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Effective Adsorption of Azure B Dye from Aqueous Solution Using Snail Shell Powder

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Abstract

Azure B dye was removed by using snail shell (Rostellaria) Powder as an adsorbent. A series of experiments was done in a batch adsorption technique to examine the effects of the process variables i.e. concentration, initial pH, temperature and absorbent dose .Optimal state adsorption of Azure B was realized at the weight of 0.02 g of adsorbent, 7.00 mg/L of dye concentration, 20 minutes as the contact time, and the temperature of 298 K. The removal data using Freundlich, Langmuir and Temkin models were analyzed at various temperatures varying from 298 to 338 K. The thermal dynamics of the adsorption process ΔH, ΔG and ΔS were found exothermal, spontaneous, and decreasing in randomness at the solid/ solution interface. The shapes of the isotherms were received from the experimental data which were found to be similar in all cases of the (S- curve) type according to Giles rating.

Keywords: Adsorption, Snail Shell, Azure B, Isotherms, Langmuir, Freundlich and Temkin.

Introduction

Water is an essential factor for living organisms to maintain their lives on earth. The living organisms can utilize only the freshwater supplier which represents 3% of the available water suppliers on the earth. The water has been distributed in the following proportions , 68.7% is in the form of snow, 29.9% as groundwater and only 0.26% as the surface water in reservoirs, lakes and rivers (Sahoo et al., 2012).Textile industries has been producing colour dye effluents which are toxic and cause a lot of damages to the environment (Ankita et al., 2013). Different processing technologies such as precipitation, adsorption, oxidation-ozonation, coagulation, coagulation-flocculation, biological and ion exchange methods have been utilized at the moment of necessity to eliminate the dyes and organic effluents produced by industries (Duraisamy et al., 2015). Dyes have been widely employed for coloring purposes and many of dyes have been considered as dangerous, and 2 % of the produced dyes has been emptying instantly into aqueous effluents, with a further 10% which is lost during the textile coloration process (Rosales et al. 2012). Synthetic dyes have been existing in wastewater streams from many industrial sectors including paper, textile, leather, cosmetics, plastic, electronics, printing, food ,pharmaceutical, etc. (Xu et al. 2016). In the coloring process, some amounts of dyes are absorbed in the product, and some of them will end up in the wastewater. Presently, thousands of synthetic dyes are obtainable in the market. Some of them are safe to human and can be used to color food and beverages, but some of them are harmful or even risky to human health (Fabryanty et al., 2017). Adsorption is a surface phenomenon, where substances' ions, molecules or atoms (adsorbate) are attracted in their gas or liquid state on the surface of the solid called (adsorbent), even the equilibrium arrives between the adsorbed molecules, and those molecules are still freely scattered in the carrying gas or liquid. The adsorption phenomenon is dependent on the interrelationship between the surface of the adsorbent and the adsorbed species (Ambali et al. 2015). The adsorption operation is an influential and interesting proposition to examine the dye contaminated wastewater. This theory can be deemed as an economical alternative because it does not need any additional pre-treatment steps if low-cost adsorbents are employed. Therefore, recently, a lot of research studies have been focused on finding a cheap and locally available material to substitute using activated carbon (Vimonses et al. 2009). The data on the equilibrium and adsorption properties, generally known as adsorption isotherms, have explained how pollutants interact with the adsorbent materials, and it is therefore necessary to refine the use of the adsorbents (Piccin et al. 2011). Therefore, the study of the adsorption ability of these dyes is much necessary for different physical and chemical processes and understanding many phenomena for instance: explanation and pollution of industrial liquid wastes (Al-Rufaie et al. 2016).

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Methods and Materials

Materials

All chemicals used in the study were of analytical grade obtained from Chemistry Department, University of Kerbala.

Specifications of the dye

Organic Azure B dye was used. All the chemicals were of high purity and commercially available. Azure B dye solution was prepared with the concentration of 100 mg/L by dissolving 0.01g from dye in 100 ml of distilled water. The properties of the selected dye have been given in Table (1), and their structures have been shown in Fig. (1).

