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A fast and environment-friendly method for determination of chemical oxygen demand by using the heterogeneous Fenton-like process ($H_2O_2/Fe_{3-x}Co_xO_4$ nanoparticles) as an oxidant

Lorena C.R. Esteves [a], Thaís R.O Oliveira [a], Elias C. Souza Jr. [a], Cleide A. Bomfeti [a], Andrea M. Gonçalves [a], Luiz C.A. Oliveira [b], Fernando Barbosa Jr. [c], Márcio C. Pereira [a], Jairo L. Rodrigues [a,*]

[a] Instituto de Ciência, Engenharia e Tecnologia, Universidade Federal dos Vales Jequitinhonha e Mucuri, Teófilo Otoni 39803-371, Minas Gerais, Brazil
[b] Departamento de Química, ICEx, Universidade Federal de Minas Gerais, 31270-901 Belo Horizonte, Minas Gerais, Brazil
[c] Faculdade de Ciências Farmacêuticas de Ribeirão Preto, Universidade de São Paulo, 14040903 SP, Brazil

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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 $H_2O_2/Fe_{3-x}Co_xO_4$ system. The $Fe_{3-x}Co_xO_4$ 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 $2.0–50\ mg\ L^{-1}$ with a sample throughput of 25 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%).

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 $^{\bullet}OH$ 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

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

[*] Corresponding author. Tel./fax: +55 33 35226037.
E-mail address: jairo.rodrigues@ufvjm.edu.br (J.L. Rodrigues).

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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-Fe_2O_3), [12] goethite (α-FeOOH), magnetite (Fe_3O_4), [13,14] akaganèite (β-FeOOH), [15] lepidocrocite (γ-FeOOH) [16], δ-FeOOH, [17] and Co-doped magnetite ($Fe_{3-x}Co_xO_4$) [18,19] have been the most frequently described. However, Co-doped magnetite ($Fe_{3-x}Co_xO_4$) 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 H_2O_2 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 $Fe_{3-x}Co_xO_4$ nanoparticles is proposed herein. With this new approach, the initial and residual H_2O_2 amounts have been previously determined whereas the COD values are obtained from only the H_2O_2 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 MΩ 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 $Fe_{3-x}Co_xO_4$ nanoparticles

$Fe_{3-x}Co_xO_4$ nanoparticles were prepared by coprecipitation of ferrous (Fe^{2+}), ferric (Fe^{3+}) and cobalt (Co^{2+}) ions by NaOH in aqueous solution. In short, 4.8219 g of $NH_4Fe(SO_4)_2 \cdot 12H_2O$, 7.8428 g of $(NH_4)_2Fe(SO_4)_2 \cdot 6H_2O$ and 0.2379 g of $CoCl_2 \cdot 6H_2O$ 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, $Fe_{3-x}Co_xO_4$. The black precipitate was washed with ultrapure water several times and dried in a vacuum desiccator at room temperature.

2.1.2. Characterization of $Fe_{3-x}Co_xO_4$ nanoparticles

Powder X-ray diffraction (XRD) data were collected from 15° to 70° 2θ by using Cu Kα ($\lambda = 1.540560$ 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. ^{57}Fe Mössbauer spectra were collected with the sample at 298 K in constant acceleration transmission mode with a 20 mCi ^{57}Co/Rh source. Data were stored in a 512-channel MCS memory unit and numerically fitted using the NORMOS^{TM} program. Isomer shift values are quoted relative to α-Fe. The morphology of the produced $Fe_{3-x}Co_xO_4$ 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 H_2O_2 catalyzed by $Fe_{3-x}Co_xO_4$ nanoparticles. The initial and residual H_2O_2 concentrations were spectrophotometrically determined and then, the COD values were obtained relatively to the amounts of H_2O_2 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 H_2O_2 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 μL of H_2O_2 (3%) and 30 mg of $Fe_{3-x}Co_xO_4$ nanoparticles were mixed and maintained under stirring for 5 min, at room temperature. The $Fe_{3-x}Co_xO_4$ catalyst was recovered by using a hand magnet and the residual H_2O_2 was determined with the Merck Quant method for quantifying H_2O_2 (simple method for spectrophotometric determination of peroxides), using a UV–visible Spectrophotometer SP 220. Since the initial H_2O_2 concentration was predetermined, the amount of H_2O_2 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

