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Removal of Reactive Dyes from Aqueous Solutions by Sugar Beet Pulp and Modified Products of Sugar Beet Pulp in a Fixed Bed Column

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Abstract. Sugar beet pulp (SBP), saponified sugar beet pulp (SSBP) and esterification product of saponified sugar beet pulp with phosphoric acid (SSBP-PA) were used as sorbent for the removal of Reactive Black 5 (RB5) and Reactive Blue 21 (RB21) from aqueous solution in a fixed bed column. The experiment was performed in column mode at room temperature (25 ^{o}C) and effect of bed depth on breakthrough curves was presented. Maximum dye removal in continuous mode experiments with SSBP-PA for RB5 and RB21 were found to be 43.28 and 32.85 mg/g, respectively. These findings revealed that SSBP-PA has a high sorption potential and it can be used for the treatment of reactive dye containing wastewater.

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

1. Introduction

The coloring of wastewater from the production of dyes and pigment, as well as from industries that use these colorants, such as leather, textile, fiber, carpet, paper, printing, automotive, plastic, ceramic, glass, food coloring, cosmetics, pharmaceutical and other industries has always been a major problem [1]. Generally, presence of aromatics ring, metal ions and halides, especially chlorides in dyes structure increase their toxicity, carcinogenicity, genotoxicity, mutagenic and teratogenic property to living beings [2]. The conventional methods for treating dye containing wastewaters are coagulation and flocculation, reverse osmosis, electroflotation, membrane filtration, irradiation and ozonation and active carbon sorption. At present, the most common treatment for effective dyes removal is sorption due to its effectiveness, efficiency, economy and no secondary pollution but it is expensive [3]. Many studies have focused on seeking cheap, locally available and effective sorbents. Various natural or wasted materials have been extensively explored and investigated for the sorption removal of different contaminants from aqueous solutions [4], [5].

In this work, sugar beet pulp (SBP) was simply modified with sodium hydroxide and phosphoric acid. SBP, saponified sugar beet pulp (SSBP) and esterification product of saponified sugar beet pulp with phosphoric acid (SSBP-PA) were proved effective in elimination of Reactive Black 5 (RB5) and Reactive Blue 21 (RB21) in a fixed column mode.

2. Materials and Method

2.1. Modification of Sorbent

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 the modification methods specified by Marshall et al., 1999 [6] and Wafwoyo et al., 1999 [7], respectively. The procedure of preparation of sorbents is proposed in Fig. 1. The some characteristics of sorbents are given in Table I.

2.2. Preparation of Dye Solutions

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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.

