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Removal of Anthraquinone Dyes from Aqueous Solutions Using Activated Carbon Fiber Prepared from Polyacrylonitrile Waste

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Abstract

In this study, the adsorption of three different blue anthraquinone dye classes (Reactive, Acid and Disperse dyes) were investigated using activated carbon fibre prepared from polyacrylonitrile (PAN) waste. The use of polyacrylonitrile based activated carbon fiber (PAN-ACF) for the adsorption of these dyes has been examined using exhaustion method at different operational conditions such as dye concentration and adsorption temperature. It was found that the adsorption of the anthraquinone dyestuffs on PAN-ACF increased with increasing temperature. In addition, the prepared ACFs exhibited higher adsorption capacities for the non-ionic anthraquinone based disperse dye than those of the anionic anthraquinone based reactive and/or acid dyes.

*Keywords***:** Adsorption; Activated carbon fiber; Polyacronitrile; Anthraquinone blue dyes: Reactive dyes; Acid dyes; Disperse dyes

.

1. Introduction

Activated carbon fiber (ACF) is well-known as smart adsorbing material due to its physical and chemical properties. It can be used in many applications, particularly in removal of several pollutants such as dyes [1-7], heavy metals [8-10] or pesticides [11, 12]. ACFs have gained a particular interest over the traditional adsorbents owing to their large surface area and microporosity character. The adsorption capacity of ACF is mainly influenced by many factors including high surface area, wide range of porosity and surface chemistry [13].

The surface chemistry is substantially governed by the distribution and type of the surface functional groups (SFGs) and the heteroatoms on the surface structure. ACF is a microporous material comprising a three-dimensional network of micrographitic layers, as their have a considerable amount of active functional groups (such as –COOH, -OH, -CO-, -O-) and extended bonds. The huge surface area (up to 3000 m^2/g) is another important criterion of ACF. Several studies have devoted to the properties of activated

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carbon fiber made from different precursors [14]. Among these precursors, about 90% of the world's total productions of ACF are based on polyacrylonitrile fiber (PAN) as precursor material [15-19].

PAN-based fibers contained carbon-oxygen functional groups with considerable amount of nitrogen functional groups, which was supposed to affect fiber adsorption. Also, the chemical structure of the adsorbed dye and its chromophoric system have an important influence on the ACFs adsorption process [20]. The adsorption process of different dye compounds by ACFs depends on whether the dyes are nonionic, cationic or anionic. The adsorption of various commercial azo dyes has already been an area of extensive research. [21], however, limited information exists in case of anthraquinone-based dyes. Among the textile commercial dyes, azo and anthraquinone dyes constitute the two principles important chemical classes of dyes [21, 22].

Anthraquinone dyes are used extensively in the textile industry as both water soluble anionic reactive and acid dyes as well as water insoluble non-ionic dispersion and vat dyes due to their brightness and strong lightfastness. However, most of these dyes are toxic, carcinogenic, mutagenic and they are much difficult to degrade [23, 24]. Moreover, they are not readily removed by typical wastewater treatment processes due to their fused aromatic structures which remain colored for long periods of time. Therefore, the process of decolorization of anthraquinone dyes has received much attention [25-35]. Due to its alternate supply, low cost, and superior adsorption efficiency, activated carbons are the most often used adsorbent in industrial wastewater treatment.

The present work aims to evaluate the adsorption performance of activated carbon fibers prepared form the waste of polyacrylonitrile fiber for different commercial anthraquinone blue dyes, which are known for their excessively application on almost all textile fabric. Three examples of anionic reactive dye (CI Reactive 19), anionic acid dye (CI Acid Blue 40) and nonionic disperse dye (CI Disperse Blue 56) were chosen as the models of blue anthraquinone-based dyes, based on were proposed. The structural correlation between the dye chemistry and the texture or surface chemistry of the PAN-based activated carbon was studied. The influence of dye concentration and temperature on the removal efficiency of color was thoroughly investigated.

