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Acid Dyes Removal from Aqueous Solutions Utilizing Amidoximated Jute Fibers Under the Effect of Gamma Irradiation

M.S. Hassan, R.M. Attya, M.H. Zohdy, A.M. Rabie
Radiation Chemistry Department, National Center for Radiation Research and Technology, Atomic Energy Authority, Cairo, Egypt

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Jute fibers were graft-copolymerized with acrylonitrile using gamma radiation technique. The nitrile groups attached to the grafted fibers were converted into amidoxime groups, through an amidoximation process, for using as an adsorbent for the acid dyes from the textile wastewater. The graft yield as a function of the irradiation dose was investigated. The amidoximated Jute fibers were characterized by Fourier transform infrared (FTIR) and X-ray diffraction (XRD). The thermal stability of modified Jute fibers was also investigated by thermogravimetric analysis (TGA). The kinetic parameters of the adsorption process and the effective conditions on the adsorption capacity, such as the pH and contact time, were also investigated. The grafting of the Jute fibers with ACN and the amidoximation process of the nitrile groups were confirmed using FTIR technique. The results indicated that, the dye adsorption was enhanced at low pH of 4 and obeyed the pseudo second order kinetic model.

Keywords: *Jute fibers, Acrylonitrile, Amidoxime, Gamma radiation, Acid dye, Adsorption*

Introduction

The presence of dyes in the wastewaters of the textile industries, industrial effluents and water supplies can cause environmental damage. The waste dyes are known by their biodegradation resistance and their significant mutagenicity [1]. Dye pollutants are harmful to the human health, on which they have dangerous effects against the different biological systems of the body [2]. Some dissolved dyes have toxic effects against the aquatic life [3]. On the other hand, the water containing the waste dyes could reduce the sunlight penetrations, which hinder the photosynthesis process [4].

Different techniques were used to purify the wastewater from dyes. The used techniques include biological or chemical procedures [5, 6] or physical techniques, including the filtration and the adsorption on different absorbents [7, 8]. The adsorption processes are becoming increasingly popular method for dyes removal from wastewater. The dye adsorption procedures can be classified according to the type of interactions between dyes and adsorbent either physically (via van der Waals forces) or through chemical process. The adsorbent materials can be classified into: (a) mineral supports such as activated carbon**,** (b) vegetal material, such as sunflower stalks and (c) modified biopolymers such as aminated sawdust and cellulose bearing active groups [9]. Various dye adsorbent substrates were used including: peels [10], activated carbon [11], soil [12], fly ash [13], silica [14], chitosan and chitosan derivatives [15-16] and the modified cellulosic materials [17]. The adsorption efficiency of the different adsorbents towards the dye from aqueous solution could be affected by many factors such as the pH [18-20], the dye concentration in the aqueous solution [20, 21], the ionic strength of the dye solution [19, 22], contact time [20, 21] and the temperature of the dye aqueous solution [22].

Corresponding author: mah5moud@hotmail.com
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There are different applications of the irradiation process, especially on the polymeric materials, either trough its polymerization and crosslinking effects, or by introducing new functionalized reactive groups upon the irradiated materials [23-25]. For example, the irradiation can be used to modify the cellulosic substrates to gain new properties as dye absorbents, which help in the dye removal and play an important role in the decreasing of the water pollution, especially in the textiles wastewater [17].

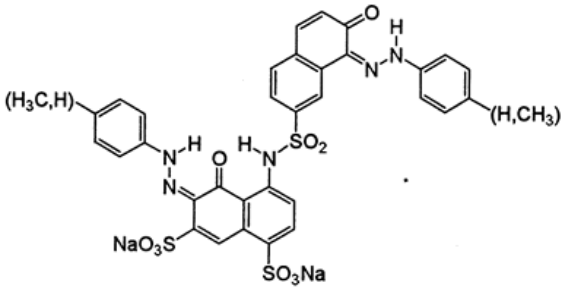
Jute, as an example of the cellulosic materials, can be chosen as a suitable dye adsorbent, which is characterized by its durability, low cost and its eco-friendly properties, although it possesses some undesirable properties as it contains a high percentage of hemicellulose and lignin, which increase its overall crystallinity and stiffness [25]. Hence, Jute fibers must be pre-treated before being used to enhance their chemical reaction [26, 27].

