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Batch Adsorption Study for Removal Acid Red 114 Dye from Aqueous Solution by Using Kenaf

Maytham Kadhim Obaid[1, 2], Luqman Chuah Abdullah[1], Intidhar Jabir Idan[1,2], Siti Nurul Ain Binti Md. Jamil[3] , Dalia Sadiq Mahdi[4]

[1]Department of Chemical and Environmental Engineering, Faculty of Engineering, University Putra Malaysia, 43400 Serdang, Selangor, Malaysia
[2]Department of Environmental Engineering, Faculty of Engineering, University babylon, Hilla, Iraq, Babylon
[3]Faculty of Science, University Putra Malaysia, 43400 Sardang, Salengor, Malaysia
[4]faculty of Biotechnology, University of Al- Qasim Green Babylon, Iraq

Abstract: **In this study, kenaf core fibre KCF with size 0.25–1 mm, was successfully by treating with (CHMAC) as quaternization agent. The MKCF was characterised by Brunauer, Emmett and Teller (BET) analysis, Fourier Transform Infrared Spectroscopy (FTIR), Scanning Electron Microscope (SEM), with pH = 6.5 and constant shaking rate of 150 rpm. Was developed to stimulate the adsorption of AR114 by MKCF under varying parameters such as pH, dosage, dye concentration and speed. In addition, isotherms and kinetics adsorption studies were estimated for determination of the equilibrium adsorption capacity and reactions dynamics; respectively on adsorption by modified kenaf core fibre was investigated. Results showed that the best dosage of MKCF was 0.1 g/100 mL, the maximum removal of AR114 Was 99.14 at 30^{0}C. The results also showed that the equilibrium data were represented by Freundlich isotherm with correlation coefficients R2= 0.8395 and the kinetic study followed the pseudo-second-order kinetic model with correlation coefficients R2= 0.9953 mg/L. Furthermore, the maximum adsorption capacity 238.1 mg/g. Adsorption through kenaf was found to be very effective for the removal of the Acid dyes.**

Keywords: **Acid Red Dye, Modified Kenaf Center Fiber, Adsorption, Freundlich, Langmuir, Temkin.**

1. INTRODUCTION

The effluents from the textile industry and a number of other industries contain different types of synthetic dyes. Most of these dyes are resistant to light and oxygen. The AZO group of dyes is the most popular in the textile industry (Gupta and Suhas, 2009). Moreover, 60% of the food colours are nitrogen colours (AZO) (Shadeera et al., 2015). Around 20% of the global water pollution results from the emissions of the textile industry (Batmaz et al., 2014). This enormous amount of water pollution is in essence the primary source of pollution. There are endless uses of water, right from cleaning equipment to cooling, rinsing, and preparing products colours. Even small amounts of dyes (below 1 ppm) are clearly visible and impact the water environment significantly, where the dyes become toxic agents with mutagenic, allergenic, carcinogenic, non-degradable and resistant properties to aerobic digestion, thereby causing serious environmental problems (Gupta et al., 2016). About 15% concentration of dyes is discharged into the water (Shamel, 2016). Hence, the dyes could directly or indirectly reach streams, ponds, rivers, and other water bodies. Of late, there has been an increased interest in finding ways to decolonise these effluents (Shadeera et al., 2015). The removal of colours from the wastewater is usually considered to be more necessary than the removal of other colourless organic substances. Treating the disposed water from textile industries has gained a lot of attention due to the increase in interest in environmental affairs globally (Fatemeh, et al., 2016). Out of the numerous techniques that are used to get rid of dyes from wastewater, the most commonly used one is adsorption (Yusuf et al., 2015). adsorption have the simplicity and high impact, ease of use and desired outcomes, and indifference to harmful substances, making it the best and most suitable for use superior to traditional methods, the chemical, physical, biological and other common methods did not mention [12]. Most these methods theories and there is no actually, Expensive, or difficult in implementation. Or resulted do not tantamount to making them a dependent way. Or be of good results, but expensive, such as the use of activated carbon. The researchers came to find alternative materials and inexpensive and widely available was the reliance on agricultural crops or agricultural residues such as (show in table1). In this research, the adsorption material kenaf is an agricultural crop (figure 1: a, b), the kenaf was modified treatment in order to increase the adsorption capacity dye from solution. Was selected acid red114, the aim to find out absorption capability absorption properties of kenaf modified for redosage and primary dye focus are Check it out in batch method. Adsorption isotherm data were fitted to Langmuir model, with cationic sites. Those it is called classes of these dyes are azo, utilized acid red 114 (AR114) color in this analyses. The kenaf was modified treatment in order to increase the adsorption capacity dye from solution, was selected acid red114. The target of this papers to knowledge the KENAF properties and its ability to assimilation. All properties have been related to analysis to understand behavior the kenaf and dye. The effects of diverse factors on the adsorption as, period time, acidity degree.

