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Investigation of Kinetics and Equilibrium Isotherms of Direct Red 12B Dye Adsorption on Hazelnut Shells

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Abstract: In this work, efficiency and performance of Hazelnut shells (HS) adsorbent was examined for the removal and recovery of Direct Red 12B (DR12B) from wastewater. The absorbance of DR12B was measured spectrophotometrically at λmax=523 nm before and after adsorption of DR12B. The maximum removal was 99.8% for 30 mg L^{-1} of DR12B concentration on 0.3 gr HS adsorbent. Acidic pH was favourable for the adsorption of DR12B. The influence of variables including pH, concentration dye, particle size, amount of adsorbent, temperature, in column method and kinetics, isotherm, contact time on the dye removal has been investigated in batch method by one at a time optimization method. The effect of foreign cations, anions and other dyes was investigated on removal efficiency. In order to investigate the efficiency of DR12B adsorption on the HS, pseudo-first-order, pseudo-second-order, Elovich and intra-particle diffusion kinetic models were studied. The graphical correlation of various adsorption isotherm models like, Langmuir, Freundlich and Tempkin have been carried out for this adsorbent.

Key words: Direct Red 12B, Adsorption, Isotherm, Hazelnut shells, Kinetics.

INTRODUCTION

Most dyes are considered to be non-oxidizable substances by conventional biological and physical treatment because of their complex structure and large molecular size. The adsorption process provides an attractive alternative treatment, especially if the adsorbent is inexpensive and readily (Sivaraj *et al*, 2001). hazelnut shells is the most popular adsorbent and has been used with great (Dogan *et al*, 2009).

High volumes of aqueous effluents contaminated with dyes are generated by different industries (Salvadori *et al*, 2007). The removal of dyes from industrial waste before they discharged in to the water bodies is very important, because most of these dyes are toxic, causing allergy, skin irritation, besides most of then are Mutagenic and/or carcinogenic (Tsuboy *et al*, 2007; Carita *et al*, 2008). Therefore, industrial effluents containing dyes need to be treated before being delivered to environment (Pavan *et al*, 2008 ; Pavan *et al*, 2007). Treatment of the effluent from the dyeing and finishing processes in the textile industry is one of the most significant environmental problems. Since most synthetic dyes have complex aromatic molecular structures which make them inert and biodegradable difficult when discharged into the environment. Coloured wastes are harmful to aquatic life in rivers, lakes and Sea where they are discharged (Shenai, 1996; Greene and Baughman , 1996; Pavan *et al*, 2008).

The methods of color removal from industrial effluents include biological treatment, coagulation, flotation, adsorption, oxidation and hyperfiltration (Santhy *et al*, 2006; Khan *et al*, 2002). Among the treatment options, adsorption has been found to be superior to other techniques for water treatment in terms of initial cost, simplicity of design, ease of operation and insensitivity of toxic substances. Subsequently, the adsorbent can be regenerated or kept in a dry place without direct contact with the environment (Mckay *et al*, 1999).

Application of biological processes to treat coloured wastewater is yet to be fully established. Among treatment technologies, adsorption is rapidly gaining prominence as a method of treating aqueous effluent. Activated carbon is the most effective and widely used adsorbent (El-Geundi and nassar, 1991).

However, its high cost has prevented its application, at least in developing countries, so it is necessary to search for an alternative low-cost adsorbent which can be used as a substitute for activated carbon. A number of low cost adsorbents are reported in the literature. These include bagasse pith (El-Geundi and Nassar, 1991), maize cobs (McKay *et al*, 1988), sunflower (Sun *et al*,

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1997), fly ash (Gupta *et al*, 2000), peat (Ramakrishna *and* Viraraghavan, 1996), saw dust (El-Nabarwy and nassar, 2000), marine algae (Zhao *et al*, 2003), fungal biomass (Basibuyuk *et al*, 2003), wasted activated sludge(Annadurai *et al*, 2003), digested sludge (Weng *et al*, 2001) , red mud (Namasivayam and Arasi,1997), coir pith (Namasivayam *et al*., 2001), Neem leaf (Bhattacharyya and Sarama, 2003), waste organic peel (Namasivayam, 1996), tree fern (Chiang *et al*, 2005). However, sorption potential of most of these low cost sorbents is generally low.

Biosorption can be defined as sequestering of organic and inorganic species including metals, dyes and odour causing substances using live or dead biomass or their derivatives. Since the 1980s, biosorption has been continuously studied for the removal of heavy metals and other pollutants from wastewater, so it could be a promising alternative to replace or supplement present dye bearing wastewater treatment processes. Biosorption, if compared with other available technologies above, gives comparable performance at a very low cost. Apart from cost effectiveness and competitive performance, other advantages are possible regeneration at low cost, availability of known process equipment, sludge free operation and recovery of the sorbate (Lorenc-Grabowska and Gryglewiez, 2007).

The biosorption capacity of a biosorbent depends on several factors. It includes type of biosorbent (species, age), type of sorbate, and presence of other competing ions and method of biomass preparation, along with several physico-chemical factors (temperature, pH, and ionic concentration).