The present study was undertaken to prepare graft copolymerization of Jute fibers with acrylonitrile under the effect of gamma irradiation, and then the nitrile groups upon the grafted Jute fibers were converted into amidoxime groups, to be used as an adsorbent substrate for acid dye (C.I. Acid red 158). The role of the effective parameters on the adsorption efficiency such as the pH range and the contact time were studied. The kinetic parameters of the adsorption process were also studied.

Experimental

Materials

Acrylonitrile monomer (AN), MW of 53.06 was obtained from Ranbaxy, India.The raw Jute fibers were obtained from the Egyptian Company for Jute Production, Egypt. The analytical grades of sodium hydroxide, sodium carbonate and glacial acetic acid were obtained from El-Nasr Pharmaceutical Chemicals Co., Egypt. Telon Fast Red ER (C.I. Acid Red 158) (the chemical structure shown in **Scheme 1**). was obtained from Bayer, Germany. The distilled water was used to prepare all the solutions.



Scheme (1): Telon Fast Red ER (C.I. Acid Red 158)

Grafting of Jute fibers with acrylonitrile

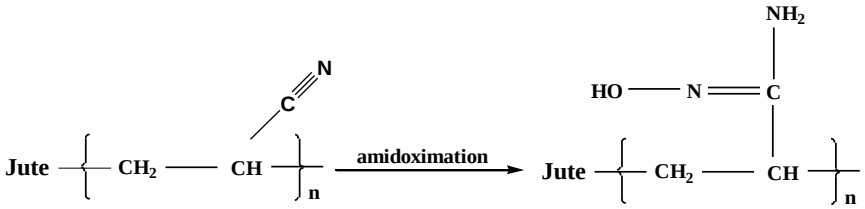
The raw Jute fibers were first pre- soaked in a concentrated solution of NaOH for 24 h and washed and neutralized with dilute acetic acid. The samples were then dried and weighed **(W_o)**. The pretreated Jute fibers were put into glass tubes containing acrylonitrile monomer, distilled water and solvent. Direct irradiation was used at different doses. The unreacted monomer and produced homopolymer upon the grafted fibers were removed, dried and weighed **(W_g)**. The total graft yield was calculated as described in **Eq 1**:

$$\text{Graft yield (\%)} = [(W_g - W_o)/W_o] \times 100 \qquad (1)$$

The gamma irradiation was carried out in Co^{60} gamma cell unit (made in India), installed at the National Center for Radiation Research and Technology (NCRRT), Cairo, Egypt at a dose rate (during the work) of 2.5 kGy/h.

Amidoximation

The nitrile groups upon the Jute-g- PAN were transformed into amidoxime groups by reacting with hydroxylamine hydrochloride. The dried samples of grafted Jute -g-PAN were put into an aqueous solution of hydroxylamine hydrochloride, and then boiled for 4 h, under reflux, after adjustment of pH using sodium carbonate. The treated Jute fibres were washed for several times and then dried using hot air [28] Scheme (2) describes the transformation process:



Scheme (2): Amidoximation reaction of Jute-g-PAN

Characterization of the amidoximated Jute fibers

Fourier transform infrared **(FTIR)** in wide range wavenumbers (400 - 4000 cm^{-1}) using Mattson 5000 FTIR spectrometer, Mattson Instruments, Madison, WI., was used to analyze the amidoximated Jute fibers. X-ray diffraction **(XRD)** using Philips (PW 1390) unit was utilized to examine the treated Jute samples, in which the diffractograms were scanned from 2^o to 40^o at room temperature. Thermogravimetric analysis **(TGA)** made by Shmadzu-30 (TGA-30), Japan at a heating rate of 10^oC/min in air, over temperature range of 30 -600^oC, was used to study the thermal stability of the treated Jute samples

