Journal of Basic and Applied Engineering Research
p-ISSN: 2350-0077; e-ISSN: 2350-0255; Volume 6, Issue 1; January-March, 2019, pp. 27-32
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http://www.krishisanskriti.org/Publication.html

Biosorption of dye from the Synthetic Solution by Using Rice Husk Activated Carbon (RHAC): Equilibrium Studies

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Graphical Abstract

Abstract—*In this study, the elimination of Basic Yellow 28 (BY28), from synthetic solutions by rice hush activated carbon (RHAC) was examined. Wastewater effluents comprise synthetic dyes which cause a potential hazard to the atmosphere therefore these dyes essential to eliminate from the water bodies. The influence of contact time, pH, temp, concentrations of adsorbent and initial dye concentration were calculated. The results have revealed that the optimum pH was found to be 7 with optimum dose 3.0 gm. In the higher percentage removal was found at 20–40 ^{0}C. The percentage elimination of dye increased with the increase in RHAC concentration upto 4.0 gm and thereafter become constant. Hence 4.0 g/L was considered as the optimum dose of biosorbent. The predictive abilities of six types of isotherm models were examined for RHAC. Redlich-Peterson model was found as best fitted models for the biosorption of dye in present study. Thus, in view of experimental explanations it can be concluded that RHAC can be used as an efficient biosorbent for dye elimination from the synthetic solution.*

Keywords: *Dye; Biosorption; Wastewater; Rice Husk Activted Carbon (RHAC).*

1. INTRODUCTION

[redacted]dustries, mostly in [redacted]lastic and rubber [redacted]000 commercially [redacted]han 7 × 105 ton of [redacted] (Gong, R.; et.al. 2008). Industrial wastewaters including dyes can cause water pollution problems. The existence of dyes in waste water reduce light penetration and has a unpleasant influence on photosynthesis process. Furthermore, dyes can also cause skin irritations, allergies, dermatitis and also provoke cancer. Then, the elimination of dyes from waste water becomes important. Dyes can be categorized in three categories: cationic, anionic and non-ionic. Among them, cationic dyes have widespread industrial applications such as for dyeing leather, paper, silk, wool and cotton. But, cationic dyes are more harmfull than anionic dyes. They can easily act together with negatively charged cells Membrane surfaces and can enter into cells and concentrate in the cytoplasma (Bayramoglu, .et.al. 2009) Basic Yellow 28 (BY28), is the one of the most dangerous cationic dyes, which is widely used in dyeing textile fabrics silk and acrylic. BY28 has numerous toxic effects. It is destructive when it is swallowed and in contact with skin. Furthermore, it is very poisonous to aquatic life with long-lasting effects. Therefore, BY28 was carefully chosen as the adsorbate in the current study. Though, to date, only a very few studies have been showed on the biosorption of BY28 from aqueous solutions. Yener et al. have studied the biosorption of Basic Yellow 28 onto clinoptilolite and amberlite XAD-4 (Yener, J.; 2006). Albanis et al. have studied the elimination of Acid Orange 7, Acid Yellow 23, Disperse Blue 79, Basic Yellow 28 and Direct Yellow 28 from solutions by biosorption on mixtures of fly ash and soil in batch and column techniques (Albanis, T.A.; 2000)

In recent years, several chemical, physical and biological decolorization methods such as coagulation, precipitation, filtration, biosorption, ozonation, oxidation, reverse osmosis, ion exchange and aerobic and anaerobic microbial degradation processes have been used for the elimination of dyes from aqueous solutions. Among these methods, biosorption is one of the most favourable methods for its easy operation, high efficiency and low cost. Consequently, various biosorbents, such as waste materials (Bharathi, S and Ramesh, S.T. 2013) natural minerals,(Elmoubarki, R.; et.al. 2015) bio -absorbents, (Daneshvar, E.; et.al. 2012) magnetic (Zhang, et.al.2015) and carbon nanomaterials,(Ramesha, G.K.; et.al 2011), have been used in dye biosorption studies. There are very few studies reported to use rice husk activated carbon as an biosorbent for the elimination of dyes from aqueous solutions.

