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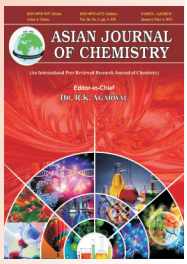

Preparation and Fractal Research of Activated Carbon from Sludge with $ZnCl_2/CuCl_2$ as Activating Agent

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Activated carbon was prepared with sewage sludge as raw material and $ZnCl_2/CuCl_2$ as activating agent by low tempertaure carbonization method. The optimum preparation conditions were activation temperature 534 °C, activation time 60 min, $ZnCl_2$ concentration 3 mol/L, $CuCl_2$ concentration 0.3 mol/L, the iodine adsorportion value was 534 mg/g. The prepared sludge carbons have a large amount of micropores, also have mesopores and macropores, with a BET surface area at 784.89 m^2/g and a Langmuir surface area at 1053.69 m^2/g. Adsorption of pharmaceutical wastewater on sludge activated carbon was conducted. The data were fitted by Freundlich equation. The sludge activated carbon had fractal characteristics, the iodine adsorportion value grow with the fractal dimension and the roughness.

Keywords: Activated carbon from sludge, Preparation, Fractal dimension, Adsorption.

INTRODUCTION

Preparation of activated carbon using excess sludge of sewage treatment plant, not only solves the covering problem of sludge disposal process, but also realizes the resource utilization of waste. Sludge activated carbon preparation and application has become a hot research topic at home and abroad. Methods for the preparation of activated carbon include chemical activation method[1,2], physical activation method[3] and chemical and physical activation method[4,5]. The effect of chemical activation method is relatively preferable, but the shortcoming of traditional chemical activation method rests with activator itself or activation process producing corrosive materials, which can corrode equipment and pollute environment. Because organic matter content from sludge itself is relatively low, by physical activation method the effect of preparation of activated carbon using sludge as raw material is unsatisfactory. While, physical and chemical activation method will be carried out in the high temperature, demand of protective gas is much more and the production process is quite complex, the production cost is relatively high.

This study chooses $ZnCl_2$ and $CuCl_2$ to prepare the composite activating agent, prepares activated carbon by low temperature carbonization and mesothermal activation method. At the same time, the study still researches the fractal characteristics of samples, in order to provide theoretical basis for its industrial application.

EXPERIMENTAL

Zinc chloride, hydrochloric acid, iodine and potassium iodide, soluble starch, sodium thiosulfate and chloride, which all are analytically pure. It still includes TOC tester, tubular resistance furnace, the pH tester, *etc*.

The experimental sludge is from some sewage treatment plant in Chongqing, whose moisture content is 74.58 %, ash content is 57.13 %, content of organic matter is 39.25 %. The experimental wastewater is from the waste water after UASB treatment of some pharmaceutical factory in Chongqing, the concentration of COD is 200-1100 mg/L, pH value is 8-9.

Preparation of activated carbon from sewage sludge: Add 2 % sawdust (mass fraction) in air-dry raw sludge natural to increase the carbon content, prepare it according to m (solid): m (liquid) = 1:2 ratio and dip it in $ZnCl_2/CuCl_2$ solution with a certain concentration for 12 h. After drying, put it into tube resistance furnace, conduct carbonization and activation under the protection of nitrogen. And then, naturally cool it to room temperature under the protection of nitrogen. Clean it with dilute hydrochloric acid until the solution is clear, then washing it to neutral with hot distilled water. Dry it to constant weight in a drying box to obtain the sludge activated carbon.

Structure determination: Using ASAP2010 specific surface area of hole diameter analyzer from the United States Micromeritics company, using liquid nitrogen as the carrier, determine the adsorption isotherm of nitrogen of the sludge

activated carbon at 77.3 5 K. The samples and KBr are grinded and flaked. Measure them by Japan's SHIMADZU IR Prestige-21 Fourier transform infrared spectroscopy instrument and determine the surface functional groups of activated carbon from sewage sludge.

Pharmaceutical wastewater treatment: Weigh some sludge activated carbon samples and add it into several 250 mL conical flask with plug. Add 100 mL pharmaceutical wastewater with known concentrations in each conical flask, oscillate them for a period of time at 35 °C, filtrate them after reaching adsorption equilibrium, detect COD detection and TOC concentration of the filtrate. Measure the treatment effect of activated carbon on pharmaceutical wastewater with the removal rate of COD and TOC after adsorption.

