Thesis Review. Integrated technologies based on the use of activated carbon and radiation to remove contaminants present in landfill leachates

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Objectives and novelty

Industrial and commercial growth in many countries around the world in the past decades has been accompanied by rapid generation of municipal and industrial solid waste, which creates the most serious environmental problems related to landfill such as the generation of leachates during the decomposition process. Among the emerging contaminants that have been detected in landfill leachates, wastewater, ground water and surface water are plastic additives and herbicides with range 0.01 µg/L to 30 mg/L. Phthalic acid (PA), bisphenol A (BPA), and diphenolic acid (DPA) are the most common monomeric plasticizers used to produce plastic material; and 2, 4- dichlorophenoxyacetic acid (2,4-D) and 4-chloro-2-methylphenoxyacetic acid (MCPA) are widely used herbicides in the world. They have potential toxicity towards humans and animals, and are suspected mutagens, carcinogens, and endocrine disruptors even at a low concentration. Numerous studies have been reported that the conventional wastewater treatments are not effective to remove these pollutants, therefore alternative treatments are necessary. The adsorption process and advanced oxidation processes (AOPs) are widely used to eliminate similar compounds from aqueous solution, taking advantage of their respective adsorbent and oxidizing properties. Activated carbon (AC) has been signaled as a promising catalyst of AOPs, however, there are few available data concerning the interaction mechanism that takes place through the AOPs in the presence of AC. With this background, the present work aimed to investigate the elimination of the above selected contaminants present in landfill leachates through different technologies such as: adsorption/bioadsortion on ACs, AOPs based on the use of UV radiation (UV, UV/H_2O_2, UV/$K_2S_2O_8$, UV/Na_2CO_3 and UV/TiO_2/AC) and gamma radiation.

Results

The overall adsorption rate of selected contaminants on two commercial ACs denominated as S and C was interpreted using diffusion models (external mass transport, intraparticle diffusion, pore volume diffusion, and surface diffusion) and kinetic models. Results showed that the external mass transport did not affect the overall adsorption rate of these contaminants on AC samples, the contribution of pore volume diffusion represented more than 92% of intraparticle diffusion on both ACs (Figure 1). The kinetic models were satisfactorily fitted to experimental data and the second-order kinetic model was better fitted these data than the first-order kinetic one.

The ACs used in this study had a high adsorption capacity which was largely attributable to dispersion and electrostatic adsorbent-adsorbate interactions. The solution pH had a major effect on PA adsorption on ACs, however, PA adsorption was not affected by the presence of electrolytes (ionic strength) in solution but was enhanced by the presence of microorganisms by around 15%, which was explained by an increase in carbon surface hydrophobicity of the AC due to the production of extracellular polymeric substances by microorganisms adsorbed on AC surface. PA removal varied as a function of the water type, increasing in the order: ground water < surface water ≃ ultrapure water < wastewater. The adsorption yield was much lower in dynamic versus static regime, attributable to difficulties of PA diffusion into the carbon pores and the shorter adsorbent-adsorbate contact time in dynamic regime.

Concerning the AOPs, results showed that UV radiation was not effective to remove these pollutants from the medium, due to their low quantum yield. The addition of radical promoters such as H_2O_2, $K_2S_2O_8$, or Na_2CO_3 markedly increased the effectiveness of UV radiation through the generation of $HO^{\bullet}$, $SO_4^{\bullet-}$, or $CO_3^{\bullet-}/HCO_3^{\bullet}$ radicals, respectively. The rate constants of reactions between these radicals and BPA were , , and . The solution pH had a major effect on BPA degradation with these three systems. These oxidation systems showed 100% effectiveness

