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BATCH SORPTION EXPERIMENTS: DUBININ-KAGANER-RADUSHKEVICH (DKR) ISOTHERM STUDIES FOR THE REMOVAL OF INDIGO DYE ON RICE BRAN AS A LOW-COST ADSORBENT

ABDULLAHI MOYOSORE
Department of Chemistry
Federal College of Education, Katsina, Nigeria
GSM: +2348036567981
Email: abdullahimoyosore82@gmail.com

&

KAMALDEEN ABDULLAHI
Department of Chemistry
Isa Kaita College of Education, Dutsin-ma, Katsina

Abstract

Adsorption of indigo dye onto rice bran has been studied using batch-adsorption techniques. This study was carried out to examine the adsorption capacity of the low-cost adsorbent for the removal of the dye. The influence of contact time, pH, temperature, adsorbate concentration and adsorbent dose on the adsorption process was also studied. Results revealed that adsorption rate initially increased rapidly with the aforementioned parameters. The values; 40 minutes, 3.0, 0.3g, 40 mgL^{-1}, and 55 ^{0}C gave the optimum contact time, pH, adsorbent dosage, adsorbate concentration and temperature, respectively. The adsorption isotherm was well fitted by the Dubinin-R model with R^2 as high as 0.95. The sorption energy of 0.7kJmol^{-1}obtained from the Dubinin-R isotherm reveals that physisorption was the dominant adsorption mechanism. Results indicate that the freely abundant, locally available, low-cost adsorbent, rice bran can be treated as economically viable for the removal of indigo dye from industrial effluents.

Keywords: indigo dye, Dubinin-R isotherm, adsorption, low-cost adsorbent, adsorbate.

Introduction

Dyes are colored substances retained on substrate by adsorption. These are soluble completely or partially soluble in a media from which they are applied in contrast with pigments. Dyes must possess a specific affinity to the substrate from which they are used.

Indigo dye has however indisputably remained the most versatile of all the natural dyes found among the people. Aside from indigo dye being used on its own, it is required to obtain a range of other colours which ordinarily would not have been obtainable from nature. Indigo dye consequently remains the commonest, the most popular and the most extensively used compared to other natural dyes and colours (Khalilu and Areo, 2015).

Dyes get into the environment through industrial effluents from food, drug, cosmetic, textile and dyestuff factories (Mathur *et al*., 2005; Christie, 2001; Rahman *et al*., 2009). A number of dyes and chemicals used by these textile industries are highly structured polymers and are very difficult to decompose biologically. They belong to different groups based on their chemical composition and application. A typical dye is composed of chromophores and auxochromes. The Chromophores are the nitrogen, carbon, oxygen and sulphur that have alternate single and double bonds while the Auxophores are the amino, carboxyl, hydroxyl, and sulphonic groups which are responsible for the various colour patterns and intensity of the textile products (Nupur et al., 2012).

Due to the complex aromatic structure and stability of these dyes, conventional biological pre-treatment methods are ineffective for degradation (Sanni*et al*., 2018). They are thus a potent hazard to the natural sources like soil, water, flora, fauna, livestock and human population. Since large quantities of dyes are used, pollution due to dyes may occur on a significant scale (McLaughlin *et al*., 1991).

The excessive and indiscriminate use of these dyestuffs has become increasingly a subject of environmental concern and as such the need to devise efficient and cost-effective method of disposing them accordingly has become necessary.

1.0 Materials and Experimental Procedure

2.1. Reagents and Solutions. Dark blue crystalline powder of indigo dye was used for the preparation of standard indigo dye stock solution. DMSO was used as a solvent. The main characteristics of the dye are λmax= 681.5 nm, pH = 13, Chemical formula = $C_{16}H_{10}N_2O_2$, and M.W.= 262.27 g/mol

2.2. Preparation of Adsorbent*:* Rice bran was collected and dried in direct sunlight for three days. After three days, the bran was put in oven at 60^{o}C for twenty-four hours. Dried rice bran was thoroughly washed with distilled water to remove all dirt and was dried at 100^{o}C till constant weight. Then the dried wheat bran was grinded and sieved with a30-mesh sieve, to prepare homogenous particle size. This bio sorbent was again washed with distilled water to remove adhering dirt and foreign particles. Then, it was kept in ovenat 60^{o}C for 24 hours. The average particle size of adsorbents was measured and it was 496μm.

