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Removal of Acid Yellow by Agricultural Waste

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Abstract

This work presents the removal of acid yellow 24(AY 24) dye from aqueous solutions using the low cost activated carbon of Lufa Acutangula Seed hull (LAS) was produced from agricultural waste.The activated carbon from agricultural waste could increase economic return and reduce pollution. The effectiveness of LAS adsorbent had been tested for the removal of colour from aqueous solution containing acid yellow 24. Batch adsorption experiments were carried out as a function of pH, agitation time and initial concentration of the adsorbate. The desorption study also carried out for the evaluation of regenerability of the activated carbon. The equilibrium adsorption uptake capacity of the process were analysed with the Freundlich, Langmuir and Temkin isotherm parameters. The dynamics of adsorption process was tested with pseudo second order mechanism. The best results were achieved with Freundlich isotherm equilibrium model and with the pseudo-second order kinetic model.

Keywords: Acid Yellow, Effluent Treatment, Textile Dye, Lufa Acutangula, Freundlich Isotherm, Temkin Isotherm.

1. Introduction

Dyes and pigments represent common and dangerous pollutants, originating in large quantities from various industries like textile, leather, rubber, plastics, pulp and paper industries. Recent reports indicate that, approximately, 12% of the synthetic textile dyes were lost in every year during the manufacture and processing operation and 20% of these dyes enter to the environment through their effluents.They are entered into wastewaters and they being one of the recalcitrant, persist for long time in water, affect photosynthetic activity of aquatic plants, reduce the growth of aquatic biota by preventing sunlight and consume the dissolved oxygen content in water. Some dyes may cause allergic dermatitis, skin irritation, cancer and mutation problems to human beings and animals [1]. Different physical,chemical and biological colour removal processes were used to remove the various dyes. Some processes, such as electrochemical techniques and ion pair extraction, are relatively new for textile waste treatment, while others have been used in the industry for a long time. Adsorption has been found to be superior to other techniques for water re-use in terms of initial cost, simplicity of design, use of operation and insensitivity to toxic substances [2]. The removal of coloured and colourless organic pollutants from industrial wastewater is considered as an important application in adsorption processes [3]. At the present, there is a growing interest is to utilize the low cost as well as commercially available materials has been chosen for the adsorption of dyes. A wide number of reports are found in literature for the preparation of activated carbons by acid activation methods from cheaper and readily available materials like bamboo [4], peach stones [5], grass and wood [6], from the agricultural wastes like coir pith [3; 7] ,Cajanus Cajan(L)Milsp seed shell [8],sun flower seed hull [9],rice husk [10],fruit peel [11],castor seed [12] and from the industrial waste product like fly ash [13]and black slurry [14;15].

In this study, activated carbon was prepared from the agricultural waste, Lufa Acutangula Seed hull using sulphuric acid as charring agent for the dye removal and it was collected in the premises of Govt arts college cheyyar india. Luffa acutangula is a very versatile plant that is widely grown in India and Asia. The vines and fruits resemble a cucumber, when dried and peeled reveals a fibrous, spongy skeleton. The Luffa plant is a fast-growing in all climatic conditions. In particular, the adsorption properties and efficiency of the activated carbon have been studied. This work analyzes the effect of dye removal using isotherms and kinetic for the adsorption properties of activated carbon. The characterization for the presence of surface functional groups of the activated carbon was determined by using Fourier Transform Infrared (FTIR) spectroscopy.

2. Materials and Methods

2.1 Materials

Activated carbon was prepared from Lufa Acutangula Seed hull. The material was washed in hot distilled water to remove impurities and dried in a sun light. It was carbonized with concentrated sulphuric acid in the weight ratio of 1:1(w/v). The carbonization and activation was completed by heating for twelve hours in a furnace at 400°C. The resulting carbon was washed with distilled water until the neutral pH of the slurry was reached. Then the carbon was dried for four hours at 100°C in a hot air oven. The dried material was ground well to a fine powder and sieved with desired size. All chemicals used in this study were of high purity, commercially available Analar grade. Stock solutions of 1g/l of dyes were prepared using doubly distilled water.