Therefore, in the present study, rice husk activated carbon was used as biosorbent for the elimination of BY28 from aqueous solutions. The effect of temperature, pH, initial dye concentration and biosorbent dosage were examined. The isotherm models were fitted to experimental data.

2. MATERIALS AND METHODS

2.1. Adsorbate and biosorbent preparation

All AR grade chemicals were used without further treatment and supplied by Himedia Laboratories Pvt. Mumbai, India. Basic Yellow 28 (C21H27N3O5S, molar mass 433.52) was used as an adsorbate. All experimental solutions of dye were prepared by diluting the stock solution with appropriate amount of millipore water. Rice husk obtained from local market of Ujjain, INDIA was cleaned and washed with millipore water. After washing, rice husk was dried in an oven for 12 hours and carbonized in muffle furnace at 300 ^{0}C for 2 hours. The acid activation of carbonized rice husk was carried out by 2N H_2S0_4 at atmospheric temperature with periodic stirring for about 24 hours. The rice husk activated carbon (RHAC) was washed with millipore water to remove residual chemicals and dried at 60^{0}C for 24 hour in an oven to completely remove moisture. This RHAC was used throughout the study as biosorbent. The surface characteristics of RHAC are as follows: BET surface area: 210 m^2/g, porosity: 0.51 ml/g, moisture content: 4.5%, and ash content: 2.0%.

2.2 Instrumentation

The concentration of dye in supernatant solutions before and after biosorption was determined by UV–vis spectrophotometer (Hach, USA) (APHA,2001). The BET (Brunauer–Emmett–Teller) surface area of RHAC was calculated by using a surface area analyzer (ASAP 2010 Micrometrics, USA). The pH of solutions was measured by standard methods using pH meter provided by WTW® Germany (makes pH 720) (APHA,2001). The SEM images of loaded and unloaded biosorbents were collected by using a scanning electron microscope (LEO 435 VP). The bulk density of biosorbent was determined by using a MAC bulk density meter.

2.3 Biosorption experiments

The batch experiment for elimination of dye from aqueous solution were carried out in an incubator cum orbital shaker at 120 rpm for 5 hours. The residual concentration of dye in the supernatant liquid after centrifugation was determined by UV-Spectrophotometer. For optimization study of biosorbent dose, a fixed amount of biosorbent dose (5-60 g/L) was added in each flask. To obtain the effect of pH and temperature the range 4-10 and 20-40^{0}C were selected respectively. Various pH levels of the dye solution were adjusted by adding a few drops of diluted hydrochloric acid (0.1 N HCl) or sodium hydroxide (0.1 N NaOH). Initial concentrations of dye was maintained at 100 mg/L, except in those where the initial dye concentration effects is to be studied. In all these studies, the samples were remaining in contact until equilibrium condition had been attained. All the experiments were conducted in triplicate and average results were used. The uptake at time t and equilibrium sorption capacity of dye were determined by the following equations (1-2):

$$Q_t = \frac{(C_i - C_t)V}{M} \tag{1}$$

$$Q_{eq} = \frac{(C_i - C_{eq})V}{M} \tag{2}$$

Where: Q_{eq} is the amounts of dye adsorbed on to the per unit mass of adsorbent at equilibrium(mg/g),

Q_t is the uptake of dye at time t(mg/g),

C_t is the liquid phase concentration of dye at time t (min),

C_i is the initial pollutant concentration (mg/L),

C_{eq} is the concentration of adsorbate at equilibrium (mg/L),

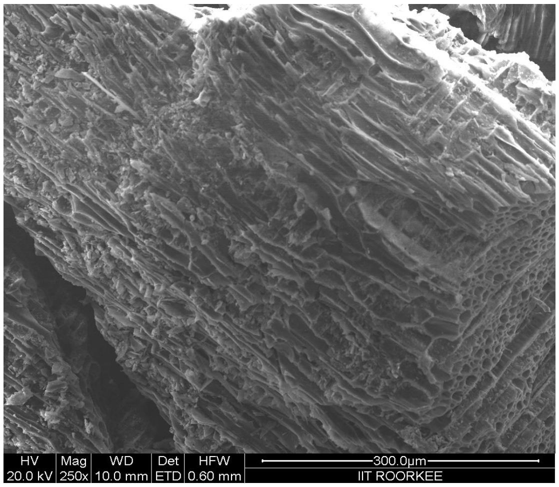
V is the volume of the solution (L),

M is the weight of the biosorbent (g).

