Decolorization of bismarck brown R and crystal violet in liquid phase using modified pea peels: non-linear isotherm and kinetics modeling

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Abstract The batch adsorption studies to assess the adsorption efficiency of citric acid modified pea peels (CAPP) for uptake of bismarck brown R (BB) and crystal violet (CV) from liquid phase were performed. The dyes uptake was found to increase with increase in agitation time, adsorbent dosage, temperature, solution pH and with decreasing initial dyes concentrations. The non-linear isotherm modeling revealed that Freundlich and Sips isotherm model correlated the data well indicating multilayer adsorption onto heterogeneous CAPP surface. Langmuir adsorption capacity, Q_m for BB and CV was 5.37 and 17.61 mg/g, respectively. The separation factor, $R_L < 1$ and Freundlich constant, $n > 1$ indicated favorable adsorption. The kinetic studies showed that the pseudo-second order rate equation correctly explained the adsorption process, supporting the adsorption of one dye molecule onto two adsorption sites, with intra-particle and liquid-film diffusion as the rate controlling steps. The negative values of ΔG° (−20 to 0 kJ/mol) suggested the spontaneous and physical adsorption. The positive ΔH° and ΔS° values suggested endothermic adsorption and increased entropy at solid-solution interface. The CAPP proved to be an inexpensive and efficient adsorbent for BB and CV removal from wastewater.

Keywords Modified pea peels · Dyes · Non-linear isotherms · Kinetics · Thermodynamics

Introduction

The decolorization of colored effluents emanating from textile, paper and pulp, and tanneries is environmentally important as the color blocks the transmission of sunlight into the aqueous streams, which inhibit the growth of aquatic biota due to reduced photosynthetic action. Some of these dyes may be non-biodegradable and harmful to living organisms. Various physico-chemical technologies for dyes/metals removal from wastewater have been reported, which include electrocoagulation (Ali et al. 2012), photocatalytic degradation (Saleh and Gupta 2012), and adsorption (Khan et al. 2015b; Khan and Nazir 2015). Adsorption process is most preferred over other methods largely due to its cost-effectiveness, ease of operation, flexibility and simplicity of design, insensitivity to toxic pollutants and partly to the high quality treated effluent and non-formation of harmful substances. In recent years, various natural and agricultural materials (Khan and Singh 2010; Salleh et al. 2011; Khan et al. 2014b) are reported for adsorptive removal of pollutants from liquid phase. However, the raw lignocellulosic wastes have limited applicability as adsorbents because of generally lower adsorption capacity, and release of soluble organic content in the treated water. However, their treatment with organic acids increases the carboxyl groups on the adsorbent surface, increasing the surface net negative charge which enhances the cationic dye adsorption (Gong et al. 2008; Sajab et al. 2011; Zou et al. 2012). In present work, the efficiency of citric acid modified pea peels (CAPP) for the removal of cationic dyes, bismarck brown R (BB) and crystal violet

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(CV) from aqueous solution was investigated. The objectives of the present work was to evaluate the adsorption capacity of CAPP towards maximum BB and CV uptake from aqueous solution, and to optimize various adsorption parameters influencing the adsorption process (contact time, initial BB/CV concentration, CAPP dose, pH, and temperature). The adsorption isotherm and kinetic parameters have been evaluated using non-linear regression method, which is considered to be better than the linear method (Ho 2006).

Materials and methods

Chemicals and reagents

BB (CDH, New Delhi, India), CV (HiMedia, Mumbai, India) and citric acid (CA), NaOH and HCl (all Merck, Mumbai, India) were used as procured. The FTIR spectra of PP and CAPP were recorded with Perkin Elmer 3 λ spectrophotometer. Scanning electron micrographs (SEM) of the adsorbent was obtained using scanning electron microscope (JEOL, model 3300). The pH adjustment was done using NaOH or HCl solution (both 0.1 M). The initial and residual dye concentrations were determined with a UV–Vis spectrophotometer (Decibel, India).

