

Article

Valorization of Biomass Hydrolysis Waste: Activated Carbon from Humins as Exceptional Sorbent for Wastewater Treatment

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Abstract: Humins, waste from biomass hydrolysis, are the main factor limiting the utilization efficiency of biomass carbon. In the present study, waste humins were employed for activated carbon production through KOH activation in a temperature range of 500–900 °C. The structure and properties of the activated carbons were studied, and a honeycomb-like macropore structure was observed. High activation temperature was demonstrated to be capable of promoting the formation of activated carbon with high surface area, high pore volume and high adsorption capacity. The activated carbon obtained by carbonization at 800 °C (KOH800) was selected as sorbent to adsorb methylene blue (MB) and phenol in aqueous solution, and the adsorption process can be explained by pseudo-second-order kinetic model. The adsorption behavior complies with Langmuir isotherm model and exhibits superior adsorption capacity of 1195 and 218 mg/g for MB and phenol, respectively. The impacts of surface area, acidic active sites and pore structures were also investigated, and it was found that the adsorption of approximately 44.0% MB and 39.7% phenol were contributed by the pores with apertures from 1.7 nm to 300 nm.

Keywords: humins; biomass hydrolysis; activated carbon; phenol; methylene blue

1. Introduction

Acid-catalyzed hydrolysis of biomass-derived hexoses to produce platform chemicals, such as 5-hydroxymethylfurfural and levulinic acid, has attracted considerable attention recently [1–4]. One of the state-of-the-art processes is the Biofine process, which can produce levulinic acid in commercial-scale [5]. Glucose, the monomer of cellulose, is usually the reactant for levulinic acid and 5-hydroxymethylfurfural production in biomass hydrolysis process. The acid-catalyzed hydrolysis process, however, inevitably forms low-value-added byproducts, humins [6,7], and the humins yield in pure glucose acid hydrolysis can reach 21–36 wt. % (listed in Table 1) [8–12]. For levulinic acid production through cellulose hydrolysis, 30–50 wt. % of cellulose carbon was converted to humins [13]. Therefore, developing cost-effective methods for converting humins to high value products is essential.

As humins are stable carbon-rich polymer [14,15] containing 50–66 wt. % of carbon [12,16–19], humins are regarded as a potential feedstock for carbon material production, e.g., activated carbon. Activated carbon has become one of the most used materials in wastewater treatment. Generally, activated carbons can be generated from biomass and coal through chemical (e.g., KOH, H₃PO₄ and ZnCl₂) and physical (e.g., steam and CO₂) activation methods. Tables 2 and 3 summarize the recent

works on the production of activated carbons and their application for dye methylene blue (MB) and phenol adsorption. Phenol and MB are two of the most used model contaminants for adsorption studies, as a large quantity of wastewater containing phenolics and dyes has been produced in modern industry. In the present work, humins were employed for activated carbon production through a KOH activation process. The structure and properties of the activated carbon were investigated and the feasibility of being utilized as adsorbent for removing phenol and MB in aqueous solutions was also explored.

Table 1. Comparison of yield of humins from catalytic conversion of glucose.

Glucose Concentration	Catalyst	Temperature	Humins Yields	Ref.
200 g/L	0.2 M H ₂ SO ₄	170 °C	21.0 wt. %	[8]
18 g/L	0.1 M H ₂ SO ₄	125 °C	29 wt. %	[9]
270 g/L	0.055 M H ₂ SO ₄	180 °C	36 wt. %	[10]
360 g/L	0.01 M H ₂ SO ₄	220 °C	35 wt. %	
50 g/L	0.05 g/L ZrPO ₄	135 °C	29 wt. %	[11]
~50 g/L	0.5% H ₂ SO ₄	175–180 °C	21 wt. %	[12]

Table 2. Recent works on preparing activated carbon for phenol adsorption.

Raw Material	Activation Methods	Adsorption Temp. (°C)	Surface Area (m ² /g)	Adsorption Capacity (mg/g)	Ref.
Humins	KOH impregnation activation at 800 °C	30	1765	218	This work
Polyethylene terephthalate	Carbonization at 800 °C, followed by steam activation at 850 °C or at 900 °C with CO ₂	24	1850	278	[20]
Waste fiberboard	Carbonization at 500 °C, followed by KOH impregnation activation at 850 °C	30	1876	217.39	[21]
Waste fiberboard	Carbonization at 500 °C, followed by K ₂ CO ₃ impregnation activation at 800 °C	40		208	[22]
eucalyptus seed husk	NaOH/H ₂ SO ₄ impregnation activation at 550 or 750 °C	20	670–780	199	[23]
Bamboo residues	Carbonization at 500 °C, followed by K ₂ CO ₃ impregnation at 850 °C	35	1120	163.82	[24]
Bituminous activated carbon	-	25	676.7	157.91	[25]
Waste tires	KOH impregnation activation at 800 °C	30	273.26	156.25	[26]
Rattan sawdust	Carbonized at 700 °C, followed by KOH impregnation activation at 850 °C	30		149.25	[27]
Vetiver roots	Carbonization at 800 °C, followed by steam activation at 800 °C	25	1185	145	[28]
Water hyacinth	H ₂ SO ₄ carbonization at 150 °C, followed by CO ₂ stream activation at 700 °C	30	632.7	112.8	[29]
Commercial activated carbon	-	R.T.		112.36	[30]
Hazelnut bagasse	ZnCl ₂ impregnation activation method	45	1489	99.27	[31]
Activated carbon R3-ex	Carbonization at 1500 and 1800 °C	25	530–1390	62.9–226.6	[32]
Tobacco residue	KOH impregnation activation at 700 °C	20–50	998–1474	45.49	[33]
Peach seeds	Carbonization (450 °C) followed by CO ₂ gasification at 600 to 900 °C	25	159–793	11.1–45.8	[34]
Activated carbons from coal, coconut shell, charcoal	-	25	>900	10.29–24.96	[35]

Table 3. Recent works on preparing activated carbon for MB adsorption.

