Synthesis of Nanocellulose from Indigenous Sources and Application in Dye Removal

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Abstract. The synthesis of an adsorbent that is low cost, effective and sustainable, from two main indigenous agricultural and domestic wastes namely rice husk and lemon peel was conducted in the study to inspect its potential to remove Congo Red, a hazardous anionic dye capable of gravely polluting water bodies. The synthesis of nanocellulose from these sources was catered via a combined approach of chemical and mechanical treatments, involving dependence on acid hydrolysis and sonication. Adsorption kinetics were performed post-synthesis to determine which among the two sources performed better in Congo Red dye adsorption. These studies were carried out by subjecting varying amounts of nanocellulose adsorbent to different quantities of dye and their adsorption capacities were evaluated under changing conditions of pH and contact time. Adsorption isotherms such as linear, Freundlich, and Langmuir were used so that the adsorption capacity of the adsorbents could be predicted. The results demonstrated that lemon peel behaved as a better adsorbent at pH 3.0 for an absorbent dose of 0.3g and showed maximum adsorption at a dye concentration of 80 mg/L.

Keywords. Nanocellulose, adsorption, rice husk, lemon peel, agricultural wastes

1. Introduction

Water bodies stained with dyes are a visually prominent form of water body pollution. Dyes not only impart colour but gravely affect the marine life residing in these water bodies and makes the water unfit for use. These dyes that are released as pollutants are by products of industrial waste produced mainly in textile industries. India is estimated to annually produce 11,000 tonnes of dye, of which 7,000 tonnes are directly discharged into the environment without treatment causing grave danger. The dye production and utilization estimates for India lies at 6.6% of the total dye production in the world, including the production of acidic dyes (example, Congo Red), substantive or direct dyes (example, Indigo) and other basic

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dyes (example, Methylene Blue and safranin) contribute to pollution affiliated with textiles, pharmaceuticals, paper printing, plastics and food industries. Dyes cater to three main types of environmental crises, firstly water waste, chemical accumulation in the groundwater, and heavy metal discharge, which is used in the process of dyeing. Industries involved in product dyeing, are known to lodge a water wastage of 93 billion cubic meters every year, the release of 72 toxic life threatening chemicals damaging our ecosystems and the discharge of carcinogenic heavy metals including mercury, cadmium, and chromium VI (Kulczycki, 2021).

Congo Red is affiliated largely with hazardous dye pollution in water bodies, due to its being in the textile industry. It being a synthetic azo-dye, causes environmental damage due to its composition that includes aromatic amine compounds which are hazardous, and additionally because these compounds are hardly eliminated during aerobic process of waste treatment (Afkhami and Moosavi, 2009). In the past few decades, removal of dye for recovering and reusing dye wastewater has also been given importance to reduce dependability on clean fresh water in the industry (Katheresan et al., 2018). Of the three methods for removing dyes from wastewater, physical, chemical and biological, the physical method is the most prominent method due to its simplicity and efficiency. Adsorption, flocculation or coagulation, membrane filtration, reverse osmosis, ion exchange, are some of the physical methods of removing dyes. Adsorption is commonly used as top quality treatment procedure for the removal of dissolved organic pollutants because it does not produce any toxic by-product (Cao et al., 2014). Adsorption is a surface-phenomenon where materials get concentrated on the surface of solid bodies. (Kanidasa et al., 2016).

Lately, due to its availability and cost effective prices, the use of agro waste as bio-adsorbents has become a matter of great interest (Dai et al., 2012). Activated charcoal is highly preferred as an adsorbent and tends to have very high adsorption capacity. However, it is also highly priced and the process of regeneration being extremely difficult, makes it ineffective in terms of more frequent usage. In this regard, in an attempt to overcome these limitations and to reduce the carbon footprint, other sustainable waste based adsorbents synthesized from agricultural or domestic wastes could be used. India is estimated to produce 350 million tonnes of agricultural waste every year (ICAR, 2020). Although they are biodegradable and less hazardous than other solid wastes, they contribute to a huge amount of solid stagnant wastes on land, especially agro wastes such as rice residues that make up most of the agro wastes produced in India. Due to having 50% of our population be directly dependent on agriculture for their livelihoods, unearthing methods and technologies to carry out effective agro-waste management becomes crucial (Obi et al., 2016). Alongside management, finding methods to develop these wastes into becoming useful adsorbents for dye removal can be another effective approach to combat both agro wastes as well as pollution caused by hazardous dyes, such as Congo Red.

