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Comparison of spectrophotometric, potentiometric and voltammetric methodologies for the determination of nitrite and nitrate in industrial effluents and in watercourses

Comparação de metodologias espectrofotométrica, potenciométrica e voltamétrica para a determinação de nitrito e nitrato em efluentes industriais e em cursos de água

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Abstract

The study addresses the importance of treating wastewater, such as water from human activities (domestic, industrial, agricultural), before it is discharged into the environment. The presence of nitrate and nitrite ions in these waters is a concern, as they are harmful to human health. The objective of this study is to evaluate different analytical techniques to measure the amount of these ions in industrial effluents and river water. The water samples were collected in Timóteo, a region with steel industries. The collections were made at three treatment points of a steel industry and at different points of the Timotinho Stream. These samples were filtered and analyzed in the laboratory using three different techniques, UV-Vis Spectrophotometry, Potentiometry with ion-selective electrodes and Differential Pulse Voltammetry. The results showed that all three techniques analyzed were effective in determining nitrite and nitrate in the water samples. However, there were some important considerations: UV-Vis spectrophotometry is quite accurate, but can be affected by interferences in the sample, such as the presence of other substances that absorb light at the same wavelength; potentiometry with ion-selective electrodes, despite being a simpler and lower-cost technique, also presented good results. Because it is more affordable, it is considered an excellent option for use in routine analyses, especially in places where resources are limited; and finally, differential pulse voltammetry, which is a more complex technique, but offers high sensitivity and can be useful in cases where very low concentrations of ions need to be detected. It is concluded that all three techniques can be used to measure nitrate and nitrite in industrial effluents and river waters, with variations in choice depending on the context. This is the main idea of the study: to identify effective techniques for measuring hazardous contaminants (such as nitrate and nitrite) in wastewater, choosing the most appropriate technique based on accuracy, sensitivity, and cost.

Keywords: Nitrite. Nitrate. Industrial effluents. Watercourses. Spectrophotometry. Potentiometry. voltammetry.

Resumo

O estudo aborda a importância do tratamento de águas residuais, como águas provenientes de atividades humanas (domésticas, industriais, agrícolas), antes de serem lançadas no meio ambiente. A presença de íons nitrato e nitrito nessas águas é preocupante, pois são prejudiciais à saúde humana. O objetivo deste estudo é avaliar diferentes técnicas analíticas para mensurar a quantidade desses íons em efluentes industriais e águas de rios. As amostras de água foram coletadas em Timóteo, região com indústrias siderúrgicas. As coletas foram feitas em três pontos de tratamento de uma indústria siderúrgica e em diferentes pontos do Córrego Timotinho. Essas amostras foram filtradas e analisadas em laboratório por meio de três técnicas diferentes, Espectrofotometria UV-Vis, Potenciometria com eletrodos íon-seletivos e Voltametria de Pulso Diferencial. Os resultados mostraram que todas as três técnicas analisadas foram eficazes na determinação de nitrito e nitrato nas amostras de água. No entanto, houve algumas considerações importantes: a espectrofotometria UV-Vis é bastante precisa, mas pode ser afetada por interferências na amostra, como a presença de outras substâncias que absorvem luz no mesmo comprimento de onda; a potenciometria com eletrodos íon-seletivos, apesar de ser uma técnica mais simples e de menor custo, também apresentou bons resultados. Por ser mais acessível, é considerada uma excelente opção para uso em análises de rotina, principalmente em locais onde os recursos são limitados; e, por fim, a voltametria de pulso diferencial, que é uma técnica mais complexa, mas oferece alta sensibilidade e pode ser útil em casos em que concentrações muito baixas de íons precisam ser detectadas. Conclui-se que todas as três técnicas podem ser usadas para medir nitrato e nitrito em efluentes industriais e águas fluviais, com variações na escolha dependendo do contexto. Esta é a ideia principal do estudo: identificar técnicas eficazes para medir contaminantes perigosos (como nitrato e nitrito) em águas residuais, escolhendo a técnica mais adequada com base na precisão, sensibilidade e custo.

