL of the 1-Naphthyl amine dye solution was then measured into the five flasks. The flasks were further labeled for different time intervals of 20, 40, 50, 60, 80 and 100 min. The concentration of the dye ions was estimated using DR 2010 spectrophotometer.

Effect of adsorbent dosage

The effect of adsorbent dosage on the adsorption of 1-Naphthyl amine dye ion by the orange peels adsorbent was conducted following the description of Sumanjit *et al.* (2007). 2, 3, 4, 5 and 6 g of the orange peels were weighed into five flasks. 50 mL of the 1-Naphthyl amine dye solution was then measured into these five flasks. The flasks were then labeled for different dosage of 2, 3, 4, 5 and 6 g. The flasks were then tightly covered and further agitated for 20 min. The resulting suspensions were then filtered with Whatman No 45 filter paper and centrifuged. The 1-Naphthyl amine dye concentration by the use of DR 2010 spectrophotometer.

Effect of initial dye concentration

The effect of dye ion concentration on the removal of 1-Naphthyl amine dye was performed following the previous works of Sumanjit *et al.* (2007). Standard dye solutions of 10, 20, 30, 40 and 50 mg/L were prepared. 50 mL of 1-Naphthyl amine dye solution was added to an accurately weighed 2±0.01 g modified adsorbent in five different flasks before it was agitated for 20 min towards the end of each time interval, the suspensions were filtered with the aid of Whatman No 45 filter paper and centrifuged. The dye ion concentrations were estimated using DR 2010 spectrophotometer.

Effect of temperature

The effect of temperature on the adsorption process was conducted according to the work of Mishra *et al.* (2009). A 2 g of the orange peels was measured and poured into five conical flasks. 50 mL of the dye solution (10 mg/L) was measured into the five flasks. The flasks were then labeled for temperature readings of 30, 40, 50, 60, and 70°C. The flasks were tightly covered and heated at the various temperatures using thermostatic water bath for 20 min time interval. Towards the end of each time intervals, the flasks were brought out and further agitated for another 5 min. The resulting suspensions were filtered using a Whatman No. 45 filter paper and then centrifuged. The of 1-Naphthyl amine dye ion concentrations were determined by DR 2010 spectrophotometer.

Data evaluation of adsorption data

Estimation of the degree of 1-Naphthyl amine dye removed

The quantity of dye removed by the orange peel (adsorbent) during the various batches of experiments were determined by the mass balance equation presented in equation 1.

$$qe = (Co - Ce) \frac{V}{M} \tag{1}$$

Where: qe = dye concentration on the orange peels (biomass) (mg/g) at equilibrium; Co= The initial dye concentration in solution (mg/l); Ce = 1-Naphthyl dye concentration in solution (mg/l) at equilibrium; M= the mass of adsorbent used (g); V = the volume of dye solution used (mL)

Adsorption kinetics

In order to understand the mechanism of adsorption process, the models of Pseudo – First order and Pseudo – Second order models were applied to treat the adsorption data (Horsfall *et al.*, 2003).

The linear equation for Pseudo-First order model kinetics is given as equation 2.

$$\ln (qe - qt) = \ln qe - kt \tag{2}$$

Where: k = The equilibrium rate constant; qe = The mass of dye adsorbed at equilibrium (mg/g); qt = The mass of dye adsorbent at time t (mg/g)

A plot of ln (qe – qt) against t confirms the model.

The Pseudo-second equation is given in equation 3

$$t/qt = 1/ho + t/qe \tag{3}$$

Where: ho = The initial adsorption capacity (mg/g min); qt = The amount of dye ion on the adsorbent surface mg/g) at time t; qe = The amount of dye ion adsorbed at equilibrium (mg/g) The initial adsorption rate, ho is further defined by the equation 4

$$ho = k_2 qe^2 \tag{4}$$

However, k₂ is the Pseudo-Second order rate constant (g/mg min).

