RESEARCH ARTICLE

# Removal of Basic Yellow 51 Dye by Using Ion Exchange Resin Obtained by Modification of Byproduct Sugar Beet Pulp

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**Abstract** The removal of dyestuffs, which are an important pollutant group in textile wastewater, is an important environmental problem. Various chemical and physicochemical methods are used in the purification of these wastewaters. Recently, it is known that a wide variety of agricultural materials and their modified products have been investigated for dye removal using the adsorption process, which is a promising removal method. In this study, the removal of Basic Yellow 51 dyestuff from aqueous solutions of sugar beet pulp, first activated by saponification with NaOH solution and then modified by heating with citric acid, was investigated. For this purpose, the effects of parameters such as solution pH, sorbent dose, initial concentration, contact time and temperature on the sorption of Basic Yellow 51 dye to modified sugar beet pulp were investigated. As a result, it was found that the functional groups of pectin and cellulose substances in sugar beet pulp, which are effective in sorption, were activated and their number increased, thereby increasing the dye removal efficiency. It was found that sorption efficiency increased with increasing contact time and temperature and decreased with increasing initial concentration. It was determined that the sorption equilibrium data fit the Langmuir isotherm better and that the sorption process was endothermic and spontaneous. The $q_e$ value was obtained from the Langmuir isotherm as approximately 200 mg/g. As a final result, it has been demonstrated that the modified product of sugar beet pulp can be used effectively in removing basic dyes from the aquatic environment.

**Keywords** Sugar beet pulp · Basic yellow 51 · Adsorption · Ion exchange

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## Introduction

In the processes applied in the textile industries, large amounts of water and chemicals are consumed and various wastewaters with various properties and in large quantities are formed. Dyestuffs constitute a significant part of the pollutants in textile wastewater. The carcinogenicity of benzidine, from which many dyestuffs are made, and some aromatics raises concerns (Chung 2016). It is stated that azo and nitro compounds are reduced in living organisms to form amines with toxic properties (Grirrane et al. 2010; Kurtan et al. 2016). It is stated that carcinogenic amines are formed from these substances in anaerobic conditions in the environment (Chung and Stevens 1993). It is stated that anthraquinone-type dyes containing combined aromatic rings are very difficult to degrade by natural cycles in nature. In addition, some disperse-type dyes were found to accumulate in living organisms (Aldalbahi et al. 2021).

The structure of the dyes is also important in the purification technique. Dyes are generally classified structurally as cationic, anionic and non-ionic (or disperse). Anionic dyes are further subdivided into direct, acid and reactive dyes (Kawabata and Taylor 2007). Brightly colored, water-soluble acid and reactive dyes are resistant to conventional treatment (El-Gohary and Tawfik 2009). Aerobic treatment systems based on biological treatment of domestic wastewater are ineffective in the treatment of these dyestuffs (Singh and Arora 2011).

In recent years, importance has been given to the use of adsorption methods in the removal of dyestuffs from wastewater, and intensive research has been carried out on the use of many adsorbents in this area. In addition to substances such as various clays, fly ash, peat charcoal and activated carbon, a wide variety of agricultural products such as orange peel, apple pulp, banana peel, cotton scraps, tree bark, bagasse, corn cob, corn husk, wheat straw, barley husk and duckweed residues and biomass have been investigated in this area. In addition, the adsorption of dye wastewater by some microorganisms has been intensively investigated. These cited studies are summarized in some articles (Arslanoğlu et al. 2020a; Waranusantigul et al. 2003; Robinson et al. 2001). The most effective material among them is activated carbon. Since commercial activated carbon is very expensive, carbonized materials obtained from a wide variety of materials such as coconut shell, walnut shell, rice shell, saw bran of the coconut tree has been investigated in dye adsorption from the aquatic environment.

Ion exchangers are also being investigated in the treatment of wastewater contaminated with paint residues, in the removal of dyes that form ionic species when dissolved in water, such as acidic or basic dyes. Due to the high cost of polymer-based ion exchangers, it is found in the literature that natural ion exchangers such as clays and zeolites, minerals such as alunite and cellulosic-based substances made from agricultural residues are investigated in removing dye from water (Orthman et al. 2003; Arslanoğlu 2021; Sezer et al. 2017; Gücek et al. 2005; Crini 2006; Forgacs et al. 2004; Gong et al. 2006, 2007; Seyrek et al. 2020; Baskaralingam et al. 2006). Zeolites have also been investigated in removing reactive dyes.

Sugar beet pulp, which is the pulp remaining from the extraction of sugar in factories where sugar is produced from sugar beet, mainly contains pectin and cellulose, and a lesser amount of lignin. It is now considered the main animal feed. It is stated that the pectin in its content is a polygalacturonic acid and has ion exchange properties (Dronnet et al. 1996; Kartel et al. 1999) and this substance is being investigated in the removal of heavy metals (Sharma and Foster 1994; Dronnet et al. 1997; Reddad et al. 2002). By esterification of cellulose-containing materials with polyacids, carboxyl groups are introduced into the cellulose molecule, giving it the ability to exchange ions. It is known that these substances are investigated in the removal of heavy metals from water (Wartelle and Marshall 2000). It was reported that the copper binding capacity of sugar beet pulp increased after esterification with citric acid (Altundogan et al. 2007).

In this study, various modified products were obtained from sugar beet pulp by saponifying and then esterifying with citric acid, and BY 51 removal was investigated by using these modified products with some characteristics. The saponification process and subsequent esterification processes applied to sugar beet pulp stabilize the sugar beet pulp by improving its swelling and water retention properties. Another important point to be noted is that esterification processes with citric acid increase the cation exchange ability of sugar beet pulp. In general, BY 51 removal increases as the modified material dose, contact time and temperature are increased.

