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Influence of ultrasound on phenol removal by adsorption on granular activated carbon

Milena Landi*, Vincenzo Naddeo, Vincenzo Belgiorno

Department of Civil Engineering, University of Salerno, 84084 Fisciano (SA), Italy
Tel. +39089969337; email: mlandi@unisa.it

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ABSTRACT

One of the most popular means for removal of natural organic matter found in small concentration is by adsorption. Recent studies have found that ultrasound enhances adsorption properties of different adsorbents for many contaminants in aqueous solution. This work describes the results of investigation carried out to examine the adsorption process of phenol, as an organic matter indicator, both from aqueous solution and from domestic wastewater on granular activated carbon (GAC) in absence and presence of ultrasound (US). The influence of ultrasonic power on the oxidation of phenol was also investigated at three different densities (1.06, 1.60 and 3.20 W/ml). The effects were monitored in terms of UV-absorbance at 270 nm, TOC and COD. Reduction of UV-absorbance and TOC have been negligible with US treatment alone and the performances have been better with adsorption into GAC. However, the adsorption rate of phenol in wastewater in presence of ultrasound, for an acoustical power of 1.06 W/ml, was twice higher than that obtained by simple stirring. Indeed, the combined employment of GAC adsorption and US can drastically remove organic substance thanks to a produced synergistic effect. Therefore, the combination of ultrasound and stirring for the adsorption process was shown to be of interest for the treatment of wastewater.

Keywords: Advanced oxidation process (AOPs); Adsorption rate; Cavitation; Sonolisys; Wastewater

1. Introduction

Phenol and its derivates belong to a group of common environmental contaminants [1]. Phenols are widely used for the commercial production of many materials, such as disinfectants, resins and adhesives, herbicides and pesticides, plastic materials and polyamide for various applications, dyes and common drugs (e.g., aspirin). They are considered as priority pollutants since are harmful to organisms at low concentrations and many of them have been classified as hazardous pollutants because of their potential harm to human health [1]. Most of these compounds are recognized as toxic carcinogens [2]. The US-EPA regulations call for lowering phenol content in the wastewater to less than 1 mg/l. Therefore, it is considered necessary to remove the phenol from industrial effluents before discharging into the water stream. Therefore, also low concentrations of it can be an obstacle to a possible reuse of water and wastewater.

There are many methods such oxidation, precipitation, ion exchange, solvent extraction and adsorption for removing phenols from aqueous solutions [3]. Adsorption process has been shown to be highly efficient [4]. Activated carbons are the most widely used adsorbents because they have excellent adsorption capacities for the aforementioned pollutants [5,6]. Furthermore use of cavitation for the degradation of phenol has been widely investigated in the recent past [7,8]. Recent studies have investigated on the effects of ultrasound on adsorption/desorption processes of phenolic compounds [9,10].

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*Corresponding author.

The aim of this study is to give a strongly evaluation of the adsorption of phenol with granular activated carbon (GAC) enhanced by ultrasound (US) processes.

US cavitation and sonochemical reaction contribute to the decomposition of chemical compounds [11–13] as well as the oxidation of natural organic matter (NOM) in water [14] and wastewater [15,16]. The reason why US power can produce chemical effects is through the phenomenon of cavitation. Cavitation is the production of microbubbles in a liquid that are formed when a large negative pressure is applied to it [17]. Compression and rarefaction waves rapidly move through the liquid media. If the waves are sufficiently intense they will break the attractive forces in the existing molecules and create gas bubbles. As additional US energy enters the liquid, the gas bubbles grow until they reach a critical size. Upon reaching a critical size, the gas bubbles either implode or collapse [18,19]. High power ultrasound produces strong cavitation in aqueous solutions causing shock waves and reactive free radicals (e.g., $^{\bullet}OH$, HO_2 and $O^{\bullet}$) through the violent collapse of the cavitation bubbles. These effects should contribute to the physical disruption of microbial structures and inactivation [20,21] as well as the decomposition of toxic chemicals [22].

The performances of ultrasound in phenol degradation depend on the ultrasonic conditions and in particular on the frequency. Many studies were carried out on sonochemical degradation of phenol and chlorophenols [23]. The better conditions to degrade that compounds are at high frequencies [24,25]. The bigger efficiency could depend on the location of the radicals in the solution: in higher frequencies the radicals are distributed in all the volume, whereas at low frequencies they are located intensely around the surface of the transducer [26].

