December 2009 Volume 4 Issue 6

Trade Science Inc.

Environmental Science

An Indian Journal

Current Research Papers

ESAIJ, 4(6), 2009 [502-506]

Study on the adsorption characteristica of expanded graphite for phenyl organic molecules

Xiu-yan Pang*, Li-li Zhang, Li-juan Xu, Ya-juan Su

College of chemistry and environmental science, Hebei University, Baoding 071002, (PEOPLE' REPUBLIC OF CHINA)

E-mail : pxy833@163.com

Received: 31st August, 2009 ; Accepted: 10th September, 2009

ABSTRACT

Adsorption characteristics of expanded graphite (EG) for phenyl organic molecules in single component solution have been investigated. Four used adsorbates are Phenol, Benzoic acid, Benzenesulfonic acid and P-Methylbenzene sulfonic acid. EG is characterized by expanded volume, specific surface area and pore cubage. Adsorption isotherm, Langmuir constants and free energy change (ΔG°) are detected and calculated, respectively. Influence of pH, temperature and ion strength on adsorption capacity of EG is investigated. It is demonstrated that adsorption of phenyl organic molecules on EG are multilayer, and the process is spontaneous. Both molecular weight and molecular structure of these adsorbates affect saturation adsorbance. High ion strength and proper pH can improve adsorption capacity. There isn't obvious relationship between equilibrium adsorbance and temperature. Adsorption capacity of EG for phenol organic molecular is low.

KEYWORDS

Expanded graphite;
Phenyl organic molecules;
Adsorption thermodynamics;
Adsorption isotherm;
pH;
Ion strength.

INTRODUCTION

Organic infectants existing in wastewaters commonly come from petroleum factory, oil refineries, plastic, leather, paint, pharmaceutical, dyes, pesticide, and steel industries, etc. Among them, phenyl organic molecules are the main infectants. Because they are both toxic and relatively water-soluble compared with other petroleum infectants, their entry into surface and drinking water has cause people' major concern.

Adsorption is a kind of effective measure used for the elimination of contaminants, active carbon[1-4], mesoporous silica[5,6], barrier-discharge plasma[7], ion exchange resin[8], organobentonite[9] have been tested in the treatment of phenyl organic molecules. With Polypropylene fibre as adsorbent and under suitable condition of pH[10], temperature, and flow rate, recovery rate of phenol in coking waster water can arrive to 99.5%. Adsorbance of phenol on active carbon prepared with reed lignin can arrive to 136.2 $mg \cdot g^{-1}$ and adsorption can well be described by Langmuir Model[11].

EG is a kind of eco-material and possesses environmental consciousness and biological compatibility. It has 4 levels pores with the size ranging from nanometer scale to micron scale[12]. Its abundant porous structure makes it have capability as adsorbent. But its adsorption characteristics for phenyl organic molecules from wastewater have been reported not so much. The objective of the present research is to study adsorption thermodynamic characteristics of EG for these phenol

organic molecules, investigate adsorption isotherm, influence of pH, temperature and ion strength on adsorption capacity. In this work, Phenol, Benzoic acid, Benzenesulfonic acid, p-Methylbenzene sulfonic acid are used as reference compounds.

EXPERIMENTAL

Adsorbent

Expandable graphite is firstly prepared according to literature[13], and then it is expanded in KSW heating oven (Huacheng Oven Factory of Tientsin) at 900°C. EG is obtained. Its structural parameters are characterized by expanded volume (0.300g expandable graphite is heated at 900°C), surface area, pore cubage as listed in TABLE 1.

TABLE 1 : Structural parameter of EG

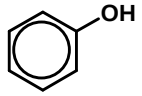
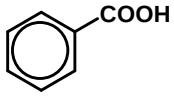
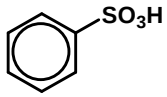
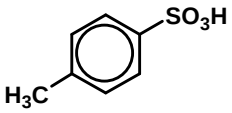
EV ($mL \cdot g^{-1}$)	Total intrusion volume ($cm^3 \cdot g^{-1}$)	Total pore area ($m^2 \cdot g^{-1}$)	Median pore diameter (volume) (Å)	Median pore diameter (area) (Å)	Average pore diameter (4V/A) (Å)	Bulk densit ($g \cdot mL^{-1}$)	Porosity (%)
320	30.1145	1044.99	163117	44	1153	0.0308	92.73

Adsorbates

Phenol, Benzoic acid, Benzenesulfonic acid and p-Methylbenzene sulfonic acid are used as reference compounds. Their chemical structure and molecular weight are showed in TABLE 2.

