

Equilibrium sorption of anionic dye from aqueous solution by palm kernel fibre as sorbent

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Abstract

Palm kernel fibre was investigated for its ability to perform as a suitable sorbent for anionic dye from aqueous solution. The effect of sorbent dose and temperature was investigated using a batch sorption technique. The results revealed the potential of palm kernel fibre, an agricultural waste, as a low-cost sorbent for the anionic dye examined. The isotherm data were closely fitted to the Langmuir equation and the dye sorption capacity of palm kernel fibre increased as the sorbent dose decreased. Maximum saturated monolayer sorption capacity of palm kernel fibre for 4-bromoaniline-azo-1,8-dihydronaphthalene-3,6-disodiumsulphate was 38.6 mg/g. Thermodynamic parameters such as change in the free energy, the enthalpy, and the entropy were also evaluated. In addition, relationships between sorbent dose and Langmuir constants were developed and are presented.

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1. Introduction

As a result of the total ban on importation of textile and leather products by the Federal Government of Nigeria, there has been increased activity in the local textile, finishing and dyeing industries so as to meet the demands for textile and colored products. Large volumes of wastewater are therefore expected to be generated during the dyeing and finishing processes which are usually characterized by components high in both color and organic content [1]. It is suspected that this generated wastewater may contain as much as 10–15% of the dyes released during the dyeing process [2]. Majority of these dyes are synthetic in nature and are usually composed of aromatic rings in their structure, which makes them carcinogenic and mutagenic [3], inert and non-biodegradable when discharged into waste streams [4]. Therefore, the treatment of

such wastewater containing soluble dyes thus requires complete removal followed by secure disposal [5].

Sorption of colored components from aqueous solution has proven to be an excellent way to treat effluent and also a cost effective technique. Several studies have shown that numerous low-cost materials have been successfully applied in the removal of dyes from aqueous solution, some of which are sugar cane dust for basic dyes, namely Basic Violet 10, Basic Violet 1, and Basic Green 4 [6], giant duckweed for Methylene Blue [7], Neem leaf powder for Brilliant Green [8], peat for Basic Blue 69 and Acid Blue 25 [9], rice husk for Malachite Green [10], tree fern for Basic Red 13 [4], and Fuller's earth for Methylene Blue [11].

The search for new, cheap, available and economic sorbent especially in developing countries like Nigeria is eminent; so as to meet the purification needs for the large volume of textile industry effluents produced on a daily basis. Research reports by Onwuka et al. [12] from Nigeria showed that a variety of household wastes and crop residues exist in the environment and a common residue of interest is the palm kernel and its

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fibre. These crop residues are used in varying extents but, in some cases, they are burnt or left unutilized on the fields. According to their findings, over 66% of the palm kernel and its fibre are burnt, a little above 5% are used as feed to animals and over 29% are left on the fields. Palm kernel fibre is a waste product of palm oil production and it consists mainly of cellulose, fibre, and residual oils.

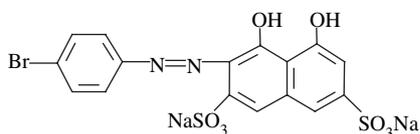
This study is aimed at investigating the possibilities of the use of palm kernel fibre, a local readily available agricultural waste product in Nigeria for the removal of anionic dye (4-bromoaniline-1,8-dihydronaphthalene-3,6-disodiumsulphate) from aqueous solution. This class of dyes is the most problematic, because they tend to pass through conventional treatment systems unaffected [13]. The system variables studied include sorbent dose, initial concentration of the dye, and temperature.

2. Materials and methods

2.1. Materials

Palm kernel fibre used in this study was obtained from the Nigerian Institute for Oil Palm Research (NIFOR), Benin City, Nigeria. The palm kernel fibre was allowed to dry with the residual oil, after processing for about two months. The raw fibre was dried in an oven at 80 °C for 6 h, grounded and screened through a set of sieves to obtain particles of size 50–60 µm. The sieved fibre was steeped in 0.02 mol/dm³ HCl overnight. The acid solution was filtered off and the fibre was washed with distilled water until the pH of the washes becomes neutral. The fibre was dried at 80 °C for 24 h and stored in an air-tight container.

