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Effect of Binders on Porous Properties, Surface Chemical Properties and Adsorption Characteristics of Granular Adsorbents from Sewage Sludge

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To investigate the influence of binders on porous properties, surface chemical properties and methylene blue adsorption characteristics of granular adsobents from sewage sludge, four samples (G1, G2, G3 and G4) respectively using soluble starch, sodium carboxymethyl cellulose, sodium silicate and calcium sulfate as binders and a sample without binder (G0) were prepared by carbonization method. The pore structure and surface characterization of samples prepared show that G1 and G2 have many microporous and mesoporous pores while the activation of sodium silicate and calcium sulfate cause that G1 and G2 are typical mesoporous adsorbents. The FTIR spectra of all samples suggest that the major differences of surface functional groups are between (1000 – 1200) cm^{-1} and (400 – 800) cm^{-1}. Langmuir model fitted the methylene blue (MB) adsorption data better, and the MB adsorption of G0, G1, G2, G3 and G4 are 56.50, 40.32, 33.44, 29.33 and 71.94 mg/g, respectively.

Keywords: granular adsorbents; sewage sludge; binders; porous and surface chemical properties; methylene blue adsorption.

1. INTRODUCTION

In recent decades, sewage sludge is being generated in an ever increasing amount due to the rapid urbanization in China. Several methods have been used for sewage sludge disposal, such as landfills, forestry and land reclamation, sea dumping, and application to farmland and incineration [1]. But, each of these options has important limitations [2]. Therefore, the development of new ways on sewage sludge treatment is in dire need.

Since almost any carbonaceous material can be used as the precursor for the preparation of activated carbon, sewage sludge has been suggested as a suitable raw material for the production of activated carbon due to its richness in volatile components [3]. In this way, it would improve sludge management while also granting economic value to waste as a material for producing adsorbents [4]. In recent years, much attention has been paid to the preparation of powdered activated carbons from sewage sludge by chemical or physical activation [5, 6], and the products have been investigated for the adsorption of pollutants in liquid, such as heavy metals [7, 8] and dyes [9, 10]. Although, granular activated carbons have more advantages than powdered activated carbons in applications [11], there is a few report on preparation and application of granular activated carbons from sewage sludge [12].

For granular activated carbons (GAC), the binder is another important factor which also has great influence on GAC properties [13, 14]. The binders usually used in preparation of GAC are coal tar [11], resin [15], clay [13] and other viscous substances.

In this study, soluble starch, sodium carboxymethyl cellulose, sodium silicate and calcium sulfate were chosen as binders to prepare granular adsorbents from sewage sludge. The effects of binders on adsorbents properties were evaluated. For avoiding the effect of other factors, the preparation process was carbonization method. And in order to compare the adsorption capacities of prepared products with samples reported, the behaviors of methylene blue removal from aqueous solution were studied. The equilibrium data of the adsorption process were analyzed to study the adsorption isotherms of methylene blue.

2. EXPERIMENTAL AND METHODS

2.1. Preparation of granular activated carbons

The raw material for granular activated carbon preparation was dewatered surplus sludge from Dadukou municipal wastewater treatment plant in Chongqing, P.R. China. Approximate analysis of the raw materials is shown in Table 1. Four substances, soluble starch ($(C_6H_{10}O_5)_n$), sodium carboxymethyl cellulose (R_nOCH_2COONa, CMC), sodium silicate ($Na_2SiO_3 \cdot 9H_2O$) and calcium sulfate ($CaSO_4 \cdot 2H_2O$), were used as binders, respectively.

Table 1. Ultimate and proximate analysis of the raw materials (results are expressed in a dry basis, except for the moisture content)

Moisture, %	Volatiles, %	Ash, %	Fixed carbon,%	C, %	H, %	N, %
71.2	45.7	47.45	6.85	16.82	3.26	3.12

The sludge sample was first dried at 105 °C for 48 h, crushed and sieved into particles with a size of less than 2 mm. Briefly, sludge powder was mixed with binder, in an optimized weight proportion of 10 : 3. After this, about 20 mL of water was added to obtain paste for extrusion.

