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Adsorption of Basic Blue 41 from Aqueous Solution onto Coconut Fiber Particles

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Abstract

In this research, adsorption experiments were carried out for removal of Basic Blue 41(BB41) dye from an aqueous solution, using coconut fiber particles (CFP) as a low-cost biosorbent. The characteristics of coconut fiber particles weredeterminedwith a scanning electron microscope (FE-SEM) and Fourier Transform Infrared (FTIR) techniques. The effects of initial pH, biosorbentdose, contact time, dye concentration and agitation speed were studied. The Langmuir, Freundlich, Temkin, BET, Dubinin-Radushkevich(D–R) and Harkins–Jura adsorption isotherm models were applied to describe the equilibrium isotherms. The Langmuir isotherm model fit the equilibrium data for the sorbent well, compared to other models. The results indicated that CFP could be employed as an excellent and low-cost sorbent for removal of Basic Blue 41 dye from an aqueous solution.

Keywords*: *Coconut fiber particle, Adsorption isotherm, Biosorption, Basic dye.

Introduction

Dyeing and finishing of textile fabrics are generally performed in water-based media. That process has environmental problems, including water pollution due to discharge of various chemical additives [1, 2]. Many industries have been set up to mitigate the continuously increasing demand for dyes and pigments [3]. Dyes are synthetic organic compounds that are increasingly being produced and used as colorants in many industries worldwide, including textiles, plastic, paper, etc. [4, 5]. Total dye consumption by the textile industry worldwide is in excess of 107 kg per year [6]. Of that, approximately one million kg/yr of dye is discharged into water streams by the industry [7]. Dye producers and users are interested in stability and fastness and, consequently, dyestuffs are being producedthat are more

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difficult to degrade after use [8]. Unless properly treated, dyes present in wastewaters can affect photosynthetic activity due to reduced light penetration and may also be toxic to certain forms of aquatic life [9]. Several wastewater treatment methods have been being used in recent years. Those methods include chemical oxidation [10-12], filtration [13-15], biologicaltreatment [16,17], and adsorption [18-20]. Among the methods mentioned, adsorption processes are attractive because of their high efficiency, low cost, availability, and ease of design. However, it should be noted that solid waste disposal is more costly and unfavorable for adsorption than it is for liquid treatment [21-23].Activated carbon is the most commonly used sorbent for the treatment of dye-bearing wastewaters. However, that process has proved to be uneconomical due to the high cost of activated carbon and also the additional cost involved in regeneration [24]. Adsorption produces a high quality product, and is aneconomically feasibleprocess [25]. In recent years agricultural wastes and by-products such as rice straw [26], palm ash [27, 28], banana pitch [29], hazelnut shell [30] , Brazilian pine-fruit shell [31-33], tree leaves [34], wood shavings [35], coffee beans [36], babassu [37] and marine algae [38] have been widely studied for the removal of dyes from synthetic effluents. Coconut fiber waste accumulates in agro-industrial yards, has no significant industrial or commercial uses, and contributes to serious environmental problems. Therefore, any attempt to reutilize coconut waste would be useful [39].Currently, it has been used as an effective adsorbent [36-43].

In the present work, finecoconut fiber particles (CFP) were used as an alternative to other biosorbents for removing Basic Blue 41 dye from an aqueous solution. The effectof varingparameters including solution pH, biosorbentdose, contact time and dye concentration were studied to determine the optimum biosorption process.

Experimental

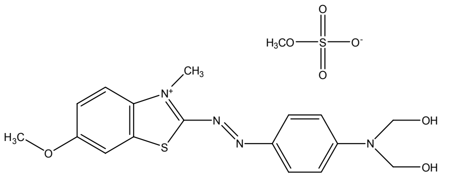
Material and Methods

Adsorbate

Basic Blue 41 (BB41) was purchased from the Ciba chemical company and used without further purification. Table 1 illustrates some characteristics of BB41. All other chemicals were prepared bythe Merck chemical company. The dye stock solutions were prepared by dissolving accurately weighed dyes in distilled water to a concentration of 1000 mg L-1 and subsequently diluted when necessary.