2 Experimental

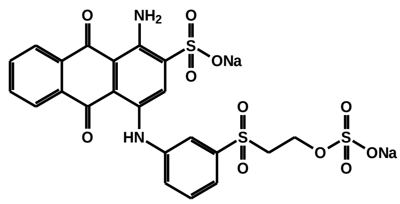
2.1 Materials and Methods

2.1.1 PAN Activated Carbon Fiber

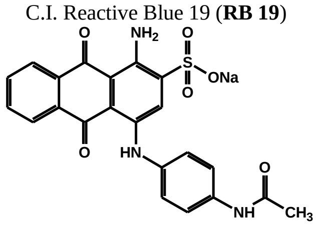
Activated carbon fibers were prepared from polyacrylonitrile fiber (PAN) waste. The pre-treatment of the fibres took place between 200 and 300 °C. Carbonization takes place next at 700–900 °C in an inert environment. The activation at 900–1100 °C with a steam-and/or–CO2 combination was the last stage. Table 1 lists the main features of the prepared PAN-based ACF. The fibres were dried at 105°C after being rinsed in de-ionized water before being used.

2.1.2 Dyes

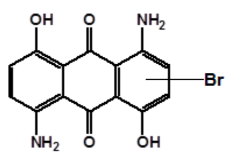
Three commercial anthraquinone-based dyes, Sunzol Brilliant Blue R Special 150% (C.I. Reactive Blue 19) (**RB19**) was obtained from Ohyoung Ind. Co., Ltd; Foron Yellow SE-FL (C.I. Disperse Blue 56) (**DB56**) was kindly supplied by Clariant GmbH; and C.I. Acid Blue 40) (**AB40**) was obtained from Sinochem Ningbo. The chemical structures of the dyes are shown in Figure 1.



C.I. Reactive Blue 19 (**RB 19**)



C.I. Acid Blue 40 (**AB 40**)



C.I. Disperse Blue 56 (**DB 56**)

Figure 1: Anthraquinone dye structures **(RB19**, **AB40** and **DB56)**

2.1.3 Dye Adsorption

The three commercial anthraquinone-based dyes, RB19, AB40, and DB56, were produced as stock solutions (1 g/L) and diluted to the appropriate concentrations with distilled water. Acetic acid and NaOH solutions were used to change the pH from its initial state. Assuming that equilibrium had been established, stoppered Erlenmeyer flasks holding 50 mL of dye solution and ACF dose (0.1 g/L) were stirred for 30 min. at 60 rpm. The samples were filtered out, and the residual dye concentration was analyzed using Shimadzu UV-2401PC UV-Visible spectrophotometer. The absorbance was measured at λ_{max}593, 618 and 623 nm for **RB19**, **AB40** and **DB56**, respectively. The dye adsorption of neutral pH solutions by ACF was studied at a various concentrations of 100, 200 and 300 mg/L. The dye adsorption was repeated at various temperatures 40, 60, 80 and 100 °C, to determine the effect of temperature on the dye adsorption by ACF.

The percentage of dye removal, R%, was calculated according to Eq. (1). The amount of dye adsorbed onto PAN based ACF (mg/g) was obtained using Eq. (2).

$$R\% = \left(\frac{A_1 - A_2}{A_1}\right) \times 100 \qquad (1)$$

Where, A_1 and A_2 are, respectively, the absorbance of the initial and final dye bath solution.

$$D_f = (D_1 - D_2)V/W \qquad (2)$$

Where D_f is the concentration of dye per gram of fibre. The starting and equilibrium dye concentrations in the dye bath are denoted by the letters D_1 and D_2 respectively (in mg/L). W refers for the fibre's weight in grams and V for the dye solution's volume in litres. The Lambert-Beer law was used to calculate the concentration of dye solutions in relation to the individual calibration curves of dyes RB19, AB40, and DB56.

3 Results and Discussion

3.1 Characterization of PAN activated carbon fiber

The microporous structure of PAN based ACF plays an important role on the adsorption capacity. Table 1 shows the textural characteristics of the prepared ACF. From which, high surface area, micropore area, micropore volume and average pore diameter of PAN based ACF was observed. FT-IR spectra of the reference PAN-ACF and **RB19**, **AB40** and **DB56** loaded PAN-ACF were recorded over the wavenumber range 400–4000 cm^{-1} as shown in Figure 2. Same significant bands at 3448, 2958, 1629, 1558 and 1137 cm^{-1} for both PAN-ACF and **RB19**, **AB40** and **DB56** loaded PAN-ACFs were observed. The bands of **RB19**, **AB40** and **DB56** loaded PAN-ACF shifted to higher intensities, which indicated the presence of dye molecules onto PAN-ACF.

