Optimization and Removal Efficiency of Basic Textile Dyestuffs Using Perfluorosulfonic Acid-Based Polymer

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ABSTRACT: *The removal of basic dyestuffs (Basic Red 46 and Basic Blue 41) from synthetic dye solutions was examined by using perfluorosulfonic acid-based polymer for the first time in the present study. The effects of four different variables, such as pHs (3.0, 5.0, 7.0, 9.0, and 11.0), temperature (25 °C, 35 °C, 45 °C, 55 °C, and 65 °C), initial dyestuffs concentration (20, 40, 60, 80 and 100 mg/L) and treatment time (20, 40, 60, 80 and 100 min.) on the removal performance were investigated. The optimum conditions were determined for R46 as pH: 6.5; temperature: 54.1 °C; concentration: 97.4 mg/L; time: 60.8 min. and for B41 as pH: 7.5; temperature: 54.6 °C; concentration: 67.1 mg/L; time: 69.5 min. by using Response Surface Methodology. Removal performance values for R46 and B41 were determined respectively 99.9% and 99.5% at the optimum conditions. Also, perfluorosulfonic acid-based polymer was able to regenerate up to 20 cycles without significant performance change for the dyestuff removal process.*

KEYWORDS: *Acrylic fiber; Central composite design; Color removal; Textile dyestuffs; Perfluorosulfonic acid-based polymer.*

INTRODUCTION

The textile industry is one of the biggest and major players in Turkey's economy. The rapid growth of this industry reveals the necessity of confronting a large amount of effluent problem that needs to be discharged into the environment. Dyeing and de-sizing process are the main sources of wastewater from the textile industry dye houses in the textile industry are mainly responsible for large amounts of colored wastewater which strongly

Anf negatively affects aquatic life due to low sunlight transmittance [1, 2]. The textile industry mainly utilizes three main groups of dyestuff materials namely anionic, cationic, and nonionic based on their chemical structures. Basic dyes that are most promising cationic-based dyestuffs frequently take part in dyeing processes in the textile industry because of their advantages such as bright colors, water-solubility, easy applications, and low energy

requirements [3]. Basic dyestuffs are in the form of hydrochlorides of organic bases or acetate salts. Basic dyestuffs are mainly used to dye acrylic fibers [4]. Dyestuffs containing a positive charge in their molecules are called "cationic dyestuffs" or "basic dyestuffs". Positive charge carriers contain N and S atoms. Ionic moieties of basic dyestuff in the aqueous solution bring the fiber-dyestuff salt into the water with the anionic groups of the fiber, since they act basically [4, 5]. The most characteristic properties of basic dyestuffs are brightness and color intensity [6]. In the textile industry, wastewater may have different pHs values depending on process conditions related to fiber type and dye class [7]. These wastewaters have become the main objectives for the treatment processes for environmental protection. It is known that the dyestuffs are dangerous for aquatic life and form undesirable colors in the water. Some of the dyestuffs are carcinogenic and prevent sunlight from aquatic life [1]. For these reasons, treatment is necessary because of the mentioned above risks. Physical, chemical, or biological methods can be named according to the nature of the process and these methods can be preferred either separately or together depending on the characteristics of the wastewater. Also, more specific methods such as electrocoagulation, nanofiltration, membrane, electrochemical, microbial, biosorption, photocatalytic, enzymatic, and adsorption have been studied in the last decades for wastewater treatment [7–10]. Due to their advantages such as high flexibility in design, physical superiority viz. porosity, uniform pore size distribution, high surface area, chemical stability, feasible regeneration, and thermal durability polymeric adsorbents were frequently employed in color removal processes [11]. They have available many forms to meet different requirements. Natural polymers and synthetic polymers can be given as an example of the main classification. Because of their particular structure, physicochemical characteristics, chemical stability, high reactivity, and excellent selectivity towards heavy metal ions and dyes, resulting from the presence of reactive chemical groups in polymer chains, natural polymers have become interesting and attractive alternatives for adsorption. It can be seen that studies in this field have recently been focused on polysaccharides especially starch, alginate, cyclodextrin, cellulose, and chitosan. Polysaccharides are abundant, renewable, and biodegradable resources that have the capacity to associate by physical and chemical interactions with a wide variety of molecules.

Recently, synthetic polymers have been examined as an alternative to conventional adsorbents such as clay, and activated carbon, due to their large surface area, mechanical rigidity, adjustable surface chemistry, and ability to regenerate under mild conditions. Synthetic polymers have also additional advantages in comparison to other adsorbent materials; for instance, they can be readily prepared in a wide range of properties (e.g. form, size, size distribution, porosity, and hydrophilicity) and they are able to modify by attaching various ligands into the structure in order to produce more specific adsorbents. Synthetic polymers perform dye removal through functional groups in their structures. Amine, sulfonamide, imine, amidoamine, acrylic acid, sulfonic acid, sodium acrylate, and sodium sulfonate functionalities are the most common groups encountered in the literature to achieve adsorption [12]. There are also different approaches to using synthetic polymer for the adsorption process. These are composite forms of synthetic polymers containing traditional adsorbents and hydrogel structures. Sen et. al. have investigated the removal of Methylene Blue dye by using clay-containing polyethylene composite structures [13]. Köklü et. al. have performed a study focused on the removal performance of remazol, everzol, and eversion groups containing dyes from textile wastewaters with hydrogel-based material [14]. *Kong et. al.* reported the removal of Methylene Blue was carried out successfully using hydrogel beads [15]. Polyamines, diallyl dimethyl ammonium chlorides (DADMAC), and polyacrylamides (PAM) are cationic polymers and are used in wastewater treatment as flocculants, coagulants, and as dewatering aids in many different processes. The most prominent feature of cationic polymers is a net cation charge with the charge density depending on the nature of the polymer. Cationic polymers that have the best dye removal performance are strongly cationic ones and have high molecular weight values. These have exhibited up to 50% dye removal performance, so using cationic polymers is not typically a practical method for decolorizing textile wastewater containing hydrolyzed reactive dyes. Due to their high solubilities, cationic polymers do not form rapidly a coagulant with dyes and pigment, it has to have waited for hours or even days for the flocculence to occur. Anionic polymers are suited for dye removal for wastewater

