Adsorption of Anionic Dye Using Cationic Surfactant-Modified Kenaf Core Fibers

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Abstract

Kenaf is a widely cultivated crop, particularly in the tropics. Kenaf core fiber (KCF) is a natural cellulose fiber derived from the plant and it is an important raw material for a variety of products. An attempt was made to chemically quaternized KCF (QKCF) as an adsorbent to increase adsorption affinity towards anionic reactive red-RB dye (RR). KCF was quaternized by treating with (3-chloro-2-hydroxypropyl) trimethylammonium chloride under basic condition. The efficiency of QKCF was investigated by adsorption studies for removing anionic RR dye from aqueous solutions. All experiments were conducted at a batch system and influential parameters cover pH, adsorbent dose, initial dye concentration, agitation speed, temperature, and contact time were investigated. Studies showed that removal efficiency of RR dye increases with increasing the adsorbent dose, agitation speed, temperature, and contact time. The equilibrium data were best represented by the Langmuir isotherm model with maximum adsorption capacity of 169.5 mg/g, and the kinetic data were found to follow the pseudo-second-order kinetic model. In general, QKCF could be suggested as an efficient and low‑cost adsorbent for removal anionic dyes.

Subject Areas

Chemical Engineering & Technology, Environmental Chemistry

Keywords

1. Introduction

Water pollution due to the effluents from textile industries emerges serious concern in the world. The textile industries are a large consumer of dyes. The dyes used in the textile industries have many different structures, *i.e.*, they can be reactive, basic, acidic, disperse, azo or metal-complex dyes [1]. Because of the coloration process, a huge amount of synthetic dyes cannot bind and get discharged into the waste water stream; thus, the industrial effluents from the textile industries are seen to carry a huge amount of the dye products and other chemical additives, which increase water pollution [2].

Around 10% - 15% of the dyes get released in the environment during the complete dyeing process, which colours the waste effluent and make it aesthetically unpleasant. Moreover, the dyes can be easily transported through the rivers or the sewers due to their water solubility. The dyes in the effluent waste are difficult to remove by using the traditional water treatment processes [3]. A great number of new technologies and technical for effluent management are being developed around the world, in response to economic, environmental and societal limitations increasingly posed by conventional wastewater systems [4]. Among these ways, adsorption is looked to be one of the most promising physiochemical techniques for wastewater treatment because of suitability, the simplicity of design and easy operation. Further, this process can remove/minimize different kinds of contaminants and thus it has a large applicability in effluents control [5].

Various adsorbents have been studied for the removal of different kinds of synthetic dyes. Coal-based activated carbon is the most widely used adsorbent for the removal of many types of dyes in commercial wastewater treatment but it is non-renewable and costly because of expensive raw material and involved high energy consumption activation process. Moreover, there are many problems related to the renewal used activated carbon [6]. Therefore, many efforts have been pursued direct the use of effective and low-cost adsorbents prepared from naturally occurring materials for the removal of textile dyes from aqueous solutions [7]. Following this trend, cellulose based substrate is considered as promising material for the removal of different types of pollutants from wastewater. Cellulose is one of the most plentiful, cheap and renewable natural polymers [8].

Generally, sorption capacity of crude agricultural by-products is low. These materials are chemically modified in required to enhance their sorption ability and, by addition, their usefulness in the treatment of wastewater. These materials, in general, have high sorption capacities towards either cationic or anionic dye [9].

Cationization or quaternization is a surface chemical treatment which helps to adds NH_4^+ groups onto the surface of fiber via replace epoxy to raise affinity towards anionic substances by promoting ion-exchange adsorption [10]. The quaternized fiber had shown an increase in adsorption capacity and affinity towards anionic substrates as the quaternization treatment increase the porosity,

surface area, and chelating functional groups. However, there is still very limited research on adsorption of reactive dye by quaternized lignocellulosic fibers.

Kenaf, a member of the hibiscus family (Hibiscus cannabinus L., Malvaceae) is a warm season annual fiber crop closely related to cotton, hemp, and okra. Kenaf is a fibrous herbal plant with great biomass production and fast growth rate. Providing the suitable temperature, water, soil fertility conditions kenaf crop would grow quickly to a height of 4 - 5.6 m with stem diameter ranging 24 - 52 mm, in about 4 - 6 months [11]. Kenaf have the same characteristics as jute fibres, but kenaf fibers are stronger, whiter, and more lustrous. Kenaf has been used for thousands of years as fishnet, sacking, and canvas due to its resistance for putrefy [12].

In this study, the feasibility of quaternized kenaf core fiber to serve as an adsorbent for the removal an anionic dye from aqueous solutions was studied. Batch adsorption was conducted to investigate its performance under various parameters such as the initial dye concentration, pH, adsorbent dosage, stirring speed, contact time, and temperature.

2. Experimental

2.1. Preparation of Quaternization Kenaf Core Fibers (QKCF)

Preparation of quaternization kenaf fibers basically divided into some steps which are kenaf core fibers (KCF) obtained, clean kenaf core fibers, Mercerization process by using sodium hydroxide, and quaternization process by using quaternizing agent which is (3-chloro-2-hydroxypropyl) trimethylammonium chloride.

KCF coarse powder used in this study were collected from Institute of Tropical Forestry Product (INTROP), University Putra Malaysia. KCF coarse powder was then sieved using 1 mm and 0.25 mm stainless steel sieves to obtain the size in range of 0.25 mm to 1 mm.

For cleaning, the kenaf particles in sizes of 0.25 mm to 1 mm were rinsed with tapwater and dried overnight at 50˚C. Then the kenaf fibers were sieved again using 1 mm stainless steel sieve to collect uniform size particles in range of 0.25 mm to 1 mm. Dry and clean were very important steps to make sure kenaf particles not mix with other contaminants.

