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An enhanced counter-current approach towards activated carbon from waste tissue with zero liquid discharge



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HIGHLIGHTS

G R A P H I C A L A B S T R A C T

- Micro-porous AC was synthesized from toilet paper and KOH as the activating agent.
- An eco-friendly synthesis process was presented with 99% reduction in usage.
- Using waste tissue in a zero discharge process will comply with environmental regulation.
- A mechanistic reaction for regeneration of KOH from metallic potassium was suggested.

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ABSTRACT

We studied the applicability of advanced counter-current procedure to convert waste tissue to a highly porous activated carbon (AC) in a zero liquid discharge (ZLD) process with a minimum consumption of the KOH activating agent. AC with a maximum surface area of 1820 m²/g was synthesized by a twostep process, including carbonization at 500 °C for 1 h and KOH activation (ratio: 1–3 w/w) at 750 °C for 1 h. The water in the washing step containing residual KOH was recycled to the carbonization step for successive cycles. The recycling process continued to reach a steady-state condition. Various techniques including XRD, FTIR, TGA, BET and SEM were utilized to compare the characteristics of the AC synthesized during 10 consecutive liquid recycling steps. The results showed that KOH usage was decreased by 99% and the water requisition per cycle was limited to the make-up water to compensate for the water loss due to evaporation. The product characteristics were found entirely similar to the product obtained with fresh water and KOH. The results of this research can be considered as a promising approach for the synthesis of high product quality sorbent for the eco-environmental applications.

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1. Introduction

Activated carbons (ACs) are broadly used as adsorbents for a wide variety of applications such as removing environmental pollutants from air and water streams [1-3]. With the intensification of environmental pollution, the need for AC is increasing [4]. A

wide range of carbonaceous raw materials have been examined for the preparation of AC [1,5–9]. Coal, wood and coconut shells have been used to produce commercial activated carbons [2]. In recent years, various waste materials for the production of AC have been investigated due to their economical appeal and availability [10–15].

To prepare ACs, carbon based precursors need to be activated in some fashion. Activation of precursors can be carried out by various physical, chemical or combined methods. The advantage of



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chemical activation is low energy requirements, as chemical activation is usually conducted at lower temperatures, while providing higher yields and higher porosity [2,4,16]. Potassium hydroxide (KOH) is often used as the activating agent for the synthesis of AC. It has been reported that ACs with a very large surface area and large micro-pore volume can be synthesized by KOH activation [8,17–20].

One of the greatest disadvantages for large scale production of AC is the demand for a high volume of washing liquid. The resulting liquid discharge used in the filtering and washing steps must be treated before discharge. For example, to prepare 1 g of AC, we found that approximately 5–8 liters of water were required for washing the product. The liquid discharge from the washing process, with a high or low pH depending on the type of the activating agent, has to be treated [8,17–20]. To the best of our knowledge, there are no published research reports on the mitigation of the activated carbon synthesis process to minimize the environmental impact.

There are many studies on the production of low cost ACs from various lignocellulosic wastes. Some of these studies are presented in Table 1. Valizadeh et al. [21] prepared porous carbon by a onestep chemical activation process (KOH and K₂CO₃) from the cones of Iranian pine trees with different impregnation ratios at 700 °C. The highest surface area using KOH activation was $1164 \text{ m}^2/\text{g}$ with a char/KOH ratio of 1:0.75. Ello et al. [22] used African palm shells to produce micro-porous AC by KOH activation. The AC was synthesized with a weight ratio of KOH to char in the range from 1:1 to 5:1 by heating the mixture at 850 °C for 1 h. The sample with a weight ratio of 5:1 had the highest surface area of $1890 \text{ m}^2/\text{g}$. Nahil and Williams [2] prepared AC using cotton stalks and phosphoric acid as the activating agent at different H₃PO₄ to cotton stalk impregnation ratios (0.3-3 w/w) and various pyrolysis temperatures ranging from 500 to 800 °C. The highest surface area obtained was 1720 m²/g with a H₃PO₄:cotton stalk ratio of 1.5:1 at 500 °C. In other work [23], AC was synthesized from cotton stalks by a one-step process using both chemical activation by H₃PO₄ or KOH, and thermal activation by steam pyrolysis. The porosity increase was in the order KOH > H₃PO₄ > steam. The highest KOH to cotton stalk ratio of 3:1 resulted in a product with a surface area of 1307 m^2/g and high micro-porosity.