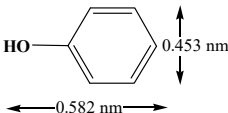
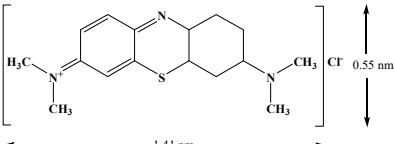
Raw Material	Activation Methods	Adsorption Temp.	Surface Area (m ² /g)	Adsorption Capacity (mg/g)	Ref.
Humins	KOH impregnation activation at 800 °C	30	1765	1195	This work
Flamboyant pods	NaOH activation	25	2854	890	[36]
Coal powder	KOH activation at 1000 °C	25	2075	871	[35]
Bituminous coal	Steam activation at 1000 °C	20	857.1	580	[37]
Salix psammophila	KOH impregnation activation at 850 °C	30		519.63	[38]
Bamboo chips	ZnCl ₂ impregnation activation at 500 °C	25	2050	435	[39]
Vetiver roots	H ₃ PO ₄ impregnation activation at 600 °C	25	1004–1272	423	[28]
Tomato waste	ZnCl ₂ impregnation activation at 600 °C	30	1093	400	[40]
Lignite	ZnCl ₂ impregnation activation at 450 °C	30	600	370.37	[41]
Delonix Regia pods	Microwave assisted ZnCl ₂ impregnation activation	62		370	[42]
Granular activated carbon	-	50	1306	357.14	[43]
Salix psammophila	H ₃ PO ₄ impregnation activation at 550 °C	30		347.13	[44]
Tea seed shells	ZnCl ₂ impregnation activation at 500 °C	20	1530.67	324.7	[45]
Dead leaves	ZnCl ₂ impregnation activation at 600 °C	45	1483	285.7	[46]
Bituminous activated carbon	-	25	676.7	130.88	[25]
Activated carbons from coal, coconut shell, charcoal	-	25	>900	130–135	[35]
Aloe vera wastes	Carbonization at 550 °C	25		129.87	[47]
Tamarind seed	H ₃ PO ₄ impregnation activation at 500 °C	50	594.04	102.77	[48]
Waste paper	KOH impregnation activation at 500 °C		66	68	[49]
Epicarp of Ricinus communis	Concentrated H ₂ SO ₄ carbonization	32	-	62.5	[50]
Buch-ham bark	Concentrated H ₂ SO ₄ at 400 °C	30–60	-	60.61–62.50	[38]
Hull of Lophira Lanceolat	Orthophosphoric acid impregnation activation at 400 °C	RT	-	55	[51]
Ficus carica bast	Concentrated H ₂ SO ₄ carbonization	25–50	-	40–50	[52]
Jatropha curcas, seed coats	Carbonization at 500 °C	28	50.29/75.70	37.84/17.44	[53]
Sunflower oil cake	H ₂ SO ₄ impregnation carbonization at 600 °C	25	240.02	16.43	[54]

2. Materials and Methods

2.1. Materials

Humins were produced through glucose (1 mol/L) acid hydrolysis for levulinic acid production at 170 °C with a reaction time of 6 h [18]. The humins were obtained by filtration from aqueous solution and dried at 100 °C before the use. Methylene blue (MB) and phenol were obtained from Macklin Reagent (Shanghai, China), and utilized with no further purification. The physicochemical properties of phenol and MB are listed in Table 4. Before the adsorption process, the phenol and MB were dissolved in deionized (DI) water.

Table 4. Physicochemical Properties of phenol and MB [55,56].

Properties	Phenol	MB
Chemical formula	C ₆ H ₅ OH	C ₁₆ H ₁₈ ClN ₃ S
Molecular weight	94.11 (g/mol)	319.85 (g/mol)
Acid-base properties	Acidic	Basic
Molecular structure		
Three dimensions	0.582 nm × 0.453 nm × 0.152 nm	1.41 nm × 0.55 nm × 0.16 nm

2.2. Activation Processes

Activation of humins was conducted by using KOH as activating agents through impregnation method. 3.0 ± 0.1 g humins were mixed with 6.0 ± 0.1 g KOH in 10 mL water and stirred for 12 h. The slurry obtained was dried at 120 ± 1 °C for 12 h, and then heated in a horizontal cylindrical furnace at 500–900 °C (heating rate 5 °C/min) for 2 h, with a nitrogen flow of 80 mL/min. Six carbonization temperatures were conducted with 100 °C increment. The activated samples were then neutralized by HCl solution (1 mol/L) and washed repeatedly with DI water until the water solution's pH = 7. The sample was dried at 120 °C for 12 h and weighed afterwards. The humins derived activated carbon produced with KOH at X carbonization temperature was labeled as KOHX. For example, KOH800 means an activated carbon prepared at 800 °C.

2.3. Sample Characteristics

To measure the thermal stability of the activated carbon, thermogravimetric (TG) test was conducted under air by a Netzsch 209F3 (Selb, Germany). X-ray diffraction (XRD) patterns was used to investigate the crystalline (or amorphous) structure of the activated carbon, by using a Rigaku D/max-III A X-ray diffractometer (Austin, TX, USA). Fourier transform infrared spectroscopy (FT-IR, Tensor 27, Bruker, Karlsruhe, Germany) were used to analyze the functional groups of activated carbons, pure phenol, pure MB, and phenol and MB adsorbed KOH800. The surface morphology of the samples was investigated by using an environmental scanning electron microscopy (SEM) system (JEOL JSM-6701F, Tokyo, Japan). The pores and special surface area were measured by nitrogen adsorption at 77.4 K using a Micromeritics Instruments TriStar II (Atlanta, GA, USA). The Brunauer-Emmett-Teller (BET) surface area and total Barrett-Joyner-Halenda (BJH) pore volume (pores from 1.7 to 300 nm) were analyzed according to the nitrogen adsorption-desorption isotherms. KOH800 was also analyzed by nitrogen adsorption at 77.4 K in an Autosorb-iQ-C chemisorption-physisorption analyzer (Quantachrome, Boynton Beach, FL, USA) in order to measure the micropores with size <1.7 nm in diameter. Boehm titration method was used to measure the total acid groups and alkaline groups, in which phenolphthalein was used as indicator [25,28].

2.4. Batch Equilibrium Processes

Adsorption experiment was performed in 50 mL sealed glass bottles, where 30 mL of phenol (or MB) solution was placed in each bottle without any pH adjustment. The initial concentration of phenol and MB was 100–400 mg/L and 800–2000 mg/L, respectively. 0.05 g activated carbon prepared was added to each bottle, and then the adsorption was conducted in an isothermal shaker at 200 rpm and 30 °C for up to 24 h. After each adsorption process, the activated carbon and the solution were separated by filtration. The concentration of phenol and MB remained in the solutions were analyzed by an UV-vis spectrophotometer (Specord® 210 Plus) at 269 and 663 nm, respectively.

For the desorption experiments, KOH800 (0.05 g) was first used for a routine adsorption in 400 mg/L phenol or 2000 mg/L MB solutions for 24 h. The MB or phenol adsorbed KOH800 were

then soaked in desorption solvents (30 mL) at 30 °C for 2 h, with a shaking speed of 200 RPM. Several solvents, including 0.1 mol/L HNO₃, 0.1 mol/L HCl, 0.1 mol/L NaOH, methanol and acetone, were used for the desorption.

The adsorption and removal efficiency of phenol and MB were calculated using Equations (1) and (2), respectively:

$$q_e = (C_0 - C_e)V/M \quad (1)$$

$$\text{Removal (\%)} = \frac{C_0 - C_e}{C_0} \times 100\% \quad (2)$$

where q_e (mg/g) is the adsorption content of MB or phenol on activated carbon, C_e and C_0 (mg/L) are equilibrium and initial concentration of MB or phenol, respectively, V is solution volume, and M is the mass of the activated carbon.

