

Preparation of adsorbents made from sewage sludges for adsorption of organic materials from wastewater

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Abstract

The carbon-bearing adsorbents were prepared from biochemical and surplus sludges by physical activation and chemical activation. The results indicated that the adsorbents made by way of chemical activation were better, with the optimum activator being complex of $ZnCl_2$ and H_2SO_4 . Moreover, the optimum preparation conditions were concentration of two activators 5 mol/L (the ratio of $ZnCl_2$ and H_2SO_4 was 2:1), at the activating temperature of 550 °C, in the proportion of solid to liquid 1:2.5, in a period of 2 h. Contrasting the active carbon, the carbon-bearing adsorbents were characterized by X-ray diffraction (XRD), energy dispersive X-ray spectrometer (EDS), scanning electron microscope (SEM), BET and BJH. By application of those adsorbents to treatment of wastewater of urban, the treatment effect of the carbon-bearing adsorbents were better than the active carbon. On the condition that the concentration was 0.5%, the COD, *P* and chromaticity color removal rates of carbon-bearing adsorbent made from the biochemical sludge of sewage were higher, which were 79.1, 98.3 and 87.5%, respectively, and the dynamic adsorption capacity was 47.8 mg/g.

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1. Introduction

Growing concerns about the environment have resulted in the development of new environmentally technologies, new materials, and new ways to reduce and minimize wastes [1–4]. One of the wastes produced by contemporary society in abundant quantity is municipal sewage sludge. Activated sludge process is the high class processing technique that deals with wastewater of urban and industry, which produces a great deal of surplus sludge at the same time. Various methods have been used to dispose of or utilize municipal sewage sludge, including incineration, land filling, road surfacing, conversion to fertilizer, compression into building blocks, et al [5–8]. Continuous increase in the quantity of sludge produced, call out for efficient and environmentally friendly approaches to its utilization. One of these is conversion of sewage sludge into adsorbents. Because the biochemical sludges contain the carbon more, can be made into the cheap adsorbents of price through the chemistry path, many

researches focused on making use of sludges to prepare the carbon-bearing adsorbents by different activating ways [9–11], and application of the adsorbents to the removal of organics in the final stages of water cleaning and to the removal of chlorinated organics [12,13]. Sewage-sludge-derived adsorbents have been also tested for their ability to remove acidic gases such as sulfur dioxide and hydrogen sulfide from air streams [14–16]. Physical activation can enhance the adsorbents' pore structure due to a partial oxidation of the carbonized materials by gases such as CO/CO_2 or steam, and it is useful for the formation of micropore structure [17]. Chemical activation involves impregnation of the raw materials with chemicals such as phosphoric acid [18], potassium hydroxide [19], and zinc chloride [20,21]. Corresponding the iodine values of the carbon-bearing adsorbents made by chemical activation and physical activation are about 400 and 10 mg/g, and the specific surface areas are about 100 and 50 m^2/g , respectively.

In this study, three kinds of carbon-bearing adsorbents were prepared by making use of biochemical sludges and surplus sludge as raw materials, characterized with various techniques, and applied of those adsorbents to treatment of wastewater of urban.

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2. Materials and methods

2.1. Preparation of carbon-bearing adsorbents

The materials were biochemical sludge and surplus sludge from the sewage treatment plant (BS and SS), and biochemical sludge from the petrochemistry company (PS). The stainless steel tube was placed in a SK-2-10 electric stove, and the dry sludge was packed to fill quantity about 30 g. The pyrolysis must be protected by the nitrogen atmosphere (the flow was about 20 L/h), heating rate was kept at 5 °C/min. The following activation methods were employed for preparing the carbon-bearing adsorbents.

2.1.1. The physical activation

The sludge sample was first dried at 103 °C for 24 h, then pyrolyzed at 550 °C for 2 h. The carbonization product was opened into the water vapor (the flow was maintained at 12 L/h), the temperature was kept at 550 °C to activate for 2 h. The product was dried at 103 °C for 24 h, crushed and sieved into a uniform size of 1 mm approximately.