Table 1: Specifications of Azure B (Eman & Rusul 2013; Rosales et al. 2012)

Chemical name	Azure B , Methylene Azure B , Tri methylthionine chloride
Empirical Formula	C15H18ClN3S
Class	Thiazine
Source	Aldrich
Solubility in water	Soluble
Molecular Weight	305.83 g/mol
Dye Content	89%
λ max	646 nm
C. I. No	52010

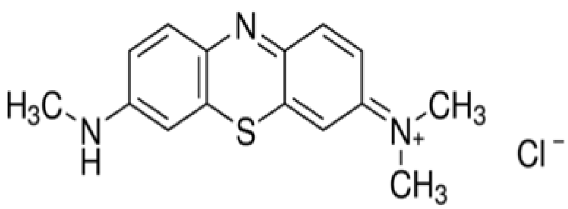

Figure 1: Structural formula of Azure B dye (Ankita & Shipra 2015)

Specifications of the adsorbent (snail shell powder)

Snail shell was gathered from dump site, and then washed carefully with tap water first, and then with deionized water to remove the particulate materials from their surface. Thereafter, it was dried in an oven at l00 C^0 for 24 hrs before being pulverized and sieved with the aid of a mechanical sieve.

The snail shell has been specified by three layers, which have bestowed it sufficient strength to withstand the external conditions and shocks that it may be exposed to. The properties of the snail shell have been given in Table (2).

Table 2: Specifications of Snail shell (Ambali et al. 2015)

Hardness (mohs scale)	4-3
Appearance	White powder
CaO	52.70
SiO2	2.40
Al2O3	0.68
Fe2O3	0.44
MgO	1.5
SO3	0.28
PH	6.8
Moisture Content, %	24.33
Bulk Density	1.25
Porosity	0.0249
Surface Area m2/g	295

After identifying most of the characteristics of the snail powder, it was used to remove the dye Azure B.

Batch Adsorption Experiments

0.02 g adsorbent with 25 ml of dye solutions of 7.000 mg/L at 150 rpm was used on a thermo stated shaker water bath. The unadsorbed supernatant liquid of the residual dye in each treatment solution was analyzed by Shimadzu UV-Vis 1800 digital double beam instrument at a wavelength corresponding to the λ max. The PH and temperature effects were studied. The amount of adsorption was identified by the ratio x/m which was determined as the amount of adsorbate in mg held by the weight of the adsorbent g.

$$\text{Removal \%} = [(C_0 - Ce)/C_0] \times 100 \qquad (1)$$

Where:

C_0 and C_e denote the initial concentration and final residual concentration of dye in mg/L; respectively (Akinyeye et al. 2016).

Results and Discussion

Effect of Contact Time

The rapport between contact time and percentage of Azure B dyes was done through batch experiments to achieve the balance as shown in Fig.2. The results showed that balance time was reached within 20 minutes.

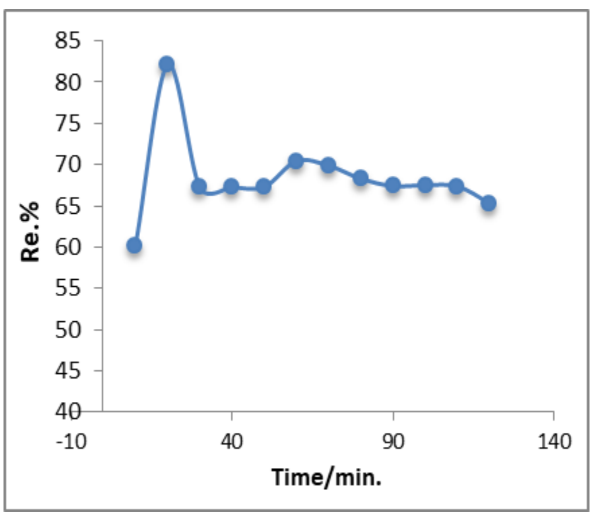

Figure 2: Effect of contact time on the adsorption of Azure B by Snail shell at Temperature 298 K, Conc. of dye 7 mg/L and the adsorbent weight of 0.02 g.

Effect of adsorbent weight

Adsorption experiments were performed by changing the adsorbent weight from 0.01-0.08 g. The initial concentration of the dye was 7 mg/L, and the temperature was 298 K (As can be observed in Fig.3).

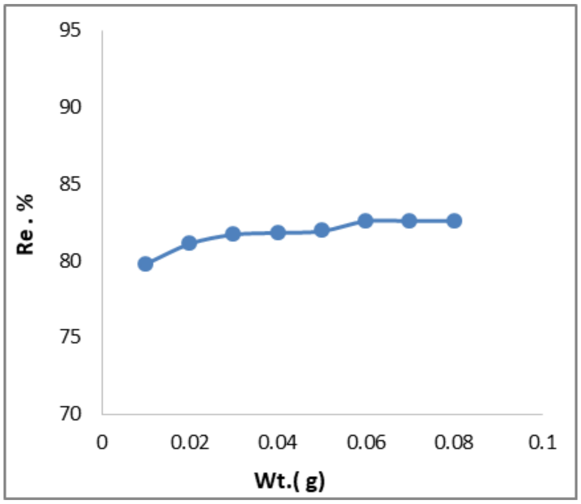

Figure 3: Effect of adsorbent weight on the adsorption of Azure B by Snail shell at Temperature 298 K.

