


Biosorption studies on waste cotton seed for cationic dyes sequestration: equilibrium and thermodynamics

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Abstract The immature *Gossypium hirsutum* seeds—an agricultural waste was converted into a novel adsorbent and its effectiveness for cationic dyes removal was discussed in this study. Characterization revealed that sulfuric acid activated waste *Gossypium hirsutum* seed (WGSAB) contains surface area $496 \text{ m}^2 \text{ g}^{-1}$. The ability of WGSAB to adsorb basic red 2 (BR2) and basic violet 3 (BV3) from aqueous solutions has been studied. Batch adsorption studies were carried out at different initial dye concentrations ($100\text{--}300 \text{ mg l}^{-1}$), contact time (1–5 h), pH (2–12) and temperature (293–323 K) to understand the adsorption mechanism. Adsorption data were modeled using Langmuir, Freundlich and Toth adsorption isotherms. Equilibrium data of the adsorption process fitted very well to the Toth model for both dyes. The Langmuir maximum adsorption capacity was 66.69 mg g^{-1} for BV3 and 50.11 mg g^{-1} for BR2 at optimum conditions. The near unity value of Toth isotherm constant (BR2: 0.999 and BV3: 1.0) indicates that WGSAB surface is heterogeneous in nature. The maximum adsorption capacity predicted by Toth isotherm of BV3 (66.699 mg g^{-1}) is higher than BR2 (50.310 mg g^{-1}). The kinetic investigation revealed that the BR2 and BV3 were chemisorbed on WGSAB surface following Avrami fractional order kinetics. Further, the fractional order and rate constant values are almost similar for every concentration in both the dyes. The thermodynamic parameters such as ΔH^0 , ΔS^0 and ΔG^0 were evaluated. The dye adsorption process was found to be spontaneous and endothermic for the two dyes.

Regeneration of WGSAB exhausted by the two dyes could be possible via acetic acid as elutant.

Keywords Adsorption · *Gossypium hirsutum* seed · Isotherm · Kinetic · Thermodynamic

List of symbols

ΔG^0	Gibbs free energy change (J mol^{-1})
ΔH^0	Enthalpy change (J mol^{-1})
ΔS^0	Entropy change ($\text{J mol}^{-1} \text{ K}^{-1}$)
b_L	Langmuir model constant (l mg^{-1})
C_0	Final concentration (mg l^{-1})
C_i	Initial and final concentration (mg l^{-1})
C_t	Concentration at any time t
h	Ho initial sorption rate ($\text{mg g}^{-1} \text{ min}^{-1}$)
k_A	Avrami rate constant (min^{-1})
K_F	Freundlich isotherm constant (l g^{-1})
k_{Ho}	Ho rate constant ($\text{g mg}^{-1} \text{ min}^{-1}$)
K_T	Toth isotherm constant
M	Amount of WGSAB (g)
n_A	Avrami model exponent
N_F	Freundlich exponent
n_T	Toth isotherm exponent
$q_{e, Ho}$	Biosorption capacity from Ho equation (mg g^{-1})
q_{mL}	Langmuir maximum monolayer biosorption capacity (mg g^{-1})
q_{mT}	Toth maximum monolayer biosorption capacity (mg g^{-1})
q_t	Dye adsorption capacity (mg g^{-1})
R	Gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$)
R_L	Separation factor
T	Absolute temperature (K)
t	Time (min)
V	Volume of dye solution (l)
λ_{max}	Optical density

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Abbreviations

BET	Breuner–Emmet–Teller
BR2	Basic red 2
BV3	Basic violet 3
FTIR	Fourier Transform Infra Red
SEM	Scanning electron microscope

Introduction

Process industries such as paper, textile, plastic, leather, cosmetic, and food employ dyes to color their products. The residual dye bearing effluents of those processes are discharged into the water bodies as such (Rangabhashiyam et al. 2013; Sivarajasekar et al. 2008, 2009). Among, the variety of dyes (cationic, anionic and neutral), the cationic dye is more toxic (Sivarajasekar et al. 2008; Sivarajasekar and Baskar 2013). These dyes have been reported to cause allergy, irritation, cancer and even mutation in human beings (Sepúlveda-Cuevas Luisa et al. 2008; Sivarajasekar and Baskar 2014a). Hence, the removal of these dyes from effluents before discharge to public water sources is an urgent and challenging requirement.