Hazelnut shells as food industry waste. Its major use today is as combustible material owing the considerable calorific value. This material was considered in some works as a source for activated carbon mostly utilized in removal of heavy metals. Hazelnut shells have the some polar functions such as alcoholic, carbonylic, carboxylic and phenolic groups, which are potentially involved in bonding with sorbed pollutants (Fu and Viraraghavan, 2001).

The present work aims to study a convenient and economic method for DR 12B removal from water by adsorption on a low cost and an abundantly available adsorbent, to gain an understanding of the adsorption kinetics, to describe the rate and mechanism of adsorption, to determine the factors controlling the rate of adsorption and to calculate the activation energy of system. The effects of initial DR 12B concentration, solution pH, amount of adsorbent, particle size and temperature on DR 12B adsorption rate have been evaluated.

MATERIAL AND METHODS

Materials

Hazelnut shells were firstly separated, before their use, all the sorbents were washed thoroughly with deionized water and oven dried at 100 ◦C for 24 h (Yasemin Bulut et al., 2007). Crushed in a ball mill and seived the samples with stainless steel mesh screens to obtain different particle sizes of adsorbent.

All reagents used are of analytical grade chemicals and were obtained from Merck. Stock solutions of the test reagent were made by dissolving the dyes in doubly distilled water. The structure of the dyes, Direct Red 12B (C.I. 29100 Direct Red 31, anionic direct dye; formula: $C_{32}H_{21}N_5Na_2O_8S_2$; Molecular weight=713.646 gr mol^{-1}; maximum wavelength=523 nm) is shown in Fig. (1). Dye concentration determination was performed on a UV–vis spectrophotometer model shimadzu at 523 nm. The pH measurements were made using a pH metrohm, model 827 Lab, Hyderabad, India. Orbital shaker machine (countery sowies) was used for batch adsorption studies.

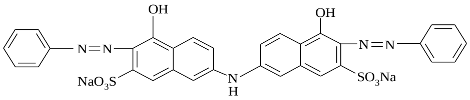

Fig. (1): Structure of Direct red 12B (C.I. No. 29100 Direct Red 31).

EXPERIMENT

Column Method

To study the effect of important parameters like the pH, adsorbent dosage, contact time, initial dye concentration and temperature on the adsorptive removal of DR12B Column experiments were conducted.

An aliquot of the DR12B solution, at in three concentrations 20, 30 and 40 mg L^{-1} pH=2.5 and 25±1°C was passed through a mini column containing 0.3 gr powder hazelnut shells 100 mesh (0-177 µm). The absorbance of Direct Red 12B was measured spectrophotometrically at λmax = 523 nm before and after passing of DR12B through the column. Finally, the percent of removal of DR12B was calculated by using a calibration curve of

DR12B. The concentration of dye in aqueous solution determined spectrophotometrically before and after passing the solution through the columnThe percentage removal of dye was calculated using the following relationship:

$$\%\mathrm{DR12BRemoval} = \frac{C_0 - C_t}{C_0} \times 100 \quad (1)$$

where Co (mg/L) and Ct (mg/L) are the initial dye concentration and dye concentration at time t, respectively.

Batch Method

To study the effect of contact time, kinetics and isotherm on the adsorptive removal of DR12B batch experiments were conducted. For each experimental run, 50 mL of DR12B solution of different concentrations (10-70 mg/L), pH and amount of the adsorbent were taken in a 100 mL Erlenmeyer flask with middle magnet. This mixture was agitated on stirrer at a constant speed in a temperature controlled. Samples were with drawn at different time intervals (01 –20 min for HS) and kinetics, isotherm and other parameters of adsorption was determined by analyzing of remaining dye concentration from aqueous solution. Experiments were carried out at pH=2.5 that the initial pH of the solution was adjusted by addition of aqueous solutions of HCl or NaOH. The percentage removal of dye was calculated using the following relationship (1).

For adsorption isotherms, dye solutions of different concentrations (10-70 mg/L) and at temperature (25 °C) were agitated with known amounts of adsorbents until the equilibrium was achieved. Equilibrium adsorption capacity was calculated from the relationship:

$$qe = \frac{(C_0 - C_t)V}{W} \quad (2)$$

where C_0 and C_e are the initial and equilibrium dye concentrations in solution, respectively (mg/L), V the volume of the solution (L) and W is the mass (g) of the used adsorbent (Kavitha *et al*, 2008).

RESULTS AND DISCUSSION

Effect of pH on DR12B Adsorption

The pH is one of the most important factors controlling the adsorption of dye onto suspended particles. The pH of the solution affects the surface charge of the adsorbents as well as the degree of ionization of different pollutants. The hydrogen ion and hydroxyl ions are adsorbed quite strongly and therefore the adsorption of other ions is affected by the pH of the solution. Change of pH affects the adsorptive process through dissociation of functional groups on the adsorbent surface active sites. This subsequently leads to a shift in reaction kinetics and equilibrium characteristics of adsorption process. As the pH increases, it is usually expected that the cationic dye adsorption also increases due to increasing of the negative surface charge of adsorbents (Dogan *et al*, 2004). The effect of initial pH of the dye solution on the amount of dye adsorbed was studied by varying pHs under constant process parameters. Since pH is the most important parameter affecting the removal of the dye, 50 mL of solutions containing various concentrations of DR12B (20, 30 and 40 mg L^{-1}) were passed from a packed column containing 0.3 g hazelnut shells mesh 60 (210 - 297 µm) The effect of pH on removal of DR12B (figure .2) was studied in range of 2-10 at temperature 25±1^0C. It was found that percent Removal of reactive dye increased with decreasing pH.

