

Kinetic Study of Basic Violet 7 Sorption from Aqueous Solutions onto Sodium Hydroxide and Citric Acid Modified Sugar Beet Pulp

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Abstract. The present research was focused on the study of sorption kinetic of Basic Violet 7 (BV7) onto sodium hydroxide and citric acid modified sugar beet pulp (SCMSBP) from aqueous solutions. The research was performed in the temperature interval 25-55 °C and concentration range of 0.1-2.5 mmol/L. In batch experimental set-up, optimum conditions for quantitative removal of BV7 by SCMSBP was attained following searching effect of variables such as sorbent dose and initial pH. The sorption kinetic data were analyzed by pseudo-first-order, pseudo-second-order, intraparticle diffusion, modified Freundlich and Banghman kinetic models. The sorption kinetic was found to follow pseudo- second order kinetic model. Based on the rate constants obtained by pseudo-second-order kinetic model using Arrhenius equation, the activation energy was determined to be 10.82 kJ/mol. The results of this study indicate that SCMSBP might be a useful sorbent for BV7 contained in waste streams generated in dye processes.

Keywords: Sorption, kinetic study, modification, citric acid, sugar beet pulp

1. Introduction

Many industries often use dyes and pigments to color their products. The dye containing coloured wastewater damages the aesthetic nature of water and enhances the chances of toxic impact on the aquatic flora and fauna. These water-soluble dyes offer considerable resistance for their biodegradation due to their complex structures and high thermal and photostability. Hence, removal of dyes from wastewaters using economical means has become a real challenge to global scientists [1]. Various processes have been employed in the past for the removal of dyes from dye containing effluents. But sorption method has been found to be more effective technique for treating wastewaters. Activated carbon is the most widely used sorbent for sorption purpose because it has a high capacity for sorption of organic matter, but its use is limited because of its high cost [2]. A notable and growing trend is to evaluate the feasibility and suitability of natural, viable, renewable and low-cost materials which will be used as sorbent to combat the menace of dye pollution. This study reports on the feasibility of applying Sodium hydroxide and citric acid modified sugar beet pulp (SCMSBP) as low-cost sorbent for Basic Violet 7 (BV7) removal from aqueous solution. Sorption kinetic parameters were also evaluated and reported. The use of low-cost, non-toxic, high surface area as eco-friendly sorbent has been investigated as an ideal alternative material for expensive and/or toxic sorbent to removal basic dyes from dye containing effluents.

2. Materials and Methods

2.1. Preparation of SCMSBP

Sugar beet pulp was obtained from Elazığ Sugar Factory in Elazığ. Sugar beet pulp was cropped in a blender and sieved to retain the +16-30 mesh fraction. SCMSBP was prepared according to the modified

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methods reported at literature [3], [4]. The procedure of modification of sugar beet pulp is proposed in Fig. 1. The characteristics of SCMSBP are shown in Table I.

