

ADSORPTION EQUILIBRIA BETWEEN ACTIVATED CARBON AND PHENOL DISSOLVED IN LIQUID AND SUPERCRITICAL AQUEOUS SOLUTIONS

G. Mancini, G. Sambenedetto, G. Del Re, G. Di Giacomo*

Dipartimento di Chimica, Ingegneria Chimica e Materiali - Università di L'Aquila.

I-67040 Monteluco di Roio, L'Aquila, ITALY

*Corresponding author: Tel +39 0862 434225,

Fax +39 0862 434203, digiaco@ing.univaq.it

Activated carbon can be used as a proper adsorbent to remove almost completely phenolic compounds dissolved in liquid water. In addition, regeneration of exhausted bed can be usefully obtained by supercritical water, which can be directly feed to a Supercritical Oxidation plant to destroy the polluting compounds; the regenerated bed can be in turn reused for a new adsorption cycle. To this purpose, new equilibrium data for the system activated carbon-phenol dissolved in liquid and supercritical water have been measured and are reported in this paper. All the experimental equilibrium ranging from liquid to supercritical water conditions have been correlated using the Langmuir model and the numerical values of the model parameters are also reported.

INTRODUCTION

Purification of water contaminated by organic compounds such as phenols, PCB, PAH, dioxins and others, can be usefully obtained by adsorption on fixed bed of activated carbon. In addition, since Supercritical Water (SCW) behaves as an organic solvent, it can also be used to regenerate the spent carbon bed which, in turn, can be reused for new adsorption cycles giving to the process significant economic viability [1, 2]. A further advantage in using SCW for regenerating the saturated carbon bed is related to the possibility of directly feeding the fluid mixture of SCW and polluting compounds to a Supercritical Water Oxidation (SCWO) section of the purification plant along with an oxygen rich gaseous stream where all the toxic compounds are definitely destroyed [3, 4].

In order to develop, design and optimise both the adsorption and the regeneration section of such a plant [5] phase equilibrium as well as kinetic data for the system activated carbon-polluting compounds dissolved in liquid and supercritical water are required, along with a proper model for calculating the concentration of the organic compounds in both the solid and the fluid phase in the whole range of all possible operating P and T conditions.

The aim of this paper is to show how equilibrium simulation can be systematically approached using phenol as model compound. This includes validation of proper procedures and apparatuses for collecting a sufficient number of reliable equilibrium data under liquid and supercritical water conditions, along with validation of a proper simulation model parametrised with all the available equilibrium data.

I - MATERIALS AND METHODS

The main characteristics of activated carbon supplied by SICAV (Italy) are reported in Table 1.

The as-received activated carbon was sieved and the 125÷150 µm fraction was used to perform the equilibrium experimental tests.

Phenol was bought from Aldrich (art. 43,151-6).

Deionized water was obtained from a reverse osmosis laboratory device (ROS-50T).

The operating procedures and apparatuses used for measuring adsorption equilibrium data in the whole range from liquid to supercritical conditions, are reported in detail elsewhere [5, 6].

In particular the liquid equilibrium data were obtained under adsorption mode at 298 K and 308 K, while the data in supercritical water conditions were obtained under desorption mode in pressure and temperature range 27.9÷33.8 MPa and 673.15÷803.15 K, respectively.

Table 1 Activated carbon characteristics.

BET Surface Area	m ² /g	327
Langmuir Surface Area	m ² /g	442
Pore Volume	cm ³ /g	0.24
Iodine Number	mg/g	800
Apparent Density	kg/m ³	400
Moisture	%	3.1
Single Point Total Pore Volume of pores less than 1272 Å at P/P ₀ = 0.9845	cm ³ /g	0.2214
Average Pore Diameter	Å	20.02

RESULTS AND DISCUSSION

Experimental equilibrium data for adsorption of phenol dissolved in aqueous solutions are reported in table 2, where C_e and q_e represent the concentration of phenol in the fluid phase and the concentration of phenol in the solid phase on a phenol free base, respectively.