Determination of the adsorbed acid dye by amidoximated Jute fibers

The amount of the acid dye absorbed by amidoximated Jute fibers was calculated through the determination of the remaining dye concentration in the solution, The UV/Vis spectrophotometer (Unicom UV2 series) was used to determine the wavelengths of the dye solutions [29]. A standard curve representing the relation between the known concentrations of the used dye and the corresponding light absorption was taken as a reference to determine the unknown dye concentrations. The amount of adsorbed dye *q* (mg/ g) was calculated according to the Eq 2:

$$q = (Co - C_e)\, V/ W \qquad (2)$$

Where C_o and C_e represent the dye solution concentrations at initial point and at equilibrium (mg/L), respectively, *W* represent the weight of used treated Jute fibers (g), *V* is the volume of dye solution (L)[20].

Results and Discussion

Gamma radiation-induced grafting of acrylonitrile monomer onto Jute fibers

In previous studies, it was reported that water/alcohol binary mixture is the suitable solvent for the grafting of cellulosic materials with AN, in which, the chance of macro-polymeric radicals to attach with the empty active sites upon the swelled cellulose fibers with water, leading to the increase of the obtained graft yield [30]. The most suitable solvent mixture in the grafting process of Jute fibres was H2O/EtOH (1:1), depending on the swelling parameters of both cellulosic fibres and AN. The effect of monomer concentration on the obtained graft yield were studied, and it was found that the highest monomer concentration was 40%, which gave the optimum and homogenous graft yield and to avoid homopolymer formation. The effect of irradiation dose on the graft yield was also studied, as shown in Fig. (1). It can be seen that the graft yield was increased by increasing the irradiation dose as a result of the increasing of the formed free radicals, up to irradiation dose of 30 kGy, and the yield then tended to slightly increase at a slow rate due to the formation of homopolymer [31]. The highest homogenous graft yield obtained (16 %) of PAN onto the Jute fibres was achieved by the use of 40% monomer concentration, 30kGy irradiation dose and solvent mixture of H2O/EtOH (1:1).

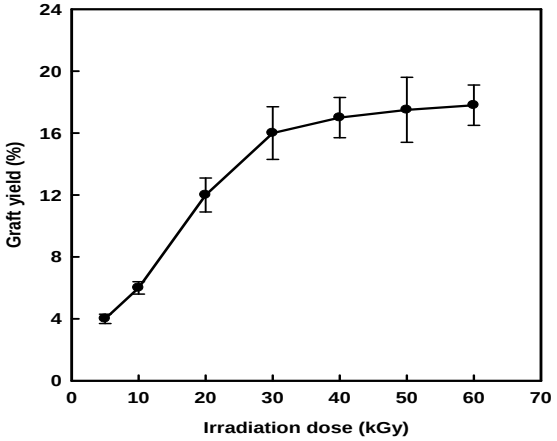


Fig. (1): Effect of irradiation dose on the graft yield of PAN onto Jute fibres

Characterization of amidoximated Jute fibers
Fourier-transform infrared (FTIR)

The structural changes of untreated Jute fibres, and those grafted with PAN and after amidoximation process, were analyzed by FTIR spectroscopy as shown in Fig. (2). The IR spectrum of Jute fibres, as cellulosic materials showed an absorption bands at 3448cm^{-1}, 2923cm^{-1}, 1650-1640cm^{-1} due to the stretching vibration of –OH, C-H stretching vibration and corresponding to water associated with cellulose, respectively. In addition, it showed absorption bands at 1375-1320 cm^{-1} and at 1047-1004cm^{-1} representing the C-H bending vibration of cellulose, and the stretching vibration of C-O, respectively as shown in Fig. (2a). The absorption band seen at 2245cm^{-1}, represents the nitrile group (–CN) as result of the grafting process of Jute fibres with PAN as shown in Fig. (2b) [32]. After amidoximation process, the characteristic band of -CN group at 2245 cm^{-1} disappeared, accompanied with the appearing of a broad band at 3000-3500 cm^{-1} for (N-H and O-H stretching vibration), at 1650 cm^{-1} for (C=N stretch vibration) and a broad band at 920cm^{-1} for (N-O stretch vibration), as shown in Fig. (2c) [33].

