New water treatment by integrated technologies based on the use of advanced oxidation/reduction processes and activated carbon

I. Velo Gala

Presented in 2013, Departamento de Química Inorgánica (F. de Farmacia). Universidad de Granada, 18071 Granada, Spain.

Supervisors: M. Sánchez-Polo (Universidad de Granada, España) and J. J. López Peñalver (Universidad de Granada, España).

Objectives and novelty

Numerous pharmaceutical compounds are being studied as part of a group of emerging unregulated pollutants that pose a potential risk for ecosystems and human health. These compounds resist removal by conventional urban wastewater treatments. Iodate contrast media, notably sodium diatrizoate (DTZ), are considered as model compounds of these pollutants due to their persistence and detection in urban wastewaters, surface water and ground waters. Conventional techniques used in urban wastewater treatment plants have proven ineffective for its removal, leading to the accumulation of DTZ and degradation products in the environment.

Advanced Oxidation/Reduction Processes appear to be a promising technology for removing organic compounds that are resistant to conventional biological treatments. In this context, the present study analyses the role of activated carbon in catalytic processes that require the use of ionizing and no-ionizing radiations. First, it was analysed the effectiveness of ultraviolet light (UV) and gamma irradiation to transform DTZ in aqueous solution determining the role of oxidizing and reducting species on DTZ degradation. In addition, the effectiveness of Fenton's reagent, Iron (III) and Iron (VI) salts, and oxidation processes based on UV, UV/H_2O_2 and UV/$K_2S_2O_8$, for DTZ degradation in aqueous phase were studied. With this background, the main aims of these studies were to identify the origin of the catalytic behaviour of activated carbons to remove DTZ in the presence of UV light and gamma radiation. For this purpose, we selected four commercial carbons (Ceca, Merck, Sorbo and Witco) and sixteen gamma-radiated carbons derived from these. The specific objectives were to study: (i) the DTZ photodegradation with low-pressure UV radiation; (ii) the DTZ degradation by radiolysis process; (iii) the mechanism underlying DTZ degradation with UV light in the presence of AC, determining the role of the physical and chemical properties of AC in this process; (iv) the mechanisms involved in DTZ removal with the combined use of AC and radiolysis and the influence of the physical and chemical characteristics of the ACs on the outcomes of this combined treatment.

In addition to their catalytic properties, ACs have many varied applications, which take advantage of their extraordinary textural and chemical properties that largely depend on the hetero-atoms on their surface. The presence of oxygenated groups determines many interesting carbons properties. Various methods have been proposed to modify the oxygen content of ACs and the nature and concentration of their surface groups. Practically all of the procedures augment the surface oxygen content but they also modify the textural properties of the ACs. In this way, we propose the utilization of ionizing radiation to modify AC surface chemistry as an alternative without damage textural properties of ACs. We evaluate the utilization of ionizing radiation to modify the electrical, chemical and textural properties of four commercial ACs, irradiating them directly in the air or in aqueous medium. The influence of each species ($HO^{\bullet}$, $H^{\bullet}$ or e^-_{aq}) on the characteristics of the treated activated carbons was also studied.

Results

The different advanced oxidation/reduction processes that have been studied shown positive results in the DTZ degradation. They were improved through the addition of AC in the UV light and gamma radiating processes. The radiolysis/AC system is more effective to remove DTZ in comparison to radiolysis in the absence of AC. It has been detected that AC has a synergetic effect on DTZ degradation by the combined process radiolysis/AC. Moreover, the synergic effect observed is independent of the textural properties of the AC but is dependent on its surface chemistry. The oxygen content of the AC influences the degree of this synergic effect in radiolysis, which was greatest in the AC with highest oxygen content. Related to the mechanism involved in the radiolysis/AC process used, the results obtained show that the solvated electrons formed during water radiolysis may interact with the AC surface, giving rise to areas with high reactivity due to the stabilization of the radicals by the quinone groups on the surface. The influence of this mechanism would be greater with higher quinone content. The analysis of the radical species produced by water radiolysis shows that adsorbate–adsorbent electrostatic interactions are necessary to obtain a synergic effect on pollutant degradation.