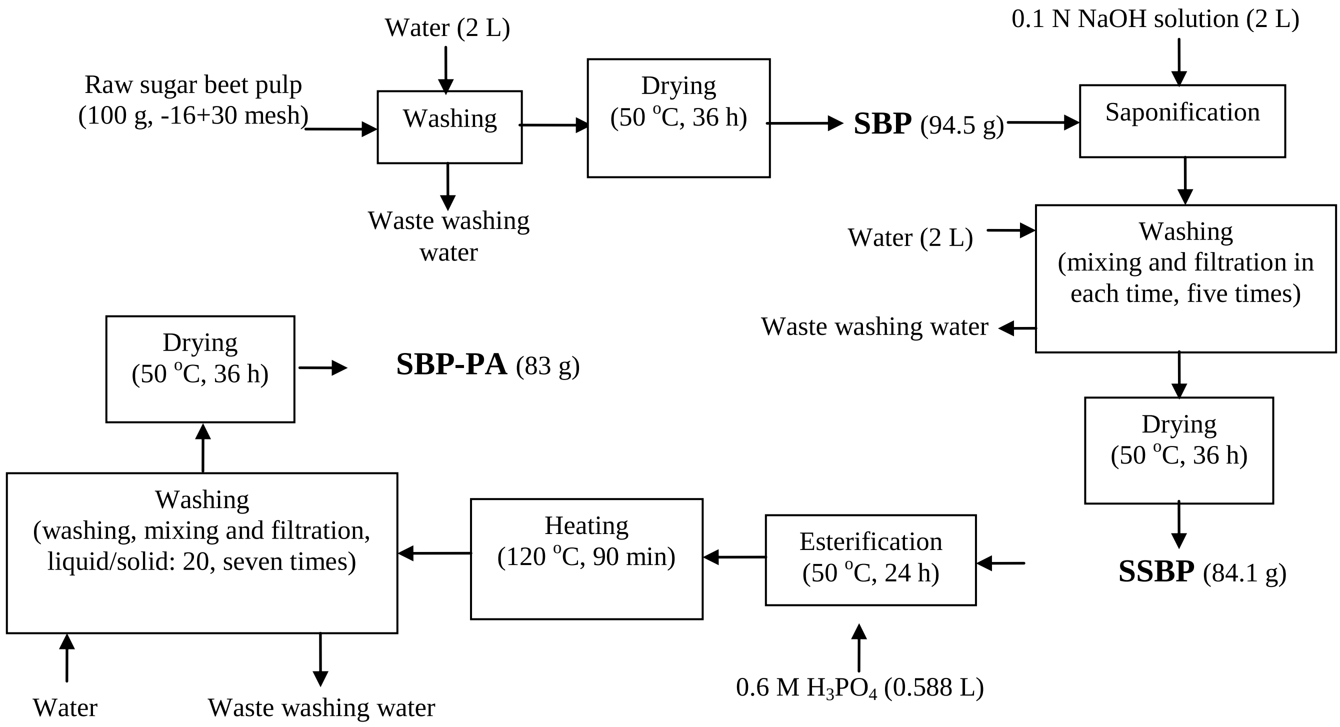

Fig. 1: The procedure of preparation of sorbents

Table 1: The some 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
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

Table 2: The Characteristics of RB21 and RB5

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

2.3. Column Studies

The fixed bed experiments were carried out in four glass cylindrical columns (internal diameter of 1.1 cm and height of 8.3, 13.6, 18.9 and 24.2 cm) packed with SBP, SSBP and SSBP-PA (bed packed depth: 5.3, 10.6, 15.8 and 21.2 cm) and coupled to a peristaltic pump (Lab Pump Jr, RHSY)). The effects of the type of dye (RB5 and RB21) were investigated. The pH of the dye solutions with HCl was adjusted to be pH 4.0. The dye solutions (250 mg/L and 25 ^{o}C) were pumped upward through the column at flow rate of 4 mL/min. At the column top, samples were collected at regular time intervals until the bed saturation, and the dyes concentration was determined by spectrophotometry (Shimadzu UV-1201). The bed saturation was considered when the outlet dye concentration was the same that the initial dye concentration. The experiments were carried out in duplicate.

2.4. Column Data Analysis

When the effluent concentration (C) from the column to reach about 10% of the influent concentration (C_o) the breakthrough point is attained. The breakthrough curve was expressed by C/C_o vs. bed volume number. The effluent volume, V_{eff} (mL), can be calculated from (1):

$$V_{eff} = Q.t_t \quad (1)$$

where Q is the volumetric flow rate (mL/min) and t_t is the total flow time (min). The value of the total mass of adsorbed dye, q_t (mg), can be calculated from the area under the breakthrough curve (2):

$$\mathbf{q_t = \frac{Q}{1000}\int_{t=0}^{t=t_t} C_s\, dt} \quad (2)$$

where C_s is the sorbed dye concentration (mg/L).The equilibrium dye uptake or maximum capacity of the column, qm (mg/g) is calculated by (3):

$$\mathbf{q_m = \frac{q_t}{m}} \quad (3)$$

where m is the dry weight of sorbent in the column (g). The total amount of dye in the column (m_t) is calculated from (4):

$$\mathbf{m_t = \frac{C_o Q t_t}{1000}} \quad (4)$$

3. Results and Discussion

One of the most important advantages to carry out chemical modifications in the native biomass is related to improve the mechanical stability in their application in continuous flow experiments. In addition, native materials used in column fillings can promote clogging due to the biomass swelling [8]. As seen Table I, SBP has high water retention capacity and swelling capacity. Apart from improving uptake capacity and extending binding sites, material modifications provide appropriate rigidity and swelling characteristics of biosorbent particles [8]. SSBP and SSBP-PA have higher copper sorption capacity from SBP.

