Full Length Research Paper

Equilibrium studies on sorption of an anionic dye onto acid activated water hyacinth roots

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The inappropriate disposal of dyes in wastewater constitutes an environmental problem and can cause damage to the ecosystem. Present investigation deals with the utilization of water hyacinth roots (collected from the ponds) as adsorbent for the removal of anionic dye from its aqueous solutions. Batch studies were conducted to evaluate the adsorption capacity of the dye, Congo red on the sorbent with respect to the variations in initial pH, contact time and initial dye concentration and the adsorbent. The effective pH for better adsorption of Congo red on water hyacinth roots was found to be 6.0. Equilibrium reached in about 3 h contact time. Equilibrium isotherms for the adsorption of Congo red on water hyacinth root were analyzed by the Freundlich, Langmuir and Redlich–Peterson isotherm equations. Results showed that Redlich–Peterson isotherm best-fits with the Congo red adsorption isotherm data on all initial dye concentrations. The Freundlich isotherm also showed comparable fit.

Key words: Water hyacinth roots, dye, sorption, isotherms.

INTRODUCTION

There has been increasing scientific concern about the hazardous effects of coloured dyes, which are widely used in textile industries (Mohamed 2004; Aksu and Tezer; 2000; Banat et al., 1996). Textile industry (and especially its part focused on the dyeing process) belongs among important sources of contamination responsible for the continuous pollution of the environment. The production of textile industry, as well as the volume of waste water containing processed textile dyes, steadily increases. The release of dyes into the environment constitutes only a small proportion of water pollution, but dyes are visible even in small quantities due to their brilliance. Many dyes reaching the water sources are difficult to decompose and may cause problems due to their possible carcinogenicity etc.

Textile dyes differs in their chemical composition and stability and that's why different approaches have to be used to lower their content in water sources. In general, chemical, physical and biological treatment procedures can be used for this purpose. The individual procedures differ in their efficiency to remove or degrade the dyes and also in the cost required for the treatment of the comparable volumes of polluted water. Recently, dye removal

became a research area of increasing interest, as government legislation concerning the release of contaminated effluent becomes more stringent. Physical and chemical methods such as adsorption, coagulation-flocculation, oxidation, filtration, and electrochemical methods may be used for wastewater decolorisation. Unfortunately, these methods are quite expensive and show operational problems such as development of toxic intermediates, lower removal efficiency, and higher specificity for a group of dyes, among others (Ho and McKay, 1999).

Adsorption processes have been investigated as an efficient and effective method to remove dyes from wastewater. Activated carbons have been extensively utilized in various industrial adsorption and separation processes. These porous carbons are usually prepared by the carbonization of various raw materials followed by physical or chemical activation (Safarik et al., 2002; Chiou, 2003; Cripps et al., 1990; Fu and Vijayaraghavan, 2003).

However, there are a number of problems associated with activated carbons such as combustion at high temperature, pore blocking, and hygroscopicity. To overcome these problems, various modifications must be developed to prepare the activated carbon to achieve the require-

ments for better abatement of organic pollutants. Due to its higher cost and considering the large quantity of wastewater normally produced by the textile industries, research has recently been novel low cost adsorbents (Chiou et al., 2003).

Various cheap adsorbents have been tested and reported to give encouraging results in several areas of application (Chiou et al., 2003; Ho, 1998; Lakshmi et al., 1994; Low and lee, 1990). Activated silica has proved useful in treating textile mill effluent and also for the adsorption of basic dyes. Activated alumina has been used for the removal of phosphates from wastewaters. Carbonaceous materials such as peat wood and lignite have been used for the removal of colour and metal ions in effluents. Other materials include fly ash and rice husk, tree bark and human hair (Ho and McKay, 1999).

However, the adsorption capacities of the above adsorbents are not very high; In order to improve the efficiency of the adsorption processes, it is necessary to develop cheap and easily available adsorbents with high adsorption capacities.

