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Adsorption Mechanism of Expanded Graphite for Oil and Phenyl Organic Molecules

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Expanded graphite shows higher adsorption capacity for oils (*e.g.*, salad oil and thermal oil) than for phenyl organic molecules (*e.g.*, phenol, benzoic acid, benzene sulfonic acid, *p*-methylbenzene sulfonic acid). To illustrate their different adsorption mechanism, adsorption capacities of expanded graphite for these pollutants are firstly detected. And then stepwise adsorption for oils is carried out with expanded graphite which has been saturated first by phenyl organic molecules. Then the difference between stepwise adsorbance of oil is checked with deviation analysis. Scanning electronic microscopy (SEM) analysis is used to show structure difference of expanded graphite adsorbed different adsorbates. It is testified the adsorption isotherms of phenyl organic molecules on expanded graphite are all type II. Deviation analysis for stepwise adsorbances of oil shows no statistical significance. Expanded graphite saturated first by phenyl organic molecules, still has an average adsorption capacity of 79 g/g for salad oil or thermal oil and it does not change with the initial phenyl organic molecules concentration. Scanning electronic microscopy photos illustrate the adsorption of oil on expanded graphite is mainly filling. In the adsorption of phenyl organic molecules, there is severe breakage of the V-type pore and shrinkage of the particles.

Key Words: Expanded graphite, Stepwise adsorption, Phenyl organic molecules, Oil, Adsorption mechanism.

INTRODUCTION

Accidents of oil tankers and oiliness wastewater have caused serious environmental problems. The adsorption treatment with porous material[1] is one of current methods to solve this pollution. Phenyl organic molecules are another kind of pollutants, both chemical and physical methods have been employed for removal of phenyl organic compounds, the former has not been very successful. Adsorption[2-4] is a kind of popular method to treat these organic compounds wastewater.

Expanded graphite is a kind of porous material. It has attracted attentions of scientists and engineers as an absorbent with a high adsorption capacity for organic materials, such as heavy oil and organic molecules. Pores in expanded graphite are described using a 4-level model[5,6]. The first-level pores are V-type open ones with

dimension of about several hundreds micrometers on the surface of expanded graphite particles. The second-level pores are willow leaf-type ones between the sub-lamella which is perpendicular to the axis of worm-like particles and have a dimension of few micrometers. The third-level pores are the ones on the surface of sub-lamellas with dimension from 0.1 to several micrometers, situated in the worm-like particles. The fourth-level pores with nanometer size can only be measured through nitrogen adsorption method. These four level pores are expected to act quite differently in adsorption performance of expanded graphite for various liquids. In the adsorption of heavy oils[7,8], large open space among entangled worm-like particles, first-level and second-level pores of expanded graphite are founded to be very important, but microporous or mesoporous pores are useless. Japanese research group classified pores in a lump of expanded graphite into three parts[9-11], large open spaces among worm-like particles, crevice-like or cleavage-like pores on the particles and pores in the particles. The adsorbance of grade A heavy oil was detected as 83.0 g on 1 g of expanded graphite with a bulk density[12] of 0.006 g/cm^3 and the pores with the size of 0.004-4.000 μm was too low to explain the adsorption capacity of the measured oil. In the adsorption study of expanded graphite for oils with viscosity ranging from 0.001-0.850 Pa/S, Inagaki[13] indicated the adsorption isotherms were all type I and effective sorption coefficient strongly depends on viscosity of oil.

In the adsorption of phenyl organic molecules[14], bentonite may function as a recyclable surfactant support for these pollutants. Charcoals are another kind of adsorbent with microporous structure, which are only a few molecular diameters in width[15]. Mikhail[2,16] found vapour of phenyl organic molecules could be adsorbed on microporous silica gel. The porous structure of expanded graphite ranging from several nanometers to hundreds micrometers makes it have adsorption capacity for phenyl organic molecules.