Preparation of adsorbent

Pea peels (PP) were obtained from the Sabzi Mandi (Vegetable Market), Okhla, New Delhi, washed with water, oven dried at 70–80 °C for 3 h, mechanically ground and sieved to 180 μ m size. For modification (Gong et al. 2008; Khan et al. 2012) 20 g PP was mixed with 0.5 M CA solution in 1:12 ratio (PP: CA, w/v) and mechanically stirred for 30 min. The slurry was dried in an electric oven at 50 °C. After 24 h, the temperature was raised to 120 °C for 90 min when the thermochemical reaction between acid and pea peels was complete. After cooling, the CAPP was washed with distilled water, filtered and suspended in 0.1 M NaOH solution (200 mL). The suspension was stirred for 60 min, filtered, washed with distilled water to remove residual alkali, dried at 50 °C in an electric oven, and finally sieved to less than 75 μ m particle size.

Estimation of pH_{pzc} of CAPP

0.01 M NaCl solution (50 mL) were placed into different 250 mL Erlenmeyer flasks with the initial pH_is adjusted between 2 and 10 by addition of HCl or NaOH (0.1 M). CAPP (0.2 g) was added to each flask and the suspensions were left to stand for 48 h. They were centrifuged, and the final pH_fs of the solutions were determined. The pH_{pzc}

corresponds to the point where pH = 0 in the pH_i vs. Δ pH plot (Δ pH = pH_i – pH_f).

Adsorption studies

BB and CV solutions (100 mg/L) were prepared in double distilled water. The experimental solutions of desired dye concentration (5–60 mg/L) were prepared by appropriately diluting the stock solution using double distilled water.

For adsorption experiments, dye solutions (20 mL) of desired concentration were equilibrated with a known amount of adsorbent in 50 mL conical flask for a predetermined time interval at constant temperature. After equilibrium was attained, the adsorbent was removed by centrifugation. The centrifugate was then analysed spectrophotometrically for the remaining dye concentration (C_t) at 450 and 590 nm for BB and CV, respectively. Kinetic studies were performed in the same manner using fixed adsorbent dosage and adsorbate concentration (5–60 mg/L) with varying contact time. For pH variation studies, the initial pH of the dye solutions (2–10) were adjusted with dilute HCl or NaOH solution. The effect of temperature was evaluated between 298 and 308 K. The amount of dye adsorbed (q_e , mg/g) was calculated using Eq. (1):

$$q_e = (C_o - C_t)/m \quad (1)$$

where C_o is dye concentration in mg/L before adsorption, C_t is dye concentration at time t and m is the amount of CAPP (g/L of dye solution). The percentage adsorption was calculated from the relationship:

$$\% \text{ adsorption} = (C_o - C_t / C_o) \times 100 \quad (2)$$

Results and discussion

Characterization of CAPP

The FTIR spectrum (Fig. S1, Supplementary data) indicated the lignocellulosic composition of PP (Khan et al. 2014a). A broad intense band at 3267 cm^{-1} is assigned to –OH stretching vibrations of hydroxyl groups (lignin). The C–H stretch band due to methyl group and –OCH₃ band due to methoxy group of lignin was observed at 2840 and 2920 cm^{-1} . The band at 1620 cm^{-1} may be attributed to C=C stretching vibration of lignin. The bands at 1420 and 1321 cm^{-1} may reasonably be assigned to C–H deform of CH₂ and syringyl ring breaking C–O stretch of phenol. The ν (C–O) stretch band due to acetyl and phenolic groups is observed at 1290 cm^{-1} . The peaks at 1106 and 1009 cm^{-1} may be ascribed to C–O–C (antisym bridging) vibration in cellulose and hemicelluloses, and C–OH stretch vibration

of the cellulosic backbone, respectively. After modification, the spectrum displayed peaks attributed to the presence of carbonyl groups at 1721 cm^{-1} and a broad peak due to carboxylic O–H groups at 2950 cm^{-1} (Gong et al. 2008).

