Kinetic, Equilibrium and Sorption studies of reactive orange -16 from aqueous solution using nut shell of arachis *hypogaea*

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ARTICLE INFO	ABSTRACT
	This paper presents the sorption studies of reactive orange -16 by using the nut shell of Arachis hypogaea. Batch experiments were conducted to study the effect of sorbent dosage, solution pH and initial dye concentration. Sorbent, net shell of Arachis hypogaea was characterized by Fourier Transform Infrared spectroscopy (FTIR) and Scanning Electron Microscopy (SEM). Langmuir and Freundlich adsorption isotherm models were used to represent the equilibrium data. The Langmuir isotherm model was found to be fitted well with the experimental data. The results of sorbent dosage showed that the equilibrium uptake capacity was found to be increase from 7.23mg/g to 25.53mg/g with decrease in amount of Sorbent from 0.5g to 0.1g. The equilibrium uptake capacity was increase from 10.283mg/g to 26.950mg/g when increasing the initial dye concentration from 50mg/L to 200mg/L. This indicates that the dye removal was influenced by the initial dye solution concentration. The sorption results were analyzed for pseudo first order, pseudo second order kinetic and intra particle diffusion model. The values of dimensionless separation factors (R_L) and Freundlich constant (n) showed that net shell of Arachis hypogaea could be used to remove reactive orange -16 from their aqueous solution.

Introduction

Dyes are used in order to colour their products by many industries such as cosmetics, leather, paper, printing, textile finishing and also consume a lot of clean water which becomes coloured wastewater poured into the environment. The presence of dyes that resist against light and heat in the effluent water is the major contaminant causing different type of risks. The presence of very small amount of dyes in water is highly visible and undesirable, reducing photosynthetic activity and causing difficulties in the environment. Introducing dye compounds into the environment also means the bad appearance of colour in the environment (Banat *et al*.1996, Crini 2006, Robinson *et al*. 2001). Among the various kinds of water-soluble dyes and brightly colored acid and reactive dyes are the most problematic as they tend to pass through conventional decolorization systems unaffected (Aksu 2005, Won *et al*. 2005,2006). Reactive dyes are extensively used for colouring fabrics, because they present medium to high fastness to cellulose fibers (Matyjas and Rybicki 2003). High volumes of aqueous effluents contaminated with dyes are generated by textile industries. The removal of synthetic dyes from aquatic systems, is extremely important from the healthiness viewpoint because most of these dyes are toxic, causing allergy, skin irritation, besides most of them is mutagenic and/or carcinogenic. Therefore, industrial effluents containing dyes need to be treated before being delivered to environment (De Lima *et al*. 2007, Sponza 2006, Pavan *et al*. 2007). Traditional physical or chemical decolorization techniques include membrane filtration, ion exchange, ozonation, electrochemical destruction, electro flotation and physical– chemical flocculation combined with flotation based on the use of activated carbon and air mixtures (Fu and Viraraghavan 2001, Banat *et al*. 1996). However the applications of the above mentioned techniques in the large scale are usually restricted due to several disadvantages such as relatively high price, high operating cost, regeneration problem, formation of hazardous by-products and intensive energy requirements (Padmesh *et al*. 2005). Most commercial systems currently use activated carbon as sorbent to remove dyes in wastewater because of its excellent adsorption ability. Activated carbon adsorption has been cited by the US Environmental Protection Agency as one of the best available control technologies (Derbyshire *et al*. 2001). However, activated carbon is a preferred sorbent, its widespread use is restricted due to high cost. In order to decrease the cost of treatment, attempts have been made to find inexpensive alternative adsorbents.

A successful adsorption process not only depends on dye adsorption performance of the adsorbents, but also on the constant supply of the materials for the process. So it is preferable to use low cost adsorbents, such as an industrial waste, natural ores, and agricultural byproducts. Recently, numerous approaches have been studied for the development of cheaper and effective adsorbents. The dye sorption abilities of various agricultural origin materials or those of the by-products have been investigated so far. Powdered peanut hull (Gong *et al*. 2005), sugarcane dust (Ho *et al*. 2005a), apple pomace and wheat straw (Robinson *et al*. 2002), tree fern (Ho *et al*. 2005b), coir pith (Namasivayam *et al*. 2001), neem sawdust (Khattri *et al*. 2000), raw date pits (Banat *et al*. 2003) and banana peel (Annadurai *et al*. 2002) just a few examples of these materials.

