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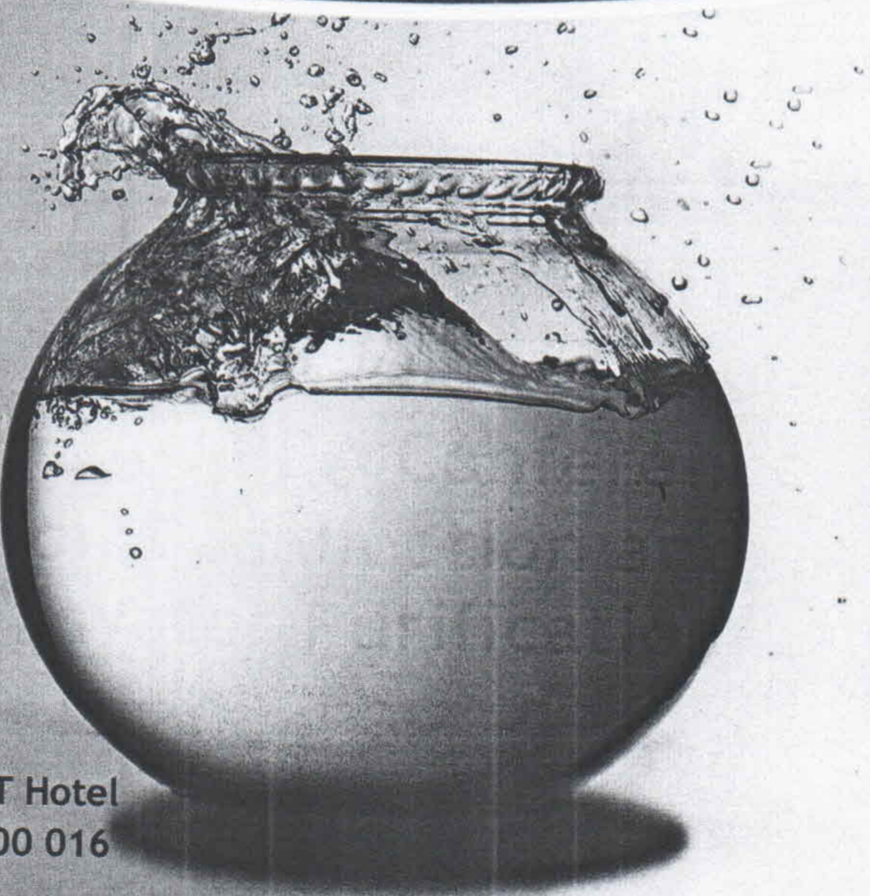

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Nano*sensor applied to Water Quality - Developing low cost pH sensor to natural water, and application of other techniques.*

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ABSTRACT

The low-cost optical sensor built in strip, was developed from a composite obtained with application of *in-situ* chemical polymerization, using polyaniline in the emeraldine oxidation state, doped with HCL onto poly(ethylene terephthalate) (PET) film, used to measured the pH of water. The absorption of UV-Vis spectra was used to evaluate the optical response to pH change of natural water. The strip showed a reversible color change upon variation of the pH. The pH ranges used to calibrate the optical sensor were from 2.0 to 12.0. These kinds of sensor show the potentiality to investigate the pH of the natural water, to application to limnologic studies, as well as, to investigate the influence of the ionic strength. In this paper were showed new techniques that can be use to conduct research with pesticides in water using electrochemistry and biosensor, and electronic tongue with conductive polymers to global quality evaluation.

Key words: disposable nanosensor, optical, low cost, conductive polymers, water quality, new techniques

Introduction

The evaluation and monitoring of water quality are of fundamental importance for the sustainable use of water resources. The contamination of the environment and its direct relation to human health, the management of livelihood and the maintenance of ecosystems, has raised standards aimed at the disposal of chemical waste. The increasing use of pesticides in agriculture and its harmful effects such as contamination of soils and waters has drawn the attention of society and scientists to the issue of sustainable development [1].

In South Ásia total renewable freshwater resources amount to 3655 km^3 and total withdrawals for agriculture are 842 km^3 per year which is by far the highest consumptive use of water [2].