In a world of rapid assimilation of natural resources, any attempt at the utilization of agricultural waste augments the raw material stock and also provides additional employments and income to marginal farmers and landless agricultural laborers, especially in developing countries. In an agrarian country like India, where 80% of population depends on the land for a living, the utilization of agricultural waste is of great significance.

Water hyacinth, an aquatic plant found widely in India, is listed as one of the most productive plants on earth and is considered one of the world's worst aquatic plants. It forms dense mats that interfere with navigation, recreation, irrigation, and power generation. These mats competitively exclude native submersed and floating-leaved plants. Due to vegetative reproduction and extremely high growth rate (Low et al., 1994, Martina et al., 2004, Mall et al., 2005), water hyacinth has attracted the attention of scientists to use it as a potential biomass for the production of biogas because of its high growth yield and availability in large amount throughout the year and allover the world. In the light of afore-mentioned studies, this research study is conducted to utilize the water hyacinth roots as a potential adsorbent to remove Congo red from its aqueous solutions. Equilibrium isotherms and agitated batch contact time studies have been performed.

MATERIALS AND METHODS

Preparation of sorbent

The water hyacinth roots used in this study were obtained from a pond near by Department of Chemical engineering, Annamalai University, Annamalainagar, Tamilnadu, India. The collected biomaterial was extensively washed with tap water to remove soil and dust and sliced into pieces. The sliced material was dried by exposure to the sunlight for 3 days and subsequently at 80°C for 3 h in a hot air convection oven. The dried material was milled into a powder using 'domestic preethi mixie' and was allowed to pass

through a +65 to -80 mesh opening size sieve. For further studies the sieved powder was treated with 2.0 N HCl for 24 h (Low et al., 1995). After that, the samples were filtered and rinsed with distilled water .The treated material was dried again at 80°C for 6 h, sealed in plastic bags, and stored in desiccators for use.

Preparation of aqueous dye solutions

Congo red was used without any purification. All other reagents were of analytical reagent grade and were obtained from Merck chemicals, UK. A calculated amount of the dye was dissolved separately in 1 L of deionized water to prepare stock solutions, which were kept in dark coloured glass bottles. For batch study, an aqueous solution of this dye was prepared from stock solutions in deionized water. NaOH and HCl solutions were used as buffers for pH studies.

Effect of pH

The pH of initial solution was adjusted between 1.97 and 10.1 by the addition of dilute 0.1 N HCl or 0.1 N NaOH using Oakton Bench top pH 510 m. In this study, 50 ml of 100 mg/l dye solution was agitated with 0.1 g of acid treated water hyacinth roots at room temperature and at a constant speed of 200 rpm. Samples were then analyzed for reduction in absorbance using Hitachi U-1100 UV/V spectrophotometer.

Effect of sorbent dosage

The effect of quantity of acid treated water hyacinth roots on the amount of color adsorbed was studied by agitating 50 ml of 100 mg/L dye solution with different amounts of sorbent addition such as 0.1, 0.2, 0.3, 0.4 and 0.5 g. All these studies were conducted at room temperature and at a constant speed of 200 rpm.

Effect of initial dye concentration and contact time

For conducting the kinetic studies, sets of ten samples agitating at equal time intervals were used. Contact time experiments were carried out by agitating with 50 ml of dye solutions whose concentrations were 25, 50, 75 and 100 mg/l at an optimum pH of 6 with 0.1 g of acid treated water hyacinth roots at room temperature. The speed of agitation was maintained constant at 200 rpm. The colour reduction profiles were obtained using the absorbance measurements.