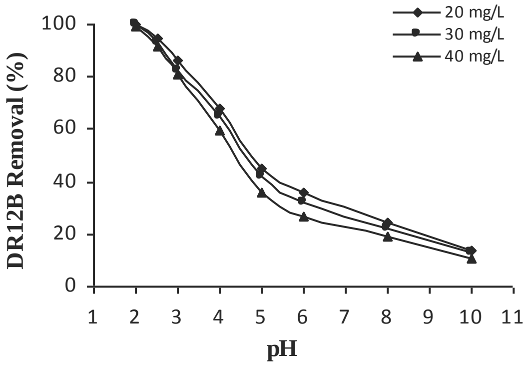

Fig. (2): Effect of pH on adsorption of DR12B (20, 30 and 40 mg/L) onto HS (0.3 g/50 mL) at temperature 25 ± 0.5 °C.

Two possible mechanisms of adsorption of DR12B on the HS adsorbent may be considered: (a) electrostatic interaction between the adsorbent and the DR12B molecule, (b) a chemical reaction between the DR12B and the adsorbent. At acidic pH the H+ ion concentration in the system increased and the surface of the HS acquired positive charge by absorbing H+ ions. As the pH of the system increases, the number of negatively charged sites increases. Surface sites on the HS do not favour the adsorption of DR12B anions due to the electrostatic repulsion. Also lower adsorption of DR12B at alkaline pH is due to the presence of excess OH^- ions. The most effective pH was 2.5 and it was used in further studies.

Effect Adsorbent Dosage

Removal of colors directly depends on the mass of adsorbent. The study of adsorbent dosages for removal of the DR12B from aqueous solution was carried out using mass of HS adsorbent ranging from 0.05 to 0.35 gr and fixing the initial DR12B concentration at 20, 30 and 40 mg/L. It was observed that highest amount of DR12B removal was attained for adsorbent mass of at least adsorbent (Fig. 3).

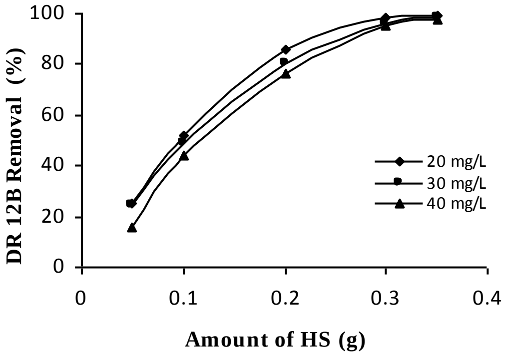

Fig. 3. Effect of HS amount on DR12B removal, Co = 20,30 and 40 mg/L at pH= 2.5, and temperature 25 ± 0.5 °C

Effect of Particle Size

To study the effect of particle size, For column adsorption experiments, three different particle sizes viz .0- 177μm, 210- 297μm and 345-500 μm HS mesh were selected and difference in the amount adsorbed was noticed by using different mesh sizes. Effect of sieve size of adsorbent on the adsorption was studied at 25 ± 0.5 ◦C, 0.3 g of HS, pH=2.5 and DR12B concentration of 20, 30 and 40 mg/L. Fig. 4 presents the effect of sieve size of adsorbent on the adsorption. It was observed that adsorption has been found to increase with the 100 mesh sizes. (Fig. 4)

Effect of Temperature

As various textile dye effluents are discarded at relatively high temperature (35- 45^0C), so temperature will be an important design parameter affecting the adsorption in the real application adsorption by DR 12B in future. 50 mL volumes of solutions containing various concentrations of the dye (20, 30 and 40 mgL^{-1}) were passed from a packed column containing 0.3 gr hazelnut shell (mesh 40).The effect of temperature (fig. 5) was studied in the temperature rang 15- 45±1^0C at pH=2.5 of DR 12B. It was found that percent removal of reactive dye increased with increased of temperature.

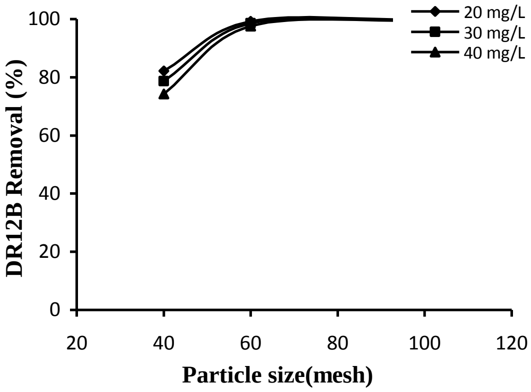

Fig. 4. Effect of particle size on DR12B removal, Co = 20,30 and 40 mg/L onto HS (0.3 g/50 mL) at pH= 2.5, and temperature 25±0.5 °C.