2.3* Indigo dye Stock Solution*: Stock solution of indigo standards was prepared by dissolving 1.04 mg synthetic indigo (95%) in Dimethylsulphoxide (DMSO) solvent to 10 ml volumetric flask. Solution was warmed for about 30 minutes in boiling water until all indigo was dissolved. Indigo concentration in stock solution obtained was 98.80 mg/l. With the help of double beam spectrophotometer, absorbance of the dye was measured at wavelength of 620nm in a 1.0 cm matched quartz curettes against a reagent blank on thorough mixing. At this wavelength all the experiments were performed. Beer Lambert law was obeyed. This general method was adopted for the rest of the experiments.

2.4 Procedure: The adsorption of indigo dye on rice bran was studied by a batch technique. 0.1 g of the dried sieved rice bran was equilibrated with 10 cm^3 of the dye solution of the known concentration in a stopper Pyrex glass flask at fixed temperature in a shaker for a known period of time. The suspension was centrifuged in a stopper tube for 10 minutes at

3500 rpm. The concentration of the dye in a known volume of the supernatant was determined spectrophotometrically. The amount of the dye adsorbed on the wheat bran was thus determined. Adsorption was determined in terms of equilibrium concentration (*Ce*), percentage Removal *P*%, and Adsorption Capacity, qe.

The effect of pH was observed by studying the adsorption of dye over the pH range from 1 to 9**.** The pH of the dye solution was adjusted by using NaOH or HCl solution and a pH meter. The sorption studies were carried out at different temperatures. The amount of equilibrium adsorption, $q_e(mg/g)$, was calculated using the formula in equation 1;

$$q_e = \frac{(C_0 - C_e)V}{W} \qquad (1)$$

The dye removal percentage can be calculated using equation 2:

$$(\%) \text{ of dye removal} = \frac{(C_0 - C_e)}{C_0} x\ 100 \qquad (2)$$

where $C_0$and *Ce* (mgL-1) are the initial and equilibrium concentrations of the dye in solution.

2.0 Results and Discussion

3.1 Effect of Contact Time: The adsorption of indigo dye on rice bran was studied as a function of shaking time at 35^0C. A sample of 50 cm^3 of the dye solution was taken in nine titration flasks, labeled them from 1–10, and shaken with0.1g of rice bran in each flask for different intervals of time ranging from 10 to 70 minutes in a shaker. After equilibration the suspension was centrifuged at 3500 rpm. After 20 minutes all the solutions were filtered and absorbance was determined photometrically at wavelength of 650 nm to obtain the equilibrium concentration (*Ce*), and percentage removal. Equilibrium time was determined by plotting a graph between different time intervals and percentage removal. The variation of percentage adsorption as a function of shaking time is depicted by fig.1. The result shows that the adsorption of indigo dye on rice bran is proportionally time dependent. The plateau observed after 40 minutes connotes that the equilibrium time is 40 minutes. Thus, for all other experiments shaking time was kept 40 minutes. At 40 minutes, the maximum adsorption is observed owing to attraction between the adsorbent and the adsorbate. Initial adsorption of dye is on exterior surface of rice bran followed by the entrance of the dye to the inner surface of the adsorbent via pores. After 40 minutes' desorption takes place.