Effect of pH

One of the important factors studied was pH which controls the adsorption processes (Muneer et al. 2017; Baseri et al. 2012) (See Fig.4). The effect of pH on the adsorption of Azure B on the Snail shell appears at the temperature of 298 K, and pH ranging from 2 to 12. The dye removal was minimum at pH 2, and the dye adsorbtion increased as the pH was increased from 2 to 8. Then, after pH 8, there was no notable change. For this reason, pH 8 was selected for further experiments**.**

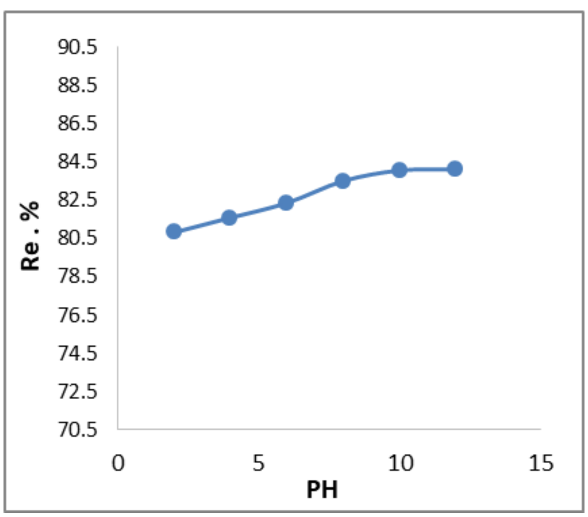

Figure 4: The Effect of pH on the adsorption of Azure B by Snail shell at Temperature Of 298K

Effect of Temperature

Azure B was studied using Snail Shell at a range from 298 to 338 K. The determination of thermodynamic parameters such as free energy (ΔG), enthalpy (ΔH) and entropy (ΔS) was done using the equations 2 to 5, which have been given in table 3 (Muneer & Noor, 2017; Jaism et al. 2015). (See figure.5 & Table.3).

$$\Delta G = -RT \ln Keq \quad (2)$$

$$Keq = (Qe\ m)/Ce\ v \quad (3)$$

$$\ln Keq = (-\Delta H/RT) + con \quad (4)$$

$$\Delta S = (\Delta H - \Delta G)/T \quad (5)$$

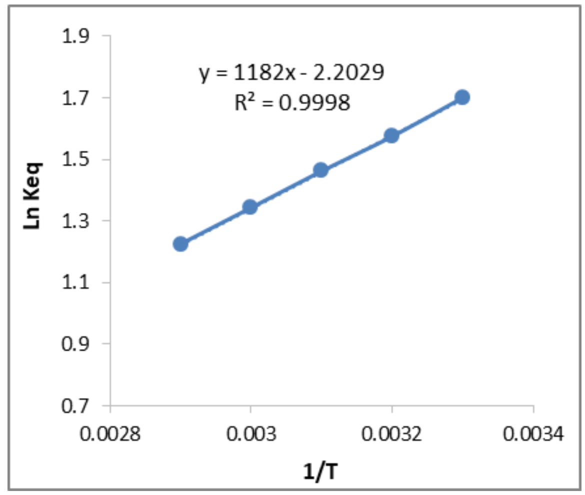

Figure 5: The Effect of the temperature on the adsorption Azure B dye on the Snail shell.

Table 3: Thermodynamic parameters of ΔG, ΔH and ΔS of Azure B dye on the adsorbent surface of Snail shell at (298-338) K

Adsorbate	Temp. K	ΔG (KJ/mol)	ΔH (KJ/mol)	ΔS (J/mol)
Azure B	298	-4.2133	-9.8271	-18.8382
	308	-4.0326		-18.8134
	318	-3.8661		-18.7454
	328	-3.6628		-18.7934
	338	-3.4435		-18.8864

Negative values of (ΔG, ΔH and ΔS) indicated the automatic nature of adsorption (Emeniru et al., 2015), the process is exothermic (Oguntimein et al., 2014), and reduction in randomization in the solid interface / solution during the adsorption process (Fairooz et al. 2015).Respectively

Adsorption Isotherm

The equilibrium data from this study were described with three adsorption isotherm models i.e. Langmuir, Freundlich and Tempkin. The acceptability and relevance of the isotherm equation to the equilibrium data were based on the values of the correlation coefficients r^2 predestined from the linear regression

(Adeogun & Balakrishnan 2017). The adsorption experiments were led by using 25 ml stoppered conical flasks at temperature from 298 to 338 K. The equilibrium state at the optimum conditions was achieved at following conditions: 0.02 g of the adsorbent materials,7 ppm of dye concentration and the time of 20 min. After filtration, the dye concentration in the filtration solution was analyzed by using UV-Vis 1800 digital double beam instrument at a wavelength corresponding to the 646. (See Figure 6). The amount of the adsorbed material was calculated from the following equation:

$$Qe= V (C_o – Ce) /m = x /m \qquad (6)$$

(Vijayakumar et al. 2012).