2.1.2. The chemical activation

The sludge sample was first dried at 103 °C for 24 h, then the dry sludge was impregnated into activator for 24 h at room temperature, the complex of ZnCl₂ and H₂SO₄ was used as optimum activating agent in different ratios of 3:1, 2:1, 1:1, 1:2 and 1:3 by volume proportions. After the supernatant liquid was removed, it was dried at 103 °C for 24 h and subsequently pyrolyzed at 550 °C for 2 h. Following pyrolysis, the product was washed with 500 mL of 3 mol/L HCl to remove acid-soluble inorganic matter, and then washed with distilled water until the pH of leached solution was 5–6 to remove excess acid, and dried at 103 °C for 24 h, crushed and sieved into a uniform size of 1 mm approximately.

2.1.3. The physical and chemical activation

The chemically activated, dried and crushed sludge was heated for 2 h at 550 °C in a mixture of nitrogen atmosphere and water vapor, then dried for 24 h.

2.2. Analytical methods

The water content were the weight loss of the three sludges by heating at 150 °C for 2 h. The content of volatile matter and ash were evaluated using thermal analysis. The thermal decomposition process of the dry sludges were investigated by simultaneous thermogravimetric and differential thermal analysis (TG-DTA) using a Shimadzu TG-DTA-50 thermal analyzer from room temperature to 800 °C, with a heating rate of 20 °C/min in nitrogen atmosphere, and the elements content of sludges were analyzed by using a Rapid Element analyzer.

A number of authors have used iodine as adsorbate in the characterization of sludge-derived-adsorbent, the iodine value of the carbon-bearing adsorbents and the active carbon (AC) were measured by titrimetric method [22,23]; production rate was calculated by the weight method (weight specific value of

product and experiment dry sludge). The BET surface areas and BJH pore distributions were measured on a Beckman Coulter SA3100 Plus instrument using N₂ adsorption at –196 °C. The scanning electron microscope (SEM) images were obtained on LEO-1530VP scanning electron microscope. X-ray diffraction (XRD) measurements were performed on a Bruker D8 Advance X-ray diffraction using Cu K α radiation. The main elements content were analyzed by energy dispersive X-ray spectrometer (EDS).

The water quality parameters measured were chemical oxygen demand (COD, closed reflux, titrimetric method), total and *ortho*-phosphate *P* (*P*_{tot} and PO₄-*P*, respectively) (ascorbic acid method), and the chromaticity color (colorimetric method). They were tested in accordance with the standard methods [24].

2.3. The wastewater adsorption experiment

The static adsorption experiment was performed to determine the optimum concentration of adsorbents. The adsorbents of 0.1–0.9 g were added to the wastewater of 100 mL relatively, and put to mix quickly on a stirring mixer for 10 min at room temperature. The wastewater was filtrated soon, and the COD and *P* value were measured. The COD, *P* and chromaticity color removal rates were calculated.

The dynamic adsorption test was carried out to evaluate the capacity of adsorbents for organics removal. Adsorbent samples were packed into the glass column (length 23.5 cm, diameter 1.2 cm, bed volume 5 cm³), then wastewater was passed though the column of adsorbents at room temperature with the flow of 40 mL/h. The COD values of different period were measured, and the dynamic breakthrough curves were made. The breakthrough COD value was 60 mg/L, and the adsorption capacities in terms of gram of COD per gram of adsorbent were calculated by integration of the area above the breakthrough curves and from the COD value of the inlet wastewater, flow rate, breakthrough time, and mass of adsorbents.

All adsorption tests were carried out three times, and each figure or table point representing the average of three readings.

