

**THE DEVELOPMENT OF A MONITORING TOOL TO WATER QUALITY CONTROL OF PIRAJUÇARA
URBAN STREAM, SÃO PAULO, BRAZIL**

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ABSTRACT

The ceramic sampler – CS has been developed as a monitoring tool for water quality control of urban stream with dense pollution, flood events, which cross big cities and located just a few meters of squares, streets, industries and residences. The study was carried through adsorption processes (with adsorption rate in the range of 7 to 5 $\text{mg.g}^{-1}.\text{min}^{-1}$) and the analysis of the adsorbed toxic compounds on saturated adsorbent material was correlated with the values obtained for water quality parameters of the urban stream during one hydrologic year of May of 2005 to July of 2006. The comparison between the measured values and the water parameters for surface water bodies classification described at CONAMA - Resolution 375, determined that the Pirajuçara stream belongs to the class 4 with high phosphorous content and low values of dissolved oxygen – DO.

RESUMO

Um amostrador cerâmico-CS foi desenvolvido como ferramenta para monitoramento da qualidade da água de córrego urbano densamente poluído, com eventos de enchente, que cruza grandes cidades e se localiza a poucos metros de praças, ruas, indústrias e residências. Foram realizados ensaios de adsorção (com velocidade de adsorção de 5 a 7 $\text{mg.g}^{-1}.\text{min}^{-1}$) e a análise dos teores de compostos tóxicos presentes no material adsorvente saturado foi correlacionada

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com os valores de compostos tóxicos obtidos em monitoramento da qualidade de água do córrego durante o período hidrológico de maio de 2005 a julho de 2006. Comparando os valores obtidos com os parâmetros de classificação de corpos de água - Resolução CONAMA 375 determinou-se que o córrego Pirajuçara pertence à classe 4 com elevados teores de fósforo e baixos valores de oxigênio dissolvido – OD.

INTRODUCTION

The water resources have been continuously suffering the environmental degradation due domestic and industrial waste discharge, urban rivers and streams with flooding events, which cross big cities and located just a few meters of squares, streets, industries and residences are now a testimony of the environmental impact of unplanned urban expansion.

Many research projects have been carried out trying to develop technologies to reduce or minimize the environmental impact on urban surface water, chemical processes are developed to treat wastewater effluents to reach the permissible limits for environmental regulation to direct discharge on water bodies. The development of monitoring and control tools for urban water quality analyzes and control will help to identify and quantify the discharge of pollutants in urban water body.

Many projects have been developed trying to perform the diagnosis of water and soil contaminated by industrial discharge, domestic sewage and solubilized products of toxic solid waste deposits. In spite of those studies there is a lack on the diagnosis and monitoring of the surface water located inside big cities with dense population. Exploratory studies indicate the urban stream as a system with high complexity with the variation of the water quality parameters measured seasonally, monthly, daily and also during the day, with the variation of the results

performed in the morning in comparison with the results obtained in the afternoon.

The development of the Ceramic Sampler - CS can add important information of the evaluation and control of the water quality of urban surface water, performed by the development of the adsorbent material with remains fixed under the water for few days allowing the measurement and control the discharge of toxic compounds. After the saturation the CS will have the tendency to show a toxic compound concentration equivalent of those present at the monitoring time on the surface water. The CS main composed by diatomite can be also used as artificial substrate for bioindicators growing followed by the quantification and identification of the algae community.

The use of diatomite pellet as adsorbent material is providing important information about the urban surface water diagnosis, about the presence of toxic metals, organic compounds, water eutrophication and the toxic condition of the water which cross big cities. The project is now providing addition information which can help the water quality measurements of similar urban surface water with dense pollution, with flooding events, as Pirajuçara urban stream located in metropolitan area of Sao Paulo.

The Pirajuçara stream

The Pirajuçara Stream is an example of the urban surface water with dense pollution, a testimony stream which receive many years of raw sewage discharge, a reflection of the historical concept of raw sewage discharge in the nearest available surface water, which can not now considered adequate. The Pirajuçara represents nowadays a water body with high phosphorous content, low concentrations of dissolved oxygen and a problem difficult and expensive to be solved (Shreve, 1977).

The Pirajuçara stream is located in metropolitan area of the São Paulo and cross many municipalities as Embú Guaçú, Taboão da Serra and São Paulo. The Pirajuçara river basin drains an area of 72 km², mostly urban areas with predominance of the residential use. It is located in the left side of the inferior canal of Pinheiros river. The table 1 shows the classification of the areas on Pirajuçara river basin (DAEE, 1999).