Table 1: Total surface area (m^2/g), Microporous surface area (m^2/g) Meso and Macroporous surface area (m^2/g) of PAN based ACF

Surface Area (m^2/g)		Pore Volume (ml/g)	
Total surface area	1085	Total pore volume	0.511
Microporous surface area	813	Microporous pore volume	0.388
Meso and Macroporous surface area	272	Meso and Macroporous pore volume	0.123

Figure 3 shows the SEM images of the **RB19**, **AB40** and **DB56** loaded PAN-ACFs and its pure PAN-ACF sample. It could be seen that the fiber diameter of dye-loaded PAN-ACF were in a higher range of 2-4 nm compared to fiber diameter of PAN-ACF, indicating that dyes were adsorbed on the meso- pore or micropore. Also Figure 3 illustrates that the increase in fiber diameter of dye loaded PAN-ACF following the order **DB56** > **AB40** > **RB19**, as the adsorption capacity of the PAN-ACF and was found to be affected by the dye type.

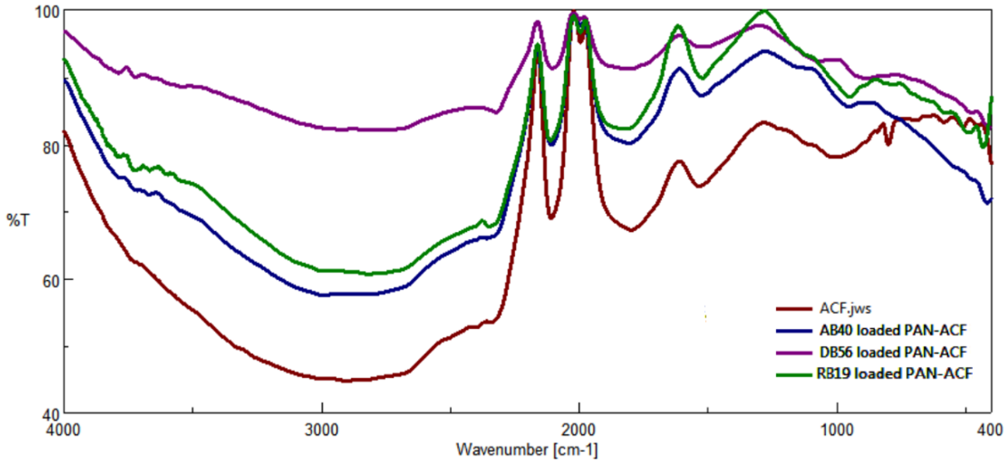


Figure 2: FT-IR spectra for both PAN, PAN-ACF and **RB19**, **AB40** and **DB56** loaded PAN-ACF

