

Adsorption thermodynamics and prediction of phase equilibria for activated carbon synthesized from waste grease.

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ABSTRACT

The research is conducted to evaluate the thermodynamic parameters of adsorption processes and to predict the phase equilibria for carbon produced from a mixture of waste grease and raw sulfur. Phenol and p-nitrophenol were used for adsorption isotherm at different concentrations and temperatures. Thermodynamic functions such as Gibbs function (ΔG), enthalpy (ΔH) and entropy (ΔS) changes during adsorption were calculated. The melting point measurements of waste grease and raw sulfur mixtures were obtained for different ratios. The lever rule is used to represent a quantitative determination in the two-phase region of a phase diagram using a certain equation. The phenol adsorption was mostly an endothermic process while the p-nitrophenol adsorption was an endothermic process for all samples as indicated by positive values of the enthalpy. Generally the adsorption processes were spontaneous as pointed out by entropy and free energy values. Various phases and boundaries were occurred at three regions with 2-phase while 1-phase is exist in the system especially at high temperatures. The ratio of liquid/solid was increased with reducing temperature and the amounts of liquid were reduced.

Introduction

Solid phase and mesophase (a phase intermediate between solid and liquid) equilibria data were of great role in thermodynamics. This importance arises from a testing and extension of fluid mixtures theories. Atkins stated that ((The mesophase may arise when molecules have highly anisotropic shape, such as being long and thin, or disk-like))(1). Meanwhile, the mesophase can be classified as a smectic phase, nematic phase or cholesteric phase.

In the last few decays, a great progress has been achieved in the field of predictive thermodynamic models. Whereas a powerful group contribution of state can be applied to predict the required pure component properties such as densities, enthalpies, heat capacities for different phases at given conditions, the various phase equilibria and excess properties for nonpolar, polar and supercritical compounds and strong electrolytes (2). Since a lot of results for pure component properties, phase equilibria and excess properties have already presented in different publications (3-5).

As already demonstrated for poly-functional molecules (6-8), the proximity of two identical or different groups has a strong influence on interaction parameters. These parameters have been measured

and successfully interpreted in terms of group contribution theory in the approximation (9,10).

The addition of grease plays a great role in decreasing a friction coefficient and increases the load-bearing capacity of the friction part in mechanical systems (11,12). However, the waste-oil products such as grease can be used as a source of raw materials in activated carbon synthesis. Active carbon in its broadest sense is a term that includes a wide range of amorphous carbonaceous materials that exhibit a high degree of porosity and an extended inter-particulate surface area (13), large adsorption capacities, fast adsorption kinetics, and relative ease of regeneration (14).

Activated carbon is produced from nearly all carbon-containing organic materials, mainly wood, sawdust, nutshells, fruit stones, peat, lignite, coal, petroleum coke, etc.(15,16). Activated carbon, also known as porous carbon, has been widely used as an adsorbent in the separation and purification of gases or liquids. The application of these carbons has been considered a major unit operation in the chemical and petrochemical industries (17).

Following up the thermodynamic functions is consider in concern due to energy transfer of adsorption processes, besides the existence of phases in the mixture of grease and sulfur that used in synthesis of activated carbon.

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Materials and Methods

Activated-carbon characteristics

The synthesis and characteristics of activated carbon synthesized from wasted grease and raw sulfur were determined as mentioned previously (18) and shown in Table (1).

Adsorption thermodynamics

Phenol and p-nitrophenol were used for adsorption isotherm at different concentrations and temperatures as mentioned previously (18). Thermodynamic functions such as Gibbs function (ΔG), enthalpy (ΔH) and entropy (ΔS) changes during adsorption can be calculated from following equations:

$$K_c = C_{Ae}/C_e$$

$$\Delta G = -RT \ln K_c$$

$$\log K_c = \Delta S/2.303R - \Delta H/2.303RT$$

Where K_c = equilibrium constant

C_e = equilibrium concentration, mg/L

C_{Ae} = equilibrium concentration at solid phase, mg/L

The values of ΔH and ΔS were evaluated from the slope and the intercept of plots of $\log K_c$ versus $1/T$.

