Adsorption of cationic dye (MB) and anionic dye (AG 25) by physically and chemically activated carbons developed from rice husk

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Abstract

Dye removal from waste water via adsorption by activated carbons (ACs) developed from agricultural wastes represents an ideal alternative to other expensive treatment options. Physical and chemical ACs were prepared from rice husks. The textural properties of the ACs were characterized by Brunauer-Emmett-Teller- N_2 adsorption and scanning electron microscopy. The chemistry of the carbon surface was investigated by Fourier transform infrared spectroscopy, base and acid neutralization capacities, pH of the active carbon slurry, and pH_{pzc} . The adsorption capacities of the ACs for the basic dye (methylene blue) and acid dye (acid green 25) were determined using parameters such as contact time, pH, and temperature. NaOH-ACs showed the highest surface area and total pore volume, whereas steam- ACs showed the lowest ones.

Key words: activated carbon, rice husk, dyes, adsorption

1. Introduction

Activated carbons (ACs) are well known for their expanded surface areas and large total pore volumes [1]. This is why they show large adsorption capacities from both gaseous and liquid phases [2]. ACs are widely used in decolorization, deodorization, filtration and purification [3,4]. ACs have also been used as catalyst support and battery capacitors [5]. Recently, ACs have been used in gas storage for natural gas vehicles [6] and more recently in hydrogen storage [7]. The conventional methods for synthesis of ACs are physical and chemical activation of carbon rich precursors. By physical activation with CO_2 , steam, or air, it is possible to obtain ACs with surface area S_{BET} values up to about $1800 \text{ m}^2 \text{ g}^{-1}$ and pore volumes up to 1.3 mL g^{-1} [8]. Chemical activation with $ZnCl_2$, H_3PO_4 , and $NaOH/KOH$ yields ACs with S_{BET} values approaching $3000 \text{ m}^2 \text{ g}^{-1}$ and with total pore volumes higher than 2.5 mL g^{-1} [9].

Agricultural byproducts are used as precursors for the preparation of ACs in order to reduce the expenses of their production. Rice husk (RH) is a large scale agricultural waste that has practically no commercial application.

Dyes are extensively used, especially in several industries. The discharge of effluents from these industries is a major source of color in water resources [10]. Dyes are generally undegradable and are harmful to flora and fauna; some of these dyes have been reported to be carcinogenic and mutagenic [11]. Colored water inhibits solar radiation into the water surface, leading to a significant reduction in photosynthesis. Treatments of colored water discharged from dyeing processes, including flocculation, precipitation, photochemical oxidation, ozonation, and adsorption have been investigated [12-15]. Because of the significant amount of organics in dye molecules, most of the conventional treatment methods fail to recover the dyes from the effluents [16]. However, adsorption has been recognized as one of the best methods for the removal of dyes from water and wastewater [17,18]. Among many adsorbents, AC is a prominent adsorbent for the removal of dyes from colored effluents [19].

This article reports the preparation of low-cost ACs from RH using phosphoric acid, sodium

Table 1. Elemental composition of ash component of RH by inductively coupled plasma atomic emission spectroscopy (ICP-OES)

Component	wt%	Component	wt%	Component	wt%
K ₂ O	2.15	Al ₂ O ₃	0.12	CuO	0.02
Na ₂ O	2.32	ZnO	0.02	Cr ₂ O ₃	0.01
CaO	1.11	Mn ₂ O ₃	0.07	SiO ₂	95.81
MgO	0.26	Fe ₂ O ₃	0.11		

hydroxide, and steam activation. This paper is occupied with the determination of textural properties and the chemistry of the surface of the carbons and their roles in the removal of cationic dye (methylene blue, MB) and anionic dye (acid green 25, AG). The kinetics and equilibrium adsorption of these hazardous materials from their aqueous solution is the main object of the present work.

