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A fast and environment-friendly method for determination of chemical oxygen demand by using the heterogeneous Fenton-like process ($\text{H}_2\text{O}_2/\text{Fe}_{3-x}\text{Co}_x\text{O}_4$ nanoparticles) as an oxidant



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ABSTRACT

An easy, fast and environment-friendly method for COD determination in water is proposed. The procedure is based on the oxidation of organic matter by the $\text{H}_2\text{O}_2/\text{Fe}_{3-x}\text{Co}_x\text{O}_4$ system. The $\text{Fe}_{3-x}\text{Co}_x\text{O}_4$ nanoparticles activate the H_2O_2 molecule to produce hydroxyl radicals, which are highly reactive for oxidizing organic matter in an aqueous medium. After the oxidation step, the organic matter amounts can be quantified by comparing the quantity of H_2O_2 consumed. Moreover, the proposed COD method has several distinct advantages, since it does not use toxic reagents and the oxidation reaction of organic matter is conducted at room temperature and atmospheric pressure. Method detection limit is 2.0 mg L^{-1} with intra- and inter-day precision lower than 1% ($n=5$). The calibration graph is linear in the range of $2.0\text{--}50 \text{ mg L}^{-1}$ with a sample throughput of $25 \text{ samples h}^{-1}$. Data are validated based on the analysis of six contaminated river water samples by the proposed method and by using a comparative method validated and marketed by Merck, with good agreement between the results (t test, 95%).

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1. Introduction

Chemical oxygen demand (COD) represents the organic pollution level in water and is therefore one of the most commonly utilized parameters for monitoring water quality. Typically, for COD determination in water, the organic compounds are completely oxidized by using a strong oxidant such as dichromate, persulphate, iodate or permanganate, and then the result is estimated by determining the amount of the consumed oxidant and expressed in terms of its oxygen equivalence. The classic method for COD determination consists of back titration of the excess of dichromate, used to oxidize organic matter in acidic medium, with ferrous sulfate and ammonium. The content of organic matter is then calculated from the oxygen consumption, which is equivalent to the dichromate amount needed to oxidize

all the organic matters [1]. However, this method has several limitations including low sensitivity, a long time-consuming (2–4 h) reflux process to allow the complete oxidation of organics and the use of expensive (e.g. Ag_2SO_4), corrosive (e.g. concentrated H_2SO_4), and highly toxic reagents (e.g. Hg(II) and Cr(VI)). Due to these limitations, the development of simpler, sensitive and “green” methods for COD determination in natural waters and wastewaters is of great interest.

Nowadays, the use of Advanced Oxidation Processes (AOPs) for water and wastewater treatment is increasing due to its high efficiency and low cost [2]. AOPs are based on the generation of •OH radicals, which are capable of oxidizing organic matter that is refractory from attack by conventional water treatment oxidants. Moreover, AOPs are clean processes that can effectively oxidize, in a non-selective manner, various organic and inorganic compounds in water [3]. These characteristics make the AOPs a promising system for utilization in environmental monitoring and/or remediation processes.

Several types of AOPs such as the Fenton process, [4–6] ozonation, [7] electrochemical oxidation, [8] wet air oxidation, [9] and

Abbreviations: COD, Chemical oxygen demand; AOPs, Advanced oxidation processes

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photocatalysis [10] can be used to oxidize organic compounds in water. Among them, the Fenton process has been reported to be the most suitable, due to not only the simplicity of its system but also the low cost of iron and hydrogen peroxide reagents [11].

Among the iron compounds used as catalysts in the heterogeneous Fenton-like process for the oxidation of organic compounds in water, iron oxides such as hematite (α -Fe₂O₃), [12] goethite (α -FeOOH), magnetite (Fe₃O₄), [13,14] akaganèite (β -FeOOH), [15] lepidocrocite (γ -FeOOH) [16], δ -FeOOH, [17] and Co-doped magnetite (Fe_{3-x}Co_xO₄) [18,19] have been the most frequently described. However, Co-doped magnetite (Fe_{3-x}Co_xO₄) seems to exhibit a higher degree of Fenton-like activity [18,19] which motivates its use as a green catalyst in COD determination processes for environmental monitoring. On the other hand, the conventional oxidation approaches based on the application of the Fenton-like process may lead to an overestimation of COD, due to a residual H₂O₂ at the end of the reaction [20,21].

Therefore, to avoid the previous mentioned limitations, a novel method for COD determination, based on the oxidation of organic matter by the Fenton-like process catalyzed by Fe_{3-x}Co_xO₄ nanoparticles is proposed herein. With this new approach, the initial and residual H₂O₂ amounts have been previously determined whereas the COD values are obtained from only the H₂O₂ amount consumed during the oxidation of the organic matter. Finally, the applicability of the method to the analysis of contaminated water samples is also demonstrated.

2. Materials and methods

2.1. Materials

All reagents used were of analytical-reagent grade. High purity deionized water (resistivity 18.2 M Ω cm) obtained using a Milli-Q water purification system (Millipore, Bedford, MA, USA) was used throughout. Cobalt (II) chloride hexahydrate (Merck), ammonium iron (III) sulfate dodecahydrate (Sigma Aldrich), ammonium iron (II) sulfate hexahydrate (Vetec), potassium hydrogen phthalate (Merck), sodium hydroxide (Sigma Aldrich), hydrogen peroxide 30% w/v (Sigma Aldrich) and Peroxid Test (Merckquant, Germany) were used.