The effects of bed height on the adsorption performances of SBP, SSBP and SSBP-PA have been investigated over a range from 5.3 to 21.6 cm at 25 ^oC. The flow rate was fixed at 4 mL/min and the initial concentration and pH of RB5 and RB21 solution were 250 mg/L and 4.0, respectively. The effects of the dye type and of bed height (5.3 cm [bed volume: 5 mL], 10.6 cm [bed volume: 10 mL], 15.9 cm [bed volume: 15 mL] and 21.2 cm [bed volume: 20 mL]) on the breakthrough curves are shown in Fig. 2. From Fig. 2, it was found that the breakthrough volume number increased with increasing bed height as expected. It was due to the fact that as the bed height increased, reactive dye had more time to contact with sorbents. The performance of the fixed bed column was evaluated by the breakthrough curves, being considered, the operation characteristics like, effluent volume (V_{eff}), total mass of dye adsorbed (q_t) and maximum capacity of the column (q_m) for C/C_o of 0.1, 0.5 1.0. The operation characteristics are given Table III. Taking into account that the same flow rate was used in all the columns, the C/C_o of 1.0 for RB5 sorption onto SBP, SSBP and SSBP-PA were obtained from the column (bed volume: 20 mL) by passing 1000, 600, 1160 mL of solutions, respectively (Table III). Increasing in column depth increased the throughput volume treated due to higher contact time. For RB21 removal with SSBP-PA, the treated solution volume varied from 160 mL to 390 mL and from 260 to 680 mL as the bed height was increased from 5.3 cm to 21.2 cm at C/C_o= 0.5 and C/C_o= 1.0, respectively. Furthermore, the sorbed dye capacity is raised 20.74 mg/g at C/C_o= 0.5 and 24.50 mg/g at C/C_o= 1.0.

In relation to the effect of the dye type, in general, the best column performance was obtained for the RB5 with SSBP-PA (Fig. 2 and Table III). For RB5, the total bed volume number was highest. It can be seen in Fig. 2 and Table III that, for all sorbent and dyes, the bed volume increase from 5 to 20 mL caused an increase in V_{eff}, q_t but q_m decreased. As consequence, the effluent volume, total mass of sorbed dye and maximum capacity of the column were highest for RB5 with SSBP-PA.

