Removal of Hg (II) from Aqueous Solution on Powdered Coal-Based Activated Carbon: Experimental Design of Microwave Assisted Preparation, Equilibrium and Kinetic Study

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Summary: Preparation of activated carbon from anthracite through microwave-assisted activation was optimized by response surface methodology (RSM). The satisfactory conditions were obtained as follows: 693 W of microwave power, 10 min of irradiation time and 1:1 of the ratio of KOH to coal, and the corresponding adsorbance of iodine and methylene blue (MB) were of 799.32 and 132.03 mg/g, respectively. The production was characterized using nitrogen adsorption isotherm, scanning electron microscopy (SEM) and Fourier transforms infrared spectroscopy (FTIR). The resultant powdered activated carbons were applied for removing Hg(II) from aqueous solution at different dosage of activated carbon, concentrations of Hg(II), adsorption temperature and pH. The Langmuir isotherm was excellently correlated to equilibrium data of Hg(II) adsorption, showing Langmuir adsorption capacities of Hg(II) was 145.41 mg/g.

Key words: Hg(II); Adsorption; Coal-based activated carbon; Response surface methodology.

Introduction

Mercury and its compounds pollution had received increasing attention during the last decades because of the risk of toxic effects which well known as bio-accumulate, even to very low concentrations [1]. Thus, it is necessary to develop methods to decrease the concentration of mercury in drinking water and industrial wastewater. Many methods, such as chemical reduction, ion-exchange resins and adsorption by porous carbon materials, have been developed to lower mercury presence in contaminated wastewater to innocuous level, and the method of adsorption by activated carbon (AC) was the most attractive method for Hg (II) removal [2].

Many raw materials, such as waste rubber tire[3, 4], sewage sludge[5], waste lignin[6] ,waste tea[7], coconut shell [8] and sugar beet pulp[9], have been chosen to prepare powder and granular ACs which were used for Hg (II) removal [2, 10, 11]. All the chosen material obeys the local specific circumstances. Xinjiang, which is an Autonomous Region of China, contains exceeding 2.19 million tons of coal. In order to promote the development of national economic, it is essential to develop high

value-added coal chemical products. Preparation of AC is a good choice in the background of construction of coal chemical industry.

The properties of AC was obviously influenced by many independent variables in the preparation process. D. Lozano-Castelló and M.A. Lillo-Ródenas *et al.* prepared AC fromSpanish anthracite by different activator (KOH and NaOH), and obtained different BET specific surface area [12, 13]. Otherwise, G. Gong *et al.* prepared AC using KOH as activator from Taixi anthracite in different condition, and also obtained different BET specific surface area as a result[14]. Additionally, different raw materials (shells of Macoré fruit[15], chlorella-based algal residue [16] and hazelnut shell [17]) were used for AC preparation, and resulted ACs with different property were obtained. It is clear that different activator, raw material and other variables could distinctly influence the property.

In the last decades, microwave-assisted method was carried out for preparation of AC due to its high energy conversion efficiency. In this process,

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energy is directly to carbon skeleton at molecular level by dipole-dipole rotation and friction within matrix [6]. The previous studies showed that microwave-assisted heating could change properties and modify surface functional group effectively in the preparation of AC [6, 18-20].

Although microwave-assisted heating has been used to produce AC, the correlative literature about coal-based activated carbon (CAC) was limited. In the present study, microwave assisted preparation of AC by KOH activation from Xinjiang anthracite was optimized by response surface methodology (RSM), and influences of variables (such as weight ratio of KOH to coal, microwave power and irradiation time) on responses (adsorption capacity for iodine and MB) were studied. Meanwhile, equilibrium, and kinetic experiments of Hg(Ⅱ) removal were carried out.

Experimental

Anthracite as precursor was obtained from Que er gou, Hutubi, Xinjiang Uygur Autonomous Region, P.R.China. Before use, the anthracite was crushed and sieved to 100 meshes, and then rinsed exhaustively with deionized water to remove carbon fines, finally dried at ambient temperature of 105°C. All reagents were analytical grade and used without further purification.

Design of Experiments

RSM is a statistical and mathematical techniques that uses quantitative data from appropriate experiments to determine regression model equations and operating conditions [21]. Meanwhile, it is a good facility to analyze the influences between different variables. Box-Behnken design (BBD), which is one of the RSM, develop mathematical model by a spherical and revolving design, regarded as a cube and consisted of a central point and middle points of the edges [22].

The experiment number of BBD was calculated as follow:

$$N = k^2 + k + c_p \qquad (1)$$

where N stands for experimental number; k and c_p are the factor number and replicate number of the central point, respectively.

In present study, three independent variables (ratio of KOH to anthracite, microwave power and

time which were named as X_1, X_2, X_3, respectively.) and two responses (adsorption capacity of iodine and MB) were selected from the published data. According to the BBD, a 17 group experiment design was shown at Table-1, together with the experimental results.

Table-1: Variable levels and response of the yield activated carbon and adsorption capacity for iodine and methylene blue.

Run	Variable levels			Responses	
	X_1	X_2 (W)	X_3 (min)	Absorbance of iodine (mg/g)	Absorbance of MB(mg/g)
9	1:2.0	495	9	426.11	30.76
3	1:1.5	297	10	415.16	61.88
16	1:1.5	495	10	476.58	83.97
11	1:2.0	495	11	412.89	38.19
17	1:1.5	495	10	482.39	88.30
8	1:1.5	693	11	478.30	96.19
4	1:1.0	693	10	778.94	124.25
5	1:1.5	297	9	324.04	42.52
2	1:2.0	693	10	429.72	59.12
15	1:1.5	495	10	469.47	89.01
1	1:2.0	297	10	152.47	20.73
6	1:1.5	693	9	649.05	97.92
13	1:1.5	495	10	473.05	85.21
12	1:1.0	495	11	677.89	117.42
14	1:1.5	495	10	468.48	84.01
7	1:1.5	297	11	156.06	42.52
10	1:1.0	495	9	636.09	119.25

Preparation of Coal-Based Activated Carbon

The preparation process was carried out at a microwave reactor. The device was operated at 2.45 GHz under varying microwave level (100-900 W). The power selector and timer controller were native knob. Meanwhile, the vacuum pump was connected the refitting microwave to keeping a vacuum environment. To preparation of CAC, the potassium hydroxide was selected as activating agent. The preparation condition of CAC was yield in Table-1. The activated production was washed by 10% hydrochloric acid, hot deionized water and cool deionized water, successively, until the filtrate reached neutral and then dried. The activated carbon was hereafter referred to as MCAC.

