CERAMIC SAMPLER STUDIES AND WATER QUALITY MEASSUREMENTS OF PIRAJUÇARA STREAM, SÃO PAULO, BRAZIL

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ABSTRACT

The results of physical and chemical analyses allows to classify the Pirajuçara urban stream as surface water class 4 by Brazilian National Environmental Council - CONAMA on the Resolution nº 357 , with an indication of eutrophication process, with high nutritional enrichment with possible qualitative and quantitative environmental impact in the aquatic communities. The toxic metals: nickel, zinc and copper were present in solution at stream water samples, they shows higher concentrations in winter, the dry season and their behavior shows resemblance with Lorents curves observed during four years. The adsorption process using diatomite (CS) and soluble phosphate and lead ions in similar conditions of pH, temperature and initial concentration of the water samples collected at Pirajuçara urban stream shows spontaneous and endothermic adsorption processes.

INTRODUCTION

Surface water resources located in metropolitan areas have been continuously suffering the environmental degradation due domestic and industrial waste discharge. The lower water quality of many urban rivers and streams which cross big cities are now a testimony of the environmental impact of the unplanned urban expansion. In summer season, some of those streams show also the occurrence of flooding events and they are located just a few meters of squares, streets, industries and residences.

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 to be placed in the monitoring water body will add important information to the evaluation and control of the urban surface water.

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(CETESB,

1978) (PIVELLI, 2006). The phosphate and chlorophyll concentration will indicate the tropic level of different systems. The raw domestic sewer in Brazil shows typically the concentration of phosphate ranging from 6 to 10 mg L^{-1}.

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 (SHREVE, 1977). The ecological systems with hipereutrophic 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 phytoplancton biomass present in water column and the tropic level of lagoons, rivers and reservoir of surface water. In green plants and phytoplancton concentration constitutes approximately 1% to 2% of the dry weight, (Udy et al, 2005; DAEE,1999).

The Pirajuçara stream is located in metropolitan area of the Sao Paulo and cross many municipalities as Embú Guaçú, Taboão da Serra and Sao Paulo. The Pirajuçara river basin drains an area of 72 km^2, mostly urban areas with predominance of the residential use. It is located in the left side of the inferior canal of Pinheiros river.

The analytical measurements performed for water quality evaluation by physical and chemical methods presents many difficulties, most of them occurs when toxic compounds remain in solution on low concentrations. Additionally 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. The use 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.

The study was carried through adsorption processes and the comparison between the adsorption results and the measured water parameters for surface water bodies' indicate, on the classification of the Brazilian Environmental Agency CONAMA - Resolution 375, the Pirajuçara stream is belonging to the class 4 with high phosphorous content and low values of dissolved oxygen – DO.

The water quality measurements are performed by the development of the adsorbent material with remains fixed under the water for few days allowing the measurement and control of the toxic compounds discharge in the water course. 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 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 can also provide addition information for water quality measurements of similar urban surface water, with dense pollution, flooding events, located in big cities, as Pirajuçara urban stream located in metropolitan area of Sao Paulo.

Thermodynamic studies

The adsorption processes are usually studied by the determination of the adsorption removal percentage, the calculation of the adsorption rate, the kinetic model, the thermodynamic behavior and the agreement with the Langmuir and Freundlich

adsorption models. The thermodynamic behavior of the adsorption processes can be studied experimentally by the determination of the variation of the entalpy and the entropy, in this study, the adsorption of the dissolved ions of lead and phosphate (Namasivayam,1993; Namasivayam, 1994) due their importance on the adsorption process performance at CS designing. (Ortiz, 2001; Namasivayam, 1995).

$$Log\ Kc = \Delta S^o/2{,}303R - \Delta H^o/2{,}303RT \qquad \text{I}$$

$$Kc = Cac/Ce \qquad \text{II}$$

Where:
R: 8,314 JK^{-1} mol^{-1}.
T: Temperature (K).
ΔH^o : The enthalpy change (kJ mol^{-1}).
ΔS^o : The entropy change (kJ mol^{-1}).
Kc : Thermodynamic equilibrium constant
Cac: Concentration of adsorbed compound in the adsorbent (mg L^{-1}),
Ce: Concentration of the toxic compound in equilibrium of the adsorption process (mg L^{-1}).

