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Supercritical Water Technology Applied to the Purification of Waters Contaminated by Toxic Micro-Polluting Organic Compounds

Gabriele Di Giacomo, Luca Taglieri
Department of Chemistry, Chemical Engineering and Materials, University of L'Aquila, L'Aquila, Italy
Email: gabriele.digiacomo@univaq.it

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ABSTRACT

Purification of water contaminated by toxic organic compounds at low and very low concentration is a quite interesting challenge from both the technical and the economical point of view. In fact, the direct destruction of organic compounds dissolved in very diluted aqueous solution is very costly and hardly achievable. To overcome this problems it was studied and developed a new water purification process which is made of three steps: 1) removal of the diluted and toxic polluting compounds by adsorption on activated carbon beds operating at ambient P ant T; 2) regeneration of the exhausted carbon bed with supercritical water in order to obtain a mixture of water and polluting compounds significantly more concentrated than the contaminated liquid water; 3) destruction of the toxic compounds in a continuous Supercritical Water Oxidation Reactor. Step 1) was studied at laboratory scale in order to obtain all the required information for modeling the adsorption operation; step 2) was modeled by using literature experimental data and, step 3) was validated at pilot plant scale. In all the above mentioned steps, phenol was used as representative of polluting compounds.

Keywords: Supercritical Water Oxidation; Water Purification Process; Solid-Liquid Adsorption; Gas-Solid Regeneration

1. Introduction

Millions of tons of organic compounds are manufactured each year. Most of these compounds are toxic, poorly biodegradable, and persistent, sometimes give biological magnification. An important class among these chemicals is aromatic chlorinated hydrocarbons such as chlorobenzene, chloronitrobenzene, poly-chlorinated biphenyls (PCB), polycyclic aromatic hydrocarbons (PAH) and dioxins. These chemicals contaminate very large amount of wastewater (often originated from chemical process industry both using and producing organic compounds) and drinking water (when spills or soil pollutants reach the groundwater level). A process commonly used for the purification of waste waters contaminated by low concentrations of organic compounds is the adsorption on activated carbon beds [1,2]. Two main problems arise from this process: the regeneration of activated carbon and the ultimate disposal of polluting organic compounds. It has been demonstrated [3,4] that the Supercritical Water (SCW) can be efficiently used for regenerating the spent activated carbon bed; coherently with the fact that SCW behaves as an organic liquid solvent. In addition, many researchers have shown the effectiveness and the wide range of applicability of Supercritical Water Oxidation (SCWO) in destroying toxic organic compounds [5-9]. The purpose of this paper is to develop and to describe a new process (obtained by properly combining an adsorption section with a SCWO section) characterized by high efficiency in both water purification and destruction of polluting materials without producing any hazardous by-product.

2. Materials and Methods

Activated carbon and phenol, as representative polluting compound, were purchased from SICAV (Chieti, Italy) and Aldrich, respectively. All the thermodynamic and kinetic details related to the adsorption section were studied at laboratory scale and reported in previous papers [1,2], while all the details related to the regeneration of the spent activated carbon bed with SCW were reported by [3] and [4].

The SCWO of the gaseous stream containing the pollutants removed from the activated carbon bed was validated by using a pilot plant which can operate at pressure up to 80 MPa and at temperature up to 1000 K. The continuous SCWO plant was made by a 0.9 m, 9/16" OD,

3/16” ID AISI 316 tube. Pre-heaters and SCWO reactor are equipped with 3 PID controllers in order to maintain the reaction temperature at a fixed value. The gaseous stream obtained by cooling to room temperature the supercritical solution coming out from the SCWO reactor is measured with an accuracy of ±0.1% by a mass flow meter which also acts as totalizer (MICRO MOTION D6).

3. Results and Discussion

By using the results on both equilibrium and kinetics adsorption of compounds polluting liquid aqueous solutions [1,2], along with the results of [3] and [4], on the regeneration of activated carbon with SCW, it was developed a new process which enables one to remove almost completely the polluting compounds from the liquid water which, in turn, are completely destroyed in the SCWO section of the process shown in **Figure 1**.

For this process, the material balance along with the values of P and T of each stream are reported in **Table 1**.

As can be seen the SCW required to regenerate the spent activated carbon bed is about 20% of the treated contaminated water. As a consequence the quantity of the water processed in the SCWO section is 5 times lower, while the concentration of the polluting compound is 5 times higher. Since the SCWO section is characterized

