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Basic Red 46 Removal from Aqueous Solutions by Using Sodium Hydroxide and Epichlorohydrin Modified Sugar Beet Pulp

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Abstract. In this study, the removal of Basic Red 46 (BR46) from aqueous solutions was investigated using sodium hydroxide and epichlorohydrin modified sugar beet pulp (SEMSBP) as sorbent. The sorption behavior of SEMSBP was examined through pH and equilibrium experiments. Sorption was pH dependent. The optimum pH was found to be 7.0±0.5. The experimental data were analyzed using the Langmuir, Freundlich and Dubinin-Radushkevich isotherm models. Equilibrium data could be fitted into Langmuir and Dubinin-Radushkevich isotherms. Maximum sorption capacity calculated from Langmuir isotherm is 0.447mmol/g (178 mg/g) at 25^{o}C. SEMSBP has the potential of being used as an efficient sorbent for removal BR46 in textile wastewaters.

Keywords: Sorption, Basic Red 46, sugar beet pulp, modification, epichlorohydrin

1. Introduction

Several dyes make their presence strikingly visible as they impart colour to the water bodies. Colour in water bodies effect aquatic diversity by blocking the passage of sunlight. Further, a colour in water bodies has an adverse aesthetic effect [1]. Sorption techniques employing solid sorbents are widely used to remove certain classes of chemical pollutants from waters, especially of those that are hardly destroyed in conventional wastewater treatment plants [2]. Activated carbon is the conventionally adopted sorbent for removing dyes from wastewaters. However, the high cost of activated carbon limits its use a sorbent [3]. This has impelled the search for cheaper substitutes like the solid wastes generated from agricultural industry.

The aim of this study was to investigate the potential of sodium hydroxide and epichlorohydrin modified sugar beet pulp (SEMSBP) as a sorbent in the removal of Basic Red 46 (BR46) from aqueous solutions.

2. Materials and Methods

2.1. Modification of Sorbent

Sugar beet pulp was obtained from Elazıg Sugar Factory of in Elazıg. Sugar beet pulp was cropped in a blender and sieved to retain the +16-30 mesh fraction. SEMSBP was prepared according to the modified methods reported at literature [4, 5]. Sugar beet pulp was base treated by stirring 100 g batches of sieved pulps in 2 L of 0.1 N NaOH. The slurry was stirred at 200 rpm for 1 h. The saponified pulps were rinsed with distilled water. This procedure was repeated five more times to ensure removal of base from saponified pulps .They were then dried overnight at 50 ^{o}C. The procedure of modification of saponified sugar beet pulp with epichlorohydrin is proposed in Fig. 1.

2.2. Preparation of Basic Red 46 Solution

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The structure of Basic Red 46 is seen in Fig. 2. Basic Red 46 (Name: Basic Red X-GRL; Color index name: Basic Red 46; Color index number: 110825; Chemical abstracts service number: 12221-69-1; Type:

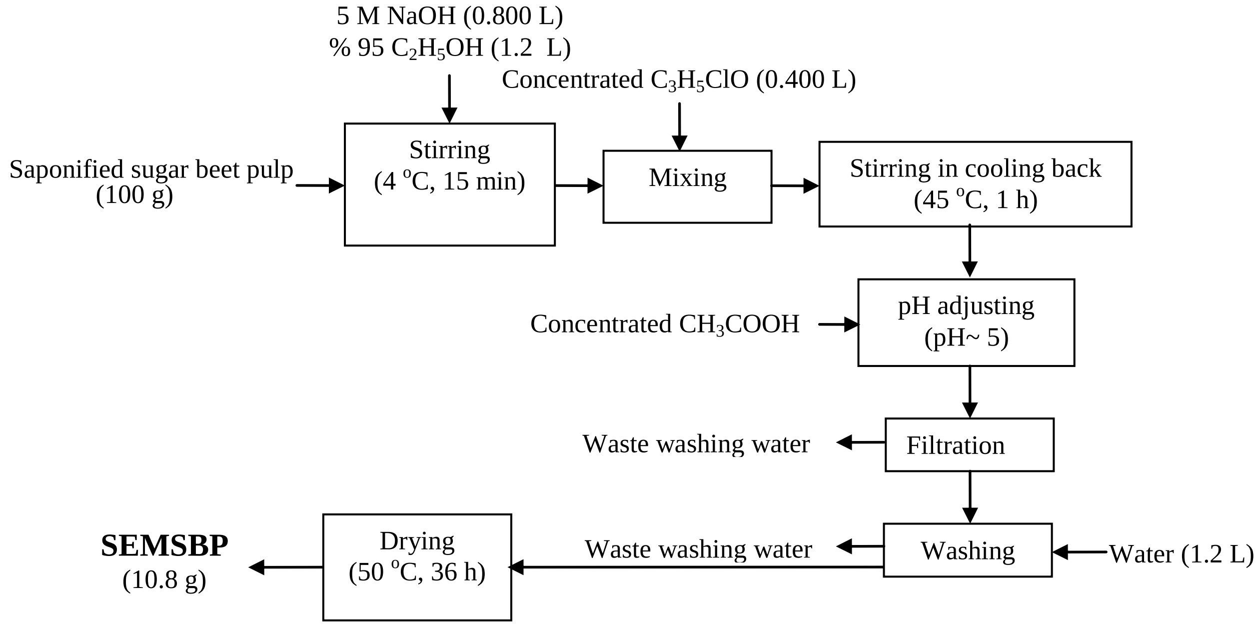


Fig. 1: The procedure of modification of saponified sugar beet pulp with epichlorohydrin

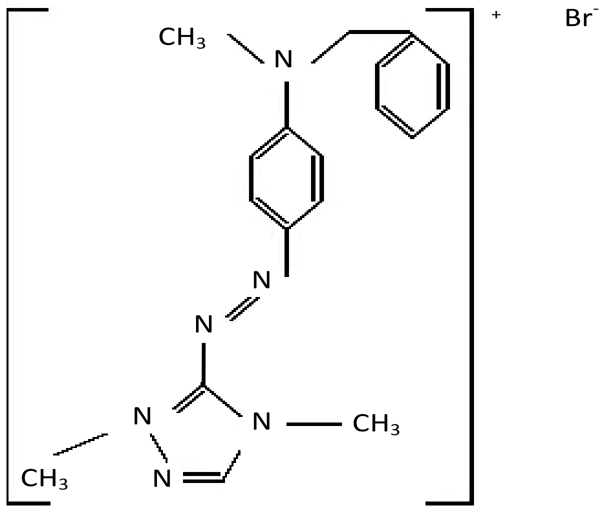


Fig. 2: The structure of Basic Red 46

Cationic; Class: Monoazo; Counter ion: Br; Molecular formula: $C_{18}H_{21}BrN_6$; Formula weight: 401.31 g/mol; λmax: 531 nm; Dye content: 71 %) was used without further purification. Standard BV7 solutions of 2.50 mmol/L were prepared as stock solutions and subsequently diluted when necessary.

2.3. Sorption Experiments and Calculation

All sorption experiments were carried out in a rotary shaker at 200 rpm (Selecta, Rotabit). The effect of sorbent dose and initial pH of dye solution on the sorption capacity of SEMSBP was investigated at 25 °C with 0.5 mmol/L of BR46 solutions which were adjusted a range of pH value 2-10 using dilute HCl or NaOH and agitated with 0.5, 1.0, 2.0, 5,0 and 10.0 g/ L of SEMSBP dose for 12 h. Sorption isotherm data were obtained at four different temperatures (25, 35, 45, 55 °C) by equilibrating various dye concentrations (0.10, 0.25, 0.50, 0.75, 1.00, 1.50 and 2.50 mmol/L) of BR46 with a fixed SEMSBP dose of 2.0 g/L for 360 min. After agitating for equilibrium or predetermined time intervals, samples were filtered through 200 mesh sieve and the filtrate was analyzed for residual dye concentration using a spectrophotometer (Shimadzu UV-1201) at 541 nm. pH was measured using pH meter (Mettler Delta 3000).

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:

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

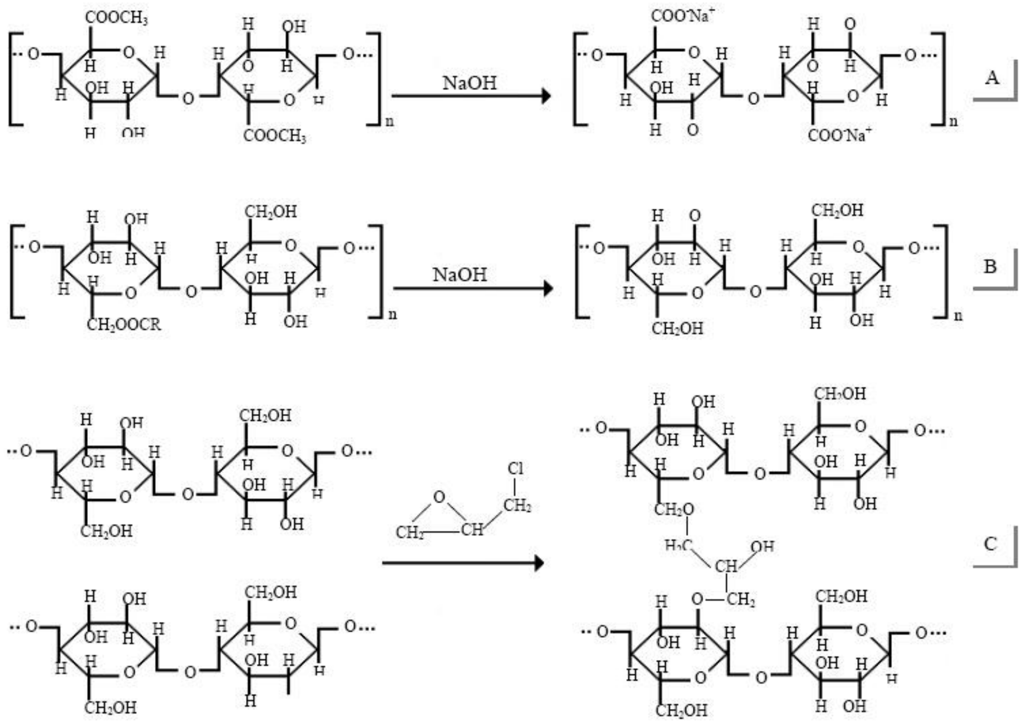
where C_o and C_t (mmol/L) are the initial and final BR46 concentrations, respectively, V (L) is the volume of BR46 solution and W (g) is the mass of SEMSBP. The amount of BR46 adsorbed was expressed as percentage of removal and was calculated using the equation:

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

where R is the percentage of BR46 removal.

3. Results and Discussions

The chemical modification of sugar beet pulp can be schematically express by equations (A-B: saponification of sugar beet pulp with sodium hydroxide, C: modification of saponified sugar beet pulp with epichlorohydrin):



Some characteristics of SEMSBP were determined such as bulk density (0.422 g/mL), mater soluble in water (0.56%), mater soluble in HCl (3.02 %), ash content (2.74 %), mechanical moisture content (7.67 %), cation exchange capacity (1.19 meq/g), water retention capacity (1.03 g/g) and swelling capacity (0.79 mL/g).

3.1. Effect of Sorbent Dose and Initial pH

The effect**s** of initial pH and sorbent dose on sorption of BR46 are shown in Fig. 3. First of all, the influences of sorbent dose and initial pH were investigated. The initial pH of BR46 solutions was researched over a range from 2 to 10. As elucidated in Fig. 3, the percentage of BR46 sorbed increased as the initial pH was increased from pH 2 to 10. But beyond pH 8, the colour of the BR46 solution is decomposed spontaneously. For this reason, pH 7±0.5was selected for sorption of BR46.

Also, the effect of sorbent dose on removal rations of BR46 are shown in Fig. 3.When the sorbent dose was increased from 0.5 t0 2 g/L at pH 7.1, the percentage of BR46 sorbed increased from 46.67 to 83.96 %.

Above 5 g/L of sorbent dose, the sorption percentages of BR46 were reached about 100 % for beyond pH 7. So, the sorbent dose of 2.0 g/L was chosen for equilibrium experiments.