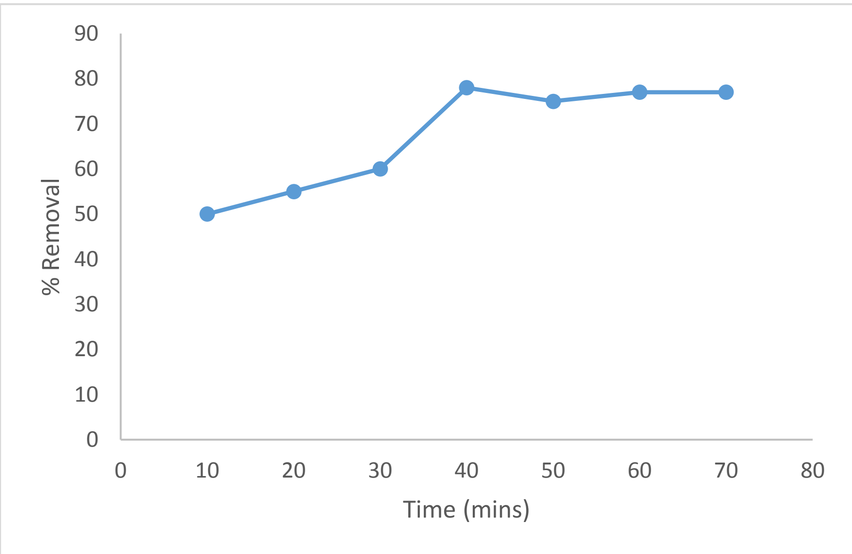

Figure 1: Effect of contact time on adsorption of the dye by rice bran.

3.2. Effect of pH: The adsorption of the dye on rice bran was studied as a function of varying pH keeping all other parameters constant. After equilibration, the suspension was centrifuged for 30minutes at 3500 rpm. After 20minutesall the solutions were filtered and absorbance was determined photometrically at wavelength 650 nm. Figure 2 gives the plot of pH against percentage removal. The result shows that the adsorption of the dye on rice bran increases with increasing pH and attains maxima at pH 3.0, indicating that equilibrium pH is obtained at this value. Thus, other experiments were carried out at pH 3.0. The increase in adsorption at lower pH may be due to the increased positive charges on the surface of adsorbent that attracts the functional groups of a dye carrying negative charge via electrostatic attraction.

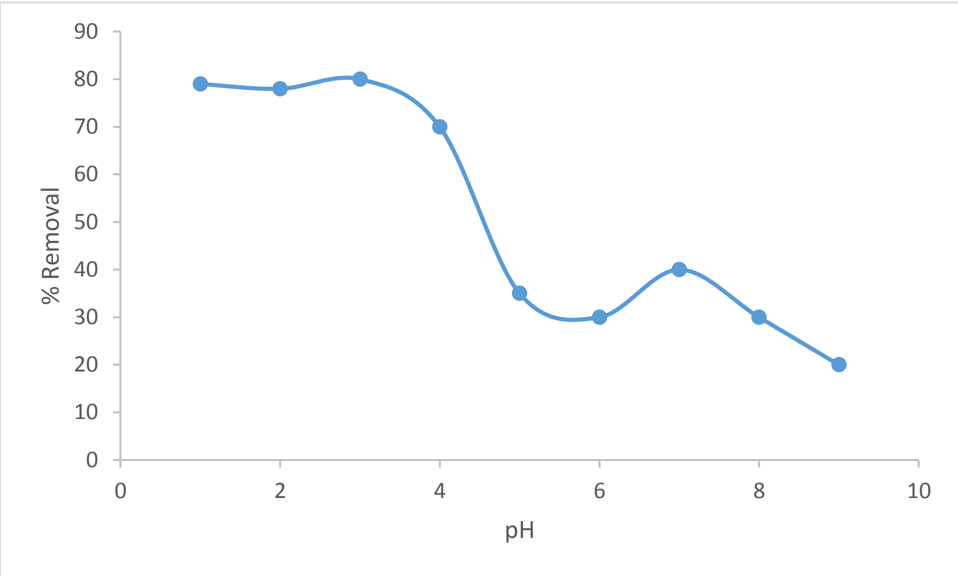

Figure 2: Effect of pH on adsorption of the dye by rice bran.