Different adsorption mechanism should cause different adsorption capacity of expanded graphite for oils and phenyl organic molecules. With salad oil, thermal oil, phenol, benzoic acid, benzene sulfonic acid, *p*-methylbenzene sulfonic acid as reference compounds and based on adsorption experiment, purpose of this study is to testify their different adsorption mechanism on expanded graphite. Adsorption thermodynamics, SEM observation, stepwise adsorption and deviation analysis of stepwise adsorption are carried out simultaneously.

EXPERIMENTAL

Preparation and structural characteristics of expanded graphite: Expanded graphite is firstly prepared with 50 mesh graphite raw material according to literature[17] and then it is expanded in KSW heating oven at 900 °C. Structural parameters of expanded graphite are characterized by expanded volume, surface area, pore cubage as listed in Table-1. These data are detected with PoreMaster 60GT instrument (Quantachrome Instruments, USA) under varying pressures of 0.818-59667.199 PSIA.

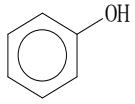
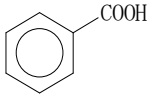
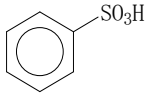
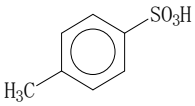
TABLE-1
STRUCTURAL PARAMETERS OF EXPANDED GRAPHITE

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

Adsorbates characteristic: Thermal oil and salad oil are used in the experiment, their viscosities are determined as 0.059 and 0.016 [100 mL/g], repectively at 25 °C with an Ubbelohde viscometer. Pure substances are used in the experiment.

Phenol, benzoic acid, benzene sulfonic acid, *p*-methyl benzene sulfonic acid are selected as adsorbates. The chemical structure and molecular weight of these compounds are showed in Table-2. Simulated phenyl organic molecules wastewaters are prepared by dissolving the different amount of the adsorbate in distilled deionized water at various concentrations. All measurements are carried with a New Century-T6-spectrophotometer (Pgenera, China) operating in the visible range on absorbance mode. Absorbance values are detected at wavelength for maximum absorbance (λ_{max}) corresponding to each phenyl organic molecules (Table-2) and its solution is initially calibrated for concentration in terms of absorbance units.

TABLE-2
CHEMICAL STRUCTURE AND MOLECULAR
WEIGHT OF PHENYL ORGANIC MOLECULES

Phenyl organic molecules	Structure	m.w.	λ_{max} (nm)
Phenol		94.1	209.8
Benzoic acid		122.1	225.0
Benzene sulfonic acid		158.2	213.4
p-Methylbenzene sulfonic acid		172.2	221.8

Adsorption for oil: Batch adsorption experiments have been carried out with about 0.200 g expanded graphite (m_1) and 100 mL oil in 250 mL flask with plug and mixed well gently. At different intervals of time, expanded graphite is filtrated with wire gauze and quantified for estimation of balance adsorbance for oil. Balance time is detected *ca.* 24 h at 25 °C. Incremental weight of wire gauze is calculated as m_2. Adsorbance q_e of oil on expanded graphite is calculated according to eqn. 1:

$$q_e = (m_2 - m_1)/m_1 \quad (1)$$

Adsorption for phenyl organic molecules: Static adsorption experiments have been undertaken by taking about 0.200 g expanded graphite (m_1) with 100 mL (V) phenyl organic molecules solution of known initial concentrations C_0 in different glass flasks with plug. The mass of expanded graphite to volume of solution is standardized as $m_1/ = 0.200/0.1 = 2.0$ g/L. Adsorbance is determined according to eqn. 2:

$$q_e = V(C_0 - C_e)/m_1 \quad (2)$$

C_e is equilibrium concentration of benzene organic molecule in solution (mg/L).