Adsorption is generally realized as an effective technique for the treatment of dye-containing wastewater (Rangabhashiyam et al. 2014; Akar et al. 2013). Among the different adsorbents identified, activated carbon was generally preferred in removal of dyes from waste water due to its relatively high sorption capacity for a wide variety of dyes. Commercially available activated carbons obtained from either wood or coal are usually expensive (Sivarajasekar and Baskar 2014b) and therefore, developing cost-effective adsorbent will encourage the industries to employ adsorption as a primary process for waste water treatment. Recently, the research has been focused toward production of activated carbon from agricultural byproducts and waste materials (Sivarajasekar 2007; Srinivasan et al. 2010; Ramaraju et al. 2014). Agricultural byproducts or wastes are rich source of organic matter containing hydroxyl, carboxyl and amine groups which can easily facilitate binding of cations such as cationic dyes (Sivarajasekar and Baskar 2015a).

Cotton (*Gossypium hirsutum*) is one of the industrial crops which plays a major role in the economics of many countries. India is the third largest country in the world which produces cotton approximately 6×10^3 tons per year (Sivarajasekar and Baskar 2015b). After harvest, the cotton seeds separated from cotton fibers are used for oil extraction. The immature cotton seeds unfit for germination and oil extraction are discarded as waste in large quantity, in India (Sivarajasekar 2014). To best of our knowledge this cheap and renewable waste material is not yet tried by the researchers as a source material for adsorbent preparation.

Therefore, in this study, an attempt was made to prepare a novel adsorbent from waste *Gossypium hirsutum* seeds, characterize it and investigate its adsorption potential for two different cationic dyes namely, basic red 2 and basic violet 3. Detailed isotherm and kinetic studies to understand the mechanism of dye adsorption were also reported.

Materials and methods

Preparation of dye solution

Basic red 2 (BR2) and Basic violet 3 (BV3) were obtained from S.D. Fine Chemicals Ltd, Mumbai. All other chemicals were obtained from Merck India Ltd, Mumbai. The structure of BR2 and BV3 is shown in Fig. 1. The stock solution of dye was prepared by dissolving 1 g of dye in 1 l of deionized water. All working solutions were prepared by diluting the stock solution to the desirable concentration. The initial pH of working solution was adjusted to the experimental conditions by stepwise adding of 0.1 N HCl or 0.1 N NaOH solutions before mixing the adsorbent with the dye solution. The concentration of dye in the sample was analyzed using a double beam UV–Vis spectrophotometer (ELICO–SL244, India) at its maximum wavelength.

Activated biomass preparation

Waste *Gossypium hirsutum* seeds were obtained from seed manufacturers, Tamil Nadu, India. The collected seeds were washed thoroughly and dried at 313 K in a temperature controlled oven for 3 days. The dried biomass was soaked with concentrated sulfuric acid in the weight ratio of 1:4. The acid soaked biomass was stirred occasionally and kept for 12 h to achieve complete adsorption of H_2SO_4 . The resultant black slurry was carefully washed with deionized water and 0.1 N sodium bicarbonate solution to remove the traces of acid. The resultant material,

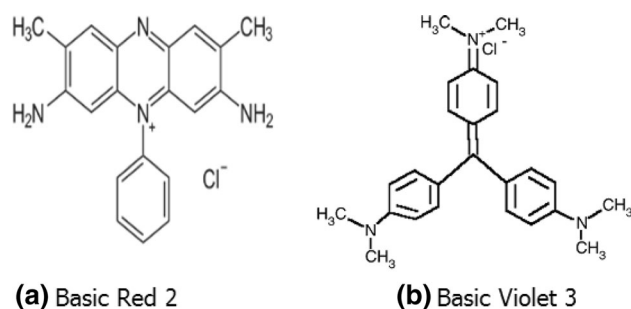


Fig. 1 Details of the cationic dyes: **a** basic red 2—Cl: 50,240, molecular weight: 350.84 mol, λ_{max} : 543 nm; **b** basic violet 3—Cl: 42,555, molecular weight: 407.98 mol, λ_{max} : 591 nm

waste *Gossypium hirsutum* seed activated biomass (WGSAB), was dried, finely ground, and stored in an air tight container for subsequent adsorption experiments.