3.3. Effect of Adsorbent Dosage*:* In order to understand the effect of adsorbent dosage, the adsorption of the dye was studied as a function of different amount of adsorbent, ranging from 0.1–1.0 g, while keeping all other parameters that is, adsorbate concentration (10 ppm), shaking time (40min), and pH (3.0), of the suspension constant. The variation of % adsorption as a function of different amount of adsorbent is depicted by Figure 3.The results show that the adsorption of dye on rice bran increases spontaneously with increasing adsorbent concentration (dye adsorption efficiency was increased with increase in adsorbent dose). Extrapolation of the plot reveals 0.3g as optimum adsorbent dosage. The spontaneous increase in adsorption with adsorbent concentration may be due to the fact that adsorption sites remain unsaturated during adsorption reaction whereas the number of sites increases by increasing the adsorbent dose (Desta, 2013).

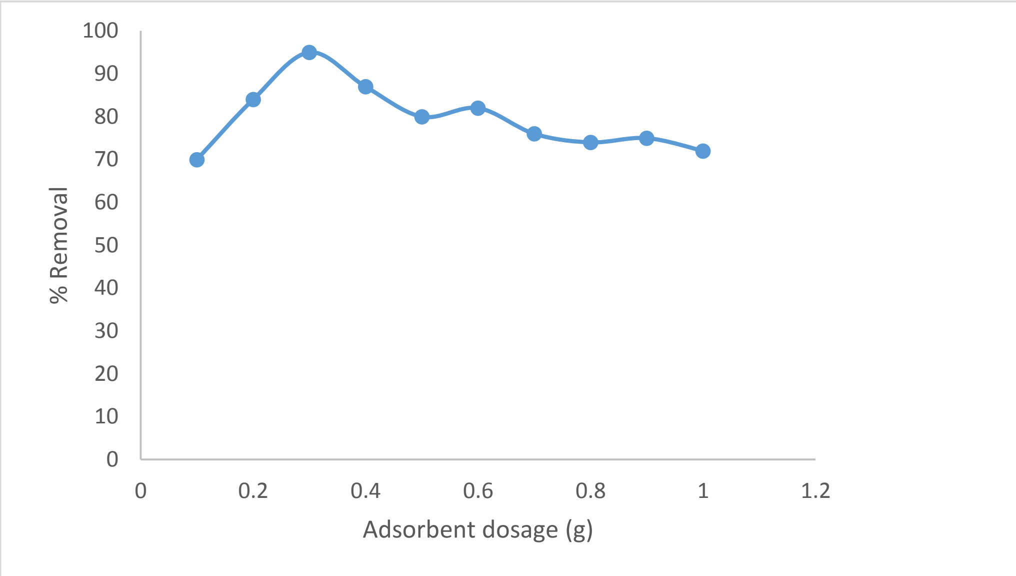

Figure 3: Effect of adsorbent dosage on adsorption of the dye.

3.4. Effect of Sorbate Concentration. The adsorption of the dye on rice bran was studied as a function of its different concentrations, that is, 10–60 mgL^{-1}, while keeping all other parameters constant. Figure 4 shows the variation of percentage adsorption as a function of different sorbate concentrations. The results show that the adsorption of the dye on rice bran increases spontaneously with increasing sorbate concentration till40 mgL^{-1} and then become constant onward. This indicates that the initial concentration adsorbate strongly affects adsorption capacity.

