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Fenton and photo-Fenton like at neutral pH for the removal of emerging contaminants in water and wastewater effluents.

ABSTRACT

Water scarcity is among the main problems to be faced by many societies and the scientific community around the entire world. In particular, one of the most important focuses of the scientists is to find alternative sources of water in order to reduce the pressure on freshwater resources. Wastewater treatment plants (WWTPs) represent one of the most interesting options to achieve this goal but, to respect the appropriate levels of water quality, specific treatments are required. Advanced oxidation processes (AOPs) are suitable to remove also recalcitrant compounds named contaminants of emerging concern (CECs), which properties of persistence and bioaccumulation are of great concern for the human health. AOPs are wastewater treatments technologies based on the production of hydroxyl radicals which allow oxidize or even mineralize almost all the organic molecules with production of CO_2, H_2O and inorganic ions. These treatments include several processes such as ozone, UV light based processes with H_2O_2, Fenton and photo Fenton processes. Photo Fenton process is particularly powerful to achieve CECs elimination from wastewater. Nevertheless, some setting requirements have limited its application at industrial scale, among these the necessity of working in a narrow range of pH in order to avoid iron loss. In fact, when the pH solution is higher than 3.0, iron used as catalyst for HO· radical production, precipitate as inactive oxyhydroxide species. Scientific community is working on the improvement of the operating conditions of this treatment in order to make possible its utilization in real wastewater treatments. The processes resulting from a modification of conventional Fenton are named Fenton-like processes.
The main goals of this thesis were the study of the treatment viability and the setting of the operating conditions of photo Fenton like at circumneutral pH to achieve the wastewater effluent quality required for reuse purpose. In this study the use of chelating agents to keep the iron soluble in a wider range of pH was investigated in order to make possible its applicability without the use of great amounts of chemicals to reduce the influent pH.
In this study was firstly confirmed the suitability of Fenton based processes in recalcitrant compounds removal. Fenton, UV-A photo-Fenton and UV-C photo-Fenton were, in fact, applied for atrazine removal from secondary effluent (SE) of municipal wastewater treatment plant (MWWTP). UV-A and UV-C photo-Fenton allowed remove 50% and 100% of the initial atrazine content respectively.
Then to answer to the main objective of this thesis the assessment of photo-Fenton's suitability for recalcitrant contaminant at circumneutral pH was carried out. Thus, homogeneous photo-Fenton like at neutral pH was applied for sulfamethoxazole (SMX) removal. In order to avoid iron precipitation, chelating agents were used to keep soluble the iron at circumneutral pH. The chelating ability of four chelating agents (ethylenediaminetetraacetic acid-EDTA, nitrilotriacetic acid-NTA, oxalic acid and tartaric acid) was tested. Then, once determined the optimum molar ratio L:Fe for iron chelation (1.5:1 for EDTA and NTA, 10:1 for tartaric acid and 20:1 for oxalic acid), their catalytic activity was evaluated when employed in photo-Fenton like for SMX removal. The highest SMX percentage removal (83% against 77% when using EDTA, 66% when

using OA and only 14% when using TA), together with the minimum chelating agents required and the better property of biodegradability and low toxicity, demonstrated the suitability of NTA for the purpose.
A further study on the stability of the chelates under reaction was carried out. The operating conditions adopted for the treatment significantly influence the stability of the chelate solution. Thus, in order to proper control the parameter set up the behavior of chelates has been study under thermal, oxidative and photochemical stress. It was demonstrated as the temperature control can represent an interesting tool to extend the chelates lifetime under oxidative and photochemical stress. By adopting different H_2O_2 doses, a linear correlation between doses and chelate decomposition could be identified. The better suitability of UV-A irradiation, against UV-C and Xe lamp, to preserve the iron chelate solution was demonstrated.
Moreover, the influence of the influent characteristics on the process efficiency needed to be also considered. Thus, different water matrices were used for the experiments. The efficiency of photo-Fenton like catalyzed by Fe(III)-NTA has been compared when applied to different aqueous matrixes (Milli-Q water, tap water, secondary effluent wastewater and well water). It was demonstrated as the ions content, especially Ca^{2+} and Mg^{2+}, significantly compromise the process of chelation. High alkalinities and organic matter, instead, mainly influenced the phase of process, when acting as radicals scavengers, reduced the amount available for SMX oxidation. Some strategies were then adopted to promote SMX removal. Between them, Mn2+ mediated photo-Fenton like showed somehow possibility for improvement. Highest removal rate was in fact exhibited in the first minutes of reaction when adding Mn^{2+} to the solution in ratio molar Mn:Fe 0.5:1. The conclusive study of the thesis regarded the assessment of the Br- presence on the efficiency achievable in recalcitrant compounds removal when applying UV/PS/Fe2+ for removal of benzophenone-4 (BZ4), nitrobenzene (NB), nitrobenzoic acid (NBA), atrazine (ATZ), and ampicilline (AMP). Br- demostrated to be a strong inhibitor in the removal of all the considered contaminants except for NB when, the removal was instead enhanced in bromide containing water.