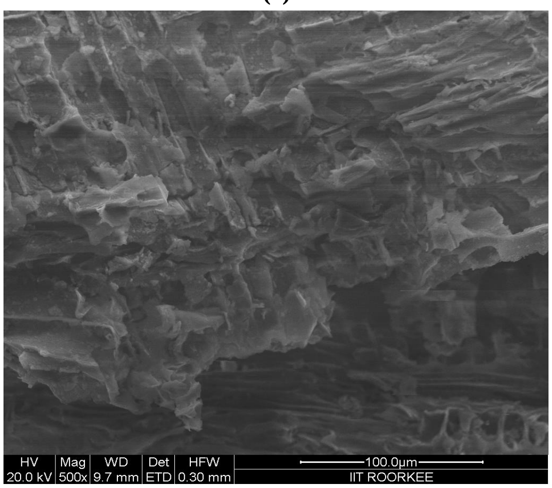
3. RESULTS AND DISCUSSION

3.1 Biosorbent characterization

Scanning electron microscope (SEM) analysis of RHAC before biosorption and after biosorption was shown in fig.1a and 1b respectively. The porous structure and smooth morphology of RHAC makes it appropriate biosorbent. The surface morphology of biosorbent was found to be changed from smooth to rough and occupation of pores shows biosorption of dye onto the pores and biosorbent surface giving it a rough texture (fig 1b).



(a)



(b)

Figure 1: (a) SEM image of biosorbent before biosorption (b) SEM image of biosorbent after biosorption

3.2 Effect of pH

The effect of initial pH on biosorption of BY28 onto RHAC was studied from pH of 4.0 to 12.0 at 30°C and constant initial dye concentration of 100 mg L^{-1}. The effect of initial pH on the biosorption of BY28 onto RHAC is shown in Fig. 2. As can be seen from Fig. 2., the adsorption capacity of BY28 increased with increase of pH from 4.0 to 7.0 thereafter become constant. BY28 is cationic dye which dissociates to the methyl sulfate anion and the positively charged cationic dye, where the positive charge is localized on a single nitrogen atom. The surface of RHAC contain oxygen groups in form of hydroxylic (–OH) functional groups. At basic pH, hydroxylic groups are deprotonated to the anionic form (–O–) and generate electrostatic attraction force with BY28 cations. At acidic pH, hydroxylic groups are protonated to the cationic form ($–OH^{2+}$) . As the pH increases, the number of positively charged sites decreases and the number of negatively charged sites increases, which favor the biosorption of cationic dye BY28 due to the electrostatic attraction. Therefore, the biosorption of BY28 onto RHAC increased with increasing pH of the solution.