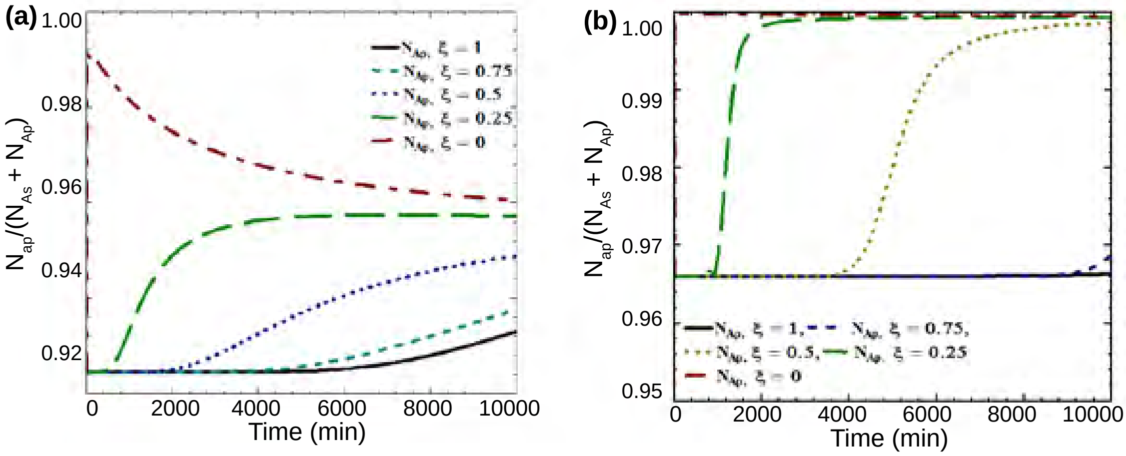

Figure 1. Contribution of pore volume diffusion to intraparticle diffusion at different radial positions, a) PA on carbon C; b) BPA on carbon S.

to remove BPA from wastewater, due to its large content of natural organic matter. The lowest BPA degradation was detected in ground water due to its higher content of metal species and bicarbonate ions. The mineralization of organic matter was more effective with the UV/$K_2S_2O_8$ system, followed by UV/H_2O_2 and UV/Na_2CO_3 systems. The lowest toxicity of byproducts was reached when using the UV/$K_2S_2O_8$ system.

The photocatalytic degradation of 2,4-D was investigated by using the integrated UV/TiO_2/AC system. Three commercial ACs denominated as S, M, and W were used in this study. Sample W was oxidized with ozone for 30 min and 120 min. Results obtained showed that the presence of AC during the catalytic photodegradation (UV/TiO_2) of 2,4-D considerably increased its percentage removal. The highest 2,4-D degradation was obtained in the presence of the ozonated ACs with a high carboxylic groups content. Carboxylic groups in the graphene planes of the activated carbon participate in the additional generation of $HO^{\cdot}$ radicals by interacting with the electrons produced by the UV/TiO_2 system. Consequently, the contribution of $HO^{\cdot}$ radicals to the global 2,4-D degradation process is greater at the beginning of the photocatalytic treatment in the presence of ozonated AC, which confirmed the proposed mechanism (Figure 2).

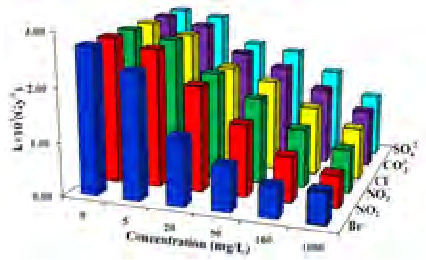

Figure 3. Variation in dose constant as a function of the species concentration present in the water. Dose rate = 1.66 Gy/min, $[DPA]_0$ = 50 mg/L, and T = 25°C.

The advanced oxidation/reduction process based on gamma radiation was also used to remove the above pollutants. The degradation process of these pollutants mainly took place via oxidation pathway. DPA degradation was reduced in the presence of Br^-, Cl^-, CO_3^{2-}, NO_2^-, NO_3^-, or SO_4^{2-}, and this decrease was greater at high concentrations of these anions, largely due to their competition with DPA for the reactive radicals generated, particularly $HO^{\bullet}$ (Figure 3). The dose constants were lower in wastewater and surface water than in ultrapure water because they contain organic matter and HCO_3^-, Cl^-, SO_4^{2-}, and NO_3^- ions that react with the radiolytically generated reactive radical species ($HO^{\bullet}$, $H^{\bullet}$ and e_{aq}^-). The total organic carbon (TOC) and toxicity of the medium were reduced during the DPA degradation by gamma radiation.

