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ORIGINAL ARTICLE

An Orthogonal Experimental Design to Prepare Activated Carbon from Sewage Sludge

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ABSTRACT
Orthogonal experiments were performed to produce activated carbon from sewage sludge based on $ZnCl_2$ activation-tubular furnace pyrolysis, in order to optimize the operating parameters such as concentration of activator $ZnCl_2$, pyrolysis time and temperature, as well as liquid to solid ratio. The typical experimental results obtained at optimized conditions were adsorption capacity of 41.97 mg/g for methylene blue, specific surface area of 298.76 m^2/g and yield of 48.9%, respectively. Other characterizations such as observation of microscopic morphology, measurements of specific surface area and heavy metal leaching from the sludge and the sludge derived activated carbon were also conducted.
***Key words**: Sewage sludge, Activated carbon, Orthogonal experimental design*

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INTRODUCTION

Annual amounts all the world of sewage sludge from wastewater treatment are increasing rapidly, particularly from developing countries as China due to the urbanization and industrialization as a result of high-speed economical development. Various approaches have been reported to treat the sludge, including landfilling, agricultural applications of the nutrients as well as energy recovery whether as gaseous state or solid carbon [1-8]. However, it still remains as a severe environmental concern without satisfactory solution and requires worldwide attention for further investigations to improve efficiency or propose new approach for final practical applications. On the other hand, soil contamination is another serious environmental concern in China [9-11] and efforts are highly required to remove the contaminants such as heavy metals.

Our goal is to prepare an adsorbent based on activated carbon to remove heavy metals from the contaminated soils. It is known that various organic precursors can be used to prepare activated carbon. Recently many reports on activated carbon preparation have involved the applications of industrial or agricultural residues. Sewage sludge normally contains large part of organic composition with the solid residue base and could be used as a precursor for activated carbon preparation [12-15]. As the first step of our research, preparation of activated carbon from the sludge was conducted with a $ZnCl_2$ activation-tubular furnace pyrolysis. It is known that the properties of activated carbon depend on the methods used and many parameters should be considered. We designed an orthogonal arrangement [16-17] for the experiments with four main conditions of concentration of $ZnCl_2$, pyrolysis temperature, pyrolysis time and liquid to solid ratio and report the obtained experimental results. The second step will be introduced in next report to prepare magnetic composite of the activated carbon and magnetite powders for easy recovery after absorption of heavy metal from soil.

EXPERIMENTAL PROCEDURE

Preparation of sludge activated carbon

The sludge sample was obtained as dewatered one from Minhou waste water treatment facility, Daxue city, Fuzhou, China. Chemical reagents of $ZnCl_2$ was purchased from Yongda Chemicals limited, Tianjin and HCl from Damao Chemicals Factory, Tianjin and used as received. The sludge sample was first dehydrated at 105 degrees in a drying oven until no weight change when checked. The dehydrated sludge was then ground to have the particles passing through 100 mesh with a sieve and kept in a dryer for next experiments. The dehydrated sludge was mixed with the solution of $ZnCl_2$ as activator at certain ratios and heated in water bath at 85 degrees for 1 hour and further dried in an oven for under 105 degrees for 24 hours. The prepared sludge with activator was heated in a tubular resistance furnace with N_2 gas flowing with heating rate of 20 degrees / per minute to produce activated carbon at temperature range from 650 ~ 850 degrees and pyrolysis time range from 30 to 90 minutes. After natural cooling, the pyrolysis products were washed with 3 M HCl solution for three times. The sample was then repeatedly washed with distilled water, until the pH of the water reached 6. Finally the water-washed products were put in an oven to dry up at 85 degrees until no weight change, named sludge-derived activated carbon (SAC) for next experimental uses.

The orthogonal experiment design

To obtain optimal conditions for the preparation of SAC, the following four factors for orthogonal experiment were chosen with concentration of $ZnCl_2$, pyrolysis temperature, pyrolysis time and $ZnCl_2$ liquid to solid ratio. Characterizations of the prepared SAC with methylene blue adsorption value, specific surface area (S_{BET}) and yield of the obtained SAC were conducted to judge the selected factors with the detailed information shown in Table 1 and 2, respectively.