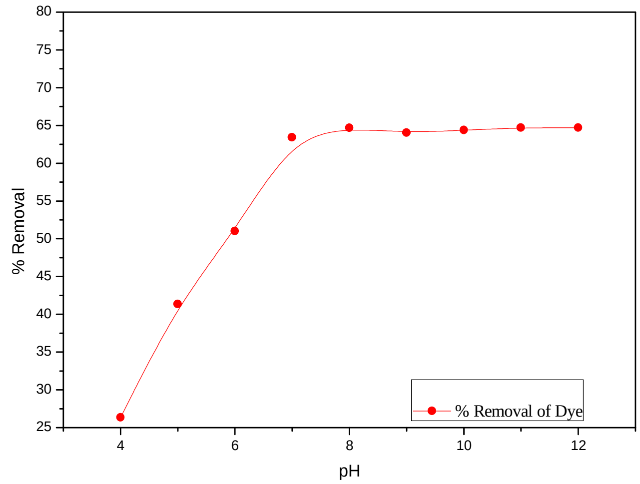


Fig. 2 Influence of pH on percentage removal,

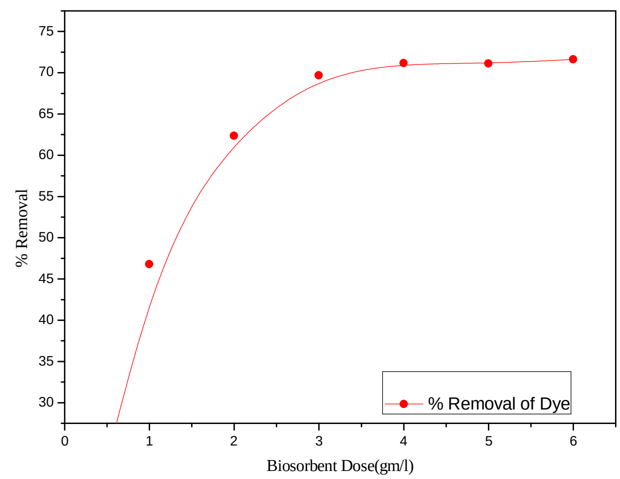


Fig. 3 Influence of biosorbent dose on percentage removal

3.3 Effect of biosorbent dose

It was evident from experimental results shown in fig.3 that the percentage removal of dye gradually increased with increased biosorbent concentration. The effect of biosorbent dose on the processes were varied from 0.5-6.0 g/L. It was also noticed that the percentage removal was constant after 3.0 g/L for biosorption process. With the increment of biosorbent concentration, the active site for biosorption and surface area increases, which leads the increment of percentage removal of dye. The increment in percentage removal of pollutants was not too high after biosorbent concentration 3.0 g/L. This is owing to the fact that the pollutant concentration onto biosorbent surface and concentration of pollutant in solution come into equilibrium with each other. Hence, the optimum dose of RHAC for removal of dye can be selected as 3.0 g/L for biosorption process.