Phase Equilibria

Samples of waste oil (used grease) and sulfur were collected from local industrial factories. The melting point measurements of mixtures were obtained for different ratios by using melting point apparatus (SMP30 Stuart Bibby Scientific).

The lever rule is used to represent a quantitative determination in the two-phase region of a phase diagram. The following equation is normally used as lever rule;

$$n\alpha l\alpha = n\beta l\beta$$

$n\alpha$ = The amount of phase α

$n\beta$ = The amount of phase β

$l\alpha$ and $l\beta$ = Distance along the horizontal tie line through the phases.

Results and Discussion

Adsorption thermodynamics

Adsorption of phenol and p-nitrophenol on activated-carbon produced from waste grease decreased with temperature. The phenol adsorption was mostly an endothermic process while the p-nitrophenol adsorption was an endothermic process for all samples (Tables 2 and 3) as indicated by positive values of the enthalpy. In general, the phenol adsorption is increased by increasing temperature which is dependent highly on the raw materials and adsorbate (19).

The positive values of entropy and negative values of Gibbs function indicated a spontaneous adsorption process. It has been known that ΔG values

up to -20 kJ/mol are highly related to the electrostatic interaction between sorption sites and the adsorbate (physical adsorption), while ΔG values of more negative than -40 kJ/mol consistent a charge sharing or transfer from the adsorbent surface to the metal ion to form coordinate bond (chemical adsorption) (20). The ΔG values obtained in this study for phenol and p- nitrophenol are mostly less than -20 kJ/mol, which indicates that physical adsorption is the predominant mechanism in the sorption process except few cases which showed a chemical adsorption (21).

Phase Equilibria

Table (4) shows the mole fraction of sulfur (X_s) at different amounts of sulfur and grease mixtures with experimental melting point temperatures (T). Meanwhile, the relation between X_s and T is presented in Fig.1 which showed various phases and boundaries. There are three regions with 2-phase while 1-phase is exist in the system especially at high temperatures. The point a1 is representing a liquid cooling while a2 is on the line between a1 and a3. At the same time, the point a3 showed a sulfur precipitating while a4 and a5 indicated an eutectic freezing (e) and solid cooling respectively. However, the lines in Fig.1 are representing boundaries between different phases at various temperatures. The line of a1 \rightarrow a2 clarified that some solid sulfur is deposited and the remaining liquid is richer in grease, meanwhile, the line of a3 \rightarrow just below a3 indicated that a sample is entirely solid and consisting of solid sulfur and solid mixture of sulfur and grease.

At another investigated regions, the line b1 \rightarrow b2 showed no change until at b2 when solid sulfur begins to deposit whereas a line of b2 \rightarrow b3 indicated that a solid sulfur deposits but at b3 a reaction occurs to form sulfur and grease. At this stage, the liquid sulfur/grease mixture is in equilibrium with a little solid sulfur and grease but there is still no liquid compound. The line of b3 \rightarrow b4 showed that as cooling continues, the amount of solid compound increases until b4, the liquid reaches its eutectic composition. It then solidifies to give a two-phase solid consisting of solid grease and solid mixture of sulfur and grease.

Taking region2 in consideration practically at point T1 in Fig.1, the ratio of l_{solid}/l_{liquid} is almost infinite for this tie line, so n_{liquid}/n_{solid} is also almost infinite and there is only a trace of solid present. When the temperature is reduced to T2, the value of l_{solid}/l_{liquid} is about 0.12 so $n_{liquid}/n_{solid} = 0.12$ and the amount of liquid is about 0.12 times the amount of solid. When the temperature has been reduced to T3, the value of l_{solid}/l_{liquid} is about 0.22 so $n_{liquid}/n_{solid} = 0.22$ and the amount of liquid is about 0.22 times the amount of solid. When the temperatures have been reduced more and more until

reaching a completely solid due to Isolid/Iliquid value of almost zero which conclude that there is only a very small amounts of liquid present.