contaminated with cationic dyes. There are various types of anionic polymers, for instance, sulfonated novolac, acrylic, modacrylic, urethanes, and methacrylates [16]. Anionic polymers can be easily ionized and have the ability to ion-exchange adsorption because of carrying acidic functionalities such as sulfonic acid, carboxylic acid, and acrylic acid so they are called also cation exchangers. Cation exchanger polymers that carry highly ionizable sulfone moieties are preferred among other ones. PFSA was chosen as the adsorbent material in our study, due to the above-mentioned advantages of synthetic polymers over typical adsorbents and sulfone groups in their structure. In the literature, studies subjected to the usage of perfluorosulfonic acid-based polymer (PFSA) in dye removal processes as an adsorbent has not come across. There are few investigation attempts that focused on the preparation of hybrid structures containing anatase titanium dioxide, nanoparticles, and graphene using PFSA as a matrix material for especially photocatalytic processes [17–22]. Also, studies are presently directed to PFSA which was utilized as a separator in electro-membrane reactors for electrochemical degradation processes of dyestuffs [23, 24]. However, it has not come across that perfluorosulfonic acid-based polymer serves as an adsorbent in dyestuff removals. Hence, the lack of studies using PFSA as an adsorbent directly in the literature is one of the main motivation sources of this study. The main contribution of our study can be evaluated as enlightening this deficiency in the literature. Response Surface Method (RSM) is a statistical method that applies quantitative data from appropriate experiments to solve multivariate equations to obtain the optimal conditions for achieving the best response. Central Composite Design (CCD) is the most popular method of making a second-order RSM in process optimization. It is a good alternative to full factorial design to obtain more data with a lower experimental number. In contrast to other methods, CCD uses axial points and therefore needs two more experiments for each parameter at the highest and lowest levels [25, 26]. Using an effective statistical analysis, the minimum number of experiments can effectively determine the relationship between parameters and responses [27-28].

This study was aimed at investigating of utilization, reusability, and removal performance of PFSA as an absorbent material in the removal process of basic dyestuffs. The removal of basic dyestuffs was evaluated by Response Surface Methodology Based on the CCD with four factors such as pH, temperature, concentration, and time. It also examined the interaction between the parameters and optimal conditions using limited experiments, and the RSM was employed to find a reliable predictive model under CCD.

EXPERIMENTAL SECTION
Materials
The dyestuffs which are Basic Blue 41 (B41) and Basic Red 46 (R46) were kindly provided by acrylic fiber manufacturer Aksa Akrilik Kimya Sanayii A.Ş. in Yalova, Turkey. The characteristic properties and chemical structures of the B41 and R46 dyestuffs were given in Table 1, Fig.1, and Fig. 2. Perfluorosulfonic acid-based polymer (Nafion® N-117, PFSA) was purchased from Alfa-Aesar, PFSA has 0.180 mm thickness and ≥ 0.9 meq/g ion exchange capacity values. Acetic acid (Fluka), hydrogen peroxide 30% (Merck) sodium phosphate dibasic (Riedel-de Haen), monobasic phosphate (Riedel-de Haen), disodium citrate buffer (0.05 M, pH: 3.0), phosphate buffer (0.1 M, pH: 7.0) and sodium acetate buffer (0.05 M, pH: 5.0) were of analytical grade and all materials were used as received without any further purification. Ultrapure water was obtained from the Millipore MilliQ system.

Removal Experiments
Stock solutions were prepared in distilled water at a concentration of 1000 mg/L (Basic Blue 41 and Basic Red 46). Stock dyestuff solutions were diluted to desired concentrations. Experiments were carried out with the PFSA. 50 mg of the PFSA was used as an adsorbent for the 10 mL synthetic dye solution.

The wavelengths which perform maximum absorption values were measured by Shimadzu UV-1800 UV-Vis. spectrophotometer in the range of 200-800 nm and given in Table 1. Dyestuff removal performance values were evaluated by absorbance measurements at maximum absorbance wavelengths before and after the removal process respectively then dyestuff removal performances of PFSA were calculated according to the following equation (Eq.1) [1, 5, 29].

$$\text{Removal Performance (\%)} : \quad\quad\quad (1)$$
$$\frac{(\text{Abs}_{(i)} - \text{Abs}_{(t)})}{\text{Abs}_{(i)}} \times 100$$

Table 1: Characteristic properties of the textile dyestuffs.

Dyestuff name	Molecule Formula	CAS		Molecular weight (g/mol)	Maximum absorbance wavelength (λ_{max}) (nm)	Usage
Basic Blue 41 (B41)	C20H26N4O6S2	12270-13-2		482.6	609	Dyes, Textiles, apparel, and leather manufacturing
Basic Red 46 (R46)	C18H21BrN6	12221-69-1		401.3	530	Dyes, Hair dying

Table 2: Dyestuff concentration, adsorbent dosage, and the ratio of them in the removal process.