Characterizations of WGSAB

The iodine and methylene blue numbers of WGSAB were calculated based on the ASTM 4607–86 standards at 298 K. The specific surface area of WGSAB was measured using a surface analyzer (Micromeritics ASAP 2020). Surface morphology was examined using a scanning electron microscope (SEM: JSM–6390LV–JEOL Ltd., Japan). Surface functional groups were determined based on a Boehm titration method. The surface pH of the WGSAB was determined by adding 1 g of carbon to 100 ml of deionized water and agitated at room temperature for 24 h. The supernatant liquid was centrifuged and pH was noted as the pH of WGSAB. Zero surface charge was found using solid addition method. FTIR analysis was done using a Thermo Nicolet, Avatar 370 FTIR spectrometer over a spectral range of 4000–400 cm^{-1} at a resolution of 4 cm^{-1} .

Batch adsorption

Batch adsorption experiments were conducted for the selected parameter ranges such as pH (2–12), temperature (293–313 K), initial concentration (100–300 mg l^{-1}) and contact time (1–5 h). Known amount of adsorbent was agitated with 200 ml of dye solution taken in Erlenmeyer flasks by means of a thermo-regulated shaker (GeNei SLM–IN–OS–16, India) operating at 100 rpm. The samples were withdrawn from the flasks at predetermined time intervals for kinetic experiments and at equilibrium time for isotherm studies. Collected samples were centrifuged and analyzed for the residual dye concentration using double beam UV–Vis spectrophotometer (ELICO–SL244, India). Experiments were repeated 3 times to obtain accurate data. Percentage of dye removal from bulk dye solution was calculated using the following equation:

$$\%R = \frac{C_i - C_0}{C_i} \times 100 \quad (1)$$

where C_i and C_0 (mg l^{-1}) are initial and final concentrations of the dye in the aqueous solution. The dye adsorption capacity q_t (mg g^{-1}) at any time t was determined as

$$q_t = (C_i - C_t) \times \frac{V}{M} \quad (2)$$

where C_t (mg l^{-1}) is concentration of dye at any time t , V (l) is volume of dye solution, and M (g) is amount of WGSAB. The exhausted WGSAB was regenerated using

hot water, acetone, dilute hydrochloric acid and dilute acetic acid in order to find the suitable solvent.

Isotherms

The batch equilibrium data obtained for five different initial concentrations (100, 150, 200, 250 and 300 mg l^{-1}) at pH 12, temperature 313 K and contact time 180 min were fitted to following isotherms.

Langmuir (1918):

$$q_e = \frac{q_{mL} b_L C_e}{1 + b_L C_e} \quad (3)$$

Freundlich (1932):

$$q_e = K_F C_e^{1/n_F} \quad (4)$$

Toth (1971):

$$q_e = \frac{q_{mT} C_e}{(K_T + C_e^{n_T})^{1/n_T}} \quad (5)$$

Kinetics

Batch experiments were carried out for different concentrations (100, 150, 200, 250 and 300 mg l^{-1}) with pH 12, temperature 313 K and contact time 180 min to investigate the kinetics. Kinetic equations including Ho and Avrami were employed for testing the batch kinetic data.

Ho (2006):

$$q_t = \frac{q_{e, Ho}^2 k_{Ho} t}{1 + k_{Ho} q_{e, Ho} t} \quad (6)$$

Avrami (Ho and McKay 2003):

$$q_t = q_{e, A} [1 + \exp(-k_A t)]^{n_A} \quad (7)$$

Thermodynamics

Batch experiments were carried out for differential temperatures (293, 303, 313 and 323 K) with pH 12, initial concentration 150 mg l^{-1} and contact time 180 min to examine the thermodynamic parameters. They were calculated from following (Smith and Van Ness 1987) Eqs. 8–9:

$$\ln\left(\frac{q_e}{C_e}\right) = \frac{\Delta S^0}{2.303R} - \frac{\Delta H^0}{2.303RT} \quad (8)$$

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \quad (9)$$

$$\Delta H_{is} = \frac{d(\ln C_e)}{d(1/T)} \quad (10)$$

where R is gas constant (8.314 $\text{J mol}^{-1} \text{K}^{-1}$) and T is the absolute temperature (K).

