
eba 10 2014
X Encontro Brasileiro sobre Adsorção
27 a 30 de Abril de 2014
Guarujá - SP

PROCESS WATER STERILIZATION AT VOLATILE SOLVENTS RECOVERY USING ACTIVATED CARBON ADSORPTION

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ABSTRACT: The aim of this work is to study the liquid adsorption process, using activated carbon, with and without colloidal silver for decreasing the microbiological activity at the process water circuit of the volatile organic compounds recovery system, normally used in polymer processing for different purposes. The best results were achieved with the samples of colloidal silver activated carbon and smaller granulometry.

KEYWORDS: adsorption process; activated carbon; granulometry; colloidal silver.

1. INTRODUCTION

Processing of different polymers to get several products requires its dissolution in volatile solvents, demanding, after obtaining the product, the solvent recovery for economical and environmental reasons, using conventional separation unit operations. It is what happens at the converters, printing of flexible packages, for different purposes, using ethyl acetate as solvent, as well as, for the production of gaskets, where toluol is the use of semi permeable films of cellulose acetate, using acetone as solvent, also applicable to the production of membranes, pointing-out that the process of dialysis, where this polymers is the best, mainly for medical use of hemodialysis. There are also the textile use of the cellulose acetate for producing different filaments, fibers and yarns, which are processes requiring huge installations for the solvent recovery; the extreme solubility of the cellulose acetate characterizes very well the process steps for handling the polymer, common to any of quoted uses, where the main issue is the obtaining of high viscosity collodium, resulting from homogeneous solution with high cellulose acetate content in acetone, which is recovered very efficiently in the industrial unities (ULLMANN'S, 1994; KIRK-OTHMER, 1984). Due to the industrial, economical and technological importance of the cellulose acetate processing, it will be used as the basis for developing this work, mainly in reference to the experience with the recovery of acetone, the solvent universally used for this compound.

Traditionally, acetone is absorbed in cold water using columns provided with sieve trays (HENLEY & SEADER, 1981). The air stream coming from the several polymer processing steps is cooled and fed to the bottom of column, below the trays; cold water is fed at the top of the column, above the trays. The acetone absorption occurs by the contact of the gas stream, containing acetone, going up, with the descending cold water, guaranteed by the adequate tray geometry, which for this service is generally a sieve tray, requiring less liquid height above the tray, resulting in a smaller pressure drop and consequently less energy consumption, issue very important considering the nature of the process, as, for safety requirements, deals with low acetone content at the gaseous stream seeking work below the lower explosion limit, avoiding explosion risks. Also for environmental and economical reasons, the unit recycles the sump water, cooled at the distillation heat exchangers and a chiller up to 7°C, being fed again to the absorption columns. To avoid any type of interaction with the cellulose acetate, as well as with the equipments, no addition of chemical is allowed at the process water circuit, resulting in microbiological activity all over it, what in the columns can be observed by a biofilm build-up at the trays, increasing the pressure drop in 15%, what is not significant, when considered that the usual pressure drop is 13,5 kPa, that is to say, normally high. When the maximum pressure drop is achieved, a shutdown of the column is required for cleaning, performed by filling the column with water and stream bubbling.

The transposition of the sieve trays to structured packing initiated by establishing the local conditions (BIRD et al, 2002) of the original situation, setting a coherent simulation with data taken from the normal operation of an absorption column provided with trays. The local conditions can also be designated by Photography of the original situation, meaning the modeling by any means of scientific calculation that reliably reproduces the studied operating situation. The described basic set has been established by using the vapor liquid equilibrium model NRTL-HOC, working process simulator Aspen Plus (NASSER & TAQUEDA, 2008).

Taking the hydraulic data from this basic simulation set the hydrodynamic rating has been performed, using the empirical formulary and methodology practiced by the structured packing supplier, obtaining the equilibrium stage height, HTO_G, height theoretical overall gas, as this process is paced by the gaseous stream (RIEMER, 2007).

The industrial implementation of the transposition was extremely successful, validating the used method. For the same column dimensions, 2077-mm diameter and 7785-mm height, the number of equilibrium stages increased from 7 to 15, increasing the acetone recovery, decreasing drastically its emission to the environment at the top, as well as a remarkable acetone concentration increase could be reported at the bottom, decreasing the steam consumption at the distillation, what means an economical issue, but also very significant for the environment. The most important aspect of this quoted work is related to the capacity and pressure drop; the processing flow rate increased in 300%; for this achieved flow rate the pressure drop decreased 90% if compared to that observed at the original configuration (NASSER & TAQUEDA, 2008).

