RESEARCH NOTES

Removal of Thiophene from Benzene from Coal Source by Liquid Adsorption on Modified ZSM-5 Synthetic Zeolite*

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1 INTRODUCTION

It is of great importance to remove thiophene to obtain a highly-purified benzene product. A number of methods practiced in industry involve the catalytic sulfuric acid desulfurization and/or catalytic hydrodesulfurization. With catalytic sulfuric acid desulfurization, large quantities of effluent which contaminate to the environment are being discharged in addition to acid corrosion on process equipment. Whereas, high capital investment and more stringent operating conditions appear to be the major drawbacks of the catalytic hydrodesulfurization. Apparently, these methods are not applicable in small-scale chemical plants. Furthermore, in these methods, some benzene will be lost by reacting with thiophene and converted into other compounds. Extractive distillation is an effective process for separating thiophene from benzene, but it cannot be applied when thiophene is present as a trace or minor impurity[1]. Comparatively speaking, more and more interests have been focused on the adsorption technology because it can remove thiophene completely from benzene from coal source and the thiophene removed can also be recovered. Adsorbents having been studied and used in recent years are primarily ion-exchange synthetic zeolites such as X-type, Y-type and ZSM-5 molecular sieve[2-4]. It has been found that the modified ZSM-5 zeolite is the most effective adsorbent, for the loading capacity of thiophene is perhaps above 10 mg per gram of adsorbent. The aim of the present paper is to contribute a better understanding of the removal of thiophene with modified ZSM-5 molecular sieve thermodynamically, and therefore to provide theoretical and basic data for its industrial application.

2 EXPERIMENTAL

2.1 Preparation of adsorbent

The sample of ZSM-5 zeolite in granular form used in the experiments was supplied by the Industrial Catalyst Plant of the Dalian University of Technology. The zeolite was ground into spherical pellets and then were treated with 600 ml of a boiling aqueous solution of $Cu(NO_3)_2$ (7% by mass) and $La(NO_3)_3$ (1%—2% by mass) for 2 hours. This ion-exchange procedure was carried out two times. It was found that further repetition did not bring about any promotion in the ion-exchange process. The treated zeolite was then dried at 120 ℃ for 4—5 h, and finally calcined for 24 h at 500°C.

2.2 Adsorption equilibrium measurement

The adsorption equilibrium experiments were carried out in an enclosed vessel in which a known amount of zeolite (1.5—2 g) was contacted with 20—40 ml of benzene-thiophene solution formerly concocted accurately at different levels of thiophene concentration. Being used for the experiments, the adsorbent was calcined at 500 °C for 12 h or so, leading to about 3% mass lost. The enclosed vessel was put in a hot water bath at a thermostatic temperature for 48 hours to attain the equilibrium state. The residual concentration in the solution after adsorption was analyzed, and thus the equilibrium adsorptive capacity may be calculated by the following equation

$$q_e = V_b(c_0 - c_e)/W_c \tag{1}$$

2.3 Analytical method

The solutions were analyzed by gas chromatography with FPD (flame photometric detector) as detector. The chromatographic column was a Φ5 mm$\times$2 m stainless steel tube filled with 17% PEG (polyethylene glycol) coated 102 white carrier (60—80 mesh). The analytical procedure and calculating method were described in a previous paper[5].

3 RESULTS AND DISCUSSION

3.1 Experimental results

Experimental data of the adsorption equilibrium are reported in Table 1. Equilibrium concentrations are taken in the range of 0 to 1.8×10^{-3} g·ml^{-1}, as normally practiced in industry.

Table 1   Experimental data for adsorption equilibrium

21°C		36°C		47°C		61°C	
$c_e \times 10^3$, g·ml^{-1}	$q_e \times 10^3$, g·g^{-1}	$c_e \times 10^3$, g·ml^{-1}	$q_e \times 10^3$, g·g^{-1}	$c_e \times 10^3$, g·ml^{-1}	$q_e \times 10^3$, g·g^{-1}	$c_e \times 10^3$, g·ml^{-1}	$q_e \times 10^3$, g·g^{-1}
0.1198	2.728	0.0578	2.504	0.0428	2.673	0.0107	1.631
0.2632	3.221	0.1434	3.293	0.1327	3.115	0.0293	2.451
0.3296	4.034	0.2600	4.248	0.3809	4.626	0.0984	3.715
0.4900	4.649	0.5478	5.545	0.6013	5.698	0.2878	4.519
0.7544	5.326	0.9138	6.570	0.9523	7.310	0.4334	5.826
1.0197	6.166	1.3214	8.025	1.3568	8.862	0.7105	6.578
1.4381	7.094	1.6661	9.125	1.6788	10.243	0.9544	8.419
1.6906	8.394					1.5141	10.378

Despite the large amount of research performed in this field, fundamental knowledge about the adsorption phenomena on zeolites is still rather limited. Even though a number of modellings have been proposed, they are so complex as to be hardly applied in practice.

However, since our purpose is only to relate the experimental data, the following simple equations have been employed
Langmuir isotherm

$$q_e = \frac{q_\infty K_L c_e}{1 + K_L c_e} \tag{2}$$

Freundlich isotherm

$$q_e = K_F c_e^{1/n} \tag{3}$$

Temkin isotherm

$$q_e = K_T \ln b c_e \tag{4}$$

The Langmuir isotherm is based on the assumption of local adsorption on the homogeneous surface of a single molecule layer whereas the Freundlich isotherm is normally applied to the

description of liquid adsorption system, and the Temkin equation is primarily suitable for the chemical adsorption on the heterogeneous surface with a medium coverage.