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But new, low cost, locally available and highly effective alternative dye adsorbent materials were still needed to search.

It is therefore of interest to investigate the possibilities of the use of nut shell of Arachis hypogaea, a local readily available agricultural waste product, for the removal of reactive orange -16 from aqueous solution.

Material and methods
Sorbate

The reactive orange was obtained from Sd-fine chemicals, India. All other chemicals used in this study were of analytical reagent grade. Stock solution was prepared by dissolving accurately weighed dye in double distilled water. Experimental solutions of the desired concentrations were obtained by diluting the stock solution by using distilled water.
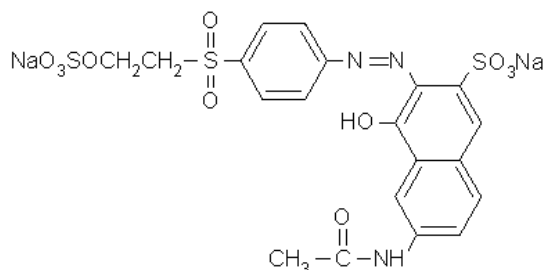
Fig. 1 Structure of Reactive orange 16

Sorbent

The nut shell of Arachis hypogaea used in this work was collected from farm in Virudhunagar, India. The nut shell of Arachis hypogaea was washed with distilled water to remove dirt and soil that are adhered on the surface of the sorbent. Then it was spread on tray and oven(Neolab, Mumbai, India)dried at 60 °C for 48 hours. The dried sorbent was ground and sieved in a 60 mesh size sieve. No other chemical or physical treatments were used prior to adsorption experiments.

Batch studies

Batch adsorption experiments were carried out by adding a fixed amount of sorbent (0.1 g) into 100 ml of different initial dye concentrations such as 50, 100, 150 and 200 mg/L of dye solution. The initial and equilibrium dye concentrations were determined by absorbance measurement using UV spectrophotometer (Shimadzu, Graphicord 240) at maximum wavelength 494 nm. The amount of adsorption at equilibrium, q_e (mg/g), was calculated by

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

where C_0 and C_e (mg/L) are the liquid-phase concentrations of dye at initial and equilibrium respectively. *V* is the volume of the solution (L) and *W* is the mass of sorbent used (g).

To study the effect of sorbent dosage 50mg/L dye solution was prepared from the stock solution and the different amount of sorbent was added (0.1, 0.2, 0.3, 0.4 and 0.5 g) to the 100ml of dye solution and the system is agitated in a shaker(Neolab, Mumbai, India) for the equilibrium time of 4 hours. To study the effect of pH on equilibrium uptake capacity of Nut shell of Arachis hypogaea was measured by adding a fixed amount of sorbent (0.1 g) into 100 ml of 50 mg/L Reactive orange -16 dye solution having different pH such as 2, 4, 6, 8, 10 and 12 of dye solution. The pH of the dye solution was varied by using 0.1N H_2SO_4 and 0.1N NaOH. The initial and equilibrium dye concentrations were determined by absorbance measurement using UV spectrophotometer at maximum 494 nm.

