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Efficient removal of reactive blue 19 dye by co-electrospun nanofibers

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Abstract: The present work demonstrates the new nanofiber mats prepared through co-electrospinning of two different polymers i.e. corn protein namely Zein and Nylon-6. The composite nanofiber membrane was used as an effective adsorbent material for the removal of toxic reactive dye i.e. Reactive Blue 19 (RB 19) from water solution. These co-electrospun nanofibers had good mechanical strength compared to zein nanofibers alone. Experimental results suggested that zein/nylon nanofibers have greater potential for total removal of RB19 at room temperature within 10 min of contact time from aqueous solution. The maximum capacity was found to be 70 mg/g of nanofibers. The mechanism of RB19 removal on proposed nanofibers is mainly through hydrogen bond and electrostatic means.

Keywords: Zein; nanocomposite membrane; adsorption; wastewater; RB19.

1. Introduction

Industries like textile, leather, paper, rubber and many other produce large amount of wastewater that is characterized by strong color content, high COD and other total suspended and dissolved solids [1, 2]. The discharge of dye loaded effluent in water environment is highly undesirable for both aquatic health and esthetical point of view [3]. Moreover, some of the azo dyes and their metabolites are known to be potentially toxic and carcinogenic, due to their complex chemical structure [4]. Therefore, the removal of such dyestuff is highly desirous. For the removal of dyes, various treatment methods have been employed such as; photo-chemical degradation, advance oxidation, ozonation, coagulation-flocculation and etc. [5]. Among these aforementioned methods, adsorption is the most simple, low cost and highly efficient process for exclusion of various pollutants including synthetic dyestuff [6]. However, the major concern in this method is selection of adsorbent material with superior adsorption capacity and cheapness [7]. Previously, a wide range of low cost adsorbents such as; cashew apple bagasse [8], pomegranate based activated carbon [9], rice straw fly ash [10], peanut hull [11], spent tea leaves [12], etc. were utilized for the removal of reactive dyes from aqueous solution. However, the adsorption capacities of these materials were low and

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required longer pre-treatment steps [13].In context to this, the exploration of one dimensional nanoscale adsorbent especially nanofibers possess good performance due to their unique properties; such as high surface to low volume ratio, highly porous morphology and better interconnectivity [14]. To produce the nanofibers, one of the simple low cost methods is electrospinning in which an external electric field is imposed to polymer solution to fabricate a nanofibers with a diameter of submicron to nanoscale [15].

In recent years, the electrospinning of natural biopolymer from renewable sources such as Zein has received much attention, due to its economic and environmental perspectives [16]. Zein is a biological macromolecule that is biodegradable, nontoxic and biocompatible polymeric protein. It is used for several applications including food packaging, drug delivery, encapsulation and etc. [17]. Apart from these applications zein nanofibers membrane is also reported as an adsorbent for reactive dyes removal through surface modification [18]. However, the poor stability and strength of zein nanofibers in aqueous medium is still a matter of concern to be fixed [19]. When zein nanofiber immersed in aqueous solution, the nanofiber mates get swollen and eventually collapse into films owing to distortion of interconnected pore structure [20]. One of the approach to improve the properties of zein nanofiber is the blending of material that should be strong and water stable [21]. Therefore, in this study zein was incorporated with nylon-6 via co-electrospinning technique to enhance the material strength and stability in water. The objective of this study is to explore the feasibility of zein/nylon co-electrospun nanofibers as adsorbent for the removal of commonly used anionic dye i.e. Reactive blue19, from aqueous solution by studying the influence of several parameters including contact time, adsorbent dosage, dye concentration, and pH of solution.

2. Materials and Methods

Zein from corn (melting point 266-283°C) was purchased from Wako Pure Chemical Industries, Ltd. Japan, Nylon-6((*Mw*~ 25,000 g/mol), Formic acid (98%) purity was supplied by Sigma Aldrich. C.I reactive blue 19 ($C_{22}H_{16}N_2Na_2O_{11}$) with a molecular weight (626.54 g/mol) were supplied by the Sumitomo Chemical Company, Ltd., Japan. The chemical structure of the used dye is given in the Fig-1.

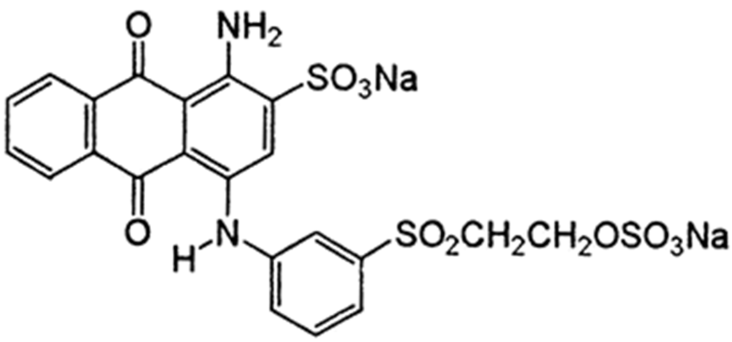

Fig-1. Chemical structure of Reactive blue (RB19)