As a final result, it can be stated that sugar beet pulp, which is a sugar factory residue, can be used for further treatment of a dyestuff such as BY 51 by modifying it under simple conditions using harmless and cheap chemicals.

In this study, a research was conducted on the use of sugar beet pulp, which is obtained as a by-product in sugar factories, for the removal of basic dyes from aqueous media after esterification with citric acid. For this purpose, systematic studies were carried out with the selected Basic Yellow 51 dyestuff, and the effects of the parameters affecting the removal were investigated, calculations related to isotherms were made and thermodynamic parameters were also determined.

## Materials and Method

Citric acid $((CH_2CO_2H)_2)$, Hydrochloric acid (HCl), Sodium hydroxide (NaOH), Basic Yellow 51 $(C_{20}H_{25}N_3O_4S$ (403.5 g/gmol)) and other chemicals used in the experiments were of analytical purity and were obtained from Sigma-aldrich and Merck companies.

### Supply of Sugar Beet Pulp and Preparation for Experiments

The sugar beet pulp used in the experiments was procured from the Elazig Sugar Factory in the 2005. Dried sugar beet pulp was ground in 50 g batches with the help of a blender and sieved through a series of sieves. It was decided to use the fraction with grain size of -30 + 50 mesh

(0.3 < x < 0.6 mm) in the study. The material prepared in this way was dried in an oven at 50 °C for 24 h.

## Modification of Sugar Beet Pulp

The modification of sugar beet pulp was carried out in the first step by interacting with NaOH solution in order to remove the small molecule substances by solubilization, on the other hand, to liberate the esterified carboxyl groups on the side groups of the pectin chain by hydrolyzing, and on the other hand, to liberate the esterified primary alcohol groups in the cellulose molecule.

The pulp reacted with the NaOH solution was converted to citric acid ester in the second step by heating after being treated with the citric acid solution. Sugar beet pulp samples with -30 + 50 mesh (0.3 < x < 0.6 mm) grain size were first treated with NaOH solution and saponification process was applied. For this purpose, 100 g −16 + 30 mesh fraction of sugar beet pulp sample was mixed in 5 L PET jars with 2 L of NaOH solution at 0.1 N concentration with the help of a mechanical mixer at 200 rpm for 1 h. After this process, the sugar beet pulp was separated from the liquid. The liquid portion was discarded and some distilled water was passed over the solid portion. Then, this material was mixed with the help of a mechanical mixer at 200 rpm for 30 min with the addition of 2 L of distilled water. The liquid portion was removed by filtration. This washing process was repeated by following the pH of the washing water until there was no pH change. The washing process was terminated when the final wash pH was around 8. The solid product obtained from the last wash was spread in front of a blower and dehumidified by blowing air. Then it was dried in an oven at 50 °C for 24 h. The saponified sugar beet pulp obtained under the above-mentioned conditions was subjected to esterification with citric acid solution. For this purpose, 25 g of saponified samples were mixed with 0.6 M citric acid solution at a rate of 7 times their weight in a glass tray. After a while, the solid material absorbed the solution and increased in volume. The mixture was kept in an oven at 50 °C for 24 h. Its weight was determined. Then, it was heated in an oven at 120 °C for 90 min to remove the water formed during esterification with the water in the body. At this stage, the weight was determined. The product obtained was rinsed with distilled water at a rate of 40 times its weight for 60 min until no citric acid remained in the washing water, and the water was removed. The presence of citric acid in the washing water was determined by adding $Pb(NO)_3$ solution to the washing water sample and determining whether there was precipitation. When no precipitation was observed, the washing process was terminated. The final solid product was dried in an oven at 50 °C for 24 h, its weight was determined and stored in closed containers for use in experiments (Arslanoglu and Tumen 2012).

## Preparation of Basic Yellow 51 Dyestuff Solutions

In the study, Basic Yellow 51 dyestuff with closed formula $C_{20}H_{25}N_3O_4S$ (403.5 g/gmol) was used. The clear formula of Basic Yellow 51 is shown in Fig. S1. A stock solution containing 1000 mg/L Basic Yellow 51 was prepared. Working solutions were prepared by appropriate dilution of this stock solution.

## Basic Yellow 51 Dyestuff Removal Studies

All experiments were carried out in 250 ml capped flasks with the help of a Zcheng 200D shaking incubator with adjustable shaking speed and temperature. The initial pH of the prepared dye-containing solutions was measured. After adding the sorbent samples to the solutions taken into the flasks, the mixtures were shaken at a speed of 200 rpm at the prescribed time and temperatures and then taken from the incubator, solid–liquid separation was performed by filtering through a filter paper, and their pH was measured. The dyestuff (Basic Yellow 51) analysis was performed spectrophotometrically in the solutions.

In the preliminary study, raw sugar beet pulp (SBP), NaOH solution activated (saponified) sugar beet pulp (SSBP), citric acid esterified sugar beet pulp (SSBPSAE) samples after being reacted with NaOH solution were used in 100 g of sorbent dose. It was mixed with solutions containing mg/L dye and shaken for 24 h. Basic Yellow 51 analyzes were performed on the samples taken from the solution after filtration.

