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Preparation of activated carbon from paper mill sludge by KOH-activation

Hwa-Young Kang†, Sang-Sook Park* and Yu-Sup Rim**

Dept. of Civil and Environment, Hanyeong College, 19, Yeoseo-dong, Yeosu 550-704, Korea
*Division of Civil and Environmental Engineering, **Dept. of Bio-environmental Chemistry,
Sunchon National University, 315, Maegok-dong, Suncheon 540-742, Korea
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Abstract−The purpose of this study is the preparation of activated carbon using paper mill sludge collected from biological wastewater treatment plant. The char produced from pyrolysis of paper mill sludge was chemically activated with potassium hydroxide. A systematic investigation of the effect of activation agent ratio, activation temperature and time on the properties of the char was carried out in a rotary kiln reactor. The chemically activated carbons were characterized by measuring iodine and methylene blue number and specific surface area. The activated carbon prepared from char of paper mill sludge in this study had maximum iodine and methylene blue number of 726.0 mg/g and 152.0 mg/g, and specific surface area of 1,002.0 m^2/g, respectively. The result of estimation on adsorption capacities of metals, the Freundlich isotherms, yields a fairly good fit to the adsorption data, indicating a monolayer adsorption of metals onto activated carbon prepared from char of paper mill sludge using a potassium hydroxide as the activating agents.

Key words: Activated Carbon, Chemical Activation, Adsorption, Paper Mill Sludge

INTRODUCTION

Carbonaceous materials have been used as adsorbents since ancient times. Activated carbons are increasingly used as an economic and stable mass separation agent for the removal of surfactants to raise the final product quality in many industrial processes. Activated carbons also play an important role in many areas of modern science and technology such as purification of liquids and gases, separation of mixtures, and catalysis [Kenneth, 2002]. Adsorption of activated carbon is governed by the chemical nature of the aqueous phase, the solid phase, and the chemical nature of the adsorbing organic [Bilal et al., 1996; Kim et al., 2005].

Activated carbon can be prepared from a wide range of carbonaceous raw materials including peat, coal, lignite, wood and various agricultural by-products, by either a physical method or a chemical method [Jia and Aik, 2002]. The method of preparation, including the characteristics of the raw starting material, activation agents, activating process, etc., can strongly influence the microstructure of the carbons and hence their function.

The physical method consists of carbonization of the precursor followed by gasification of the resulting char in steam or carbon dioxide [Hsisheng et al., 1998; Satya Sai et al., 1997; Hong et al., 2000; Lee and Lee, 2001]. The formation of the porous structure is achieved by elimination of a large amount of internal carbon mass [Li-Yeh and Hsisheng, 2000]. The development of the porosity, i.e. the size and the ratio of the mesopores and micropores, is determined by the extension of the elementary graphitic crystallites [László et al., 1998]. The other method, chemical activation, is performed by carbonizing the raw material that has been impregnated with a chemical reagent such as zinc chloride, phosphoric acid and potassium hydroxide. Because of the dehydrogenation properties, the chemical reagents may promote the formation of cross-links, leading to the formation of a rigid matrix, less prone to volatile loss and volume contraction upon heating to high temperatures [Caturla et al., 1991; Jagtoyen et al., 1992].

Preparation of adsorbents from carbon materials precursors by potassium hydroxide activation was originally developed by the AMOCO Corporation in the late 1970s [Kenneth et al., 2002]. Since then, a number of works have systemically studied how to obtain high surface area and extraordinary adsorptive capacity activated carbon from raw materials with KOH activation [Ahmadpour et al., 1998; Tsai et al., 2001]. Otowa et al. [1990] developed high surface area (over 3,000 m^2/g) from a mixture of coconut shell or petroleum coke by chemical activation with KOH at 600-900 °C in an inert atmosphere. Hu and Stinivasan [1999] also prepared high-surface-area activated carbon, which was a BET surface area and pore volume of as high as 2,451 m^2/g and 1.21 cm^3/g, respectively. The prepared activated carbons exhibited a much higher adsorption capacity for phenol, 4-chlorophenol and it-nitrophenol from aqueous solution.