Palavras-chave: Nitrito. Nitrato. Efluentes industriais. Águas residuais. Espectrofotometria. Potenciometria. Voltametria.

1. Introduction

Wastewater resulting from various human activities, whether domestic, industrial or agricultural, cannot continue to be discarded without prior treatment. Treatment plants consist of a series of physical, chemical and biological processes, the purpose of which is to improve the quality of the treated water, in order to use it again for human consumption or, at least, to discard it with minimal consequences that harm the environment (Batalha & Parlatore, 1977).

As a result, and also with the increase and greater efficiency of inspection carried out by government agencies in the area, industries, whose processes are polluting by nature, have become more concerned with installing equipment to treat their effluents (COPAM, 1987).

In addition to other polluting agents, there has been growing concern regarding the presence of nitrate and nitrite ions in water supplies, as they are considered highly harmful to health (Bruning & Kaneene, 1993).

Conventional and modern methods for the detection and determination of nitrite and nitrate in water include those based on spectrophotometry, potentiometry and voltammetry. Conventional methods, although offering a number of advantages, have certain disadvantages, such as considerable time consumption and sometimes requiring expensive equipment (Wang *et al.*, 2017; Wierzbicka, 2019; Singh *et al.*, 2019).

The aim of this study was to evaluate the analytical methodologies for the quantitative determination of nitrate and nitrite ions in industrial effluents and river waters. The techniques selected for the analysis of these ions were UV-Vis spectrophotometry, potentiometry with ion-selective electrodes and differential pulse voltammetry.

The samples that served as models for the evaluation of the three analytical methodologies were collected in the municipality of Timóteo, Minas Gerais State, Brazil. Thus, it was possible with these three methodologies to evaluate the concentration of nitrite and nitrate in the waters of the Timotinho Stream and in the liquid effluents resulting from a steel industry.

2. Materials and Methods

The samples of industrial effluents and water from the Timotinho Stream were collected in the municipality of Timóteo, in the central-eastern part of the state of Minas Gerais, in the region known as Vale do Aço, which is home to large steel companies. Timóteo is bordered to the north by the municipality of Coronel Fabriciano, to the south by Marliéria, to the east by Caratinga and Bom Jesus do Galho, and to the west by Antônio Dias and Jaguaraçu.

The water and effluent samples were collected sequentially every 12 days during the rainy season. The collection period was between October and November.

The sites included samples from the Chemical Bath Tank (TQ1), the Equalization Tank (TQ2), and the Final pH Correction Tank (TQ3) of the ETE of a steel industry. In the Timotinho stream, samples were collected upstream and downstream of the ETE discharge outlet. In this watercourse, site RT4 is located 1,100 m and site RT5 is 250 m upstream of the discharge. Site RT6 is located 750 m and site RT7 is 1,000 m downstream. The choice of sites in the Timotinho stream was based on, among other factors, ease of access to the site. In addition to the sites already mentioned, samples were also collected from an outfall (EM8) of the steel industry.

The water samples from the stream and industrial effluents were collected manually using a PVC collector and then transferred to 1000 mL polyethylene bottles, previously decontaminated in the laboratory, in sequence with a 10% nitric acid solution, a 10% hydrochloric acid solution, a concentrated detergent bath, deionized water and water from the collection site itself (Agudo, 1987).

To preserve the samples, they were kept under ice cooling in Styrofoam boxes until they arrived at the laboratory. The maximum recommended storage for nitrite and nitrate determinations is 48 h, according to the American Public Health Association (Greenberg *et al*., 1992; Cunniff, 1998).

Before analysis, the water samples were filtered using a vacuum pump through 0.45 m porosity cellulose membrane filters to remove suspended particles. During filtration, the first 60 mL were discarded so that the collection bottle could be washed with the sample itself and to eliminate possible contamination.

