Solid-Fluid Equilibrium for the System Activated Carbon and Aqueous Solutions of Phenol under Supercritical Water Conditions

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Activated carbon beds can be successfully used for safe and affordable purification of waste waters contaminated by toxic organic compounds, like PCB and Dioxins, as shown in previous works, using Phenol as model compounds. Furthermore, Supercritical Water Oxidation (SCWO) can be used for safe and efficient final destruction of the above mentioned toxic compounds. Therefore, regeneration of spent carbon beds using Supercritical Water (SCW) is quite interesting. To this purpose, the starting point is the quantification of Solid-Fluid Equilibrium (SFE) for the system made by activated carbon, Phenol, and SCW. A number of SFE measurements were made at laboratory scale under supercritical water conditions using a proper experimental apparatus along with a proper procedure. These data were used in combination with previously measured Solid-Liquid Equilibrium (SLE) data for the same system, in order to develop a new model able to quantitatively describe the phase equilibrium of the system under consideration from ambient to SCW P and T conditions. A Freundlich based equation was chosen and it was parameterized for comparison with the experimental data. As expected, since SCW behaves as an apolar solvent, the results obtained show that SCW can be successfully used for regenerating spent activated carbon under P and T values around 35 MPa and 720 K, respectively.

1. Introduction

Purification of very large amount of water micro polluted by toxic organic compounds like PCB and Dioxins is a challenge from both technological and economic point of view. In fact the purification must be done with a simple and economic affordable technology able to remove almost completely the much diluted pollutants from the aqueous stream and, at the same time, concentrate the pollutants on some other phase. Than the subsequent problem is the safe and complete destruction of the toxic compounds. In a previous paper (Di Giacomo and Del Re, 2001) a process which enable one to meet both these requirements was developed and described. It was obtained by connecting a nano-filtration section with a Supercritical Water Oxidation section fed with the retentate stream coming from the membrane filtration plant. This approach was presented with the purpose to make clear the basic idea; however, there are some complications related to the accumulation of the pollutants on the surface of the nano-filtration modules other than to the difficulties of destroying the polluted membranes. For these reasons we started with a new experimental and theoretical research program based on the following steps, using always phenol as representative of micro-polluting compounds:

- Experimental and theoretical characterization of the Solid-Liquid equilibrium of the pseudo ternary system made by activated carbon and polluted water;
- Experimental and theoretical characterization of activated carbon fixed beds adsorption of polluting compound from a liquid contaminated aqueous stream;
- Experimental and theoretical characterization of the solid-fluid equilibrium for the pseudo ternary system made by activated carbon and polluted SCW under different P and T conditions;

- Experimental and theoretical characterization of desorption of polluting compound from the spent fixed beds activated carbon using supercritical water;
- Experimental and theoretical characterization of the performance of a SCWO section, fed with the stream coming from the desorption section;
- Development of a new process which enables one to affordably remove micro-polluting compounds from contaminated waters and to destroy the toxic compounds.

Some results related to the above mentioned steps of the research program have been already published (Di Giacomo et al., 2007; Di Giacomo and Taglieri, 2011; Di Giacomo and Taglieri, 2012; Carozza, 2012) or are available from the literature (Salvador et al., 2002). The main purpose of this paper is to present and to discuss the experimental results related to the characterization of the pseudo ternary solid-fluid equilibrium of the system made of activated carbon, Phenol, and water under SCW conditions in sufficiently wide ranges of P and T. A further purpose is to develop a new Freundlich based model which can be used to quantitatively describe the Solid-Fluid equilibrium under the operating process parameters of the regeneration of spent activated carbon with supercritical water, in sufficiently wide range of P and T values.

2. Materials and Methods

2.1 Materials

Granular activated carbon and Phenol where purchased from SICAV (Chieti, Italy) and Aldrich, respectively; the main characteristics of these materials were reported in a previously published paper (Di Giacomo and Del Re, 2001). Deionised water is obtained using a reverse osmosis laboratory device (ROS-50T) and then deoxygenated using an ultrasonic bath (Branson-5200).