Table 1 Factors and levels of orthogonal design

Levels	Factors			
	the concentration of $ZnCl_2$ (mol/L) A	pyrolysis temperature (degree) B	pyrolysis time (min) C	liquid-solid ratio (X : 1) D
1	1	650	30	1
2	2	750	60	1.5
3	3	850	90	2

Table 2 Orthogonal experimental arrangements

Serial number	Range and levels			
	A	B	C	D
1-1	1	650	30	1
1-2	1	750	60	1.5
1-3	1	850	90	2
1-4	2	650	60	2
1-5	2	750	90	1
1-6	2	850	30	1.5
1-7	3	650	90	1.5
1-8	3	750	30	2
1-9	3	850	60	1

Characterizations

The internal structure and surface morphology of the prepared SAC at optimized conditions from the orthogonal experimental design and a commercial activated carbon (AC) as a reference were characterized by scanning electron microscopy (SEM) (S-3400N, Hitachi, Japan). The specific surface area and pore structure of the dehydrated sludge, the SAC and AC were measured with JW - BK micro analyzer, Beijing JWGB Sci & Tech Co., Ltd, Beijing based on static nitrogen adsorption. The measurement conditions were temperature of 77.4 K and relative pressure range (P/P_0) of 10^{-6} ~ 1 with sample degas-treated for 2 hours at 105 degrees by vacuum heating. BET equation and BJH equation were used to calculate the specific surface area, specific pore volume and average pore diameter, respectively.

In order to examine heavy metals contents of the prepared SAC, leaching tests of the sludge and sludge activated carbon were conducted under Standard HJ/T299-2007, Environmental Ministry, China. Leaching solution of pH 3.2 with 2:1 of sulfuric acid and nitric acid was first prepared and 10g samples were put in the prepared solution 250 ml and agitated for 20 hours. Concentrations of several typical heavy metals of lead, cadmium, chromium copper nickel arsenic and zinc leached in the filtrate were measured by ICP method.

RESULTS AND DISCUSSION

Orthogonal experimental results

Table 3 Experimental results with orthogonal arrangements

Serial number	Variables				Responses		
	A	B	C	D	Methylene blue adsorption value（mg/L）	Specific surface area S_{BET}（m^2/g）	Yield（%）
1-1	1	1	1	1	26.43	265.88	60.9
1-2	1	2	2	2	27.31	305.96	49.8
1-3	1	3	3	3	36.42	255.44	40.1
1-4	2	1	2	3	31.34	299.42	54.4
1-5	2	2	3	1	36.85	293.12	48.5
1-6	2	3	1	2	44.78	227.95	43.6
1-7	3	1	3	2	41.14	311.63	46.7
1-8	3	2	1	3	42.56	300.32	62.8
1-9	3	3	2	1	42.46	262.87	42.4

Response values of methylene blue adsorption value, specific surface area S_{BET} and yield of the prepared SAC to the factor levels are listed in Table 3. The properties of the SAC are clearly dependent on the factor and its level. Two important parameters in a range analysis: Kij and Rj were used to show which factor is more important one and the results are shown in Table 4. Kij is defined as the average value of the Kji of all level (i, i =1, 2, 3) in each factor (j, j = A, B, C, D) and used to determine the optimal level and the optimal combination of factors. Rj is defined as the range between the maximum and minimum value of Kij and is used to assess the importance of the factors.