Where:
Qe = x/m the quantity of adsorbed material (mg) /g adsorbent
V = volume of pesticide solution (L) that was used
C_0 = Initial concentration of the dye (mg/L)
Ce = Equilibrium concentration (mg/L)
m = weight of adsorbent (g)

The amount of the adsorption was expressed by the ratio x/m which was defined as the quantity of adsorbate in (mg) held by the weight of adsorbent (g).

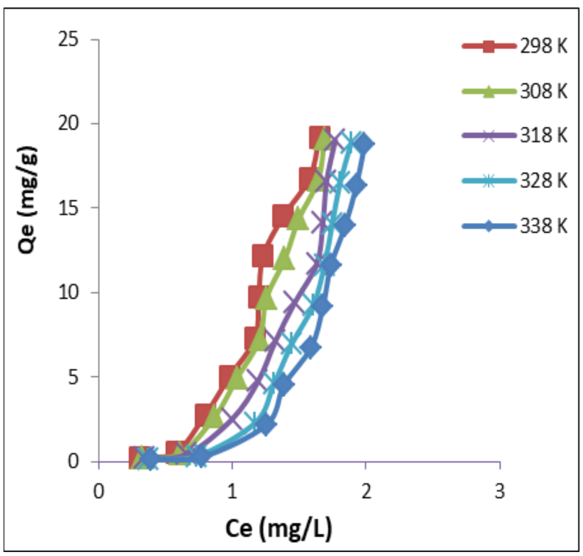

Figure 6: Adsorption Isotherm of Azure B adsorption from aqueous solution on the surface of the Snail shell at different temperatures

The shapes of the isotherms received from the experimental data were found to be similar in all cases to the (S- curve) type according to Giles rating. The results were received on the adsorption of Azure B which were analyzed by the well-known models given by Langmuir, Freundlich and Temkin.

Langmuir isotherm

The linear form of the Langmuir isotherm model was given by the following equation:

$$Ce/Qe = 1/ab+ Ce/a \qquad (7)$$

Where:
Ce: is the equilibrium concentration of the adsorbate Azure B mg/L
Qe: the amount of adsorbate adsorbed per unit mass of adsorbate mg/g
a and **b** are the Langmuir constants (Bello et al. 2010).
The values of **a** and **b** were determined from the slope and intercept of the plot respectively. The feasibility of the adsorption process was calculated through using the separation factor R_L, which was defined by equation 8:

$$R_L = 1 / (1 + b\,Co) \qquad (8)$$

Where:-
C^0 is the initial dye concentration in solution mg /L
b is the Langmuir constant L/mg

The value of **R_L** indicated the type of the isotherm to be either favorable ($0 < R_L < 1$), unfavorable ($R_L > 1$), linear ($R_L = 1$) or irreversible ($R_L = 0$) (Jiankun et al., 2014). (See Figure.7)

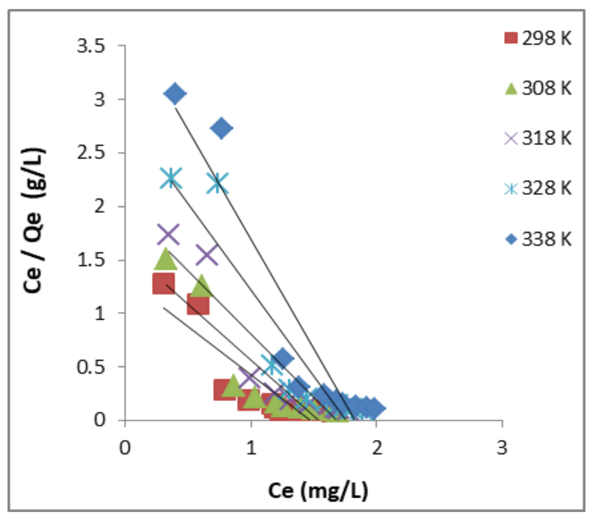

Figure 7: The Langmuir isotherms for Azure B dye at different temperatures

Freundlich Isotherm

The Freundlich isotherm assumed the multilayer sorption on a heterogeneous surface. The linear form of Freundlich equation can be expressed as:

$$\log Qe = \ln K_f +1/ n \log Ce \qquad (9)$$

Where:
Qe and **Ce** are the same as defined above, and **K_f** and **n** are the Freundlich constants (Lei et al. 2017). (See Figure 8).