Simulated wastewaters of these phenyl organic molecules are prepared by dissolving these adsorbates in distilled deionized water at various concentrations. All quantitative analysis are achieved with spectrophotometer.

TABLE 2 : Chemical structure and molecular weight of phenyl organic molecules

Phenyl organic molecules	Structure	Molecular weight	λ_{max} (nm)
Phenol		94.1	209.8
Benzoic acid		122.1	225.0
Benzenesulfonic acid		158.2	213.4
P-Methylbenzene sulfonic acid		172.2	221.8

Methods

Static adsorption and equilibrium adsorbent

In static adsorption experiments, the mass of EG to volume of solution is standardized as M/V=0.2 g / 0.1 L = 2.0 g/L. The jars are sealed and placed in a shaker for 4.0 h under a steady temperature until equilibrium reached. Adsorbance is determined as follows:

$$Qe = V(C_0 - C)/M \quad (1)$$

C_0 Initial concentration of adsorbate in solution, mg/L; C Equilibrium concentration of adsorbate in solution, mg/L; M Mass of adsorbent, g; V Volume of solution, L; Qe Equilibrium adsorbance, mg/g.

Adsorption capacity of EG in the influence of ion strength, pH and temperature

NaCl and Na_2SO_4 are used to investigate their influence on adsorption capacity of EG, and pH of the solutions is adjusted by HCl or NaOH. Different temperatures of 5°C, 25°C and 45°C are controlled in order to determine their influence on adsorption capacity. Equilibrium adsorbance is calculated according to equation (1).

RESULTS AND DISCUSSION

Investigation of adsorption isotherm and thermodynamic parameter

Static adsorption capacities of EG corresponding to adsorbates' different equilibrium concentrations are measured as Figure 1. It reveals a typical II isotherm, and adsorbance increased quickly with the increasing equilibrium concentration, which is the

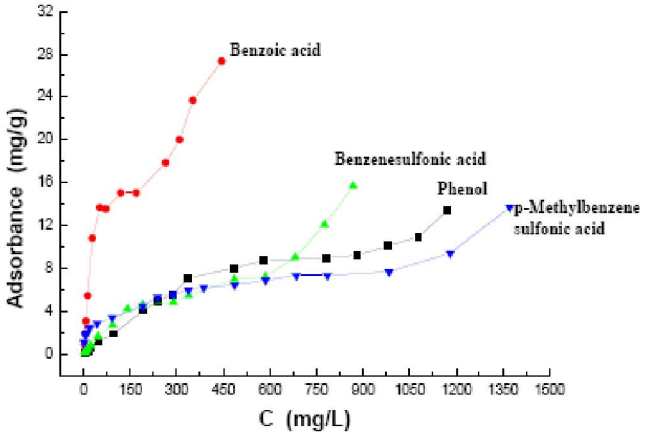


Figure 1 : Adsorption isotherm of phenol, benzoic acid, benzenesulfonic acid, p-Methylbenzene sulfonic acid at atmospheric pressure and 25°C

Current Research Paper

result of multiplayer adsorption of molecules[14]. In the adsorption of Ovalbumin, Serum albumin, Bovine serum albumin, Lysine, Basic fuchsine, Acid brilliant red 3B, Benzene sulfonic acid, p-Aminobenzene sulfonic acid, 2-Naphthol-3, 6-disulfonic acid and p-Diphenylamine sulfonic acid, similar results are obtained[15-17].

In the condition of monolayer adsorption, adsorption constant can be obtained from Langmuir equation[18]:

$$1/Q = 1/Q_0 + A\cdot/(Q_0 \times C) \quad (2)$$

Q_0 — The maximum adsorbance of adsorbate on EG in forming complete monolayer, mg/g; A — Equilibrium concentration of adsorbate corresponding to half saturation adsorbance, mg/mL.