Characterization

The pore structure of MCAC was determined by nitrogen adsorption isotherm at 77 K using BET equation. SEM (JSM-6490LV) was completed on raw and MCAC. FT-IR spectrum (KBr pellets), which was detected the surface functional groups, were recorded on an AVATAR360 Fourier transform spectrometer with a scanning range of 4000-500 cm⁻¹. The Surface acidity/basicity was determined by titration using the NaOH and HCl. The pH of the point of zero charge,

pH_{PZC} was determined using so-called pH drift method[23].

Hg(II) Removal

Stock solutions (1.00 g·L^{-1}) of Hg(II) ions was prepared with 5% nitric acid solution by using analytical grade $HgCl_2$. The stock solution was diluted with double distilled water and to standard solutions of appropriate concentrations (20-100 mg/L). The adsorption studies of MCAC for Hg(II) were determined by the following procedure: the amount of MCAC (0.05-0.50 g) was added to 0.05L Hg(II) solution with agitating 120 rpm for 3h at various temperature. Before adsorption, the pH of solution which detected by a pH meter was adjusted by adding 0.10 M HCl or NaOH. The initial and equilibrium concentrations of Hg(II) were determined by Hydra II C Mercury Analyzer. The calculated formula of adsorbance of Hg(II) (q_e) was follows:

$$q_e = \frac{(C_0 - C_e)V}{m} \tag{2}$$

where C_0 (mg/L) and C_e (mg/L) are initial and equilibrium concentration of Hg(II), respectively. V (L) and m (g) represent the volume of the solution and the mass of MCAC used, respectively.

In order to study the adsorption equilibrium, batch adsorption experiments were carried as follows: the mixture of 0.10g MCAC and 0.05L aliquots of 100 mg/L Hg(II) solutions was shaken with 120 rpm at room temperature for 12h. The absorbance of Hg(II) (q_t) was calculated as follow:

$$q_t = \frac{(C_0 - C_t)V}{m} \tag{3}$$

where C_0 (mg/L) and C_t (mg/L) are concentrations of Hg(II) at initial stage and time t, (min) respectively. V (L) represents the volume of the solution and m (g) stands for the mass of MCAC used.

Adsorption isotherms were fitted with Langmuir and Freundlich equation as described below[24, 25]:

A. Langmuir equation:

$$q_e = \frac{Q_0 K_L C_e}{1 + K_L C_e} \tag{4}$$

where Q_0 (mg/g) and K_L (L/g) are Langmuir constants related to adsorption capacity and rate of adsorption, C_e (mg/L) is the equilibrium concentration of the Hg(II), and q_e (mg/g) is the mount of Hg(II) adsorbed per unit mass of adsorbent.

B. Freundlich equation:

$$q_e = K_F C_e^{1/n} \tag{5}$$

where K_F (mg/g) (L/mg)$^{1/n}$ and $1/n$ are Freundlich adsorption constant and a measure of adsorption intensity, respectively

Adsorption Kinetics Study

Adsorption kinetics aimed to confirm the rate constant of adsorption and the absorbance of equilibrium. In the present study, the pseudo-first [26] and pseudo-second order equation[27] were considered for adsorption kinetics. The kinetics equations were defined as:

$$\frac{dq}{dt} = k_1(q_e - q_0) \tag{6}$$

$$\frac{dq}{dt} = k_2(q_e - q_0)^2 \tag{7}$$

where q_e (mg/g) and q_0 (mg/g) stand for the equilibrium and initial concentration of Hg(II), respectively; k_1 (mg/g·h) and k_2 (mg/g·h) represent the adsorption rate constant of pseudo-first and pseudo-second order equation, respectively.

Results and Discussion

Optimization by RSM

The preparation conditions of MCAC which covered the parameters such as ratio, microwave power and irradiation time were generated by the software of Design Expert 7.1, and the absorbance of iodine and MB as responses were compiled in Table-1. As can be seen in Table-1, the adsorption of iodine (778.94 mg/g) and MB (124.61 mg/g) were found to be the optimization on the 4th run. The experimental data were fitted to a second order polynomial

regression model which coefficient is positive indicates synergistic effect; conversely, negative indicates antagonistic effect [28] as follow:

$$Y_1 = 473.99 - 135.86X_1 + 161.04X_2 - 38.77X_3 - 21.63X_1X_2$$
$$-13.75X_1X_3 - 0.69X_1X_3 + 53.23X_1^2 - 83.15X_2^2 + 11.02X_3^2 \quad (8)$$

$$Y_2 = 86.10 - 34.25X_1 + 26.23X_2 + 0.48X_3 - 6.00X_1X_2$$
$$+2.31X_1X_3 - 0.43X_2X_3 - 6.49X_1^2 - 13.11X_2^2 - 3.20X_3^2 \quad (9)$$

where Y_1 and Y_2 represents the adsorption capacity of iodine and MB, respectively; X_1, X_2 and X_3 are the ratio of KOH to anthracite, microwave power and irradiation time, respectively.