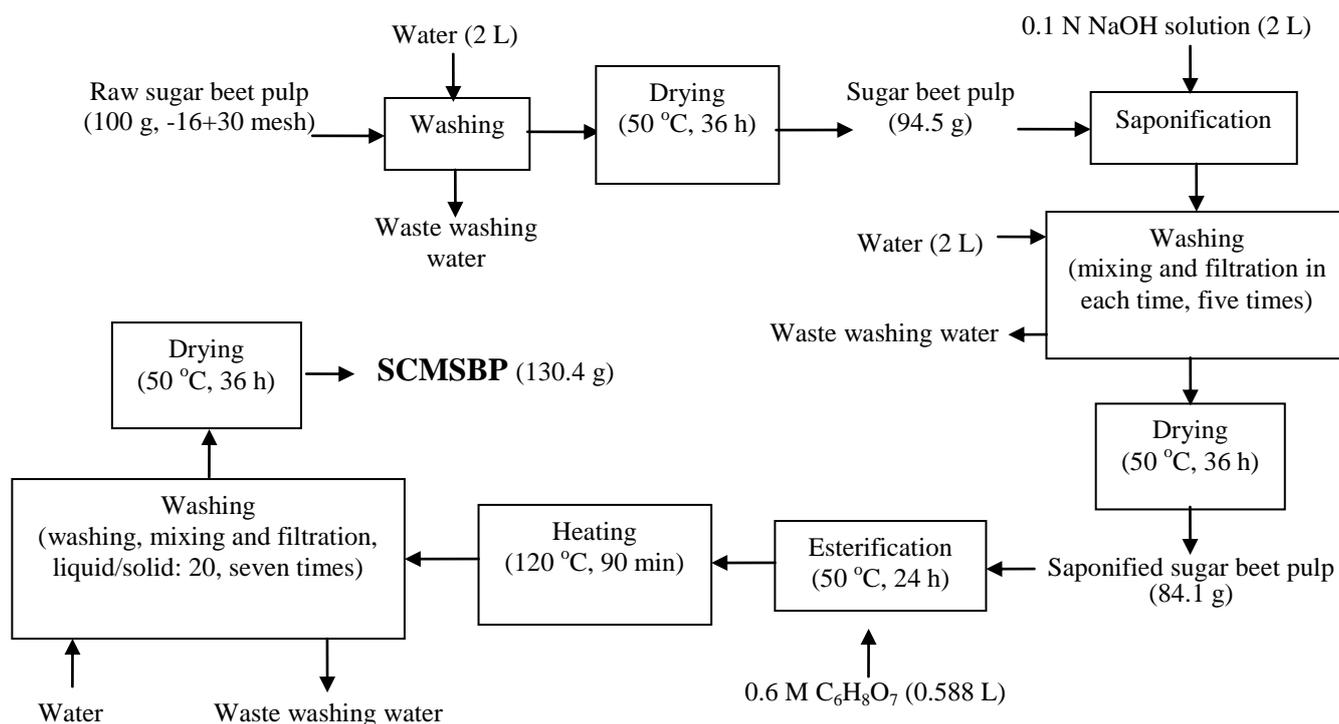


Fig. 1: The procedure of modification of sugar beet pulp with sodium hydroxide and citric acid

Table 1: The Characteristics of SCMSBP and BV7

The characteristics of SCMSBP		The characteristics of BV7	
Bulk density (g/mL)	0.359	Name	Cationic Violet 7
pH (% 1 solution)	3.89	Colour index number	48020
Mater soluble in H ₂ O (%)	0.96	Chemical abstracts service number	6441-82-3
Mater soluble in HCl (%)	3.57	Type	Cationic
Ash content (%)	4.68	Class	Metin
Mechanical moisture content (%)	6.83	Counter ion	Cl
Cation exchange capacity (meq/g)	3.49	Molecular formula	C ₂₄ H ₃₀ N ₂ Cl
Water retention capacity (g/g)	4.92	Formula weight	417.41 g/mol
Swelling capacity (mL/g)	3.89	λ _{max}	542 nm
Copper sorption capacity (meq/g)	3.32	Dye content	65 %

2.2. Preparation of BV7 Solutions

The characteristics of BV7 are shown in Table I. BV7 was used without further purification. The BV7 stock solution was prepared by dissolving accurately weighted dye in distilled water to the concentration of 2.50 mmol/L. The stock solution was then appropriately diluted to get test solutions of desired concentrations.

2.3. Sorption Experiments, Measurements and Calculations

The effects of sorbent dose and initial pH of BV7 solution on the sorption capacity of SCMSBP were investigated at 25 °C. All sorption experiments were carried out in a rotary shaker at 200 rpm (Selecta, Rorabit). pH of BV7 solutions (0.5 mmol/L) were adjusted from 2 to 10 using dilute HCl or NaOH and agitated with a range of SCMSBP dose (0.5, 1.0, 2.0, 5.0 and 10.0 g/L) for 12 h.

The kinetic data were obtained at four different temperatures (25, 35, 45 and 55 °C). Kinetic of BV7 sorption onto SCMSBP was followed by taking various concentrations (0.10, 0.25, 0.50, 1.00, 2.50 mmol/L) for different time periods (5-720 min).

The dye solutions were separated from the sorbents by filtration using 200 mesh sieve. The pH of dye solutions were adjusted at pH 7 before analysis. BV7 concentration was estimated spectrophotometrically by

monitoring the absorbance at 542 nm using UV-vis spectrophotometer (Shimadzu UV-1201). pH was measured using pH meter (Mettler Delta 3000).