During laboratory analyses, the water samples were kept in a freezer at 4 °C for as long as necessary (Greenberg *et al*., 1992).

2.1. Spectrophotometric measurements

Nitrate and nitrite ions in water and liquid effluents were determined by UV-Vis spectrophotometry using a Hitachi U-2000 spectrophotometer interfaced to a computer with data acquisition and management by a program developed in Visual Basic. The data were acquired and stored in ASCII format and later processed in the Origin 9.0.0 graphics program (Microcal Origin, 2013).

Nitrate determinations were made at 220 nm and because organic matter interferes with the nitrate analysis, as it also absorbs at 220 nm, a second measurement was made at 275 nm, where only organic matter is absorbed. The true nitrate absorbance was obtained by difference.

Potassium nitrate was used to construct the analytical curve, dried in an oven at 105 °C for 24 hours (Morita & Assumpção, 1983).

The determination of nitrite consisted of comparing the colors produced by treating the samples with sulfanilamide and N-(1-naphthyl)-ethylenediamine dihydrochloride. Sulfanilamide reacts with the nitrite ion to form the diazonium salt.

N-(1-naphthyl)-ethylenediamine dihydrochloride reacts with the diazonium salt to form p-(4-ethylenediamino-1-naphthylazol) benzenesulfonamide, which absorbs at 543 nm (Greenberg *et al*., 1992).

The salt used to construct the calibration curve was sodium nitrite, previously dried in a desiccator (Morita & Assumpção, 1983).

2.2. Potentiometric measurements with selective electrodes

The procedures for determining the two anions were performed using Orion selective electrodes for nitrite and nitrate (Orion, 1996a, 1996b), an Ag/AgCl reference electrode and a Digimed potentiometer.

For the determinations of nitrite and nitrate, the technique used was direct measurement, a simple procedure for measuring a large number of samples. This method requires only one reading for each sample and calibration is performed with a series of standards.

For both the determinations of nitrite and nitrate, Interference Suppression Solution was added to all standards and samples, which ensures the same ionic strength and pH and allows the removal of several interfering ions.

The calibration was performed by obtaining analytical curves with five standards, with the potential values (mV) versus the logarithm of the standard concentrations. Then, sample determinations were made using analytical curves (Orion, 1996a, 1996b).

2.3. Voltammetric measurements

The instrument used for voltammetric measurements was the P.A.R. polarograph, model 384B (EG&G Parc, 1988; Pizeta & Branica, 1988), interfaced to a computer with data acquisition and management by a program developed in Visual Basic. The data were acquired and stored in ASCII format and subsequently processed in the Origin 8.0 graphics program, from Microcal.

The voltammetric technique used was differential pulse polarography, with the hanging drop mercury electrode (HMDE) as the working electrode, the platinum electrode as the auxiliary electrode and the Ag/AgCl electrode as the reference electrode (Reis *et al*., 2021; Annino & McDonald, 1961).

The potential range explored was from -0.9 to -1.2 Volts, with a potential increment of 4 mV and pulse amplitude of 60 mV, using the supporting electrolyte citric acid 2 mol L^{-1}, pH 2.5, for nitrite determinations (Annino & McDonald, 1961) and zirconium oxychloride 0.05 mol L^{-1} for nitrate determinations (Cunniff, 1998). The supporting electrolytes were deoxygenated for 240 seconds and, subsequently, between the addition of the sample and the additions of standard, the solutions were deoxygenated for 60 seconds.

The quantification technique used was standard addition, with an initial volume of supporting electrolyte of 5 mL, adding 50 μL of sample and four successive additions of 50 μL of standard, with the determinations being made in triplicate for each subsample.

3. Results and Discussion

The UV-Vis spectrophotometric technique, described for the determination of nitrate and nitrite ions (Greenberg et al., 1992), was used as a standard method for comparison with the potentiometric and voltammetric techniques.

