DIATOMITE ADSORPTION TOOL TO MONITOR THE WATER QUALITY OF PIRAJUÇARA STREAM LOCATED IN SÃO PAULO - BRAZIL

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RESUMO

Um amostrador cerâmico foi utilizado como ferramenta de medida de qualidade de água de córregos urbanos com densa carga de poluentes e que se encontram perto de espaços públicos, ruas, indústrias e residências. Processos de adsorção foram realizados para obter as porcentagens de remoção e as velocidades de adsorção. Os parâmetros de qualidade de água foram medidos para Córrego Pirajuçara durante um ano hidrológico de maio de 2005 a maio de 2006 e os resultados obtidos são discutidos com o auxílio de uma tabela de correlação. Uma comparação foi feita entre os resultados obtidos e aqueles esperados para águas de superfície indicando que o Córrego Pirajuçara pertence a Classe 4 , com elevado teor de fósforo e baixos valores de oxigênio dissolvido.

Descritores: *Adsorvedor; Diatomito; Pirajuçara; Córrego; Urbano.*

ABSTRACT

A ceramic sampler was developed for use as a monitoring tool to control the quality of water of urban streams that are prone to heavy pollution, floods, and are close to public places, streets, industries and residences. This investigation was based on adsorption processes and used the results of removal percentage and adsorption rates. The water quality parameters of the stream Pirajuçara were measured during one hydrological year, from May 2005 to July 2006, and the results are presented as a correlation table. Comparison of the measured water parameters with those required of surface water bodies, indicate that the Pirajuçara stream belongs to surface water class 4, with high phosphorous content and low dissolved oxygen values.

Keywords: *Adsorber; Diatomite; Pirajuçara; Stream; Urban.*

INTRODUCTION

Urban surface waters are a feature of unplanned urban expansion and its impact on the environment. It is prevalent all over the world,but mostly in large cities of underdeveloped countries. Urban water sources which cross big cities are prone to environmental degradation due to discharge of raw domestic and industrial wastewater. In the rainy season, environmental degradation tends to increase with the occurrence of floods. Many projects carry out diagnostic studies of soil and water contaminated by discharge of toxic industrial wastes and other soluble products. However, there is a marked lack of diagnostic studies and monitoring of surface waters located inside densely populated big cities. Exploratory studies have indicated that an urban stream is a highly complex system with water quality parameters that vary seasonally, monthly, daily and even during the day. The development of a tool to monitor and control water quality is essential to help identify, quantify and minimize the discharge of pollutants into urban water bodies.

Brazil, with an estimated population of 186 million is the most populated South American country and ranks 5 th in the world. Most of the Brazilians live in the industrial metropolitan areas of São Paulo, Rio de

Janeiro, and Belo Horizonte. Urban growth has been rapid and in 2005, about 81% of Brazil´s population lived in urban areas. This growth has aided economic development but has also created serious social, security, environmental and political problems for major contiguous urban built-up areas which have merged together. The Metropolitan area of São Paulo is one of them. As the capital of the state of São Paulo, its population is 18.24 million and ranks as the seventh most populous metropolitan city in the world [1].

The Pirajuçara stream runs for about 17 Km through metropolitan São Paulo, and includes the municipalities of Embu das Artes, Taboão da Serra and São Paulo. Located on one side of the Pinheiros river. The Pirajuçara Stream is a classic example of urban surface water and also exemplifies the shifting of pollutants by the water flow from one municipality to another. It is a body of water with high phosphorous content, low concentrations of dissolved oxygen and a problem that is difficult and expensive to solve [2][3]. Many projects are underway to reduce the environmental impact of the stream on the community in its vicinity. Most of the projects are focused on reducing flow rates, which is usually in the range of 21.2 m^3/s to 114 m^3/s. The flow rates tend to reach critical levels during the rainy season, about 240m^3/s, causing floods and losses for the community. In the dry season, the São Paulo prefecture project is focuses on cleaning the stream by dredging and removing the sediments, composed mainly of contaminated soil and solid residues [4][5].

The main source of phosphate in urban surface waters is the discharged raw sewer and industrial effluents [6]. Hypereutrophic environments with high nutrient contents favor the appearance and growth of algae[7].