Table 4 Range analysis results

Indicators	Levels	Factors			
		A	B	C	D
Methylene blue adsorption value	K_{1j}	30.05	32.97	37.92	35.25
	K_{2j}	37.66	35.57	33.70	37.74
	K_{3j}	42.05	41.22	38.14	36.77
	R_j	12.00	8.25	4.43	2.50
	The optimal solution	A_3	B_3	C_3	D_2
Specific surface area S_{BET}	Levels	Factors			
		A	B	C	D
	K_{1j}	275.76	292.31	264.72	273.96
	K_{2j}	273.50	299.80	289.42	281.85
	K_{3j}	291.61	248.75	286.73	285.06
	R_j	18.11	51.05	24.70	11.10
	The optimal solution	A_3	B_2	C_2	D_3
Yield	Levels	Factors			
		A	B	C	D
	K_{1j}	50.27	54.00	55.77	50.60
	K_{2j}	48.83	53.70	48.87	46.70
	K_{3j}	50.63	42.03	45.10	52.43
	R_j	1.80	11.97	10.67	5.73
	The optimal solution	A_3	B_1	C_1	D_3

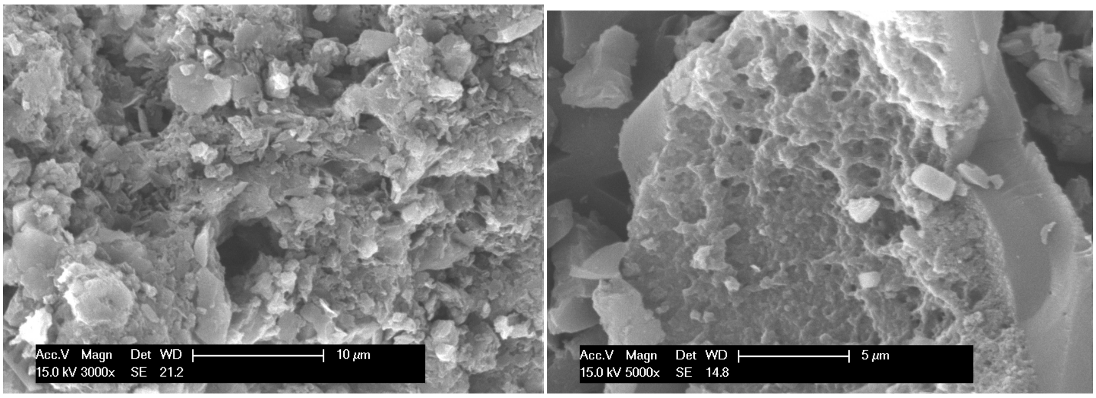
With methylene blue adsorption value: the optimal level combination of the four factors was $A_3B_3C_3D_2$, denoting that $ZnCl_2$ concentration A_3, pyrolysis temperature B_3, pyrolysis time C_3, and liquid-solid ratio D_2 are 3 mol/L, 850 degrees, 90 min and 1.5:1 respectively. Range analysis results for Rj are in the order of $R_A > R_B > R_C > R_D$, indicating that SAC methylene blue adsorption value is most affected by $ZnCl_2$ concentration, followed by pyrolysis temperature.

With specific surface area S_{BET}: the optimal level of various factors combination was $A_3B_2C_2D_3$, by the levels for $ZnCl_2$ concentration of 3 mol/L, pyrolysis temperature of 750 degrees, pyrolysis time of 60 min and liquid-solid ratio of 2:1 respectively. Range analysis results for Rj are in the order of $R_B > R_C > R_A > R_D$, showing that the SAC specific surface area is most affected by pyrolysis temperature, followed by the pyrolysis time.

With the SAC yield: the optimal level of various factors combination was $A_3B_1C_1D_3$, by the levels for $ZnCl_2$ concentration of 3 mol/L, pyrolysis temperature of 650 degrees, the pyrolysis time of 30 min, liquid-solid ratio of 2: 1, respectively. Range analysis results for Rj are in the order of $R_B > R_C > R_D > R_A$, giving the results that SAC yield depends most on pyrolysis temperature, followed by the pyrolysis time.

Characterizations of the prepared SAC at optimized conditions

From the range analyses of the orthogonal arrangement, factor combination as $A_3B_2C_2D_2$ is determined as the optimized parameters: namely namely $ZnCl_2$ concentration of 3 mol/L, pyrolysis temperature of 750 degrees, pyrolysis time of 60 min, liquid-solid ratio of 1.5 to 1, respectively. The prepared SAC sample at the conditions was characterized with results as the methylene blue adsorption value of SAC 41.97 mg/g, S_{BET} of 298.76 m^2/g and yield of 48.9%. Comparison between the prepared SAC with a commercial activated carbon (AC) and the raw sewage sludge was also conducted to show the typical feature of activated carbon.



