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RESEARCH ARTICLE

Adsorption Thermodynamic Study of Congo Red Dye on Electrospun Nanofibers Mat of Polyacrylonitrile

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Abstract

The present study intends to prepare nanofibers mat of polyacrylonitrile by electrospinning technique and investigates their adsorption capacity to Congo red dye from the aqueous solution, after characterize it by different techniques such as FTIR, SEM, EDA, XRD and BET. The influence factors on adsorption were studied including adsorbent dosage, initial concentration, contact time, pH and ionic strength. The results confirmed that the increasing in pH decreases the adsorption capacity. So, the optimum adsorbent dosage, initial concentration and contact time were 0.006 g, 25 mg/L and 150 min respectively. The isotherm models of Freundlich and Langmuir were applied on the experimental adsorption data to evaluate the maximum capacity and energy of adsorption. The experimental data was founded more fitted with Langmuir model. Additional, the thermodynamic parameter changes such ΔG, ΔH and ΔS of adsorption were estimated. The results explained that the adsorption process was exothermic and non-spontaneous.

Keywords: *Electrospinning, Congo red dye, Polyacrylonitrile, Nanofiber, Adsorption.*

Introduction

At recent years, nanofibers mat were occupied a great and wide attention. This due to their superlative properties such as the high ratio of surface area to volume and good mechanical characteristic compared to classical membranes [1]. Electro pinning is easy and simple process to produce a fine fiber through applying a high voltage to overcome surface tension forces in polymer solution.

The droplet (conic form) is distorted at the tip of the syringe where the polymer drop extends towards the grounded collector, during this the solvent dries and is collected as network of fine fibers which has a typical diameter of several hundred nanometers [2-8]. The presence of large surface area in nanofibers is one of the most effective factors in adsorbent surfaces [9, 10]. Polyacrylonitrile is a commercial and cheap material and studied many time to produce nanofibers as adsorbent because of its high adsorption capacity, high recycling rate, high chemical resistance, thermal stability, low flammability and good mechanical properties [11, 20].On the other hand, dyes are among the most prominent industrial pollutants in the aquatic environment which are a great concern to possess their toxic and dangerous substances [21].Congo red among of these dyes which widely used in the textile industry. Furthermore, this dye is toxic, mutagenic and carcinogenic, so it causes many problems for living organism and human, such as gastrointestinal and respiratory diseases as well as the eye and skin irritation.

Thus, removing this dye from water and wastewater is necessary and essential [22, 23]. The physico-chemical processes were used to treat and remove the coloring of industrial wastewater including coagulation, filtration, flocculation, adsorption, ozonoalysis and UV radiation [24, 26]. Adsorption is the simplest and cheapest technique which used in the pollution removal scale. In the present study, a nanofibers mat of polyacrylonitrile was spun by electrospinning technique and characterized by FTIR, SEM, EDA, XRD and

BET techniques. The prepared nanofibers mat considered as an adsorbents to remove Congo red dye from aqueous solution. Many influence factors on the adsorption adsorbent dosage, initial concentration, contact time, pH and ionic strength were scrutinized. Besides, Freundlich and Langmuir isotherm models were applied on the experimental adsorption data to evaluate the maximum capacity and energy of adsorption. Isotherm models of Freundlich Langmuir and were applied on the experimental adsorption data, then thermodynamic study carried out to investigate the adsorption characteristics.

Experimental

Chemicals

Polyacrylonitrile $(C_3H_3N)n$, congo red dye ($C_{32}H_{22}N_6Na_2O_6S_2$), dimethylformamide (DMF), hydrochloric acid (HCl), Sodium hydroxide (NaOH), sodium chloride (NaCl), sodium carbonate (Na_2CO_3) and potassium chloride (KCl). All chemical materials were supplied by Sigma Aldrich.

Instruments

Electro spinning Instrument/NE300/ Invoke noseLTD/ Turkish, spectro photometer/ S8400/Shimadzu/ Japanese, Shaking Water Bath/ S W B-25/ HYSC/ Korean, Hotplate stirrer/ LMS-1003/ LabTech/ Thailand, Mechanical stirrer/ HS-30D /Wisest iv/ Korean, Electronic balance/CPA-22/ Sartorius/ German, Mechanical cutter, Scanning electron microscope/S8000 TESCAN/French, X-Ray diffraction spectrophotometer/ XRD-6000/Shimadzu /Japanese, Atomic force microscope/AA-3000/ Phywe/ German, Thermo gravimetric Analyzer TT-1000/ STA/ German.

Electrospinning Nanofibers Mat

Electro spinning Instrument the electrospinning solution of polyacrylonitrile was prepared with concentration 7% wt/v using DMF as a solvent by continuous stirring at 50° C for 4 h to obtain a homogeneous polymer solution. PAN solution was transferred to a 20 mL plastic syringe connected to a nozzle with diameter 0.9 mm. The electrospinning process was carried out under 30 kV, where the polymer solution was then extended towards the collected cylinder which wrapped with aluminum sheet and the rotating rate was 50 rpm. The distance between the nozzle and the collected electrode was 19 cm and the following rate 0.01 mL/min. The resulting nanofibres mat was placed in a vacuum oven (60° C, 3 h) to evaporate the residual solvent.

Adsorption Experiments

The optimal adsorbent dosage of CR dye adsorption process was studied (10mL) of initial concentration (25 mg/L) at 25° C and for 2 h. The adsorbed quantity of dye by 0.006 g of nanofibres mat was investigated at different values of pH (2, 3, 4, 5 and 6) with (10 mL) of an initial concentration (25 mg/L) at 25° C and for 2 h.