In recent years, nano-sized materials have been gaining much importance due to their ability to display high functionality due to large surface area. Properties such as improved bioavailability, enhanced aqueous solubility and enhanced drug targeting, have increased both the demand and need for nanoparticles. They are used to reinforce polymers, paper and membranes which make them bio-nanocomposites that are biodegradable, environment-friendly and improve remarkably the properties of a materials compared to polymer matrices used in the conventional macro composite materials. Nanocellulose is a sustainable and biocompatible polymer that takes in its abode an array of applications. It exists naturally in varying forms as cellulose nanocrystals (CNC), nanofibrillated cellulose (NFC), nanocrystalline cellulose (NCC), and bacterial cellulose (BC). The improvements that nanocellulose can cause to a material's properties is attributed to factors such as good barrier properties, high modulus and tensile strength and the ease at which chemical surface modification can be performed (Ramos et al., 2016). Its remarkable mechanical and physical properties are attributed to the various hydroxyl groups and strong hydrogen bonding networks present in the cellulose fibril structures.

Nanocellulose is a natural bio adsorbent with high adsorption affinity, high mechanical strength, biodegradability and hydrophilic surface (Norrahim et al., 2021). Many classes of environmental contminants including dyes, heavy metals, and oil are adsorbed by nanocellulose. In view of this, the present work used two wastes of agricultural and domestic origin, rice husk and lemon peel to extract nanocellulose to use it as a natural adsorbent. The presence of lignocellulosic biomass in these agro-waste samples can be manipulated to synthesize nanocellulose to be used as an adsorbent, thus reducing both land waste and domestic wastage and also introducing sustainable bio-based adsorbents for removing toxic dyes. Rice husk as well as lemon peel are very common agro wastes that can be easily sourced and can be made available abundantly and are very prominent wastes generated in Indian households due to the population's frequent consumption of rice and lemon. Since cellulose for synthesis of nanocellulose is extracted from lignocellulosic biomass, chemical pretreatments such as alkaline pretreatment and acid pretreatment with a weak acid are used since they can effectively remove lignin and hemicelluloses (Vincent et al., 2021). Cellulose obtained can be further reduced to nanoscale by chemical, mechanical or enzymatic treatment. While acid hydrolysis is a chemical treatment procedure, cryocrushing, micro fluidisation and sonication are mechanical approaches to synthesize nanocellulose (Nilsson, 2017). Therefore, this study aimed at broadening the usage of cellulose for dye adsorption by reducing it to nanoscale and studying the parameters necessary to carry out kinetics and isotherm studies in order to determine via what approach and what source the adsorption is dominant. This study predominantly used acid treatment for cellulose extraction and ultrasonication for nanocellulose production.

2. Methodology

2.1 Cellulose extraction

Approximately 150 g of each source boiled in 500 mL of distilled water for about 10 min and filtered. This step was carried out to eliminate phenolic compounds as well as a portion of water-soluble polysaccharides. The residue was treated with 500 mL of 1 M sulphuric acid solution at 85 ^{0}C with constant stirring for 30 min. This step was repeated twice; subsequently, the residue was filtered. This treatment was conducted to remove the pectic polysaccharides. Following this, the residue was suspended in 500 mL of 1 M sodium hydroxide solution (NaOH) and stirred at 50 ◦C for 30 min to remove lignin and hemicelluloses. This procedure was repeated thrice following which the residue was filtered. This was continued with the bleaching procedure where the residue was treated with sodium hypochlorite solution (1-2%) at around 95 ◦C for nearly 60 min. This step was repeated multiple times until the color of the residue changes to milky white. The bleached precipitate thus obtained was cellulose. This precipitate was washed with double distilled water until a neutral pH of the filtrate was obtained (Mateo et al., 2021). Darker the pigment of the source, the longer the bleaching process takes. Washing the source each time with distilled water after every step could minimizes the time for bleaching.

2.2 Nanocellulose synthesis

The cellulose samples previously extracted were laid out on petri plates and placed in a hot air oven at 80°C for drying. After drying, the cellulose samples were powdered and suspended in water in test tubes. The samples were sonicated for 45 minutes in an ice bath to facilitate size reduction to the nanoscale. The sonicated samples were then filtered and dried again to obtain powdered nanocellulose (Mateo et al., 2021; Naz et al., 2015).

2.3 Nanocellulose estimation

Preliminary confirmation of cellulose extraction from rice husk and lemon peel sources was carried out using some of the common laboratory reagents such as iodine solution, Fehling's solution, Schultz's reagent, and additionally by Safranin test. Confirmation on nanocellulose formation was obtained through UV-Vis spectroscopy (using Genesys 10S UV-Vis spectrophotometer, Thermo Scientific). UV-visible spectrophotometer peaks were obtained for both cellulose and nanocellulose for each of the samples at a wavelength range of 200 nm - 800 nm to confirm size reduction.