3. Results and Discussion

3.1. Characteristics of Activated Carbon

3.1.1. Surface Area and Pore Distribution

As shown in Figure 1 and Table 5, humins were solids cumulated by microspheres and their BET surface area and BJH pore volume were only 5.7 m²/g and 0.0045 cm³/g, respectively. Pyrolysis of humins at 500 °C improved the formation of pores, though the SEM images of the humins pyrolysis product (humins500) did not changed much as compared with that of the humins. The BET surface area and BJH pore volume of the solid increased to 73.8 m²/g and 0.014 cm³/g, respectively. The structure of humins, however, changed significantly and porous carbon materials were formed after the KOH activation treatment (shown in Figure 1). The BET surface area and BJH pore volume can reach 428–1975 m²/g and 0.03–0.66 m³/g, respectively, when the KOH activation temperature is in the range of 500–900 °C (listed in Table 5). Figure 2 showed the N₂ adsorption isotherms for the activated carbons produced at 500–900 °C. The KOH500–KOH900 exhibited isotherms of type I according to the IUPAC classification. A sharp curve was observed at relatively low pressures ($P/P_0 < 0.1$) and a greater volume adsorption was observed afterwards, illustrating the small pore size region held a wider pore size distribution. The pore size distribution of KOH800 is shown in Figure 3, which indicates that the pore volumes are mainly attributed to the pores with diameter between 0.5 and 4 nm, and the average diameter is about 1.92 nm.

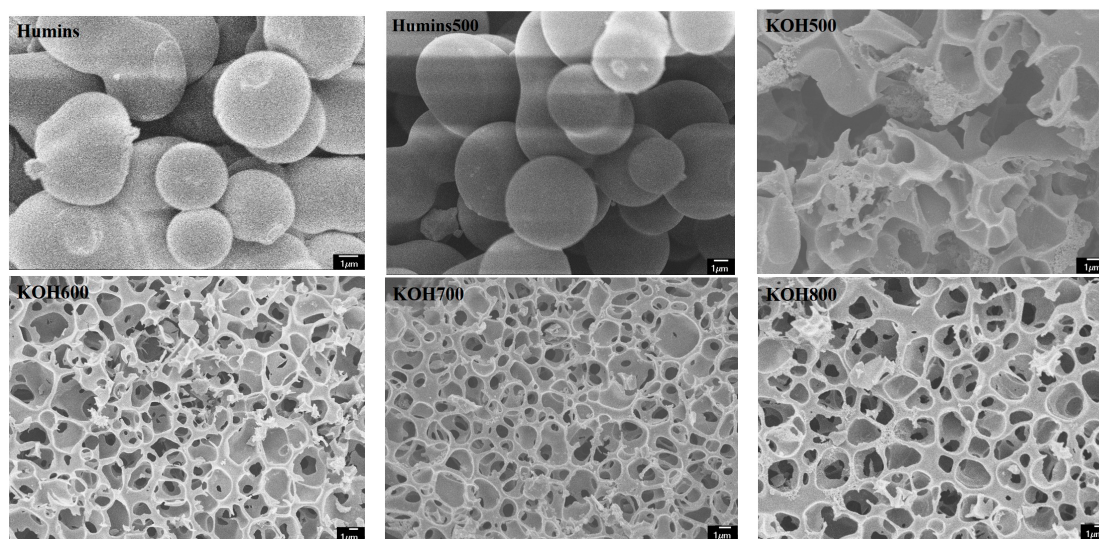


Figure 1. Cont.

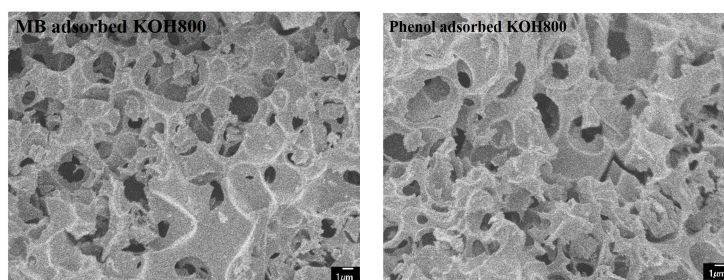


Figure 1. SEM images of humins, KOH500–KOH800, MB adsorbed KOH800, phenol adsorbed KOH800, and the humins500 which was obtained by pyrolysis of humins at 500 °C without KOH activation.

Table 5. Properties of humins and humins carbonization products.

Sample	Yields (wt. %)	BET Surface Area (m ² /g)	BJH Pore Volume ¹ (cm ³ /g)	Total Acidity (meq g ^{−1})	Total Basicity (meq g ^{−1})
Humins	-	5.7	0.0045	-	-
Humins500 ²	55.8	73.8	0.014	-	-
KOH500	39.2	428	0.025	3.0	0.17
KOH600	30.8	665	0.068	3.3	0.28
KOH700	26.2	1041	0.10	3.2	0.48
KOH800	23.1	1650	0.32	3.3	0.51
KOH900	15.0	1975	0.66	3.1	0.56
Phenol adsorbed KOH800 ³	-	927	0.22	-	-
MB adsorbed KOH800 ⁴	-	67.2	0.013	-	-

¹ Measured between 1.7 nm and 300 nm width; ² Humins carbonization at 500 °C without KOH activation; ³ 0.05 g KOH800 used for adsorption in 30 mL 400 mg/L phenol solution for 24 h; ⁴ 0.05 g KOH800 used for adsorption in 30 mL 2000 mg/L MB solution for 24 h.

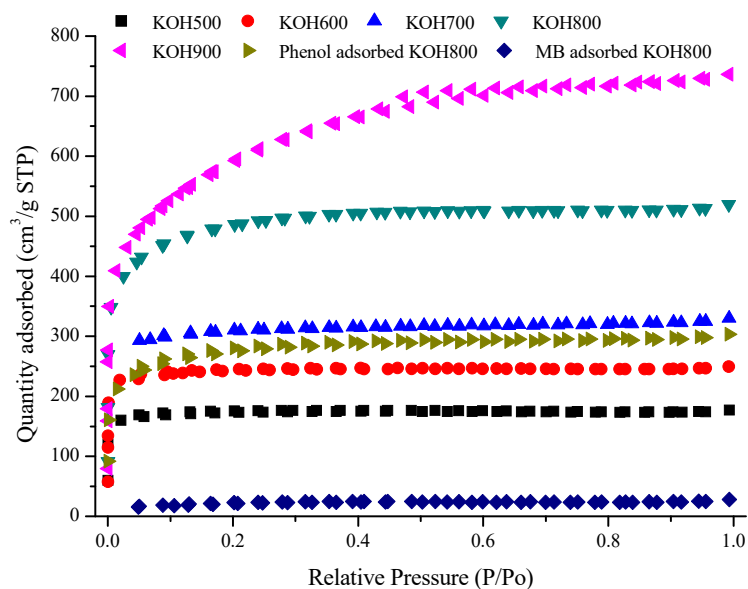


Figure 2. Adsorption isotherms of nitrogen for various activated carbons at 77 K.