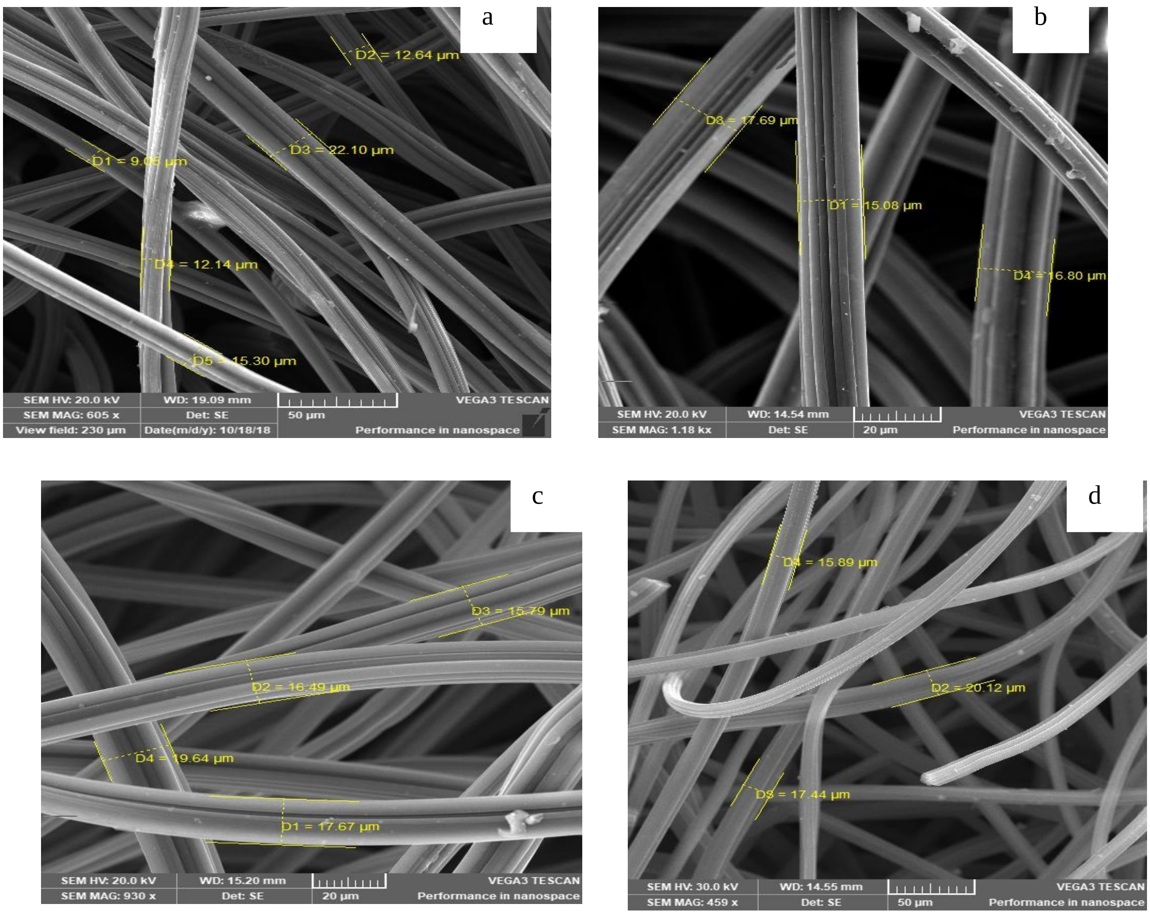


Figure 3: SEM micrographs of (a) PAN-ACF and (b) **RB19** loaded PANACF; (c) **AB40** loaded PAN-ACF; (d) **DB56** loaded PAN-ACF.

3.2 Effect of dye concentration

An essential driving element in the adsorption process is the initial dye concentration. Its impact is crucial in overcoming the impedance to mass transfer between the liquid and solid phases. [36, 37]. Figure 4 shows efficient dyes removal % by ACF which lies on the range of 60-95%. The results obtained from the effect of dye concentration within the range studied (100-300 mg/l) showed that the percentage of dye removal by sorption decreases with increasing the initial dye concentration. This is due to the decrease in the surface area and pore sites available on the surface of ACF with increasing dye concentration. The increase in the numbers of dye molecules will oblige and delay the entrance into the porous structure of ACF. Low removal efficiency of the investigated anthraquinone dyes at higher concentrations is mainly depending on the dye type and the available charges on the dye structures.

The presence of charge on the dye structure will facilitate the physical and/or chemical bond formation with the active groups on the ACF. This can explain why the charged Reactive Blue 19 and Acid Blue 40 dyes are more adsorbed than the uncharged Disperse Blue 56 on ACF structure.

3.3 Effect of temperature

Effect of temperature on the anthraquinone dyes ability to adhere to activated carbon fibre was further investigated by performing the experiment at different adsorption temperatures (40, 60, 80 and 100°C). The relationship between dye adsorption capacity at different concentrations and temperature conditions was presented in Figures 5-8. From which, it was apparent that the highest capacity for adsorption of RB19, AB40 and DB56 increased with increasing temperature. This trend is also applicable even at higher dye concentrations. This phenomenon may be attributed to that, at higher temperature the dye molecules tend to escape from the solid phase into bulk phase [38]. Additionally, the adsorption capacity improved as the starting concentration was raised from 100 to 300 mg/L by raising the temperature from 40 to 100°C, the solutions with greater beginning concentrations had stronger adsorption driving forces compared to the solutions with lower initial concentrations [39]. Also, at high temperature the porous structure of ACF becomes more open for dyes molecules to penetrate through it.