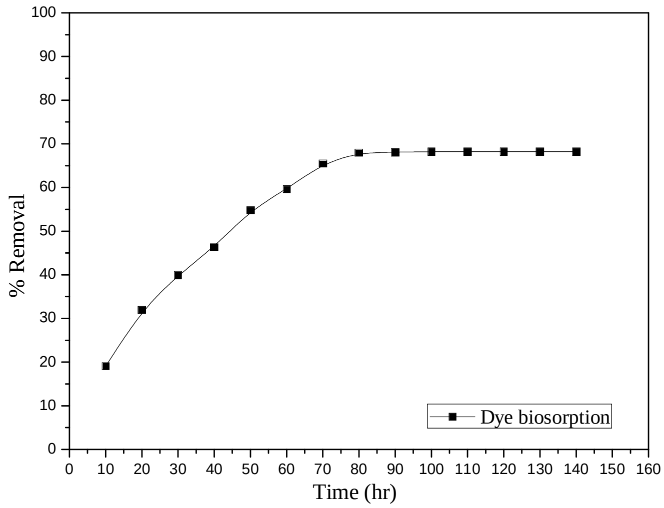


Fig. 4 Influence of contact time on percentage removal,

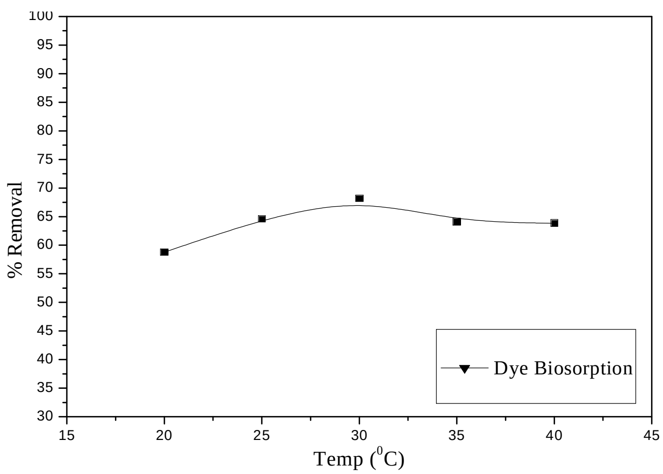


Fig. 5 Influence of temperature on percentage removal

3.5. Effect of contact time

From **Fig 4** it was observed that the uptake of dye onto dye increases rapidly at initial time intervals and then constant until the equilibrium is reached. The time required to reach equilibrium was found to be 1 h. The amounts of dye adsorbed at equilibrium are found to be 99.5 %, at an initial concentration of mg/L at a pH of 7.0 at 30^0 C. The high efficiency in uptake at an initial step is due to the availability of adsorption sites on the surface of biosorbent. After a rapid uptake, there takes place a transitional phase in which the rate of removal was slow and reaches a constant value. The effect of dye concentration on the biosorption by RHAC was investigated by varying the initial dye concentration between 100 and 1000 mg/L at an initial pH of 7.0 at 30 ^{0}C (**Fig. 4**). From the results it was observed that the increase in concentration increases the dye removal.

3.6. Effect of temperature

The effect of temperature on removal of dye were investigated in the range of 20^0C to 40^0C (Fig.5). The removal of dye is increased from 25^0C to 30^0C slightly and after that it starts to decrease. The maximum removal efficiency was found at 30^0C for biosorption process. The increment of temperature helps the adsorbate transport within the pores of biosorbent this may be due to decrease in solution viscosity with increase in temperature (Mall et.al., 1996). Diffusion of adsorbate from the bulk phase into pores of biosorbent have been detected in some of the biosorption processes of endothermic nature (Mall et.al. 1996). 30^0C was selected as the optimum temperature for all the studies.

3.6. Effect of initial concentration

The effect of initial concentration was studied in the range of 100-1000 mg/L for dye keeping pH, temperature, time and dose constant. Fig 6 indicate the effect of initial concentration of dye onto RHAC for biosorption studied. It was found that percentage removal by biosorption process, decrease with increase initial concentration this is due to fact that as initial concentration of substrate increase the active sites available on surface of RHAC decreased (Olgun, A 2009). The surface of RHAC becomes saturated after some time as a result the capacity of biosorbent is high at initial stage.

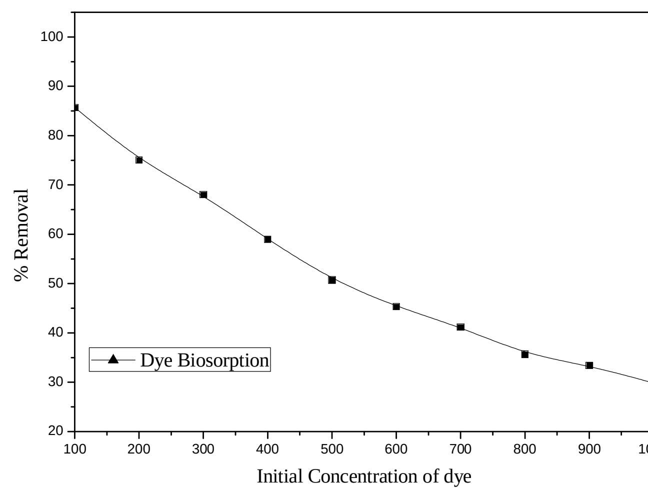


Fig. 6 Influence of initial concentration on percentage removal

3.7 Isotherm Modelling

Adsorption equilibrium data is used to describe the efficiency of an adsorptive removal process. The equation used for adsorption isotherm indicates the diffusion of adsorbate from liquid phase to the solid phase at equilibrium condition. Several mono component isotherm models such as Langmuir, Freundlich, Redlich-Peterson Toth and Fritz-Schlunder isotherm models were used in this study and compared with experimental data.