Results and Discussion

Influence of contact time on adsorption

The response of time on the removal of the removal of 1-Naphthyl amine dye were studied within the intervals of 20 min and were further varied from 20 to 100 min. The Fig. 1 below illustrates the adsorption trend of dye at varying time duration. As contact time for the process was increased from 20 to 100 min the quantity of dye removed also increased as well from 0.110 to 0.215 mg/g. The Figure also revealed that the amount of 1-Naphthyl amine dye removed increased with increase in the time and the percentage of dye removed with maximum percent (86.0%) was obtained at 100 min. This observation could be linked to the fact that the dye solution adsorbent system when agitated at longer time, more of the molecules of the dye appear to accumulate on the adsorbent surface until an equilibrium is attained. However, similar observations have been made by some other researchers (Sumanjit *et al.*, 2007; Hajira *et al.*, 2008; Mishra *et al.*, 2009).

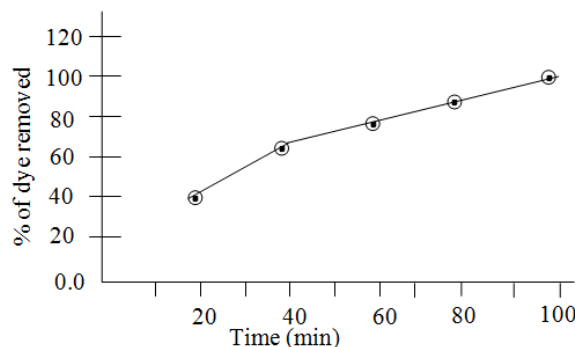


Fig. 2: Effect of contact time on the adsorption of the dye by orange peels adsorbent

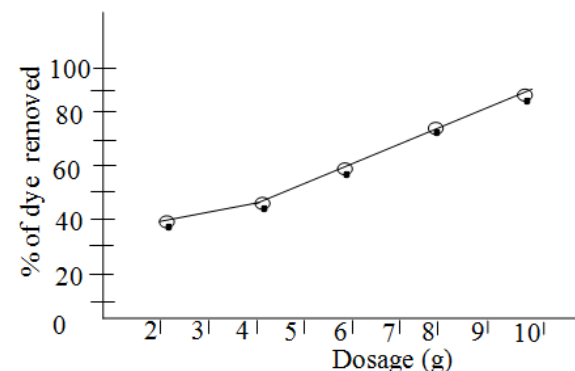


Fig. 3: effect of adsorbent dosage on dye adsorption

Influence of adsorbent dosage on dye adsorption

The effect of the amount of adsorbent (orange peels) on the removal of 1-naphthyl – amine dye was conducted. The dosage of adsorbent was varied from 2 – 6 g. Fig. 2 represents the response of adsorbent dosage on the adsorption of the dye. The quantity of dye removed increased from 0.098 to 0.219 mg/g as the adsorbent dosage was increased from 2 – 6 g.

From the plot, it is evident that the optimized adsorbent dose was 6 g where 0.219 mg/g of dye was adsorbed. Similarly, the maximum percent (87.8%) of dye adsorbed was obtained at this dosage 6 g which is represented in Fig. 3. The observed increase in dye uptake could be linked to certain behaviours.

According to Mishra *et al.* (2009), increase in dye uptake can be attributed to the fact that increasing adsorbent dosage creates more binding sites for adsorption.

Influence of dye ion concentration on adsorption

Results of the removal of 1-naphthyl amine dye by orange peels (adsorbent) at various initial dye ion concentrations are represented in Fig. 3. The adsorption capacity of the adsorbent increased from 0.188 to 1.093 mg/g when the dye concentration was increased from 10 to 50 mg/L with maximum adsorption of 1.093 mg/g at 50 mg/L.

Similarly, the actual percent removal of the dye was observed to increase with increase in the initial dye concentrations. This may be attributed to the fact that as the dye concentration is increasing, more dye was made available for adsorption on the adsorbent. Moreover, the effect of concentration gradient which appears to be the main driving force for the adsorption process could contribute.