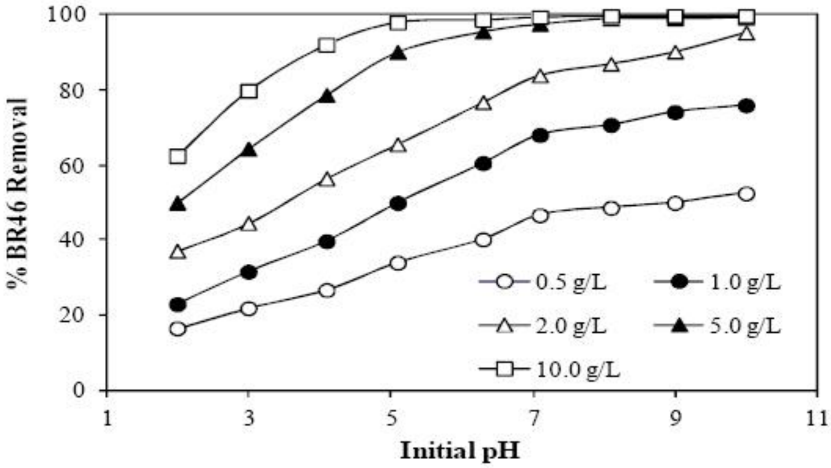


Fig. 3: The effect of initial pH and sorbent dose on sorption of BR46 (Initial dye concentration: 0.5 mmol/L, temperature: 25 ^oC, time: 12 h, agitation speed: 200 rpm).

3.2. Sorption Isotherms

The sorption isotherms indicate how the sorbate molecules distribute between the liquid phase and the solid phase when the sorption process reaches an equilibrium state. In this study, Langmuir, Freundlich and Dubinin-Radushkevich isotherms was used. The linear forms of isotherms are shown in Table I.

The linear plots of Ce/qe versus Ce show that the sorption obeys Langmuir isotherm model (Eq. 3). The Langmuir isotherm theory is based on assumption of a structurally homogeneous sorbent and monolayer coverage [6]. That is, once a molecule occupies a site, no further sorption can take place at that site. The essential characteristics of Langmuir isotherm can be expressed by a dimensionless constant called equilibrium parameter, R_L and R_L indicates the type of the isotherm to be either unfavorable (R_L>1), linear (R_L=1), favorable (0<R_L<1) or irreversible (R_L=0).

Table 1: The Linear Forms and Other Equations of Langmuir, Freundlich and Dubinin-Radushkevich 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)	[6]	**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) **E_o:** Energy for Dubinin-Radushkevich isotherm (kJ/mol) **ε:** Dubinin-Radushkevich isotherm constant (J/mol) **β:** Dubinin-Radushkevich isotherm constant (mol^2/J^2)
Freundlich	$\ln[q_e] = \ln[k_F] + \frac{1}{n_F}\ln[C_e]$ (5)	[7]	
Dubinin-Radushkevich	$\ln[q_e] = \ln[q_{DR\,m}] - \beta.\varepsilon^2$ (6) $\varepsilon = \left[RT\ln\left(\frac{1}{C_e}+1\right)\right]$ (7) $E_o = \frac{1}{\sqrt{2\beta}}$ (8)	[8]	

The Freundlich isotherm model assume that the sorption takes place on heterogeneous surfaces and sorption capacity depend on concentration of sorbate at equilibrium [7]. Dubinin-Radushkevich isotherm is generally applied to express the sorption mechanism with a Gaussian energy distribution onto a heterogeneous surface [8]. The model has often successfully fitted high solute activities and the intermediate range of concentrations data well. The approach was usually applied to distinguish the physical and chemical sorption of ions with its mean free energy, E_o per molecule of sorbate [9].

Table II has shown the results of isotherms analyses calculated for sorption of BR46 dye on SEMSBP. Equilibrium data could be fitted into Langmuir and Dubinin-Radushkevich isotherms. Maximum sorption capacities calculated from Langmuir isotherm at 25 and 55 ^{o}C are 0.447 and 0.495 mmol/g, respectively.

Table 2: The Parameters of Langmuir, Freundlich and Dubinin-Radushkevich Isotherms

		25 ℃	**35 ℃**	**45 ℃**	**55 ℃**
Langmuir	R^2	0.998	0.998	0.999	0.999
	q_m, mmol/g	0.447	0.458	0.478	0.495
	b, L/mmol	15.108	18.104	24.244	28.795
	R_L	0.026	0.022	0.016	0.014
Freundlich	R^2	0.955	0.947	0.944	0.939
	n_F, g/L	2.824	2.830	2.985	3.019
	k_F, mmol/g	0.467	0.498	0.539	0.576
Dubinin-Radushkevich	R^2	0.982	0.988	0.991	0.993
	β, $(mmol/J)^2$	0.011	0.010	0.008	0.007
	q_{DRm}, mmol/g	0.391	0.413	0.438	0.462
	E, kJ/mol	6.901	7.217	7.956	8.452

4. Conclusion

Sodium hydroxide and epichlorohydrin modified sugar beet pulp is much effective for sorption of Basic Red 46. Therefore, the sorbent is expected to be economically feasible for removal of basic dyes from aqueous solutions.

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