（a） SAC （b） AC

Figure 1 SEM observation of both SAC and AC samples

Figure 1 shows the SEM morphology of the prepared SAC and commercial AC. It can be seen that, compared with the relatively small and even distributions of holes, the prepared SAC presents clearly different features: with an irregular shape, uneven similar cellular structure and large holes. Possible applications may be put especially on the removal of heavy metal ions and macromolecular organic pollutants.

Specific surface area, pore volume and average pore diameter are shown in Table 5 for the three samples. Compared with the smaller specific surface area of 5.9 m^2/g and specific pore volume of 0.03 cm^3/g from the raw sewage sludge, these values have been significantly increased for SAC sample up to 298.76 m^2/g and 0.32 cm^3/g, respectively, a typical feature for activated carbon. Although these values are still smaller than that of a reference commercial AC sample, Average pore diameter of the prepared SAC is much larger than that of the commercial one. A easier adsorption of macromolecular substances and heavy metals and a quicker diffusion of the pollutants into the structures may result from the larger pore diameter.

Table 5 Specific surface area, pore volume and diameter of various samples

Sample	S_{BET}/ （m^2/g）	Specific pore volume / （cm^3/g）	Average pore diameter/ （nm）
Sludge	4.67	0.03	25.69
SAC	298.76	0.32	4.28
AC	726.86	0.68	3.74

Since the prepared SAC sample is used later for heavy metal adsorption from contaminated soils, leaching behaviors of several heavy metals were examined and the results are shown in Table 6. With the Chinese standard for the regulation of toxicity leaching identification (GB5085.3 2007), all the concentrations of seven heavy metals after leaching test are clearly at very low values, particularly even without observable extraction of Cd, Ni and As, suggesting it is safe and feasible to use the prepared SAC for applications. It is more interesting to note that the concentrations of the leached metals from SAC are lower than that from raw sewage sludge, except Zn only. The relatively high concentration of Zinc from the sample means that the washing process for the sample preparation if not sufficient and needs further improvement to take out the remaining Zn chloride. It is understood that, from the lower concentrations of all the other metals, the activated carbon may have the capacity to hold the heavy metals inside the structures.

Table 6 Heavy metal contents from the prepared samples in leaching liquid (mg/L)

Sample	Pb	Cd	Cr	Zn	Cu	Ni	As
sludge	0.0133	0.0016	0.0142	0.0351	0.0164	0.0284	—
SAC	0.0112	—	0.0098	0.1051	0.0084	—	—
GB 5085.3-2007 the maximum allowable concentration	5	1	15	100	100	5	5

The next step of the research is to prepare magnetic composites of SAC and magnetite powders for an easy recovery and reuse from the practical application of the prepared sample to absorb heavy metals from contaminated soils.

CONCLUSION

In this research zinc chloride activation was used to prepare SAC by thermal pyrolysis. The main experimental conclusions are made as follows:

(1) The optimized processing conditions for preparing SAC were zinc chloride concentration of 3 mol/L, pyrolysis temperature of 750 ℃, pyrolysis time of 60 min, and liquid-solid ratio of 1.5:1, with typical experimental results: adsorption value of methylene blue as 41.9 mg/g, specific surface area as 298.76 m^2/g and yield as 48.9%, respectively.

(2) Comparison between the raw sewage sludge, the prepared SAC and a commercial AC by various analyses such as SEM microstructure characterization and determination of specific surface area analysis has shown that, although property such as specific surface area from the prepared SAC has not been increased as high as that of commercial AC, typical feature of activated carbon from the prepared sample has been observed, particularly with the mesoporous structure and larger pore diameter. Less solution of heavy metals during leaching test compared with that of raw sewage sludge suggests the possibility of the prepared SAC to hold the metals inside activated carbon structure.

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