2.2 Methods

Acid yellow 24 (AY24) dye solution was prepared with a known concentration. From that, 50 ml of 100 mg/l dye solution was taken and loaded with the 75mg of activated carbon. Then the solution was shaken in a mechanical shaker at a definite time intervals. After that sample was withdrawn from the shaker and filtered. Then the filtrate were analysed in UV-Visible spectrophotometer (ELICO - SL 150). Desorption studies were carried out using the spent carbon. The carbon loaded with dyes was separated and gently washed with distilled water to remove any unabsorbed dyes.The dye-loaded carbon was agitated with 50 ml of water adjusted to various pH values for 60 min and analyzed.

2.3 Batch adsorption studies

2.3.1 Adsorption experiments

Batch mode experiments were carried out using Lufa Acutangula Seed hull activated carbon (mass 75 mg) as an adsorbent to investigate the factors influencing the rate and extent of uptake efficiency of the dye by the adsorbent such as contact time, dosage of adsorbent, pH and desorption study.

2.3.2Effect of Contact time

Studies were carried out about 50 ml of dye solution for the concentration of 100 mg/l and the 75mg mass of adsorbent in a 250 ml conical flask which was shaken by 180rpm of speed.The experiment was carried out in a pH of 7 and the room temperature of 29°C.The contact time were varied from 10 mins to 120 mins with the 10mins time intervals.

2.3.3 Effect of adsorbent dose

The effect of the adsorbent dose on the equilibrium uptake efficiency of 50 ml of aqueous solution of dye concentration with 100 mg/l was investigated by agitating with different doses of adsorbent (0.1- 2.5 g) for a time greater than their equilibrium time for 180 rpm at its pH of 7.

2.3.4 Effects of pH

The effects of pH on the equilibrium uptake of the dye were investigated by using 50 ml of100 mg/l dye solution and known concentration of the adsorbent.The initial pH values were adjusted with 0.1M Hydrochloric acid or 1M Sodium hydroxide to attain a pH range from 2-12. The suspensions were agitated for 75 min.

2.3.5 Desorption studies.

Based on various pH (2 - 12) of 50 ml aqueous solutions were conducted by using 75mg of dye loaded adsorbent. The suspension was agitated greater than its equilibrium time at 180 rpm.

3. Results and Discussion

3.1 Effect of Contact Time.

The effect of contact time on the amount of AY24 dye adsorbed on the Lufa Acutangula Seed hull activated carbon was investigated at initial concentration of 100 mg/l. The contact time for different intervals were investigated this was presented in Fig.1.The results indicate that the rate of dye removal progressively increased with the time shows that a rapid adsorption of the dye at the initial stages of the adsorption and equilibrium was attained within 70 min.Such uptake indicates a high degree of affinity towards the AY 24 molecules via chemisorption.The increase of the rate of dye removal with contact time may be attributed to the decrease in the diffusion layer thickness surrounding the adsorbent particles and attained a plateau after a equilibrium adsorption of adsorbent.The maximum Quantitative removal 93.41% was obtained at an adsorbent dose of 75mg.

3.2 Effect of adsorbent dose

The effect of adsorbent dose was also investigated for the removal of dyes from aqueous solution. The experiments were carried out with adsorbent dose varied from 0.05 to 2.5g with keeping other parameters are constant. The removal percentages of dye were found to be 73 to 93.5% (Fig.2).The increase of dosage increases adsorbent sites that is the surface area of contact with the dyes increases [1:8].Therefore the amount of dye uptake capacity increases and consequently leads to a better adsorption. This trend is mainly due to the increase in sorptive surface area and availability of more adsorption site. Similar results have been reported by the other investigators [16;17].