The preparation of coelectrospun nanofibers is mentioned as :

A solution of 60 %(wt./v) zein was prepared in DMF followed by stirring for 2 hour at room temperature. Nylon-6 polymer of 22 %(wt. /v) was also prepared separately in formic acid under constant stirring for 24 h at room temperature to obtain a homogeneous solution. Both these solutions were loaded separately onto 5 ml plastic syringes with an inner diameter of 0.6 mm and were positioned oppositely at an angle of 10° from the horizontal plane, and co-electrospinning was performed simultaneously, at 20kV having tip to collector distance of 15 cm an 20 cm for both zein and nylon-6 solutions, respectively, the grounded rotating metallic drum covered with aluminum

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foil was used for the deposition of zein/nylon electrospun nanofibers. After completion of co-electrospinning, the samples were dried overnight at room temperature prior to adsorption experiments. The average thickness of zein/nylon nanofibers was found to be 51±2µm.

The adsorption behavior of anionic dye RB19 from aqueous solution on zein/nylon co-electrospun nanofiber membrane were studied at room temperature using the batch mode, the experiments were performed on an automatic gallenkamp shaker by mixing a fixed adsorbent dose (20±0.2 mg) of nanofiber membrane in 5ml of 50mg/l of dye concentration at 200rpm, the solution was shaken until the equilibrium was achieved. In order to evaluate the efficacy of dyes removal by the adsorbent, following parameters were analyzed; Contact time (1-10min), pH solution (1-9), adsorbent dosage (5-25mg), and initial dye concentration (50-300ppm).After the dye adsorption, the nanofiber membrane were separated out manually and the samples were analyzed by Uv-vis spectrophotometer for the residual dye concentration at wavelength of (λmax-592nm) for RB19.

Dye removal percentage (AE %) was determined according to the following eq.

$$\text{Dye removal (AE \%)} = \frac{(C_o - C_t)}{C_t} \times 100 \qquad (1)$$

Where C_0 (mg/l) and C_t (mg/l) are the initial and final dye concentrations at time t, respectively. To compare the validity of kinetic and isotherm models, error analysis was also established using following relation.

$$\textbf{SSE} = \sum_{i=1}^{N} (q_{cal} - q_{\exp})^2 \qquad (2)$$

Where, q_{cal} and q_{exp} are the calculated and experimental adsorption capacities of zein/nylon nanofibers, respectively.

The surface morphology of zein/nylon co-electrospun nanofibers membrane before and after adsorption was examined using SEM (S3000N by Hitachi, japan) with accelerating voltage of 10kV and maximum magnification of 300,000x after sputtering with Au/Pd. The average diameter of nanofiber was measured using J-image analysis software (image pro R plus, version5.1, Media cybernetics, Inc.) from SEM micrographs. The chemical structure of zein/nylon nanofibers membrane was characterized by FTIR spectroscopy (IR presige-21 by Schimadzu, japan) using ATR mode. Ultraviolet-visible (uv-vis) spectrophotometer (Perkin Elmer, USA) was used to measure absorbance of dye solution before and after adsorption experiments. Tensile properties of the zein/nylon nanofibers membrane was determined using titan universal tester (titan 3-910) at jog speed of 1000mm/min. All the tests were performed at room temperature (23–25 ^{0}C) followed by ASTM D-638 Standard test method.

3. Results

3.1. Characterization

The SEM images of neat Zein, Nylon-6 and composite of zein/nylon nanofibers is presented in Fig-2 (a, b and c). The morphology of zein and nylon-6 nanofibers were bead free and smooth. The average mean diameter of zein, nylon-6 and zein/nylon nanofiber were found to be 130, 100, 150 nm respectively (Fig-2 d, e and f)