Figure 1 illustrates the scanning electron micrographs (SEM) of CAPP, which showed a network of irregular grooves and ridges along with large number of pores that is considered helpful for the accessibility of dyes to the adsorbent surface. The SEM images of CAPP after adsorption of BB and CV exhibited accumulation of dyes on the edges of the rough surfaces as well as in the pores, which indicated that when the adsorption on the exterior surface reached saturation, the dye molecules entered into the interior CAPP pores.

Effect of adsorbent dose

The adsorptive removal of BB and CV by CAPP was studied by varying the amount of adsorbent while keeping the initial dye concentration, temperature (298 K) and pH (7.0) constant at different contact times. The results shown in Fig. 2 demonstrated that the rate of adsorption of dyes increased with increase in the CAPP mass before equilibrium was attained. As the CAPP dose was increased from 2 to 10 g/L the percent BB uptake increased from 58 to 88. Similarly, CV removal increased from 69 to 95 % when adsorbent dose was increased from 1 to 5 g/L. However, after optimum dosage (10 g/L for BB and 5 g/L for CV) no significant change in the % removal was observed and saturation occurred as a result of the decrease in equilibrium concentration of dye molecules per active sites of the adsorbent. The phenomena of increased dye removal with adsorbent dose might be due to the presence of abundant adsorbent surface sites for adsorption of dye molecules.

Effect of contact time

The effect of contact time was studied at constant initial dye concentration, temperature (298 K) and pH (7) with optimum adsorbent dose for the respective dyes as a function of time as shown in Fig. 3. The percentage removal of BB and CV by CAPP increased from 56 to 88 and 58 to 95 when the contact time increased from 10 to 60 and 10 to 70 min, respectively before attaining equilibrium. Therefore, the optimum contact time was considered to be 60 and 70 min for BB and CV, respectively.

The observed trend in adsorption of dyes with contact time can be explained on the basis that initially large number of vacant surface sites was available for adsorption causing increase in adsorption with increase

Fig. 1 SEM images of CAPP; CAPP loaded with bismarck brown R and crystal violet

in contact time. The slower adsorption later may be result of decrease in the number of available vacant surface sites and increase in the repulsive forces between dye molecules adsorbed onto CAPP surface and in the solution phase.

Fig. 2 Effect of adsorbent dose

Fig. 3 Effect of contact time

Effect of initial dyes concentration

The initial concentration of the adsorbate is an important parameter for adsorption studies because a given mass of adsorbent can adsorb only a fixed amount of adsorbate. The effect of initial dye concentration on adsorption was investigated at different initial concentrations of dyes with fixed adsorbent dosages at 298 K and pH 7. The results are shown in Fig. 4. The percent dyes adsorption showed a general decrease with increase in initial concentration. With increase in initial CV concentrations from 10 to 50 mg/L the % removal decreased from 99 to 94. In case of BB a decrease in % removal from 96 to 87 was observed with increase in dye concentration from 5 to 30 mg/L. It was, therefore, inferred that surface saturation was dependent on the initial dyes concentration. The rapid rate of adsorption at lower initial concentrations might be due to the fact that initially sufficient numbers of adsorption sites are available for adsorption, making fractional adsorption independent of initial dye concentration. However, at high concentrations the number of available sites for adsorption

Fig. 4 Effect of initial dye concentration

became fewer and hence the percentage removal became dependent on initial concentration.

Effect of temperature

The adsorption capacity of an adsorbent is largely affected by temperature. The removal of the BB and CV were studied at three different temperatures 298, 303 and 308 K for solution of different concentrations. The results are presented in Fig. 5. The extent of adsorption of the dyes was found to be temperature dependent. With increase in temperature from 298 to 308 K, the % adsorption increased from 83 to 89 for BB and 86 to 95 for CV, which suggested endothermic adsorption. The higher dye uptake with rise in temperature might be ascribed to decrease in escaping tendency of dye molecules from the adsorbent surface, change in pore size, and enhanced rate of intraparticle diffusion.

