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Heterogeneous catalytic wet peroxide oxidation of paraquat in the presence of modified activated carbon

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ABSTRACT

The catalytic wet peroxide oxidation (CWPO) method was applied to the degradation of paraquat, a widely used and highly toxic herbicide. The effect of ammonia pre-treatment and iron impregnation on Fenton-driven reaction efficiency was first investigated. Iron amendment and acidic oxygen-surface groups were found to promote the catalytic activity towards paraquat degradation. The effects of three significant operational parameters (hydrogen peroxide concentration, catalyst dosage and temperature) on catalytic performance of the most promising catalyst (AC-Fe) were then investigated. The best degradation yield (71.4% of COD abatement in a 20 mg L^{-1} solution) was obtained with 12.5 mmol L^{-1} H_2O_2, 1 g L^{-1} catalyst dosage and $T = 70\,^{\circ}C$, although ambient temperature could be preferred for application convenience.

A nearly complete degradation of paraquat and its intermediates (~92% of COD removal) was achieved after 12 h treatment, when proceeding at ambient temperature via regular sequential additions of the spent amount of H_2O_2 in the presence of optimal catalyst dosage. A reasonably good stability of the catalyst was demonstrated during consecutive re-use of the same recovered sample, in long-term CWPO runs. Only a slight decrease of catalytic performance (from 92% to 85% of COD removal) was observed after five consecutive cycles, probably due to high stability of the supported iron species.

Time evolutions of aromatic intermediates and short-chain carboxylic acids were recorded using HPLC analysis, and clearly indicated that CWPO is capable of effectively degrading the paraquat herbicide.

1. Introduction

The environmental impact of pesticides and herbicides has attracted much attention due to their increasing and widespread usage in agriculture to preserve crops from pests. In addition to direct spreading on cultures, important quantities of pesticides are discharged in the environment from applicator rinsates and industrial wastewaters generated from agricultural and veterinary factories. Generally due to their slow biodegradation and high mobility in the environment, these substances pass to surface and ground water, causing a potential danger for human and animal health. To reduce environmental and health impact of these pollutants, considerable human and economic resources were invested, over the past three decades, in the development of powerful and practical treatment processes for the degradation and/or removal of hazardous organic compounds from contaminated wastewaters.

Conventional wastewater treatment methods have limitations since most of pesticides are resistant to traditional chemical and biological treatments [1]. Among novel technologies developed during the past two decades, advanced oxidation processes (AOPs) emerge as the most promising methods of depolluting contaminated water from applicator rinsates and industrial effluents, owing to their high potency to degrade and completely mineralize many refractory compounds including pesticides.

AOPs are those oxidation processes based on generation and use of powerful hydroxyl radicals ($^{\bullet}OH$) by means of chemical, photochemical or photocatalytic methods. These radicals react unselectively and at a very high rate (k in the range of 10^7 to $10^{10}\,M^{-1}\,s^{-1}$) with a wide range of organic compounds leading to their mineralization. Over the last three decades, several AOPs such as (conventional Fenton, photo-Fenton, electro-Fenton, O_3/UV, O_3/H_2O_2, H_2O_2/UV, UV/TiO_2 and plasma) have been conceptualized and successfully applied to the degradation of various organic compounds [2–10]. Nevertheless, Fenton reaction-based chemical oxidation still stands as the most studied degradation method in wastewater systems [11–15]. The conventional Fenton reagent is a well-known and very effective remediation system, based on the in situ generation of hydroxyl radicals via homogeneous reaction between hydrogen peroxide and ferrous ions or other low valence transition metal ions such as Cu(II), Co(II) and Mn(II). However, the necessary high dosage of iron and hydrogen peroxide, to achieve a high mineralization yield of the pollutant, as well as the continuous loss of catalyst and the important amount of generated iron hydroxide sludge, needing further separation

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step to comply with environmental regulations, constitutes the main evident drawbacks of the homogeneous Fenton system. One of the most practical and interesting ways proposed to circumvent these limitations is the use of Fenton-like heterogeneous catalysts involving iron minerals [16,17], crystalline Fe_2O_3/SBA-15 nano-composites [18] or transition metal ions immobilized on solid supports such as alumina [19], zeolites [20–22], pillared clays [23–25], ion exchange resin [26] and activated carbon [27]. This technology, known as catalytic wet peroxide oxidation (CWPO), represents a highly attractive alternative to classic Fenton method since it can promote the oxidation of different organic pollutants without sludge formation and with the possibility to recycle the iron catalyst. Since the early works of Fajerweg et al. [20] and Lücking et al. [28] reporting successful heterogeneous Fenton-like treatment of organic pollutants, numerous studies have aimed to develop and apply new solid catalysts to CWPO of model compounds and real industrial wastewaters [18,29]. Activated carbons offer most of desirable properties required for catalytic supports such as extended surface area, well-developed porosity and variable surface chemistry [30]. Therefore, they have attracted increasing interest over the last decade [27,28,31,32], which allowed a better understanding of the relation between the chemical and textural properties of the carbon and its catalytic efficiency. However, most of published studies were focused on the degradation of phenolic compounds and nothing had been reported concerning the application of CWPO method to the degradation of pesticide contaminants in the presence of active carbon supported catalyst.