The dye solution was prepared in distilled water using 4-bromoaniline-azo-1,8-dihydronaphthalene-3,6-disodiumsulphate (BDH); all working solutions were prepared by diluting the stock solution with distilled water. The structure of the dye molecule is shown below. The wavelength of maximum sorption in the visible light range is 534 nm, molecular weight is 547.29 and melting point is 165 °C.



4-bromoaniline-azo-1,8-dihydronaphthalene-3,6-disodiumsulphate

2.2. Methods

The proximate composition of the coconut copra meal was determined using the Association of Official Analytical Chemist (AOAC) [14]. The IR spectra of the copra meal sample were recorded using KBr wafers in conjunction with a Perkin–Elmer infrared spectrophotometer. KBr wafers

were prepared by mixing a given sample with KBr crystals and the resulting mixture was ground to a fine powder and heated for 1 h at 373 K. Finally, the mixture was pressed into a KBr wafer under vacuum conditions and used as such for IR studies.

2.2.1. Effect of sorbent dose at constant dye concentration

The effect of sorbent dose on the equilibrium uptake of dye ions was investigated with sorbent masses of 0.25, 0.75, 1.25, 1.75, and 2.25 g. The experiments were performed by adding the known weights of palm kernel fibre to five 100 ml beakers containing 50 ml of 0.25 mmol/dm³ solution at pH 5.00. The flasks were shaken at 150 rpm and 297 K for 4 h and the equilibrium concentration of the remaining dye was determined spectrophotometrically.

2.2.2. Isotherm experiment using 0.25 g of fibre

Equilibrium uptake of dye ions was investigated at 297 K with sorbent mass of 0.25 g of palm kernel fibre in contact with 50 ml of dye solutions of concentrations ranging from 0.25 to 4.00 mmol/dm³ and at pH 5.00. The flasks were shaken at 150 rpm and 297 K for 4 h and the equilibrium concentration of the remaining dye was determined spectrophotometrically.

2.2.3. Effect of sorbent dose at various initial concentrations

Equilibrium uptake of dye was investigated at 297 K with sorbent masses of 0.25, 0.75, 1.25, 1.75, and 2.25 g of palm kernel fibre in contact with dye solutions of concentrations ranging from 0.25 to 4.00 mmol/dm³ and pH 5.00. The flasks were shaken at 150 rpm and 297 K for 4 h and the equilibrium concentration of the remaining dye was determined spectrophotometrically.

2.2.4. Effect of temperature

Batch sorption was performed at temperatures ranging from 297 to 328 K, using sorbent weights of 0.25, 0.75, 1.25, 1.75, and 2.25 g and initial dye concentration from 0.25 to 4.00 mmol/dm³ set at pH 5.00. The flasks were shaken at 150 rpm for 4 h and the equilibrium concentration of the remaining dye was determined spectrophotometrically.

2.2.5. Sorbent re-generation

The sorbents (0.25, 0.75, 1.25, 1.75, and 2.25 g) that were used for sorption of 0.25 mmol/dm³ of dye solution were separated from the dye solution by centrifugation. The dye-loaded sorbents were filtered using Whatmans filter paper and washed gently with water to remove any unadsorbed dye. Then the spent sorbents were agitated in 50 ml of distilled water (the pH was left at 5.00) and the desorbed dye was then estimated.

3. Results and discussion

Basic forms of Langmuir isotherm [15] have reasonable agreement with a large number of experimental systems

including those, which have different interfaces between the two phases. The rate of sorption to the surface should be proportional to a driving force times an area. The driving force is the concentration of the solution and the area is the amount of bare surface. If the fraction of covered surface is ϕ , the rate per unit of surface is:

$$r_a = k_a C(1 - \phi) \quad (1)$$

The desorption from the surface is proportional to the amounts of surface covered:

$$r_d = k_d \phi \quad (2)$$

where k_a and k_d are the rate constants, r_a is the sorption rate, r_d is the desorption rate, C is the concentration in the solution and ϕ is the fraction of the surface covered.

The two rates are equal at equilibrium and we find that:

$$\phi = \frac{k_a C_e}{k_d + k_a C_e} \quad (3)$$

and

$$K_a = \frac{k_a}{k_d} \quad (4)$$

Since q_e is proportional to ϕ :

$$\phi = \frac{q_e}{q_m} \quad (5)$$

The saturated monolayer sorption capacity, q_m , can be obtained. When ϕ approaches 1, then $q_e = q_m$.

