

Preparation of Carbonaceous Hydrochar Adsorbents from Cellulose and Lignin Derived from Rice Straw

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IN THIS paper, carbonaceous hydrochar adsorbents with highly functionalized surface active sites were prepared from cellulose and lignin constituents of rice straw via hydrothermal treatment at 180°C for 20hr followed by carbonization process at 500°C for 2hr without external gas flow. Two carbonaceous samples were obtained from cellulose and lignin and denoted as RC-C and RL-C, respectively. The resulting hydrochar adsorbents were characterized using means of SEM, TEM, FTIR, Boehm's titration and adsorption of N₂ gas at -196°C. Kinetic and equilibrium adsorption studies using methylene blue (MB) dye as model pollutant compound in industrial wastewaters were determined. The calculated adsorption efficiencies of the adsorbents were considerably depended on the initial dye concentration, contact time and temperature. The obtained adsorption results were found to describe well using the pseudo-second order kinetic and Langmuir isotherm models. Monolayer adsorption capacity of RC-C and RL-C reached to 100 and 40 mg/g towards MB dye, respectively. Based on these findings, the produced hydrochars from cellulose and lignin of rice straw can be emerged as low-cost and valuable adsorbents for removing dye contaminants from wastewater.

Keywords: Hydrothermal Treatment, Hydrochar, Cellulose, Lignin, Adsorption, Cationic Dye.

Introduction

Due to their thermal and chemical stability, high concentration of surface functional groups, high degree of aromaticity and polarity, hydrochar materials derived from lignocellulosic wastes have received great attention in the recent years [1-5]. These materials are currently prepared using hydrothermal carbonization process (HTC) of wet biomass at moderate temperatures (*ca.* 180–250°C) under self-generated pressures at approximately 20-30 bars [5]. HTC process is a powerful technique for the synthesis of a carbon-rich solid product dispersed in water containing soluble organic substances from various biomass wastes. Additionally, the hydrothermal carbonization, as a wet carbonization, is more efficient than the conventional dry carbonization, because it operates at low temperature and thus does not consume high energy for decomposition of biomass materials such as cellulose, hemicellulose and lignin [1-5]. The aromaticity of carbon structures produced in hydrochars are similar to that obtained in either biochar or activated carbon materials. Moreover, this process involves sequence of chemical reactions like hydrolysis, dehydration, decarboxylation, polymerization

and aromatization to form polymerized hydrochar [2,3]. Carbonaceous hydrochar materials have been offered to be used as adsorbents for water and air purification, as electrodes in energy storage, as catalysts for fuel cells and as heterogeneous catalysts [5]. However, low porosity developed in hydrochars [1, 3], thus post-carbonization treatment is required to enhance its porosity. Recently, different hydrocarbons and biomass wastes such as glucose, cellulose, macroalgae, coconut husk fibers, etc., have been employed for preparation of carbonaceous hydrochars under varying conditions of HTC process [1-5].

It is well-known that cellulose, hemicellulose, and lignin are the three key components of biomass and they in general cover respectively 40–60%, 20–40% and 10–25% of lignocellulosic biomass [6]. Accordingly, cellulose is the most copious natural polymer with total production of 10¹¹–10¹² tons/year [3,7,8]. It has a molecular formula (C₆H₁₀O₅)_n and made up of glucose units [8]. Lignin is the second most plentiful natural raw material after cellulose [9] and composed of complicated phenylpropane units [10]. In addition its annual production amounts to more than 50 million tons/year. Both cellulose and lignin by-products

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DOI : 10.21608/ejchem.2017.1311.1080

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are discharged from paper and wood pulping industries in large quantities, and thus represent a major problem of disposal [10]. It is important to mention that cellulose and lignin materials have a considerable carbon content and thus they have been used for preparation of activated carbons [8, 10]. In recent work, Jindo *et al.* [11] studied the effect of carbonization temperature on the physicochemical characteristics of biochars prepared from different agricultural wastes (e.g. rice husk, rice straw, wood chips of apple tree and oak tree). Thereof, preparation of carbonaceous hydrochars from cellulose and lignin components derived from rice straw to be used as adsorbent materials is an important issue.

To the best of our knowledge this is the first study looking at the preparation of carbonaceous hydrochar-free silica from cellulose and lignin components extracted from rice straw using hydrothermal carbonization at 180°C for 20hr followed by post-thermal treatment at 500°C for 2h to be used as adsorbents. In this paper the possibility to use the hydrochar products derived from rice straw as low-cost and alternative adsorbents to the commercial activated carbons was examined also. The adsorption efficacy of the prepared hydrochar adsorbents towards removal of methylene blue dye (MB) was investigated through kinetic and equilibrium adsorption studies. Furthermore, the influences of initial dye concentration, contact time of hydrochar with dye molecules and temperature of the adsorption process on the effectiveness of adsorption were studied in order to establish the optimal adsorption conditions.

Experimental

Preparation of cellulose fibers and lignin powder

Prior hydrothermal treatment, the rice straw was collected from Delta region in Egypt, washed thoroughly with hot water for several times then dried overnight at 80°C. Rice straw was milled, sieved in range of 0.4–0.8 mm. The method described by Elanthikkal *et al.* [12] with slight modification was employed to prepare cellulose fibers. Fifty grams of the cut rice straw was transferred into a 2-L beaker and added 700mL of 10% w/v NaOH solution. The mixture was heated with occasional stirring for 4 hr at a temperature of 60–70°C and left overnight at room temperature in order to remove the lignin, hemicellulose and other substances. Then, the mixture was filtered and washed several times to separate the insoluble pulp and to remove the excess NaOH also.

