

Removal of Cationic Neutral Red Dye from Aqueous Solutions Using Natural and Modified Rice Straw

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MODIFIED colloidal carbons were prepared by reacting colloidal carbon obtained from rice straw with thermal oxidation, nitric acid and urea treatment. The textural and chemistry characteristics of the surface of non-modified and modified carbons were obtained from nitrogen adsorption at -196°C, elemental analysis and fourier transform infrared (FTIR) techniques. The uptake of cationic neutral red (NR) dye from aqueous solutions by these carbons was determined by kinetic and equilibrium experiments. The surface area and the total pore volume decreased, whereas the pore radius increased after the treatment with nitric acid. The surface pH of un-modified carbon was basic while those of modified carbons were acidic. Urea treated carbons with the lowest acidic character and high nitrogen content presented the lowest NR dye uptake capacity. The maximum removal of NR dye was obtained at a pH of 4. The amount of adsorption by the investigated carbons was found to depend on the amount of surface acidity. The adsorption results were analyzed considering Langmuir, Freundlich and Dubinin-Radushkevich(D-R) models. The adsorption of NR dye onto the assessed adsorbents is of the physical sorption type following pseudo – first – order kinetic. Nitric acid modification brought about a significant rise in NR dye adsorption which was ascribed to the formation of oxygen containing acidic groups on the surface of adsorbent. The equilibrium adsorption data of NR dye were well fitted with Langmuir and D-R models.

Keywords: Rice straw, Colloidal carbon, Adsorption, Neutral red dye, Surface chemistry

INTRODUCTION

The properties of carbon materials as adsorbents are strongly dependent on the textural features and on the chemical surface functionalities [1-4]. The textural characteristics are described by the porosity and surface area while the surface functionalities are mainly composed of surface oxygen containing groups classified as acidic, basic and neutral groups [3,4]. The surface functional groups are capable to play an important role in the adsorption performance of carbons as these groups in pore entrances can influence not only the access of adsorbents but also the selective adsorption of individual species [5-8].

Surface functional groups responsible for the carbon characteristics comprise carbonyl, carboxyl, phenol, quinone, lactone and others bound to edges of the graphite-like layers [9,10]. The nature and concentration of these groups

might be modified by different oxidizing agent treatment methods [11-14]. Thermal treatment is used for dry oxidation and concentrated nitric acid and concentrated urea are applied in wet oxidation. Oxidation may also influence the pore structure development. Alternatively, other modification processes were described, such as urea, ammonia and other nitrogen containing substances [12,13].

Activated carbons are generally employed for the removal of dyes from water and wastewater owing to their high sorption capability for inorganic and organic pollutants. Adsorption has proved to be one of the most effective physicochemical methods for textile wastewater treatment. Extensive studies were performed to improve the sorption capacities of activated carbon prepared from agricultural by-products for dye removal but relatively less work is reported to physical or chemical modified carbons [14, 15].

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The aim of this work was to modify colloidal carbon prepared from rice straw with sulphuric acid using dry modified (thermally treated at 600 °C for 4 hr) and wet modified treatment with either concentrated nitric acid or saturated urea solution then thermally treated at 600°C to enhance the weakly acidic functional groups and the surface nitrogen groups respectively. Such modifications can improve the adsorption capacity of the colloidal carbon. The adsorption of cationic dye, neutral red (NR), on the modified colloidal carbon was investigated. The study also comprises characterization of the adsorbents and the determination of the factors influencing the sorption, including the contact time, pH and temperature.

Experimental

Materials and methods

Adsorbent preparation

Rice straw was collected and washed several times to ensure the removal of dust and ash. It was subsequently rinsed several times with distilled water and dried in hot air-oven at 50 °C overnight. The dried rice straw was ground to pass through a 1mm sieve and designated as sample RS sample. Colloidal carbon was obtained by reacting 10 g of RS with 100 ml (12 mol/L) sulphuric acid at 30 °C for 24hr. The resulting black mixture was allowed to cool and then filtered using a Buchner funnel. The carbonized product was washed several times with distilled water until the pH neutral (pH =7) which did not give a precipitate with barium chloride solution. The product known as colloidal carbon was denoted as (C).

To prepared modified colloidal carbons, three alternative treatment steps were applied to colloidal carbon surface which included:

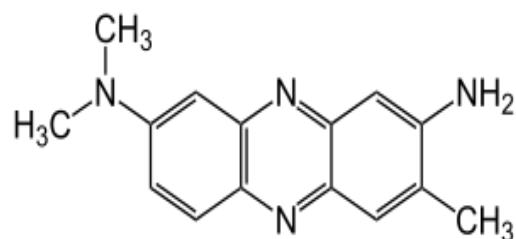
- Thermal partial oxidation by air.
- Liquid phase oxidation by conc.Nitricacid solution.
- Thermal treatment of urea treatment carbon sample.

Thermal oxidation of colloidal carbon (C) obtained was carried out in a fixed bed reactor at 600°C for 4 hr to generate C-Th. Liquid phase oxidation took place by oxidizing (C) with 30%V/V concentrated nitric acid at room temperature for 48 hr. The ratio of carbon to acid was 1:3 (V/V). Humic compounds formed were leached out of the carbon by washing with distilled water until the pH reached neutral and

finally rinsed with double distilled water and then the carbon sample was dried overnight at 110°C prior to being used. HNO₃- oxidized carbon was designating as C-N. The urea impregnation procedure included the addition of about 5 g of C in a glass beaker containing 150 ml of saturated urea solution. The mixture was stirred for 1 h at 30 °C. The treated sample was then filtered off, washed by distilled water to remove any excess of urea and dried at 100°C. The heat treatment was carried out in the fixed bed reactor at 450°C for 1 h. Urea treated colloidal carbon was labelled as C-u.

Neutral Red Dye (NR)

A basic dye was used in experiments as an adsorbate which is widely used in the textile industry ; its molecular formula is written as 3-amino-7-dimethyl amino -2-methyl phenazine with molecular weight of 288.78 g/mol, the corresponding structure is illustrated in Scheme 1.



