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STUDY OF MUSTARD STEM HUSK FOR THE REMOVAL OF COMASSIE BRILLIANT BLUE R250 DYE BY ADSORPTION TECHNIQUE

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Abstract

Dyes are usually toxic and harmful for living organisms, due to their stability and non degradable nature. Many industrial effluents contain different types of dyes, which are then sent to the water streams. In present studies the removal of comassie brilliant blue R250 (CBB) dye was carried out by using Mustard stem husk (MH). The batch adsorption method was adopted for the removal of dye under the optimized conditions of amount of adsorbent, contact time, concentration of dye and temperatures. Spectrophotometric technique was adopted for the measurement of concentration of dye before and after adsorption. The adsorption isotherm models such as Langmuir, Freundlich, and Dubinin Radushkevich were applied to elaborate the respective constants. By obtaining 0.980 r^2 value it was estimated that Langmuir isotherm is the best fitted model. pH of point zero charge was also evaluated. Thermodynamic parameters such as the changes in enthalpy (ΔH°), entropy (ΔS°), and Gibbs' free energy (ΔG°) were determined to find out the nature of adsorption process. The kinetics models were considered to evaluate the rate constant. The value of rate constant was found to be 2.6×10^{-3} by applying pseudo second order kinetics. The morphology of MH was evaluated before and after adsorption of dye by scanning electron microscopy (SEM). Preliminary adsorption studies have shown that mustard stem husk possess a good affinity for dye and about 62% removal of CBB was observed. The present work can be used for the safety of living organisms from harmful diseases caused by using polluted water.

Introduction

Many industries use dyes and pigments to color their products. Most of the dyes are inert and non-toxic at the concentrations discharged into the receiving water, however, they impart color which is undesirable to the water user. Color removal from textile effluents is a major environmental problem because of the difficulty in treating such streams by conventional physicochemical and biological treatment methods (Mane and Bhusari, 2012; Pearce *et al.*, 2003; Annadurai *et al.*, 2003; Robinson *et al.*, 2001; Ponraj *et al.*, 2011,).

Various studies have been conducted for the removal of dyes by employing physicochemical methods. These include the use of coagulants, oxidizing agents, membrane filtrations, electrochemical, and adsorption techniques (Hassan and Jamal 2012; Hua Hu, and Chih Hu, 2013; Juang *et al.*, 2007). The adsorption method has been found to be an efficient and economical process to remove dyes and also to control biochemical oxygen demand (Bhatnagar and Minocha, 2006; Gupta and Suhas, 2009; Jahangiri-Rad *et al.*, 2013, Olukanni *et al.*, 2006).

CBB is commonly used for staining proteins in analytical biochemistry. This particular dye was previously used as acid wool dye. There are so many other types of Comassie but only Comassie R-250 and G-250 have vital importance in biochemical analysis. The suffix “R” in brilliant blue R-250 is an abbreviation for “red” as the blue color of the dye has a slight reddish tint. The color produced by the dye and their λ_{max} depends on pH. It exhibits different color and λ_{max} at different pH values. The color of the two dyes depends on the acidity of the solution. At pH less than 0 the dye has a red color with an absorption maximum at a wavelength of 470 nm. At a pH of around 1 the dye is green with an absorption maximum at 620 nm while above pH 2 the dye is bright blue with a maximum adsorption at 595 nm.

Natural biosorbents are well known and familiar to mankind from the earliest days of civilization. Because of their low cost, large abundance, high sorption properties and potential for ion exchange, biological materials are used as strong adsorbents (Gayatri and Ahmaruzzaman, 2010; Nayak and Singh, 2011; Feldblyum *et al.*, 2013). The adsorption capabilities resulted due to net negative charge on the structure of biosorbent. This negative charge gives the capability to adsorb positively charged species. Their sorption properties also come from their high surface area and high porosity (Forsgren et al 2013, Gosh 2011).

The mustard husk (MH) has the largest surface area and cation exchange capacity. Chemically it is hydrated cellulose along with other species (Onal, 2006). It is used as a nano adsorbent and is applicable in the areas to reduce the environmental burden. The MH is highly effective chemical, in granular form for the purification of waste water . It can also be used as a desiccant due to its adsorption properties (Dabrowski, 2001) and photochemical reaction field (Costa Saab, 2003).