2.4 Experiments on adsorption kinetics

To establish the appropriate adsorption conditions for the removal of Congo Red dye by the extracted nanocellulose adsorbent, dye adsorption tests were done taking four criteria into consideration, which included the dye concentration (40mg/L - 200mg/L), adsorbent dose (0.1g - 0.5g), pH (3.0 - 8.0), and contact time (0 – 120 min). The ranges were chosen based on previous literature (Cao et al., 2014).
(I) *To determine the influence of pH on adsorption,* six test tubes with 10 mL of the dye solution of concentration 40 mg/L were taken and 0.2 g of the nanocellulose adsorbent extracted from each source was added to each tube. The test tubes were maintained at different pH values varying from 3.0 to 8.0. 0.1M HCl and 0.1M NaOH were used to maintain the required pH value. The test tubes were kept for 90 min under shaking at 100 rpm, after which the absorbance was measured at 539nm after 90 min, to determine the optimum pH for each adsorbent.

(II) *To understand the effect of dye concentration,* 0.2 g absorbent was added to 5 test tubes containing Congo Red dye solution of varying concentrations from 40 mg/L to 200 mg/L at pH 3.0, and the absorbance readings were taken at 539 nm after 90 min to determine optimum dye concentration for each of the adsorbents.

(III) *To understand the effect of adsorbent dose,* 0.1g, 0.2g, 0.3g, 0.4g and 0.5g adsorbent were added to 5 test tubes containing 80 mg/L of Congo Red dye solution at pH 3 and their absorbance readings were taken after 90 min at 539nm, to determine the optimum adsorbent dose for each of the adsorbents.

(IV) *To understand the effect of contact time*, five absorbance readings starting from the zeroth reading were taken at an interval of every 30 min. 80mg/L dye concentration, adsorbent dose of 0.3 g, and pH 3.0 were the conditions used to check the ideal contact time for each of the adsorbents. The effect of contact time was determined by using 0.3 g adsorbent in 10 mL dye solution having an initial concentration of 80 mg/L. Absorbance was recorded at 539nm after each contact period.

Following each trial, the percent removal efficiency of the adsorbent towards the dye was calculated as follows:

$$\% R = ((C_0 - C)/C_0)*100 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{(1)}$$

where C_0 is the initial dye concentration and C is the final dye concentration (mg/L).

The optimum conditions for dye adsorption were chosen based on the maximum values of % R.

2.5 Adsorption kinetic models

The kinetics of Congo Red dye adsorption was measured using various kinetic models such as the pseudo first-order and pseudo second-order models (Sandesh et al., 2012). The Lagergren's first-order rate equation is one of the most commonly used kinetic models for solute adsorption from solutions. This model is of the form:

$$dq/dt= K_1 (q_e-q_t) \quad (2)$$

where, q_e (mg/g) is the amount of the metal ions adsorbed on the adsorbent at equilibrium, and K_1 (/min) is the rate constant of the first-order adsorption. Upon integration and application of boundary conditions qt = 0 at t = 0 and qt = qt at t = t, the integral form of equation (2) becomes:

$$\ln (q_e-q_t)= \ln (q_e)-K_1.t \quad (3)$$

The pseudo first-order model assumes that the rate of occupancy of adsorption sites corresponds to the number of vacant sites. The value of K_1 and q_e can be obtained from the slope and intercept of the linear plot of ln (q_e-q_t) versus t, respectively.

The second-order kinetic model, on the basis of the adsorption equilibrium capacity, is as follows:

$$dq/dt = K_2 (q_e-q_t)^2 \quad (4)$$

where K_2 (g/mg min) is the rate constant of the second-order equation, and q_e (mg/g) is the maximum dye adsorbed. After definite integration by applying the boundary conditions q_t = 0 at t = 0 and q_t = q_t at t = t, Eqn (4) becomes the following:

$$(t/q_t) = (1/K_2q_e^2) + (1/q_e) \quad (5)$$

If the second-order kinetic model is appropriate, the plot of t/q_t vs t should yield a straight line, from which q_e and K_2 can be calculated using the slope and intercept

2.6 Adsorption isotherms

To understand the adsorption mechanism, the examination and inspection of adsorption isotherm values were performed. Three adsorption isotherms, namely linear, Langmuir, and Freundlich adsorption isotherm were used to deduce the temperature effects on the adsorption capacity (Sandesh et al., 2012). These isotherm models were used to establish a link between the amount of dye absorbed and the equilibrium concentration in the aqueous solution.

The temperatures chosen were 27°C, 32°C, and 37°C. The equilibrium studies were performed using 0.2 g of each of the adsorbents in 10 mL Congo Red dye solutions at varying concentrations of 40 mg/L- 200 mg/L. For each temperature, test tubes containing each of the adsorbents were agitated in a temperature-controlled shaker for 30 mins and their absorbance were measured at 539nm. The capacity to adsorb was evaluated by making use of the formula:

$$q = [(C_0\text{-}C)*V] / M \quad (6)$$

Where, C_0 is the initial dye concentration and C is the equilibrium concentration (mg/L), V is the volume of the dye solution (mL) and M is the amount of adsorbent (g).