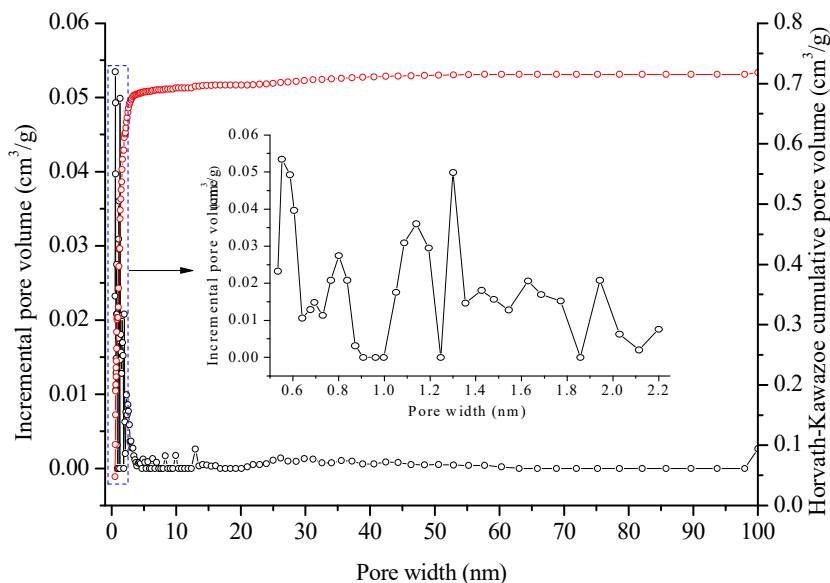


Figure 3. Pore size distribution of KOH800.

3.1.2. Impacts of Activation Temperature

Carbonization temperature is a crucial factor for the activation process. Higher activation temperature usually results in higher micropore volume and surface area, as high temperature is generally preferred in the gasification process and can increase the surface porosity [57]. The yield of activated carbon, however, decreases with the carbonization temperature. The yield decreased from 39.2 wt. % to 15.0 wt. % with a temperature increased from 500 °C to 900 °C. It has been reported that the pore development and the carbon loss may result from the formation of tar and gasses through intercalation effects of K^+ in the carbon framework [57]. The macropores present in the activated carbons were visible by the SEM images and distributed densely on the KOH500–KOH800. Interestingly, KOH700 and KOH800 have more honeycomb-like macropores (0.5–5 μm) on surface. Our results suggest that higher activation temperature is preferred for the formation of pores and results in higher BJH pore volume and surface area, but sacrifices the carbon yield.

3.1.3. Carbon Framework

As in the case of humins, the carbon framework of the KOH500–KOH900 is amorphous, as indicated by the XRD analysis (see Figure 4). Broad diffraction peaks were found located at around $2\theta = 22^\circ$ and 44° for all the activated carbons owing to the (002) and (100) planes of the carbon [58–61]. The broad peak at around $2\theta = 22^\circ$ could result from the amorphous carbon structures which were randomly arranged [62,63]. Figure 5 showed the FT-IR spectra of the KOH500–KOH900, indicating that all the activated carbons obtained have similar functional groups, i.e., hydroxyl groups (around 3450 cm^{-1}), carbon-carbon double bonds (around 1630 cm^{-1}), and carbon oxygen bonds (around 1100 cm^{-1}) [64,65]. The acidic and alkaline groups of the KOH500–KOH900 were between 3.0 and 3.3 mmol/g and 0.17–0.56 mmol/g, respectively (see Table 5). Interestingly, the concentration of alkaline group increases with the carbonization temperature. The acidic group enhances the adsorption of MB (alkaline solute), while the alkaline group improves the adsorption of phenol (acidic solute) [25,28].

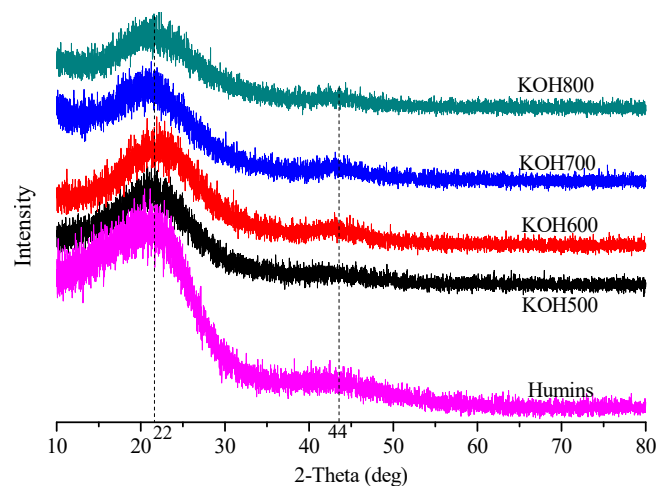


Figure 4. XRD spectra of humins and KOH500–KOH800.

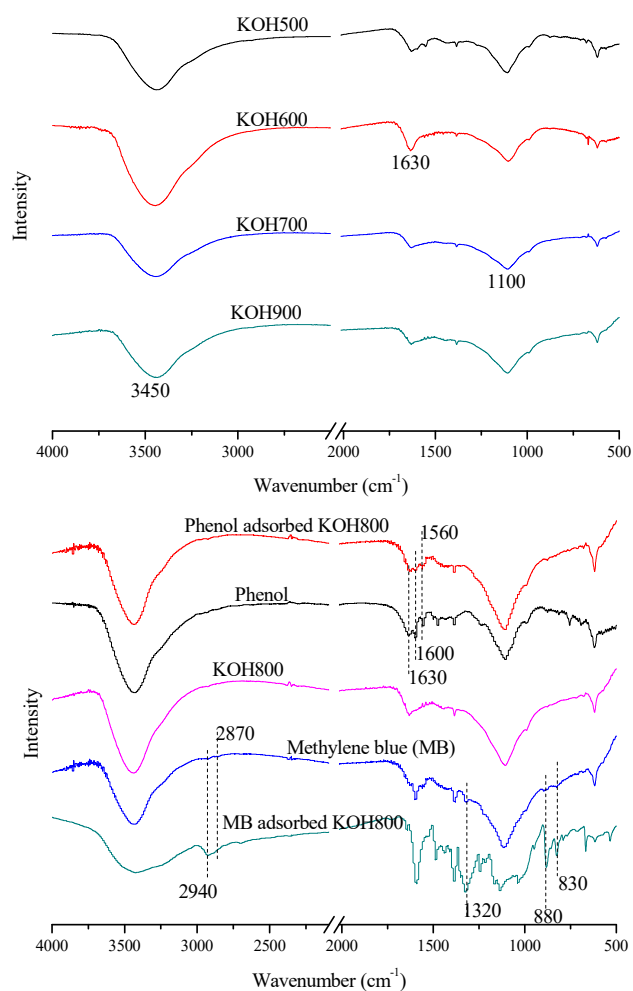


Figure 5. FT-IR spectra of activated carbon, MB, phenol, and MB and phenol adsorbed KOH800.

3.1.4. Thermal Stability

The activation and preparation of the activated carbons were conducted under N_2 atmosphere, whereas the utilization of activated carbons is usually under the air atmosphere. KOH500 and KOH800, therefore, were selected to investigate their thermal stability under air atmosphere and the results were

shown in Figure 6. Generally, a less loss of weight with the increase of pyrolysis temperature means a better thermal stability. Compared with humins, both KOH500 and KOH800 exhibited improved thermal stability. The major weight loss of KOH500 and KOH800 started at 400 and 450 °C, respectively, indicating that KOH500 and KOH800 are stable when the temperature is below 400 °C. A higher temperature of carbonization is preferred in considering of the thermal stability of the activated carbons under air atmosphere.