2.2 Apparatus and operating procedure

The experimental Solid-Fluid equilibrium under supercritical water conditions was measured at temperatures from 673 to 803 K and at pressures from about 28 to 34 MPa, using a 0.225 L AISI 329 stainless steel autoclave (NOVA SWISS, T_{max} = 773 K at P_{max} = 70 MPa) having three openings on the top and equipped with a variable speed magnetic stirring system. A constant operating temperature is obtained by inserting the autoclave into an electrical oven equipped with two heating resistances (Watlow, MT03L3AP-3000, 200 V, 1000 W) and with an automatic temperature control (CAL Controls, 3300); the oven is open on the top. A type J thermocouple connected to one of the three openings available on the top with an high pressure pipe having an inside diameter of 0.001 m, is inserted into the autoclave in order to continuously detect the temperature inside the cell with an accuracy of ±0.2 K while the pressure inside the cell is measured by a pressure transducer (Haenni EDR430) with an accuracy of 0.15 % and it is continuously displayed by a digital indicator. Two high pressure micro-metering valves are used for pressurizing and depressurizing the cell. Figure 1 shows schematically this apparatus. The quasi static technique used for the first time for measuring the solubility of metallorganic compounds in supercritical carbon dioxide described in a previous paper (Di Giacomo et al., 1991) has been used for this research with minor modifications. Shortly, a weighted amount, about 1 g, of exhausted activated carbon having a known composition of Phenol, is loaded inside three cylinders of 0.001 L made of stainless steel; the cylinders are placed on a supporting plate suspended from the lid of the autoclave. Then the cell is hermetically closed and evacuated using a vacuum pump (Barnant & Co., 400-1902) up to about 10 kPa to eliminate most of the oxygen before starting with an experiment. To start, a small amount of deionized and deoxygenated water is loaded inside the cell by connecting one of the opening on the top with an water container and opening the micro-metering valve. When the cell is ready, the temperature is raised to a stable desired values, the pressure is also monitored, and the stirring is started. The time required to reach stable values of P and T is about 1.5 to 2 h, while a further 3 h are required to obtain the equilibrium conditions. To measure the equilibrium concentrations, the autoclave is removed from the oven and placed to cool in air until reaching the desired temperature inside the cell; then is opened in order to recover and to measure the concentration of Phenol in the liquid and in the solid phase.
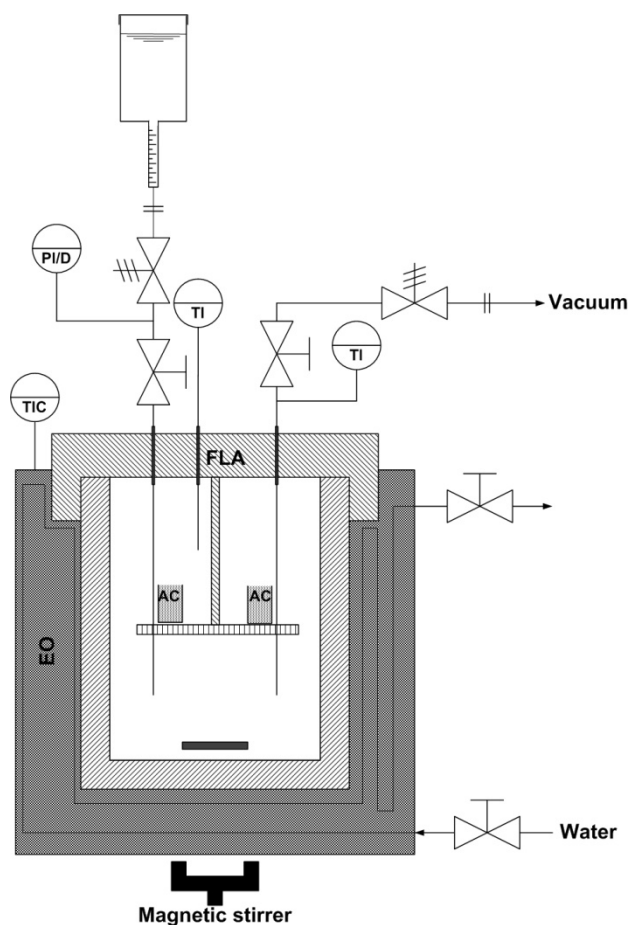
Figure 1: Schematic representation of the experimental apparatus used for measuring Solid-Fluid equilibrium data under SCW conditions (EO: Electric Oven; FLA: Flanged Lid of Autoclave; AC: Activated Carbon)

2.3 Analytical methods

The value of the equilibrium concentration of Phenol in the liquid phase is obtained by measuring the COD of the aqueous solution, previously filtered to eliminate some small amount of solid phase eventually dropped from the solid phase containers. To this purpose, sticks LCK 614 in the range 50-300 mg/L of O_2 and sticks LCK 314 in the range 15-150 mg/L of O_2 along with a digester (Thermostat LT 1W, LTG037) and a spectrophotometer (Cadas 50, LPG 221) are used. The value of the equilibrium concentration of Phenol in the solid phase is obtained by the material balance. Since Phenol can pyrolyze at the operating temperature values, an UV-VIS spectrophotometric double ray (Perkin Elmer, Lambda 2S) was used in five experiments to verify that the pyrolytic degradation of phenol is practically negligible. This result was further verified in one case by using the GC-MS analytical method (GC Varian 3400 and detector Varian Saturn 2000).