The evaluation of surface water quality by physical and chemical measurements has been given an indication of the water environmental contamination just when the measurements are made. These limitations increase when the surface water is a lotic system, a stream or a river, where the water is continuously renewed at each point [8]. The use of adsorbent materials for monitoring water quality has the advantage of concentrating some toxic compounds to be measured. It provides information about the environmental effect of discharged contaminants during a period of time and is capable of providing information about a condition that is not encountered at the moment of conducting physical and chemical verifications.

The adsorption process can be studied from the variations in the concentration of adsorbable compounds (equation 1) in solution and measurement of the increase in the adsorbate content on the surface[9][10]. When the adsorption process reaches the equilibrium time – te, the concentration of adsorbable compound in the solution remains constant despite further increase in stirring time and the adsorption rate can be calculate (equation 2) [11][12][13].

$$R = [(C_i - C_e)/C_i] * 100 \quad (1)$$

$$\log(C - C_e) = \log C_e - (K_{ab}/2.303)\, t \quad (2)$$

Where:

K_{ab}: Adsorption rate (mg g^{-1} min^{-1}),
t: Stirring time (min),
R: Removal percentage (%),
C_i: Initial concentration (mg L^{-1}),
C_e: Concentration at equilibrium (mg L^{-1}),
C: Concentration at time t (mg L^{-1}).

The adsorbed compounds (or adsorbate) concentrate on the surface and the adsorbate saturation level can be determined using scanning electron microscopy – SEM coupled to X-ray energy dispersive spectroscopy – EDS. The latter helps determine the surface composition. The morphology can be used to determine the composition of the adsorbed compound [14][11][15].

The main objective of this project was the development of a Ceramic Sampler – CS, composed mainly of diatomite pellets as the adsorbent material. This was immersed for a few days in the water to be monitored and subsequently analyzed. This enabled the measurement and control of the toxic compounds in waters with toxic metals, organic compounds and products of eutrophication.

METHODS

The water sampling studies were carried out during one hydrological year, starting in June 2005 and finishing in June 2006. The geographical coordinates of the sampling point were 23°33'55.78"S 46°42'50.61"W and correspond to the mouth of the Pirajuçara stream located in the metropolitan area of São Paulo. The sampling procedure and measurement of the physical and chemical parameters in the field were performed once every 20 to 30 days.

The water quality parameters were chosen based on the Brazilian standards CONAMA Resolution nº 357 of March 17th, 2005. The parameters were: turbidity, measured by the nephelometry method (Tecnopon TB 1000); sediments, determined with Imhoff glass; dissolved oxygen, measured with a portable oxymeter (Hanna HI 8043), total phosphate content and water temperature [16].

The Ceramic sampler (CS) consists of 250g of diatomite pellets packed in an acrylic mesh. Diatomite pellets, weighing about 1g and about 1 cm in diameter were used. The CS was positioned in the stream at a depth of about 50 cm. At the end of this period, the saturated pellets were dried, fixed in a resin and cut longitudinally. The resulting hemispheres were examined by scanning electron microscopy and the chemical composition determined by EDS. This procedure enabled the chemical composition profile of the pellet to be determined from the surface to the center. This can be used to determine the percolation depth of the adsorption process and the presence of surface incrustations.

The adsorption processes were studied in the laboratory using diatomite pellets and aqueous solutions containing lead. Dissolved lead ions were chosen as the toxic metal ion to be adsorbed in the laboratory studies to determine the adsorption behavior and efficiency. This study was carried out to determine the adsorbate removal percentage (%) and the adsorption rate (mg g^{-1} min^{-1}) in a controlled environment.

The adsorption processes were studied in batch experiments with magnetic agitation. A 1 g pellet was added to 500 mL of lead solution at controlled temperatures and pH values. The lead concentration during the adsorption experiments was determined with the aid of an Inductively Coupled Plasma Spectrometer–ICP/AES. The temperature and pH were varied in the range that is normally found in stream waters.