In this study, the effects of activation temperature and time, and impregnation ratio of potassium hydroxide-to-char on the quality of the activated carbon prepared from char of paper mill sludge were investigated. Ultimately, the research is identifying the proper activation conditions of char of paper mill sludge by analysis of iodine and methylene blue number and specific surface area on prepared activated carbon. Batch reactor adsorption of metals was also carried out to evaluate the adsorptive capacity of activated carbon prepared from char of paper mill sludge.

MATERIALS AND METHODS

1. Sample Preparation

Paper mill sludge waste from a biological wastewater treatment plant was used as the starting material. Fig. 1 shows a schematic

†To whom correspondence should be addressed.
E-mail: khy9792@hanmail.net

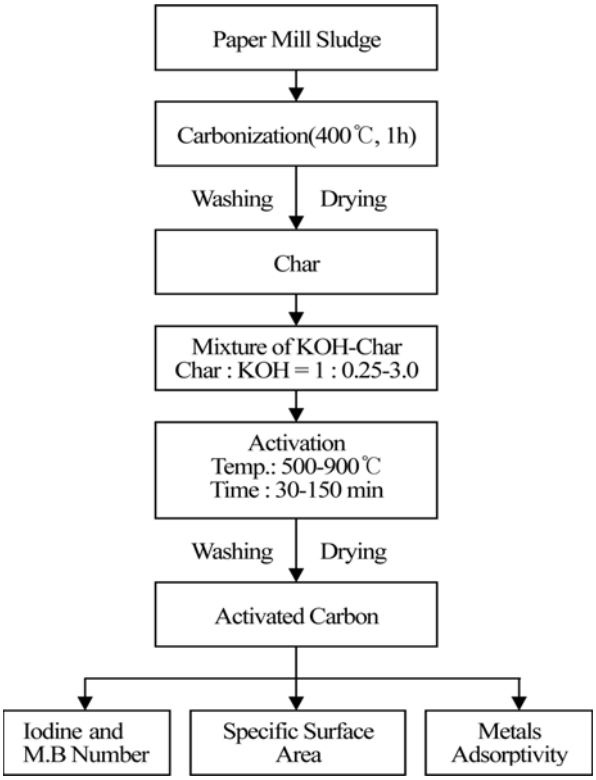

Fig. 1. Schematic representation for the preparation of activated carbon from paper mill sludge with potassium hydroxide.

representation for the preparation of activated carbon from paper mill sludge. The raw paper mill sludge was dried in an oven at 110 °C for 1 day and crushed mechanically by using a mixer. The crushed samples were sieved to obtain particles sizes of 1-2 mm to be suitable for the carbonization and activation process. The sieved paper mill sludge was carbonized by different temperature (200-600 °C), and than the carbonized samples were soaked with 3 N HCl at 80 °C for 1 h followed by washing with 500 ml of distilled water to remove residual tar and inorganic matter. The char of paper mill sludge pyrolyzed at 400 °C had the higher iodine number 216.0 mg/g and surface area of 279.7 m^2/g with yield of 34.1% as shown in Table 1. To ensure a complete reaction between activation agent and char, the char produced from suitable carbonization condition (400 °C, 1 h) was mixed with various amounts of KOH (ratios of KOH to char: 0.25, 0.5, 1.0, 2.0, and 3.0) at 90 °C for 2 h. The char mixed with various amounts of KOH was activated at 500-900 °C for 30-150 min. Upon completion of the activation with KOH, the activated products were soaked with 4% NaOH at 80 °C for 1 h, and followed by repeated washing with distilled water to remove residual potassium and inorganic matter, and air dried overnight at 100 °C.