The first study on combined process date back 1998 by Rege and co-workers [9]. They studied the desorption of phenol by ultrasound on activated carbon. The results showed that the desorption rate in presence of ultrasound at 40 kHz was greater than that obtained in the non sonic case. Moreover the ultrasound at 1.44 MHz was still higher because a higher frequency prevents the pulverization of carbon. They also found that the ultrasonic method for desorption were favored by high temperature and by the increase in power intensity.

The combined process (GAC + US) was tested also for the adsorption of phenol. Schuller and Yang [27] found that for the adsorption in a batch adsorber, ultrasound acts like a mixer, improving the mass-transfer coefficient through cavitation and acoustic streaming. The second one appears to be the more important of the two. In the same years, Breitbach and Bathen [28] noted that ultrasound not only promote desorption but also enhances mass transfer of adsorption processes. Hamdaoui and co-workers [29] studied effects of ultrasound (20 kHz) adsorption process of p-chlorophenol (p-CP) on GAC. The kinetic curves showed that the rate of p-CP adsorption was much higher under ultrasound than was obtained by simple stirring. Therefore, this rate of p-CP adsorbed onto GAC decreased with increasing intensity, probably because more cavitation events occurred and more molecules were desorbed [29]. This effect, which is more dominant at the megahertz frequencies, could reduce the adsorption enhancement induced by ultrasound. In a following research [10] they studied the same process but in presence of high frequency ultrasound. The results obtained have the opposite tendency: increasing ultrasonic intensity the amount of p-CP adsorbed increases. This is explainable probably because at lower frequency the adsorption is controlled by different mechanisms. At lower frequencies the growth time of the cavitation bubbles increases, the bubbles size is bigger and the collapses are more violent. Therefore, although the high frequencies enhance the phenol removal in sonication treatments, in adsorption into GAC with US at low frequencies the pulverization of carbon is maximized and increases the specific surface of the GAC [9].

The aim of this study was to investigate the adsorption processes of phenol into GAC in presence and in absence of low frequency of ultrasound. In order to make a practical evaluation of possible performances in a plant scale the process was implemented with domestic wastewater spiked with phenol. A comparison between the adsorption rate of phenol in aqueous solution and in wastewater was also studied and discussed.

2. Materials and methods

2.1. Activated carbon, solutions and ultrasonic reactor

Phenol (CAS N.108-95-2) supplied by Fluka Analytical (Sigma-Aldrich, USA) at 99.5% of purity was used as an adsorbate. Solutions of desired concentration were prepared by dissolving the appropriate amount of phenol in ultra pure water (Millpore MilliQ, USA). The tested phenol concentration has been of 100 mg/l.

Granular activated carbon (GAC) employed as the adsorbent in the present study was supplied by Sigma-Aldrich (USA). The carbon was pretreated by boiling in deionized water for 1 h and washed with deionized water until the washing water UV absorbance was equal to zero. The washed GAC was dried in a oven at 110°C to constant weight and stored in a drier prior to use. The BET (Brunauer-Emmett-Teller) specific surface area (875 m^2/g) was obtained from N_2 adsorption isotherms at 77 K. The GAC has a mean granulometry of 2.5 mm.

The treatments were conducted also on domestic wastewater spiked to 100 mg/l of phenol. The samples were taken in the large biological wastewater treatment plant (WWTP) of Salerno (700,000 eq-hab), in the south of Italy, downstream of secondary sedimentation tank.

Oxidation tests, as adsorption tests, were conducted in an ultrasonic cleaner (Elma® TS 540), working at a frequency of 35 kHz and an electrical nominal power of 160 W.

2.2. Experimental procedures

The sonication tests were carried out using 250 ml flasks (Pirex, USA) where phenol solutions were added into. The densities were modified changing the volume of phenol solutions in the flask. In particular the densities tested were 1.06, 1.60 and 3.20 W/ml.

Batch adsorption experiments were also carried out using 250 ml flasks (Pirex, USA) where 0.15 g of GAC was added into 150 ml of phenol solutions.

In GAC adsorption tests, the samples were shaken using a magnetic stirrer (Heidolph, MR 3001) with a stirring speed of 125 rpm. In the adsorption with GAC and US tests (Fig. 1), instead, effects associated with hydrodynamic phenomenon due to cavitation were used to make a perfect mixing of reactor content [10]. In both cases, the glass reactor was provided of uniform mixing conditions. The temperature was maintained constant and equal to 25°C.

After the treatments and before the measurements, the activated carbon and the treated solution were separated by filtration with Millipore (USA) filter of 0.45 μm. It should be noted that phenol concentration remained unchanged during filtration operation.