Amount of dye adsorbed

The formula used to find the Amount of dye adsorbed, q_e, was as shown below:

$$q_e = \frac{V(C_o - C)}{M} \qquad (1)$$

q_e (mg/g) is the amount of dye adsorbed at equilibrium, V (L), is the volume of the solution dye, C_o (mg/L) is the initial dye concentration, C (mg/L) is the dye concentration at any time and M (g) is the adsorbent dosage.
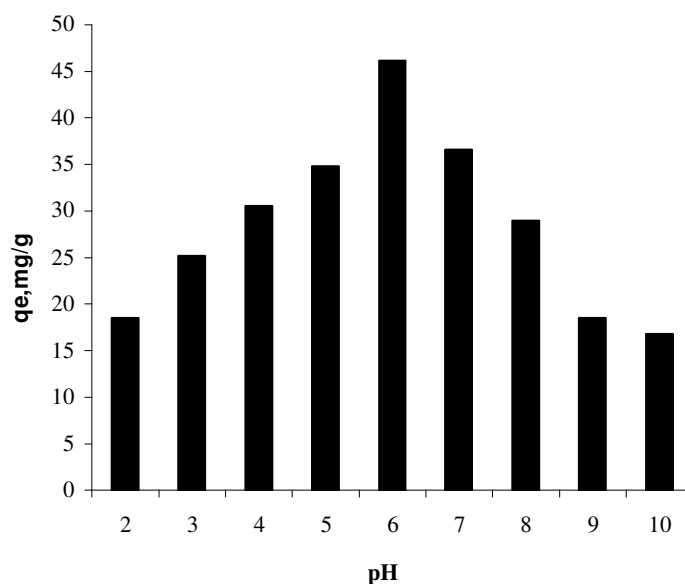
Figure 1. Effect of pH on equilibrium uptake of Congo Red (M:0.1 g;V:50 ml;Co:100 mg/L;Temp:30°C)

RESULTS AND DISCUSSION

Effect of pH

From the set of experiments conducted to find the effect of pH on adsorption phenomenon, it was observed that pH influences both the water hyacinth roots surface dye binding sites and the dye chemistry in water. Figure 1 shows the amount of dye adsorbed, q_e, using acid activated absorbent at different initial pH values. In this set of experiments, the initial dye concentration was fixed at 100 mg/l.

From the shake flask experiments, better colour removal of the dye, Congo red, was observed at pH of 6.0 .The uptake of Congo red was found to be optimal at pH 6.0 with the maximum dye uptake of 46.15 mg/g . In the pH range of 2.0 to 5.0 a decreasing trend in q_e values was observed. Identically, the q_e values were found to decrease in the alkaline pH range of 7.0 - 10.1. Similar results are reported (Low et al., 1995; Vijaraghavan et al., 2004).

Effect of adsorbent dosage

Figure 2 show the effect of adsorbent dosage on the amount of dye adsorbed q_e (mg/g). It was observed that the amount of dye adsorbed varied with initial adsorbent dosage. The amount adsorbed decreased from 46.15 - 30.34 mg/g for an increase in sorbent dosage from 0.1 – 0.5 g. An increase in % colour removal was observed with

an increase in adsorbent dosage. The decrease in q_e may be due to the solute transfer rate on to the adsorbent surface ,that is, the amount of solute adsorbed onto unit weight of adsorbent get splitted with increasing adsorbent dosage. The relationship between the amount of dye adsorbed at equilibrium (q_e) and the adsorbent dosage [M] is given by

$$q_e = 46.175 M^{-0.2465} \tag{2}$$

Biosorption equilibrium

The equilibrium isotherm is of fundamental importance in the design of adsorption. The isotherm expresses the relation between the mass of dye adsorbed at constant temperature per unit mass of the adsorbent and liquid phase concentration.

