Waste tire char valorization by preparing Ni-Cu carbocatalyst for applications in sulfate radicals based advanced oxidation processes (SR-AOPs) : Degradation of metronidazole emerging pollutant

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Waste tire amounts have continuously increased in the last decades presenting a great potential for harmful effects to the environment. Pyrolysis was applied lately as an effective recycling method in order to recover energy and produce valuable products. Tire char (TC) represents an attractive by-product that can be modified to produce adsorptive and catalytic materials of significant industrial relevance. In this study, a series of Ni-Cu-TC catalysts with different weight ratios was synthesized and applied towards the degradation of metronidazole (MTZ) by advanced oxidation processes (AOPs), through activation of peroxymonosulfate (PMS, HSO_5^-) and peroxydisulfate (PDS, $S_2O_8^{2-}$) oxidants. MTZ was studied as a model emerging pollutant since it is one of the widely used antibiotics worldwide, with high solubility and diffusion in aqueous media, frequently detected in various wastewaters. Physicochemical characterization of TC catalysts was performed by scanning electron microscopy (SEM), X-ray diffraction (XRD), ATR-FTIR spectroscopy, Raman spectroscopy, porosimetry, and elemental analysis. XRD pattern of TC_10%Cu was ascribed to cubic Cu_5Zn_8 with diffraction peaks at 43.37º, 50.46º, 74.14º and 89.96º. Three characteristic diffraction peaks of TC_10%Ni appeared at 37.25º, 43.28º and 62.88º, which are indexed as (111), (220) and (220) planes, correlated to NiO cubic structure. The best catalytic systems were tire char with 10% (w/w) loading Cu (TC_10%Cu/PDS) and 10% (w/w) loading Ni (TC_10%Ni/PMS), with 100% degradation of MTZ in 30 min and 15 min, respectively. The optimal dosage of PMS, PDS and Ni-Cu tire carbon catalyst, was 100 mg/L, 250 mg/L and 500 mg/L, respectively. In order to identify the major reactive species generated, scavenging experiments have been conducted. For PMS/10%Ni-TC system singlet oxygen ($^1O_2$) was revealed as the dominant species followed a non-radical mechanism, while for PDS/10%Cu –TC system $SO_4^{-\bullet}$ radicals were the major oxidative species. Finally, mass spectrometry (LC-HR-MS) analysis was followed to identify transformation products (TPs) during MTZ catalytic degradation by TC_10%Cu and TC_10%Ni, and TP with *m/z*=128.0450 Da was the major one. Further experiments on characterization of the catalysts were in progress (e.g. XPS analysis, contact angle) in order to correlate catalytic performance and mechanisms with surface properties of the prepared catalysts.