Although high volume production of toilet paper, a hygienic product with almost pure cellulose, is annually being produced in the world; to the best of our knowledge, no attempt has been made in in AC synthesis. Therefore, in the present study, this accessible cellulosic material, after being carbonized, was used as a precursor for the synthesis of AC with zero liquid discharge along

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S	vnthesis	of	AC	from	various	lignocellulosic	materials.
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Source	Method of activation	Surface area (m²/g)	Authors
Macadamia nut shells	Physical/CO ₂ (1100 °C)	602	Poinern et al. [45]
Rice husk	Chemical/ZnCl ₂ (700 °C)	811	Kalderis et al. [46]
Grape stalk	Chemical/ZnCl ₂ (700 °C)	1760	Ozdemir et al. [47]
Cyperus alternifolius	Chemical/H ₃ PO ₄ (450 °C)	1066	Sun et al. [48]
Cotton stalks	Chemical/H ₃ PO ₄ (900 °C)	1720	Nahil & Williams
Cotton stalks	Chemical/H ₃ PO ₄ /KOH (700 °C)	1307	El-Hendawy [23]
Eucalyptus camaldulensis	Chemical/H ₃ PO ₄ /KOH (900 °C)	2595	Heidari et al. [5]
African palm shells	Chemical/KOH (850 °C)	1890	Ello et al. [22]
Toilet paper	Chemical/KOH (750 °C)	1820	Present study

with an outstanding reduction of the activating agent usage. The alkaline effluent from the washing stage was collected and reused for the next consecutive activation step.

2. Materials and methods

Toilet paper (Merfin, USA) purchased from the local market, was cut into small pieces $(25 \times 12 \text{ cm sizes})$ with a scissors, and was stored in a sealed container before use. The characteristics of highly cellulosic toilet papers (97.8%) with an approximate weight of 1000 ± 30 g roll⁻¹ were analyzed with ASTM techniques. In the analysis, the contents of moisture (4.17%), volatile matter (80.36%), ashes (3.21%) and fixed carbon (12.26%) were determined. Potassium hydroxide (Sigma-Aldrich, USA) was analytical grade and used as received without further purification. Deionized water was used to prepare alkaline solution and for washing of synthesized activated carbon in the first washing stage. A furnace (Lindberg/Blue M, USA) and an in-house-made stainless steel reactor with an inner dimension of 17×3 cm under Argon gas were used. A centrifuge (IEC Centra-HN, USA) and a pH meter (EcoMet, CE) were used to separate solid/liquid phases and measure the alkalinity of the solution, respectively. A two-step procedure was applied: carbonization and activation.

2.1. Carbonization procedure

The carbonization process was carried out at 400 °C based on TGA results of toilet paper. Therefore, a three-step thermal treatment under argon atmosphere was applied to obtain char as follows: (i) increasing the temperature from ambient to 400 °C using a heating rate of 10 °C/min, (ii) maintaining the temperature at 400 °C for 1 h, and (iii) decreasing the temperature from 400 °C to ambient in about 1.5 h [18]. Ten grams of tissue paper were put in a tubular reactor (Fig. 1) and at the end of the process the char was weighed for the activation stage.