3. Results and discussion

3.1. The abilities of the carbon-bearing adsorbents

Table 1 shows the properties of biochemical and surplus sludges. From the Table 1 we can know that the sludges have high water content and low fixed carbon content, and the volatile matter content of biochemical sludges are high. Based on the results of previous studies, the total organic matter in the biochemical sludges are about 60% (wt.%) and the ash are about

Table 1
Properties of different sludges (wt.%)

Sludge	Water	Fixed carbon	Volatile matter	Ash
BS	95.0	17.4	53.5	29.1
PS	84.3	16.0	50.0	34.0
SS	93.0	15.1	34.2	50.7

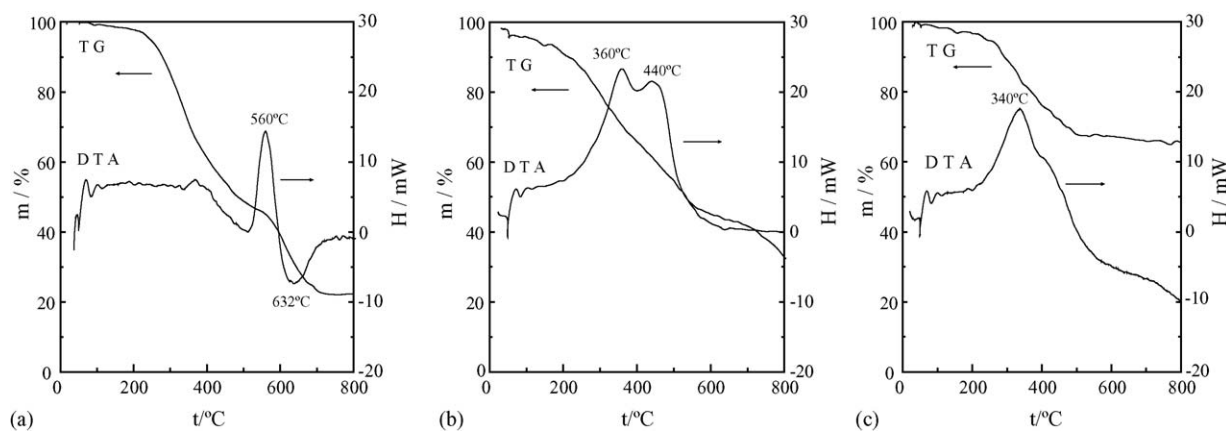


Fig. 1. Thermal analysis curves of (a) BS; (b) PS; (c) SS.

Table 2
Content of N, H and heavy metal elements of different sludges (wt.%)

Sludge	N	H	Ni	Pb	Cr	Cd	Cu
BS	1.08	0.23	0.1	0.04	0.2	0.0004	0.02
PS	1.60	0.63	0.05	0.002	0.06	0.001	0.03
SS	2.72	1.79	0.07	0.005	0.2	0.0005	0.02

30% [25,26], so the fixed carbon content are relatively low. The elements content are shown in Table 2, showing that sludges have lower N, H and heavy metal elements, which is agreement with the previous studies [27].

The result of the thermal analysis of the dry sludges are presented in Fig. 1(a)–(c). The TG and DTA curves show that the stage of weight loss of the three dry sludges occurred at approximately 200–600 °C by TG curves, at the corresponding temperature well-defined exothermal peak in DTA curves, associating with the gradual volatilisation of part of the organic materials contained within the sludges. The residue after heating to 800 °C are the ash, and about 80% of the ash are consist of inorganic oxides such as Al_2O_3 , SiO_2 , and Fe_2O_3 [28].

Adopt different raw materials of BS, PS, SS and activations to prepare carbon-bearing adsorbents, the iodine values and production rates are shown in Table 3. It is clearly seen that

the abilities of the products prepared by the chemical activation of different sludges are better, and the iodine values of the biochemical-sludges-derived adsorbents are higher.