Figure 1: (A) Kenaf Plant **Figure 1: (B) Section Of Kenaf Plant**

Figuer2: (A) Kenaf Before Treatment **Figure2: (B) Kenaf After Treatment**

Table 1: Agricultural waste used previously in studies as absorbent

Dyes	Adsorbents	q_{max} (mg/g)	References
Methylene blue	Modified Durian Leaf Powder	125	Hussin et al., 2015
Reactive Blue19	Wheat Straw	4.22	Khalidet al., 2015
Reactive Yellow 2(RY2)	Cocoa (Theobroma Cacao) Shell	333.33	Mylsamyet al., 2012.
Phenol	carbonized coir pith	48.31	Kavitha et al., 2016.
Red denoted as RR	Green Carbon	28.25	Yargıç, et al., 2013.
brilliant blue reactive (RBBR)	pomegranate peel activated carbon	370.86	Azmier et al., 2014.
Reactive orange	hyacinh root powder	17.24	M.soni et al., 2014.
Methylene blue	corn cob powder calcined	41.33	Miyaha, et al., 2016.
Methyl Red	Montmorillonite	84.28	Omidi, et al., 2016.
mercury ion	fir wood sawdust	129	Miyaha et al., 2016
lead(II)	rubber leaf powder (CARL)	97.19	Faisal et al., 2016
Reactive red 228	Quaternized Flax shive	190.0	wang et al., 2013
Acid red 114	Modified kenaf core fibers	238.1	This work

2. MATERIALS AND METHODS

Preparation of Modified Kenaf Core Fibres (MKCF):

The pulverisation pro. These modified Kenaf core fibres were then heated and dried at 50^0C and preserved in a desiccator show figure: 2 (a). With the help of a stainless steel sieve, the KCF was sieved in order to extract fibres in the range of 0.25–1 mm. The modification of KCF to fibres included three steps: cleaning, mercerisation and quarterisation. During the cleaning process, the KCF was extensively washed with distilled water. The KCF was then made to undergo the drying process where it was heated in an oven at 50^0C for 24 hours. Following this, the clean and dry Kenaf core fibres were soaked in 20% weight of NaOH solution for 24 hours in order to complete the mercerisation process. The alkaline solution made the walls of the fibres swell up and become active, in turn enhancing the resilience, lustre, and absorption capability of the fibres. The mercerised Kenaf fibres were again washed with distilled water and dried by heating in an oven at 500C. During the quarterisation process, every gram of KCF was mixed with 62.5 mmol of CHMAC and 37.0 mmol of NaOH. The mixture was preserved in a locked beaker container at room temperature for 24 hours. The mixture was then washed with 0.2% acetic acid solution in order to end the reaction. It was again washed with distilled water so that the pH level could be neutralised, then be ready for use show figure 2: (b) before treat.

Preparation stock solution dye:

1 g of dye was liquefied in 1 L of distilled water in a volumetric flask in order to prepare the stock solution. The mixture was stored at room temperature for 24 hours in a bottle with a screw cap to ensure that the stock solution becomes homogeneous. The mixture was also kept away from light so that it is not affected by external factors. A specific volume of the stock solution was prepared to achieve the expected concentration. Table 2 presents the typical properties of acid red 114 dyes. Figure 3 illustrate the chemical structures of acid red 114 dyes. A spectrophotometer UV- 1800 (SHMADZU) was used for measuring absorbance. The absorption of dyes onto adsorbents was measured by using UV. The wavelength of AR114 dye is known to be 518 nm. To ascertain the concentrations of dyes that have not been absorbed by the adsorbents, the calibration curves were used. With the help of the calibration curves, the concentrations were determined during experimental work in the lab. For all the experiments, MKCF was separated from the MKCF-dyes mixture solution with the use of a filter paper prior to the analysis. The filter paper was used to filter and isolate Kenaf from the solution before the UV spectrophotometer analysis was carried out. Those all properties for chose acid red 114(AR114) color demonstrated to table 2, and the all compound structure in figure 3. In this study, the decolorization of the watery result might have been contemplated over clump mode.

To absorbance measurements, a spectrophotometer UV-1800 (SHMADZU) might have been utilized. The greatest wavelength λmax for those AR114 color might have been measured during 518nm. Focuses Throughout test worth of effort were dead set from A standard alignment bend. The color result might have been separated through channel paper with separate those adsorbent in the recent past running the UV spectrophotometer examination. The rate evacuation effectiveness (R %) were ascertained utilizing Equations (1) Also (2), separately.

$$q_e=(C_i-C_e)*V/W \qquad (1)$$

$$R\ (\%) = (C_i-C_e/C_i)*100 \qquad (2)$$

Where: $C_{i=}$ initial dye concentrations (mg/L). C_e = final dye concentrations (mg/L). V = volume of liquid (L). W = weight (MKCF) (g).

Table2. General properties about acid red 114.

Name of the commercial dye	Acid red 114
λ max (nm)	518 nm
Molecular weight (g/mol)	830.81
Physical state	Dry powder
Dye content	45 %
Chemical formula	C37H28N4Na2O10S3

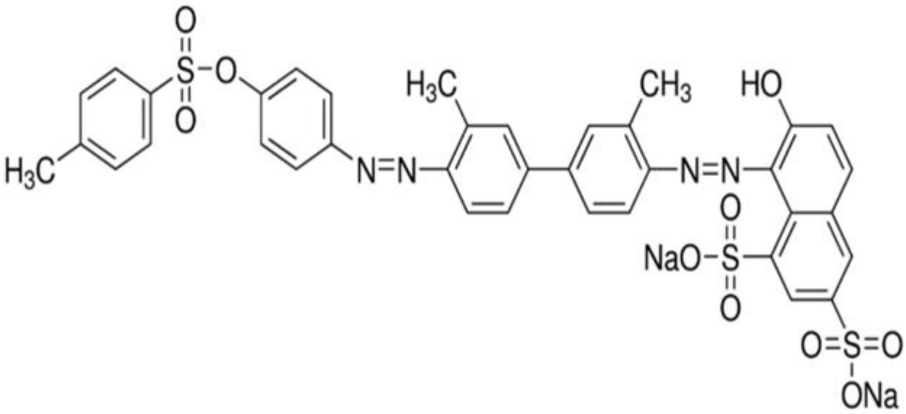

Figure3: Chemical structure of acid red114.