2.2. Activation procedure

The carbonization process was followed by the activation of carbon in the same reactor shown in Fig. 1. In each experiment, a mixture of a 1.07 M KOH alkali solution (3 g potassium hydroxide in 50 mL deionized water) and 2 g of char obtained from the carbonization stage were heated and mixed in a glass beaker on a heater-stirrer device. After homogenizing at room temperature for 2 h, the mixture was subjected to heat in the oven at 110 °C for 24 h to evaporate all moisture from solid. The obtained solid was ground manually to produce a uniform powder of 75–150 μ m (100–200 mesh) of KOH-carbon (KOH/carbon ratio: 3:1).



Fig. 1. Experimental Set-up used for production of AC.

Then, the fine powder was placed in the reactor for the activation stage under Argon atmosphere at 750 °C for 1 h [24]. The increasing and decreasing temperature profiles were similar to those in the carbonization stage. It should be noted that for the next consecutive experimental runs, the alkaline solution from the washing step was recycled to the activation step with fresh carbonized powder, after adjusting its pH.

2.3. Washing steps

The AC particles obtained in the carbonization stage were subjected to a stage-wise counter-current washing with de-ionized (DI) water. The proposed stage-wise operation has several industrial benefits compared to a one-stage washing operation and reduces the need for wash water remarkably [25]. The AC was washed with Deionized water in 25 stages (i.e. 50 mL, each). The process flow diagram of the AC preparation with zero discharge effluent and the detail of washing process in a counter-current manner is depicted in Fig. 2. In the washing step and in the start-up operation, fresh DI-water was used in all 25 stages of washing (50 mL in each stage). However, in the steady state operation, fresh water (50 mL) was used only in the last stage of washing (i.e. stage 25). The start-up operation refers to the first step of the counter-current approach which uses fresh DI-water (50 mL) in all the 25 consecutive stages of washing process, while the steady state operation refers to the other subsequent washing process in which the recycled aqueous stream was used. In addition, the simultaneous application of centrifugation and filtration was performed to facilitate the washing and to easily separate the supernatant for the next stage. The 25 consecutive washing steps required 5 min of centrifugation and filtration. Finally, the time required for complete washing steps was about 125 min. While, in the common washing methods, in spite of the higher water volume usage and lower overall efficiency, the required washing time is at least 7-8 h. In this approach, the supernatant liquid phase of the *i*th washing stage was decanted to recover KOH solution and was used for the preceding stage (i.e. stage 1) under steady-state operation. The solution pH decreased in each washing stage from stage 1 to stage 25. Twenty-five stages of washing were chosen to assure that the alkalinity of the final solid product decreased to an acceptable level. Multiple stage counter-current washing process removes the majority of potassium hydroxide from the AC product. Supernatant liquid (50 mL) collected from the first washing stage had the highest pH. The alkalinity of this solution was adjusted by adding appropriate amounts of potassium hydroxide before being used in the next synthesis run. The aforementioned operation, minimized the overall use of fresh water and activating agent. The recycled solution was initially subjected to an activation operation with 2 g fresh carbonized powders.

At steady state operation, 0.1 g of potassium hydroxide was added to the alkali solution (i.e. 50 mL supernatant liquid) collected from the preceding washing operation to make up and adjust the alkalinity of the solution for the next activation run. It should be noted that the need for potassium hydroxide in the steady state operation and successive runs (i.e. 0.1 g) is much lower compared to the start-up stage (i.e. 6 g) because of residual potassium hydroxide in the alkali supernatant collected from the preceding runs. The steady-state operation was started by adding 2 g carbonized powder to the recycled alkali supernatant before the drying step. In the steady-state washing process, the water collected from the second washing stage of the preceding run served as the washing water in the first stage of the current run; the water collected from the third stage served as the washing water of the second stage, and so on. Only 50 mL of fresh water was used in the 25th stage of washing as the make-up water. This make-up water compensated the water loss during the drying stages.

The washed AC undergoes a normal drying process at 80 °C in the oven overnight. Overall, the developed zero liquid discharge process comprises of a main start-up step that uses a fresh solution of potassium hydroxide and fresh DI-water followed by a steadystate stage, in which only 50 mL of fresh water is used for the entire process.