KCF mercerized by soaking it in 20% weight of aqueous NaOH solution for 24 hours. Mercerization is a treatment of fibers with an alkali. The alkali causes the fibers walls to swell and become round, and increasing absorbency. Mercerized kenaf core fibers were rinsed with distilled water and dried at 50˚C for 24 hours.

For quaternization process, each gram of dried mercerized kenaf core fibers was reacted with a solution consisting of 1.5 g of NaOH: 6.67 mL of (3-chloro-2-hydroxypropyl) trimethylammonium chloride sol (60%wt in water): 2.5 Ml of distilled water. The mixture was preserved in sealed bowl at room temperature for 24 hours. After that, the QKCF was washed with 0.2% acetic acid solution to stop the reaction and followed by rinsed with distilled water until pH 7 which is a neutral condition. Then, QKCF was dried at 50˚C for 24 hours and stored in a

desiccator before to use.

The structure morphologies of QKCF was identifying by Scanning Electron Microscope (SEM). Samples were prior plated with a fluffy layer of gold. The SEM apparatus was operated at 15 kV, and scanning electron photographs were recorded at an enlargement of 100 um.

Infrared (IR) spectra were registered on Fourier Transform-Infrared (FT-IR) Spectrometer 100. All spectra were plotted as the percentage of transmittance against wave number (cm^{-1}) at a range of 650 - 4000 cm^{-1} at room temperature. FTIR spectrum was used in this study to identify the characteristic functional groups in QKCF. Hence, discovery quaternary amine group in the spectra will point out as an index for success quaternization treatment. Specific surface area was finding by BET surface area analyzer.

2.2. Preparation of Dye Solution

A stock solution of the reactive red-RB(RR) dye was prepared by dissolving 1.0 g of dye in 1000 ml distilled water to prepare a stock solution of 1000 mg /L. The experimental solution was prepared by diluting definite volume of the stock solution to get the desired concentration. The general properties of selected reactive red RB dye showed in Table 1, and molecular structure was shown in Figure 1.

For absorbance measurements a spectrophotometer UV-1800 (SHMADZU) was employed. The absorbance for the RR dye was measured at the maximum wavelength (λ_{max}) equal to 288 nm. Concentrations during experimental work
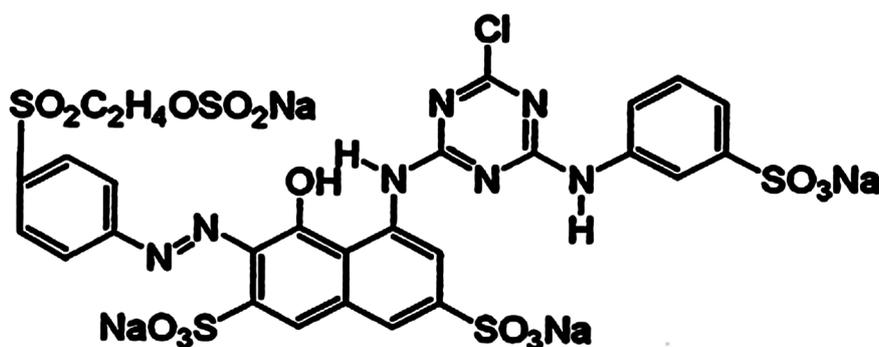
Figure 1. Molecular structure of reactive red RB dye.

Table 1. General properties of reactive red RB dye.

Name of the commercial dye	Remazol red 198
C.I Name	Reactive red 198
No. Of azo bonds	Monoazo
maximum wavelength (λ_{max})(nm)	288
Molecular weight (g/mol)	967.5
Chemical formula	$C_{27}H_{18}C_1N_7Na_4O_{15}S_5$

were determined from a standard calibration curve. The dye solution was filtered through filter paper to separate the adsorbent before running the UV spectrophotometer analysis. The amount of adsorbate adsorbed at equilibrium condition, q_e (mg/g) was calculated by using Equation (1) and the percentage of dye removal calculated from Equation (2).

$$q_e = \left(C_o - C_e\right)\frac{V}{W} \tag{1}$$

$$\% \, \text{Removal} = \frac{C_o - C_e}{C_o} * 100 \tag{2}$$

where: C_o and C_e represent the initial and final RR concentrations (mg/L), respectively, W is the weight of adsorbent (g) and V is the volume of solution (L).

2.3. Adsorption Experiments

All the experiments were done in batch system using 250 mL Erlenmeyer flasks. In each flask, the volume of dye was 100 mL, and the dosage of QKCF used was 1g/L (0.1 g/100 ml). All flasks were sealed properly using aluminum foil to keep sample from leakage. The speed of incubator shaker was set at 200 rpm for 3 hours and at temperature of 25˚C for all adsorption experiments.

To determine the effect of NaOH concentration during mercerization step on removal efficiency of QKCF, Reactive Red-RB (RR) dye solution at an initial dye concentration of 100 mg/L was prepared and 0.1 g of QKCF mercerized with NaOH of 5 wt%, 10 wt%, 20 wt%, 40 wt% and 60 wt% was added to each flask contained 100 mL of dye solution respectively. All flasks were shaken at 150 rpm at 25˚C for 2 hours. This experiment is very important to get optimum reaction efficiency.

The primarily adsorption test was carried out on both the natural kenaf core fiber (NKCF) and (QKCF) to compare their percentage of RR dye removal. A fixed amount of each adsorbent (0.1 g/100 mL) was added into two flasks containing 100 mg/L of RR dye solution and then placed in an incubator shaking at 150 rpm for 2 hours.