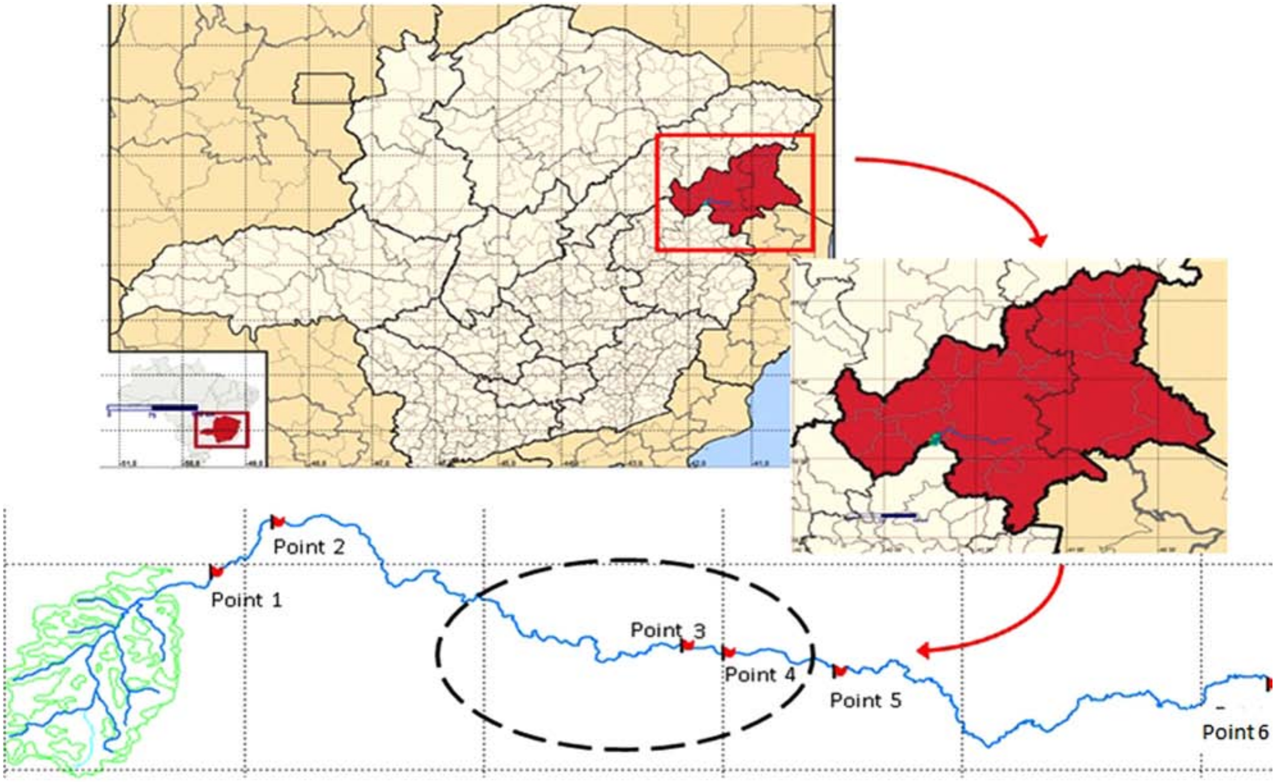

Fig. 1. Map showing points of water collection from a contaminated river in Brazil (Todos os Santos River, Minas Gerais state, Brazil).

(and Poté-MG/Baixinha Poté-MG/Valão), two in urban Teófilo Otoni and two points after crossing the urban area city (Teófilo Otoni-MG/Pedro Versiani). The geographical location and altitude regarding samples were 17 °50′ (S) 41 °40′ (W) and 598.4 m (P-1), 17th 48′ (S) 41 °39′ (W) and 550.8 m (P-2); 17 °51′ (S) 41 °30′ (W) and 328.5 m (P-3), 17 °52′ (S) 41 °29′ (W) 319 m (P-4), 17 °52′ (S) 41 °27′ (W) and 310 m (P-5); 17 °52′ (S) 41 °18′ (W) and 272.5 m (P-6).

3. Results and discussion

3.1. Catalyst characterization

Chemical analysis of the prepared sample showed the $Fe_{3-x}Co_xO_4$ catalyst consisted of 13 wt% Co and 58 wt% Fe. TEM images (Fig. 2) showed that an agglomerated of pseudo-spherical particles with average particle size of 23 nm was produced.

