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Removal of Reactive Dyes from Aqueous Solutions by Sugar Beet Pulp and Modified Products of Sugar Beet Pulp in Batch System

Nurdan Bahar [1 +]

[1] Tunceli University Faculty of Engineering, Department of Chemical Engineering, 62000, Tunceli, Turkey

Abstract. The present research was focused on the study of sorption of Reactive Blue 21 (RB21) and Reactive Black 5 (RB5) onto sugar beet pulp (SBP), saponified sugar beet pulp with sodium hydroxide (SSBP) and esterification product of saponified sugar beet pulp with phosphoric acid (SSBP-PA) from aqueous solutions. The research was performed in the temperature interval 25-55 ^{o}C in and in the concentration range of 50-600 mg/L. Batch study was conducted in order to determine the optimal initial pH and the optimal initial pH was selected to be 4. Langmuir and Freundlich models were fitted to the experimental data. It was found that the Langmuir isotherm model presented satisfactory fit with the experimental data. The maximum sorption capacity onto SSBP-PA after 6 h at 25 ^{o}C could reach 204 and 192 mg/g for RB21 and RB5, respectively. The sorption process of RB21 and RB5 onto SSBP-PA were endothermic.

Keywords: Reactive dye, dye removal, sorption, sugar beet pulp, modification

1. Introduction

Nowadays, with the rapid development of modern industries, the problem of water pollution has become increasingly serious. Industrial effluents (main environmental pollution source) contain highly colour dyes with large amount of organic solids.The discharge of such contaminated water into public streams is a great environmental challenge not only due to its treatment for reuse but also its toxicity to human beings and animals by contaminating underground water reservoirs [1].

Reactive dyes are typically azo-based chromophores combined with different types of reactive groups. They have the favourable characteristics of bright colour, water-fast, simple application techniques and low energy consumption and are used extensively in textile industry but nearly 50% of reactive dyes may be lost to the effluent after dyeing of cellulose fibers. Reactive dyes cannot be easily removed by conventional wastewater treatment systems they are stable to light, heat and oxidizing agents. [2]. Furthermore, any degradation by physical, chemical or biological treatments may produce small amount of toxic and carcinogenic. On the other hand, the development of sorption technique represents a powerful alternative for the removal of reactive dyes and other pollutants like heavy metals from industrial wastewaters [3].

The purpose of the present work was to study the effect of initial pH and sorbent type on the sorption of Reactive Blue 21 (RB21) and Reactive Black 5 (RB5) onto sugar beet pulp (SBP), saponified sugar beet pulp with sodium hydroxide (SSBP) and esterification product of saponified sugar beet pulp with phosphoric acid (SSBP-PA), as well to determine a isotherm model which would optimally describes the experimental data.

2. Experimental

2.1. Modification of Sugar Beet Pulp

Sugar beet pulp was obtained from Elazıg Sugar Factory in Elazıg. Sugar beet pulp was cropped in a blender and sieved to retain the +16-30 mesh fraction. SSBP and SSBP-PA were prepared according to

[+] Corresponding author. Tel.: +905324659417; fax: +904282131861.
E-mail address: nbahar@tunceli.edu.tr.

the modification methods specified by Marshall et al., 1999 [4] and Wafwoyo et al., 1999 [5], respectively. The procedure of preparation of sorbents is proposed in Fig. 1. The characteristics of sorbents are given in Table I.