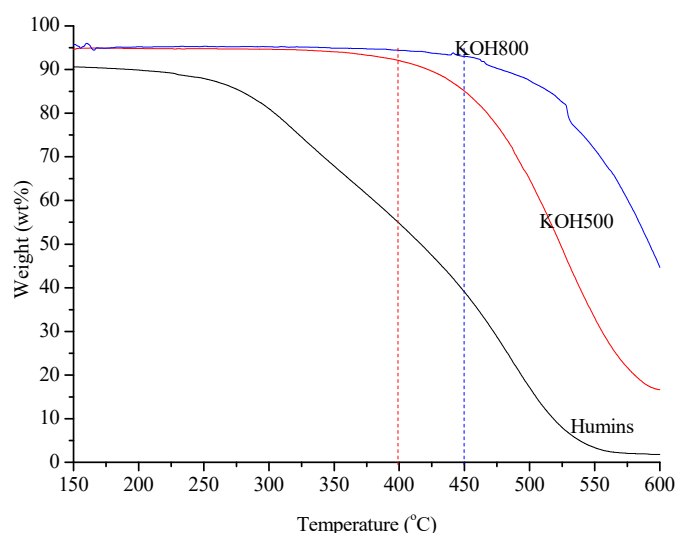


Figure 6. Thermal stability of humins, KOH500 and KOH800 in air atmosphere.

3.2. Application of Activated Carbons in Adsorption

3.2.1. Adsorption Capability

The adsorption effects of KOH800 was investigated by comparing the results from FT-IR, SEM, N₂ adsorption isotherm, pore volume and surface area analysis. Figure 5 showed the FT-IR analysis results of KOH800 before and after the dye adsorption. The phenol has three peaks at 1650, 1600 and 1450 cm⁻¹ owing to the existence of benzene ring structure [64,65], and all these peaks were also measured in the FT-IR spectrum of phenol adsorbed KOH800. The MB peaks at 2940 and 2870, 1320, 880 and 830 cm⁻¹ attribute to the C-H stretch, C-N stretch (aryl) and C-H bend, respectively [64,65]. Similar as phenol, all of these peaks were observed in KOH800 adsorbed with MB. The SEM image of KOH800 adsorbed with MB and phenol have much less pores on the surface in comparison with fresh KOH800, indicating that the pores were blocked or covered after the adsorption. This was demonstrated by BJH pore volume and BET surface area analysis. After the phenol adsorption (shown in Table 5), the BET surface area and BJH pore volume of KOH800 decreased by 43.8% and 31.3%, to 927 m²/g and 0.22 m³/g, respectively. The changes after the MB adsorption were more significant and the BET surface area and BJH pore volume decreased by 95.9% and 95.9%, to 67.2 m²/g and 0.013 m³/g, respectively. The decrease of BJH pore volume and surface area after the phenol and MB adsorption were also reflected by the change of N₂ adsorption capacity. The N₂ adsorption capacity of the fresh KOH800 is 510 cm³/g STP at 77 K, and this value decreased to 280 and 23 cm³/g STP after phenol and MB adsorption, respectively. In brief, the FT-IR SEM, N₂ adsorption capacity, surface area and pore volume results all indicate that KOH800 can effectively adsorb phenol and MB and the KOH800 showed better adsorption capacity of MB than that of phenol.

The adsorption capacity and removal efficiency of KOH500–KOH900 were also investigated. All of these activated carbons were employed to adsorb 400 mg/L phenol and 800 mg/L MB, and the results are shown in Figure 7. It is obvious that all the KOH500–KOH900 can effectively remove phenol and MB from aqueous solution. For instance, KOH800 is capable of removing approximately

85% phenol and almost all MB. In addition, the activated carbon prepared at higher temperature is more efficient in phenol and MB removal, i.e., the removal efficiencies of KOH500–KOH900 on phenol and MB follow the order: KOH900 > KOH800 > KOH700 > KOH600 > KOH500. The increase of adsorption capacity of these activated carbons can be interpreted by the increase of pore volumes and surface area. The increase of total alkaline sites with carbonization temperature (listed in Table 5) also leads to better phenol adsorption [28], as the alkaline sites would promote the adsorption of acidic phenol by π - π dispersion force [66].

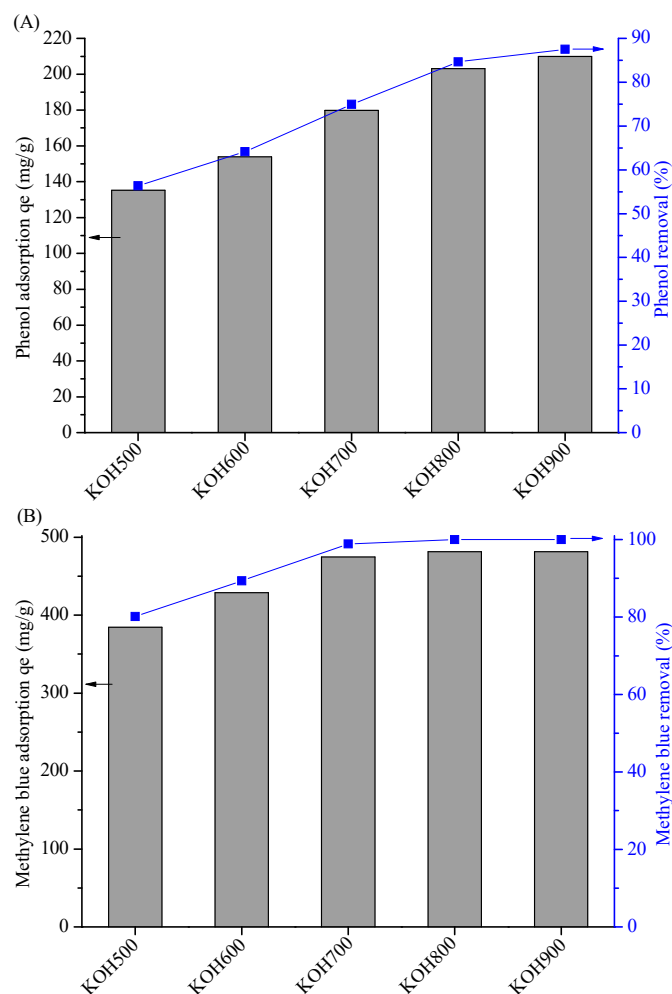


Figure 7. Comparison of phenol and MB adsorption capacity and removal efficiency. (A) Phenol adsorption; (B) MB adsorption. Experimental conditions: 0.05 g activated carbon in 30 mL of 400 mg/L phenol or 2000 mg/L MB solution for 24 h.