In Brazil the semi-arid 18% of the national territory and includes 29% of the population of the country, with an extension of 858.000 km2, representing about 57% of the territory northeast, and the area designated as "Drought Polygon" (occurrence of droughts) is estimated at 1,083,790.7 km^2. It is estimated that only in semi-arid, the area occupied by naturally saline soil is more than 90,000 km^2, predominantly within the Drought Polygon.

Besides, the growing demand for water in industrial processes may affect the local environment in a significant way. Likewise, water scarcity, especially in the semi-arid northeast of Brazil, makes water reuse a factor of high priority and attractiveness [3].

Thus it is important to have methodologies to assess the impact of agricultural activities on soil and water. More specifically, in the case of application of inputs such as fertilizers and pesticides (herbicides, insecticides, fungicides), and substances such as nitrates, nitrites, heavy metals, ions and humic substances, it is essential to constant monitoring of the environment in order to know well the effects and destination of such products in natural resources [4, 5]. In this case, the tests are almost always expensive and require the use of sophisticated laboratory equipment. Therefore, the developments of sensors that allow the determination of these substances in the laboratory or field, with techniques of low cost and simple to perform, are highly desirable. An important feature of the monitoring and surveillance of these substances in the environment [6, 7] is the need for a large number of tests and measures, both spatially and temporally. To this end, we seek to increasingly sensors, equipment and the most simple, cheap and fast. The study of conducting polymers has attracted an enormous scientific and technological interest due to the need of active materials for sensors in many applications. These polymers become electroactive through the process of doping, with a variety of substances, which allows an increase of its versatility for use in sensor devices.

The potential impact of nanotechnology on the sensor market is huge in the developing and developed world alike. For example, industry analyst NanoMarkets reports that nanotech sensors generated global revenues of US$2.7 billion in 2008 and estimates it will reach US$7.2 billion in 2012.

In Brazil, The National Nanotechnology Laboratory Applied to Agribusiness, housed at Embrapa's agricultural instrumentation unit in São Paulo, has developed a cheap optical sensor incorporating nano-assembled films to evaluate the acidity of natural water supplies. And 'electronic tongues' – another kind of polymer sensor developed at Embrapa – can be used to distinguish between different mineral waters and between pure water and water contaminated by organic matter.

New sensor technology co
powerful micro-and nanoma
will lead to tiny sensors, p
high accuracy for detectin
and biochemical's. The pote
of nanotechnology sensor ma
For example, the nano market i
States reached $ 190 million
should grow at an average a
26% to $ 592 million by the
[8].

One of the major challe
century will certainly be the d
of electronic devices based
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are beginning to be demonst
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that in 1994 a Field Effect Tra
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of substrate for the producti
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device. However, other mat
on organic compounds, ca
such as polyaniline, polyp
polythiophene conductive [9].

Line Patterning Technique

The sensor technology
conducting polymers has s
interesting results, espec
related to the development o
devices [10-11]. It has been sh
miniaturization and thin film
could be the best way to have s
working with good performan
the techniques which usually
achieve such systems are not s
due high costs and many comp
to build up such sensors. M
and collaborators [12] dev
Line Patterning Technique, w
used to fabricate inexpensive,

electronic devices [13]. This process is relatively simple and easy to be carried out. In this process, commercially available office supplies, as for example overhead transparency and paper can be used as a substrate for the fabrication of electrodes. Therefore, it is a new possibility to fabricate disposable and inexpensive sensors.

The pH of the water is an important parameter to water quality, because the value could determine the toxic effects of the substances found in the solution. (runoff from agricultural, domestic, and industrial areas may contain iron, aluminum, ammonia, mercury or other elements). The measurement of the pH in the water has high weigth in the Water Quality Index (WQI). The WQI are compound by the following parameters: a) Dissolved oxygen; b) Fecal coliform; c) pH; d) Biochemical oxygen demand; e) temperature; f) total phosphate; g) Nitrates; h) Turbidity and i) Total solids. [22].