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The insoluble pulps which constitute the cellulose were bleached with 500mL of 1% w/v sodium hypochlorite (NaClO) solution and buffered to pH of ~ 5 by an acetate buffer. The extracted cellulose was washed at least three times with distilled water until the pH of the washing becomes neutral. The cellulose was air dried at 80°C and denoted as RC.

To extract lignin, the soluble pulp (filtrate) was acidified with concentrated sulfuric acid to pH ~3 and then the precipitated solid was collected and washed with hot water for several times till pH~5.5, filtrated and dried overnight at 80°C. The produced lignin powder was designated as RL. For simplicity, R, C and L letters are abbreviations of rice straw, cellulose and lignin, respectively. Figure 1 shows the preparation scheme of carbonaceous hydrochars from cellulose and lignin wastes of rice straw.

Preparation of carbonaceous hydrochars

A definite weight of cellulose fiber (RC) or lignin powder was added to~ 1.66 N of NaOH solution (2g in 30 mL distilled water) and stirred for 30 min prior to hydrothermal treatment. Then, the mixture was changed into a 100 mL Teflon-lined autoclave tube inside a stainless steel reactor then heated in an electrical muffle at 180°C for 20hr. The produced hydrochar was taken out of autoclave and then heated in a vertical stainless tube at 500°C for 2hr without flow of any external gases. After carbonization process, the produced hydrochar samples from cellulose and lignin were labeled as RC-C and RL-C, respectively, where the latter C is referred into carbonization. For comparison sake, the morphology and surface properties of pretreated rice straw with NaOH as starting material before hydrothermal treatment was studied also.

Characterization of the prepared hydrochars

The morphology characteristics of the prepared samples were determined using field emission scanning electron microscope (FE-SEM, FEI Quanta FEG-250). High resolution transmission electron microscope (HR-TEM, JEM-1230, Japan) operated at 120 kV was used to study the shape and size of nanoparticles. Prior to nitrogen adsorption measurements, the samples were degassed in vacuum at 300°C. The textural parameter, such as the BET- surface area (S_{BET} , m²/g), total pore volume (V_{T}) and mean pore diameter (R_{p}) were evaluated from BET- equation using BEL-Sorp (Microtrac Bel Crop, Japan) by using N₂ gas adsorption at -196°C. The changes

in surface functional groups were identified by fourier transform infrared (FT-IR) spectroscopy in the range of 4000-400 cm^{-1} using a JASCO 6100 FT-IR spectrometer, and the KBr disc technique. In addition, the total acidic and basic sites on the surface of solid hydrochars were also determined by the Boehm's titration method [13] as follows; fine powder of hydrochar was added into each 0.1 M NaOH and HCl aqueous solutions under shaking for 48 h at room temperature. Then the supernatant solutions were back-titrated with 0.1 M HCl or NaOH, respectively.

Adsorption studies of Methylene blue dye

To determine the adsorption capacity of prepared carbonaceous hydrochar adsorbents, liquid-phase adsorption studies towards methylene blue dye (MB) were considered.

In batch adsorption experiment, 50 mL of methylene blue dye (MB) solutions with initial concentrations ranging from 25 to 300 mg/L were added into a set of 100 mL conical flasks and conducted with 100 mg solid adsorbent at the initial pH of dye solution (~ 6). The flasks were kept in a shaker at a speed of 200 rpm. After agitation, the dye solutions were separated from the adsorbent by filtration and their absorbance was measured at the wavelength characteristic of MB dye, $\lambda_{\text{max}} = 664 \text{ nm}$ by using a UV-Vis spectrophotometer (Shimadzu-2401PC).

The amount of MB dye adsorbed onto hydrochar adsorbents at equilibrium (q_e , mg/g) or at time t (q_t , mg/g) was calculated according to the following equations:

$$q_e = \frac{(C_0 - C_e)}{m} V \quad (1)$$

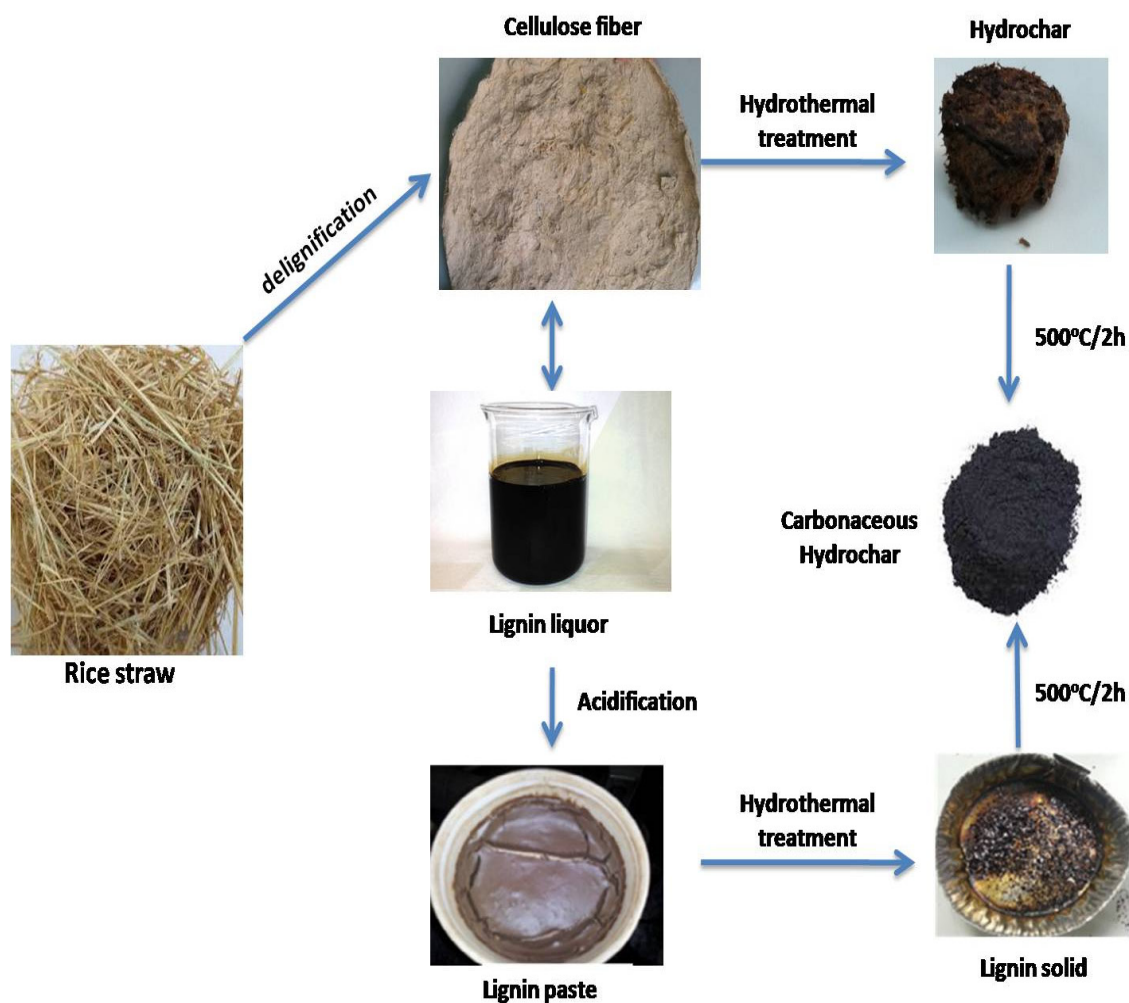


Fig.1.Preparation scheme of the carbonaceous hydrochar adsorbents from cellulose fiber and lignin precursors.

$$q_t = \frac{(C_0 - C_t)}{m} V \quad (2)$$

where C_0 , C_e , and C_t are initial, equilibrium and time concentrations (mg/L) of MB dye, respectively. V is the volume of solution (mL) and m is the mass of dried hydrochar adsorbent (mg). The effect of the following parameters on the kinetic removal of MB dye was studied: (i) initial dye concentration (25, 50 and 100 mg/L), (ii) agitation time: (10–240 min) at a constant temperature (25°C) and at initial dye pH~ 6 and (iii) temperature (25 and 40°C) at different dye concentrations ranging from 5 to 60 mg/L at agitation time of 120 min and at pH 6. All absorbance measurements were performed in two replications. The maximum deviation of the MB dye amount adsorbed onto hydrochar adsorbents was less than 3%.

Results and Discussion

Morphological studies

Alkali pretreatment with NaOH has been employed to remove lignin from biomass and to increase the biodegradability of cellulose [14]. Figure 2 (a-c) shows the morphological features

of the pretreated rice straw with NaOH, RC-C and RL-C hydrochar samples. As seen in Fig. 2a, the pretreated rice straw with NaOH shows a rough surface with the presence of cracks through fibrous structure. While SEM image of the hydrochar produced from cellulose (RC-C) exhibits formation of aggregates with spherical shape (Fig.2b). Probably such morphology results in the strong delignification process of rice straw to produce cellulose free of amorphous lignin and hemicellulose. Regardless, these spherical shapes can be thermodynamically more stable as compared to other particle shapes [2].

On the other hand, the SEM photograph of hydrochar obtained from lignin (RL-C) elucidates the formation of irregular platlets (layers) with rough surface and few pores (Fig.2c). Pua *et al.* [15] have reported the same result with the kraft lignin char which has been prepared from the *Jatropha* oil. Additional thorough investigation using TEM on RC-C sample was done and indicated that the produced spheres show nanowhiskers (needle-like) which are derived from cellulose fiber [16] (Fig. 2d). This ultra-structure property may provide appropriate surface for uptaking dye molecules by the hydrochar obtained.