The ANOVA of the quadratic model for absorbance of iodine and MB were listed in Table-2 and Table-3. It can be found that the high *F*-value of 16.46 and 24.51 and low *P*-values less than 0.05 for the adsorbance of iodine and MB implied significance of the model. Besides, the effect of variables were ordered by linear terms (X_1 and X_2), followed by squared terms (X_1^2 and X_2^2), and then interaction terms (X_1X_2 and X_1X_3).

The three-dimensional response surface graphs were showed in Fig. 1. The three-dimensional response surfaces, which were constructed to the important two variables (ratio of KOH to coal and microwave power) on the adsorption capacity of iodine and MB at constant irradiation time (10 min), was shown in Fig. 1a and 1d. Evidently, absorbance of iodine enlarged from 152.47 to 778.94 mg/g, and MB from 20.73 to 124.25 mg/g with the ratio increased form 0.5 to 1.0, and then a flat slope was kept along at constant irradiation time (10 min). This clearly shows that ratio and microwave power were important process variable to the adsorption capacity. The optimal adsorbance of iodine (778.94 mg/g) and MB (124.61 mg/g) were determined at fixed irradiation time (10 min).

Fig. 1b and Fig. 1e showed that the three-dimensional response surfaces of the combined effect of ratio and irradiation time at constant microwave power of 495 W. The trends of absorbance of iodine and MB were drastic ascent with increasing ratio. Ratio is likely an important factor influencing the adsorption capacity at invariable microwave power. The influence of irradiation time and microwave power was displayed in Fig.1C and 1F. Approximately identical adsorbance with the increase of irradiation time was occurred at the microwave power range used. It is clearly demonstrated that irradiation time slightly influenced decolourization which is corresponding with the result of ANOVA analysis. In the process, pore structure could develop easier at a higher microwave power as the reaction between KOH and the carbon precursor was more blazing, moreover, the tar or volatile matter components were easier removed at a higher temperature, and pore structure expand as a result, which caused the change of adsorbance [29].

The optimization conditions for the preparation of MCAC were obtained as ratio of KOH to coal of 1:1, microwave power of 637 W and irradiation time of 9 min and the resultant adsorbance of iodine and MB were of 799.32 and 132.03 mg/g, respectively.

Table-2: ANOVA for response surface quadratic model for adsorption capacity of iodine.

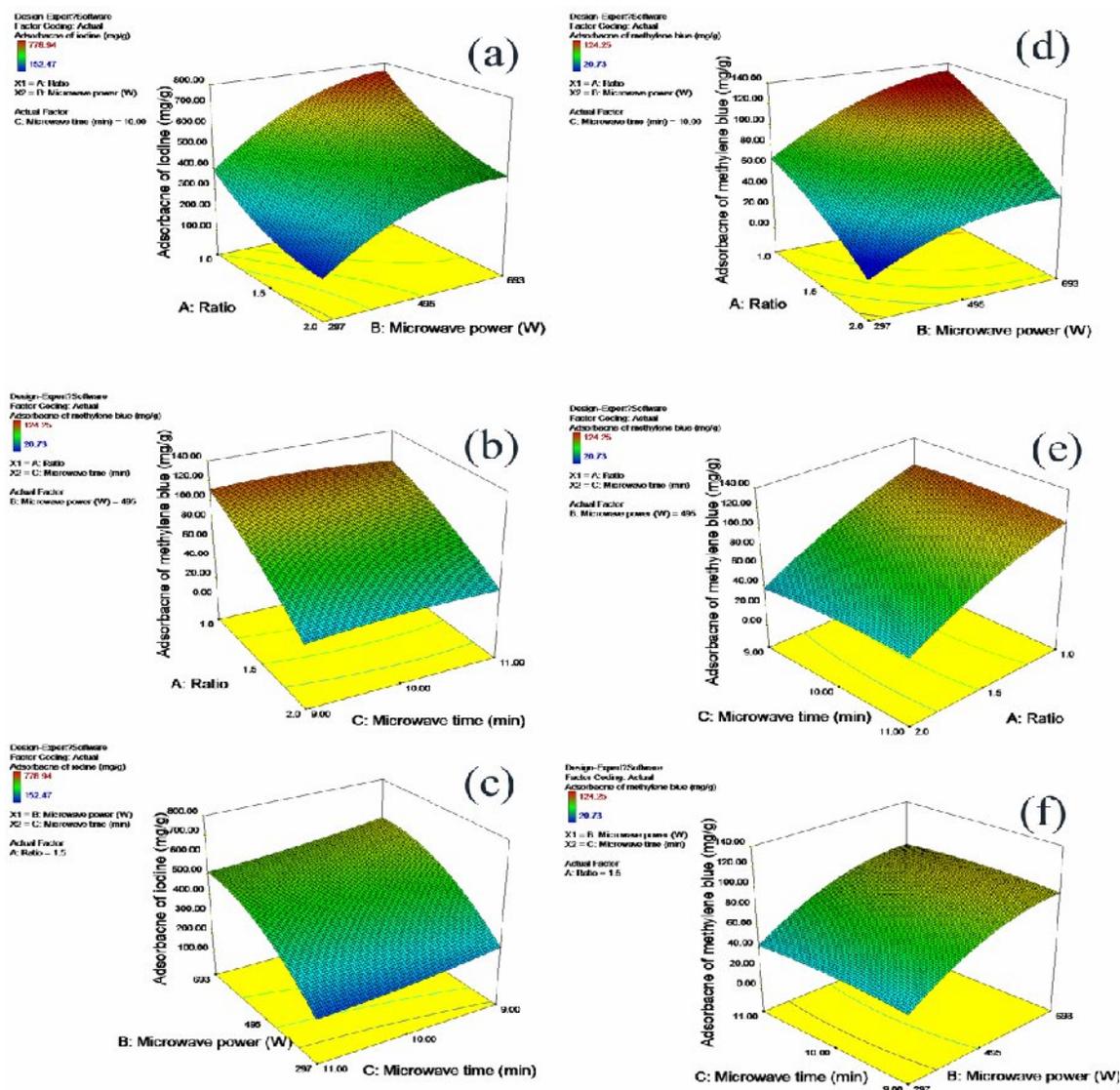| Source	Sum of Squares	df	Mean Square	*F*-Value	*p*-value Prob > *F*	
Model	4.093E+005	9	45482.22	16.46	0.0006	significant
X_1	1.477E+005	1	1.477E+005	53.44	0.0002	
X_2	2.075E+005	1	2.075E+005	75.08	< 0.0001	
X_3	12024.13	1	12024.13	4.35	0.0754	
X_1X_2	1871.86	1	1871.86	0.68	0.4376	
X_1X_3	756.80	1	756.80	0.27	0.6169	
X_2X_3	1.92	1	1.92	6.942E-004	0.9797	
X_1^2	11930.47	1	11930.47	4.32	0.0763	
X_2^2	29112.65	1	29112.65	10.54	0.0141	
X_3^2	511.37	1	511.37	0.19	0.6800	
Residual	19342.09	7	2763.16			
Lack of Fit	19213.14	3	6404.38	198.67	< 0.0001	significant
Pure Error	128.94	4	32.24			
Cor Total	4.287E+005	16				