The contact time of determined by contacting 0.006g of nanofibres mat with (10 mL) of an initial concentration 25mg/L 25° C for different times in range (15-180 min). The studies of adsorption isotherm were done by placing (0.006 g) of nanofibers mat with (10 mL) of concentration series of CR dye solution (5, 10, 15, 20, 25 and 30 mg / L) at different temperatures (25, 30, 35 and 400° C) and for the equilibrium time of (150 min). The adsorption quantity was investigated by measuring the absorbance of CR dye solution with UV/V spectrometer at the maximum wavelength, using the following equation [27]:

$$q_e = \frac{(C_o - C_e)V}{w} \dots\dots\dots (1)$$

Where C◦ is the dye initial concentration mg/L, Ce is the equilibrium concentration dye mg/L, V is the dye solution volume L and w is the membrane weight g.

Fig.1: Real Photograph of the prepared nanofibers mat

Preparation of the Adsorbent Mats

The prepared nanofibers mat was cut to a circular piece with a diameter of 2 cm using a mechanical cutting tool, Fig. (1), which were used as an adsorptive surfaces in the adsorption study.

Results and Discussion

FTIR Technique

Infrared spectrum was recorded for PAN nanofibers mat at the frequency range (600-4000 cm^{-1}), Fig. 2. Generally, There are many peaks attributed to groups CH_2, C≡N, C=O, C-O and C-H. The absorption peaks at the range (2940–2870 cm^{-1}) range were assigned to the stretching vibration of the C-H group in CH_2 and CH_3, respectively [28]. While a characteristic absorption peak was observed in the range (2240–2260 cm^{-1}) which attributed to nitrile group C≡N in polyacrylonitrile chains. In addition, the appearance of an absorption peaks at 1735 cm^{-1} and 1234 cm^{-1} were indicated to the presence of C=O and C-O groups respectively due to the oxidation of polyacrylonitrile in the air and the residues of the solvent which used in the electrospinning process.

The peaks at 1527 cm^{-1} and 1620 cm^{-1} were attributed to the resonance of C=O bond . So, the peak appearance at 1450 cm^{-1} relates to the stretching vibration of C-H group [29]. Absorption peaks appeared at 1342 cm^{-1} and 1369 cm^{-1} due to the vibrations of aliphatic group C-H from different positions in CH and CH_2, respectively [29].

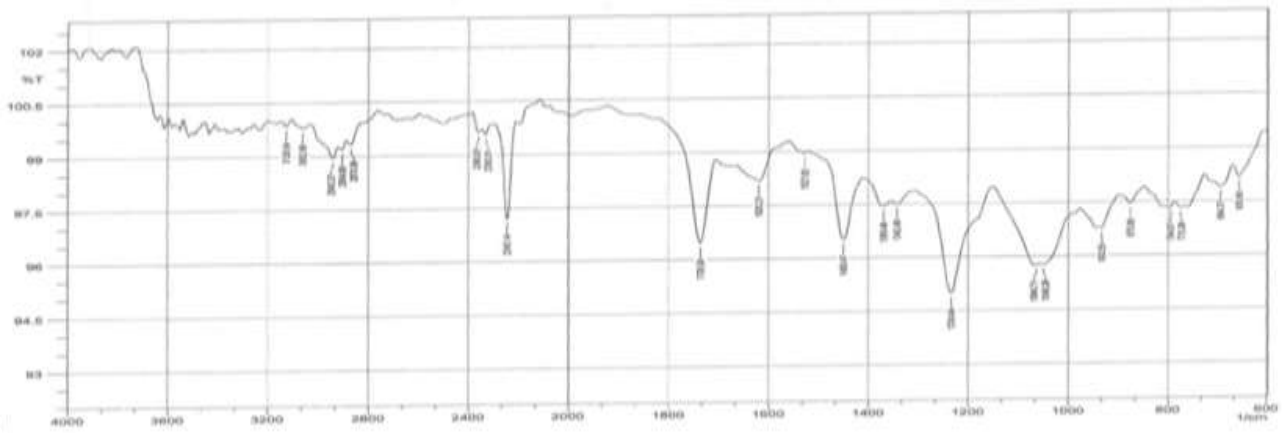


Fig.2: Infrared spectrum of the prepared PAN nanofibers mat

SEM Technique

The SEM micrographs of PAN nanofibers mat are shown in Fig. 3. It can be observed an uniform fibers net and without any drops and beads. Also, the average diameter of the electrospun nanofiber 100 and 200 nm.