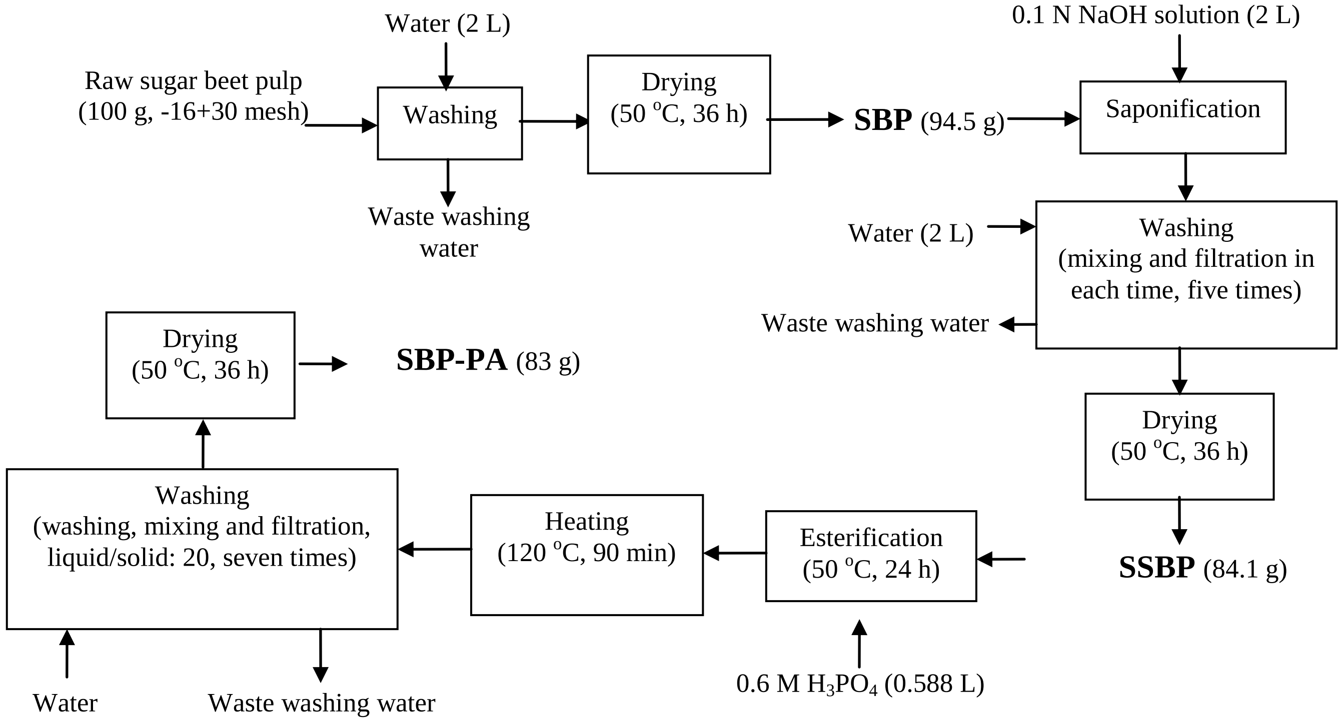

Fig. 1: The procedure of preparation of sorbents

Table 1: The Characteristics of Sorbents

Parameters	**SBP**	**SSBP**	**SSBP-PA**
Bulk density (g/mL)	0.294	0.315	0.348
pH (% 1 solution)	5.33	8.16	3.70
Mater soluble in H_2O (%)	4.64	3.29	0.73
Mater soluble in HCl (%)	7.58	5.36	1.96
Ash content (%)	3.81	5.37	5.05
Mechanical moisture content (%)	6.73	7.91	6.63
Water retention capacity (g/g)	7.94	6.78	2.25
Swelling capacity (mL/g)	6.72	4.27	1.91
Copper sorption capacity (meq/g)	0.75	0.98	0.91

2.2. Preparation of Dye Solutions

RB21 and RB5 (commercial purity) were used without further purification. Standard RB21 and RB5 solutions of 1000 mg/L were prepared as stock solutions and subsequently diluted when necessary. The characteristics of RB21 and RB5 are given Table II.

Table 2: The Characteristics of RB21 and RB5

	RB21	**RB5**
Name	Reactive Turquoise Blue G	Reactive Black B
Chemical Abstracts Service Number	12236-86-1	17095-24-8
Type	Reactive	Reactive
Class	Copper phthalocyanine	Diazo
λ_{max}, nm	623	600
Formula weight, g/mol	576	992
Dye content	73%	68%

2.3. Sorption Procedure

Batch sorption experiments were conducted by dose of 5.0 g/L of sorbents (SBP, SSBP and SSBP-PA) in 150 mL-PE bottles containing 100 mL of aqueous solutions at different concentrations of RB21 and RB5. The mixtures were stirred at 200 rpm in a thermostatic rotary shaker (Selecta Rotabit) for 12 h of contact period. After shaking for a certain time, the sorbents by filtration with a 200 mesh stainless sieve and the concentration of dyes after the sorption were analyzed by Spectrophotometer (Shimadzu UV-1201).

The effects of initial pH (2-10) on the removal efficiency were investigated. The pH of dye solutions were adjusted to 2-10 using hydrochloric acid and sodium hydroxide. Sorption experiments were carried out by adding with a dose of SSBP-PA of 5.0 g/L into dye solutions (50-600 mg/L) at different temperatures (25-55 ^{o}C).

All experiments were carried out in duplicate, in which all data was calculated, and the average values were taken to represent a result. The amount sorbed was calculated using the following equation:

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

where C_o and C_t (mmol/L) are the initial and final concentrations of dyes, respectively, V (L) is the volume of reactive dyes solution and W (g) is the mass of sorbents. The amount of sorbed dye was expressed as percentage of removal and was calculated using the equation:

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

where R is the percentage of dye removal.