Scheme 1: Chemical structure of cationic Neutral Red dye (NR)

Techniques

Instruments used for adsorbent characterization

The textural parameter, such as the BET-surface area (S_{BET} , m²/g), total pore volume (V_T) and average pore diameter (r) were evaluated from BET- equation using Quantachrome Nova Automated N₂ gas adsorption at -196 °C. In addition, an estimate for micropore (V_{micro} , ml/g) and non-micropore ($V_{non-micro}$, ml/g) volumes using the t-plot method was obtained [16].

For the chemical characterization of prepared carbons, CHN analysis was performed. The carbon, hydrogen, and nitrogen contents of the three samples were determined automatically by a VARIO Microanalyzer System. The different types of functional groups were identified by fourier transform infrared (FT-IR) spectroscopy in the range of 4000-400 cm⁻¹ using a Perkin Elmer Paragon 1000 FT-IR Spectrometer (USA), and the KBr disc technique.

The chemistry of the surface as determined from the surface pH and the relative concentrations of different surface functional groups in investigated carbons were determined according to the Boehm's titration method [12-15, 17]. The surface pH values were measured in a suspension of 1g of carbon 20 ml of CO₂- free distilled water after a contact time of 48hr at 25 °C. The pH- meter used was of digital type (Pope Model No. 1501).

The kinetic experiments of neutral red (NR) dye sorption were carried out using all investigated carbons at 30°C and pH=4. A 250 ml of 200ppm dye solution was prepared. The stirrer speed was maintained at 1000 rpm. All kinetic experiments were conducted for 1 hr and repeated twice. Equilibrium adsorption studies of NR were undertaken at 30°C and pH=4 over all carbons investigated. An equilibrium time of 24 hr was allowed to ensure the attainment of equilibrium conditions. The residual dye concentration was determined using a UV-Vis spectrophotometer (Shimadzu Model PC-2401) with 1.0 cm length -path cell. Absorbance measurements, of the property diluted filtrates, were made at the maximum wavelength of 530 nm.

Results and Discussion

Elemental analysis

Table 1 comprises the elemental analysis of the investigated carbons. Results in the table depicts that the starting colloidal carbon (C) has a small oxygen content (0.98% wt) confirming the presence of a small number of oxygen - containing groups on its surface, whereas the oxidized and urea treated carbon have much higher amounts of oxygen, *i.e.* 10.7, 21.8 and 7.79% for C-Th, C-N and C-u, respectively. Thus oxidation with nitric acid slightly increased the nitrogen content; whereas treatment with urea produced a large increase in the nitrogen content [11-15]. Nitrogen may react with oxygen-containing surface groups and or with the mineral admixtures contained in the oxidized carbon with nitric acid [18, 19].

Oxidation of colloidal carbon was found to be associated with a decrease in the ash content. This decrease is more pronounced in case of oxidation with nitric acid which is more likely associated with a reaction of this acid with some inorganic constituents. Most of

these ashes are silica and silicate compounds and other elements oxides present in the rice straw such as K₂O, CaO, and MgO as reported in the literature [20].

Textural properties

The representative adsorption/desorption isotherms of nitrogen onto C, C-N and C-u, at -196°C, are shown in Fig. 1. The nitrogen adsorption isotherms of all investigated carbons belong to type IV of IUPAC classification. The N₂ adsorption results were carefully analyzed using the conventional BET method and the t- method [16] to determine the specific surface area, the total pore volume, the mean pore radius and the volumes of micro- and non-micropores. Table 2 lists the textural properties of the prepared carbons and reveals the following results; (i) After thermally oxidizing treatment at 600° C, the surface area, total pore volume, mean pore radius and non micropore volume increased to different degrees, for example, the non micropore volume increased about 70 %, while the increase in r_m value of C-Th was calculated to be 2%. (ii) The surface area decreased while total pore volume and mean pore radius increased upon oxidation with concentrated nitric acid, where about 18% increase in the mean pore radius was obtained. Thus concentrated nitric acid treatment may induce destruction of the carbon texture. The non-micropore volume ($V_{non-mic}$, ml/g) of sample C-N represents 92.5% of its total pore volume (V_p , ml/g). The decrease in the surface area was associated with about 23.7% increase in the mean pore radius. (iii) The treatment of carbon with concentrated urea and then heated at 400°C (C-u), severely affected the porosity of carbon, where the total surface area and total pore volume increased about 3.2% and 17.6%, respectively. The volume of non-micropore (*i.e.* mesopores) decreased about 9 % than the original carbon and accompanied with a large increase in the micropore volume. Urea treatment carbon, a number of complex reactions taking place between the carbon and the urea involves a number of complex reactions under heat treatment [19,21]. The textural changes depend among other factors on the oxidizing agent or post treatment used. It was reported that the liquid phase oxidation does not notably change the texture of the activated carbon [3,11,22]. However, under more harsh conditions (concentrated acid, heating until complete evaporation) a decrease in surface area and micropore volume was observed while the non-micropore volume increased owing to the collapse of the pore walls [22].

Chemistry of the carbon surface

The chemistry of the carbon surface is attributable to the presence of the carbon - oxygen functional groups of basic or acidic character. The

TABLE 1. Elemental analysis of the investigated carbons.