Langmuir isotherm

The Langmuir, Freundlich isotherms are the most frequently used two parameter models in the literature describing the non-linear equilibrium between amount of dye adsorbed on the acid treated water hyacinth roots (q_e) and equilibrium concentration of solution (C_e) at a constant temperature(30°C). The Langmuir equation, which is valid for monolayer sorption onto a homogeneous surface with a finite number of identical sites, is given by equation (3).
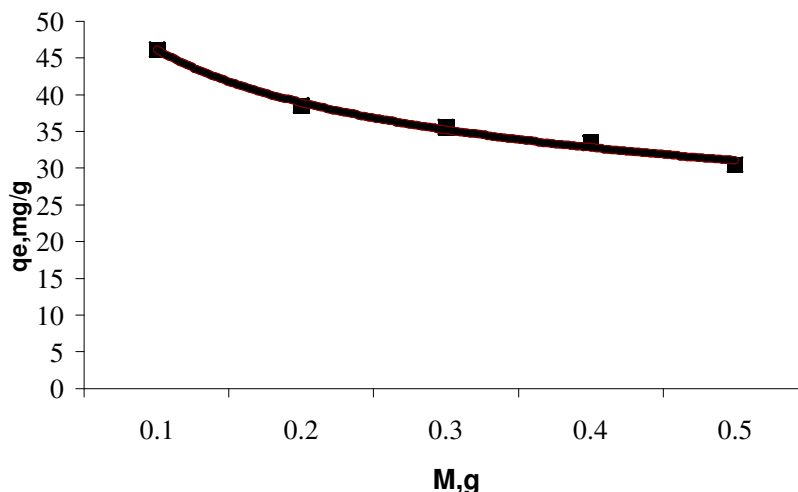
Figure 2. Effect of sorbent dosage on uptake of Congo red (Co:100 mg/L;V:30 ml;pH:6).

$$q_e = \frac{q_o k_L C_e}{1 + k_L C_e} \tag{3}$$

Where; parameters q_o and k_L are Langmuir constants related to maximum adsorption capacity (monolayer capacity) and bonding energy of adsorption, respectively, which are functions of the characteristics of the system as well as time. The values of q_o and k_L can be determined from the linear plot of C_e/q_e versus C_e. The Langmuir equation is used for homogeneous surfaces.

$$h = k_L q_o \tag{4}$$

$$\frac{C_e}{q_e} = \frac{1}{h} + \frac{k_L C_e}{h q_o} \tag{5}$$

The Langmuir adsorption isotherm assumes that the adsorbed layer is one molecule in thickness. The strength of the inter-molecular attractive forces is believed to fall of rapidly with distance. Figure 3 illustrates the linear plot of the Langmuir equation 2. From the plot it is evident that there is some deviation from linearity. The isotherms can be divided into three discrete regions. The isotherm constants h and k_L, together with the concentration range over which the constant hold, are presented in Table 1.

The Langmuir isotherm constant q_o in equation 1 is a measure of the amount of dye adsorbed when the monolayer is completed. The higher adsorption capacity, q_o (>>1) indicates the strong electrostatic force of attraction. Theoretically, this value of q_o should remain a constant.

The isotherm constant h, defined as the product of q_o and k_L, is obtained from the reciprocal of the intercept of the linear plot represented by equation 2. As h should remain constant independent of the solution concentration, the change in slope of the isotherm line is a function of k_L and q_o. The slope is represented by $1/q_o$ and hence a reduction in slope implies an increase in the monolayer capacity, q_o.

Freundlich isotherm

The Freundlich isotherm model assumes neither homogeneous site energies nor limited levels of sorption. The Freundlich model is the earliest known relationship describing the sorption equilibrium and is expressed by the below mentioned equation (6):

$$q_e = K_F C^{1/n} \tag{6}$$

Where; K_F and n are the Freundlich constants related to adsorption capacity and adsorption intensity. Equation 6 can be linearized in logarithmic form and Freundlich constants can be determined.