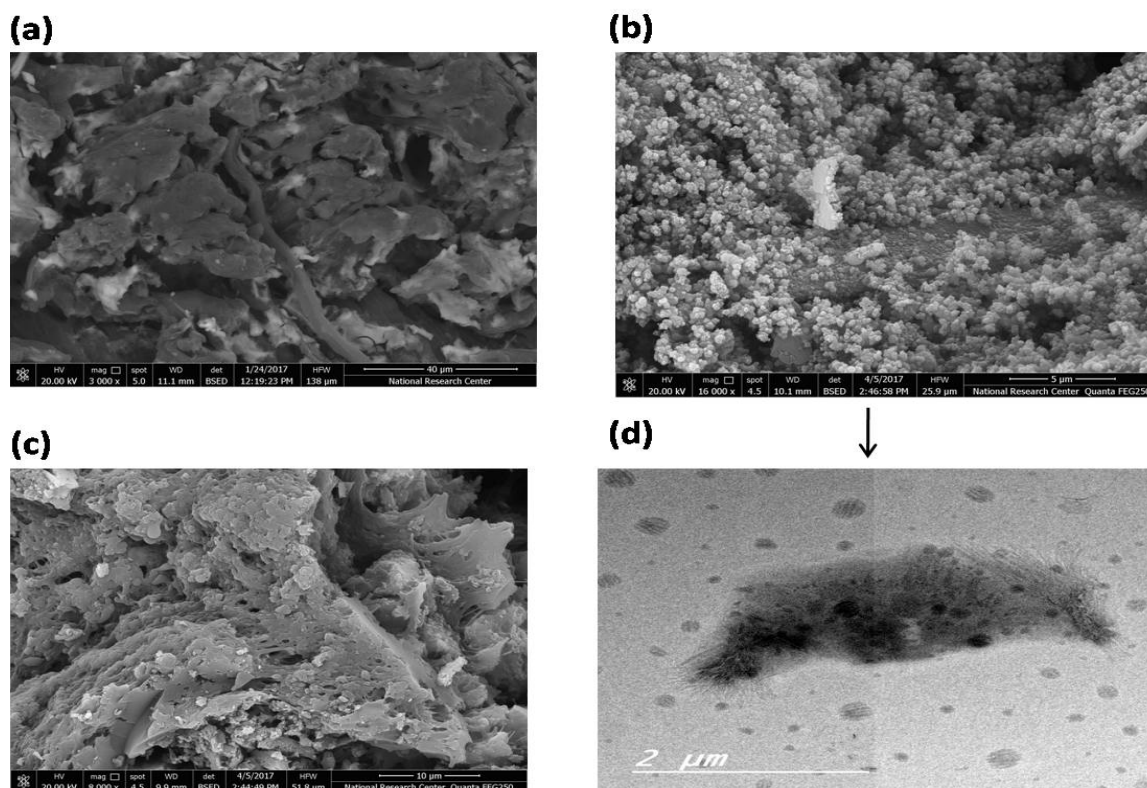


Fig. 2. SEM images of pretreated rice straw (a), hydrochar-cellulose (b), hydrochar-lignin (c) and TEM photograph of hydrochar-cellulose (d).

Surface and textural studies

Sevilla and Fuertes [2] proposed the carbonization mechanism of hydrochar during HTC of cellulose. They reported six steps as follows: (i) hydrolysis, (ii) dehydration and destruction of cellulose into soluble products, (iii) polymerization of these products, (iv) aromatization of the polymers thus formed, (v) formation of spherical nuclei and (vi) growth of the nuclei to form microspheres on the surface of cellulose. Thus, significant changes in their surface characteristics could be obtained as a result of these chemical reactions. To investigate these changes in the surface chemical groups through the chemical treatment of rice straw, the FTIR technique was applied. Figure 3 illustrates the FTIR spectra of pretreated rice straw, hydrochar-cellulose (RC-C) and hydrochar-lignin (RC-L). It was found that some chemical transformations happened when the cellulose and lignin extracted from rice straw were converted to carbonaceous hydrochar materials. For example, the absorption peak at 1450 cm^{-1} is due to $-\text{CH}$ deformation for both lignin and cellulose is shifted to 1437 cm^{-1} in hydrochar-lignin. Its intensity is significantly decreased after delignification of rice straw process as seen in FTIR spectra of both hydrochars. It has been reported that this peak is mainly attributed to cellulose more than lignin in the origin rice straw [3, 17]. However, the broad peaks between 1160 and 1036 cm^{-1} are apparently observed in hydrochar-cellulose and hydrochar-lignin and pretreated rice straw, respectively. Such peaks are ascribed to ether linkages (C–O–C) asymmetric stretching in cellulose, hemicellulose and lignin, however, their intensities increased after delignification process in RC-C [18]. The presence of sharp peaks at 1640 cm^{-1} in all samples can be attributed to conjugation of carbonyl groups with aromatic ring. Also another small absorption band at 1720 cm^{-1} is ascribed to C=O vibrations in carbonyl, quinone, ester or carboxyl [19]. Moreover, the appearance of peaks at $3000\text{--}3800\text{ cm}^{-1}$ as a wide band centered at 3430 cm^{-1} is attributed to the presence of O–H stretching vibrations in hydroxyl or carboxyl groups [3]. The stretching of $-\text{CH}$ in the aliphatic structure appears at 2840 cm^{-1} . In all spectra, the appeared peaks at 480 and 870 cm^{-1} are referred to C–H out-of-plane bending vibrations in the aromatic ring.

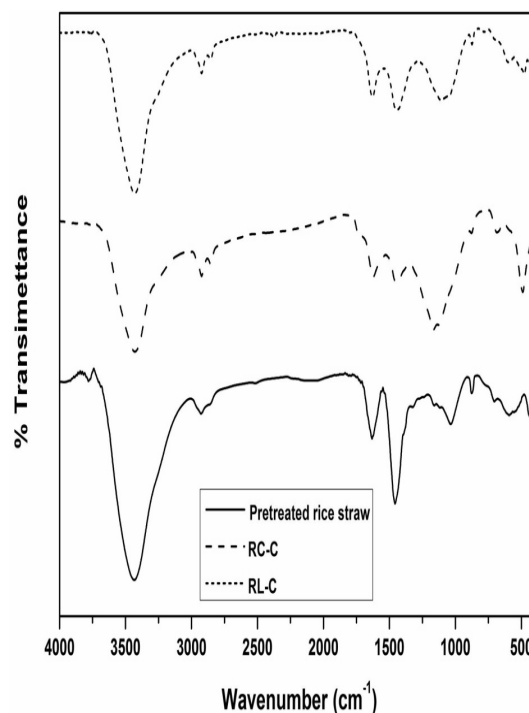


Fig. 3. FTIR spectra of the as-prepared samples.

Therefore, FTIR results show that well functionalized carbonaceous hydrochar materials were produced by means of the hydrothermal of cellulose or lignin at temperature of 180°C for 20hr followed by carbonization at 500°C for 2h under its own atmosphere. This property will enhance the adsorption efficacy of the prepared carbonaceous hydrochar materials. In order to identify the functional groups containing oxygen on the hydrochar surface, the total acidic and basic groups were determined by Boehm's titration and their amounts in mmol/g are listed in Table 1. It was found that the total acidity of RC-C sample is slightly higher than that of RL-C, confirming the introduction of acidic groups including carboxylic acid, lactonic, and phenolic groups as well as few amounts of basic functional groups such as quinone and carbonyl groups [20]. Overall, it can be deduced that the as-synthesized hydrochars bear high amounts of different oxygen sites on the surface. Boehm's titration corroborates the presence of both acidic and basic active sites which agrees with the results in FTIR spectra also.