Linear adsorption isotherm model was obtained by plotting q (mg/g) against C(mg/L). Langmuir adsorption isotherm model was obtained by plotting 1/q (g/mg) against 1/C (L/mg). Freundlich model was obtained by plotting log q against log C.

3. Results and Discussion

3.1 Nanocellulose estimation

3.1.1 Yield measurements

The yield of nanocellulose obtained per 30 g of cellulosic materials considered, lemon peel and rice husk, were calculated and the results obtained are presented in Table 1.

Table 1. Nanocellulose yield

Source	Initial weight (g)	Final weight (g)	Yield percentage
Rice Husk	150	24.7	16.46
Lemon peel	150	56.9	37.93

Four qualitative tests, namely, Iodine test, Fehling's test, Schultz's test and Safranin test were performed to determine the presence of cellulose and absence of lignin in the sample. The results obtained are given in Table 2.

Table 2. Qualitative tests for cellulose

Sample	Iodine test	Fehling's reagent	Schultz's reagent	Safranin test
Rice husk	Colourless	Colourless	Purple	Colourless
Lemon peel	Colourless	Colourless	Purple	Colourless

Due to the absence of helices, cellulose cannot hold iodine, and therefore it shows no colour change when iodine is added. Fehling's test is a confirmatory test for monosaccharides, and since cellulose is a polysaccharide, no colour change is observed. Schultz's reagent is exclusively used to detect the presence of cellulose, and it turns the sample purple. Safranin stains lignin, and therefore no colour change indicates the absence of lignin. Hence the results obtained confirm that the extracted product is cellulose and lignin is absent.

3.1.2 UV- Visible Spectrophotometry

The absorbance peaks for nanocellulose extracted from both sources were around 270 nm, which correspond to UV regions. Decrease in peak intensities compared to cellulose implies the conversion of cellulose in the original sample to nano-form and therefore confirms presence and formation of nanocellulose after the treatment procedure employed in the study. The differences in the absorbance values as obtained using UV-Vis spectroscopy for the original sample and the treated samples where nanocellulose is extracted are given in Table 3.

Table 3. Absorbance values for source samples and corresponding nanocellulose

Source	Cellulose absorbance	Nanocellulose absorbance
Rice Husk	3.780	1.940
Lemon Peel	4.070	2.090

Interestingly, UV-Vis spectroscopy results suggest the percent conversion of cellulose to nanocellulose is almost the same for both sources, and is close to 50%.

3.2 Kinetic studies

3.2.1 Effect of pH

To know the effect of pH on % dye removal by nanocellulose adsorbents, the pH was varied between 3.0 and 8.0. The variation in percent removal for different pH values is shown in Fig. 1, which indicate that the reduction percentage is higher at pH 3.0 for both rice husk and lemon peel sources.

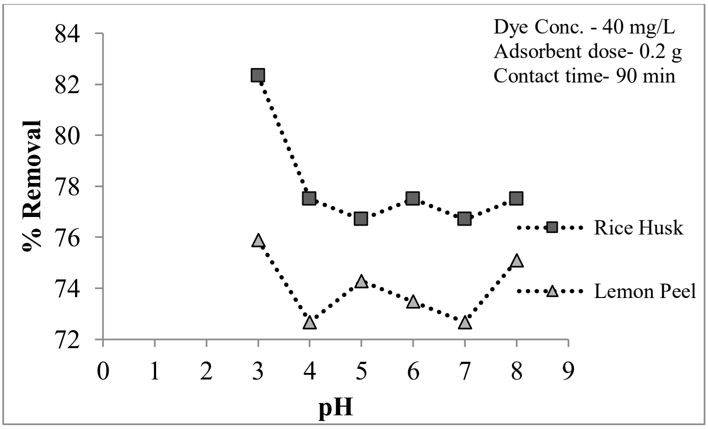

Fig. 1. Effect of pH on % dye removal

The results obtained are similar to the result of previous work conducted on Congo red dye adsorption (Kaur et al., 2013 & Cao et al., 2014).

3.2.2 Effect of dye concentration

Adsorbent concentration of 0.2 g was added to 10 mL of Congo Red solution of varying concentration (40-200 mg/L) to evaluate the effect of the concentration of the dye. For this study, solution pH was fixed at 3.0 based on previous observation made for pH studies. The contact time of 90 min was considered.

From Fig. 2, it is observed that at dye concentration of 80 mg/L, percent reduction was maximum for both sources. Hence, 80 mg/L is the optimum dye concentration for maximum adsorption by nanocellulose under study.