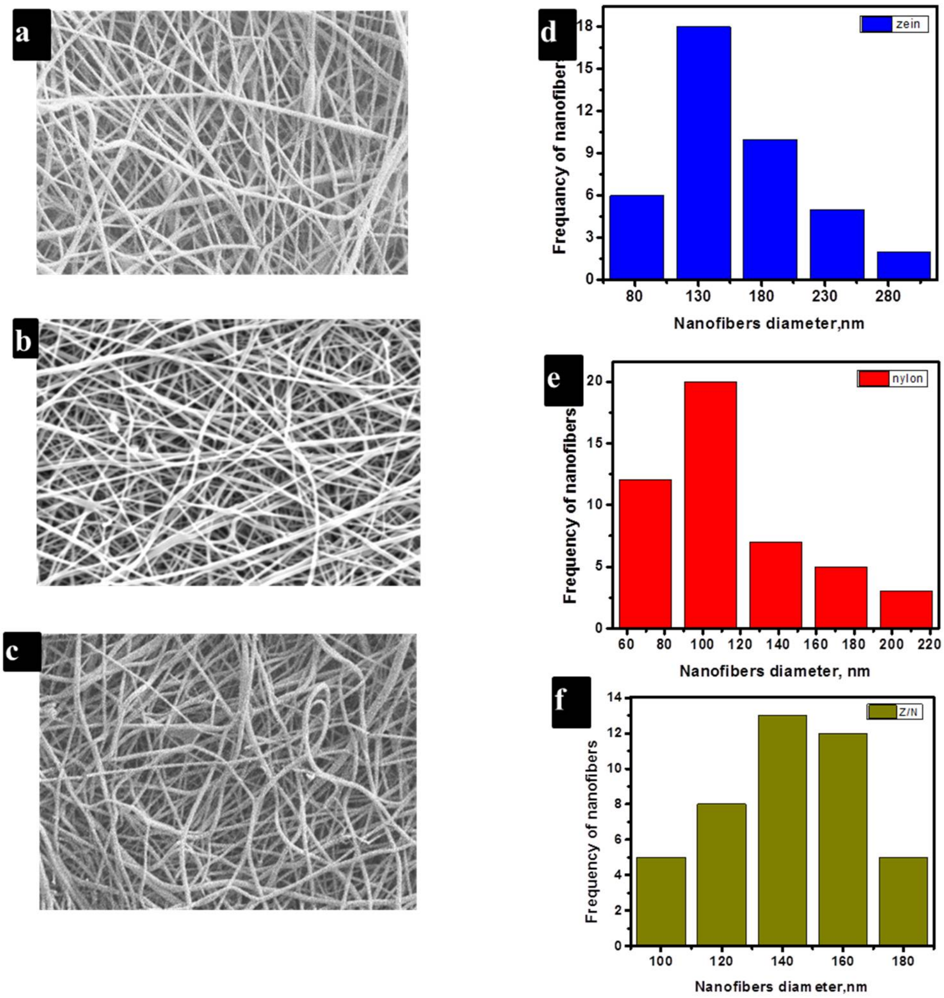

Fig-2 (a, b, c) shows the SEM images of zein, nylon and zein/nylon nanofibers with their respective diameter distribution diagram (d, e, f)).

The chemical analyses of neat zein, pure nylon and blended zein/nylon nanofibers were performed using ATR-FTIR, in order to corroborate functional groups present in the nanofibers. The FTIR spectra of nanofibers in the range of 1000-4000 cm-1 are demonstrated in Fig-3.The broad absorption peak at 3300 cm-1 of neat zein nanofibers as shown in spectrum Fig -3(a) related to (-NH2 stretching vibration). Whereas, the characteristic bands indicative of amide vibrational bands at 1655, 1584, 1478 and 1335 cm−1 indicated amide I, amide II, and amide III; correspond to(C=O) stretching ,(N-H) bending and axial deformation vibrations of (C-N) stretching respectively [23]. On the other hand spectrum (b) shows the absorption band of nylon-6. The peaks at 3308 cm^{-1} and 2850 cm^{-1} is mainly related with NH stretching and –CH symmetric stretching vibrations, respectively. The amide vibrational bands at 1642cm−1 (amide I, C=O stretch), and 1542 cm−1 (amide II, C–N stretch and CO–N–H bend). Additionally, the peak at 680 is indicative of (O-C-N) bending [24]. The peak of 1616 cm−1 (amide I) is observed for the zein /nylon which is attributed to the amino groups of blend nanofibers. The spectrum (c) of blended zein/nylon nanofibers show that the, amide I, amide II, peaks were slightly shifted to lower wavenumber for zein/nylon nanofibers when compared to pure zein and nylon nanofibers. For instance, the amide I peak was observed at 1616 for zein/ nylon, similarly, the amide II peak was shifted to lower wavenumber as absorption peak of amide II was observed at 1536, for zein/nylon. The peak shift of amide I and amide II to lower wavenumbers for zein/nylon nanofibers suggested the interaction became more pronounced for nanofibers samples. In fact the region from 3400-2800 of zein/nylon nanofibers resembles with nylon-6 FTIR region,

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while the region from 1700-500 cm-1 closely resemble with zein component. This confirms successful blending of two different polymers.