Carbon	Elements-(%)					Ash%
	C	H	N	S	O*	
C	83.2	0.50	0.37	0.65	5.21	4.6
C-Th	80.18	0.94	0.74	0.52	10.70	4.0
C-N	73.89	0.91	1.05	0.47	21.79	2.7
C-u	79.45	0.89	6.30	0.48	7.78	4.3

*obtained by the difference between the percentage content

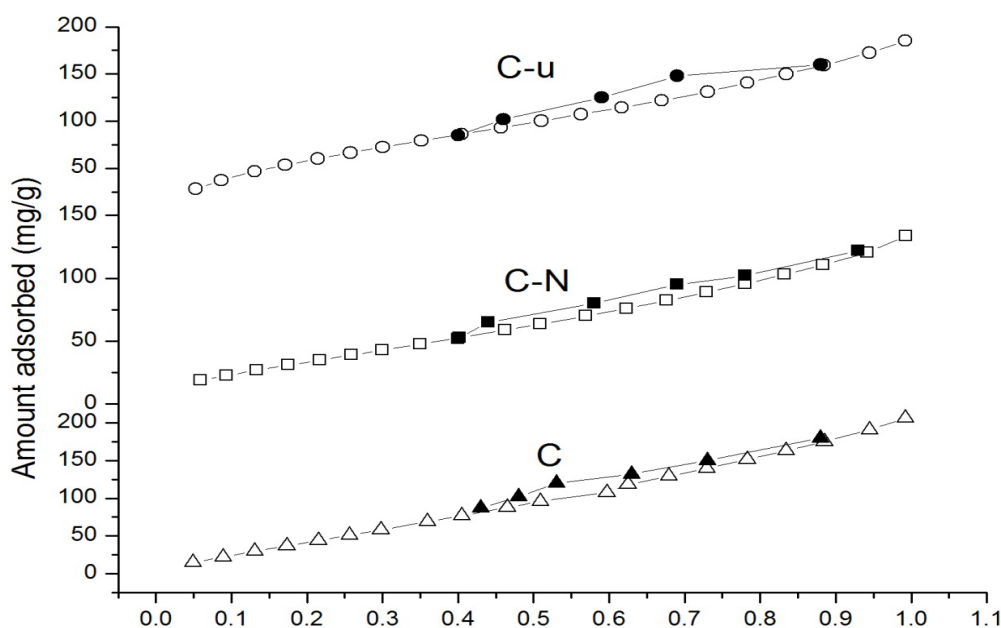


Fig. 1. Nitrogen adsorption / desorption isotherms for C, C-N and C-u.

pH of the aqueous slurry of a carbon affords a suited indicator on the acidity of this carbon. The functional groups on the surface of investigated carbons (C, C-Th, C-N and C-u) were determined by Boehm's titrations and their results are listed in Table 3 together with the surface pH. Urea treatment resulted in sample (C-u) with weak acidic characters owing to the presence of carbonyl groups. However, the Boehm's titration was not employed in this sample as nitrogen containing groups may behave as acids in water solutions. Table 3 reveals that the surface pH of the colloidal carbon C is basic whereas those of its oxidized derivatives are acidic. However, surface acidic and basic functional groups are existing in all the investigated carbons; the concentration of the acidic groups in the surface of carbon (C) is very low. The increase in the concentration of these acidic groups is observed during treatment of this carbon with oxidizing agents. Thus

oxidation with nitric acid brought about 1.75 fold increases whereas about 1.41 fold increases for oxygen thermally treated rice straw at 600°C (C-Th). The surface pH of the all investigated carbons was examined for oxidation resulted in a decrease in the surface pH due to deposited oxygen functional groups [18]. Oxidation led to the development of new functional groups, such as carboxylic acid, lactones and anhydride, carbonyl and phenol groups. The treatment with contracted urea resulted in pH increase. Urea treatment increased the basic character of the modified carbon, in comparison with the colloidal carbon [4]. This increase in surface basicity may partly due to formation of nitrogen – containing groups which are able to bind with protons. Nevertheless, it can also be connected with decomposition of some oxygen – containing acidic groups that can shadow the π electrons of graphene layer [13, 15].

Figure 2 shows the FTIR spectra for the

colloidal carbon in comparison with the (a) after dry oxidation treatment, (b) after treatment with nitric acid and saturated urea in order to identify the oxygen functional groups on their surfaces. Normally, the band recorded at 3640-3410 cm^{-1} represents the -OH stretching of polymeric compounds. The band of 3000-2800 cm^{-1} is ascribed to the stretching vibration of C-H. The band obtained at 1740-1725 cm^{-1} donates the stretching vibration of COO- and C=O. The bands at 1324, 1376 and 1000 cm^{-1} are assigned to the carboxyl, carbonate or carboxylic salt and metal carbonate, respectively. For oxidation thermally at 600 °C for 4 hr in absence of any active agents may be leaving a less contaminated surface (tarry materials and hydrocarbons) ready to interact with the residual and combined oxygen [2,4,15, 19], thus creating oxygen C = O groups either of acidic or basic groups type [2]. Nitric acid is a good oxidizing agent for the conversion of basic groups. It was indicated that the increase in the intensities of the bands at 1625, 1390 and 3425 cm^{-1} after the nitric acid treatment can increase the binding capability of carbon used. Figure 2b also shows that the same peaks appeared after carbon modified with concentrated urea and heated at 450 °C for 1hr. Clear bands were seen that they could be related to nitrogen – containing species. For the C-u carbon, the presence of both N-H at (1412 cm^{-1}) and C-N at (1078 cm^{-1}) bands might indicate the formation of amide and amine groups [15]. Therefore, the resulting modified carbon C-u contains to some extent oxygen – containing groups with a basic nature, however; it is still acidic in character.

Effect of pH and temperature on adsorption

Among the factors affecting the adsorption of an adsorbate from its aqueous solution,

the pH, temperature, initial concentration and equilibrium time are of great significance. Preliminary experiments have been performed for the determination of the appropriate pH which leads to maximum NR dye adsorption. Figure 3 shows the effect of pH on adsorption of NR dye by different carbon samples. Obviously, when all other adsorption conditions are the same apart from the solution pH, the maximum NR dye adsorption from solution was occurred at pH=4. This trend was true for all the investigated carbons. Adsorption kinetic and isotherms of NR dye were undertaken at pH=4.

The effect of adsorption temperature may be indicated by comparing the capacity of colloidal carbon (C) at different temperatures of 30 – 50°C (figure not shown here). This carbon shows increase of about 21.6% in the adsorption capacity upon rising the adsorption temperature from 30 to 40°C. Moreover, about 37.3% increase upon further rise in the adsorption temperature from 40 to 50°C. The increase in temperature can lead to higher diffusion rates accompanied by decreasing viscosity and density of the solute, enhancing the extent of adsorption [23]. The recorded increase in magnitude of the equilibrium adsorption with increasing temperature also indicated that the adsorption of NR dye onto colloidal carbon C was endothermic in nature.