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \tag{7}$$

The Freundlich equation predicts that the dye concentration on the adsorbent will increase so long as there is an increase in the dye concentration in the liquid. The experimental evidence indicates that an isotherm is reached at a limiting value of the solid phase concentra-
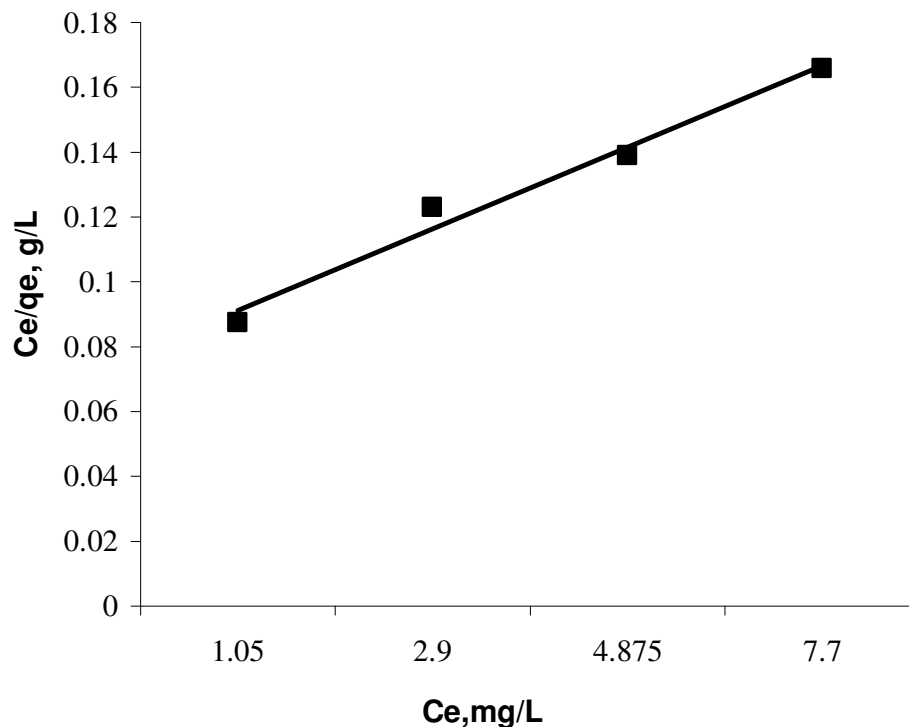
Figure 3. Langmuir plot for Congo red sorption onto water hyacinth roots. (M: 0.1 g; V: 50 ml; pH:6; Temp:30°C).

Table 1. Equilibrium isotherm constants at 30°C.

Freundlich isotherm			Langmuir isotherm			
K_F **(mg/g) (L/g)^n**	**1/n**	**R^2**	k_L **L/mg**	q_o **mg/g**	**h**	**R^2**
1.545	0.1892	0.9607	0.544	13.4646	7.33	0.9557

tion. The equation itself does not have any real physical significance. Figure 3 illustrates the plot of the Freundlich expression for the Congo red sorption onto water hyacinth roots. Freundlich isotherm fitted well to the data with correlation coefficient values of 0.9607. The calculated Freundlich isotherm constants at 30°C are as shown in Table 1. The value of Freundlich exponent n = 5.157 lying in the range of 1 - 10, indicate favorable adsorption.

Redlich-Peterson isotherm

Jossens and co-workers modified the three-parameter isotherm first proposed by Redlich and Peterson (1959) to incorporate features of both the Langmuir and Freundlich equations (Jossens et al., 1978). It can be described as follows:

$$q_e = \frac{K_R C_e}{1 + a_R C_e^{b_R}} \qquad (8)$$

Table 2. Redlich- Peterson equilibrium isotherm constants at 30°C.

Redlich-Peterson isotherm			
k_R	a_R	b_R	**R^2**
18.23	0.5423	0.3018	0.9948

At low concentrations the Redlich-Peterson isotherm approximates to Henry's law and at high concentrations its behavior approaches that of the Freundlich isotherm. The linearized form of the equation 8:

$$\ln\left(\frac{K_R C_e}{q_e} - 1\right) = b_R \ln C_e + \ln a_R \qquad (9)$$

The Redlich-Peterson isotherm constants k_R, a_R and b_R the coefficients of correlation are presented in Table 2. Since the method used to derive the isotherm parameters

maximizes the linear correlation coefficient, it is unsurprising that in all cases the Redlich-Peterson isotherms exhibit extremely high R^2 values. The solubility of a dye is an essential property to enable the dye to penetrate into the porous structure of the water hyacinth roots. Clearly it could it could be expected that small, highly soluble molecules would be ideal molecules for adsorption process. However dyes will associate in aqueous solution to form dimmers and possibly larger micelles. Such larger groups of molecules will not have an easy progression through the porous structure of the water hyacinth roots. The process will be assisted if the dye is ionic and the adsorbent carries an opposite charge. This is the case for the water hyacinth roots-anionic dye sorption process currently under study. The different dye ions will experience different physical and electrical attraction forces according to their structure molecular size and functional groups.