Results and discussion
Effect of initial dye concentration

Different concentrations of 50,100,150 and 200 mg/L dye solution was prepared and then 0.1g of sorbent was added and the system was agitated in a mechanical shaker and the dye concentration was measured with time interval of 10,20,to 240 min. The variation in dye uptake (qt) with contact time at different initial dye concentrations (50 to 200 mg/L) is shown in the Fig. 2. From the Fig. 2, it was observed that the dye removal occurs in the first rapid phase (60 min) and thereafter the sorption rate was found to decrease. The higher sorption rate at the initial period (60min) may be due to an increased number of functional sites available at the initial stage. The increased in concentration gradients tends to increase in dye sorption at the initial stages. As time precedes this concentration is reduced due to the accumulation of dye particles in the functional sites leading to a decrease in the sorption rate at the larger stages from 60 to 240 min. The Fig. 2. shows that as the initial concentration of the dye increases from 50mg/L to 200mg/L the equilibrium uptake capacity increases from 10.28 mg/g to 26.95 mg/g.
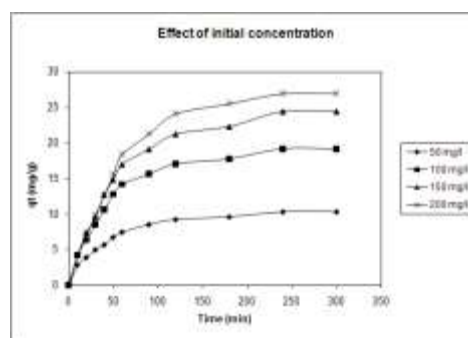

Fig. 2. Effect of initial concentration on adsorption of reactive orange - 16 using nut shell of Arachis hypogaea

Effect of Sorbent dosage

The effect of sorbent dosage was found by adding different amount of sorbent to a fixed concentration of dye solution. 50mL of 50mg/L dye solution was prepared from the stock solution. To this solution different amount of sorbent added (0.1, 0.2, 0.3, 0.4, 0.5 g) and the system is agitated in a shaker for four hours. The Figure.3 shows the effect of sorbent dosage on sorption of reactive orange 19 by Arachis hypogaea. Equilibrium dye uptake capacity q_e decreased from 25.53 mg/g to 7.23mg/g with increase in dosage of the sorbent from 0.1 to 0.5g.The decrease in equilibrium uptake due to the solute transfer rate onto surface of the sorbent.
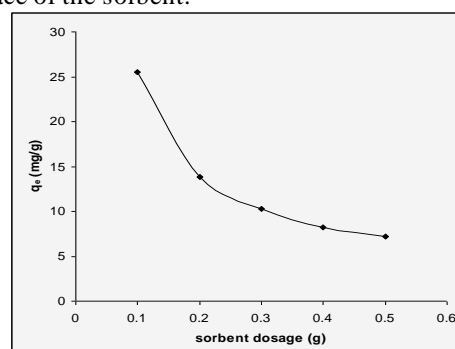

Fig. 3. Effect of adsorbent dosage on adsorption of reactive orange - 16 using nut shell of Arachis hypogaea.

Effect of pH

The effect of pH on the sorption of reactive orange -16 by nut shell of Arachis hypogaea was investigated. Experiments

were performed using different initial pH of the dye solution in the range of 2 to 12. Figure. 4. shows the plot of effect of solution pH on the equilibrium uptake of reactive orange - 16 using nut shell of Arachis hypogaea at 30°C. The dye uptake capacity was found to be more at pH 2. This may be due to two sulfonate groups of reactive orange - 16 are easily dissociated at pH 2. Therefore pH 2 was taken as optimum value. The dye uptake capacity is decreased with increase the pH of the solution. This can be due to the surface charge of the nut shell of Arachis hypogaea. At low pH the active site on the sorbent is positively charged and can adsorb the reactive orange - 16 dye, due to opposite charge attraction between negatively charged dye anions and positively charged adsorption sites. At high pH the surfaces are probably negatively charged which repulse negatively charged dye anions. The similar type of results were obtained for sorption of Acid red 138 from aqueous solutions onto rice bran (Hashemian *et al.* 2008).
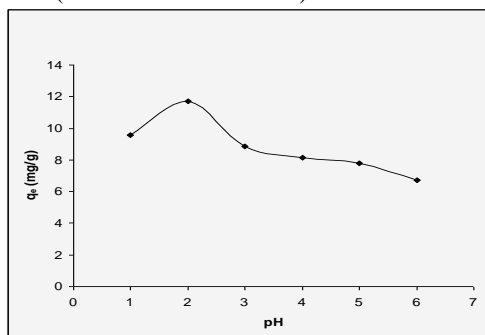

Fig. 4. Effect of pH on adsorption of reactive orange -16 using nut shell of Arachis hypogaea

