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 though 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 H₂SO₄         | 170 °C      | 21.0 wt. %    | [8]  |
| 18 g/L                | 0.1 M H₂SO₄         | 125 °C      | 29 wt. %      | [9]  |
| 270 g/L               | 0.055 M H₂SO₄       | 180 °C      | 36 wt. %      | [10] |
| 360 g/L               | 0.01 M H₂SO₄        | 220 °C      | 35 wt. %      | [11] |
| 50 g/L                | 0.05 g/L ZrPO₄      | 135 °C      | 29 wt. %      | [12] |
| ~50 g/L               | 0.5% H₂SO₄          | 175–180 °C  | 21 wt. %      |      |

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

| Raw Material          | Activation Methods                                      | Adsorption Temp. (°C) | Surface Area (m²/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 CO₂ | 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 K₂CO₃ impregnation activation at 800 °C | 40                    | 208                 |                            | [22]   |
| Eucalyptus seed husk  | NaOH/H₂SO₄ impregnation activation at 350 or 750 °C    | 20                    | 670–780             | 199                        | [23]   |
| Bamboo residues       | Carbonization at 500 °C, followed by K₂CO₃ impregnation activation 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                    | 183                 | 145                        | [28]   |
| Water hyacinth        | H₂SO₄ carbonization at 150 °C, followed by CO₂ stream activation at 700 °C | 30                    | 632.7               | 112.8                      | [29]   |
| Commercial activated carbon | -                                                      | R.T.                  |                     | 112.36                     | [30]   |
| Hazelnut bagasse      | ZnCl₂ 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 CO₂ 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 (m²/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          | ZnCl₂ impregnation activation at 500 °C         | 25               | 2050                | 435                       | [39] |
| Vetiver roots         | H₃PO₄ impregnation activation at 600 °C         | 25               | 1004-1272           | 423                       | [28] |
| Tomato waste          | ZnCl₂ impregnation activation at 600 °C         | 30               | 1093                | 400                       | [40] |
| Lignite               | ZnCl₂ impregnation activation at 450 °C         | 30               | 600                 | 370.37                    | [41] |
| Delonix Regia pods    | Microwave assisted ZnCl₂ impregnation activation | 62               |                     | 370                       | [42] |
| Granular activated carbon |                                    | -                | 1306                | 357.14                    | [43] |
| Salix psammophila     | H₃PO₄ impregnation activation at 550 °C         | 30               |                     | 347.13                    | [44] |
| Tea seed shells       | ZnCl₂ impregnation activation at 500 °C         | 20               | 1530.67             | 324.7                     | [45] |
| Dead leaves           | ZnCl₂ impregnation activation at 600 °C         | 45               | 1483                | 285.7                     | [46] |
| Bituminous activated carbon |                              | -                | 676.7               | 130.88                    | [25] |
| Activated carbons from coal, coconut shell, charcoal | | | | | |
| Aloe vera wastes      | Carbonization at 550 °C                         | 25               | >900                | 130-135                   | [35] |
| Tamarind seed         | H₃PO₄ 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 H₂SO₄ | 32               |                     | 62.5                      | [50] |
| Buch-ham bark         | Concentrated H₂SO₄ at 400 °C                   | 30-60            | -                   | 60.61-62.50               | [38] |
| Hull of Lophira Lancelot | Orthophosphoric acid impregnation activation at 400 °C | RT | - | 55 | [51] |
| Ficus carica bast     | Concentrated H₂SO₄ 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    | H₂SO₄ 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.
was added to each bottle, and then the adsorption was conducted in an isothermal shaker at 200 rpm (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].

2.2. 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-IIIA 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

| Table 4. Physicochemical Properties of phenol and MB [55,56]. |
|---------------------------------------------------------------|
| **Properties** | **Phenol** | **MB** |
| Chemical formula | C₆H₅OH | C₁₆H₁₂ClN₂S |
| Molecular weight | 94.11 (g/mol) | 319.85 (g/mol) |
| Acid-base properties | Acidic | Basic |
| Molecular structure | CH₃-Cl-N(k) |  |
| Three dimensions | 0.582 nm × 0.453 nm × 0.152 nm | 1.41 nm × 0.55 nm × 0.16 nm |
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:

\[ q_e = \frac{(C_0 - C_e)V}{M} \]  \hspace{1cm} (1)

\[ \text{Removal (\%)} = \frac{C_0 - C_e}{C_0} \times 100\% \]  \hspace{1cm} (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 change 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 m²/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.](image-url)
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 (m²/g) | BJH Pore Volume 1 (cm³/g) | Total Acidity (meq g⁻¹) | Total Basicity (meq g⁻¹) |
|-------------------------|----------------|-------------------------|---------------------------|-------------------------|--------------------------|
| Humins                  | -              | 5.7                     | 0.0045                    | -                       | -                        |
| Humins500               | 55.8           | 73.8                    | 0.014                     | 3.0                     | 0.17                     |
| 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  | -              | 927                     | 0.22                      | -                       | -                        |
| MB adsorbed KOH800      | -              | 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.
which were randomly arranged \[62,63\]. Figure 5 showed the FT-IR spectra of the KOH500–KOH900, (acidic solute) \[25,28\].

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 um) 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 2θ = 22° and 44° for all the activated carbons owing to the (002) and (100) planes of the carbon \[58–61\]. The broad peak at around 2θ = 22° 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) \[25,28\].
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 lesser loss of weight with the increase of pyrolysis temperature was observed.
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 absorbed 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) | $\Delta q$ (%) | $R^2$ | $k_2$ (g/mg h) | $q_{e,cal}$ (mg/g) | $\Delta q$ (%) | $R^2$ |
| 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           | 0.7197 | 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:

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

(3)

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

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

(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 $\Delta q$ (%) was also used to analyze the applicability of the two models, and the $\Delta q$ (%) is expressed as:

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

(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 $\Delta q$ 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 $R^2$, $\Delta q$, 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 adsorbtion 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.](image)

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]:

$$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{1}{q_m} C_e$$

(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   | $q_m$ (mg/g) | $K_L$ (L/mg) | $R^2$   | $R_L$ \(^1\) | $K_F$   | $n_F$ | $q_m$ |
|----------|--------------|--------------|---------|---------------|---------|-------|-------|
| MB       | 1195         | 6.787        | 1.000   | $7.4 \times 10^{-5}$ (1.8 \times 10^{-4}) | $8.4 \times 10^{-15}$ | 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 \([27]\):

$$\ln q_e = \ln K_F + \frac{1}{n_F} \ln C_e$$

(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 $8.4 \times 10^{-15}$ 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.

$$R_L = \frac{1}{1 + K_L C_0}$$

(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, $1.8 \times 10^{-4}$–$7.4 \times 10^{-5}$ (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 HNO₃     | 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 HNO₃     | 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, and 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 cm\(^3\)/g and 0.22 cm\(^3\)/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 cm\(^3\)/g) is equivalent to the total volumes of 0.52 \times 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 \(\pi-\pi\) 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 cm\(^3\)/g (0.3 \times 1021 nm\(^3\)) pore volume of KOH 800, which is capable for absorbing 2.84 \times 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 um) 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 cm\(^3\)/g, indicating that about 0.292 (=0.32 – (1 + 1.184) \times 0.013) cm\(^3\) of the initial pore volume with aperture \(\geq 1.7\) 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 \times 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 \(\pi-\pi\) 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 cm\(^2\)/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 m\(^2\)/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 m$^2$/g), and better adsorption capacity of N$_2$, 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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