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Characterisation of silica-supported Fe–Ni bimetallic nanoparticles and kinetic study of reductive degradation of the drug nimesulide

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ABSTRACT

Ni–Fe bimetallic nanoparticle assemblies with diameter of 20–200 nm were synthesised on surface of silica and applied for reductive degradation of the drug nimesulide in aqueous solution. The bimetallic nanoparticles was synthesised as a function of the Ni content: 8 wt.% Ni + 92 wt.% Fe, 18% wt.% Ni + 82 wt.% Fe, and 34 wt.% Ni + 66 wt.% Fe. SEM images confirmed that the nanoparticles were uniformly anchored on silica. EDS analysis confirmed the presence of Fe, Ni and silica in the samples, while XRD analysis showed presence of the Fe^0 and Fe_2O_3/Fe_3O_4 structures. The reductive degradation of nimesulide with silica-supported bimetallic nanoparticles containing 8 wt.% Ni was carried out under batch conditions using an agitation frequency of 250 rpm. The formation of by-products was monitored using the LC-ESI–MS technique. A complete removal of nimesulide (50 mg L^{-1}) was achieved after 15 min of reaction with silica-supported bimetallic nanoparticles containing 8 wt.% Ni (6.0 g L^{-1}). The influence of the external and internal mass-transfer limitations were evaluated and a theoretical analysis of the reductive reaction was presented. It was verified that the degradation of nimesulide is characterised by reduction of the nitro group and removal of the sulphonyl group with formation of an amine and thioester aromatic derivative product. The present work indicates that the reductive treatment process making use of silica-supported bimetallic nanoparticles containing Fe and Ni is very promising for the elimination of the nitro moiety present in nimesulide.

1. Introduction

The scientific community is verifying with increasing frequency that many chemicals which have not historically been considered as contaminants are present in the environment on a global scale. These “emerging contaminants” caused by anthropic activities are commonly found in municipal, agricultural, and industrial wastewater sources. In recent years, monitoring studies have revealed the occurrence of several different types of emerging contaminants (e.g., drugs, pesticides, personal care products, etc.) in wastewater, as well as in contaminated natural waters, such as rivers and lakes neighbouring urban areas [1–4].

The impact of most of the emerging contaminants on the health of people and aquatic life remains unclear because these pollutants show up in low levels (e.g., parts per billion or parts per trillion). However, aquatic life and humans are not exposed to just one pollutant at a time but, rather, to a whole mix of different substances. From these considerations, there is a common sense that better water treatment technologies are needed in order to ensure that water of high quality is delivered to the population [3–5]. Therefore, pollution control in contaminated waters must be addressed by making use of non-conventional treatment technologies, such as advanced water treatment technologies that can adequately convert the recalcitrant pollution burden to less environmentally harmful substances [6,7].

In this scenario, the drug nimesulide (NMS) belongs to the class of emerging contaminants because it can be found in domestic sewage as well as in hospital wastewaters [3,4]. For instance, a concentration value of 9.731 $\mu g\,L^{-1}$ for NMS was recently reported by Papageorgiou et al. [3] for the effluent of a wastewater treatment plant. Nimesulide, or *N*-[4-nitro-2-(phenoxy)phenyl] methanesulphonamide, which is a nitro aromatic compound

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(NAC), is a selective non-steroidal anti-inflammatory drug (NSAID) belonging to the sulphonanilide group. This drug is one of the ten best-selling drugs in Brazil due to its superior efficacy when compared to other similar drugs such as ibuprofen, diclofenac and piroxicam [8]. Fig. 1 shows the molecular structure of nimesulide ($C_{13}H_{12}N_2O_5S$), which consists of two rings (e.g., phenyl and nitrophenyl groups) interconnected by an oxygen atom, forming an angle of 74.69° in the crystalline form [9].

The deleterious effects of NACs in the environment are caused by the nitro aromatic moiety present in the molecule [10]. Fortunately, these undesirable effects can be avoided by chemical reduction of the nitro group using metallic nanoparticles such as zero-valent iron (e.g., ZVIn) [10]. The introduction of a second metal (e.g., Co, Ni or Pd) together with iron in order to obtain bimetallic nanoparticle systems (e.g., bNP-Fe–Ni) allow us to modulate the catalytic activity of the iron nanoclusters towards the reductive degradation/removal of organic pollutants [11–15]. In fact, due to differences in the standard redox potentials of the different metals, the use of bimetallic systems presents an advantage over the monometallic systems (e.g., ZVIn) since they permit the catalytic cleavage of the hydrogen molecules generated during oxidation of Fe^0 thus originating the $H^{\bullet}_{(ads)}$ radicals adsorbed on surface of the more noble metal (e.g., Ni^0). Afterwards, by means of "bimetallic interface reactions" the catalytic degradation of organic pollutants is caused by incorporation of the adsorbed atomic hydrogen (e.g., H.(ads) radicals) in the molecular structure of the target pollutant thus leading to the reductive degradation reaction [16].

From the above considerations, the choice of Ni as a second metal is of great interest due to its less negative redox potential ($E^0(Ni^{2+}/Ni^0) = -0.23$ V) in relation to iron ($E^0(Fe^{2+}/Fe^0) = -0.44$ V). For instance, in the case of cobalt the difference in the redox potential in relation to iron is less pronounced since $E^0(Co^{2+}/Co^0) = -0.28$ V and, therefore, the catalytic activity of this metal for the reductive degradation reaction would be less pronounced in comparison to nickel. In addition, the use of Ni instead of Co requires a lower cost.