Fig. 1: Three-dimensional response surface plot of activated carbon adsorbance for iodine (a, b and c) and MB (d, e and f).

Table-3:   ANOVA for response surface quadratic model for adsorption capacity of MB.

Source	Sum of Squares	df	Mean Square	F-Value	p-value Prob > F	
Model	16075.56	9	1786.17	24.51	0.0002	significant
X_1	9384.50	1	9384.50	128.75	< 0.0001	
X_2	5503.58	1	5503.58	75.51	< 0.0001	
X_3	1.87	1	1.87	0.026	0.8772	
X_1X_2	143.76	1	143.76	1.97	0.2030	
X_1X_3	21.44	1	21.44	0.29	0.6044	
X_2X_3	0.75	1	0.75	0.010	0.9221	
X_1^2	177.55	1	177.55	2.44	0.1625	
X_2^2	723.81	1	723.81	9.93	0.0161	
X_3^2	43.15	1	43.15	0.59	0.4668	
Residual	510.21	7	72.89			
Lack of Fit	487.21	3	162.40	28.24	0.0038	significant
Pure Error	23.01	4	5.75			
Cor Total	16585.78	16				

Characterization

The nitrogen adsorption-desorption curve and the surface physical parameters of MCAC were demonstrated in Fig. 2 and Table-4, respectively. As can be seen in Fig. 2, the adsorption isotherm curve was similar to an intermediate between type I and type II isotherms according to the existence of microporous and mecroporous structure illustrated by International Union of Pure and Applied Chemistry (IUPAC). A hysteresis loop, which was presented in the desorption branch at high relative pressures, indicated the presence of mesoporosity. Meanwhile, it can be observed that the BET surface area, Langmuir surface area, total pore volume and average pore size of MCAC were 849.31 m^2/g, 1281.46 m^2/g, 0.476 cm^3/g and 22.43 Å, respectively (Table-4).

Table-4: Porous structure parameters of the MCAC.

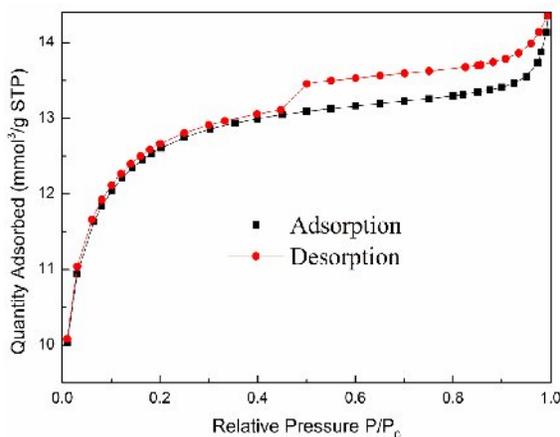| Properties	MCAC
BET surface area (m^2/g)	849.31
Micropore surface area(m^2/g)	579.30
External surface area(m^2/g)	270.01
Langmuir surface area(m^2/g)	1281.46
Total pore volume (cm^3/g)	0.476
Micropore volume (cm^3/g)	0.318
Average pore size (Å)	22.43

Fig. 2: Nitrogen adsorption-desorption curves of MCAC at 77 K.