3. RESULT AND DISCUSSION

Morphological characterization (SEM):

The morphological features and surface characteristics of natural kenaf core fibres (NKCF) and modified kenaf core fibres (MKCF) were analyzed by using Scanning Electron Microscopy (SEM). The SEM images are shown in Figure 4. for NKCF, Mercerized KCF, MKCF and MKCF after adsorbent dye respectively. Figure 4, demonstrates the changes in the surface microstructure and porosity of the kenaf core fibres after quaternization process. From the figure, it can be clearly seen that the surface of raw kenaf particles was appeared fibrously, smooth, and constituted by sheaves of narrower fibres surrounded by a lingo-cellulosic cover (Eduardo et al., 2008). For MKCF, 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 to dye. Hence, the surface area of MKCF could provide the area for the adsorption to occur.

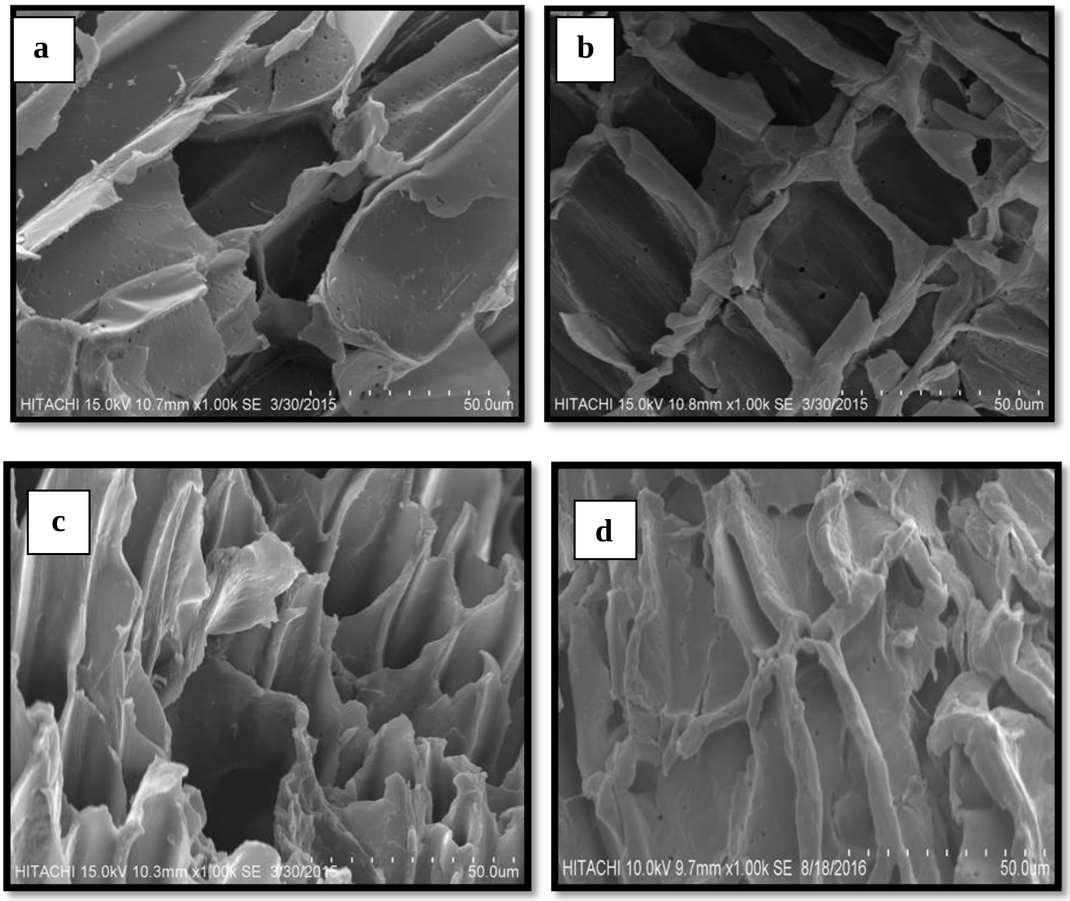

Figure 4: SEM micrograph for (a) NKCF (b) Mercerization KCF (c) MKCF and (d) MKCF after adsorption dye.

Fourier Transform Infrared (FTIR) Spectroscopy:

The FTIR spectrum is a primary tool to identify the characteristic functional groups which can contribute to enhance adsorption efficiency of the MKCF for adsorption dyes. The major and minor peaks recorded for natural kenaf core fibres (NKCF) and modified kenaf core fibres (MKCF) are showed in Figure 5, and listed in Table 3.