2. JUSTIFICATION

Structured packing consists of thin metallic corrugated strips placed vertically in the upward flux of the gas stream. The strips are continuously grooved and discontinuously perforated, being welded at the edges, resulting in a reasonably rigid spatial structure of a beehive. They are supplied in layers of about 190-mm height, split in circular elements to allow assembly at the column. Each layer is assembled with a gap of 45° in relation to the previous layer in order to increase turbulence improving mass and heat exchange (RIEMER, 2007).

Due to the above described characteristics of the structured packing, the biofilm build-up, as also observed for the original configuration, showed to be more critical, as the new configuration is more sensible to any pressure drop increase, affecting significantly the column performance, and increasing the frequency of shut down for maintenance. A new cleaning method for structured packing column has been developed, requiring the use of biodegradable detergents, a final step with hydrogen peroxide, as well as its continuous dosing during operation, for its bactericide nature. However, the operating discontinuity of the new configuration of the absorption column due the biofilm build-up shows that it is not enough to sterilize the water process.

The conventional technique used in water disinfection is chlorination. Besides chlorine is efficient against pathogenic microorganisms, its use promotes the formation of disinfection by-products as triahalomethanes and haloacetic acids (Lalley et al., 2014). For this reason, the study of process water sterilization by using alternative methodologies to replace the conventional chlorination process is highly desirable and of great importance to minimize operating costs as well as for environmental health.

It is therefore justifiable to study the development of an effective process using adsorption with activated carbon with and without silver impregnation to decrease the microbiologic activity at the process water circuit during column operation.

3. FUNDAMENTALS

Adsorption is a time-related phenomenon that is diffusion controlled. The adsorption process can be described in three steps: Initially, as a liquid or gas contacts activated carbon particles, the impurities in the bulk liquid come into contact with the external surface of the carbon particles. Next, the adsorbates diffuse into the internal pore structure. The final step is relatively fast and involves the attraction of the adsorbates to the surface of the pore walls, where they are held by chemical or electrostatic forces.

Adsorption can be classified in two types: physical and chemisorption.

In physical adsorption, the adsorbates are held on the surface of the pore walls by weak electrostatic forces of attraction (van der Waals).

Chemisorption involves relatively strong forces of attraction, or in some cases actual chemical bonds between the adsorbates and oxygen complexes on the pore wall surface. Therefore, the efficiency of an activated carbon for removing impurities will be influenced by diffusion effects, pore size characteristics surface complexes and accessible surface area.

For liquid-phase applications, the first two steps of the adsorption process are relatively slow, and involve diffusion of impurities into the internal porosity of carbon particles. As a result, adsorption rate is to some degree diffusion controlled. In any application of activated carbon, whether powdered, granular or extruded, there is some minimum time required for adsorption to occur.

Adsorption in liquid phase is also affected by many chemical and physical parameters, such as the species being adsorbed, its concentration, temperature and pH. Generally, non-polar organic species are readily adsorbed by activated carbon.

Adsorption trends often follow the relative solubility of substances – the more soluble a substance, the less likely it is to be adsorbed. Therefore, variables such temperature, concentration and pH affect both solubility and adsorptive capacity.

Activated carbon has been recognized as one of the oldest and widely used adsorbent for the water and wastewater treatment for removing organic and inorganic pollutants. The high surface area, large porosity, well developed internal pore structure consisting of micro-, meso- and macropores as well as a wide spectrum of functional groups present on the surface of activated carbon make it a versatile material which has numerous applications in many areas (BHATNAGAR et al., 2013)

Different carbons can also impact the relative adsorptive capacity or adsorption rate. If a solution contains many large molecules, such as color bodies or polymer species, a carbon with a high macro and mesoporosity will perform better. With small molecules, the converse may not always be true because other factor besides microporosity, such as the surface chemistry or pore wall, may have an overriding effect. Laboratory or plant trials are the only true test of a carbon's performance (BOPPART et al, 1996).