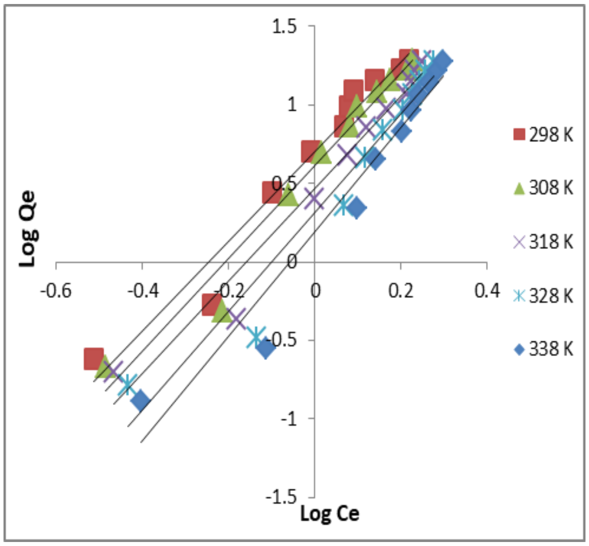

Figure 8: The Freundlich isotherms for Azure B dye at different temperatures.

The Temkin Isotherm

The Temkin isotherm has been generally applied in the following form:

$$qe = B \ln A_T + B \ln Ce \quad (10)$$

Where:

A_T is the equilibrium binding constant that corresponds to the maximum binding energy

B is the constant which is related to the heat of adsorption (Hameed et al. 2008). (See Figure.9 & Table.4).

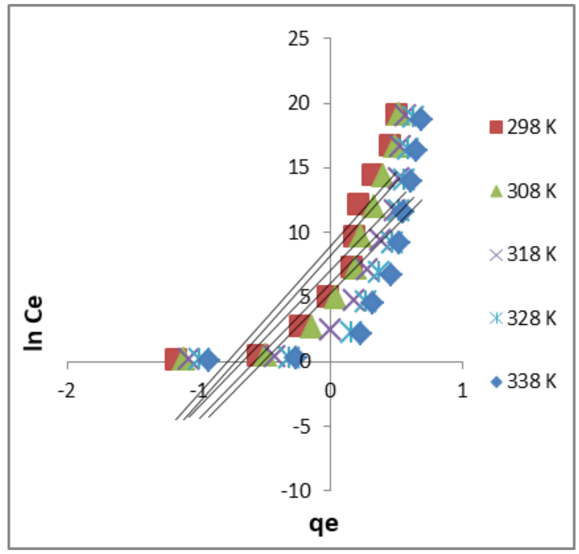

Figure 9: The Temkin isotherms for Azure B dye at different temperatures.

Table 4: Langmuir, Freundlich and Temkin parameters of adsorption isotherms at (298 – 338) K

Adsorbate Azure B										
Temp. K	Langmuir isotherm				Freundlich isotherm			Isotherm Temkin		
	a (mg/g)	b (mg/L)	(r2)	RL	(Kf)	(n)	(r2)	B	AT	(r2)
298	-1.1032	-0.6787	0.7557	-0.2666	5.0722	0.3496	0.9642	11.412	2.2025	0.7606
308	-0.9576	-0.6511	0.7783	-0.2810	4.1238	0.3381	0.9693	11.383	2.0610	0.7505
318	-0.8438	-0.5976	0.8422	-0.3141	2.9437	0.3386	0.9551	10.591	1.9473	0.6863
328	-0.6179	-0.5700	0.8603	-0.3344	2.0749	.31730	0.9444	10.451	1.7922	0.6371
338	-0.4906	-0.5469	0.8741	-0.3535	1.5573	0.3004	0.9493	10.432	1.6766	0.6291

Conclusion

1. The present study proved that snail shell can be used as an effective adsorbent for the elimination of Azure B dye from aqueous solutions.
2. Besides minimizing the wastes, the results also availability additional benefits to industrial wastewater treatment.
3. It was found that the equilibrium data were very compatible with Freundlich isotherm model, indicating a monolayer adsorption on a homogenous surface.
4. Thermodynamic studies mentioned that the adsorption process was exothermic, and the degrees of freedom decreased at the solid- liquid values spontaneously in nature.

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