Isotherm studies

The adsorption data were analyzed with two adsorption isotherm models, namely Langmuir, and Freundlich. The Langmuir adsorption model [Langmuir (1918)] is based on the assumption that maximum adsorption corresponds to a saturated monolayer of solute molecules on the adsorbent surface. The expression of the Langmuir model is given by the following equation:

$$q_e = \frac{Q_0 b C_e}{1 + b C_e} \qquad (2)$$

where q_e (mg/g) and C_e (mg/L) are the amount of adsorbed dye per unit mass of sorbent and unadsorbed dye concentration in solution at equilibrium, respectively. Q_0 is the maximum amount of the adsorbed dye per unit mass of sorbent to form a complete monolayer on the surface bound at high C_e (mg/g), and b (L/mg) is a constant related to the affinity of the binding sites. The linear form of Langmuir isotherm is

$$C_e/q_e = \frac{1}{Q_0 b} + \frac{C_e}{Q_0} \qquad (3)$$

The Langmuir constants Q_0 and b were determined from the slope and intercept of the plot of C_e/q_e against C_e and are presented in Table 1. The Freundlich model [Freundlich (1906)] is an empirical equation that assumes heterogeneous adsorption due to the diversity of adsorption sites. The Freundlich equation is expressed as

$$q_e = K_F C_e^{1/n} \qquad (4)$$

where K_F (mg/g (L/mg)1/n) is roughly an indicator of the adsorption capacity and $1/n$ is the adsorption intensity. The magnitude of the exponent, $1/n$, gives an indication of the

favorability of adsorption. Values of $n > 1$ represent favorable adsorption conditions (Treybal 1968, Ho and McKay, 1978). Eq.4 may also be written in the logarithmic form as

$$\ln q_e = \ln K_F + (1/n) \ln C_e \qquad (5)$$

values of K_F and n are calculated from the intercept and slope of the plot and are listed in Table 5.

The Langmuir and Freundlich isotherms for the adsorption of reactive orange - 16 onto nut shell of Arachis hypogaea at 30°C temperatures are shown in Figs. 5 and 6. The Langmuir and Freundlich adsorption constants evaluated from the isotherms at 30°C temperature with the correlation coefficients is listed in Table 1. As seen from the Table 1, very high regression correlation coefficient was shown by the Langmuir model. This indicates that the Langmuir model was very suitable for describing the sorption of reactive orange16 by nut shell of Arachis hypogaea. The maximum capacity Q_0 determined from the Langmuir isotherm defines the total capacity of the adsorbent for the dye as 38.46 mg/g. The reason that the Langmuir isotherm fits the experimental data very well may be due to the homogenous distribution of active sites on the of adsorbent surface.
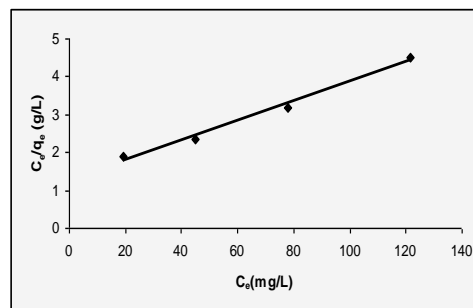

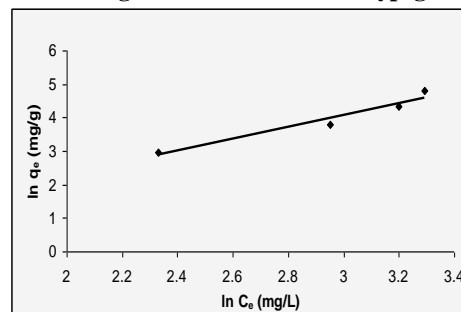**Fig. 5. Langmuir isotherm for adsorption of reactive orange - 16 using nut shell of Arachis hypogaea**

Fig. 6. Freundlich isotherm for adsorption of reactive orange - 16 using nut shell of Arachis hypogaea

Adsorption kinetics

The adsorption mechanism and potential rate controlling steps have been investigated by using the pseudo first, pseudo second order kinetic and intra partical diffusion models. The linear form of Lagergren's pseudo first order rate equation is as follows (Lagergren (1898):

$$\log(q_e - q_t) = \log q_e - \frac{K_1}{2.303} t \qquad (6)$$

where K_1 is the rate constant (1/h), q_e the amount of solute adsorbed on the surface at equilibrium (mg/g), q_t the amount of solute adsorbed at any time (mg/g). The value of the adsorption rate constant (k_1) for *reactive orange-16* sorption by nut shell of Arachis hypogaea was determined from the plot of log ($q_e - q_t$) against t.