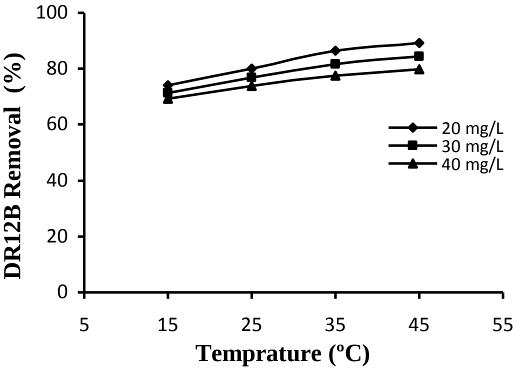

Fig. 5. Effect of temperature on DR12B removal, Co = 20, 30 and 40 mg/L onto HS (0.3 g/50 mL) and pH= 2.5 at mesh 40.

Effect of Initial Dye Concentration

Dye concentration also affects the efficiency of colour removal. Hence a higher initial concentration of dye may enhance the removal of dye. 50 mL volumes of solutions containing various concentrations of the dye (10-100 mg L^{-1}) were passed from a packed column containing 0.3 gr hazelnut shell (mesh 100). The effect of initial concentration of dye (fig. 6) was studied in pH 2.5. It was found that percent removal of dye increased with decreasing of initial concentration of dye.

Interference Studies

The influence of some ions and dyes on the removal of DR 12B was studied. Various amounts of other species were added to a solution containing DR 12B and the recommended procedure was applied. An error of less than or equal to ±5% in the absorbance reading was considered tolerable. The results presented in Table (2) show the good selectivity of the procedure. The interference effects of the dyes (Blue 56, Methylen blue, Direct Red 23 (Scarlet), Acid Blue129, Blue G, Congo Red) were studied in solution of DR 12B .

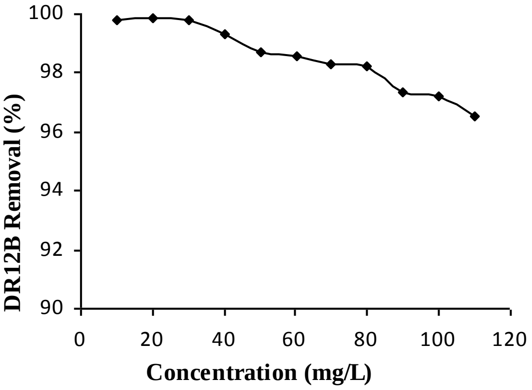

Fig. 6.Effect of concentration dye on DR12B removal, onto HS (0.3 g/50 mL) and pH= 2.5 at mesh 100.

Table (2) : Effect of interferent ions and dyes the HS efficiency Of DR 12B

Interferences	Ratio interferenence
Cl^-, CO_3^{2-} ,SO_4^{2-} , F^- , I^-, NO_3^-, Br^- , Mn^{2+},Ca^{2+} , NH_4^+, Fe^{3+}, Fe^{2+} , Pb^{2+} , Co^{2+} ,K^+ , Na	1000
Ni^{2+}, Mg^{2+} , Cu^{2+}	800
Blue 56, Methylen blue	50
Blue 56, Methylen blue	40
Acid Blue 129	30
Blue G	25
Congo Red	20

Regeneration of Hazelnut Shell

Desorption studies help to elucidate the nature of adsorption and to recycle of the spent adsorbent and the dye. Columns can be re-restoration, research has shown that the hazelnut shell particles with HCl and NaOH 0.1 M of pH (2 to 10) can be rebuilt, then restored. 50 ml of color with a 100 mesh particle size in the pH=2.5 adjusted solution is passed through the column. After crossing the first color of the column volume 25ml of a mixture of NaOH and HCl pH in different colors wash solution will pass through it. The results showed that the acidic pH column, but column cannot be washed up to three times the color is able to absorb alkaline pH and in particular pH=10 and desorption is best. Column eight is able to revive. To remove the paint is 98%.

The results showed that hazelnut shell could be used for several sorption- desorption cycles with similar efficiency (figure 7).

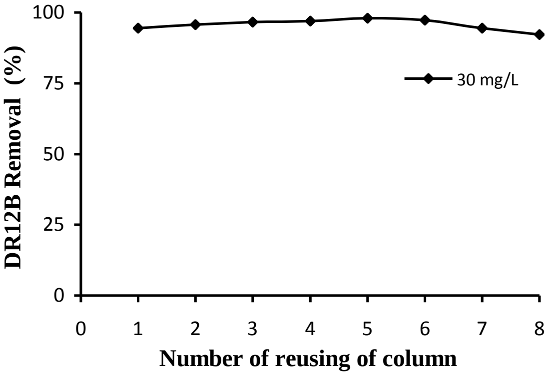

Fig. 7. Regeneration onto HS (0.3 g/50 mL) and desorption at pH=10 in mesh 100.