Nomenclature:

RH	Rice husk
ACs	Activated carbons
K	Absolute temperature
SLC	Steam-activated carbon from HF-leached RH
PLC	H ₃ PO ₄ -activated carbon from HF-leached RH
NC	NaOH-activated carbon from unleached RH
NLC	NaOH-activated carbon from HF-leached RH
MB	Methylene blue dye
AG	Acid green 25 dye
C ₀	The initial concentration (mg/L)
C _e	The equilibrium concentration (mg/L)
C _t	The solute concentration at time t (mg/L)
q _e	The equilibrium amount adsorbed (mg/g)
q _t	The amount adsorbed at time t (mg/g)
K ₁	Pseudo first order rate constant (h ⁻¹)
K ₂	Pseudo second order rate constant (mg/g min)
K _d	Rate constant of intraparticle diffusion (mg/g h ^{0.5})
T	Time (h)
S _{BET}	Surface area (m ² /g) from the BET method
S ^α	Surface area (m ² /g) from the α method
V _T	Total pore volume of the sorbent (mL/g)
$\bar{r}$	Mean pore radius (nm)
S _m ^α	Surface area of micropores (m ² /g)
S _n ^α	Surface area of non micropores (m ² /g)
V _m ^α	The volume of micropores
V _n ^α	The volume of non-micropores
b	Langmuir adsorption constant (L/mg)
K _d	Distribution coefficient (L/g)
ΔG ⁰	Free energy change in adsorption
ΔH ⁰	Standard enthalpy change
ΔS ⁰	Standard entropy change

2. Experimental

2.1. Materials

RH from the rice mill of El-Mansoura City (Egypt) was used

as raw material. RH was first washed with distilled water to remove dust and other adhering impurities, and then dried at 383 K for 48 h. Finally, the dried product was ground and sieved to different particle sizes. This study focused on the size fraction 0.3-0.5 mm. The RH used contained about 22 wt% lignin, 42 wt% cellulose and 20 wt% of hemicelluloses. The moisture content of as received RH was about 5.2%. Ash content was 18.6 wt%. The elemental composition of the ash was previously determined in our laboratory as shown in Table 1.

Two carbonization products C and LC were prepared; the former was obtained by the carbonization of dried RH, whereas the latter was obtained by carbonization of dried RH pre-leached with hydrofluoric acid, HF. Leaching was done at room temperature using 25% analytical grade HF. The acid solution volume to mass ratio was 2.5:1. The slurry was stirred for 30 min, and then the solid was separated and washed with distilled water until neutralization and then oven dried at 383 K for 24 h. Dried RH and dried HF-leached RH were calcined separately in absence of air in batch process using a stainless steel reactor at a rate of 10 Kmin⁻¹ from room temperature up to 773 K, followed by soaking at this final temperature for 3 h. An A-K-type thermocouple and a digital temperature controller were used to set and control the sample temperature.

Steam AC (SLC) was obtained by gasifying a portion of LC carbon with a mixture of nitrogen and steam at 1173 K to burn off = 29 wt%. After this, sample LC pre-carbonized at 773 K was contained in a stainless steel tube (40 cm length and 4 cm internal diameter) positioned vertically in a tubular muffle furnace. The entering gas mixture was passed through the "LC" bed, which was supported on a fine chromel screen. The flow rate was sufficient to keep the sample "Jiggling." Details on steam activation have been reported elsewhere [20].

An activated sample (PLC) was prepared by soaking LC in 50 wt% analytical grade phosphoric acid at room temperature for 3 days. The acid solution volume to the solid mass was 3:1. The slurry was occasionally stirred; the solid was then separated and heated gradually in absence of air in a stainless steel reactor at a rate of heating = 10 Kmin⁻¹ up to 773 K; it was then maintained at this temperature for 3 h. After cooling, the carbonized mass was washed thoroughly with distilled water until the washing attained a PH value of 6.0, at which point the washed material was dried. Details of the method are reported elsewhere [21].

Two additional ACs, NC and NLC, were prepared by soaking the carbonization products C and LC, respectively, in the presence of substantial weight of analytical grade NaOH, dissolved in the least amount of water for 48 h (carbon: solid NaOH = 1:3 w/w). The paste was then dried. Thereafter, the dried product was calcined at 1123 K at a rate of 10 Kmin⁻¹, and by maintaining the maximum temperature for 2 h. After cooling to room

Fig. 1. Adsorption-desorption isotherms of N_2 at 77 K by (a) SLC, (b) PLC, (c) NC, (d) NLC.

temperature, the activated product was ground and sieved, and the fraction of size 0.3–0.5 mm was washed with doubly distilled water and dried at 383 K for use in adsorption and analytical investigations. Details of the apparatus and the experimental methods are reported elsewhere [22].