The values found for the analyses using the three methods are shown in Tables 1 and 2, respectively for nitrite and nitrate. It is possible to observe that the concentrations of nitrite and nitrate obtained through the three analytical methodologies employed showed good repeatability among themselves, in each collection performed, and any of them can be chosen to be used in routine analysis. Due to availability reasons, samples were not collected in the first sampling of Emissario Novo.

Table 1. Nitrite determinations by the three analytical methodologies.

Collections[a]	**Place**	**NO_2^- (mg L^{-1})**[b]		
		Spectrophotometry	**Potentiometry**	**Voltammetry**
First	1TQ1	255 ± 32	255 ± 15	251 ± 25
	1TQ2	0.14 ± 0.04	≥ 1.64[c]	0.13 ± 0.04
	1TQ3	5.9 ± 0.2	5.5 ± 0.1	6.7 ± 0.6
	1RT4	0.20 ± 0.01	≥ 1.64	0.010 ± 0.001
	1RT5	0.63 ± 0.09	≥ 1.64	0.57 ± 0.26
	1RT6	0.58 ± 0.05	≥ 1.64	0.63 ± 0.04
	1RT7	2.10 ± 0.02	2.10 ± 0.01	2.5 ± 0.2
Second	2TQ1	292 ± 29	286 ± 13	291 ± 9
	2TQ2	4.7 ± 0.1	4.7 ± 0.1	4.6 ± 0.1
	2TQ3	10.8 ± 0.2	10.4 ± 0.1	10.8 ± 0.1
	2RT4	0.16 ± 0.02	≥ 1.64	0.16 ± 0.01
	2RT5	0.13 ± 0.01	≥ 1.64	0.140 ± 0.002
	2RT6	1.2 ± 0.1	≥ 1.64	1.10 ± 0.02
	2RT7	1.2 ± 0.1	≥ 1.64	1.10 ± 0.01
	2EM8	4.10 ± 0.03	4.00 ± 0.02	4.1 ± 0.1
Third	3TQ1	262 ± 45	264 ± 36	261 ± 41
	3TQ2	0.07 ± 0.02	≥ 1.64	0.05 ± 0.01
	3TQ3	3.5 ± 0.1	3.50 ± 0.03	3.5 ± 0.1
	3RT4	0.20 ± 0.01	≥ 1.64	0.20 ± 0.01
	3RT5	0.21 ± 0.01	≥ 1.64	0.22 ± 0.01
	3RT6	0.40 ± 0.01	≥ 1.64	0.40 ± 0.02
	3RT7	0.42 ± 0.02	≥ 1.64	0.42 ± 0.02
	3EM8	1.10 ± 0.02	≥ 1.64	1.10 ± 0.01
Fourth	4TQ1	262 ± 45	264 ± 36	261 ± 41
	4TQ2	0.07 ± 0.02	≥ 1.64	0.05 ± 0.01
	4TQ3	3.5 ± 0.1	3.50 ± 0.01	3.5 ± 0.1
	4RT4	0.20 ± 0.01	≥ 1.64	0.20 ± 0.01
	4RT5	0.21 ± 0.01	≥ 1.64	0.22 ± 0.01
	4RT6	0.40 ± 0.01	≥ 1.64	0.40 ± 0.01
	4RT7	0.42 ± 0.02	≥ 1.64	0.42 ± 0.02
	4EM8	1.10 ± 0.03	≥ 1.64	1.10 ± 0.02

[a] Samples collected on a non-rainy day, during the rainy season.

[b] Average of three subsamples ± standard deviation.

[c] Values preceded by the symbol ≥ indicate detection limit.

In terms of availability, the most viable method in financial terms and with the fastest analysis is the potentiometric method, since it involves a potentiometer available in almost all laboratories and is normally equipped with combined electrodes for pH measurements. Therefore, it is sufficient to replace these combined electrodes with other ion-selective electrodes. On the other hand, the detection limit is higher than that of the other two techniques, spectrophotometric and voltammetric, and this is a limitation.