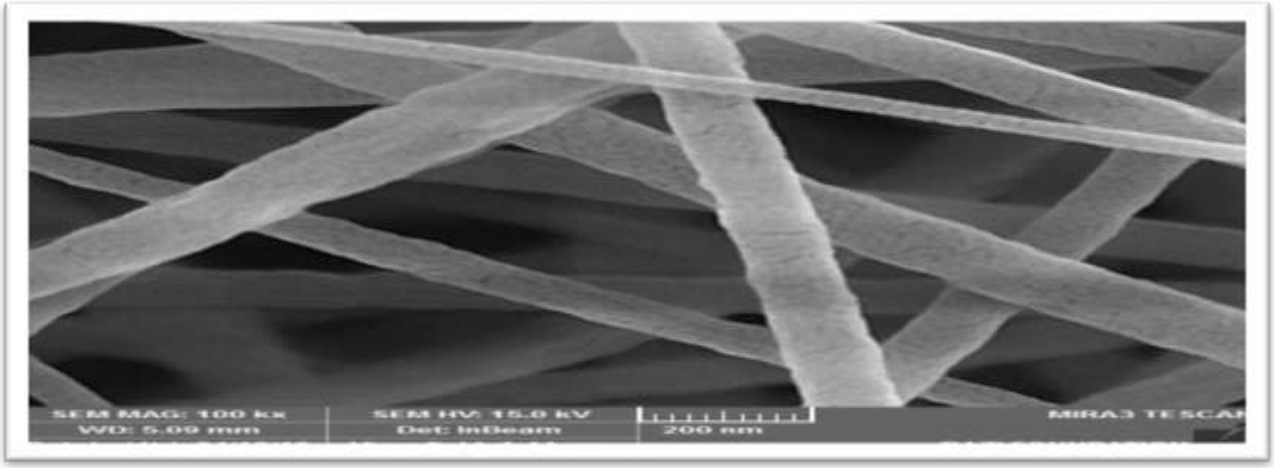
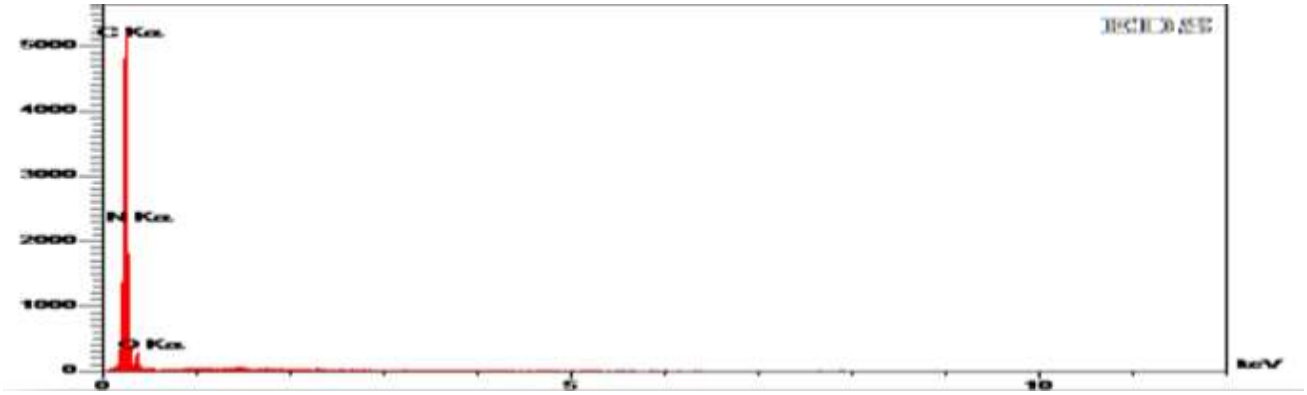


Fig.3: SEM micrograph of SEM the prepared PAN nanofibers mat

EDS Technique

Fig.4 shows the spectrum of (EDX) of PAN nanofibers mat are shown in Fig.4 which indicates the presence of the carbon and nitrogen elements as a main constituents. So, the ratio of oxygen element attributed to the polymer oxidation and solvent residues.



Elt	W%
C	54.97
N	36.78
O	8.25
	100.00

Fig.4: EDS diagram of the prepared PAN nanofibers mat

XRD Technique

Fig.5 shows the X-ray diffraction pattern of PAN nanofibers mat.

It can be seen that, the absence of any sharp peak which indicates to the amorphous form of nanofibers mat.

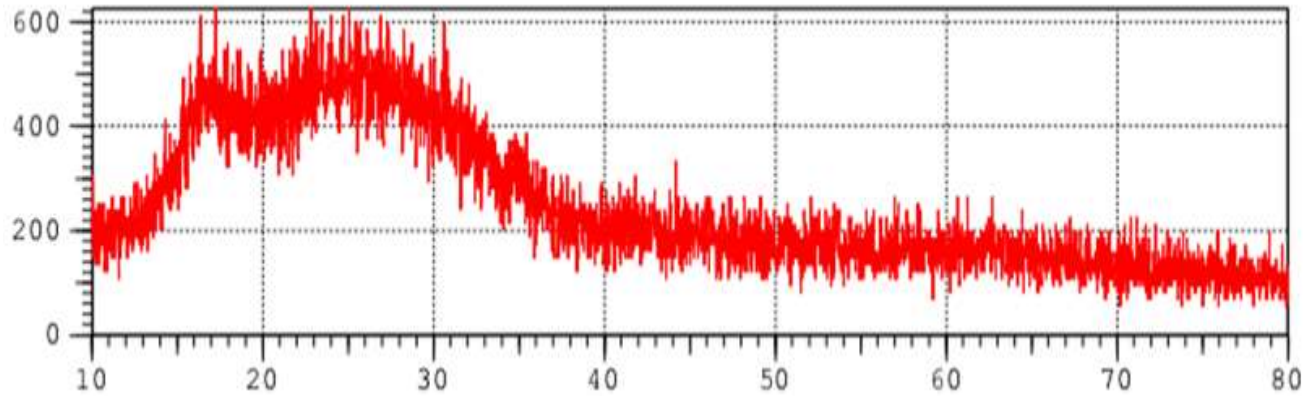


Fig.5: X - ray diffraction patterns of the recorded membrane

TGA Technique

TGA was performed to investigate the thermal degradation of PAN nanofibers mat throw heated to 6000° C with rate 10° C min^{-1} under an atmosphere of argon. Fig. 6 shows the thermo gram of nanofibers mat which had four steps. The first decomposing temperature was 280.80° C with a weight loss 10.7% that may be due to the moisture evaporation. While the second step with a weight loss 32.5% at 350.50° C that attributed to the degradation of fibers structure. The third step with a weight loss 28.6% at 482°C which refers to the nitrile group decomposition. The last loss step was at 594°C with a weight loss 14.6% that indicates to the chains degradation of polymer. It can be noticed, the thermal stability of PAN nanofibers is higher than PAN powder as a result to the increasing of surface area of nanofibers.