2.1.1. Synthesis of Fe_{3-x}Co_xO₄ nanoparticles

Fe_{3-x}Co_xO₄ nanoparticles were prepared by coprecipitation of ferrous (Fe²⁺), ferric (Fe³⁺) and cobalt (Co²⁺) ions by NaOH in aqueous solution. In short, 4.8219 g of NH₄Fe(SO₄)₂ · 12H₂O, 7.8428 g of (NH₄)₂Fe(SO₄)₂ · 6H₂O and 0.2379 g of CoCl₂ · 6H₂O were solubilized in 100 mL of ultrapure water and precipitated at room temperature with 100 mL of 0.1 M NaOH under vigorous stirring for 30 min. This led directly to the product, Fe_{3-x}Co_xO₄. The black precipitate was washed with ultrapure water several times and dried in a vacuum desiccator at room temperature.

2.1.2. Characterization of Fe_{3-x}Co_xO₄ nanoparticles

Powder X-ray diffraction (XRD) data were collected from 15° to 70° 2 θ by using Cu K α (λ =1.540560 Å) radiation in a Rigaku Geigerflex diffractometer equipped with a graphite diffracted-beam monochromator. Silicon was used as an external standard. The Rietveld structural refinement was performed with FULLPROF 2012 program. ⁵⁷Fe Mössbauer spectra were collected with the sample at 298 K in constant acceleration transmission mode with a 20 mCi ⁵⁷Co/Rh source. Data were stored in a 512-channel MCS memory unit and numerically fitted using the NORMOS™ program. Isomer shift values are quoted relative to α -Fe. The morphology of the produced Fe_{3-x}Co_xO₄ was monitored with transmission electron microscopy (TEM), using a JEOL transmission electron microscope,

model JEM 2000EXII. Total Fe and Co contents were measured by atomic absorption analyses (Carls Zeiss Jena AAS). Magnetization measurements were performed with a portable magnetometer with a fixed magnetic field of ca. 0.3 T calibrated with a metallic nickel.

2.2. Methods

2.2.1. The COD method

The method for COD quantification proposed in this work was based on the oxidation of organic matter by H₂O₂ catalyzed by Fe_{3-x}Co_xO₄ nanoparticles. The initial and residual H₂O₂ concentrations were spectrophotometrically determined and then, the COD values were obtained relatively to the amounts of H₂O₂ consumed during the oxidation reaction of organic matter in water. Basically, the method was developed as follows: a calibration curve was made by fitting the potassium hydrogen phthalate (a COD standard) concentration as a function of the H₂O₂ concentration consumed during the oxidation of hydrogen phthalate. In short, 5 mL of each 5, 10, 20, 25, 30, 40 and 50 mg L⁻¹ COD standard, 40 μ L of H₂O₂ (3%) and 30 mg of Fe_{3-x}Co_xO₄ nanoparticles were mixed and maintained under stirring for 5 min, at room temperature. The Fe_{3-x}Co_xO₄ catalyst was recovered by using a hand magnet and the residual H₂O₂ was determined with the Merck Quant method for quantifying H₂O₂ (simple method for spectrophotometric determination of peroxides), using a UV-visible Spectrophotometer SP 220. Since the initial H₂O₂ concentration was predetermined, the amount of H₂O₂ consumed in the reaction can be readily calculated. The determination of COD in real samples was obtained similarly, except for the use of a contaminated water sample instead of COD standard.

2.2.2. Method validation

The validation of the COD method was based on studies of precision, sensitivity, accuracy, linearity and by comparing the results obtained in the analysis of six water samples by the proposed COD method and a standard method marketed by Merck Chemicals [22].

The precision tests were performed by measuring the intra-day and between-days COD for the samples. The detection limit of the method was defined as three times the standard deviation divided by the white slope of the calibration curve. For the accuracy test, the results obtained with the developed method were compared with the standard method commercialized by Merck Chemicals.

2.2.3. Collection of water samples

Ordinary water sample collection was conducted at six points located in selected TSR sections (see Fig. 1) for COD determination. Of these points, two were located before the selected urban area and near the origin of the river; two were located after the urban area, and two within the urban area, which was located in a region with major contamination. At each sample site, the water sample was collected according to the Environmental Technology Company (CETESB) standards [23]. The samples were stored at 4 °C prior to analyses.

The georeferencing information of the TSR Basin is important for controlling the water quality along the river because it helps identify the most critical contamination points with accuracy. From a georeferenced map, one can obtain parameters that facilitate data analysis, e.g., the distance between collected points or the proximity to a specific point of interest. The contaminated water collection points ($n=6$) were defined based on several parameters, such as the proximity to urban centers and water use and with a radius of 74 km. The geographic coordinates of each point were determined using a Garmin 60CSx GPS receiver. These coordinates were used for the additional analysis. Collection points, identified as P-1 to P-6 are two points near the source

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