In the present study MH was used as an adsorbent for the removal of comassie brilliant blue R250 (CBB). The adsorption study was carried out under optimized conditions to get maximum removal of dye through adsorption process. Adsorption isotherms were used to calculate the values of respective constants related to the equilibrium of adsorption phenomena. The maximum removal of CBB was about 62% using MH as an adsorbent. Many parameters including sorption capacity, sorption energy, enthalpy, and entropy change were determined. These parameters would be useful in the understanding of sorption removal of heavy metals by biosorbents from an aqueous environment.

Materials and Methods

Materials: The comassie brilliant blue R250 dye (CBB) was obtained from BDH laboratory suppliers. The molecular formula of CBB is $C_{45}H_{44}N_3NaO_7S_2$, molecular weight is 825.97 g/mole, and color Index (C.I) is 42660, having maximum limits of impurities about 5%. It was used as an adsorbate, dissolved in Methanol 99.85% and distilled water.

Preparation of CBB (R-250) dye solution: The comassie brilliant blue R250 dye was used for the preparation of standard stock solution. CBB is insoluble in cold water and slightly soluble in hot water. It was first dissolved in methanol and then the solution was made up to desired concentration with distilled water. The stock solution of CBB was prepared i.e. 100 ppm (1.2× 10-4 mol/dm3). Maximum wavelength of dye solution was recorded by taking spectrum using double beam spectrophotometer. The prepared stock solution was used for the adsorption and thermodynamic studies. The structure of CBB is shown in Figure 1.

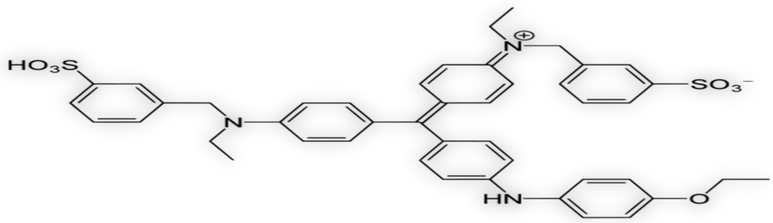

Fig. 1. Chemical structure of comassie Brilliant Blue(R-250)

Preparation of Adsorbent: The MH was used as an adsorbent. The stems of mustard were collected from its fields in Multan district, Punjab province (Pakistan). They were dried and then sieved to particle size of 100 µm (Blott and Pye, 2001). Then it was applied as an adsorbent for the removal of CBB.

Adsorption studies: The process of adsorption is preceded by various pathways. Some adsorbents are held loosely by Vander Waals forces indicates the physical adsorption, while those held firmly indicates the chemical adsorption (Andrade *et al.,* 2011).

Determination of optimum amount of adsorbent: For the optimization of amount of MH, 4.84×10^{-5}M solution of dye CBB was prepared in 500 cm^3 volumetric flask. 50 cm^3 volume of the dye solution was added in five separate conical flasks. Different amount of MH were added in respective flasks and then placed in shaking incubator for 30 minutes shaking at 120 rpm. After 30 minutes solutions were filtered and absorbance was recorded at 591 nm. The amount, at which optimum dye removal was obtained selected for further studies (Jahangiri-Rad *et al.,* 2013).

Determination of optimum time of adsorbent: Optimum shaking time for adsorption was determined by preparing five flasks containing 50cm^3, 4.84×10^{-5} M solution of CBB and 0.9g of MH. The flasks were then placed in shaking incubator at 120 rpm. After the 5 minutes of interval each flask was removed, filtered and absorbance was recorded by UV visible spectrophotometer. In this way the time at which optimum removal was observed is selected for further studies.

Determination of optimum shaking concentration of adsorbent: In order to evaluate the concentrations at which maximum adsorption was observed, 50 ml volume of dye with different concentrations ranging from 2.42×10^{-5} to 7.26×10^{-5}M were taken and 0.9g of adsorbent was added in each flask. The flasks were placed in shaking incubator by keeping optimum time and concentration at 120 rpm. After specific time period the flasks were drawn from shaking incubator, filtered and the absorbance of filtrate was recorded by using UV-Visible spectrophotometer at particular wavelength λ_{max}.

Adsorption at different temperatures: Fifty ml of the dye solution having various concentrations of dye CBB was taken in separate conical flasks. Optimum amount of MH were added in separate flasks and placed in shaking incubator by keeping optimum conditions and desired temperatures ranging from 303-318 K (±2K). After specific optimum time i.e. 20 minutes flasks were taken out from shaking incubator, filtered and absorbance was recorded for the determination of concentration of dye in the solution.

