Adsorption Removal of Inhibiting Compounds by Modified Activated Carbon

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Abstract: The effects of modification on the surface properties and inhibiting compounds (formic acid, acetic acid, 5-hydroxymethylfurfural and furfural) removal performance of activate carbon (AC) were investigated. The raw and modified ACs were characterized, the result showed that the surface chemistries of the modified ACs were significant changed, but only the porous structure of modified by HNO_3 were slightly damaged, and the others no obvious change. The formic acid and acetic acid removal performance of modified AC had a certain amount of improvement compared to the raw AC, but it is still relatively low (15% and 14%), so AC adsorption is not suitable for removal formic acid and acetic acid. And the 5-hydroxymethylfurfural (5-HMF) and furfural removal performance of modified AC by $ZNCl_2$ is good (89% and 81%). the process of adsorption of 5-HMF and furfural by activated carbon belongs to the process of exothermic physical adsorption and is the entropy reduction process. The adsorption is best carried out at low temperature.

Keywords: Inhibiting Compounds, Modified Active Carbon, Adsorption, Kinetics, Isotherms

1. Introduction

The low economic value and high availability of lignocellulosic materials result that the lignocellulosic materials is the most promising sources of renewable raw material for various biotechnological processes. The main ingredients of lignocellulosic is cellulose, hemicellulose and lignin. These materials have fibrous structure of rigid [1; 2]. In order to use these materials, it was selectively separated of the main fractions in biotechnological processes, the methods include different physical, chemical and various combinations thereof [3]. During acid hydrolysis, the sugars and lignin are degraded into several toxic compounds, which can inhibit microbial metabolism. The inhibiting compounds include furan-derivatives (furfural and 5-hydroxymethyl furfural), phenolic compounds and weak acids (formic acid and acetic acid) [4]. Thus detoxification of the hydrolysate is an important aspect to be considered for the improvement of fermentation processes from hydrolysates [5].

Various methods have been proposed to remove inhibiting compounds from hydrolysate to levels that would not inhibit the fermentation process [6; 7]. Adsorption by activated carbon (AC) is one of the most frequently used methods because of the remarkable adsorption capacity and the simplicity in operation [8]. The AC has several different classification, according to the method of manufacture activated carbon can be divided into chemical (Phosphoric acid, sodium hydroxide, zinc chloride, etc) and physical methods of activated carbon. According to the raw material of manufacture activated carbon can be divided into coconut shell, coal quality and wooden activated carbon, etc, the different AC have the difference of porous structure, surface area and surface functional groups, which can affect the performance of adsorption by AC [9; 10]. In previous studies, activated carbon adsorption research focus on the hydrolysate and adsorption conditions [11; 12]. The adsorption of lignin and associated impurities by three commercial AC were investigated by the literature [13] for xylo-oligosaccharides separation from autohydrolysis liquor of almond shells. This work revealed that the increase of AC elevated the removal of lignin-derived species to 80%. The study of adsorption of

furan-derivatives and weak acids by AC is less.

In this work, AC carbon was modified by HNO_3, $ZNCl_2$, KOH and HCl to the preparation of modified activated carbon samples (ACs), properties of the ACs were characterized by N_2 adsorption/desorption, Boehm titration and FTIR. The adsorption of formic acid, acetic acid, 5-HMF and furfural from aqueous solution on raw and modified ACs were investigated systematically, and the adsorption kinetics, isotherms and adsorption thermodynamics were analyzed.

2. Methods

2.1. Materials

Commercial AC was activated with phosphoric acid and in powder form with 200 mesh particle size, it was supplied by Guangzhou Hanyan Activated Carbon Manua'cturing Co. Ltd. The formic acid, acetic acid, 5-HMF and furfural were supplied by Tianjin Ruijin Chemical Co. Ltd.

2.2. Preparation of ACs

The activated carbon (AC) were modified using solutions of 1 mol/L HNO_3 (AC-N samples), $ZNCl_2$ (AC-ZN samples), KOH (AC-K samples) and HCl (AC-Cl samples) as impregnating agents, and one other AC were impregnated by deionized water (AC-raw samples); the proportion of AC and impregnating agents ratio was 1:4 w/w. Those impregnations were agitated at 80°C for 12 h; after this time, they were washed with deionized water until constant pH was obtained and were then dried in oven at 105°C for 72 h.