The standard discharge of wastewater from dyeing and finishing processes of textile industry for the pH was less than 10; therefore, the initial pH of 100 mg/L RR dye solutions was adjusted from pH (2 - 10). RR dye solution was adjustment by using 0.1 N HCl and 0.1N NaOH to the desired pH. The pH meter (EUTECT INSTRUMENTS-Malaysia) was used and calibrated by pH buffer solutions of 4.0, 7.0 and 10.0 to prevent error.

For the effective of initial dye concentration, the solutions of RR with concentration 10 - 200 mg/L were prepared.

The effect of the agitation speed was investigated by changing the stirring speed from 75 rpm to 250 rpm.

To study the effective of temperature, four different temperatures (15˚C, 25˚C, 35˚C and 45˚C) were applied to observe the influence of temperature on the

adsorption capacity and percentage of dye removal.

The effect of the sorbent dosage was investigated by varying amount of QKCF from 0.05 to 1.6 g/L and added to RR dye solutions of 100 mg/L. The flasks were shaken for 24 hours. From this experiment, the adsorption isotherm was determined.

The study of the impact of contact time was achieved by changing the RR dye concentrations from 20 to 100 mg/L. The samples were withdrawn at growing time periods ranging from 15 min to 180 min. From this study, the kinetics of adsorption was determined.

In order to minimize error, all the above experiments were triplicated and the average value was used for further analysis.

3. Results and Discussion

### 3.1. Characterization of Adsorbent

SEM is helpful for find out the particle shape and suitable size distribution of the adsorbent. In addition, SEM is the main device for characterizing the surface morphology and fundamental physical properties of the adsorbent surface. The textural structure of granular NKCF and QKCF were observed by SEM images shows in **Figure 2**. From the figure, it is observed the enlargement of pores had turned into splitting exposing additional original cellulose so that the previously unreachable inner part of the fiber was able to react with dye. Moreover, considerable pores are more suitable for adsorption of bulky substrates such as reactive dyes [13].

The FT-IR spectra of NKCF and QKCF are shown in **Figure 3**. From Figure it can be see many peaks for QKCF, from 3843 to 3263 cm^{-1} which indicate O-H stretching vibration and C-H stretching at 2878 cm^{-1} and 2341 cm^{-1} respectively. From the spectrum, the peaks at 1783 cm^{-1}, 1654 cm^{-1} and 1592 cm^{-1} on QKCF can be assigned to aromatic C=C stretch [14]. Furthermore, peaks at 1474 cm^{-1} and 1419 cm^{-1} with nearly equal intensity that assigned to C-H stretching of tert-butyl group is an evident of quaternary ammonia group reacted to QKCF. C-O stretch mode in C-O-C cellulose linkage appeared at 1059 cm^{-1} and 1062 cm^{-1} for NKCF and QKCF, respectively. The bands at QKCF and NKCF from 787 cm^{-1} to 706 cm^{-1} are assigned to CH$_2$ rocking.

