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FeO_x-kaolinite catalysts prepared via a plasma-assisted hydrolytic precipitation approach for Fenton-like reaction

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ABSTRACT

Iron oxides (FeO_x) supported on clay minerals are efficient catalysts for the Fenton-like degradation of organic pollutants in water. This study explores a new preparation route for such catalysts by exploiting the use of gliding arc plasma at atmospheric pressure for the precipitation-deposition of FeO_x particles onto kaolinite. The physicochemical properties of the synthesized catalysts and their activity in the degradation of the azoic dye Acid orange 7 (AO7) are herein evaluated. Results show that the catalysts consist of nanosized goethite fibres onto clay particles. The BET surface area of the catalysts was greater than that of kaolinite and depended on the Fe weight percentage in each catalyst. As a consequence, these materials were very active when tested in the catalytic degradation of AO7 ($C_0 = 25$ mg L^{-1}). Abatement efficiencies of 86% and 50% in terms of bleaching and degradation respectively were obtained after 120 min, in the presence of 0.2 g L^{-1} of catalyst with 9.4 wt% of Fe. Increasing the catalyst dosage enhanced the abatement efficiency. For the catalyst dosage of 3 g L^{-1}, the bleaching and degradation efficiencies were 100% and 80% respectively after only 80 min. Moreover, the catalyst was still active in neutral and basic media, even if lower abatement efficiencies were obtained for neutral and basic dye solutions. On the other hand, the AO7 abatement efficiency of catalyst with 4.4 wt% of Fe was almost equal to that with 9.4 wt%, suggesting that 4.4% of iron in the catalyst is sufficient to transform in a reasonable time, all H_2O_2 into hydroxyl radicals. Finally, the recycling tests showed that the catalysts remain active even after three consecutive uses.

1. Introduction

During the last decades, heterogeneous Fenton catalysis has been pointed as a promising advanced oxidation process to degrade organic pollutants in wastewater. Such process was developed in order to overcome the drawbacks of classic homogeneous Fenton. Indeed, it has been shown that the homogeneous Fenton reaction requires a very low operation pH, and that a large amount of iron sludge is formed during the reaction [1,2]. Consequently, many research works have been done aiming at preparing iron-based materials which can serve as Fenton-like solid catalysts.

In our previous works, we demonstrated that the exposure of an iron (II) aqueous solution to the gliding arc plasma discharge in humid air induces the formation of amorphous iron oxyhydroxide which, in temporal post-discharge, can be transformed into nanostructured porous goethite [3]. The material was rather active as heterogeneous Fenton catalyst for the degradation of Orange II dye. Unfortunately, the nanostructured materials are not highly recommended in industry for applications in real systems because of their small size and their mechanical instability which does not facilitate the removal of the catalyst from solution after reaction [4]. For this purpose, the use of nanosized iron oxides as heterogeneous Fenton catalysts must consider facilitating the catalyst separation at the end of the reaction. This can be done by depositing them onto microsized materials such as sand [5,6], activated carbon [7], zeolites [8], resins [9], etc. Recent studies showed that the use of silica-

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alumina support can improve the performances of the iron oxide based Fenton-like catalyst [10–12]. Such improvement has been attributed to the good dispersion of iron oxide on the surface of support, and to the low hydroxyl radicals scavenging effect of silica compared to that of pure iron oxide [13]. Moreover, previous researches indicated that the alumina added to the catalyst might prevent the iron leaching from the solid catalyst, and thus enhance its recyclability [11]. For this purpose, clay minerals which are layered silica-alumina materials have been intensely investigated as support for heterogeneous Fenton catalysts. For instance, Hassan and Hameed investigated on the Fenton-like bleaching of Reactive Blue 4 using Fe-ball clay prepared by the impregnation method [14]. Daud and Hameed also used Fe-Kaolinite prepared by impregnation for Fenton-like bleaching of Acid Red 1 [15]. More recently, the precipitation method was used by Fida et al. to prepare La-Fe montmorillonite catalyst for the degradation of Methylene blue and Rhodamine B [16]. Finally, Fe-pillared clays were investigated in many works as heterogeneous (photo)Fenton catalysts [17,18]. Unfortunately, the impregnation and pillarization techniques are quiet expensive, since they sometime require the use of precipitating reagent (strong bases), high temperatures (400 °C–500 °C) and long processing time (several ours).