Effect of Contact Time on DR12B Removal

The adsorption rate, obtained for DR12B adsorption on HS was observed by decrease of the concentration of DR12B within the adsorption medium with contact time. The time necessary to reach equilibrium for the removal of the DR12B molecules at three concentrations of (20, 30 and 40 mg L^{-1}) by HS from aqueous solution was established about 18 minutes. After equilibrium, the amount of adsorbed dye did not change significantly with time in (Fig. 8)

At 20 mg/L of DR12B, the removal rate in the first varies from 61.8% to 96.8% of the maximum removal onto HS. For instance, the adsorbents exhibited three stages, which can be attributed to each linear portion of the figure. The first linear portion was attributed to the diffusion process of DR12B to the adsorbent surfaces (Guo *et al*, 2003; Chingombe *et al*, 2006), hence, was the fastest adsorption stage. This result is corroborated by the factionary-order kinetic model. The second linear portion was attributed to intra-particle diffusion, which was delayed process. The third stage may be regarded as the diffusion through smaller pores, which is followed by the establishment of equilibrium (Guo *et al*, 2003; Chingombe *et al.*, 2006), The surface of HS may contain a large number of active sites and the solute adsorption can be related to the active sites on equilibrium time. Also up to 94 - 96% of the total amount of DR12B adsorption was found to occur in the first rapid phase (18 min) and there after the adsorption rate was found to decrease. The higher adsorption rate at the initial period (first 14 min) may be due to too number of vacant sites available at the initial stage. As a result there exist too concentration gradients between adsorbate in solution and onto adsorbent surface. This increased in concentration gradients tends to increase in DR12B adsorption at the initial stages.

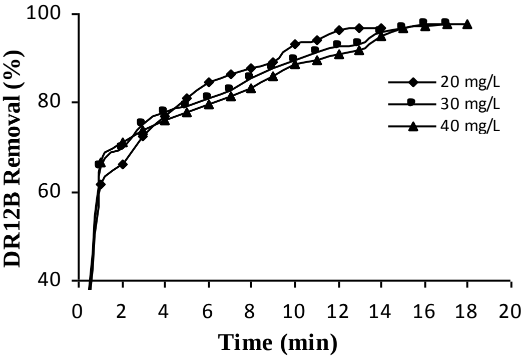

Fig. 8. Effect of contact time : with initial concentration 20, 30 and 40 mg/L at on optimum condition: HS amount 0.3 g/50mL, contact time 20 minutes and pH=2.5.

Adsorption Kinetics Study

Kinetic models are used to examine the rate of the adsorption process and potential rate controlling step. The adsorption rate is strongly influenced by several parameters related to the state of the solid, generally having very heterogeneous reactive surface, and to the physicochemical conditions under which adsorption is carried out. In order to investigate the adsorption processes of DR12B on the adsorbent, pseudo-first-order, pseudo-second-order, Elovich and intra-particle diffusion kinetic models were studied.

The Pseudo First-Order Equation

The rate constant of adsorption is determined from the pseudo first-order equation given by Langergren and Svenska (Lagergren *et al.,* 1898):

$$\log (qe - qt) = \log qe - k_1 t \qquad (3)$$

The values of log (qe −qt) were linearly correlated with t. The plot of log (qe −qt) vs. t should give a linear relationship from which the values of K_1 were determined from the slope of the plot (Table 3). In many cases, the first-order equation of Lagergren does not fit well with the whole range of contact time and is generally applicable over the initial stage of the adsorption processes (Fig. 9) (Ahmed *et al,* 2007). The calculated qe values are not close to the experimental qe values which indicate that the adsorption of DR12B onto HS is not a first order reaction.

Pseudo-Second-Order Model

The pseudo second-order equation based on equilibrium adsorption (Mckay *et al.,* 1998) . is expressed as:

$$1/q_t = 1/k_2qe^2 + (1/qt)\ t \qquad (4)$$

Where k_2 (g/mg h) is the rate constant of the second- order adsorption. If the second-order kinetics is applicable, the plot of t/q versus t should show a linear relationship. There is no need to know any parameter beforehand and qe and k_2 can be determined from the slope and intercept of the plot. Also, this procedure is more likely to predict the behaviour over the whole range of adsorption. The linear plots of t/q versus t (Fig. 10) show a good agreement between experimental and calculated qe values (Table 3).

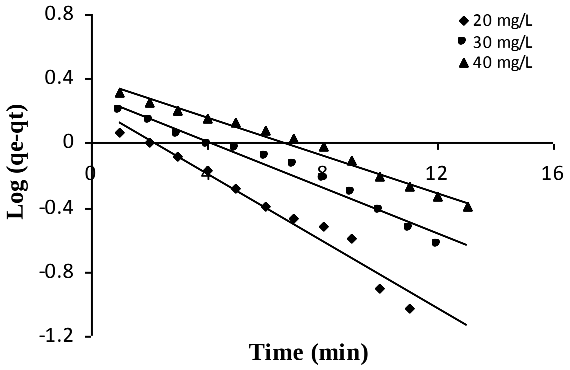

Fig. 9. Pseudo-first-order kinetic model plot for the adsorption of DR12B with concentrations 20, 30 and 40 mg/L, at temperature 25 ± 0.5 °C on optimum condition: HS amount 0.3 g/50 mL, contact time 18 min and pH=2.5.