X-ray diffraction (XRD)

The XRD spectra of the raw Jute fibre, Jute-g-PAN and Jute-g-PAO were studied as shown in Fig. (3). A definite characterized peak was noticed at 2θ= 22.45^{o} of Jute fibres, which indicates the high crystalline nature of Jute fibres, as a result of the high crystalline lignin [27]. However, the intensity of the peak was decreased after grafting with PAN, which has a lower crystal lattice than that of the virgin Jute fibres. After the amidoximation process, a slight increase in the crystallinity was noticed as a result of the conversion of the nitrile groups to amidoxime groups with higher crystal lattice.

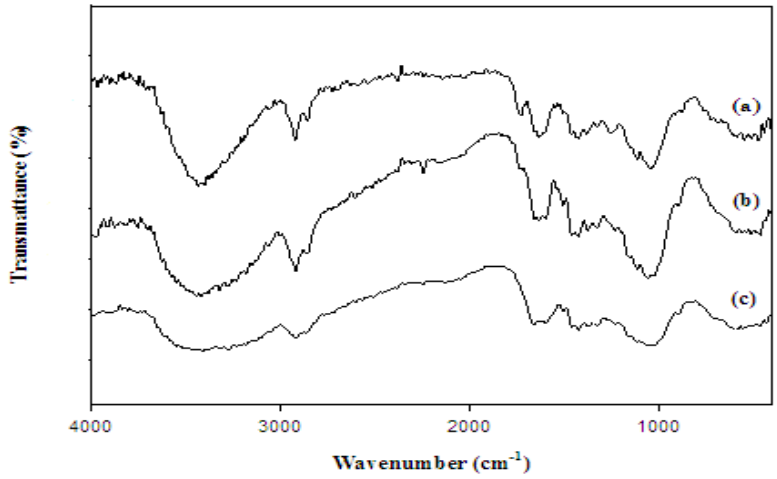


Fig. (2): FTIR spectra of: (a) pure Jute, (b) Jute-g-PAN and (c) Jute-g-PAO fibres

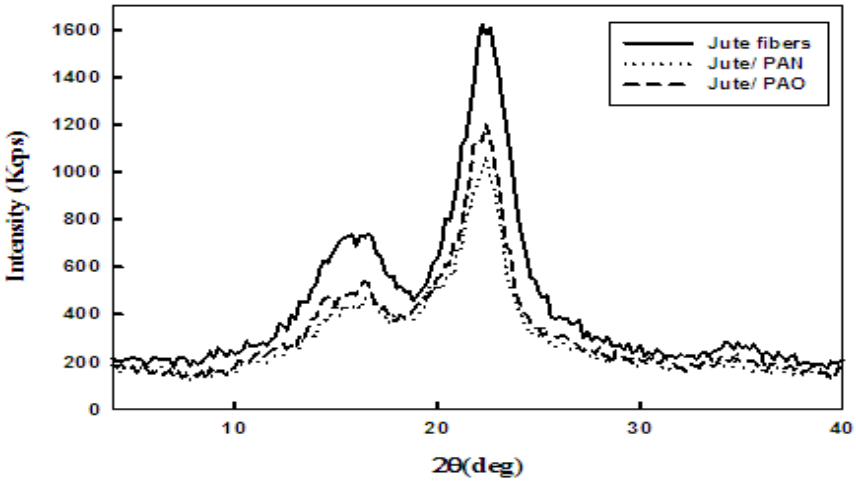


Fig. (3): XRD scans of untreated Jute, Jute-g-PAN and Jute-g-PAO fibres

Thermogravimetric analysis (TGA)

The TGA thermograms and the corresponding rate of thermal decomposition reaction curves of untreated Jute fibres, Jute-g-PAN and Jute-g-PAO are illustrated as shown in **Fig. (4)**. It was found that the thermal stability of grafted Jute fibres with PAN and amidoximaed fibres was higher than the untreated Jute fibres as a result of the formation of crosslinked polymer (PAN) formation upon the Jute fibres [34]. As seen in **Fig. (4)**, it can be noticed that there is an increase in the temperature of the maximum rate of the thermal decomposition reaction (T_{max}) by grafting with PAN and after amidoximation process. The T_{max} for Jute, Jute-g-PAN and Jute-g-PAO were found to be 362, 372 and 380^{o}C, respectively, while, the weight remaining (%) were 5, 13 and 28 % at 500^{o}C for Jute, Jute-g-PAN and Jute-g-PAO, respectively. This could be attributed to the high stability of each component (amidoxime group, backbone graft chain and the cellulosic chain), which accordingly need more heat to be decomposed forming multiple stages of degradation and higher temperature range. Also, the rate of thermal decomposition values was found to follow the order:

Jute-g-PAO > Jute-g-PAN > Jute fibres

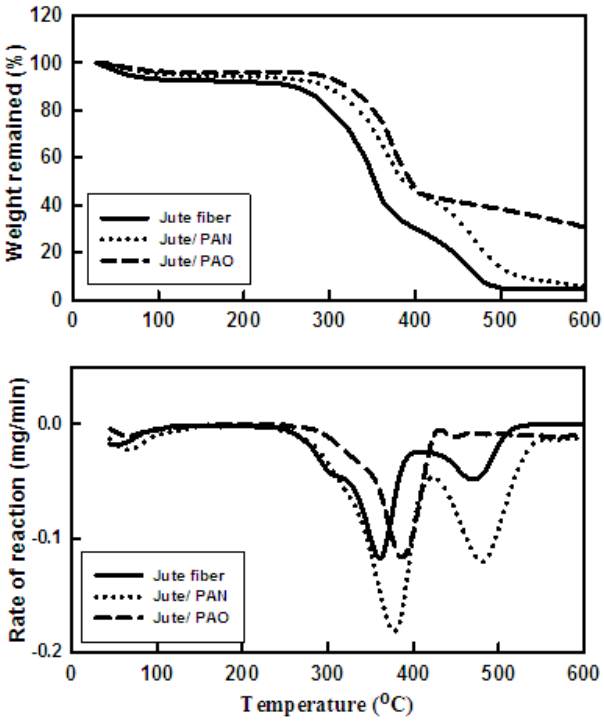
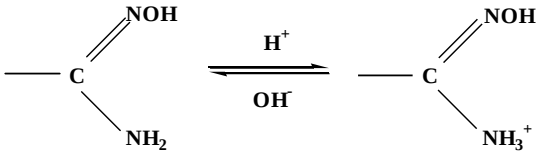


Fig. (4): TGA thermograms and the corresponding rate of thermal decomposition curves of: untreated Jute, Jute-g-PAN and Jute-g-PAO fibres

Dye adsorption by amidoximated Jute fibers

Adsorption mechanism of acid dye by amidoximated Jute fibers

The raw Jute fibers have no affinity for the adsorption of acid dyes, while, the amidoximated Jute fibers have an acceptable affinity as an adsorbent towards acid dyes. This could be due to the presence of amidoxime groups, which possess two lone pairs of electrons, one of them on the oxygen atom and the other on the N atom [35]. With the variation of the pH range, the amidoxime chelating functional group acts as an amphiprotic compound due to its two possible isomerization equilibriums, as shown in **Scheme 3.** It is observed that in acidic medium, the amidoxime functional group behaves as a cation group for adsorption of anionic dyes (acid dye) through electrostatic attraction.



Scheme (3): Isomerization equilibriums of the amidoxime functional groups

Effect of pH on dye adsorption

The amount of the adsorbed dye **(*q*)** by amidoximated Jute fibers as a function of different pH values, while keeping of the dye concentration at 50 mg/L was determined as illustrated in **Fig. (5)**. It can be seen that, the amount of adsorbed dye was decreased by increasing of the pH range of the dye solution. The highest adsorbed amount of acid dye was achieved within the pH range 3-4. This could be attributed to the action of the amidoxime groups, which have the amphiprotic ability and tends to turning into cation molecules via accepting of hydrogen ions (H^{+}) at low pH range, which can adsorb the acid dye (anion dye) through electrostatic attraction [35], as described in Scheme 4.