The BET surface areas and the average pore diameter of the NKCF and QKCF are revealed that the surface area (S$_{BET}$) increased from 2 m^2/g for NKCF to 4 m^2/g for QKCF. The average pore diameter of NKCF is 106 nm which is macropores, and QKCF has an average pore diameter of 283 nm. Enlargement of the pore size is due to the dissolved lignin and hemicellulose in NaOH solution during the treatment process. Macropores acts as tunnels which enables the dyes to enter inside the smaller pores at the interior side of the QKCF where they can be adsorbed and retained. Furthermore, pore volume slightly decreased from 0.1699 cm^3/g for NKCF to 0.1128 cm^3/g for QKCF. It is attributed to the smoother texture of KCF surface after quaternization process [15].
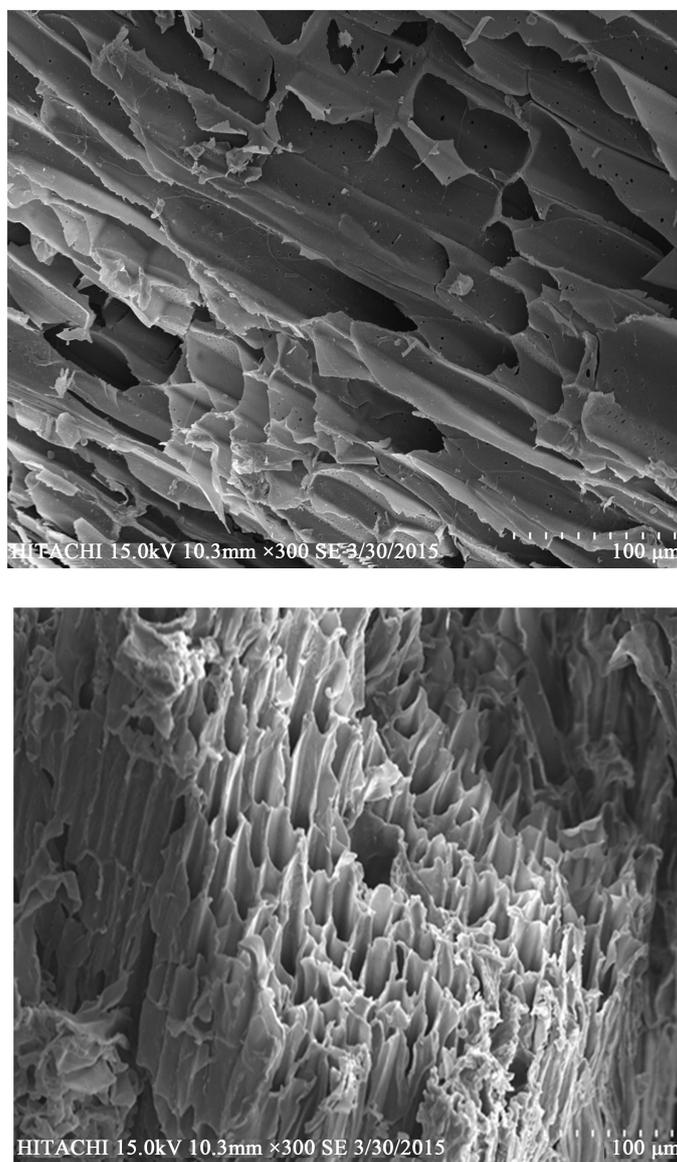
Figure 2. SEM images (a) NKCF and (b) QKCF.
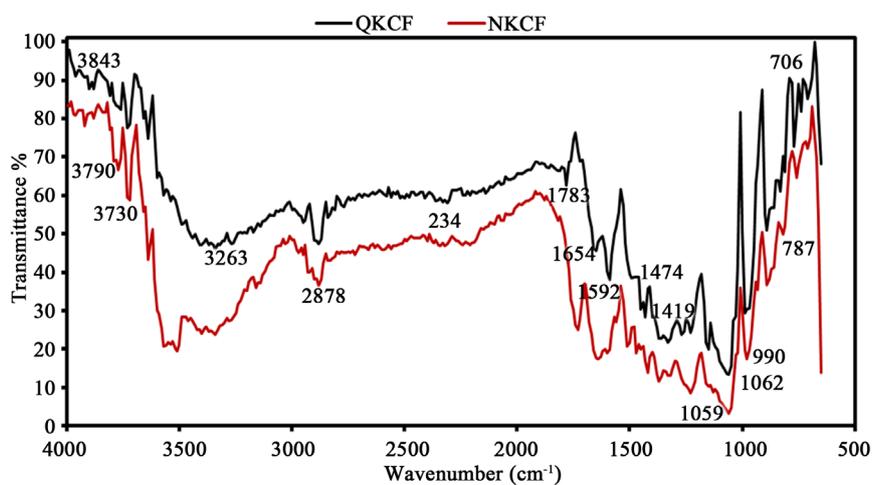
Figure 3. FTIR spectra for NKCF and QKCF.
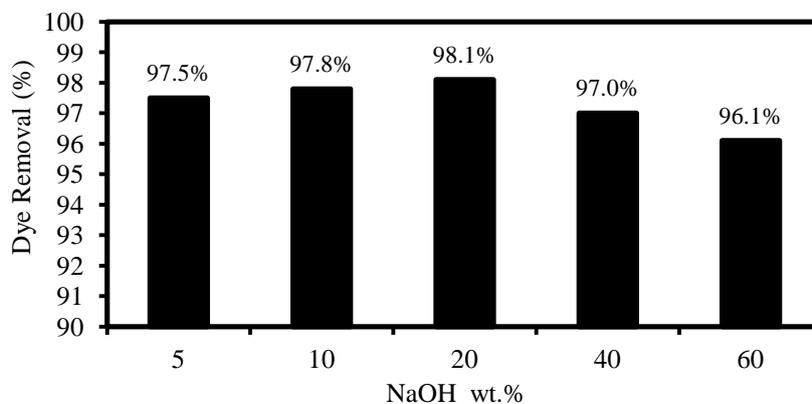
3.2. Effect of Mercerization

Figure 4 showed the removal efficiency of RR dye by QKCF with the NaOH concentration 5, 10, 20, 40 and 60 wt% during mercerization step. From the figure, it can be seen that the optimum NaOH concentration is 20%, which give the best removal efficiency (98.1%). Goswami [16] reported that fiber treated with increasing sodium hydroxide concentration showed increasing amorphous structure and porosity. Furthermore, NaOH more than 20 wt% is too viscous with a low wetting ability which is not suitable to use. Therefore, 20 wt. % NaOH solution was used in mercerization process to prepare all the QKCF for adsorption experiment.

3.3. Effect of Quaternization

The influence of quaternization proses on natural kenaf core fiber as adsorbent was tested by adsorption study on 100 mg/L RR dye solution. RR dye removal of 98.1% and 5.7% was achieved by using QKCF and NKCF respectively. From the result, it can see that QKCF had the highest percentage in removal RR compared to NKCF, this experimental result proved that chemical modification of NKCF was successfully increased the performance adsorption capacity of NKCF in removal anionic dye from aqueous solution.

3.4. Effect of pH

pH is a so significant parameter in absorption process and affected on absorption capacity, dye solubility, solution chemistry and the surface of the absorbent pore [17]. The effect of pH on the percentage removal was shown in **Figure 5**. The dye adsorption is unaffected by pH over the whole range explored, and from pH 5 to 10, adsorption rate did not vary significantly and the removal percentage was steady around 98%. Hameed and Ahmad [18] reported similar results for the adsorption of MB onto garlic peel; this behavior attributed to the availability of senior number of effective sites on the adsorbent surface, and related the solute (dye) uptake to the active sites and as well to the chemistry from the solute in the solution.