The microscopic structure of coal and MCAC were shown in Fig. 3. As can be seen, the surface of coal is planar without pore structure. After activation, there are lots of small pores and crevices on the surface, which well developed pore network[18]. This shows that the activation stage mainly creates macro and mesoporous which significantly increases the surface area of MCAC.
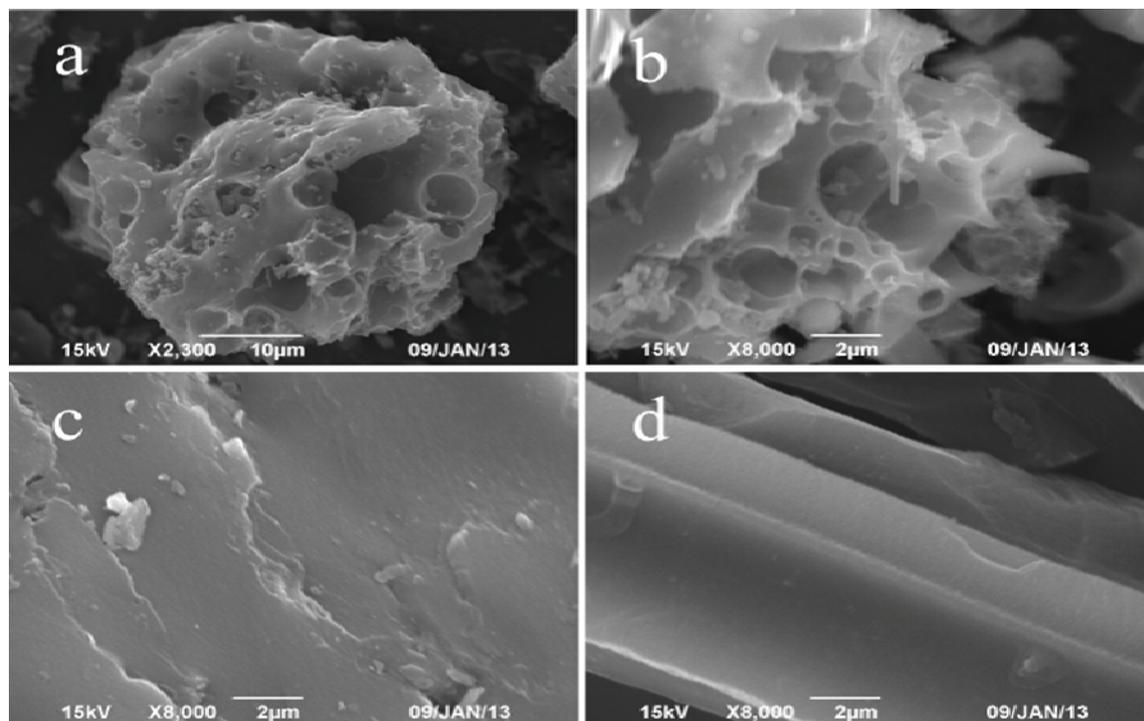

Fig. 3: SEM Micrographs of the MCAC (a and b) and coal (c and d).

To characterize surface groups of MCAC, FT-IR spectra were obtained (listed in Fig. 4.). The absorbance band at 3433.66 cm^{-1} was related to -OH groups[19], and the region between 1627.47-1450.86 cm^{-1} of the carbonyl group[30]. The signal at 2354.54 cm^{-1} was identical to the C≡C (alkynes)[31]. Similarly, the presence of C=O functional groups of anhydrides showed the transmittance at 1038.76 cm^{-1}[31]. It was obviously that amounts of acidic surface functional group were presented. Therefore, MCAC exhibited acidic character with a surface acidity of 1.66 mmol/g and surface basicity of 0.56 mmol/g. Meanwhile, the pH$_{pzc}$ was found to be 6.98.
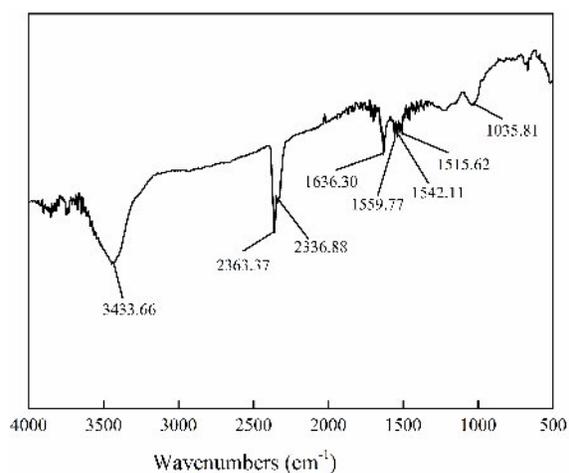

Fig. 4:　　FTIR spectra of MCAC.

Hg(Ⅱ) Removal

The Influence of Dosage

Fig. 5a displayed the effect of MCAC dosage on Hg(II) adsorbance. In this case, the adsorbance was decreasing as the dosage increasing, because of particles electrostatic interactions, interfacing metal binding sites or mixing problems. The optimum dosage corresponded to the least amount of MCAC with the highest Hg uptake: 0.5 g/L. This phenomenon could explained by that superfluous dosage.

The Influence of Initial Hg(II) Concentration

As can be seen from Fig. 5b, the adsorbance of Hg(II) increased rapidly with the initial concentration enlarging. The result shows that it had stronger mass transfer driving force between the mercury solution and MCAC with higher concentration force. Similar results were reported by other authors[2, 32].

The Influence of Temperature

According to Fig. 5c, it was noticed that the adsorbance of Hg(II) by MCAC decreased from 24.30 to 8.51 mg/g with increasing temperature from 20 to 60°C. On one hand, the hydrogen bond of carboxy group and hydroxyl group was unsteadiness at higher temperature contributed to the less binding site which resulted in lower adsorbance. On the other hand, the adsorption was reversible and exothermic reaction, and the reaction was occurred towarded opposite orient as elevated temperature. According to Li, Li [33], it had been reported that AC contained many carboxylic acids groups which were thermally less stable and more easily decomposed to carbon dioxide and carbon monoxide. The less functional group led to the lower adsorbance. As well as AC surface chemistry, aqueous pH greatly influences Hg(II) speciation therefore influencing removal.

The Influence of pH

As can be seen Fig. 5d, the adsorbance of Hg(II) reached maximum at a pH of 4, and the adsorbance gradually decreased as pH aggrandizement. This may be caused by the different retention of Hg(II), in the acid medium, the Hg(II) exists as the species of Hg^{2+} and Hg(OH)$^+$ which could exchanges H$^+$ with carboxyl groups in AC[32, 34].

