Adsorption of paracetamol onto carbon nanomaterials and degradation by ultrasonic and gamma radiation

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Abstract

Processes integration does the treatment of wastewater with pharmaceuticals a more efficient process. The adsorption of pollutants on different materials (e.g carbon based materials or silica ones) is one of the technologies most studied for water decontamination. On the other hand, the advanced oxidation processes (AOP) are among the emergent technologies for pharmaceuticals degradation. A novel approach to treat polluted waters can be the integration of the adsorption and AOP. This work shows the results of the paracetamol adsorption in multiwalled carbon nanotubes (MWCNT) and graphene (G), and the ulterior degradation and desorption of the paracetamol with ultrasound at high (USh) and low (USl) frequency and gamma radiation. The adsorption of paracetamol on MWNTC and G was experimentally determined, being the adsorption on MWNTC higher than that on G. Also fit to theoretical models were developed for a better understanding of the processes. Saturated nanostructures were washed with ethanol and dried under 60 ºC .Then saturated nanostrustures were treated with USh at a frequency of 862 kHz and a power of 30.6 W, desorption and degradation of the paracetamol was observed at the same time. With USl at 42 kHz, only a partial desorption of the studied pharmaceutical was observed and degradation was not reached. For gamma radiation, the intensification of the process was also studied with hydrogen peroxide and it was observed that, starting from 40 kGy, the corresponding signal of the pharmaceutical in the chromatogram disappears. The mineralization was determined with a Total Organic Carbon analyzer, obtaining the best results for the gamma radiation with hydrogen peroxide, with values between 92.8 and 94.1%. These results show the perspective of process integration of adsorption on carbon nanomateriales and the degradation with ultrasound and gamma radiation for the treatment of pharmaceuticals polluted waters.

Keywords: Carbon nanoparticles, adsorption, persistent organic pollutants, ultrasound, gamma

1. INTRODUCTION

Nowadays thousands of new different molecules are used to prevent or fight diseases[1]. The last 20 years, several reports have evidenced that pharmaceuticals are a new kind of environment pollutant.

Biological treatment systems are not efficient to eliminate persistent organic pollutants and that is the reason why these pollutants have been detected in treatment plant effluents[2]. Paracetamol can be found in polluted waters. Laboratory studies have shown that paracetamol is low biodegradable[3, 4]. Metabolites of paracetamol are hepatotoxics, that is the case of N-acetil-p-hydroquinone[5]. Adsorption is among the technologies most studied for water decontamination. Advanced Oxidation Processes (AOP) are being evaluated as emergent technologies for degradation of Persistent Organic Pollutants POP. An interesting approach might be the integration of adsorption and AOP. Processes integration could be an efficient tool to improve the treatment of wastewater contaminated with POP.

The aim of this work is evaluate the adsorption of paracetamol on carbon nanotubes and graphene and drug degradation into them by ultrasonic and gamma irradiation.

2. EXPERIMENTAL

2.1. Strategy

At first time MWCNT and G was saturated with paracetamol. Then, both were washed and dried at 50 ºC. After this, the treatment with low (USl) and high (USh) frequency ultrasound and gamma radiation in aqueous phase was carried out. Finally the effect of these processes were evaluated.

2.2. Carbon Nanoestructures

Carbon nanotubes are multiwalled with an external between 10 y 25 nm and specific surface of 240 m^2/g. Graphene in few layer between 4 y 8 nm and an specific surface of 48 m^2/g.

2.3. Equipment

An ultrasound multifrequency generator (MEINHARDT ULTRASCHALLTECHNIK) connected to a stainless steel-made transducer, operating in continuous mode at a frequency of 860 kHz and power output of 32 W was used for the sonication experiments. Reactions were carried out in a 1.0 L cylindrical glass reaction vessel. Low frequency experiments were carried out in an ultrasonic Bransonic 151OE operating in continuous mode at a frequency 42 kHz. A gamma irradiator model ISOGamma-LLCo with a ^{60}Co source was used at 5, 40,100 and 200 kGy.

2.4. Adsorption isotherm measurements

Equilibrium adsorption experiments have been carried out to evaluate the adsorption capacity of the adsorbents. In a single experiment, 30 mL of a paracetamol solution (initial concentration between 0.075 and 2.000 g/L) and a fixed amount of MWCNT and G (0.025 g) are mixed during 24 h at 25°C. The concentration of paracetamol in solution is measured by a SHIMADZU UFLC using a diode array detector DAD UV/Vis SHIMADZU SPD-M20A (wavelength 248 nm), a column Phenomenex model Synergi 4µ Fusion-RP 80Å, 30 x 4.60 mm 4 µm. The equilibrium concentration of paracetamol on solid phase is calculated from initial and final concentrations in aqueous solution. Each experiment is repeated threefold under identical conditions. In this work, the pH of the solutions is left free during adsorption experiments.