3. Results and Discussions

3.1. The Effect of Sorbent Type and Initial pH

The variation of equilibrium dye removal with sorbent type and initial pH is given in Fig. 2 for an initial dye concentration of 300 mg/L at 25 ^{o}C for a contact time of 12 h. As seen from Fig. 2, sorption of RB21 and RB5 were maximum at pH 2.0 and decline sharply with further increase in pH and reached to zero at pH 9. pH 2.0 is very acidic pH. So the working pH value for removal of RB21 and RB5 was chosen as 4.0 and other sorption experiments were performed at this pH value. At higher pH values, a negatively charged surface site on the sorbent does not favour the sorption of dye anions due to electrostatic repulsion. The reactive dyes release coloured dye anions in solution. SBP is dominated by negatively charged sites that are largely carboxylate groups together with some weaker acidic groups of heteropolysaccharides and nitrogen-containing functional groups of proteins [6]. So, the increase of OH- ions with the increasing pH cause a competition with the dye anions for sorption sites resulting in a decrease in sorption [7].

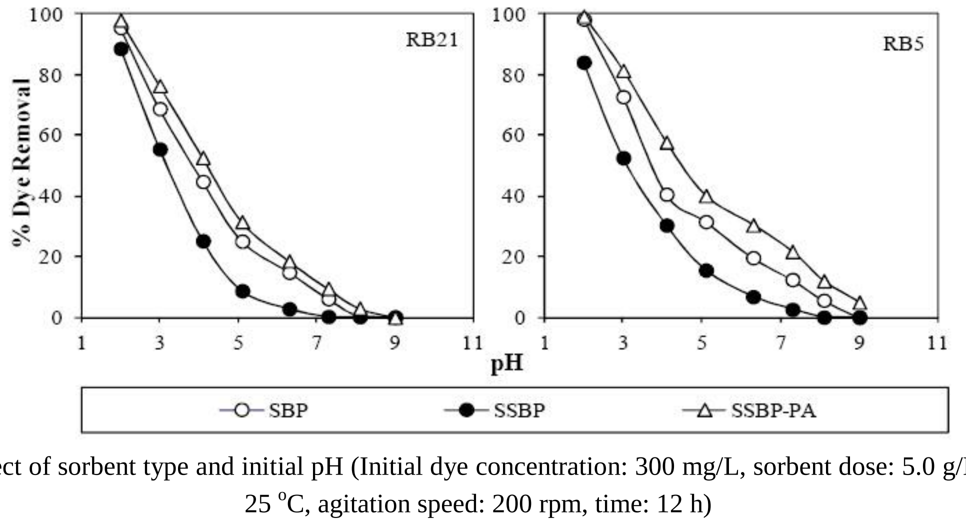

Fig. 2: The effect of sorbent type and initial pH (Initial dye concentration: 300 mg/L, sorbent dose: 5.0 g/L, temperature: 25 ^{o}C, agitation speed: 200 rpm, time: 12 h)

As shown in Fig. 2, the effective sorbent for removal of RB21 and RB5 is SSBP-PA. The removal percentages of RB21with SBP, SSBP and SSBP-PA are 27.56, 45.42 and 57.8 %, respectively. This values for RB5 are 30.16, 40,57 and 59.07, respectively.

3.2. Sorption Isotherm

Fig. 3 shows the experimental isotherm data of RB21 and RB5 on SSBP-PA at different temperatures (25-45 ^{o}C). The uptake of the dye anions increase with an increase in temperature thereby indicates the process to be endothermic.