Experimental equilibrium data for desorption of phenol in supercritical water are reported in table 3, where ρ_{fluid} is the density of the fluid phase.

All the experimental data reported in table 2 and in Table 3 are shown in Figure 1.

Our equilibrium data under liquid water conditions are in good agreement with literature data [7, 8, 9]; equilibrium data under supercritical water conditions are not available in the literature.

All the data were fitted by using the Langmuir model:

$$q_e = \frac{Q_a^0 \cdot b \cdot C_e}{1 + b \cdot C_e} \quad (1)$$

where Q_a^0 represents the maximum adsorption capacity, while the parameter b is closely related to the heat of adsorption.

Q_a^0 and b under subcritical water conditions are given by equations (2) and (3):

$$Q_a^0 = 0.043 + 2.97 \cdot 10^{-3} (T - 298.15) \quad (2)$$

Table 2. Experimental equilibrium data for the system activated carbon - phenol - liquid water.

298.15 K			308.15 K		
Test	C_e (fluid phase) [g/l]	q_e (solid phase) [g/g]	Test	C_e (fluid phase) [g/l]	q_e (solid phase) [g/g]
1	0.0051	0.016	17	0.0400	0.0515
2	0.0056	0.016	18	0.0380	0.0518
3	0.0140	0.021	19	0.0310	0.0535
4	0.0160	0.021	20	0.0300	0.0538
5	0.0290	0.027	21	0.1070	0.0546
6	0.0290	0.027	22	0.1070	0.0546
7	0.0350	0.031	23	0.1280	0.0644
8	0.0360	0.031	24	0.1210	0.0664
9	0.0860	0.032	25	0.1270	0.0751
10	0.0790	0.033	26	0.1260	0.0756
11	0.0790	0.033	27	0.0050	0.0152
12	0.0880	0.033	28	0.0034	0.0154
13	0.0710	0.035	29	0.0045	0.0229
14	0.0865	0.042	30	0.0067	0.0230
15	0.0816	0.043	31	0.0120	0.0269
16	0.1350	0.047	32	0.0120	0.0269

Table 3. Experimental equilibrium data for the system activated carbon – phenol – supercritical water.

Test	T [K]	P [MPa]	ρ_{fluid} [kg/m ³]	C_e (fluid phase) [g/l]	q_e (solid phase) [g/g]
1	703.15	30.2	180.19	0.6278	0.0433
2	703.15	28.6	159.40	0.5220	0.0477
3	703.15	32.0	207.83	0.5770	0.0400
4	703.15	31.1	193.40	0.7060	0.0816
5	703.15	30.8	188.87	0.7914	0.0780
6	803.15	31.0	108.58	0.9400	0.0894
7	803.15	27.9	94.68	0.9937	0.0878
8	738.15	30.5	138.80	0.9150	0.0828
9	734.15	32.5	158.97	0.8990	0.0760
10	703.15	33.8	240.44	0.7060	0.0710
11	673.15	29.0	309.07	0.5470	0.0695