Table 2. Relative error between nitrite determinations by comparison between the three techniques.

Collections[a]	Place	NO_2^- (mg L^{-1})		
		Error 1 (%)[b]	Error 2 (%)[c]	Error 3 (%)[d]
First	1TQ1	0.00	1.57	1.57
	1TQ2	ND[e]	7.14	ND
	1TQ3	6.78	-13.56	-21.82
	1RT4	ND	95.00	ND
	1RT5	ND	9.52	ND
	1RT6	ND	-8.62	ND
	1RT7	0.00	-19.05	-19.05
Second	2TQ1	2.05	0.34	-1.75
	2TQ2	0.00	2.13	2.13
	2TQ3	3.70	0.00	-3.85
	2RT4	ND	0.00	ND
	2RT5	ND	-7.69	ND
	2RT6	ND	8.33	ND
	2RT7	ND	8.33	ND
	2EN8	2.44	0.00	-2.50
Third	3TQ1	-0.76	0.38	1.14
	3TQ2	ND	28.57	ND
	3TQ3	0.00	0.00	0.00
	3RT4	ND	0.00	ND
	3RT5	ND	-4.76	ND
	3RT6	ND	0.00	ND
	3RT7	ND	0.00	ND
	3EN8	ND	0.00	ND
Fourth	4TQ1	-0.76	0.38	1.14
	4TQ2	ND	28.57	ND
	4TQ3	0.00	0.00	0.00
	4RT4	ND	0.00	ND
	4RT5	ND	-4.76	ND
	4RT6	ND	0.00	ND
	4RT7	ND	0.00	ND
	4EN8	ND	0.00	ND

[a] Samples collected on a non-rainy day, during the rainy season.

[b] Relative error between spectrophotometric and potentiometric techniques.

[c] Relative error between spectrophotometric and voltammetric techniques.

[d] Relative error between potentiometric and voltammetric techniques.

[e] ND – Not determined.

Table 3. Nitrate determinations by the three analytical methodologies.

Collections[a]	Place	NO_3^- (mg L^{-1})[b]		
		Spectrophotometry	**Potentiometry**	**Voltammetry**
First	1TQ1	105300 ± 1752	104775 ± 4463	105441 ± 2498
	1TQ2	457 ± 74	406 ± 43	443 ± 36
	1TQ3	519 ± 21	529 ± 22	542 ± 11
	1RT4	11.2 ± 1.9	12.5 ± 2.1	13.3 ± 2.5
	1RT5	54.6 ± 0.9	54.5 ± 1.3	52.6 ± 5.1
	1RT6	44.6 ± 0.3	45.4 ± 2.9	45.6 ± 1.2
	1RT7	166 ± 8	163 ± 4	153 ± 8
Second	2TQ1	139133 ± 1986	132928 ± 7615	138712 ± 2259
	2TQ2	443 ± 4	437 ± 11	438 ± 2
	2TQ3	1266 ± 27	1279 ± 30	1274 ± 7
	2RT4	7.3 ± 1.8	5.8 ± 0.1	6.8 ± 1.3
	2RT5	5.7 ± 0.2	4.9 ± 0.5	5.3 ± 0.2
	2RT6	83.8 ± 4.2	87.8 ± 4.3	83.2 ± 1.1
	2RT7	87.2 ± 6.5	89.1 ± 6.4	88.1 ± 4.7
	2EN8	482 ± 4	518 ± 12	482 ± 2
Third	3TQ1	58407 ± 8226	55030 ± 5661	58239 ± 8308
	3TQ2	466 ± 98	415 ± 68	434 ± 66
	3TQ3	571 ± 17	697 ± 15	567 ± 14
	3RT4	3.7 ± 1.3	3.6 ± 1.2	3.9 ± 1.1
	3RT5	6.3 ± 0.6	6.5 ± 1.1	6.3 ± 0.3
	3RT6	34.6 ± 0.9	34.2 ± 1.0	34.4 ± 0.8
	3RT7	25.4 ± 2.8	24.3 ± 3.1	25.5 ± 1.9
	3EN8	169 ± 4	172 ± 14	168 ± 4
Fourth	4TQ1	58407 ± 8226	55030 ± 5661	58239 ± 8308
	4TQ2	466 ± 98	415 ± 68	434 ± 66
	4TQ3	571 ± 17	697 ± 13	567 ± 14
	4RT4	3.7 ± 1.3	3.6 ± 1.2	3.9 ± 1.1
	4RT5	6.3 ± 0.6	6.5 ± 1.1	6.3 ± 0.3
	4RT6	34.6 ± 0.9	34.2 ± 1.0	34.4 ± 0.8
	4RT7	25.4 ± 2.8	24.3 ± 3.1	25.5 ± 1.9
	4EN8	169 ± 4	172 ± 14	168 ± 4