2.2 Techniques

2.2.1. Low temperature adsorption of nitrogen

The textural properties (surface area and porosity) of the ACs were investigated using a volumetric apparatus of conventional type. The adsorbent was degassed at 473 K under reduced pressure of 10^{-5} torr for 8 h prior to adsorption measurements. The adsorption of N_2 at 77 K was followed until near saturation, i.e., until a relative pressure = $P/P_0 > 0.95 < 1$.

2.2.2. Scanning electron microscopy

Scanning electron microscopy (SEM): micrographs of SLC, PLC, and NLC were obtained using a SEM (JEOL, model 6400). Prior to the analysis, the samples were dried at 110°C for 4 h. A thin layer of gold was coated on the samples for charge dissipation.

2.2.3. Surface functional group determination

Fourier transform infrared (FTIR) spectroscopy: FTIR spectra were recorded between 4000 and 400 cm^{-1} using a Mattson 5000 FTIR spectrometer. Discs were prepared by first mixing 1 mg dried carbon sample with 500 mg of KBr (Merck for spectroscopy) in an agate mortar and then pressing the resulting mixture at 5 tonne/ cm^2 for 5 min and 10 tonne/ cm^2 for 5 min under vacuum.

2.2.4. Determination of pH of the slurry

Zero point five gram of carbon sample was shaken with 25 mL (CO_2 free distilled water); then, the pH of the filtrate was measured.

2.2.5. Determination of PH_{pzc}

Initially, 50 mL of NaCl was placed in several closed Erlenmeyer flasks. The PH within each flask was adjusted to a value between 2–12 by adding either HCl (0.1 M) or NaOH (0.1 M). Then, 0.15 g was added to each flask, the flasks were agitated for 48 h, and the final PH was then measured. The PH_{pzc} is defined as the point where the curve PH_{final} vs. $PH_{initial}$ crosses the line $pH_{final} = pH_{initial}$ [23].

2.2.6. Selective neutralization analysis

Acid and basic functional groups on the AC surface were determined by the method proposed by Boehm [24]. Solutions of $NaHCO_3$ (0.05 N), Na_2CO_3 (0.05 N), NaOH (0.05 N and 0.15 N) and HCl (0.05 N) were prepared using CO_2 -free distilled water. A 25 mL volume of these solutions was added to vials containing 0.25 g of AC. These samples were shaken until equilibrium. When equilibrium was reached the carbon was separated from the solution by filtration. The excess of base or acid was determined by back titration using (HCl 0.05 and 0.15 N) and NaOH (0.05 N) solutions [25].

3. Results and Discussion

3.1. Textural properties

The nitrogen adsorption-desorption isotherms at 77 K of SLC, PLC, NC, and NLC are shown in Fig. 1. The isotherms show the characteristics of type I and type II of the Brunauer, Deming, Deming and Teller (BDDT) classification [26]. The isotherms exhibit a steep initial part and a well developed knee bend at $P/P_0 = 0.1$ – 0.2 . The narrow closed hysteresis loop exhibited by the investigated sorbent may be taken as evidence of capillary condensation in the micropores [27]. The conventional

Fig. 2. The α plots of nitrogen adsorption at 77 K by (a) SLC, (b) PLC, (c) NC, (d) NLC.

Table 2. Textural properties of the investigated carbons as determined from nitrogen adsorption at 77 K

Carbon sample	S_{BET} (m^2/g)	V_{T} (mL/g)	$\bar{r}$ (nm)	S^{a} (m^2/g)	S_{m}^{a} (m^2/g)	S_{n}^{a} (m^2/g)	V_{m}^{a} (mL/g)	V_{n}^{a} (mL/g)
SLC	770	0.679	1.76	830	701.5	128.5	0.3081	0.3709
PLC	1172	0.850	1.45	1213	827	386	0.41	0.44
NC	1958	1.123	1.25	2050	1451	599	0.570	0.550
NLC	2254	1.380	1.22	2275	1808	467	0.690	0.690

SLC: steam-activated carbon from HF-leached RH, PLC: H₃PO₄-activated carbon from HF-leached RH, NC: NaOH-activated carbon from unleached RH, NLC: NaOH-activated carbon from HF-leached RH, S_{BET} : surface area (m^2/g) from the BET method, V_{T} : total pore volume of the sorbent (mL/g), $\bar{r}$: mean pore radius (nm), S^{a} : surface area (m^2/g) from the α method, S_{m}^{a} : surface area of micropores (m^2/g), S_{n}^{a} : surface area of non micropores (m^2/g), V_{m}^{a} : the volume of micropores, V_{n}^{a} : the volume of non micropores.