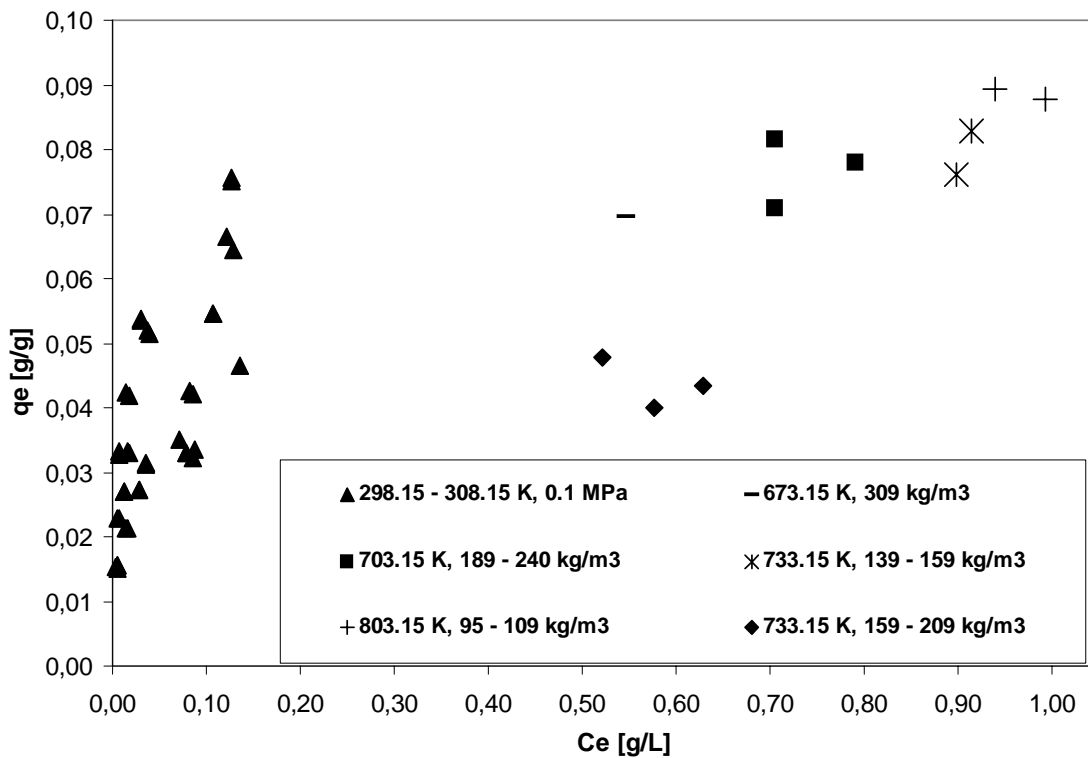


Figure 1. Experimental equilibrium data for phenol in liquid and supercritical water on activated carbon.