[a] Samples collected on a non-rainy day, in the rainy season.

[b] Average of three subsamples ± standard deviation.

Table 4. Relative error between nitrate determinations by comparison between the three techniques.

Colections[a]	Place	NO_3^- (mg L^{-1})		
		Error 1 (%)[b]	Error 2 (%)[c]	Error 3 (%)[d]
First	1TQ1	0.50	-0.13	-0.64
	1TQ2	11.16	3.06	-9.11
	1TQ3	-1.93	-4.43	-2.46
	1RT4	-11.61	-18.75	-6.40
	1RT5	0.18	3.66	3.49
	1RT6	-1.79	-2.24	-0.44
	1EN7	1.81	7.83	6.13
Second	2TQ1	4.46	0.30	-4.35
	2TQ2	1.35	1.13	-0.23
	2TQ3	-1.03	-0.63	0.39
	2RT4	20.55	6.85	-17.24
	2RT5	14.04	7.02	-8.16
	2RT6	-4.77	0.72	5.24
	2RT7	-2.18	-1.03	1.12
	2EN8	-7.47	0.00	6.95
Third	3TQ1	5.78	0.29	-5.83
	3TQ2	10.94	6.87	-4.58
	3TQ3	-22.07	0.70	18.65
	3RT4	2.70	-5.41	-8.33
	3RT5	-3.17	0.00	3.08
	3RT6	1.16	0.58	-0.58
	3RT7	4.33	-0.39	-4.94
	3EN8	-1.78	0.59	2.33
Fourth	4TQ1	5.78	0.29	-5.83
	4TQ2	10.94	6.87	-4.58
	4TQ3	-22.07	0.70	18.65
	4RT4	2.70	-5.41	-8.33
	4RT5	-3.17	0.00	3.08
	4RT6	1.16	0.58	-0.58
	4RT7	4.33	-0.39	-4.94
	4EN8	-1.78	0.59	2.33

[a] Samples collected on a non-rainy day, during the rainy season.
[b] Relative error between spectrophotometric and potentiometric techniques.
[c] Relative error between spectrophotometric and voltammetric techniques.
[d] Relative error between potentiometric and voltammetric techniques.

4. Conclusion

In this study, three analytical methodologies were compared UV-Vis spectrophotometry, potentiometry with ion-selective electrodes, and differential pulse voltammetry, for the determination of nitrate and nitrite ions in samples of industrial effluents and river water collected in the municipality of Timóteo, MG. The results showed that the three techniques present good repeatability and consistency in the values obtained for nitrite and nitrate concentrations. Therefore, any of the methodologies can be used for routine analyses, depending on the resources available in the laboratory. Specifically, UV-Vis spectrophotometry was used as the standard method due to its wide acceptance and application in environmental analyses. However, the potentiometric technique stood out for its financial viability and speed of analysis, although it presents a higher detection limit compared to the other two methodologies, which may limit its application in cases of low ion concentrations.

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