ABB41 concentration graph for the standard solution versus absorbance at the 617 nm wavelength was prepared and used to determine the concentration of an unknown solution. The absorbance of dye solution was monitored for each adsorption procedure. Then the concentrations of dye in the residual solution and the dye uptake were estimated using the standard graph. After that, the adsorption rate of BB41 on the biosorbent was plotted.

Table 1. The characteristics of Basic Blue 41.

Name and color index(C.I)	structure	λ_{max}(nm)	Molecular Weight
Basic Blue 41;11,105		617nm	482.57 g $mole^{-1}$

Preparation and characterization of biosorbent

Coconut fiberwas collected from Malaysia. The biosorbent was washed completely with hot distilled water to remove particles adhering to the surface and water-soluble materials. It was sliced, spread on trays and dried at 105 °C for 24 h. The dried slices were ground and sieved with a planetary mill (Planetry Ballmill/ PM100) to obtain smaller-size particles, and the material was stored in a plastic bottle for further use.

The pH measurement of solutions was done using a pH meter (Metrohm 691, Metrohm, Riverview, FL, USA). The pH of a solution was adjusted by adding H_2SO_4 or NaOH. A Unico 4802 UV-Visible spectrophotometer was employed for absorbance measurements using a quartz cell of 1 cm path length.

Fourier Transform Infrared (FTIR-2000, Bruker Tensor 27) analysis was applied to the undyed CFP and dye-adsorbed CFP to investigate the surface characteristic functional groups, where the spectra were recorded from 4000 to 400 cm^{-1}.

Scanning electron microscope (SEM) data of samples were obtained by a scanning electron microscope (XL30-Philips, Japan). For studying the biosorbent surface texture, scanning electron microscopy (SEM) analysis was done on the powdered coconut fiber particle before and after BB41 adsorption. The size distribution of the CFP was analyzed by dynamic light scattering.

Adsorption procedure

All experiments were conducted with the biosorbent samples in 250 mL conical flasks containing 100 mL BB41 solutions in a water bath to elucidate the optimum values of the experimental parameters including solution pH (3-11), biosorbent dose (0.1-0.8 g), dye-concentration (50–800 mg L^{-1}), contact time (5-120 min) and mixing speed (120-600 rpm). After equilibration time, the samples were taken out and centrifuged at 5000 rpm for 10 minutes with a Hettich EBA20 for solid–liquid separation. The spectrophotometer analyzed residual dye concentration in the solution.

Biosorption equilibrium

0.2 gram of CFP was used for adsorption of BB41 at 60 min, pH 9 and different initial dye concentrations (50-800 mg L^{-1}).The adsorbed amounts of BB41 were calculated using the equation:

$$q_e = (C_0 - C_e)V / W \qquad (1)$$

Where C_0 and C_e are the initial and equilibrium dye concentrations (mg L^{-1}), qe is the amount of dye adsorbed on the biosorbent (mg g^{-1}) at equilibrium, V is the volume of the BB41 solution (L) and W is the weight of biosorbent (g).

Results and discussion

Characterization of sorbent

In order to investigate the surface of the CFP, FTIR spectroscopy was studied (Figure1). The broad peaks were at 3417.38 cm^{-1} (O-H stretch), 2920.41 cm^{-1} (C-H stretch), 1738.56 cm^{-1} (Conj. C=O stretch), 1611.47 cm^{-1} (Conj. C=C stretch) and 1057.22 cm^{-1} (C-Ostretch). We can conclude that some of the peaks are shifted. The changes observed in the spectrum indicated changing in bonding energy in the corresponding functional groups [39].