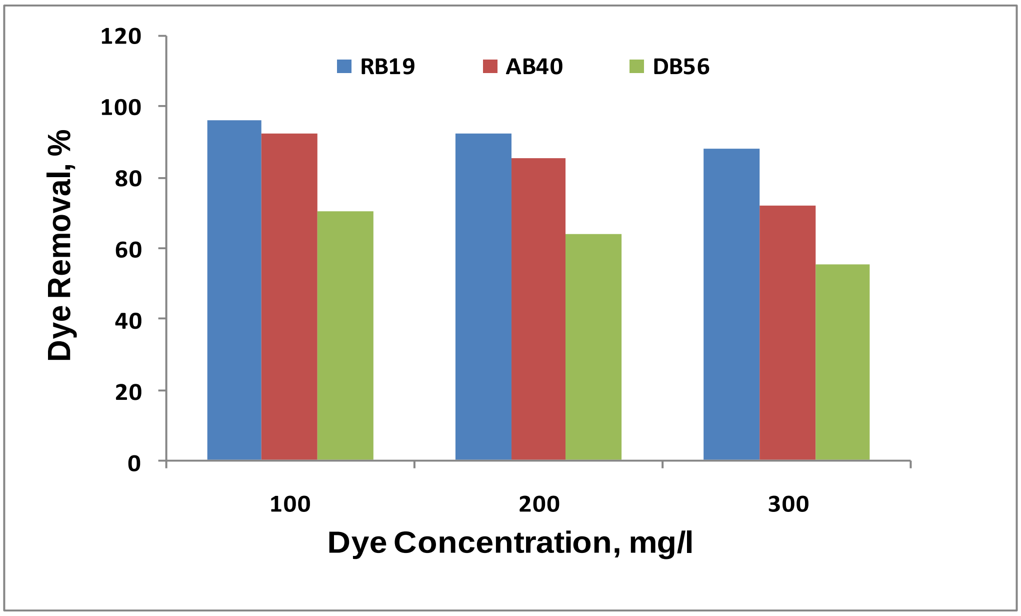


Figure 4: Effect of the dye concentration removal of **RB19**, **AB40** and **DB56** on PAN-ACF (PAN-ACF: 0.1 g, time: 30 min, pH: 7, temperature: 40±1°C).

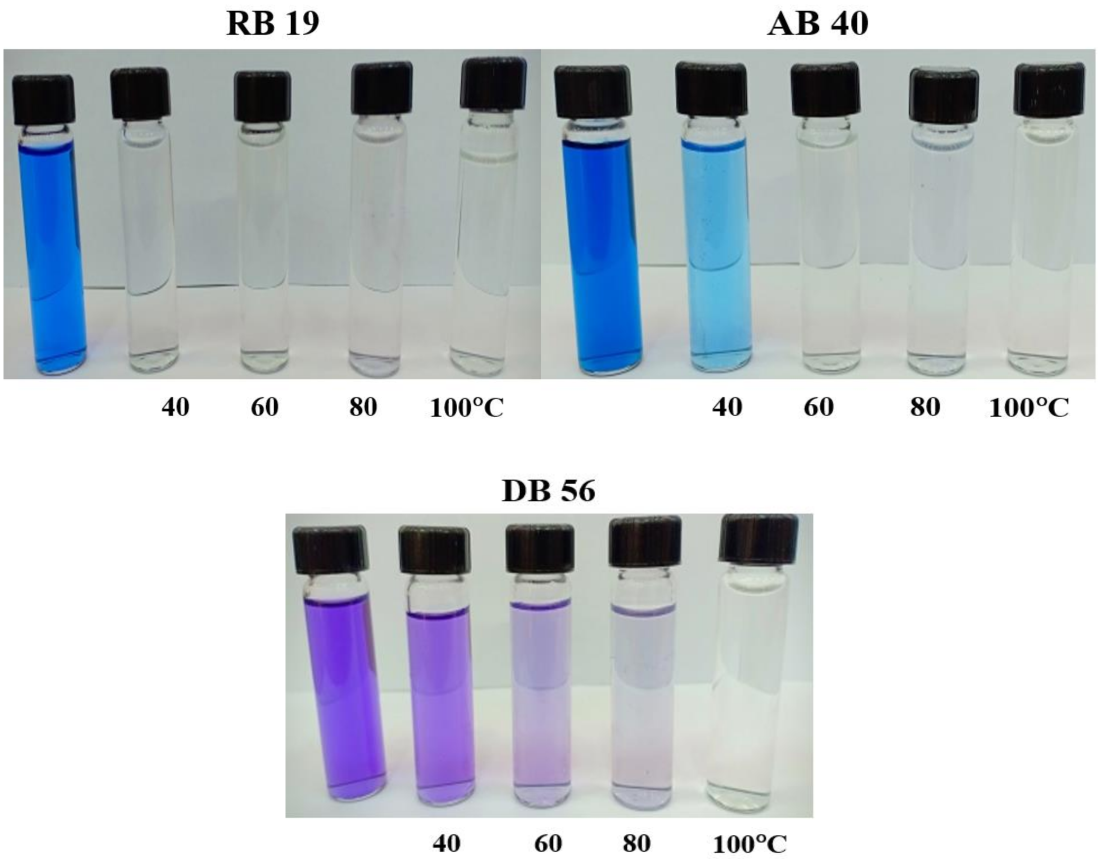


Figure 5a: Effect of temperature on the dye removal of **RB19**, **AB40** and **DB56** on PAN-ACF (Dye concentration: 100 mg/l, PAN-ACF: 0.1 g, time: 30 min, pH: 7 and temperature 40°C, 60°C, 80°C, 100°C).

