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Wastewater quality monitoring

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A new concept for monitoring basic water pollution based on a sequential injection analysis system (SIA) provided with two simple spectrophotometric detectors is proposed. The dissolved organic carbonaceous pollution – expressed as TOC (total organic carbon), COD (chemical oxygen demand) or BOD (biological oxygen demand) – and particulate pollution (TSS, total suspended solids) can be estimated using advanced UV spectrophotometry. Moreover, the nitrogenous and phosphorous compounds are determined either directly (nitrate for example) or by addition of a simple reagent, followed by UV–visible detection.

1. Introduction

The European Community decided in 1991 to oblige all EU Member States to equip with wastewater treatment plants all cities whose wastewater organic load is greater than 15 000 equivalent-inhabitants (to be implemented before 31 December 2000) and 2000 equivalent-inhabitants (to be implemented before 31 December 2005). The characterization of wastewater at the inlet and outlet of the treatment plants is an effective way to control the process efficiency and to verify the final quality of treated waters. Usually, wastewater quality is characterized both by global parameters like biological oxygen demand (BOD), chemical oxygen demand (COD), total organic carbon (TOC) or total suspended solids (TSS), and by nitrogen and phosphorus compounds. All values must be lower than the maximum permissible values, depending on specific regulations. These dispositions are of great importance but unfortunately the monitoring

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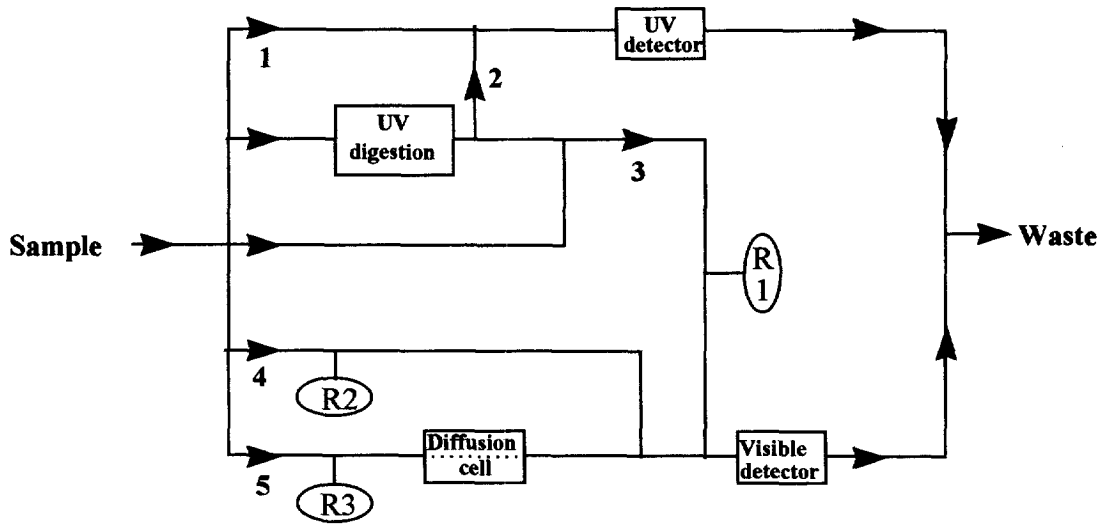

Fig. 1. Block diagram of the final monitoring system.

procedures presently performed are not very satisfactory because they involve sampling, storage and laboratory analysis – a succession of sample handlings which considerably enhances the risk of errors. There is now an increasing need to limit sample handlings and to develop fast and accurate devices enabling a range of parameters to be monitored by direct field measurements.

The aim of this study was to develop a simple wastewater quality monitoring system based on spectrophotometric methods for the measurement of BOD, COD, TOC, TSS, global N and total P. Other parameters such as nitrate, nitrite, ammonium, orthophosphate or detergents can be directly measured with the system.

The proposed multiparametric monitoring system is built around a sequential injection analysis (SIA) system coupled with two simple spectrophotometric detectors. All parameters are measured using one of the two following principles: the direct exploitation of the UV spectrum of the sample, and a chemical reaction with one stable and simple reagent.

2. General design

Spectrophotometric methods were chosen for their versatility and flexibility, enabling them to be adapted to various sample treatments and analyses, with the lowest maintenance and reagent consumption. The analytical methods have been designed using either a multiwavelength exploitation of the UV spectra or the classical absorbance measurement, both applied in combination with SIA. This technique is more versatile and robust than flow injection systems and allows total automation of the whole procedure.