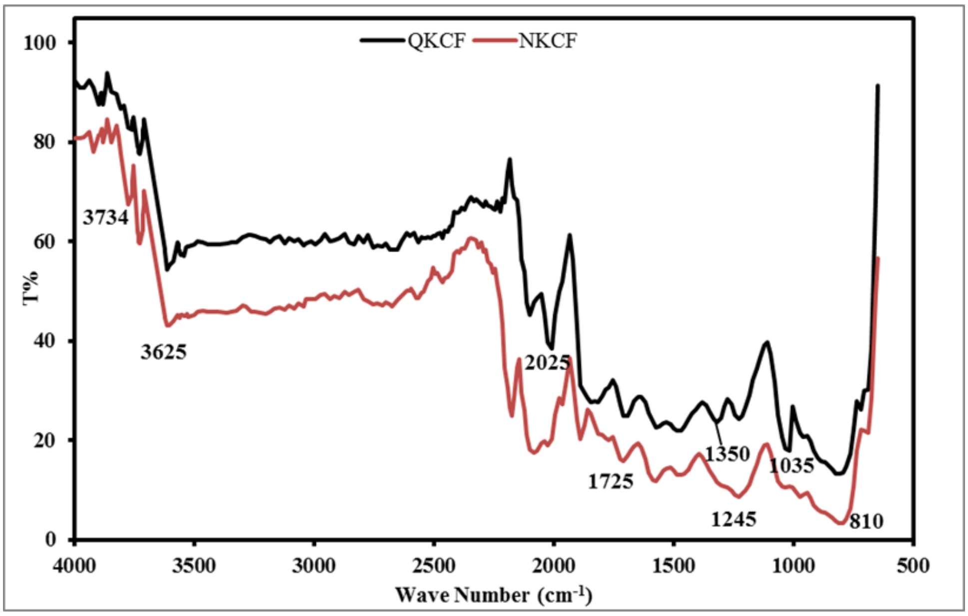

Figure 5: FTIR spectra for NKCF and MKCF

Table 3: Analysis of FTIR spectra of NKCF and MKCF

Frequency for NKCF (cm^{-1})	Frequency for MKCF (cm^{-1})	Assignment
3734	3734	O-H stretching
3625	3625	O-H stretching
-	2025	C-H stretching
1725	1725	C = O stretching
-	1350	O-H bending
1245	1245	C-O stretching
-	1035	C-O-C stretching
810	810	CH_2 rocking

BET Analysis:

The BET analysis of MKCF and NKCF has revealed that the surface area (SBET) increased from 2.3 m^2/g for NKCF to 4 m^2/g for MKCF and the average pore diameter increased from 105.5 nm for NKCF to 283 nm for MKCF. Enlargement of the pore size is due to the dissolved lignin and hemicellulose in NaOH solution during the mercerization process. Hence, increase the surface area of cellulose that can react to quaternizing agent. Furthermore, pore volume slightly decreased from 0.1699cm^3/g for NKCF to 0.1128 cm^3/g for QKCF. It is attributed to the smoother texture of KCF surface after chemical quaternization.

Particle size distribution:

Particle sizes for MKCF with a log-normal distribution are shown Figure 6. The most widely used method of describing particle size distributions are D values. The D10, D50 and D90 are commonly used to represent the midpoint and range of the particle sizes of a given sample. From the results of Particle size distribution, the D10, D50 and D90 were 15.391, 71.342 and 502.201µm respectively. Particle sizes distribution is a very important parameter to be considered when selecting suitable adsorbent particle size. Smaller particle size yields better removal efficiency because smaller particle sizes have larger surface area and that will increase the number of active sites for adsorption, however, fine particles that have difficult and long settling time are not favored as they will cause a problem in separation after the adsorption process. Therefore, the adsorbent particle size must be choosen according to their removal efficiency, settling time, and cost factor.

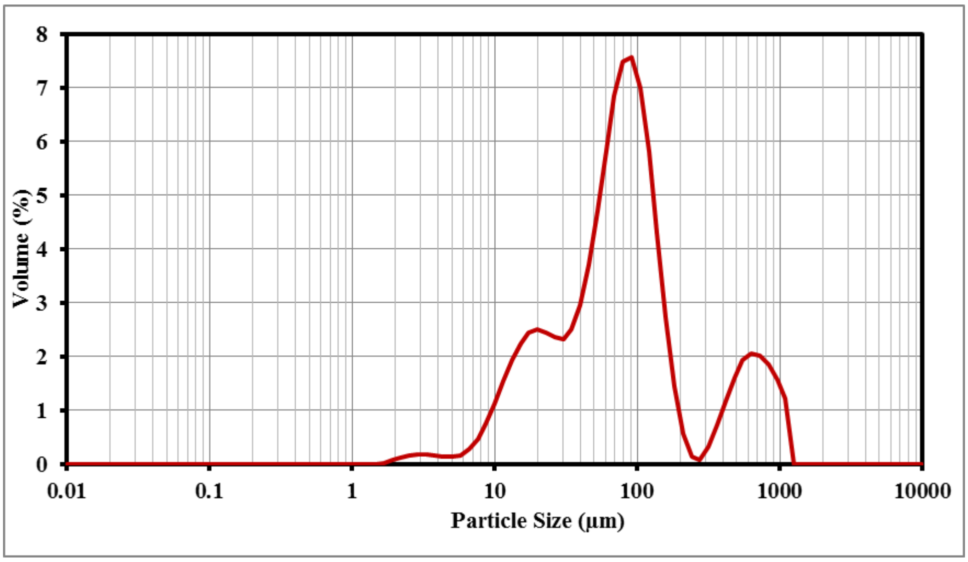

Figure 6: Particle Size Distribution for MKCF.

Dosage effect:

Adsorbent dosage is an important parameter in adsorption studies. All experimental were conducted at the temperature of 30 ^{0}C, and speed 150 rpm, with a period of time 24 hours. Dye concentration of AR114 in this liquid was 0.1g/100mL and the (MKCF) varied dosage were 0.2, 0.16, 0.14, 0.12, 0.1,0 .08, 0.06 and 0.04 g/100 ml respectively, Figure 7, shows the effect of adsorbent dose on the removal of AR114 by MKCF. From the figure it can be seen that an increase of adsorbent dosage from 0.02 to 0.1 g/100ml causes an increase in percentage removal from 45% to 99.14 %. This is due to the fact that, increase in MKCF dosage increase area available for adsorption. Moreover, a further increase in adsorbent dosage resulting in a slight percentage of dyes removal due saturation point. For subsequent adsorption experiments a 0.1 g/100 ml dosage of MKCF was selected because it is the least amount used and showed the best removal for both dyes.