Under the same conditions (the concentration of activators: 5 mol/L, proportion of solid to liquid: 1 g:2.5 mL, activating temperature: 550 °C, activating time: 2 h), the screening results of different activators are given in Table 4. For

Table 4
The effect of different activators on the adsorbent abilities

Sludge	Activator	Iodine value (mg/g)	Production rate (wt.%)
BS	ZnCl ₂	432.22	45.9
	H ₂ SO ₄	83.50	38.9
	KOH	2.90	31.8
	FeSO ₄	2.34	30.8
PS	ZnCl ₂	403.79	70.8
	H ₂ SO ₄	79.85	65.3
	KOH	1.36	54.1
	FeSO ₄	1.99	50.1
SS	ZnCl ₂	332.09	51.1
	H ₂ SO ₄	53.62	64.3
	KOH	1.20	52.4
	FeSO ₄	2.97	49.8

Table 3
The effect of different raw materials and activations on the adsorbent abilities

Activation	Sludge	Iodine value (mg/g)	Production rate (wt.%)
The carbonization	BS	8.80	42.9
The physical activation		10.39	41.6
The chemical activation		432.22	45.9
The physical and chemical activation		333.81	43.8
The carbonization	PS	6.90	66.3
The physical activation		11.59	62.3
The chemical activation		403.79	70.8
The physical and chemical activation		308.95	68.3
The carbonization	SS	5.50	50.5
The physical activation		13.15	50.4
The chemical activation		332.09	51.1
The physical and chemical activation		277.81	53.8
	AC	473.16	–

Table 5
The effect of the ratio of complex activator on the adsorbent abilities

Sludge	ZnCl ₂ :H ₂ SO ₄ (V:V)	Iodine value (mg/g)	Production rate (wt.%)
BS	3:1	489.64	52.9
	2:1	596.58	51.8
	1:1	349.86	45.9
	1:2	318.31	41.5
	1:3	249.62	38.6
PS	3:1	375.63	68.7
	2:1	438.31	67.5
	1:1	213.56	63.4
	1:2	179.63	60.8
	1:3	123.45	56.8
SS	3:1	309.60	88.1
	2:1	488.02	86.6
	1:1	296.30	76.9
	1:2	238.96	72.4
	1:3	188.28	68.6

all the sludges, the activators of ZnCl₂ and H₂SO₄ are better.

Based on the screening results, 5 mol/L ZnCl₂ and H₂SO₄ of the same concentration reply to go together to activate. Table 5 shows that the abilities of the carbon-bearing adsorbents prepared by complex of ZnCl₂ and H₂SO₄ are better, and the optimum ratio of ZnCl₂ and H₂SO₄ is 2:1.

By taking surplus sludge as raw material, the influential factors on the adsorbents abilities are studied. Orthogonal design of L₉ (3⁴) is adopted in the orthogonal experiment. Table 6 shows the result, from the analysis of variance (*R* and *S*) can know that the main influential factor is activating temperature, sub-

sequent is activator concentration, the effect of proportion of solid to liquid and activating time are relatively littler. The optimum preparation conditions are concentration of two activators are 5 mol/L (the ratio of ZnCl₂ and H₂SO₄ is 2:1), activating temperature is 550 °C, the proportion of solid to liquid is 1:2.5, activating time is 2 h. The experiment under the same conditions are repeated for five times, and the iodine values of all the activated products are 480–488 mg/g.

3.2. The characterization of the carbon-bearing adsorbents

The carbon-bearing adsorbents made from BS, PS and SS by the chemical activation with the activator of complex of ZnCl₂ and H₂SO₄ are designated as BSC, PSC and SSC. The specific surface area and pore structure of the carbon-bearing adsorbents

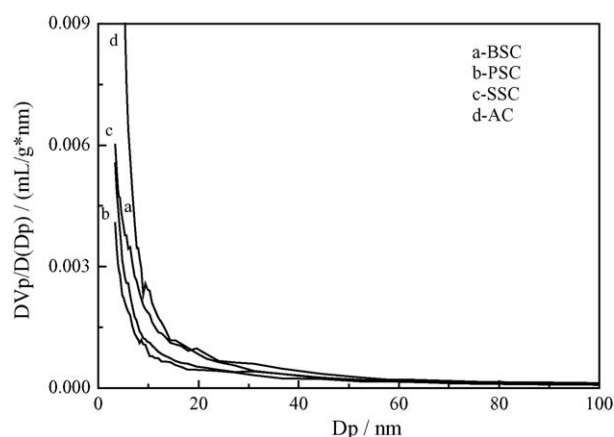


Fig. 2. Pore distribution curves of adsorbents.