Data analysis

The isotherm and kinetic parameters were determined using MATLAB® non-linear curve fitting tool. The statistical parameters such correlation coefficient (R^2) and root mean square error (RMSE) were considered for examining the correlations. The R^2 close to unity and smaller RMSE is the index to select the suitable correlation.

Results and discussions

Characterization of WGSAB

The amount of micropores (1.0–2.8 nm) developed on the carbon surface is estimated using Iodine number, whereas the development of mesopores (around 1.5 nm) is understood via methylene blue number (Kasaoka et al. 1989). The Iodine number and methylene blue number of WGSAB were measured to be 510 and 42 mg g⁻¹, respectively. The BET surface area was found to be 496 m² g⁻¹ which conferred the development of pores on its surface. The SEM micrograph (Fig. 2c) showed that the WGSAB surface was full of uneven sized micro pores due to effective chemical activation by sulfuric acid. In addition to the porosity, the reactive functional groups on the surface strongly influence biosorption behavior of the WGSAB. Boehm titration provides evidence for the existence of surface functional groups such as carboxylic, lactonic, phenolic and carbonyl contributing to surface acidity (Boehm 1966). The surface of the WGSAB was found to be chemically heterogeneous, and the basicity (1.24 mmol g⁻¹) was less compared to the surface acidity (5.37 mmol g⁻¹). The surface pH was estimated to be 6.5. The point of zero charge was estimated to be 6.4. The FTIR analysis (Figure not shown) revealed that WGSAB surface

was comprised with OH (3419 cm⁻¹), COOH (1704 and 1625 cm⁻¹), and S=O (1380 cm⁻¹) functional groups.

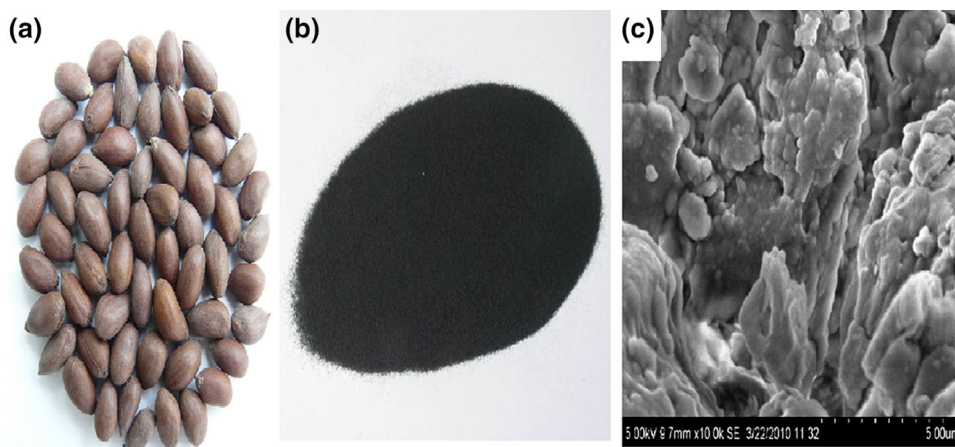
Effect of pH

To achieve a maximum dye removal by an adsorbent, the hydrogen ion concentration is to be monitored carefully in the adsorption process. It replaces some of the positive ions found in the active sites and alters the degree of ionization of the dye during the adsorption (Srinivasan and Viraraghavan 2010; Rafatullah et al. 2010; Amran et al. 2011). The effect of initial pH on the adsorption of BV3 and BV2 is represented in Fig. 2. The percentage of BV3 and BR2 sorption onto WGSAB showed an increasing trend as the pH changed from 2 via 12. The percentage dye removal increased from 68.5 to 94 % for BV3 and 65.5 to 90.26 % for BR2. The maximum adsorption was found at pH 12 for both the dyes. Cationic adsorption is favorable at pH value higher than surface pH (18). Hence, increase in the pH led reduction of H⁺ ions concentration on the sorption sites and electrostatic attraction between the dye molecule and WGSAB which increased the percentage dye removal (Gupta and Suhas 2009; Rafatullah et al. 2010; Arslan and Yiğitoğlu 2008).