The amount of residual concentration of phenol in the solution was measured considering the wavelength of 270 nm using a UV Visible Spectrophotometer (Perkin Elmer, Lambda 12). The calibration curve were prepared by measuring the absorbance of 10 aqueous solutions of phenol with different concentrations ranged from 0.1 to 100 mg/l. After each treatments, the measurement of the absorbance of the sample yielded the actual concentration from the calibration curve. The amount of phenol adsorbed, q_t (mg/g), at time t (h) was calculate as follows (Eq. 1)

$$q_t = \frac{(C_0 - C) \cdot V}{W} \qquad (1)$$

where C_0 (mg/l) and C_t (mg/l) are the phenol concentration at initial time to and at any time t, respectively, V (l) is the volume of the solution and W (g) is the weight of dried carbon used in the mixtures.

Total organic carbon (TOC) was measured with TOC analyzer (Shimadzu TOC-5000A, China). Chemical oxigen demand (COD) was analyzed according to standard methods (procedures #410.4) [30] using a DR/890 colorimeter (Hach Company, USA).

3. Results and discussion

3.1. TOC removal by ultrasound

The performance in degradation of phenol by US in low frequency conditions was not noticeable for all densities tested. The efficiencies in TOC reduction also were very low: around 4% after 2 h of treatment (Fig. 2). Fig. 2 shows also that increasing density the performances did not significantly change.

Choosing the lowest density between those tested also prolonging treatment time the efficiencies in TOC reduction have been no more than 8% after 5 h of treatment and the trend of TOC removal versus time is

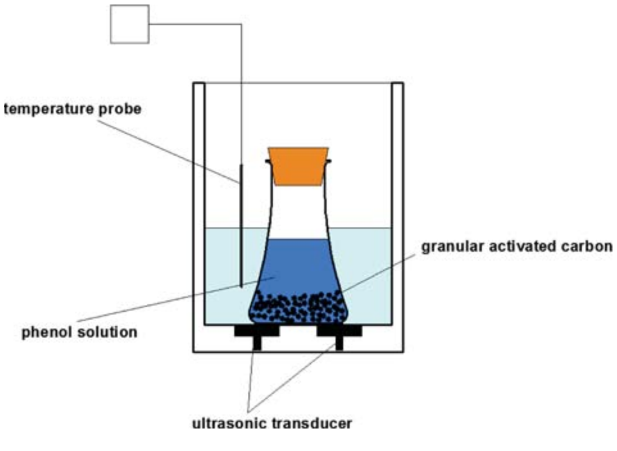

Fig. 1. Schematic equipment for adsorption with GAC and US.

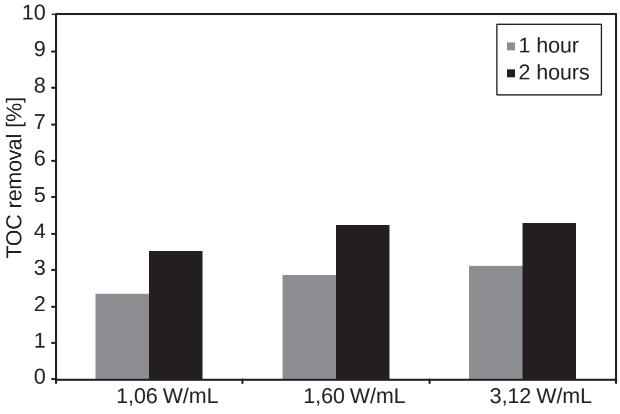

Fig. 2. TOC reduction (%) versus ultrasound density (W/ml) for 1 and 2 h of US treatments of 100 mg/l phenol aqueous solution.

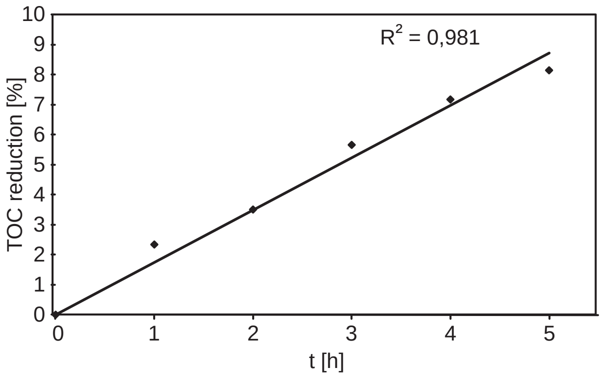

Fig. 3. TOC reduction (%) versus time (h) in US treatments of 100 mg/l phenol aqueous solution with 1.06 W/ml.

characteristic of zero-order kinetics (Fig. 3). The performances have been very similar also varying the US density.