Conclusions

Both diffusion and kinetic models successfully fitted the adsorption experimental data; however, we recommend the use of diffusion models since their assumptions are nearer to the real adsorption process than those of kinetic models. AOPs based on the use of UV radiation (UV, UV/H_2O_2, UV/$K_2S_2O_8$, UV/Na_2CO_3 and UV/TiO_2/AC) and gamma radiation represented alternative processes for the removal of the selected contaminants. Moreover, the UV/$K_2S_2O_8$ system was the most effective to remove both pollutant and TOC. The presence of ozonated ACs with a high carboxylic groups content greatly increased the pollutant photodegradation by the UV/TiO_2 system.

Related publications

[1] Abdel daiem MM, Rivera-Utrilla J, Ocampo-Pérez R, Sánchez-Polo M, López-Peñalver JJ, Treatment of water contaminated with diphenolic acid by gamma radiation in the presence of different compounds, Chem. Eng. J., 2013; 219, 371–379.

[2] Rivera-Utrilla J, Sánchez-Polo M, Abdel daiem MM, Ocampo-Pérez R, Role of activated carbon in the photocatalytic degradation of 2, 4- dichlorophenoxyacetic acid by the UV/TiO_2/activated carbon system, J. Appl. Catal: B Environ., 2012; 126, 100–107.

[3] Ocampo-Pérez R, Abdel daiem MM, Rivera-Utrilla J, Méndez-Díaz JD, Sánchez-Polo M, Modeling adsorption rate of organic micropollutants present in landfill leachates onto granular activated carbon, J. Colloid Interface Sci., 2012; 385, 174–182

[4] Abdel daiem MM, Ocampo-Pérez R, Rivera-Utrilla J, Sánchez-Polo M, Méndez-Díaz JD, Environmental impact of phthalate acid esters and their removal from water and sediments by different technologies - A review, J. Environ. Manage., 2012; 109, 164–178.

[5] Méndez-Díaz JD, Abdel daiem MM, Rivera-Utrilla J, Sánchez-Polo M, Bautista-Toledo I, Adsorption/Bioadsorption of Phthalic Acid, an Organic Micropollutant Present in Landfill Leachates, on Activated Carbons, J. Colloid Interface Sci., 2012; 369, 358–365.

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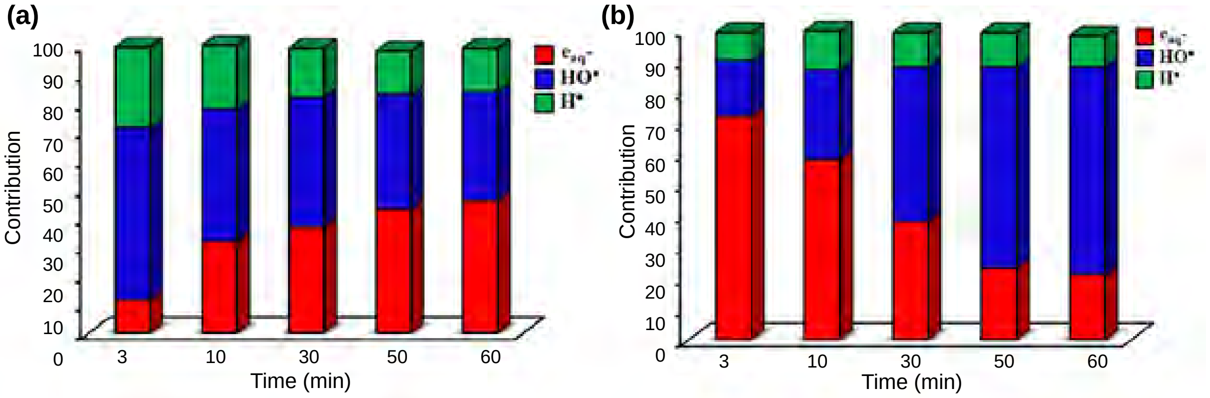

Figure 2. Contribution of radical species to 2,4-D removal by the a) UV/TiO_2/AC system and b) UV/TiO_2 system. T = 25º C, pH = 7, [2,4-D] = 50 mg/L, mass of TiO_2 and AC = 5 mg.