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Natural diatomites: Efficient green catalyst for Fenton-like oxidation of Orange II

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ABSTRACT

The Fenton-like oxidation of the anionic azo-dye Orange II (100–500 mg/L) was batchwise performed using commercial grade diatomites (3.5% Fe content) thermally treated.

Solid samples were thoroughly characterized by several techniques. Peroxidation experiments were performed varying the diatomite calcination temperature (500, 700, 1000 °C), reaction temperature (50, 60, 70, 80 °C), catalyst load (0.47, 0.94, 1.89 and 3.78 g), H_2O_2 concentration (11.0, 13.7, 20.6 mmol/L) and dosing, pH (2–3.5) and initial dye concentration (0.28, 0.57, 1.43 mmol/L). The influence of NaCl and oxalic acid on the catalytic performance and stability was also addressed.

The best results were obtained with samples calcined at 700 °C, with initial pH 3, at 70 °C and using the stoichiometric amount of H_2O_2, since complete decoloration, TOC reduction close to 67% and negligible Fe leaching were achieved. The stability of the catalyst maintains after 20 h of usage, with a final Fe loss of 2.25%. An average of 0.88 mg/L of iron leached after each run, which is below the discharge limit.

1. Introduction

Diatomite occurs as abundant sedimentary accumulations of siliceous skeletons (frustules) of microscopic aquatic plants known as diatoms [1]. Its composition mainly includes opal or hydrous silica (SiO_2–H_2O), usually 70–90%, but also alumina (0.6–8%), iron (0.2–3.5%), alkali metal oxides, Na_2O and MgO (less than 1%), CaO (0.3–3%) and minor amounts of other impurities, such as P_2O_5 and TiO_2 [2]. Sand, clay, carbonate and organic material are typical contaminants, however the latter ones decompose into gaseous CO_2, SO_2 and H_2O during calcination, leaving the bulk of diatomite [3]. Due to its extremely porous structure, low density and high surface area, they are used for adsorption of organic chemicals [2,4–8] and heavy metal removal [9–13].

Diatomite has also been employed as a catalyst support for several reactions: oil hydrogenation [14], hydration of acrylonitrile [15], Fischer–Tropsch synthesis [16], hydrocarbons oxidation [1], photodegradation of industrial wastes [17,18], photoelectro-Fenton of industrial wastewaters [19], and phenol hydroxylation [20]. Nevertheless, the use of diatomite as a catalyst rather as catalyst support has not been extensively studied [21], although, the presence of a high percentage of iron would enable its use as a heterogeneous Fenton-like catalyst without requiring major modifications.

The closest antecedent to the employ of this material in Fenton processes is the use of zeolites, clays and natural oxides. These materials have been widely tested in Fenton-like oxidation reactions, giving in several cases a high level of mineralization and reduced leaching of the active phase [22–24]. Also, the study of pillared clays (PILC) as Fenton catalysts has been frequently reported, being the preferred materials for the degradation of organic pollutants [24].

There is not a full consensus about the Fenton-like mechanism with supported iron species and this is related to the variation in the Fe coordination environment in diverse materials, such as pure iron oxides, clays or diatomites.

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Lin and Gurol [25] studied the decomposition of H_2O_2 on iron oxide and summarized the mechanism of Fe^{3+}-initiated chain reaction through the following sequence:

$$—Fe^{III}—OH + H_2O_2 \leftrightarrow (H_2O_2)_S$$

$$(H_2O_2)_S \rightarrow —Fe^{II} + H_2O + HO_2^{\bullet}$$

$$—Fe^{II} + H_2O_2 \rightarrow Fe^{III}—OH + {}^{\bullet}OH$$

$$2HO_2 \leftrightarrow H^+ + O_2^{\bullet -}$$

$$—Fe^{III}—OH + HO_2/O_2^{\bullet -} \rightarrow -Fe^{II} + H_2O/OH^- + O_2$$

The initiation reaction in systems involving iron oxides is expected to be the interaction of H_2O_2 with Fe(III) sites on the surface. The reactions are initiated by the formation of a precursor surface complex of H_2O_2 with the oxide surface. The protonation equilibria of unoccupied surface groups, that is, the species $—Fe^{III}—OH_2^+$ and $—Fe^{III}—O^-$, affects the H_2O_2 decomposition. Furthermore, under acidic conditions the dissolution of iron oxides occurs and the presence of some organic compounds generates the iron solubility via complexation and reductive dissolution, which promotes the homogeneous Fenton contribution [26].

The different activity of iron supported catalysts is influenced by the cation dispersion in the support, iron valence, surface area, point of zero charge, and the presence of different iron species, for example in clays, iron could be in the form of free iron oxides, structural iron in the clay lattice or complexed iron [27].