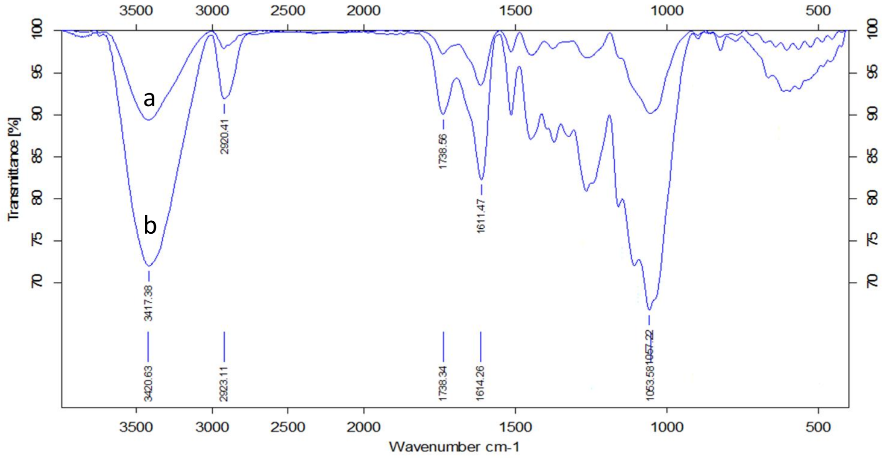


Figure 1. FTIR spectrum of (a) CFP (b) BB41 adsorbed on CFP.

Figure 2 shows the SEM micrographs of CFP samples before and after dye adsorption. Figure 2 indicates that the biosorbent exhibits overlapping and aggregation of sorption sites. The surface of dye-loaded adsorbent, however, shows that the surface of biosorbent is covered with dye molecules (Figure 2(b)).

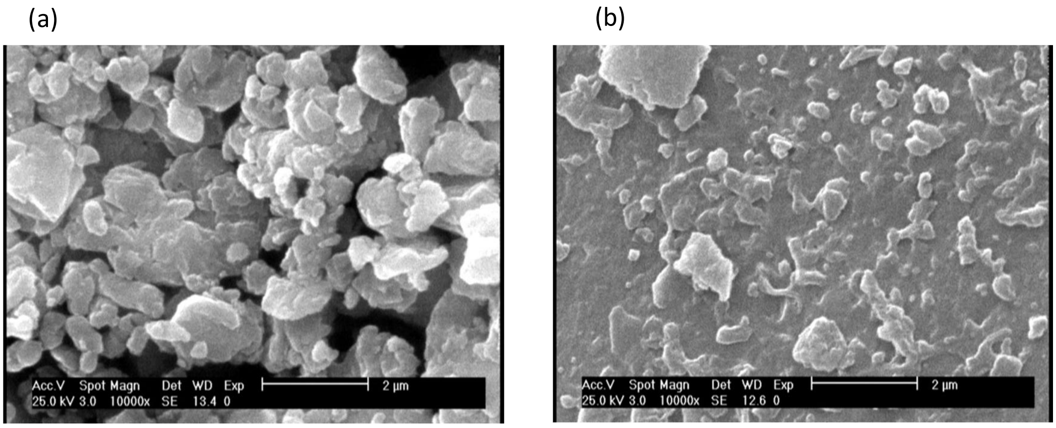


Figure 2. Scanning electron microscope of (a) CFP and (b) BB41 adsorbed on CFP.

Effect of adsorbent dose on dye adsorption

The effect of CFP dose on the amount of BB41 adsorbed was studied by adding different amounts (0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, and 0.8 g) of biosorbent into 100 ml of dye solution, with an initial dye concentration of 100 mg L^{-1}. The test was done at room temperature for 1 hour. Then, the residual amount of dye was calculated by spectrophotometer. Biosorption capacity was measured. The plot of dye removal percentage versus adsorbent dose (g) is shown in Figure3. The results show that the adsorption of dye increased with the increase of adsorbent dose up to 0.2 g. That can be attributed to increased effective contact area of adsorbent. But a higher adsorbent dose leads to a decrease in dye adsorption.The result may be attributed tooverlappingof adsorption sites, resultingin adecreaseintotaladsorbentsurface area availableto the dye [40]. Similar results regarding the effect of biosorbent dose on dye biosorption capacity have been observed and discussed in the articles for different types of biosorbents [41-42].