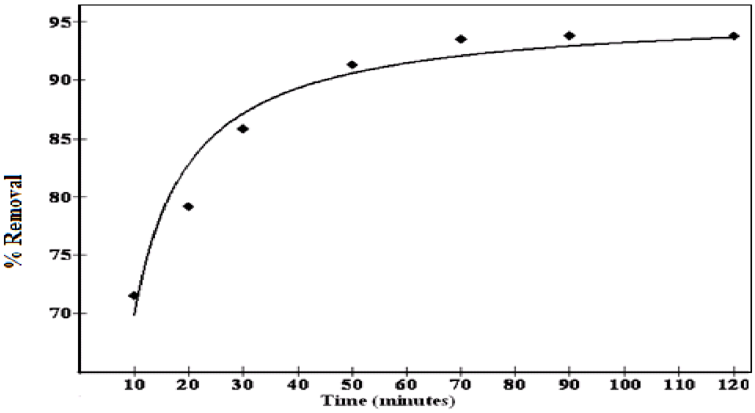

Figure: 1 Effect of Time

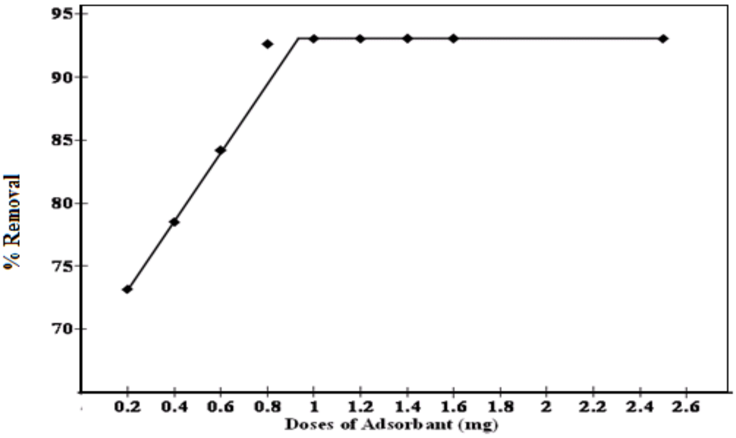

Figure: 2 Effect of Adsorbent Dose

3.3Effect of pH

The pH of the solution is an important factor that affects the rate of adsorption process, since it determines the interaction between the adsorbate and adsorbent surface. This interaction phenomenon implies which type of species (anions or cations) are liberated or surrounded on the surface of adsorbent during the adsorption. The effect of solution pH on the adsorption of AY24 by LAS was shown in Fig. 3. The amount of adsorption decreases when the pH increased. The Low pH (2 - 4) was found to be favourable condition for maximum adsorption of AY24. Similar results of pH effect were also reported for the adsorption of on banana pith [18], coir pith [19] and orange peel [11]. Two possible mechanisms of adsorption of AY24 may be considered: (a) electrostatic interaction between the protonated groups of carbon and acidic dye and (b) the chemical reaction. At pH 2 and 3 favouring significantly high electrostatic interaction exists between the positively charged surface of the adsorbent and anionic dye.

As the pH of the system increases, the number of the negatively charged sites increases and the number of positively charged surface site decreases (Fig. 3). A negatively charged surface site on the adsorbent does not favour the adsorption of dye anions due to the electrostatic repulsion. Low adsorption of AY24 at higher pH values due to the presence of excess OH^- ions competing with the dye anions for adsorption of the anionic dye on the adsorbent. At alkaline pH significant adsorption of the anionic dye on the adsorbent still occurred. This proves that the second mechanism, i.e., chemisorption, might be operative [20].

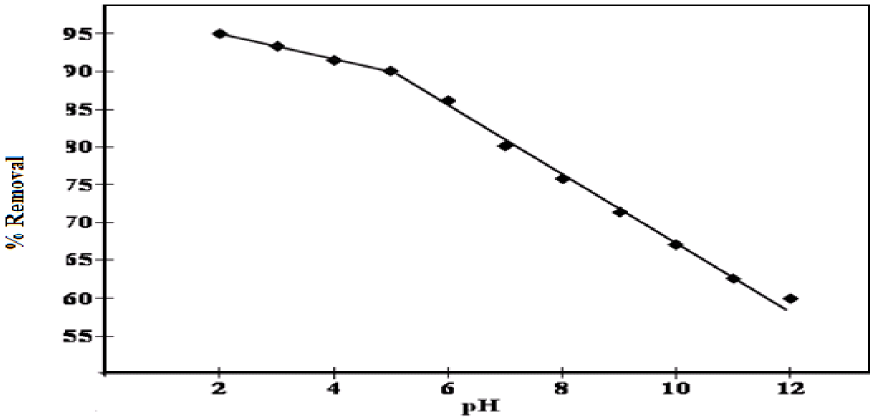

Figure: 3 Effect of pH.