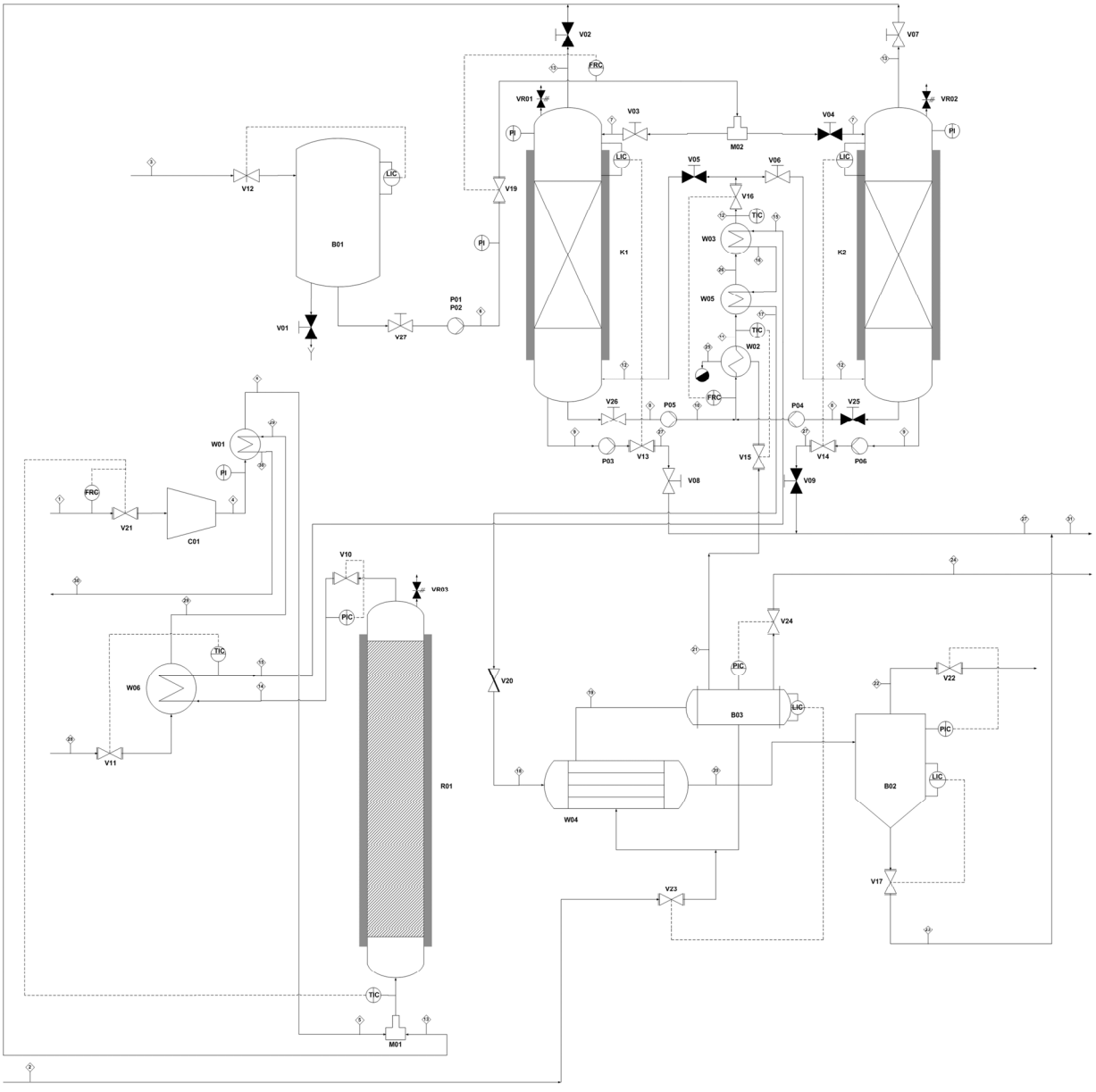

Figure 1. Flow sheet of the proposed process.

Table 1. Material balance of the process shown on Figure 1, based on 100 m^3/h of micro-polluted water.

Stream n.	Description	Temperature (˚C)	Pressure (bar)	Mass flow rate (kg/h)
1	Air	25	1	522
2	Demineralized water	25	1	171,422
3	Contaminated water	25	1	100,000
4	Air	-	350	522
5	Air	440	350	522
6	Contaminated water	25	1.75	100,000
7	Contaminated water	25	1.75	100,000
8	SCW	25	1	19,828
9	Purified water	25	1	80,070
10	SCW	25	350	19,828
11	SCW	78	350	19,828
12	SCW	450	350	19,828
13	SCW and desorbed contaminants	450	350	19,854
14	Gaseous mixtures from SCWO reactor	450	350	20,374
15	Gaseous mixtures from SCWO reactor	470	350	20,374
16	Gaseous mixtures from SCWO reactor	374	350	20,374
17	Water and gas	300	350	20,374
18	Water and gas	300	1.2	20,374
19	Steam	120	1.2	171,422
20	Water and gas	40	1.2	20,374
21	Recovered steam	120	1.2	1807
22	Gas	40	1.2	532
23	Purified water	40	1.2	19,843
24	Steam	120	1.2	169,615
25	Condensed water	99	1.2	1807
26	SCW	179	350	19,828
27	Purified water	25	1	80,070
28	Flue gas	800	2	7118
29	Flue gas	460	2	7118
30	Flue gas	426	2	7118
31	Purified water	40	1.2	99,913

by high investment and operating costs in comparison with the adsorption section, the proposed process allows one to purify the water and to destroy the toxic computing compounds in an optimal way from both the technical and economical point of view.

In **Table 2** are reported the list of symbols used in the process flow sheet along with the corresponding significance.

4. Conclusion

It has been found that by properly combining an adsorption section with SCWO section it is possible to efficiently purify polluted and micro-polluted water and to

Table 2. Description of the symbols used in Figure 1.

Symbol	Description
W01	Overheater
W02	Preheater
W03	Overheater
W04	Condenser
W05	Vaporizer
W06	Overheater
C01	Compressor
B01	Feed tank
B02	Gas-liquid separetor
B03	Tank
P01/06	Pumps
R01	SCWO reactor
K1	Fixed bed adsorber
K2	Fixed bed adsorber
V01/27	Valves
VR01/03	Ropture disk
M01/02	Mixer

efficiently destroy the toxic polluting organic compounds in an optimal way. In fact, the process developed in this study allows one to take advantage of the best characteristics of the combined technologies. In addition, since the regeneration of the spent activated carbon bed in done by using SCW, it is possible to avoid the production of any kind of polluting stream and the consumption of any kind of chemicals.

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