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Improved membrane flux recovery by Fenton-type reactions

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ABSTRACT

Fenton reactions were applied to the degradation of dissolved organic matter (OM) and fouling removal of iron oxide membranes. Humic acid (HA), bovine serum albumin (BSA) and sodium alginate (SA), were used as models of humic substances, proteins and polysaccharides respectively. The degradation reaction was performed with H_2O_2 1 mM at pH of 2.5 and the reactant concentration was measured over time by total organic carbon (TOC) and HPLC. Dissolved and particulate iron were efficient catalyst, achieving mineralization rates of 80%, 40% and 85% for HA, BSA and SA respectively. The H_2O_2 solution was applied as a cleaning agent on membranes previously fouled by the compounds individually, as well as their mixtures. Hydraulic cleaning of the membrane surfaces did not show significant improvement; Fenton treatment produced a flow recovery of 97% for HA, 86% for BSA and 88% for SA. Flux recovery was slightly lower for mixtures, where chemical interactions between foulants yielded a more compact, recalcitrant layer. Membrane surfaces were characterized by scanning electron microscopy (SEM) and atomic force microscopy (AFM), showing residual foulants after treatment, regardless of the flux recovery achieved. The results showed the cleaning ability of this reagent with a very good recovery of the initial flux.

1. Introduction

Fouling has been recognized as the main limiting effect on membrane performance, efficiency and therefore widespread application of membrane technology. There is a wealth of research dedicated to fouling. However, reports on membrane cleaning treatments are considerably less [1]. Operating conditions for filter modules as well as the modification of membrane surfaces [2] are ongoing research issues to predict the behavior of fouling.

Cleaning approaches for microfiltration and ultrafiltration membranes are mainly physical cleaning or backflushing (i.e. reversing the flow through the membrane, followed by "relaxation" or temporary interruption of permeate flux) and chemical cleaning, which consists mainly of basic, acid and oxidizing solutions applied as cleaning agents [3–7]. Despite of the increasing research and understanding of the membrane fouling process itself, it remains a challenge to develop efficient techniques for fouling removal [3,8].

Fouling is primarily observed as a flow decrease in the filtrate with time, and it can be reversible if removed by a simple water rinsing, or irreversible, when compounds are bonded to the membrane surface causing permanent changes in the membrane performance [9].

Membrane fouling during natural water filtration is mainly attributable to three kind of compounds: microbial [10], organic compounds [11–15] and inorganic substances or minerals [8,16,17]. Nevertheless, among these foulants, natural organic matter (NOM) was found to have the most detrimental effects on membrane performance as it can result in fast irreversible fouling during surface water filtration [18].

We have previously reported on a novel fabrication process for iron-oxide ultrafiltration ceramic membranes [19], with an average pore size of 24 nm and BET surface area of 75.6 m^2/g. The Molecular Weight Cut Off (MWCO) was measured to be 150,000 Da, which falls in the ultra-filtration range.

The introduction of new, chemically active materials for ceramic membranes opens a broad range of application possibilities, such as adsorbents [20], disinfectants [21], or catalysts [22]. Additionally, the precursor particles are synthesized in aqueous media under low to moderate temperatures, which results in significant improvements in the environmental impacts and economic aspects, one of the main drawbacks of ceramic membranes today compared with their polymeric counterparts. Their fouling characteristics have also been investigated. In spite of their promising features, fouling by dissolved organic compounds may be the limiting factor for water treatment application of these new membranes [23].

Inorganic membranes have been investigated as catalytic materials or catalysts supports [24–26]. In particular, iron is a well-

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known catalyst for advanced oxidation through Fenton processes. Fenton reactions use dissolved iron as a catalyst for the generation of hydroxyl radicals [27]:

$$\mathrm{Fe(II)} + H_2O_2 \rightarrow \mathrm{Fe(III)} + OH^- + HO^\bullet \quad (1)$$

$$\mathrm{Fe(III)} + H_2O_2 \rightarrow \mathrm{Fe(II)} + H^+ + HO_2^\bullet \quad (2)$$

$$\mathrm{Fe(III)} + HO_2^\bullet \rightarrow \mathrm{Fe(II)} + H^+ + O_2 \quad (3)$$

In all the cases, the hydroxyl radical (HO•) reacts rapidly and non-selectively with most organic matter (OM), e.g. humic acids, producing chemical decomposition (Eq. (4)).

$$OM + HO^\bullet \rightarrow OM_{oxid} \quad (4)$$

Fenton reactions are most efficient at acidic pHs, and their effectiveness decay rapidly at $pH > 6$ due to precipitation of Fe(III) oxide. Several authors discussed the feasibility of the Fenton reaction in heterogeneous phase [28–30], although the exact reaction mechanism is still subject of debate. In general, homogeneous Fenton reaction predominates in acidic media due to dissolution of the surface iron oxide in catalytic amounts; at $pH > 4.5$, a probable mechanism of reaction in heterogeneous phase was proposed, but with much lower efficiency [31].