The integrated linear form of pseudo-second-order equation is (McKay and Ho, 1999)

$$\frac{t}{q_t} = \frac{1}{k_2 \, q_{2e}} + \frac{1}{q_e} \, t \qquad (7)$$

where k_2 (g/mg min) is the pseudo-second-order rate constant determined from the plot of t/q_t versus t.

The intraparticle diffusion model which refers to the theory proposed by Weber and Morris is thus tested to identify the diffusion mechanism [Furusawa and Smith (1974)]. According to this theory:

$$q_t = k_i t^{1/2} + C \qquad (8)$$

where k_i is the intraparticle diffusion rate constant (mg/g min$^{1/2}$) and C (mg/g) is a constant that gives an idea about the thickness of the boundary layer. If the Weber–Morris plot of qt versus $t^{1/2}$ gives a straight line, then the sorption process is controlled by intraparticle diffusion only.

The straight line plot of t/q_t against time for the pseudo-second-order reaction of the sorption of reactive orange - 16 onto ground net shell are shown in Figs. 7. The calculated value of pseudo-first-order rate constant (k_1), pseudo-second-order rate constant (k_2), equilibrium dye uptake capacity (q_e) and their corresponding regression coefficient values (R^2) are presented in Table 2. It can be seen from Table 2, that the coefficients for the pseudo-first-order kinetic model obtained at all the studied concentrations were low. Also the theoretical q_e values found from the pseudo-first-order kinetic model did not give reasonable values. This suggests that this sorption system is not a first-order. The calculated q_e values agreed very well with the experimental values for the case of pseudo-second-order kinetics, and a regression coefficient of above 0.98 shows that the model can be applied for the entire sorption process.
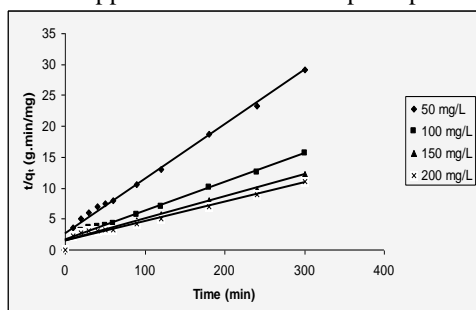
Fig.7. The pseudo second order kinetic model of adsorption of Reactive orange - 16 aqueous solution using nut shell of Arachis hypogaea.

The plot of q_t vs $t^{1/2}$ for intra-particle diffusion in the adsorption of reactive orange - 16 onto nut shell of Arachis hypogaea at various concentrations (Figure 8) was used to obtain the diffusion rate parameters. The correlation coefficients for intra-particle diffusion (R^2 = 0.9540, 0.9583, 0.9649 and 0.9751) were lower than for the pseudo-second-order kinetics. This indicates the present system may be followed by intra-particle diffusion. Furthermore, the plots don't pass through the origin, an observation that suggests some degree of boundary layer control.