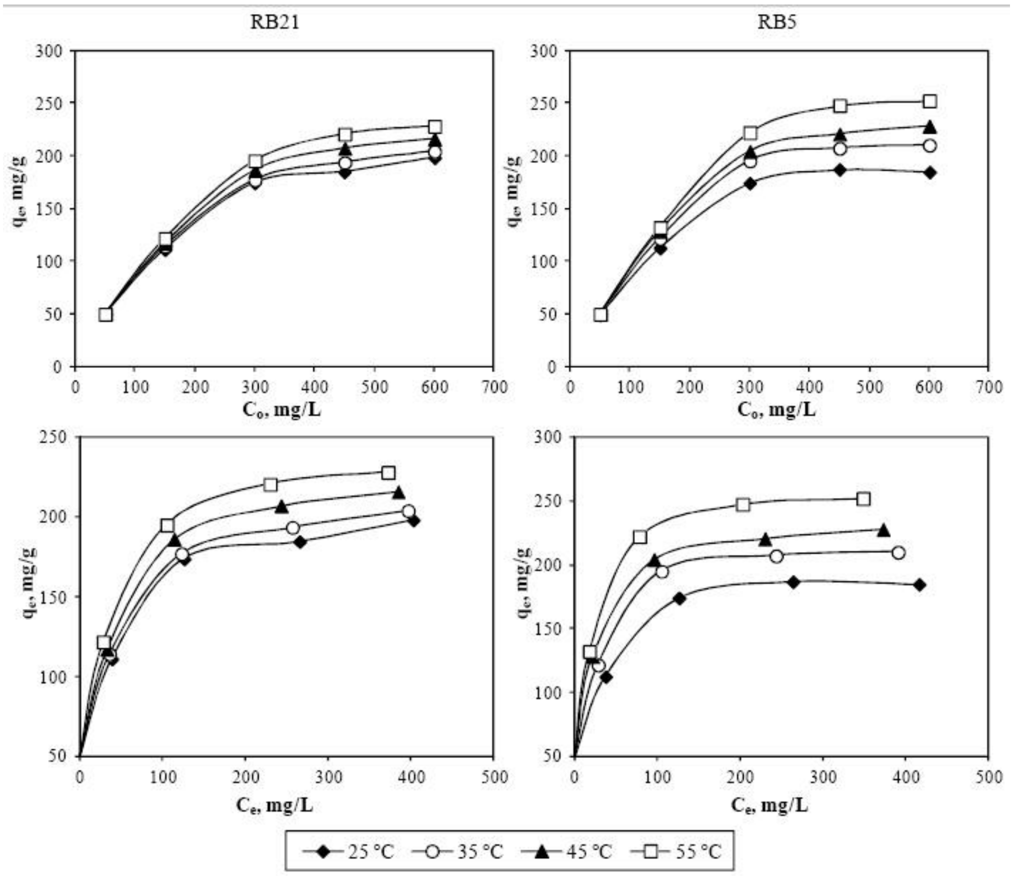

Fig. 3: The effect of initial dye concentration on sorption capacity at equilibrium and non-linearized sorption isotherms (pH: 4, dose: 5.0 g/L,agitation speed 200 rpm, time: 6 h).

In this study, Langmuir and Freundlich were used. The linear forms of isotherms are shown in Table III. The Langmuir equation is valid for monolayer sorption onto a completely homogeneous surface with a finite number of identical sites and with negligible interaction between sorbed molecules. The Freundlich equation assumes neither homogeneous site energies nor limited levels of sorption and the Freundlich isotherm is shown to be consistent with exponential distribution of active centres, characteristic of heterogeneous surfaces. The parameters of isotherms are presented in Table IV. Equilibrium data could be fitted into Langmuir.

Table 3: The Linear Forms and Other Equations of Langmuir and Freundlich Isotherms

Isotherm name	Linear form and other equations of isotherm	Reference	Nomenclature
Langmuir	$\frac{C_e}{q_e} = \frac{1}{q_m.b} + \frac{C_e}{q_m}$ (3) $R_L = \frac{1}{1+bC_o}$ (4)	[8]	**C_e:** Dye concentration at the beginning (mol/L) **q_e:** Amount of sorbed at equilibrium (mol/g) **q_m:** Maximum amount of sorbed (mol/g) **R_L:** Equilibrium parameter for Langmuir isotherm **b:** Langmuir isotherm constant (L/mol) **k_F:** Freundlich isotherm constant (mol/g) **n_F:** Freundlich isotherm constant (g/L)
Freundlich	$\ln[q_e] = \ln[k_F] + \frac{1}{n_F}\ln[C_e]$ (5)	[9]	

Table 4: The Parameters of Langmuir and Freundlich Isotherms

Isotherm	Constant	RB21				RB5			
		25 ℃	35 ℃	45 ℃	55 ℃	25 ℃	35 ℃	45 ℃	55 ℃
Langmuir	R^2	0.994	0.995	0.995	0.996	0.997	0.997	0.998	0.998
	q_m, mg/g	204	208	222	238	192	217	233	256
	b, L/mg	0.054	0.057	0.059	0.064	0.077	0.087	0.090	0.097
	R_L	0.880	0.875	0.872	0.863	0.838	0.821	0.816	0.805
Freundlich	R^2	0.980	0.984	0.980	0.980	0.980	0.980	0.985	0.980
	n_F, g/L	5.25	5.10	5.22	5.27	4.27	4.43	4.15	3.83
	k_F, mg/g	63.1	63.7	69.4	74.8	49.7	58.8	60.2	61.6

4. Conclusions

In this work, SSBP-PA has been proved to be an efficient sorbent for the removal of RB21 and RB5 from aqueous solutions. Temperature-dependent sorption experiments suggest that the sorption process is endothermic nature. The maximum sorption capacities for RB21 and RB5 were estimated at 204 and 192 mg/g according to the Langmuir model at 25 ^oC.

5. References

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