Conclusion

- Adsorption of phenol and p-nitrophenol on activated-carbon decreased with temperature.
- The phenol and p-nitrophenol adsorption was mostly an endothermic and spontaneous process.
- Physical adsorption was dominant process for phenol and p-nitrophenol.
- Various phases and boundaries were occurred at three regions with 2-phase and 1-phase exist.
- The ratio of nliquid/nsolid was increased with reducing temperature and the amounts of liquid were reduced .

References:

1. Atkins, P. Physical Chemistry. 6th. Addition, Oxford University Press (2001).
2. Gmehling, J. Pure Appl. Chem. 75:875-888 (2003).
3. Ahlers, J. and Gmehling, J. Fluid Phase Equilib. 191: 177-188 (2001).
4. Ahlers, J. and Gmehling, J. Ind. Eng. Chem. Res. 41: 3489-3498 (2002).
5. Ahlers, J. and Gmehling, J. Ind. Eng. Chem. Res. 41: 5890-5899 (2002).
6. Grolrier, J. and Kehiaian, H. J. Chim. Phys. 70: 807-810(1973).
7. Polo, C.; Gutierrez, C.; Kechavaraz, M. and Kehiaian, H. Phys. Chem. 84:525-529(1980).
8. Kehiaian, H.; Tine, M.; Lepori, L.; Matteoli, E. and Marongiu, B. Fluid Phase Equilib. 46: 131-177(1989).
9. Cancellu, D.; Marongiu, B. and Porcedda, S. Thermochem. Acta 178: 33-49 (1991).
10. Dahmani, A.; Kaci, A. and Jose, J. Fluid Phase Equilib. 134: 255-265 (1997).
11. Lee, J.; Cho, S.; Hwang, Y.; Lee, C. and Kim, S. Tribol. Lett. 28:203-208 (2007).
12. Lee, K.; Hwang. Y.; Cheong, S.; Choi, Y.; Kwon, L.; Lee, J. and Kim, S. Tribol. Lett. 35:127-131 (2009).
- 13- Bansal, R.C., Goyal, M. and Raton, B., "Activated Carbon Adsorption", Taylor & Francis Group(2005).
- 14- Prahas, D., Kartika, Y. and Indraswati, N. Chem. Eng. J. 140: 32-42 (2008).
- 15- March, H., and Reinoso, F.R., "Activated Carbon", Elsevier Science & Technology Books, 2006.
16. Al-Khateeb, I. I. Al-Mehemdy, A., O. J. Chem. Chem. Eng. 5: 715-719 (2011).
- 17- Sricharoenchaikul V., Pechyen C. and Atong D., " Preparation and Characterization of Activated Carbon from the Pyrolysis of Physic Nut (Jatropha

- curcas L.) Waste", American Chemical Society Magazine (2007).
- 18- Ali, H. M.Sc. Thesis. Al-Anbar University, Iraq. (2011).
- 19- Zawani, Z., Luqman, C. and Thomas, S., Eur. J. Sci. Res., 37, 67, (2009).
- 20- Horsfall, M., Spiff, A. and Abia, A. Bull. Korean Chem. Soc. 25:969-976 (2004).
- 21- Abdel Ghani, N. and Elchaghaby, G. Inter. J. Enviro. Sci. Tech. 4:451-456 (2007).

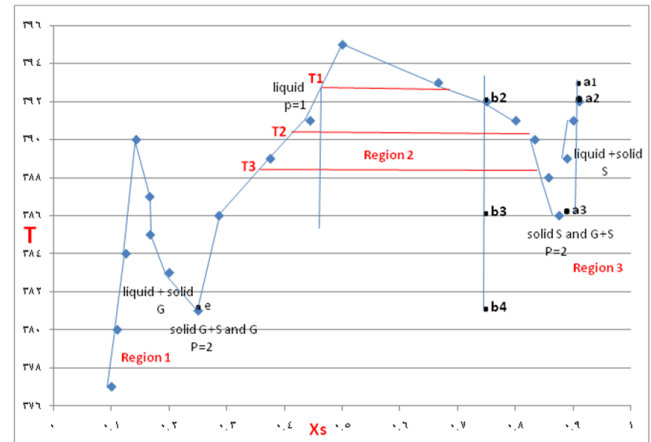


Fig.1: Relation between sulfur- mole fraction (Xs) and temperature.