Effect of temperature

The effect of aqueous phase temperature on the adsorption of BV3 and BR2 is shown in Fig. 3. An increasing trend was noticed in percentage dyes removal while changing the solution temperature from 293 to 313 K. Percentage dye removal increased from 74.9 to 94.9 % for BV3 and 71.24 to 92.18 % for BR2. This illustrated that adsorption of these dyes was endothermic and the raise in solution temperature promoted the kinetic energy of both the dyes which enhanced the rate of diffusion of dye molecules

Fig. 2 Details of adsorbent: **a** immature *Gossypium histurum* seeds, **b** WGSAB, **c** SEM micrograph of WGSAB



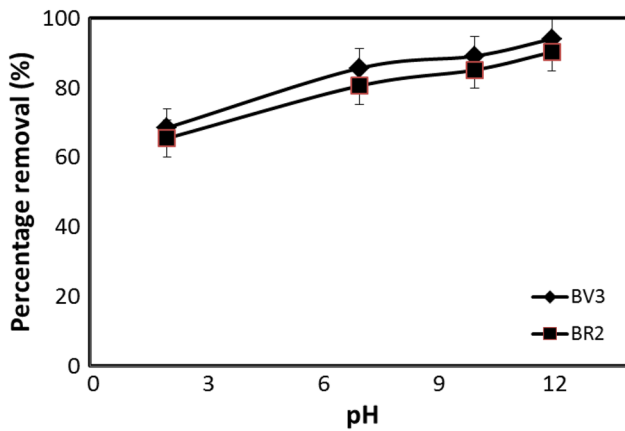


Fig. 3 Effect of pH on percentage dye removal (conditions: initial concentration: 150 mg l⁻¹, dosage: 1 g l⁻¹, temperature: 303 K, contact time: 360 min)

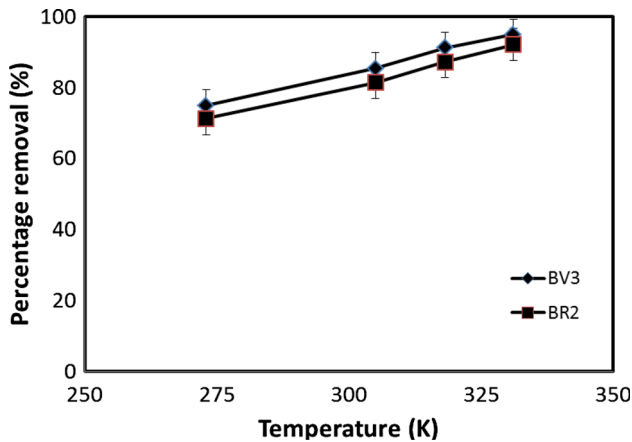


Fig. 4 Effect of temperature on percentage dye removal (conditions: initial concentration: 150 mg l⁻¹, dosage: 1 g l⁻¹, pH: 12, contact time: 360 min)

across the boundary layer and into the WGSAB pores (Farah et al. 2007; Rafatullah et al. 2010).

Effect of initial concentration and contact time

To find equilibrium time, the sorption of dyes onto WGSAB was observed as a function of time until the amount of dyes adsorbed became constant (Figs. 4, 5). Maximum percentage of dyes removal was noted within 30 min in both cases of dyes. This rapid adsorption uptake of dyes indicated the chemisorption nature of sorption onto WGSAB (Gulnaz et al. 2004). After this quick uptake the percentage dyes removal was gradually increased until 180 min and after there was only a slight difference in the percentage dyes removal. Hence, the equilibrium time was fixed to be 180 min for all experiments independent of the initial dyes concentrations. The percentage dyes removal