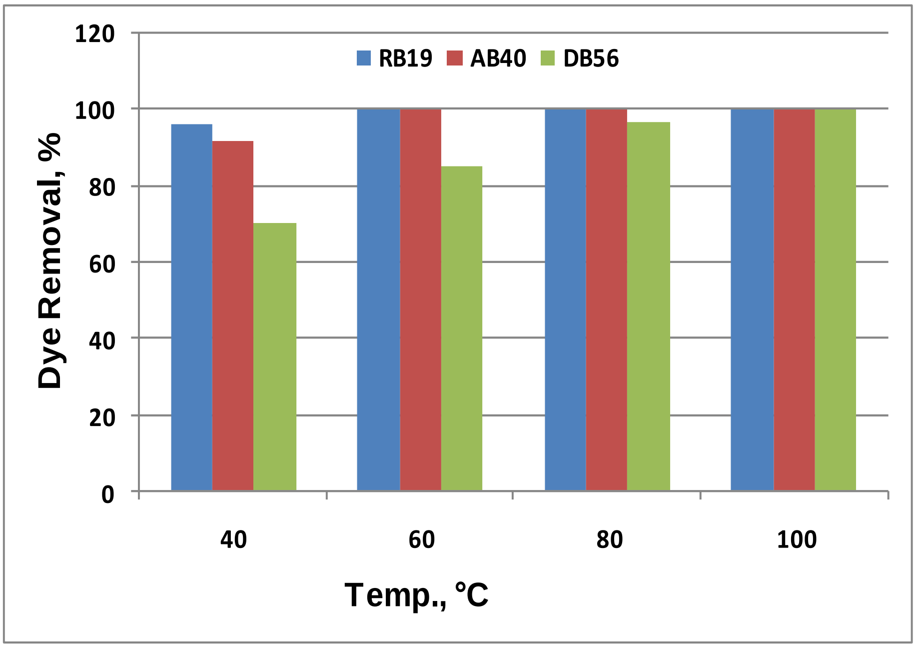


Figure 5b: Effect of temperature on the dye removal of **RB19**, **AB40** and **DB56** on PAN-ACF (Dye concentration: 100 mg/l, ACF: 0.1 g, time: 30 min, pH: 7).