Qualitative analysis of the powder XRD (Fig. 3) indicated the existence of a single crystallographic phase corresponding to magnetite (JCPDS card number 1-1111). To confirm whether an isomorphic substitution of Fe by Co was occurring in the magnetite, a structural analysis was performed. The subsequent Rietveld refinement of XRD data with pseudo-Voigt peak fitting gave the structural parameters. The Rietveld refinement yielded a profile residual factor, R_p, of 1.4, indicative of a good quality refinement model. The XRD pattern of $Fe_{3-x}Co_xO_4$ was indexed on a cubic lattice with parameter $a=8.3856(2)$ Å. The lattice parameter for pure magnetite has been reported to be 8.3960 Å [22]. The decrease in the lattice parameter of prepared sample may be due to two factors: (i) partial oxidation of Fe^{2+} (ionic radium of 78 pm in octahedral coordination) into Fe^{3+} (65 pm) and (ii) isomorphic replacement of Fe^{2+} by Co^{2+} (74 pm). Since the formation of individual cobalt oxides was not detected in the

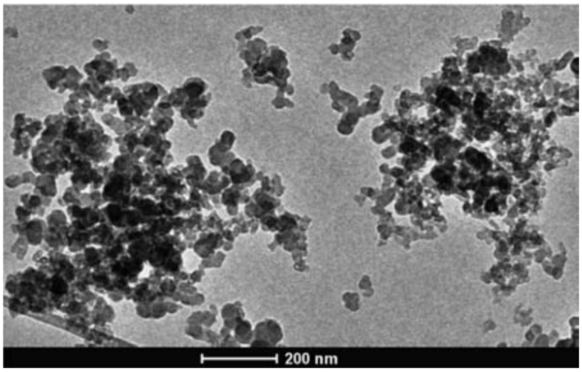

Fig. 2. TEM images for the $Fe_{3-x}Co_xO_4$ nanoparticles.

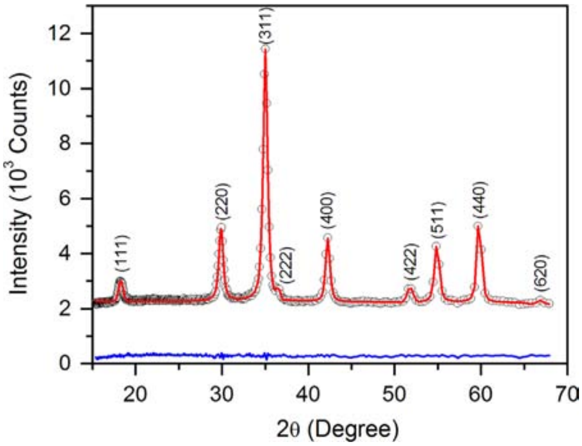

Fig. 3. Rietveld refinement of the XRD pattern of the $Fe_{3-x}Co_xO_4$ nanoparticles.

XRD pattern (Fig. 3), we suggest the incorporation of Co into the magnetite structure.

To corroborate the XRD data, ^{57}Fe Mössbauer measurements were carried out to confirm the formation of $Fe_{3-x}Co_xO_4$, as this technique is specific for the study of the Fe environment. The room temperature Mössbauer spectrum for the prepared sample (Fig. 4) can be fitted with two sextets and one doublet. One sextet (δ=0.29 mm s^{-1} and B_{hf}=49.0 T, relative area=40%) corresponds to Fe^{3+} in tetrahedral coordination (A site – Fig. 4), whereas another (δ=0.66 mm s^{-1} and B_{hf}=45.5 T, relative area=41%) corresponds to $Fe^{2+/3+}$ in octahedral coordination (B site – Fig. 4) in magnetite structure. The doublet (δ=0.32 mm s^{-1} and Δ=0.62 mm s^{-1}) contributes 19% of the total Fe and can be assigned to small particle size magnetite or some another iron oxide resulting from the oxidation of magnetite. The area ratio between octahedral and tetrahedral sites occupancies ($RA_{B/A}$) is 1.88 for pure magnetite. For the prepared sample the area ratio was 1.03, suggesting that the Fe in the octahedral site was replaced by Co ions in magnetite structure, as verified by XRD data. The results of magnetization measurements corroborate this interpretation of XRD and Mössbauer data: as expected, the isomorphic substitution of Fe by Co induced a strong decrease in magnetization values for the prepared sample (30 emu g^{-1}) compared with those expected for pure magnetite (100 emu g^{-1}).