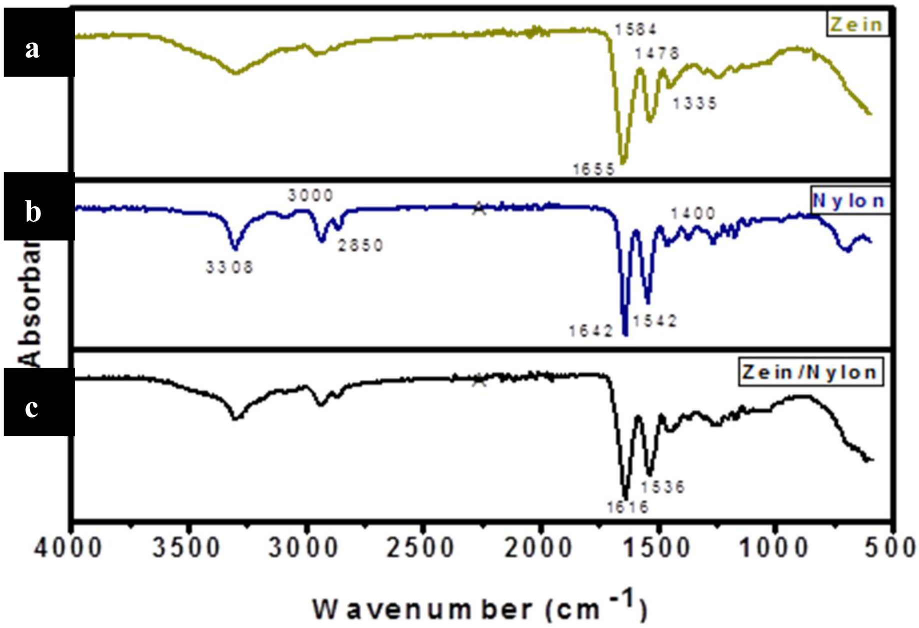

Fig-3 ATR-FTIR spectra of (a) zein (b) nylon and (c) blended zein/nylon nanofibers

Fig-4 shows the mechanical behavior of zein, nylon-6 and both zein/nylon-6 nanofibers. The low tensile force of zein nanofibers indicate poor mechanical strength. Incorporation of nylon with zein nanofibers increase the amide linkages between the zein and nylon resulting more compact structure, thus slippage is reduced and elasticity improved which provide good mechanical properties. Tensile strength of zein/nylon was found to be 3MPa at break of 40%.

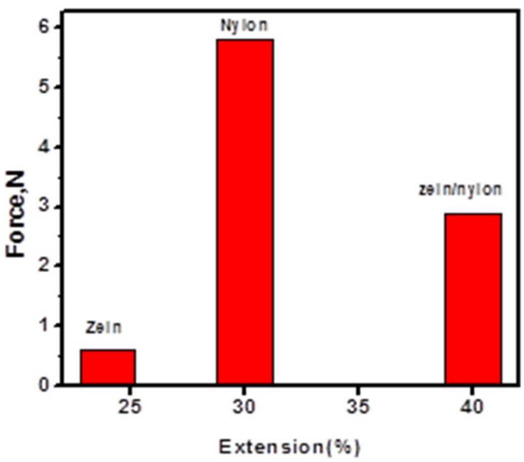

Fig -4. Typical force-elongation performance of zein, nylon and zein/nylon-6 nanofibers

3.2. *Adsorption study of nanofibers*

3.2.1. **Effect of contact time** :

In order to reach to the best material for RB19 removal, it was realized to compare the adsorption efficiencies of Zein nanofiber, Nylon-6 nanofiber and Zein/Nylon-6 nanofibers. The preliminary results suggested that Zein/Nylon-6 nanofibers were comparatively better for RB19 removal followed by Zein nanofibers and Nylon-6 nanofibers. Therefore, further optimization was made on composite nanofibers. Decolorization of RB19 from aqueous solution was investigated at different time intervals to attain the maximum adsorption by the zein/nylon nanofibers as presented in the Fig-5. It is clearly shown that, the rapid and significant removal of RB19 by the nanofibers membrane. was found to be 85% in just 60 seconds of contact and within 10min of shortest equilibrium time, the total dye was decolorized, which is relatively higher than other well-known adsorbents. The rapid uptake of dye is due to faster rate of dye mobility towards the abundant vacant sites of the adsorbent. After certain period of time the rate of adsorption was observed to be slightly down this trend may be due to accretion of dye molecules onto available sites [26]. This breakthrough performance of zein/nylon nanofibers is significant for industrial application due to its high efficiency at minimum time.

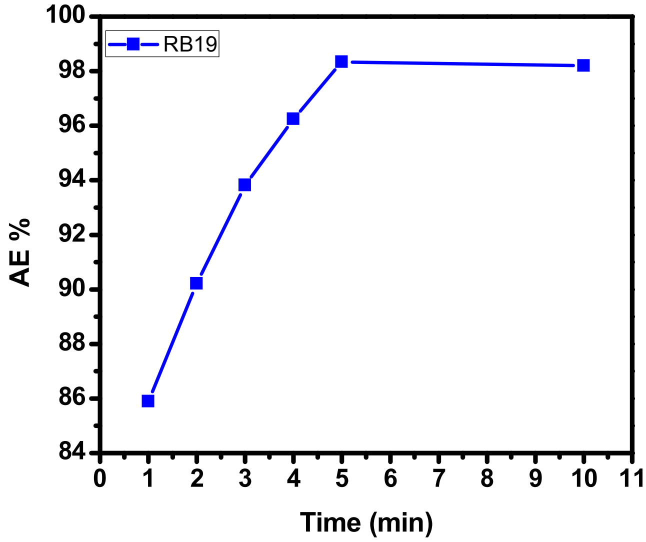

Fig-5. Effect of contact time on adsorption of dye

To calculate the amount of dye adsorbed, different models such as, pseudo-first-order (Eq 1), pseudo-second -order kinetic (Eq 2) and intraparticle diffusion models (Eq 3) were used [27-29].