Then, 1 g/L SSBPSAE was mixed into the dye solutions of 100 mg/L concentration at different initial $pH_i$ and shaken for 24 h. Basic Yellow 51 determinations were made in the filtrates. With these experiments, the effect of initial pH on dye removal was investigated. In order to determine the effect of the amount of SSBPSAE on dye removal, 0.5–10.0 g/L SSBPSAE was added to the dye solutions at a concentration of 100 mg/L prepared at natural pH and agitation was performed for 24 h. With these experiments, the effect of the dose (sorbent amount) was examined. The effects of temperature and time on the removal of Basic Yellow 51 from aqueous solutions were investigated by comparing the results obtained in experiments performed at 20-50ºC temperatures with 50–250 mg/L concentrations of Basic Yellow 51 solutions using SSBPSAE at a dose of 1 g/L. In this study, in which the equilibrium time was determined, the results obtained with Basic Yellow 51 solutions at different initial concentrations and the time selected as the equilibrium time were applied to the Langmuir and Freundlich

isotherms and thermodynamic equations. Adsorption capacity, adsorption enthalpy, free energy and entropy evaluations were made in the SBPSAE-dye solution system within the limits of the studied parameters.

## Analysis of Solutions

Basic Yellow 51 concentrations in solutions were calculated based on absorbance measurements at 425 nm using a Shimadzu brand (UV 1201 Model) visible region spectrophotometer. In order to convert the measurements into healthy results, the absorbance values obtained in the appropriate blind trials were taken into account. After the solution concentrations were determined after the sorption process, the Basic Yellow 51 removal efficiency and the amount of Basic Yellow 51 retained per unit sorbent amount were calculated using the following equations.

$$Removal,\% = (C_o - C_s)\frac{100}{C_o} \qquad (1)$$

$$q = \frac{(C_o - C_s)V}{m} \qquad (2)$$

In these equations, $C_o$ and $C_s$ represent the initial and final Basic Yellow 51 concentration of the solution (mg/L), q the Basic Yellow 51 amount adsorbed by the unit mass of the adsorbent (mg/g), V the volume of the solution (l), and m the mass of the sorbent used (g) shows.

pH measurements in solutions were carried out using Metler Delta 350 pH meter. The pH adjustments in the related experiments were made using dilute HCl and NaOH solutions in the presence of the mentioned pH meter.

In order to see the reproducibility of the color removal results, it was determined that the results were within $\pm 5\%$ by performing 10 experiments with the same conditions for each material and evaluating the results that were closer to each other. All characterization tests and decolorization experiments in this study were performed by repeating twice. Because of the above finding, a third experiment was performed when the two results differed from each other by more than 5%. The average of the two experimental results was evaluated.

## Results and Discussion

In the preliminary study, using raw sugar beet pulp (SBP), saponified sugar beet pulp (SSBP) by reacting with NaOH solution, and sugar beet pulp (SBPSAE) esterified with citric acid after saponification, the amount of these substances at a dose of 1 g/L, in a pH 4.8 buffer medium Basic Yellow 51 removal efficiencies after 24 h from Basic

Yellow 51 solution at 100 mg/L concentration prepared (0.03 M acetic acid-0.07 M sodium acetate) are given in Table S1.

Comparing the removal efficiencies in Table S1, it can be stated that the interaction of SSBP with NaOH solution did not increase the sorption efficiency much, but esterification with citric acid increased the sorption efficiency of SSBP-SAE more than twice.

It can be said that NaOH hydrolyzes the ester groups in pectin and cellulose molecules to reveal acid groups (as carboxylates) in pectin (Eq. 3) and free primary alcohol groups in cellulose (Eq. 4). It can be stated that extra carboxyl groups are introduced into the molecule (Eq. 5) by subjecting the SBP activated with NaOH solution to esterification with citric acid. Thus, it can be explained that the substances with increased anionic active groups keep the dyestuffs forming cation groups more effectively. These explanations can be better understood by examining the following equations (Eqs. 3, 4 and 5) (Arslanoglu and Tumen 2012).

**Table 1** Some properties of the grape pulp and modified product used in experiments

| Property | SBP | SSBP | SSBPSAE |
|---|---|---|---|
| Bulk density (g/cm³) | 0.301 | 0.326 | 0.359 |
| pH[a] | 5.12 | 8.13 | 3.97 |
| Solubility in water (%)[b] | 4.42 | 3.07 | 0.96 |
| Solubility in acid (%)[c] | 7.99 | 5.45 | 3.57 |
| Ash (at 900 °C) (%)[d] | 3.65 | 5.47 | 4.68 |
| Moisture (%)[e] | 6.12 | 7.76 | 6.83 |
| COD (mg-$O_2$/L)[a] | 177.0 | 48.1 | 75.3 |
| CEC (meq/g)[f] | 0.93 | 1.46 | 3.44 |
| Water retention capacity (g/g)[b] | 7.75 | 6.69 | 4.92 |
| Swelling capacity (ml/g)[g] | 6.55 | 4.31 | 3.89 |
| Methylene blue adsorption (meq/g)[h] | 200.8 | 238.7 | 311.5 |

[a]Measurements made on the liquid obtained by balancing 1 g of substance with 100 ml of water for 24 h

[b]Measurement of solid matter obtained by equilibrating 1 g of substance with 100 ml of water for 24 h

