Development of an adsorption/desorption process to remove pharmaceuticals from wastewater: from sorbent screening to fixed-bed column tests.

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Pharmaceuticals are frequently detected in wastewater treatment plant effluent, and traditional wastewater treatment plants (WWTPs) are often ineffective in their removal. Due to their accumulation and to their toxic effects even at very low concentrations (from ng/L to μg/L), the new EU wastewater directive 2024/3019 requires large WWTPs to achieve an 80% removal of several pharmaceuticals, including diclofenac, carbamazepine and chlarithromycin. This work is focused on the removal of these compounds, that are representative of different pharmaceutical categories: anti-inflammatory, anti-epileptic and antibiotic, respectively. Adsorption was selected as removal technology, thanks to its flexibility, ease of operation and low cost. The tested sorbents include both commercial ones (activated carbon Norit, taken as the benchmark, and polymeric resin XAD16N), and Molecularly Imprinted Polymers (MIPs), developed in the UNIBO laboratories to selectively adsorb target pharmaceuticals. The sorbent screening phase was conducted by means of batch isoterm tests resulting in higher performance of the commercial materials with respect to MIPs. For this reason, Norit and XAD16N were selected for further investigation in fixed-bed column tests with a particular focus on chemical regeneration. The first continuous tests were conducted at a 3 minute Empty Bed Contact Time (EBCT) and a 15 cm bed height, with a WWTP effluent spiked with carbamazepine, diclofenac and chlarithromycin. On XAD16N, diclofenac showed the poorest adsorption, reaching 20% breakthrough (BP) at 8700 BVs, while clarithromycin performed the best, reaching 10% BP at 15500 BVs. On Norit, both clarithromycin and diclofenac reached 20% BP in less than 2600 BVs, making XAD16N a more promising sorbent under these conditions. The possibility of in-situ regeneration was studied by testing the effectiveness of methanol, ethanol and 2-propanol at ambient temperature. XAD16N was easily regenerated with 10 to 20 BVs of solvent, with ethanol being the most promising one in terms of consumption and efficiency; on the other hand, chemical regeneration of Norit proved inefficient, even with high amounts of solvent. Pharmaceutical adsorption on XAD16N was effectively simulated thanks to the adsorption module of AspenPlus. The LCA and cost-benefit analysis of the process are in progress. This work demonstrated the effectiveness of XAD16N and Norit in removing pharmaceuticals from wastewater, and the feasibility of in-situ regeneration of XAD16N with 10-20 BVs of ethanol. These results represent a significant step towards the development of a reliable and cost-effective adsorption/desorption process for the removal of micropollutants from municipal wastewater.

Keywords: *pharmaceuticals, adsorption, wastewater, chemical regeneration, process simulation.*