Optical pH disposable nanosensor.

The line patterning technique was used to make a mask to developing a low-cost optical sensor, built in the stripe of poly(ethylene terephthalate) (PET) film, using a thin film of polyaniline (PANI) in the emeraldine oxidation state [14-15] doped with HCl, by *in-situ* chemical polymerization. The measurements occured with conductive polymers doped and dedoped, and were used to evaluate the pH of natural water. The absorption of UV-Vis spectra was investigated to evaluate the optical response of the pH change to natural water, and the comparison with common technique (Horiba system) used to measure the value of water pH in the natural condition. The sensitivity and reproducibility was evaluated.

In this paper are demonstrated the potential application of low cost sensor to investigate influence of ionic strength to desalinization investigation, carry out study of pH in natural water (limnologic and portable water), new other techniques to evaluate de concentration of pesticide in water (Electrochemistry and biosensor) and global water quality (electronic tongue).

Materials and Methods

Development of optical pH sensor using Line Patterning Technique (LPT)

The LPT was used to design the mask and polyaniline deposition. In the figure 1 the sequence for the manufacture of optical pH sensor: a) Design of the mask, b) negative image of the mask, c) printing of the mask on PET, d) in-situ synthesis of PANI, e) removal of the toner with toluene and methyl ethyl ketone (MEK).

The size of the strip was designed compatible with PET to the size of portable electronics. The size of the square to deposition of the active layer (PANI) was determined according to the place where the light beam will not be dispersed.

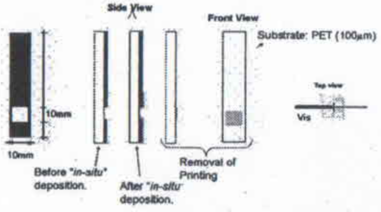

Fig. 1. Sequence for the development of optical sensor using line patterning technique.

Emeraldine-HCl By *in situ* Deposition of Polyaniline from a 1 mol*l^{-1} Hydrochloric Acid Aqueous Solution.

The overhead transparency was place in a 1.0 M hydrochloric acid solution with 0.1M aniline and 0.1M ammonium persulfate. The polymerization at 0.0^{0}C was done, with the reaction time of 90 minutes. Thin strips of PET coated with PANi were cut with 1.0 cm and 6.0cm. The ribbons were used as sensor of pH in the natural waters. All the measurements were carry out at room temperature.The absorbance measurement were taken from UV-Vis spectrometer Shimadzu 1610, to evaluate the colorimetric response of the polyaniline in the emeraldine base oxidation, onto poly(ethylene terephthalate) (PET). The polymerization of the composites, used as a pH sensor, showed a formation of polyaniline (PANi) in the doped emeraldine salt (ES) form. All the aqueous solution used in this experiment was prepared with Milli-Q water. Aniline (Aldrich, Sao Paulo, Brazil) was used after distillation under reduced pressure. Other chemicals were used as received.

UV-Vis spectroscopy of the PET/PANI stripe with different pH

The spectrum of polyaniline obtained by chemical oxidation is pH dependent between a pH 2 -12. In this range the apparent p*K* is around 7, which is in the physiological pH range. The electronic absorption band of polyaniline sensitive to pH change is very broad. The figure 2 showed the absorption response of the composite (*in-situ* deposition of polyaniline coated PET) with fifteen different pH (2.0, 3.0, 4.0, 4.5, 5.0, 5.5, 6.0, 6.5, 7.0, 7.5, 8.0, 9.0, 10.0, 11,0 and 12.0).

Measurement in natural water

The developed system was used to determine the pH of natural water dammed. The water used in the experiment was collected on January 6, 2009 at 16:30 in Carlos Botelho (Lobo-Broa) reservoir, Itirapina, São Paulo, Brazil
11′ 40.87″ S, longitude 47^0 53
the surface area is 6.8 Km^2
around 22 x 10^6 m^3. We col
water samples at different
30 and 45 cm), to obtain the
samples from the Lobo-Br
with the optical system. The
PANI was maintained for fiv
1M HCl solution, and after dr
same used for the calibration
system. After calibration, th
placed for five minutes in the
measured the pH, being inse
system for measuring pH. The
with the optical system was co
the values obtained with a co
meter (Analion).