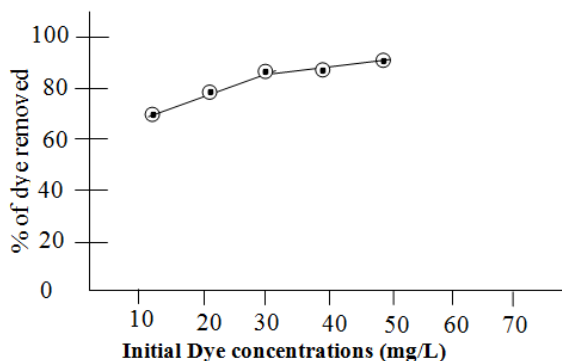


Fig. 4: Effects of concentration on dye removal

The Effect of temperature on dye adsorption process

The dependence of dye removal on temperature was monitored within the range of temperature 30 – 70°C at the interval of 10°C. The observation is shown in the Fig. 5. The amount of dye adsorbed increased from 0.130 to 0.144 mg/g with increase in temperature from 30 to 70°C.

Furthermore, increase in the amount of dye removal with temperature increase was not much significant. Hiroyuki *et al.* (1994) noted that higher dye removal due to increase in temperature may be attributed to chemical reaction taking place between the functional groups of the adsorbate/adsorbent and the dye. Moreover, at high temperature there is always an increase in the mobility potential of large dye ion producing a swelling effect within the internal structure of the adsorbent. This enabling the large dye molecules to penetrate further (Ho *et al.*, 1996).

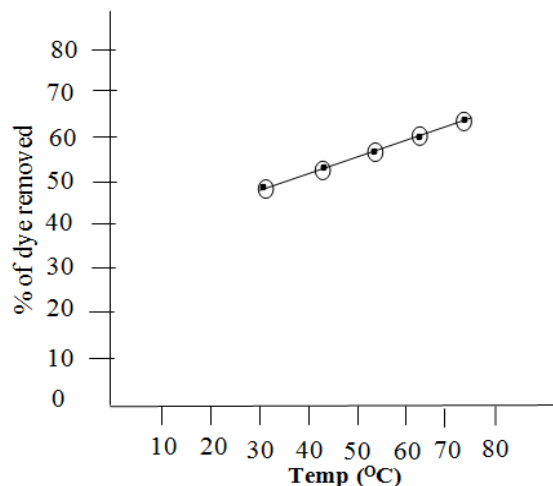


Fig. 5: Effect of temperature on dye removal

It is important to note that the behaviour of increased adsorption with increased temperature has also been reported by other researchers (Gunmany 2002; Hajira *et al.*, 2008).

The Langmuir isotherm

Langmuir isotherm model was adopted to estimate the maximum adsorption capacity over complete monolayer coverage on the biomass surface. The plot of specific adsorption (ce/qe) to the equilibrium concentration (ce) is presented in Fig. 6 and the linear isotherm parameters Qm and KL and the coefficient of determinations are presented in the Table 1.

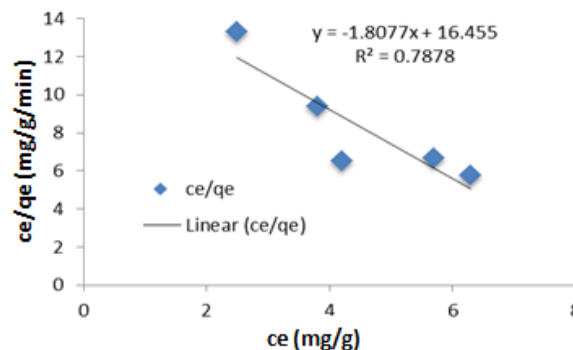


Fig. 6: Langmuir plot for concentration

The R² value revealed that the Langmuir isotherm appears to provide a good model of the adsorption process. The favorability of the sorption process was tested using the essential features of the Langmuir isotherm, expressed in terms of a dimensionless constant referred to as separation factor (S_f) proposed by Poots *et al.*(1978). The separation factor S_f is described by the relationship.

$$S_f = \frac{1}{1 + k_1 C_o} \quad (5)$$

C_o = the initial dye ion concentration of 10 mg/l; K₁ = the Langmuir isotherm constant; S_f indicates the shape of the model as noted below;

S_f = 0 irreversible isotherm; S_f > 1 unfavourable isotherm; 0 < S_f < 1 favourable isotherm; S_f = 1 linear isotherm

The separation factor for the process is less than one indicating that orange peel biomass appears to be an excellent adsorbent for the 1-naphthyl amine dye. The separation quantity and other Langmuir isotherm quantities are presented in Table 1.