Table 6
Orthogonal design of chemical activation

Order number	<i>C</i> (mol/L)	<i>T</i> (°C)	<i>D</i> (1:X)	<i>T</i> (h)	Iodine value (mg/g)
1	3	450	2.5	1	165.17
2	3	550	4.0	2	286.34
3	3	650	5.5	3	282.01
4	5	450	4.0	3	221.18
5	5	550	5.5	1	226.43
6	5	650	2.5	2	347.60
7	7	450	5.5	2	195.37
8	7	550	2.5	3	464.77
9	7	650	4.0	1	431.59
<i>K</i> ₁	244.51	193.91	325.85	274.40	–
<i>K</i> ₂	265.07	325.85	313.04	276.44	–
<i>K</i> ₃	363.91	353.73	234.60	322.65	–
<i>R</i>	119.40	159.82	91.25	48.25	–
<i>S</i>	24449.35	43730.39	14641.23	4468.85	–

Table 7
Pore characteristics of adsorbents

Adsorbent	Pore volume (mL/g)	Micropore volume (mL/g)	Average pore diameter (nm)	Specific surface area (m ² /g)
BSC	0.07	0.02	38.81	114.53
PSC	0.06	0.02	34.89	128.96
SSC	0.05	0.02	32.51	144.47
AC	0.10	0.07	18.27	633.39

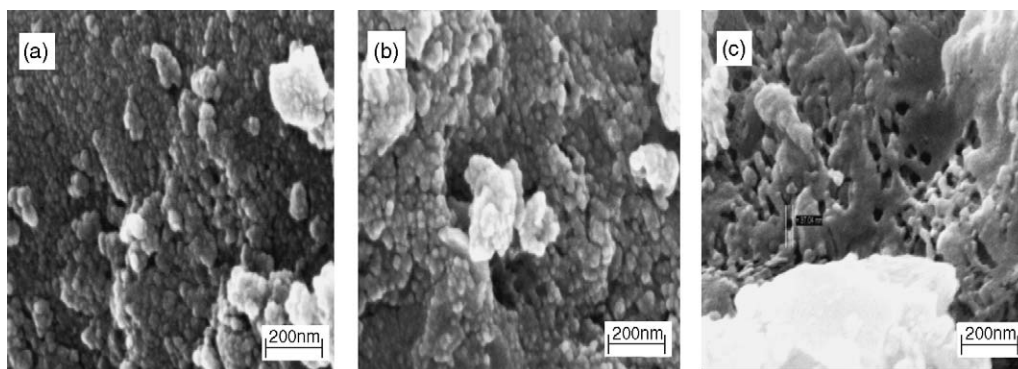


Fig. 3. SEM images of adsorbents of (a) BSC; (b) PSC; (c) SSC.

and the active carbon are measured, as a result seeing the Table 7. Fig. 2(a)–(d) shows the pore path distribute curves. The pore path distribute of the active carbon is more narrow, and is mainly cellular structure. The pore path distribute of the carbon-bearing adsorbents are wider, and are mainly transition pore structure, corresponding the specific surface areas are lower than the active carbon.

Many researches [29,30] have found that the synergistic action of the complex activator accelerates the activation process of dewatering, condensation, wetting and expansion, and making the carbon-bearing chemical compound within the sludges condense to non-volatile carbon. It's activation effect is better than the single activator, and the transition pore structure of the activated products are more flourishing, corresponding the abilities of the carbon-bearing adsorbents increase greatly.

Fig. 3(a)–(c) shows the SEM images of the carbon-bearing adsorbents, and the pore structure of the carbon-bearing adsorbents are heterogeneous, and are mainly transition pore structure. The SEM images are anastomosing with the measurement result of the pore structure.