2.3. Characterization Methods

The BET surface area and pore structure characteristics of the ACs were determined by N2 adsorption/desorption at 77 K using a surface area analyzer (v-sorb2800p, Gold APP Instrument Corporation China). The surface functional groups of the ACs were quantitatively measured using Boehm's titration method [14]. The surface functional groups of the ACs were also determined with a Fourier transform infrared spectrometer (VERTEX70, Bruker) in the scanning range of 4000-400 cm-1.

The concentration of formic acid, acetic acid, furfural, and 5-HMF were measured using a Shimadzu LC-20T HPLC system equipped with a Waters C18 symmetry column (4.6-150 mm, 5μm) and a UV detector. Samples were run at 30°C and eluted at 1.0 mL/min with a gradient elution mode of mobile phase A and B, mobile phase A was a mixture of 0.02 mol/L NaH_2PO_4 and acetonitrile with a volume ratio of 95:5 at pH 2.8 adjusted by H_3PO_4. Mobile phase B was a mixture of acetonitrile and methanol with a volume ratio of 50:50. All analyses were carried out in duplicates at a minimum. The average data were reported. The standard deviations were calculated as measurement errors.

2.4. Adsorption Experiments

Batch experiment for inhibiting compounds (formic acid, acetic acid, 5-HMF and furfural) adsorption by the ACs was carried out in a temperature-controlled water bath magnetic stirrer with a stirring rate of 400 rpm. The effect of contact time (0-5min), initial pH value (2-11), temperature (20-50°C) initial concentration of inhibitor (10-1000 mg/L) on the adsorption performance were investigated.

100 mL inhibitor solution with certain concentration and magnetic rotor were added into the 150 mL conical flask. NaOH and HCl were adopted to adjust pH value before adsorption experiments. After the adsorption process, the solution was filtered through a 0.22 μm nylon membrane and then the filtrate was analyzed by HPLC to determine the concentration of inhibitor. The adsorbed amount of dyes was calculated according to the following Eq. (1),

$$q_t = (C_0 - C_t)V/m \qquad (1)$$

Where q_t is the adsorbed amount after time t, C_0 and C_t are initial concentration and concentration of the adsorbate after time t, respectively, mg/L; V is the volume of the solution, L, and m is the weight of the AC used, g.

When the adsorption reach equilibrium state, the equilibrium adsorption amount of phenol (q_t, mg/g) was calculated according to the following Eq. (2),

$$eq_e = (C_o - C_e)V/m \qquad (2)$$

Where Ce (mg/L) is the equilibrium concentration of phenol.

The percentage removal of the inhibitor was calculated using the following Eq. (5),

$$\%Removal = (C_0 - C_t)/C_0 \times 100 \qquad (3)$$

3. Results and Discussions

3.1. Characterization of the ACs

3.1.1. Porous Structure and Surface Area of the ACs

Porous characteristics and surface area of the ACs are listed Table 1. The total surface area (SBET) and total pore volume (Vtotal), micropore surface area (Smicro) and volume (Vmicro), mesopore surface area (Smeso) and volume (Vmicro) of the AC-N, AC-Cl, AC-Zn and AC-K are no obvious change. But the AC-N slightly decrease compared to the other ACs, the decrease of surface area and pore volume may be break by erosion or collapse of pores by modification treatment.

Table 1. *Surface area and structural characteristics of ACs.*

Sorbents	Surface area (m²/g)			Pore volume (cm³/g)		
	SBET	Smiro	Smseo	Vmicro	Vmeso	Vtotal
AC-raw	1207	750	420	0.36	0.66	1.11
AC-N	1084	687	336	0.32	0.58	0.96
AC-Cl	1202	750	446	0.37	0.69	1.12
AC-Zn	1225	750	395	0.36	0.65	1.12
AC-K	1205	757	408	0.35	0.65	1.11

3.1.2. Surface Chemical Properties of ACs

The amounts of functional groups on ACs surface detected

by Boehm titration were listed in Table 2. It showed that the acidic function groups (carboxylic, lactonic and phenolic) and basic groups on the ACs surface. It is clear that the acidic function groups on the ACs modified by HNO_3, HCl and $ZnCl_2$ increased compared to that of AC-raw. And the acidic function groups on the AC-K surface decreased. But the basic groups has not been detected on the AC-K surface, it is may

because the AC was activated with phosphoric acid, the acidic function groups on the AC surface were stronger, and the modification by KOH was feeble. Besides, the different chemical properties of the HNO_3, HCl and $ZnCl_2$ result in the amount of the carboxylic groups, lactonic groups and phenolic groups on the ACs surface is different.