Dyestuff concentrations (mg/L)	20	40	60	80	100
Adsorbent dosage (g/L)	5	5	5	5	5
(Dyestuff concentration)/(adsorbent dosage) ratio (mg/g)	4	8	12	16	20
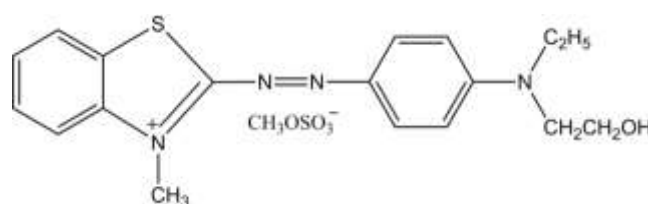
Fig. 1: Chemical structure of Basic Blue 41.
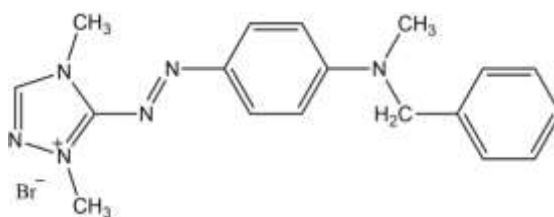
Fig. 2: Chemical structure of Basic Red 46.

$Abs_{(i)}$ is the absorption value of the dyestuff in the maximum wavelength.

$Abs_{(t)}$ is the absorption value at the maximum wavelength at the end of the adsorption time after the addition of the PFSA.

Adsorption and Regeneration

Adsorption of dyestuff is strictly dependent on the surface chemistry of the adsorbent materials. Functional groups on the surface of the polymeric adsorbent are fully responsible for the adsorption process. PFSA materials contain three main functional parts, the first is a polytetrafluoroethylene (PTFE) mainchain, the second is side chains that consist of fluorinated carbon which act as a bridge between the polymer backbone and the third part and the third is ionic groups (sulfonic acid) which

can serve as a proton donor and have ion exchange capability. Due to the nature of sulfonic acid groups which can easily proton release and ion exchange, PFSAs are frequently utilized in Fuel Cells as membrane materials. Proton conductivity and as a result electricity is provided by sulfonic acid groups in PFSA materials, *via* releasing protons. Therefore adsorption and ion exchange processes can be also easily realized with PFSA materials because of mentioned characteristics of sulfonic acid groups.

The adsorption process onto PFSA samples used in the present study as adsorbent is mainly driven by electrostatic interactions involving sulfonic acid groups on the surface. PFSAs are charged negatively after the loss of proton in properly hydrated or aqueous mediums, hence they became an attraction point for positively charged particles. Consequently, basic dyes which exist in textile wastewater

Fig. 3: The chemical structure of PFSA and the proposed mechanism of adsorption and regeneration processes.

and are positively charged using sulfonic acid groups of PFSAs as the connecting port. Thus dyes were captured by PFSA and textile, and the wastewater was decolorized.

Regeneration is defined as taking back ions that have been picked up during the process from exhausted (fully loaded) ion exchange materials, so the ion-exchanger can continue to be used. The first step in regeneration is to backwash the system sequentially by running water and treating it with proper solvents. Then ion exchanger was regenerated with a specific solution or other regenerated chemicals. In order to regenerate PFSA, the method proposed in the literature was used [30]. After each removal cycle, PFSA was washed with ultrapure water and PFSA soaked in a beaker containing isopropanol and boiled for 30 min. Then PFSA has been treated by boiling a 3-5% H_2O_2 solution in an Erlenmeyer until the color of PFSA disappeared. The chemical structure of PFSA and the proposed mechanism of adsorption and regeneration of PFSA were given following respectively in Fig. 3.

The proposed mechanism of regeneration of PFSA was given following.

$$PFSA - SO_3H^+ + BD^+_{(aq)} \rightarrow PFSA - SO_3BD^+$$

(Adsorbent)   (Basic Dye)

$$PFSA - SO_3BD^+ + H_2O_{2(aq)} \rightarrow$$

(Exhausted Adsorbent)   (Hydrogen peroxide)

$$PFSA - SO_3H^+ + O - OH^-_{(aq)}$$

(Regenerated Adsorbent)   (Hydroperoxide)

The schematic representation of the removal process was given in the graphical abstract in Fig. 4.

Experimental design

It aimed to determine optimum conditions for dye removal by using the experimental design. For this aim, to evaluate the removal efficiency of basic dyes, a central composite design with a response surface method was used at five levels. In this study, the effects of four parameters such as pH, temperature, concentration, and time were examined. Table 3 shows the levels of parameters set for the central composite design. The high, middle and low levels of factors are delineated as +1, 0, -1 and the axial points are +β, -β. The coded values of axial points were computed according to Eq. (2).

$$\alpha = [2^4]^{1/4} \qquad (2)$$

The dyestuff removal process was evaluated using Design-Expert Software, Version 7.0 (Stat-Ease, Minneapolis, USA) in terms of experimental differentiations. To practice the central composite design method, the total number of experimental runs was fixed 30 covering 24 factorial points and 6 central points according to Eq.(3).

$$N = 2^k + (2.k) + C_0 \qquad (3)$$

Where *k* is the number of factors and C_0 is the number of central points.

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Table 3: Factors and their levels for the removal process.

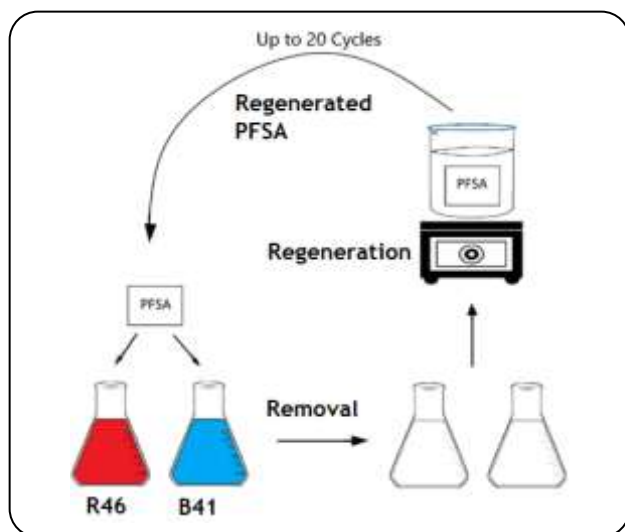| Factors	Unit	Code	Levels				
			- β	-1	0	1	B
pH		A	3	5	7	9	11
Temperature	°C	B	25	35	45	55	65
Concentration	mg/L	C	20	40	60	80	100
Time	min	D	20	40	60	80	100

Fig. 4: Graphical abstract; a schematic representation of the removal process.