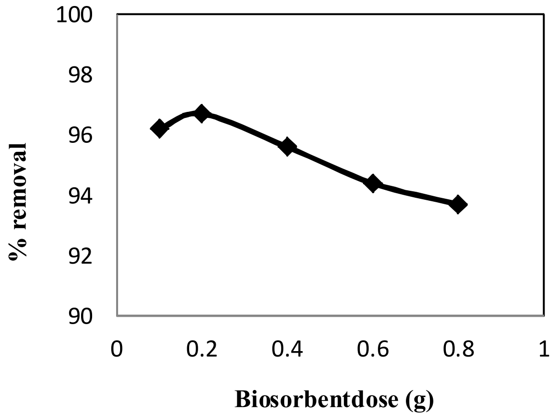


Figure 3.Effect of adsorbent dose on the adsorption of BB41 by CFP.

Effect of solution pH

The pH of the dye solution affects several items such as: the surface charge of the biosorbent, the degree of ionization of the materials, the dissociation of functional groups on the active sites of the biosorbent and the structure of the dye molecule [43].The biosorption capacity of BB41 by CFP at different pH values (3 to 11) is plotted in Figure4.As Figure4 shows, biosorption capacity of BB41 by CFP increased with increasing pH. As initial solution pH increased, the number of negatively charged sites increased and positively charged sites decreased. Therefore, the electrostatic repulsion between the adsorbent site and positively charged dye ion was lowered, which may have resulted in an increase of adsorption. Also, lower adsorption at acidic pH was probably due to the presence of excess of H+ ions competing with cation groups on the dye for adsorption sites.The results show that the maximum biosorption of BB41 was observed at pH 9.0. Maximum biosorption capacity of BB41 was found to be 48.68 at optimum pH. Similar pH trends were also reported by other researchers for princess tree leaf [40] and kaolin [47].

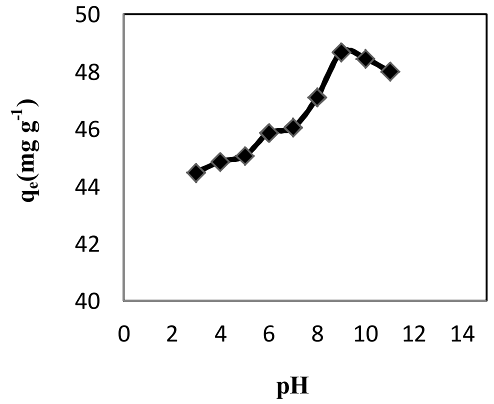


Figure 4. Effect of pH solution on the adsorption of BB41 byCFP.

Effect of agitation speed

Agitation is an important parameter in adsorption phenomena. Agitation influences the distribution of the solute in the bulk solution and the formation of the external boundary film. Agitation speeds of 120, 240, 360, 480 and 600 rpm were used within a contact time of 60 min. Figure5 indicates that the adsorption capacity significantly increases as the agitation speed increased from 120 rpm to 240 rpm. This can be attributed to increased possibility of contact of dye molecules with adsorbent surface. On the other hand, the experimental errors between the agitation speeds of 240, 360, 480 and 600 rpm show that the effect of agitation seemed to be negligible at above 240 rpm. The effect can be attributed to the increase in turbulence and reduction in boundary layer thickness around the adsorbent particles as a result of increase in the degree of mixing [46]. Tsai et al. [46] and Nandi et al. [47] found these results for the adsorption of dye onto ground eggshell and kaolin, respectively.