The developed procedure was continued for 10 consecutive cycles in order to achieve stable and steady conditions to prove feasibility of this approach. The composition of the recycled alkali supernatant reached a quasi-steady-state after the forth recycling step. The effect of the recycled alkali supernatant on the quality of the AC was studied for up to 10 consecutive recycles. The pH of the resulting supernatant from washing at different stages was chosen as a criterion for reaching a stable condition.

2.4. Chemical and textural characterization

Adsorption characterization of the ACs produced from toilet paper was determined by nitrogen adsorption at -196 °C (i.e. 77 K) and a relative pressure (P/P_0) range of 0.001–0.1 using a Micromeritics ASAP 2020, USA. The Brunauer-Emmett-Teller (BET) specific surface area was calculated from the adsorption isotherms by means of the BET equation where monolayer coverage of nitrogen molecules is anticipated to be complete. The pore size distribution was obtained by the Barrett-Joiner-Halenda (BJH) equation during the desorption phase [26]. The BJH method according to the Kelvin equation, relates the relative pressure of nitrogen in equilibrium with the porous solid to the size of the pores where capillary condensation takes place. The pore size radii covered by the BJH calculations ranged from 1.7 to 300 nm [27]. The pore width range was separated into three groups based on the IUPAC classification concerning porous materials (micropores below 2 nm, meso-pores between 2 and 50 nm and macrospores above 50 nm) [28]. Then, the cumulative pore volumes were calculated. The Fourier transform infrared (FTIR) spectra of the samples were recorded on solid state by a Vector 22 spectrometer (MA, USA). Spectra were performed in the 4000–400 cm^{-1} region, with resolution of 4 cm⁻¹. A Rigaku-Mini Flex powder diffractometer (Japan) was used to collect XRD data of the synthesized samples using CuKa (λ = 1.54059 Å) over the range of 5° < 2 θ < 80° with a step width of 0.02°. Thermal analysis (TGA/SDTA 851eMettler Toledo, Switzerland) was conducted under nitrogen flow to determine the thermal stability of the produced AC samples. The heating rate was fixed at 10 °C/min from 25 °C to 900 °C. The surface morphology of the prepared samples was studied using scanning electron microscopy (SEM, Model LEO 1530) micrographs. Moreover, the produced carbonaceous materials were characterized via Raman spectroscopy using an HR 800 Horiba multi-channel spectrometer. The AC production yield (Y) was calculated as follows:

$$Y(\%) = \frac{W}{W_o} \times 100 \tag{1}$$

where W is the mass of the produced AC (g) and W_o is the mass of the carbonized tissue before impregnation in KOH solution (g). It should be noted that the AC samples synthesized with ith liquid recycling were called as "AC-i".

3. Results and discussion

3.1. Transition and steady state condition

To determine the required number of recycling stages to achieve steady-state conditions, the variations of pH of filtrates (supernatant liquid) of each washing stage were measured, as illustrated in Fig. 3. Fig. 3a shows the variation of pH in the first



Fig. 2. Process flow diagram of the synthesis of AC (a), the propsed zero discharge process with washing in 25 stages in a counter-current manner (b).

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and last runs of the experiment. The pH of filtrate increased as the number of recycling steps increased. The most significant variations were observed for stages 1–5 (Fig. 3b). Although after 4 times of recycling, the composition of the filtrate (in each stage) reached a quasi-steady-state level.

3.2. XRD analysis

The XRD patterns for some selected produced AC samples, i.e. AC-1, AC-5 and AC-10 (Fig. 4) presented a broad peak around $2\theta = 22^{\circ}$ and an obvious peak around 44.64° which could be ascribed to the reflection from the (002) and (100) planes [29]. These broad peaks are the specifications of amorphous carbon with carbon rings stacked up in a disorganized fashion. Hence, some degree of micro-crystallinity with turbostratic graphite structure in the obtained ACs is indicated. The existence of micro-pore struc-

ture is observed in the attained ACs around 20: 20° [30]. It is obvious that after 10 consecutive experimental runs, with an aim to develop a zero liquid discharge technique and decrease the activating agent usage (KOH), the XRD patterns demonstrate no remarkable difference.