Fig. 4(a)–(d) shows the X-ray diffraction diagrams of adsorbents, the carbon-bearing adsorbents are all hexagonal crystal structure, and the active carbon is adventitious carbon. The carbon content of BSC and PSC are relatively higher.

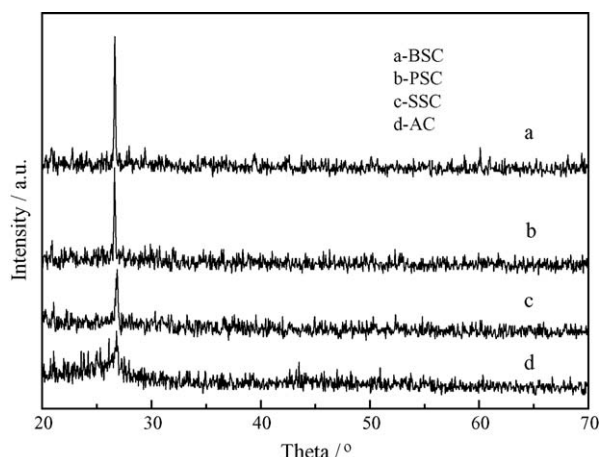


Fig. 4. X-ray diffraction diagrams of adsorbents.

EDS was performed to confirm the composition of the carbon-bearing adsorbents. The images of the three carbon-bearing adsorbents and the active carbon are presented in Fig. 5, and the elements content are shown in Table 8, showing that the carbon-bearing adsorbents are composed of carbon and some inorganic compounds such as zinc and aluminium salts and silica.

3.3. Application in treatment of wastewater of urban

In static adsorption experiment, the effect of concentration of adsorbents sees the Fig. 6. It can be seen that the adsorbents concentration has important effect on the adsorption of the organic substances in wastewater treatment, and the removal rate of COD increase with the rise of the adsorbents concentration, and increase gently after the concentration of 0.5%. On the condition that the carbon-bearing adsorbents concentration is 0.5%, contrast the active carbon and make use of the carbon-bearing adsorbents to treatment of wastewater (pH: 8.5, COD value: 302.4 mg/L, *P* value: 19.7 mg/L), the COD and *P* value of the wastewater of urban are not very high. Table 9 shows that under the same processing condition the adsorption effect to organic materials and *P* and chromaticity color of wastewater of the carbon-bearing adsorbents are better than the active carbon, and the biochemical-sludge-derived adsorbents perform much better than the adsorbent made from surplus sludge.

As indicated elsewhere [31,32], the possibilities of granular activated carbon was normally investigated using a dynamic state experiment. In dynamic adsorption experiment, the breakthrough curves for our samples are shown in Fig. 7. The calculated capacities are summarized in Table 10. It is clearly seen that the capacities of the sludge-derived adsorbents are more than the active carbon, and the breakthrough time of the active carbon decrease greatly comparing to the sludge-derived adsorbents. The treatment effect of adsorbents made from the biochemical sludges are better, which is anastomosing with the result of static adsorption experiment.

Because the sludge-derived adsorbents are mainly transition pore structure, and beneficial to adsorb the big member organic materials, however the active carbon is mainly cellular structure and the velocity of liquid diffusion is slower. The micropore volume of the biochemical-sludges-derived adsorbents are