[c]Measurement of solid substance obtained by equilibrating 1 g of substance with 100 ml of 0.25 M HCl solution for 24 h
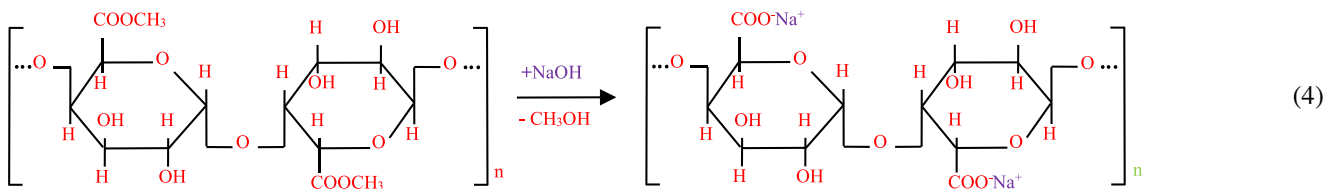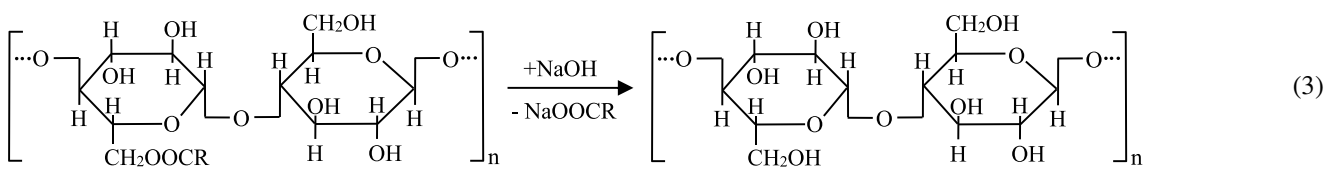
[d]The result of ash at 900 °C

[e]Constant weighing result at 105 °C

[f]The cation exchange capacity (CEC) was determined by the back titration method based on the saturation of samples with a specific standard acid solution (ASTM 1974)

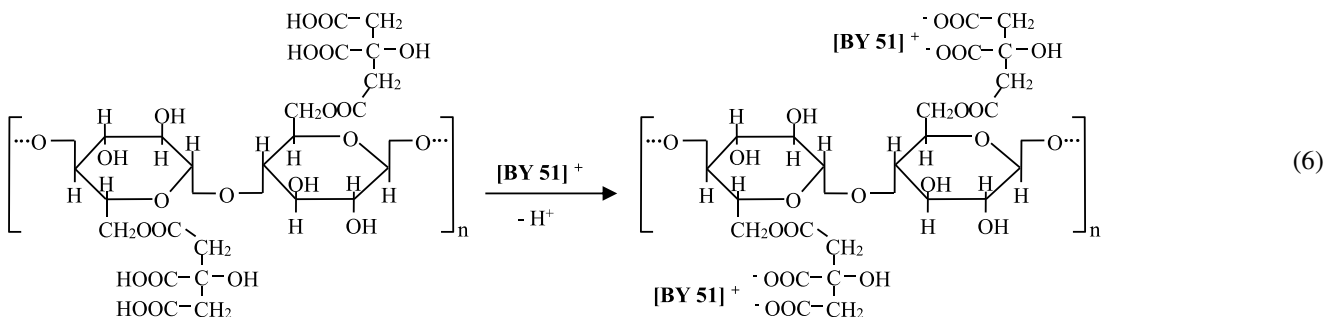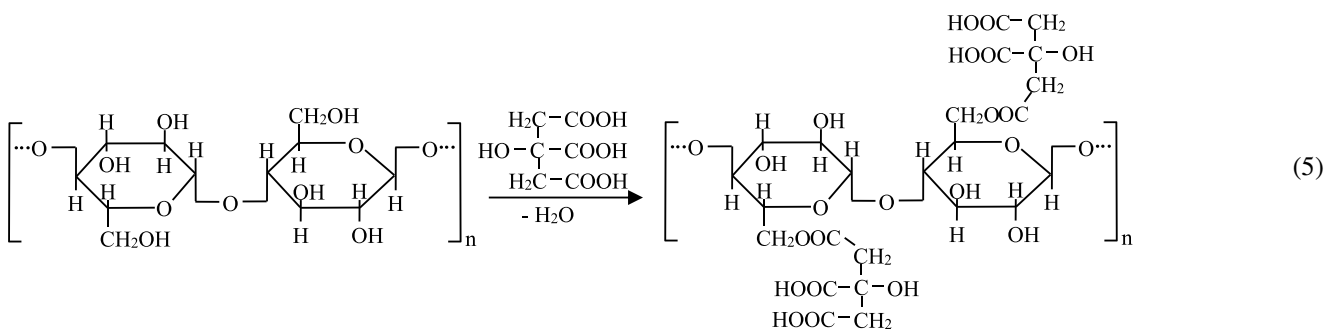[g]Swelling caused by keeping 1 g of substance in 0.1 N $NaNO_3$ solution for 24 h

[h]The result of the analysis made in the solution by shaking 1 g of the substance with 200 ml of 500 mg/L methylene blue solution for 24 h with pH 4.8 buffer solution

$$\text{(cellulose structure)} \xrightarrow[- \text{NaOOCR}]{+\text{NaOH}} \text{(cellulose structure)} \qquad (3)$$

$$\text{(pectin structure with COOCH}_3\text{)} \xrightarrow[- \text{CH}_3\text{OH}]{+\text{NaOH}} \text{(structure with COO}^-\text{Na}^+\text{)} \qquad (4)$$

Sugar beet pulp consists mainly of pectin, cellulose and hemicellulose, while citric acid is a tricarboxylic acid. Some properties of sugar beet pulp and its modified products were determined in a previous study (Table 1) (Arslanoğlu and Tumen 2012). It can be stated that the retention of BY-51 in aqueous solutions by this cellulose and pectin-based material is due to the negatively charged active centers in the structure. Free and esterified alcoholic and acidic functional groups and oxygen bridges in the structure of the substances in sugar beet pulp constitute an active center for the retention of cations. In the studies, it was determined that the cation exchange capacity of cellulosic materials modified with polyacids such as citric acid increased (Altundogan et al. 2007).