Results and Discussion

Effect of amount of adsorbent: The effect of amount of MH on the adsorption of CBB was studied. The amount of MH was varied from 0.30 to 1.50g, in 4.84×10^{-5}M concentration of CBB. The adsorption of dye was increases as the amount of adsorbent increases and then shows constant behavior. 0.9g of MH was selected as optimum. The K_D and % removal values for the adsorption were found to be 40.84 and 62.20% respectively.

Effect of the shaking time on adsorption: Optimum amount of adsorbent was taken in same concentration of adsorbate at different time intervals, the amount of adsorbent interact with adsorbate increases as their contact time increases, and after few instant the equilibrium was established and % removal of dye became constant. For CBB-MH system, the optimum adsorption was attained within 20 minutes.

Effect of concentration of adsorbate: The effect of concentration of dye by using optimum amount of MH was studied. The concentrations of CBB applied were in the range from 2.12×10^{-5} to 7.20×10^{-5}M. The optimum concentration of adsorbate was determined for the MH was 4.74×10^{-5}M.

Effect of Temperatures on Adsorption: The effect of temperature for the adsorption of CBB on MH was studied. The temperatures were varied from 303 to 318 K (±2K). It was observed that the adsorption was decreased as the temperature of the system increased.

Adsorption Isotherm: In order to understand the design of adsorption process, various equilibrium curves have been described by the scientists. An adsorption isotherm is a graphical representation showing the relationship between the amount adsorbed by a unit weight of adsorbent and the amount of adsorbate remaining in a test medium at equilibrium (Tahir et al 2012). To optimize the design of an adsorption system for the adsorption of dye molecules, appropriate correlation for the equilibrium curve was established.

The comassie brilliant blue R250 dye concentration was varied from 20 to 60 ppm by keeping all optimum parameters and their constants are given in Table 1.

Table. 1. Langmuir Isotherm for the removal of CBB by using mustard husk

Temperature (K)	$k \times 10^2$	Vm	R^2
303	2.36	6.605	0.903
308	5.29	14.29	0.932
313	11.1	8.873	0.857
318	4.72	8.025	0.980

By using the adsorbed amount of CBB and equilibrium concentration (*Ce*), the adsorption isotherms of CBB on MH were evaluated by plotting a graph between extent of adsorption (log *q*) and equilibrium concentration log *Ce* (M). The adsorption data was fitted in adsorption model like Langmuir, Freundlich and Dubinin-Radushkevich adsorption isotherms.

Langmuir Adsorption Isotherm: By applying Langmuir isotherm, the values of Langmuir constants were evaluated as shown in equation 1.

$Ce/X/m = (1/kV_m) + Ce/V_m$ --------------- (1)

Where Ce: equilibrium concentration, V_m: monolayer sorption capacity, X/m: maximum possible amount of dye that can be adsorbed per unit dry weight of sorbent, K: Langmuir empirical constant, also called binding constant (Chilton et al 2002).

From the slope 1/Vm and intercepts 1/K.Vm were evaluated from its graph.

Freundlich adsorption isotherms: The Freundlich isotherm is representing as;

$\mathrm{Log}X/m = \mathrm{Log}K + 1/n\ \mathrm{Log}Ce$ ------------------ (2)

Where “Ce” is the equilibrium concentration of the dye solution(mgL^{-1}). K is Freundlich constant related to the sorption capacity, and 1/n is an empirical parameter related to sorption intensity, (Wahab, 2007) which varies with heterogeneity of the material as presented in Figure 2. Freundlich plots were obtained at various temperatures. By plotting log X/m versus log Ce and the values of 1/n and K were interpreted.

D-R Adsorption Isotherm: The Dubinin-Radushkevich equation is also used to find out the mean free energy values of sorption. It is representing as (Iqbal and Ashiq 2007):

$LnX/m = K\varepsilon^2 + LnXm$ -------------- (3)

Where X/m is maximum possible amount of dye that can be adsorbed per unit weight of sorbent, Xm is monolayer capacity, K is the constant related to sorption energy and $\acute{\varepsilon}$ is the Polanyi potential.