3.2.2. Adsorption Kinetics

Considering the adsorption capabilities and yields, KOH800 was selected for adsorption kinetics and isotherm studies, which are important for modeling the adsorption process. As KOH800 has better adsorption capability on the MB, the aqueous solutions with comparably high initial MB concentrations, i.e., 800, 1000, 1500 and 2000 mg L⁻¹, were employed for the kinetic studies [28,36–38,44–46,49,52]. The data obtained from MB and phenol adsorption by KOH800 were utilized for pseudo first and second order kinetic models, and the results are listed in Table 6. The pseudo-second order model illustrates a chemisorption process involving valency forces [36,67] and the pseudo-first order model defines the adsorption rate depended on the adsorption capacity [68].

Table 6. The parameters for the Pseudo-first-order and Pseudo-second-order kinetic models.

Solute	C ₀ (mg/L)	q _{e,exp} (mg/g)	Pseudo-First-Order Kinetic Model				Pseudo-Second-Order Kinetic Model			
			k ₁ (h ⁻¹)	q _{e,cal} (mg/g)	Δq (%)	R ²	k ₂ (g/mg h)	q _{e,cal} (mg/g)	Δq (%)	R ²
Phenol	100	59.7	1.74	1.4	103	0.7769	5.61	59.5	1.1	1.000
	204	117.6	0.73	2.0	104	0.9572	1.81	117.6	1.2	1.000
	301	165.5	0.57	2.9	104	0.7776	0.91	166.7	1.6	1.000
	401	204.6	0.37	7.96	103	0.8741	0.24	204.1	6.4	1.000
MB	801	481.3	3.88	10.8	102	0.8083	1.44	476.2	1.1	1.000
	1002	604.3	1.61	24.5	101	0.7107	0.27	588.2	3.3	1.000
	1501	907.4	0.91	107.2	96.7	0.8384	0.04	909.1	1.5	1.000
	2000	1184.0	0.29	222.9	95.6	0.886	0.007	1250	6.3	1.000

The pseudo-first-order rate equation is listed as:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (3)$$

The linear form of pseudo-second-order rate is listed as:

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

where q_t (mg/g) is the adsorbed content of phenol (or MB) on the sorbent at time t (h). k_1 (h⁻¹) and k_2 (g/mg h) are the constants of first order rate and pseudo second order rate, respectively. Table 6 listed the correlation coefficients (R^2) and the kinetics parameters, which were calculated through linear regression. Normalized standard deviation Δq (%) was also used to analyze the applicability of the two models, and the Δq (%) is expressed as:

$$\Delta q (\%) = 100 \times \sqrt{\frac{\sum \left[\frac{q_{exp} - q_{cal}}{q_{exp}} \right]^2}{(n - 1)}} \quad (5)$$

where n means the number of data points, and the subscripts 'cal' and 'exp' indicates the calculated and experimental values, respectively.

The correlation coefficient R^2 of second order kinetic model ($R^2 = 1.000$) are higher than that of the first order kinetic model ($R^2 = 0.7769$ – 0.9572) for the phenol adsorptions, whereas the Δq for the pseudo-first-order kinetic model ($\Delta q = 1.1$ – 6.4) is much lower than those for the pseudo-second-order kinetic model ($\Delta q = 103$ – 104) (listed in Table 6). Similar phenomena were observed in the MB adsorption test results. The experimental q_e values ($q_{e,exp}$) for both MB and phenol adsorption are significantly different from the calculated values ($q_{e,cal}$) obtained from the pseudo-first-order kinetic model, whereas the $q_{e,exp}$ matches well with the $q_{e,cal}$ obtained from pseudo-second-order model. All these R^2 , Δq , and the similarity between $q_{e,exp}$ and $q_{e,cal}$ indicate that the adsorption characteristics of phenol and MB complies with pseudo-second-order reaction kinetics. This is consistent with results reported before that the pseudo-second-order kinetics was a better simulation model for MB and phenol adsorption by biomass derived activated carbons [20,31,54,69–71]. In addition, the good fit of the pseudo-second-order kinetic model indicated the adsorption process was dominated by chemisorption.

3.2.3. Adsorption Isotherm

Figure 8 showed the influence of contact time on adsorption of phenol and MB with a series of initial concentrations (100–400 mg/L phenol, and 800–2000 mg/L MB). The saturation curves rise sharply firstly, and then level off with the contact time. Adsorption of MB and phenol was almost stopped when the saturation curves became a plateau line. The change of adsorption rate results from the change of the solute concentration and the available adsorbent sites on KOH800. As the number of available adsorbent sites and solute concentration are high at the initial stage, solute can

occupy the macro and mesopores rapidly, which results in quick MB and phenol adsorption on the external surface of KOH800. When most of the available surface adsorbent sites are occupied and the solute concentration decreases, MB and phenol have to diffuse into the micropores. The adsorption rate became very slow and a plateau of the curves was gradually reflected, due to the lack of available sites for further adsorption. The contact time for saturated adsorption of both phenol and MB was approximately 3 h, when the initial concentrations were 100–401 and 800–1500 mg/L, respectively (shown in Figure 8). Longer contact time for saturated adsorption of MB, however, was required with higher initial concentration (e.g., 2000 mg/L). It is noted that with the initial phenol concentration increased from 100 to 401 mg/L, the adsorption capacity at equilibrium (q_e) increased from 59.7 to 204.6 mg/g. Similarly, the q_e increased from 481.3 mg/g to 1184.0 mg/g when the initial MB concentrations increased from 801 to 2000 mg/L.

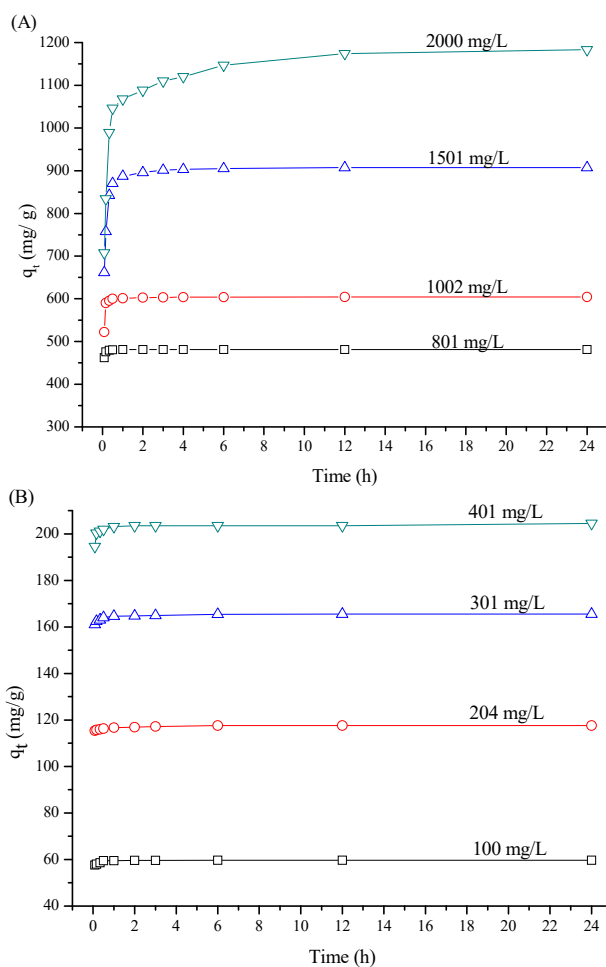


Figure 8. Adsorption isotherms of MB (A) and phenol (B) with various concentrations.