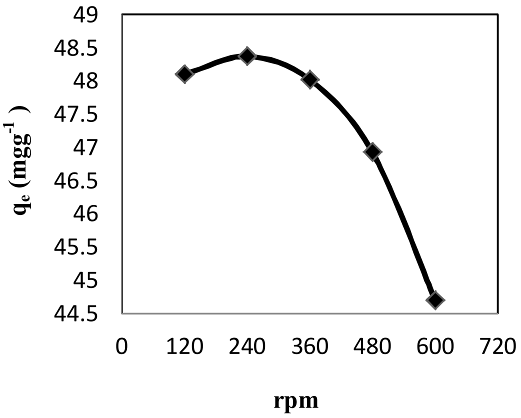


Figure 5.Effect of agitation speed on the adsorption of BB41

Effect of contact time and dye concentration

The contact time between the adsorbate and the biosorbent is one of significant importance for practical application in the wastewater treatment process [48]. The effects of initial dye concentration on the adsorption capacity of BB41 onto the CFP are investigated in Figure6. The amount of BB41 adsorbed at equilibrium (q_e) increased from 22.31 to 393.836 mg g^{-1} as the initial concentration was increased from 50 to 800 mg L^{-1}, attributed to the increase in the driving force between the aqueous and solid phases and the number of collisions between dye ions and adsorbents [49]. Also it shows rapid adsorption of BB41 in the first 15 min, thereafter, the adsorption rate decreases gradually till it reaches equilibrium. Equilibrium was established at 60 min for all the initial concentrations studied.

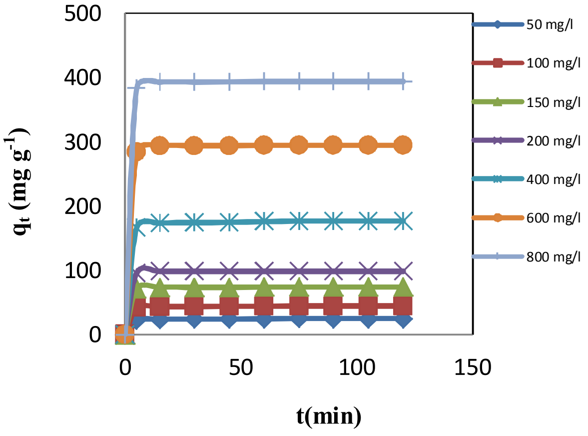


Figure 6. Effect of the time on the adsorption of BB41 byCFP.

Adsorption isotherms

To describe the biosorption equilibrium between an adsorbent and a sorbate, five models were used, including the Langmuir, Freundlich, TemkinBET, Dubinin-Radushkevich(D–R) and Harkins-Jura equations.

Langmuir isotherm

The Langmuir theory suggests that the biosorption onto the adsorbent surface is homogeneous in nature. The most widely used equation describing the adsorption process is the Langmuir equation. The linear form of the Langmuir equation can be found in the following equation [50]:

$$\frac{1}{q_e} = \frac{1}{Q} + \left(\frac{1}{QbC_e}\right) \qquad (2)$$

Where Q is the amount of the dye adsorbed on biosorbent to form complete monolayer coverage on the surface bound at equilibrium, C_e is the equilibrium concentration of dye solution, q_e is the amount of dye biosorbed on biosorbent at equilibrium, and b is the Langmuir constant related to the affinity of the binding sites. The value of Q is the maximum adsorption capacity. The values of Q and b can be calculated from intercepts and slopes of the straight lines of plot of $1/q_e$ against $1/C_e$ (Figure7). The values of Q and bare listed in Table 2.