The original treatment for obtaining drinking water used sand-anthracite filter, which was replaced by granular activated carbon, preceded by ozonation to minimize taste and odors, improve disinfection, reduce the formation of trihalomethane and haloacetics, as well as oxidize many trace organic contaminants and increase the organic carbon biodegradability. The biological granular activated carbon filters can effectively remove some algae toxins, ammonia, biodegradable organic carbon and many trace organic contaminants including taste and odor compounds. However, the ability of such systems to effectively remove pathogens is limited. The effective removal of these pathogens could be achieved by adding UV disinfection following ozonation and biological granular activated carbon filtration. However, this would significantly increase the capital and operating costs of the system. Low pressure membrane processes of microfiltration and ultrafiltration, using porous membranes of different configurations can effectively remove particulate contaminants, including protozoan parasites. But, membranes cannot remove dissolved natural organic matters, synthetic organic compounds and those responsible for taste, odor and color. To improve treatment performance, the low pressure membranes processes have been coupled with other processes, mainly coagulation, ozonation and adsorption, being the last, the one which has received increasing consideration over the last two decades. The scientific literature mostly focuses on the hybrid membrane process, which combines activated carbon and low pressure membranes under a variety of configurations: i. activated carbon prior to the low pressure membrane; ii. both processes integrated in the same vessel, where the hollow fiber membranes are submerged and the activated carbon is suspended, keeping the content under turbulence by strong aeration at the bottom; iii. the activated carbon treatment is done after the low pressure membrane at the permeate stream. Although any of the described configurations is completely developed, they are cheaper than UV application followed by ozonation and very effective (STOQUART et al, 2012).

Silver has been used as a water disinfectant for many years, although this disinfection mechanism is not known for sure. It is believed that the Ag atoms bind to thiol groups (–SH) in enzymes and subsequently causing the enzyme deactivation. Other theories postulate that Ag^+ ions enter the cell intercalate between purine and pyramidine base pairs, denaturing the DNA molecule. Though other metals are effective at bacterial inactivation, silver has proven to be the most efficient, and for this reason the most investigated. There are numerous surfaces which can serve as support for silver decontaminating particles, being granular activated carbon a very effective material as it adequately removes pathogenic microorganisms (LALLEY et al, 2014).

Activated carbon is more efficient for removing organic compounds than metals and other inorganic pollutants. The treatment of the surface chemistry of activated carbons is a way to provide new application to activated carbon in different fields. This modification of activated carbon involves oxidation, surface grafting by chemical, electrochemical, plasma and microwave methods to introduce functional groups, impregnation and so on, being this last mentioned treatment of major interest is this study. The impregnation of activated carbons with metals such as silver, copper, aluminum and iron is gaining interest because the enhanced adsorption capacity, bactericide action, but mainly due the adsorption potential towards fluoride, cyanide and heavy metals like arsenic in water. Arsenic removal can be achieved by iron modification of the activated carbon. At a different pH the same iron modification proves to be efficient for copper removal. Aluminum impregnated activated carbon is efficient for removing fluoride from aqueous solution. The efficiency of silver and nickel for removing cyanide from aqueous solution was also evaluated (BHATNAGAR et al, 2013).

The biological impregnation of activated carbon is also effective for improving drinking water quality, removing organic matter and ammonium, requiring, however, a long time (30-60 days) to achieve sufficient amount of biomass to recover all the activated carbon surface, as well as an ultraviolet disinfection to prevent the invasion of indigenous bacteria, guaranteeing the stability of the process (ZHANG et al., 2013).

When activated carbon with no impregnation is used to purify drinking water, bacteria preferably adhere to it because of its good biocompatibility, breeding on it during the purification process so that the activated carbon itself becomes a pollutant. Then, to achieve the drinking water quality required by the World Health Organization, antibacterial activated carbons are required. Silver ions possess significant antiseptic and bacteriostatic properties, very effective with the most kinds of bacterias, which is achieved by the release of the silver ions from the silver-based antibacterial composites. To guarantee the effectiveness three factors need to be optimized: surface area, antibacterial activity and amount of silver lost. The impregnation usually occurs with Ag NO_3, soaking the activated carbon in a solution of $AgNO_3$ followed by reduction with agents such hydrazine or simply by heating (thermal decomposition of $AgNO_3$ to Ag^o). For this composite prepared in this way, large silver particles are usually distributed randomly on the surface of the activated carbon, resulting in leaching of silver during the water purification, due the trivial solubility of elemental Ag^o, slowly decreasing the effectiveness of the system with time. An alternative method is the vacuum impregnation, which consists of exchanging the internal gas occluded in open pores for an external liquid phase, resulting in a uniform deposition of silver (ZHAO et al., 2013).

4. METHODOLOGY

The activated carbon samples were supplied by the company PICA and their main characteristics are briefly specified at Table 1.