Table 2. Contents of surface oxygen-containing functional groups of raw and modified ACs.

Sorbents	Carboxylic groups (mmol/g)	Lactonic groups (mmol/g)	Phenolic groups (mmol/g)	Total acidic groups (mmol/g)	Basic groups (mmol/g)
AC-raw	0.0431	0.34496	0.6036	0.9917	0
AC-N	0.6468	0.2156	0.6468	1.5092	0
AC-Cl	0.0431	0.0862	1.3798	1.5092	0
AC-Zn	0.9055	0.3018	0.1724	1.3798	0
AC-K	0.0431	0.0431	0.5174	0.6036	0

Fourier transformation infrared spectrum of the ACs is shown in the Figure 1. The modified and raw AC show semblable adsorption peaks. The broad adsorption band of 3200-3600 cm^{-1} with the peak around 3433 cm^{-1} is ascribed to the hydroxyl stretching vibration. The band around 1615 cm^{-1} is corresponding to the stretching vibration of the carbonyl (C=O) groups and C=C groups.
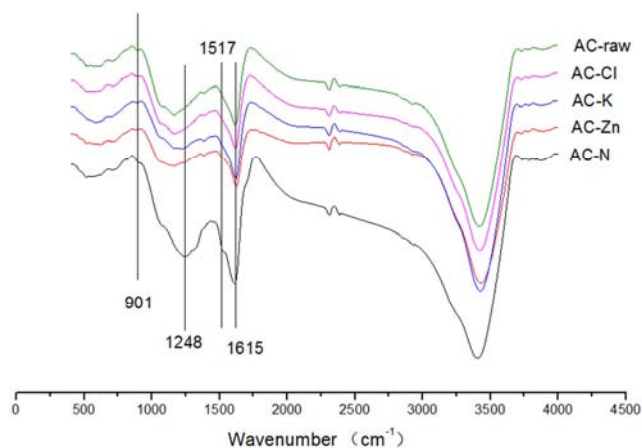

Figure 1. FTIR spectra of raw and modified ACs.

3.2. Experiments for the Inhibitor of Fermentation by ACs

3.2.1. Ph Effect on Removal Percentage

In this study, ACs was used as an adsorbent to remove the inhibiting compounds in the aqueous solution at a pH range of 2-11, as shown in Figure 2. It isn't observed that the removal percentage has significantly affected by the pH value. But the difference of the removal percentage of the inhibiting compounds consist in the adsorption by the different modified ACs. Compared with AC-raw, the effect of AC-Cl adsorption of formic acid increased, AC-N and AC-Zn having the similar adsorption and the effect of AC-Zn adsorption decreased; the effect of AC-N and AC –K adsorption of acetic acid increased, AC-Cl having the similar adsorption and the effect of AC-Zn adsorption decreased; the effect of AC-N adsorption of 5-HMF and furfural, the other ACs having the similar adsorption of 5-HMF and furfural.

The different adsorption of the formic acid and acetic acid

by the different ACs attributed to the difference of the amounts functional groups on ACs surface, and the different adsorption of the 5-HMF and furfural by the different ACs attributed to the difference of the Porous characteristics and surface area of the ACs.

Figure 2 show the highest removal percentage of formic acid, acetic acid, 5-HMF and furfural is the adsorption by AC-Cl, AC-k, AC-Zn and AC-Zn respectively. So select AC-Cl, AC-k, AC-Zn and AC-Zn to adsorb formic acid, acetic acid, 5-HMF and furfural to explore the effect of initial solution pH on inhibiting compounds removal by ACs.

3.2.2. Effect of Solvent Temperature

Solvent temperature has an important effect on the mass transfer rate and diffusion rate of inhibiting compounds during the adsorption process. And with the increase of solvent temperature, the activated molecules on AC surface increase. The adsorption capacity of 5-HMF and furfural for the ACs decrease with the increased temperature (20-50°C), while the Change of formic acid and acetic acid decrease slightly. (Figure 3.). This indicates that the adsorption process of the inhibiting compounds is exothermic.