Brunauer-Emmett-Teller (BET) equation [28] was applied to determine the BET surface area S_{BET} (m^2/g) of each carbon. The total pore volume V_{T} (mL/g) of each carbon was also calculated from the volume of nitrogen adsorbed near saturation, i.e. at $P/P_0 = 0.95$. Another textural parameter, i.e., the mean pore radius $\bar{r}$ (nm), was calculated from the relationship:

$$\bar{r} = \frac{2V_{\text{T}} \times 10^3}{S_{\text{BET}}} \quad (1)$$

The α method of using [29] was also used to determine the total surface area S^{a} (m^2/g) of each carbon, taking the standard data for the adsorption of N₂ at 77 K on non-porous carbon as

a reference [30]. The α method allows the determination of the volumes of micropores and of non micropores, V_{m}^{a} and V_{n}^{a} , respectively, and also the surface located in these types of pores, i.e. S_{m}^{a} and S_{n}^{a} .

Fig. 2 shows the α plot of nitrogen adsorbed at 77 K.

Inspection of Table 2 reveals that (i) The S_{BET} values are comparable to their corresponding values determined from the α -method with a difference not exceeding 7.7%. (ii) The mean pore radius of the sorbents investigated is less than 1.8 nm. Thus suggests the existence of both micro and non micropores. Evidently, the values of V_{m}^{a} and V_{n}^{a} are comparable, particularly for chemically ACs. The SLC showed the lowest surface area, but showed the

Fig. 3. Scanning electron microscopy for activated carbons: (a) SLC, (b) PLC, (c) NLC.

Fig. 4. Fourier transform infrared spectra of the investigated activated carbons.

largest mean pore radius. This might be ascribed to the slight pore widening brought about by the erosion of the pore walls during gasification with steam to a burn off = 29%. More pronounced effects on the porosity are perhaps expected upon gasification with oxidizing gases to higher burn off. (iii) The surface located in the micropores was higher than that located in non micropores; this was found to be true for all the carbons investigated.

SEM: the SEM images in Fig. 3 show that ACs have an irregular shape and size with no definite morphology; this situation may be ascribed to the preliminary treatments, which include crushing, impregnation, carbonization, and activation at different temperatures. The SEM micrographs obtained at a magnification of 350x clearly indicate the porous structure of the ACs.

3.2. Chemistry of the carbon surfaces

The chemistry of the carbon surface is attributed to the ex-

istence of carbon-oxygen groups of acidic or basic character depending on the carbonization temperature, the condition and methods of carbonization, and the activation. The infrared spectra in Fig. 4 give information on the chemical structure of the ACs. All the carbon samples show a wide band at about 3250-3425 cm^{-1} due to the O-H stretching mode of the hexagonal group and adsorbed water. The sample shows absorption bands due to aliphatic C-H near 2800-2950 cm^{-1} [31]. Bands around 2322-2390 cm^{-1} may be assigned to C=O stretching in the ketone group [32]. The very small peak near 1700 cm^{-1} is assigned to C=O stretching vibrations of ketones, aldehydes, lactones, or carboxyl groups. The weak intensity of this peak indicates that the prepared ACs contain small amounts of carboxyl group. The bands near 1600 are due to C=C stretching vibration in the aromatic ring [33]. A broad band between 1250 and 1100 cm^{-1} is observed; this band may be assigned to C-O stretching in acids, alcohols, phenols, and esters. The appearance of bands at 900-1300 cm^{-1} could be also due to phosphorous species resulting from phosphoric acid activation [34].

Although this analysis can't be considered as quantitative, it can give information on the carbon-oxygen groups on the surface of AC prepared in the present work.