RESULTS AND DISCUSSION

Physical and chemical results

Table 1 shows the following parameters that were measured: turbidity, amount of sediments, dissolved oxygen, phosphate content and temperature of the Pirajuçara stream water. The DO values were always below 2.0 mg/L, which is the lower limit for surface water Class 4. This indicated that the surface water can be used only for navigation purposes according to CONAMA Resolution nº 357. A few measurements were found to be at the limit of Class 3 and Class 4. As has been indicated earlier, some variations in the measured results are acceptable due to the complexity of an urban water system [16].

The values obtained for phosphate content were always high for surface waters. These were in the range of 0.01 to 1.08 mg.L-1 and in accord with a hipereutrofic system. The water temperature measured at the site was in the range 17.3oC - 26.9oC and the average was 22.2oC. The pH was in the range 6 - 8, and averaged 7.2. The average temperature and pH can be considered to be high for surface waters and this clearly indicated pollution due to discharges with high organic matter. These results were used in the laboratory experiments to study the adsorption process using diatomite pellets.

The values of turbidity were relatively low, in the range 16 - 72 NTU, and this can be defined as almost Class 3 surface water, which is up to 100 NTU. An exception was observed on April, 2006, when the turbidity was 948 NTU. This sample also showed large amounts of sediments, about 5 $mL.L^{-1}$. This could be attributed to erosion of soil from the banks and its inclusion in the stream bed. The amount of sediments was generally low, averaging about 0.3 $mL.L^{-1}$. However these values are not in compliance with Resolution nº 357 which stipulates the waters to be free of sediments, to prevent flooding of shipping channels.

Tabela 1: Values of DO (mg.L^{-1}), phosphate (mg.L^{-1}), turbidity (NTU) and sedimented solids (mL.L^{-1}) measured in water samples of the Pirajuçara stream.

Date	Temp (°C)	DO (mg .L^{-1})	Phos. (mg.L^{-1})	Turb. (NTU)	Sed. Solids (mL.L^{-1})
06/06/05	21.1	2.0	0.01	38.4	0.2
07/14/05	18.7	1.4	0.73	36.9	0.3
08/31/05	23.0	2.4	0.17	43.0	0.1
10/05/05	24.0	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	0.5	0.88	32.9	0.3
12/14/05	25.1	1.6	1.08	39.0	0.5
01/11/06	26.9	2.7	1.06	23.8	0.1
01/26/06	21.0	0.6	1.08	36.2	0.1
02/08/06	25.6	1.8	1.08	53.4	1.0
03/06/06	25.7	3.5	1.08	71.6	0.2
03/20/06	24.0	2.0	0.88	16.0	0.5
04/03/06	23.1	2.6	0.69	16.5	0.5
04/17/06	**21.6**	**1.5**	**0.88**	**948**	**5.0**
05/09/06	21.1	1.2	0.78	43.1	0.5
05/22/06	20.1	1.2	0.88	31.0	0.5
06/14/06	19.0	0.5	0.90	50.6	0.5

On the basis of the results of physical and chemical parameters the Pirajuçara stream can be classified as surface water Class 4, as per CONAMA Resolution nº 357, with indications of eutrophication processes with nutritional enrichment and quantitative environmental impact on the aquatic communities.

Quantitative chemical analysis of the main dissolved compounds was also performed. The results of the physical and chemical parameters measured during the year the stream was monitored were used to prepare a correlation table shown in Table 2.

Table 2: Physical and chemical parameters during the year

	A	B	C	D	E	F	G	H	I	J	K	L	M
A	1												
B	0.19	1											
C	0.06	0.38	1										
D	0.21	0.08	0.10	1									
E	0.32	0.12	0.02	0.72	1								
F	0.06	0.67	0.30	0.02	0.06	1							
G	0.06	0.40	0.20	0.14	0.11	0.35	1						
H	0.37	0.31	0.67	0.46	0.60	0.77	0.15	1					
I	0.83	0.52	**0.91**	**0.90**	0.22	0.33	0.88	0.56	1				
J	0.48	0.76	0.17	0.30	0.76	0.88	0.01	0.47	0.03	1			
K	0.69	0.42	0.78	0.50	0.03	0.18	0.30	0.48	0.59	0.29	1		
L	0.83	0.51	**0.94**	**0.90**	0.18	0.35	0.86	0.57	**0.99**	0.03	0.65	1	
M	0.35	0.02	**0.92**	0.89	0.39	0.81	0.57	0.70	0.74	0.53	0.58	0.77	1

A: Monitoring days –1st day on 06/06/05 and 389th day on 29/06/06
B: Water Temperature (°C);
C: Dissolved oxygen - DO (mg.L^{-1});
D: Turbidity (NTU);
E: Sediments (mL.L^{-1});
F: Temperature (°C);
G: Pluviometer index (on 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}).