3.4 Desorption study

It is necessary to recycle the used adsorbent to make this process as more economical and surplus availability. As pH was increased, the percent of desorption decreased from 43.45(pH 2) to 23.5 (pH 12) (Fig.4). Very low desorption dyes proved that chemisorptions might be influenced the adsorption of dye on adsorbent.

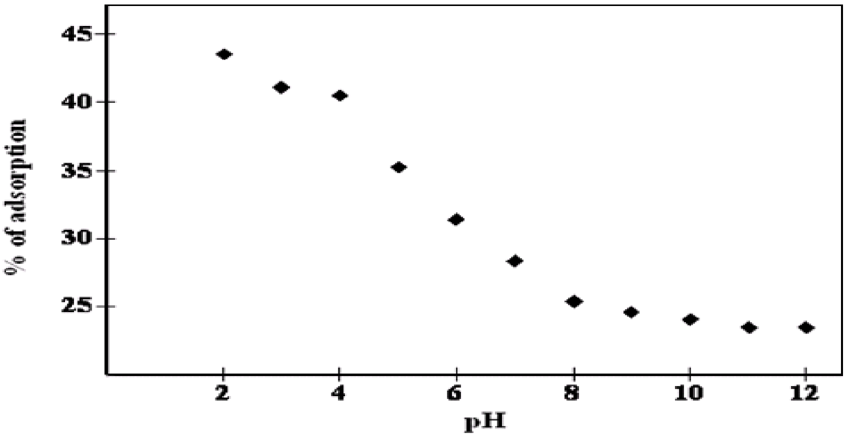

Figure: 4 Desorption Study

3.5 Adsorption isotherm

The experimental data were analyzed according to the linear form of the Langmuir, Freundlich and Temkin isotherms. The theoretical Langmuir isotherm [21] is valid for sorption of a solute from a liquid solution as monolayer adsorption on a surface containing a finite number of identical sites. Langmuir isotherm model assumes uniform energies of adsorption on to the surface without transmigration of adsorbate in the plane of the surface [22]. Therefore, the Langmuir isotherm model was chosen for estimation of the maximum adsorption capacity corresponding to complete monolayer coverage on the sorbent surface.The Langmuir isotherm is represented by the following equation (Langmuir and Amer, 1918).

$$\frac{Ce}{Qe} = \frac{1}{Qm\,b} + \frac{Ce}{Qm} \qquad \text{... (1)}$$

Here *Ce* is the equilibrium concentration (mg/l), *Qe* is the amount adsorbed at equilibrium (mg/g) and *Qm* and *b* are Langmuir constants related to the adsorption efficiency and energy of adsorption, respectively.The linear plots of $\frac{Ce}{Qe}$ versus *Ce* suggest the applicability of the Langmuir isotherms (Fig. 5). The values of, Q_m and *b* were determined from the slope and intercept of the plots as 92.7 and 0.0866 respectively. From the results, it was found that adsorption efficiency Q_m and adsorption energy *b* of the carbon. From the values we can conclude that the maximum adsorption corresponds to a saturated mono-layer of adsorbate molecules on an adsorbent surface with constant energy and no transmission of adsorbate in the plane of the adsorbent surface occurs. This trend shows that the adsorbent prefers to binding of acidic ions and that special ion predominates on the sorbent characteristics, when ion exchange is the predominant mechanism. To confirm the favourability of the adsorption process, the separation factor (RL) value was found to be 0.0865 and confirm that the ongoing adsorption process was favourable [23].

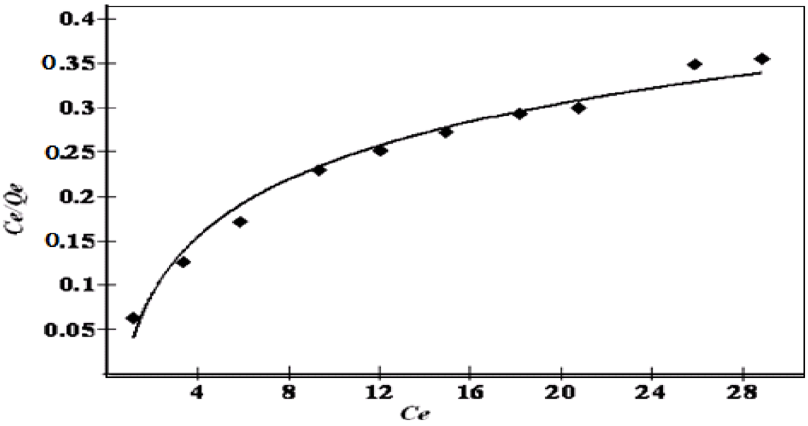

Figure: 5 Langmuir Isotherm

The Freundlich isotherm model [24] is the earliest known equation describing the adsorption process (Fig. 6).The Freundlich equation was also employed for the adsorption of Acid Yellow 24 (AY24) dye on the adsorbent.The Freundlich isotherm (Freundlich, 1906) is represented as