Similar results were obtained by Juang and co-workers [31] for phenol concentrations. They found that phenol concentrations remains nearly unchanged and with GC analyses degradation products were not detected in the solutions. Their tests were conducted with different systems (US bath respect US horn) and the results were the same [31]. The low phenol removal percentages can be explained as both the systems worked at low frequencies. Indeed, the low frequency can entail the delimitation of the degradation at only a small part of the reactor and a non uniform distribution of the degradation percentage inside the reactor. One more reason could be due to a better release of hydroxyl radicals into the bulk solution at higher frequency than at the lower one [24].

3.2. *Influence of US on the GAC adsorption*

Initial concentration of 100 mg/l of phenol was investigated to study the influence that the US has on the adsorption into GAC. Fig. 4 shows the data obtained for the reduction of phenol concentration by adsorption into GAC both in aqueous solution and in wastewater with (GAC+US) and without the simultaneous irradiation of US. The adsorption rate in aqueous solution increases with treatment time and is higher, at the same treatment time, with GAC+US processes. The adsorption rate into GAC after 5 h of treatment changes no more. Indeed 5 h is the equilibrium time. Instead in the GAC + US process the equilibrium time is achieved in only 4 h. This is a validation that the US irradiation enhances the GAC adsorption, not only because reduces the equilibrium time but, especially, increases the removal performances.

The process is less efficient in terms of phenol removed in wastewater than in aqueous solution. Therefore the equilibrium point in wastewater is reached in lower time both with and without US. It can be due at the presence of natural organic matter in the wastewater that was adsorbed into GAC, saturating the pores and limiting the adsorption of the phenol, but reducing equilibrium time.

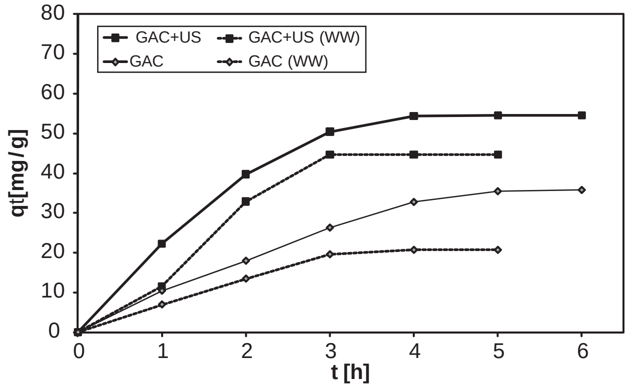

Fig. 4. Adsorption kinetics of phenol in both aqueous solution and wastewater (WW) with (GAC + US) and without (GAC) US irradiation (initial phenol concentration 100 mg/l, GAC 1 g/l, US density 1.06 W/ml).

The comparison of the kinetic curves shows that the rate of phenol adsorption is much higher in presence of US than in simple stirring, both for aqueous solution and in wastewater. It can be noted that the slope of the curve in presence of US is higher than in absence at the beginning of the test. That slopes becomes similar with time.

It can be explained relating to the different steps of the adsorption process. In particular, adsorption happens through an initial mass transfer from the liquid to the particle surface across the boundary layer thickness, a next diffusion within the porous particle and a finally adsorption itself phase on the surface of the GAC [29]. The fact that the initial slope is more marked indicates that the first step, mass transfer, is favored in presence of US. Indeed the sonication generates violent collapse of the cavitation bubbles, which, collapsing near the adsorbent surface, produce shockwaves. Near to cavitation, the other effect that happens is acoustic streaming, that is the movement of the liquid induced by ultrasonic waves. The extreme turbulent conditions, due to cavitation and acoustic streaming, enhances the rate of the mass transfer into the bulk solution as well as at the boundary layer [10].

The coupling of the processes yielded phenol degradation that are not similar to those predicted from the linear combination of the individual sonication and adsorption into GAC experiments. Indeed, the degree of phenol removal was also monitored by the measurement of TOC concentration remained in solution (Fig. 5).