3.3. Adsorption Kinetics

The removal efficiency of different inhibiting compounds using ACs versus time are shown in Figure 4. It was noted that the adsorption equilibrium for 5-HMF and furfural was achieved within 0.83 min, slightly slowly compared to the formic acid and acetic acid, which achieved equilibrium using about 0.58 min. The removal efficiency of 5-HMF and furfural reached 89.0% and 81.0% at adsorption equilibrium respectively, but the removal efficiency of formic acid and acetic acid only reached 14.0% and 13.8% respectively, which demonstrated that the modified ACs can be utilized for the adsorption of 5-HMF and furfural at a low dosage, and can't be utilized for the adsorption of formic acid and acetic acid.

The adsorption kinetics illustrates the inhibiting compounds adsorption rate and eventually explores the mechanism of adsorption and the rate limiting steps involved. Investigating the adsorption process is inhibiting compounds

on the modified ACs, the pseudo first-order, pseudo second-order, and intraparticle diffusion models were used to fit the experimental results. The equations are expressed as follows,

First order kinetic model:

$$\log(q_e - q_t) = \log q_e - k_1 t / 2.303 \qquad (4)$$
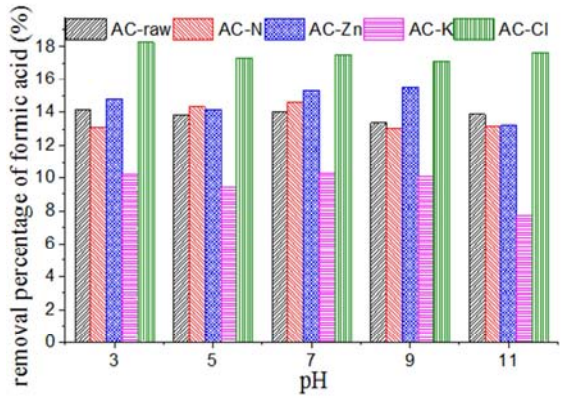
Second order kinetic model:

$$t/q_t = 1/(k_2 q_e^2) + t/q_e \qquad (5)$$

Intraparticle diffusion model:

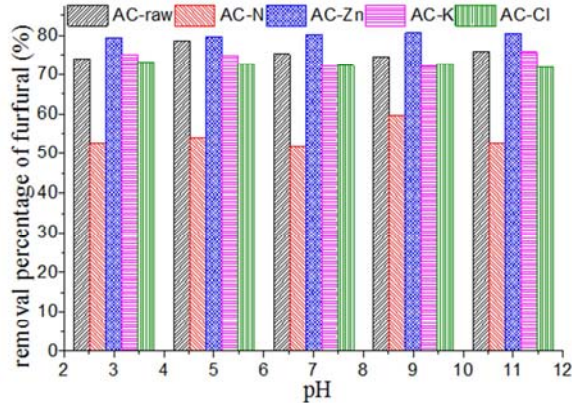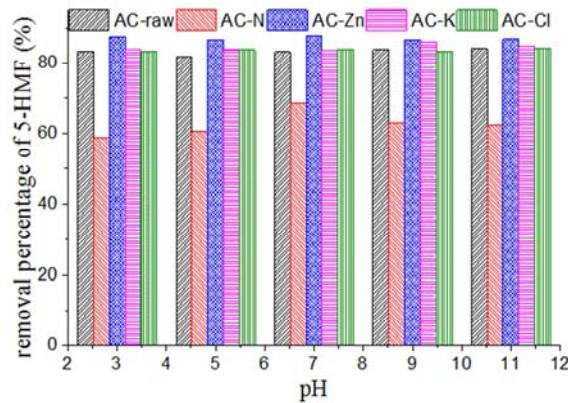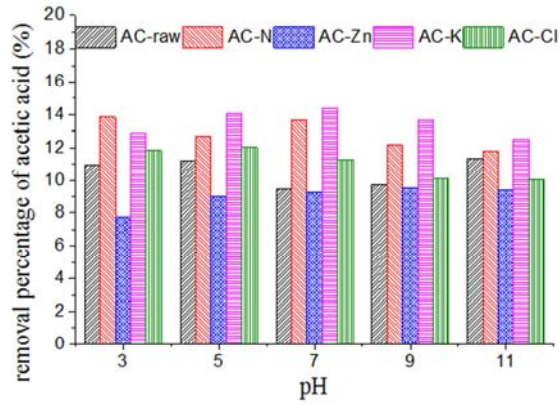$$q_t = k_{id} t^{0.5} + c \qquad (6)$$