2.4 Theoretical model

The Freundlich equation ($q_e = K_F C_e^n$) was used to fit the Solid-Fluid equilibrium data measured under adsorption and regeneration conditions. In particular, under adsorption conditions K_F has been expressed as linear function of temperature in the range between 298.15 K and 308.15 K, while under regeneration conditions K_F has been expressed with the following equation:

$$K_F = K_C \cdot exp\left[K_T(T - T_C) + K_P(P - P_C) + K_\rho(\rho - \rho_C)\right] \tag{1}$$

Where:
K_C represents the value of K_F at the critical point of the water;
T_C is the critical temperature of the water;
P_C is the critical pressure of the water;

ρ_C is the density of the water at its critical point.

As can be seen, the Freundlich based equation used under SCW conditions is characterized by five adjustable parameters (K_C, K_T, K_P, K_ρ, and n) and can only be used inside the supercritical region. Therefore, the equilibrium concentrations of Phenol in the solid phase under SCW conditions, q_e (grams of phenol/grams of activated carbon), can be calculated as function of C_e (grams of Phenol/liter of fluid aqueous solution) using the following equation:

$$q_e = K_C \cdot exp\big[K_T(T - T_C) + K_P(P - P_C) + K_\rho(\rho - \rho_C)\big] \cdot C_e^n \qquad (2)$$

to be applied with $T > T_C$ and $P > P_C$.

3. Results and discussion

The adsorption experimental equilibrium data along with the values of the three model parameters were reported and discussed in a previous paper (Di Giacomo et al., 2007). The regeneration experimental equilibrium data obtained under supercritical water conditions are reported in Table 1, along with the numerical values of the operating parameters which characterize each experimental test.

Table 1: Solid-Fluid equilibrium concentrations measured under supercritical water conditions; W and AC are water and activated carbon, respectively

Test N°	W (g)	AC (g)	Phenol (g)	T (K)	P (MPa)	q_e (g/g)	C_e (g/L)
1	51	1	0.118	703.15	31.1	0.0816	0.7060
2	50	1	0.118	703.15	30.8	0.0780	0.7914
3	60	1	0.113	703.15	33.8	0.0710	0.7060
4	30	1	0.118	803.15	31.0	0.0894	0.9400
5	30	1	0.118	803.15	27.9	0.0878	0.9937
6	38	1	0.118	738.15	30.5	0.0828	0.9150
7	42	1	0.113	734.15	32.5	0.0760	0.8990
8	80	1	0.113	673.15	29.0	0.0695	0.5470
9	50	1	0.079	703.15	30.2	0.0433	0.6278
10	51	1	0,079	703.15	28.6	0.0477	0.5220
11	50	1	0.069	703.15	32.0	0.0400	0.5770

Comparing these data with the corresponding Solid-Liquid equilibrium data (Di Giacomo et al., 2007) one can observe that, for a given values of q_e, the concentration of phenol in supercritical water is one order of magnitude higher than in the liquid water. This result is very interesting since it means that the amount of contaminated SCW to be treated in the SCWO section, for the final destruction of the toxic compounds, is ten time lower than the amount of polluted water purified in the adsorption section. The data reported in Table 1 were used to obtain the numerical values of the adjustable parameters of the model described above; to this purpose, the following least squares function (SR) was minimized:

$$SR(K_C, K_T, K_P, K_\rho, n) = \sum_i \big(q_e^{exp} - q_e^{cal}\big)_i^2 \qquad i = 1, 2, \dots, N \qquad (3)$$

The results of the model parameterization are reported in Table 2 while, the performance of the theoretical model in simulating the Solid-Fluid equilibrium under consideration in the whole range including both adsorption and regeneration operating conditions, is shown in Figure 2. Furthermore, Figure 3 shows the behavior of the absolute difference between calculated and experimental q_e values as function of C_e under SCW and equilibrium conditions. As can be seen, although similar experimental data are unavailable in the literature, Figure 2 and Figure 3 show that the model can be confidently used for predicting the distribution of phenol between the solid and the fluid phase, from ambient to SCW conditions.