Spectral studies:

The Fourier Transform Infrared spectroscopy (FTIR) analysis was carried out to confirm the existence of amine, carboxyl and phosphonate group in nut shell of Arachis hypogaea biomass. The FTIR spectroscopy analysis (figure.9) had showed a strong band in the range of 1730-1750cm^{-1}

indicative of C=O of the carbonyl in carboxylic group. The peaks at 1644, 1370 and 1264 cm^{-1} representing carboxyl groups. some absorption bands(P=O) stretching at 1103 cm^{-1} and the P-OH stretching at 1055cm^{-1}where the phosphonate group is present. The spectrum showed some characteristic absorption of amine group: N-H bonding band at 1512 cm^{-1} and also C-N stretching band at 1264 cm^{-1}.
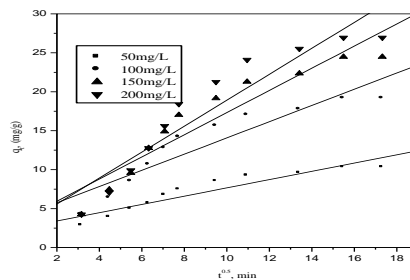
Fig.8. The intra particle diffusion model of sorption of Reactive orange - 16 from aqueous solution using nut shell of Arachis hypogaea
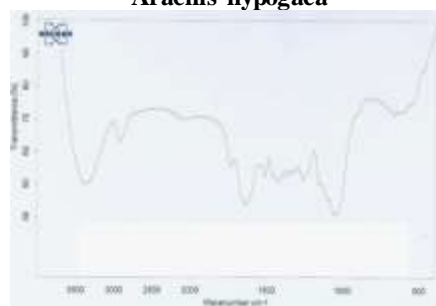
Fig. 9. FTIR spectrum of nut shell of Arachis hypogaea (before adsorption)

The Figure.10. shows the Scanning Electron micrograph of nut shell of Arachis hypogaea. Scanning Electron micrograph shows that the nut shell of Arachis hypogaea surface is homogeneous pores and cavities, providing a large exposed surface area for the sorption of Reactive orange - 16 dye. The presence of pores indicates that there is a good possibility for Reactive orange - 16 dyes to be trapped and adsorbed into the surface of the nut shell of Arachis hypogaea.
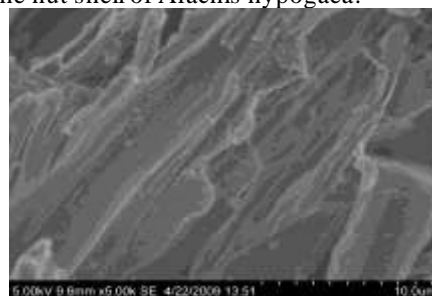
Fig. 10. Scanning electron microscope of nut shell of Arachis hypogaea (before adsorption)

Conclusion

The sorption of Reactive orange -16 from aqueous solution using nut shell of Arachis *hypogaea* was systematically investigated under different conditions. Sorption equilibrium correlated reasonably well by Langmuir isotherm than Freundlich isotherm. The sorption capacity at equilibrium was found to be increased with increase initial dye concentration. The pseudo second order kinetic model agreed very well with the dynamic behavior for the adsorption of reactive orange - 16 onto nut shell of Arachis hypogaea. The results indicated that

reactive orange - 16 onto nut shell of Arachis hypogaea was chemical in nature and net shell of Arachis hypogaea could be used as sorbent to remove reactive orange -16 from their aqueous solution.

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Table 1 : Langmuir and Freundlich parameters for sorption of reactive orange - 16 onto nut shell of Arachis *hypogaea*

Isotherm	Parameters
Langmuir	
Q_0(mg/g)	38.46
b(L/mg)	0.02052
R^2	0.9901
Freundlich	
K_f (mg/g(L/g)$^{1/n}$)	0.2811
n	0.5607
R^2	0.954

Table 2 : Pseudo-first-order and Pseudo-second-order rate constants for the sorption of reactive orange - 16 onto nut shell of Arachis *hypogaea*

Initial conc.	q_e,exp (mg/g)	Pseudo first order kinetic model			Pseudo second order kinetic model		
		K_1(L/min)	$q_{e,cal}$ (mg/g)	R^2	K_2 (g/mg.min)	$q_{e,cal}$ (mg/g)	R^2
50	10.2836	0.0078	5.933	0.7749	0.00303	11.286	0.9886
100	19.1489	0.0104	12.531	0.8969	0.00142	21.322	0.9848
150	24.4680	0.0113	18.420	0.949	0.00085	28.011	0.9762
200	26.9503	0.0122	21.122	0.930	0.00064	31.948	0.9649