The pH of the aqueous slurry of the carbon material provides convenient indicators of the surface groups on the carbons. The PH values of the slurries of SLC, PLC, NC, and NLC were found to be 6.06, 5.82, 7.43, and 6.99 respectively. This may be taken as evidence that acid functional groups slightly predominate on the surface of SLC and PLC, whereas the base functional groups very slightly predominate on the surface of NC. On the other hand, the level of acid functional groups is equivalent to that of the basic functional groups on the surface of NLC. The

Table 3. Functional groups (meq/g), surface pH, and PH_{PZC} of the investigated carbons

Carbon	Carboxylic	Lactonic	Phenolic	Carbonyl	Total acidic	Total basic	Surface PH	PH_{PZC}
SLC	0.33	0.07	0.36	1.15	1.91	1.10	6.06	7.39
PLC	0.20	0.46	0.86	0.16	1.68	0.35	5.82	6.71
NC	0.05	0.21	0.10	0.07	0.43	0.76	7.43	6.96
NLC	0.07	0.24	0.07	0.07	0.45	0.31	6.99	6.56

HP_{PZC} : point of zero charge.

Fig. 5. The structure of methylene blue and acid green.

chemistry of the surface of the ACs is better determined from their base neutralization capacities (meq/g). NaHCO_3 neutralizes carboxylic groups, whereas those groups that are neutralized by Na_2CO_3 but not by NaHCO_3 were believed to be lactones. The weakly acidic groups neutralized by NaOH but not by Na_2CO_3 were postulated to be phenols. Neutralization with 0.15 N NaOH was assumed to determine all the acidic functional groups on the surface, including carbonyl groups.

The functional groups on the surfaces of the ACs are listed in Table 3, expressed as (meq/g).

3.3. Adsorption of MB and AG25 dyes from their aqueous solutions

Fig. 5 shows the chemical structure of MB ($\text{C}_{16}\text{H}_{18}\text{ClN}_3\text{S}_2\cdot 2\text{H}_2\text{O}$) and of AG ($\text{C}_{28}\text{H}_{20}\text{N}_2\text{Na}_2\text{O}_8\text{S}_2$). MB and AG were obtained from Sigma-Aldrich. The molecular wt of MB is 319.9 and its λ_{max} is 663 nm; the molecular wt of AG is 622.59 and its λ_{max} is 642 nm.

3.3.1. Effect of dye solution pH

Adsorption from solution depends on both the pH, particularly when the solute is charged, and also on the contact time between the solid adsorbent and the adsorption solution. Preliminary experiments have been carried out to determine the effect of pH on the amount of dye adsorbed at 298 K when a contact time of 48 h is allowed in order to ensure the attainment of equilibrium conditions.

A series of five 250 mL conical flasks filled with 200 mL of the

dye solution of initial concentration 400 mg/L were used. The initial pH values of the adsorption solution were adjusted at 2, 4, 6, 8, and 10 using HCl , and NaOH . Then, 0.2 g of the carbon sample was added to each flask. The mixtures were agitated at a speed of 100 rpm using a thermostatted water bath shaker (Kottermann Labortechnik). The procedure was repeated for the other carbons. After equilibrium the flasks were removed from the shaker and the equilibrium concentrations were determined using the equation:

$$q_e = \frac{(C_0 - C_e)V}{M} \quad (2)$$

where C_0 and C_e are the initial and equilibrium concentrations (mg/L), respectively, V is the volume of adsorption solution (L), and M is the mass of carbon (g). Fig. 6 depicts the change of q_e (MB) and (AG) with the initial pH of the solution.

Fig. 6 shows that q_e is pH dependant. However, the trend is not the same for the two dyes. Thus in the case of MB adsorption, q_e increased with the increase of initial pH, whereas for AG q_e decreased with the increase of initial pH. AC may be regarded as being composed of amphoteric solids because of the existence of both negatively and positively charged sites on the surface when it is placed in aqueous solution; which type of site dominates depends on the solution pH. When the surface of the carbon is negatively charged ($\text{pH} > \text{pH}_{\text{pzc}}$), it can attract cationic dye molecules such as MB from solution. This explains the increase of q_e of MB with the increase of dye solution pH from 2 to 10. The decrease of q_e of AG25 with the increase of solution pH from 2 to 10 may be ascribed to the high concentration of negatively charged-OH ions and the repulsion between the negatively charged adsorbent and the anionic dye molecules. Also, at high pH values no more exchangeable anions exist on the surface of the adsorbent [35,36], considering the value of q_e at some intermediate initial pH values, i.e., at an initial dye solution of pH 6-7. Evidently, q_e values are between 70 and 80% of the maximum q_e . However, it is still preferable to remove dyes from their aqueous solution by their adsorption at neutral pH, using ACs. This is simple, convenient, and cost-saving.