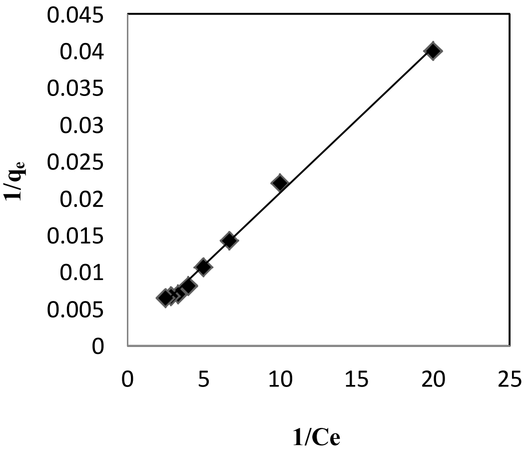


Figure 7.Langmuir isotherm for BB41 sorption onto CFP.

The results showed that the Langmuir model was the best-fitted for BB41, which indicated that a chemisorption mechanism is involved in the adsorption of dye on CFP. The essential characteristic of the Langmuir isotherm can be expressed by the dimensionless constant separation factor, R_L, defined by [40]:

$$R_L = \left(\frac{1}{1+bC_0}\right) \qquad (3)$$

Where C_o is the initial dye concentration (mg L^{-1}) and b is the Langmuir constant (L mg^{-1}). R_L shows the nature of the biosorption mechanism.

R_L values indicate the type of isotherm to be irreversible (R_L=0), favorable (0<R_L<1), linear (R_L=1) or unfavorable (R_L>1) [40].

In this study, the value of R_L was found to be in the range of 0–1 (Figure8). The R_L values indicated that the biosorption process is favorable for BB41.

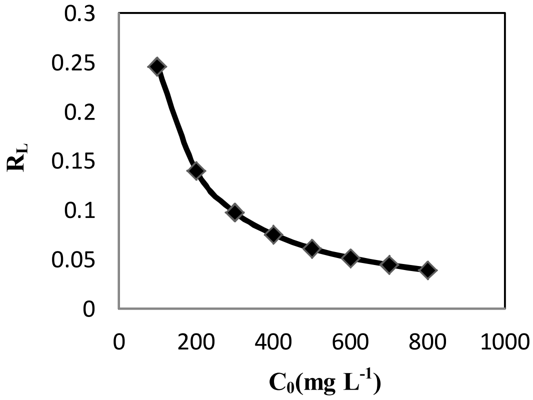


Figure 8. The separation factor for BB41 onto CFP.

Table 2. Equilibrium values for the BB41 biosorption on CFP.

Adsorption model	**Isotherm constants**		
Langmuir	**Q(mg g^{-1})**	**b (L mg^{-1})**	**R^2**
	1000.00	0.50	0.996
Freundlich	**Q_f**	**N**	**R^2**
	1.79	1.07	0.989
Temkin	**K_{Te}**	**B**	**R^2**
	355.31	68.13	0.948
BET	**X_m**	**K_B**	**R^2**
	138.89	4.23	0.858
Dubinin-Radushkevich(D–R)	**q_m(mg g^{-1})**	**K**	**R^2**
	222.07	4.00×10^{-8}	0.975
Harkinson-Jura	**A**	**B**	**R^2**
	625.00	-0.50	0.803

Freundlich isotherm

The Freundlich equation is another model which is often used to shown an empirical relationship between the concentration of a sorbate on the surface of an adsorbent and the concentration of the sorbate in the solution. The equation is presented below [40]:

$$\ln q_e = \ln Q_f + \frac{1}{n}\ln C_e \qquad (4)$$

Where Q_f is the Freundlich isotherm constant (mg g^{-1}) related to the bonding energy. Q_f is defined as the distribution coefficient and suggests the amount of dye adsorbed on CFP for unit equilibrium concentration.

The value of n indicates whether the biosorption process is favorable or not. The value of Q_f, correlation coefficient and n of CFP are calculated from Figure9 and presented in Table 2. The R^2 value for BB41 showed that the experimental data was also very well fitted to the Freundlich isotherm model at higher doses. The values of n are greater than 1, indicating that the biosorption of BB41 onto CFP is a favorable physical process. The results indicated that biosorption of BB41 onto CFP also involved some physical forces such as electrostatic interactions between adsorbates and adsorbent.