Table 1: Classification areas of the Pirajuçara river basin.

CLASSIFICATION	Area (km²)	% Total Area
High dense urban area	47.49	65.96
Low dense urban area	16.74	23.26
Green areas	7.77	10.79
Total of urban areas	64.23	89.22
Total of green areas	7.77	10.78
Totals	72.00	100.00

Source: DAEE, 1999.

Physical and Chemical Parameters of Water Quality Analysis

There are some physical and chemical parameters to be measured for water quality classification of surface water bodies; the classification will also indicate the possible use. The National Environmental Commission – CONAMA on the Resolution 357 establish the limits for each class of surface water based on the results obtained for turbidity, DO - dissolved oxygen, concentration of nitrogen compounds, pH values, the concentration of toxic metals, phosphate and chlorophyll (Branco, 1984) (CONAMA, 2005). The phosphate is one of the most important nutrients for the biological processes and one of the most important parameters in effluent characterization, higher values of phosphate will enhance the eutrofização processes of polluted surface waters. In table 2 the concentration of phosphate and chlorophyll a can be observed, they will indicate the systems on different trophic levels. The raw domestic sewer in Brazil shows

typically the concentration of phosphate ranging from 6 to 10 mg L⁻¹.

Table2: Phosphate and Chlorophyll a measurements for water bodies on different trophic levels

Level	Phosphate (mg L ⁻¹)	Chlorophyll a (µg L ⁻¹)
Oligotrophic	<0.010	<2.5
Mesotrophic	0.010-0.035	2.5-8.0
Eutrofic	0.035-0.100	8.0-25.0
Hipereutrofic	>0.100	>25

Fonte: Lobo, 2002.

The common source of phosphate content in superficial waters is the fertilizer leaching and solubilization applied in agricultural areas, the decomposition of organic materials, the discharge of raw sewer and industrial effluent, as the fertilizers, pesticides, chemistries in general, nourishing, freezing conserves and dairy industry which represents large amounts. The ecological systems with hipereutrofic levels are favorable to the appearance of superior aquatic plants which limits the use of the water body and enhance the appearance of parasites, which can cause many diseases. The quantification of chlorophyll a is used to estimate the phytoplankton biomass present in water column and the trophic level of lagoons, rivers and reservoir of surface water. In green plants and phytoplankton concentration constitutes approximately 1% to 2% of the dry weight, Table 2(Udy et al, 2005)(Barroso, 1998). One of the main methods of analysis of chlorophyll a is the spectrofluorimetry, where the intensity of emitted energy is quantified from the absorption of radiating energy under the light form.

The evaluation of the water quality by physical and chemical methods represents many difficulties to perform the analytical measurements, mainly when toxic compounds remain in solution on low concentrations. The physical and chemical results represent an instantaneous knowledge of the water conditions, only the environmental contamination of the surface water

when the measurements are made. These limitations become higher when the surface water is a lotic system, a stream or a river, where the water is continuously renewed in each point. However, the measurements performed monthly during a long time increase significantly the informative value of physical and chemical methods, reducing the discrete character of the information (Lobo, 2000). The used of adsorbent materials for water quality monitoring present the advantage to offer information of environmental effect of contaminant discharge with the capability to reflect a condition not more existing at the moment of the verification.

Adsorption processes

The adsorption processes are usually studied by the determination of the adsorption removal percentage, the calculation of the adsorption rate, the kinetic model and the concordance with the Langmuir and Freundlich adsorption models. This project was performed emphasizing the calculations of adsorption removal percentage (equation I) and the adsorption rate (equation II) due their importance on the adsorption process performance under the water, during the monitoring time. The adsorption process have to be available during all the expose time for surface water monitoring.(Ortiz, 2001)(Namasivayam, 1995).

$$R = C_i - C_e / C_i * 100 \quad \text{I}$$

$$\log (q_e - q) = \log q_e - (k_{ab} / 2.303) t \quad \text{II}$$

Where:

q_e : Mass for adsorbed compound for adsorbent mass at equilibrium time(mg g^{-1}).

q: Mass for adsorbed compound for adsorbent mass at t time(mg.g^{-1}).

k_{ab} : Adsorption rate ($\text{mg g}^{-1} \text{min}^{-1}$).

t: Stirring time (min).

R: Removal percentage (%).

C_o : Inicial concentração (mg L^{-1}).

C_e : Concentration at Equilibrium (mg L^{-1}).