It has been stated that ion exchange is also effective as a mechanism in the removal of BY 51 from aqueous solutions by using modified sorbent based on sugar beet pulp (Arslanoğlu and Tumen 2012). The esterification of the cellulose in the lemon peel and inner fibers with citric acid and the binding of this modified product to the BY 51 dyestuff can be expressed by the hypothetical reaction equation in Eq. 6. The introduction of carboxyl groups into the cellulose molecule with the modification process and thus the enrichment of the material with acidic groups can explain the removal of BY 51, a cationic dyestuff, by the modified sorbent.

Considering these results, citric acid esterified sugar beet pulp (SSBPSAE) was chosen as the sorption material

$$\text{(cellulose)} \xrightarrow[- \text{H}_2\text{O}]{\begin{array}{c}\text{H}_2\text{C}-\text{COOH} \\ \text{HO}-\text{C}-\text{COOH} \\ \text{H}_2\text{C}-\text{COOH}\end{array}} \text{(citric acid esterified cellulose)} \qquad (5)$$

$$\text{(SSBPSAE)} \xrightarrow[- \text{H}^+]{[\text{BY 51}]^+} \text{(BY 51 bound product)} \qquad (6)$$

for Basic Yellow 51 removal work and this material was used in the following experiments. The results of the studies performed at different initial pHs are shown in Fig. S2. In order to make a sound evaluation, the final pH values obtained in the experiments are given together in Fig. S2. By increasing the initial pH of the solution, the pHs measured in the solution obtained after the experiment increase for values between 2 and 4 initial pHs. However, for values with an initial pH greater than 5, the final pH$_f$ values are lower than the adjusted initial pH$_i$. As can be seen from Eq. 5, the SSBPSAE used is acidic. For this reason, SSBPSAE removes the basicity of the solution it contacts and brings it to the acidic area. Even the initial pH of the solution was 10, and the final pH was measured around 5. Basic Yellow 51 removal also follows a trace. Considering that the initial pH of the solution containing 100 mg/L Basic Yellow 51, which was prepared without adding any acid–base, is around 7.1, and it is taken into account that the removal values obtained above this pH do not increase much, it can be used at higher pHs. The study does not appear to be of any practical use. For example, approximately 94% removal is obtained in the solution at natural pH, while the removal in the solution with the initial pH adjusted to 9 or 10 is approximately 98–99%. For this reason, in the next part of the study, solutions with pH around 7.1 were studied without adding acid–base (Yaras and Arslanoğlu 2018).

The pH$_{ZPC}$ value is the net surface neutrality of the adsorbent. It is an important feature that determines the pH when it has a pH value. In our study, the pH$_{ZPC}$ value of SSBPSAE was found to be 5.93 (approximately 6.0). Above pH 7, especially pH 6–7 seems to be much more suitable for BY 51 removal. It is expected that pH values above 5.93, which is the pHzpc value, are more suitable for BY 51 removal (Şenol 2022). Therefore, the pHzpc value also confirms the optimal pH found. With increasing pH, negative loading of the adsorbent surface above the pHzpc value becomes more effective for the positively charged cationic BY 51 adsorption. As a result, it can be said that the optimum pH for BY 51 adsorption in the fixed bed column using ion exchange resin prepared from sugar beet pulp is around 6.

The effect of the SSBPSAE dose on the removal of Basic Yellow 51 from the solution at a concentration of 100 mg/L is given in Fig. S3. As can be seen from the figure, and as expected, the percentage of Basic Yellow 51 removal increases as the SSBPSAE dose is increased. For example, when using SSBPSAE at a dose of 1 g/L, approximately 94% removal is achieved after 24 h. Increasing the adsorbent dose to 5 g/L results in approximately 99% removal, and increasing the dose to 10 g/L results in 99.90% dye removal. In other words, no significant increase in removal was observed by increasing the adsorbent dose above a certain dose. For this reason, 1 g/L was chosen as the SSBPSAE dose and subsequent experiments were performed with this sorbent dose.

The effects of concentration, temperature and time on the sorption of Basic Yellow 51 were investigated by conducting experiments with solutions containing Basic Yellow 51 at initial concentrations of 50–250 mg/L at temperatures of 20–50 °C and for periods varying between 15–1440 min. The results are given in Fig. S4.

When Fig. S4 is examined in general, at the four temperatures studied, the removal increases with the increase of the time and reaches a plateau. However, the time to reach equilibrium is shortened at higher temperatures. For example, at 20 °C, the time to reach equilibrium was observed to be approximately 360 min at all five different initial concentrations studied. In the experiments carried out at 30 °C, this time was approximately 240 min, and in the experiments carried out at 40 and 50 °C, the time to reach equilibrium was observed to be approximately 120 min. When the relevant values are compared with each other, it can be stated that the temperature also affects the Basic Yellow 51 removal positively (Arslanoğlu et al. 2021).

The adsorption isotherm was the relationship curve between the adsorption capacity of the adsorbent at constant temperature and the concentration of the adsorbate in the equilibrium state, which usually provided information about the adsorption mechanism and surface properties (Arslanoğlu et al. 2021).

The Langmuir model assumes that under the premise that there is no interaction between the adsorbed particles, the energy of the adsorption center of each particle is the same, they are evenly distributed on the surface of the adsorbent, and the adsorption process is monolayer adsorption. The model expression is shown below (Arslanoğlu et al. 2021; Yaras and Arslanoğlu 2018).

$$\frac{C_e}{q_e} = \frac{1}{q_{max}b} + \frac{C_e}{q_{max}} \tag{7}$$

where $C_e$ (mg/L) is the equilibrium adsorption concentration, $q_e$ (mg/g) is the equilibrium adsorption capacity, $q_{max}$ (mg/g) is the maximum adsorption capacity of the adsorbent, and $b$ (l /mg) is the adsorption equilibrium constant related to the affinity of binding sites.