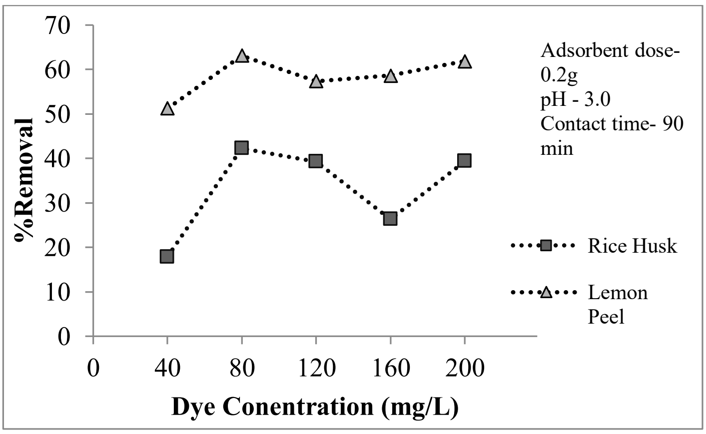

Fig. 2. Effect of dye concentration on % dye removal

3.2.3 Effect of the adsorbent dosage

To 10 mL of 80 mg/L dye solution at pH 3, varying quantities of adsorbent (0.1- 0.5 g) was added for a contact time of 90 min. 80 mg/L of dye concentration was chosen since it was previously determined to be optimum. The reduction in dye concentration after the contact time is as shown in Fig. 3.

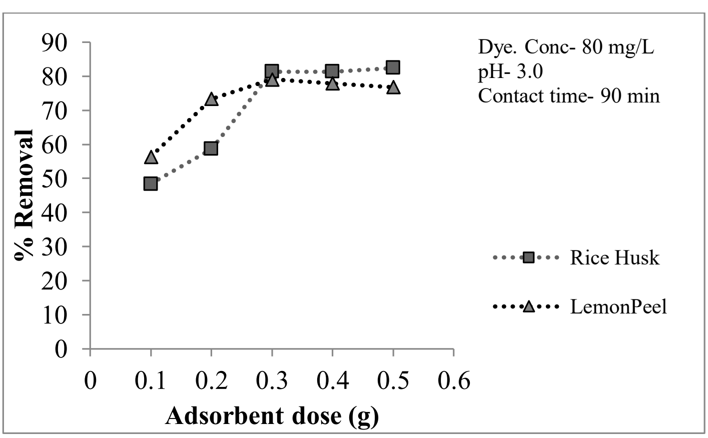

Fig. 3. Effect adsorbent dose on % dye removal

Both for lemon peel and rice husk nanocellulose, the optimum adsorbent loading was found to be 0.3 g. In the previous work 24.76 g/L was the optimum value obtained for Congo Red dye adsorption which is comparable to the results obtained in this work, that is 33.3 g/L (Ponnusamy and Subramaniam, 2013)

3.2.4 Effect of time of contact

To 10 mL of 80 mg/L dye solution having a pH 3.0, optimum value of adsorbent dose i.e., 0.3 g was added and readings were taken at an interval of 30 min until desorption was observed. The adsorption and desorption rends can be seen in Fig. 4.

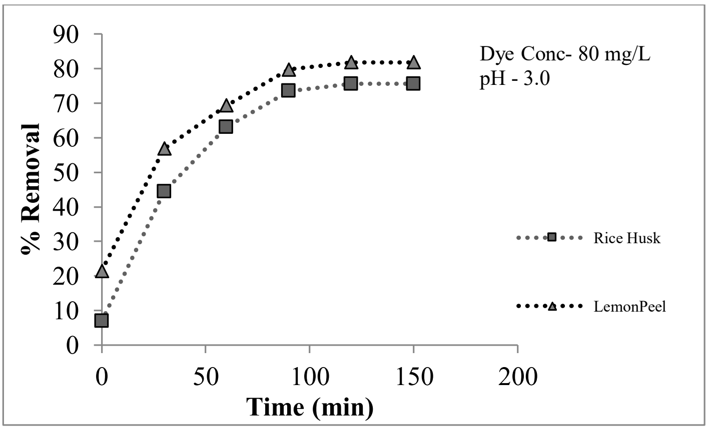

Fig. 4. Effect of time of contact on % dye removal

It was observed that %R was highest at contact time of 90 min for lemon peel. This is in line with result obtained in the previous work (Chukki et al., 2018). On the other hand, the percent reduction was highest at a contact time of 120 min for nanocellulose from lemon peel, which can further be correlated to previous works (Lafi et al., 2019).

3.3 Adsorption kinetics models

Kinetic models are used to test the experimentally determined data so as to understand the mechanism of adsorption. Pseudofirst- order and pseudosecond- order models were used in the present study. It was assumed that the measured concentrations and surface concentrations are equal.