TABLE 1. Surface active groups and textural properties of the prepared hydrochar adsorbents.

Samples	Surface active groups		Textural parameters		
	Total acidic groups (mmol/g)	Total basic groups (mmol/g)	S_{BET} (m^2/g)	V_{T} (cm^3/g)	R_{p} (nm)
RC-C	3.21	0.80	181	0.0326	7.20
RL-C	2.84	1.22	88.6	0.0122	5.51

Figure 4 shows the adsorption-desorption isotherms of nitrogen gas onto the prepared adsorbents at -196°C . The isotherms are characteristics of type I and IV combinations according to IUPAC classification with hysteresis loops of type H4, confirming that the prepared adsorbents contain micropores and mesopores in their porous structure. The textural parameters of the prepared hydrochars are collected in Table 1. According to the data presented in this table, the prepared hydrochar from cellulose (RC-C) shows better BET-surface area, total pore volume and mean pore diameter than that of hydrochar obtained from lignin (RL-C). It can be deduced that the total surface area of RC-C increase by about 51% as compared to that of RL-C hydrochar. Thus the feedstock type affects the surface of hydrochar property and on the porosity development inside the porous structure of hydrochar-based carbon.

Adsorption studies

Effect of initial dye concentration, contact time and temperature

The effect of initial dye concentration and

contact time on the adsorption process of MB dye molecules is shown in Fig. 5. Results of this figure illustrate that the RC-C adsorbent has higher adsorption amount of MB dye as compared with that obtained using RL-C adsorbent, attaining 3.7 folds increase in the adsorption amount of MB dye of 50mg/L . This result can be related to the high surface area of RC-C hydrochar resulting in an increase a number of active sites responsible for adsorption.

The adsorption kinetics of MB dye on the prepared hydrochars show an initial fast adsorption followed by a much slower adsorption. The amount of adsorbed dye increased sharply after the first 10 min of the contact interval and then increased slightly upon the equilibrium established at around 120 min. Adsorption of MB dye onto the obtained RC-C hydrochar enhanced with raising the concentration of dye from 25 to 50 mg/L and then decreased when the initial concentration was 100 mg/L . With increasing dye concentration its molecules are densely packed on the adsorbent surfaces. It can be seen that

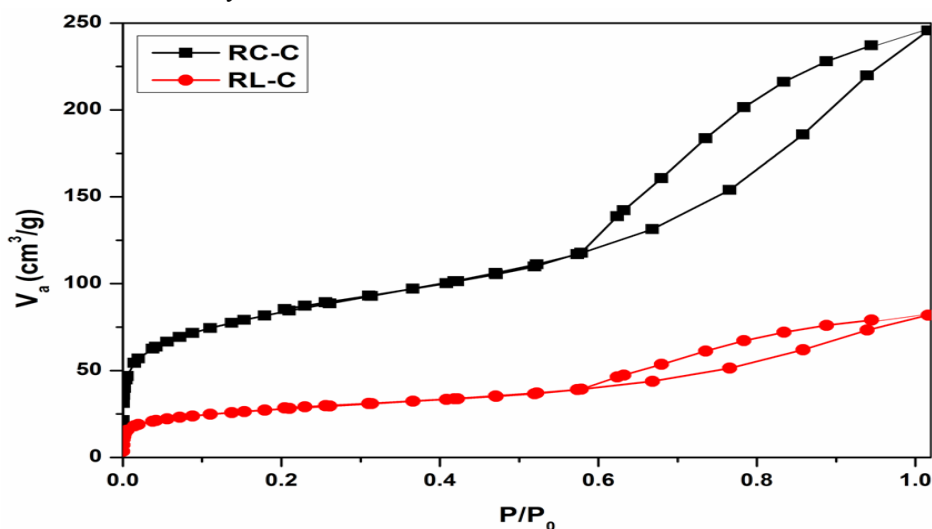


Fig.4. Adsorption/desorption isotherms of nitrogen at -196°C for RC-C and RL-C samples.

there is an instantaneous adsorption phenomenon indicating in turn that the RC-C hydrochar sample has a strong adsorption affinity toward MB dye as a basic dye.

Additionally, the adsorption capacities of RC-C and RL-C adsorbents were analyzed with respect to the change in temperature and initial dye concentration as depicted in Fig. 6. The increase in initial dye concentration from 5 to 60 mg/L and temperature from 25 to 40°C leads to the enhancement in uptake amounts of the

MB dye, suggesting that the adsorption process is endothermic in nature. When the temperature increased, the intraparticle diffusion rate of the MB dye molecules increased during the external boundary layer and the internal pores of the hydrochars. Therefore, the adsorption process probably is controlled by a chemical process. Other studies have been reported the same obtained results [21-23].

Kinetic studies

Three common kinetic models were used so as to investigate the adsorption mechanism

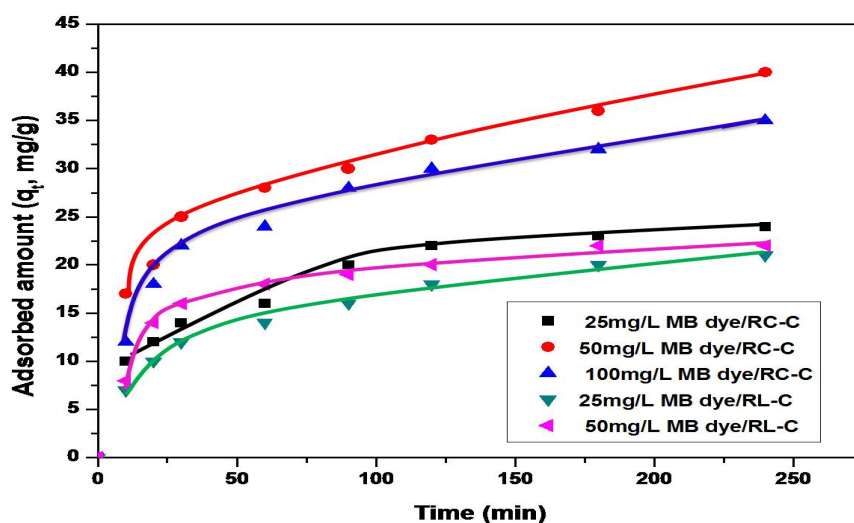


Fig. 5. Effect of initial dye concentration and contact time on the adsorption of MB dye by the prepared hydrochars (adsorbent mass= 0.1g, pH= 6, and T=25°C).