Table 1 – Specification of activated carbon commercial samples

Sample	**Sample Code (X)**	**SW (g/cm^3)**	**SA (m^2/g)**
PicahydroS21	A	0.460	956.8
PicahydroS05*	B	0.495	939.3
PicahydroS23	C	0.420	1011.5
PicahydroS23S5*	D	0.452	931.9

* Samples impregnated with silver, SW - Specific Weight, and SA - Superficial Area

Table 2 indicates the sample mass of activated carbon used in each trial and their concentration in the treated water.

Table 2 – Description of the trials

Concentration Code **#**	**Weight of Activated Carbon** **(g)**	**Concentration of Activated Carbon** **(kg/m^3 of water)**
1	0.2	1.0
2	2.0	10.0
3	0.006	0.03
4	4.0	20.0

From Tables 1 and 2 the testing was organized and identified by a letter followed by a number (X#) as follows:

- X is the sample code of the activated carbons , indicated at Table 1;
- # is concentration code of activated carbon, as indicated at Table 2.

For instance, in trial A1, the used sample was the Picahydro S21 (Table 1), with the concentration of 1 kg of activated carbon per cubic meter (Table 2).

The testing was initially developed at the batch mode and then in continuous using industrial process water. In batch the testing used glass flasks, magnetic stirrers, analytical balance. In continuous the activated carbon bed was constructed with a glass column and the continuous feed was provided by using a peristaltic pump. The installation for the continuous testing provides 2 hours of residence time of the water in the circuit, identical to the observed for the process water at the industrial installation.

In both cases the results of process water sterilization using activated carbon were achieved by using the Nutrilab F kit, where treated water samples are applied and kept at 35°C during 5 days. The obtained results were compared with the Template (Figure 1) to make the counting of the Colonies Formed Units – CFU, per ml of treated process water.

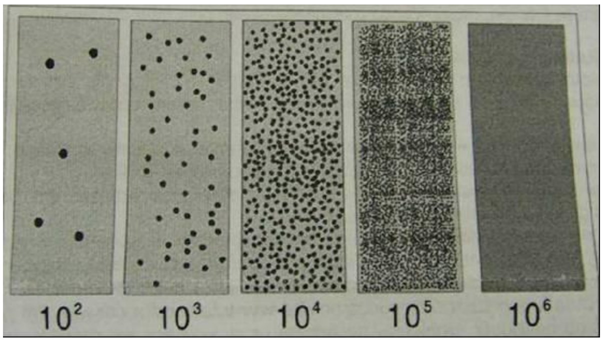

Figure 1 – Template to evaluate the results.

5. RESULTS

As the residence time in the industrial unit is 2 hours, the initial testing at the batch mode was performed with this time. However,, the complete elimination of biological activity was not achieved. As both A1 and C1 showed no reduction of the microbiological activity at all they were disregarded in the following trials. The next step of the testing was also at the batch mode, but during 24 hours, with all the combination of samples, with the exception of A1and C1. In this case, although the complete elimination of the microbiological activity was not achieved, it was possible to perform a screening of the combinations, suggesting that the combinations A4, B4 and C4 are effective, all of them reducing in 100 time the counting of colonies forming unities. It is also important to observe that A4 and B4 have higher granulometry and C4 smaller than, as well as B4 is impregnated with colloidal silver. These results can be observed at Table 3.

Based on these results with the references A4, B4 and C4, the testing in continuous was organized in order to increase the contact of the process water and the activated carbon, at the beginning in order to compare the impact of the granulometry, that is to say, excluding B4, which is colloidal silver impregnated.

Table 3 – Results of the 24-hour batch mode trials.

Trial	Time (h)	
	0	24
A2	10,000	1,000
A3	10,000	10,000
A4	10,000	100
B2	10,000	10,000
B3	10,000	10,000
B4	10,000	100
C2	100	100
C3	100	100
C4	100	0
D2	100	100
D3	100	100
D4	100	100

The first continuous testing took place for 24 hours as illustrated by Table 4.

Table 4 – 24-hour continuous mode testing with samples of activated carbon without silver

Time (h)	CFU	
	A4	C4
0	10,000	10,000
12	100	0
15	100	0
18	100	0
21	100	07
24	100	0

The higher efficiency of low granulometry (smaller mean particle size) activated carbon is clearly stated as after 12 hours the counting nil has been achieved. It is important to point-out that the same mass of activated carbon was uses for both samples.