Bragg's equation was utilized for calculation of the interlayer spacing as follows:

$$d = \frac{\lambda}{2\sin\theta} \tag{2}$$

where λ is the X-ray wavelength (k = 0.154 nm) and θ is the scattering angle of the peak position. The determination of the crystallite size along the c-axis (crystallite height), L_c, and along the a-axis (crystallite width), L_a, was carried out by Scherrer's equation [30]:

$$L = \frac{K\lambda}{B\cos\theta}$$
(3)



Fig. 3. Alkalinity of washing liquid in different stages of washing process (a) startup and steady-state condition (b) transition and steady state condition.



Fig. 4. XRD pattern of synthesized AC with recycling liquid.

where K is the shape factor, 0.94 for (002) and 1.84 for (100) [31], and B is the full width half maximum of the peak in radian. Table 2 provides the values of d_{002} , d_{100} , L_c and L_a . In the investigated cases, the interplanar spacing d_{002} values were in the range of 0.39 to 0.40 nm, which is larger than the calculated value for graphite (d_{002} = 0.335 nm) [30]. According to the results, the XRD spectrum indicates that the synthesized AC contains uncorrelated small graphitic layers [32], which is in accordance with previous studies [16,33]. The high d_{002} indicates that our AC is disordered demonstrating that appropriate graphitization had not occurred [30,33]. However, it is confirmed that disordered AC consists of better porosity and consequently the higher surface area which enhances the application of AC as a good adsorbent [16,30,33].

3.3. TGA analysis

The TGA graphs of the toilet papers and synthesized ACs are shown in Fig. 5. The TGA/DTA curves of toilet paper (Fig. 5a) indicate three weight loss stages at 75 °C with 2.08 wt% loss (water evaporation), 330 °C with 40.6 wt% loss (hemicellulose decomposition and volatilization of organics), and incessant slight volatilization due to cellulose decomposition [4,30,34].

The TGA results of synthesized ACs (Fig. 5b) shows a weight loss at around 85 °C which corresponds to the water evaporation in the first stage of weight-loss [35]. The second stage amount of weight loss of the AC samples occurred around 250–400 °C. This indicates the decomposition of most tightly detained organic volatiles within the carbon matrix [30,34]. The last weight loss ranged from 400 to 900 °C, representing the thermal degradation by pyrolysis of cellulose in the ACs [30]. As a result, the small amount of the overall mass loss for AC samples during the carbonization process demonstrated that the synthesized ACs has no significant impurities.