Adsorption kinetics

Effect of initial concentration on NR dye

Figure 4 shows the extent of NR dye adsorption onto colloidal carbon (C) as a function

TABLE 2. Textural properties of the investigated carbons obtained from nitrogen adsorption –desorption at -196°C.

Sample	S _{BET} m ² /g	V _T ml/g	\bar{r} nm	V _{micro} ml/g	V _{non-micro} ml/g
C	256	0.1861	1.39	0.007	0.1791
C-Th	265	0.2111	1.42	0.004	0.2041
C-N	153	0.2291	1.72	0.017	0.2121
C-u	265	0.2198	1.74	0.057	0.1620

TABLE 3. Surface functional groups (meq /g) and the pH of the investigated carbons.

Carbons	Carboxylic	Lactonic	Phenolic	Carbonyl	Surface pH
C	0.06	0.09	0.01	0.20	7.9
C-Th	0.54	0.42	0.55	0.67	6.7
C-N	0.83	0.40	0.50	0.91	4.0
C-u	–	–	–	–	6.9

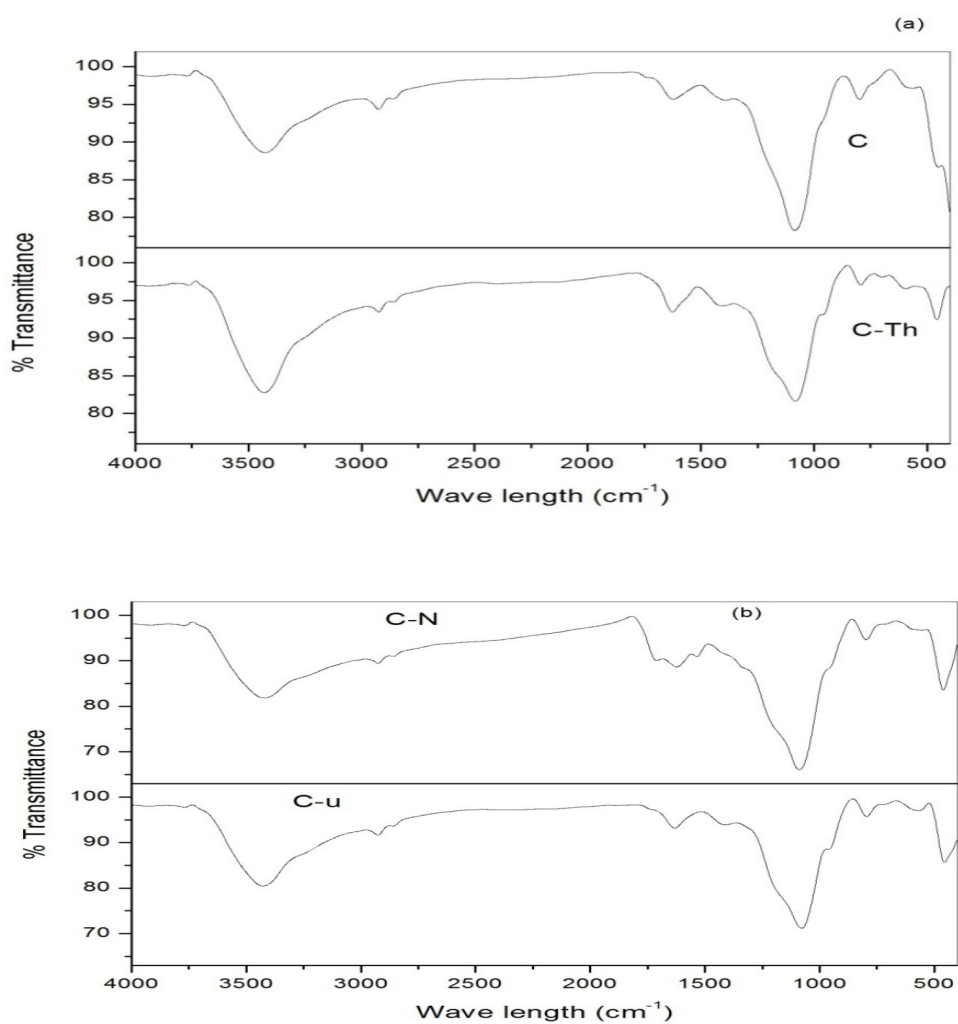


Fig. 2. Representative FTIR patterns. (a) Samples C and C-Th (b) samples C-N,C-u.