The experimental design matrix of the dyestuffs removal process is presented in Table 4.

RESULTS AND DISCUSSION
Removal Performance

In this work, the removal of basic dyestuffs (B41 and R46) which are used for the dyeing of acrylic fiber in the textile industry was carried out successfully and investigated under various parameters such as time, temperature, pH, and initial dye concentration by using PFSA. High removal performances were achieved at moderately high temperatures for both basic dyes. In the perspective of mechanism, our study subjected the removal process of basic dyestuffs (B41 and R46) from textile wastewater using PFSA is based on ion-exchange adsorption. Ion-exchange adsorption is defined as, "the process of releasing", one kind of ion and adsorbing another same kind of ion by an adsorbent. In accordance with this definition, PFSA and basic dyestuffs can be classified as adsorbent and adsorbed ions respectively in our study. Due to the working mechanisms they exhibit, adsorbents used in ion-exchange processes are frequently called as ion-exchangers. Ion exchangers are generally insoluble high molecular weight synthetic polymers that have charged functional groups attached to them with covalent bonds. They can exchange the ions on the charged functional groups against ions of the same charge from the surrounding medium. Ion exchange is a reversible and stoichiometric process. The type of charge owned by the functional group is a criterion for the classification of ion exchangers. Ion-exchange materials can be differentiated mainly as cation exchangers have structurally bound anions, anion exchangers have structural bound cationic groups, and there are also amphoteric ion exchangers, containing both ion types at the same time. Cation exchangers are employed only in the mediums containing cations and are prepared with modification of synthetic polymers *via* reaction with suitable agents that can attach anionic moieties such as $-SO_3^-$ and $-COO^-$. Because of high ionization values of sulfone moiety, cation exchangers which have $-SO_3^-$ functionality are labeled as strong acidic. In an ion-exchange process that employed strong acidic cation exchangers, cations are replaced from the solution to attached groups of polymers via electrostatic interactions. The parameters affecting the kinetics and thermodynamics of this process have two different ionic fluxes can be summarized as follows. Porosity and surface area of adsorbent, process temperature and pH, cations numbers, cations concentration, cations valences, and cations masses or volumes in the solution are evaluated as key factors [31-34].

In light of the info mentioned above, while under the same conditions, all parameters are the same -ceteris paribus- for basic dyes so there is only one evaluation criterion to consider for our results and it is cation masses

Table 4: Experimental design matrix of the removal process.

Experiment number	pH	Temperature	Concentration	Time
1	-1	-1	-1	-1
2	1	-1	-1	-1
3	-1	1	-1	-1
4	1	1	-1	-1
5	-1	-1	1	-1
6	1	-1	1	-1
7	-1	1	1	-1
8	1	1	1	-1
9	-1	-1	-1	1
10	1	-1	-1	1
11	-1	1	-1	1
12	1	1	-1	1
13	-1	-1	1	1
14	1	-1	1	1
15	-1	1	1	1
16	1	1	1	1
17	-β	0	0	0
18	β	0	0	0
19	0	-β	0	0
20	0	B	0	0
21	0	0	-β	0
22	0	0	B	0
23	0	0	0	-β
24	0	0	0	β
25	0	0	0	0
26	0	0	0	0
27	0	0	0	0
28	0	0	0	0
29	0	0	0	0
30	0	0	0	0