3.3.2. Batch equilibrium and kinetic studies

Adsorption experiments were carried out by adding a fixed amount of adsorbent (0.25 g) to a series of 250 mL conical flasks filled with 200 mL diluted solutions of 50-500 mg/L. The flasks

Fig. 6. Representative illustrations for the effect of pH on adsorption of methylene blue and acid green 25, respectively.

Fig. 7. Kinetic adsorption curves of methylene blue, (a) by SLC, (b) by PLC and of acid green, (c) by NC and (d) by NLC.

were then sealed and placed in water bath shaker and were shaken at 100 rpm for the required adsorption time at 298, 308, and 318 K and neutral pH. The flasks were then removed from the shaker and the equilibrium concentrations were measured. The amount of dye adsorbed at equilibrium q_e (mg/g) by the carbon sample was calculated from Eq. (2).

The procedure of kinetic measurements at 298 K was identical to the equilibrium procedures, except for the contact time. Samples from the adsorption solution were taken at different time intervals and the concentrations of the dye in the sample were similarly measured.

All the absorption measurements were carried out using a Unicam 5625 UV/Vis spectrophotometer.

The amount of dye adsorbed at time t , q_t (mg/g) was calculated using:

$$q_t = \frac{(C_0 - C_t)V}{M} \quad (3)$$

where C_0 and C_t (mg/L) are the initial concentration and the concentration of the dye adsorption solution at time t ; V and M have been previously defined.

Representative adsorption curves of MB and AG are shown in Fig. 7.

The kinetic models, used in order to investigate the mechanism of adsorption, were the pseudo first order, the pseudo-second order and the intraparticle diffusion models. The differential form of the pseudo-first order model of adsorption can be expressed as [37]:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \quad (4)$$

where q_e and q_t (mg/gm) are the amounts of dye adsorbed at

equilibrium and at time t , respectively, and k_1 is the equilibrium constant (min^{-1}).

Integration is performed for Eq. (4) and by applying the initial conditions $q_t = 0$ at $t = 0$

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303t} \quad (5)$$

The differential form of the pseudo-second order reaction equation may be written as [38]

$$dq_t/dt = k_2(q_e - q_t)^2 \quad (6)$$

where k_2 is the pseudo-second rate constant (mg/g min), as shown in Table 4. After integration, considering the boundary conditions, the linearized form of this model is given as

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (7)$$

The intraparticle diffusion model was first proposed by Weber and Morris [39], who concluded that the uptake was proportional to the square root of the contact time during the course of adsorption, i.e.,

$$q_t = K_d t^{0.5} + C \quad (8)$$

where K_d is the rate constant of the intraparticle transport (mg/g $\text{h}^{0.5}$). The value of K_d is obtained from the slope of the straight line where C is the intercept.

Evidently the application of the pseudo-first order model to the kinetic adsorption curve of MB and AG gave q_e values that were significantly lower than the corresponding experimental ones. Also, the values of the correlation coefficient R^2 were rela-

Fig. 8. Representative Pseudo-second-order kinetic plots for adsorption of methylene blue, (a) by SLC, (b) by PLC and of acid green, (c) by NC and (d) by NLC.

Fig. 9. Representative intraparticle diffusion plots for the adsorption of methylene blue, (a) by SLC, (b) by PLC and of acid green, (c) by NC and (d) by NLC.

tively low compared with those obtained when the pseudo second order model was considered, as shown in Fig. 8.

Intraparticle diffusion model: according to the intraparticle diffusion model, multilinearity may be obtained when q_t is plotted versus $t^{0.5}$, as shown in Fig. 9. This indicates that more than

one step occurred. Evidently, two steps could be present in the current investigation. The first sharper portion stands for the external surface adsorption. The second portion was the gradual adsorption, referring to the intraparticle diffusion controlled adsorption process. If the lines don't pass through the origin, the