Performance evaluation method: The determination methods of iodine adsorption value of sludge activated carbon, moisture content and ash content are in accordance with GB/T 2496.8-1999 (determination standard of iodine adsorption value), GB/T 12496.3-999 (determination of ash content) and "GB/T 12496.4-1999 (determination of moisture content). The determination of solution COD is in accordance with GB 11914-89 (potassium dichromate method). TOC is determined by TOC measuring instrument.

RESULTS AND DISCUSSION

Adsorption isotherms of sludge activated carbon: According to B-D-D-T classification[6], adsorption isotherms of sludge activated carbon obtained belongs to type I isotherm (Fig. 1). When the relative pressure is closes to 0.1, adsorption quantity of sample is close to saturated. When the relative pressure is greater than 0.1, with the increase of pressure, the adsorption amount increases slowly. This indicates when the relative pressure is low, adsorption is mainly from micropore, at the same time, the sample also contains a certain amount of mesopores and macropores. Table-1 shows the specific surface area of sludge activated carbon.

IR spectra of sludge activated carbon: FTIR spectra of sludge activated carbon is as shown in Fig. 2, 3450-3400 cm^{-1} is the stretching vibration absorption peak of O-H key, 1100-1000 cm^{-1} is the stretching vibration absorption peak of C-OH key, at 1600 cm^{-1} there appears the stretching vibration absorption peak of C==C key and C==N key. Therefore, sludge activated carbon may contain C, H, O, N elements and after the activation they form C==C, C-OH, C==N structure.

Preparation of sludge activated carbon

Effects of activation temperature: Under the conditions of activation time being 60 min, the concentration of $ZnCl_2$ being 3 mol/L and the concentration of $CuCl_2$ being 0.3 mol/L, change the activation temperature, investigate the effect of activation temperature on the iodine value. Fig. 3 shows that the effect of activation temperature change on iodine value is quite obvious. At 400-600 °C, the change of iodine value is