The values of the equilibrium parameters have been determined by fitting the experimental data with the above models, and are summarized in Table 2.

Table 2   Parameters of adsorption equilibrium isotherms

T, °C	Langmuir model			Freundlich model			Temkin model		
	$K_L \times 10^{-3}$ $ml\cdot g^{-1}$	$q_\infty \times 10^3$ $g\cdot g^{-1}$	RR	$K_F,$ $(g\cdot ml^{-1})^{1/n}$	n	RR	$K_T \times 10^3$	$b \times 10^{-3},$ $ml\cdot g^{-1}$	RR
21	4.424	7.268	0.937	0.1163	2.364	0.988	2.084	21.914	0.959
36	8.330	7.235	0.949	0.0992	2.624	0.997	1.917	44.399	0.969
47	12.829	7.104	0.907	0.0914	2.767	0.980	1.952	53.549	0.929
61	31.217	6.189	0.957	0.0918	2.840	0.991	1.581	147.880	0.934

It can be seen from Table 2 that the Freundlich isotherm agrees with the experimental data much better than the other two models. This is also shown in Fig.1. Fig.2 shows the plots of the Freundlich parameters, n and K_F, against temperature, indicating the approximate linear relationships between them.

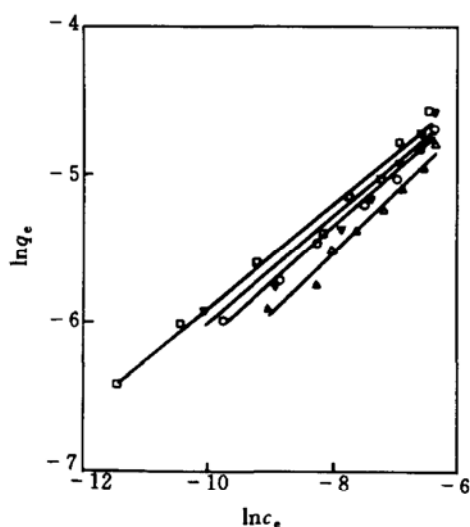$$K_F = 0.1524 - 6.24 \times 10^{-4}T \tag{5}$$

$$n = 2.1519 + 0.01204T \tag{6}$$

Figure 1   Comparison of experimental data
with Freundlich isotherm
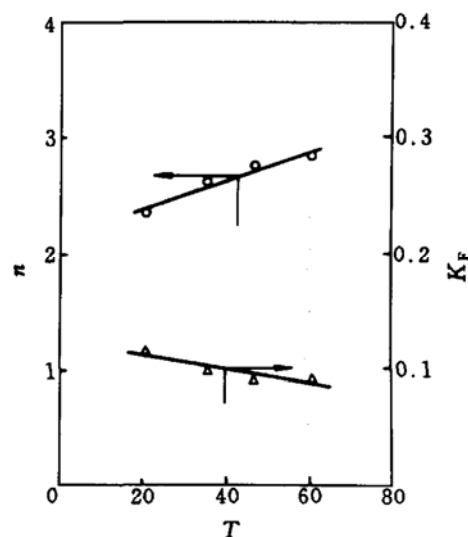$T/°C$: △ 21; ○ 36; ▽ 47; □ 61

Figure 2   Relationship between Freundlich
parameters and temperature

However, it should be mentioned that the employment of these equations must be restricted within the concentration and temperature limits stated in the present paper since they are only empirical relationships obtained from the experimental data.

3.2 Discussion

It has been found that ZSM-5 zeolite, a product of thoroughly ion-exchange treatment with Cu(II)-La(III), is a selective adsorbent for thiophene, and its loading capacity increases with increasing adsorption temperature. The adsorption equilibrium can be demonstrated best with the Freundlich isotherm rather than with the Langmuir isotherm in a wide range of temperatures

and concentrations. This suggests that thiophene is not adsorbed physically on a single molecular layer but mainly adsorbed chemically onto the modified ZSM-5 zeolite adsorbent. Further studies on the adsorption mechanism should be carried out.

4 CONCLUSIONS

The adsorption equilibrium of thiophene in benzene with modified ZSM-5 zeolite may be described by the Freundlich isotherm, which is related to the adsorption temperature as given in Eqs.(5) and (6) presented in this paper.

NOMENCLATURE

b	equilibrium parameter of the Temkin isotherm[Eq.(4)], $ml \cdot g^{-1}$
c_e	equilibrium concentration of thiophene in the solution, $g \cdot ml^{-1}$
c_0	initial concentration of thiophene in the solution, $g \cdot ml^{-1}$
K_F	equilibrium parameter of the Freundlich isotherm[Eq.(3)], $(g \cdot ml^{-1})^{1/n}$
K_L	Langmuir constant, $ml \cdot g^{-1}$
K_T	equilibrium parameter of the Temkin isotherm [Eq.(4)]
n	concentration exponent parameter of the Freundlich isotherm [Eq.(3)]
q_e	equilibrium content of thiophene on the adsorbent, $g \cdot g^{-1}$
q_∞	maximum loading capacity in the Langmuir model, $g \cdot g^{-1}$
RR	relevance coefficient
T	temperature, °C
V_b	volume of solution, ml
W_c	mass of adsorbent, g

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