Based on the results of chemical analysis, Mössbauer spectroscopy, and Rietveld refinement of XRD data (occupancy factors for tetrahedral and octahedral crystallographic sites), we calculated that the chemical formula of the prepared sample was $[Fe]\{Fe_{1.31}Co_{0.50}\square_{0.19}\}O_4$, where [ ] represents tetrahedral sites, { } octahedral sites and □ cation vacancies. From these data, it was possible to determine the structure of the Fenton-like catalyst prepared in this work. Fig. 5 shows the graphical representation of the crystal structure of the $[Fe]\{Fe_{1.31}Co_{0.50}\square_{0.19}\}O_4$ nanomaterial. The iron ions occupy both tetrahedral and octahedral sites, whereas Co ions occupy only the octahedral sites. Green circles represents Fe in the octahedral site, yellow circles corresponds to Fe in the tetrahedral site, blue circles are Co in octahedral sites and empty circles corresponds to cation vacancies.

3.2. The COD method

The feasibility of a rapid, safety and environment-friendly method for COD determination based on the use of $Fe_{3-x}Co_xO_4$ nanomaterial as a catalyst was evaluated.

During the process of organic matter oxidation, the $Fe_{3-x}Co_xO_4$ nanoparticles can activate the H_2O_2 molecules to achieve efficient oxidization of any organic compounds in water. By determining the initial and residual H_2O_2 concentrations, it is possible to calculate the COD value from standards or water samples. The initial and residual H_2O_2 concentrations can be quantified by several methods; however, we have selected the colorimetric method commercialized by Merck (MerkQuant for peroxides).

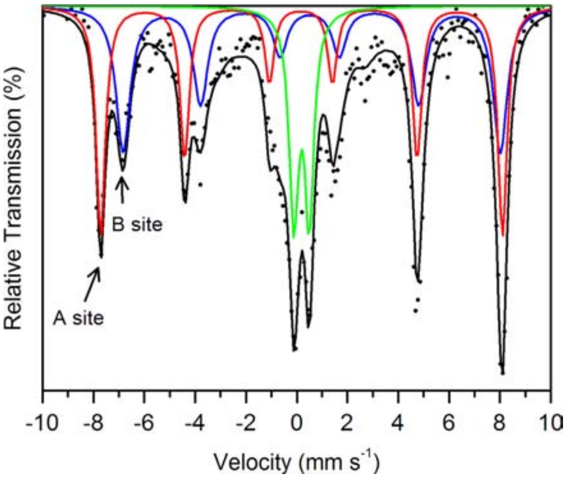

Fig. 4. 298 K Mössbauer spectra of the $Fe_{3-x}Co_xO_4$ nanoparticles.

The optimization of the COD method was carried out by analyzing the optimal H_2O_2 amount required to oxidize all organic matters in water (Fig. 6). It can be noted that increasing the H_2O_2 amounts also augments the analytical signal. For values above 40 μL, the method no longer presented linearity; thus, the H_2O_2 volume adopted for further experiments was 40 μL.

3.3. Validation and analytical characteristics of the proposed COD method

The detection limit of the method was 2.0 mg L^{-1}, a value sufficient for the analysis of COD in water samples. The linear range was from 2.0 to 50.0 mg L^{-1} with a sample throughput of 25 samples h^{-1}. The respective within-day and between-day precisions of 0.42% and 0.59% indicate a good precision of the proposed method. Table 1 summarizes the analytical characteristics of developed method.

Method validation was carried out by comparing the results obtained for COD in six water samples (collected in Todos os Santos River, see Fig. 1) by applying the proposed procedure and by applying the method marketed by Merck Chemicals (Table 2). Previous studies of Blanc et al. [24] demonstrated elevated organic

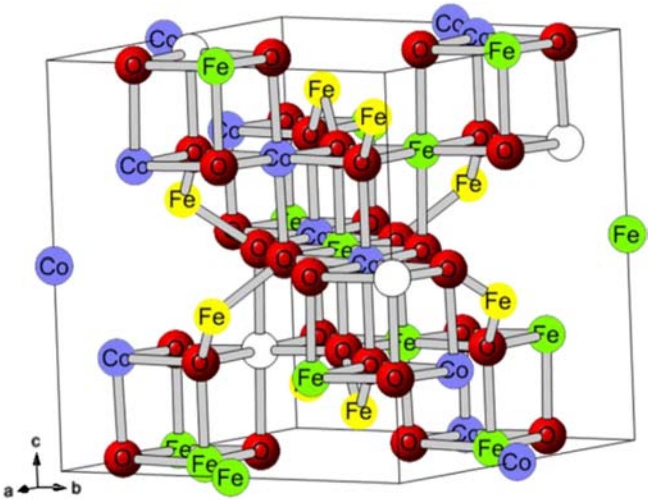

Fig. 5. Graphical representation of the crystal structure of $[Fe]\{Fe_{1.31}Co_{0.50}\square_{0.19}\}O_4$ catalyst. (For interpretation of the references to color in this figure, the reader is referred to the web version of this article.)