Table 2: Numerical values of all the adjustable model parameters

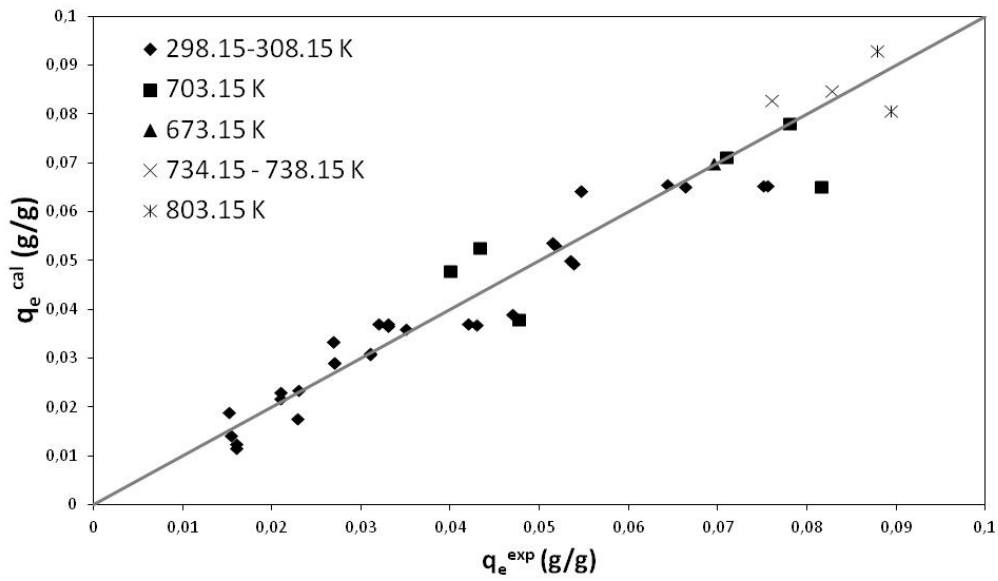| K_C	K_T	K_P	K_ρ	n
0.24705	0.000579	-0.003359	0.003791	1.65

Figure 2: Graphical representation of the performance of the model in simulating the Solid-Fluid equilibrium in the whole range of operating conditions including both adsorption and regeneration
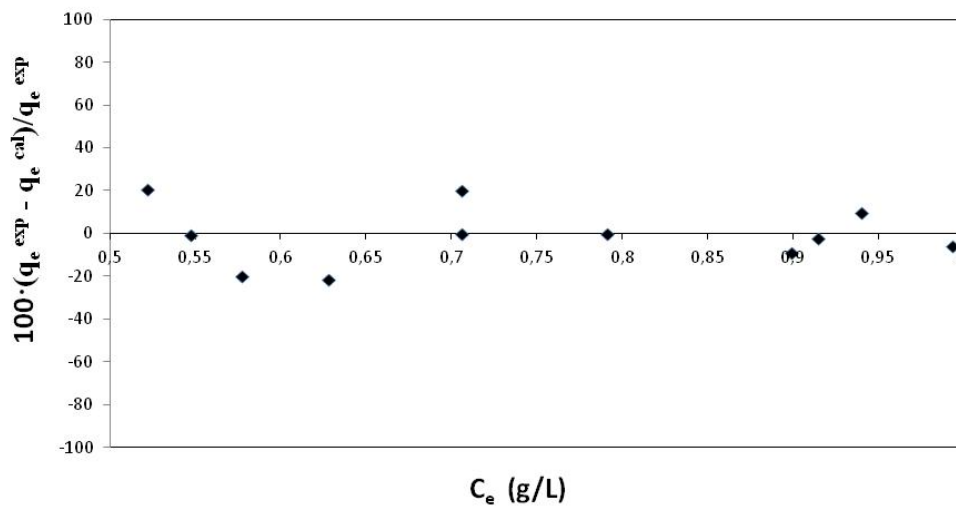

Figure 3: Percent relative deviation between experimental and calculated values of q_e under SCW and equilibrium conditions

In particular, the values of the Percent Average Absolute Error (PAAE) defined by:

$$PAAE = 100/N \sum_i \left(\left| q_e^{exp} - q_e^{cal} \right| / q_e^{exp} \right)_i \qquad i = 1, 2, \dots, N \tag{4}$$

is equal to 10.0, with a maximum percent error (EPMX) = 21.6
These values are quite similar to the corresponding values obtained in previous papers (Brandani et al., 2006) for PAAE and EPMX.

4. Conclusions

New experimental reliable data unavailable in the literature and concerning the distribution of phenol between activated carbon and supercritical water under equilibrium condition were obtained using an already tested experimental laboratory apparatus and related operating method. In addition, a model based on the Freundlich equation was developed to predict the distribution of phenol between activated carbon and supercritical water. This model was parameterized with the above mentioned experimental data and can be satisfactorily used to this purpose, under equilibrium conditions. Finally, it was found that the concentration of phenol in supercritical water is of one order of magnitude higher than in the liquid water. This means that the amount of SCW to be treated in the SCWO section for the final destruction of the toxic compounds, is ten time lower than the amount of polluted water purified in the adsorption section.

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