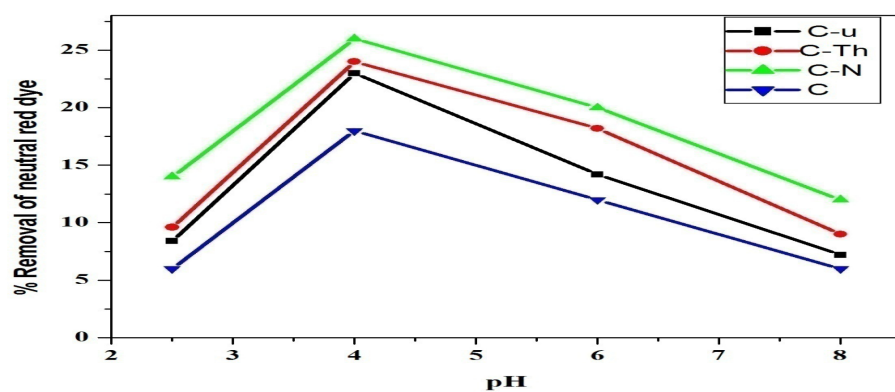


Fig. 3. Effect of pH on the adsorption of NR dye over all investigated samples

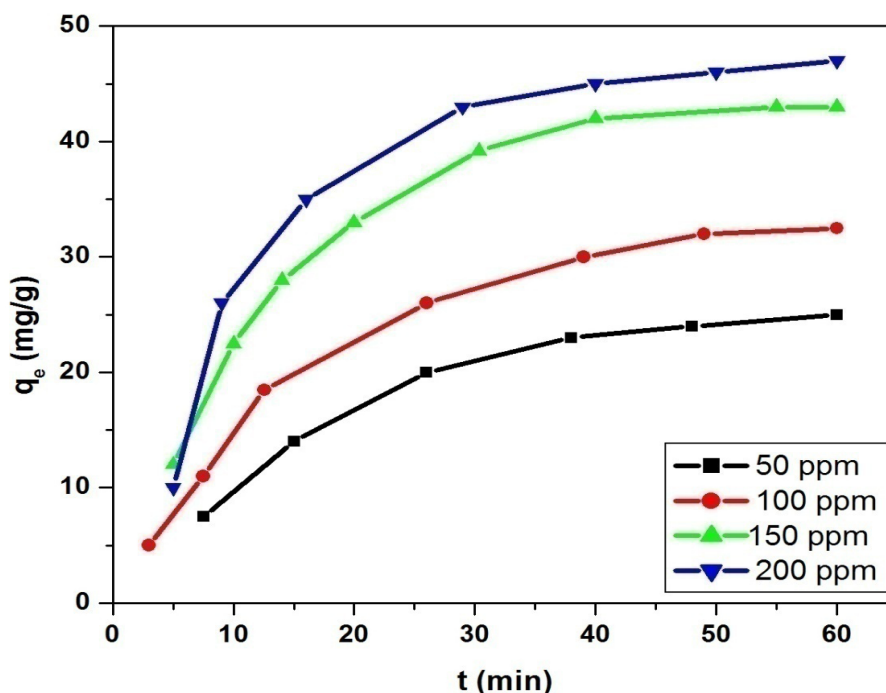


Fig.4. The extent of NR dye adsorption of colloidal carbon (C) as a function of time and initial concentration.

of time and initial concentration. The quantity of NR adsorbed per unit mass increased from 20 to 39 mg/g as the NR concentration increased from 50 to 200 mg/L. The equilibrium was attained at 40 min for all the initial concentration studied indicating completely monolayer adsorption. The surface of colloidal carbon contains a number of active sites and the solute (NR) uptake can be correlated to the active sites on equilibrium time. Furthermore, up to 95% of total amount of dye uptake was found to occur in the first rapid phase (40 min) and then the adsorption rate was found to decrease. The increase in adsorbed amount with an increase in initial concentration is attributable to the increase in the mass transfer driving force. From the above mentioned discussion, the surface of colloidal carbon contains a large number of acidic sites.

The kinetic models used in order to investigate the mechanism of adsorption were the pseudo first order (Eq.(1)) and pseudo second order kinetic model (Eq. (2)) and the intra-particle diffusion model (Eq. (3)). The adsorption of NR onto the investigated carbons C, C-Th, C-N and C-u with an initial concentration 200 mg/L and temperature 30°C were examined.

$$\log (q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \quad (1)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (2)$$

where q_e and q_t are the adsorbed amounts of NR dye at equilibrium and at time t (mg/g), respectively. k_1 is the pseudo-first order adsorption rate constant (min^{-1}), and k_2 is the pseudo-second order adsorption rate constant (g/mg.min).

If intra-particle diffusion is assumed to be the rate-limiting step in the adsorption process, the equivalent equation may be written as the equation of Weber and Morris.

$$q_t = k_{id} t^{0.5} + C \quad (3)$$

where k_{id} is the intra-particle diffusion constant ($\text{mg/g.min}^{0.5}$) and C is constant.

The adsorption kinetic curves of the NR dye adsorption onto all investigated carbons are shown in Fig. 5. The kinetic parameters evolving from the application of the three models are given in Table 4.

The first order kinetic equation was applied to the obtained data; adequate straight lines were obtained with high values of correlation R^2 (Table 4). For the pseudo – first order equation is shown in Fig 6. The correlation coefficient (R^2) values are presented in Table 4 which approached unity and indicate the applicability of the pseudo first-order kinetic model for NR adsorption onto all investigated carbons. It is obvious from Table 4 that the adsorption capacity q_e at equilibrium very close to the experimental q_e (exp). On the other hand, by examining the pseudo-second order kinetic model, the data of the experimental values of q_e (exp) were not consistent with the calculated ones. Also, the values of correlation coefficients R^2 of the adsorption of NR dye onto all investigated carbons are approaching unity as listed in Table 4. This suggests the postulation that the adsorption of NR on the studied carbons followed pseudo- first order kinetics.

In order to predict the rate limiting step intra-particle diffusion applied through the use of Eq. (3). Figure 7 shows that the lines do not pass through the origin. For intra-particle diffusion is not the only rate limiting step indicating the effect of film diffusion (boundary layer diffusion). As seen in Fig 7, all the plots show a linear portion extending up wards to a curved plateau. The initial line section represents the surface or film diffusion and the second one is the intraparticle or pore diffusion. Thus the adsorption process of NR is controlled by both film and pore diffusions, respectively. The values of k_{id} and C were estimated and given in Table 4.

The intra-particle diffusion constant k_{id} also exhibits a significant rise with the increase in the acidity (number of acidic sites) of sorbent which is in agreement with the surface pH values of the investigated carbons. The k_{id} value increases in the order $8.79 > 8.20 > 7.89 > 6.31$ for C-N, C-u, C-Th and C, respectively. These indicate that modification of colloidal carbon C with concentrated nitric acid to give C-N resulted in a considerable increase in k_{id} , i.e. a nearly 1.4 fold increase. While modification of C with concentrated urea and then heated at 450 °C is associated with nearly 1.3 fold increase in the value of k_{id} . It seems that modification of colloidal carbon with concentrated nitric acid or with saturated urea then heated at 450°C for 1 hr resulted in generally the same increase in k_{id} .