The monitoring system consists of three basic parts: a flow driving system (programmable automatic burette), a multiway valve module, and the detection systems. All the operations related to the defined analytical procedures, as well as any modifications and data acquisition are PC-controlled.

The block diagram of the final monitor is shown in Fig. 1, and the analytical procedure depends on the studied parameter. For the analysis of BOD, COD, TOC, TSS, nitrate and detergents (line 1), a direct exploitation of the UV spectrum is used. For total nitrogen and organic phosphorus, UV photodigestion is needed. Line 2 corresponds to the direct final nitrate determination with the previous procedure, whereas in line 3 a reagent (R1) has to be added in order to determine either inorganic orthophosphates or total phosphorus (also as orthophosphates after mineralization). Line 4 is used for nitrite determination using a standard colorimetric method (reagent R2). It should be noted that nitrite could also be determined through line 1. Finally, ammonium is analyzed in line 5 by a colorimetric method after conversion to ammonia with reagent R3 and its diffusion through a hydrophobic membrane.

The whole system is integrated in a $60 \times 60 \times 30$ cm box with a weight of about 20 kg. It can be installed near to a fast sample loop connected to a filtration unit for lines 3, 4 and 5 corresponding to the SIA part.

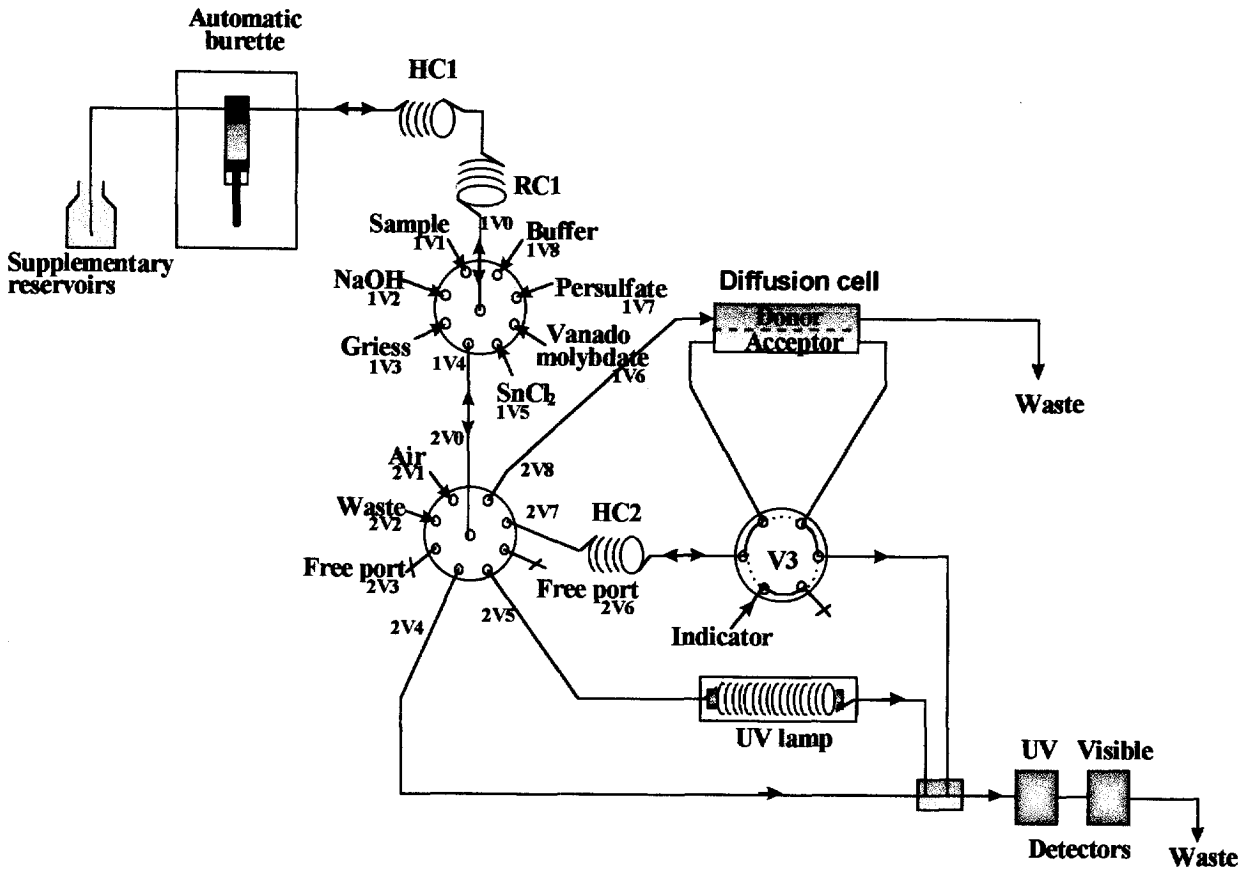

Fig. 2. SIA set-up of the monitoring system.

3. Instrumentation

3.1. UV–visible spectrophotometric detectors

Two compact spectrophotometric detectors with low power consumption were designed for the project. One 8 photodiode polyphotometer was used as SIA detector for the visible region, and one 16 diode array for the UV region. For the visible detector, the wavelengths were chosen in order to cover the main colorimetric needs (405, 430, 470, 495, 530, 550, 585, 640 nm). One supplementary diode was added at 800 nm for refraction index correction, and the flow cell has a 10 mm pathlength. For the UV detector, the light source is a pulsed deuterium lamp, and the range is 200–350 nm with 10 nm bandwidth. This latter is equipped with a self-cleaning cell including a quartz cylinder cell which incorporates a moving piston for cleaning.

Both polyphotometric detectors are reliable, very simple, compact and cheap.

3.2. Sequential injection analysis (SIA)