or volumes. R46 basic dye has a smaller molecular weight and molecular volume comparison to B41 basic dye, so R46 can be more easily transported from the solution to PFSA matrix and also it was affected less by steric hindrances. Thus, it can be understood why R46 basic dye has higher removal efficiency values than B41 basic dye. Selected studies in the literature where this phenomenon is observed are summarized below. A study by Langlois revealed as the molar rate of adsorption decreases with the increased molecular weight of adsorbed ions linearly [35]. In the study which focused determination of adsorption characteristics of various amino acids onto sulfonated polystyrene-divinylbenzenes, Jones et. al. have found that selectivity values (S) are smaller for larger molecules because steric hindrance prevents full utilization of the exchange capacity of sulfonated polystyrene-divinylbenzene material [36]. *Albroomi et al.* have performed a study with commercially available activated carbon (5.0 g/L) for the removal of Methylene Blue basic dye at pH: 3.0, 7.0, and 10.0 and, found removal values 82%, 93%, and 95% respectively. They have reported that with increasing pH of the solution number of available hydroxyl groups of the adsorbent used was also increased and, therefore higher dye removal values for pH 7.0 and pH 10.0 could be reached [37]. *Wang et al.* have carried out the removal of MB basic dye at pH: 3.0, 5.0, 7.0, 9.0, and 11.0 using carboxymethyl chitosan alginate microspheres and removal values found as 26%, 33%, 40%, 46%, and 100%, respectively [38]. Ebrahimi et. al. have used fishbone as an adsorbent (2.5 g/L) for the removal of basic dyes Basic Blue 41 (B41) and Basic Yellow 37 (BY28). They have determined the lowest values for dye removal at pH 2.0 (for B41 25% and for BY28 28%) because of the protonation of functional groups, which makes the surface of the adsorbent more positive and causes the repulsion between dye molecules and adsorbent. They have reached the highest removal value at pH: 11 (for B41 93% and for BY28 80%) due to the absorbent surface being negatively charged and attracting the dye molecules. Also, they found removal values at pH: 7.0 86% and 62% for B41 and BY28 respectively [29]. *Humelnicu et. al.* have examined for removal B41 using 2.5 g/L natural zeolitic tuff for 20 hours. They have reported the dye removal values as 92%, 94%, 86%, and 95.7% for pH: 3.0, 5.0, 6.0, and 8.0 respectively. They have reached higher removal values at pH: 5.0 and 8.0 [39]. The study was performed by
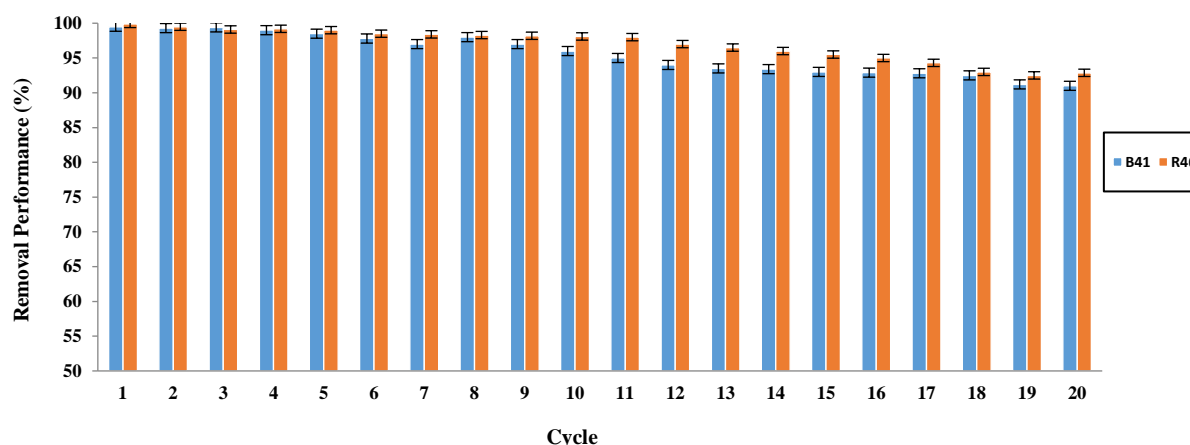
Fig. 5: Removal performance values of B41 and R46 by using regenerated PFSA material according to cycle numbers.

Elazioutti et al. Maghnia Montmorillonite clay (1.0 g/L) adsorbent was used to remove Methylene Blue cationic dye. They have concluded that optimum removal performance for dye removal could be reached at neutral pHs [40]. *Kyzas et. al.* have used Kenaf fibers (10 g/L) for the removal of Basic Yellow 37, and reported that Kenaf fibers have exhibited 10%, 66%, 70%, 59%, and 78% of removal values for pH 2.0, 4.0, 6.0, 8.0 and, 10.0 respectively for 24 hours period. It was also reported that Kenaf fibers could be regenerated only 10 times [41].

In the present study, we have reached relatively high dye removal values by using PFSA at acceptable concentrations in a short time for a wider range of pH range in comparison to similar studies in the literature. For the solutions at basic pH's, -SO₃H groups of PFSA can release more easily H^+ ions, so the ion-exchange adsorption process has become more efficient and rapid. However, ionization and transportation of the basic dyes have been sustained easily at acidic pH values of solutions. Therefore, the phenomenon of reaching maximum dye removal values at pH 7.0, it can be stated that the most appropriate combination of these two opposite effects leads us to the conclusion that pH 7.0 was the most proper condition for study. So, in terms of pH values, the highest values have been reached at neutral pH for B41, R46 with the same removal performance (98%). In light of these results, it can be said that PFSA can be evaluated as a suitable adsorbent for basic dye removal processes that perform under various pH values. With increasing initial dye concentration, while removal values of B41 decrease, there is no remarkable change in removal performances

that were observed for R46. Generally, the removal performance of both basic dyes gets better with longer contact time between adsorbent and dyes, however, it was also seen removal performance of both basic dyes was not changed further with contact times beyond 80 min. One of the basic knowledge gains of our study can be noted as a basic dye that has a relatively lower molecular weight has shown better removal performance values as against the one that has a higher molecular weight. The most important contribution of our study to the literature was the investigation of the ability to use PFSA adsorbent for the first time in the removal of basic dyes. Furthermore, it demonstrated the reusability of PFSA as an adsorbent with high removal performance values up to 20 cycles for the removal of basic dyes in our study. From the the perspective of reusability, PFSA has been differentiated from regular adsorbents with remarkable removal performance values up to 90% even at the 20th regeneration cycle at pH:7.0, dye concentration (60 mg/L) for 100 min. (Fig.4). Regeneration experiments were performed at least three times and results are expressed as the mean values in Fig. 5.

Regression model

The results corresponding to the specified experimental conditions are shown in Table 5. Due to the lower standard deviation and the higher R^2 value, the quadratic model is seen as the most suitable model for these conditions. Response values were given as Y_1 (R46) and Y_2 (B41) belonging to the predicted model, and were specified as coded values obtained from Eqs. (4) and (5).

Table 5: The experimental results obtained at the experimental conditions designed according to the central composite design.