$$\log Qe = \log K_f + \frac{1}{n}\log Ce \qquad ... (2)$$

Here Q_e is the amount of AY24 adsorbed (mg/g), C_e is the equilibrium concentration of dye in the solution (mg/l) and K_f and n are constants incorporating all factors affecting the adsorption capacity and intensity of adsorption, respectively. Linear plot of $\log Q_e$ versus $\log C_e$ shows that the adsorption of AY24 dye follows the Freundlich isotherm (Fig.6). The values of K_f and n found to be 15.996 and 2.164 respectively showed the increase of negative charge on the surface that enhances the electrostatic force between the carbon surface and the dye ion, which increases the adsorption of dyes.The values clearly show the dominance of adsorption capacity. The intensity of adsorption is an indication for the bond energies between dye and the adsorbent and the possibility of a slight chemisorptions rather than physisorption. The possibility of multilayer adsorption of dyes through the percolation process could not be ruled out. However, the values of n are greater than one indicating that the adsorption is much more favourable than Langmuir isotherm [25].

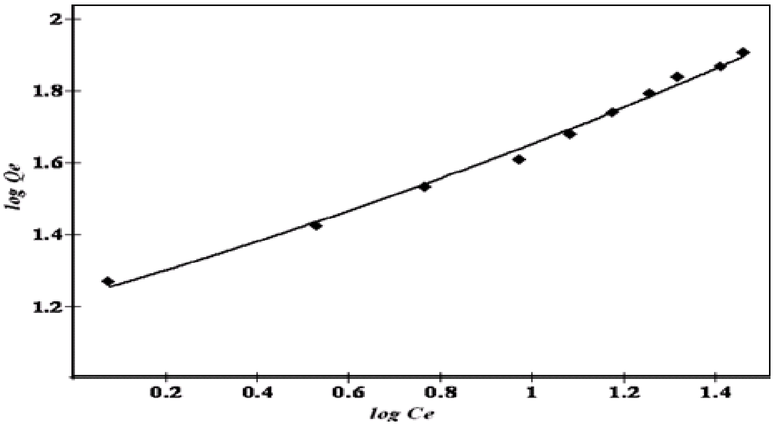

Figure: 6 Freundlich Isotherms

Temkin adsorption isotherm model [26] was used to evaluate the adsorption potential of the adsorbent for AY24 (Fig.7)

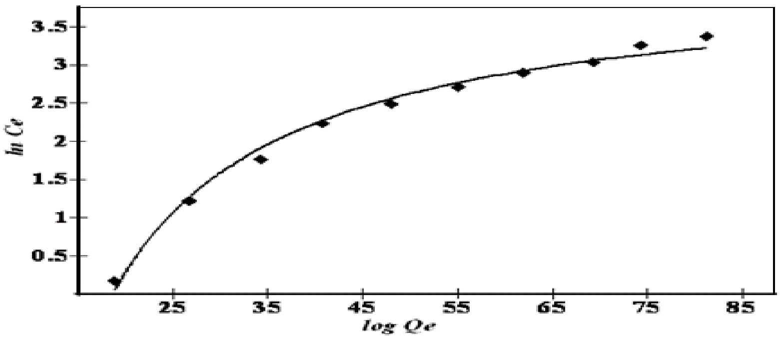

Figure: 7 Temkin Isotherm

The Temkin equation was also employed for the adsorption of Acid Yellow 24 (AY24) dye on the adsorbent. The Temkin equation is represented as

$$Qe = \beta_\tau \ln K_\tau + \beta_\tau \ln Ce \qquad \text{... (3)}$$

β_τ is theTemkin constant related to heat of adsorption (kJ mol^{-1}) .K_τ is the equilibrium binding constant(Lmol^{-1}) corresponding to the maximum binding energy. The values of Temkin constant and equilibrium constant were 0.045 and 1.2213 respectively.The correlation coefficient (R^2) for Langmuir, Freundlich and Temkin isotherms were 0.917,0.999,0.871 respectively.From the correlation coefficient value it was concluded that Freundlich isotherm fitted well compare to other isotherms.