Stepwise adsorption of oil: A series simulated phenyl organic molecules wastewaters are prepared with concentrations of 100, 300 and 500 mg/L. Adsorption experiments for these compounds are first carried out according to the method mentioned in as in case of adsorption for oil. Expanded graphite, saturated by different concentration of phenyl organic molecules solution, is filtrated with wire gauze and placed for 0.5 h and then it is successively used for the adsorption of oil. After equilibrium, filtration with wire gauze and placed for 0.5 h, it is dried at 110 °C for about 7 h to ensure a constant of m_2. The stepwise adsorbance of oil is calculated according to eqn. 1.

RESULTS AND DISCUSSION

Adsorption capacity of expanded graphite for oil: Static adsorption experiments of oil have revealed that mass of expanded graphite increases quickly during the first several minutes and then adsorption rate decreases with time. For oil with higher viscosity, a longer adsorption equilibrium time is needed[18]. In the adsorption of oil, saturated adsorbance during 24 h is used to show its adsorption capacity. The value is detected as 131.3 g thermal oil and 127.8 g salad oil for each gram of expanded graphite with a bulk density of 0.0048 g/mL.

Adsorption capacity and sorption isotherm of expanded graphite for phenyl organic molecules corresponding to concentrations of 100, 300, 500 mg/L, are detected. Results listed in Table-3 show saturated adsorbance increases with phenyl organic molecules concentration. Expanded graphite holds higher adsorbance for benzoic acid than other tested phenyl organic molecules.

The isotherm of expanded graphite for these tested adsorbate is detected and showed in Fig. 1. Adsorption isotherms of the four phenyl organic molecules are all type II. The adsorbance increases quickly with the increasing equilibrium concentration, which is a result of multilayer sorption of molecule[19].

SEM analysis of saturated expanded graphite: Study of static adsorption has testified expanded graphite shows higher adsorption capacity for oils (higher than 100 g/g) than for phenyl organic molecules (less 100 mg/g within the tested equilibrium concentration). To test their different adsorption pattern, SEM analysis is carried out for expanded graphite (a), expanded graphite saturated by phenol (b), expanded graphite saturated by thermal oil (c), expanded graphite saturated by

TABLE-3
SATURATED ADSORBANCE OF EXPANDED GRAPHITE FOR PHENYL ORGANIC MOLECULES

Phenyl organic molecules	Initial concentration (mg/L)	Absorbance (mg/g)
Phenol	100	1.91
	300	5.60
	500	8.05
Benzoic acid	100	13.57
	300	17.87
	500	27.34
Benzene sulfonic acid	100	2.75
	300	4.88
	500	7.02
p-Methylbenzene sulfonic acid	100	3.43
	300	5.58
	500	6.48

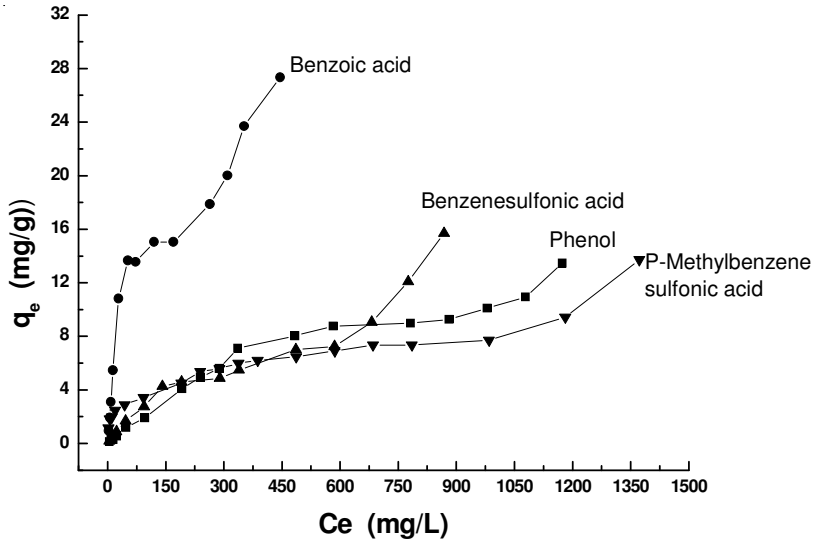


Fig. 1. Adsorption isotherms of phenyl organic molecules at atmospheric pressure and 25 °C