The adsorption process performance can be follow by the variation of the concentration of the adsorbed compound in solution and measuring the increase content at adsorbent surface. When the adsorption process reaches the equilibrium time – *te* the concentration on the adsorbent and in solution will keep constant in spite of continuing the time stirring.

The main goal of the project has been the determination of the thermodynamics constants which better represents the adsorption process thermodynamics behavior during different time stirring and deposition. The information's have been used to the designing of the adsorbent material for Ceramic Sampler – CS construction.

MATERIALS AND METHODS

The water sampling procedures were performed on three hydrological years with four winter seasons, starting in June, 2004 and finished at September, 2007. The geographical coordinates of the sampling point were 23º33'55.78"S and 46º42'50.61"W correspondent with the river month of Pirajuçara Stream, located in metropolitan area of Sao Paulo. The water sampling procedure and the physical and chemical measurements in the monitoring field were performed monthly, with about 20 to 30 days of time interval.

Water quality physical and chemical parameters were measured in different depth and distances from the margin of the Pirajuçara water flow accordingly with the scheme observed at Figure 2. The temperature, conductivity, dissolved oxygen-DO and pH parameters were measured using the YSI 556 probe with a flexible cab of 20 m on different depths: 7,5 m from the sampling point on the bridge (surface water), 8 m (0,5m depth), 9 m (1,5 m depth), 10 m (2,5m depth), 11 m(3,5 m depth) and 12 m (reaching the bottom of the cannel). The measurements were also performed on 5 m and on 10 m from the margin (representing the middle of the cannel with total width of 20m).

The results of physical and chemical analyses as expected allows to classify the Pirajuçara urban stream as surface water class 4 by Brazilian National Environmental Council -CONAMA on the Resolution nº 357 , with an indication of eutrophication

process, with high nutritional enrichment and resultant qualitative and quantitative environmental impact in the aquatic communities.

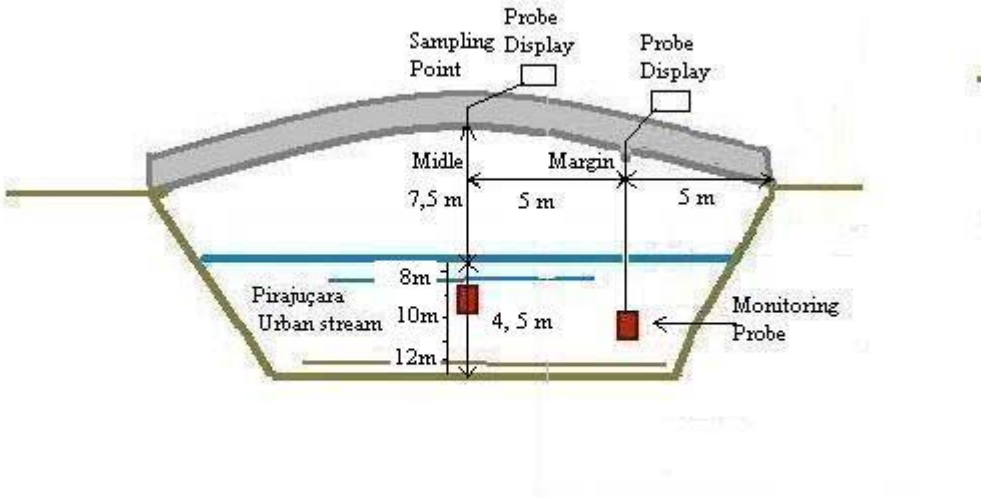

Figure 2: Sampling point of Pirajuçara stream and the schematic measurements performed at different depth and distance from the margin.

The adsorption processes

The adsorption processes for the ceramic sampler designing were performed at the laboratories using the diatomite pellets and water solutions of phosphate and lead. The lead ions were chosen to be used as soluble toxic metal compound in laboratory experiments as an indication of the metal behavior due it's efficiency on adsorption response. The phosphate ions was chosen to be used in adsorption experiments due its high content measured at water samples and its content is an indication of the eutrofication problem, often to be facing on water quality monitoring processes of urban surface water bodies.

The adsorption procedures were performed aiming the determination of the thermodynamics constants of the adsorption process. After those studies the adsorbent material can be modified accordingly with the requirements to increase it's efficiency as water quality monitoring tool.

