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Application of Hyparrheniahirta– A novel biosorbent for the effective removal of reactive dyes

M.K. Raman[1] and G. Muthuraman*

[1]Department of chemistry, Sri Sairam Engineering College, Chennai-600044, Tamil Nadu, India.
*Department of Chemistry, Presidency College, Chennai – 600005, Tamil Nadu, India.

Abstract: Among the various pollution, color pollution of water is chronic issue of nearby textile industries, but it is cost-effective problem of the textile industries to treat the effluent. Since Hyparrheniahirta -a novel biosorbent, which is locally available, used to treat one of the reactive textile dyes. The biosorbent was prepared from Hyparrheniahirta by various methods and tested their adsorption efficiency by adsorption of reactive dye using batch adsorption technique. It was found that, Sodium hydroxide washing increases adsorption efficiency. Batch adsorption experiment was carried out as a function of effect of pH, adsorbent dose, initial dye concentration and contact time. Equilibrium isotherms were analyzed by Freundlich, Langmuir, Tempkin and Redlich-Peterson isotherm equation using correlation coefficients. Pseudo-first-order, pseudo-second-order and intra particle diffusion models were used to fit the experimental data and the kinetic study showed the adsorption process could be described the pseudo second order kinetics. It was also evidenced by FT-IR and SEM analysis. Therefore like the other adsorbents, Hyparrheniahirtais also one of the good adsorbent for the dye adsorption.
Key words : Hyparrheniahirta, Lemon yellow, Waste water, Reactive dye, Adsorption.

Introduction

Dyes can be classified into anionic (direct, acid and reactive dyes), cationic (basic dyes) and non-ionic (disperse dyes) [1].Reactive HE dyes are the most common textile dye used in the local dying industries which are not biodegradable. In aqueous solution, the anionic dyes carry net negative charge, while cationic dyes carry a net positive charge due to the presence of protonated amine or sulfur containing groups [2]. Due to their strong interaction with many surfaces of synthetic and natural fabric, reactive dyes are used for dyeing wool, cotton nylon, silk, and modified acrylics [3]. Therefore, the treatment of coloured effluent from the dyeing industries is necessary.In recent years, the research interest in the production of inexpensive adsorbents. Consequently, a number of low cost and easily available materials, such as biomass, are being studied for the removal of different dyes from aqueous solution at different operating conditions[4].

Hyparrheniahirta- a novel kind of low cost adsorbent used to study their adsorption efficiency with one of the reactive HE dye namely Lemon Yellow HE-4G (LYHE-4G)from aqueous solution. The adsorption studies were carried out using effect of pH, adsorbent dose, initial dye concentration and contact time. The results were evaluated by four kinetic models and four adsorption models.

Materials and methods

Materials

The reactive dye Lemon Yellow HE-4G (LYHE-4G) [C.I. Reactive Yellow-81, λ_{max} : 380 nm], anionic in nature is most commonly used dye in cotton dyeing was collected from local dyeing industry, Thiruvallur district, Tamil Nadu. It was used as received without further purification. A stock solution of LYHE-4G (500 mgL^{-1}) was prepared and suitably diluted to the required initial concentration.

Adsorbent Carbon (AC) preparation

The **Hyparrheniahirta(HH)**was collected from a mountains in Thiruvallur District was washed several times with distilled water and left to dry in sun light, then it was cut into small pieces and then carbonized by two different methods. (i) The pieces were kept in china dish covered with aluminium foil and normally carbonized (NHH), (ii) The pieces were soaked into Sodium hydroxide solution for four days which removes coloring matter in HH and then washed with distilled water, dried were kept in china dish covered with aluminium foil and carbonized (SWHH).The carbonization was carried out in muffle furnace for one hour at 250°C. It was then ground and the portion between 0 and 100 µm sieves was used in all the experiments.

Adsorption studies

Batch adsorption experiments were carried out at the temperature (30 ± 1°C). Exactly 50mL of reactive dye solution of known initial concentration (10–100 mg L^{-1}) was shaken at the constant agitation speed (150 rpm) with a required dose of adsorbents (0.4–2 g L^{-1}) for a specific period of contact time (300 min) in a orbital shaker, after noting down the initial pH of the solution. The percentage removal of dye was calculated using the following relationship:

$$\%\ Removal of dye = \frac{C_i - C_e}{C_i} X\ 100$$

where, $C_i$and$C_e$aretheinitial and final(equilibrium) concentrations of dye (mgL^{-1}), respectively.