All the experiments were carried out in duplicate and the means values were used for calculation. The amount of sorption at time t , q_t (mmol/g), was calculated by:

$$q_t = \frac{V(C_o - C_t)}{W} \quad (1)$$

where C_o and C_t (mmol/L) are the initial and final BV7 concentrations, respectively, V (L) is the volume of BV7 solution and W (g) is the mass of SCMSBP. The amount of BRV7 adsorbed was expressed as percentage of removal and was calculated using the below equation. Where R is the percentage of BV7 removal.

$$R = \frac{(C_o - C_t)100}{C_o} \quad (2)$$

3. Results and Discussion

3.1. Effect of Initial pH and Sorbent Dose

Fig. 2 shows the effects of initial pH and sorbent dose. The initial pH exerts profound influence on the ability of sorbent surface for interaction and dye molecule tendency for binding to solid surface. These phenomena presumably are due to its influence on the surface properties of the sorbent and ionization/dissociation of the sorbate molecule. The effect of initial pH on the percent removal of BV7 by SCMSBP was evaluated within the pH range 2-10 at initial dye concentration of 0.5 mmol/L and contact time 12 h. It was observed that the removal of dye increased with the increasing pH. At an acidic pH condition, the hydroxyl and carboxyl groups on the surface of SCMSBP are protonated and they inhibit the binding of the BV7 dye cation. The excess H^+ ions compete with the dye cations for the sorption sites. With an increasing pH of the dye solution, the surface groups will be deprotonated resulting in an increase of negatively charged sites that favour the sorption of the cationic dye (BV7) due to electrostatic attraction. But beyond pH 8, the colour of the BV7 solution is decomposed spontaneously. For this reason, pH 7 ± 0.5 was selected for sorption of BV7.

The sorption of BV7 onto SCMSBP was studied by changing the quantity of sorbent dose (0.5-10 g/L) in dye solution while keeping the initial dye concentration (0.5 mmol/L). As can be seen from Fig. 2, the percent removal increased from 46.14% to 82.14% with the increase in the sorbent dose from 0.5 to 2 g/L. The subsequent increase in the SCMSBP quantity in dye solution to 10 g/L led to an insignificant increase in the removal percent (99.73%). The maximum sorption capacities for BV7 with sorbent doses of 2.0 and 10.0 g/L were determined to be 0.205 and 0.050 mmol/g, respectively. For this reason, optimum sorbent dose for BV7 removal was selected to be 2.0 g/L.

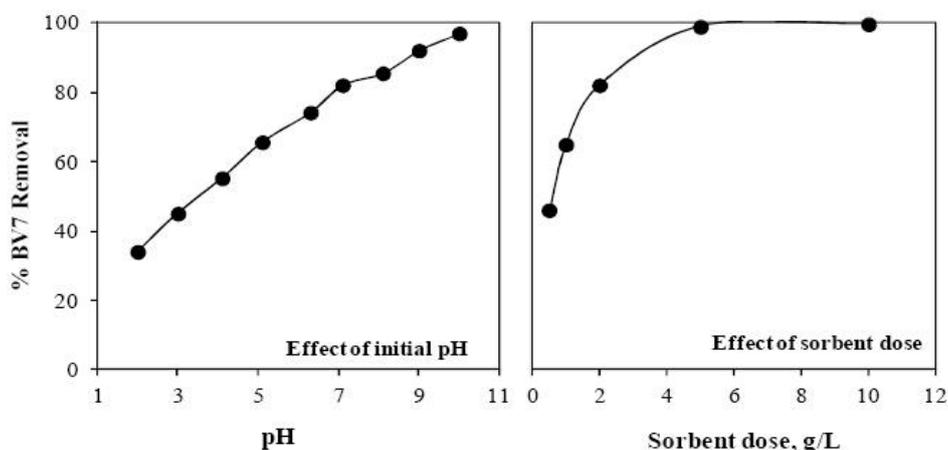


Fig 2: The effects of initial pH and sorbent dose (Initial dye concentration: 0.5 mmol/L, temperature: 25 oC, time: 12 h, agitation speed: 200 rpm. Sorbent dose for effect of initial pH is 2.0 g/L and pH for effect of sorbent dose is 7.1)

3.2. Kinetic Study

Kinetic modeling not only allows estimation of sorption rates but also leads to suitable rate expressions characteristic of possible reaction mechanisms. The kinetic experimental data were analyzed by pseudo-first-order, pseudo-second-order, intraparticle diffusion, modified Freundlich and Banghman kinetic models in this study. The linear forms of kinetic models and parameters calculated from kinetic models are seen Table II and Table III, respectively. It can be seen that the linear correlation coefficients for second-order model is good. In this model, the rate-limiting step is the surface adsorption that involves chemisorption, where the removal from a solution is due to physicochemical interactions between the two phases [5]. Based on the comparison between experimental and theoretically calculated q_e values, it was found that these values are close to each other for removal of BV7 by SCMSBP.