Table 1: Linear Langmuir isotherm quantities

Dye ion	qm (mg ⁻¹)	K _L (Lg ⁻¹)	R ²	S _r
1-NA	1.808	0.109	0.788	0.478

R² = Coefficient of determination; S_r = Separation factor; K_L = Langmuir constant; qm = Dye concentration at equilibrium; Dye ion = dye concentration

The Freundlich isotherm evaluation

Freundlich isotherm adopted to estimate the adsorption capacity of the dye on the adsorbent surface. The linear forms of the isotherms for the process are presented in Fig. 7. The plot revealed that Freundlich isotherm is also appearing as an appropriate model to describe the adsorption process. Table 2 shows the linear Freundlich sorption isotherm constants and the coefficient of determination (R²). The linear pattern of the Freundlich isotherm appears to produce a reasonable model which describes the adsorption process under consideration based on the value of R².

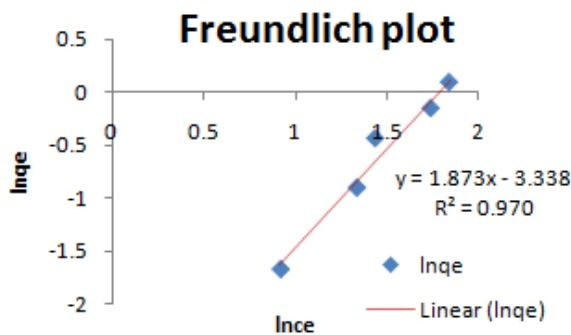


Fig. 7: Freundlich plot

Table 2 Freundlich isotherm constant

Dye ion	1/n	n	R(Lg ⁻¹)	R ²
1-NA	1.873	0.534	0.035	0.970

Dye ion = dye concentration; 1/n = Adsorption intensity; n = Adsorption coefficient; R = Affinity of adsorbent towards the adsorbate; R² = Coefficient of determination

Adsorption kinetics

Pseudo-first order model

The kinetics of the adsorption process is probably the most important factors for predicting the rate in which adsorption takes place for a given system. The plot of ln(qe - qt) against t as presented in Fig. 8 gave the Pseudo - First order kinetics. From the flow, it was observed that the relationship between dye ion diffusivity, ln(qe - qt) and the time is linear which confirm the model. In Table 3 and Fig. 8, the values of the coefficient of determination R² are shown. The values obtained indicated that the Pseudo -First order model provides a good description for the adsorption of 1-naphthyl amine dye by the orange peel biomass.

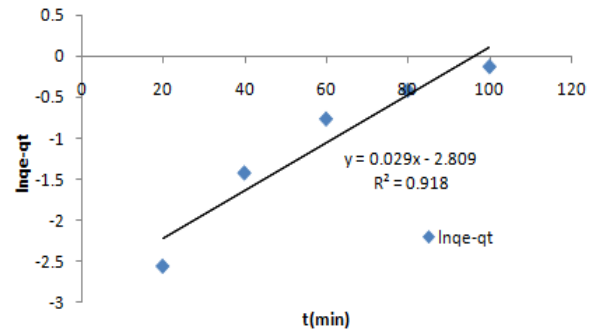


Fig. 8: Pseudo-first order plot

Table 3: Values of pseudo first order kinetic parameter

Dye ion	K ₁	qe (mg/g)	R ²
1-NA	0.029	0.060	0.919

Dye ion = dye concentration; K₁ = pseudo first order rate constant; qe = amount of dye adsorbed at equilibrium; R² = Coefficient of determination