Adsorption Study

Adsorption Equilibrium

The adsorption isotherm attested molecules distribute between adsorbent and adsorbate while the adsorption process reached an equilibrium state[6]. In present study, isothermal models of Langmuir and Freundlich were used to fit the results. A better correlation coefficient (R^2=0.9431) of Langmuir was found in Table-5 and Fig.6. That is to say, the process of Hg(II) adsorption on MCAC was monolayer adsorption[33].
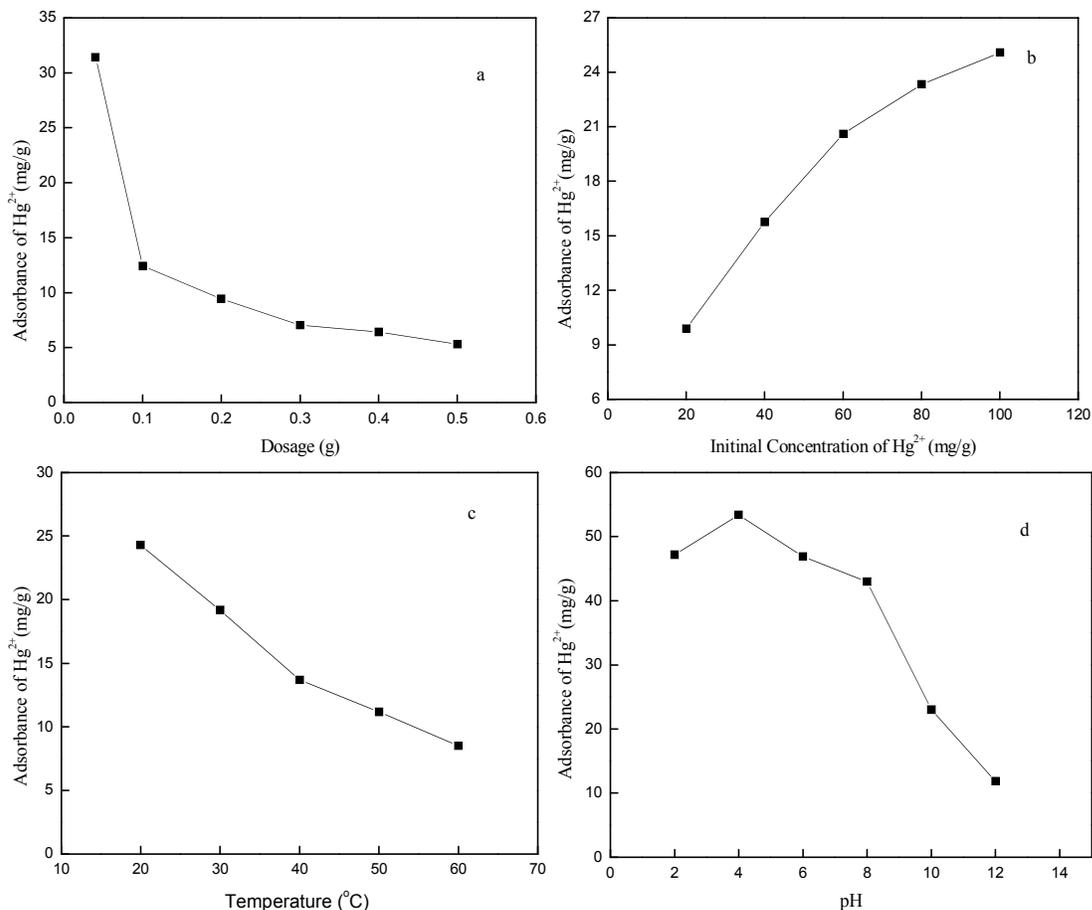
Fig. 5:   The influence factor of Hg adsorbance on MCAC: (a)Dosage; (b)Initial concentration; (c)Temperature; (d)pH.

Table-5: Isotherm and kinetic parameters for the adsorption of Hg(II) onto CAC at 30°C.

Model	Constant		R^2
Langmuir	Q_o (mg/g)	K_L (L/mg)	R^2
	145.41	0.1263	0.9349
Freundlich	n	K_F (mg/g).(L/mg)$^{1/n}$	R^2
	2.3841	29.4516	0.8505
Pseudo-first-order	K_1(1/min)		R^2
	0.0050		0.9289
Pseudo-second-order	K_2(g/mg h)		R^2
	0.0445		0.9964

Adsorption Kinetics

Pseudo-first and pseudo-second order model have been proposed to predict the mechanism of Hg(II) adsorption by MCAC. The adsorption data were fitted using the plots of $\ln(q_e-q_t)$ against t for pseudo-first order model and t/q_t versus t for pseudo-second order model. Table-5 and Fig. 7 showed that the pseudo-second order model, indicating a chemisorption mechanism, could better fit the experimental data with an correlation coefficient of 0.9964.
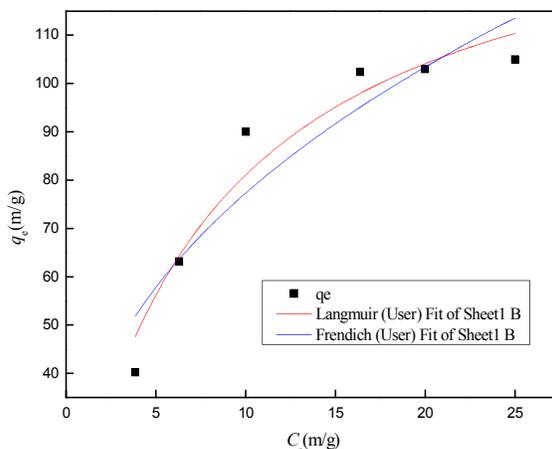