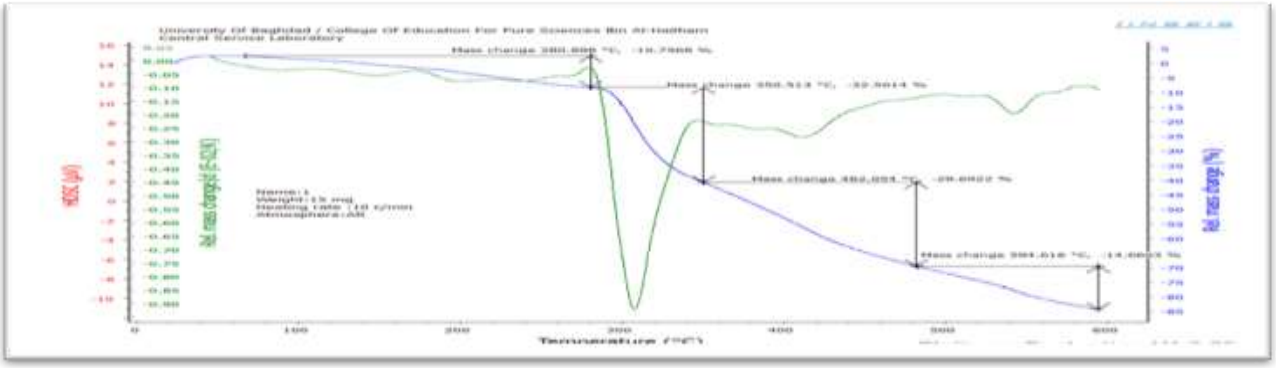


Fig.6: TGA thermograph of the prepared PAN nanofibers mat

BET Technique

The BET and BJH techniques were done to investigate the specific surface area and porosity of the materials. Fig.7 shows Brunner-Emmett-Teller plot of the physical adsorption of nitrogen gas on the surface of PNA nanofibers mat to determine the surface area of nanofibers when the adsorption is multilayer. Nitrogen gas adsorption decreases with increasing gas pressure, which may be due to the insufficient of gas molecules to bind with the nanofibers surface or the morphological incompatibility of the nanofibres surface, while a slight increasing occurs in the amount of adsorptive gas at pressure (P/P_0=0.2269) followed by a larger increasing at pressure (P/P0=0.354). Based on the adsorption data, we note that PAN nanofibers owned a large surface area (5.0524 m^2g^{-1}) and that the total pore size was 0.002255 cm^3g^{-1}, while the pore diameter rate was 1.7853 nm which indicates to that the studied nanofibers is micro pores.

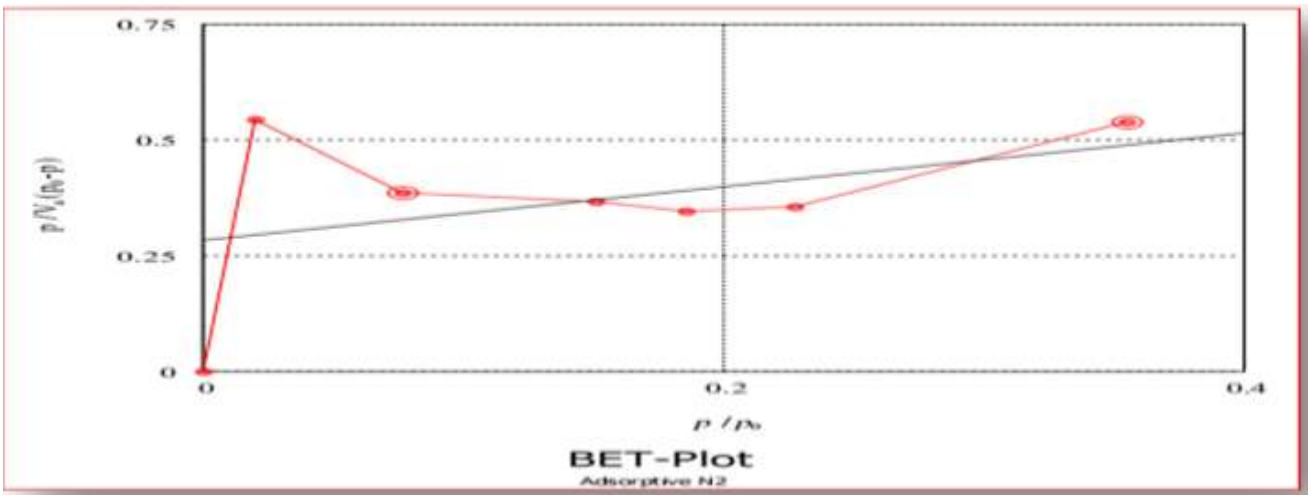


Fig.7: BET plot of the prepared PAN nanofibers mat

The Adsorption Studies

The Adsorbent Weight Effect

The effect of adsorbent weight of the adsorption of CR dye PAN nanofibers mat was studied an initial concentration 25 mg/L at 25 ° C as shown in Fig.8.

The quantity of adsorptive dye increased with increasing the weight of nanofibers mat that attributed to the increasing of the effective adsorption sites. The optimum value was 0.006 g, higher than that the weight becomes ineffective because the arrival of saturation state [30].