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Cylindrical extrudates (with, in average, 4 mm diameter and 9mm long) were dried for 12 h at 105 °C. And then, a subsequent heat treatment was made under nitrogen flow (0.6 L/min). The temperature was raised (5 °C/min) up to 300 °C and 700 °C, respectively, and held for 1 h. Last, the samples were cooled in the nitrogen atmosphere. The granular adsorbents were designated in accordance with the binder used, which include G1 (with soluble starch as the binder), G2 (with sodium carboxymethyl cellulose as the binder), G3 (with sodium silicate as the binder), and G4 (with calcium sulfate as the binder). In order to investigate the impact of binders on adsorbents properties, a sample without binders was also prepared with the same method, and named for G0.

2.2. Characterization of granular activated carbons

The specific surface area and pore structural parameters of the samples were determined from the adsorption isotherm of nitrogen at 77 K (Micromeritics ASAP 2020M). The total specific surface area (Stotal) was calculated by the Brunauer-Emmett-Teller (BET) equation. The total pore volume (V_{total}) was estimated to be the liquid volume of N2 at a relative pressure (p/p_0) of 0.995. The specific microporous volume (V_{micro}) and mesoporous volume (V_{meso}) were estimated from the t-plot method and BJH model, respectively. The pore-size distribution was determined by density functional theory.

The surface physical morphology was observed by scanning electron microscopy (SEM, FEI Quanta250). The qualitative estimation of the surface functional groups was performed by Fourier Transform Infra-Red spectroscopy (FTIR, Perkin-Elmer Spectrum GX). Pressed potassium bromide (KBr) pellets were spanned and recorded between 4000 cm^{-1} and 450 cm^{-1}.

2.3. Methylene blue adsorptive properties

Dye, methylene blue (MB), which has a chemical formula of $C_{16}H_{18}N_3CINS{\cdot}3H_2O$ and a molecular weight of 373.90, was chosen as the targeted adsorbate in this study. MB samples were obtained from Kelong, Chengdu, P.R. China.

Equilibrium adsorption studies were conducted in a set of 250 mL Erlenmeyer flasks containing 0.20 g adsorbent and 200 mL dye solutions with various initial concentrations (50, 100, 200, 300, and 400 mg/L). The flasks were agitated in an isothermal water-bath shaker at 120 rpm and 25 °C until the equilibrium was reached. MB uptake at equilibrium, q_e (mg/g), was calculated by Eq. (1):

$$q_e = \frac{(C_0 - C_e)\cdot V}{W}, \quad (1)$$

where C_0 and C_e (mg/L) are the liquid-phase concentrations of dye at initial and equilibrium, respectively, and C_e was determined by UV-vis spectrophotometry at a wavelength of 665 nm. V (L) is the volume of the solution, and W (g) is the mass of adsorbent used.

The obtained data were fitted to Langmuir's and Freundlich's isotherm models. Langmuir's model (Eq. 2) is a theoretical model which assumes that adsorption occurs in a saturated monolayer of molecules of adsorbate on the surface of the adsorbent.

$$\frac{C_e}{q_e} = \frac{1}{Q_0 K_L} + \frac{1}{Q_0} C_e, \quad (2)$$

where Q_0 (mg/g) and K_L (L/g) are Langmuir constants related to adsorption capacity and rate of adsorption, respectively.

Furthermore, the separation factor from Langmuir's model, r is defined [16] as equation (3).

$$r = \frac{1}{1 + K_L C_0}. \quad (3)$$

The value of r indicates whether the type of isotherm is reversible ($r = 0$), favorable ($0 < r < 1$), linear ($r = 1$) or unfavourable ($r > 1$) [17].

Freundlich's isotherm is an empirical equation which considers the adsorbent surface energetically heterogeneous.

$$\log q_e = \log K_F + \frac{1}{n} \log C_e, \quad (4)$$

where K_F (mg/g) (L/mg) and $1/n$ are the Freundlich adsorption constants, and a measure of the adsorption intensity. The value of n indicates favorable adsorption when $1 < n < 10$, the more favorable the lower its value within this range [18].

3. RESULTS AND DISCUSSION

3.1. Characterization of GAC samples

3.1.1. Pore structure

The nitrogen adsorption isotherms of all samples are illustrated in Fig. 1, a. According to IUPAC classification, the isotherms of G1 and G2 possess combination of type I and type II which indicates simultaneous presence of micropores and mesopores. And the isotherms of G0, G3 and G4 represent type II isotherm which are traditionally attributed to mesoporous solids with some contribution by micropores. When $p_0/p > 0.95$, the tailings of isotherms show that there are a few macropores in all samples.