Effect of initial pH

The variation in the adsorption of the BB and CV onto CAPP with increase in pH of the solution (2–10) is shown in Fig. 6. The % dye adsorbed increased from 75 to 92 and 73 to 99 with increase in pH from 2 to 10 for BB and CV, respectively. The pH of the solution primarily affects the degree of ionization of the dyes and the surface properties of the adsorbents. At pH below pH_{pzc} (5.20), the surface of CAPP was positively charged and the adsorption of cationic dyes decreased due to the repulsive forces. At $pH > pH_{pzc}$, the CAPP surface acquired negative charge resulting in increased adsorption due to greater electrostatic attraction.

Adsorption isotherms

The equilibrium data for adsorption of dyes onto CAPP was modeled using non-linear Langmuir (1918), Freundlich (1906), Redlich–Peterson (1959), Sips (1948) and

Fig. 5 Effect of temperature

Fig. 6 Effect of pH

Radke and Prausnitz (1972) isotherm models using SigmaPlot 13 software (Trial version):

$$q_e = Q_m b C_e / (1 + b C_e) \quad (\text{Langmuir}) \quad (3)$$

$$q_e = K_f C_e^{1/n} \quad (\text{Freundlich}) \quad (4)$$

Fig. 7 Non-linear plots for Langmuir isotherm

$$q_e = K_{RP} C_e^{g_{RP}} / (1 + \beta_{RP} C_e^{g_{RP}}) \quad (\text{Redlich–Peterson isotherm}) \quad (5)$$

$$q_e = K_s a_s C_e^{\beta_s} / (1 + a_s C_e^{\beta_s}) \quad (\text{Sips isotherm}) \quad (6)$$

$$q_e = a_R r_R C_e^{\beta_R} / (a_R + r_R C_e^{\beta_R - 1}) \quad (\text{Radke and Prausnitz}) \quad (7)$$

where, Q_m and b are the Langmuir saturation adsorption capacity and adsorption equilibrium constant, respectively, and C_e is the equilibrium concentration (mg/L), K_f and n are the Freundlich coefficients. K_{RP} (L/g), β_{RP} (L/mg) are the Redlich–Peterson isotherm constants, and g is the exponent. K_s is the Sips adsorption capacity (mg/g), a_s is the related to the energy of adsorption and β_s is the exponent. The a_R and r_R are the Radke–Prausnitz isotherm constants and β_R is the exponent.

The Langmuir adsorption isotherm is used to evaluate the saturation adsorption capacity and is valid when all the adsorption sites are energetically homogenous. The Freundlich model assumes non-uniform adsorption over the heterogeneous surfaces as well as multilayer adsorption.

The values of Q_m and b , calculated from the non-linear Langmuir adsorption isotherms plots (q_e vs. C_e) for BB and CV (Fig. 7) are tabulated in Table 1. The calculated saturation adsorption capacity (Q_m) of CAPP for BB (5.37 mg/g) was lower or comparable to that of other adsorbents, while for CV (17.61 mg/g) it was higher (Table 2). The separation factors (R_L) were between 0.20–0.44 for BB and 0.35–0.33 for CV indicating favourable adsorption (Hall et al. 1966).

Non-linear Freundlich isotherm plots for BB and CV at three temperatures (Fig. 8) with correlation coefficient $R^2 = 0.986$ –0.999 indicated that the data obeyed the Freundlich isotherm model. The greater than unity values of n (1.54–1.73 for BB and 1.83–2.01 for CV) indicated that