This recent technique is based on the same principles as flow injection analysis (FIA) but offers major assets over the earlier technique. The primary difference between FIA and SIA lies in the fact that the latter uses a switching valve rather than an injector to accurately deliver measured volumes of carrier, sample and reagent solutions to a holding coil by means of a piston pump featuring a precisely controlled forward-stop-backward motion. In this work, a titration autoburette was used as a liquid driver. This alternative device is much more easy to operate than the sinusoidal flow pump (i.e. piston pump) initially proposed for this technique.

The designed system was fully automated by coupling it to a personal computer and by developing the appropriate software for burette and valve controls, and also for data acquisition and treatment. A 5 ml automatic burette and a two valve module (all provided with the appropriate RS232C interfaces) were used as liquid drivers.

Table 1
Comparison of the results of the monitoring system with reference methods

Parameter	Reference method	Range (unit)	Correlation coefficient	Validity test
TSS	Gravimetric	5–300 mg/l (SS)	0.87	+
BOD	Dilution	5–300 mg/l (O_2)	0.73	–
COD	Potassium dichromate	10–500 mg/l (O_2)	0.91	+
DOC	High temperature	5–150 mg/l (C)	0.92	+
Organic nitrogen	Kjeldahl (and ammonium)	5–60 mg/l (N)	0.94	+
Ammonium	Indophenol blue	2–60 mg/l (NH_4)	0.88	+
Nitrite	Griess	0.5–25 mg/l (NO_2)	0.99	+
Nitrate	Ion chromatography	1–200 mg/l (NO_3)	0.99	+
Orthophosphate	Vanadomolybdate	0.5–50 mg/l (PO_4)	0.97	+
Organic phosphorus	Acid persulfate digestion	0.5–20 mg/l (PO_4)	0.98	+
Anionic detergents	Standard addition	0.5–20 mg/l (MBAS)	0.99	+

4. Methods

4.1. Robust deconvolution method of UV spectra

The qualitative study of the UV spectrum has led to a large amount of work mainly dealing with waste and natural waters. The best way to obtain a quantitative relation for a non-specific parameter estimation is to use a deconvolution method [1–3]. In practice, the shape of the unknown UV spectrum, and the associated value of the studied parameter, can be considered a linear combination of better defined spectra (reference spectra) related to characteristic states or specific compounds in the water, each of them having its own parameter value. An optimized deterministic basis was chosen with five reference spectra corresponding to the different phases of absorbent matter (suspended, colloidal and dissolved), and to specific compounds (nitrate and detergents). Application of this deconvolution procedure concerns the measurement of global parameters (organic pollution, suspended solids) and of specific compounds (nitrate, detergents) in wastewaters [3,4].