MATERIALS AND METHODS

The water sampling procedures were developed for one hydrological year, started in June of 2005 until June of 2006, the geographical coordinates were 23°33'55,78"S 46°42'50,61"W in the river mouth of Pirajuçara Stream, SP, Brazil. The water samples and the physical and chemical measurements were performed monthly, with about 20 to 30 days of time interval.

The physical and chemical parameters of water quality were performed accordingly with those establish by the CONAMA Resolution nº 357 of March 17th, 2005. The parameters were the turbidity by the nephelometry method (Tecnopon TB 1000), sediment solids based on Imhoff glass, dissolved oxygen – DO measured by portable (Hanna HI 8043), the total phosphate for colorimetric method by the synthesis of blue molybdenum complex with the measurement of absorbance/transmittance in spectrophotometer UV - Visible on $\lambda = 880 \text{ nm}$ and the water temperatures were measured by digital thermometer.

The Ceramic Sampler –CS as a monitoring tool

The Ceramic sampler –CS is main composed by diatomite pellets with 1 cm of diameter and mass of 1g. About 250g of the pellets were placed in a package made by acrylic screen. This

set was placed in the stream water with 50 cm of maximum depth; it remained there for 20 to 30 days. After the monitoring time the saturated pellets were dried and analyzed.

The saturated pellets were fixed in resin; suffered longitudinal cut and one half spheres were analyzed by scanning electron microscopy – SEM with EDX chemical analysis. These procedures allow measuring the chemical composition of the saturated pellets from the surface to the bulk, to measure and controlling the percolation depth of the adsorption process.

The adsorption processes

The adsorption systems was studied using the diatomite beds and water solutions of lead and phosphate with similar composition of the analyzed Pirajuçara water samples for the determination of the adsorption removal percentage (%) and the adsorption rate($\text{mg g}^{-1} \text{min}^{-1}$). After those studies the adsorbent material can be modified accordingly with the requirements to be most efficient to perform the measurements of toxic compounds present at urban water.

The adsorption processes were studied in batch with magnetic agitation. The concentration of lead and phosphate in adsorption experiments were controlled by complex titration and inductive coupled plasma spectrometry–ICP/AES. The parameters of the adsorption systems studied were: the variation of the agitation time and the variation of the initial concentration of the solutions. The temperature and the pH values are similar with those found on the stream water samples and were kept constant. The obtained results had allowed the determination of the removal percentage and the adsorption rate.

RESULTS AND DISCUSSION

Physical and chemical results

The values of turbidity, sedimented solids, dissolved oxygen, phosphate and water

temperature of Pirajuçara stream can be observed at Table 3. The DO values were always below the lower limit of 2,0 mg/L expected for surface water Class 4, destined to the navigation accordingly with Resolution nº 357. One or two measurements were found almost in the limit for Class 4, they can be considered as an effect of the rain.

The phosphate content is not limited for CONAMA surface water Class 4. However they were always high, in the range of 0,01 to 1,08 mg.L⁻¹, This phosphate content represents an hipereutrofic system which enhances the growth and the proliferation of aquatic vegetal organisms.

The values of turbidity during the year were relatively low, in the range of 16 to 72 NTU, almost in the condition demanded for Class 3 surface water, up to 100 NTU. Except the value obtained in April, 2006, with 948 NTU, this sample was also observed a increase on sedimented solids values, it was measured 5 mL.L⁻¹. The effect can be related to an isolated event of edges erosion of the stream or an uncommon rain event. The values of sedimented solids had been low during all monitoring time, with the average of 0,3 mL.L⁻¹. However the Resolution nº 357 demands their absence in order to prevent the flooding events of ships canals.

The results of physical and chemical analyses allows to classify the Pirajuçara stream as surface water Class 4 by the CONAMA Resolution nº 357, with an indication of eutrophication process, with nutritional enrichment and severe qualitative and quantitative environmental impact in the aquatic communities.

A correlation table was prepared based on Person Coefficient applied on physical and chemical measurements during the monitoring year, Table 4. The positive correlation of 0,99 was observed for potassium and sodium content, this effect was expected due those chemical elements are related and common chemical compounds of soaps and detergents directly related

with domestic sewage discharge. The negative correlation $-0,94$ and $-0,91$ was observed for DO and sodium content and DO and potassium content which represents more soap and detergent discharge less DO present in surface water. The turbidity has a negative correlation with sodium and potassium content, it was observed mainly during the raining season, the rain has the tendency to increase the turbidity and also to dilute the domestic sewage discharge, and as a result can dilute the sodium and potassium content.