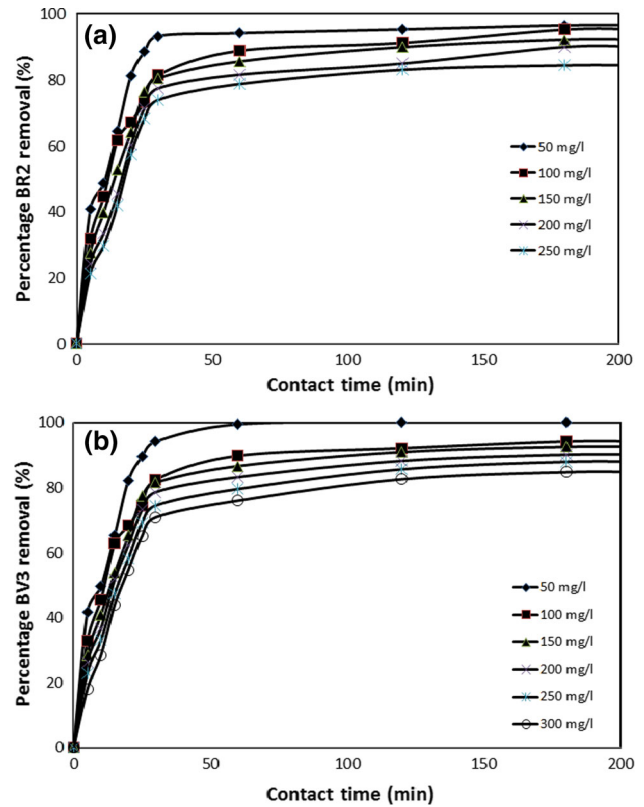


Fig. 5 Effect of initial concentration and contact time on percentage dye removal (conditions: contact time: 360 min, dosage: 1 g l⁻¹, pH: 12, temperature: 313 K)

Table 1 Optimum parameters and statistical values for isotherms

Isotherm	Constants	BR2	BV3
Langmuir	Q_{mL} (mg g ⁻¹)	50.310	66.699
	b_L (l mg ⁻¹)	0.126	0.065
	R_L	0.033	0.081
	R^2	0.9906	0.9945
	RMSE	1.7805	1.3297
Freundlich	K_F (l g ⁻¹)	8.688	8.705
	n_F	2.231	2.132
	R^2	0.9697	0.9924
	RMSE	3.1990	1.5618
Toth	q_{mT} (mg g ⁻¹)	50.105	66.699
	n_T	0.999	1.000
	R^2	0.9907	0.9945
	RMSE	1.7738	1.3297

onto WGSAB was decreased with the increase of initial dyes concentrations due to the boundary layer resistance (Garg et al. 2004; Malik 2003), unavailability of active sites and pores to dye molecules on WGSAB particles (Srinivasan and Viraraghavan 2010; Amran et al. 2011).

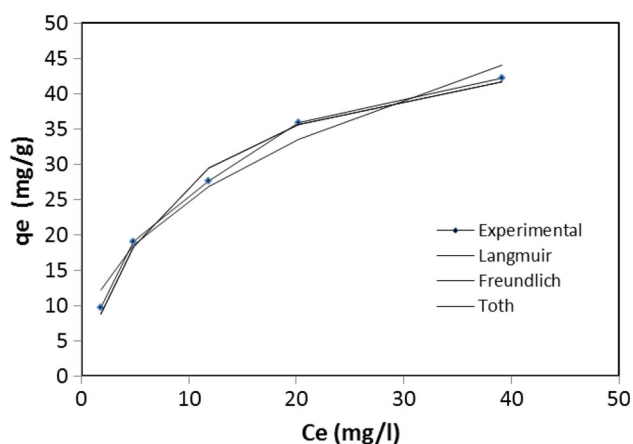


Fig. 6 Comparison of isotherms

Isotherms

The optimum parameter set for each isotherm model, R^2 and RMSE values are displayed in Table 1. The goodness of the models to explain the equilibrium data was in the order: Toth > Langmuir > Freundlich. The Toth isotherm was developed from potential theory to enhance the outcomes of Langmuir isotherm and also to be applicable for heterogeneous sorption systems. The high values of R^2 and low values of RMSE indicate that Toth isotherm properly correlated the adsorption data better than other two isotherms. The near unity value of Toth isotherm constant (n_T) indicates the WGSAB surface is heterogeneous in nature. The maximum adsorption capacity predicted by Toth isotherm of BV3 (66.699 mg g^{-1}) is higher than BR2 (50.310 mg g^{-1}). Therefore, WGSAB is more suitable for removal of BV3 than BR2. Figure 6 illustrates the comparisons of the isotherm data.