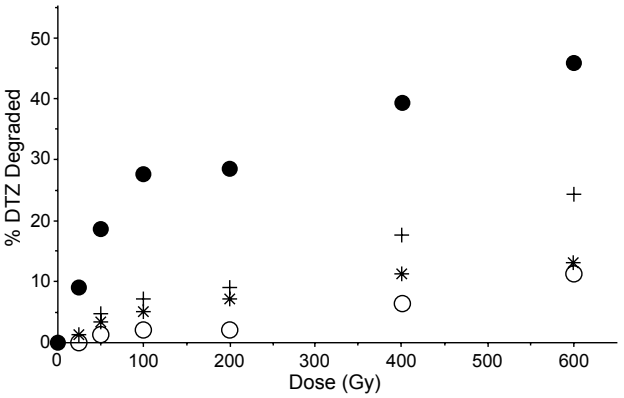

Fig. 1 – Percentage DTZ removal by: (*) radiolysis without AC; (●) radiolysis in the presence of AC; (○) DTZ adsorption on AC; and (+) theoretical sum effect of adsorption plus radiolysis. $[DTZ]_0$ = 1000 mg L^{-1}. Amount of AC Merck = 0.06 g. T = 298 K. pH = 6.5. Dose rate = 1.66 Gy min^{-1}.

The results of this study demonstrate that the presence of activated carbon during the DTZ photodegradation process markedly increases the removal rate, regardless of the activated carbon used. The results

obtained indicate that activated carbon Witco exerts the greatest synergic effect on DTZ removal by the UV/AC system, with a synergic contribution >53% at one minute of treatment. Regardless of the activated carbon sample considered, its synergic activity is in general, enhanced by the gamma radiation treatment. The textural and chemical properties of the activated carbons used show no clear relationship with their synergic contribution. However, the synergic activity of the activated carbon is more greatly enhanced by the samples with higher percentages of surface oxygen and, among these, the samples with higher percentages of carbon atoms with sp2 hybridization. Determination of the activated carbon band gap demonstrated that these materials behave as semiconductor materials and therefore as photoactive materials in the presence of UV light, because all Eg values are <4 eV. In general, the gamma radiation treatment reduces the band gap energy of the materials and, within the same series of activated carbons, lower Eg values correspond to higher k_{ob} values. We indicate that the percentage of carbon atoms with sp2 hybridization is increased in the gamma radiation modified materials, explaining their usually superior behavior in DTZ photodegradation. We highlight that: (i) the photocatalytic activity of reutilized activated carbons is similar to that of the original carbons, (ii) the presence of dissolved oxygen enhances DTZ removal by UV/AC, and (iii) UV radiation produces very slight chemical modifications on the activated carbons. The Witco series show the highest performance in synergic removal due to the presence of sulphur hetero-atoms in its composition. Based on these results, an action mechanism for the photo-catalytic removal of DTZ in the presence of activated carbon is proposed, in which the activated carbon acts as a photocatalyst, promoting electrons of the valence band to the conduction band and increasing the generation of $OH^{\bullet}$ radicals in the medium.

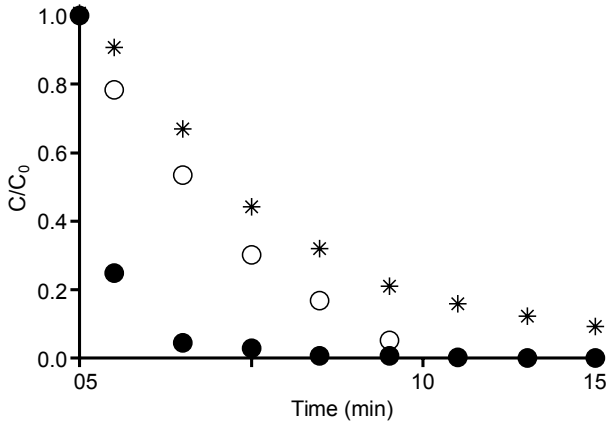

Fig. 2 –DTZ removal by the UV/AC system. (*) Direct photolysis; (●) UV/AC; (○) UV + adsorption on AC. $[DTZ]_0$ = 25 mg L^{-1}. Amount of AC Witco = 0.06 g. T = 298 K. pH = 6.5.

