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Efficiency of natural clay as heterogeneous Fenton and photo-Fenton catalyst for phenol and tyrosol degradation

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ABSTRACT

Advanced oxidation processes (AOPs) are particularly useful for cleaning toxic or non-biodegradable materials in wastewater. Among these processes, the advantage of the Fenton processes is the potentially complete mineralization of organic substances. In this work, a naturally containing Fe-clay naturally red clay (NRC) was used as heterogeneous catalyst for the Fenton and photo-Fenton oxidation of two organic pollutants (phenol and tyrosol). NRC was characterized by several complementary methods including chemical analysis, X-ray diffraction, temperature programmed reduction, scanning electron microscopy, and energy-dispersive X-ray spectroscopy. The influence of different parameters like calcination's temperature and initial H_2O_2 concentration were examined considering both the pollutant conversion and the total organic carbon (TOC) abatement. This catalyst was very efficient for the mineralization of both compounds in aqueous medium under mild experimental conditions. Indeed, 100% pollutant conversion could be achieved for both pollutants with a TOC abatement of 90 and 85%, respectively, for phenol and tyrosol by photo-Fenton oxidation. Catalytic activity of NRC was mainly attributed to the amount of iron oxide species (12 wt.%) present naturally in the clay.

Keywords: Clay; Phenol; Tyrosol; Fenton; Photo-Fenton; TOC abatement

1. Introduction

Industrial processes generate a wide variety of wastewaters containing organic pollutants with negative impact for ecosystems. In accordance with the increasingly stringent environmental legislation, the effective pollutants degradation or removal is a challenging task that is implying the development of advanced and economic viable advanced oxidation processes (AOPs) [1]. These processes aim to the mineralisation of the organic pollutants to CO_2, H_2O and inorganics or, at least into harmless products [2]. Only

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wastes with relatively small chemical oxidation demand (COD) content ($\leqslant 5\,\mathrm{g\,L^{-1}}$), could be suitably treated by means of these processes. Higher COD contents would require the consumption of too large amounts of expensive reactants, they can be more conveniently treated by wet oxidation or incineration [3].

One of the most promising AOPs is based on the use of the Fenton reagent ($H_2O_2 + Fe^{2+}$), commonly carried out in homogeneous phase. Oxidation with the Fenton's reagent has already proved to be effective and promising for the destruction of several compounds, and consequently for the treatment of a wide range of wastewaters, as described in several reviews [4,5]. The photo-Fenton process is rather similar to the Fenton one, but employing also radiation. However, in order to overcome the major drawbacks of the homogeneous system (iron removal, etc.), heterogeneous Fenton-type systems have been developed to catalyse the oxidation of various organic compounds in mild reaction conditions [6].

A wide range of solid materials, such as transition metal-exchanged zeolites, pillared interlayered clays containing iron or copper species, and iron-oxide minerals have been proposed as heterogeneous catalysts for the oxidative degradation of organic compounds through the Fenton-like reaction [4]. By combining the efficiency of the homogeneous Fenton process with the advantages of heterogeneous catalysis, these materials show great promise for the treatment of highly recalcitrant organic pollutants. The use of clays as catalysts for Fenton-like reactions is therefore a promising alternative for decontamination of soils, groundwater, sediments, and industrial effluents because they are natural, abundant, inexpensive, and environmentally friendly [5].

To avoid all the disadvantages of catalysts synthesis, natural containing Fe-clay (NRC) could be an interesting alternative as heterogeneous catalyst. In this study, the efficiency of a Tunisian containing Fe-clay was investigated in the Fenton-like and photo-Fenton-like oxidation of two harmful pollutants (phenol and tyrosol) in aqueous media, under mild experimental conditions (ambient temperature and pressure). The influence of different parameters like calcination's temperature and initial pollutant concentrations were examined considering both pollutant conversion and total organic carbon (TOC) abatement.