Table 1: Characteristics of activated carbon synthesized from wasted grease and sulfur

Samples	Treatment	(C) %w	Surface area m ² g ⁻¹	pH	Bulk density g cm ⁻³
Wo	No activate r/O ₂	24.2	32.4	8.88	0.61
Wo - N	No activa tor/N ₂	21.8	117.7	7.71	0.59
Zn-20	20%Zn Cl ₂ / O ₂	45.6	110.3	5.13	0.59
Zn-20N	20%Zn Cl ₂ / N ₂	49.2	115.2	4.95	0.67
Zn-40	40%Zn Cl ₂ / O ₂	62.5	64.7	4.97	0.59
Zn-40N	40%Zn Cl ₂ / N ₂	57.5	110.7	4.90	0.67
Na-10	10%Na Cl/ O ₂	29.4	139.9	5.18	0.48

F.S - 20N	F.S - 20	F.S - 10N	F.S - 10	Na- 20N	Na- 20	Na-10 N
20%/food salt/ N ₂	20%/food salt/ O ₂	10%/food salt/ N ₂	10%/food salt/ O ₂	20%/Na Cl/ N ₂	20%/Na Cl/ O ₂	10%/Na Cl/ N ₂
30.5	37.3	20.3	31.6	33.3	34.4	26.3
123.6	66.6	201.9	120.6	146.4	144.0	156.3
5.24	4.85	5.01	5.00	4.63	4.40	5.46
0.48	0.43	0.43	0.43	0.41	0.40	0.46

Table 2: Thermodynamic parameters of phenol adsorption on activated carbon.

Na- 10N-P	Na- 10-P	F.S- 20N-P	F.S- 10N-P	F.S- 10-P	Wo - N-P	Wo - P	Initial Phenol Concn. (mg/L)	ΔH kJmol ⁻¹	ΔG, kJmol ⁻¹			
									ΔS J K ⁻¹ mol ⁻¹	283K	293K	313K
-2.73	-2.26	4.92	5.88	2.87	1.57	0.34	200	8.0	-1.79	-2.14	-2.39	-2.04
31.2	31.1	59.1	61.5	44.3	20.1	8.0	200	8.0	-3.75	-4.58	-5.40	-4.24
-11.62	-10.98	-11.43	-11.05	-10.10	-3.75	-1.79	200	8.0	-10.10	-10.19	-11.27	-11.55
-13.02	-12.57	-11.44	-11.52	-10.19	-4.58	-2.14	200	8.0	-10.19	-10.19	-11.27	-11.55
-11.72	-11.46	-13.09	-12.66	-11.27	-5.40	-2.39	200	8.0	-11.27	-11.27	-11.27	-11.27
-12.49	-12.32	-15.38	-15.57	-11.55	-4.24	-2.04	200	8.0	-11.55	-11.55	-11.55	-11.55

Zn- 40N-P	Zn- 40-P	Zn-20N-P	Zn-20N-P	Na- 20N-P	Na- 20-P
200	200	200	200	200	200
6.22	1.37	4.92	3.42	1.37	6.15
63.9	29.1	52.4	48.5	39.4	68.3
-11.01	-6.49	-9.05	-9.78	-12.41	-12.50
-12.16	-7.38	-10.29	-10.69	-13.95	-14.64
-14.67	-8.09	-12.09	-12.59	-12.40	-12.99
-14.36	-7.42	-12.31	-12.09	-14.77	-17.91

Table3: Thermodynamic parameters of p-nitrophenol adsorption on activated carbon.