Table 1 Non-linear adsorption isotherm constants

Isotherm constant	BB			CV		
	298 K	303 K	308 K	298 K	303 K	308 K
Langmuir						
Q_m (mg/g)	5.37	5.12	5.04	14.71	17.61	15.74
b (L/mg)	0.78	0.27	0.36	0.22	0.42	0.69
R_L	0.20	0.43	0.443	0.349	0.398	0.325
R^2	0.983	0.981	0.959	0.955	0.957	0.941
SSE	0.077	0.094	0.216	2.171	2.574	3.626
SE	0.124	0.137	0.208	0.737	0.802	0.952
Freundlich						
K_f (L/g)	0.88	1.14	1.36	3.08	5.28	6.27
n	1.54	1.65	1.73	1.83	1.79	2.01
R^2	0.996	0.999	0.989	0.989	0.989	0.986
SSE	0.018	0.007	0.054	0.543	0.674	0.889
SE	0.060	0.037	0.104	0.368	0.410	0.471
Redlich–Peterson						
K_{RP} (L/g)	1704954737.0	244595005.01	435473092.61	24818079640.77	433710377.49	1804728065.5
β_{RP}	1931291345.34	2112817459.10	319515890.65	8063812088.04	176700439.60	287697773.12
g	0.35	0.39	0.42	0.45	0.44	0.50
R^2	0.996	0.999	0.989	0.988	0.989	0.986
SSE	0.019	0.007	0.054	0.542	0.674	0.889
SE	0.067	0.041	0.116	0.425	0.474	0.544
Sips						
K_s	221.5	238.0	440.3	1105.0	1488.0	1552.0
a_s	0.004	0.005	0.003	0.0028	0.0035	0.0040
β_s	0.655	0.611	0.581	0.315	0.561	0.499
R^2	0.997	0.999	0.998	0.993	0.985	0.996
SSE	0.019	0.007	0.110	0.524	0.649	0.868
SE	0.054	0.019	0.035	0.314	0.251	0.280
Radke and Prausnitz						
a_R	15795082.4	52532082.8	−43558779.5	185744794.90	173781046.48	−63398818.8
r_R	0.96	1.11	1.25	2.05	3.23	3.72
β_R	0.37	0.35	0.32	0.45	0.46	0.41
R^2	0.981	0.979	0.956	0.984	0.979	0.975
SSE	0.087	0.103	0.230	0.763	1.249	1.542
SE	0.148	0.1604	0.249	0.504	0.645	0.717

both dyes are favourably adsorbed onto CAPP. The K_f value for BB and CV were between 0.88 and 1.36 and 3.07 and 6.27, respectively.

Redlich–Peterson, a three-parameter adsorption isotherm, is used to evaluate whether the data follows Langmuir or Freundlich isotherm (Fig. S2, Supplementary data). If the Redlich–Peterson exponent (g) is close to zero, the adsorption process follows Freundlich isotherm. If g is close to unity, the process obeys Langmuir isotherm. The values of K_{RP} , β_{RP} and g along with R^2 , sum of square error (SSE) and standard error (SE) are presented in Table 1. The close to zero g values (0.349–0.420 for BB and

0.441–0.502 for CV supported that the adsorption process followed Freundlich isotherm model.

Sips adsorption isotherm, which is a combination of Langmuir and Freundlich isotherms, is better suited to describe adsorption onto heterogeneous adsorbent surface. It reduces to Freundlich isotherm at lower dye concentration, while at higher concentration it predicts the Langmuir equation indicating monolayer adsorption (Foo and Hameed 2010). The Sips constants K_s , a_s and β_s calculated from q_e vs. C_e plots (Fig. S3, Supplementary data) are summarized in Table 1 along with R^2 , SSE and SE. The far from unity values of β_s (Table 1), indicated that the Freundlich isotherm was