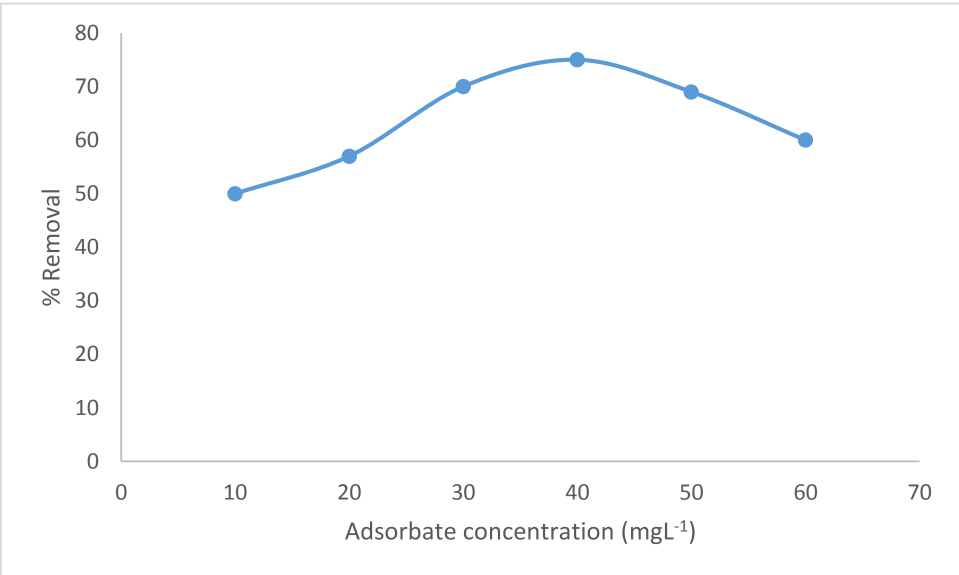

Figure 4: Effect of concentration of dye (adsorbate) on adsorption.

3.5. Effect of Temperature: To observe the effect of temperature, adsorption studies of indigo dye onto rice bran were performed at eight different temperatures: 30, 35, 40, 45, 50, 55, 60 and 65 °C. The percentage adsorption at the various temperatures were calculated and plotted against the temperature values (Figure 5). The results show that percentage adsorption increases linearly with increasing temperature till 55^0C then decreases. The increase in adsorption at elevated temperature could be due to the enlargement of pore size of the adsorbent facilitating adsorption of more adsorbate.

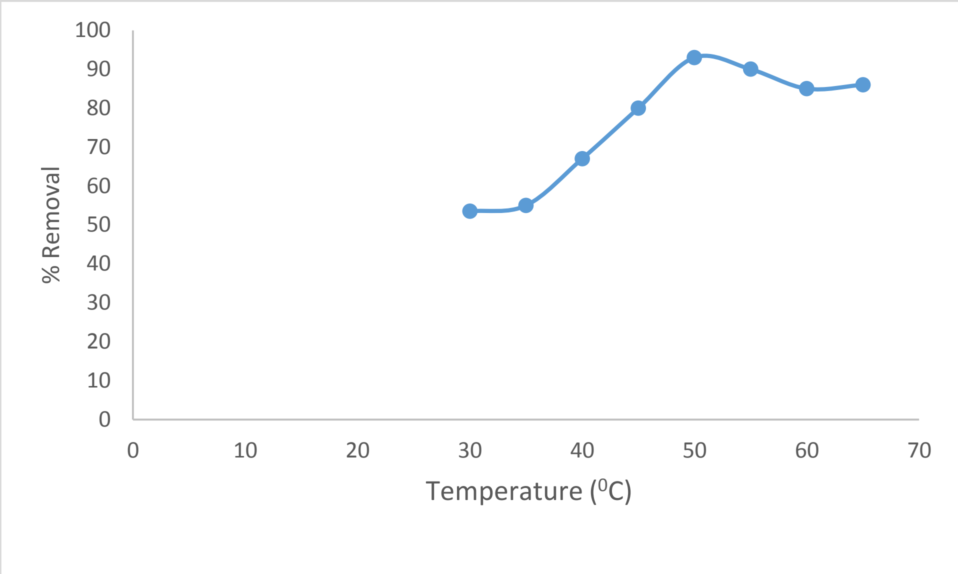

Figure 5: Effect of temperature on adsorption of the dye by rice bran.

3.6 Dubinin-Kaganer-Radushkevich Equation: This equation is used to determine sorption mean energy which enables estimation of whether adsorption is carried out by ion exchange mechanism, physisorption or, chemisorptions [Hameed, 2009]. The mathematical expression is shown in equation 3.