From this testing a new trial was planned in order to check whether the colloidal silver is effective, keeping the smaller granulometry. The final continuous testing took place for 12 hours as summarized by Table 5.

Table 5 – 12-hour continuous testing with activated carbon with and without silver

Time (h)	CFU	
	A4	C4
0	57,000	57,000
1	3,400	500
2	1,200	500
3	900	250
4	900	150
5	900	100
6	700	100
7	600	0
8	600	0
9	400	0
10	400	0
11	350	0
12	250	0

In this comparison of samples without (C4) and with silver (D4), both of them with smaller granulometry (smaller mean particle size), the results clearly stated that the action of the colloidal silver is positive as it presented a reduction greater than 300 times after 4 hours and after 7 hours the bacterias were completely eliminated. Although the other sample also presented a good performance, also remarkably reducing the number of colonies forming units, it could not eliminate completely the bacterias.

This can be observed by the picture of the Nutrilab kit, where the bacterial presence can be clearly observed.

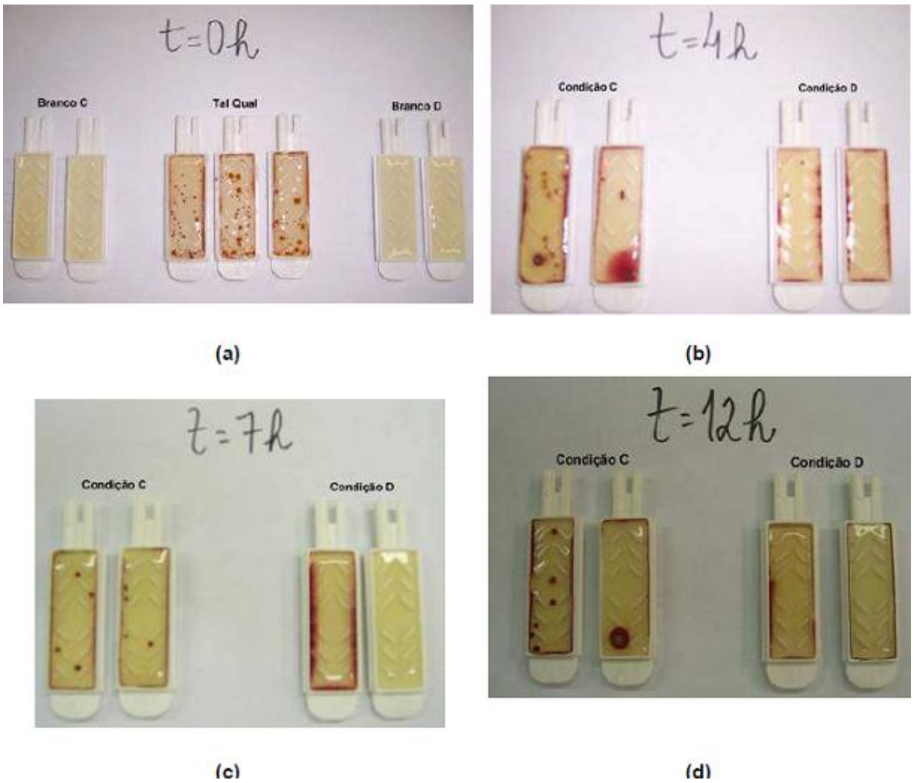

Figure 2 – View of the evolution of the results with Nutrilab kits for the continuous testing comparing effectiveness of activated carbon with (Sample D) and without silver (Sample C): (a) 0 h, (b) 4 h, (c) 7 h and (d) 12 h

6. CONCLUSIONS

The continuous testing showed that the adsorption process with low granulometry (smaller mean particle size) activated carbon without colloidal silver impregnation Picahydro S23, referred in this study as C4, is effective after 12 hours of recirculation, eliminating the presence bacterias' colonies.

In the same way, the continuous testing comparing the previously mentioned low granulometry activated carbon with the also low granulometry (smaller mean particle size) activated carbon Picahydro S23 S5 with colloidal silver impregnation, in this study referred as D4, showed that this one is more effective as the bacterias were eliminated after 7 hours of recirculation.

Those results proved the effectiveness of the proposed adsorption process with activated carbons for the process water sterilization. Its implementation will avoid biofilm formation inside the packed column, increasing the operating time before maintenance stops, as well as the packing efficiency.

ACKNOWLEDGEMENT

Jacobi Carbons and Quebecor are acknowledged for supporting the development of this work providing the studied samples and technical information.

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