3.4. FTIR spectra

Toilet paper is manufactured from almost pure cellulose. The chemical nature of the functional groups on the precursor and AC surface was confirmed by FT-IR as indicated in Fig. 6. The FT-IR spectra of the precursor revealed the strong O-H stretching absorbing band from vibration in surface -OH groups of cellulose structure and adsorbed water molecule at 3370 cm⁻¹, the C–H stretching at 2900 cm⁻¹, the HCH and OCH in-plane bending vibrations at 1430 cm^{-1} , the CH deformation vibration at 1375 cm^{-1} , the bending vibration of CH₂ at 1316 cm⁻¹, the vibration bond of C–O at 1259 cm⁻¹, the asymmetric vibration of C–O–C at 1162 cm⁻¹, the stretching vibration of glucose ring at 1111 cm⁻¹ and 898 cm⁻¹, and the stretching vibration of C–O at 1032 cm⁻¹. Moreover, the C-OH out-of-plane bending mode appeared at 668 cm⁻¹, 700, 756 cm⁻¹ [36,37]. These peaks confirm the cellulose content in the sample. The spectra of the ACs after 10 successive runs remained nearly unchanged. Most of the peaks assigned in precursor also appeared in ACs with the small differences in their intensity. For instance, the O-H stretching vibration of adsorbed water is assigned not only with higher intensity at 3425 cm⁻¹ but also at 1630 cm⁻¹. Toilet paper is a lignocellulosic material, with cellulose as the main component. This polymeric structure releases most of the noncarbon elements, mainly hydrogen, oxygen and nitrogen in the form of liquids and gases during activation or carbonization by pyrolytic decomposition, leaving behind a porous carbon skeleton in the form of aromatic sheets and strips [38]. The C–H bond stretching of carboxylic acids is at 2853 cm⁻¹, the C=O stretching in lactones at 1711 cm⁻¹, the skeletal C=C vibrations in aromatic rings at 1505 cm⁻¹, the $-CH_2$ deformation at 1433 cm⁻¹, the asymmetric stretching vibrations of C–O–C in ethers at 1255 and 1015 cm⁻¹, the C–O–C stretching

Table 2 Interlayer spacing (d) and crystallite size (L) of the AC samples.

Sample	d ₀₀₂ (nm)	d ₁₀₀ (nm)	Lc (nm)	La (nm)
AC-1	0.40	0.21	1.77	3.22
AC-5	0.39	0.20	1.79	3.34
AC-10	0.43	0.20	1.74	3.17



Fig. 5. TGA/DTA thermo-grams for the (a) Toilet paper (b) Activated carbons.

of β -(1 \rightarrow 4)-glycosidic linkages at about 894 cm⁻¹, the =C–H bending vibrations of alkanes and alkynes in the region 685–516 cm⁻¹ [21,39].

3.5. Raman analysis

Totally ordered mono-crystalline carbon (i.e. graphite) shows a peak at 1582 cm⁻¹, while disordered amorphous carbon has two humps of graphite (G) band at almost 1600 cm⁻¹ and disorder-carbon (D) band at 1350 cm⁻¹ [40,41]. Fig. 7 shows the Raman spectra for ACs in consecutive runs. The presence of the G (1334 cm⁻¹) and D (1592 cm⁻¹) bands demonstrates the existence of ordered graphitic and disordered carbon [32,40,42]. There is no sign of cellulose band which affirms that the carbonization process was complete [32,43], corroborating the TGA results.

The comparison of synthesized ACs in 10 consecutive runs was performed by calculating the R ratio, between the intensity of the (D) and (G) bands. The R ratio and the percentage of graphitic carbon and disordered carbon are illustrated in Table 3. Similar R ratios demonstrate the similarity of AC characteristics during successive runs.



4000 3600 3200 2800 2400 2000 1600 1200 800 400 Wavenumber (cm⁻¹)

Fig. 6. FTIR spectra of synthesized AC with recycling liquid.



Fig. 7. Raman spectroscopy of synthesized AC with recycling liquid.

Table 3

Graphitic and disordered carbon proportions in the AC samples.

Proportion	AC-1	AC-5	AC-10
R ratio (I _D /I _G)	0.996	0.992	0.944
Graphitic carbon (%)	42.93	37.55	35.71
Disordered carbon (%)	57.07	62.44	64.29

Similar properties of the AC samples, especially after steady state conditions are reached, are obvious by comparison of the R ratios. Also, the crystalline size of graphite along the (100) plane in all cases was around 3 nm, which is in agreement with the XRD results. According to the XRD and Raman results, it can be concluded that the cellulose contents in the AC samples decom-



3.6. SEM analysis

The SEM images of prepared ACs with consecutive recycling of liquid are presented in Fig. 8. As revealed in these micrographs, chemical activation along with pyrolysis was effective in expanding the carbon pore structure. The SEM images demonstrate that activation with KOH creates cavities that are smooth with many different sizes and shapes of the synthesized AC. Many micropores are formed, as well as a quantity of *meso*-pores which provide the resulting high surface area. No significant morphological difference was observed from the first to tenth samples.