$\varepsilon = RTLn\ (1+1/Ce)$ ------------- (4)

The plot of ln X/m versus $\acute{\varepsilon}^2$ is a straight line with slope K and intercepts ln Xm as shown in Figure 3. By using K, the mean free energy of sorption is calculated as,

$Es = 1/\ (2k)^{1/2}$ ---------------- (5)

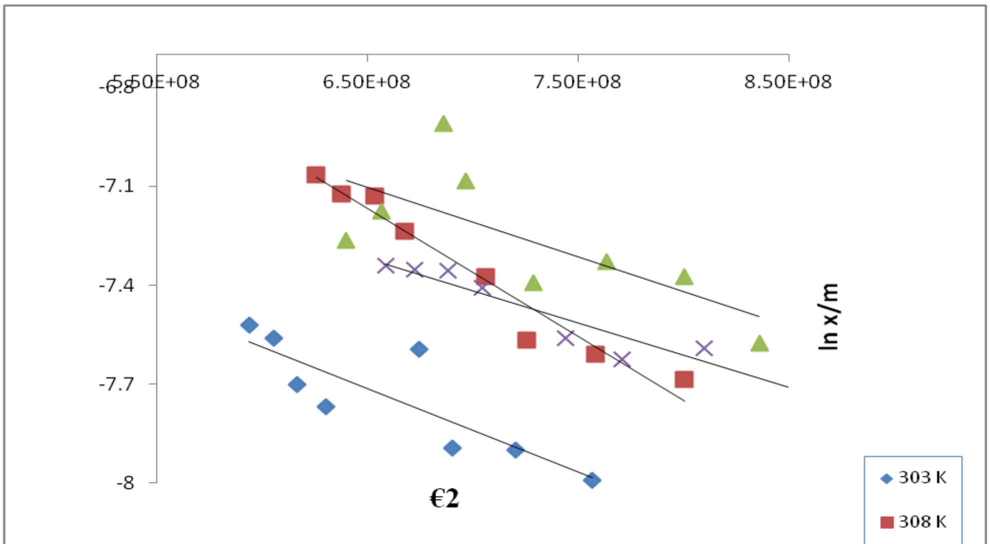

Figure 3: D R Isotherm Plot for Mustard stem husk (MH)-Comassie Brilliant Blue R250 (CBB) System

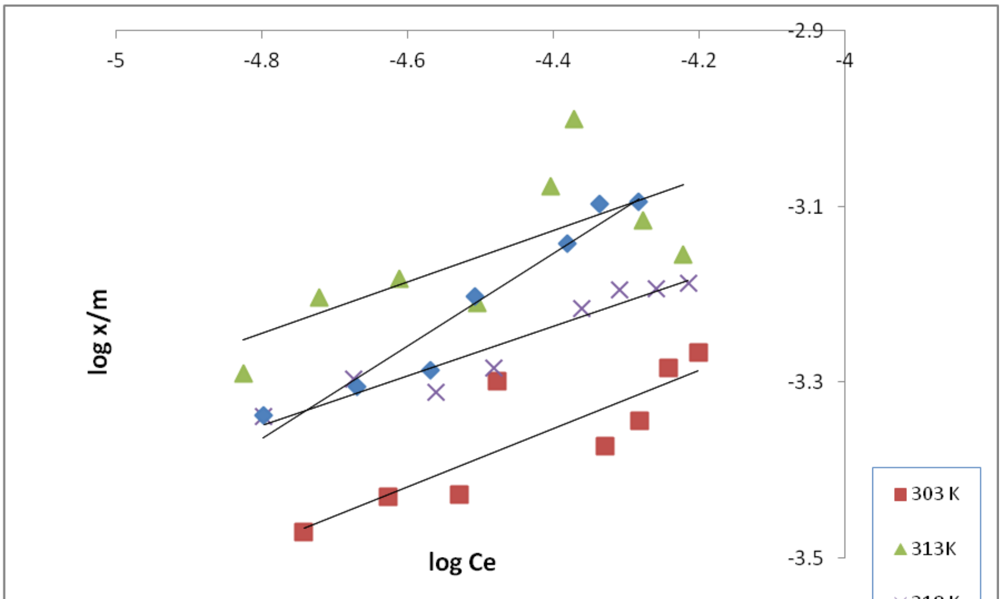

Figure 2: Freundlich Isotherm Plot of Mustard stem husk MH-Comassie Brilliant Blue R250 (CBB) System