Experiment number	Independent variables				Experimental value	
	A	B	C	D	Y_1	Y_2
1	5.00	35.00	40.00	40.00	85.1	67.5
2	9.00	35.00	40.00	40.00	89.9	71.7
3	5.00	55.00	40.00	40.00	97.4	77.3
4	9.00	55.00	40.00	40.00	96.1	92.3
5	5.00	35.00	80.00	40.00	79.2	57.4
6	9.00	35.00	80.00	40.00	77.8	54.0
7	5.00	55.00	80.00	40.00	96.0	85.9
8	9.00	55.00	80.00	40.00	95.7	86.4
9	5.00	35.00	40.00	80.00	98.2	84.3
10	9.00	35.00	40.00	80.00	99.5	88.6
11	5.00	55.00	40.00	80.00	99.6	94.3
12	9.00	55.00	40.00	80.00	99.4	99.2
13	5.00	35.00	80.00	80.00	97.7	63.1
14	9.00	35.00	80.00	80.00	96.7	62.9
15	5.00	55.00	80.00	80.00	99.6	98.5
16	9.00	55.00	80.00	80.00	99.5	98.9
17	3.00	45.00	60.00	60.00	98.7	75.5
18	11.00	45.00	60.00	60.00	96.0	80.0
19	7.00	25.00	60.00	60.00	93.5	75.3
20	7.00	65.00	60.00	60.00	99.5	99.5
21	7.00	45.00	20.00	60.00	99.2	96.2
22	7.00	45.00	100.00	60.00	99.7	68.3
23	7.00	45.00	60.00	20.00	93.7	73.3
24	7.00	45.00	60.00	100.00	99.9	69.6
25	7.00	45.00	60.00	60.00	99.0	88.0
26	7.00	45.00	60.00	60.00	99.2	87.6
27	7.00	45.00	60.00	60.00	99.5	92.5
28	7.00	45.00	60.00	60.00	99.0	94.8
29	7.00	45.00	60.00	60.00	99.2	90.1
30	7.00	45.00	60.00	60.00	99.0	90.3

A= pH, B= Temperature (°C), C= Concentration (mg/L), D= Time (min), Y_1 = (R46), Y_2 = (B41).

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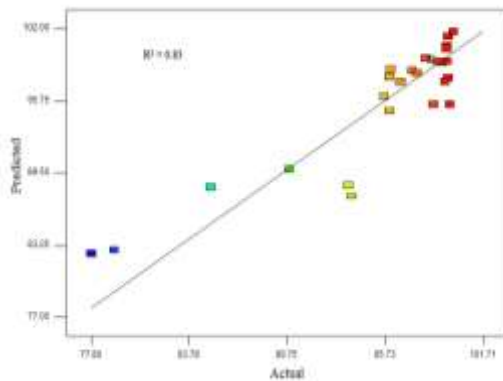
Fig. 6: Predicted response versus actual response for removal of R46.

$$Y_1 = 99.15 - 0.15\,A + 2.97\,B - 0.92\,C + 3.56\,D - \qquad (4)$$
$$0.35\,AB - 0.46\,AC - 0.11\,AD + 1.23\,BC - 2.95\,BD +$$
$$1.04\,CD - 1.00\,A^2 - 1.21\,B^2 - 0.48\,C^2 - 1.14\,D^2$$

$$Y_2 = 90.55 + 1.45\,A + 9.65\,B - 5.16\,C + 3.75\,D + \qquad (5)$$
$$0.99\,AB - 1.94\,AC - 0.43\,AD + 5.08\,BC + 0.04\,BD -$$
$$1.12\,CD - 3.13\,A^2 - 0.72\,B^2 - 2.00\,C^2 - 4.70\,D^2$$

Coded values *A, B, C*, and *D* corresponded to selected process factors pH, temperature, concentration, and time respectively. While the positive values exhibit a synergistic effect and the negative values mean simply an antagonistic effect.

Statistical analysis

In order to define the compatibility of the regression model, ANOVA analysis based on the central composite design was performed using the Design Expert Software. The statistical model also describes the effects of quadratic terms and linear terms on the interactions between variables and responses.

In terms of model significance, Prob>F values can be appraised as a cornerstone, it is known that while the Prob>F values are below 0.05, the model is meaningful [27, 28]. With 5.11 and 8.92 F values (data not shown), the quadratic model based on the ANOVA method was to exhibit the most fitted model for the responses Y_1 and Y_2. Statistically significant model terms of the response Y_1 (R46) were determined as B, D, and BD which are given in Table 6. The time parameter (D) stands out as the most important effect on the removal performance of the R46 with a 27.06 (data not shown) of F value, and was followed by temperature term (B) and interaction between
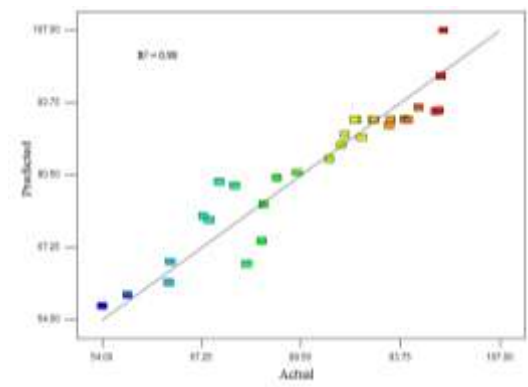
Fig. 7: Predicted response versus actual response for removal of B41.

temperature and time terms (BD) can be seen in Table 6. However, it can be said that other model terms B, C, D, BC, A^2, and D^2 are also statistically significant for response Y_2 (B41)

The correlation plots between predicted and actual values for the response (R46) and (B41) are shown in Fig.6 and Fig.7. According to the statistical test results, the quadratic model showed a sufficient agreement between the predicted and actual data for each response, depending on the distribution of most of the experimental data near the straight line.

Interaction effect of process variables on responses

Fig. 8. and Fig. 9. show the graphical representation of the 'size effect' of each of the parameters upon the dyestuffs removal performance for R46 and B41 respectively. From these figures, it can be seen that temperature (B) and time (D) have a positive effect, while pH (A) and concentration (C) harm the yield of removal R46. Also, pH (A), temperature (B), and time (D) have a positive effect, while concentration (C) has a negative effect on the yield of removal B41. The second-order terms and interaction terms affect to process at various ratios.

