Adsorption of ciprofloxacin and diclofenac using humics and silica-coated Fe_3O_4 nanoparticles

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The emerging pollutants such as non-steroidal anti-inflammatory drugs (diclofenac sodium, DCF) and antibiotics (ciprofloxacin, CIP) have aroused increasing concerns, and the efficient removal of pharmaceuticals from wastewater is becoming an urgent problem. An eco-friendly composites consisting of Fe_3O_4 nanoparticles modified by humic acids (HA) and/or 3-aminopropyl-triethoxysilane (APTES) have been fabricated via an in-situ/sol-gel method, characterized and used for CIP and DCF adsorptive removal. XRD, SEM, Mossbauer spectroscopy, zeta potential (DLS), N_2 adsorption-desorption measurements and elemental analysis were employed to characterize all synthesized composites: Fe_3O_4/APTES, Fe_3O_4/HA, Fe_3O_4/APTES/HA. The adsorption kinetics, isotherms as well as various influence factors, e.g., pH, ionic speciation and strength on the CIP and DCF removal were systematically investigated. The CIP and DCF recovery was studied from 0.1 mM solutions at solid:liquid ratio 1:1000, pH 7.5, and the contact time 24 h. The equilibrium concentrations were determined spectrophotometrically.

Fe_3O_4 conjugation with humic acids lead to increase specific surface from 117 to 142 m^2/g for the Fe_3O_4 and the Fe_3O_4-HA20 (20 wt% of HA), respectively. The sorbents under study are characterized by a high sorption capacity regarding to ciprofloxacin. The results obtained indicate that the adsorption of CIP by the Fe_3O_4-HA20 is largely enhanced in comparison with the bare Fe_3O_4.

High uptakes of diclofenac reaching 178 and 256 mg g^{-1} for Fe_3O_4/APTES/HA and Fe_3O_4/APTES composites respectively proved that the obtained xerogels are potential candidates for removal of drugs from waters and wastewaters. The isotherm of DCF adsorption was described well by the Freundlich model.

The results showed that the presence of HA weakened the sorption capacity of Fe_3O_4/APTES, but decreased its toxicity towards *Paramecium caudatum* and *Sinapis alba*.

To maximize the removal degree for DCF, ultrasonic (US) treatment in the absence or presence of Fe_3O_4/APTES and HA was investigated. Two frequencies, three time and three pH conditions were tested (30 and 100 kHz; 5, 10, and 30 min and 3, 7, and 9, respectively). The adsorption of DCF has increased when Fe_3O_4/APTES in the presence HA was sonicated at 100 kHz, pH 3 (58%, respectively) compared with 30 kHz, pH 3 (32%, respectively) within 30 min. These facts suggested that the fabricated composites have great potential for CIP and DCF-contaminated water treatment.

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