Thermodynamic parameter: The thermodynamics parameters related to the adsorption of dyes such as free energy change (ΔG°), enthalpy change (ΔH°) and entropy change (ΔS°) were evaluated. These parameters were calculated (Lakshmi; Srivastava; Mall and Lataye (2009) by using following equations;

$\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ}$ ------------------ (6)

$\Delta G^\circ = -RTLnK$ ---------------------- (7)
$LnK = -\Delta H^\circ/RT + \Delta S^\circ/R$ ----------- (8)
The values of ΔH° and ΔS° were calculated from the slope and intercept of the linear variations of lnK with the reciprocal of temperature (1/T). The values are representing in Table 2. The negative values of ΔGº indicate the spontaneous nature of adsorption process (Havsteen, 2002). The positive values of ΔHº and E_a confirm the endothermic nature of the system

Table 2: Thermodynamic Parameters for the Adsorption of CBB onto MH.

Concentration ($M\times10^5$)	**ΔH°** (kJ/mol)	**ΔS°** (J/mol.K)	**ΔG°** (kJ/mol)			
			303 K	**308 K**	**313 K**	**318K**
2.42	7.189	06.901	-9.28	-9.31	-9.35	-9.38
3.03	7.167	07.358	-9.40	-9.43	-9.47	-9.51
3.63	5.148	14.375	-9.50	-9.58	-9.65	-9.72
4.24	0.415	29.764	-9.43	-9.58	-9.73	-9.88
5.45	4.460	17.010	-9.61	-9.70	-9.78	-9.87
6.05	4.608	16.512	-9.61	-9.69	-9.78	-9.86
6.66	1.701	26.214	-9.64	-9.77	-9.91	-10.00
7.26	0.815	29.215	-9.67	-9.81	-9.96	-10.10

pH of point zero charge onto MC: The point at which the net positive and negative charges on a surface become neutral is known as point zero charge. The method adopted here by adjusting the pH of the adsorbent between 2-12 using sodium chloride, hydrochloric acid and sodium hydroxide solutions. The ratio of adsorbent amount to solution volume used was 0.9g/20mL. The pH of initial solution was noted down. The stay time of 24 to 48 hours was given to establish the neutrality on the surface of adsorbent. Final pH of the solutions was recorded and results were summarized in Figure 4.

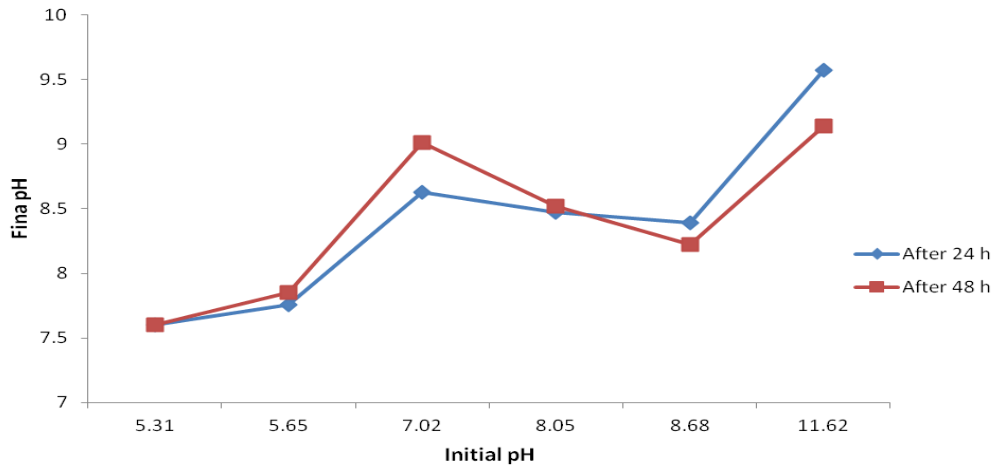

Figure 4: Effect of point of Zero Charge of MH

Adsorption Kinetics: From the optimization of shaking time the adsorption kinetics was evaluated to determine the kinetics of CBB-MH system. For this investigation pseudo first order and pseudo second order models were applied. Lagergen and pseudo second order model was adopted by the Ho and McKay. They are expressed as follows:
$Log (q_e-q_t) = log\ q_e - k_1\ t/2.303$ ---------- (9)
$t/q_t = 1/2k_2qe^2 + 1\ t/q_e$-----------(10)

Where qe and qt are the amount of the dye adsorbed on the adsorbent (mol/g) at equilibrium and time t, k_1 is the adsorption of pseudo first order rate constant (min^{-1}) and k_2 is the adsorption of second order rate constant (mol/g.min).