Results and discussion

Investigation of sorption parameters

Effect of pH

The effect of initial pH on the equilibrium uptake of the 10 mgL^{-1} of LYHE-4G solution was investigated onto 2 gL^{-1} of NHH and 1.2 $gL^{-1}$of SWHH by varying the initial pH from 1 to 6 (Fig. 1a). The dye adsorbed on carbons was higher at lower pH and it decreases rapidly as the pH increases. The adsorption is very minimum at pH 6 and it becomes zero at neutral. As the pH of the solution increased, the dye adsorbed decreased considerably. The same behavior was observed by many authors [5, 6].

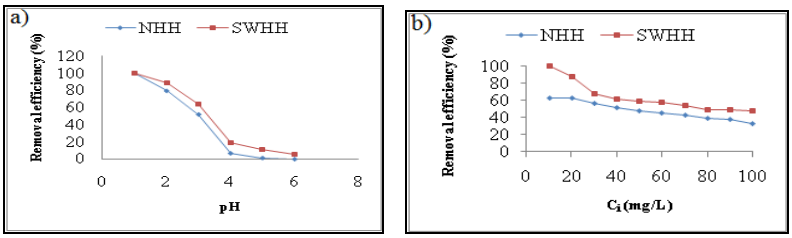

Fig. 1.a) Effect of pH on the removal of 10mgL^{-1} of LYHE-4G b) Effect of initial dye concentration in mg L^{-1} of LYHE-4G on 1g L^{-1} of adsorbents.

Effect of adsorbent dose

The equilibrium uptake of the10 mgL^{-1} ofLYHE-4G solution onto NHH an SWHH was studied by varying the adsorbent dose (2-10 gL^{-1}). The percentage removal of LYHE-4G increased with the increase in dose of adsorbent. This may be due to the increase in carbon surface area and availability of surface active sites [7, 8].

Effect of initial concentration of dye

The effect of initial concentrations (10-100 mgL^{-1}) of LYHE-4G on NHH and SWHH in terms of percentage removal was studied as shown in Fig. 1b. The percentage removal of the dye was found to decrease with the increase in initial dye concentration. At lower concentration, the ratio of initial number of dye molecules to the available surface area is low. Subsequently, the fractional adsorption becomes independent of initial concentration. However, at high concentration the available sites of adsorption become fewer and hence the percentage removal of dye is dependent upon the initial concentration [7, 9].

Effect of contact time

The effect of contact time on the percentage removal of LYHE-4G was investigated at initial dye concentration (20 mg/L. The percentage removal of dye by adsorbent was rapid in the beginning but it gradually decreased with time until it reached equilibrium. The pattern of graphs were almost same for NHH and SWHH, the percentage removal were 62.42 and87.26 respectively at equilibrium. The plots reveal that maximum percent removal of the dye after about 1 h of shaking. The rate of removal is higher in the beginning due to larger surface area available of adsorbent. After adsorption, the rate of dye uptake is controlled by the rate of dye transported from the exterior to the interior sites of the adsorbent particles.

Adsorption isotherms

Freundlich model

The Freundlich adsorption model is the earliest known equation describing the adsorption process [10]. The amount of solute adsorbed, Q_e is related to the equilibrium concentration, C_e of solute in solution by following linear equation:

$$\log Q_e = \log K_F + \frac{1}{n}\log C_e$$

where, K_F is a constant for the system, related to the bonding energy. As the value for $1/n$ below one for SWHH indicates a normal Frendlich isotherm, while $1/n$ above one for NHH, is an indicative of cooperative adsorption [11, 12]. The values of K_F and $1/n$ are determined from the intercept and slope of the linear regressions of log (Q_e) vs. log (C_e) (Table 1).

Langmuir model

A basic assumption of Langmuir[13] theory is that sorption takes place at specific homogeneous sites within the adsorbent, can be represented by the following linear form:

$$\frac{C_e}{Q_e} = \frac{1}{Q_m K_L} + \frac{C_e}{Q_m}$$

where,$Q_m$is the monolayer adsorption capacity (mgg^{-1}) and $K_L$is the Langmuir constant in Lmg^{-1} related to energy of adsorption. Fig. 2a.shows the linear plot of C_e/Q_e vs. C_e for LYHE-4G on the adsorbents,the values of Q_m and $K_L$were determined from intercept and slopes of the linear plots (Table 1). The essential feature of Langmuir isotherm can be expressed by means of dimensionless constant referred to as the separation factor or equilibrium parameter, R_L, which is defined by the following equation [14]:

$$R_L = \frac{1}{1 + K_L C_i}$$

where,C_i is the initial dye concentration (mg L^{-1}).Since theR_L values calculated between 10-100 mg $L^{-1}$are very well lie in the range of 0 to 1, the adsorption process was favorable.