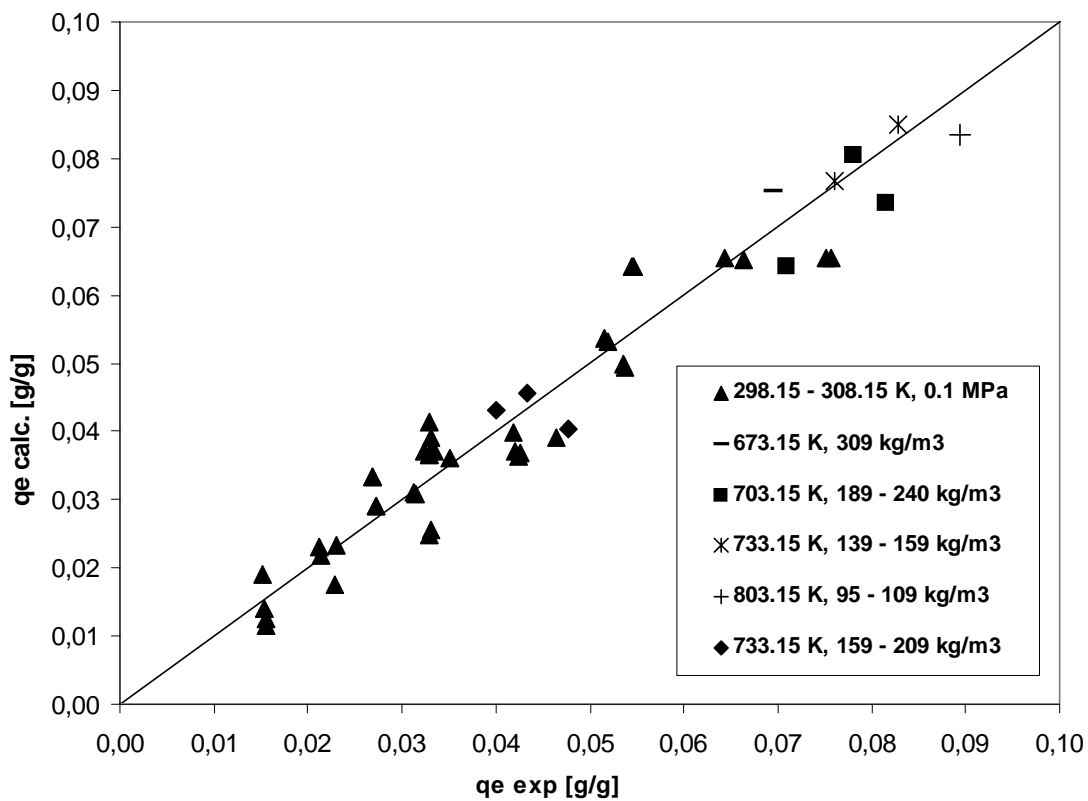


Figure 2. Comparison between experimental and calculated concentration of the adsorbate.

$$b = 34.233 \exp(224.43/T) \quad (3)$$

Q_a^0 and b under supercritical water conditions are given by equations (4) and (5):

$$Q_a^0 = 0.4244 - 4.83 \cdot 10^{-3}(T - T_c) + 3.61 \cdot 10^{-4}(\rho - \rho_c) - 1.61 \cdot 10^{-5}(T - T_c)(\rho - \rho_c) \quad (4)$$

$$b = 0.5820 \exp(2.95 \cdot 10^{-3}(T - T_c) + 9.43 \cdot 10^{-4}(\rho - \rho_c)) \quad (5)$$

where T_c e ρ_c represent the critical temperature and critical density of water, respectively. On figure 2 is shown a comparison between experimental and calculated data using Langmuir model, eq. (1), and the proper expressions for Q_a^0 and b (eq. (2) or (4) and (3) or (5), respectively).

CONCLUSION

New equilibrium experimental data for the system activated carbon-phenol dissolved in liquid and supercritical water have been obtained. Our data are in good agreement with available literature data.

In measuring data under SCW conditions, deionised water was degassed before use, in order to avoid any possible decomposition of phenol by oxidation reactions. However, under the experimental conditions used in this work, oxidation effect on the results was not important.

A simple model based on the Langmuir equation was also developed and parametrised with all the available data; using this model equilibrium of the system activated carbon-phenol dissolved in liquid and supercritical water can be satisfactorily simulated in the whole range of the interesting operating conditions of both adsorption and regeneration sections of the water purification plant.

Acknowledgements

The authors appreciate the laboratory support received by G. Spagnoli and L. Spera during this work.

REFERENCES:

- [1] Salvador F., Sanchez Jimenez C., *Carbon*, Vol. 34, **1996**, p. 511.
- [2] Salvador F., Sánchez C., Cubero R., Sánchez M.J., Salvador A., *Proc. of 4th Int. Symp. on High Pressure Process Technology and Chemical Engineering, "High Pressure in Venice", Venezia (Italy) September 22-25, 2002*, p. 220.
- [3] Del Re, G., Di Giacomo, G., *Desalination*, Vol. 138, p. 61.
- [4] Shaw R. W., Dahmen N., *Supercritical Fluids-Fundamentals and Applications*, Kiran E., Debenedetti P. G. and Peters C. J. eds., *Kluwer Academic Publishers, Dordrecht, The Netherlands, 2000*.
- [5] Sambenedetto G., Consalvi L., Del Re, G., Di Giacomo G., , *Proc. Membranes in Drinking Industrial Water Production, 22 - 26 September, Mülheim an der Ruhr, Germany, 2002*, p. 73.
- [6] Mancini G., Di Giacomo G., Del Re G., *Chemical Engineering Transactions, Ed. S. Pierucci*, Vol. 3, **2003**, p. 391.
- [7] Furuya E.G., Miura Y., Noll A., *Noll. Sep. Pur. Technol*, Vol. 11, **1997**, p. 69.
- [8] Edgehill R.U., Lu G. Q., *J. Chem. Technol. Biotechnol.*, Vol. 71, **1998**, p. 27.
- [9] Teng H., Hsieh C., *J. Chem. Technol. Biotechnol*, Vol. 74, **1999**, p. 123.]