Based on equation (2), the values of $1/Q_0$ and A are calculated from the intercepts and slopes of the straight lines. Langmuir constants for Phenol, Benzoic acid, Benzenesulfonic acid, p-Methylbenzene sulfonic acid are showed in TABLE 3. The results show a low maximum adsorbance in forming complete monolayer, and it has no obvious relationship between maximum monolayer adsorption amount and adsorbate molecular weight. This indicates Q_0 is influenced not only by adsorbates' molecular weight, but also their molecular structure.

Adsorption free energy change ($\Delta G°$) is calculated according to equation (3)[19]. Negative $\Delta G°$ indicates adsorption of the reference compounds on EG are all spontaneous.

$$\Delta G° = -RTlnb \quad (3)$$

b -- Langmuir equation constant, mL/mg, and b = 1/A; $\Delta G°$ -- Free energy change in the adsorption.

TABLE 3 : Adsorption constants and thermodynamic parameter

Adsorbates	Molecular weight (g/mol)	Q_0 (mg/g)	A (mg/mL)	$\Delta G°$ (kJ)
Phenol	94.1	6.1	0.206	–3.87
Benzoic acid	122.1	124.1	0.393	–2.33
Benzenesulfonic acid	158.2	29.1	0.760	–0.68
p-Methylbenzene sulfonic acid	172.2	2.97	0.0042	–13.56