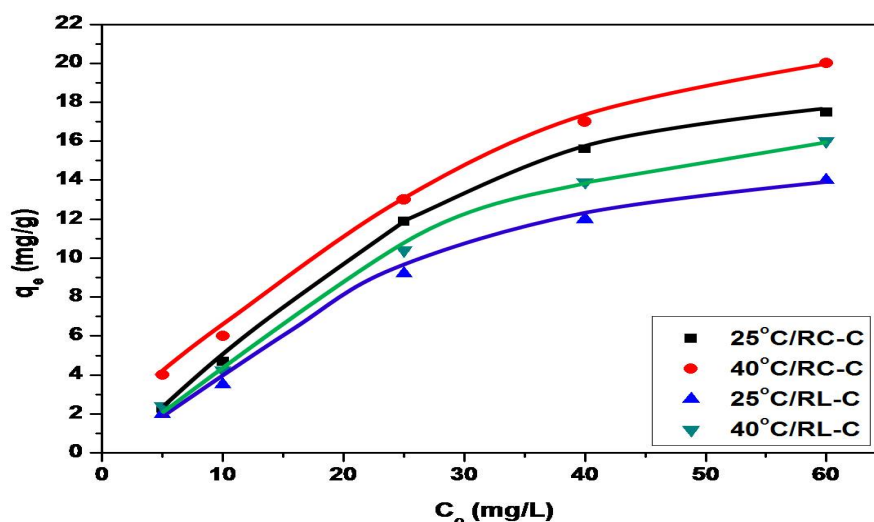


Fig. 6. Effect of temperature on the equilibrium adsorption of MB dye on the prepared hydrochars (adsorbent mass= 0.1g and pH= 6).

of MB dye onto hydrochar adsorbents. Firstly, the Lagergren-first-order kinetic model can be described by the equation [24]:

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \quad (3)$$

Secondly, a linear form of pseudo-second-order kinetic model is expressed by the equation [25]:

$$t/q_t = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (4)$$

where q_e and q_t are the amounts of MB dye adsorbed (mg/g) at equilibrium and time t (min), respectively; k_1 is the rate constant of the Lagergren-first-order kinetic model (min^{-1}). The values of k_1 were calculated from the plots of $\log(q_e - q_t)$ versus t (Fig. 7a). In equation (4), k_2 is the rate constant (g/mg min) of pseudo-

second-order kinetic model of adsorption. The slope and intercept of the linear plots t/q_t against t yield the values of $1/q_e$ and $1/k_2 q_e^2$ (Fig. 7b).

Thirdly, the model proposed by Weber and Morris [26], i.e. an intra-particle mass transfer diffusion model, is described by the equation:

$$q_t = k_{id} t^{1/2} + C \quad (5)$$

where C (mg/g) is the intercept and k_{id} is the intra-particle diffusion rate constant ($\text{mg/g min}^{1/2}$), which can be calculated from the slope of the linear plots of q_t versus $t^{1/2}$ (Fig. 7c). All the calculated kinetic parameters are summarized in Table 2.

As speculated from this table, the correlation coefficients (R^2) of both pseudo-first-order and pseudo-second order models are relatively close (between 0.966 and 0.999). However, the