The objective of the present study is to explore the application of Fenton-type reactions in the cleaning of iron oxide ceramic membranes during filtration of organic substances. The treatment was applied to the fouling caused by three model organic compounds: humic acid (HA), bovine serum albumin (BSA), and sodium alginate (SA), as models of natural organic matter, proteins and polysaccharides respectively. These substances are commonly used to represent dissolved organic matter in water [11,32]. They adequately exemplify the chemistry of organic compounds commonly encountered in surface waters and/or mixed liqueur biological reactors, where ceramic membranes may be used for drinking water treatment or wastewater MBR´s; all three of them have proven to produce significant fouling, which can be further accentuated by synergistic effects when found in mixtures [23].

Cleaning experiments were carried out with membranes fouled with HA, BSA, SA, and mixtures of these fouling agents. Cleaning efficiency through Fenton-like reactions was tested and compared to basic and acidic treatments. The analyses were carried out for several filtration-cleaning cycles to assess membrane integrity and endurance.

2. Experimental

2.1. Chemicals

Industrial grade $FeCl_2$ (28–32% w/w) was obtained from PPE Argentina S.A. and anhydrous acetic acid (analytical grade, Anedra, Argentina) was used.

The organic compounds were Gallic Acid (GA) (technical grade, Carlo Erba, Italy), Humic Acid sodium salt (HA) (technical grade, Sigma-Aldrich, USA), Bovine Serum Albumin (BSA) (98%, Sigma-Aldrich, USA), and Sodium Alginate (SA) (analytical grade, Sigma-Aldrich, USA). Type I ultrapure water was used in all the experiments (18MΩ).

The cleaning reagent was prepared with Hydrogen Peroxide 30% (Anedra, Argentina), $Fe_2(SO_4)_3$ (analytical grade, Sigma-Aldrich, USA) and H_2SO_4 (98%, Anedra, Argentina). NaOH (analytical grade, Anedra, Argentina) and H_2SO_4 were used for pH adjustment.

2.2. Fabrication of FeOx nanoparticles and ceramic membranes

Iron oxide nanoparticles were synthesized in the laboratory following a previously published procedure [19]. Briefly, lepidocrocite was obtained by oxidation of $FeCl_2$ (PPE, Argentina) under controlled pH (6.7–6.8) [33]. Secondly, the prepared lepidocrocite was reacted with anhydrous acetic acid to yield iron oxide (FeOx) nanoparticles by the attack of the acid on the hydrogen bonds of the mineral structure. These nanoparticles were used as precursors to the ceramic membranes; they were deposited onto support matrices or used as a self-standing material.

The FeOx nanoparticles were sintered at 450 °C and converted to hematite powder; the material was suspended in water by magnetic stirring and used as catalyst in Fenton batch reaction experiments.

For membrane cleaning filtration experiments, alumina supports were fabricated in the laboratory by pressing of alumina powder in a custom made stainless steel mold and sintering at 1100 °C. The composite membranes were then obtained by dip-coating of flat porous alumina supports with a concentrated suspension of the iron oxide precursor. The coated supports were dried at room temperature and sintered at 450 °C for at least 4 h to produce full conversion of the FeOx particles to hematite [23].

2.3. Fenton reaction – Batch experiments

Fenton reactions were conducted in batch mode using FeOx-derived ceramics as iron source and compared with the use of soluble iron salts of same oxidation state. The oxidation of HA, BSA and SA, as models of natural organic matter, proteins and polysaccharides, respectively, was tested. Gallic acid degradation was also investigated as a reference, as it has an aromatic structure similarly to humic and fulvic acids, but it is a smaller, much simpler molecule.

The organic compounds were analyzed by UV–visible spectroscopy, total organic carbon analyzer (TOC) and/or high performance liquid chromatography (HPLC). In all cases studied, the reactions were performed in duplicate or triplicate. TOC was measured on a Shimadzu TOC Analyzer, TOC-VCPH, equipped with an autosampler ASI-V auto sampler (Kyoto, Japan). UV-visible spectroscopy was performed on a Shimadzu UV–vis 1650 pc (Kyoto, Japan) ($\lambda = 280$ nm). The HA and BSA samples were analyzed on an HP 1100 HPLC, chromatographic gel filtration column GF-250 (9.4 × 250 mm, 4 µm), mobile phase: 0.1 M phosphate buffer pH 7, flow 1 mL/min, detector UV absorbance ($\lambda = 280$ nm), injected volume 200 µl.

2.4. Filtration experiments

Membrane fouling and chemical cleaning experiments were performed in dead-end mode, in a custom made cell under constant pressure conditions, supplied by compressed air. A new membrane was used in each experiment.

Permeate flux of both as prepared and fouled membranes were determined by clean water filtration experiments. Permeate volume was recorded over time and flux determined as the slope of the linear fit of the experimental data from Darcy's equation:

$$J = \frac{dV}{dt \cdot A} = \frac{\Delta P}{\mu \cdot R_T} = \frac{\Delta P}{\mu \cdot (R_m + R_f)}$$

where J is the permeate flux ($l\,m^{-2}\,s^{-1}$), A is the effective filtration area (m^2), ΔP is the transmembrane filtration pressure (kPa), μ the solution viscosity and R_T is the total membrane hydraulic resistance, which is composed by the sum of the clean membrane resistance R_m and the fouling layer resistance R_f.