2. Materials and methods

2.1. Materials

Phenol (99 + %), H_2O_2 (30 wt.%) of analytical reagent grade (Aldrich), Tyrosol (98%) (ACROS Organics), acetonitrile, and water of high-performance liquid chromatography (HPLC) grade (Panreac) were used without further purification. A natural containing Fe-clay sampled in Jebel Tejera-Esghira (33°21´ 55.13´´ N, 10°30´35.30´´ E), 9 km Northeast Medenine (Tunisian Southeast) was used as catalyst.

2.2. Catalyst characterization

The chemical composition of the clay was determined by X-ray fluorescence with an ARL® 9,800 XP spectrometer. Characterization by X-ray diffraction (XRD) was realized using a Philips® PW 1,710 employing Cu Kα filtred radiation ($\lambda = 1.5418\,\text{Å}$). The temperature programmed reduction (TPR) profiles were recorded from 25 up to 900°C at a heating rate of $5^\circ\mathrm{C\,min^{-1}}$ in a flow of 5% H_2/Ar ($30\,\mathrm{mL\,min^{-1}}$) using an Altamira AMI-200 apparatus. Hydrogen consumption was monitored and integrated using thermal conductivity detection (TCD) over the whole temperature range. The specific surface area was determined by nitrogen adsorption at −196°C on a Qsurf M1 apparatus (Thermo Electron Corporation). Scanning electron microscopy (SEM) analysis was performed with a LEO 438VP microscope equipped with energy-dispersive X-ray spectroscopy (EDX) (ISIS 300) analyser.

2.3. Fenton and photo Fenton degradation of phenol and tyrosol

Catalytic tests were performed in aqueous medium at ambient conditions (atmospheric pressure and at room temperature) in a thermostated perfectly stirred Pyrex reactor of 250 mL. The reactor was equipped with a pH electrode to measure constantly the pH variation of the reaction medium. In each test, the reactor was loaded with 100 mL of phenol or tyrosol solution (0.5 mM, pH 3 for Fenton, and pH 5 for photo-Fenton reaction) and 100 mg of catalyst. The solution was equilibrated during 60 min, and then analyzed to confirm the absence of adsorption by the clay. About 7 mM or 10 mM of hydrogen peroxide (30 wt.%) was added to initiate the reaction in the case of phenol and tyrosol, respectively (the theoretical initial concentration required for the entire mineralization of pollutant). High performance liquid chromatography (HPLC, Waters 600) was used to measure the pollutant conversion. At given intervals, a low amount of 0.5 mL was removed from solution to follow the course of pollutant conversion. The reaction was stopped by adding 0.5 mL of methanol and the samples were filtered with 0.45 μm syringe filter before HPLC analysis. At the end of each trial, the

TOC content of the solution was measured by a Shimadzu TOC-V_{CSH} analyzer. Photo-Fenton reaction was carried in the same condition by using a low pressure UV lamp (Heliosquartz, Italy) as light source and a Pyrex reactor. Experimental tests were carried out three times. HPLC and TOC analysis were performed two times.

3. Results and discussion

3.1. Catalyst characterization

Chemical analysis of raw clay showed that NRC was mainly composed of (in wt.%) SiO_2 (54%), Al_2O_3 (24%), and Fe_2O_3 (12%). Other oxides were also present in lower amounts. The percentage of iron oxide (12 wt.%) is high when compared to the other natural clay used in catalytic wet peroxide oxidation of phenol [7]. This high iron content explains the red color of the clay. The measured specific surface area was $50\,m^2\,g^{-1}$.

These results were confirmed by XRD analysis (Fig. 1). Data were analyzed by the MAUD program.

The reduction profile of the raw clay (Fig. 2a) displayed two hydrogen consumption peaks in the 400–700°C range, typical to the reduction profile of Fe_2O_3 [8]. The first peak was attributed to the reduction of Fe_2O_3 to Fe_3O_4, and the second peak to the second reduction step from Fe_3O_4 to metallic iron [9–11].

The profile observed within 400–500°C was similar to the profile obtained with pure α-Fe_2O_3, and can be ascribed to the reduction of easily accessible trivalent cations Fe^{3+} to Fe^{2+} [12]. In the case of calcined samples (Fig. 2(b–e)), only one reduction peak was really observed. The first reduction peak seemed to be lowered or hidden in the second, which was wider for calcined samples. Moreover, a shift of the Fe_2O_3 reduction peak to low temperature was especially observed for the samples calcined at 450 and 550°C; this property could lead to a higher activity of these samples for phenol oxidation by an easier reduction of the iron species.