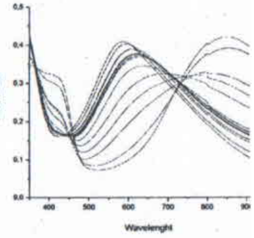

Fig. 2. Set of absorption spectra rec
film obtained by in-situ deposition of
emeraldine oxidation state, on

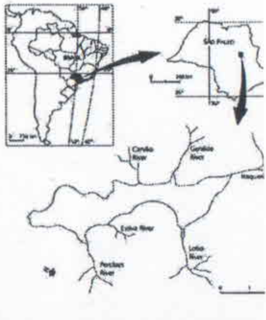

Fig. 3. Localization of Carlos Botelh
Reservoir (SP) [16].

Results and Discussion

The colour of PET/PANI stripe is pH dependent, as the protonated and non-protonated forms of the PANI have different spectral characteristics. Fig. 4 shows the calibration curve that was obtained with the wavelength of 530nm. The reproducibility was tested, and value obtained for 6 different samples were 7.6% to the same wavelength. The sensitivity of the calibration curve, using a fourth grade polynomial equation, was approximately 0.4 of pH. The minimum measurement of the pH was 1.5 and the maximum was 11.9. The equation 1 is a linear relation of the attenuation (I/I) and pH. This is considered the calibration equation of PET/PANI stripe. The reproducibility was investigated and the standard deviation is considered the measured three times, with immersion time of 5 minutes each measure.

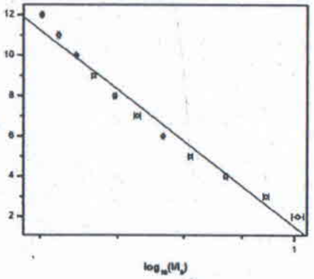

Fig. 4. Normalised attenuation curve of the PET/PANI stripe, measured at 530 nm as a function of pH

Where "I" is the measurement of the stripe under different pH and "I " is the reference before measure the pH solution.

$$pH = 1.503 - \left(43.982 * \log_{10}\left(\frac{I}{I_0}\right)\right)\left(R^2 = 0.9882\right) \qquad (1)$$

The optical device developed was used to verified the effects of the ionic strength and the nature of the ions, using buffer solutions in which different salts (NaCl and KCl) and three concentrations of 0.15, 0.30 and 0.50 mol l-1, with the solution in the same pH (7.0). Fig. 5 shows the relation between concentration (mol l-1) and attenuation response of PET/PANI stripe, obtained by using NaCl and KCl (in different concentrations).

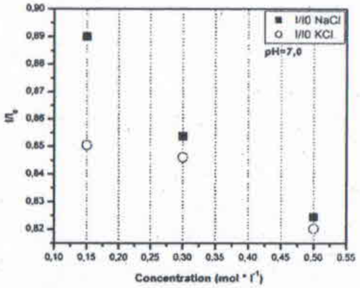

Fig. 5. Effect of ionic strength (0.15, 0.30 and 0.50 mol l-1, in the same pH (7.0)) and nature of the ions (NaCl and KCl) on the sensor response.

The results obtained show us the potentiality to be used as disposable sensor to evaluate the influence of ionic strength, and can be applied to investigate the salt concentration in the water solution.

Application of optical pH in natural water

The pH of natural water collected from various depths, in Carlos Botelho (Lobo-Broa) reservoir, Itirapina-SP, Brazil, was obtained with the PET/PANI optical sensor. The pH of the water through the optical system was compared with measurement of the commercial pHmeter. The data collected are showed in Table I. The proposed optical system has an accuracy of ± 0.4 pH units, the data obtained are in good agreement with the pH obtained with the commercial system.

Table I. Values of pH of water (Carlos Botelho reservoir) at various depths, obtained with the optical system and commercial electrode.