Tempkin isotherm model and Redlich-Peterson isotherm model

Tempkin isotherm contains a factor that explicitly takes place into account adsorbing species-adsorbate interactions [15]. Tempkin isotherm has generally been used in the linearized and rearranged form as following:

$$\mathbf{Q_e} = \beta lnK_T + \beta \ln C_e$$

where, K_T is an equilibrium constant of binding corresponding to the maximum energy of binding (mg L^{-1}) and the β is related to the heat of adsorption. A plot of $Q_e$vslnC$_e$, enables the determination of the isotherm constants K_T and β (Table 1).

Redlich-Peterson(R-P) isothermcan be applied either in homogeneous or heterogeneous system due to the high versatility of the equation[16]. It can be stated by the following equation:

$$\frac{\log C_e}{Q_e} = logK_R + \beta logC_e$$

where, β is the desorption constant and K_R is R-P isotherm constant(gL^{-1}).The isotherm constants β, K_R and the correlation coefficients, R^2 for the R-P isotherm are listed in Table 1.

Table 1 Isotherm parameters for the adsorption of LYHE-4G at 30°C

Isotherm	Parameter	NHH	SWHH
Freundlich	1/n	1.279	0.351
	K_F(mg/g)	20.045	10.715
	R^2	0.965	0.905
Langmuir	Q_m (mg/g)	45.45	58.82
	K_L (L/mg)	0.045	0.061
	R^2	0.993	0.923
R-P	B	0.444	0.948
	K_R (g/L)	0.272	0.093
	R^2	0.946	0.970
Tempkin	B	9.783	10.180
	K_T (mg/L)	0.47	1.204
	R^2	0.989	0.840

The obtained results of each model for the adsorption of LYHE-4G on carbon prepared from **Hyparrheniahirta** are presented in Table 1. The value of correlation coefficient, R^2, was used to compare the four isotherm models. As can be seen from the Table 1, R-P model showed a higher correlation coefficient. Therefore the adsorption process followsFreundlich at high concentration and Langmuir at low concentration of dye. Similar results were reported for the adsorption of Orange-G and Methyl Violet dye onto bagasse fly ash [17].

Adsorption kinetics

Lagergren's first-order kinetic model

The pseudo-first-order kinetic model of Lagergren [18] is more suitable for lower concentration of solute and its linear form is:

$$\log(Q_e - Q_t) = \log Q_e - \frac{k_1}{2.303}t$$

where, Q_t (mg g^{-1}) is the amount of adsorbate adsorbed at time t (min); k_1 (min^{-1}) is the rate constant of pseudo-first-order model. The values of k_1 and Q_e for the adsorption of dye onto adsorbent were determined from the plot of log (Q_e-Q_t) vs. time (Table 1).

Pseudo-second-order kinetic model

Adsorption kinetics was explained by the pseudo-second-order model expressed as following linear equation:

$$\frac{t}{Q_t} = \frac{1}{k_2 Q_e^2} + \frac{t}{Q_e}$$

where, k_2 is the second order rate constant (g mg^{-1} min^{-1}). The values of k_2 for LYHE-4G on adsorbent were calculated from the slopes of the respective linear plots of t/Q_t vs. t (Fig. 2b). The correlation coefficients,R^2 were 1 and 0.999 for NHH and SWHH respectively suggest a strong relationship between the parameters and also explain that the process follows pseudo second order kinetics.

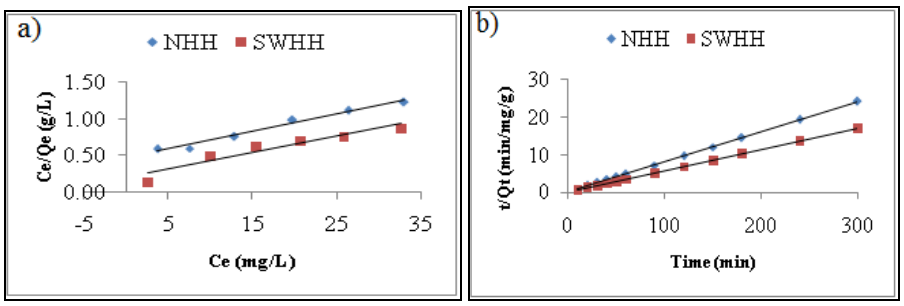

Fig. 2.a) Langmuir isotherm model b) Pseudo-second-order kinetic model

As can be seen from the table 1, the values of R^2 are closer to unity for pseudo second order model. Thus, adsorption of GYHE-R and RGHE-4BD dyes onto adsorbent obey the pseudo second order model. Furthermore, values of $Q_{e\ (cal)}$ calculated from pseudo second order model were good agreement with experimental values, $Q_{e\ (exp)}$ than those calculated form pseudo first order and Elovich model. Similar results were found for the adsorption of MB and GV onto sepiolit[19] and MB onto hazelnut shell [20].