The interaction of gamma irradiation with the ACs permits their surface chemistry to be modified without significantly altering their textural properties. Gamma irradiation produces graphitization of the irradiated ACs, due to an increase in the percentage of surface carbon atoms with sp2 hybridization and a decrease in the percentage with sp3 hybridization. ACs irradiated in media with a predominance of $H^{\bullet}$ species have a lower pHpzc in comparison to the non-irradiated AC, due to an increase in acidic functional groups and a decrease in basic functional groups. No general behaviour patterns were observed for ACs irradiated in media with a predominance of solvated electrons or hydroxyl radicals. Study of the electronic properties of the ACs showed that their Eg value is lower after irradiation. This decrease is related to an increase in the percentage of carbon atoms with sp2 hybridization and in surface oxygen content.

Conclusions

Activated carbons can play more than a mere support role in Advanced Oxidation/Reduction Processes. The presence of activated carbon during the DTZ photodegradation process by UV light markedly increases the removal rate, regardless of the activated carbon used. The results obtained indicate that the synergic activity of the activated carbon is more greatly enhanced by the samples with higher percentages of surface oxygen and, among these, the samples with higher percentages of carbon atoms with sp2 hybridization. Activated carbons behave as semiconductor materials and therefore as photoactive materials in the presence of UV light. The role of ACs in the radiolysis system is dependent on their oxygen content ant the adsorbate–adsorbent electrostatic interactions are necessary to obtain a synergic effect on pollutant degradation.

The gamma irradiation is appear to be an assuring technology for changing ACs surface chemistry to be without altering their textural properties. Gamma irradiation produces graphitization of the ACs, increase sp2 hybridization and surface oxygen content, so Eg value is lower after irradiation,

Related publications

[1] Velo-Gala I., López-Peñalver J.J., Sánchez-Polo M., Rivera-Utrilla J. Surface modifications of activated carbon by gamma irradiation. Carbon, 2013, Volume 67, Pages 236-249.

[2] Velo-Gala I., López-Peñalver J.J., Sánchez-Polo M., Rivera-Utrilla J. Role of activated carbon on micropollutans degradation by ionizing radiation. Carbon, 2013, Volume 67, Pages 288-299.

[3] Velo-Gala I., López-Peñalver J.J., Sánchez-Polo M., Rivera-Utrilla J. Activated carbon as photocatalyst of reactions in aqueous phase. Applied Catalysis B: Environmental, 2013, Volumes 142–143, Pages 694-704.

[4] Velo-Gala I., López-Peñalver J.J., Sánchez-Polo M., Rivera-Utrilla J. Comparative study of oxidative degradation of sodium diatrizoate in aqueous solution by H_2O_2/Fe^{2+}, H_2O_2/Fe^{3+}, Fe (VI) and UV, H_2O_2/UV, $K_2S_2O_8$/UV. Chemical Engineering Journal, 2013, in Press.

[5] Velo-Gala I., López-Peñalver J.J., Sánchez-Polo M., Rivera-Utrilla J. Ionic X-ray contrast media degradation in aqueous solution induced by gamma radiation. Chemical Engineering Journal, 2012, Volumes 195–196, Pages 369-376.

[6] Velo-Gala I., López-Peñalver J.J., Sánchez-Polo M., Rivera-Utrilla J. Degradation of X-ray contrast media diatrizoate in different water matrices by gamma irradiation. Journal of Chemical Technology and Biotechnology, 2013, Volume 88, Issue 7, Pages 1336-1343.