(a)





(b)





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Fig. 9. N₂ Adsorption-desorption isotherms (a) and BJH pore size distribution of ACs (b).

Table 4	
Textural parameters of the prepared A	٩0

Sample	KOH:precursor	Yield (%)	Textural parameter					
	(g/g)		S _{BET} (m ² /g)	V _{mic} (cm ³ /g)	V _{mes} (cm ³ /g)	V _{total} (cm ³ /g)	V _{mic} (%)	Average Pore Diameter (nm)
AC-1	6.0:2	37	1820	0.833	0.280	1.113	74.82	1.68
AC-2	0.1:2	32	1878	0.824	0.268	1.092	75.46	1.72
AC-3	0.1:2	31	1736	0.804	0.286	1.084	73.62	1.56
AC-4	0.1:2	32	1681	0.812	0.29	1.102	73.68	1.53
AC-5	0.1:2	34	1637	0.824	0.241	1.065	77.37	1.58
AC-6	0.1:2	32	1641	0.809	0.326	1.109	72.60	1.57
AC-7	0.1:2	33	1629	0.826	0.285	1.111	74.35	1.52
AC-8	0.1:2	32	1633	0.813	0.284	1.097	74.11	1.54
AC-9	0.1:2	34	1627	0.809	0.280	1.089	74.29	1.55
AC-10	0.1:2	31	1631	0.823	0.283	1.106	74.41	1.51
Precursor	-	-	5.31	0.004	0.004	0.008	50.00	6.47

3.7. Porosity analysis

Adsorption-desorption isotherms of N2 at 77 K and BJH pore size distribution of the precursor and the synthesized AC during 10 successive recycling stages is presented in Fig. 9. Based on IUPAC classification, the isotherms of ACs show typical Type IV adsorption/desorption isotherm shapes with hysteresis loop and sharp increases at low relative pressure, demonstrating the existence of both micro- and meso-pore structures. According to Fig. 9a, the hysteresis loop was almost identical and it showed no significant difference. Fig. 9b illustrates also the BJH pore size distribution for the AC synthesized from toilet paper. It can be observed that the pore size distribution of the AC samples is similar, although more narrowly distributed and mostly being composed of micro-pores. According to the results, the N₂ adsorption capacity of as-synthesized ACs was significantly higher than that of toilet paper and the pore diameter remarkably changed by activation process (Figs. 9a and b).

The textural properties of the precursor and the AC including S_{BET} , V_{mic} , V_{mes} , V_{total} , and yield are represented in Table 4. It can be concluded that the N_2 adsorbed volume for AC-1 to AC-5 samples is varied; however, for AC-5 to AC-10 samples, these variations decreased ($\sim 5 \text{ cm}^3/\text{g}$). This indicates that after the 5th stage recycling run, steady-state had been achieved as described in Section 3.1. The textural properties of AC samples in (Table 3) are also consistent. Also, this shows that the synthesized ACs are micro-porous, as more than 70% of the total pore volume are micro-pores. It can be also observed that the physical properties of precursor were significantly improved by the activation treatment. The results from nitrogen desorption isotherms corroborate the SEM images.

A summary of related studies for the synthesis of AC from lignocellulosic materials is provided in Table 4. In spite of the use of the recycled effluent for successive AC syntheses, the BET surface area and total pore volume values achieved in this study were higher than commercial activated carbon (CAC). In many previous studies, including those mentioned in Table 1, increasing the treatment temperature and/or the activating agent ratio or both treatments led to an enhancement of surface area and porosity. However, in the current study, the synthesized AC with a high surface area and porosity was achieved without environmental concerns and with a very high cost-effectiveness.