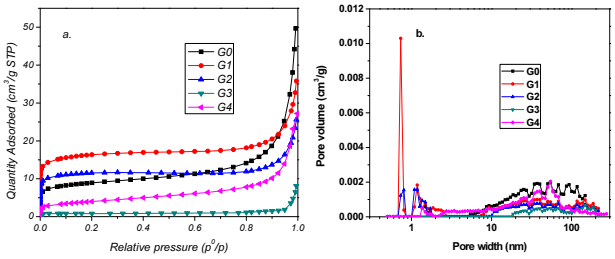

Fig. 1. Characteristics of the porous structure of samples: a – nitrogen adsorption isotherms; b – pore size distribution

The structural parameters of products prepared are measured and listed in Table 2. The total surface area and microporous volume values of G1 and G2 are greater than G0, G3 and G4. This indicates the organic binders are beneficial for the micropores formation. The micropores formation may be in two ways: (1) pyrolytic carbons from organic binders deposited in pores make their size smaller; (2) pyrolytic carbons form micropores. The mesoporous volume percentages of all samples are 75.51 %, 49.07 %, 50.50 %, 58.18 % and 88.89 %, suggesting G0, G3 and G4 are typical mesoporous adsorbents. The lowest surface area and pore volume of G3 may be due to that the silica from sodium silicate decomposition blocks a lot of pores at high temperature.

Table 2. The porous structure parameters of activated carbons

Samples	S_{BET}, m^2/g	V_{total}, cm^3/g	V_{micro}, cm^3/g	V_{meso}, cm^3/g
G0	30.79	0.0499	0.0072	0.0377
G1	55.60	0.0432	0.0180	0.0212
G2	39.06	0.0301	0.0138	0.0152
G3	2.24	0.0055	0.0021	0.0032
G4	14.27	0.0288	0.0008	0.0256

The structural parameters of products prepared are measured and listed in Table 2. The total surface area and microporous volume values of G1 and G2 are greater than G0, G3 and G4. This indicates the organic binders are beneficial for the micropores formation. The micropores formation may be in two ways: (1) pyrolytic carbons from organic binders deposited in pores make their size smaller; (2) pyrolytic carbons form micropores. The mesoporous volume percentages of all samples are 75.51 %, 49.07 %, 50.50 %, 58.18 % and 88.89 %, suggesting G0, G3 and G4 are typical mesoporous adsorbents. The lowest surface area and pore volume of G3 may be due to that the silica from sodium silicate decomposition blocks a lot of pores at high temperature.

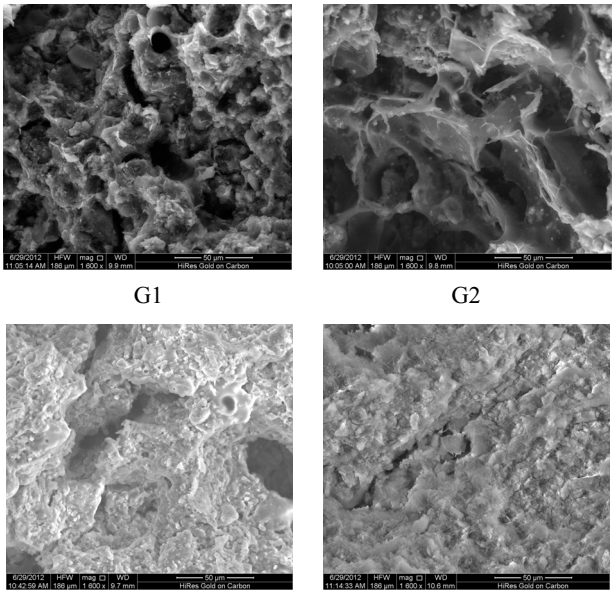

Fig. 2. SEM micro-graphs of G1, G2, G3 and G4

The surface of G1, G2, G3 and G4 were observed by SEM, and the micro-graphs are shown in Fig. 2. It can be seen that there are much pyrolytic carbons or ash in pores of G1 and G2, verifying that pyrolytic carbons actually change the pore size, and suggesting specific surface area and pore volume increase could be through activation or washing. In addition, there are obvious traces of burning on surfaces of G3 and G4, indicating that the sodium silicate and calcium sulfate might be activators besides binders. Moreover, the Elemental analysis of all samples show that carbon contents of G3 and G4 are trace, which also suggesting the sodium silicate and calcium sulfate could be activators. And the study on synthesis of nitrogen-doped porous graphitic carbons worked by Guangwen Yang et al. [19] also confirmed that calcium salt could be used as activating agent.