Several isotherm equations have been developed to interpret the equilibrium behavior. In this study, the adsorption process were investigated by using the Langmuir and Freundlich models. The linearized form of Langmuir isotherm equation employed is [27]:

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

where K_L (L/mg) is the Langmuir constant related to the sorption free energy and the affinity of binding sites. The correlation coefficients (R^2) and the isotherm parameters are shown in Table 7.

Generally, Langmuir model is employed for describing a homogenous surface, and a good R^2 indicates monolayer adsorption [27,37].

Table 7. Isotherm parameters of Freundlich and Langmuir models.

Solute	Langmuir Isotherm				Freundlich Isotherm		
	q_m (mg/g)	K_L (L/mg)	R^2	R_L ¹	K_F	n_F	q_m
MB	1195	6.787	1.000	7.4×10^{-5} (1.8×10^{-4})	8.4×10^{-15}	4.81	0.738
Phenol	217.9	0.21	0.9952	0.012 (0.045)	62.9	3.3	0.9885

¹ For the MB adsorption, the R_L outside and inside the bracket were calculated at the initial concentration of 2000 mg/L and 800 mg/L, respectively. For the phenol adsorption, the R_L outside and inside the bracket were calculated at the initial concentration of 400 mg/L and 100 mg/L, respectively.

The Freundlich isotherm is used for heterogeneous systems considering multilayer adsorption and the interaction among the molecules adsorbed. The linearized form of Freundlich isotherm equation employed is [27]:

$$\ln q_e = \ln K_F + \frac{1}{n_F} \ln C_e \quad (7)$$

The n_F is used to determine if the adsorption is linear ($n_F = 1$) [36]. $n_F < 1$ is for a chemical process, whereas $n_F > 1$ is for a favorable physical process. $1/n_F > 1$ and $1/n_F < 1$ corresponds to cooperative adsorption and normal Langmuir isotherm, respectively [21,36]. The n_F for the MB and phenol adsorption were 4.81 and 3.3. Thus, the $1/n_F$ for MB and phenol were 0.21 and 0.30, respectively. All the $1/n_F$ values are <1 for this work, indicating that adsorption is a physical process and the adsorption complies a normal Langmuir isotherm. This also explains the high R^2 of the Langmuir model, 1.000 and 0.9952 for MB and phenol, respectively. It further demonstrates that the adsorption is homogeneous but not the heterogeneous. The reliability of the homogeneous adsorption can be confirmed by the adsorption curves, which are smooth and continuous as shown in Figure 8.

K_F is the Freundlich constant and a high K_F value usually means an easy uptake of solute by activated carbon [31]. In this work, the K_F for the MB and phenol adsorption was 8.4×10^{-15} and 62.9, respectively, which is opposite to the data of adsorption capacity, i.e., the adsorption capacity of MB was much higher than that of phenol. In addition, the correlation coefficient R^2 for the Freundlich model on MB adsorption is also low (0.738). Thus, in this work, the Freundlich isotherm model is not a good choice for simulating the experimental data.

Tables 1 and 2 list the literatures about the maximum adsorption capacity for various activated carbons. These values were obtained by experiments or calculation relying on the Langmuir isotherm. In this work, the maximum adsorption capacity of the MB and phenol calculated by the Langmuir isotherm was 1195 mg/g and 218 mg/g, respectively. The adsorption capacity of both MB and phenol are very high in comparison with the previous works shown in Tables 1 and 2, especially for the MB adsorption, for which the KOH800 displayed the highest adsorption capacity. In general, the active groups, pore structure and surface area are the dominant factors that affect the adsorption capacity, and their impacts are discussed below.

The adsorption process can also interpreted by an equilibrium parameter, R_L [23,37], no matter it is “favorable” or not.

$$R_L = \frac{1}{1 + K_L C_0} \quad (8)$$

R_L is utilized to classify the type of isotherm, i.e., linear with $R_L = 1$, unfavorable with $R_L > 1$, favorable with $0 < R_L < 1$, and irreversible with $R_L = 0$. The $R_{L(phenol)}$ for phenol adsorption is between 0.012 and 0.046 (see Table 7) when the initial phenol concentration is 100–400 mg L⁻¹, indicating a favorable adsorption of phenol. The $R_{L(MB)}$ for MB adsorption is, however, very low and close to zero, 1.8×10^{-4} – 7.4×10^{-5} (listed Table 7), illustrating an irreversible adsorption, i.e., the adsorption of MB is very strong. As $R_{L(phenol)}$ is much higher than $R_{L(MB)}$, the adsorption of phenol is not as strong as the

adsorption of MB. This is in accord with the results obtained from the subsequent desorption studies, as a relative weak adsorption is good for desorption.

3.3. Desorption

A potential adsorbent for industrial application for the removal of organic wastes usually requires both excellent adsorption capacity and good desorption potential. Several conventional acid/alkali solutions (NaOH, HCl and HNO₃ solution) and organic solvents (methanol and acetonitrile), therefore, were employed for a preliminary desorption study (see Table 8).

Table 8. Impacts of solvent on the desorption ¹.

Solute	Adsorbed Content mg/g	Carbon Concentration (mg/L)	Desorption Solvent	Desorption Efficiency (%)	Irreversible Adsorption (%)
MB	1184	1667	DI water	1.7	98.3%
MB	1184	1667	0.1 mol/L HNO ₃	2.1	97.9%
MB	1184	1667	0.1 mol/L HCl	2.6	97.4%
MB	1184	1667	0.1 mol/L NaOH	<1	>99%
MB	1184	1667	Methanol	28	72
MB	1184	1667	Acetone	25	75
Phenol	205	1667	DI water	15.6	84.4
Phenol	205	1667	0.1 mol/L HNO ₃	21.5	78.5
Phenol	205	1667	0.1 mol/L HCl	31.2	68.8
Phenol	205	1667	0.1 mol/L NaOH	74.6	25.4
Phenol	205	1667	Methanol	98	2
Phenol	205	1667	Acetone	95	5

¹ Desorption conditions: MB or phenol adsorbed KOH800 were soaked in various desorption solvents at 30 °C for 2 h, with a shaking speed of 200 RPM.

The overall desorption of MB from the adsorbed KOH800 in the aqueous solution is low (desorption efficiency <3% or the irreversible adsorption >97%) disregards of the treatment aqueous solution (e.g., neutrality, acidity (0.1 mol/L HNO₃ or 0.1 mol/L HCl), alkalinity (0.1 mol/L NaOH). Organic solvents methanol and acetonitrile showed slightly higher desorption efficiency in comparison with the aqueous solution, 28% and 25%, respectively. These values, however, are still low. Thus, the MB adsorbed in the KOH800 cannot be recovered by solvent extraction and efficient desorption methods for the MB desorption needs to be developed. Desorption efficiency of phenol is much higher in comparison with that of MB, which is consistent with the results obtained on RL calculation above. The alkaline solution can more efficiently improve desorption of phenol from the adsorbed KOH800 compared to neutral and acidic aqueous solution, and the desorption efficiency can reach 74.6%. The desorption efficiency of phenol in the methanol and acetonitrile even reached 98% and 95%, respectively. Thus, methanol is a potential preferred desorption solvent, as almost all the phenol was removed from the activated carbon to the organic solvent, and recovered after low-temperature evaporation of methanol.