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}t \quad (1)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (2)$$

$$q_t = k_i t^{0.5} + c$$
(3)

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Where q_t (mg/g) is the dye concentration on nanofibers at the time t, q_e (mg/L) is the solution phase concentration of RB19 at equilibrium. k_1 (min^{-1}), k_2 (g/mg.min) and ki (mg/g.$min^{0.5}$) are the rate constants associated with pseudo first, pseudo second and intra particle diffusion models respectively. The calculated kinetics parameters and the correlation coefficients (R^2) are given in Table 1. Analysis and validation of experimental data to different models suggested that the adsorption of RB19 can be better explained by pseudo second order model rather than pseudo first order as shown in Fig-6 (a) and (b). The correlation coefficients values (R^2) for RB19 obtained from the Pseudo-second-order kinetic model were found to be over 0.99 which is greater than pseudo first order. Also the experimental values of q_e are very similar to the values calculated by the pseudo-second-order equation (q_{ecal}). Thus, the adsorption can be better described by the pseudo-second-order kinetic model rather than the pseudo-first-order kinetic model. The best fit of the second-order expression suggests that the chemisorption mechanism is involved in the adsorption [30].

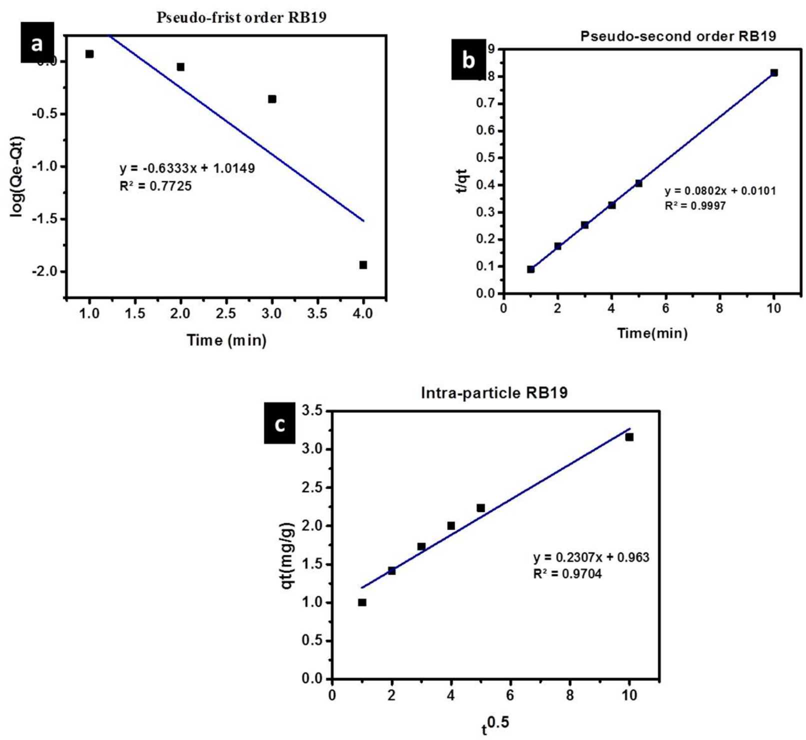

Fig-6 (a) pseudo-first (b) pseudo-second order kinetics (c) intra-particle diffusion RB19

To determine the rate-limiting step involved in the adsorption of dyes by the adsorbent, the intra-particle diffusion model was applied to analyze the kinetic data, according to this model the plot q_t vs $t^{0.5}$ must be linear and should pass through the origin for rate controlling mechanism in intra particle diffusion model. Fig-6(c) clearly shows that adsorption of RB19 on zein/nylon nanofiber consists linear plot between q_t vs. $t^{0.5}$ without passing through origin that does not favor intraparticle diffusion mechanism but external diffusion or surface adsorption is the rate controlling step.

Table 1. Kinetic fittings and parameters for the adsorption of RB19 on Zein/nylon-6 nanofibers

Pseudo-first order			
$q_{e, exp}$ **(mg/g)**	$q_{e, cal}$ **(mg/g)**	k_1 **(min^{-1})**	R^2
12.27	10.32	1.458	0.77

Pseudo-second order			
$q_{e, exp}$ **(mg/g)**	$q_{e, cal}$ **(mg/g)**	k_2 **(g/mg.min)**	R^2
12.27	12.46	0.632	0.99

Intraparticle Diffusion		
k_i(mg/g.min$^{0.5}$)	**c**	**R^2**
0.23	0.963	0.97

3.2.2 The effect of pH on adsorption.

The pH of solution is an important parameter to be considered during the adsorption process, as it can influence the degree of ionization of dye, surface charge of the adsorbent, and also dye molecule structure .The adsorption of dye RB19 onto zein/nylon nanofiber membrane was studied at different pH to determine the optimum pH for maximum adsorption as shown in Fig-7.It was found that the maximum adsorption of RB19 occurred at pH1. When the pH is low, the adsorbent surface becomes more protonated due to increase in H^+ concentration, which increase the electrostatic interaction between the dye anionic ($-SO_3$) and adsorbent surface ($-NH^{+}_{3}$) resulting more contact between each other that increase the adsorption efficiency[31]. However increasing the pH cause decrease removal efficiency, this is due to more negatively charged ions formed that cause deprotonation of amino groups in zein/nylon nanofibers; as a result adsorbent surface charge turned from highly positive to highly negative, this causing the electrostatic repulsion between adsorbent surface and dye solution.