The saturated monolayer isotherm can be represented as a linear form:

$$q_e = \frac{q_m K_a C_e}{1 + K_a C_e} \quad (6)$$

The above equation can be rearranged to the following linear form:

$$\frac{C_e}{q_e} = \frac{1}{K_a q_m} + \frac{1}{q_m} C_e \quad (7)$$

where C_e is the equilibrium concentration (mmol/dm³), q_e is the amount of dye sorbed (mmol/g), q_m is q_e for a complete monolayer (mmol/g), K_a is the sorption equilibrium constant (dm³/mmol). A plot of C_e/q_e versus C_e should give a straight line of slope $1/q_m$ and an intercept of $1/K_a q_m$.

Based on fundamental thermodynamics concept, it is assumed that in an isolated system, energy cannot be gained or lost and the entropy change is the only driving force. In environmental engineering practice, both energy and entropy factors must be considered in order to determine which process will occur spontaneously. The Gibbs free energy change, ΔG^0 , is the fundamental criterion of spontaneity. Reactions occur spontaneously at a given temperature if ΔG^0 is a negative quantity. The free energy of the sorption reaction, considering

the sorption equilibrium constant, K_a , is given by the following equation:

$$\Delta G^0 = -RT \ln K_a \quad (8)$$

where ΔG^0 is the standard free energy change (J); R is the universal gas constant, 8.314 J/K mol and T is the absolute temperature (K).

The Gibbs free energy change, ΔG^0 , can be represented as follows:

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \quad (9)$$

A plot of ΔG^0 versus T will be linear. Enthalpy change, ΔH^0 , and entropy change, ΔS^0 , were determined from the slope and intercept of the plots.

3.1. Characteristics of palm kernel fibre

The percentage proximate composition of palm kernel fibre on dry weight basis is: carbohydrate 38.15%, lipid 9.00%, fibre 19.90%, ash 6.30%, protein 14.80%, moisture 9.78%, Ca 0.63%, P 0.45% and Mg 0.29%. IR measurement of the palm kernel fibre showed the presence of the following groups: C=O (1680.1 cm⁻¹), COOH (3300–2500, 1110.8 cm⁻¹), -OH (3426.2 cm⁻¹), C=C (1.675 cm⁻¹), C-N (1030–1230 cm⁻¹), N-H (1548.8 cm⁻¹) and NH₂ (3400–3500 cm⁻¹).

3.2. Isotherm experiment

Sorption isotherm usually describes the equilibrium relationship between sorbent and sorbate, i.e. in this case, the equilibrium relationship of the ratio between the quantity of dye sorbed and that remaining in aqueous solution at a fixed temperature at equilibrium. By plotting solid phase concentration against liquid phase concentration, graphically it is possible to depict the equilibrium isotherm. The isotherm thus yields certain constants whose values express the surface properties and affinity of the sorbent. In order to optimize the design of sorption system to remove dyes from effluents, it is important to establish the most appropriate correlation for the equilibrium curve. Therefore, the most commonly used Langmuir isotherm was applied to model the experimental data. Fig. 1 shows the plot of Langmuir isotherm along side with experimental data at different sorbent doses. The Langmuir isotherm model was found to fit closely with the experimental data, as seen from the coefficient of determination in Table 1. The Langmuir isotherm model assumes a monolayer sorption of dye molecules on the sorbent surface. Langmuir isotherm model has also been successfully applied to other anionic dye-sorbent systems such as Acid Red 57 onto sepiolite [21], Procion Crimson H-EXL (PC) onto pyrophyllite [22], Acid Yellow 36 on carbon from sawdust [23], and Acid Blue 113 on activated carbon [24]. Langmuir isotherm is applicable to homogeneous sorption, where the sorption of each sorbate molecule onto the surface has equal