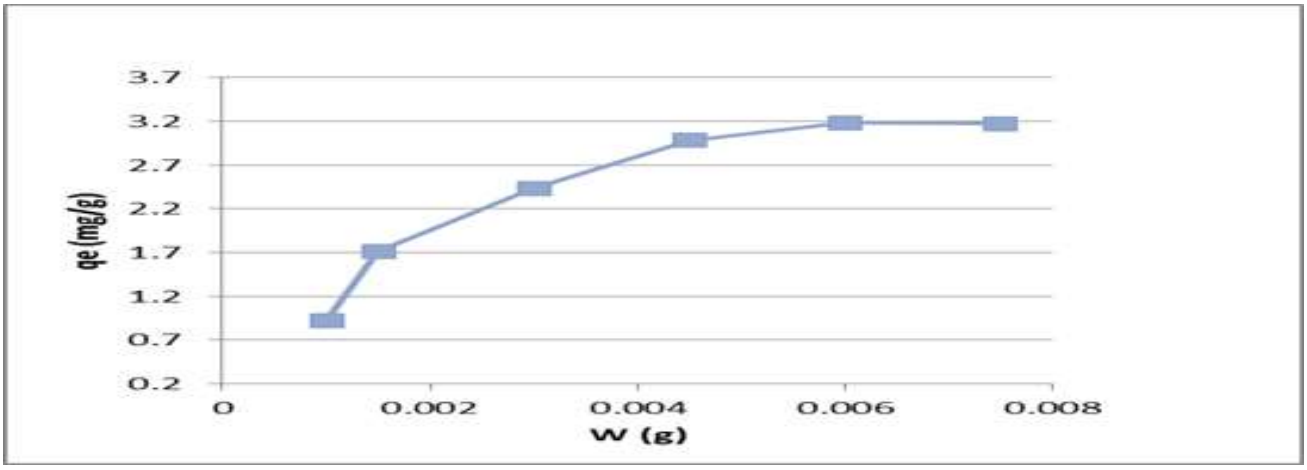


Fig.8: The effect of adsorbent weight

The Initial Concentration Effect

The initial concentration effect of CR dye on PAN nanofibers mat was studied for a range of initial concentrations (5, 10, 15, 20, 25 and 30 mg/L) with 0.006 g at 25oC, as shown in Fig.9. We observe that the adoptive quantity increases with the increasing the initial concentration of dye, as a result to the increasing of average diffusion which leads to the mass transfer on the surface of nanofiber mat [30].

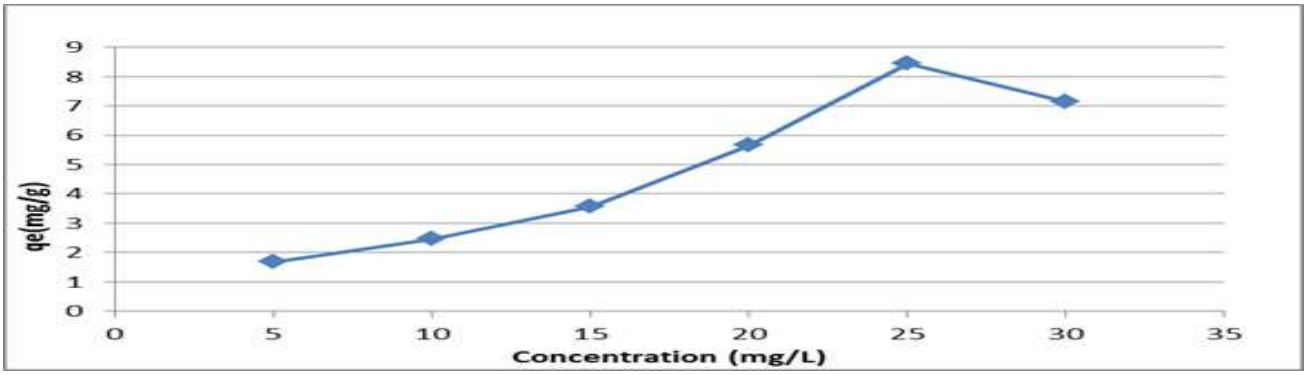


Fig.9: The effect of initial concentration of CR red dye on PAN nanofibers mat

The Contact Time Effect

The contact time effect on the adsorption of CR dye on PAN nanofibers mat was investigated with an initial concentration 25 mg/L and 0.006 g at 25oC, as shown in Fig.10.

The adsorptive quantity increases gradually with the time increasing. After 150 min, the adsorptive quantity becomes relatively slow this attributed to the equilibrium achieving within this period as a result to the occupancy of most active sites of surface nanofibers mat with the dye molecules [31].

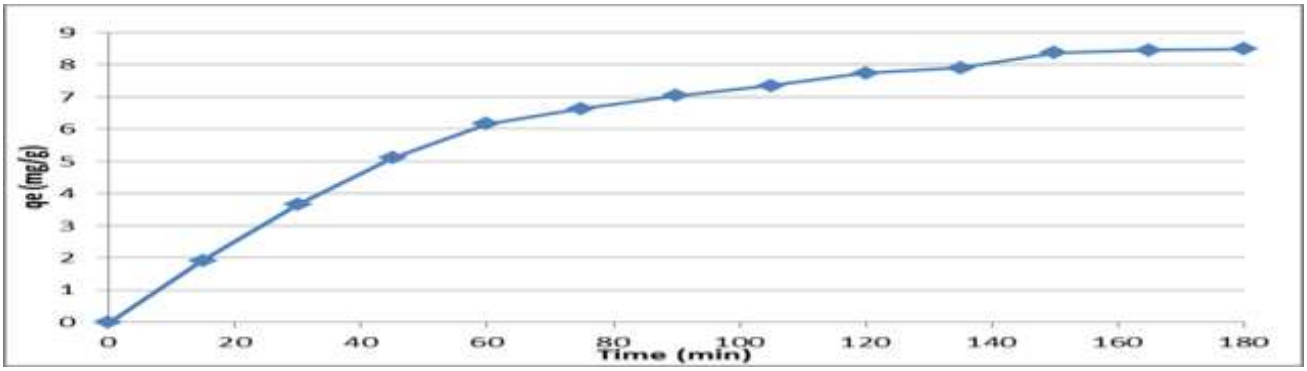


Fig.10: The effect of contact time of CR red dye on PAN nanofibers mat

PH Effect

The effect of pH of the adsorption of CR dye on PAN nanofibers mat was investigated at an initial concentration 25 mg/L and 0.006 g at 25oC, as shown in Fig. 11. The data showed that the adsorption capacity has maximum value at natural medium, then it decreased with higher pH in the solutions. So, an alkaline increases the negative charge of adsorbent which causes an electrostatic repulsion between it and the anionic dye molecules [32].