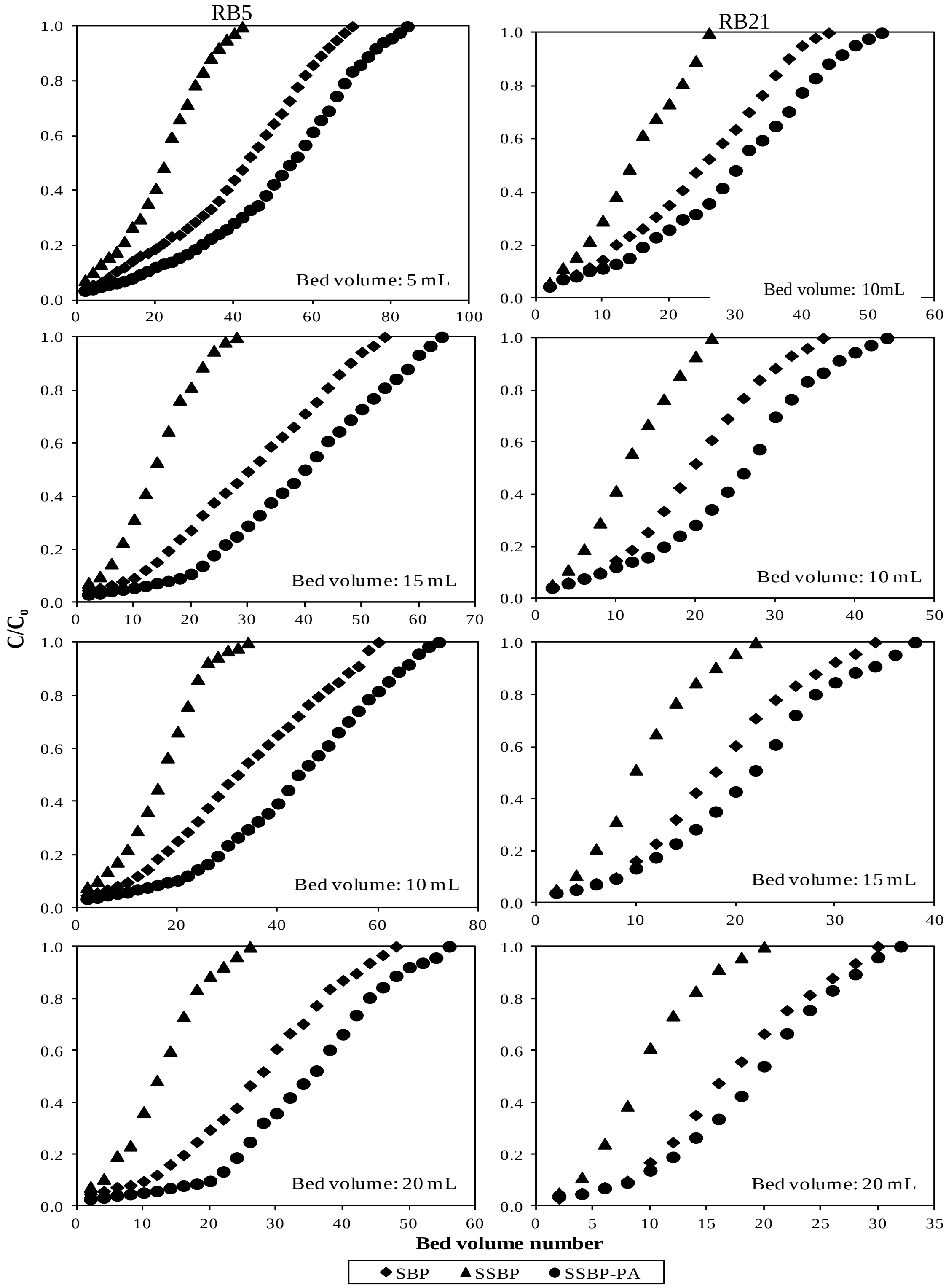

Fig. 2: The effects of the dye type and of bed height on the breakthrough curves (pH: 4.0, initial dye cons.: 250 mg/L, flow rate: 4 mL/min)

4. Conclusions

The results of continuous sorption process in the fixed column showed that the modified production of saponified sugar beet pulp with phosphoric acid (SSBP-PA) can be employed for removal of Reactive Black 5 (RB5) and Reactive Blue 21 (RB21) successfully. The effect of bed depth in performance of column was studied. Results showed that with increasing the bed depth, the dye uptake capacity of column decreases. The maximum capacity of column for SSBP-PA was found to be about 43.28 mg/g RB5 at C/C_o= 1.0 (bed volume: 5 mL, bed depth: 5.3 cm).

Table 3: The Operation Characteristics of Fixed Bed Columns

	Bed Volume (mL)	**q_t, mg**								
		C/C_o= 0.1			C/C_o= 0.5			C/C_o= 1.0		
		SBP	SSBP	SSBP-PA	SBP	SSBP	SSBP-PA	SBP	SSBP	SSBP-PA
RB5	5	11.6	4.6	21.0	40.8	20.8	46.6	48.3	24.9	61.5
	10	28.6	9.1	46.9	61.8	31.9	89.5	77.9	37.5	104.4
	15	36.0	12.7	68.3	88.1	37.4	121.7	107.0	40.1	151.1
	20	47.6	16.2	95.3	108.4	46.4	142.9	127.8	56.1	164.5
RB21	5	7.0	4.5	10.2	23.2	13.2	29.4	28.5	16.4	34.8
	10	18.6	9.2	18.6	39.3	20.2	52.7	45.8	25.8	59.0
	15	28.0	13.1	29.6	53.3	28.1	64.9	63.2	35.1	74.5
	20	37.5	14.2	39.4	66.5	32.9	77.6	79.3	41.7	87.8

	Bed Volume (mL)	**V_{eff}, mL**								
		C/C_o= 0.1			C/C_o= 0.5			C/C_o= 1.0		
		SBP	SSBP	SSBP-PA	SBP	SSBP	SSBP-PA	SBP	SSBP	SSBP-PA
RB5	5	50	20	85	115	115	137	380	240	430
	10	105	41	192	320	174	440	560	300	640
	15	155	59	296	470	200	600	900	570	1140
	20	232	66	470	548	252	710	1000	600	1160
RB21	5	35	20	45	125	70	160	230	120	260
	10	80	40	80	190	130	270	380	230	480
	15	120	60	135	270	150	330	540	330	570
	20	180	65	180	340	180	390	600	480	680

	Bed Volume (mL)	**q_m, mg/g**								
		C/C_o= 0.1			C/C_o= 0.5			C/C_o= 1.0		
		SBP	SSBP	SSBP-PA	SBP	SSBP	SSBP-PA	SBP	SSBP	SSBP-PA
RB5	5	9.86	3.45	14.80	34.57	15.74	32.85	40.94	18.89	43.28
	10	12.14	3.44	16.50	26.17	12.07	31.51	32.99	14.19	36.74
	15	10.16	3.20	16.03	24.90	9.44	28.58	30.22	10.11	35.47
	20	10.08	3.07	16.78	22.97	8.79	25.15	27.07	10.63	28.96
RB21	5	5.89	3.44	7.18	19.68	10.00	20.71	24.15	12.39	24.50
	10	7.87	3.47	6.56	16.63	7.64	18.56	19.42	9.76	20.76
	15	7.91	3.31	6.94	15.05	7.10	15.23	17.84	8.86	17.50
	20	7.94	2.70	6.93	14.08	6.22	13.66	16.79	7.90	15.46

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