Figure 2. The effect of initial solution pH on inhibiting compounds removal by ACs (inhibiting compounds concentration = 100mg/L; adsorbent dosage = 2.5g/L; environment temperature = 20°C; time = 5 min).
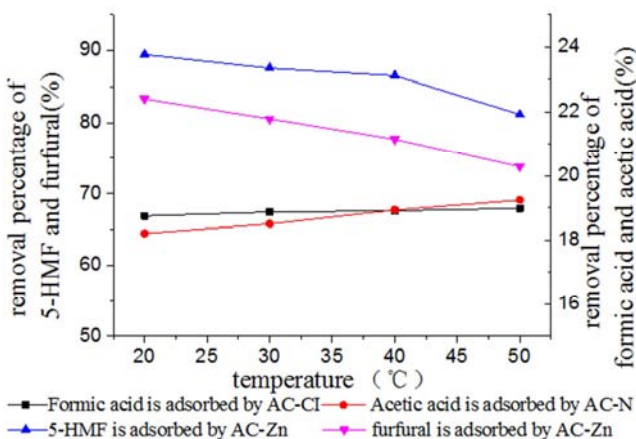

Figure 3. The effect of environment temperature on inhibiting compounds removal by ACs (inhibiting compounds concentration = 100mg/L; adsorbent dosage = 2.5g/L; initial solution pH = 7; time = 5 min).

Where, q_e and q_t are the amount of adsorbed inhibiting compounds per unit mass of adsorbent (mg/g) at equilibrium and at time t, respectively; k_1 is the pseudo first sorption rate constant (h^{-1}); k_2 is the rate constant of pseudo second order adsorption (g/mg/h); k_{id} is the rate constant of intraparticle diffusion ($mg/g/h^{0.5}$), and c indicates the thickness of boundary layer.

The kinetic parameters were calculated accordingly and listed in Table 3. The correlation coefficients for the second order model were all greater than 0.99 for 5-HMF and furfural, while those for the first model were 0.917 and 0.960 respectively, 0.983 and 0.956 for the intraparticle were relative high, indicating that intraparticle diffusion was the rate-limiting step in the adsorption process. From R^2 of various kinetics models, pseudo second order model was more suitable to describe the adsorption kinetics behaviors. Moreover, the equilibrium adsorption values calculated by the second order model ($q_{e\ cal}$) matched well with experimental adsorption results ($q_e\ exp$), which further confirmed that the kinetics of adsorption by AC-Zn for 5-HMF and furfural was best described by the pseudo second order model.

Table 3. *Pseudo first and second order parameters for the adsorption.*

Inhibiting compounds		5-HMF	Furfural
First order	K1 (min-1)	1.06	1.53
	qe cal (mg/g)	25.70	13.18
	R2	0.917	0.960
Second order	K2 (g/mg/min)	0.46	0.84
	qe cal (mg/g)	37.82	33.92
	R2	0.999	0.999
Intrapartical diffusion	kid (mg/g/min0.5)	10.58	6.98
	c	25.95	26.44
	R2	0.983	0.956
qe exp (mg/g)		35.73	32.42
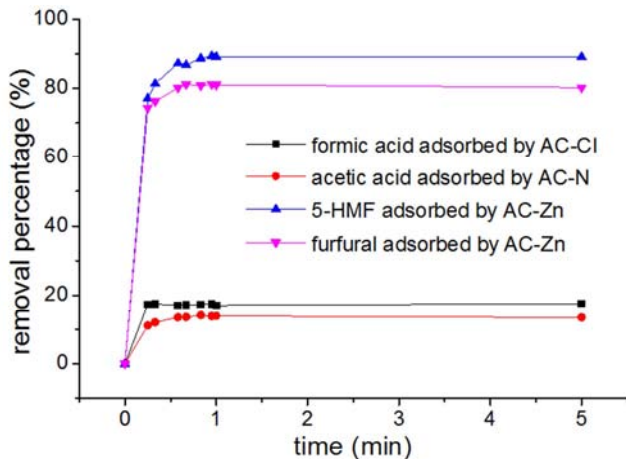
Figure 4. *Effect of time on inhibiting compounds removal by ACs (inhibiting compounds concentration = 100mg/L; adsorbent dosage = 2.5g/L; initial solution pH = 7; environment temperature =20°C).*