$ln q_e = ln q_m - \beta \varepsilon^2$ (3)

where

$\varepsilon = RT ln\,(1 + 1/C_e)$,

qm is a theoretical saturation capacity, β is a constant related with sorption energy, mol^{2}J^{-2}, ε is a polonyi potential and mean sorption energy E_s is expressed in equation 4;

$E_s = \frac{1}{\sqrt{-2\beta}}$ (4)

The Dubinin-Kaganer-Radushkevich (DKR) isotherm (Figure 6) was used to determine the value of the sorption energy E through equation 4, which can confirm the adsorption mechanism. When the value of E is in the range of 1 to 8kJmol^{-1}, it is indicative of physisorption. When it is in the range of 8 to 16 kJmol^{-1} it is indicative of ion-exchange. When it is in the range of 20 to 40 kJmol^{-1},it is indicative of chemisorption [Eba *et al.*, 2010]. The E value obtained for the dye is 0.70 kJmol^{-1}, well within 1 to 8 kJmol^{-1} which shows that the type of adsorption for the dye is physisorption.

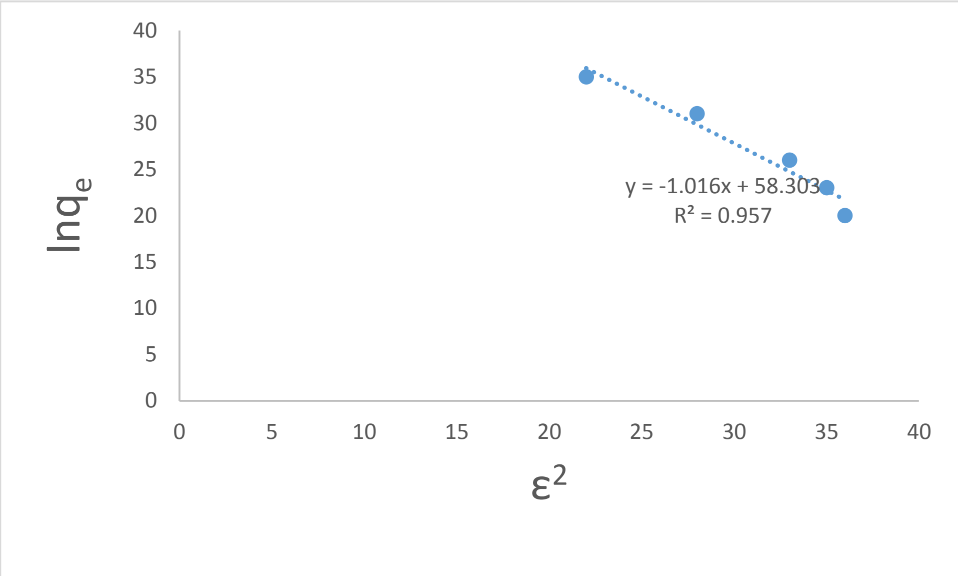

Figure 6: Plot of Polanyi potential ε and ln qe for activation energy.

3.0 Conclusion

Rice bran is an environment friendly, cost-effective, and locally available agrowaste adsorbent for the adsorption of dyes from industrial effluents. Results from this study showed that adsorption of indigo dye onto rice bran increases with the amount of the adsorbent. This may be explained because of the fact that adsorption is a surface phenomenon where adsorbate molecules occupy specific sites on the adsorbent. These sites are commonly known as active centers. The concentration of these active centers on the surface is further related to the pore size and pore volume available after impregnation. This explains why increasing the quantity of adsorbent results in increased adsorption. Results revealed that initially the % removal increase, rapidly; however, after some times the rate becomes almost constant. This is because all the available active centers on the adsorbent have been occupied and there are no further sites and hence no further adsorption is possible. The time when this phenomenon occurs, therefore, may be termed optimum time. The values; 40 minutes, 3.0, 0.3g, 40 mgL^{-1}, and 55 ^{0}C give the optimum contact time, pH, adsorbent dosage, adsorbate concentration and temperature, respectively. The adsorption isotherms could well be fitted by the Dubinin-R model with R^2 as high as 0.95. The value of sorption energy obtained from the Dubinin-R isotherm reveals that physisorption was the dominant adsorption mechanism. Since rice bran is abundant, locally available, low-cost adsorbent and has a considerable high adsorption capacity, it may be treated as economically viable for removal of dyes from textile effluents.

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