Equilibrium adsorption

In this investigation the adsorption of NR was carried out over a wide range of equilibrium concentration and pH =4. The adsorption isotherms of NR are shown in Fig. 8. The isotherms

are of L- type according to Gile's classification. Three models namely, Langmuir, Freundlich and Dubinin-Radushkevich (D-R), were applied for the equilibrium data of NR. The isotherms are similar to those characterizing the adsorption but with the steep initial portions and with slight tendency to attain constant adsorption value. The Langmuir adsorption model suggests that adsorption takes place at specific, homogeneous adsorption sites within the adsorbent, and that intermolecular forces lessen rapidly with the distance from the adsorption surface and these isotherms obey Langmuir's equation's.

$$C_e / q_e = \frac{1}{K_L Q_0} + \frac{1}{Q_0} C_e \quad (4)$$

where C_e is the equilibrium concentration (mg/L), Q_0 the monolayer capacity (mg/g) and K_L is the adsorption equilibrium constant (L/mg).

The linear Langmuir plots are shown in Fig. 9 and the equilibrium sorption data are listed in Table 5. To estimate the best adsorption isotherm model, the correlation coefficient values (R^2) were calculated and listed in Tables 5 and 6.

Freundlich isotherm model is an empirical equation that can describe the reversible adsorption onto heterogeneous surface at sites with different energy of adsorption and is not restricted to the formation of the monolayer of adsorbate. The linear form of this model is expressed as:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (5)$$

where K_F is the Freundlich constant (mg/g)/(L/mg)^{1/n}, and also referred to adsorption capacity, while n is the heterogeneity factor and related to adsorption intensity. The value of n can be used also to describe the adsorption whether is linear ($n=1$) or a physical process ($n>1$) is favorable, or a chemical process ($n<1$). The values of K_F and n are determined from the intercept and slope of the plot $\log q_e$ versus $\log C_e$, respectively, and are listed in Table 5.

Another model was also employed to the equilibrium adsorption data of NR dye onto all investigated carbons. This model adopted by Dubinin-Radushkevich (D-R) model (6). It supposes that only a small fraction of the surface is uniform in structure and energetically homogenous. The D-R equation is as the following:

$$q_e = q_m e^{-\beta \xi^2} \quad (6)$$

where q_e is the amount adsorbed substances at the equilibrium concentration C_e , q_m is the maximum amount adsorbed and it is also known as the adsorption capacity, β is a constant correlated

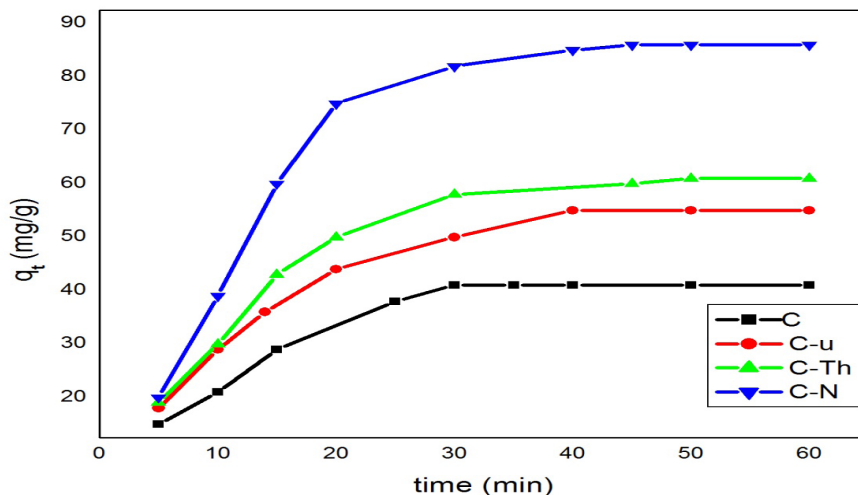


Fig. 5. Kinetic curves of dye sorption onto Carbons investigated at 30°C.

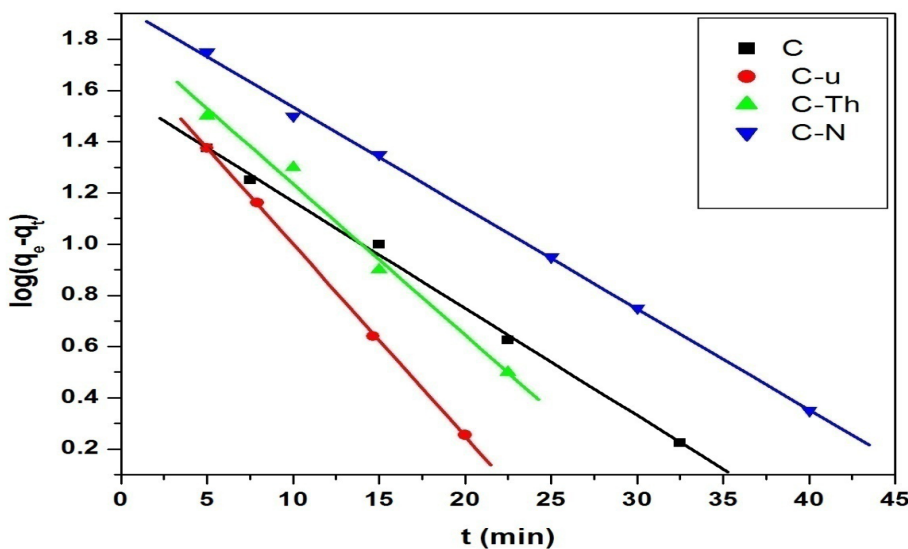


Fig. 6. Linear plots of kinetic first – order of NR dye sorption onto Carbons investigated at 30°C.

to the energy and ξ the potential energy of the surface which equal $RT \ln(1+1/C_e)$ where R is the gas constant (kJ/mol.K), T is the absolute temperature. The D-R equation can be written as:

$$\ln q_e = \ln q_m - \beta \xi^2 \quad (7)$$

A plot of $\ln q_e$ versus ξ^2 gave a straight line (not shown here). The values of q_m and β were obtained and are shown in Table 6. The intercept and slope of the straight lines obtained from the relationship:

$$E_a = 1/2(-\beta)^{0.5} \quad (8)$$

The values of E_a obtained were between 0.0318 and 0.0485 kJ/mol. The value of E_a signifies that the adsorption of NR dye onto all carbons investigated is physical forces, i.e. dispersion or Van der Waals forces. The Langmuir and D-R models exhibit higher values of R^2 (> 0.99) than that obtained from Freundlich model. Thus the adsorption of NR dye onto the prepared adsorbents is well fitted to Langmuir and D-R models.