The adsorption processes were studied in batch with magnetic agitation, 1 pellet with about 1g and 1 cm of diameter was added to 500 mL of toxic solution on controlled temperature and pH values. The variation of toxic concentration during the adsorption experiments were controlled by complex titration and inductive coupled plasma spectrometry–ICP/AES. The parameters of the adsorption systems studied were: the time stirring, initial concentration and temperatures. The temperatures and pH varies of the solutions were in the range of the water samples collected at urban stream.

RESULTS AND DISCUSSION

The results of physical and chemical analyses as expected allows to classify the Pirajuçara urban stream as surface water class 4 by Brazilian National Environmental Council -CONAMA on the Resolution nº 357 , with an indication of eutrophication process, with high nutritional enrichment and resultant qualitative and quantitative environmental impact in the aquatic communities

The collected water samples were chemically analyzed and the results of the toxic metals nickel, zinc and Copper were used to prepare Figure 1. The higher chemical content is in agreement with those found in literature for dry season. The sodium, calcium, potassium, magnesium and phosphate content were a clear indication of the domestic wastewater discharge mostly in secondary household products, the fecal coliforms were also found and will be object for specific further studies (Godoi, 2007).

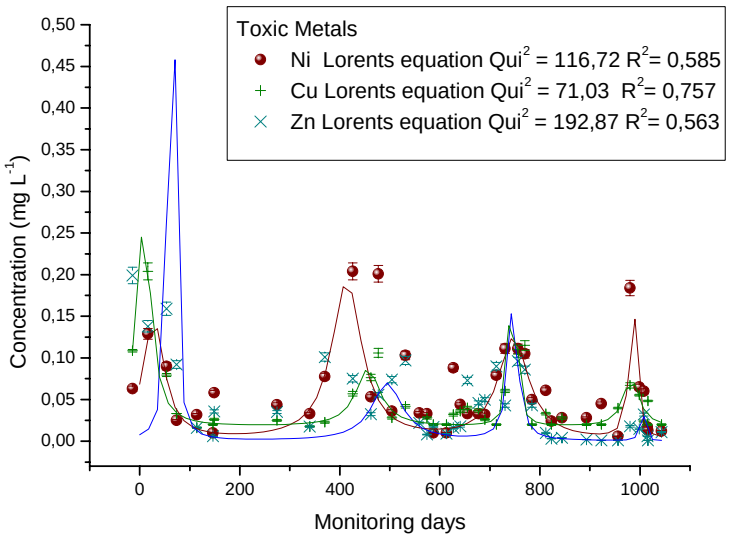

Figure 2: The concentration of the toxic metals measured on water samples collected on different hydrologic days.

The measurements of nickel, copper and zinc concentration increase during the winter, as expected for dry season, Figure 3. The concentration values obtained for the toxic metals during the monitoring time shows also a cyclic behavior an indication of their dependence of the weather conditions, the toxic metal content increase at winter and reduce at summer, the raining season.

The water samples were analyzed and nickel, copper and zinc concentration obtained during the monitoring time shows cycling behavior with Lorentz curves resemblance, for nickel the correspondence from experimental data's and the Lorentz equation found the values of Qui^2= 116.72 and R^2= 0.59, for copper was obtained Qui^2= 71,03 and R^2=0.76 and for Zinc Qui^2= 192,87 and R^2=0.56. The four distinct peaks were obtained one peak for each winter season. The first peak can be noted in the beginning of the measurements, the second can be observed after 360 days, the third one at 720 days and the fourth at 1080 days, confirming their dependence of the cycling weather conditions.

The lower concentrations of the toxic metals were observed in summer, the raining season. The increasing in raining water content can be the agent of this effect with the dilution of the soluble compounds or it can be also a result of the turbidity increase. After the solid particle settlement, the suspended solid particles may adsorb the soluble toxic metals; further measurements have to be performed to confirm the cycling behavior and the adsorption effect on surface water quality with the possibility of the use of the adsorption process to measure and control the water quality parameters.

Water quality physical and chemical parameters were measured in different depth and distances from the margin of the Pirajuçara water flow, the scheme can be observed at Figure 1. The results show little difference between the measurements performed in 5m of the margin and the 10m from the margin, in the middle of the water flow channel. The physical and chemical parameters shows also a small difference from the surface to the bottom of the channel, the exception was observed for the Oxidation Reduction Potential – ORP, changing from the surface to the bottom from an oxidant environment at 7,8m to a reduction environment, changing from aerobic condition to anaerobic condition, one of this effect can be observed by the gas bubbles production on the surface, they are resultant of the anaerobic processes resultant of those conditions.