A positive correlation of 0.99 was observed between potassium and sodium content. This correlation was expected as these elements are usually found jointly in soaps and detergents, and their secondary products are found in raw sewage discharge. Negative correlations of –0.94, –0.91 and -0.92 were observed as expected between DO and sodium, potassium and magnesium content respectively. These correlations represent soap and detergent discharges and are related to low DO in the highly impacted surface water. The turbidity has a negative correlation with sodium and potassium content. This was observed mainly during the rainy season. Rains tend to increase turbidity and also dilute the domestic sewage discharge. Consequently, increase in water content reduces the sodium and potassium levels.

The adsorption experiments

The removal percentages were calculated from the adsorbed lead ions on diatomite pellets. The removal percentage varied in the range 55.4 % - 71.4 %. The higher value of 71.4 %, was obtained at pH 7 and 20°C and the lower value at pH 8 and 30°C. The environmental conditions of the stream during the monitored hydrological year matched those found for the high removal percentage, with average pH of 7.2 and average water temperature of 22.2°C.

The higher removal percentages for adsorbed lead ions were obtained at 20°C and 30°C at pH 7. The experimental results were plotted and the curves showed a sigmoidal tendency (Boltzman equation) at pH 7 and 20°C, with Qui^2 = 0.01 and R^2 = 0.99. At pH 7 and 30°C the values of Qui^2 and R^2 were 2.71 and 0.97 respectively, as shown in Figure 1.

The initial lead ion concentration in the solution was in the range 12 mg L^{-1} – 290 mgL^{-1}. The calculated final lead concentrations adsorbed onto diatomite pellets were 10.36 mg L^{-1} and 176 mgL^{-1} at 20°C and 30°C respectively. Figure 1 shows the sigmoidal curves and indicates 30 min as equilibrium time – te, after which the system reached equilibrium. Continued stirring did not result in any increase in the adsorbed mass on the diatomite surface.

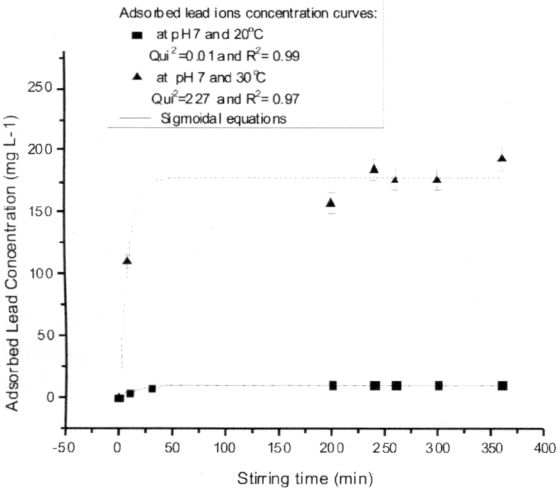

Figure 1: Adsorption curves for adsorbed lead ions on diatomite pellets.

The adsorption rate values (K_{ab}) were calculated using equation II and the measured lead concentrations (C and C_e). Figure 2 shows the linear equation of the systems with higher removal percentage and they were used to perform the K_{ab} calculations. The linear coefficient corresponds to log C_e and the declivity corresponds to ($-K_{ab}/2.303$).

The linearized adsorption curves used to calculate K_{ab} can be seen in Figure 2. These curves reveal two different tendencies. The one corresponding to higher initial concentrations shows higher adsorption rate and improved linear aspect. The adsorption systems with lower initial concentrations show lower adsorption rates and lower linear aspect. This effect was expected considering that at higher initial concentrations, more molecules are available for adsorption and the collision frequency with the pellet surface is higher, increasing thus the adsorption rate. The initial dilute solutions provide reduced amounts of available molecules, and thus are more affected by the intra molecule and intra particle collisions. This reduces the adsorption rate and the linear aspect.