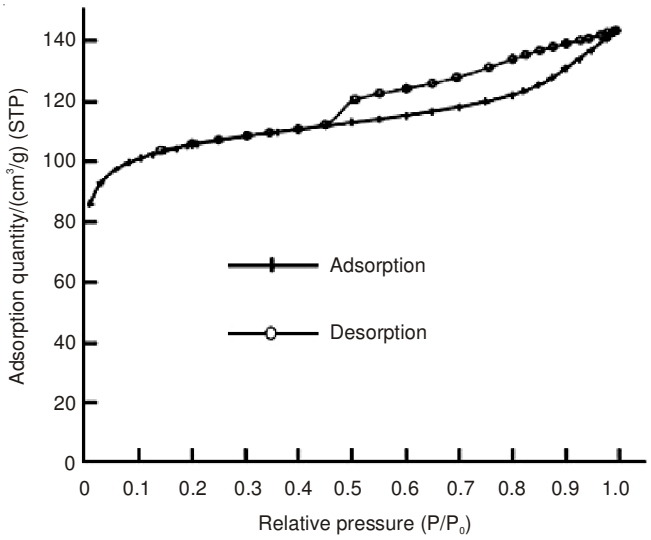

Fig. 1. N_2 adsorption isotherms of sludge activated carbon at 77 K

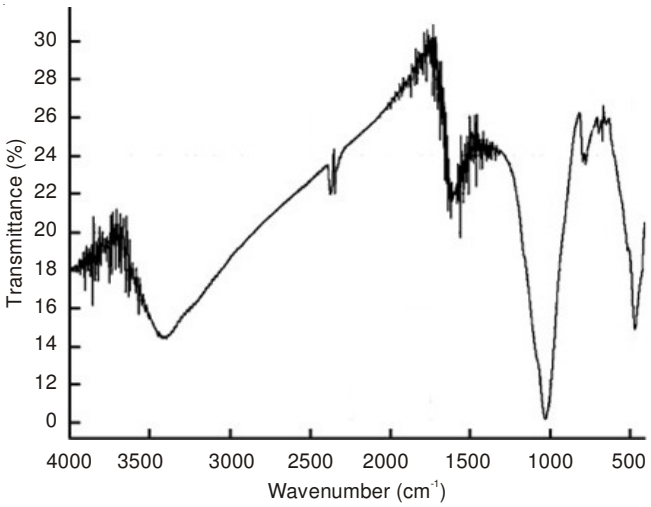

Fig. 2. IR spectra of sludge activated carbon

near 250 mg/g, at 500 °C iodine value can achieve the best. With increasing activation temperature, volatile components increase continually, the etching effect of $ZnCl_2$ and $CuCl_2$ increases. Close to 500 °C, $CuCl_2$ achieves its melting point and its etching effect is further strengthened. New pore structure becomes much more abundant. In the course of temperature rising from 400 °C to 500 °C, form abundant micropore, adsorption capacity is enhanced. With increasing temperature sequentially, micropore wall is burn through, part of micropores are expanded into mesopores or macropores, as a result, their specific surface area is reduced, the iodine adsorption value is also decreased.

Effects of activation time: In the conditions of the activation temperature being 500 °C, concentration of $ZnCl_2$ being 3 mol/L and $CuCl_2$ concentration being 0.3 mol/L, examine the effect of activation time on iodine value. Fig. 4 shows that

TABLE-1
SPECIFIC SURFACE AREA OF SLUDGE ACTIVATED CARBON

Sample	BET specific surface area (m^2/g)	Micropore specific surface area (m^2/g)	Langmuir specific surface area (m^2/g)	Mean pore size (Å)	Micropore volume (m^3/g)
AC-1	784.89	558.52	1053.69	21.64	0.26

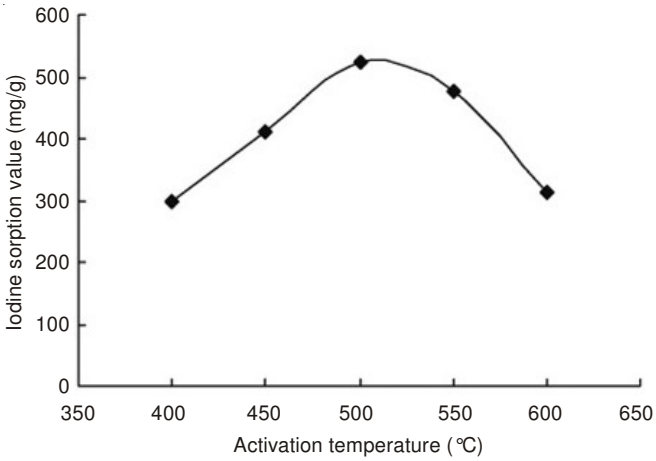

Fig. 3. Effects of activation temperature on iodine value

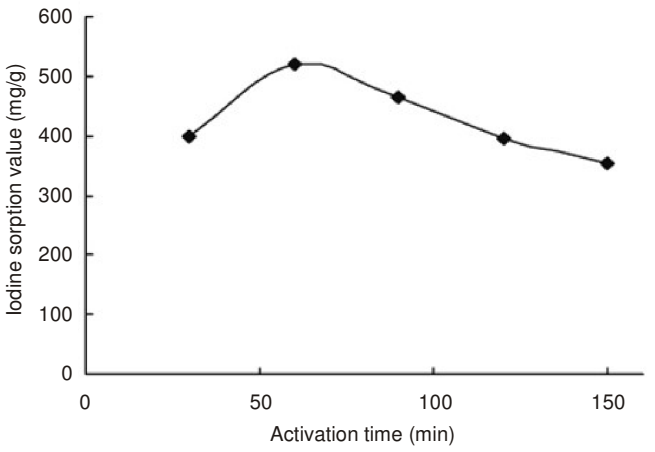

Fig. 4. Effects of time temperature on iodine value

with the increase of activation time, the etching of $ZnCl_2$ and $CuCl_2$ will make the inside of carbon particles form more and more micropore, the micropore surface area also increases gradually, so that the iodine adsorption value increases. When the activation time is more than 1 h, due to activation time being prolonged, part of micropore is extended to mesopore and macropore, which results in a corresponding reduction in the iodine adsorption value.