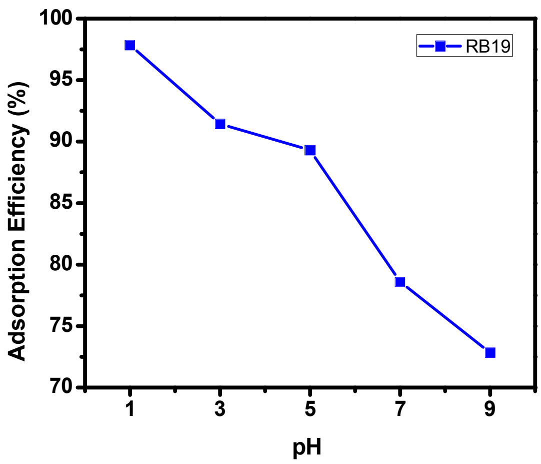

Fig -7 Effect of pH on dye removal by Zein/Nylon nanofiber membrane

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3.2.3 **The effect of adsorbent dosage**

The adsorbent dose is an important parameter in adsorption studies which define the removal efficiency of dye in the given mass of adsorbent. In this study, the removal efficiency of RB19 on the certain mass of nanofiber was investigated at initial dye concentration of 50mg/l under optimum conditions of pH and time. Fig-8 shows that the adsorption of RB19 in the acidic medium increased with the increase in the adsorbent dosage, this is because at higher dosage more binding sites were available and greater surface area that tended to increase dye adsorption. The maximum adsorption efficiency of nanofiber was about 98% at 20 mg nanofiber mass at room temperature.

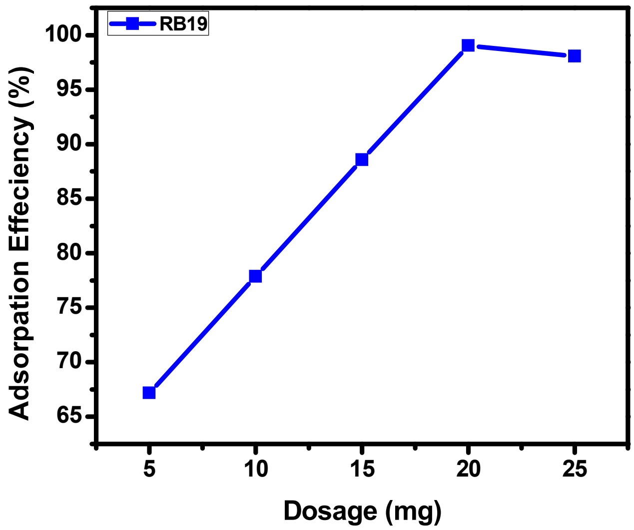

Fig-8 Effect of adsorbent dosage on adsorption of RB19

3.2.4 **The effect of initial dye concentration and Adsorption Isotherms.**

The adsorption is greatly influenced by the concentration of the analyt . The adsorption of RB19 on the adsorbent surface of zein/nylon was studied at different initial concentration ranging from 50-300 mg/l at constant temperature and optimum conditions of time, pH and nanofiber mass Fig-9. The dye adsorption capacities onto adsorbent increased with the increase of the concentration of dye solutions, the maximum adsorption capacities for RB19 reached 61.2 mg g-1. It was observed that the removal efficiency of dyes declined slightly with rise in initial dye concentration. This may be due to more vacant number of active sites and large specific area which was subsequently occupied by the dye molecule leading to saturation stage and reduction in further removal of RB19 from aqueous phase.