Table 3: Values of DO (mg.L^{-1}), phosphate (mg.L^{-1}), turbidity (NTU) and sedimented solids (mL.L^{-1}) of the Pirajuçara stream.

Date	Temp (°C)	DO(mg.L^{-1})	Phosphate (mg.L^{-1})	Turbidity (NTU)	Sedimented Solids (mL.L^{-1})
06/06/05	21,1	2	0,01	38,4	0,2
07/14/05	18,7	1,4	0,73	36,9	0,3
08/31/05	23	2,35	0,17	43	0,1
10/05/05	24	0,6	0,79	29,3	0,1
10/21/05	23,2	0,2	0,92	32,6	0,2
11/17/05	23,8	0,53	0,88	32,9	0,3
12/14/05	25,1	1,6	1,08	39	0,5
01/11/06	26,9	2,72	1,06	23,8	0,1
01/26/06	21	0,59	1,08	36,2	0,1
02/08/06	25,6	1,75	1,08	53,4	1
03/06/06	25,7	3,52	1,08	71,6	0,2
03/20/06	24	1,99	0,88	16	0,5
04/03/06	23,1	2,56	0,69	16,5	0,5
04/17/06	21,6	1,5	0,88	948	5
05/09/06	21,1	1,2	0,78	43,1	0,5
05/22/06	20,1	1,2	0,88	31	0,5
06/14/06	19	0,5	0,90	50,6	0,5

Table 4: Correlation table of the physical and chemical measurements.

	A	B	C	D	E	F	G	H	I	J	K	L	M
A	1												
B	-	1											
C	0,06	0,38	1										
D	0,21	-	-	1									
E	0,32	-	-	0,72	1								
F	0,06	0,67	0,30	0,02	-	1							
G	-	0,40	-	-	-	0,35	1						
H	0,37	-	-	-	0,60	-	0,15	1					
I	0,83	0,52	-	-	-	-	0,88	0,56	1				
J	0,48	0,76	0,17	0,30	-	0,88	0,01	0,47	-	1			
K	0,69	0,42	-	-	0,03	-	0,30	0,48	-	0,29	1		
L	0,83	0,51	-	-	-	-	0,86	0,57	0,99	-	0,65	1	
M	-	0,02	-	0,89	-	0,81	-	-	-	0,53	-	-	1

A: Monitoring days – 1^o day in 06/06/05 and 389^o day in 29/06/06;

B: Water Temperature (°C);

C: Dissolved oxygen - OD (mg.L⁻¹);

D: Turbidity (NTU);

E: Sedimented Solids (mL.L⁻¹);

F: Temperature (°C);

G: Pluviometer index (average 3 days before the sampling) (mm);

H: Phosphorus Concentration (mg.L⁻¹);

I: Potassium concentration (mg.L⁻¹);

J: Calcium concentration (mg.L^{-1});

K: Iron concentration (mg.L^{-1});

L: Sodium concentration (mg.L^{-1});

M: Magnesium concentration (mg.L^{-1}).

The adsorption experiments

The removal percentages and adsorption rates were calculated for adsorption systems with soluble lead ions and phosphate, Table 4. The higher removal percentage was obtained for lead ions in solution, it was 59,93% for pH 7 at 20°C and the lower value of lead removal percentage was 40,42 % at pH 8 and 30°C which indicates the environmental condition is more favorable for the adsorption process development. The lower removal percentages were observed for phosphate on pH 7, low pH value increase the removal percentage from 3,60 to 17,33.

Table 4: Removal percentage of phosphate and lead ions in solution;