Metallic (e.g., zero-valent iron, ZVIn) and bimetallic (e.g., bNP-Fe–Ni) nanoparticles are promising candidates for the removal of heavy metals and organic pollutants from water, wastewater and soil [10–11,15–26]. Due to their intrinsic magnetic properties, these nanoparticles are prone to agglomeration; therefore, the metallic nanoparticles are sometimes stabilised (e.g., encapsulated) with carboxymethyl cellulose (CMC) or stabilised/supported with chitosan and silica [13,21,27]. Silica (SiO_2) is a low-cost and abundant material that can be used in order to promote stabilisation of the assemblies of magnetic metallic nanoparticles

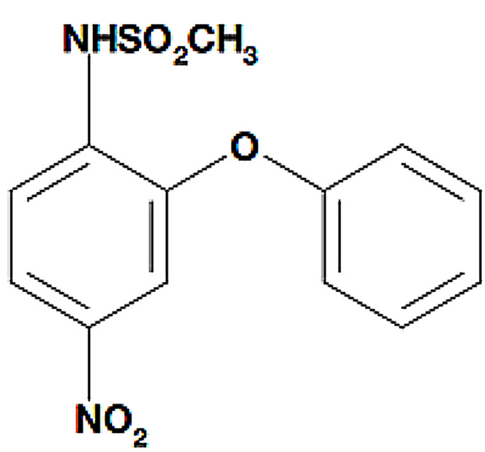

Fig. 1. Molecular structure of nimesulide (NMS).

by means of supporting the latter (e.g., anchoring process), i.e., the anchoring process can minimise the undesirable agglomeration of nanoparticles by avoiding the formation of three-dimensional assemblies exhibiting a reduced surface area [27]. As a result, the effective surface area exhibited by the metallic nanoparticles for the reductive degradation reaction is increased and the rate of the heterogeneous surface redox reaction is also increased.

According to Reddy and Lee [28], magnetic chitosan composites (MCCs) are also a promising material for the removal of different kind of pollutants since they exhibit fast adsorption rate and high adsorption efficiency. In short, MCCs consist of a chitosan polymer matrix and a dispersed phase containing magnetic particles. More recently, Reddy and Yun [29] reported that the spinel ferrite (SF) magnetic materials comprise an important class of composite metal oxides with unique properties that can be used for treating a wide range of aqueous pollutants such as metal ions, dyes, and pharmaceuticals.

In the present study, supported bimetallic nanoparticles containing Fe and Ni denoted as bNP/SIL were synthesised in the presence of silica, characterised, and then applied for the reductive degradation of NMS in aqueous solution. The major factors affecting degradation of NMS, such as NMS and bNP/SIL concentrations as well as the agitation frequency, were studied. By-products formed during the reductive treatment were identified using the liquid chromatography electrospray mass spectrometry (LC-ESI–MS) technique.

2. Materials and methods

2.1. Materials

Nimesulide ($C_{13}H_{12}N_2O_5S$, M.W. = 308.1 g mol^{-1}) was purchased from Fluka, while ferrous sulphate ($FeSO_4 \cdot 7H_2O$) was purchased from Synth (Brazil). Silica (SiO_2) was purchased from Vetec (Brazil). Sodium borohydride ($NaBH_4$), nickel nitrate ($Ni(NO_3)_2 \cdot 6H_2O$), sodium hydroxide (NaOH), acetonitrile (C_2H_3N), methanol (CH_3OH) and trifluoroacetic acid ($C_2HF_3O_2$) were purchased from Sigma–Aldrich. "Purum p.a." products were used throughout. All solutions were prepared using ultra-pure water obtained using a model Classic Di-MK2 water purification system from PURELAB (Brazil).

2.2. Synthesis of bimetallic nanoparticles containing Fe and Ni supported on silica

The Ni–Fe bimetallic nanoparticles supported on silica (SiO_2), denoted as SIL, containing different Fe:Ni ratios, denoted as bNP/SIL, were synthesised in aqueous solution through the chemical reduction of Fe^{2+} and Ni^{2+} ions and using SiO_2 as the support (average particle size of 2.0 μm and specific surface area of 400 m^2 g^{-1}), according to the modified procedure described by Zhu et al. [27]. In short, $FeSO_4 \cdot 7H_2O$ was reacted in the presence of SiO_2 with an excess of $NaBH_4$, resulting in hydrogen evolution with the formation of a black powder under suspension containing the supported Fe^0/SIL nanoparticles (see Eq. (1)) [30]:

$$Fe^{2+}_{(aq.)} + 2BH_4^-{}_{(aq.)} + 6H_2O_{(l)} + SiO_{2(s)} \rightarrow SiO_{2(s)} - Fe^0 + 2B(OH)_{3(s)} + 7H_{2(g)} \quad (1)$$

The SiO_2 used in the preparation of bNP/SIL plays a very important role in dispersability of the Fe^0 nanoparticles due to its high surface area [27]. Thus, the obtained black suspension containing the bNP/SIL nanoparticles was not prone to agglomeration. Fe^{2+} solutions were prepared using 25 mL of a 0.14 M $FeSO_4 \cdot 7H_2O$ solution in the presence of 1.0 g of SiO_2 (250 rpm and 30 min). The pH was adjusted to 6.8 using an NaOH solution. Then