Three-dimensional response surface graphs were plotted for R46 and B41 removal efficiency. The surface response graphs were composed by varying two parameters and other variables were kept constant at zero levels. Fig. 10 and Fig. 11 exhibited the interaction effect among pH, temperature, concentration, and time on the removal performance of R46 and B41. According to Fig. 10, the removal performance of R46 increased with rising
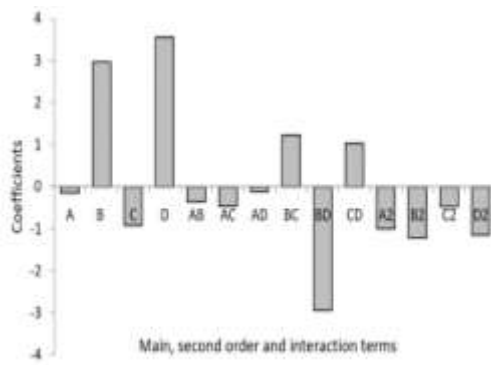
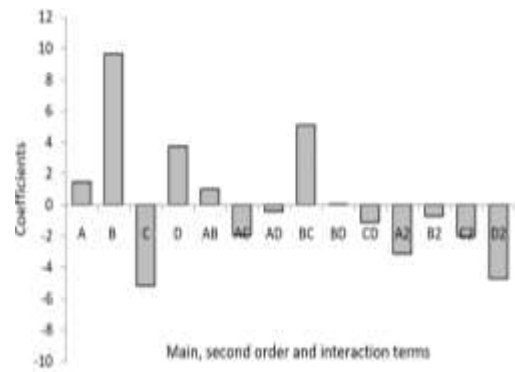***Fig. 8: The significant main, second-order and interaction terms for removal of R46.***

Fig. 9: The significant main, second-order and interaction terms for removal of B41.
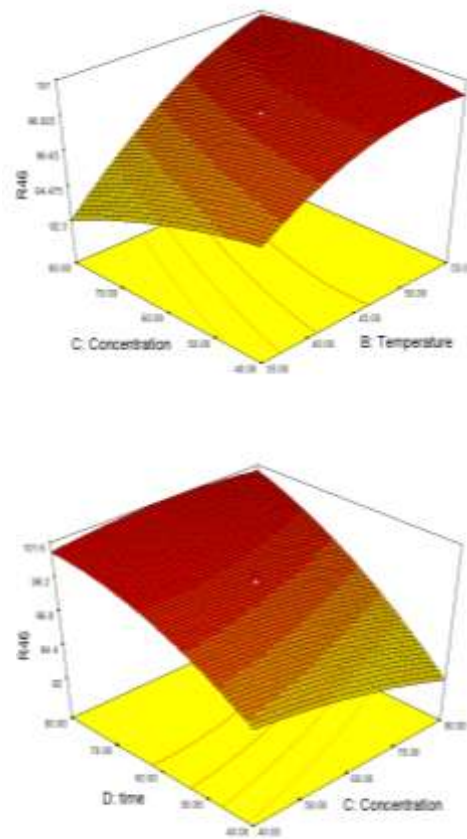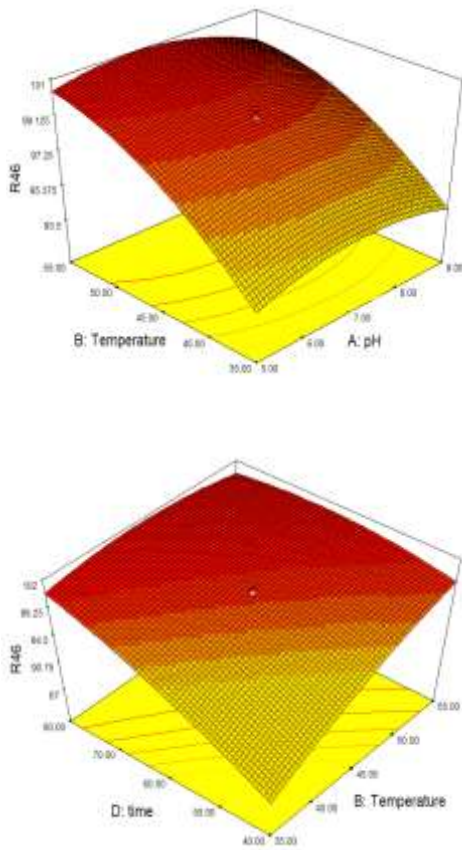

Fig. 10: Three-dimensional (3D) response surface plot for removal of R46.

temperature and time. The increase in the pH and concentration causes a negative effect on the yield in a small amount. According to Fig. 11, the removal performance of B41 raised with increasing pH, temperature, and time while decreasing with high concentrations.