Table 1. Iodine number, surface area and yield for char produced from pyrolyzed of paper mill sludge (pyrolysis time: 1 h)

Temperature (°C)	200	300	400	500	600
Iodine number	142.0	136.0	216.0	205.0	185.0
S_{BET} (m^2/g)	198.6	225.3	279.7	263.9	245.2
Yield (%)	42.1	38.3	34.1	31.2	26.6

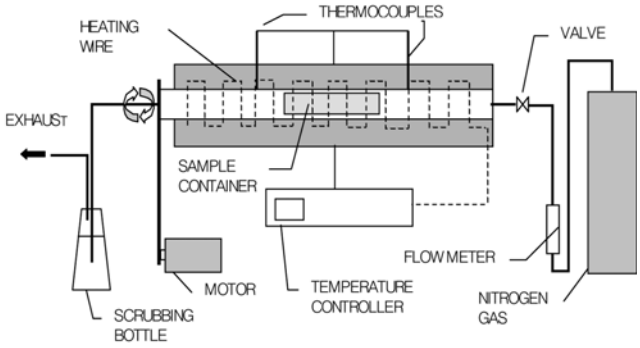

Fig. 2. Schematic diagram of rotary kiln reactor for pyrolysis of paper mill sludge.

After drying in air, the activated carbons were characterized by iodine and methylene blue number, specific surface areas, yields and metal adsorptivity.

2. Rotary Kiln Reactor

As shown in Fig. 2, a 160 cm long rotary kiln reactor of 7.5 cm o.d. and 7 cm i.d. was used to produce activated carbons from the paper mill sludge. The temperature of the carbonization and activation sections was raised to the required level before feeding materials. Reactor temperature was recorded by using type K thermocouples and can be raised to a maximum temperature of 1,200 °C. Pure nitrogen with a flow rate of approximately 100 ml/min was used as the inert gas flushing through the reactor right from the pyrolysis process. A condenser was connected to the other end of the reactor, and the condensed material was collected in a beaker.

3. Analysis Methods

The iodine and methylene blue number were determined by KSM 1802 (Korean Standard Methods 2000). Iodine number is defined as the number of milligrams of iodine adsorbed by 1 g of carbon when the equilibrium concentration in the supernatant liquor is 0.02 N. Methylene blue number is defined as the number of milligrams of methylene blue adsorbed per gram of carbon. Adsorption capacities of metals on the prepared activated carbons were determined by the standard method [Arnold et al., 1992]. For each experiment, 0.5 g of the prepared activated carbon was weighted and placed in 100 ml of Copper, Cadmium or Chromium solutions of desired concentrations (1-100 mg/*l*) and pH 6.0. Adsorption was carried out in a thermostatted bath shaken at 200 rpm at 20 °C for 2 h. After this time, the solution was filtered by membrane filter with 0.45 μm and the concentration of metal in each solution was measured by using Atomic Absorption Spectrophotometry (AA-6701G; Shimadzu Inc., Japan).

Specific surface area of activated carbon prepared from char of paper mill sludge was analyzed by N_2 adsorption/desorption isotherm at 77 K using a Quantasorb surface area analyzer (Quanta Chrome, USA). The Brunauer, Emmett and Teller (BET) surface area was calculated by using the adsorption data in a relative pressure of 0.30 [Gregg et al., 1982]. Total pore volume was automatically calculated from the amount of N_2 vapor adsorbed at a relative pressure about 0.95. The Thomas. and Thomas [1997] method was employed for determination of the pore size distribution. This method employs the Kelvin equation for determination of the pore size distribution and assumes a cylindrical pore shape.

RESULTS AND DISCUSSION

1. Impregnation Ratio and Activation Temperature

Among the activating agents used for the prepared of activated carbon from carbon materials, KOH has been proven to be one of the most effective chemical activators [Otowa et al., 1990; Hu and Srinivasan, 1999]. Therefore, we performed for the char that had been impregnated with a potassium hydroxide. The temperature and time range of activation employed in the present study were 500-900 °C and 60 min. The adsorption properties of activated carbons are determined to a substantial extent by their pore structures [Dubinin, 1996]. In view of such correlations, iodine and methylene blue numbers as well as specific surface area were measured for the prepared activated carbon. A high specific surface area is a primary requirement for an activated carbon for gas treatment; nevertheless, the need for large pores for purification of water is also important. Iodine number represents the surface area contributed by pores larger than 10 Å [Satya Sai and Jaleel, 1997]. Methylene blue is a relatively large 'colour body' molecule. Therefore, iodine number provides a good indication of the capacity of an activated carbon for sorption of pollutants of small molecule size from water; the other side, methylene blue provides an indication of the capacity of an activated carbon to remove organic compound adsorption (microcystin, alpechine, colour bodies, etc.) from water.