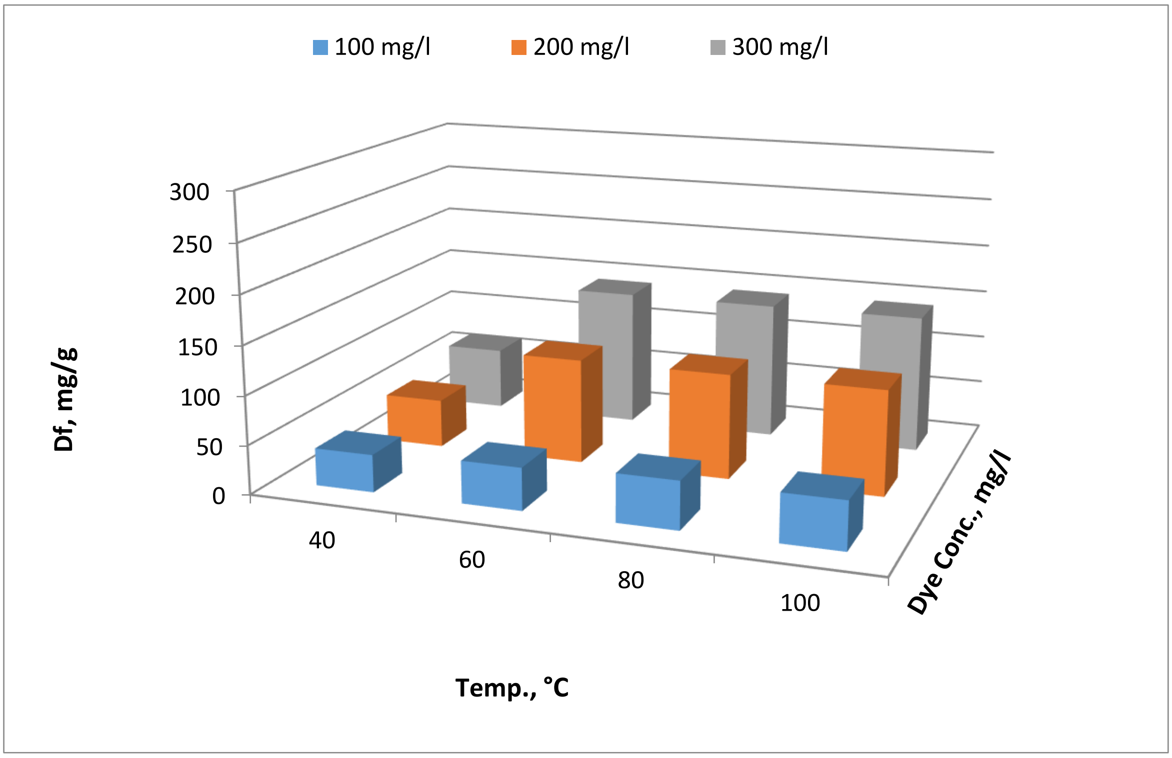


Figure 6 Effect of temperature on the adsorption capacity of **RB19** on PAN-ACF at various dye concentration (RB19 concentration: 100-300 mg/l, PANACF: 0.1 g, time: 30 min, pH: 7)

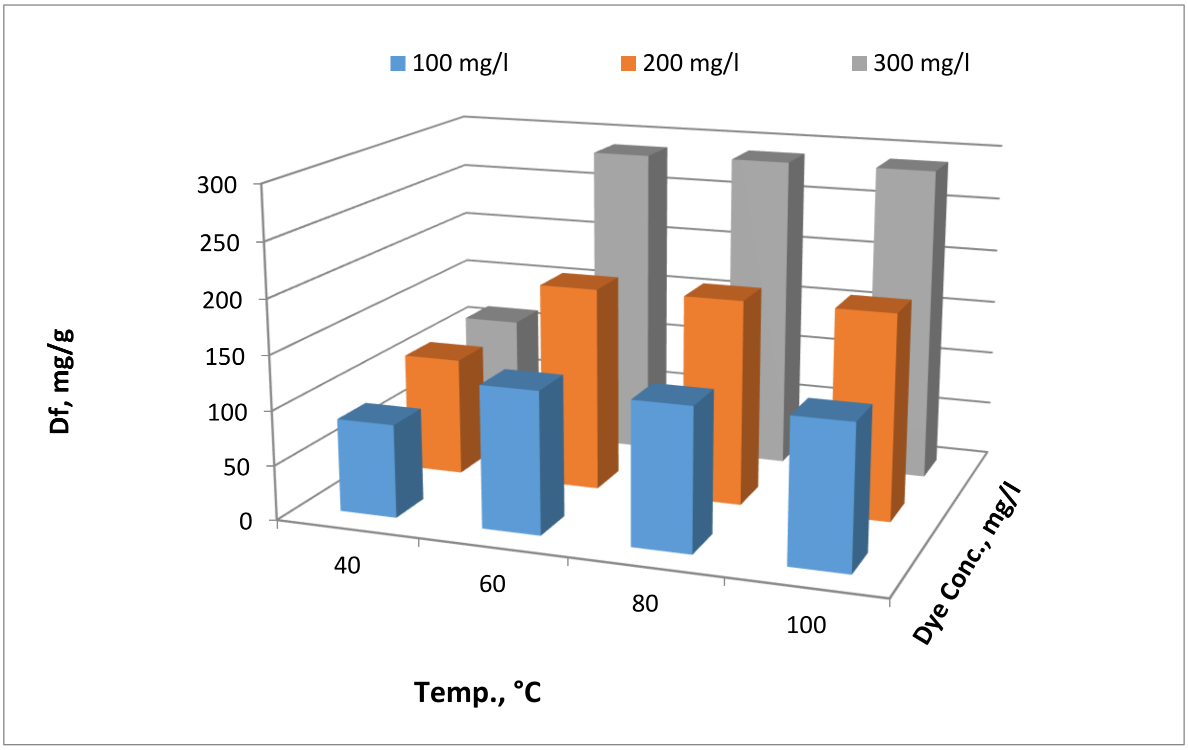


Figure 7: Effect of temperature on the adsorption capacity of **AB40** on PAN-ACF at various dye concentration (AB40 concentration: 100-300 mg/l, PANACF: 0.1 g, time: 30 min, pH: 7)