Table 2 Comparison of Q_m of different adsorbents for BB and CV adsorption

BB			CV		
Adsorbent	Q_m (mg/g)	Refs.	Adsorbent	Q_m (mg/g)	Refs.
3,4-Dihydroxyphenylacetic acid grafted chitosan	39.27	(Chao et al. 2004)	Sugar cane stalk	18.7	(El-Sayed et al. 2011)
3,4-Dihydroxybenzoic acid grafted chitosan	26.18	(Chao et al. 2004)	Citric acid modified pea peel	17.61	This work
4-Hydroxybenzoic acid grafted chitosan	17.78	(Chao et al. 2004)	Jalshakti polymer	12.9	(Dhodapkar et al. 2006)
Blast furnace sludge	8.2	(Bhatnagar and Jain 2005)	<i>Citrullus lanatus</i> rind	11.99	(Suyamboo et al. 2012)
Citric acid modified pea peel	5.37	This work	bottom ash	11.44	(Nidheesh et al. 2012a)
Blast furnace dust	4.6	(Bhatnagar and Jain 2005)	bottom ash	5.24	(Nidheesh et al. 2012b)
Blast furnace slag	2.7	(Bhatnagar and Jain 2005)	Tin(IV)molybdovanadate	1.7	(Vinisha and Janardanan 2013)

Fig. 8 Non-linear plots for Freundlich isotherm

more favourable than the Langmuir isotherm and adsorption occurred onto heterogeneous adsorbent surface.

The Radke–Prausnitz isotherm equation is valid for wide range of concentrations. When the exponent β_R approaches zero, the Radke–Prausnitz adsorption isotherm is reduced to Freundlich isotherm model. The Radke–Prausnitz isotherm parameters, a_R , r_R and β_R evaluated from q_e vs. C_e plots (Fig. S4, Supplementary data) are presented in Table 1 along with R^2 , SSE and SE. The values of β_R between 0.37 to 0.32 for BB and 0.46 to 0.41 for CV suggested that the data conformed to Freundlich model.

Estimation of best fitted isotherm models

The best fit non-linear isotherm model was evaluated by error analysis (Fig. 9) using correlation coefficients (R^2),

sum of square error (SSE) and standard error (SE). In two-parameter isotherms, highest R^2 value (0.996–0.999 for BB and 0.986–0.989 for CV) and lowest values of SSE (0.007–0.054 for BB and 0.543–0.889 for CV) and SE (0.037–0.104 for BB and 0.368–0.471 for CV) indicated that the Freundlich isotherm is most appropriate model. Among the three-parameter isotherms, Sips isotherm described the data better having highest R^2 (0.997–0.999 for BB and 0.985–0.996 for CV) and lowest values of SSE (0.007–0.110 for BB and 0.524–0.8868 for CV) and SE (0.019–0.035 for BB and 0.251–0.314 for CV). The Sips exponent was closer to zero than unity, which supported that the adsorption of dyes onto CAPP was more fitted to Freundlich than Langmuir model.

Adsorption kinetics

Lagergren's pseudo-first order (Lagergren 1998) and pseudo-second order (Ho and McKay 1998) models were used to fit the kinetic data. The pseudo-first order model assumes the adsorption of one dye molecule onto one adsorption site whereas in pseudo-second order model one dye molecule is adsorbed onto two active sites (Khan et al. 2015a). The kinetic parameters were evaluated using non-linear pseudo-first order (Eq. 8) and pseudo-second order rate equations (Eq. 9):

$$q_t = q_e(1 - e^{-k_1 t}) \quad (8)$$

$$q_t = (k_2 q_e^2 t) / (1 + k_2 q_e t) \quad (9)$$

where q_e and q_t (mg/g) are the amount of dye adsorbed per unit mass at equilibrium and at time t , k_1 (1/min) and k_2 (g/mg/min) are pseudo-first-order and pseudo-second-order rate constants, respectively.

Fig. 9 Comparison of error analysis for non-linear isotherm models

The values of k_1 , k_2 and $q_{e(\text{calc})}$ were obtained from non-linear plots of q_t vs. t at 298 K (Figs. 10, 11), and are given in Table 3 together with R^2 , SSE and SE. A good agreement between $q_{e(\text{exp})}$ and $q_{e(\text{calc})}$, together with higher R^2 , and lower SSE and SE values for the pseudo-second-order kinetic model revealed that the kinetics of the adsorption process followed pseudo-second-order rate equation indicative of one dye ion occupying two adsorption sites.