Influence of ion strength on adsorption capacity

NaCl, Na_2SO_4 is used respectively to adjust solu-

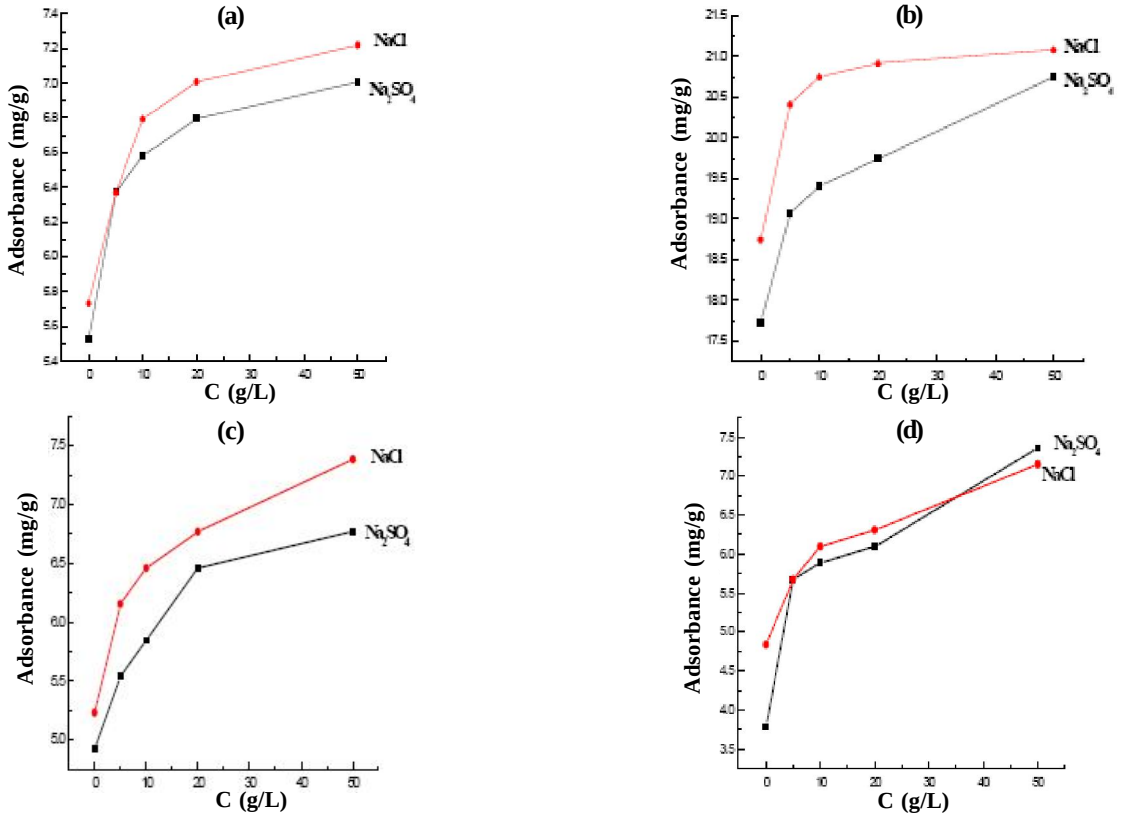


Figure 2 : Influence of ion strength on adsorption capacity: (a) Phenol; (b) Benzoic acid; (c) Benzenesulfonic acid; (d) P-Methylbenzene sulfonic acid

tion ion strength. Adsorbing research is carried out using a 300 mg/L of different phenyl organic molecule solutions corresponding to different ion strength ranging from 0 to 50 g/L. Influence of ion strength on adsorbance (showed in Figure 2) indicates that presence of salt ion enhances adsorption of EG for these tested adsorbates.

Influence of pH on absorbency and adsorption capacity

Ionic phenyl organic molecules can release polluted phenyl organic molecule anions/cations in solution, and absorbency change along with their existence form, which is influenced by pH. So it is important to know how pH affects absorbency and what the range of pH is before study the influence of pH on adsorption capacity. Figure 3 indicates that acidity led to a change of absorbency under a certain wavelength. To Phenol, Benzenesulfonic acid, P-Methylbenzene sulfonic acid, change of pH from 2.0 to 10.0 had no noticeable impact on absorbency; as for Benzoic acid, change of pH from 4.0 to 12.0 had no noticeable impact on absorbency. Then among the mensurated pH mentioned above, its influence on adsorption capacity is carried out. Figure 4 presents a degressive relationship between equilibrium adsorbance and pH. This might be caused by the decrease of combined phenol organic molecule. The decreasing H^+ enhanced ionization of these adsorbates in solution, and reduced the amount of unionized molecules. The lipophilic nature of EG led to the degressive adsorbance.

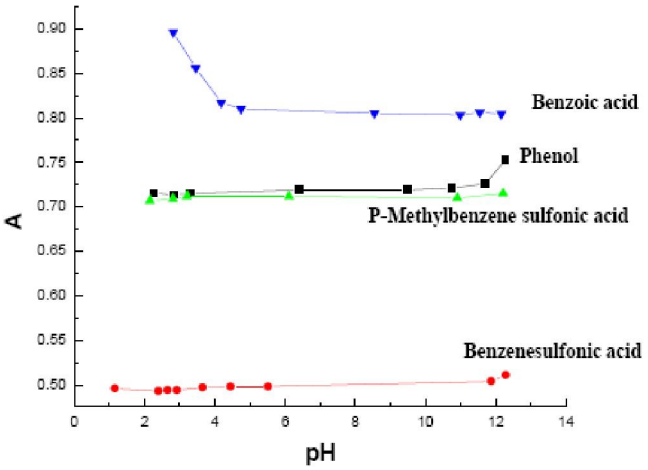


Figure 3 : Influence of pH on absorbency of phenyl organic molecules

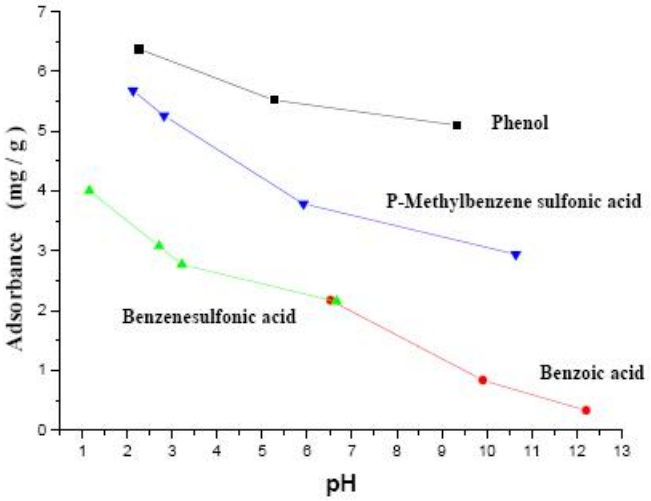


Figure 4 : Influence of pH on adsorption capacity of EG for phenyl organic molecules