3. RESULTS

3.1. Adsorption of paracetamol

Figure 1 shows adsorption isotherm of paracetamol onto MWCNT and G and the fitted to theoretical models.

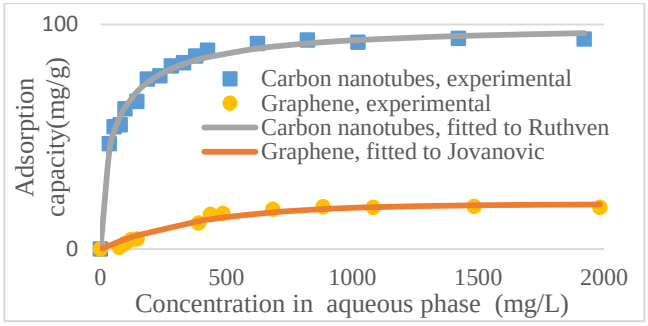

Fig 1: Adsorption isotherm of paracetamol onto MWCTN and G (T = 25 °C).

Maximum capacity adsorption of paracetamol is 91.4 mg per gram of MWCNT and 18.9 mg per gram of G. Both values are lower than obtained by Quesada et al. on activated carbons from vegetable sources[6].

3.2. Degradation using high and low frequency ultrasound

Figure 2 shows results of desorption and degradation from MWCNT and G using USl y USh. At low frequency, the physics effect of the ultrasound prevails assuring the rupture pharmaceutical-adsorbent. Paracetamol reaches total desorption from G at 30 min. For MWCNT a held increased was observed at the studied hour. This should be studied until desorption equilibrium is reached. At low frequency, degradation was not observed.

Desorption and simultaneously degradation of paracetamol from nanoparticles was observed for USh. Desorption was observed during the first 15 min after which an equilibrium between desorption and degradation was observed (15-60 min). After 60 min, degradation prevailed over desorption for MWCNT and G. USh promotes formation of free radicals ($OH^{\bullet}$), and that is the reason cause sonochemist effect appears side to physical effects.

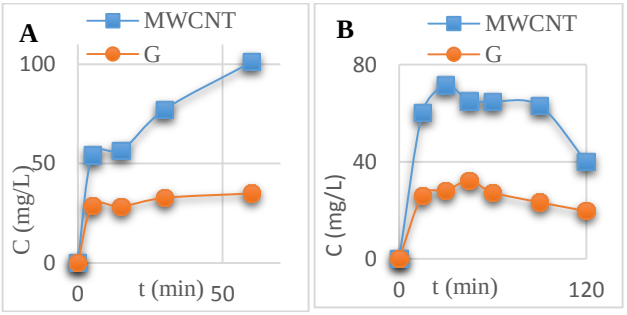

Fig 2: Desorption and degradation from MWCNT and G using (A) USl (40 kHz, 70 W, T=30 ºC) and (B) USh (F=862 kHz, P=32 W y T=30 ºC).

3.3. Degradation using gamma radiation

Results of gamma irradiation experiments are shown on figure 3. Gamma irradiation showed desorption and degradation of the pharmaceutical from 5 kGy. At 40 kGy the paracetamol degradation was 100%. The increase in reaction rate with hydrogen peroxide addition was evaluated with gamma radiation and the signal of the pollutant does not appear for G, meaning that degradation occurs even at lower doses.

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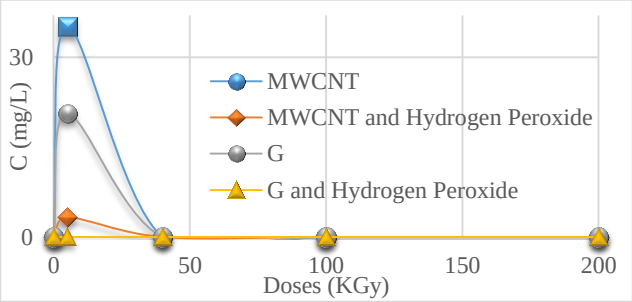

Figura 3: Desorption and degradation of paracetamol using gamma irradiation.