Conclusion

Batch studies were conducted the effective pH of 6.0 for adsorption of Congo red onto water hyacinth roots. Equilibrium reached in about 3 h contact time. Optimum dosages were found to be. 1g/l. Equilibrium isotherms for the adsorption of Congo red on water hyacinth root was analyzed by the Freundlich, Langmuir and Redlich–Peterson isotherm equations. Result showed that the R–P isotherm best-fits the Congo red adsorption isotherm data on all adsorbents. The Freundlich isotherm also shows comparable fit.

REFERENCES

Aksu Z, Tezer S (2000). Equilibrium and kinetic modeling of biosorption of Remazol Black B by *Rhizopus arrhizus* in a batch system: Effect of temperature, Process Biochem. 36: 431–439.

Banat IM, Nigam P, Singh D, Marchant R (1996). Microbial decolourization of textile-dye containing effluents: a rev. Bioresour. Technol. 58: 217–27.

Chiou MS, Ho PY, Li HY (2003). Adsorption Behavior of Dye AAVN and RB4 in Acid Solutions on Chemically Cross-Linked Chitosan Beads J. Chin. Inst. Chem. Eng. 34(6): 625-634.

Cripps C, Bumpus JA, Aust SD (1990). Biodegradation of Azo and Heterocyclic Dyes by *Phanerochaete chrysosporium*. Appl. Environ. Microbiol. 56(4): 1114-1118.

Fu Y, Viraraghavan T (2003). Column studies for biosorption of dyes from aqueous solutions on immobilized *Aspergillus niger* fungal biomass. Water SA 29 (4): 212-217.

Ho YS, Mckay G (1999). A kinetic study of dye sorption by biosorbent waste product pith Resources, Conserv. Recycling 25: 171–193.

Lakshmi KC, Narayan R, Krishnaiah AK (1994). Colour removal from a dyestuff industry effluent using activated carbon. Indian J. Chem. Tech. 1:13–19.

Low KS, Lee CK, Tan KK (1995). Biosorption of basic dyes by water hyacinth roots. Bioresour. Technol. 52: 79-83.

Low KS, Lee CK (1990). Removal of arsenic from Biosorption of basic dyes by water hyacinth roots (*Eichhornia crassipes (Mart) Solms*). Ibid, 13 (1): 129-131.

Low KS, Lee CK (1990). "The removal of cationic dyes using coconut husk as an absorbent" 13(2): 221-228.

Low KS, Lee CK, Heng L (1994). Sorption of basic dyes by *Hydrilla verticillata*. Environ. Technol. 15: 115-124.

Mall ID, Srivastava VC, Agarwal NK, Mishra IM (2005). Removal of congo red from aqueous solution by bagasse fly ash and activated carbon: Kinetic study and equilibrium isotherm analyses, Chemosphere 61: 492–501.

Martina M, Jozefa F, Aleksander P (2004). Decoloration of the diazo dye Reactive black 5 by immobilised *Bjerkandera adusta* in a stirred tank bioreactor. Acta Chim. Slov. 51: 619–628.

Mohamed MM (2004). Acid dye removal: comparison of surfactant-modified mesoporous FSM-16 with activated carbon derived from rice husk. J. Colloid Interface Sci. 272: 28–34.

Safarik I, Ptackova L, Safarikova M (2002). Adsorption of dyes on magnetically labeled baker'syeast cells, Eur. Cells Mater. 3(2): 52-55.

Vijayaraghavan K, Jegan JR, Palanivelu K, Velan M (2004). Removal from aqueous solution by marine algae *Ulva reticulata*. Electronic J. Biotechnol.*,* 7(1):[online] Available from internet: http://www.ejbiotechnology.info/ content/vol7/issue1/full/4/.