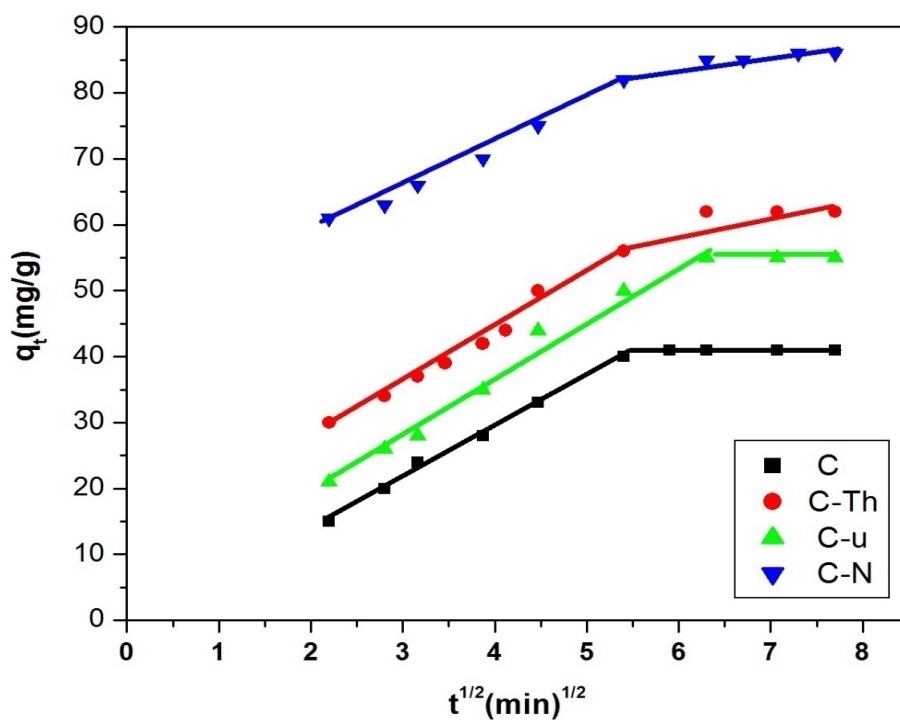


Fig. 7. Intraparticle diffusion plots for the adsorption of NR onto Carbons investigated at 30°C.

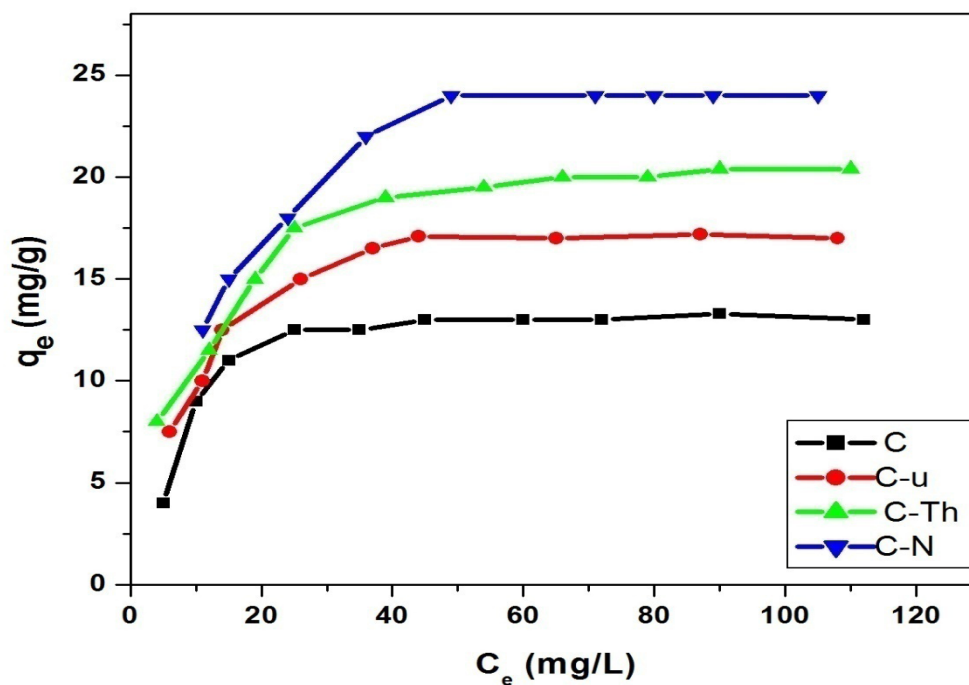


Fig. 8. Equilibrium adsorption isotherms of dye onto investigated carbons at 30°C and pH = 4.

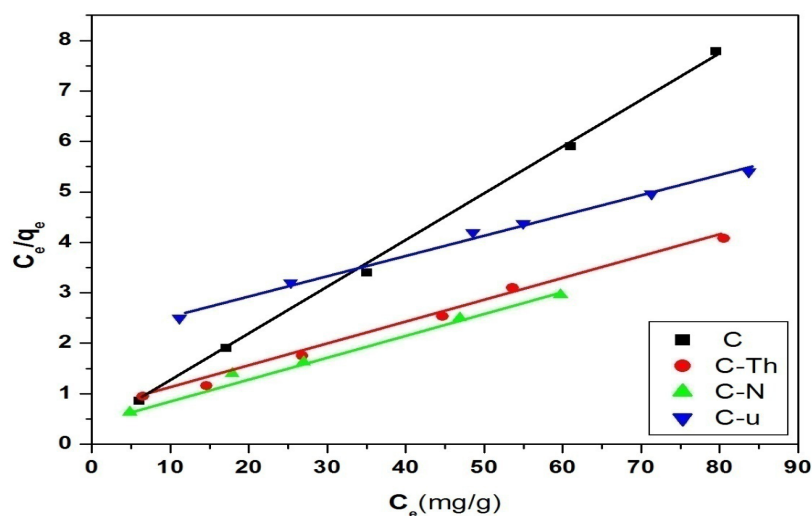


Fig. 9. Representative Langmuir of the adsorption of NR dye onto investigated Carbons.