From ln (qe-qt) *versus* time plot (Fig. 5), pseudofirst- order K_1 and qe were calculated and tabulated in Table 4.

Table 4. Pseudo first- order model constant, qe and R^2 values

Sample	**qe (exp) (mg/g)**	**qe (cal) (mg/g)**	**K_2 (g/mg.min)**	**R^2**
Lemon Peel	3.522	3.184	0.049	0.994
Rice Husk	3.33	3.039	0.038	0.988

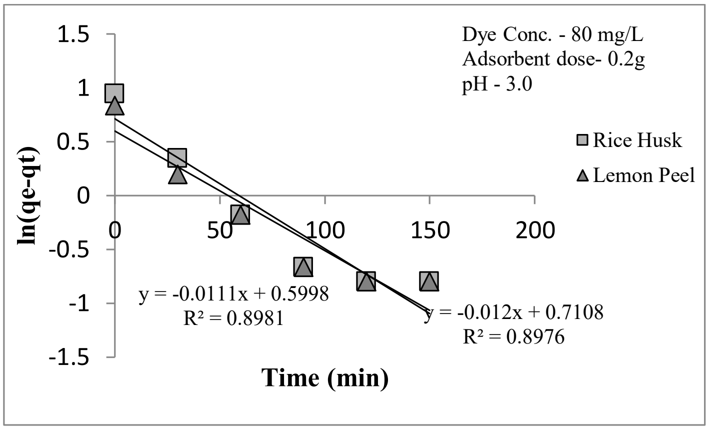

Fig. 5. Pseudo first-order model equation for Congo Red adsorption

The calculated qe and R^2 values are not satisfactory, hence pseudosecond- order model was carried out.

Table 5. Pseudo second- order model constant, qe and R^2 values

Sample	**qe (exp) (mg/g)**	**qe (cal) (mg/g)**	**K_1 (mg/g.min)**	**R^2**
Lemon Peel	3.522	1.8202	0.011	0.898
Rice Husk	3.33	2.0339	0.012	0.897

From the plot of t/qt *versus* time (Fig. 6), K_2 and qe were calculated. These constants and value of R^2 for both sources is listed Table 5. It can be observed that qe (cal) value is in-line 5with the experimental qe value and R^2 value is also satisfactory indicating pseudo second-order model fits well for adsorption of Congo red by nanocellulose produced from both sources.

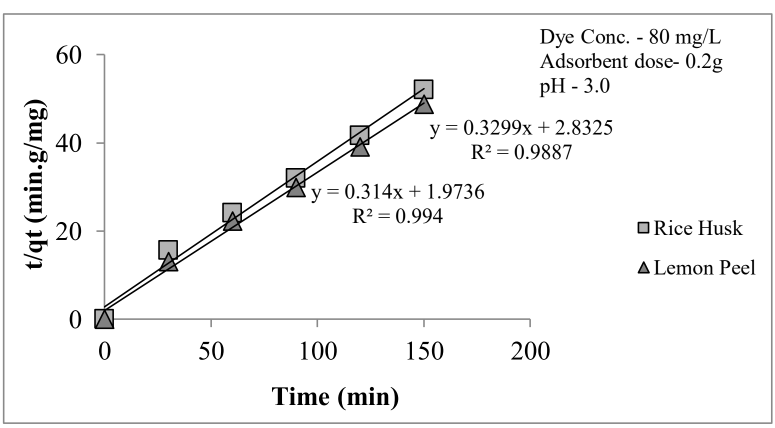

Fig. 6. Pseudosecond-order model equation for Congo Red adsorption

3.4 Adsorption isotherms

The linear, Langmuir and Freundlich isotherm was carried out to understand adsorption equilibrium. Experimental trials were carried out using 0.3 g adsorbent at different concentrations of the Congo red dye solution (40 -200 mg/L) at three defined temperatures (27ºC, 32ºC and 37ºC). Plots of q (amount of dye solution adsorbed per gram of the adsorbent) versus C (equilibrium concentration of the solution), 1/q versus 1/C, and log q versus log C for nanocellulose adsorbent obtained from rice husk are shown in figures 7, 8, and 9, respectively, and those for nanocellulose from lemon peel are shown in figures 10, 11, and 12.