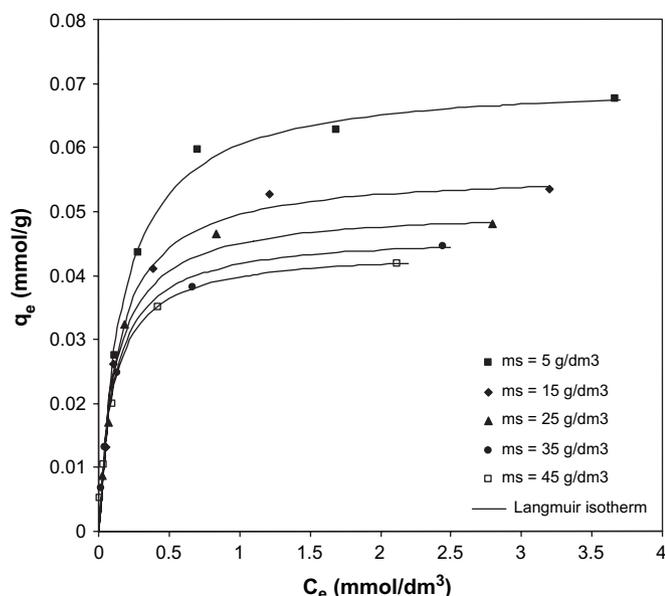


Fig. 1. Langmuir isotherm for the sorption of anionic dye using palm kernel fibre at various doses. Solution pH: 5.00; agitation speed: 150 rpm; temperature: 297 K.

sorption activation energy [15]. The Langmuir constants q_m and K_a were calculated and their values are given in Table 1.

3.3. Effect of sorbent dose

The effect of changing sorbent dose on the removal and sorption capacity of various dye/palm kernel fibre systems was examined using isotherm experiments with the data analyzed with the linear form of the Langmuir isotherm which was found to give the best fit with the experimental data. Isotherms were determined for five palm kernel fibre dose ranging from 5 to 45 g/dm³ with contact time of 4 h. Fig. 2 shows an increase in the palm kernel fibre dose from 5 to 45 g/dm³, increases the percentage of dye removal, R_m , from aqueous solution from 55.2 to 95.6%, but decreases the monolayer capacities, q_m , from 0.0705 to 0.0439 mmol/g. It is apparent that by increasing the dose of the palm kernel fibre, the number of sorption sites available for sorbent–biosolute interaction is increased, thereby resulting in the increased percentage of dye removal from the solution. The decrease in sorbent capacity, i.e. the amount of dye sorbed per unit weight of sorbent with increase in palm kernel fibre dose, may be attributed to two reasons. The increase in sorbent dose at constant dye concentration and volume will lead to unsaturation of sorption sites through the sorption process [25,26] and

Table 1
Langmuir isotherm constants for anionic dye at various doses

m_s (g/dm ³)	q_m (mmol/g)	K_a (dm ³ /mmol)	r^2
5	0.0705	5.95	1.000
15	0.0561	7.53	0.999
25	0.0503	8.42	0.999
35	0.0464	9.10	1.000
45	0.0439	9.65	1.000

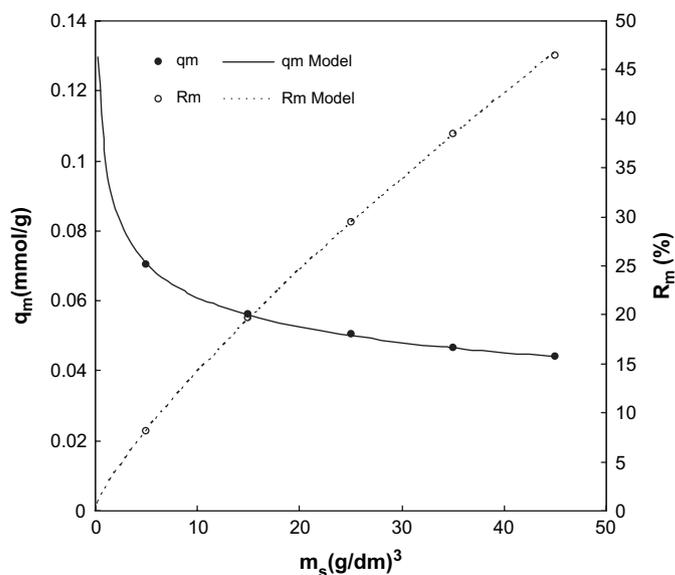


Fig. 2. Effect of palm kernel fibre dose, m_s , on the percentage of dye removal, R_m , and amount of dye sorbed, q_m . Sorbent dose: 5 g/dm³; solution pH: 5.00; agitation speed: 150 rpm; temperature: 297 K.