Pseudo-second order model

The plot of t/qt against t presented in Fig. 9 gave the Pseudo-second order kinetics. From the graph, it was observed that the relationship between t/qt and t is linear confirming the model. Similarly, the initial sorption rate (ho), the equilibrium adsorption capacity qe, the pseudo - second order rate constant k₂ and the coefficient of determination R² are presented in Table 4. The values of coefficient of determination R² it indicated that the Pseudo-Second order model provide a better description for the adsorption process than the Pseudo-First order model. This observation was also reported by Arami *et al.* (2005) for the adsorption of dyes from coloured textile wastewater by orange peels adsorbent.

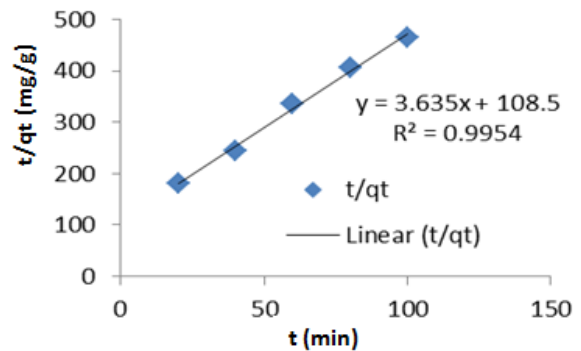


Fig. 9: pseudo second order plot

Table 4: Values of pseudo second order kinetic variables

Dye ion	ho(mg/g/min)	K ₂ (g/mg(min))	qe (mg/g)	R ²
1-NA	0.009	0.119	0.275	0.995

Dye ion = dye concentration; ho = initial adsorption capacity; K₂ = pseudo second order rate constant; qe = amount of dye adsorbed at equilibrium

Thermodynamic parameters

The values of the thermodynamic quantities like enthalpy (ΔH°), free energy (ΔG°), and entropy (ΔS°) of the adsorption process were determined from the Langmuir constant K adopting the following equations;

$$\Delta G = -RT \ln K \quad (6)$$

$$\ln K = \Delta S - \Delta H \quad (7)$$

$$\Delta G = \Delta H - T\Delta S \quad (8)$$

The values of ΔH° and ΔS° were thus calculated from the slope and intercept of the linear graph of $\ln K$ with the reciprocal of temperature ($1/T$). The thermodynamics quantities of the process at various temperatures are shown in Fig. 9.

The linear variation graph of $\ln k$ against $1/T$ is given as shown in Fig. 10.

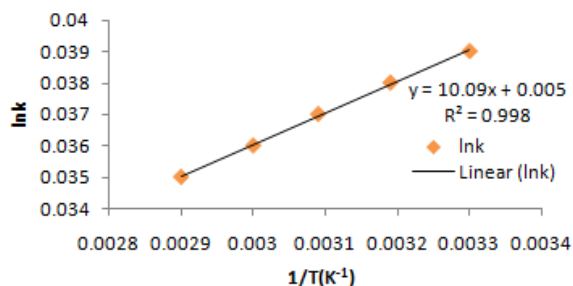


Fig. 10: linear variation of $\ln k$ against $1/T$

From the Table 4, the free energy ΔG° is the fundamental criterion of spontaneity but its corresponding value in this sorption process is positive showing that the process is Non-spontaneous. The values of enthalpy are also positive which revealed the endothermic situation of the process. The values of the entropy are very low; however positive indicating the process is physical.

Conclusion

The effects of 1-naphthyl amine ion concentration on adsorption capacities of orange peels waste biomass revealed 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 in the initial dye ion concentrations. The effect of contact time and temperature on adsorption showed the same trend in the increase on the amount of dye adsorbed and the actual percent removal. Consequently, the equilibrium data fitted Langmuir and Freundlich isotherms adequately and the separation factor obtained from the Langmuir isotherm revealed that the adsorption of the dye ions onto the orange peel biomass was favorable.

Conflict of Interest

Author declares there is no conflict of interest related to this study.

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