3.6 Adsorption kinetics

The study of kinetics is important for the analysis of solute adsorption rate which controls the retention time of adsorption at the solid-solution interface. The results would be of undeniable importance for the process optimization in industry. The kinetics of AY24 adsorption on the LAS was analyzed using pseudo first-order rate expression and pseudo second order model [27].High correlation coefficient for pseudo second-order equation indicated that the pseudo second-order model could successfully describe the kinetic of AY24 adsorption on LAS.

3.6.1 Pseudo first order model

The Langergren equation a pseudo second-order equation, describes the kinetics of adsorption process as follows Equation

$$\log(Qe - Qt) = \log Qe - \frac{k_1}{2.303} \qquad \text{... (4)}$$

Where Q*t* is the amount of dye adsorbed (mg/g) at time *t*, Q*e* is the amount of dye adsorbed at equilibrium, and k_1 is the rate constant of first-order sorption (min^{-1}).In the figure 8 , correlation coefficient value (R^2 = 0.8639) shows that, this model does not favour the adsorption process of the dye with the adsorbent.

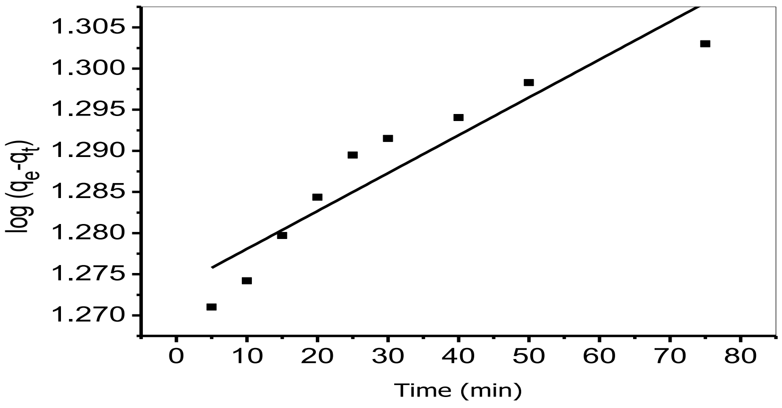

Figure: 8 Pseudo first order model

3.6.2 Pseudo Second-Order Model

The second order kinetic model can be given by

$$\frac{t}{Qt} = \frac{1}{k_2} . Qe2 + \frac{1}{Qe} . t \qquad \text{... (5)}$$

Where k_2 is the rate constant of second-order sorption (g mg^{-1} min^{-1}).The plot of $\frac{t}{Qt}$ versus *t* showed a linear relationship with high regression coefficient (R^2= 0.9995).Fig.8 showed a linear relationship with high regression coefficient (R^2 = 0.9995).The kinetics of AY24 adsorption on the LAS was analyzed using pseudo first-order rate expression and pseudo second order model [28].High correlation coefficient for pseudo second-order equation indicated that the pseudo second-order model could successfully describe the fitness of the adsorption and also explained that the chemisorptions were the rate determining step. Similar reports were given in various studies [29; 30].

Table 1. Kinetic parameters for the adsorption of AY 24 dye.

Pseudo-first order			Pseudo second order			
K_1	q_e	r^2	q_e.exp	K_2	q_e.cal	r^2
0.0011	0.10498	0.8639	24.84	0.1366	4.8966	0.9995