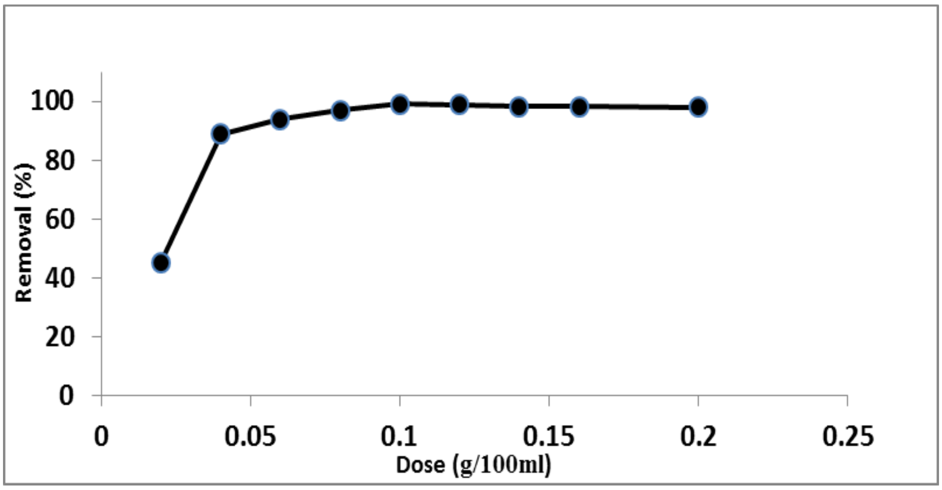

Figure 7: impact of (MKCF) dosage in AR114 removal

PH effect:

PH has a significant impact on adsorption process as it affects the adsorption capacity, dye solubility (Iscen et al., 2007). The degree of acidity used is between 2 and 12 at 30°C. Add caustic soda or Hydrochloric acid, the solution is adjusted to pH up to the required. The percentage removal of AR114 dye is slightly affected by pH over the whole range explored Figure 8, and it is clear that the best initial pH of the sorption from pH 6 to 8 and above this value decreased with 100 mg/L fixed initial dye concentrations, adsorption rate did not vary significantly and the removal percentage was steady around 99%. The authors attributed this behavior caused sites willing to absorb and which cannot be estimated, but undoubtedly many and these places have the ability to absorb the dissolved and related the solute uptake to the effective venues.

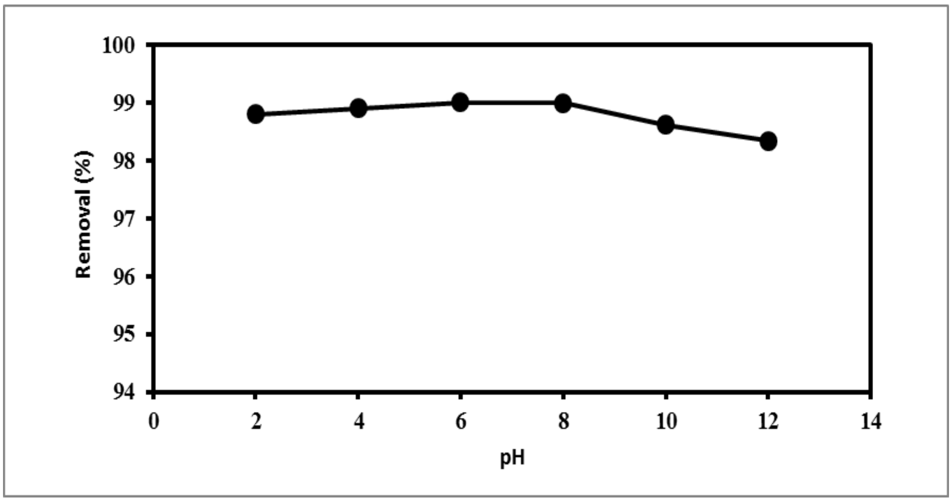

Figure: 8 impact of pH in AR114 removal

Effects of an initial concentration and contact time:

Many important things have an effect is evident in the systems treatment and models of water and effluent water and aqueous solution, Equilibrium time as it affects the size of the interaction [25]. In the beginning, it was acting Alltel with pigment red 114 High-absorption, because to provide surface and interior spaces empty, after this the then-Speed decline gradually to that reach a state of balance After 190 minutes, we see so clearly in Figure 9. The sorption of AR114 was carried out at different initial solution concentrations used in this study (5, 25, 75 and 100 mg/L), at pH 6.5, and Speed vibration 150 rpm