Table 4. Kinetic parameters for adsorption of methylene blue and acid green 25

Dye	Sample	Pseudo- second order			Intraparticle diffusion		
		K ₂ (mg/gm min)	q _e (mg/gm)	R ²	K _d (mg/gh ^{0.5})	C (mg/gm)	R ²
MB	SLC	0.025	231.48	0.998	4.495	204.28	0.978
	PLC	0.0359	370.370	0.999	5.067	334.57	0.997
	NC	0.00281	473.93	0.998	14.748	392.984	0.9308
	NLC	0.00582	606.06	0.999	1.994	588.25	0.998
AG 25	SLC	0.043	84.03	0.999	1.0447	77.919	0.989
	PLC	0.0359	168.06	0.999	3.029	158.432	0.962
	NC	0.00128	256.41	0.997	18.257	139.432	0.991
	NLC	0.00142	304.870	0.997	29.759	131.937	0.999

K₂: pseudo second order rate constant, q_e: the equilibrium amount adsorbed, K_d: rate constant of intraparticle diffusion, C: constant of intraparticle diffusion equation indicating thickness of boundary layer, R²: regression coefficient.

Table 5. Langmuir isotherm constants for adsorption of MB and AG 25 onto activated carbons

Dye	Sample	25			35			45		
		q _{max} (mg/g)	b (L/mg)	R ²	q _{max} (mg/g)	b (L/mg)	R ²	q _{max} (mg/g)	b (L/mg)	R ²
MB	SLC	226.24	0.092	0.995	238.095	0.128	0.999	256.4	0.156	0.997
	PLC	377.35	0.240	0.995	389.105	0.376	0.995	408.163	0.40	0.999
	NC	492.610	0.086	0.998	537.63	0.143	0.997	571.428	0.162	0.994
	NLC	740.740	0.066	0.998	751.87	0.1201	0.998	793.56	0.225	0.999
AG25	SLC	82.78	0.040	0.996	93.457	0.0502	0.998	103.199	0.073	0.999
	PLC	164.47	0.132	0.997	178.587	0.171	0.997	190.476	0.1973	0.998
	NC	224.719	0.194	0.999	278.551	0.237	0.996	304.878	0.300	0.998
	NLC	278.551	0.156	0.996	342.465	0.202	0.995	367.64	0.221	0.999

q_m: maximum adsorption capacity, b: Langmuir constant related to the heat of adsorption.

intraparticle diffusion is not the only rate limiting step and this indicates the effect of film diffusion (boundary layer diffusion) on the adsorption of dyes. A high value of C indicates the increase of the thickness of the boundary layer and consequently its pronounced effect, as can be seen in Table 4.

3.3.3. Equilibrium adsorption isotherm

The isotherm data were obtained by plotting the amount of dye adsorbed on the solid (mg/g) against the remaining concentration of dye in the solution (mg/L). The Langmuir adsorption isotherm [40] assumes that adsorption occurs at specific homogeneous sites within the adsorbent and makes the estimation of adsorption capacities under various condition a simple task.

The model can be written as

$$\frac{1}{q_e} = \frac{1}{bq_m} + \frac{1}{c_s} \quad (9)$$

where q_e is the equilibrium dye concentration on the adsorbent (mg g⁻¹), C_e is the equilibrium dye concentration in the solution

(mg dm⁻³), and q_m is the maximum adsorption capacity (mg g⁻¹). The Langmuir adsorption model is based on the formation of only a monolayer. Based on this, q_m is frequently considered to be the monolayer capacity and can be designated q_{mon} (mg g⁻¹); b (L mg⁻¹) is known as the Langmuir constant and is related to the heat of adsorption. The linear form of the Langmuir isotherm equation can be represented as the following:

$$\frac{c_e}{q_e} = \frac{1}{bq_{mon}} + \frac{1}{q_{mon}} C_e \quad (10)$$

The plots of C_e/q_e versus C_e for the adsorption of methylene blue onto AC give a straight line of slope = (1/q_{mon}) and an intercept = (1/bq_{mon}).

The Langmuir isotherm parameters for adsorption of MB and AG 25 are listed in Table 5.

Representative equilibrium adsorption isotherms of MB and AG measured at 298, 308, and 318 K on the investigated ACs are shown in Fig. 10 and their linear plots are shown in Fig. 11; these linear plots indicate that the adsorption of both dyes by

Fig. 10. Representative isotherms for the adsorption of methylene blue (MB) on activated carbon at diff temp of MB, (a) by SLC, (b) by PLC and of acid green, (c) by NC and (d) by NLC.