The Freundlich model assumes that the heterogeneous adsorption surface has different adsorption energies. This model was shown in the following equation.

$$x/m - K_f C_e^{1/n} \tag{8}$$

where $K_F$ (l/g) is the Freundlich adsorption equilibrium constant, which indicates the adsorption capacity and represents the strength of the adsorptive bond, and n is the heterogeneity factor, which represents the distribution.

As expected from examination of the same figure, it can be seen that the % of Basic Yellow 51 removal decreases with the same dose as the initial concentration is increased.
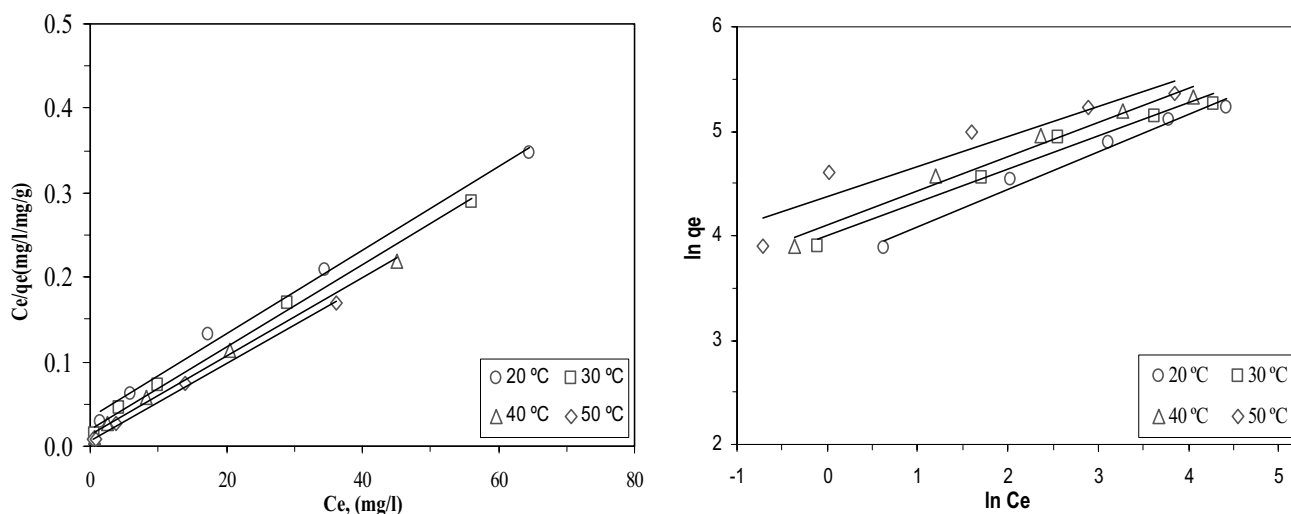
**Fig. 1** Langmuir and Freundlich isotherm (Experimental conditions: Initial conc.: 50; 100; 150; 200; 250 mg/L; Sorbent dose: 1 g/L; Shaking time: 6 h; Shaking speed: 200 rpm)

This also applies to all temperatures. The isotherms created by considering the values in 360 min selected as the equilibration time are given in Fig. 1. The constants and regression coefficients obtained from the Langmuir and Freundlich isotherms are shown in Table S2.

When the non-linear isotherm (Fig. S5) is examined, it can be said that the Basic Yellow 51 sorption of SSBPSAE reached a saturation under operating conditions. From its isotherm shape, it can be stated that it is an L-type isotherm. The results of applying the equilibrium data to the Freundlich and Langmuir isotherms show that the Langmuir isotherm is more suitable for this system within the operating conditions. Calculations (Langmuir constant $q_{max}$) have shown that the sorption capacity of Basic Yellow 51 of SSBPSAE under operating conditions is 200–222 mg/g. Using the obtained Langmuir constant (b), the dimensionless r constant values were found to be between 0.007 and 0.118 (Table S3). The r values between 0 and 1 showed that the sorption was favorable (Altundoğan et al. 2007).

$$r = 1/(1 + bC_0) \tag{9}$$

$$\frac{m}{V} = \frac{C_0 - C_e}{\frac{q_{max}bC_e}{1+bC_e}} \tag{10}$$

Calculated dose values are shown in Table S4. Accordingly, a dose of approximately 4 g/L SSBPSAE is needed to achieve 99% removal from the solution at 20℃ containing, for example, Basic Yellow 51 at a concentration of 100 mg/L. The dose that can remove with the same efficiency from the solution at 50℃ at the same concentration has been calculated as approximately 1.2 g/L. This explains

the effective role of temperature in removing Basic Yellow 51.

$$\ln b = \ln b' - \Delta H°/RT \tag{11}$$

$$\Delta G° = -RT \ln b \tag{12}$$

$$\ln b = -\frac{\Delta H°}{RT} + \frac{\Delta S°}{R} \tag{13}$$

The thermodynamic parameters calculated on the basis of the b values calculated (Fig. S6) from the Langmuir isotherm are shown in Table S5. Accordingly, the positive enthalpy value ($\Delta H° = 35.785$ kJ/mol) indicates that the Basic Yellow 51 removal process of SSBPSAE from aqueous solutions is endothermic. The negative free energy change ($\Delta G° = -5.791$ kJ/mol) indicates that this sorption process is spontaneous, that is, it will occur spontaneously. Small positive entropy change ($\Delta S° = 0.142$ kJ/mol.K) may be caused by the increase in irregularity at the solution sorbent interface and the changes that may occur on the adsorbent surface during sorption (Arslanoğlu et al. 2021; Yaras and Arslanoğlu 2018).