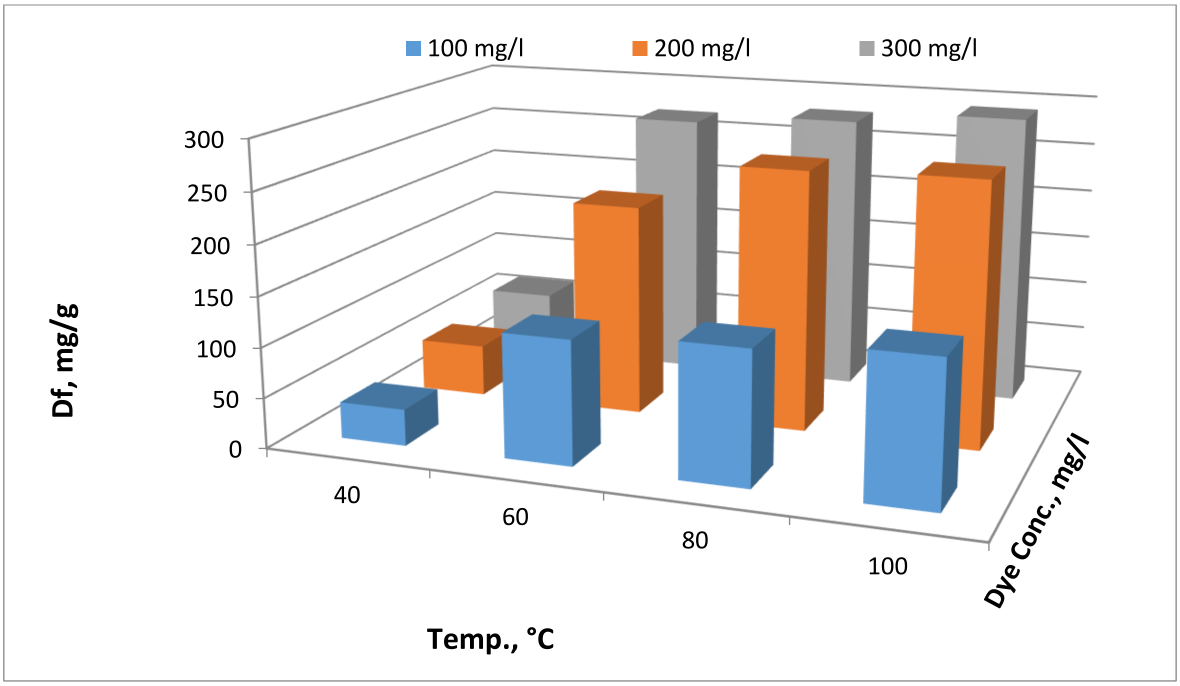


Figure 8: Effect of temperature on the adsorption capacity of **DB56** on PAN-ACF at various dye concentration (DB56 concentration: 100-300 mg/l, PANACF: 0.1 g, time: 30 min, pH: 7)

In this context, the adsorption capacity of PAN-ACF on the removal of the nonionic disperse dye **DB56** from aqueous solutions reaches approximately 290 mg/g at 100 °C. This result is similar to the observation of anionic acid dye **AB40**. While, the adsorption of the anionic reactive dye **RB19** exhibited a moderate value of approximately 142 mg/g at the same temperature.

4. Conclusion

The Polyacrylonitrile based activated carbon PAN-ACF is prepared and applied to the adsorption removal of some commercial nonionic and anionic antharaquinone textile dyes from their aqueous solutions. The PAN-ACF exhibited higher adsorption capacities for the non-ionic antharaquinone disperse dye than those of the anionic based reactive or acid dyes. The adsorption capacity of PAN-ACF on the removal of the nonionic disperse dye **DB56** and the anionic acid dye **AB40** from aqueous solutions reached approximately 290 mg/g at 300 mg/L of the initial dye concentration. The adsorption of the anionic reactive dye **RB19** exhibited a moderate value of approximately 142 mg/g when applied at the same concentration. The adsorption of dyestuffs on PAN-ACF increased with increasing temperature. This success in process optimization for better dye removal at lower dye temperatures would suggest the viability of PAN based ACFs application in industrial scale.

5. Acknowledgements

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6. Conflicts of interest

The authors have no conflicts of interest to declare.

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