The data presented in Table 2 compare the maximum monolayer adsorption capacity of the different types of adsorbents used for the removal of BR2 and BV3. The value of (q_m) in this study is moderately larger than those in most of the previous work.

Kinetics

The determined parameter set, R^2 and RMSE values for each kinetic model are presented in Table 3. On comparison of the selected models, the higher values of R^2 and smaller values of RMSE over the selected concentration range show Avrami model correlated the kinetic data better than Ho model. It is also seen from the Table 3 that while the concentration increased the rate constant (K_A) values subsequently decreased and uptake capacity ($q_{e,A}$) increased. Further, the fractional order (n_A) and rate constant (K_A) values are almost similar for every concentration in both the dyes. This meant that the higher concentration

Table 2 Comparison of maximum adsorption capacities for BV3 and BR2 adsorption

Adsorbent	q_m	References
BV3 adsorption		
Coniferous pinus bark	32.78	Ahmad (2009)
<i>Calotropis procera</i> leaf	4.14	Ali and Muhammad (2008)
Orange peel	14.3	Annadurai et al. (2002)
Palm kernel fiber	78.9	El-Sayed (2011)
Sugarcane dust	3.8	Ho et al. (2005)
Neem sawdust	3.8	Khattri and Singh (2000)
Wood apple	19.8	Jain and Jayaram (2010)
Coir pith	2.56	Namasivayam et al. (2001a)
Treated coir pith	94.7	Namasivayam et al. (2001b)
Japonica	82.83	Wang et al. (2008)
Rice bran	42.25	Wang et al. (2008)
Wheat bran	80.37	Wang et al. (2008)
Treated waste cotton seed	66.69	This study
BR2 adsorption		
Treated olive stone	526.3	Aziz et al. (2009)
Spent bleaching earth	194.8	Mana et al. (2007)
Natural zeolite	0.055	Qiu et al. (2009)
Treated waste cotton seed	50.11	This study

favored the uptake of both the dyes but led unavailability of active sites to the dye molecules (Aziz et al. 2009; Jain and Jayaram 2010).

Thermodynamics

Thermodynamic parameters including the changes in Gibbs free energy ΔG^0 (J mol^{-1}), enthalpy ΔH^0 (J mol^{-1}) and entropy ΔS^0 ($\text{J mol}^{-1} \text{K}^{-1}$) must be considered to illustrate spontaneity of the adsorption process (Smith and Van Ness 1987). The values of enthalpy and entropy changes were obtained from Fig. 7 and are given in Table 4. As seen, the adsorption of dyes by WGSAB was spontaneous with the negative values of ΔG^0 (Eren et al. 2010). The value of ΔH_0 was positive which described that the dyes adsorption was endothermic and chemisorptive (Vinod and Aniruthan 2001). The positive ΔS^0 indicated the some structural changes in the WGSAB particles as well as dye molecules during the adsorption process (Senthilkumar et al. 2006).

Regeneration

The production charge for WGSAB is only based on the sulfuric acid cost as immature cotton seeds are naturally available in plenty. The cost of WGSAB can be further reduced if it could be regenerated for further use. From

Table 3 Optimum parameters and statistical values for kinetics

Model	Parameter	BR2					BV3				
		100 (mg l ⁻¹)	150 (mg l ⁻¹)	200 (mg l ⁻¹)	250 (mg l ⁻¹)	300 (mg l ⁻¹)	100 (mg l ⁻¹)	150 (mg l ⁻¹)	200 (mg l ⁻¹)	250 (mg l ⁻¹)	300 (mg l ⁻¹)
Ho	k_{Ho} (g mg ⁻¹ min ⁻¹)	0.011	0.004	0.002	0.002	0.001	0.011	0.004	0.002	0.002	0.001
	$q_{e,Ho}$ (mg g ⁻¹)	10.799	20.671	31.108	40.710	49.557	10.799	20.671	31.108	40.710	49.557
	R^2	0.9632	0.9899	0.9749	0.9628	0.9548	0.9632	0.9899	0.9749	0.9628	0.9548
	RMSE	1.3220	1.2920	3.0751	4.9106	6.5949	1.3220	1.2920	3.0751	4.9106	6.5949
	Avrami	n_A	0.287	0.269	0.252	0.240	0.235	0.287	0.269	0.252	0.240
	K_A (min ⁻¹)	0.287	0.269	0.252	0.240	0.235	0.287	0.269	0.252	0.240	
	$q_{e,A}$ (mg g ⁻¹)	9.808	18.246	27.187	35.043	42.185	9.808	18.246	27.187	35.043	42.185
	R^2	0.9811	0.9931	0.9920	0.9839	0.9824	0.9811	0.9931	0.9920	0.9839	0.9824
	RMSE	0.9322	1.0641	1.7326	3.2261	4.1185	0.9322	1.0641	1.7326	3.2261	4.1185