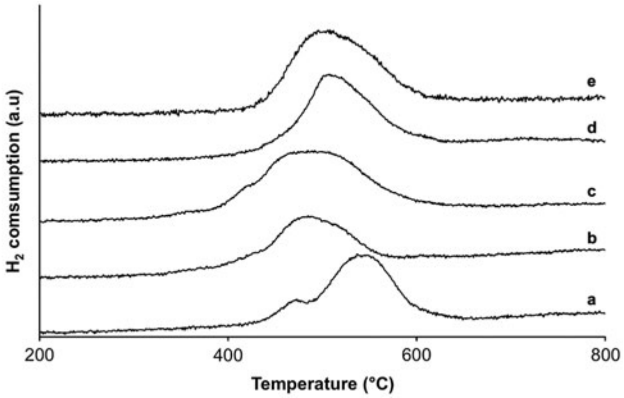

Fig. 2. TPR of NRC (a) not calcined, calcined at (b) 450°C, (c) 550°C, (d) 650°C, and (e) 800°C.

The SEM images (Fig. 3) show the morphologies of the clay before and after calcination. There was no significant change on the morphology and on the raw (Fig. 3a) and calcined clay (Fig. 3b). EDX analysis indicated that the clay is Si- and Al-rich with low Mg and K, and high Fe contents.

3.2. Catalytic activity

3.2.1. Fenton and photo Fenton like reaction

The phenol conversion curves obtained by Fenton oxidation of phenol with sieved samples

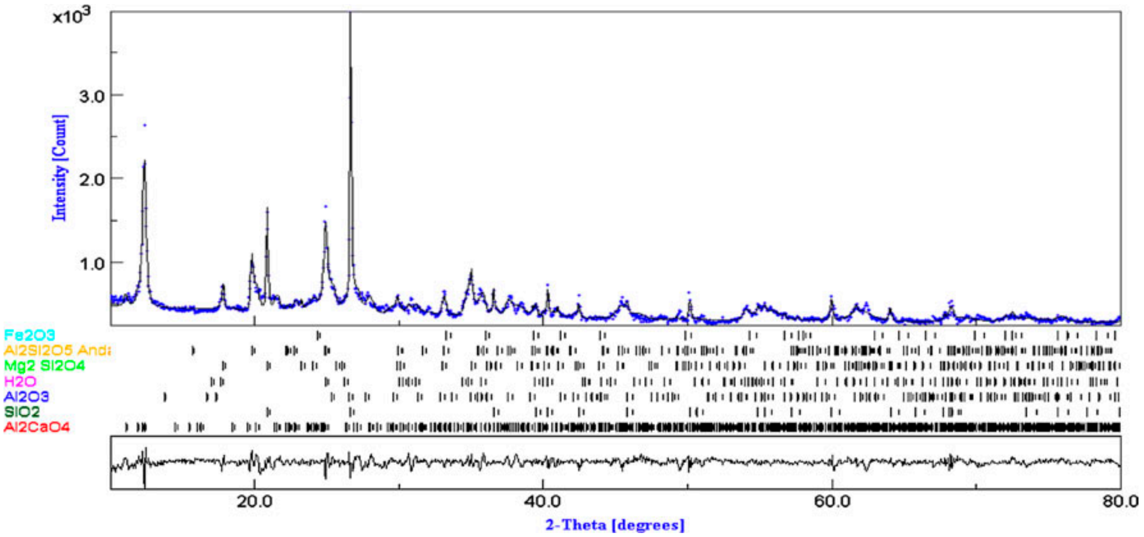

Fig. 1. XRD of NRC.