Concentration of Total Organic Carbon (TOC) decreases for MWCNT and G to 7.0 mg/L (Fig. 4) at 200 kGy with and without degradation intensification with hydrogen peroxide. The origin of that value is because not identified degradation products remains in solution as reported by Andreozzi et al[7].

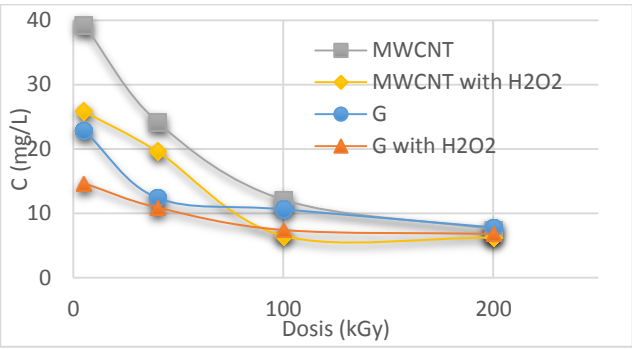

Figure 4: Variation of total organic carbon concentration in aqueous phase for gamma irradiation experiments.

Mineralization reaches values between 72.5 and 92.8 % at 200 kGy for paracetamol desorbed from G and MWCNT respectively. In presence of hydrogen peroxide, mineralization slightly to 76.5 and 94.1 % respectively.

These results highlight the perspective for integrating the drug adsorption on carbon nanostructures and advanced oxidation processes for the treatment of waste water contaminated with persistent organic pollutants.

4. CONCLUSIONS

The adsorption isotherms of paracetamol onto two carbon nanoparticles (Multiwalled Carbon Nanotubes and Graphene) show that MWCNT has the highest adsorption capacity when compared with G, as expected, due to the higher specific surface area. At low frequency ultrasound, the physics effect of the ultrasound prevails assuring the rupture pharmaceutical-adsorbent. Nevertheless, degradation of the pharmaceutical was not confirmed. When using high frequency (862 kHz, 30,6 W, T 30 ºC) desorption and degradation was observed at the same time, reaching mineralization values, at two hours reaction time, of 38.3 % and 62.7 % for G and MWCNT respectively. Gamma radiation revealed better results at 200 kGy, showing degradation in presence and absence of hydrogen peroxide between 72.5 – 76.5 % y 92.8 – 94.1 % for G and MWNT respectively.

Adsorption on carbon nanoparticles and treatment with AOPs appears as a very effective solution to remediate paracetamol and could be considered as a tertiary treatment for pharmaceutical wastewaters before discharge.

references

[1] E. Zuccato, Castiglioni, S., Fanelli, R., Identification of the pharmaceuticals for human use contaminating the italian aquatic environment. , J. Hazard. Mater., 122, 205-209, 2005.
[2] I. Quesada, Jáuregui-Haza, U., Wilhelm, A. M., Delmas, H., Contaminación de las aguas con productos farmacéuticos. Estrategias para enfrentar la problemática, Revista CENIC Ciencias Biológicas, 40, 173-179, 2009.
[3] A. Joss, Zabczynski, S., Gobel, A., Hoffman, B., Loffler, D., Mcardell, C., Ternes, T., Thomsen, A., Siegrist, H., Biological degradation of pharmaceuticals in municipal wastewater treatment: Proposing a classification scheme., Water Research, 1686-1696, 2006.
[4] K. Sang, Jaeweon, C., In, K., Brett, V., Shane, S., Occurrence and removal of pharmaceuticals and endocrine disruptors in South Korean surface, drinking, and waste waters., Water Research, 1013-1021, 2007.
[5] A. Ziylan, Ince, N. H., The occurrence and fate of anti-inflammatory and analgesic pharmaceuticals in sewage and fresh water: Treatability by conventional and non-conventional processes., Journal of Hazardous Materials, 187, 24-36, 2011.
[6] I. Quesada, Julcour, C., Jáuregui, U.J., Wilhelm, A.M., Delmas, H. , Degradation of paracetamol by catalytic wet air oxidation and sequential adsorption - Catalytic wet air oxidation on activated carbons, Journal of Hazardous Materials, 221-222, 131-138, 2012.
[7] R. Andreozzi, Caprio, V., Marotta, R., Vogna, D., Paracetamol oxidation from aqueous solutions by means of ozonation and H_2O_2/UV system, Water Research, 37, 993-1004, 2003.