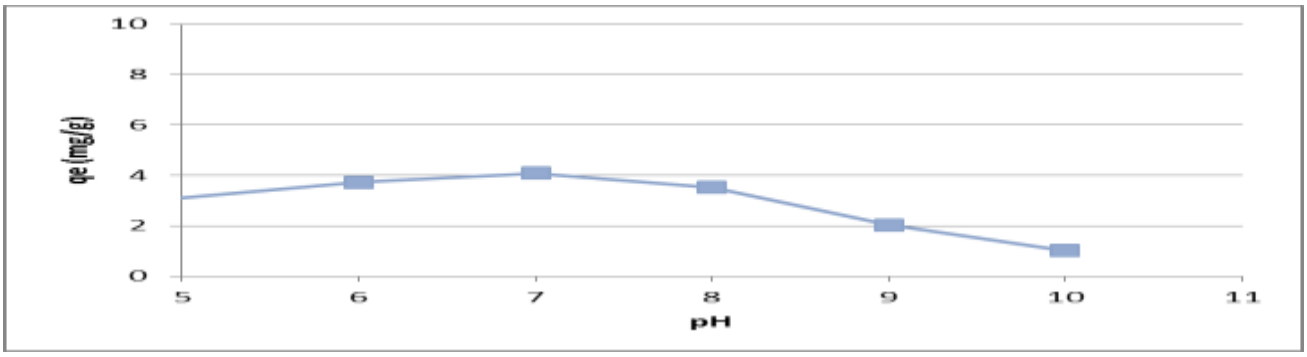


Fig.11: The effect of pH of CR red dye on PAN nanofibers mat

The Ionic Strength Effect

The ionic strength effect of the adsorption of CR dye on PAN nanofibers mat was illustrated by using (0.1, 0.2, 0.3 and 0.4 M) of NaCl and KCl aqueous solutions with an initial concentration 25 mg/L and 0.006 g at 25°C, as shown in Fig. 12.

The results showed that the adsorption capacity increases with the ionic strength increasing. That is due to the fact that the salt in the solution aggregates the molecules of dye and reduces the dye molecule size which leads to the hydrophobicity increasing [33].

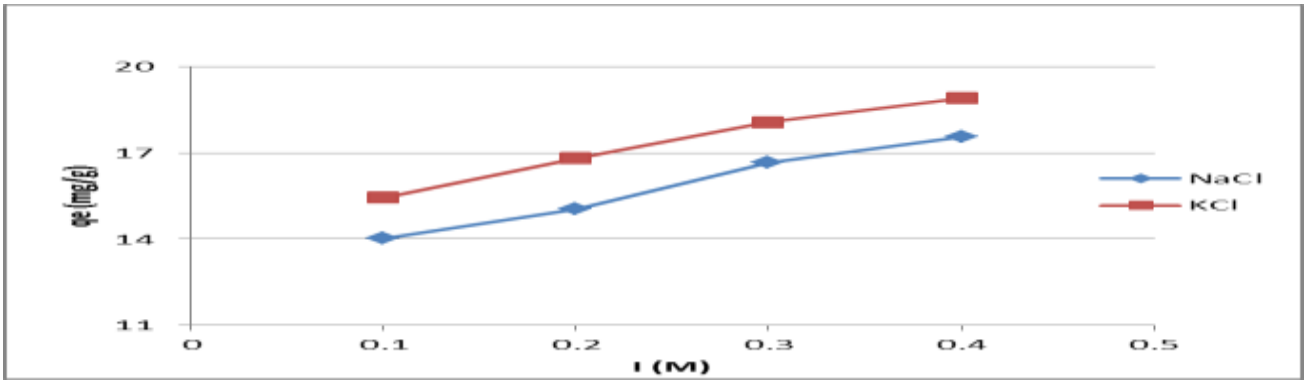


Fig.11: The effect of ionic strength of CR red dye on PAN nanofibers mat

Adsorption Isotherms

The adsorption isotherms represent the relationship between the solution concentration and the adsorbed quantity on adsorbent surface at equilibrium when a temperature is constant. So, the adsorption isotherms describe the nature of the interaction between the adsorbent and adsorbate that are necessary in determining the optimum conditions of the adsorption process [27].

The present study illustrated the adsorption of CR dye from its aqueous solution on PAN nanofibers mat. Langmuir and Freundlich isotherm model have been applied on the adsorption data. Langmuir isotherm confirms the adsorption occurring in a specific site in the adsorbent surface when the adsorption is a monolayer, so the energy of adsorption is distributed homogeneously on the adsorbent surface. The linear form of Langmuir can be expressed as following [34]:

$$\frac{C_e}{q_e} = \frac{1}{q_{max} k_L} + \frac{C_e}{q_{max}} \dots\dots\dots (4)$$

Where qe is the adsorbed dye at equilibrium mg/g, Ce is the adsorbed concentration dye at equilibrium mg/L while q_{max} and k_L is the experimental Langmuir constants.

The values of both Langmuir constants q_{max} and $k_L$can be found through plotting Ce/qe versus Ce. The slope of the straight line represents q_{max} and the intercept illustrates k_L.