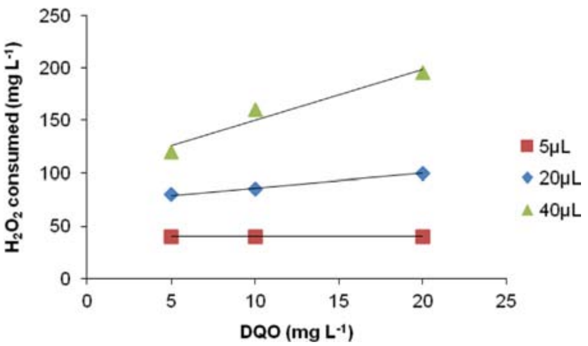

Fig. 6. Optimization of the H_2O_2 amounts used in the method of COD determination.

Table 1
Analytical characteristics of the proposed method for COD determination.

Analytical parameters	Results
Linear coefficient correlation (R^2)	0.998
Slope (L mg^{-1})	1.2143
Within-day precision (%) ($n=5$)	0.42%
Between-day precision (%) ($n=5$)	0.59%
Method detection limit (mg L^{-1})	2.0
Linear range (mg L^{-1})	2.0–50.0
Accuracy	No statistical difference between proposed and standard method

Table 2
Comparison between the proposed and a standard method for COD determination in water samples. Samples were collected from Todos os Santos River, Brazil (see Fig. 1 and text for details).

Samples	COD (SD) mg L^{-1}	COD (SD) mg L^{-1}
Point 1	16.5(0.7)	15.9(1.0)
Point 2	19.3(0.8)	21.4(1.2)
Point 3	50.0(1.1)	53.0(2.1)
Point 4	35.5(1.1)	33.2(1.6)
Point 5	40.0(0.9)	38.8(1.9)
Point 6	18.1(1.0)	18.4(1.3)

Table 3
Analytical performance parameters for determination of chemical oxygen demand and comparison between published methods.

Analytical parameter	Proposed method	Wang et al. (2013a) [25]	Wang et al. (2013b) [26]	Li et al. (2003) [27]	Almeida et al. (2012) [28]
Method detection limit (mg L^{-1})	2.0	18.3	15.0	2.0	0.93
Procedure	($H_2O_2/Fe_{3-x}Co_xO_4$ nanoparticle) as oxidant	TiO_2 nanorod sensor	CuO_2-loaded TiO_2 nanotube	Luminol–H_2O_2 chemioluminesce	Flow injection microwave solid phase extraction of activated carbon
Linear range (mg L^{-1})	2.0–50.0	20–280	20–300	4–4000	2.78–850
Sample throughput (samples h^{-1})	25	Not provided	Not provided	40	18

contamination in this river. No statistical differences were observed between the methods (*t* test, 95% confidence interval), indicating a good accuracy of the proposed method.

A comparison of the figures of merit of the proposed method and of four previous publications for COD determination is shown in Table 3. The proposed method presents comparable or better detection capability in the table and shows very good sample throughput, requiring a very low sample volume.

4. Conclusion

A simple, fast, low-cost and environment-friendly method for COD determination in water was developed. The present procedure presents several distinct advantages when compared to classical methods for routine determination of COD in water samples:

(i) the use of $Fe_{3-x}Co_xO_4$ nanoparticles in the presence of H_2O_2 take a highly oxidant system, due to in situ formation of hydroxyl radicals ($^\bullet$OH), which are highly reactive species and non-selective, capable of oxidizing any type of organic matter present in an aqueous medium;

(ii) the standard reduction potential of the hydroxyl radicals ($E^\circ=2.80$ V), generated in the $Fe_{3-x}Co_xO_4/H_2O_2$ system, is higher than the standard potential of oxidizing agents most commonly used for organic matter oxidation in an aqueous medium, such as permanganate ($E^\circ=1.51$ V), and dichromate ($E^\circ=1.33$ V). Consequently, the organic matter oxidation in the presence of $Fe_{3-x}Co_xO_4/H_2O_2$ occurs more effectively than in cases involving dichromate or permanganate;

(iii) since $Fe_{3-x}Co_xO_4$ has magnetic properties, it can be easily recovered by using an external magnet and then be reused by several reaction cycles without significant loss of activity;

(iv) since the initial and residual H_2O_2 concentrations are determined, there is no interference of H_2O_2 amounts on the COD values.

Acknowledgments

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