TABLE 4. Kinetic parameters for the adsorption of NR dye onto investigated carbons.

Adsorbents	Pseudo-first -order				Pseudo-second-order			Intraparticle diffusion	
	$q_e(exp)$	k_1	q_{e1}	R^2	k_2	q_{e2}	R^2	k_{id}	C
C	39	0.0114	42.2	0.998	1.024×10^{-3}	62.5	0.993	6.31	2
C-Th	51.1	0.36	56.1	0.994	7.8×10^{-4}	80	0.996	7.89	12
C-N	75.3	0.61	79.3	0.997	4.9×10^{-4}	125	0.974	8.79	46.2
C-u	46.0	0.49	50.2	0.998	6.5×10^{-4}	83.3	0.997	8.20	4

TABLE 5. Langmuir and Freundlich equation coefficients for NR dye adsorption onto investigated carbon.

Adsorbents	Langmuir parameters			Freundlich parameters		
	K_L	Q_o	R^2	K_F	n	R^2
C	0.285	10	0.996	4.79	4.0	0.956
C-Th	0.057	25	0.997	3.16	2.27	0.975
C-N	0.64	24.2	0.981	3.47	2.5	0.963
C-u	0.022	22.5	0.997	3.39	1.5	0.988

TABLE 6. D-R isotherm constants

Adsorbents	E_a (kJ/mol)	q_m (mmol/g)	$\beta \times 10^{-3}$ (mol ² k/L ²)	R^2
C	0.046	0.0019	0.236	0.997
C-Th	0.0318	0.0013	0.317	0.996
C-N	0.0485	0.0053	0.212	0.999
C-u	0.046	0.0015	0.228	0.998

Conclusion

Colloidal carbon developed from rice straw exhibited surface area of 256 m²/g and total pore volume of 0.04861 ml/g. Nevertheless, a large fraction of this area is located in range of micropore sizes. Basic properties are dominant for untreated colloidal carbon. Thermally, nitric acid, and urea modified colloidal carbons were prepared. These sorbents were characterized by determining their physical and chemical properties including N₂ adsorption, elemental analysis, FTIR and surface acidity. The cationic NR dye was highly adsorbed on nitric acid – modified form, particularly at pH=4. Oxidation of colloidal carbon with oxidizing agent thermally or acid treated was associated with a decrease of surface area and total pore volume but, with an increase in the pore dimensions. On the other hand, urea modified carbon was associated with increase of surface area and increase in the basic character. This might be partly attributed to formation of nitrogen groups. The adsorption was of the physical adsorption type and the adsorption data followed Langmuir and D-R models and followed pseudofirst –order kinetics. The equilibrium adsorption data followed Langmuir and D-R models. The mean energy (E_a) obtained indicated the physical nature of sorption process. The adsorption capacities of non – modified and modified carbon toward NR dye adsorption were found to increase in the subsequent order C-N > C-Th > C-u > C.

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إزالة الصبغ الاحمر المتعادل الكاتيوني من المحاليل المائية باستخدام قش الأرز الطبيعي والمعدل

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تم تحضير مواد كربونية غروية معدلة عن طريق تفاعل الكربون الغروي الناتج من قش الأرز مع الأكسدة الحرارية، حامض النيتريك والمعالجة باليوريا. تم الحصول على الخصائص النسبجية والكيميائية لسطح المواد الكربونية غير المعدلة والمعدلة باستخدام تقنيات امتزاز غاز النيتروجين عند درجة حرارة 196^o -م، التحليل العنصري وطيف الأشعة تحت الحمراء (FTIR). تم دراسة امتزاز الصبغ الاحمر المتعادل الكاتيوني (NR) من المحاليل المائية بواسطة هذه المواد الكربونية من خلال التجارب الامتزاز الحركية والانتزانية. ولقد انخفضت مساحة السطح وحجم المسام الكلي، في حين زاد نصف قطر المسام بعد المعالجة مع حامض النيتريك. وكان الرقم الهيدروجيني السطحي للكربون غير المعدل قلوية بينما قيمتها للمواد الكربونية المعدلة كانت حمضية. اظهرت المادة الكربونية المعالجة باليوريا اقل حامضية وأعلى محتوى نيتروجين وعليه قدم أقل قدرة امتزازية تجاه الصبغة. تم الحصول على الحد الأقصى لإزالة الصبغة عند درجة الحموضة 4. وقد وجد أن كمية الامتزاز من قبل المواد الكربونية قيد التحقيق تعتمد على كمية الحموضة السطحية. وقد تم تحليل نتائج الامتزاز تبعاً لنماذج لانجمير، فريونديتش و دوينين-رادوشكفيتش (D-R). امتزاز الصبغة (NR) على الممتزات المعينه هو من نوع الامتزاز الفيزيائي وينبع معادلة حركية من الرتبة الاولى. وعليه فإن المعالجة بحامض النيتريك جلبت زيادة كبيرة في امتزاز الصبغة (NR) وذلك يعزى إلى تشكيل مجموعات الأوكسجين التي تحتوي على مجموعات وظيفية حمضية على سطح المادة المازة الناتجة. وتبين أن نتائج الامتزاز الاتزانى للصبغة قد توافقت جيداً بشكل جيد مع نماذج لانجمير و دوينين-رادوشكفيتش (DR).