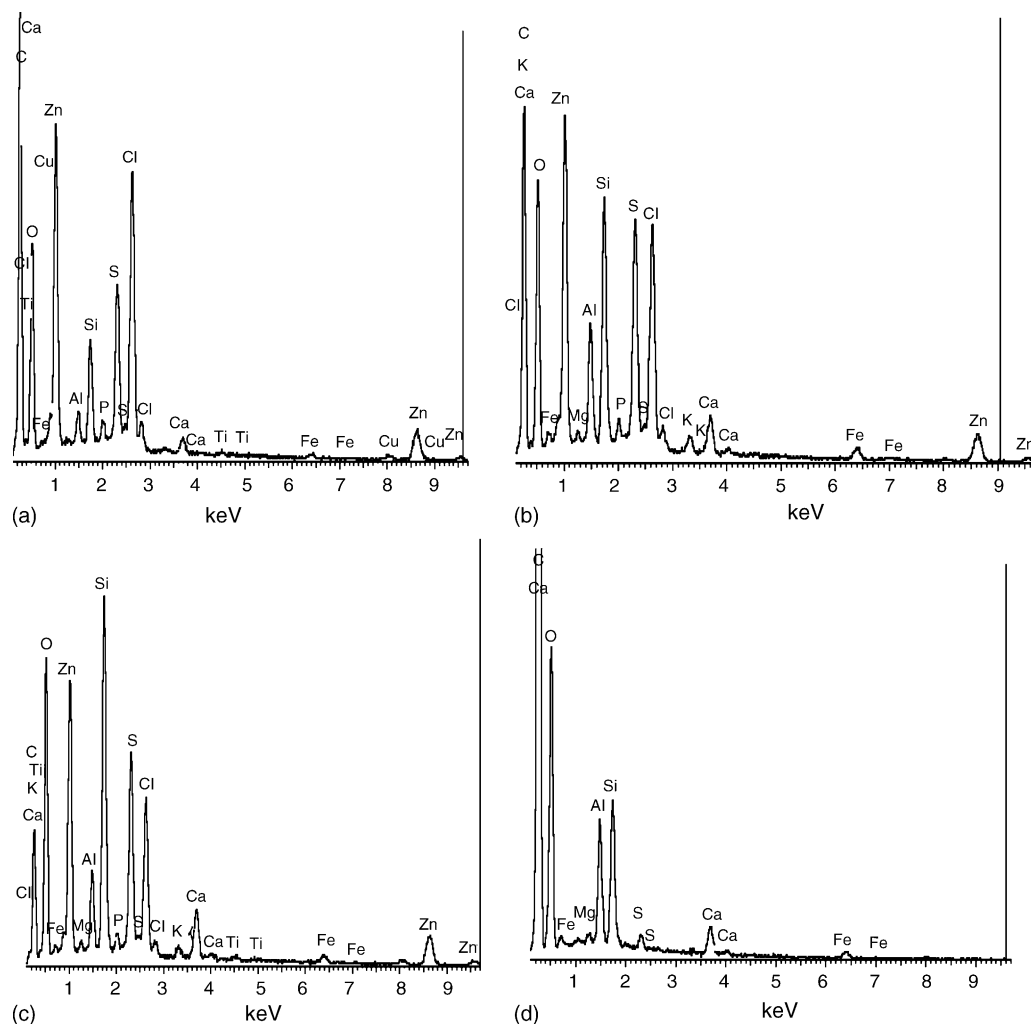


Fig. 5. EDS spectra of adsorbents of (a) BSC; (b) PSC; (c) SSC; (d) AC.

Table 8
Content of elements of adsorbents (wt.%)

Adsorbent	C	O	Zn	Si	Al	Fe	Ca	Mg	K	Ti	Cl	S	P
BSC	52.5	18.3	12.7	2.1	0.6	0.6	0.6	0	0	0.1	8.1	3.9	0.5
PSC	45.5	20.2	12.5	4.5	2.0	1.5	1.4	0.2	0.5	0	6.1	5.2	0.4
SSC	28.0	27.4	15.1	9.2	1.9	1.4	2.6	0.3	0.5	0.2	6.3	6.5	0.6
AC	70.9	23.0	0	2.2	1.7	0.9	1.0	0.1	0	0	0	0.2	0

Table 9
Treatment effect of adsorbents to wastewater

Adsorbent	BSC	PSC	SSC	AC
pH value	7.1	7.4	7.2	8.7
COD value (mg/L)	63.2	74.2	96.2	178.7
COD removal rate (%)	79.1	75.5	68.2	40.9
P value (mg/L)	0.3	0.3	0.7	17.7
P removal rate (%)	98.3	98.3	96.6	10.2
Chromaticity color removal rate (%)	87.5	87.5	87.5	75.0