When there is possibility of the diffusion of dye species into the interior pores of the adsorbent the intraparticle diffusion plays a significant role in controlling the kinetics of adsorption process (Eq. 10) (Weber and Morris 1963).

$$q_t = k_i t^{0.5} + C_i \quad (10)$$

where (k_i) ($\text{mg/g min}^{0.5}$) is the intraparticle diffusion rate constant and C_i , is intercept, which gives an idea about the

Fig. 10 Non-linear plots for pseudo-first order kinetic model

thickness of the boundary layer (larger the intercept greater the boundary layer effect).

If q_t vs. $t^{0.5}$ plot is a straight line, which passes through the origin then the rate limiting step is solely due to intraparticle diffusion. When the plots do not pass through the origin, boundary layer control along with intraparticle diffusion is involved. The magnitude of k_i was obtained from the slope of the straight line q_t vs. $t^{0.5}$ plots (Fig. S5, Supplementary data), and are listed in Table 4 along with corresponding R^2 .

The intraparticle diffusion plots showed multi-linearity indicating that adsorption occurred in two or more steps. The first sharper region in the intraparticle diffusion plot indicated the instantaneous external surface adsorption, which was completed within 50 min for BB and 60 min for CV. The second region is the gradual adsorption stage of intraparticle diffusion, which was attained in 60 min for BB and 70 min for CV. This implied that both the surface adsorption and intraparticle diffusion were likely to control the kinetics of the BB and CV adsorption.

The kinetic data was fitted into the liquid-film diffusion model in its linear form (Eq. 11) (Boyd et al. 1947):

Fig. 11 Non-linear plots for pseudo-second order kinetic model

$$\ln(1 - q_t/q_e) = -K_{fd}t \quad (11)$$

where, $(q_t/q_e = F)$ is the fractional attainment of equilibrium and K_{fd} is the adsorption rate constant.

A linear plot of $-\ln(1-F)$ vs. t (Fig. S6, Supplementary data) with zero intercept suggests that kinetics of adsorption process is controlled by the liquid-film diffusion. The liquid-film diffusion plots were linear but did not pass through the origin, which indicated that liquid-film diffusion did not solely determine the mechanism of the adsorption of BB and CV onto CAPP. The values of K_{fd} and R^2 are given in Table 4.

Thermodynamic studies

Thermodynamic parameters such as standard Gibbs free energy change (ΔG°), standard enthalpy change (ΔH°) and standard entropy change (ΔS°) were calculated using the following equations (Eqs. 12, 13):

$$\log K_c = (-\Delta H^\circ / 2.303 RT) + (\Delta S^\circ / 2.303 R) \quad (12)$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (13)$$

Table 3 Non linear kinetic parameters and statistical data

Parameters	BB (mg/L)						CV (mg/L)					
	5	10	15	20	25	30	10	20	30	40	50	60
Pseudo-first order												
q_e (mg/g)	0.471	0.916	1.341	1.755	2.185	2.622	1.867	3.631	5.426	7.175	9.069	10.775
k_1 (1/min)	0.159	0.113	0.092	0.083	0.071	0.068	0.275	0.221	0.179	0.161	0.157	0.155
R^2	0.864	0.911	0.920	0.932	0.932	0.931	0.612	0.585	0.666	0.729	0.853	0.857
SSE	0.001	0.005	0.016	0.627	0.052	0.062	0.086	0.557	1.294	2.088	1.806	2.530
SE	0.014	0.033	0.057	0.074	0.102	0.103	0.120	0.305	0.464	0.590	0.549	0.649
q_e (exp)	0.48	0.93	1.36	1.78	2.2	2.61	1.98	3.88	5.76	7.60	9.40	11.16
Pseudo-second order												
k_2 (g/mg/min)	1.019	0.504	1.535	2.037	2.595	3.143	2.034	4.050	6.160	8.237	10.432	12.417
q_e (mg/g)	0.172	0.618	0.082	0.053	0.033	0.025	0.226	0.081	0.041	0.027	0.020	0.017
R^2	0.988	0.994	0.988	0.986	0.981	0.987	0.874	0.827	0.859	0.886	0.957	0.958
SSE	0.064	0.000	0.020	0.406	0.769	0.015	0.028	0.232	0.546	0.882	0.524	0.739
SE	0.012	0.003	0.022	0.034	0.054	0.056	0.068	0.191	0.302	0.383	0.295	0.350