Na-20N-PN	Na-20-PN	Na-10N-PN	Na-10-PN	F.S- 20N-PN	F.S- 10N-PN	F.S- 10-PN	Wo - N-PN	Wo - P	Initial p-nitro Phenol Concn. (mg/L)	ΔH kJmol ⁻¹	ΔS JK ⁻¹ mol ⁻¹	ΔG, kJmol ⁻¹			
												283K	293K	313K	333K
500	500	500	500	500	500	500	500	500	500	1.93	91.9	-4.40	-8.07	-8.32	-12.20
31.4	23.4	9.16	7.59	15.1	3.42	5.13	2.80	1.93	500	8.86	88.7	-16.72	-15.33	-17.92	-19.88
183.5	150.4	93.7	83.9	113.7	74.3	74.2	50.3	91.9	500	8.86	88.7	-16.72	-15.33	-17.92	-19.88
-16.16	-16.72	-16.20	-15.33	-15.94	-16.72	-15.33	-10.61	-4.40	500	8.86	88.7	-16.72	-15.33	-17.92	-19.88
-23.68	-21.00	-18.72	-16.87	-17.37	-17.91	-16.59	-13.06	-8.07	500	8.86	88.7	-17.91	-16.59	-17.92	-19.88
-23.49	-19.88	-18.62	-17.77	-18.62	-20.63	-17.92	-12.04	-8.32	500	8.86	88.7	-20.63	-17.92	-17.92	-19.88
-30.57	-29.96	-23.07	-20.83	-24.57	-20.19	-19.88	-13.77	-12.20	500	8.86	88.7	-20.19	-19.88	-17.92	-19.88

Zn-20-PN	500	4.38	64.9	-13.74	-14.02	-15.71	-18.04
Zn-20N-PN	500	10.9	84.1	-11.75	-12.64	-14.52	-18.48
Zn-40-PN	500	6.29	51.2	-7.53	-8.53	-8.87	-11.49
Zn-40N-PN	500	8.89	89.1	-15.56	-15.84	-18.90	-21.80

5	114	0.17
6	112	0.17
7	110	0.20
8	108	0.25
9	113	0.29
10	106	0.33
11	116	0.38
12	118	0.44
13	122	0.50
14	120	0.67
15	119	0.75
16	118	0.80
17	117	0.83
18	115	0.86
19	113	0.88
20	116	0.89
21	118	0.90
22	119	0.91

Table 4: Values of sulfur mole fraction and boiling points of grease-sulfur mixtures.

Sample No.	M.P., °c	Xs
1	104	0.10
2	107	0.11
3	111	0.13
4	117	0.14

تقدير ثرمودينامك الامتزاز وتوازن الطور للكربون المنشط والمحضر من الكريز التالف

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الخلاصة

يهتم البحث في تقييم ودراسة الدوال الثرموديناميكية لعمليات الامتزاز مع متابعة تقدير توازن الطور للكربون المنشط المنتج من خليط الكريز التالف و الكبريت الخام. تم استعمال الفينول والبارانايترو فينول لدراسة الامتزاز المتماثل حراريا عند درجات حراريه مختلفة وتراكيز مختلفة. تم حساب الدوال الثرموديناميكية كالتغيرات في الطاقة الحرة والانتالبية والانتروبية والحاصلة خلال عمليات الامتزاز. كما تم قياس درجات الانصهار لخليط الكريز التالف والكبريت الخام عند نسب خلط مختلفة لدراسة توازن الطور في حين تمثل قاعدة العتلة التقدير الكمي لمناطق الاطوار. تشير النتائج الى ان امتزاز الفينول على الكربون المنشط يتصف بكونه عملية ماصة للحرارة في معظم الحالات في حين تؤكد نتائج امتزاز البارانايترو فينول الى عملية الامتزاز هي ماصة للحرارة ولجميع النماذج و المعاملات المستخدمة في البحث. في حين ان عمليات الامتزاز بشكل عام هي عمليات تلقائية كما تحددتها القيم المستحصلة للطاقة الحرة والانتروبي. الاطوار والحدود المختلفة تم تحديدها في مناطق ثلاث وبتطورين في حين ان مناطق الطور الواحد تتواجد بشكل واضح مع ارتفاع درجة الحرارة بينما تزداد نسبة طول ذراع السائل الى طول ذراع الصلب المستحصلة من قاعدة العتلة مع الانخفاض بدرجات الحرارة والتي تؤدي الى زيادة الكميات الصلبة.