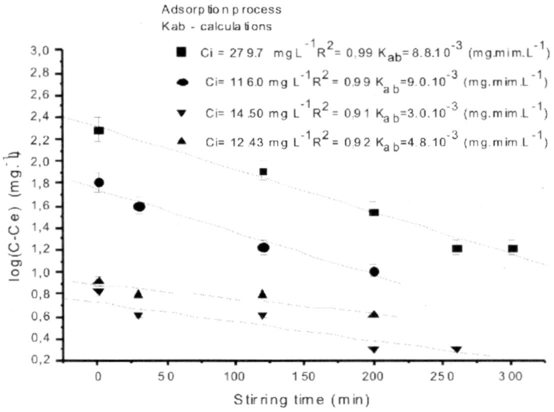

Figure 2: Linearized adsorption curves for lead ions on different initial concentrations.

The K_{ab} results reveal only slight variations and range between 3.0 10^{-3} and 9.0 10^{-3} $mg.g^{-1}.min^{-1}$. These values are similar to those reported in literature for non-conventional adsorbents. The higher values were obtained for lead adsorption at pH 7 and 30°C. Comparison of this value with the high removal percentage at pH 7 and 20°C indicate a heating process which tends to increase the adsorption process with a corresponding decrease in adsorption efficiency. These aspects need to be confirmed in experiments.

Surface analysis of immersed diatomite

SEM analysis of both the partially saturated diatomite spheres in the adsorption studies and the CS pellets indicated low concentrations of toxic metals on the surface. The deposited lead compounds on the adsorbent surface tend to be higher on the surface and decrease proportionally into the bulk. The absence of lead on the surface can be a consequence of low removal percentage in the adsorption studies. In the case of deposition on the CS from the stream, the absence of lead could be due to the high suspended solid particle content, which was observed in the stream, interfering with the surface adsorption process.

SEM studies also revealed incrustations on the CS. EDS analysis indicated that the incrustations were mainly composed of iron, calcium, magnesium, potassium, chlorine and phosphorous, suggesting these to be entrapped dried solid sludge of the steam in voids of the adsorbent. (Figure 3) Further experiments and surface analysis confirmed this observation.

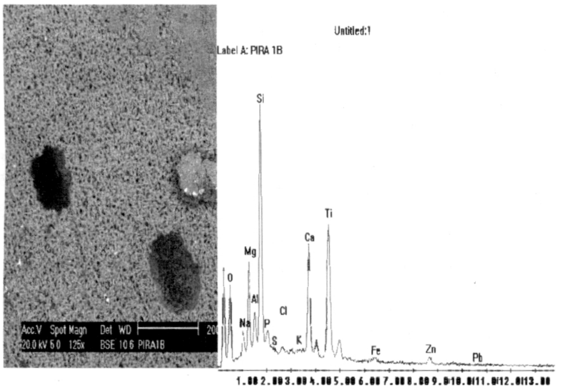

Figure 3: Incrustation located near the diatomite surface (right) and its chemical composition (left).

CONCLUSIONS

The results of analysis of the physical and chemical parameters helped classify the Pirajuçara stream as surface water Class 4 as per the CONAMA Resolution nº 357, and indicated eutrophication processes, with nutritional enrichment and severe qualitative and quantitative environmental impact on the aquatic communities. Positive correlations, with respect to physical and chemical parameters, were observed for potassium and sodium content. This was expected as these elements are found in soaps and detergents that are part of domestic sewage discharge. A negative correlation was observed between DO and sodium content as well as between DO and potassium content, indicating that with increasing soap and detergent discharge the DO in surface water decreases. Turbidity has a negative correlation with sodium and potassium content. This was observed mainly during the rainy season. The rains increase turbidity and also dilute the domestic sewage discharge. This causes dilution of the sodium and potassium content. The removal percentage and the adsorption rates for lead ions were calculated. This showed little variation, ranging from 3.0 10-3 to 9.0 10-3 mg.g-1.min-1and was similar to data reported in literature for non-conventional adsorbents.

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