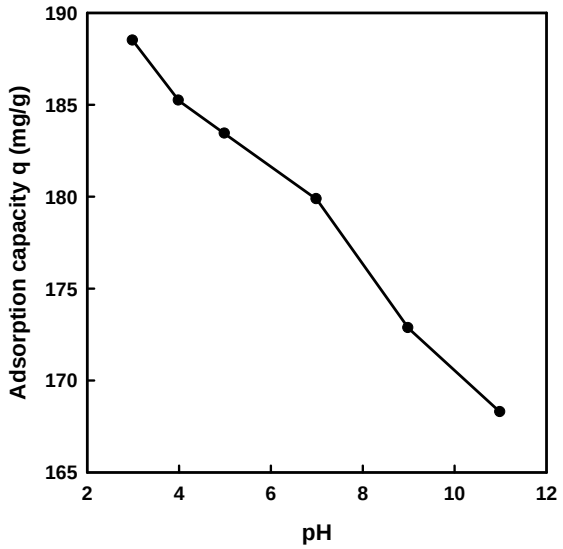
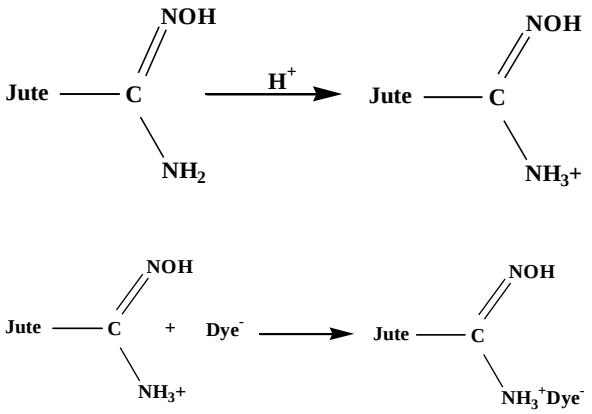


Fig. (5): Effect of different pH ranges on the dye adsorption percentage by modified Jute fibers at different temperatures



Scheme (4): The effect of the protonation process on the acid dye adsorption by the Jute-g-POA

Effect of contact time on dye adsorption

The amount of the adsorbed dye **(*q*)** by amidoximated Jute fibers as a function of the variation of the contact time, while keeping of the dye concentration at 50 mg/L and at a dye solution pH of 3, at room temperature was determined as illustrated in **Fig. (6)**. It was noticed that the amount of adsorbed dye by the amidoximated Jute fibers was increased with increasing of the contact time up to 20 min, then it tends to increase at lower rate with increasing the contact time up to 60 min, then it tended to level off with further increase of the contact time. The significant dye adsorption rate in the beginning state may be due to the presence of strong electrostatic binding between dye molecules and the protonated amidoxime molecules upon the treated Jute fibers, which contain sufficient vacant adsorption sites [36]. It was noticed also that, the rate of dye removal was decreased by increasing of the contact time, as a result of the decreasing of the available vacant adsorption sites on the treated Jute fibers.

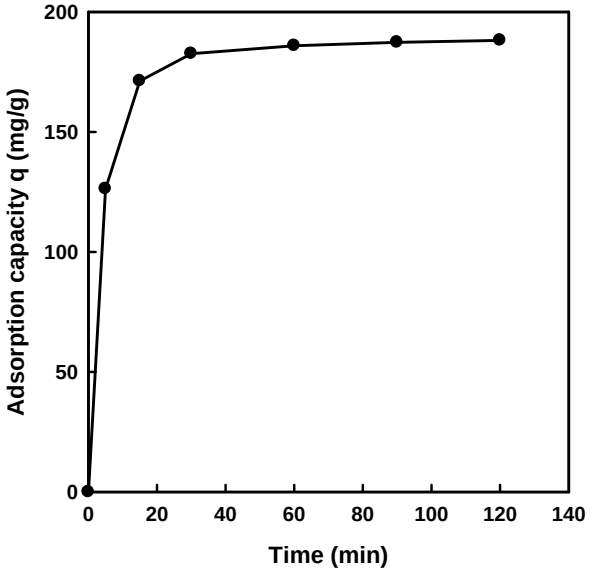


Fig. (6): Effect of contact time on the adsorption capacity of Jute-g-POA towards acid dye, at constant pH range: 3