Table 2: Kinetic parameters for the adsorption of LYHE-4G at 30°C

Kinetic model	Parameter	NHH	SWHH
Lagergren's first order model	$Q_{e\ (cal)}$ (mg/g)	3.235	10.209
	k_1	0.062	0.071
	R^2	0.991	0.971
Pseudo second order model	$Q_{e\ (exp)}$	12.48	17.45
	$Q_{e\ (cal)}$ (mg/g)	12.658	17.857
	k_2	0.077	0.030
	R^2	1	0.999

Analysis of SEM and FTIR spectra before and after adsorption

SEM Analysis

The surface morphology of the activated carbon was examined using scanning electron micrography (SEM). The Fig. 3(a) shows the smooth surface area of NHH whereas the Fig. 3(b) shows the presence of more porous surface on SWHH and hence it increases the activity of SWHH than the NHH.

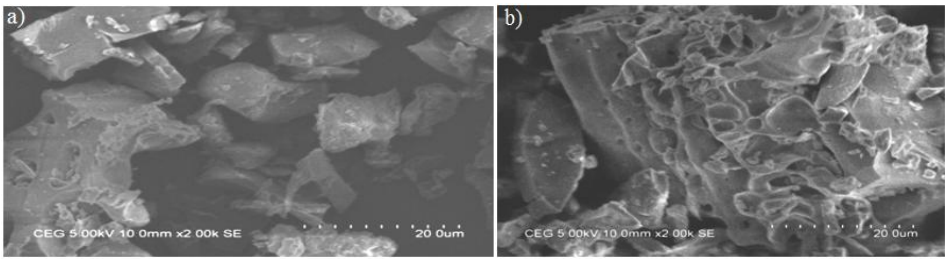

Fig. 3. SEM micrography of activated carbon a) NHH and b) SWHH

Analysis of FTIR spectra

As can be seen from the Fig. 4 the absorption frequencies of activated carbon between 2500-2000 cm^{-1} have single broad peak and it was split up into two peak after the adsorption of dyes. Also many other frequencies were shifted to different wave number with the adsorption of dyes. From these findings it is presumed that the dye was adsorbed onto the adsorbent through interaction with the active functional groups.

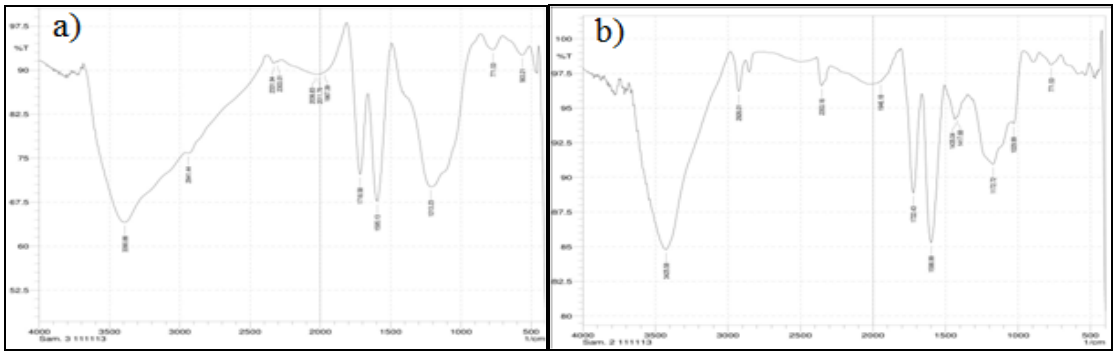

Fig. 4. FT-IR spectrum of activated carbon, a) before adsorption and b) after adsorption of dye

Conclusions

The present study shows that the activated carbon prepared from ***Hyparrheniahirta***have been used successfully for the removal of commercial textile dyes namely LYHE-4G. Although normal carbonization provides potential adsorbent, the raw material washed with sodium hydroxide increases the efficiency of adsorbent still.The percentage removal of the dye was maximum at lower pH, lower initial dye concentration and with higher adsorbent dose. The results of equilibrium adsorption were best fitted with Redlich-Peterson isotherm and the adsorption process was good agreement with pseudo second order kinetic model.

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