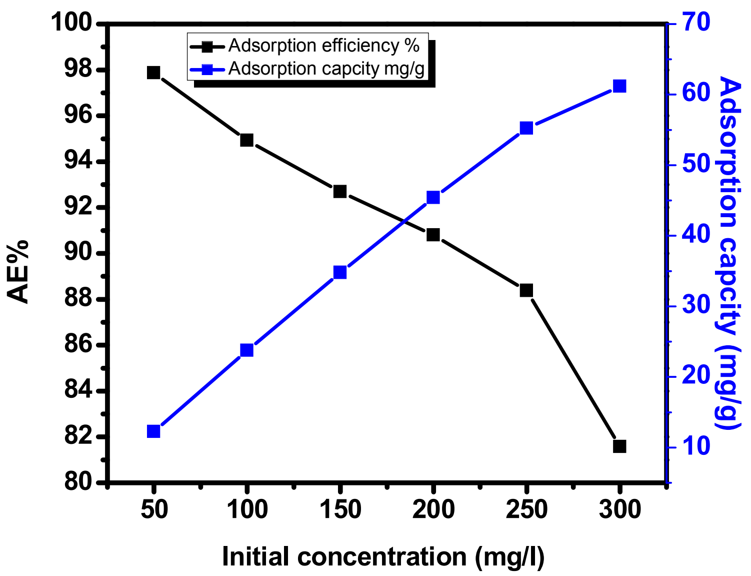

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Fig-9. Effect of initial dye concentration on adsorption efficiency of Zein/Nylon-6 nanofibers

To calculate the adsorption capacity of RB19 on the surface of adsorbent, two well-known adsorption models namely Langmuir and Freundlich [32, 33] isotherm were used respectively to analyze the adsorption isotherms illustrated as:

$$\frac{c_e}{q_e} = \frac{1}{b \times q_{\max}} + \frac{c_e}{q_{\max}}$$

(4)

$$\log q_e = \log k_f + \frac{1}{n} \log c_e$$

(5)

Where q_{max} is the maximum adsorption capacity (mg/g), C_e is the equilibrium solution phase concentration, b is related to adsorption free energy and specifies the adsorbent-dye affinity. K_f is adsorption capacity and the value 1/n from Freundlich isotherm gives information about the relative distribution of active sites; the relative parameter values calculated from the Langmuir and the Freundlich models were listed in Table 2.

For Langmuir model, q_{max} which is a measure of monolayer adsorption capacity of the zein/nylon, was calculated 70mg/g for RB19. The values of b were found to be within the range from 0 to 1, indicating that the zein/nylon adsorbent were suitable for Langmuir adsorption for RB19 as shown in Fig-10(a). For Freundlich model, Fig-10(b). The value of n reveals the favorability and degree of heterogeneity. Calculated from Freundlich model, n>1 suggesting favorable adsorption conditions. Based on R2 value and error analysis, both isotherms favor RB19 adsorptions.

Table 2. Isotherm parameters for the adsorption of RB19 on Zein/nylon-6 nanofiber at constant temperature (25°C).

DYE	Langmuir				Freundlich			
	q_{max}(mg/g)	b(L/g)	R^2	SSE	1/n	K_f (mg/g(L.mg)$^{1/n}$)	R^2	SSE
RB19	70.4	0.114	0.98	0.034	2.32	12.14	0.98	0.032

The adsorption capacity and other operational parameters of current work were compared with the previously used materials for RB19 (Table 3). It was observed that the Zein/Nylon-6 nanofibers possessed good adsorption capacity. Moreover, the adsorption time achieved from this new

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Zein/Nylon-6 composite nanofibers for significant dye removal was minimum (i.e. 5 min) that is the distinctive quality of this adsorbent compared to previously reported materials.

Table 3. Comparison of adsorption capacities and other operational parameters for Reactive blue dyes reported in literature

Dye	Adsorbent	pH	Time (min)	Temperature (K)	Amount (g/L)	Adsorption capacity (mg/g)	Reference
Reactive Blue	Natural ,modified & A.C Wheat straw	6.5	300	R.T	5g	3.2	[35]
RB19	Hollow zein N.P	9.0	1440	294.15	1	1016.0	[18]
RB19	pomegranate seed powder	3	1440	-----	5	9.26	[36]
RB19	Rice straw fly ash	1	60	300	0.9	38.24	[10]
R.B	cashew apple bagasse	2	3500	298.15	10	57.07	[8]
RB19	NiO nanoparticle	3	120	R.T	2.2	98.83	[34]
RB19	magnate/graphene oxide	3	66	R.T	10	62.5	[37]
RB19	grafted chitosan	3	420	-----	0.1g	1498	[38]
Reactive Blue 49	Coal ash	1	900	298.15	100	75.8	[39]
RB19	Zein/nylon-6 nanocomposite	1	5	R.T		70	Present study