Figure 4. Effect of NaOH concentration during mercerization proses on percentage removal of RR dye by QKCF.
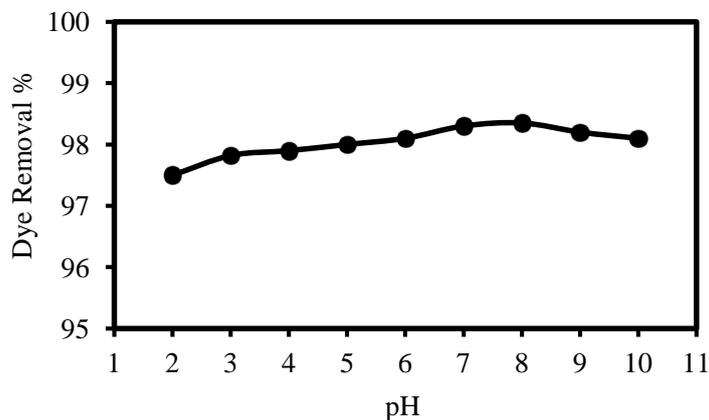
Figure 5. Effect of different pH on the removal of RR dye by QKCF adsorbent. (Dose = 0.1 g/100 ml, (C_o = 100 mg/L, Temp. = 25˚C, Speed = 200 rpm).
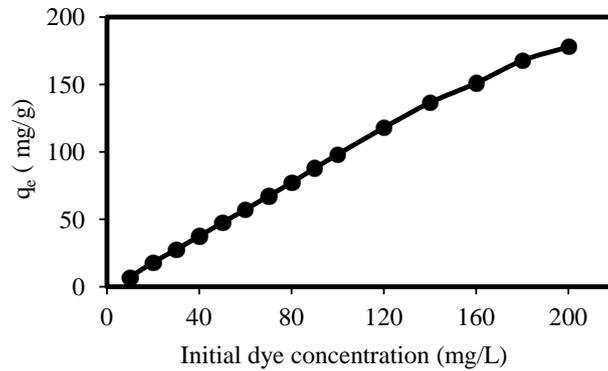
3.5. Effect of Initial Dye Concentration

In batch absorption experiment, the initial dye concentration in solution plays a significant role as a driving force that overcomes mass transfer resistance of adsorbate between the solid phase and aqueous [19]. **Figure 6** showed that with an increase of dye concentration from 10 to 200 mg/L, the adsorption capacity increases from 7 to 177.8 mg/g. The increase in adsorption capacity with an increase in dye concentration was probably due to the higher adsorption average and exploitation of all active sites ready for the adsorption at higher concentration.
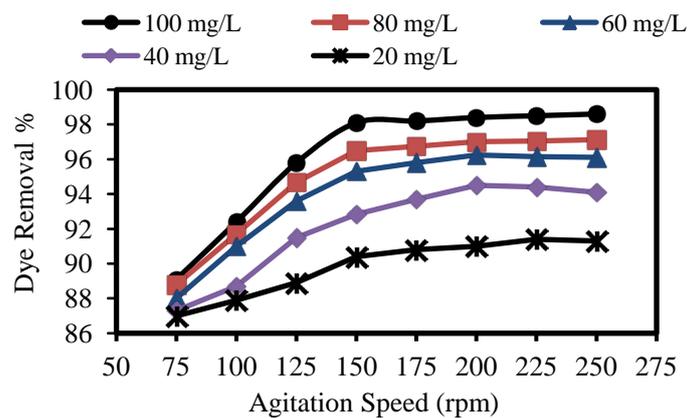
3.6. Effect of Agitation Speed

Figure 7 shows the influence of the agitation rate on the sorption of RR dye by QKCF. The results showed that the percentage removal of dyes by QKCF was enhanced with an increase in the agitation speed from 75 to 200 rpm. With the increasing of the agitation speed, the rate of diffusion of the dye molecules from the dye solution to the liquid boundary layer surrounding the adsorbent particle become higher because of an enhancement of the turbulence and a decrease of the thickness of the liquid boundary layer. Increasing agitation rate decreases the film resistance to mass transfer surrounding the sorbent particles, thus, increasing sorption of dyes molecules [20].
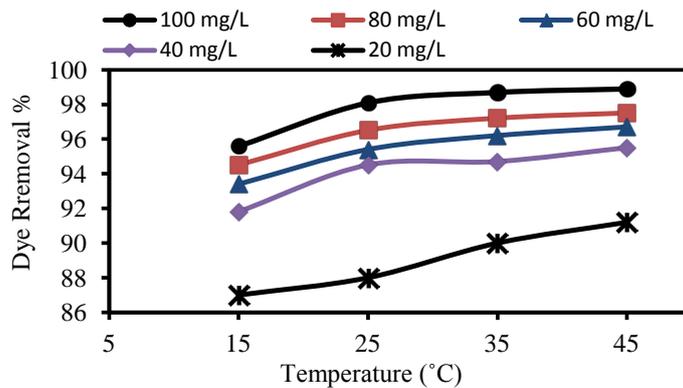
3.7. Effect of Temperature

Figure 8 shows the effect of temperature on the sorption of RR. Adsorption of RR by QKCF for all initial dye concentration the percentage removals increased with increasing temperature from 25˚C to 45˚C, indicating an endothermic process. The increment of adsorption may be due to the increased rate of diffusion of the adsorbate molecules across the surface boundary layer and by the internal pores of the adsorbent particles. An increased number of molecules may obtain sufficient energy to succumb an interaction with active sites at the surface [21]. Thus, batch mode studies were carried out at 200 rpm of agitation speed.

Figure 6. Effect of initial dye concentration on the amount of adsorbed. (Dose = 0.1 g/100 ml, Temp. = 25˚C, Speed = 200 rpm).


Figure 7. Effect of different agitation speed on the removal of RR by QKCF adsorbent (Dose = 0.1 g/100 ml, Temp. = 25˚C, Time = 3 hr).

Figure 8. Effect of different temperature on the removal of RR by QKCF adsorbent (Dose = 0.1 g/100 ml, Speed = 200 rpm, Time = 2 hr).