Effects of $CuCl_2$ content: Under the conditions of the activation temperature being 500 °C, activation time being 60 min, the concentration of $ZnCl_2$ being 3 mol/L, change the concentration of $CuCl_2$, investigate the influence of changing $CuCl_2$ content on iodine value. From Fig. 5 we can find that when $CuCl_2$ concentration is 0.3 mol/L, the best iodine adsorption value can be achieved, when the concentration is lower, the effect of forming hole is not obvious, while the concentration is larger, pore blockage is easily caused, at the same time, large amount of Cl^- can also make aperture generate horizontal expansion and form macropore[7].

Effects of $ZnCl_2$ content: Under the conditions of the activation temperature being 500 °C, activation time being 60 min, $CuCl_2$ concentration being 0.3 mol/L, change the concentration of $ZnCl_2$, investigate the influence of changing $ZnCl_2$ content on iodine value. From Fig. 6 we can find that with the increase of $ZnCl_2$ content, iodine adsorption value increases, when $ZnCl_2$ concentration reaches 3 mol/L, the

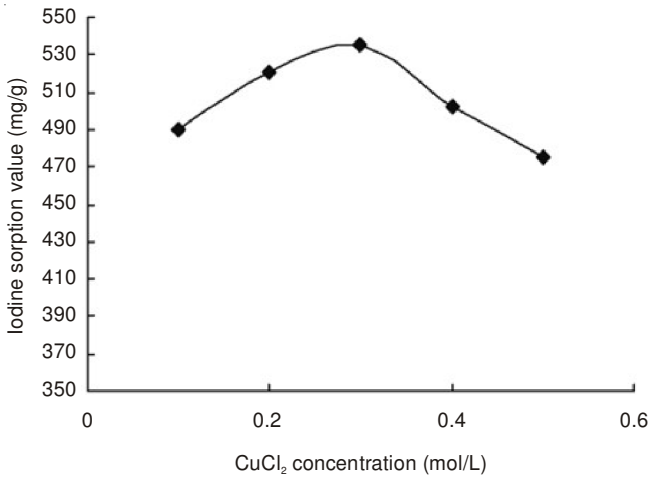

Fig. 5. Effects of $CuCl_2$ contenton iodine value

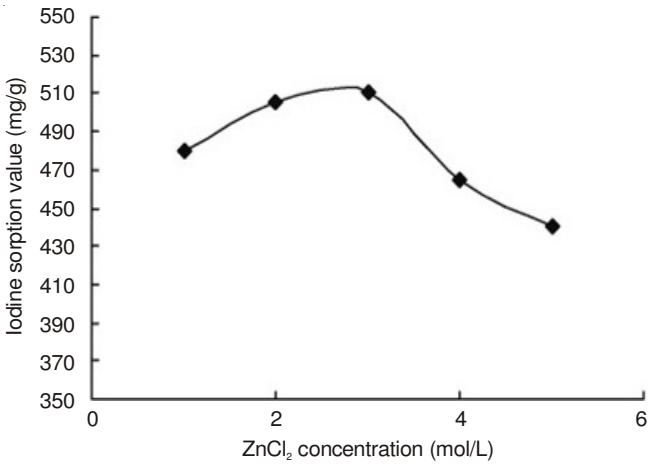

Fig. 6. Effects of $ZnCl_2$ content on iodine value

iodine adsorption value can obtain the maximum value, with $ZnCl_2$ concentration increasing sequentially, $ZnCl_2$ can make partial pore blockage and in the washing process they can not be fully removed, which make the adsorption ability decline [8].

Orthogonal experiment: Using the orthogonal experimental design of four factors and three levels, study the effect of activation temperature, concentration of $ZnCl_2$, concentration of $CuCl_2$ and activation time on iodine adsorption value. By single factor experiment and orthogonal experiment, the optimum technological conditions for the preparation of sludge activated carbon using $ZnCl_2/CuCl_2$ composite activation method is that activation temperature is 500 °C, activation time is 60 min, the concentration of $ZnCl_2$ is 3 mol/L, the concentration of $CuCl_2$ is 0.3 mol/L, the iodine adsorption value reaches 534 mg/g. According to the influence degree of the conditions on adsorption effect, from high to low in the order: activation temperature > activation time > $ZnCl_2$ concentration > $CuCl_2$ concentration.