The application of diatomite as a Fenton catalyst is attractive and innovative as it is a low cost material, widely available from a sustainable source with a high content of Fe, key in the Fenton reaction mechanism. These characteristics agree well with some of the "green chemistry" principles, such as the employment of alternative feedstocks that are more innocuous and the design of eco-compatible chemicals [28]. In this context, the aim of this study is to explore the use of natural Argentinian diatomite as a Fenton-like catalyst for the degradation of Orange II (OII), which belongs to the wide family of the azo-dyes.

Orange II, also known as Acid Orange 7, has a synthetic origin and a complex aromatic structure with two aromatic rings (a benzene ring and a naphthalene ring), a sulfonated group and an azo bond (—N=N—). This poorly biodegradable azo-dye is widely used in the dyeing of textiles and cosmetics, and extensively found in the wastewaters of the related industries [29]. For this reason, several authors have investigated the OII degradation through Fenton and Fenton-like processes as listed in Table 1.

Most researchers obtained high OII conversions, but rarely report TOC reduction data. Using heterogeneous catalysts, best results in terms of decoloration and TOC reduction (only owned to peroxidation) were obtained by Ramírez et al. [30,31] for the oxidation of 35 mg/L solutions of OII using high loaded Fe-saponite based samples. With higher OII concentrations (100 mg/L), best results were obtained with the homogeneous reaction [32].

According to the literature, there exists a complex network of interactions between the species involved in the Fenton process, which depends on the concentration of oxidant, catalyst and pollutant, catalyst nature, pH and temperature. All of these parameters define the efficiency of the process and the degree of mineralization. Therefore, in the present study, several operating conditions were studied to evaluate the performance of commercial diatomites thermally treated for their use as a Fenton-like catalyst over the oxidation of Orange II.

2. Experimental

2.1. Catalyst preparation

The diatomite sample was purchased from a local supplier (Marysol), harvested from a deposit located in Ing. Jacobacci, Río Negro, Argentina. The raw diatomite was sieved and the fraction 7–8 mesh (2.38–2.83 mm) collected. Then, it was separated in different portions, which were subsequently calcined at three different final temperatures, 500, 700 and 1000 °C, under air atmosphere in a programmable furnace, applying a heating rate of 10 °C/min, from room temperature to the selected calcination temperature. The samples were left in the furnace for 5 h at the calcination temperature.

2.2. Catalyst characterization

The Fe content of the catalyst was determined by inductively coupled plasma-atomic emission spectroscopy (ICP-OES, Spectro Arcos) after microwave-assisted digestion of the samples.

Specific surface area and pore volume of the catalysts were determined by N_2 adsorption/desorption at 77 K, using a Micromeritics ASAP 2000 surface analyzer. The samples were outgassed overnight at 523 K prior to the adsorption analysis.

Powder X-ray diffraction (XRD) patterns of the samples were obtained with a Siemens model of D5000 diffractometer employing Cu Ka radiation. The X-ray was operated at 40 kV and 30 mA. The patterns were recorded over $5° < 2\theta < 75°$ angles, and compared to the X-ray powder files to confirm phase identities.

Thermogravimetric analyses (TGA) were performed in a TGA-50 Shimadzu equipment with thermal analyzer TA-50 WSI, using a heating rate of 10 °C/min, under an oxygen flow of 30 mL/min. Diatomites were pulverized and samples of 20 mg were taken. The curves were recorded simultaneously along with the temperature increment.

The chemical composition analysis of samples was performed by X-ray fluorescence (XRF) using a Philips PW2540 Magix spectrophotometer yielding the weight percentage of each constituting element. A constraint of X-ray fluorescence spectroscopy is its inability to analyze elements with an atomic number below 11 (Na).

The surface morphology was investigated by means of a scanning electron microscope JEOL JSM-6460LV. The elemental composition was determined by energy dispersive X-ray spectroscopy (EDS) using an EDAX Genesis XM4-Sys60 equipment.

Different species in the sample were identified by Fourier transform infrared/attenuated total reflection spectroscopy, (FTIR/ATR Nicolet 6700). Spectra were recorded in the region of 4000–400 cm^{-1}, at room temperature by performing 64 scans with a resolution of 2 cm^{-1}.

Mössbauer spectra were obtained at room temperature (RT) with a conventional constant acceleration spectrometer in transmission geometry with a $^{57}Co/Rh$ source. Measurements were recorded at 10 mm/s and then fitted using the Normos program developed by Brand [44]. Isomer shift values are given relative to that of α-Fe at RT.

The point of zero charge (PZC), where the total concentration of surface anionic sites equals the total concentration of surface cationic sites, was determined by the mass titration method, reported by Preocanin and Kallay [45]. Finally, the surface charge was determined by the acid titration method [46].