Abstract

The aim of this work is to study and to compare the degradation of two anionic azo dyes (Methyl Orange (MeO) and Acid Red 14 (AR14)) in aqueous solution, by various advanced oxidation processes (AOPs) in homogeneous and heterogeneous phases.

Photolysis of both dyes at 254 nm is negligible. However, the photooxidation of the two dyes in presence of H_2O_2, halates oxidants (IO_3^-, BrO_3^-, ClO_3^-, ClO_4^-) and BO_3^- ions under UV irradiation at 254 nm was very effective, except for ClO_3^- and ClO_4^-. The degradation rate of MeO and RA14 follows pseudo-first order kinetics in all studied Oxidant/UV systems. The highest degradation rate was obtained in presence of BrO_3- for both dyes. The different systems were compared for an oxidant concentration of 10^{-2} mol. L^{-1} and the results obtained showed that the decolorization followed decay order: $BrO_3^-/UV_{254nm} > IO_3^-/UV_{254\ nm} > H_2O_2/UV_{254\ nm} > BO_3^-/UV_{254nm} > ClO_3^-/UV_{254nm} = ClO_4^-/UV_{254\ nm} = UV_{254nm}$. The optimization of the oxidant concentration for each process was determined. No degradation of MeO and AR14 in the presence of ClO_3^- and ClO_4^-, because these ions do not absorb at 254 nm, so they do not generate radical species which degrade organic pollutants.

In heterogeneous phase, the decolorization of the aqueous solutions of the two substrates by TiO_2 PC500 in the dark (adsorption) and in the presence of monochromatic UVA irradiation at λ = 365 nm was carried out. The adsorption of AR14 on the TiO_2 PC500 catalyst was judged favorable by the Langmuir isotherm, while the adsorption of MeO can be represented by the Langmuir and Freundlich isotherms. No photolysis was observed for both dyes at 365 nm, while photocatalysis significantly enhanced the removal of both substrates. The linear plot $Ln(C_0/C)$ versus time shows that the photocatalytic degradation of the two substrates follows pseudo-first order kinetics. The Langmuir-Hinshelwood model is very suitable for describing the phodegradation kinetics of the two dyes studied. The influence of many operating parameters has been released by comparing the behavior of each dye, such as the initial dye concentration, the initial catalyst mass, the irradiation source, the pH and various inorganic additives (salts and oxidants). The degradation rate constant of AR14 was higher than that of MeO in all experiments. Generally, the addition of inorganic salts influences the photocatalytic process of the two dyes differently. The addition of H_2O_2 accelerates the photodisappearance of MeO, however it inhibits the photodecomposition of AR14. Halates electron acceptors (IO_3^-, BrO_3^-, ClO_3^-, and ClO_4^-) enhance the photodegradation of both dyes, but the order of effectiveness varies with electron acceptor concentration.

 The method of experimental design was applied to model the influence of three experimental parameters (the initial dye concentration, the initial iodate concentration and the intensity of the photon flux) on the photocatalytic degradation of AR14 by the TiO_2 $P25/UV_{suntest}$ process, according to a second-degree polynominal model. This experimental design made it possible to quantify the influence of each parameter on the dye photodegradation rate and to determine the possible interactions between the three parameters studied. The optimal values of the parameters that give maximum yield were also determined.