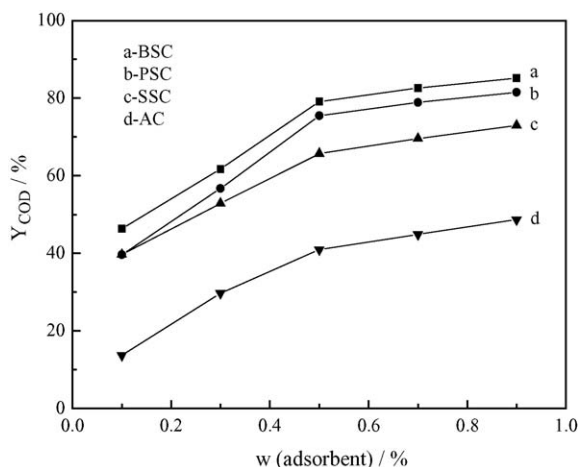


Fig. 6. Effect of the adsorbents concentration to COD removal rate.

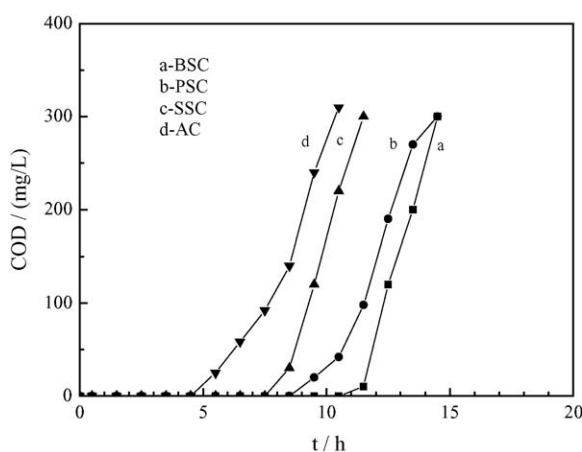


Fig. 7. Breakthrough curves of the adsorbents.

Table 10
The capacity and breakthrough time of adsorbents

Adsorbent	BSC	PSC	SSC	AC
Breakthrough time (h)	12	11	9	6
Adsorption capacity (mg/g)	47.8	45.6	41.2	30.8

lower, corresponding the specific surface areas are lower than the surplus-sludge-derived adsorbent, but the flourishing big and transition pore structure are more favorable to adsorb the organics, in addition the content of carbon are higher, so the treatment effect are better than the surplus-sludge-derived adsorbent.

4. Conclusions

The following conclusions can be made from the present experiment:

- (1) The carbon-bearing adsorbents can be prepared from biochemical and surplus sludges by chemical activation. The optimum activator is complex of $ZnCl_2$ and H_2SO_4 , and the optimum preparation conditions are concentration of two activators 5 mol/L (the ratio of $ZnCl_2$ and H_2SO_4 is 2:1),

at the activating temperature of 550 °C, in the proportion of solid to liquid 1:2.5, in a period of 2 h.

- (2) The pore path distributes of the carbon-bearing adsorbents are wider, and are mainly transition pore structure, corresponding the specific surface areas are lower than the active carbon. They are made of carbon and some inorganic compounds, and are all hexagonal crystal structure.
- (3) In static adsorption, as the concentration of the carbon-bearing adsorbents are 0.5%, the COD removal rates of adsorbents of BSC, PSC, and SSC are 79.1, 75.5, and 68.2%, the removal rates of *P* are 98.3, 98.3, and 96.6%, respectively, and the chromaticity color removal rates are all 87.5%. The treatment effect to wastewater of the sludge-derived adsorbents are better than the active carbon.
- (4) The treatment effect of the carbon-bearing adsorbents made from the biochemical sludges are better in dynamic adsorption, the adsorption abilities of the sludge-derived adsorbents are better than the active carbon, the adsorption capacities of adsorbents of BSC, PSC, and SSC are 47.8, 45.6, and 41.2 mg/g, respectively.

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