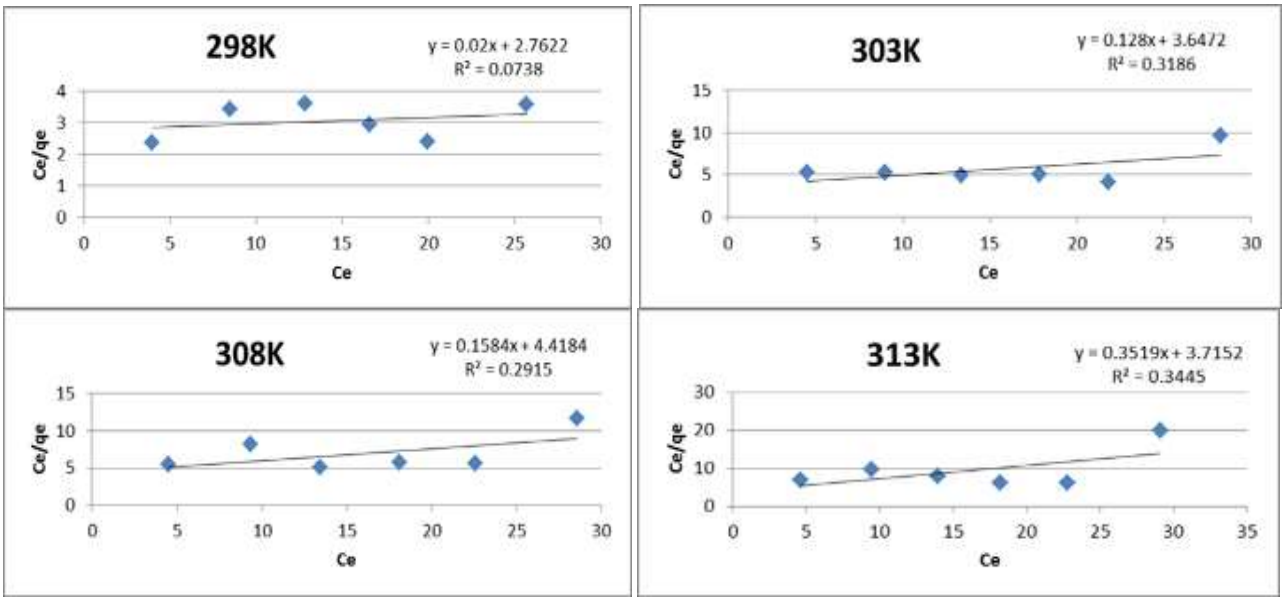


Fig.13: Langmuir isotherm plots of adsorption CR dye on PAN nanofibers mat at the studied temperatures

Table 1: Langmuir constants of adsorption of CR dye on PAN nanofibers mat at the studied temperatures

Thermal degree	R^2	q_{max} (mg\kg)	k_L(L\mg)
298	0.0738	50.76142	0.007131
303	0.3186	7.8125	0.035095
308	0.2915	6.31313	0.03585
313	0.3445	2.84099	0.094743

From the results that observed in Table 1 the values of k_L and q_{max} were oscillating at different studied temperatures. Additionally the average value of correlation coefficient R2 is 0.2571, which indicates Langmuir model is not suitable for the studied adsorption system. Freundlich isotherm model is an empirical equation, which it considers used for heterogeneous adsorbent surface in the energy distribution of active sites. It considers when the adsorption is a [35]. The linear Freundlich equation is expressed as:

$$lnq_e = lnk_F + \frac{1}{n} lnC_e \dots\dots\dots (3)$$

Where qe is the adsorbed dye quantity at the equilibrium mg/g, Ce is the adsorbed dye concentration of at the equilibrium mg/L and k_F or n is the experimental Freundlich constants. k_F and n can be calculated from intercept and slope of plotting ln qe versus ln Ce respectively.

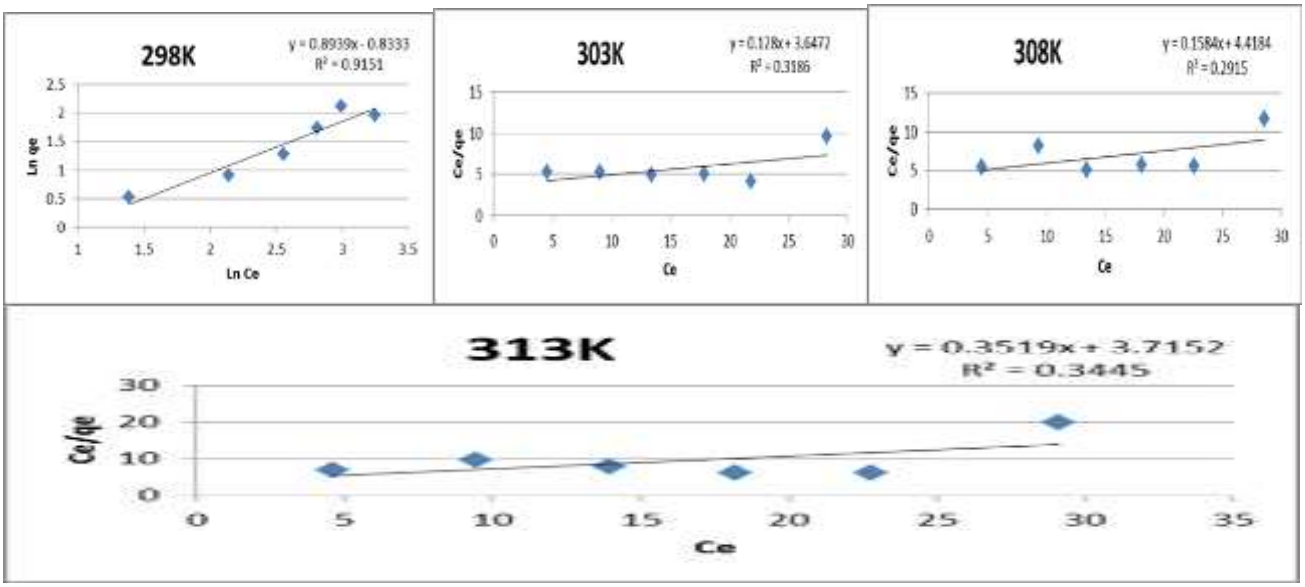


Fig.14: Freundlich isotherm plots of adsorption CR dye on PAN nanofibers mat at the studied temperatures