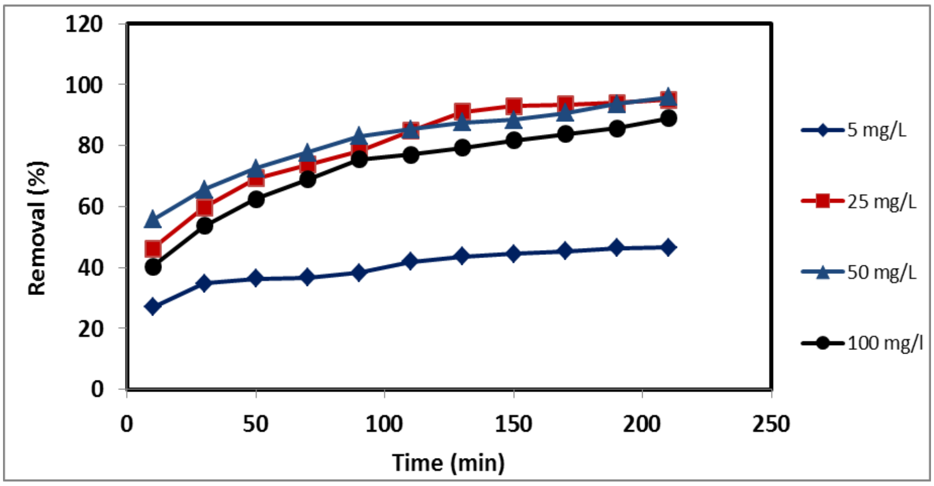

Figure 9: Impact of period time in removal efficiency of AR114 dye For Several initial concentrations

Adsorption Isotherm Study:

The processes of adsorption dyes are usually described through isotherms, which is a relationship between the amounts of adsorbate (dye) adsorbed on the surface of adsorbent (MKCF) and the amount of adsorbate (dye) remaining in a test medium at equilibrium. In this study, the most popular adsorption isotherms which are Langmuir, Freundlich and Temkin models have been studied [26, 27].

Langmuir Model:

The Langmuir isotherm principle can be described with fewer words is absorption occurs on the outer surfaces only, and this surface homogenous, As Langmuir. Isotherm is monolayer isotherm (Langmuir, 1916), the Langmuir equation (1).

$$C_e/qe=1/Kq_{max}+ C_e/q_{max} \quad (1)$$

The: C_e= equilibrium concentration (mg/L), q_{max} = equilibrium adsorption capacity (mg/g), K= Langmuir rate of adsorption (L mg/l). In Figure 10, from result C_e/q_e against C_e gets a straight line, from the sloped can be calculated q_{max}, K.

RL = 1/ (1+K.C_o) (2)

Where: K= denotes the Langmuir Constant C_o = the initial concentration.

Plot of the linear form of Langmuir equation for AR114 dye are shown in Figures 10. Analysis of linear regression of Langmuir isotherm shows that the maximum adsorption capacity (q_{max}) for adsorption of AR114 by MKCF was 238.1 mg/g. Moreover, the correlation coefficient (R^2) for AR114 was 0.9853.

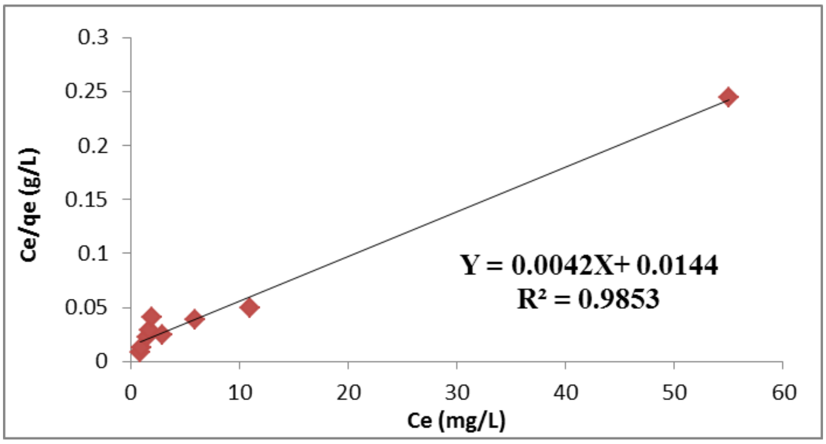

Figure 10: Langmuir adsorption isotherm for AR114

Freundlich Modle:

On heterogeneous surfaces only absorption of the dye is happening, this is what reached Freundlich, one of the experimental equations, logarithmically non liner (Freundlich, 1906). Can be written as follows, shown in Figure 11.

logqe=logKF+(1/n)logCe (3)

qe= KF*$Ce^{1/n}$ (4)

Where: K = Freundlich constant. n = adsorption intensity. 1/n= is an empirical parameter dependent on adsorption rigor. From the slope, the values of KF, n calculated directly. Figure 11, explaine the linear form of Freundlich isotherm model for AR114 dye. Figure show that the correlation coefficient (R^2) for AR114 was 0.8395.

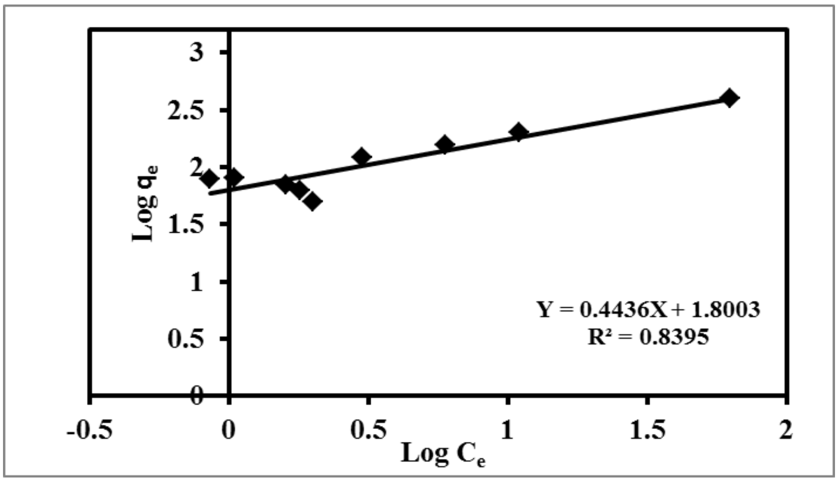

Figure 11: Freundlich adsorption isotherm for AR114 Temkin Modle.