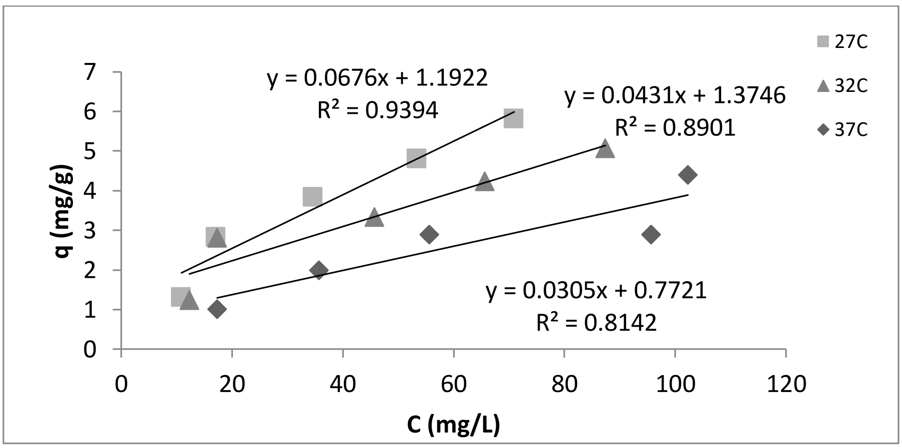

Fig. 7. Linear isotherm model for Congo Red adsorption on Rice husk adsorbent

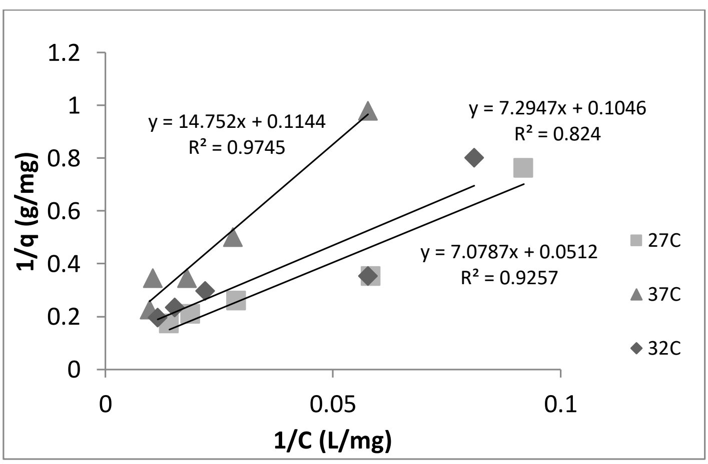

Fig. 8. Langmuir isotherm model for Congo Red adsorption on Rice husk adsorbent

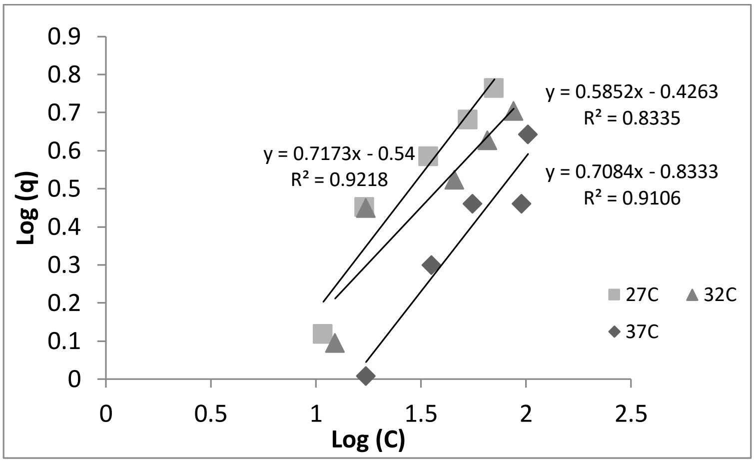

Fig. 9. Freundlich isotherm model for Congo Red adsorption on Rice husk adsorbent

The linear form of the Freundlich and Langmuir equation gives Freundlich and Langmuir constants (as represented by equations 7 and 8) using the slopes and the intercepts which is listed in tables 6 and 7 for the adsorbent from rice husk and lemon peel, respectively.

$$\log q = \log K_F + (1/n).\ \log C \tag{7}$$

$$1/q = 1/q_0 + (1/K_L.q_0)(1/c) \tag{8}$$

Table 6. Linear, Freundlich and Langmuir adsorption constants for Congo red adsorption on Rice husk adsorbent

Temperature (ºC)	Linear isotherm		Freundlich isotherm			Langmuir isotherm		
	K (L/g)	R^2	K_F(mg/g)	n	R^2	q_0(mg/g)	K_L(L/g)	R^2
27	1.192	0.94	0.58	1.39	0.92	19.6	0.007	0.92
32	1.374	0.89	0.65	1.70	0.83	9.61	0.014	0.82
37	0.814	0.81	0.43	1.41	0.91	8.77	0.007	0.97

A maximum correlation coefficient of 0.97 was obtained at 37 ºC, suggesting that Langmuir model is more suitable for rice husk adsorbent.