3.4. Adsorption Mechanism

The BET surface area of KOH800 reaches 1650 m²/g, which is higher than that of most activated carbons shown in Tables 1 and 2, even though it is not the highest, illustrating that the surface area of the KOH800 results in the good adsorption result. The surface area, however, is not the only factor that related to the excellent adsorption capacity for phenol and MB removal.

It has been reported that the size of adsorbents and the structure of solutes are critical factors that affect the adsorption efficiency [43]. The advantages of KOH800 are its pore structure and aperture. The SEM image showed that morphology of KOH800 is honeycomb-like, which can greatly improve the diffusion of solutes and the adsorption process. In addition, the pore size of KOH800 are mainly in the range of 0.6–2.4 nm diameter, accounting for approximately 68% of the total pore volumes (0.72 cm³/g) based on the Horvath-Kawazoe cumulative pore volume data (pore aperture from 0.5 to 100 nm, shown Figure 3).

The basic molecular dimensions of phenol are reported as 0.582 nm width, 0.453 nm depth, 0.152 nm thickness, respectively [55], and the phenol molecular diameter is 0.746 nm calculated by Lorenc-Grabowska's work [20]. In general, the pore width (or diameter) for slit pores (or cylindrical pores) should be wider than that of the solute molecules so that the solute molecule can diffuse into the pore and be adsorbed [55]. Pores with a diameter <0.582 nm, therefore, cannot adsorb the phenol effectively. According to the Spartan'14 calculation based on Space-filling model, the molecular volume of phenol is 0.1055 nm^3 . The BJH pore volume (1.7 nm–300 nm) in the fresh KOH800 and the KOH800 after MB adsorption were $0.32 \text{ cm}^3/\text{g}$ and $0.22 \text{ cm}^3/\text{g}$, respectively, indicating about 0.055 cm^3 ($=0.32 - (1 + 0.2046) \times 0.22$) per gram KOH800 of the initial mesoporous pore volume with aperture between 1.7 and 300 nm was filled or covered by the phenol. This volume ($0.055 \text{ cm}^3/\text{g}$) is equivalent to the total volumes of 0.52×1021 ($=0.055 \times 1021/0.1055$) phenol molecules (0.864 mmole or 81.3 mg phenol). In other words, about 39.7% ($=81.3/204.6$) of the phenol molecules were absorbed by the pores, with apertures from 1.7–300 nm, and the major part of the phenol molecules should be adsorbed by the micropores with aperture <1.7 nm. In fact, Lorenc-Grabowska et al. concluded that it is hard for micropores with a size <0.8 nm to absorb phenol, as the adsorption process is dominated by micropore filling mechanism involved the π - π dispersion in pores 1–2 times larger than phenol [20]. Thus, the phenol adsorption is dominated by the activated carbon with 0.75–1.5 nm pores size. Interestingly, the pores with 0.75–1.5 nm in diameter account for approximately $0.3 \text{ cm}^3/\text{g}$ ($0.3 \times 1021 \text{ nm}^3$) pore volume of KOH 800, which is capable for absorbing 2.84×1021 phenol molecules (4.72 mmole or 444 mg) assuming the phenol molecules are tightly packed. This value is much higher than the actual adsorption capacity of KOH800. In addition, the SEM image showed that the macropores (0.5–5 μm) in the KOH800 disappeared (Figure 1), indicating that the macropores also contributed to the adsorption of phenol.

The reported size of MB is 1.41 nm width, 0.55 nm depth and 0.16 nm thickness [43,56]. According to the Spartan'14 calculation based on Space-filling model, the molecular volume of MB is 0.297 nm^3 . Generally, the accessible pore size should be approximately at least 1.3–1.8 times greater than the dye molecule width [55]. Thus, main contribution for the outstanding MB adsorption should result from the pores with diameter larger than 1.83 ($=1.41 \times 1.3$) nm. The BJH pore volume with pore size 1.7–300 nm in the KOH800 after MB adsorption was $0.013 \text{ cm}^3/\text{g}$, indicating that about 0.292 ($=0.32 - (1 + 1.184) \times 0.013$) cm^3 of the initial pore volume with aperture $\geq 1.7 \text{ nm}$ per gram KOH800 was filled or covered by the MB. This volume (0.292 cm^3) is equivalent to the total volumes of 0.983×1021 ($=0.292 \times 1021/0.297$) MB molecules (1.63 mmole , or 521.4 mg). Thus, about 44.0% ($=521.4/1184$) MB molecules should be absorbed by the pores with aperture from 1.7 to 300 nm. Another major adsorption of the MB should be attributed to the macropores (aperture >300 nm) and the outer surface of the KOH800 (shown in Figure 1), as the honeycomb-like macropores were almost covered. The adsorption of MB on the macropores and surface probably resulted from the comparable high contents of acidic groups due to the dispersion forces resulted by π - π interactions [66]. As shown in Table 5, the KOH800 has a total acidic groups of 3.3 meq g^{-1} , which is relative high in comparison with the total acidic groups on activated carbons reported before [23,25,28,37,39,40]. In general, adsorption of MB can be governed by opposite effects in term of their physical and chemical processes [72], and acidic groups are preferred for MB adsorption. The impacts of the total acidic groups were also reflected by the adsorption performance of the KOH500, which had an extremely low pore volume ($0.025 \text{ cm}^3/\text{g}$). However, the KOH500 still exhibited a comparable MB adsorption capacity of 385 mg/g owing to the relative high density of acidic groups (3.0 meq g^{-1}) and moderate surface area ($428 \text{ m}^2/\text{g}$). Therefore, the superior MB adsorption capacity on the KOH800 can be explained by the comparable high surface area, good pore structures and high density of total acidic groups.

4. Conclusions

Humins, the major solid wastes from biomass hydrolysis, were found a potential material for activated carbon production with KOH activation from 500 to 900 °C. Although high temperature

can cause low yields (15%–39.2%), the activated carbons obtained at high temperature usually have high BJH pore volume, high BET surface area (428–1975 m²/g), and better adsorption capacity of N₂, phenol and MB. Both the adsorption of phenol and MB on the KOH800 complies with the Langmuir adsorption model with a pseudo-second-order kinetics, and the maximum adsorption capacity of phenol and MB reached 1195 mg/g and 218 mg/g, respectively. Methanol was found a potential solvent for phenol desorption and recovery, while efficient desorption methods for the MB desorption needs to be developed. The excellent MB adsorption capacity was attributed to the high surface area, high content of acidic active sites, and good pore structure. About 44.0% MB and 39.7% phenol absorption were contributed by the pores with apertures from 1.7–300 nm. The macropores and outer surface of the KOH800 are also primary impact factors for MB adsorption.

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