In practice, the acquisition of spectra is carried out between 200 and 350 nm with the UV detector. The general procedure includes a saturation test (if any absorbance value is greater than 2.5 a.u., a dilution step is necessary), a test of the restitution quadratic error (between measured and restituted spectra) for the autovalidation of the procedure, and the calculation of the parameters. The results are displayed simultaneously for the different parameters 30 s after the beginning of spectrum acquisition.

4.2. SIA methods

The overall instrumental set-up is shown in Fig. 2. All reagents are of analytical grade.

4.2.1. Ammonium

After studying the different methods available for ammonium determination [5], the selected procedure for ammonium determination is the following: using the automatic burette, the sample (75 µl) and an alkaline solution (100 µl of 0.01 mol/l NaOH) are sequentially aspirated into the holding coil RC1 through ports 1V1 and 1V2 respectively. They are then mixed by flow reversal through ports 1V4 and 2V8, to the donor shell of a gas-diffusion cell. There, ammonia diffuses through a hydrophobic membrane into the acceptor shell containing an acid-base indicator solution (1 ml of 8×10^{-5} mol/l bromothymol blue), which is propelled through V3 to the visible detector. The change in the absorbance, at 640 nm, of the acid-base indicator solution used as acceptor stream is measured through the port and referred to the ammonium content in the sample.

The gas diffusion unit consists of two symmetric methacrylate blocks each with a straight channel of dimension $52 \times 1.8 \times 0.3$ mm. The cross-section of the inner channel is rectangular. A gas-permeable hydrophobic membrane, 0.45–0.22 µm pore size, was placed between these half-shells.

4.2.2. Nitrite

The proposed method is based on a modified Griess reaction, which was chosen because of its selectivity and sensitivity. In order to determine the content of nitrite, 80 µl of sample and 160 µl of the Griess reagent (20 g/l of sulfanilamide, 0.5 g/l of

NED and 1.5 mol/l HCl) are sequentially aspirated through ports 1V1 and 1V3 respectively to the holding coil RC1, and mixed by flow reversal while being transported to the detector through ports 1V4 and 2V4. The absorbance is then read at 530 nm [6,7].

4.2.3. Total nitrogen

The digestion with UV radiation was chosen as the most convenient for the automatic monitoring system in order to avoid the potential problems caused by high temperatures and gas bubble formation usually associated with other methods (microwave). In brief, 100 µl of buffer (7 g/l of sodium tetraborate, pH 9) is first aspirated to the holding coil RC1, through port 1V8 and followed, through port 1V7, by 30 µl of oxidant (4 g/l of potassium persulfate), 50 µl of sample (port 1V1), 30 µl of oxidant (port 1V7) and finally, 100 µl of buffer (port 1V8). Thus, the sample is sandwiched between two reagent and buffer zones. The mixture is then propelled through ports 1V4 and 2V5 to the UV reactor. After 3–5 min, the mineralized mixture is pushed through the UV detector. The organic and inorganic nitrogen compounds are oxidized into nitrate which is then measured using the previous UV multiwavelength procedure.

The photo-oxidation reactor consist of a 15-W mercury lamp (λ=254 nm) placed inside an aluminum cylinder, a Teflon tube (150×1.5 mm i.d.) coiled around it and a cooling fan, which is used to keep its temperature low.

Different substances were tested for mineralization: $NaNO_3$, NH_4Cl, urea, glycine, aspartic acid, barbituric acid, EDTA, 4-aminophenol (p-AP), 4-nitrophenol (p-NP), and 2,5-pyridyl dicarboxylic acid (PDA). These compounds all have a wide variety of nitrogen forms. For all compounds, the recovery was more than 85% for 30 mg/l of N. The difference between the TN and the sum of the concentrations of nitrates and nitrites before photo-oxidation is the Kjeldahl nitrogen (TKN). The organic nitrogen can also be calculated.

4.2.4. Orthophosphate

The vanadomolybdate method was chosen for its good reproducibility and reagent stability. The procedure is as follow: 1 ml of 0.125 mol/l HCl is aspirated directly by the burette to the coil HC1 and 250 µl of reagent (0.035 mol/l of molybdate and 0.0025 mol/l of metavanadate in 0.6 mol/l of HCl) plus 250 µl of sample are sequentially aspirated respectively through ports 1V6 and 1V1 to the holding coil RC1. Then the liquid is propelled towards the detector through ports 1V4 and 2V4. The absorbance is then read at 430 nm.