Depth (cm)	pH (commercial System)	pH (Stripe (PET/PANI))
15	7.2	7.5
30	7.7	7.9
45	7.6	7.9

The data were obtained in the field, during a rainy day, in 01/2009, 16:00hs. The measurement of the pH obtained in 15 cm was possible observe a slight trend to acid regime. This could be a influence of the rain in the fisrt layer of natural water. In the depth 30cm and 45 cm basically the pH didn´t change.

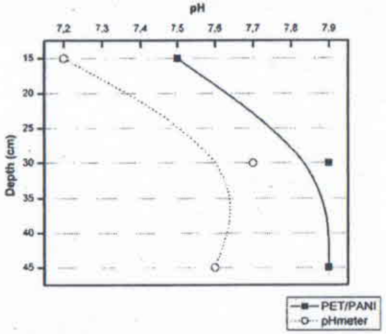

Fig. 6. The graphic contain experimental data of the relation of pH with the depth (15, 30 and 45 cm) of the Broa reservoir.

New Techniques to water quality monitoring.

Follow below some of the new techniques that were developed by researchers of the Embrapa Agricultural Instrumentation applied to evaluated water quality used in soil physics, limnology and other areas:

Nanobiosensors with AFM car for detecting herbicides

Enzyme inhibitors bind to and decrease their activity. Sinc an enzyme activity can kill a or correct a metabolic imbalar drugs are enzyme inhibitors. also used as herbicides and p Specific interactions betweer can be studied at the molec using atomic force microscop Adhesion, in particular, is go short-range intermolecular f may be controlled by appropria modification, thus leading t called Chemical Force Microsc [17, 18]. Figure 7 shows the force between glass (substrate) without herbicide (diclofop-m the tip of the Atomic Force M (AFM) coated with enzyme (a carboxylase (ACCase).

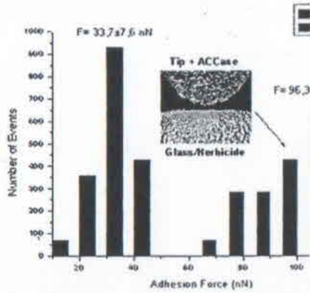

Fig.7. Force curve on glass and herb

Electrochemical detection of p using conducting polymers as

Pesticides with acidic char (2,4-D, gliphosate and bent readily sorbed on the dedoped increasing the voltammetric of the CPE2 electrode. How interaction was observed betw acidic pesticides and the polyp suggesting that electrostatic interaction are dominant in the sorption of such pesticides without doping of the polypyrrole by protonation, since the paraquat is an ionic pesticide [19].

Electronic Tongue water quality

An electronic tongue based on conducting polymers and a lipid-like material (stearic acid, SA) can be used to distinguish between different mineral waters and between pure water and water contaminated by organic matter [20].

The importance of using ultrathin films in obtaining high sensitivity, detecting sucrose, quinine, NaCl, and HCl at the parts-per-billion (ppb) level. For that were compare sensor arrays made with nanostructured Langmuir–Blodgett (LB) films and cast films from conducting polymers, a metallic complex, *mer*-$[RuCl_3(dppb)(py)]$ (dppb = $PPh_2(CH_2)_4PPh_2$; py = pyridine) (Rupy), and mixtures of conducting polymers and Rupy. This could be indicate that the manipulation of composite Rupy/conducting polymer films may be tailored to specific applications, particularly because ruthenium complexes might complex with heavy metals [21].

Conclusions

The results obtained in this work indicate that the strip built with PET - PANI nanocomposite produced during *in situ* polymerization of aniline onto PET film, is suitable for a construction of disposable optical sensor, which could be useful to measure pH of the natural water, as well the ionic strength .The sensitivity and durability of each optical sensor were obtained from the experimental results. The analysis of the data showed that could be useful to investigation in environmental condition.

In addition was showed the potentiality of new techniques (Biosensor with AFM cantilever and Eletrochemistry) applied to detection and quantification of herbicide in water, and electronic tongue to use in global water quality. In this paper was showed a brief overview of the potential application of low cost sensor to investigate influence of ionic strength to desalinization investigation, carry out study of pH in natural water.

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