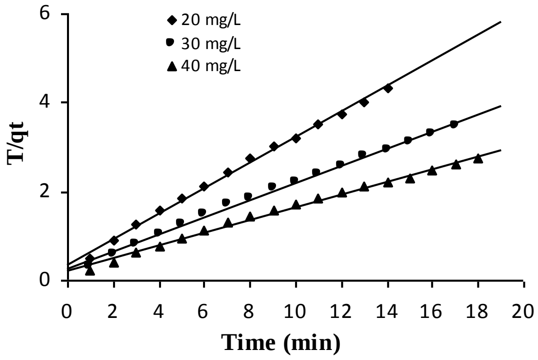

Fig. 10. Pseudo-second-order kinetic model plot for the adsorption of DR12B with concentrations 20, 30 and 40 mg/L, at

temperature 25 ± 0.5 °C on optimum condition: HS amount 0.3 g/50 mL, contact time 18 min and pH=2.5.

The correlation coefficients of all examined data were found very high ($R^2 \geq 0.990$ and 0.996) and calculated qe are almost near experimental qe values, This shows that the model can be applied for the entire adsorption process and confirms that the adsorption of DR12B dye on HS follows the pseudo-second-order kinetic model.

The Intraparticle Diffusion Model

The adsorption mechanism of adsorbtion onto adsorbent follows three steps: film diffusion, pore diffusion and intra-particle transport. The slowest of three steps controls the overall rate of the process. Generally, intra-particle diffusion is often rate-limiting in a batch reactor, while for a continuous flow system film diffusion is more likely the rate-limiting step. In order to investigate the possibility of intra-particle diffusion resistance affecting the adsorption intra-particle diffusion model (Weber *et al*, 1963) was explored.

$$q_t = K_{dif}\, t^{1/2} + C \qquad (5)$$

where K_{dif} is the intra-particle diffusion rate constant. (Fig. 11) represents a plot of qt vs. $t^{0.5}$ for all adsorbents. It shows two separate regions, the initial part is attributed to the bulk diffusion while the final part to the intra-particle diffusion. Values of C give an idea about the thickness of boundary layer (Table 3), i.e. the larger the intercept, the greater is the boundary layer effect. The data indicate that intra-particle diffusion controls the adsorption rate. Simultaneously, external mass transfer resistance cannot be neglected although this resistance is only significant for the initial period of time (Mall *et al*, 2006).

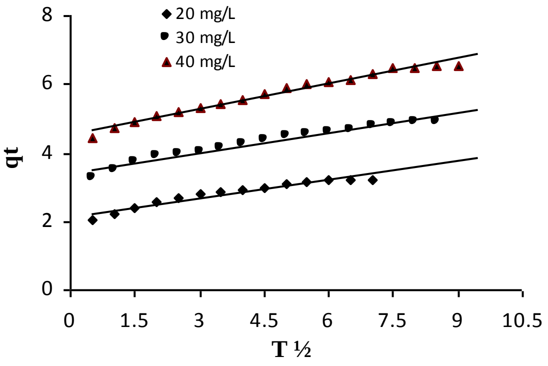

Fig. 11. Intraparticle diffusion model plot for the adsorption of DR12B with concentrations 20, 30 and 40 mg/L, at temperature 25 ± 0.5 °C on optimum condition: HS amount 0.3 g/50 mL, contact time 18 min and pH=2.5.

Elovich Kinetic Equation

The Elovich equation based on equilibrium adsorption (Chien and Clayton, 1980) is generally expressed as:

$$q_t = 1/\beta \ln(\alpha\beta) + 1/\beta \ln(t) \qquad (8)$$

where α is the initial adsorption rate (mg. g^{-1} min^{-1}), β is the desorption constant (g. mg^{-1}) during any experiment. If the adsorption fits the Elovich model, a plot of qt vs. ln(t) should yield a linear relationship with a slope of (1/β) and an intercept of (1/α) ln (αβ). The graph of the Elovich model for the adsorption of the DR 12B by Hzelnut shells at 25 °C is shown in Fig 12. The Elovich constants obtained from the slope and the intercept of the straight line reported in Table 3. The correlation coefficients R^2 are very wavy and ranged from low value to high value without definite role.

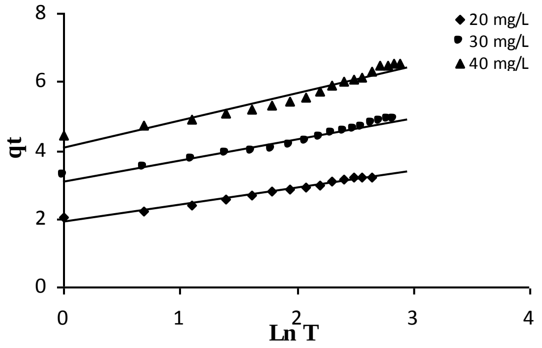

Fig. 12. Elovich kinetic model plot for the adsorption of DR12B with concentrations 20, 30 and 40 mg/L, at temperature 25 ± 0.5 °C on optimum condition: HS amount 0.3 g/50 mL, contact time 18 min and pH=2.5.

Table 3. Adsorption kinetic parameters for the adsorption of DR12B at temperature 25 ± 0.5 °C on condition optimum: HS amount 0.3 g/50 mL, contact time 18 min and pH=2.5.