In the same context, the Temkin isotherm used too to evaluate the Assimilation potential of acid dye, Principle Temkin, Interaction or the absorption occurs only on the outer surfaces with coverage of, not be the low temperature logarithmically, rather be linear .on this basis, the standard format is prevalent in energy distribution (Aharoni, 1977). The equation Written as follows (5).

q_e=(RT/b)*ln (A)+(RT/b)ln(Ce) (5)

(B=RT/b)

The: R= 8.314 J/mol, K, T= is the absolute temperature in K, (L/g), A = Temkin isotherm constant (L/g), b= is related to the heat of adsorption (J/mol). From the Temkin plot shown in Figure 12, the Temkin isotherm model cannot describe adsorption of AR114 on MKCF because it gives the lowest correlation coefficient (R^2) 0.766 for AR114. The summary of results for isotherm constants of dye is listed in Table 4. From the above results, the Langmuir isotherm model is the best in describing adsorption of AR114 dye on MKCF since it gives the highest correlation coefficient (R^2) (0.9853) as well as the lowest SSE value (7228).

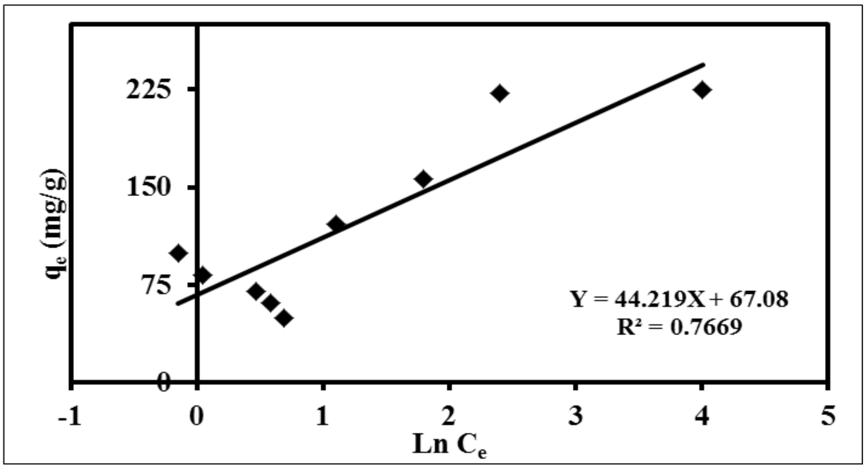

Figure 12: Temkin adsorption isotherm for AR114

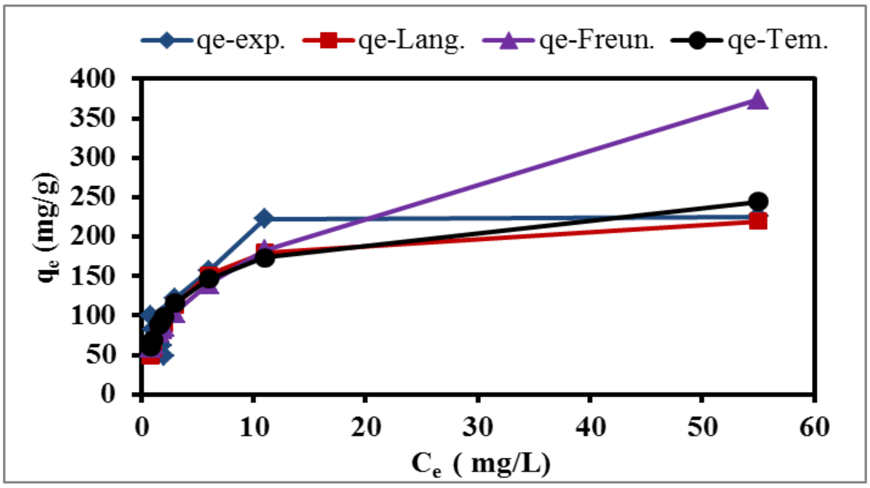

Figure 13: Adsorption Isotherms for AR114

Table 4: Isotherm constants for AR114 on MKCF

Model	Parameters	AR114 dye
Langmuir	q_{max} (mg/g)	238.1
	b (L/mg)	0.292
	K_L (L/g)	69.444
	R_L	0.0331
	R^2	0.9853
	SSE	7228
Freundlich	K_F	63.125
	1/n	0.4436
	R^2	0.8395
	SSE	28053
Temkin	A (L/g)	4.558
	B (J/mol)	44.219
	R^2	0.766
	SSE	8312

Kinetics study:

Several applications kinetic adsorption can be measured and Evaluation the efficiency of the adsorption procedure. To evaluate the rate adsorption of (MKCF), the data in Figure 14, were used with pseudo-first, pseudo-second, kinetic methods. The formula of pseudo-first, written (6) (Hossain, 2010):

$$\log(q_e-q_t)=\log q_e-(k/2.303)*t \quad (6)$$

Where: qe = value of MKCF adsorbed (mg/g) at equilibrium, qt = value of MKCF adsorbed at a time (min), k = average constant of adsorption operation (min-1) of the pseudo-first.

(K, qe_{cal}) can found from the slope (k). It can be seen in Figure 14, the data can be found in Table 5. The calculated qe values we found from this kinetic method did not satisfy the experimental one. Hence, the results obtained do not meet the ambition and we conclude that the process is going on approach the pseudo-second order.