Fig. 3 shows the effect of impregnation ratio of potassium hydroxide-to-char and activation temperature on development of iodine and methylene blue number of the activated carbon prepared from char of paper mill sludge. Higher iodine (above 600) and methylene blue (above 120) numbers can be obtained when the experiments are conducted at 700 °C and 800 °C for impregnation ratio of potassium hydroxide-to-char of 1.0 as shown in Fig. 3. It indicates insignificant activation at lower temperature and impregnation ratio of potassium hydroxide-to-char of below 0.5. The iodine and methylene blue number of activated carbon prepared by activation at 500-600 °C are lower but reach a maximum at 700 °C. The increase of iodine and methylene blue number by raising the activation temperature from 600 °C to 700 °C can be attributed to the release of tar. For activation at 800-900 °C, the decreases of adsorptive capacity may induce a shrinkage in carbon structure, resulting in a reduction in porosity [Ibarra et al., 1991]. That is, a higher temperature (800-900 °C) resulted in severe activation that had a detrimental impact on the development of porosity on activated carbons. Therefore, we identify that pore development was due to the activation reactions between char and potassium hydroxide at the appropriate temperature (700 °C).

For investigation of the effect of activation temperature and impregnation ratio of potassium hydroxide for properties of resulting activated carbon, we identify that temperature and KOH-impregnation ratio play an important role on development of iodine and methylene blue number of the chemically activated carbons. Fig. 4, also, shows that the activated carbon prepared from char impregnated of potassium hydroxide of 1.0 ratio in the rotary kiln reaction systems operated at 700 °C had a higher iodine and methylene blue number, and specific surface area of 726.0 and 124.0, and 1002.0 m^2/g with yield of 15.7%. It shows the impregnation ratio of potassium hydroxide-to-char of 1.0 was found to be the optimum ratio for activated carbons. This indicates insignificant activation at impregnation ratio of potassium hydroxide-to-char of below 0.5 and above 2.0. With raising the ratio of potassium hydroxide to char from 0.5 to 1.0, the increase of iodine and methylene blue number,