3.8. Effect of Contact Time

Figure 9 shows the effect of contact time on removal efficiency of RR dye for different initial dye concentration. RR dye was rapid remove in the first 90 min and attained equilibrium after 120 min for all initial dye concentration. The majority of dye removal occurred within 90 min and a further increase in contact time resulted in only a small increase in percent removal. This trend is in logical
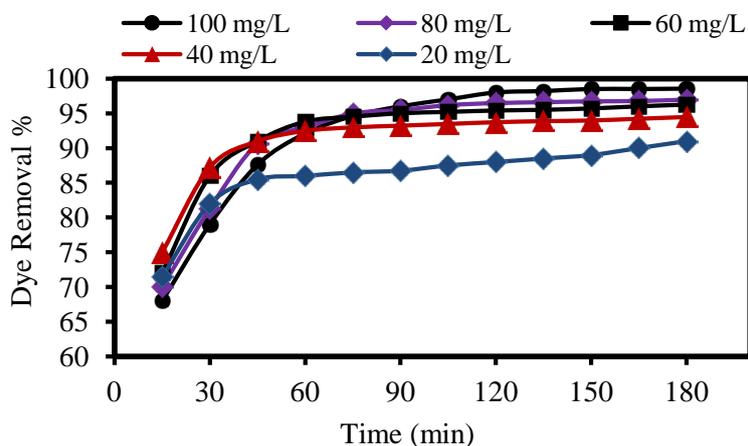
Figure 9. Effect of contact time on removal efficiency of RR dye for different initial dye concentration (Dose = 0.1 g/100 ml, Speed = 200 rpm, Temp. = 25˚C).

approval with those reported in other dye adsorption studies. The higher rate in the first can be due to the great available surface area/adsorption sites of the adsorbents while the subsequent slower rate can be due to interparticle diffusion.
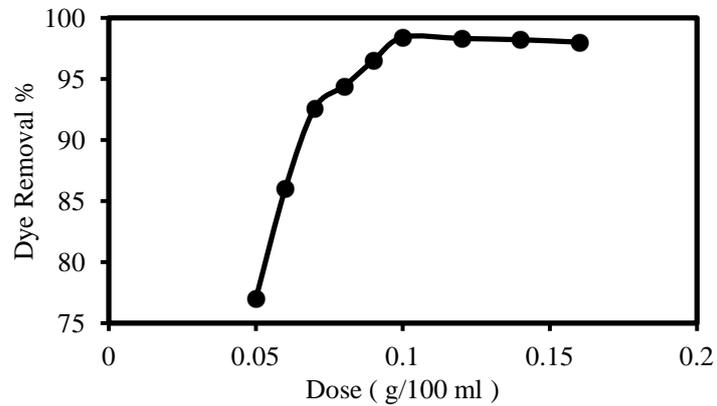
3.9. Effect of Adsorbent Dosage

Figure 10 shows the effect adsorbent dose of QKCF on the percentage removal of RR dye. It was observed that at an increase in adsorbent dosage from 0.05 to 1.0 g/L causes an increase in percentage removal of RR dye from 77% to 98.4%. This is due to the fact that, increase in adsorbent dosage increase adsorbent surface area and availability of more adsorption sites. After the critical dose of (1.0 g/L) the extent of adsorption decreased. This phenomenon was also confirmed by Mohammad [22]. The decrease in color removal is because, at the higher adsorbent dosage, there is a very fast superficial adsorption on the surface adsorbent that produces a lower solute concentration in the solution than when the adsorbent dose is lower.

4. Adsorption Isotherms

Adsorption isotherms are major design requirements for any adsorption system. Isotherm expresses the relation between the quantities of adsorbate (mg) removed from the liquid phase by unit of mass of adsorbent (g) at constant temperature. To quantify the adsorption capacity of adsorbents for the removal of adsorbate from aqueous solution, the equilibrium of a solute separated between liquid and solid phase is demonstrated by different models of adsorption isotherms like Langmuir and Freundlich isotherm models. The applicability of the isotherm equations was a comparison by referring to the correlation coefficient, R^2 [23].

The Freundlich isotherm is the closer relationship that depicting the sorption equation derived empirically in 1912. This fairly acceptable practically isotherm can be applied for non-ideal sorption that includes heterogeneous surface energy systems and is obvious by the following equation [24]:

Figure 10. Effect of adsorbent dose on the adsorption of RRdye onto QKCF (Speed = 200 rpm, Temp. = 25°C, Time = 24 hr, C_o = 100 mg/L).

$$q_e = K_F C_e^{1/n} \tag{3}$$

where:

q_e: The quantity of adsorbate adsorbed per mass unit of the adsorbent.

C_e: The equilibrium concentration of the adsorbate. (mg/l)

K_F: is roughly an indicator of the adsorption capacity of the adsorbent which can be defined as the adsorption or distribution coefficient (mg/g (l/mg)$^{1/n}$)

$1/n$: is the adsorption intensity or surface heterogeneity.

In general, as the K_F value rises, the adsorption ability of the adsorbent for a given adsorbate increases. The magnitude of the exponent ($1/n$) gives a signal of the favorability for adsorption, the value of $1/n$ ranges between (0 and 1), and the adsorption becoming more heterogeneous as $1/n$ value gets closer to zero. Values of $n > 1$ represent favorable adsorption condition. Equation (3) may be linearized by taking logarithms [24]:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \tag{4}$$

A plot of $\log q_e$ versus $\log C_e$ results in a straight line with a slope of ($1/n$) and an intercept ($\log K_F$).

Experimental data are often plotted in this manner as a convenient way of determining whether removal of material from solution is accomplished by adsorption and as means of evaluating the constants (K_F) and (n).

Langmuir's model is characterized by the conditions below:

1-The molecules are adsorbed on definite sites on the surface of the adsorbent.

2-Each site can take in only one molecule (monolayer).

3-The area of each site is a fixed quantity determined solely by the geometry of the surface.

4-Adsorption energy is the same at all sites. In addition, the adsorbed molecules

Cannot move across the surface or react with neighboring molecules [25].