Details on the porosity of the granular activated carbons produced are presented in Fig. 1, b. The G0, G3 and G4 are principally in the mesopore range and evidenced a significant pore volume increment at a pore diameter > 2 nm, respectively. The G1 and G2 have a large pore volumes in the ranges of 0.7 nm – 2.0 nm and > 8 nm.

3.1.2. Surface functional groups

The FTIR spectra of G0, G1, G2, G3 and G4 are demonstrated in Fig. 3. It is shown that the major differences of all samples are in the ranges of (1000 – 1200) cm^{-1} and (400 – 800) cm^{-1}. The bands at about 3400 cm^{-1}, 1600 cm^{-1}, 1400 cm^{-1} and 1050 cm^{-1} of all samples are assigned to the hydroxyl groups (–OH), the C=O stretching vibration of carbonyl groups, COOH groups vibration, and the C–O–C group in carboxylic and alcoholic groups [20], respectively. The bands round 1100 cm^{-1} and 1150 cm^{-1} of G4 are ascribed to C–O stretching in alcohol, ether or hydroxyl groups and asymmetric stretching vibration (–C–O–C– ring) [21]. A broad band between (400 – 800) cm^{-1} of G1, G2, G3 and G4 are assigned to bending vibration of –OH groups, or stretching vibration of C–O groups [22].

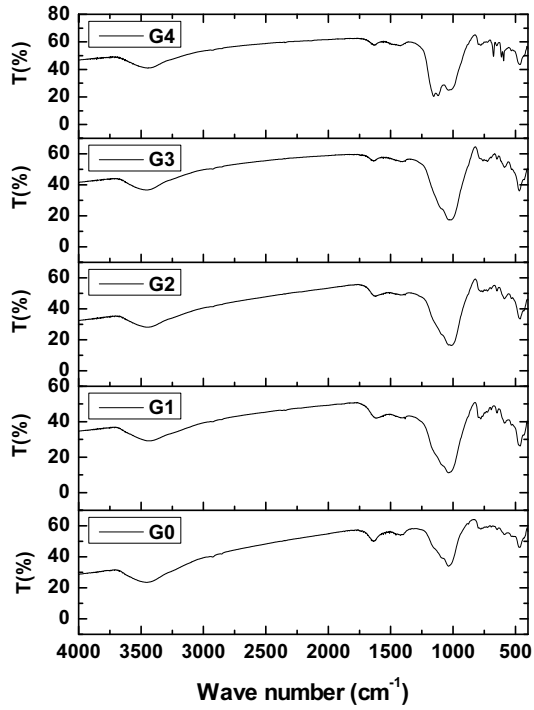

Fig. 3. FT-IR spectra of all samples

3.2. Adsorption of methylene blue

3.2.1. Adsorption equilibrium

The adsorption equilibrium curves of MB adsorbed on all samples (q_e) versus equilibrium aqueous MB concentration (C_e) at 25 °C were shown in Fig. 4. The MB adsorption capacities of all granular samples are enhanced with the increase of dye initial concentration. When the initial dye concentration is greater than 50 mg/L, the MB adsorption capacity of G4 is obviously greater than the other four samples. And with the increase of MB initial concentration, the MB adsorption amounts of G1, G2, G3 and G4 are fleetly closed to equilibrium, which may be

attributed to the influence of –OH or C–O groups between 400 cm^{-1} and 800 cm^{-1}.

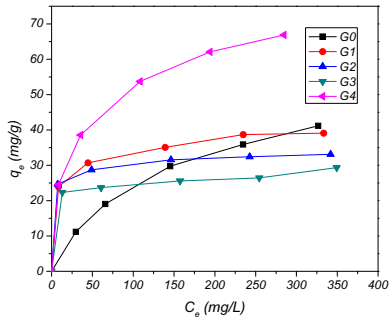

Fig. 4. Adsorption equilibrium of MB onto laboratory-produced granular adsorbents

The calculated constants of the Langmuir's and Freundlich's isotherm equations along with R2 values are presented in Table 3. Except the one from Freundlich's isotherm equation of G3, all R2 values is greater than 0.98, indicating the adsorption process of MB onto samples prepared might be a heterogeneous adsorption. However, the Langmuir model fitted the experimental data better, suggesting the adsorption of MB onto products prepared is dominantly physical adsorption and the adsorption capacity of MB is closely related to the surface area of samples. However, the MB adsorption of G4 is maximum, while its surface area is not the maximum. This may be due to the ion exchange between metal ions and MB molecules [23].