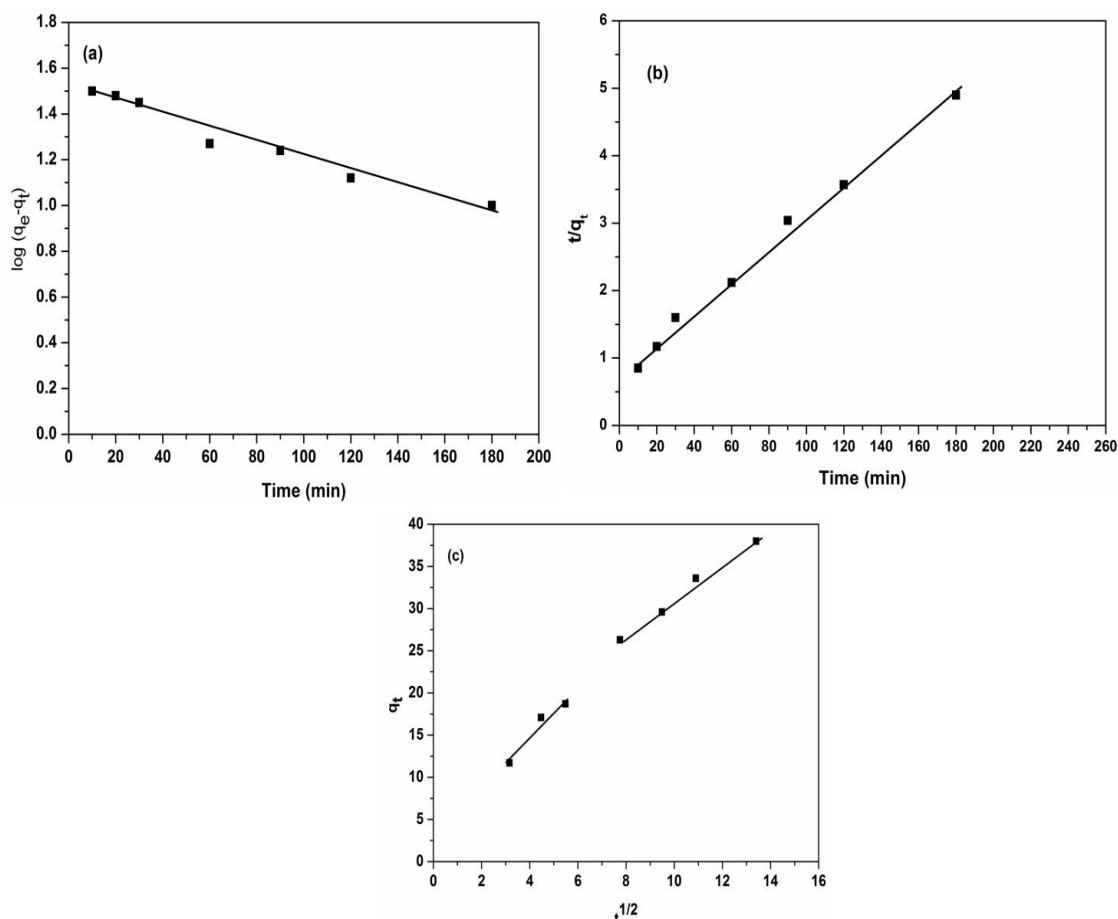


Fig. 7. Representative kinetic adsorption plots of MB dye onto RC-C adsorbent (a) pseudo-first order model, (b) pseudo-second order model and (c) intraparticle diffusion model (adsorbent mass= 0.1g, pH= 6, and T=25°C).

TABLE 2. Pseudo-first-order, pseudo-second-order kinetic model and intraparticle diffusion parameters for adsorption of MB dye at 25°C.

Adsorbents	$C_0 = 50$ mg/L	<i>Pseudo-first-order</i>				<i>Pseudo-second-order</i>			<i>Intraparticle diffusion</i>		
		$q_{e(expt)}$	k_1	$q_{e(cal)}$	R^2	k_2	$q_{e(cal)}$	R^2	k_{id}	C	R^2
		(mg/g)	(min^{-1})	(mg/g)		(g/mg min)	(mg/g)		(mg/g $min^{1/2}$)		
RC-C	47	6.91×10^{-3}	32.9	0.966	7.03×10^{-4}	43.5	0.999	2.63	4.82	0.975	
RL-C	25	0.0116	17.2	0.974	1.03×10^{-3}	23.8	0.985	1.39	2.22	0.940	

computed experimental $q_{e(expt)}$ values from the linear plot of pseudo-first-order model did not agree with those of calculated values. Also, R^2 values of pseudo-second order are slightly high, therefore, it is more expected that the adsorption of MB dye onto hydrochars can take place through the second-order mechanism. In addition, the calculated values of $q_{e(cal)}$ from this model are very close to those determined experimentally $q_{e(expt)}$, corroborated that pseudo-second-order kinetic model is the predominant model.

Furthermore, the rate-controlling step in the adsorption of MB dye was determined using the intraparticle diffusion model [26]. Figure 7c presents a representative plot of intraparticle diffusion of MB dye on the RC-C adsorbent as an example. It exhibits two linear sections and do not pass through the origin which is owing to the difference in the mass transfer rate between the initial and final stages of adsorption [27]. 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 MB is controlled by film and pore diffusions, respectively. It was noticed that the adsorption of MB dye onto RC-C brings an increase in the value of k_{id} about 1.89 fold more than that of RL-C adsorbent.

Equilibrium studies

To examine the equilibrium adsorption of MB dye onto the prepared adsorbents, thus the adsorption data were analyzed in terms of Langmuir, Freundlich, and Temkin adsorption isotherms. The linear form of the Langmuir isotherm [28] is expressed as the following equation:

$$\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{1}{q_m} C_e \quad (6)$$

where C_e is the equilibrium concentration of adsorbate (mg/L), q_e the amount of dye adsorbed at equilibrium (mg/g), and q_m is the monolayer

adsorption capacity (mg/g) and K_L (L/mg) is the Langmuir adsorption equilibrium constant. The free energy of adsorption, ΔG (kJ/mol) can also be evaluated from the parameter K_L according to the expression:

$$\Delta G = -RT \ln K_L \quad (7)$$

In addition Langmuir adsorption isotherm can be given in expression of a dimensionless constant called a "separation factor" and noted as (R_L):

$$R_L = \frac{1}{1 + C_e K_L} \quad (8)$$

The equation representing linear form of Freundlich adsorption [29] can be given as:

$$\ln q_e = \ln K_F + 1/n \ln C_e \quad (9)$$

where K_F (mg/g (L/mg) $^{1/n}$) is roughly an indicator of the adsorption capacity and $1/n$ is the adsorption intensity. Freundlich constants K_F and $1/n$ can be calculated from the intercept and slope of the linear plot with $\ln q_e$ against $\ln C_e$.

The linear form of Temkin isotherm is given by [30]:

$$q_e = B_1 \ln K_T + B_1 \ln C_e \quad (10)$$

where $B_1 = (RT/b)$ and K_T are the Temkin constants; K_T is the equilibrium binding constant (L/mol) corresponding to the maximum binding energy, b is the variation of adsorption energy (kJ/mol) and constant B_1 is related to the heat of adsorption.