The pseudo-second-order rate equation of BV7 sorption on SCMSBP is expressed as a function of temperature by Arrhenius equation, as shown below:

$$\ln(k) = \ln(A) - E_a/RT \quad (3)$$

Table 2: The Linear Forms of Pseudo-First-Order, Pseudo-Second-Order, Modified Freundlich, Intraparticle Diffusion, and Banghman Equations

Kinetic model	Linear form	Linear plot	Reference
Pseudo-first-order	$\ln(q_e - q) = \ln(q_e) - k_1 t$ (4)	$t - \ln(q_e - q)$	[6]
Pseudo-second-order	$\frac{t}{q} = \frac{1}{k_2 \cdot q_e^2} + \frac{t}{q_e}$ (5)	$t - t/q$	[7]
Intraparticle diffusion	$q = k_{int} \cdot t^{1/2} + C$ (6)	$t^{1/2} - q$	[8]
Modified Freundlich	$\ln[q] = \ln[k \cdot C_o] + \frac{1}{m} \ln[t]$ (7)	$\ln(t) - \ln(q)$	[9]
Banghman	$\log \left[\log \left(\frac{C_o}{C_o - q \cdot m} \right) \right] = \log \left(\frac{k_o \cdot m}{2.303 \cdot V} \right) + \alpha \cdot \log(t)$ (8)	$\log[t] - \log \left[\log \left(\frac{C_o}{C_o - q \cdot m} \right) \right]$	[10]

Table 3: The Values of Constants and Correlation Coefficients of Kinetic Models

Kinetic model		25 °C	35 °C	45 °C	55 °C
		$q_e(\text{Experimental}), \text{mmol/g}$	0.198	0.205	0.212
Pseudo-first-order	R^2	0.990	0.977	0.966	0.935
	$k_1, 1/\text{min}$	0.020	0.019	0.019	0.018
	$q_e, \text{mmol/g}$	0.166	0.158	0.155	0.147
Pseudo-second-order	R^2	0.996	0.997	0.997	0.996
	$k_2, \text{g}/\text{mmol} \cdot \text{min}$	0.187	0.222	0.252	0.279
	$q_e, \text{mmol/g}$	0.217	0.222	0.222	0.233
Modified Freundlich	R^2	0.979	0.979	0.977	0.991
	$k, \text{L}/\text{g} \cdot \text{min}$	0.068	0.090	0.104	0.140
	m	2.92	3.38	3.68	4.55
Intraparticle diffusion	R^2	0.912	0.884	0.866	0.828
	$k_{int}, \text{mmol}/\text{g} \cdot \text{min}^{1/2}$	0.013	0.013	0.013	0.013
	C	0.030	0.040	0.046	0.058
Banghman	R^2	0.983	0.983	0.981	0.994
	$k_o, \text{mL}/(\text{g} \cdot \text{L})$	33.00	44.05	51.61	71.67
	$\alpha, \text{mmol}/\text{g} \cdot \text{min}$	0.393	0.345	0.322	0.267

The $\ln(k)$ versus $1/T$ gives a straight line with slope $-E_a/R$. The Arrhenius activation energy calculated from the slope is found to be 10.82 kJ/mol. The positive activation energy is the energy that must be overcome for a sorption to occur [11].

4. Conclusions

It is evident that sodium hydroxide and citric acid modified sugar beet pulp is a good sorbent for Basic Violet 7 and it can be suggested for the removal of basic dye from dye containing effluents. In this study, the effective pH was 7 and the optimum sorbent dose was found to be 2.0 g/L. The kinetic study was performed based on pseudo-first-order, pseudo-second-order, intraparticle diffusion, modified Freundlich and Banghman equations. The results data indicate that the sorption follow the pseudo-second-order rate.

Nomenclature

α	Banghman model constant (1/min)	k_{int}	Intraparticle diffusion rate const. (mol/g.min ^{1/2})
C	Integral constant of intraparticle diffusion	m	Amount of sorbent (g)
C_e	Dye concentration at the beginning (mol/L)	R^2	Correlation coefficient
C_o	Dye concentration at the equilibrium (mol/L)	R	Ideal gas constant (8.314 J/mol.K)
E_a	Activation energy, kJ/mol	t	Time (min)
k	Modified Freundlich rate constant (L/g.dk)	T	Temperature (K)
k_o	Banghman rate constant (L ² /g)	q	Amount of sorbed at t time (mol/g)
k_1	Pseudofirst-order rate constant (1/min)	q_e	Amount of sorbed at equilibrium (mol/g)
k_2	Pseudo-second-order rate constant (g/mol.dk)	V	Volum of solution (L)

5. References

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