From the application of the results of the experiments performed at different temperatures for solutions with an initial concentration of 50–250 mg/L to the kinetic models, it was determined that the most suitable model was the pseudo second-order model. This is seen in Table S6, where the $q_c$ values calculated from the pseudo second-order model and the experimentally calculated $q_e$ values are quite close to each other (Altundoğan et al. 2007).

Adsorption kinetics can provide information about the adsorption rate and can be further used to analyse the

reaction mechanism and diffusion transfer mode. To explore the reaction mechanism of adsorption, the adsorption kinetic data were fitted with the pseudo-first-order kinetic model (Eq. 4) and pseudo-second-order kinetic model (Eq. 5), and the values of the parameters were listed in Table 2.

$$\log(q_e - q_t) = \log q_e - \frac{k_{1,ad}}{2.303} t \tag{14}$$

$$\frac{1}{(q_e - q_t)} = \frac{1}{q_e} + k_{2,ad} t \tag{15}$$

where $q_e$ (mg g$^{-1}$) is the equilibrium adsorption capacity and $q_t$ (mg g$^{-1}$) is the amount of adsorption at time t. $k_1$ (min$^{-1}$) and $k_2$ (g mg$^{-1}$ min$^{-1}$) are the kinetic adsorption rate constants of the Pseudo-first-order kinetics, pseudo-second-order kinetics, respectively. Obviously, the kinetic linear function of the adsorption process of BY 51 by SSBPSAE was more consistent with the pseudo-second-order model ($R^2 > 0.99$), and the calculated maximum adsorption capacity q$_e$ was close to the experimental value (Table S7). The rate-limiting step might be chemical adsorption or chemical reaction, which might involve electron sharing or exchange between BY 51 and the adsorbent (Arslanoğlu et al. 2021; Yaras and Arslanoğlu 2018).

Adsorption was a multi-stage process that consisted of (i) diffusion of solute molecules from solution to the surface of the adsorbent, (ii) diffusion within the particle to the interior of the adsorbent molecules, and (iii) adsorption of the adsorbent on the inner surface of the fine pore (slow step and speed determined)(Altundoğan et al. 2007). The pseudo-first-order and pseudo-second-order kinetic models were insufficient to determine the diffusion mechanism, thereby the intra-particle diffusion model (Weber and Morris model) was used to evaluate the diffusion process, which was expressed as follows,

$$q = k_i t^{1/2} + I \tag{16}$$

where $k_i$ [mg(g min$^{1/2}$)$^{-1}$] is the kinetic adsorption rate constant of the intraparticle diffusion model and $I$ is the intercept of the intraparticle diffusion model. The fitting results were shown in table. It could be observed that the adsorption process of BY 51 obviously contained two stages of fast and slow speed, and neither of the fitting lines passed the origin (intercept data is shown in Table 6). According to the concept of boundary layer thickness, the larger the intercept is, the greater the influence of the boundary layer. According to the above results, it could be inferred that intra-particle diffusion was not the only rate-limiting step for the adsorption of BY 51 by SSBPSAE, and other kinetic models could also control the adsorption rate (Wartelle and Marshall 2000).

The regression coefficients in the relevant evaluations also confirm this. Since it conforms to the pseudo

second-order model, the activation energies were calculated from the slope of the linear graphs obtained between the logarithms of the rate constants and 1/T by applying the data obtained from the experiments performed at various temperatures for the initial concentrations of 50–250 mg/L BY-51 to this model. The activation energy calculated from the Arrhenius equation for the sorption processes performed with 100 mg/L BY-51 solution was found to be 19.426 kj/mol (Dronnet et al. 1997).

$$k_{ad} = A\left(e^{-E_A/RT}\right) \tag{17}$$

As a result, it is possible to obtain a material with increased sorption capacity by simple processes such as removing sugar beet pulp and citric acid at 120 °C for esterification application. In the study, it was determined that Basic Yellow 51, which is a basic (cationic) dyestuff, can be effectively removed from wastewater with this modified material.

## Adsorption Mechanism

The above discussion showed that the SSBPSAE ion exchanger composite exhibited (Fig. 2) outstanding adsorption performance for BY 51, and the following was a comprehensive discussion of the adsorption mechanism based on the potential analysis, the structure and composition of the adsorbent, etc. Fig. S2 demonstrated that the adsorbent had obvious pH sensitivity, and the sensitivity was usually considered to be opportune to the desorption-cycle-regeneration of adsorbents. For the adsorption of BY 51, the removal efficiency increased gradually with increasing pH, and the removal efficiency was the highest (89%) when the pH was 8. SSBPSAE had the highest removal efficiency at pH 8, so electrostatic interaction was the most important adsorption driving force. Through FTIR analysis, it was known that SSBPSAE was highly aromatic and rich in π electrons, especially after treatment with citric acid. Moreover, SSBPSAE was rich in π electronic structures and oxygen-rich functional groups, especially under acidic conditions, and might also undergo cation-π bonding with amino or even hydrogen bonding with the dimethylamino, carbonyl, hydroxyl, amide carbonyl, and amino groups on BY 51 (Fig. S7). The above information explained the pH adsorption behavior of BY 51 by the adsorbent. Meanwhile, the adsorption under acidic conditions limited the applicable scope of the adsorbent. Similar to BY 51, π-π electron-donor–acceptor interaction and hydrogen bonding also existed between the adsorbent and BY 51 containing aromatic ring, sulfonic and imine groups. Moreover, the aromatic ring in BY 51 was prone to tilt/rotation in the structure, hence, BY 51 and SSBPSAE were also prone to π–π stacking interactions (Arslanoğlu et al. 2021; Yaras and Arslanoğlu 2018).