Optimization

One of the objectives of this study was to determine the optimum process conditions from the models obtained experimentally. For this aim, firstly, the objective of the optimization was decided, which may be either economic or technical. In this optimization study, the dyestuff
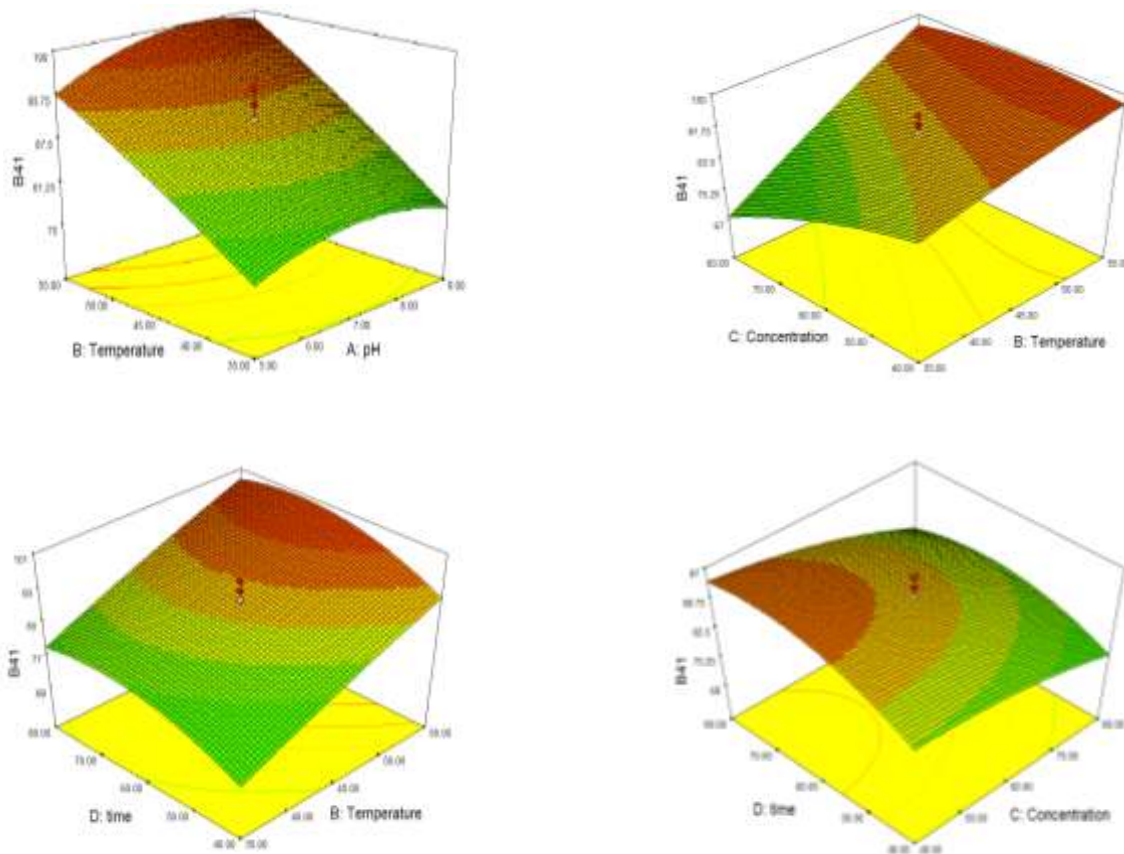
Fig.1 1: Three-dimensional (3D) response surface plot for removal of B41.

removal performance was chosen as the objective function for maximum dyestuff concentration. Besides, optimum conditions were often calculated in the presence of some constraints which ensure them to be more realistic. If the model used in the optimization study is an empirical one, axial points of the process factors in the experimental design were considered as explicit constraints to avoid extrapolation. Concerning its economic value, the temperature and time parameters were evaluated between low and high levels. Thus, the optimization problem was defined as follows;

 - Maximize Y

 - Constraints on the parameters A and C (- 1 < parameters < + β)

 - Constraints on the parameters B and D (- 1 < parameters < + 1)

The optimization was realized using a constrained optimization program supplied in the Design-Expert Software, optimization toolbox [42]. For the dyestuff removal process, the calculated optimum process conditions were given in Table 6. by taking into account the models given in Eq. (4) and Eq. (5).

Where some variable levels were rounded, based on the sensitivity of the equipment used.

Fig. 11 exhibits a decrease in the percentage of dye removal with the increasing amount of initial concentration for Basic Blue 41 dye, while the rise in initial dye concentration in the removal of other Basic Red 46 (Fig. 9) did not adversely affect dyestuffs removal. Since the molecular weight of the Basic Blue 41 dye is higher than the other dyes, it is eliminated with a lower percentage than the other dyestuffs. The percentage of dyestuffs removal performance increased with the increase of the incubation time as given in Fig. 9. and Fig. 10. The characteristic properties of the basic dyestuffs used in the study are shown in Table 1. As seen in Fig. 9. and Fig.10, removal values increased with an increasing incubation time of the adsorbent to dyestuffs. Dyestuff removal values

Table 6: Optimum conditions for dyestuff removal performance.

Dyestuff	pH	Temperature (°C)	Concentration (mg/L)	Time (min.)	Performance (%)
R46	6.5	54.1	97.4	60.8	99.9
B41	7.5	54.6	67.1	69.5	99.5

reached the maximum at 80 min. and then the dye removal values remained constant.

CONCLUSIONS

In the textile industry, basic dyestuffs are mainly used to dye acrylic fibers. Dyestuffs from dyehouse effluent are dangerous for aquatic life and form undesirable colors in the water. Perfluorosulfonic acid-based polymer was successfully utilized for the very first time to remove the basic dyestuffs which were utilized in the acrylic fiber dyeing process. The optimum conditions which were determined for the removal process using CCD were given following for both dyestuffs: - for R46 pH: 6.5; temperature: 54.1 °C; concentration: 97.4 mg/L; time: 60.8 min. - and for B41 pH: 7.5; temperature: 54.6 °C; concentration: 67.1 mg/L; and time: 69.5 min. Under these conditions, removal values were respectively 99.9% and 99.5% for R46 and B41.

Results show that R46 had higher dye removal performance values in comparison with B41 so removal performance values strictly depended on the molecular size of the dyestuffs. The most important contribution of our study is exposing that perfluoro sulfonic acid-based polymer has the capability of reusability for removal processes. It can be regenerated for reuse at the removal process up to 20 times without any significant performance loss. From the economic perspective,

the reusability of perfluorosulfonic acid-based polymeric adsorbent is the most important aspect against its relatively high price. Consequently, it can be said that this polymer which can be regenerated will be the most promising alternative in contrast to conventional methods. Perfluorosulfonic acid-based polymers can be used as an effective adsorbent material for dyestuff removal processing.

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