The well-known expression of the Langmuir model is given by Equation (5) [26].

$$q_e = \frac{q_{max} K C_e}{1 + K C_e} \tag{5}$$

where q_e is the amount of adsorbate adsorbed per unit weight of adsorbent at equilibrium (mg/g), C_e the equilibrium concentration in the solution (mg/L), q_{max} the maximum adsorption capacity and K is the adsorption equilibrium constant (rate of adsorption). The linearization form of this equation is [27].

$$\frac{C_e}{q_e} = \frac{1}{k q_{max}} + \frac{C_e}{q_{max}} \tag{6}$$

A plot of C_e/q_e versus C_e indicates a straight line of slope $1/q_{max}$ and an intercept of $1/(K q_{max})$.

The fundamental characteristics of the Langmuir isotherm have been given by the expression separation factor or equilibrium constant R_L, which is defined by on different systems as follows:

$$R_L = \frac{1}{1 + K C_o} \tag{7}$$

where C_o is the highest initial concentration of adsorbate, and K is the Langmuir constant. This signs the nature of adsorption as [28]:

$R_L > 1$ (unfavorable), $0 < R_L < 1$ (favorable), $R_L = 0$ (irreversible), and $R_L = 1$ (linear).

The Langmuir, Freundlich, and the equilibrium adsorption isotherms of RR dye adsorption onto QKCF are shown in **Figures 11-13** respectively. As the obtained isotherm parameters show (**Table 2**), QKCF has a high adsorption capacity for anionic RR dye in the solution. The experimental results indicate that sorption of RR dye onto QKCF follows the Langmuirmodel. A good fit of the

$$Y = 0.0059X + 0.0133$$
$$R^2 = 0.992$$
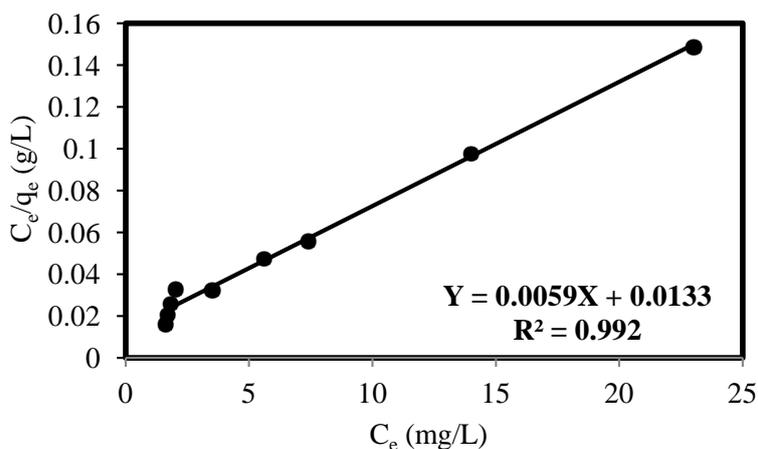
Figure 11. Langmuir adsorption Isotherm of RR onto QKCF at 25˚C.

Table 2. Langmuir and Freundlich constants of adsorption of RR on QKCF.

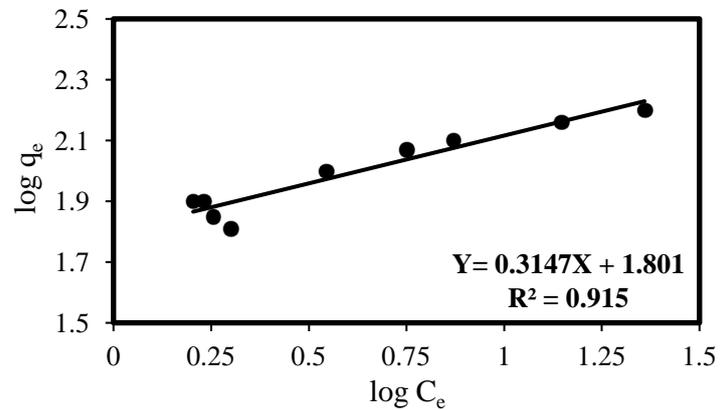| Langmuir Constants				Freundlich Constants		
q_{max} (mg/g)	K (L/mg)	R^2	R_L	K_F	1/n	R^2
169.5	0.444	0.992	0.022	63.234	0.3147	0.915

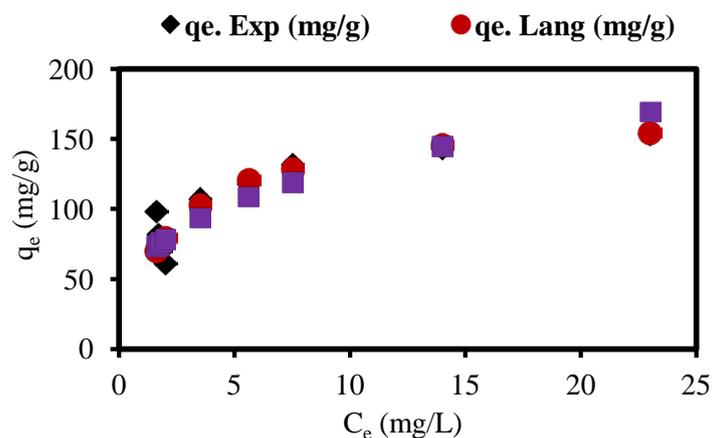**Figure 12.** Freundlich adsorption Isotherm of RR onto QKCF at 25°C.

Figure 13. Equilibrium adsorption Isotherm of RR onto QKCF at 25°C.

Langmuir isotherm to the experimental data for QKCF confirms that the adsorption is a monolayer. The R_L value for the adsorption of RR onto adsorbents is $0 < R_L < 1$ also shows that the adsorption process for QKCF is favorable.