secondly may be due to particulate interaction such as aggregation resulting from high sorbent dose [27]. Such aggregation would lead to a decrease in total surface area of the sorbent and an increase in diffusional path length [25]. The corresponding linear plots of the values of q_m , R_m , and K_a against m_s were regressed to derive a mathematical relationship with high coefficients of determination (>0.999). Therefore, q_m , R_m , and K_a can be expressed as a function of m_s as follows:

$$q_m = 0.100 m_s^{-0.215} \quad (10)$$

$$R_m = 2.28 m_s^{0.794} \quad (11)$$

$$K_a = 4.17 m_s^{0.220} \quad (12)$$

The effect of isotherm shape can be used to predict whether a sorption system is ‘favourable’ or ‘unfavourable’, both in fixed-bed systems [28] as well as in batch processes [29]. According to Hall et al. [30] the essential features of the Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor or equilibrium parameter K_R that can be defined by the following relationship:

$$K_R = \frac{1}{1 + K_a C_0} \quad (13)$$

where K_R is a dimensionless separation factor, C_0 is the initial concentration (mmol/dm³) and K_a is the Langmuir constant (dm³/mmol). The parameter K_R indicates the shape of the isotherm accordingly.

Values of K_R	Type of isotherm
$K_R > 1$	Unfavourable
$K_R = 1$	Linear
$0 < K_R < 1$	Favourable
$K_R = 0$	Irreversible

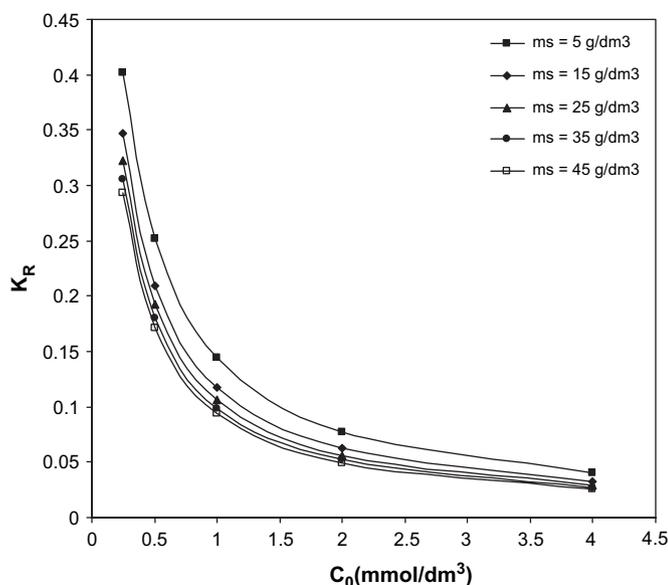


Fig. 3. Values of the separation factor, K_R , for the sorption of anionic dye by palm kernel fibre. Temperature: 297 K.

A figure with a relationship between K_R and C_0 was presented to show the essential features of the Langmuir isotherm [31]. Fig. 3 shows the values of K_R for 4-bromoaniline-azo-1,8-dihydronaphthalene-3,6-disodiumsulphate at different sorbent doses. The K_R values indicated that sorption was more favourable for the higher initial dye concentrations and sorbent doses than the lower ones.

3.4. Effect of temperature

The effect of temperature on the sorption isotherm of the dye/palm kernel fibre system was studied at 297, 306, 317,

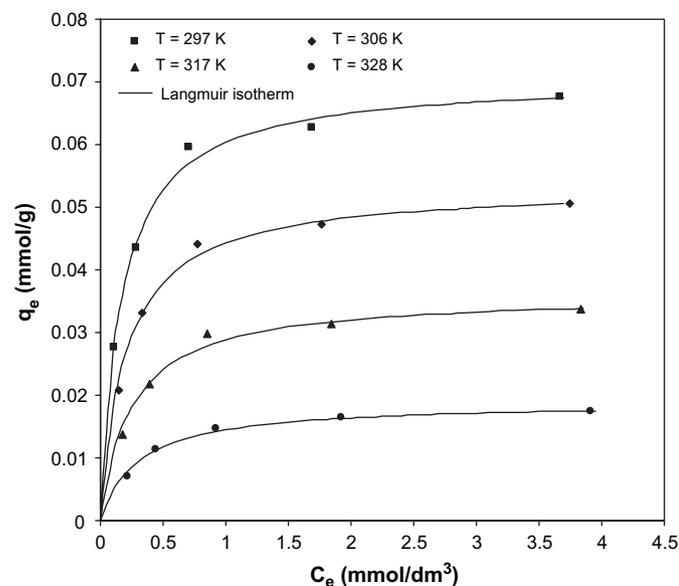


Fig. 4. Langmuir isotherm for the sorption of anionic dye using palm kernel fibre at various temperatures. Solution pH: 5.00; agitation speed: 150 rpm.