Fractal dimension of sludge activated carbon

Establishment of adsorption isotherm equation: Take 0.8 g sludge activated carbon samples, put it into five groups 250 mL conical flasks and then add waste water with the COD initial concentration being 200, 400, 600, 800 and 1000 mg/L,

TABLE-2
THE LANGMUIR AND FREUNDLICH EQUATION PARAMETERS OF SLUDGE ACTIVATED CARBON ON COD AND TOC

Processing object	Langmuir equation			Freundlich equation		
	b	$1/Q_m$	R^2	K	1/n	R^2
COD	0.0036	0.0067	0.8710	1.4048	0.7106	0.9645
TOC	0.0050	0.0229	0.9931	0.3256	0.8366	0.9976

respectively and the corresponding TOC concentration being 51.8, 79.62, 107.14, 137.93 and 169.49 mg/L, respectively. Put the five groups of samples into a homothermal oscillator, oscillate for 240 min at 35 °C (by the previous experiment, the adsorption equilibrium has been reached at 150 min). After oscillation and adsorption, filter the solution and determine the concentration of the filtered COD and TOC. The calculation of adsorption capacity of COD and TOC is shown as formula 1.

$$q = V(C_0\text{-}C)/W \quad (1)$$

While: q-the equilibrium adsorption capacity, mg/g; V-organic waste water volume, L; C_0, C-the initial and equilibrium concentrations of organic pollutants as adsorbent in wastewater, mg/L; W-the quality of sludge activated carbon, g.The fitting results of adsorption isotherm model are shown in Table-2.

The result in Table-2 indicates that the adsorption isotherm model is more suitable for Freundlich equation[9-10].

$$\text{Langmuir: } C_e/Q_e = 1/(Q_m b) + C_e/Q_m \quad (2)$$

$$\text{Freundlich: } \text{In}Q_e = \text{In } k + (1/n)\text{In } C_e \quad (3)$$

While: C_e-solute mass concentration of adsorption equilibrium, mg/L; Q_e-adsorbent adsorption capacity of adsorption equilibrium, mg/g; Q_m-saturated adsorption capacity of single molecular layer, mg/g; b-Langmuir constant, l/mg; k-Freundlich constant; 1/n-the index of Freundlich equation.

Determination of the fractal dimension of sludge activated carbon: Fractal adsorption model is based on fractal Freundlich formula[10]:

$$I/n = D\text{-}2 \quad (4)$$

While: D-The fractal dimension value.

The parameters of Freundlich equation and the formula (4) obtained can calculate the fractal dimension of sludge activated carbon, in the course of activated carbon adsorbing COD and TOC, fractal dimension is 2.7106 and 2.8366, respectively, they are within the range of the surface fractal dimension. This shows that the surfaces of sludge activated carbon have fractal characteristics, both COD and TOC adsorption process occurs in the fractal surface.

In the function of single $ZnCl_2$ activation agents, a relationship between the iodine adsorption value of the sample obtained at different activation temperature and the fractal dimension D is shown in Table-3. Adsorption properties with fractal dimension changes regularly, namely the surface roughness of activated carbon increases, the adsorption properties is much stronger.

TABLE-3
INFLUENCE OF PREPARATION TEMPERATURE ON ADSORPTION PROPERTIES AND FRACTAL DIMENSION

Temp. (°C)	450	500	550	600	650
Iodine sorption value (mg/g)	237	303	382	326	242
Fractal dimension D	2.21	2.32	2.45	2.35	2.22

Conclusion

With excess sludge of sewage plant as raw material, use $ZnCl_2/CuCl_2$ compound activator to prepare sludge activated carbon, under the conditions of activation temperature being 500 °C, activation time being 60 min, $ZnCl_2$ concentration being 3 mol/L, $CuCl_2$ concentration being 0.3 mol/L, the iodine adsorption value reaches the 534 mg/g. BET specific surface area of the sludge activated carbon prepared is 784.89 m^2/g, Langmuir specific surface area is 1053.69 m^2/g, mainly comprises micropore, also contains some mesopore and macropore. According to the index of the Freundlich equation fitted out and fractional Freundlich formula, the fractal dimension of sludge activated carbon can be calculated out, which is 2-3. This proves that the sludge activated carbon has fractal characteristics, both COD and TOC adsorption process occurs in the fractal surface.

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