Model	Parameters	Initial DR12B Conc.(mg/L)		
		20	30	40
Pseudo – First Order Model	K_1 (min^{-1})	0.239	0.163	0.133
	q_e (mg/g)	1.333	1.694	2.192
	R^2	0.962	0.973	0.981
Pseudo - Second Order Model	K_2 (g/mg/min)	0.125	0.083	0.058
	q_e (mg/g)	3.496	5.181	6.994
	R^2	0.996	0.995	0.994
	h (mg/g.min)	1.527	2.227	2.796
Intra particle diffusion model	K (mg/g/$min^{1/2}$)	0.910	1.293	1.886
	C (mg/g)	1.423	2.539	3.431
	R^2	0.962	0.974	0.981
Elovich Model	α (mg/g.min)	25.69	99.91	141.11
	β (g/mg)	2.044	1.650	1.261
	R^2	0.980	0.963	0.936

Adsorption Equilibrium Study

Adsorption isotherms are prerequisites to understand the nature of the interaction between adsorption and the adsorbent used for the removal of organic pollutants. An adsorption isotherm describes the relationship between the mount of adsorbate up taken by the adsorbent and the adsorbate concentration remaining in solution (Langmuir,1918). There are many equations for analyzing experimental adsorption equilibrium data. The equation parameters of these equilibrium models often provide some insight into the adsorption mechanism, the surface properties and affinity of the adsorbent for adsorbate (Langmuir , 1918 and Chilton *et al*, 2008; Abdelwahab and Desalin, 2008). The parameters obtained from the different models provide important information on the surface properties of the adsorbent and its affinity to the adsorbate. Several isotherm equations have been developed and employed for such analysis and three important isotherms, the Langmuir, Freundlich and Tempkin, isotherms are applied in this study.

Langmuir Isotherm

The Langmuir isotherm is based on the assumption that the adsorption process takes place at specific homogeneous sites within the adsorbent surface and that once a dye molecule occupies a site, no further adsorption can take place at that site, which concluded that the adsorption process is monolayer in nature. The Langmuir equation, which is valid for monolayer adsorption onto a completely homogenous surface with a finite number of identical sites with negligible interaction between adsorbed molecules, is represented in the linear form as follows (Desalin *et al*., 2008):

$$Ce/qe = 1/kqe + (1/qe)\, Ce \qquad (2)$$

Where Ce is the equilibrium concentration of the adsorbate (DR12B) (mg L^{-1}), qe, the amount of adsorbate adsorbed per unit mass of adsorbate (mg g^{-1}), and K and qe are the Langmuir constants related to the monolayer adsorption capacity and affinity of adsorbent towards adsorbate, respectively. When Ce/qe was plotted against Ce, a straight line with slope of 1/k was obtained (Fig. 13), indicating that the adsorption of the DR 12B on treated sawdust produced from treated sawdust follows the Langmuir isotherm. The Langmuir constants ‘qe’ and ‘k’ were calculated from this isotherm and their values are given in Table 4.

Freundlich Isotherm

The well-known logarithmic form of the Freundlich model is given by the following equation (Freundlich 1906):

$$\log qe = \log K_F + (1/n) \log Ce \qquad (3)$$

where qe is the amount adsorbed at equilibrium (mg g^{-1}), Ce the equilibrium concentration of the adsorbate (DR 12B) and K_F and n are the Freundlich constants, n giving an indication of how favourable the adsorption process and K_F is the adsorption capacity of the adsorbent. K_F can be defined as the adsorption or a distribution coefficient and represents the quantity of dye adsorbed onto treated sawdust adsorbent for a unit equilibrium concentration. The slope 1/n ranging between 0 and 1 is a measure of adsorption intensity or surface heterogeneity, becoming more heterogeneous as its value gets closer to zero. A value for 1/n below one indicates a normal Langmuir isotherm while 1/n above one is indicative of cooperative adsorption. The plot of log qe versus log Ce gives straight lines with slope of ‘1/n’ (Fig. 14), which shows that the adsorption of the DR 12B also follows the Freundlich isotherm. Accordingly, Freundlich constants (K_F and n) were calculated and recorded in Table 4.

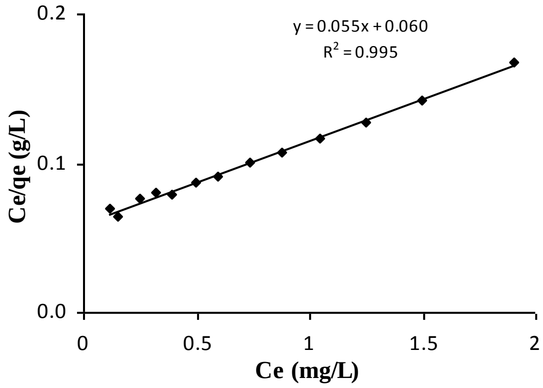

Fig. 13. Langmuir isotherm models plot for the adsorption of DR12B with concentrations 10-70 mg/L, at temperature 25 ± 0.5 °C on optimum condition: HS amount 0.3 g/50 mL, contact time 18 min and pH=2.5

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Tempkin Isotherm

The Tempkin isotherm equation assumes that the heat of adsorption of all the molecules in layer decreases linearly with coverage due to adsorbent-adsorbate interactions, and that the adsorption is characterized by a uniform distribution of the bonding energies, up to some maximum binding energy (Tempkin, 1940).The Tempkin isotherm is given as:

$$qe = B \ln K_T + B \ln Ce \qquad (4)$$

where K_T (l/g) is the equilibrium binding constant, corresponding to the maximum binding energy, and constant B is related to the heat of adsorption. K_T plot of qe versus ln Ce enables the determination of the isotherm constants B and K_T from the(Fig. 15), slope and intercept of the straight line plot. The Temkin equilibrium adsorption curves relating the solid and liquid phase concentration of DR 12B at equilibrium are given as follows Table 4.