Table 2: Freundlich constants of adsorption of CR dye on PAN nanofibers mat at the studied temperatures

Thermal degree	R^2	n	k_f (mg/kg)
298	0.9151	1.186	0.433
303	0.8122	1.170	0.294
308	0.7678	1.139	0.247
313	0.5895	1.132	0.227

From the table data, it is can be to noted that the values of Freundlich constant k_F decreases with increasing temperature, that refers to the capacity lowering of adsorption when the temperature is high. Also, the adsorption intensity n decreases with increasing temperature, thus confirming the exothermic nature of the studied adsorption system. Continually, the average value of correlation coefficient R2 is 0.77115, which supports the suitability of Freundlich model to the studied adsorption process. The thermodynamic parameter of adsorption process provides additional information relating with the changes of inherent energy [36-37]. The adsorption thermodynamic parameter such as Gibbs free energy change ΔG^o, enthalpy change ΔH^o and entropy change ΔS^o of the adsorption of CR dye on PAN nanofibers mat were estimated using the following thermodynamic equations:

$$lnk = \frac{-\Delta H^{\circ}}{RT} + constant \dots\dots\dots (5)$$

Where k is the constant of thermodynamic equilibrium, ΔH^o is the enthalpy change of adsorption, R is the universal gas constant, T is the absolute temperature Kelvin.

The enthalpy change was calculated from the slope of the straight line which results from plot of lnk versus 1/T (van't Hoff plot) as shown in Fig.15. The standard free Gibbs energy ΔG^o was estimated from the following equation:

$$\Delta G^{\circ} = -RT\ln k \dots\dots\dots (6)$$

The value of entropy changes (ΔS°) was estimated by an equilibrium Gibbs formula:

$$\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ} \dots\dots\dots (7)$$

The calculated thermodynamic parameters are abstracted in Table 3. As the showed results the negative value of the enthalpy change indicates that the adsorption process is exothermic in nature, this explains that the increase in temperature has increased the kinetic energy of the CR dye molecules which leads separate them from the surface of nanofibers mat and returns to the solution, causing lowering in the adsorption capacity. Besides, the positive value of Gibbs free energy change refers to non-spontaneously of the adsorption process. Additional, all ΔG° values increased with the temperature decreasing which supported a decrease in the CR dye adsorption with increasing temperature, as a result. This is may be due to the molecules mobility increasing of dye in solution then their instability on the surface of PAN nanofibers mat. The negative values of entropy change implies to the ordering increasing of adsorbate-adsorbent interface [38].

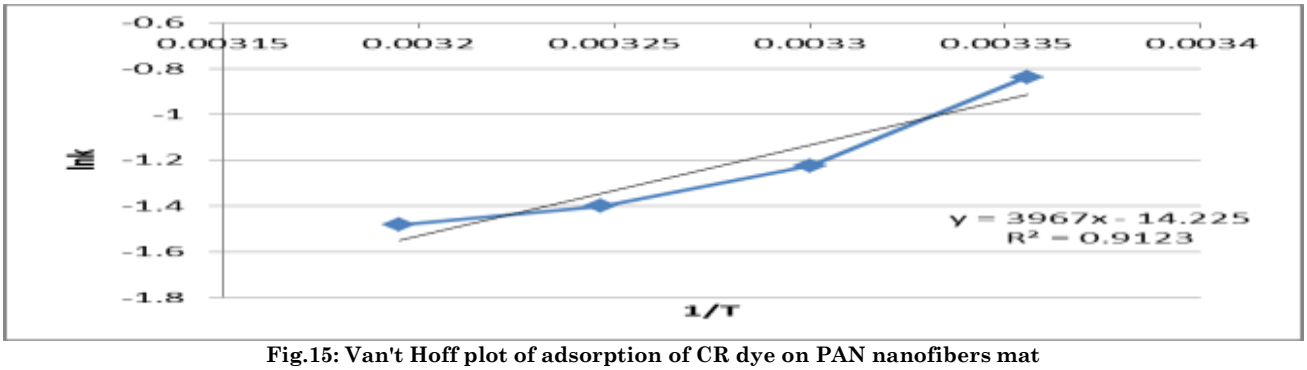


Fig.15: Van't Hoff plot of adsorption of CR dye on PAN nanofibers mat

Table 3: The calculated thermodynamic functions of adsorption of CR dye on PAN nanofibers mat

Thermal degree	S(J/mol)Δ	H(J/mol)Δ	G(J/mol)Δ
298	-119.627	-32981.6	2071.25
303	-119.018		30380.911
308	-118.721		3584.485
313	-117.7		3858.404

Conclusion

Electrospun nanofibers mat of polyacrylonitrile successfully has done for using as adsorbent in the adsorption studying of Congo Red (CR) dye from aqueous solution at a range of temperatures, then characterized by different techniques such as FTIR, SEM, EDA, XRD and BET. The influence factors on the adsorption process were studied. Freundlich and Langmuir constants have been calculated for the adsorption system. The results indicated that experimental data was more fitted with Langmuir model. So, the thermodynamic investigation showed that the adsorption of CR dye on PAN nanofibers mat was exothermic and non-spontaneous.

Acknowledgement

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