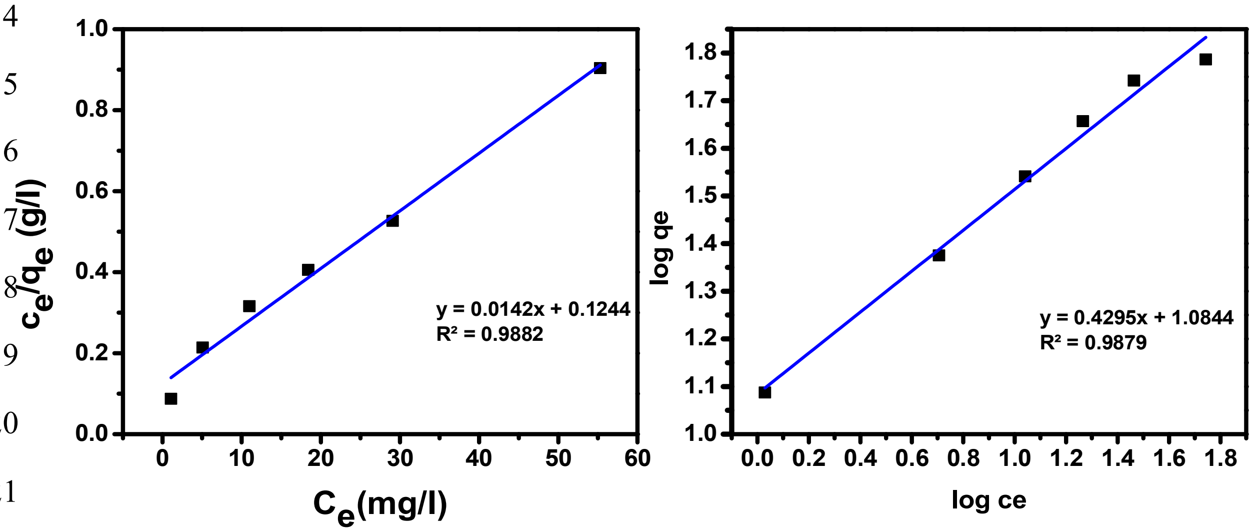

Fig-10. (a) Langmuir –isotherm (b) Freundlich- isotherm of RB19.

3.3 *The binding mechanism of dye on nanofibers.*

Fig-11(a) shows the IR of blended zein/nylon nanofiber, the broad peak at 3298 cm-1 corresponds to (–NH2 stretching vibration). The stretching at 2950 cm-1 and 2845 cm-1 are related to (-CH) asymmetric and symmetric stretching. The broad/ sharp peaks at 1640 cm-1, 1535 cm-1,1440 cm-1 and 1250 cm-1 were indicative of amide I (C=O stretching vibration), amide II (N-H bending) and amide III (axial deformation vibrations of C-N stretching) respectively. Fig-11(b) show the FTIR analysis after adsorption with RB 19 dye on blended zein/nylon nanofibers, as it can be seen that substantial changes occurred, the new bands at 1050 cm-1 and 1210 cm-1 were the peaks of –SO3 asymmetric stretchings of dye, that confirm the attachment of dye on nanofibers. The peak due to NH2 stretching also reduced in intensity that suggests that NH2 group from zein/nylon nanofibers participated in adsorption. Some bands near 1300 cm-1 also overlapped with fresh zein/nylon nanofiber sample that may due to interaction of sulphonate groups of dye with C-N groups of zein/nylon. From the FTIR study, it may be assumed that sulphonate group from dye had preferentially attacked –C-N region of zein/nylon nanofibers. This can be possible either through electrostatic means or by hydrogen bonding from NH group that may have altered C-N stretching also.

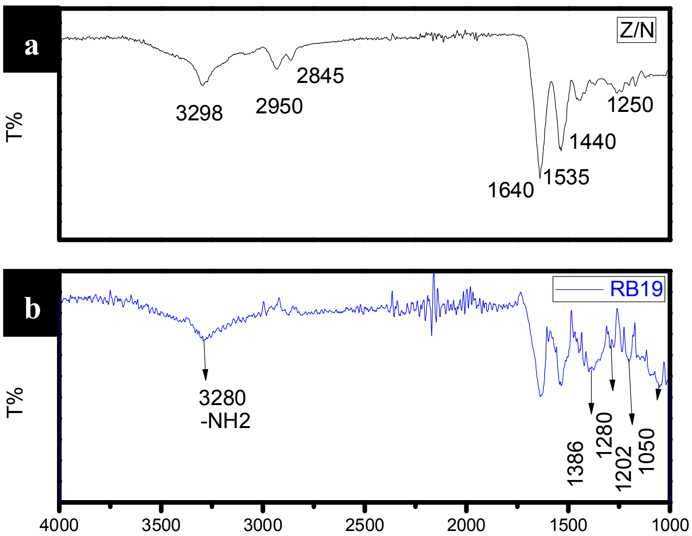

Fig-11. FTIR spectra of zein/nylon nanofibers before (a) and after dye RB19 adsorption (b).

4 Conclusion

Efficient and economically viable nanofibers were fabricated via co-electrospinning of two different polymers for RB19 removal from aqueous solution within 10 minutes of adsorption. The acidic pH was favorable for maximum adsorption of anionic dye with the removal efficiency of 94%. The dosage 20mg was sufficient enough to decolorize total dye RB19 at room temperature with adsorption capcity of 70mg/g of nanofiber which is comparatively higher than other well know adsorbents . The binding mechanism between dye and nanofibers is the result of both physical and chemical interactions. The nanofibers are simple, economic with no secondary toxic sludge and minimum waste generation, due to its high surface area and low volume. Another advantage of this nanofiber membrane is its potential application for dye filtration as blending both different polymers yielded nanofiber membrane with excellent mechanical strength.

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