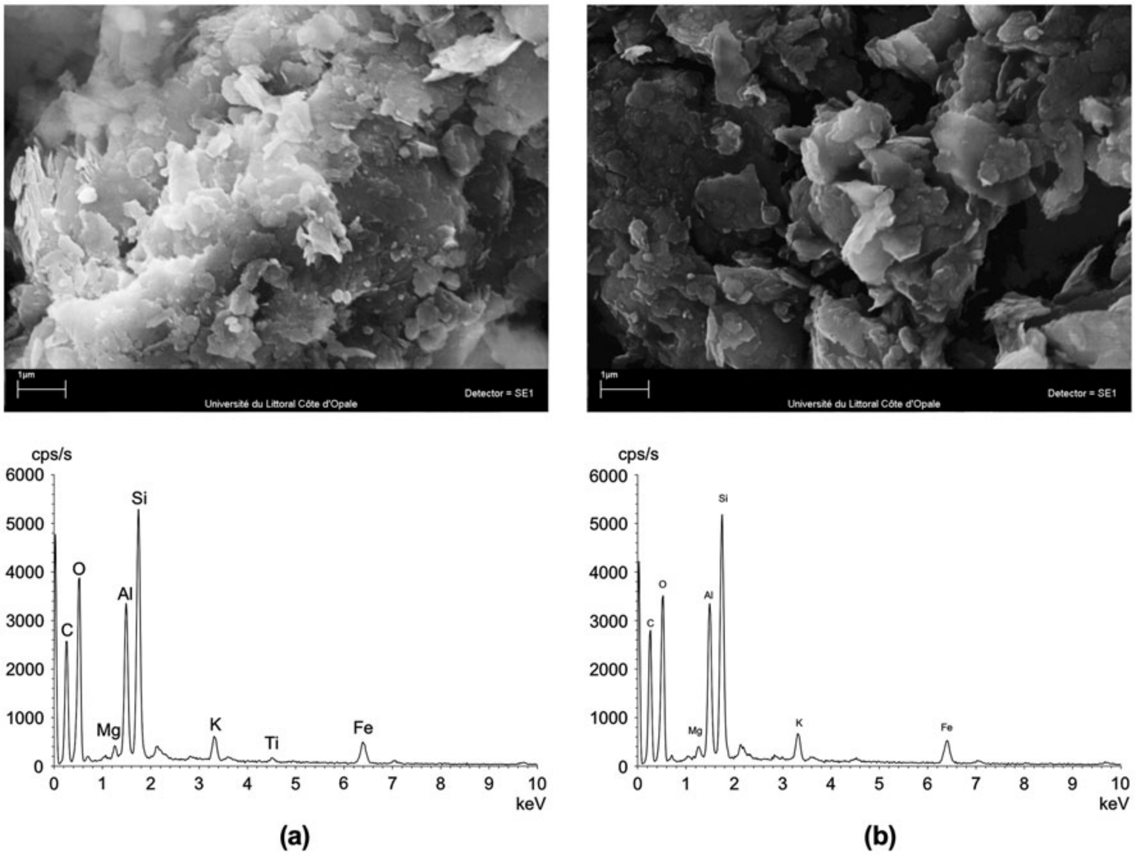

Fig. 3. SEM images and EDX analysis for (a) raw and (b) calcined clay.

(d < 50 µm) of NRC at different calcination temperatures (450, 550, 650, and 800°C) are presented in Fig. 4. All the curves displayed a sigmoidal profile with three different periods. An induction period of 3 h followed by a rapid oxidation of phenol is observed. The existence of an induction period has been observed in several studied using pillared catalysts [13]. This period was often ascribed to the time required for the activation of the surface catalyst. A very low catalytic activity is observed with the non calcined clay. The best results are obtained with the clay calcined at 450°C; calcination at higher temperature did not lead to higher catalytic activities.

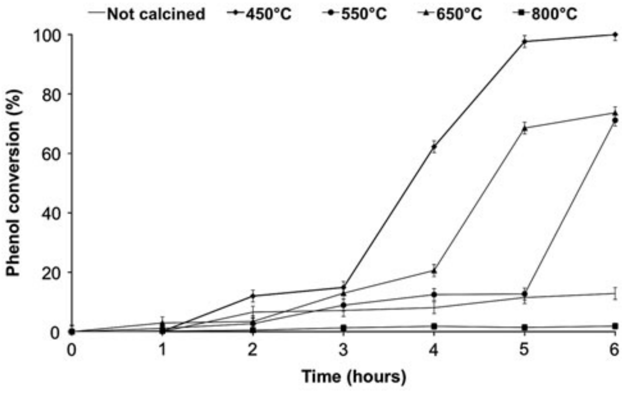

Fig. 4. Catalytic activity of NRC in the Fenton oxidation of phenol at various calcination temperature.