Adsorption kinetics

The kinetics of the dye adsorption process of the acid dye (C.I. Acid Red 158) into the amidoximated Jute fibers were studied by the pseudo first-order model [37] according to Eq. 3:

$$\log (q_e - q_t) = \log q_e - k_{pf} / 2{:}303t \qquad (3)$$

Where, $\boldsymbol{q_e}$ represents the amount of adsorbed acid dye (mg/g) at equilibrium, $\boldsymbol{q_t}$ represents the amount of the adsorbed acid dye (mg/g) at time ***t***. the pseudo first order rate constant was represented by k_{pf} (min^{-1}). The slopes and intercepts of plots of log (q_e–q_t) versus time (t) were used to determine k_{pf} and q_e as illustrated in Fig. (7). The all resulted parameters and the correlation coefficient (r^2) were summarized in Table (1).

The pseudo second-order model [38] was also used according to Eq. 4:

$$t/q_t = 1/k_2 q^2_e + t/q_e \qquad (4)$$

Where, q_e represents the amount of adsorbed acid dye (mg/g) at equilibrium and q_t represents the

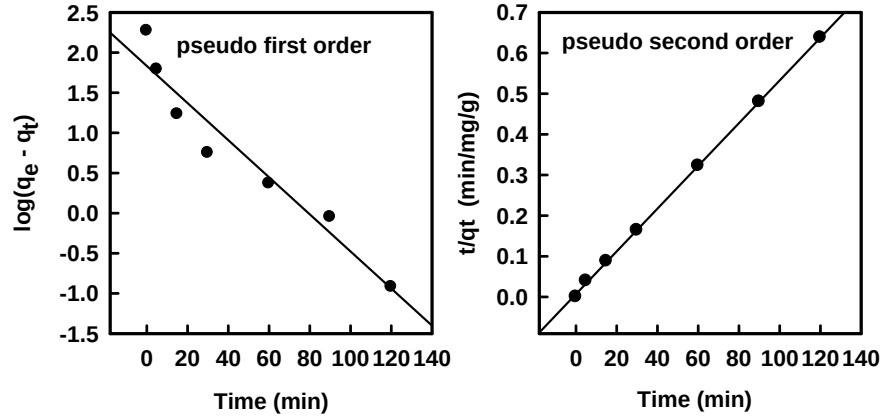


Fig. (7): The pseudo first and second order plots for the adsorption process of acid dye by Jute-g-PAO

Table (1): Kinetic parameters of the adsorption process of the acid dyes by Jute-g-PAO

Pseudo first kinetic model			Pseudo second order kinetic model		
K_{pf} (min^{-1})	q_e (mg/g)	r^2	K_{ps} (g/mg/min)	q_e (mg/g)	r^2
-4.496	**2.23**	**0.9361**	**0.005**	**0.00**	**0.9997**

amount of the adsorbed acid dye (mg/g) at time *t*, while k_2 (g/mg/min) represents the rate constant of pseudo second order adsorption. The slopes and intercepts of plots of (t/q_t) versus time (*t*) were used to determine k_2 and q_e as illustrated in Fig. (7). The resulted parameters of k_2 , q_e and the correlation coefficient (r^2) were illustrated in Table (1). It can be seen from Table (1), which summarizes the data achieved for both of the two adsorption kinetic models, the correlation coefficient was found to be 0.9361 according to the pseudo first order model, while it was 0.9997 according to the pseudo second order model, which indicate that the dye adsorption processes by the amidoximated Jute fibers follows the pseudo second order kinetic model.

Conclusions

This study showed that Jute fiber, as a cheap natural fiber, can used as an effective adsorbent for acid dyes from wastewater, by graft copolymerization with acrylonitrile, followed by amidoximation process. The effective factors on the grafting process were investigated, in which the optimum graft yield was obtained at an absorbed dose of 30 kGy and monomer percent of 40%. The dye adsorption by the modified Jute fibers was increased in acidic medium (pH: 3-4) and by increasing the contact time. It was concluded also that the dye adsorption process follows the pseudo second order kinetic model.

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