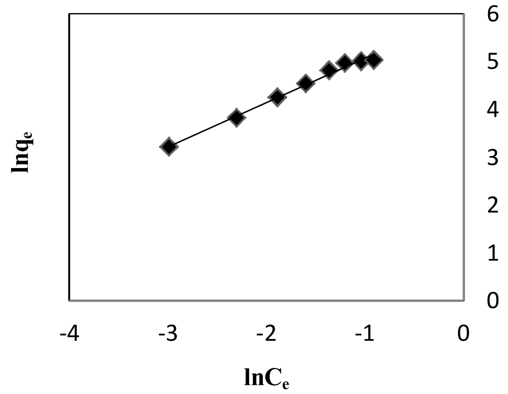


Figure 9.Freundlich isotherm for BB41 sorption onto CFP.

Temkin isotherm

The Temkin isotherm includes a factor that explicitly takes into account adsorbing species-adsorbent interactions. The Temkin isotherm is the following equation [50]:

$$q_e = \frac{RT}{b}(\ln K_{Te}C_e) \quad (5)$$

Where $B=RT/b$ and K_{Te} can be determined from the linear plot of q_e against lnC_e (Figure 10). The B and K_{Te} values are listed in Table 2. The correlation coefficients obtained by this model are above 0.94. That indicates that the experimental data does not fit well to this model.

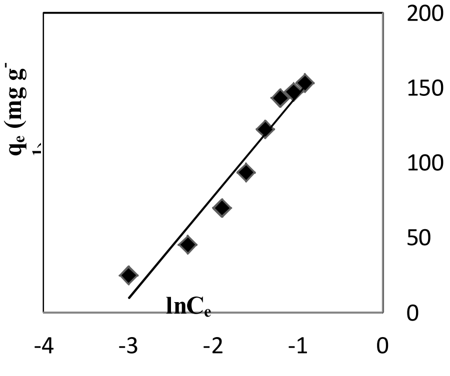


Figure 10.Temkin isotherm for BB41 sorption.

BET isotherm

The BET equation is often used to describe adsorption data for multilayer systems. The linear form of the BET isotherm can be represented in the following equation [50]:

$$\frac{C_e}{Q_e(1-C_e)} = \frac{1}{X_m K_B} + \frac{k_B - 1}{X_m K_B} C_e \qquad (6)$$

Where X_m is roughly an indicator of the adsorption capacity, K_B is the adsorption constant; C_e and Q_e are equilibrium dye concentrations in solution and biosorbent, respectively. It can be found that X_m and K_B can be determined from the linear plot of $C_e/Q_e(1-C_e)$ against C_e (Figure11). The X_m and K_B values are listed in Table 2. The correlation coefficients of this model are above 0.85. This means that experimental data does not fit well into the BET model because the regression coefficients obtained by Langmuir and Freundlich are higher than BET.

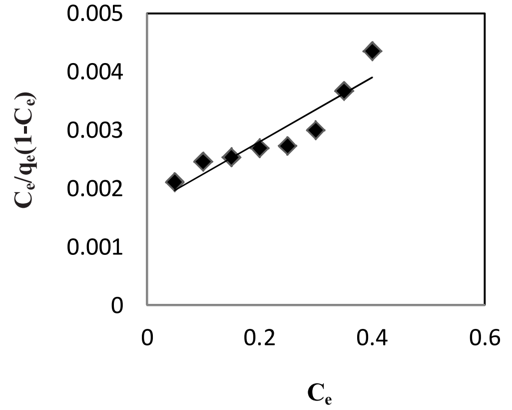


Figure 11. BET isotherm for BB41 sorption onto.