The effect of H_2O_2 dosage on phenol conversion was also examined by varying the initial concentration of H_2O_2 from 3.5 to 14 mM. A maximum of TOC conversion was obtained with a concentration of 7 mM (the theoretical initial concentration required for the entire mineralization of phenol).

The best TOC abatement (70%) was obtained with NRC (d < 50/450°C) in phenol Fenton-like oxidation (Fig. 5). This result was very promising compared with other studies using natural calcined clays, or pillared clays [7,13–15]. Indeed, in these studies, a good phenol conversion and TOC abatment are usually obtained at higher temperatures (>70°C), with higher peroxide concentrations (>50 mM) or at higher iron contents (>15 wt.%) for the same phenol concentration used in our study. No significant conversion was

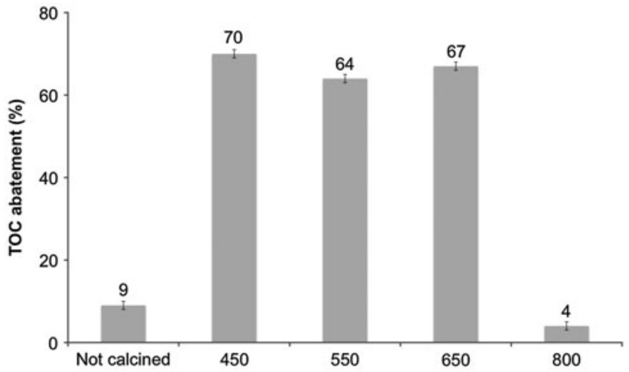

Fig. 5. TOC conversion after phenol Fenton-like oxidation using NRC.

obtained for tyrosol by Fenton oxidation in similar experimental conditions.

Moreover, in this kind of heterogeneous catalyst containing Fe^{3+} oxides the reduction of Fe^{3+} to Fe^{2+} is accelerated under ultraviolet radiation [4]. The photo-Fenton or photo-Fenton-like process is generally more efficient than the Fenton or Fenton-like process. The light source may affect significantly the performance in photo-Fenton degradation. Different light sources have been tested for phenol degradation with clay materials [16]. Results showed that the use of UV-C radiation, even at lower intensity, provided better conversion values because UV-C is absorbed more effectively by the different species present in the system (Fe (III) compounds, pollutant, and H_2O_2). Consequently, a low pressure UV lamp (15 W) with wavelength of 254 nm was used in this study.

The catalyst achieved 100% of phenol conversion in a maximum of 16 minutes whatever the calcination temperature may be (Fig. 6). In all experiments TOC abatement was up to 60%, the optimal one was 90% using sieved (d < 50) NRC calcined at 450°C (Fig. 7).

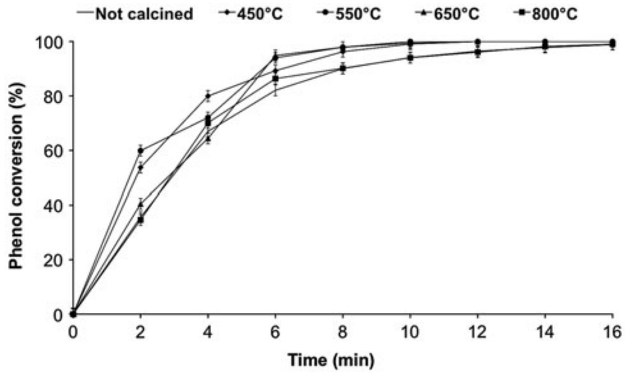

Fig. 6. Catalytic activity of NRC in phenol photo-Fenton-like oxidation.