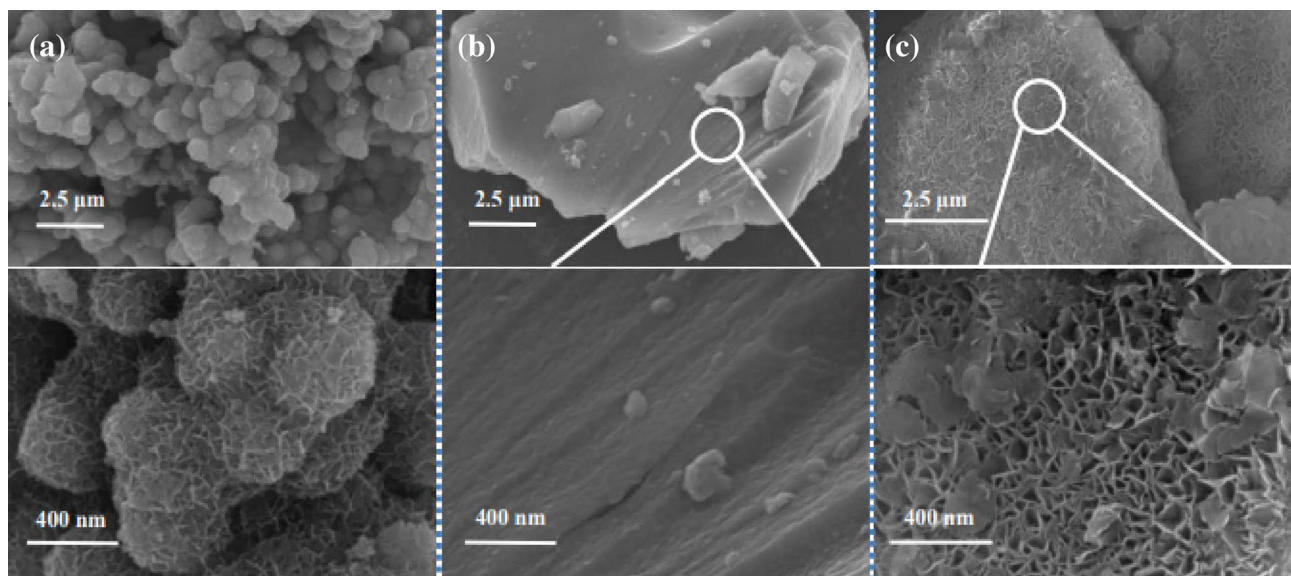**Fig. 2** SEM images of SBP (**a**), SSBP (**b**) and SSBPSAE (**c**)

FTIR spectra were conducted (Fig. 9). SSBPSAE clearly contained many active functional groups, including O–H bending vibration combined with manganese oxide (1635 and 1410 cm$^{-1}$) (Zaki et al. 2001), –O bond vibration (1055 cm$^{-1}$) (Guan et al. 2007), acid characteristic band (525 cm$^{-1}$) (Yang et al. 2010), C–O stretching vibration on the surface of resine (1100 cm$^{-1}$) and C=C stretching in the aromatic ring (1600 cm$^{-1}$), particularly the exposure of aromatic rings was conducive to the adsorption of aromatic organic compounds such as BY 51 (Arslanoğlu et al. 2020b).

The SSBPSAE used in this study was compared with other adsorbents in the literature for the removal of Basic Yellow 51 (Table S8). When the adsorption capacity of SSBPSAE adsorbent is compared with the literature data, it can be said that it provides significant dye removal and makes a positive contribution to the literature.

### Recycling of SSBPSAE Resin

In order to observe the reuse ability of the SSBPSAE, the adsorption–desorption cycle of SSBPSAE was carried out 6 times, and the adsorption capacity was calculated by Eq. (2). The regeneration method is as follows: the SSBPSAE was soaked in 0.001 M HCl, washed and decolorized, then washed with deionized water for many times to remove the HCl, and put into a sealed bag for reuse. The regeneration of SSBPSAE is its dominant feature in application (). Under the optimized conditions, the adsorption–desorption cycle was carried out continuously for 6 cycles, and the adsorption ratio of PSO were 93.2%, 89.9%, 90.1%, 85.5%, 84.3%, 62.49%, respectively. The adsorption ratio of PSO for 5 cycles showed excellent stability and recycling ability, and

the adsorption ratio of PSO decreased after 5 cycles. The adsorption ratio of X-5 resin for PSO decreased by more than 30% before the sixth cycle, which indicated that the adsorption/desorption of PSO by X-5 resin could be reused for 5 cycles without decreasing its performance (Arslanoğlu et al. 2021; Yaras and Arslanoğlu 2018).

### Conclusion

The sorption efficiency of the substance formed by the esterification of saponified sugar beet pulp with citric acid (SSBPSAE) is more than twice that of raw sugar beet pulp. It can be stated that carboxylate groups are formed as a result of hydrolysis of pectin in the structure by treating sugar beet pulp with NaOH solution, and also, free secondary alcohol groups are formed by hydrolysis of esterified alcohol groups in cellulose. The sorption capacity value obtained from the application to the Langmuir isotherm was found to be between 200–222 mg/g for different temperatures. For example, while a solution with an initial concentration of 100 mg/L requires a dose of about 4 g/L at 20 °C, a dose of just over 1 g/L was found to be sufficient for the removal efficiency at 50 °C. As a final result, it can be stated that sugar beet pulp, which is an agricultural residue, can be effectively used in the removal of basic dyes that can form cationic type ions when dissolved in water by first activating it with NaOH solution and then modifying it with citric acid.

**Declarations**

**Conflict of interest** The authors declare that there are no conflicts of interest regarding the publication of this paper.

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