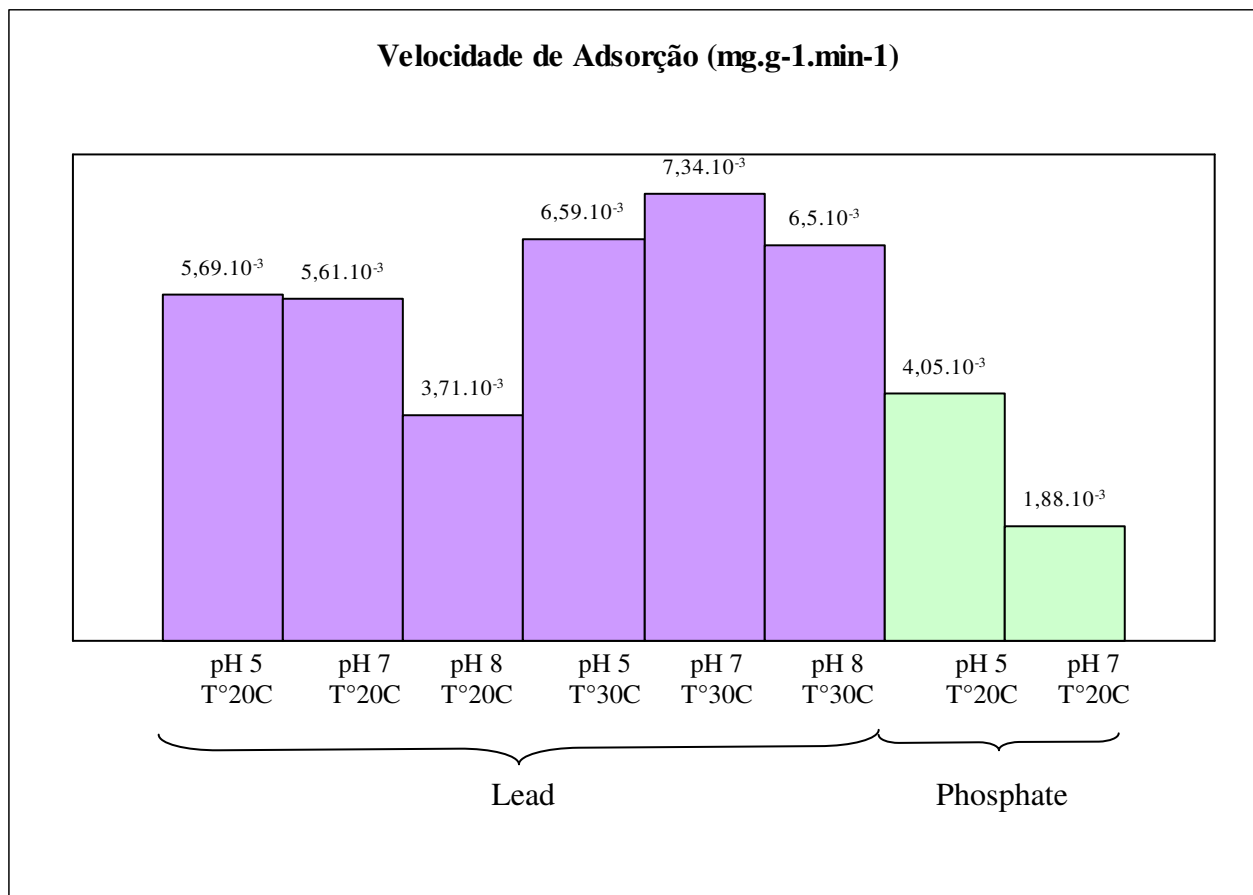
Soluble ions	pH	Temperature (°C)	Average Removal Percentage (%)
lead	5	20	45,09
		30	53,56
	7	20	59,93
		30	50,91
	8	20	46,58
		30	40,42
phosphate	5	20	17,33
	7	20	3,60

The adsorption rate values were calculated for lead and phosphate soluble ions. The results shows little variation ranging from $3,63 \cdot 10^{-3}$ to $7,34 \cdot 10^{-3} \text{ mg.g}^{-1}.\text{min}^{-1}$ and they are similar to those found in literature, for non-conventional adsorbents. The higher values were obtained for lead adsorption at pH 7 and 30°C , when this value is compared with the high removal percentage on pH 7 at 20°C was observed an indication of the heating process has the tendency to accelerate de adsorption process with a correspondent lost of adsorption efficiency.

Surface analysis of saturated adsorbent

The SEM analysis indicates low concentration of toxic compounds (lead and phosphorous) on the surface of the diatomite pellets. This effect can be an indication of the low removal percentage of the diatomite pellets, or can be also a result of the high sedimented solid particles observed at the stream which interfere with the surface adsorption process. During the SEM analysis was also observed the formation of an incrustations near the pellet surface, a EDX analysis indicate they were main composed by iron, calcium, magnesium, potassium and phosphate, as an indication of they were a result of the dried stream solid sludge. Further surface analysis will be performed to confirm this possibility.

Figure 1: Average adsorption rate for lead and phosphate adsorption process.



CONCLUSION

The results of physical and chemical analyses allows to classify the Pirajuçara stream as surface water Class 4 by the CONAMA Resolution nº 357 , with an indication of eutrophication process, with nutritional enrichment and severe qualitative and quantitative environmental impact in the aquatic communities. The positive correlation for physical and chemical parameters were observed for potassium and sodium content, this effect was expected due those chemical elements are related and common chemical compounds of soaps and detergents directly related with domestic sewage discharge. The negative correlation were observed for DO

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