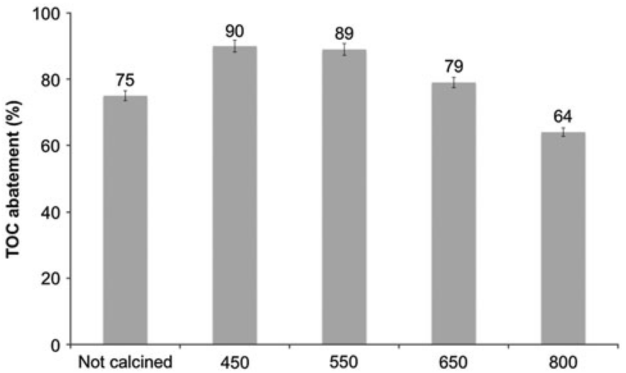

Fig. 7. TOC conversion after phenol photo-Fenton-like oxidation using NRC.

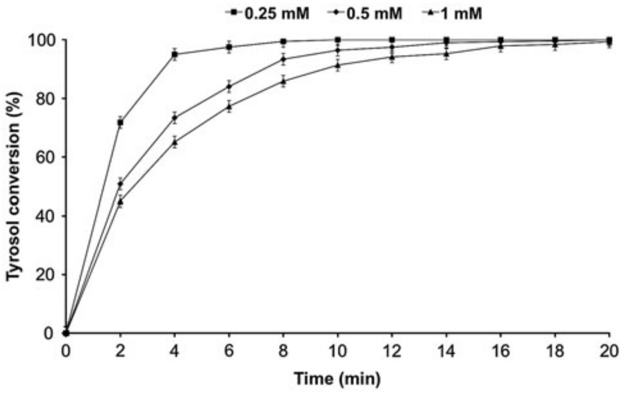

Fig. 8. Photo-Fenton degradation of tyrosol at different concentrations.

The most efficient catalyst (d < 50/450°C) was chosen as catalyst in the photo-Fenton oxidation of tyrosol. In this case, the effect of pollutant concentration was investigated (Fig. 8). 100% tyrosol conversion was reached after 18 min reaction, even for the most concentred solution (1 mM). However, the TOC abatement is dependant on the tyrosol initial concentration (Fig. 9).

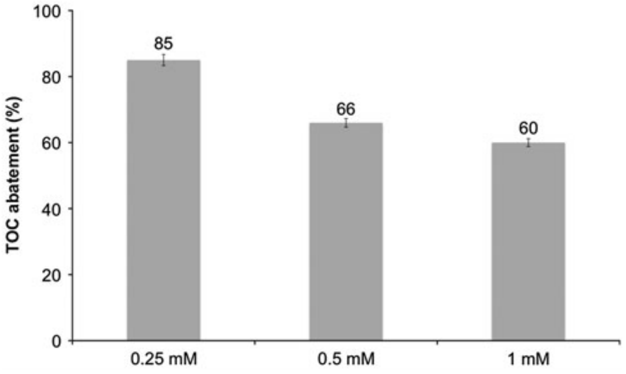

Fig. 9. TOC conversion for tyrosol photo-Fenton oxidation using NRC(d<50/450°C).

For both pollutants, no induction period was observed in the photo-Fenton oxidation contrary to the Fenton oxidation. These results demonstrated that the reduction of Fe^{3+}–Fe^{2+} is the limiting factor in the Fenton process, and that this reduction is indeed accelerated by UV radiation.

4. Conclusion

In this study, we report for the first time the use of a natural containing Fe-clay for the heterogeneous Fenton-like and photo-Fenton-like oxidation of two organic pollutant. A total phenol conversion and a 70% TOC removal were obtained within a period of 6 h at ambient temperature, atmospheric pressure and low concentration of hydrogen peroxide by Fenton oxidation using sieved and calcined NRC ($d < 50/450$°C). A total phenol and tyrosol conversion was also obtained in less than 20 min by photo-Fenton-like oxidation. Characterization of the clay has shown that the major iron species present and responsible for the catalytic performance was Fe_2O_3. The high stability of the clay in the reaction condition and its good catalytic performance in pollutant conversion and TOC abatement showed great promise for the treatment of organic pollutant in wastewater.

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