3.4. Adsorption Isotherms and Adsorption Thermodynamics Analysis

The equilibrium adsorption isotherm is also used to understand the mechanism of the adsorption. Adsorption isotherm models describe the interaction between the adsorbate and adsorbent. In this work, classic isotherm models, Langmuir, Freundlich and Sips were used to obtain the isotherm parameters for adsorption of 5-HMF and furfural onto AC-Zn. The Langmuir isotherm model is based on a monolayer adsorption onto a surface with a finite number of adsorption sites of uniform adsorption energies. It can be expressed as the following equation

$$q_e = q_m K_L C_e / (1 + K_L C_e) \qquad (7)$$

where, q_e is the equilibrium adsorption capacity, mg/g; C_e is the equilibrium concentration of adsorbate in the solution, mg/L; q_m is the maximum amount of the 5-HMF and furfural adsorbed per unit weight of the adsorbent, which also describes the formation of complete monolayer coverage on the surface at high equilibrium concentration of 5-HMF and furfural, mg/g; K_L is the Langmuir adsorption equilibrium constant related to the affinity of the binding sites and indicates the bond energy of the adsorption reaction between adsorbent and adsorbate, L/g.

The Freundlich isotherm model is an empirical equation, which is utilized to understand adsorption on heterogeneous surfaces with multiple adsorption layers [15]. It can be expressed as the following equation,

$$q_e = K_F C_e^{1/n} \qquad (8)$$

where, K_F (mg/g) and n are Freundlich constants related to the adsorption capacity and adsorption intensity and spontaneity, respectively. The value of n in the range of 1<n<10 indicates a favorability adsorption process. The greater the value of n, the better is the favorability of the adsorption.

The Sips model is a combination of Langmuir and Freundlich isotherms [16], which takes the following form:

$$q_e = q_s K_S C_e m / (1 + K_S C_e m) \qquad (9)$$

Where, q_s is the specific adsorption capacity at saturation, mg/g; K_S is Sips isotherm constant related to energy of adsorption, mL/mg, and m is the heterogeneity factor. If the value of K_S approaches to zero, Sips isotherm equation follows the Freundlich isotherm model, while the value of m equal or close to 1, the Sips isotherm equation reduced to the Langmuir isotherm.

Table 4. *Langmuir, freundlich and Sips isotherms parameters for the adsorption.*

Inhibiting compounds		5-HMF	furfural
Langmuir	qm (mg/g)	147.49	192.31
	KL (L/g)	0.031	0.012
	R2	0.944	0.957
Freundlich	KF (mg/g)	10.756	8.260
	n	2.28	2.063
	R2	0.994	0.995
Sips	qs	152.81	207.12
	KS (mL/mg)	0.102	0.058
	m	0.202	0.117
	R2	0.987	0.986
qe exp (mg/g)		140.78	164.98

The plots of the adsorption isotherms are illustrated in Figure 5, and the calculated parameters are listed in Table 4. It was shown that for the 5-HMF and furfural, the adsorption fitted the best with the Freundlich model, with an R^2 of 0.994 and 0.995 respectively, it means that the adsorption occurs as a multi-layer process. Variations in K_L values of inhibiting compounds indicated the difference of adsorption energies between the adsorbent and inhibiting compounds. High K_L value of 5-HMF is bigger than furfural, it means the faster adsorption, which was consistent with the results of the kinetic study.

Van't Hoff equation can be obtained the reaction Gibbs free energy change at different temperatures, as can determine the reaction direction and s the amount of adsorption enthalpy change. It can be expressed as the following equation,

$$\ln C_e = -\ln K_0 + (\Delta H / RT) \qquad (10)$$

Where ΔH is the adsorption enthalpy change, R is the ideal gas constant, T is the absolute temperature, K_0 is a constant, C_e is equilibrium concentration.