5. Adsorption Kinetics

The kinetic adsorption explains reaction pathways; during the times to reach the equilibrium whereas chemical equilibrium confers no information around pathways and reaction average. Therefore, a number of adsorption processes for pollutants have been studied in an effort to find an appropriate explanation to mechanisms and kinetics for sorting out environment solution. Thus, In order to analyze the sorption kinetics of RR onto QKCF, the pseudo-first-order and pseudo-second-order models were applied to the experimental data.

The linear form of the pseudo-first-order model (Equation (8)) was described by Lagergren [29]. The values of constant K_1 and calculated q_{cal} were obtained from the slope and intercept respectively of plots of $\log(q_e - q_t)$ versus time (t) as shown in **Figure 14**. The parameters and correlation coefficient (R^2) of pseudo-first order kinetic model was listed in **Table 3**. It obvious from **Table 3** that the calculated q_e values for all concentration did not agree with experimental q_e values thus the pseudo-first-order model did not fit well.
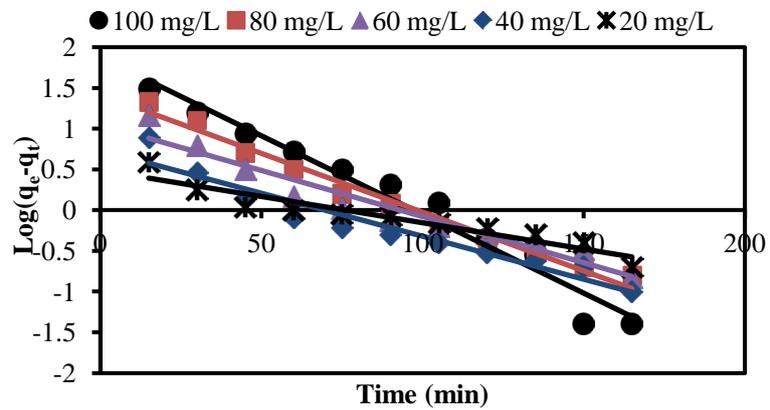
Figure 14. Pseudo-first order kinetic model for adsorption of RR on QKCF (Dose = 0.1 g/100 ml, Speed = 200 rpm, Temp. = 25˚C).

Table 3. Parameters and correlation coefficient (R^2) of pseudo-first and pseudo-second order kinetic models for adsorption of RR dye by QKCF.

| Initial dye concentration (mg/L)	q_{eexp} (mg/g)	Pseudo-first-order kinetic model			Pseudo-second-order kinetic model		
		$q_{e\,cal.}$	K_1	R^2	$q_{ecal.}$	K_2	R^2
20	18.2	3.1	0.015	0.9013	18.4	0.012	0.9996
40	37.8	5.5	0.024	0.927	38.46	0.009	0.9999
60	57.75	11.3	0.026	0.9311	59.17	0.0042	0.9998
80	77.6	26.014	0.033	0.9805	80.65	0.0023	0.9997
100	98.55	86.34	0.044	0.9639	103.1	0.00126	0.9998

$$\log\left(q_e - q_t\right) = \log q_e - \frac{K_1}{2.303}t \tag{8}$$

Pseudo-second order model Equation (9) had been achieved by plotting t/q_t versus time (t) [30]. The values of K_2 and calculated q_{cal} can be determined experimentally from the slope and intercept of a plot of t/q_t versus time (t) as shown in **Figure 15**. The parameters and correlation coefficient (R^2) of pseudo-second order kinetic model was listed in **Table 3**. From **Table 3**, it can be seen that the correlation coefficients R^2 for linear plots of the pseudo-second order model are ranges between 0.9996 to 0.9999 and the calculated q_e values are agreement with experimental q_e values. This indicates that the adsorption kinetic is better represented by the pseudo -second order model. Hence, the adsorption kinetic of RR dye on QKCF occurred by internal diffusion mechanism and chemisorption is involved based on the assumption in the pseudo-second-order kinetic model [31].

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e}t \tag{9}$$

6. Conclusion

In this work, the ability of QKCF adsorbent to remove RR dye from aqueous
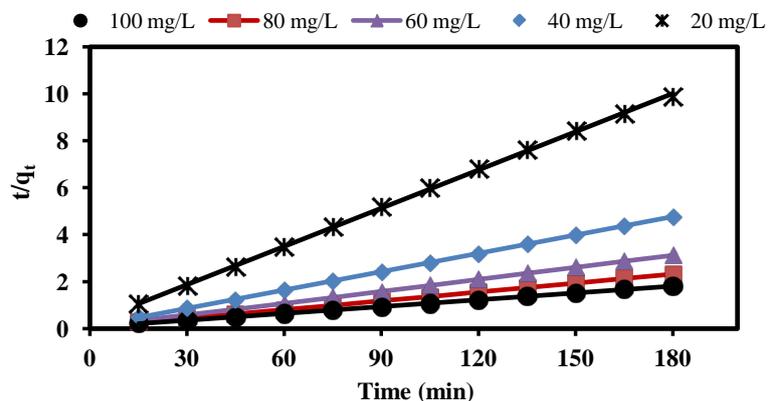
Figure 15. Pseudo-second order kinetic model for adsorption of RR on QKCF (Dose = 0.1 g/100 ml, Speed = 200 rpm, Temp. = 25˚C).

solution was investigated. Experimental results show that QKCF has higher adsorption efficiency compared with raw kenaf core fiber for removal RR dye from aqueous solution. The equilibrium adsorption data were best represented by the Langmuir isotherm model, indicating monolayer adsorption on a homogenous surface and the adsorption capacity was found to be 169.5 mg/g at 25˚C. The adsorption kinetics was described well by the pseudo-second-order model equation. Since KCF used in this work is freely and locally available, the resulting sorbent is predicted to be economically applicable for removal of reactive anionic dyes from aqueous solution. It can be concluded that the quaternization kenaf core fiber is an effective adsorbent for the removal of an anionic dye from aqueous solutions.

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