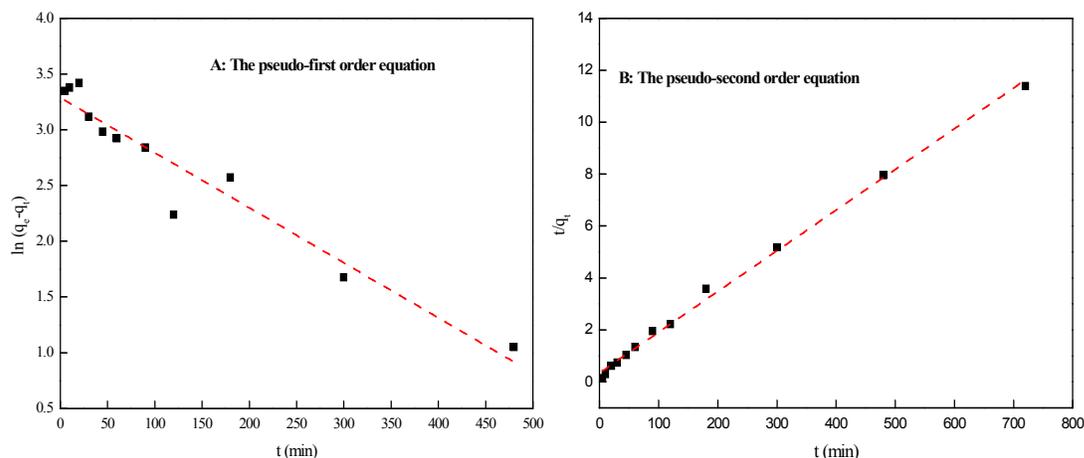Fig. 6:   Langmuir and Freundlich isotherm plot for the adsorption of Hg(II) on MCAC

Fig. 7:   Pseudo-first-order and Pseudo-second-order kinetic plot for the adsorption of Hg(Ⅱ) on MCAC.

Conclusion

It had indicated that KOH was a suitable activating agent for the preparation of AC from Xinjiang anthracite by microwave radiation. The RSM was employed to optimize the preparation conditions of MCAC. The ratio of KOH to anthracite and microwave power significantly influence the adsorbance of iodine and MB from ANOVA. The optimization conditions of ratio of KOH to coal of 1:1, microwave power of 637 W and irradiation time of 9 min were obtained. The prepared MCAC at above conditions was employed to adsorbe iodine and MB and the value of adsorbance were of 799.32 and 132.03 mg/g, respectively. The nitrogen adsorption-desorption curve was similar to an intermediate between type I and type II isotherms, and the BET surface area, Langmuir surface area, total pore volume and average pore size of MCAC were 849.31 m^2/g, 1281.46 m^2/g, 0.476 cm^3/g and 22.43 Å, respectively. FT-IR spectrum of MCAC showed many peaks belonging to different functional groups. MCAC exhibited acidic character with a surface acidity of 1.66 mmol/g and surface basicity of 0.56 mmol/g. Meanwhile, the value of pH_{pzc} was found to be 6.98. SEM micrographs showed that the external surface of MCAC was full of cavities compared with starting materials. The resulted MCAC was also used for removal of Hg(II). Adsorption was found the maximum in the pH of 4, and temperature of 20^oC. Through the Adsorption isotherm and kinetics experiment, the Langmuir adsorption capacities of Hg(II) reached 145.41 mg/g, and the adsorption were found to agree satisfactorily with the model of Langmuir and pseudo second-order model, respectively.

References

1. T. W. Clarkson, L. Magos, The Toxicology of Mercury and its Chemical Compounds, *CRC Crit. Rev. Toxicol.*, **36**, 609 (2006).
2. K. Ranganathan, Adsorption of Hg (II) Ions from Aqueous Chloride Solutions using Powdered Activated Carbons, *Carbon*, **41**, 1087 (2003).
3. V. Gupta, B. Gupta, A. Rastogi, S. Agarwal and A. Nayak, A Comparative Investigation on Adsorption Performances of Mesoporous Activated Carbon Prepared from Waste Rubber Tire and Activated Carbon for a Hazardous Azo Dye-Acid Blue 113, *J. Hazard. Mater.*, **186**, 891 (2011).
4. V. Gupta, B. Gupta, A. Rastogi, S. Agarwal and A. Nayak, Pesticides Removal from Waste Water by Activated Carbon Prepared from Waste Rubber Tire, *Water Res.*, **45**, 4047 (2011).
5. Q. Wen, C. Li, Z. Cai, W. Zhang, H. Gao, L. Chen, G. Zeng, X. Shu, Y. Zhao, Study on Activated Carbon Derived from Sewage Sludge for Adsorption of Gaseous Formaldehyde, *Bioresour. Technol.*, **102**, 942 (2011).

6. A. V. Maldhure and J. Ekhe, Preparation and Characterizations of Microwave Assisted Activated Carbons from Industrial Waste Lignin for Cu (II) Sorption, *Chem. Eng. J.*, **168**, 1103 (2011).

7. M. Auta and B. Hameed, Preparation of Waste Tea Activated Carbon Using Potassium Acetate as an Activating Agent for Adsorption of Acid Blue 25 dye, *Chem. Eng. J.*, **171**, 502 (2011).

8. A. L. Cazetta, A. M. Vargas, E. M. Nogami, M. H. Kunita, M. R. Guilherme, A. C. Martins, T. L. Silva, J. C. Moraes, V. C. Almeida, NaOH-Activated Carbon of High Surface Area Produced from Coconut Shell: Kinetics and Equilibrium Studies from the Methylene Blue Adsorption, *Chem. Eng. J.*, **174**, 117 (2011).

9. X. Ma, D. Li, Z. Wu, G. Meng, Y. Wu, H. Zhang and Z. Liu, Preparation of Activated Carbon from Sugar Beet Pulp via Microwave-Assisted Method, *J. Shihezi Univ. (Nat. Sci.)*, **32**, 349 (2014).

10. M. I. Rakowska, D. Kupryianchyk, T. Grotenhuis, H. H. M. Rijnaarts, A. A. Koelmans, Extraction of Sediment-Associated Polycyclic Aromatic Hydrocarbons with Granular Activated Carbon, *Environ. Toxicol. Chem.*, **32**, 304 (2013).