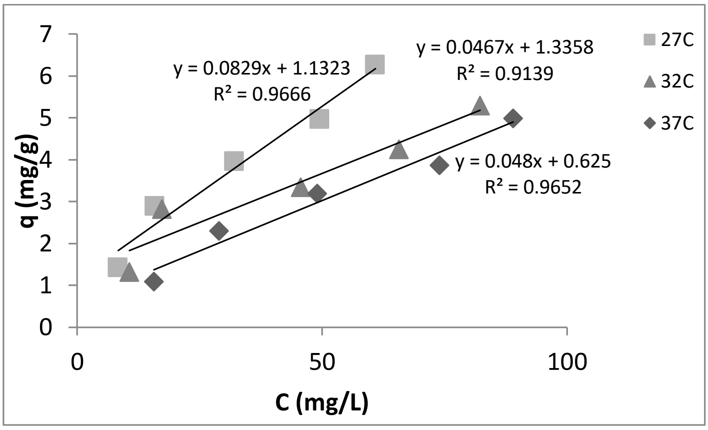

Fig. 10. Linear isotherm model for Congo Red adsorption on lemon peel adsorbent

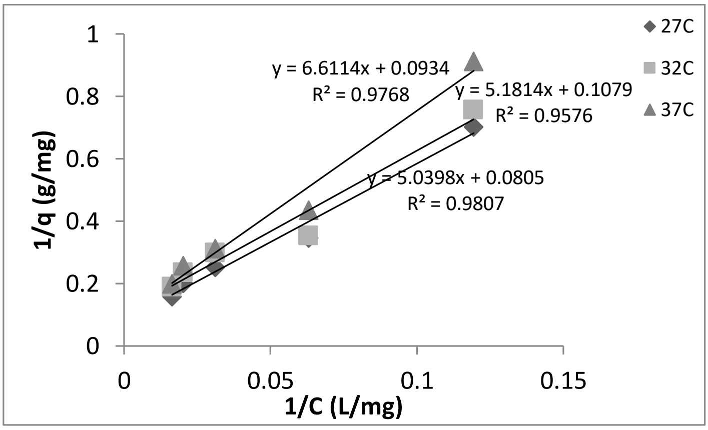

Fig. 11. Langmuir isotherm model for Congo Red adsorption on lemon peel adsorbent

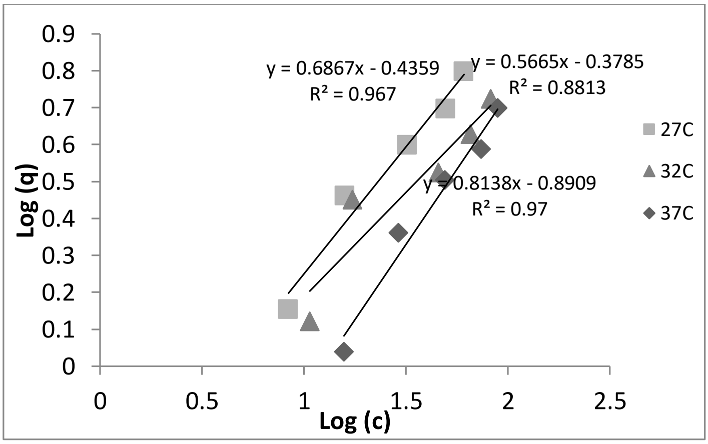

Fig. 12. Freundlich isotherm model for Congo Red adsorption on lemon peel adsorbent

Table 7. Linear, Freundlich and Langmuir adsorption constants for Congo red adsorption on lemon peel adsorbent

Temperature (ºC)	Linear isotherm		Freundlich isotherm			Langmuir isotherm		
	K (L/g)	R^2	K_F(mg/g)	n	R^2	q_0(mg/g)	K_L(L/g)	R^2
27	1.132	0.966	0.647	1.45	0.967	12.5	0.015	0.98
32	1.335	0.913	0.685	1.76	0.88	9.34	0.02	0.957
37	0.625	0.965	0.410	1.23	0.97	10.75	0.014	0.976

At all temperatures, Langmuir model can be considered more suitable for lemon peel adsorbent based on the better correlation coefficients compared to other isotherms.

4. Conclusion

The experimental results indicate that the adsorbents synthesized from agricultural wastes can be effectively utilized in the removal Congo Red dye. The used adsorbents are low cost, sustainable and effective. The adsorption kinetics carried out showed that the adsorption process depends on pH and dye concentration, and the optimum pH and dye concentration for greater dye reduction was obtained as pH 3.0 and 80 mg/L. Other factors that include adsorbent dose and contact time show that higher dye removal depend on the source from which the adsorbent is extracted. The adsorption isotherm models were used to represent the experimental data, and Langmuir model fit best both for rice husk adsorbent and lemon adsorbent. Hence, it is the occurrence of monolayer adsorption in the cases of lemon peel and rice husk adsorbents. Inexpensiveness and the rapid adsorptive ability of the synthesized adsorbents make them a promising technique for eliminating toxic dyes such as Congo Red.

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