salad oil (d), respectively. Fig. 2 (a) shows a special V-type structure of expanded graphite as mentioned in reference[5]. Compare with (a), (b) shows obvious breakage of V-type structure of expanded graphite, but pores on the surface of the worm like particles are still clear. But (c) and (d) shows expanded graphite is filled thoroughly by oil. Adsorption process of oil into expanded graphite may compose of two-unit process of absorption and filling[1]; "wrapping space", first-level and second-level pores of expanded graphite particles play important role in influence adsorbance. However, as proved above, the adsorption of phenyl organic molecules on expanded graphite belongs to multilayer adsorption.

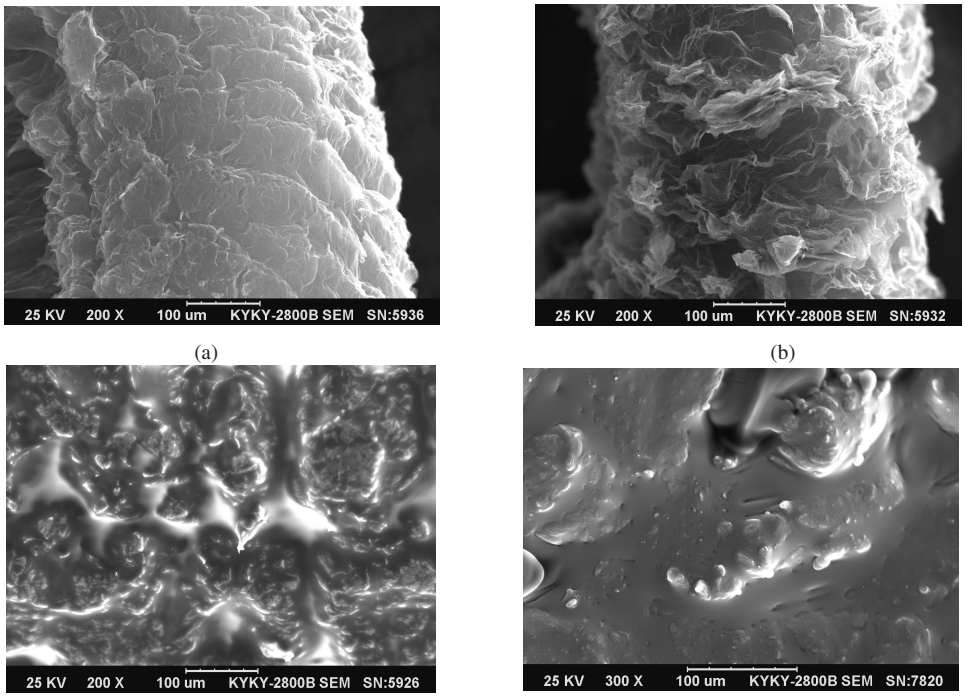
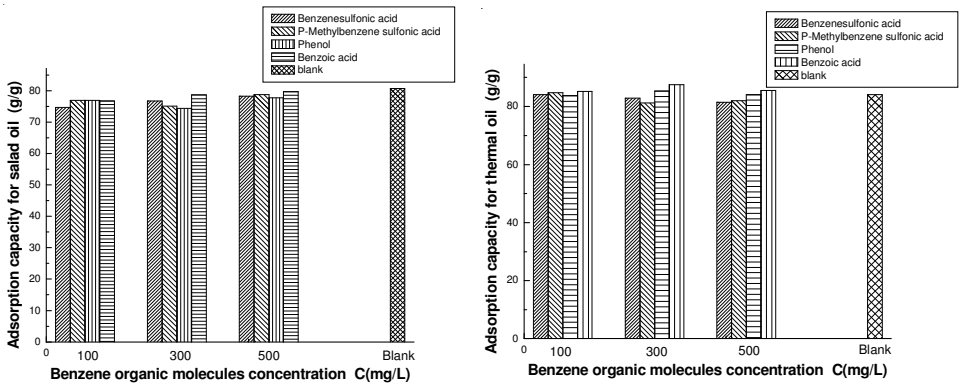