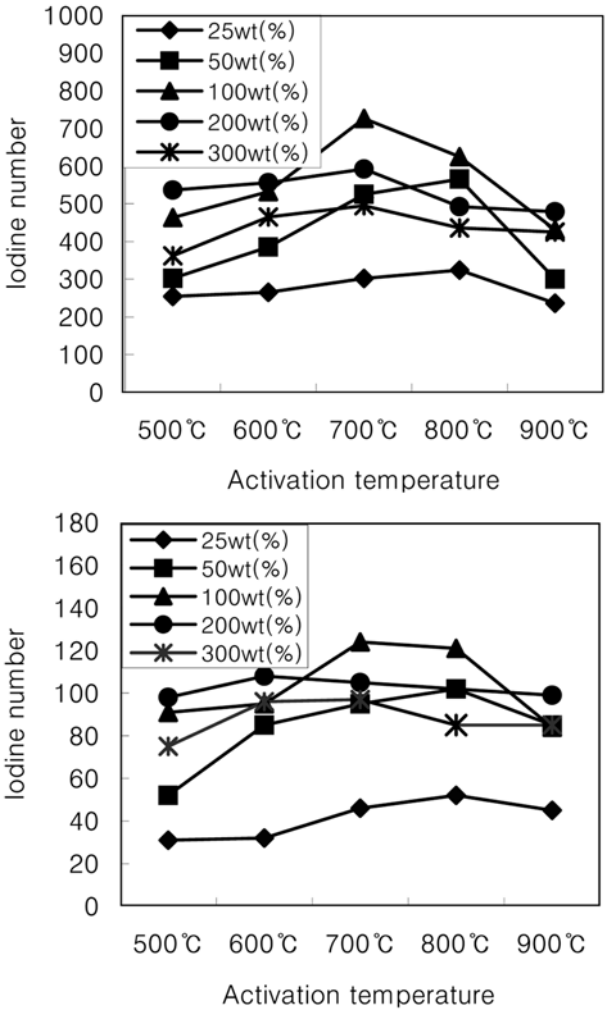

Fig. 3. Effect of activation temperature and impregnation ratio of potassium hydroxide-to-char on development of iodine and methylene blue number (activation time: 1 hr).

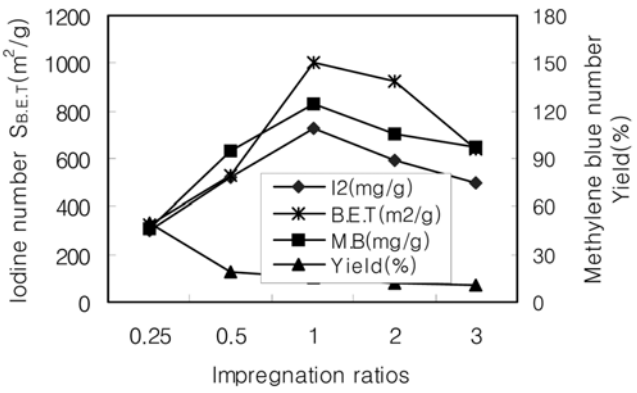

Fig. 4. Iodine and methylene blue number, specific surface area, and yield as a function of impregnation ratio of potassium hydroxide-to-char at 700 °C (activation time: 1 hr).

and specific surface area can contribute to a number of new microporosity creations and the widening of microporosity into the range of mesoporosity. For impregnation ratio of potassium hydroxide-to-char of above 2.0, the decreases of adsorptive capacity can be attributed to the severe release of tar result from severe activation of char, resulting in a larger widening of porosity. An activation temperature of 700 °C and impregnation ratio of 1.0 for KOH activation has also been recommended by Ahmadpour and Do [1996] in the preparation of activated carbons from coal by chemical activation. With increasing ratio of potassium hydroxide to char from 0.25 to 3.0, the overall yield of the activated carbons decreased as a result of accelerated activation. This can be attributed to the fact that volatile evolution, carbon oxidation to create porosity and carbon gasification are enhanced by the increase in impregnate ratios, leading to the increase in weight loss after the washing steps to remove residual potassium and inorganic matter.

2. Activation Time

Activation time is one of the important parameters for the production of activated carbon. In the present study, Fig. 5 shows the effect of activation time on development of iodine and methylene blue number, yield, and specific surface area of the activated carbon prepared from char of paper mill sludge at 700 °C for potassium hydroxide ratio of 1.0. As the activation time increases, the iodine and methylene blue number, and the specific surface area also increase, in that the result passes through a maximum adsorption capacity. Fig. 5 shows that the activated carbons by potassium hydroxide in a rotary kiln reactor had iodine number of 462.0 and methylene blue number of 92.0, and specific surface area of 749.0 m^2/g with yield of 45.8% for activation time of 30 min at 700 °C, compared with methylene blue number of 124.0 and a maximum iodine number of 726.0 and specific surface area of 1,002.0 m^2/g with yield of 15.7% for activation time of 60 min at 700 °C. Prolonging activation time from 30 to 60 min at 700 °C, from the increase of adsorptive capacity it seems that both microporosity and the larger pores develop, presumably by widening of micropores to mesopores and more micropores are being opened. For longer activation times from 60 min to 90 min, a decrease of iodine number and specific surface area was observed, whereas the methylene blue number increased from 124.0 to a maximum of 152.0 with a decrease in yield from 15.7% to 14.2% at 700 °C. This implies that longer activation times are necessary for the enlargement of the pores to convert activated carbons having maximum iodine number and specific surface area into activated carbons with maximum methylene blue numbers. For activation time of above 120 min at 700 °C, the overall decrease of the iodine and methylene blue number, and specific surface area was observed as a result of development of macropores due to coalescence or widening of micropores, and burnt out of the pores at higher reaction times.