Table 3 summarizes the parameters of the Langmuir, Freundlich and Temkin isotherms. Isotherms of MB dye adsorption on the surface of hydrochars are presented in Fig. 8. On the basis of their shape they are classified as a class of L-isotherm. As can be noticed from Table 3, the

experimental data obtained are better described by the Langmuir isotherm models, as confirmed by the high value of the correlation coefficients (R^2). The adsorption capacity of RC-C is very higher than that of RL-C by a factor of 2.5. The calculated negative values of ΔG indicate the feasibility and spontaneous nature of adsorption of MB dye onto the materials obtained. The values of separation factor (R_L) show that the adsorption process of dye onto hydrochars is favorable ($0 > R_L < 1$). The values of Freundlich constant ($1/n$) are lower than one for the adsorption of MB dye onto the tested hydrochars showing that the adsorption process is also favorable. The calculated values of B , b and K_T from Temkin model are given also in Table 2. Temkin isotherm assumes two adsorption phenomena as follows: (i) the adsorption heat of monolayer solute molecules (adsorbate) decreases linearly with an increase in the coverage due to interaction between adsorbate molecules and adsorbent surface and (ii) a uniform distribution of binding energies up to some maximum binding energy is obtained [30].

Conclusions

In summary, feasible and novel hydrochars derived from cellulose and lignin components of rice straw were prepared and characterized by

techniques such as SEM, TEM, FTIR, Boehm's titration and porosity development using N_2 gas adsorption at -196°C . Kinetic and equilibrium adsorption studies were investigated using methylene blue dye as model compound. The surface of resultant hydrochars derived from cellulose (RC-C) composed of microspheres aggregates and of irregular fibrous layers in case of lignin (RL-C). It can be found that the two hydrochars obtained are most probably containing various oxygen functional groups. The pseudo-second-order kinetic model can describe the MB adsorption and the intraparticle diffusion was not the only rate-controlling step. The equilibrium adsorption results were significantly described by the Langmuir isotherm than by others owing to the fact that the prepared hydrochars have large abundant oxygen functionalities (e.g., acidic sites amounted about 2.84-3.21 mmol/g). In this frame, the obtained low-cost hydrochars derived from cellulose and lignin could be employed to remove dye-contaminated wastewater.

Acknowledgement

The authors gratefully acknowledge the financial supports provided by the National Research Centre (NRC), Egypt, under the Project No. 11090201.

TABLE 3. Langmuir, Freundlich, and Temkin isotherm parameters for adsorption of MB dye onto the prepared hydrochars from cellulose and lignin materials.

Models	RC-C	RL-C
Langmuir		
q_m (mg/g)	100	40
K_L (L/g)	0.1724	0.0336
R_L	0.0189	0.0902
ΔG (kJ/mol)	-27.0	-23
R^2	0.999	0.957
Freundlich		
K_f ((mg/g)/(L/mg) ^{1/n})	23.2	6.93
$1/n$	0.30	0.28
R^2	0.844	0.893
Temkin		
B_1	12.8	5.84
b (J/mol)	193.3	424.3
K_T (L/mol)	10.5	1.135
R^2	0.921	0.820

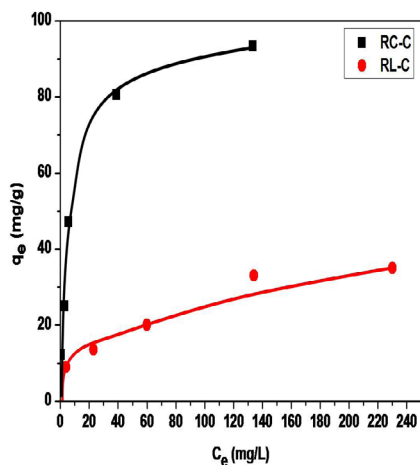


Fig. 8. Adsorption isotherms of MB dye on the surface of hydrochars (adsorbent mass= 0.1g, pH= 6, and T=25oC).

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- (Received 12 /7/ 2017;
accepted 19/ 9 /2017)

تحضير مواد هيدرومادية كربونية مازية من السليلوز واللجنين المستمد من قش الارز

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في هذه الورقة، تم تحضير مواد هيدرومادية كربونية مع مواقع وظيفية ذات نشاط سطحي من السليلوز واللجنين المستمد من قش الارز عن طريق المعالجة الحرارية المائية عند 180 درجة مئوية لمدة 20 ساعة متبوعة بعملية الكربنة عند 500 درجة مئوية لمدة ساعتين بدون تدفق غاز خارجي. تم الحصول على اثنين من العينات الكربونية من السليلوز واللجنين ويشار إليهما RC-C and RC-L على التوالي. تم توصيف العينات المازة الناتجة باستخدام وسائل مثل ميكروسكوب الكتروني ماسح (SEM)، ميكروسكوب الكتروني نافذ (TEM)، طيف حيود الأشعة تحت الحمراء (FTIR)، طريقة المعايرة لـ Boehm و امتزاز غاز النيتروجين عند 196 درجة مئوية. تم تحديد دراسات الامتزاز الحركية والتوازنية باستخدام صبغة الميثيلين الأزرق (MB) كنموذج لمركب ملوث في مياه الصرف الصناعي. وكانت كفاءة الامتزاز المحسوبة من الممتزات تعتمد إلى حد كبير على تركيز الصبغة الأولية، ووقت الاتصال ودرجة الحرارة. تبين ان نتائج الامتزاز التي تم الحصول عليها توصف جيدا باستخدام نماذج الرتبة الزائفة الثانية الحركية و إيزوثيرم لانجمير. وصلت قدرة الامتزاز أحادي الطبقة لـ RC-C و RC-L إلى 100 و 40 ملجم/جم نحو صبغة الـ MB ، على التوالي. واستنادا إلى هذه النتائج، يمكن أن تعتبر مواد الهيدرومادية المحضرة من الكربنة المائية للسليلوز واللجنين المستمد من قش الارز كمواد امتزاز منخفضة التكلفة وذات قيمة لإزالة الملوثات الاصبغ من مياه الصرف الصناعي.