Table 2

Langmuir isotherm constants for anionic dye at various temperatures

T (K)	q_m (mmol/g)	K_a (dm ³ /mmol)	ΔG^0 (kJ/mol)	r^2
297	0.0705	5.95	-4.40	1.000
306	0.0533	4.90	-4.04	1.000
317	0.0360	4.00	-3.66	0.999
328	0.0188	3.32	-3.27	0.999

and 328 K and the results were displayed in Fig. 4. The results revealed that the sorption capacity decreased from 0.0705 to 0.0188 mmol/g with temperature increase from 297 to 328 K. The maximum sorption of anionic dye onto palm kernel fibre was compared with anionic dyes other agricultural wastes in Table 3. This decrease in sorption capacity with temperature is due to the enhancement of the desorption step in the sorption mechanism indicating that the process is exothermic [32]. It is known that decreasing sorption capacity with increasing temperature is mainly due to the weakening of sorptive forces between the active sites on the palm kernel fibre and anionic dye species, and also between adjacent dye molecules on the sorbed phase. For a conventional mechanism of physisorption system, increase in temperature usually increases the rate of approach to equilibrium, but decreases the equilibrium capacity [4].

3.5. Thermodynamic parameters

The values for the sorption equilibrium constant, K_a , decreased with increasing temperature. The thermodynamic parameter Gibbs free energy change, ΔG^0 , for the sorption processes are shown in Table 2. The negative values of ΔG^0 confirm the feasibility of the process and the spontaneous nature of the sorption. The values of ΔG^0 were found to decrease from -4.40 to -3.27 kJ/mol as the temperature increases from 297 to 328 K and the low values for ΔG^0 indicate that a spontaneous physisorption process occurred [33]. Some researchers have also obtained similar results for ΔG^0 in the sorption of anionic dyes on other sorbents. For example, the sorption of Acid Orange 7 onto spent brewery grains had $\Delta G^0 = -22.8$ kJ/mol [16] and sorption of Acid Blue 193 onto Na-bentonite had $\Delta G^0 = -0.36$ kJ/mol [34].

The values of ΔH^0 and ΔS^0 calculated from the plot of Gibbs free energy change, ΔG^0 , versus absolute temperature

Table 3

Comparison of monolayer equilibrium capacity for some anionic dyes with other agricultural sorbents

q_m (mg/g)	Sorbent	Sorbate	Reference
30.50	Spent brewery grains	Acid Orange 7	[16]
22.40	Orange peel	Congo Red	[17]
19.88	Orange peel	Acid Violet 17	[18]
14.40	Peat	Acid Blue 25	[9]
4.42	Banana pith	Acid Brilliant Blue	[19]
4.26	Sugar cane dust	Rhodamine B	[20]
3.23	Orange peel	Rhodamine B	[17]
1.33	Orange peel	Procion Orange	[17]
38.6	Palm kernel fibre	4-Bromoaniline-azo-1,8-dihydronaphthalene-3,6-disodiumsulphate	This study