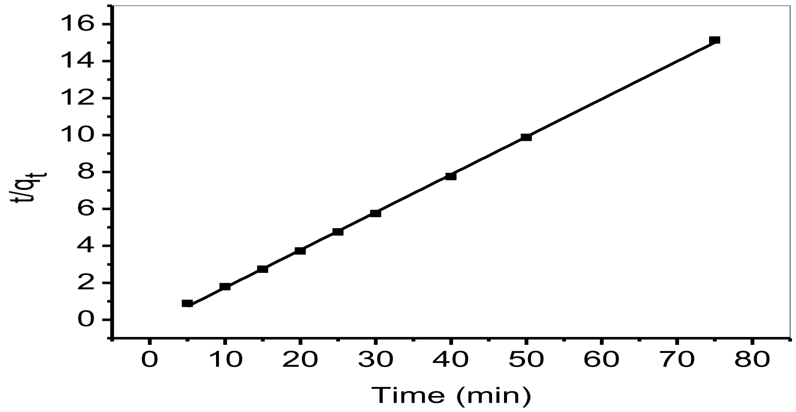

Figure: 8 Pseudo second order model

3.7. FTIR studies

FTIR studies are used for prediction of different types of functional groups present in the adsorbent material. The FTIR spectrum of carbon presented in Fig. 9.

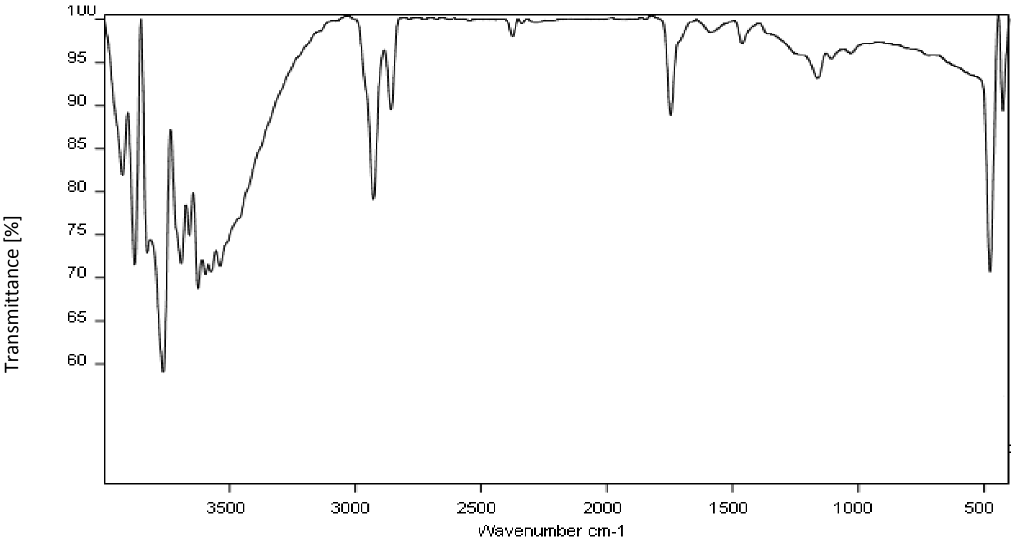

Fig. 9. FTIR spectrum Lufa Acutangula Seed hull Carbon

The carbon spectrum shows the peaks in the positions of 3763cm^{-1},3624cm^{-1},2922cm^{-1},1586cm^{-1}and1160cm^{-1}. The peak position of 3763 cm^{-1},3624 cm^{-1},indicates that the presence of stretching vibration of the OH group involves in the intermolecular or intramolecular hydrogen bonding or moisture present either in carbon or KBr. The peaks in the positions of 2922cm^{-1} indicates that the presence of C-H stretching vibrations in the carbon. The peak positions of 1586 cm^{-1}and 1160 cm^{-1} shows that the presence of alkyl group or due to the presence of C=O, C-C bond interaction respectively.The presence of functional group confirms that the AY24dye was strongly adsorbed onto the Acutangula Seed hull carbon.

Conclusion

The present study shows that the activated carbon prepared from Lufa Acutangula Seed hull is a potential adsorbent for the removal of Acid Yellow 24 (AY24) from the aqueous solution.Optimum pH for the removal of dye is less than 3. The kinetic data of adsorption were well fitted by the pseudo-second-order kinetic model. It gives the higher correlation coefficient value, this implies that the adsorption process was chemical adsorption rather than physorption.The equilibrium adsorption data were best represented by Freundlich model than langmuir and Tempkin model, It shows that the multilayer adsorption is predominant. The FTIR study of the carbon shows that the functional groups are responsible for the enhancing the chemisorption of dye molecule with the carbon.The highest adsorption capacity of prepared LAS adsorbent showed that it could be an alternative to commercially activated carbon for the removal various anionic dyes.

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