Table 4 Liquid-film and Intraparticle diffusion constants and statistical data

Parameter	BB (mg/L)						CV (mg/L)					
	5	10	15	20	25	30	10	20	30	40	50	60
Liquid-film diffusion												
K_{fd} (1/min)	0.059	0.068	0.069	0.068	0.072	0.061	0.081	0.085	0.085	0.110	0.099	0.110
R^2	0.995	0.998	0.978	0.961	0.952	0.983	0.959	0.849	0.848	0.937	0.805	0.937
SSE	0.028	0.017	0.182	0.326	0.456	0.111	0.002	0.026	0.064	0.148	0.313	0.451
SE	0.084	0.066	0.214	0.285	0.338	0.166	0.174	0.358	0.378	0.298	0.508	0.298
Intraparticle diffusion												
k_i (mg/g min ^{0.5})	0.084	0.053	0.096	0.137	0.190	0.236	0.126	0.308	0.740	0.741	0.931	1.117
C_i	0.342	0.528	0.630	0.731	0.733	0.805	1.215	2.009	3.104	3.104	3.906	4.567
R^2	0.919	0.912	0.974	0.948	0.960	0.967	0.990	0.983	0.980	0.980	0.974	0.974
SSE	0.000	0.000	0.010	0.020	0.025	0.039	0.122	0.513	0.572	0.356	1.033	0.356
SE	0.011	0.034	0.046	0.065	0.071	0.088	0.018	0.103	0.103	0.157	0.228	0.274

where, K_c is the equilibrium constant ($=C_{ae}/C_e$), C_{ae} (mg/L) is the amount adsorbed on solid at equilibrium, T is the temperature in Kelvin, and R is the gas constant (J/molK).

The values of ΔH° and ΔS° were determined from the slope and intercept of $\log K_c$ vs. $1/T$ plots. The thermodynamic parameters ΔG° values were between -3.57 to -5.40 (kJ/mol) for BB and -4.70 to -7.82 (kJ/mol) for CV over the experimental temperature (298–308 K). However, an increase in the temperature led to a change in the ΔG° to more negative values suggesting that the adsorption was more spontaneous at higher temperature. The calculated ΔG° values between -20 to 0 kJ/mol confirmed the physisorption of the dye molecules onto CAPP (Mahmoodi et al. 2010). The positive values of ΔH° (38.60 and 86.40 kJ/mol for BB and CV) demonstrated the endothermic

adsorption. The positive entropy change (ΔS°) values (0.142 and 0.306 kJ/mol/K for BB and CV) indicated the increase in randomness at the solid-solution interface.

Conclusions

The removal of cationic dyes, BB and CV by CAPP was studied. The non-linear regression analysis of the equilibrium data for adsorption of BB and CV onto CAPP, using different isotherms indicated that Freundlich and Sips isotherm best fitted the data suggesting multilayer adsorption onto heterogeneous adsorbent surface. The R_L values were in agreement with favourable adsorption process. Freundlich constant $n > 1$ supported the favourable nature

of adsorption. The ΔG° between the -20 to 0 kJ/mol indicated physical adsorption. The kinetics of the adsorption followed pseudo-second order model with the adsorption mechanism controlled by both liquid-film and intraparticle diffusion. The thermodynamic parameters indicated that the adsorption of dyes onto CAPP was spontaneous and endothermic. The positive values of the entropy change supported the increase in the randomness at the solid-solution interface. The results revealed that CAPP can be an effective and economically viable adsorbent for the removal of CV from aqueous solution.

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