11. M. Lillo-Ródenas, D. Lozano-Castelló, D. Cazorla-Amorós and A. Linares-Solano, Preparation of Activated Carbons from Spanish Anthracite: II. Activation by NaOH, *Carbon*, **39**, 751 (2001).

12. D. Lozano-Castello, M. Lillo-Rodenas, D. Cazorla-Amoros and A. Linares-Solano, Preparation of Activated Carbons from Spanish Anthracite: I. Activation by KOH, *Carbon*, **39**, 741 (2001).

13. G. Gong, J. Liu, W. Yang, Q. Xie, X. Yao and S. Tang, Regulation of Nanostructure in Coal-Based Activated Carbon and its Application for Methylene Blue Removal, *Nanotechnol.* (*IEEE-NANO*), 2012 12th IEEE Conference on, IEEE, pp. 1 (2012).

14. K. N. Aboua, Y. A. Yobouet, K. B. Yao, D. L. Goné and A. Trokourey. Investigation of Dye Adsorption onto Activated Carbon from the Shells of Macoré fruit. *J Environ. Manag.* **156**, 10 (2005).

15. Y. M. Chang, W. T. Tsai and M. H. Li. Characterization of Activated Carbon Prepared from Chlorella-Based Algal Residue. *Bioresour. Technol.* **184**, 344 (2005).

16. A. Şencan, M. Karaboyacı and M. Kılıç. Determination of Lead(II) Sorption Capacity of Hazelnut Shell and Activated Carbon Obtained from Hazelnut Shell Activated with ZnCl₂. *Environ. Sci. Pollut. Res.* **22**, 3238 (2005).

17. D. Xin-Hui, C. Srinivasakannan, P. Jin-Hui, Z. Li-Bo and Z. Zheng-Yong, Preparation of Activated Carbon from Jatropha Hull with Microwave Heating: Optimization using Response Surface Methodology, *Fuel Process. Technol.*, **92**, 394 (2011).

18. K. Yang, J. Peng, C. Srinivasakannan, L. Zhang, H. Xia and X. Duan. Preparation of High Surface Area Activated Carbon from Coconut Shells Using Microwave Heating, *Bioresour. Technol.*, **101**, 6163 (2010).

19. T. Wang, S. Tan and C. Liang, Preparation and Characterization of Activated Carbon from Wood Via Microwave-Induced ZnCl₂ Activation, *Carbon*, **47**, 1880 (2009).

20. B. Hameed, I. Tan and A. Ahmad, Preparation of Oil Palm Empty Fruit Bunch-Based Activated Carbon for Removal of 2, 4, 6-trichlorophenol: Optimization Using Response Surface Methodology, *J. Hazard. Mater.*, **164**, 1316 (2009).

21. A. Kumar, B. Prasad and I. Mishra. Optimization of Acrylonitrile Removal by Activated Carbon-Granular using Response Surface Methodology, *Can. J. Chem. Eng.*, **87**, 637 (2009).

22. H. Deng, L. Yang, G. Tao and J. Dai, Preparation and Characterization of Activated Carbon from Cotton Stalk by Microwave Ted Chemical Activation-Application in Methylene Blue Adsorption from Aqueous Solution, *J. Hazard. Mater.*, **166**, 1514 (2009).

23. I. Langmuir. The Constitution and Fundamental Properties of Solids and Liquids. Part i. Solids, *J. Am. Chem. Soc.,* **38**, 2221 (1916).

24. H. Freundlich. Over the Adsorption in Solution, *J. Phys. Chem.*, **57,** 1100 (1906).

25. Z. T. d. S. S. Lagergren, *Adsorption Geloster Stoffe,* Kungliga Svenska Vetenskapsakademiens, Handlingar, pp. 1 (1898).

26. Y. Ho, G. McKay, A Comparison of Chemisorption Kinetic Models Applied to Pollutant Removal on Various Sorbents, *Process Saf. Environ. Prot.*, **76**, 332 (1998).

27. J. Sahu, J. Acharya and B. Meikap. Optimization of Production Conditions for Activated Carbons from *Tamarind Wood* by Zinc Chloride Using Response Surface Methodology, *Bioresour. Technol.*, **101**, 1974 (2010).

28. Q. S. Liu, T. Zheng, P. Wang and L. Guo, Preparation and Characterization of Activated

Carbon from Bamboo by Microwave-Induced Phosphoric Acid Activation, *Ind. Crop. Prod.,* **31**, 233 (2010).

29. C. Saka, BET, TG–DTG, FT-IR, SEM, Iodine Number Analysis and Preparation of Activated Carbon from Acorn Shell by Chemical Activation with $ZnCl_2$, *J. Anal. Appl. Pyrolysis*, **95**, 21 (2012).

30. Z. Y. Zhong, Q. Yang, X. M. Li, K. Luo, Y. Liu and G. M. Zeng. Preparation of Peanut Hull-Based Activated Carbon by Microwave-Induced Phosphoric Acid Activation and its Application in Remazol Brilliant Blue R Adsorption, *Ind. Crop. Prod.*, **37**, 178 (2012).

31. J. Goel, K. Kadirvelu, C. Rajagopal and V. Garg, Removal of mercury (II) from Aqueous Solution by Adsorption on Carbon Aerogel: Response Surface Methodological Approach, *Carbon*, **43**, 197 (2005).

32. L. Li, X. Li, J.-Y. Lee, T.C. Keener, Z. Liu and X. Yao, The Effect of Surface Properties in Activated Carbon on Mercury Adsorption, *Ind. Eng. Chem. Res.*, **51**, 9136 (2012).

33. J. Goel, K. Kadirvelu and C. Rajagopal. Competitive Sorption of Cu (II), Pb (II) and Hg (II) Ions from Aqueous Solution Using Coconut Shell-Based Activated Carbon, *Adsorpt. Sci. Technol.*, **22**, 257 (2004).