Herein, we investigate on the use of non-thermal gliding arc plasma technique for the synthesis of FeO_x-kaolinite composites via hydrolytic precipitation, and to evaluate the catalytic performance of such materials in Fenton-like degradation of the organic Acid orange 7 (AO7) dye. Kaolinite is a clay mineral from the family of T-O phyllosilicates. The most well-known and the oldest application of this layered silica-alumina material is its use as raw material for the production of traditional ceramics [19,20]. The use of kaolinite in catalysis is not so frequent, probably because of its low surface area compared to that of other clay materials. However, the surface of the kaolinite is very rich in hydroxyl groups - the main ion exchange sites - which confers it interesting chemical properties. These characteristics of kaolinite (i.e low surface area and the presence of hydroxyl groups) served as the starting hypothesis for this work. The aim here is to obtain a composite material in which the FeO_x nanoparticles are not trapped inside the pores, but are dispersed on the surface of clay particles. Indeed, a good dispersion of FeO_x on the external surface of kaolinite will favour good contact with dye molecules, and thus enhance their abatement efficiency. This may be possible if the precipitation-deposition process of FeO_x on the clay surface is governed by a mechanism closely linked to the surface hydroxyls of kaolinite. The most important merit of the gliding arc plasma assisted hydrolytic precipitation technique as compared with other methods consists in the fact that it only requests mild conditions and a short processing time. Moreover, the only chemical used (apart the iron precursor) is humid air which is non-pollutant, available and renewable. The synthesized materials were characterized by Inductively Coupled Plasma-Atomic Electron Spectroscopy (ICP-AES), X-ray Diffractometry (XRD), Scanning Electron Microscopy (SEM), N_2-physisorption, Thermogravimetric analyses and Temperature Programmed Reduction of Hydrogen (H_2-TPR).

2. Materials and methods

2.1. Materials

Kaolinite was obtained from Local Materials Promotion Authority (MIPROMALO), Cameroon. The analytical grade ammonium iron (II) sulphate hexahydrate [$(NH_4)_2Fe(SO_4)_2 \cdot 6H_2O$] was purchased from Sigma-Aldrich (Belgium). The Acid Orange 7 dye selected as a model pollutant - because of its use in textile and food industry - was obtained from Sigma-Aldrich (CAS Number: 633-96-5; Colour Index Number: 15510) and was used without any purification.

2.2. Methods

2.2.1. Catalysts preparation

The FeO_x-kaolinite composites synthesis was done by plasma assisted precipitation-deposition of FeO_x onto the surface of clay particles, using a gliding arc batch reactor. The design of such reactor is described elsewhere [3,21]. To this end, 2 g of $(NH_4)_2Fe(SO_4)_2.6H_2O$ (i.e the FeO_x precursor) was dissolved in 400 mL of distilled water to obtain a 5 g L^{-1} iron (II) solution. A known mass of kaolinite (2 g or 4 g) was then added to the precursor solution. The whole was stirred vigorously for 30 min to ensure a good dispersion of the clay particles and then, the white suspension was exposed to the plasma discharge under magnetic stirring. After 60 min of treatment, the yellow-brown paste obtained (Fig. 1) was collected by vacuum filtration using a 0.45 μm Millipore filter, washed repeatedly with deionized water and dried at 80 °C for 24 h. The resulting material was named as K-FeOx-m/2-0H where *m* denotes the mass of kaolinite introduced into the solution containing 2 g of precursor. A part of the yellow-brown paste was further aged with the plasma shut off and without stirring in the reactor at 98 °C for 1 h–3 h, before being collected. The material obtained after ageing was named as K-FeOx-m/2-dH where *d* denotes the ageing duration.

2.2.2. Catalysts characterization

The weight percentage of Fe in the pristine clay and in the synthesized catalysts was measured by inductively coupled plasma-atomic emission spectroscopy (ICP-AES) on Iris Advantage apparatus from Jarrell Ash Corporation. The X-ray diffraction (XRD) analyses were done on a Siemens D5000 diffractometer using the Kα radiation of Cu ($\lambda = 1.5418$ Å). The 2θ range was recorded between 5° and 70° at a rate of $0.02° s^{-1}$. The ICDD-JCPDS database was used to identify the crystalline phases. Scanning Electron Microscopy (SEM) was done on a LEO 983 GEMINI microscope equipped with a field emission gun. The uncoated samples were exposed to an acceleration voltage of 1 kV. The N_2-physisorption analyses were carried out on Micromeritics Tristar 3000 equipment. Before measurement, the samples were outgassed at 90 °C overnight under vacuum. The specific surface area was calculated using the Brunauer-Emmet-Teller (BET) equation whereas the pores size and volume were calculated using the Barrett-Joyner-Halenda (BJH) model. The thermogravimetric analyses (TGA)

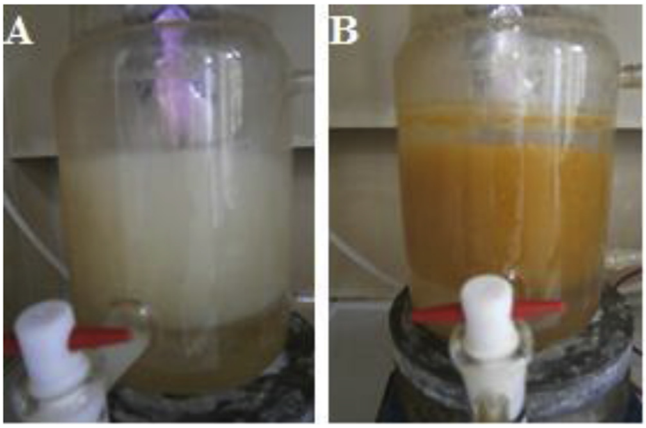

Fig. 1. Plasma reactor containing kaolinite suspension in iron(II) solution before (A) and after plasma-treatment for 60 min (B).