The activated carbon prepared from char of paper mill sludge shown Fig. 5 has a lower iodine number than the corresponding specific surface areas. These data suggest that moderate portions of microporosity developed in the activated carbons occupied microporous structure of 3.6-10 Å, because N_2 surface area represents pores larger than 3.6 Å, compared with iodine number representing pores larger than 10 Å. Comparing the number of methylene blue with the iodine, the prepared activated carbons showed greater adsorptive capacity for iodine over methylene blue dye. The same type of result was seen in the work of Robert and Nosa [1996]; they explained the result by the size of the iodine molecule, which is much smaller than the double aromatic ring molecule of the methylene blue structure, and thus could occupy more of the smaller pores in the prepared activated carbon. As shown in Fig. 6, the activated carbon prepared from paper mill sludge in the present study mostly exhibits a smaller pore size distribution as a result of the oxidation reaction catalyzed from potassium hydroxide and release of tar.

3. Adsorption of Metals

When a solution is contacted with a solid adsorbent, molecules of adsorbate transfer from the fluid to the solid until the concentration of adsorbate in solution is in equilibrium with the adsorbate on the solid. The equilibrium data at a given temperature are usually represented by an adsorption isotherm, which is the relationship between the quantity adsorbed per unit mass of solid and the concentration of adsorbate in solution. Metals, i.e., copper, cadmium and chromium, were chosen as adsorbates to evaluate the adsorptive capacity of the activated carbon prepared from char of paper mill sludge. Activated carbon with iodine number of 726.0 and meth-

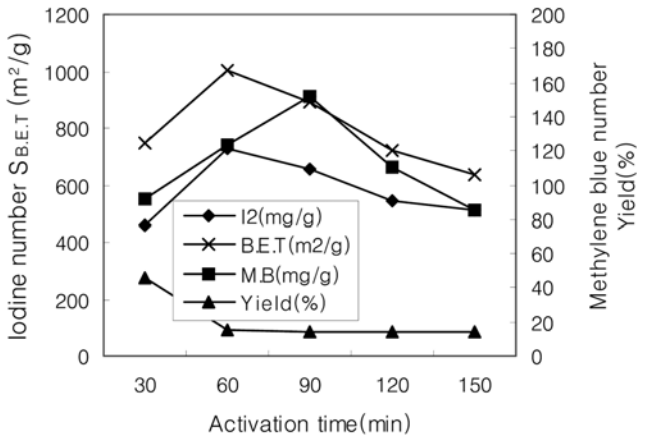

Fig. 5. Iodine and methylene blue number, specific surface area, and yield as a function of activation time at 700 °C (ratio of potassium hydroxide-to-char of 1.0).

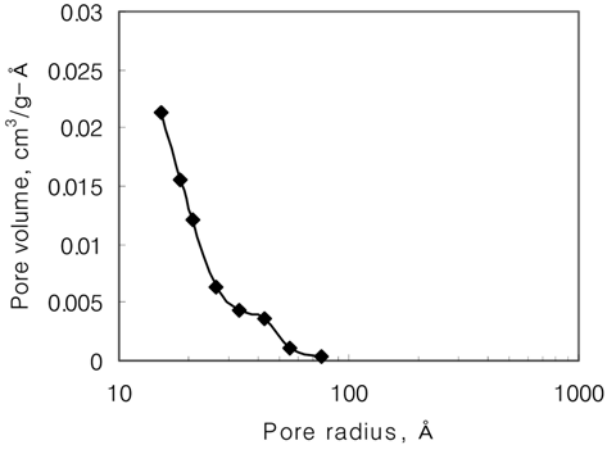

Fig. 6. Pore size distribution curve of activated carbon produced from activation at 700 °C for 60 min by using impregnation ratio of potassium hydroxide -to-char of 1.0.