Among them Langmuir, and Freundlich are two parameter models, Redlich–Peterson and Toth are three parameter models, and Fritz–Schlunder model is four parameter model. Langmuir model shows that adsorption takes place consistently on the active sites of the biosorbent, and once an adsorbate occupies an empty site, no additional biosorption can take place at this site (Annadurai et.al., 1997, Verma, et.al. 2016) The Freundlich model is based on biosorption on heterogeneous surfaces (Annadurai, et.al., 1997). Redlich and Peterson model include three parameters into an isotherm and then, can be applied both in heterogeneous or homogenous systems owing to the high adaptability of the equation (Annadurai, et.al.1997). The parameters of the five mono component isotherms and, the values of their corresponding MPSD are presented in Table 1, Based on the results shown in Table 1, best fit isotherm models for dye are observed in the order: (Redlich–Peterson >Langmuir > Toth > Fritz–Schlunder > Freundlich)

The features of Langmuir isotherms can be described by a separation factor (Annadurai, et.al, 1997).

$$R_L = \frac{1}{(1+bC_0)} \quad (2)$$

Separation factor R_L, explain the feasibility of adsorption process. An adsorption process is favourable when $R_L < 1$, unfavourable when $R_L > 1$, linear when $R_L = 1$, favourable for $0 < R_L < 1$ and irreversible when $R_L = 0$. In this study, the value of R_L was found less than 1, indicating a favourable adsorption process of dye. Marquardt's percent standard deviation (MPSD) was used to predict the equilibrium adsorption data. To define the best isotherm model, Marquardt's percent standard deviation (MPSD) may be produced as (Annadurai, et.al, 1997). comparative table (Table 2) on the basis of brief review of different biosorbents, and uptake capacity for dye ions is presented.

$$MPSD = 100\sqrt{\frac{1}{n-p}\sum_{i=1}^{p}\left(\frac{Q_{e,i}^{exp}-Q_{e,i}^{cal}}{Q_{e,i}^{exp}}\right)^2} \quad (3)$$

Table 1: Comparison of mono component isotherm model parameters for dye onto rice husk activated carbon

Mono component isotherm Models	Parameters	Dye
Langmuir	Q_o	198.50
	b	0.02
	MPSD	9.46
Freundlich	K_F	1.21
	n	5.26
	MPSD	20.94
Redlich-Peterson	K_{RP}	0.067
	a_{RP}	0.0003
	β	1.61
	MPSD	05.73
Toth Model	q_{to}	282.01
	a	0.32
	n	0.047
	MPSD	17.47
Fritz Schlunder Model	a1	0.56
	a2	-0.52
	b1	0.18
	b2	-0.0004
	MPSD	18.90

Table 2: Comparison of biosorption capacity for various biosorbents

Biosorbents	Dye	Biosorption capacity	pH	Reference
sludge	Remazol Brillient Blue	91.0mg/g	7	Santosh et al.2008.
Metal hydroxide sludge	Reactive Red 2	7.99 mg/g	7	Uçar B, Güvenç A, Mehmetoglu Ü 2011
Metal hydroxide sludge	Reactive Blue 4	4.48 mg/g	7	Uçar, Güvenç A, Mehmetoglu Ü 2011
Metal hydroxide sludge	Rhodamine B	42.19 mg/g	7	Selvam PP, Preethi S, 2008
Waste Red Mud	Congo Red	4.05mg/g	7	Namasivayam C, Arasi D 1997

4. CONCLUSION

Equilibrium isotherm aspects of the biosorption of cationic dye Basic Yellow 28 (BY28) onto Rice Husk Activated Carbon (RHAC) was investigated. The removal efficiency of BY28 increased with the increase of pH in the range of 4.0–7.0, thereafter found constant. Maximum biosorption 100 mg/L of dye was found to occur at pH: 7.0, biosorbent dose 3.0 g/L and temperature 30^{0}C. Equilibrium adsorption data showed excellent fit Redlich-Peterson isotherm model The biosorption capacity was found 198.50 mg/ g. It was found that the RHAC can effectively remove basic dyes, and also behaves as a good biosorbent.

5. ACKNOWLEDGEMENTS

The authors are thankful to the Ujjain Engineering College, Ujjain and Indian Institute of Technology Roorkee, India for making its analytical instruments available for the research work.

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