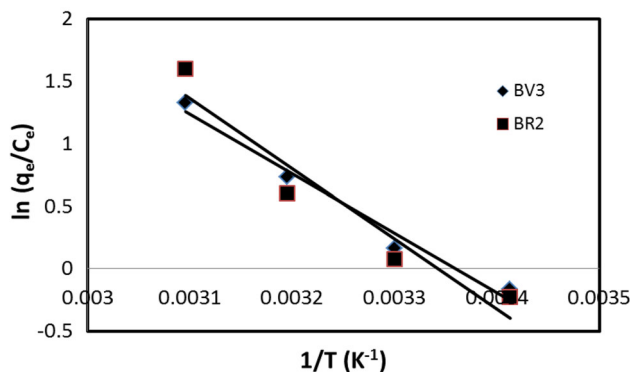


Fig. 7 Thermodynamic graph for adsorption of BV3 and BR2 onto WGSAB

Table 4 Calculated thermodynamic parameters for adsorption of BV3 and BR2 onto WGSAB

T (K)	ΔG^0 (J mol ⁻¹)		ΔH^0 (J mol ⁻¹)		ΔS^0 (J mol ⁻¹ K ⁻¹)	
	BR2	BV3	BR2	BV3	BR2	BV3
293	-45,216	-38,391	678.04	572.67	156.64	132.98
303	-46,783	-39,721				
313	-48,349	-41,051				
323	-49,915	-42,381				

Fig. 8, acetic acid was found efficient to elute BR2 as well as BV3 than other solvents. It was noticed from laboratory batch experiments that BR2 adsorbed WGSAB could be regenerated twice efficiently for further use using acetic acid. But the BV3 adsorbed WGSAB could be regenerated three times for subsequent experiments.

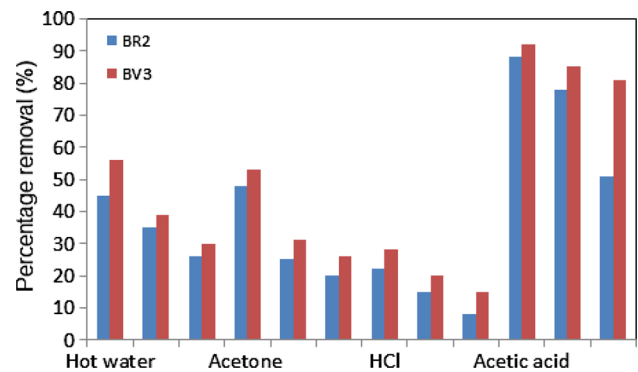


Fig. 8 Comparison of regeneration cycles

Conclusions

An adsorbent was prepared from waste *Gossypium hirsutum* seed and its efficiency to adsorb BR2 and BV3 was evaluated. Surface characterization of the adsorbent indicated that it has good number of pores, surface functional groups and adsorption capacity. The effects of process conditions such as initial dye concentrations, contact time, pH and temperature on dye removal efficiency were studied. Isotherm analysis indicated that Toth isotherm properly correlated the adsorption data and WGSAB surface is heteroporous. Kinetic modeling showed that selected cationic dyes were chemisorbed on the WGSAB surface and obeyed Avrami fractional order kinetics and higher concentrations favored the dye adsorption. Thermodynamic study indicated that desorption of BR2 and BV3 onto WGSAB was spontaneous and endothermic in nature. Regeneration of WGSAB was tried using different elutants and could be possible using acetic acid.

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