Fig. 11. Linearized form of Langmuir equation for methylene blue for activated carbons (ACs) at 298 K; graphs also depict linearized form of Langmuir equation for AG for ACs at 308 (a) SLC, (b) PLC, (c) NC, (d) NLC.

the investigated adsorbents could be represented adequately by the Langmuir model:

3.3.4. Effect of temperature

Fig. 10 shows that adsorption of MB and AG increases with the increase of adsorption temperature from 298 to 318 K. Evidently, the increase of adsorption with temperature at low equilibrium concentration was less pronounced. The increase of adsorption with increase of temperature indicates that the adsorption of MB and AG by the investigated ACs is an endothermic process. This isn't surprising to the authors because the dye molecules are relatively bulky and the pore diameters of the adsorbent are of small $\bar{r}$. It has been previously mentioned in this

paper that the pore radii of the investigated carbons lie between 1.76 and 1.22 nm. The rise of adsorption temperature probably enhanced the diffusion of dye molecules to the adsorption sites at the surfaces inside the pores [41].

3.3.5. Thermodynamic parameters

The change in standard free energy (ΔG°) of adsorption was calculated from Eq. (11). In this equation, R is the gas constant, K_d is the equilibrium constant, and T is the temperature in K. The K_d value is calculated from Eq. (12).

$$\Delta G^\circ = -RT \ln K_d \quad (11)$$

Table 6. Thermodynamic parameters for adsorption of MB and AG on activated carbons

Dye:	Sample		25	35	45	ΔS° (J/mole K)	ΔH° (KJ/mole)
MB	SLC	ΔG° (KJ/mole)	-0.120	-0.420	-0.934	40.09	11.864
	PLC		-1.221	-1.505	-1.923	35.25	9.315
	NC		-0.289	-0.857	-1.30	50.68	14.79
	NLC		-1.06	-1.28	-1.727	32.67	8.708
AG25	SLC	ΔG° (KJ/mole)	-0.693	-1.74	-2.919	111.98	32.72
	PLC		-2.207	-3.687	-5.155	9.54	20.155
	NC		-0.346	-1.638	-2.511	56.78	15.702
	NLC		-0.458	-1.828	-2.53	103.34	30.25

ΔG° : free energy change in adsorption, ΔH° : standard enthalpy change, ΔS° : standard entropy change.

$$K_d = \frac{q_e}{c_e} \quad (12) [41]$$

where q_e and C_e are the equilibrium concentrations of dye ion on adsorbent (mg/gm) and in solution (mg/L), respectively. Standard enthalpy (ΔH°) and entropy (ΔS°) of adsorption could be estimated from the Van't Hoff equation:

$$\ln K_d = \frac{-\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \quad (13)$$

The slope and intercept of the Van't Hoff plot are equal to $(\frac{-\Delta H^\circ}{R})$ and $(\frac{\Delta S^\circ}{R})$, respectively.

The values of ΔG° , ΔH° , and ΔS° are shown in Table 6.

The positive value for enthalpy change indicates that the sorption is endothermic in nature. This is also observed from the increase of the sorption capacity with temperature. The negative values of ΔG° indicate the spontaneous nature of the adsorption process; the value of ΔG° is $> 0.12 < 5.16$ KJ/mole, i.e., it is a value that is consistent with the electrostatic interaction between the adsorption sites and the adsorbing ions (physical adsorption).

The most important mechanism for adsorption of dyes is mainly between oxygen free Lewis basic sites, which are related to delocalized π electrons on the basal planes of the AC, and the free electrons of the dye molecule resulting from several aromatic rings and double bonds.

4. Conclusions

ACs of expanded surface area, well developed micropore structure, and large total pore volume were prepared from RH, a residue of agricultural activity. The textural properties of RH-based ACs depend on the methods and conditions of carbonization and activation, and on the activating agent used. NaOH-ACs exhibited the highest adsorption capacities for MB and AG; these carbons showed the highest surface areas and also the highest pore volumes. The pore size of the sorbent and the bulkiness of the dye molecule determined the dye uptake. Dye adsorption was found to be pH dependant whether the dye is of basic or acid type. The adsorption of MB and AG followed

pseudo-second order kinetics and the adsorption was controlled by intraparticle diffusion and the boundary layer effect. The adsorption was found to be spontaneous, endothermic, and of a physical nature.

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