Among numerous compounds, paraquat (PQ) (1,1′-dimethyl-4,4′-bipyridinium chloride) is one of the most widely used herbicides that is marketed as quick-acting, non-selective contact herbicide used at the weed emergence to protect a wide range of crops [33]. PQ is extremely toxic to mammalian and is considered as a potent human poison [34] that should be efficiently removed from contaminated wastewaters, in order to avoid its dangerous accumulation in the environment. Reviewing the literature revealed that there are only few reports investigating the degradation/mineralization of PQ by means of heterogeneous photocatalytic processes, in the presence of TiO_2 in slurry cell [35,36] or as immobilized films [37–39], or UV-ozonation method [40], and very recently, we reported the successful mineralization of PQ by electro-Fenton method [41].

The aim of this research was to study the catalytic wet hydrogen peroxide oxidation of paraquat in the presence of plain and modified activated carbons. The effects of various operational parameters including the AC surface chemistry, hydrogen peroxide concentration, catalyst dosage and working temperature on the kinetic of PQ degradation were carefully analyzed. The decay of paraquat and its degradation intermediates as well as the evolution of chemical oxygen demand (COD) were followed to verify the effectiveness of PQ degradation by CWPO method.

2. Experimental

2.1. Reagents

Unless otherwise stated, all chemicals and organic solvents used in this work were of analytical-reagent grade and used without further purification. Paraquat was an analytical standard purchased from Sigma (purity = 95–98%). Ammonia, sulfuric acid (98%), sodium chloride, ferrous sulfate, potassium iodide, ammonium heptamolybdate, o-phenanthroline, hydroxylamine and hydrogen peroxide (30%) were all purchased from Sigma–Aldrich (France). Methanol and acetonitrile (HPLC grade) were obtained from Prolabo (France). Oxalic, Acetic, formic and succinic acids were analytical grade products obtained from Fluka (France). Impurity-free nitrogen was used for solution de-oxygenation.

The activated carbon used in the present investigation was obtained from Panreac (France) with a particle size of 100–150 μm and a specific surface area, as measured by the BET method, of 986 $m^2\,g^{-1}$. Before usage, the original carbon was thoroughly washed in diluted hydrochloric acid (1 N) for 2 h in order to remove metal oxides components as well as residual physically adsorbed chemicals. Then the carbon was washed in boiling deionised water until circum-neutral pH of the supernatant, oven dried in thin layers at 105 °C for 24 h and kept in desiccator until used. This sample is denoted as (AC).

2.2. Preparation and characterisation of activated carbon catalysts

The plain activated carbon was submitted to various treatments in order to produce catalysts with different surface chemistries. In the first step, plain carbon was treated with 2 M ammonia solution at 25 °C for 2 h then thoroughly washed with deionised water until the pH of the supernatant was constant. Weighed portions of plain carbon (AC) and ammonia-treated carbon (AC_b) were subsequently impregnated with iron solution using a procedure adapted from Zazo et al. [27]. Calculated amount of ferrous nitrate to obtain 4% (w/w) of iron loading on the catalyst are dissolved in the minimum volume of deionised water sufficient to cover the activated carbon powder. After impregnation, all samples were left 2 h at room temperature, dried overnight at 60 °C and finally calcinated at 200 °C during 4 h. The resultant samples are labelled as (AC-Fe) and (AC_b-Fe).

Specific surface areas and pore volumes of the ACs were obtained from low temperature (77 K) nitrogen adsorption isotherms, using a computer controlled gas sorption analyser (ASAP 2000). Samples were outgassed overnight at 300 K prior to the adsorption analysis. The surface area, S_{N_2}, was calculated by applying the BET equation to the corresponding isotherms.

Surface functional groups were determined by standard neutralization-titration with HCl, NaOH, Na_2CO_3, $NaHCO_3$ (0.05 N in water) according to the Boehm procedure [42].

The point of zero charge (pH_{PZC}), was determined by the so-called pH drift method according to the procedure described in the literature [43,44].

2.3. Adsorption and CWPO degradation procedure

All degradation assays were carried out in magnetically stirred 250 mL stoppered conical flasks wrapped in aluminum foil and filled with 200 mL of 20 $mg\,L^{-1}$ paraquat solution. The solution pH was adjusted to 3.0, using sulphuric acid and a Mettler-Toledo 340 pH-meter, to favor an optimum generation of hydroxyl radicals [4]. Treatment was initiated by simultaneous addition of 50 mg powdered catalyst and the required amount of hydrogen peroxide (30%, v/v). The effect of hydrogen peroxide dosage was investigated by amending various initial concentrations corresponding to 1, 2, 5, 10 and 20 times the theoretical stoichiometric amount of H_2O_2 needed for complete mineralization of paraquat (2.41 $mmol\,L^{-1}$). To assess the role of temperature, this parameter was controlled within ±1 °C at the desired value (30, 40, 50, 60 and 70 °C) by immersing the reaction flask in a constant temperature water bath.

At regular time intervals, small volume samples (1 mL) were withdrawn from reaction flask and immediately filtered through 0.2 μm PTFE syringe top filters to remove carbon particles. The sample was then analyzed to follow the degradation of paraquat and its intermediates. To obtain quantitative mineralization of PQ, long-term assays were carried out in the presence of 1 $g\,L^{-1}$ of the