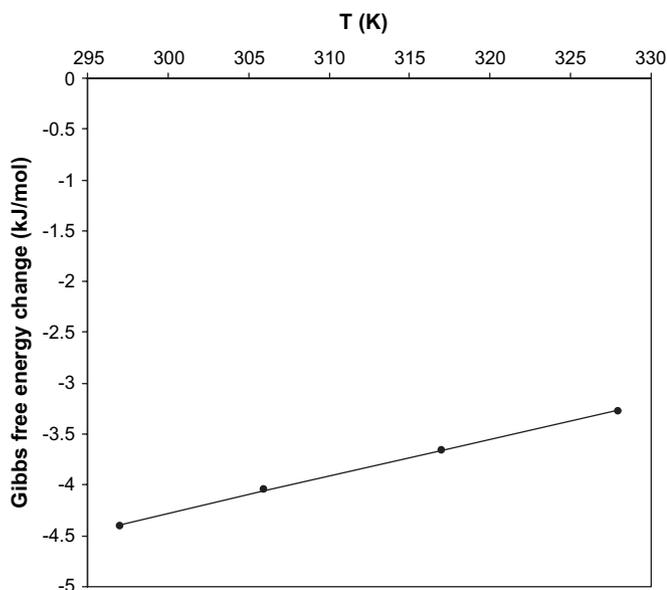


Fig. 5. Relationship between Gibbs free energy change (ΔG^0) and temperature of sorption. Solution pH: 5.00; agitation speed: 150 rpm.

(Fig. 5) are given as -15.2 kJ/mol and -0.0363 J/mol K, respectively. The enthalpy change is negative implying that the sorption process is exothermic. Enthalpy change due to chemisorption takes value between 40 – 120 kJ/mol, which is larger than that due to physisorption [21]. Therefore, the sorption of the anionic dye under examination onto palm kernel fibre is likely due to physisorption. This result shows that the interaction between the anionic dye and the palm kernel fibre is mainly electrostatic. The heat of physisorption involves only relatively weak electrostatic interactions [21]. Values for ΔH^0 for the sorption of Acid Red 57 (-26 kJ/mol) and Acid Blue 193 (-24.9 kJ/mol) onto sepiolite and Na-bentonite were also negative and in close range to that obtained in this

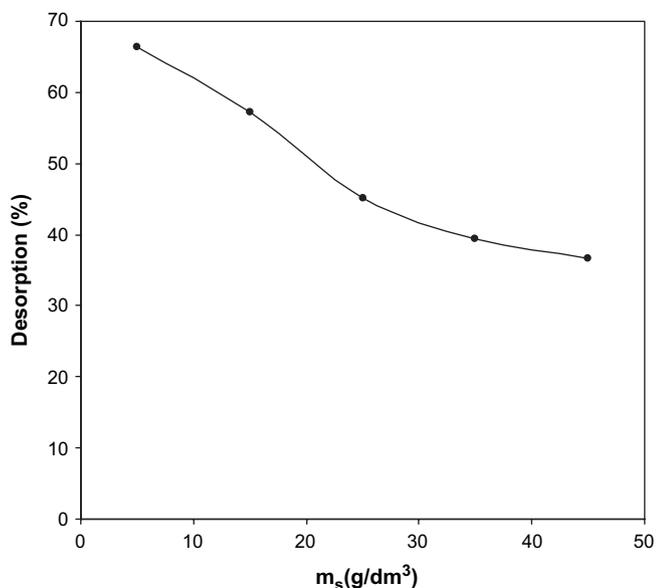


Fig. 6. Effect of sorbent dose on desorption of anionic dye from palm kernel fibre. Solution pH: 5.00; agitation speed: 150 rpm; temperature: 297 K.

study. Generally, sorption of dye is currently described as an exothermic process [35,36].

3.6. Sorbent re-generation

To evaluate the economic viability of palm fibre for water purification, it is necessary to re-generate the spent sorbent. As the dose of the sorbent used in the sorption experiment increases, the percentage of desorption decreases (Fig. 6). Percentage of desorption of this magnitude obtained in this study indicates that sorption is physical in nature and the reverse reaction in Eq. (14) is very likely to occur.



The decrease in percentage of desorption with increasing dose of sorbent is likely due to the increase in the Langmuir equilibrium constant, K_a , which is related to the bonding of the dye molecule on the sorbent. As the values of K_a decrease, the equilibrium in Eq. (14) is shifted to encourage the desorption step.

4. Conclusion

Palm kernel fibre, a very abundant agricultural by-product in Nigeria has been shown to be a good sorbent for the anionic dye examined in this study and can be suggested for the removal of anionic dyes from wastewater. Both the decrease in temperature and sorbent dose results in a higher dye loading per unit weight of the sorbent. The results obtained were very well described by the theoretical Langmuir isotherm. The equilibrium monolayer capacity of palm kernel fibre for this dye was 0.0705 mmol/g when temperature was 297 K and palm kernel fibre dose was 5 g/dm^3 . The thermodynamic analysis indicates that the system is spontaneous and exothermic, and up to 66.4% of the dye sorbed can be desorbed with distilled water.

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