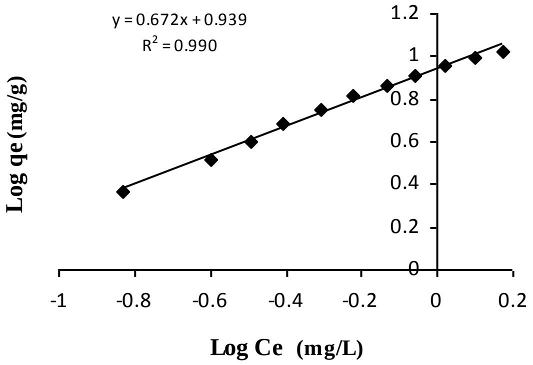

Fig. 14: Freundlich isotherm models plot for the adsorption of DR12B with concentrations 10-70 mg/L, at temperature 25 ± 0.5 °C on optimum condition: HS amount 0.3 g/50 mL, contact time 18 min and pH=2.5

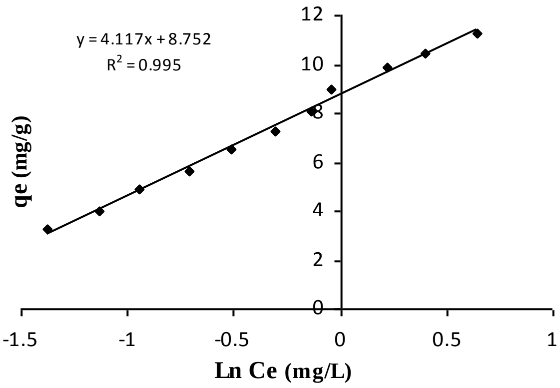

Fig. 15: Tempkin isotherm models plotfor the adsorption of DR12B with concentrations 10-70 mg/L, at temperature 25 ± 0.5 °C on optimum condition: HS amount 0.3 g/50 mL, contact time 18 min and pH=2.5

Table 4. Comparison of the coefficients isotherm parameters for DR12B adsorption onto HS

Isotherm Models	Parameters	
Langmuir	Qe (mg g^{-1})	18.240
	K(L mg^{-1})	0.913
	R^2	0.995
Freundlich	1/n	0.672
	K_f (L mg^{-1})	2.557
	R^2	0.990
Tempkin	B	4.117
	K_T (L mg^{-1})	8.379
	R^2	0.995

Table (4) shows the values of the parameters of the three isotherms and the related correlation coefficients. As seen from Table 4, the Langmuir model yields a somewhat better fit (R^2 = 0.995), Tempkin isotherm (R^2=0.995) than the Freundlich model (R^2 = 0.990). Equilibrium data fitted well with the Langmuir and tempkin model.

Application to Real Samples

In order to test the reliability of the proposed methodology, it was applied to the removal of concentrations of DR 12B in domestic Karoon river, waste water and Maroon river samples. For this purpose, various amounts of DR 12B (20, 30 and 40 mg L^{-1}) were spiked to the sample. Then, spiked samples were treated under the general procedure. The results show that good extraction efficiency are obtained and confirmed the validity of the proposed method for real samples.

Table 5. Removal of DR 12B in water samples

Sample	DR 12B(mg L^{-1})	Extraction efficiency (%)
Karoon River	20	99.65
	30	99.31
	40	99.10
Waste water	20	87.22
	30	85.06
	40	84.99
Maroon river	20	99.53
	30	99.17
	40	98.82

CONCLUSION

The present investigation showed that hazelnut shells an effective adsorbent for removal DR12B from aqueous solution. The amount of DR12B adsorbed was depended on initial solution pH, initial DR12B concentrations, contact time, and adsorbent dose. The maximum removal was attained at pH=2.5. The equilibrium adsorption is practically achieved in 18 minutes. It was also a function of adsorbate concentration and temperature of the solution. The adsorption–desorption study showed that the adsorption was reversible and followed the ion exchange mechanism. Adsorption equilibrium data follows Langmuir, Freundlich and Tempkin isotherm models. The equilibrium data fitted very well in a Langmuir and Tempkin isotherm equations. The kinetic study of DR12B onto HS was performed based on pseudo-first-order, pseudo-second-order, Elovich and intra-particle diffusion equations. The data indicate that the adsorption kinetics follow the pseudo-second-order rate with intra-particle diffusion as one of the rate determining steps. The present study concludes that the HS could be employed as low-cost adsorbents for the removal of DR12B from aqueous solution in general.

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