Influence of temperature on adsorption capacity

Influence of temperature on adsorption capacity of EG for phenyl organic molecules at 5˚C, 25˚C, 45˚C are detected. Results show no obvious change of adsorbance. It indicates that sorption between EG and phenyl organic molecules exist mainly in physical adsorption.

CONCLUSIONS

This study has provided an insight into the adsorption isotherm and thermodynamic parameter of EG for phenyl organic molecules. Adsorption of phenyl organic molecule on EG is a spontaneous process. Adsorption types of Phenol, Benzoic acid, Benzenesulfonic acid, P-Methylbenzene sulfonic acid are type II. Adsorption capacity is influenced by many factors such as the initial concentration of phenyl organic molecules, the amount of EG, ion strength, pH. While, adsorption capacity of EG for phenol organic molecular is lower than other reported adsorbents.

ACKNOWLEDGEMENTS

This study is supported by Doctor Foundation of Hebei province Education Office (China, No.B2004402) and Doctor Foundation of Hebei University. We gratefully acknowledge their support during the study.

REFERENCES

[1] M.Vladimir, K.Gun, V.T.Vladimir, et al.; Sorption, **11**, 163 **(2005)**.

[2] M.N.Daniela, C.L.Eva, G.R.Antonio, et al.; Carbon, **42**, 653 **(2004)**.

[3] Y.H.Han, X.Quan, H.M.Zhao, et al.; Frontiers of Envir.Sci.& Eng.in China, **1**, 83 **(2007)**.

[4] Z.R.Yue, J.Economy; J.Nanomater.Res., **7**, 477 **(2005)**.

[5] K.Gun, M.Vladimir; Centr.Eur.J.Chem., **5**, 420 **(2007)**.

[6] J.J.Li, X.Y.Xu, Z.P.Hao, et al.; J.Porous Mater., **15**, 163 **(2008)**.

[7] A.G.Bubnov, V.I.Grinevich, O.N.Maslova; Russ.J.Appl.Chem., **79**, 934 **(2006)**.

[8] M.Carmona, A.D.Lucas, J.L.Valverde, et al.; Chem.Eng.J., **117**, 155 **(2006)**.

[9] Y.H.Shen; Water Res., **36**, 1107 **(2002)**.

[10] Z.Z.Zhu, Z.L.Hao, Z.S.Shen, et al.; Ind.Water Treat, **26**, 50 **(2006)**.

[11] Y.Sun, J.P.Zhang, G.Yang, et al.; Envir.Prot.Treat., **27(4)**, 75-77 **(2006)**.

[12] H.Zhao, W.Zhou, N.Z.Cao, et al.; Mater.Sci.& Eng, **20**, 153 **(2002)**.

[13] X.Y.Pang, Z.Y.Dong, X.L.Li; Chinese Carbon, **2**, 35 **(2007)**.

[14] W.C.Shen, N.Z.Cao, S.Z.Wen, et al.; Carbon Tech., **3**, 1 **(1996)**.

[15] F.Y.Kang, Y.P.Zheng, H.Zhao, et al.; New Carbon Mater., **18**, 161 **(2003)**.

[16] X.Y.Pang, P.Lv, Y.Q.Feng, et al.; Envir.Sci.:An Indian J., **3**, 150 **(2008)**.

[17] X.Y.Pang, L.J.Xu, Y.J.Su, et al.; J.Mater.Sci.and Eng., **2**, 49 **(2008)**.

[18] Z.H.Shao, M.H.Zhou, L.C.Lei; Acta Sci.Circum., **25**, 655 **(2005)**.

[19] V.K.Gupta, I.A.li, M.D.Suhas; J.Colloid Interface Sci., **265**, 257 **(2003)**.