Table 3. Langmuir and Freundlich isotherm constants and regression correlation coefficients for the adsorption of MB onto samples

Sam-ples	Langmuir model				Freundlich model		
	Q_0, mg/g	K_L, L/mg	r	R^2	K_F, mg/g	n	R^2
G0	56.50	0.01	0.69	0.9974	1.88	1.85	0.9897
G1	40.32	0.08	0.23	0.9983	18.01	7.32	0.9938
G2	33.44	0.16	0.16	0.9996	21.14	12.79	0.9966
G3	29.33	0.07	0.32	0.9926	18.02	13.55	0.8701
G4	71.94	0.04	0.27	0.9948	13.58	3.48	0.9965

For Langmuir isotherm, the value of r is found to be less than 1, suggesting the samples prepared is favorable for adsorption of MB under conditions studied and the isotherms may be classified as type I. However, the values of n from Freundlich isotherm equation indicate that only G0, G1 and G4 is favorable for adsorption of MB. Due to the lower n value, the MB adsorption of G0 and G4 is more favorable.

3.2.2. Comparison of adsorbents

The maximum adsorption capacities of MB onto different adsorbents prepared from various sludge, are listed in Table 4. It can be seen that the adsorption capacities of granular samples without activators obtained in this work are greater than the powdered samples also without activating agents, suggesting it is practicable that preparation of granular activated carbons from sewage sludge for MB adsorption. And activation could observably improve MB adsorption capacities of samples. Therefore, the MB adsorption capacities of G0, G1 and G2 are enhanced by chemical or physical activation. Moreover, the adsorption capacity of G4 was 71.94 mg/g. It is lower than powdered samples prepared by ZnCl2 and atmosphere, which is due to the surface area or pore volume reduce of granular sample comparing with powdered sample. This indicates that calcium sulfate is a likely activator, while it is also a binder.

Table 4. Comparison of adsorption capacities of various adsorbents for MB

Precursor	Activating agent	Particle shape	Adsorption capacity (mg/g)	Reference
Sewage sludge of urban treatment plant	None	granular	56.50	This study
	None		40.32	
	None		33.44	
	$NaSiO_3$		29.33	
	$CaSO_4$		71.94	
Anaerobic sludge of urban treatment plant	H_2SO_4	powdered	24.5	[3]
	$ZnCl_2$		102.0	
	None		16.6	
Sewage sludge of urban treatment plant	H_2SO_4	powdered	62.3-74.7	[24]
Paper mill sewage sludge	None	powdered	25.44	[25]
	atmosphere		130.69	

4. CONCLUSIONS

In this study, sludge based granular adsorbents have been successfully prepared by carbonization, using soluble starch, sodium carboxymethyl cellulose, sodium silicate and calcium sulfate as binder, respectively. The N2 isotherms of G1 and G2 possess combination of type I and type II which indicate simultaneous presence of micropores and mesopores, while G0, G3 and G4 are the typical mesopore adsorbents. The SEM micro-graphs of G1, G2, G3 and G4 indicate that pyrolytic carbons from soluble starch and sodium carboxymethyl cellulose change pores size, and there are obvious traces of burning on surfaces of G3 and G4, which indicates that the sodium silicate and calcium sulfate might be activators besides binders. The FTIR spectra suggest that comparing with G0, G1, G2, G3 and G4 have broad bands and the major differences of surface functional groups are between $(1000-1200)\ cm^{-1}$ and $(400-800)\ cm^{-1}$. MB adsorption equilibrium data of all products prepared are fitted to the Langmuir and Freundlich isotherm models well, indicating the adsorption of MB onto products prepared might be a heterogeneous adsorption. Comparing with the powdered samples reported, it is practicable that preparation of granular activated carbons from sewage sludge for MB adsorption.

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