3.8. KOH reaction mechanism

According to the literature, the precursor, the activation agent and the synthesis conditions have a significant effect on the micro-pore properties of the AC [4,45–49]. The porosity is caused by chemical compounds remaining in the internal structure of the lignocellulosic materials that hinder their shrinkage. It was previously confirmed that KOH is the most effective agent to form micro-pores [17,19,50]. The development of porosity of the AC by KOH activation is related to gasification reactions. In this process, KOH can enter and intercalate into the carbon lamellae to make the separation of layers and pore development. As well, KOH is reduced to metallic potassium in the course of the carbonization/ activation process [51]. The reduction of hydroxide to form free potassium metal, the penetration of free metal into the lattice of the carbon, the expansion of the lattice by the intercalated potassium, and the rapid removal of the intercalate from the carbon matrix lead to the observed higher porosity [52,53]. In this work, the activation process between graphitic layers. Therefore KOH reduction could be explained by the following reaction [24,51]:

$$6KOH + 2C \rightarrow 2K + 3H_2 + 2K_2CO_3 \tag{4}$$

3.8.1. Proposed reversible reaction mechanism

The need for large amounts of washing water to decrease the pH from 10 to around 7 and a slowly decreasing rate of pH at the final stages of washing (at least 25 washings stages) are due to slow release of KOH during the washing process. During washing of the synthesized AC, the following reversible reactions may occur [19,24,51,54]:

$$2K + 2H_2O \rightarrow 2KOH + H_2 \tag{5}$$

$$K_2CO_3 + H_2O \rightarrow 2KOH + CO_2 \tag{6}$$

A temperature increase during the washing step is due to the aforementioned fast reactions and dissolution of KOH. The overall reaction is:

$$2K + K_2CO_3 + 3H_2O \rightarrow 4KOH + H_2 + CO_2 \tag{7}$$

This means that during the washing of AC samples (in the early stages of washing), the metallic potassium and potassium carbonate within the macro/meso-pores of solid react to form KOH. The reaction kinetics and molecular diffusion of KOH across the macro- and meso-pores to bulk liquid are fast phenomena which are responsible for recovering the majority of KOH and decreasing the pH from 14 to around 10.

In order to decrease the pH further from 10 to around 7, while recovering a small amount of residual KOH from samples, a large amount of water is needed. This can be explained by the three phenomena in series as follows:

- Penetration of water to micro-pores and the AC lattice (slow),
- Reaction of metallic K and K₂CO₃ with water to form KOH (fast),
- Diffusion of produced KOH from the lattice of carbon to the bulk of washing liquid across micro-pores of AC (slow).

Therefore, the overall rate of this phenomenon is slow, resulting in an increase in the number of washing stages.

Considering the forward reaction (Eq. (5)) during the activation process and reverse reaction (Eq. (8)) during the washing process, the following reaction represents the entire activation-washing process:

$$2C + 4H_2O \rightarrow +4H_2 + 2CO_2 \tag{8}$$

This overall reaction might be a reason for the loss of carbon in the form of carbon dioxide, leading to a decrease in activation yield.

4. Conclusions

Activated carbon is one of the most widely used adsorbents. Highly porous AC was developed in this work using toilet paper in a step-wise washing process with consecutive recycling. This procedure gave a zero liquid discharge effluent with a minimum usage of KOH activating agent. The criteria that were considered for synthesis of AC included: the feasibility of scaling-up the production, the eco-environmental aspects, and the stability of the ultimate production guality. The need for water and KOH (<1%)was limited to evaporation and slight-physical losses, respectively. Furthermore, with a view towards scale-up, the described approach eliminates the need for high cost wastewater treatment units. The low diffusion rate of forming KOH from micro-pores of synthesized AC to the liquid bulk is the main reason to increase the number of washing stages. The synthesized ACs had similar characteristics once the steady-state condition had been achieved. The proposed techno-economical procedure at large scale offers a novel approach for manufacturing environmental friendly adsorbents, providing a promising method to reduce pollutants entering the environment.

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