Pseudo-second order method Equation (7) had been achieved by plotting t/qt vs. (t). The values of K_2, and calculated q_{cal} .We can be found from the drawing from cross t/qt vs. (t), in Figure 15.

$$t/q_t=1/(k_2* q_e^2)+(1/q_e)*t \quad (7)$$

The data can be found in Table 5, through the value of (R^2=0.9953) found clear and high, show that the process was very good and follow to the path of pseudo-second-order. And that the adsorption process carried out correctly.

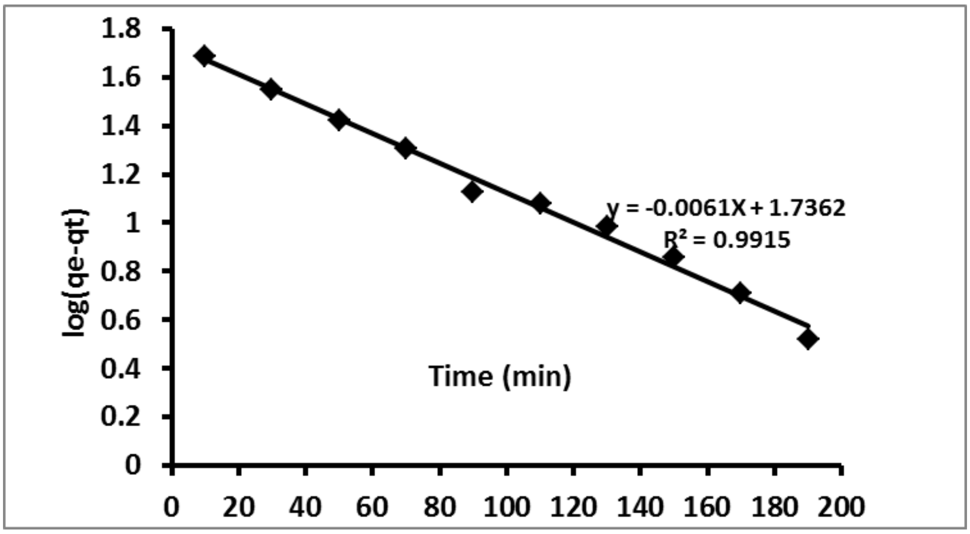

Figure 14: Kinetic study of AR114 on MKCF by using pseudo-first order kinetic method (C_o=0.1g/100mL)

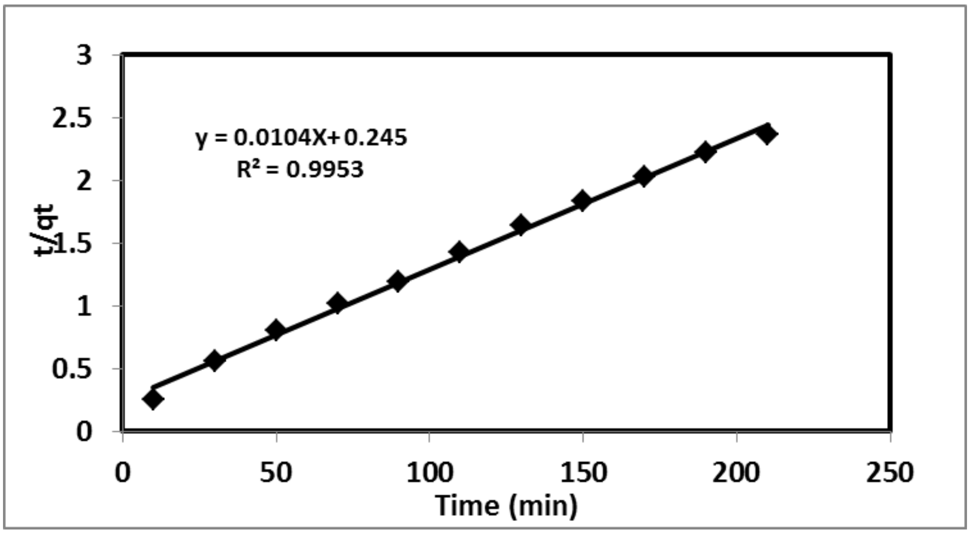

Figure 15: Kinetic study of adsorption of AR114 on MKCF by using pseudo-second order kinetic method (C_o=0.1 g/100mL)

Table 5: Parameters and pseudo-first, and second order kinetic method, for of AR114 by MKCF.

Name of dye	$q_{e\ exp}$ (mg /g)	Pseudo-first-order kinetic model			Pseudo-second-order kinetic model		
		$q_{e\ cal.}$	K_1	R^2	$q_{e\ cal.}$	K_2	R^2
AR114	88.94	54.5	0.0141	0.9915	96.153	0.0000131	0.9953

4. CONCLUSION

in this study, was successfully prepared Modified Kenaf (MKCF), improvements in terms of adsorption capacity, and removal, Results showed that modified Kenaf have higher adsorption efficiency compared with raw Kenaf (ecofriendly adsorbents and ideal alternative). Kenaf was perfect with the dye used has a good strength to remove acid dye from solutions. In this research, we used AR114 dye and was percentage removal idealism of 99.141% dye, has reached an equilibrium state in a short time at 210 minutes and optimum pH=6.5. Was studied several Requirements, like initial dye condensation, contact time, PH, dosage, SEM, FTIR, BET, Equilibrium data; It came identical with Langmuir method, Freundlich method. The best correlation was for Langmuir. The adsorption kinetics was convenient with pseudo-second order kinetic method. All data and graphs of linear equations clear well and explained to us the general behavior.

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