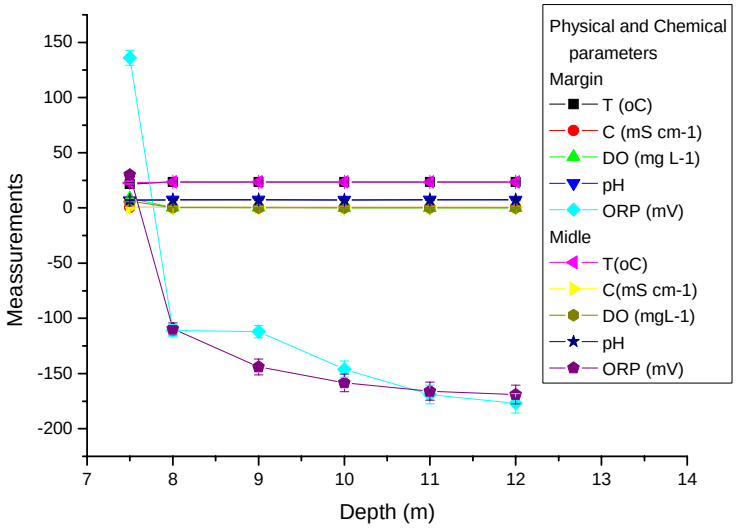

Figure 3: The measurements performed at Pirajuçara on different distance from the margin and depth. The 7,5 m represents the surface and the 12m represents the bottom of the stream channel.

The DO and conductivity – C values measured in the surface (7,5 m) in comparison with those obtained for the deepest environment from 8 to 12 m shows lower levels from the surface to the bottom of the water flow. This effect was expected as a result of oxygen and dissolved ions consumption due the degradation of high content of organic matter.

The results of physical and chemical analyses as expected allows to classify the Pirajuçara urban stream as surface water class 4 by Brazilian National Environmental Council -CONAMA on the Resolution nº 357 , with an indication of eutrophication process, with high nutritional enrichment and resultant qualitative and quantitative environmental impact in the aquatic communities.

The concentrations of lead and phosphate ions in solution during the adsorption process were experimentally measured and after that the thermodynamics

constants were calculated using the equations I and II with the determination of ΔS^o and ΔH^o. They were obtained by the determination of the linear equation, from figure with *log Kc* as dependent variable y and *1/T* as independent variable x.

Table 1: Linear equations for lead and phosphate ions adsorption by the CS and calculated ΔS^o and ΔH^o.

Phosphate Equation	ΔS^o *(kJmol $^{-1}$)*	ΔH^o *(kJmol $^{-1}$)*	*Adsorption Process*
Y=1,109-0.056x	18,11	1,07	Endothermic and Spontaneous
Lead Equation	ΔS^o *(kJmol $^{-1}$)*	ΔH^o *(kJmol $^{-1}$)*	*Adsorption Process*
Y=0,946-0,154x	21,23	2,95	Endothermic and Spontaneous

The results indicate the adsorption process using diatomite (CS) and soluble phosphate and lead ions in similar conditions of pH, temperature and initial concentration of the water samples collected at Pirajuçara urban stream were spontaneous and endothermic. Further experiments have to be performed to confirm the thermodynamics behavior and to explain why, in spite of similar thermodynamics results, the adsorption process of the diatomite and dissolved phosphate ions were less effective and most complex in comparison with the lead ions adsorption.

CONCLUSION

The results of physical and chemical parameters allows to classify the Pirajuçara stream as surface water Class 4 by the CONAMA Resolution nº 357 , with an indication of eutrophication process, with high nutritional enrichment and possible severe qualitative and quantitative environmental impact to the aquatic communities. The toxic metals: nickel, zinc and copper were present in solution at stream water samples, they shows higher concentrations in winter, the dry season and their behavior shows resemblance with Lorents curves. The adsorption process using diatomite (CS) and soluble phosphate and lead ions in similar conditions of pH, temperature and initial concentration of the water samples collected at Pirajuçara urban stream were spontaneous and endothermic.

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