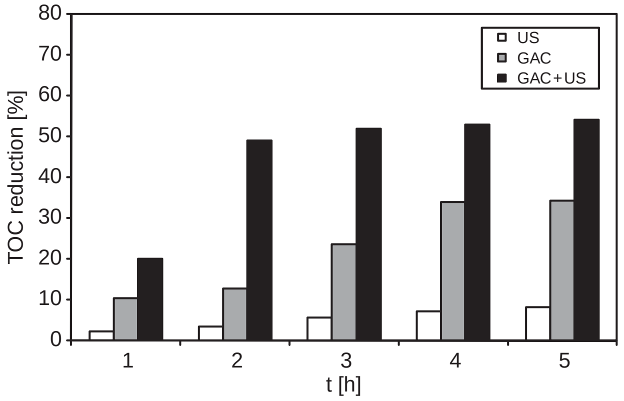

Fig. 5. TOC removal from aqueous solutions during ultrasonic (US) treatments, adsorption without (GAC) and with ultrasound (GAC + US) (initial phenol concentration 100 mg/l, GAC 1 g/l, US density 1.06 W/ml).

The TOC removal in combined process was found to be more than additive TOC degradations obtained with the sum of each treatment. As shown in Fig. 5, after 5 h of treatment TOC reduction by US alone is about 8%, the reduction by adsorption into GAC is 35% and the one by adsorption with US is more than 50%. This indicates the high synergistic effects of adsorption on GAC enhanced with US.

The effect of GAC + US treatment on the wastewater is also evaluated in terms of COD reduction. The COD is one of the most widely used analysis methods as an indicator of the organic content of a wastewater [32]. The Fig. 6 shows the characteristics of the raw wastewater spiked with phenol at different stages of the processes.

Both treatments allow a significant reduction of initial COD: the adsorption onto GAC tests achieve a performance of about 25%, while the combined application with US irradiation allows a reduction up to 40%. Furthermore, it can be noted that the reduction of COD after 3 h in adsorption onto GAC alone holds quite steady. In adsorption with US irradiation the COD reduction, instead, after only 2 h of treatment, the performances decrease drastically until to become nearly steady. This is an index that, also in wastewater, the equilibrium point can be reaching in a lower time with adsorption with US than adsorption without.

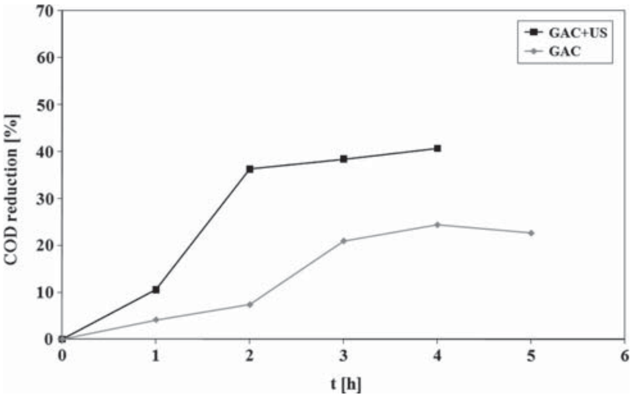

Fig. 6. COD reduction in GAC and GAC + US adsorption of domestic wastewater spiked with phenol (initial phenol concentration 100 mg/l, GAC 1 g/l, US density 1.06 W/ml).

Another noted effect was the tendency of GAC under the action of US to be pulverized at 35 kHz, the cavitation bubbles collapses impose great mechanical stress on the surface of the adsorbent [28]. At higher frequencies the pulverization of carbon was minimized [9]. It happens because when the frequency increases the growth time of the cavitation bubbles decreases. The bubbles size is smaller and the collapses are less violent.

4. Conclusions

The adsorption into GAC with and without US irradiation using phenol as a model compound for the degradation of fine organic matter in domestic wastewater has been investigated.

The results showed that low frequency US is not suitable for phenol degradation. Otherwise the US enhances the adsorption process into GAC and guarantees a higher rate of adsorption both in phenol solution that in wastewater spiked with phenol. Therefore the combined process shows a high synergistic effect estimated with TOC degradation in phenol solution. The degradation of COD in wastewater spiked with phenol was also investigated. The combined treatment (GAC + US), also in that case, has shown performances twice as high as the adsorption into GAC alone.

It has been noted that the ultrasonic treatment alone may not suitable for the phenol degradation at low frequencies, but in presence of solid particles we know that the ultrasonic effects are amplified. In the same way the carbon granules in phenol solution should act as solid particles. In this case, part of the phenol is adsorbed into GAC and a part (bigger than with only US) could be mineralized. Deeper studies are necessary to confirm this hypothesis.

However, further studies are necessary to the optimization of intensities and frequencies of ultrasonic irradiation. The knowledge acquired on the mechanisms of ultrasound assisted adsorption has to be transfer into technical applications of adsorption processes.

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