Fig. 2. SEM micrograph of expanded graphites (a) expanded graphite, (b) expanded graphite saturated by phenol, (c) expanded graphite saturated by thermal oil, (d) expanded graphite saturated by salad oil

Stepwise adsorbance of expanded graphite for oil the further evidence of adsorption mechanism: Stepwise adsorbances of oil on expanded graphite which is saturated by different concentration of phenyl organic molecules solution are detected and the results are showed in Fig. 3. Stepwise adsorbance of oil on expanded graphite, which is saturated by deionized water first in stepwise adsorption, is regarded as blank value. No obvious difference among these adsorbances is observed in Fig. 3.

To judge whether there is statistical significance or not among these adsorbances of oil in stepwise adsorption, deviation analysis has been carried out. The blank value is considered as average of deviation analysis[20]. Deviations both between average and every adsorbance of oil corresponding to various initial phenyl organic molecules concentrations (in group) and deviations between average and adsorbance of oil corresponding to different kind phenyl organic molecules (among groups) are calculated. Results showed in Table-4 give the conclusion of no statistical significance. For thermal oil and salad oil, the deviation results in group and among groups are all smaller than theoretical value of $t_{0.05,2} = 4.303$ (in group) and $t_{0.05,4} = 2.776$ (among groups), respectively. In other words, the stepwise adsorbance of oil depends neither on phenyl organic molecules concentrations nor on their structure and molecular weight.



(a) (b)

Fig. 3. Stepwise adsorption capacity of oil on expanded graphite

TABLE-4
t-TEST OF STEPWISE ADSORBANCE OF OIL ON EXPANDED GRAPHITE

		t-test (in group)		t-test (among groups)
$t_{theoretical}$		$t_{0.05,2} = 4.303$		$t_{0.05,4} = 2.776$
$t_{calculated}$	Thermal oil	Phenol	$t_{0.05,2} = 4.227$	$t_{0.05,4} = 1.649$
		Benzoic acid	$t_{0.05,2} = 2.676$	
		Benzene sulfonic acid	$t_{0.05,2} = 3.897$	
		p-Methylbenzene sulfonic acid	$t_{0.05,2} = 3.551$	
	Salad oil	Phenol	$t_{0.05,2} = 0.649$	$t_{0.05,4} = 2.664$
		Benzoic acid	$t_{0.05,2} = 2.726$	
		Benzene sulfonic acid	$t_{0.05,2} = 1.595$	
		p-Methylbenzene sulfonic acid	$t_{0.05,2} = 1.343$	

Stepwise adsorbance of oil declines markedly, for thermal oil and salad oil, it is about three-fifths of its individual adsorption capacity on expanded graphite (131.3 and 127.8 g/g). The diminished adsorbance should be caused by the breakage of V-type structure, deformation of pores and shatter of the particles under surface tension. The existence of stepwise adsorbance of oil testifies a different adsorption mechanism between expanded graphite and phenyl organic molecules, expanded graphite and oil. Expanded graphite which has been used for the treatment of phenyl organic molecules wastewater, can be used sequentially for the remove of oils contamination.

Conclusion

The study shows that expanded graphite has better adsorption capacity for thermal oil and salad oil and the adsorption is mainly due to filling. While, adsorption of phenyl organic molecules on expanded graphite is multilayer, which causes smaller adsorbance. expanded graphite, saturated by phenyl organic molecules, still holds abundant pores on the surface of the worm like particles. In the stepwise adsorption of phenyl organic molecules and oil on expanded graphite, there is no statistical significance among stepwise adsorbance of oil. The adsorbent can be used for the elimination of phenyl organic molecules and oils step by step.

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