ylene blue number of 124.0, and specific surface area of 1,002.0 m^2/g was tested as the adsorbent for metals. To estimate adsorption capacities of metals, the Freundlich model, which is the most commonly encountered model used to describe the adsorption of a material from solution, was employed:

$$x/m=K_f C_e^{1/n}$$

where, x is mass of material adsorbed on solid phase (g), m is mass of solid on which adsorption is taking place (g), K_f is the Freundlich adsorption coefficient, C_e is concentration of material being adsorbed remaining in solution at equilibrium (g/m^3), n is empirical coefficient. In the case of the Freundlich model, a higher K_f means a higher of adsorption capacity of adsorbent and an n coefficient of 2-10 means easy adsorption on adsorbent, while an n coefficient of below 0.5 means that adsorption is difficult.

The parameters of isotherm models, together with the Freundlich equations, are listed in Table 2. The order of activated carbon-metals affinity in adsorption was identified as Cu>Cd>Cr. In particular, we identify that the activated carbon prepared in the present study has a higher adsorption capacity for copper resulting from relatively higher K_f of 107.9692 and n coefficient of 2.1753. Fig. 7 shows that the Freundlich model, indicating monolayer adsorption, yields a fit expressly for metals adsorption on prepared activated carbons.

CONCLUSION

From the results of the studies reported here, it can be concluded that activated carbons with moderate surface areas and adsorptivity can be produced from char of paper mill sludge by using potassium hydroxide as the activating agent. Based on the experimental observations, it was identified that the temperature and impregnation ratio of activating agents have the greatest influence on the quality of the activated carbon during the activation step. Increase in reaction time also resulted in better activation. However, a higher temperature (800-900 °C) resulted in severe activation that had a detrimental impact on the development of porosity on activated carbons, and for higher impregnation ratio (above 2.0), decreases of adsorptive capacity were observed, which can be attributed to the severe release of tar resulting from severe activation of char, and resulting in a larger widening of porosity. Longer reaction times, also, resulted in decreased adsorptivity, which was due to coalescence or widening of previously formed pores. Activated carbon which had a maximum iodine number of 726.0 and specific surface area of 1,002.0 m^2/g was prepared from activation at 700 °C for 60 min by using potassium hydroxide-to-char of 1.0, whereas activated carbon which had a maximum methylene blue number of 152.0 was prepared from activation at 700 °C for 90 min. The adsorption isotherm of metals on activated carbon, with iodine number of 726.0 and methylene blue number of 124.0, and specific surface area of 1002.0 m^2/g, was identified as a fairly good fit of the Freundlich model indicating monolayer adsorption.

Table 2. Parameters of metals adsorption isotherms (at 20 °C) on prepared activated carbons according to the freundlich equations

Metals	Equation	K_f	n
Copper	Y=0.4597x+2.0333	107.9692	2.1753
Cadmium	Y=0.5597x+1.5228	33.3272	1.7866
Chromium	Y=0.7860x+0.0560	1.1376	1.2722

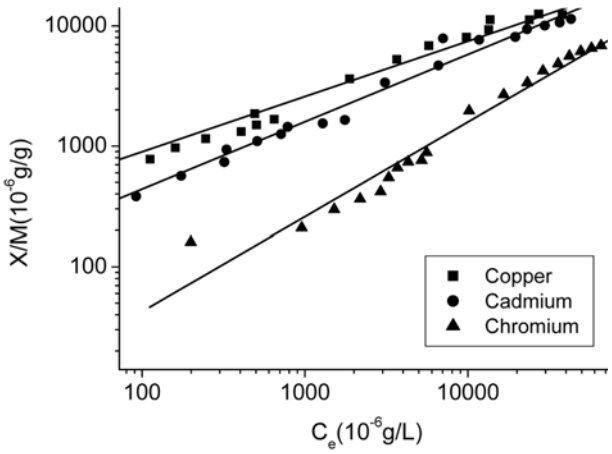

Fig. 7. Freundlich adsorption isotherms of metals on the activated carbon prepared from char activated at 700 °C for 1 hr by using impregnation ratio of potassium hydroxide-to-char of 1.0.

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