Dubinin-Radushkevich(D–R) isotherm

The Dubinin-Radushkevich(D-R) model is a more generalized model as compared to the Langmuir isotherm. The model is based on the fact that there is no homogeneous surface or constant adsorption potential. The linear form of the D–R isotherm equation can be seen below [51]:

$$\ln q_e = \ln q_m - K\varepsilon^2 \qquad (7)$$

where K is a constant corresponding to the biosorption energy, q_m the theoretical saturation capacity and ε is the Polanyi potential which is calculated from the equation below:

$$\varepsilon = RT\ln(1+\frac{1}{C_e}) \qquad (8)$$

where R (kJ mol^{-1} K^{-1}) is the gas constant and T (K) is the absolute temperature. E was calculated from the K value by the following relation:

$$E = \frac{1}{(2K)^{\frac{1}{2}}} \qquad (9)$$

The calculated parameters of D–R are calculated from Figure12 andare also given in Table 2. The E value is about 3.535 (KJ mol^{-1}). The values of correlation coefficients for dye are low, so the model is not fitted for BB41 dyes.

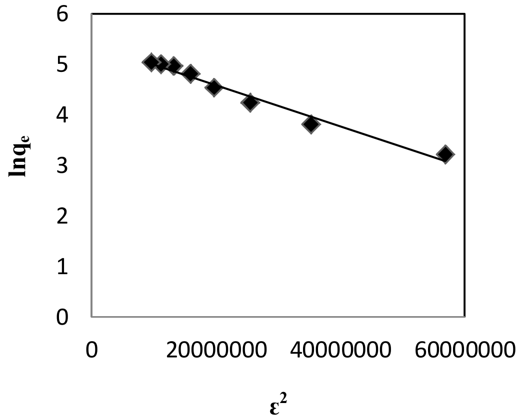


Figure 12. Dubinin-Radushkevich(D–R) isotherm for BB41 sorption onto CFP.

Harkins-Jura isotherm

The Harkins-Jura adsorption isotherm is expressed by the following equation [50] as:

$$\frac{1}{q_{e^2}} = (\frac{B}{A}) - (\frac{1}{A}) \log C_e \qquad (10)$$

The isotherm equation accounts for multilayer adsorption and can be explained with the existence of a heterogeneous pore distribution. The Harkins-Jura isotherm parameters (A,B) were obtained from the plots of $1/q_e^2$ against log C_e (Figure13). The value of A, B and R^2 are listed in table 2. The values of correlation coefficients for dye are low, so the model is not fitted for BB41 dyes.

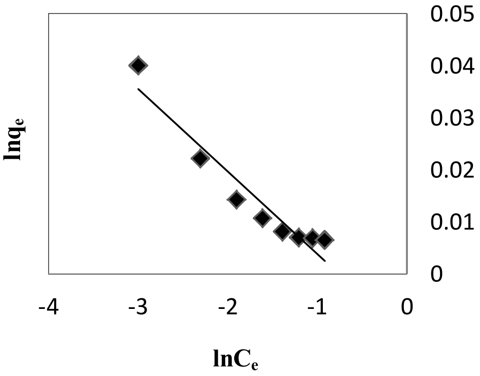


Figure 13.Harkins-Jura isothermfor BB41 sorption onto CFP.

Conclusion

Equilibrium was performed for the adsorption of Basic Blue41 from aqueous solutions onto CFP. Theresults of adsorption showed that CFP can be effectively used as a biosorbent for the removal of cationic dyes. The characteristics of CFP weredetermined by performing FE-SEM and FTIR analysis. The effect of adsorbent dose, initial dye concentration, contact time, PH and agitation speed (rpm) were experimentally studied to evaluate adsorption capacity. The results show that the best removal percentage was observed at 60 min, 0.2 g biosorbent, 240 rpm and pH 9. The adsorption isotherms of BB41 on CFP were studied by the Langmuir, Freundlich,Temkin,BET, Dubinin-Radushkevich (D–R) and Harkins–Jura models. The Langmuir isotherm model fit the equilibrium data for the sorbent well compared to other models.This study showed that CFP can be used as an economical natural biosorbent to remove BB41 dye from an aqueous solution.

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