4.2.5. Total phosphorus

The SIA manifold is basically the same as used for orthophosphate determination, but with UV digestion. The procedure is as follows: 1 ml of 0.048 mol/l HCl is aspirated directly by the burette to the coil HC1 and 240 µl of sample is inserted, through port 1V1, in the holding coil RC1 as a central zone, sandwiched between 75 µl of oxidant (16 g/l of potassium persulfate), through port 1V7, and 100 µl of the above vanadomolybdate reagent, through port 1V6. Then the flow is reversed and propelled to the UV reactor through ports 1V4 and 2V5, where the flow is stopped for a certain time (150 s) to oxidize organic phosphorus compounds into orthophosphate. Finally, the mixture is transported to the detector for orthophosphate determination by means of the vanadomolybdophosphate method.

The duration of the SIA procedures is obviously longer than that of the direct UV method. For the measurement of the different parameters, the total time required can be less than 15 min, including the cleaning and autocheck steps, depending on the number of replicates.

5. Validity of results

All results are summarized in Table 1. The results of the different parameters obtained from either real samples or synthetic solutions were compared with those of reference methods, chosen from international standards. The comparison was carried out for each parameter by calculating the correlation coefficient and by testing the validity of the following hypotheses: value of slope and intercept of the regression line (respectively 1 and 0), and validity of the linearity [8].

For global parameter estimation (TSS, BOD, COD, and TOC) and for nitrate determination, the proposed UV method has been tested for a range of real samples (85) corresponding to treated wastewaters originating from several treatment plants. The correlation coefficient values (R^2), respectively 0.87, 0.73, 0.91 and 0.92, show that BOD obviously gives the worst results, as the measurement principle of the reference method is very different. Moreover, this parameter is the only one with a negative test of validity (slope different

from 1). TOC has been replaced by DOC, taking into account the performance of commercial instruments used for the comparison.

For the other parameters (ammonium, nitrite, organic nitrogen, orthophosphate and organic phosphorus), SIA procedures have been optimized [9,10] and tested for a series of calibrant solutions and of real samples, depending on the parameter. For nitrite, 10 calibrants were prepared with a nitrite/nitrate ratio varying from 0.1 to 10, and covering a range of 0.5–20 mg/l of nitrite. For organic nitrogen, 11 wastewater samples were analyzed with the Kjeldahl method (and ammonium determination) and with the SIA–UV method. For samples with a high COD value, the mineralization is complete up to 60 mg/l N when using a persulfate concentration as high as 20 g/l. This causes a high blank signal that can be eliminated with longer irradiation times (10 min), but in this case the gas bubbles formed by the decomposition of persulfate may interfere with the spectrophotometric measurement and a separation device has to be installed. Another possibility is to use a more diluted oxidant (12 g/l) and an irradiation period of 5 min. In that case the method is linear up to 30 mg/l N.

For orthophosphate and organic phosphorus, seven wastewater samples have been used for the comparison. A complementary test of the photooxidation efficiency has been carried out with different compounds, showing that, except for condensed phosphates, the efficiency is always greater than 90%.

For anionic detergents, the method of standard addition has been preferred to the not very precise reference method (MBAS).

In conclusion, for all parameters tested, the correlation coefficient values are close to or greater than 0.9 and the validity test is always positive, showing that the proposed methods can considered equivalent with regard to the results of the reference methods.

6. Conclusions

This new simple wastewater quality monitoring system is compact, portable and multiparametric. The system rapidly gives good results for the estimation of global pollution parameters (TSS, COD, DOC) and for the determination of specific compounds (nitrate, anionic detergents) with a direct UV procedure. Non-absorbent species (ammonia, organic nitrogen, orthophosphates and organic phosphorus) are determined with the use of a set of SIA procedures (including the design of a new compact and reagent-sparing SIA manifold and of a simple digestion unit using UV oxidation).

From this work some evident advantages of SIA compared to FIA may be deduced:

- Greater multiparametric capacity
- Drastic reduction of reagent consumption
- Greater autonomy due to the better performances of the different components of the SIA system.

Some further complementary work has been done and needs to be developed, such as the determination of hexavalent chromium and applications to natural and industrial waters. The proposed monitoring system has now to be industrialized.

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