Characterization of Mustard stem husk: The characterization of MH clay was carried out by adopting SEM techniques. Scanning Electron Microscopy was used to identify the changes in the surface morphology of adsorbed MH. The SEM was performed by using Joel JSM-6380A scanning electron microscope.

SEM analysis: SEM images of MH were taken at different magnifications, before and after adsorption. Figure 5 show the surface of MH adsorbent which was unsaturated and have many adsorptive sites and pores before the adsorption with CBB.

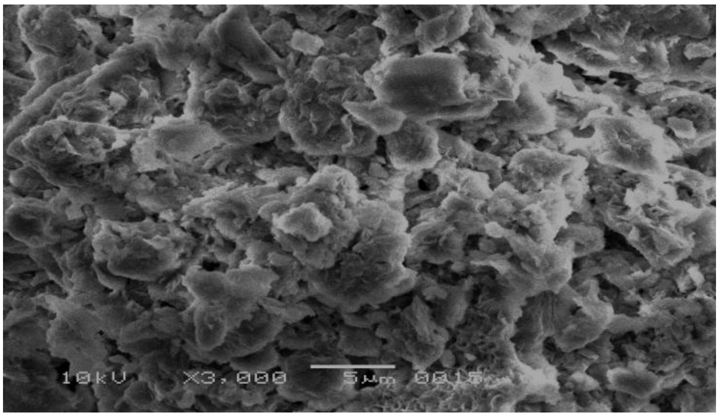

Fig. 5. SEM image of MH before adsorption

There is a formation of adsorbed layer on the surface of adsorbent seems to be no active sites are available for the further adsorption of dye as shown in Figure.

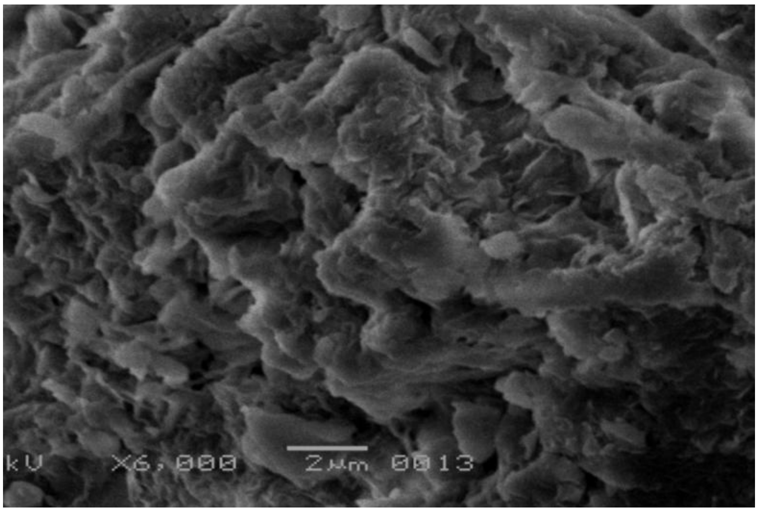

Fig. 6. SEM image of MH after adsorption

Conclusion

In the present study, experiments were carried out to investigate the adsorption potential of MH. The results of the study revealed that MH exhibit good adsorption capacity and can be used as an efficient low cost adsorbent for the removal of CBB from aqueous solutions. The adsorption process was dependent on contact time, amount of dosage, initial dye concentration and temperature. The dose of MH was 0.9g and optimum dye removal was observed within 20 minutes from the beginning of each experiment. The maximum % removal of the dye was 92.40 and the K_D value was 40.84. The adsorption isotherm models like Langmuir, Freundlich and Dubinin-Radushkevich were also applied to determine the feasibility of the adsorption process. It was concluded that Langmuir is the suitable and best fit model for the CBB-MH system. The R_L values between 0 to 1 shows the favorability of the reaction process. Thermodynamic parameters like free energy ΔG^o, enthalpy ΔH^o and entropy ΔS^o were also determined. Their values shows the spontaneous, endothermic and entropy driven process. Adsorption kinetics revealed that the system follow pseudo second order kinetics. The pH investigation data shows that the adsorbent is neutralized at basic pH.

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