The experimental data were taken into the equation that pertain to the Van't Hoff isotherm of 5-HMF

is ln C_e=0.82459-1651/T, the equation that pertain to the Van't Hoff isotherm of furfural is ln C_e =9.8016-2287.8/T. The adsorption enthalpy change (ΔH) of 5-HMF and furfural was observed by the slope, and according to the Gaussian equation and Freun dlich adsorption isotherm, we can get the
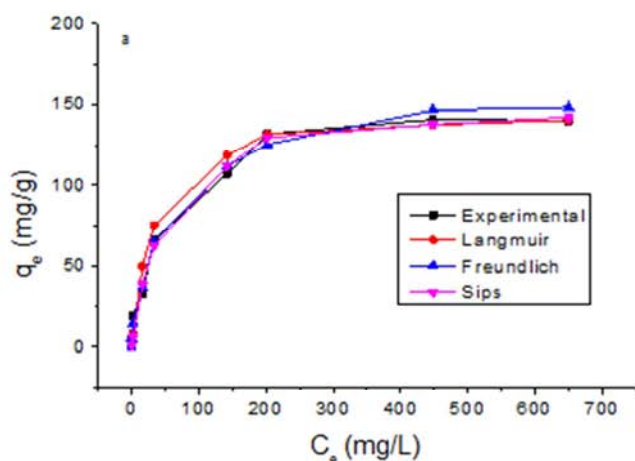
adsorption free energy variable ΔG = -nRT (which n is the Freundlich constant). The change in adsorption entropy (ΔS) is calculated from the Gibbs-Helmholtz equation. ΔS = (ΔH-ΔG) / T. And the calculated enthalpy change, the free energy change and the entropy change are shown in Table 5.
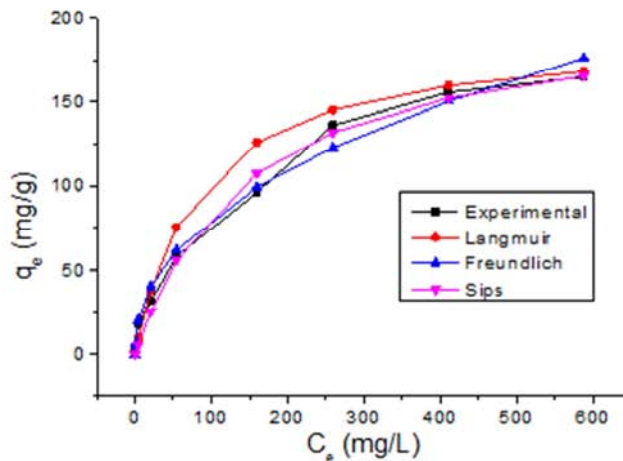

Figure 5. Various adsorption isotherms fit by AC-Zn, (a) 5-HMF; (b) furfural (adsorbent dosage=2.5g/L).

Because ΔH<0 in the table, the adsorption of activated carbon 5-HMF and furfural process is the exothermic process. No new chemical bond was generated and adsorption was mainly controlled by physical behavior in this process. And ΔG <0, indicating that the adsorption of 5-HMF and furfural by activated carbon is a spontaneous process. ΔS<0, showing that entropy in the process that the 5-HMF and furfural molecules from the disorder state in the solution to the order state on active carbon surface is reduced, activated carbon adsorption of furfural at low temperature is more appropriate.

Table 5. *The enthalpy change, Gibbs free energy and entropy change of activated carbon adsorb 5-HMF and furfural at 293.15K.*

	5-HMF	Furfural
ΔH(kJ/mol)	-13.7	-19.0
ΔG(kJ/mol)	-5.56	-5.03
ΔS(J/mol*K)	-65.70	-81.97

4. Conclusions

The objective of this study was to find a method of modified activated carbon to improve the ability of removal of inhibiting compounds by activated carbon. Activated carbon adsorption is suitable for removal of 5-HMF and furfural in the solution. At 2.5 g/L of activated carbon, 20°C, the removal rate of 5-HMF and furfural can reach 89.0% and 81.0%, respectively, when their initial concentration is 100 mg/g. And the adsorption of formic acid and acetic acid is not good. Under the same conditions the removal rate only can reach 14.0% and 13.8%, respectively.

The kinetic equation of adsorption of 5-HMF and furfural on activated carbon is in accordance with the quasi-second order kinetic equation. At the same time, the diffusion rate of 5-HMF and furfural particles is the main factor affecting the adsorption of activated carbon. ΔH, ΔG and ΔS are less than zero, and it is shown that the process of adsorption of 5-HMF

and furfural on activated carbon belongs to the process of exothermic physical adsorption and is the entropy reduction process. The adsorption is best carried out at low temperature.

Acknowledgements

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