Sequencing batch reactor for treatment of chemical laboratory wastewater

Cláudia Telles Benatti[1], Célia Regina Granhen Tavares[1*], Benedito Prado Dias Filho[2] e Mateus Pinatto Gaspar[1]

*[1]Departamento de Engenharia Química, Universidade Estadual de Maringá, Av. Colombo, 5790, 87020-900, Maringá, Paraná, Brasil. [2]Departamento de Análises Clínicas, Universidade Estadual de Maringá, Av. Colombo, 5790, 87020-900, Maringá, Paraná, Brasil. *Autor para correspondência. e-mail: celia@deq.uem.br*

ABSTRACT. The wastewater from academical chemical laboratories is generally composed of organic matter and a wide range of chemicals and heavy metals, being one of the most difficult wastewaters for treating. The treatment consisted of hydroxide precipitation and of a biological treatment using a sequencing batch reactor (SBR). Each cycle of the SBR system was operated for 24h with FILL/REACT, SETTLE and DRAW/IDLE periods in the ratio of 20:3.5:0.5. The reactor was fed with a mixture of domestic and laboratory wastewaters to minimize the inhibitory effect of laboratory wastewater on the microorganisms bioactivity. Kinetic studies conducted for the FILL/REACT and SETTLE periods showed that the effluent has difficult biodegradability, reaching a COD reduction of 11%.

Key words: laboratory wastewater, sequencing batch reactor, SBR, hydroxide precipitation.

RESUMO. Reator batelada seqüencial para o tratamento de efluente químico de laboratório. O efluente gerado em laboratórios acadêmicos de análises químicas é composto, de maneira geral, por matéria orgânica e uma grande variedade de resíduos químicos e metais pesados e consiste em um dos mais difíceis de serem tratados. O método de tratamento empregado consistia na precipitação com hidróxido e tratamento biológico em reator batelada seqüencial (RBS). Cada ciclo do sistema RBS foi operado por um período de 24h com as etapas de ENCHIMENTO/REAÇÃO, SEDIMENTAÇÃO e RETIRADA/REPOUSO na razão 20:3,5:0,5. O reator foi alimentado com uma mistura de efluente doméstico e efluente de laboratório a fim de minimizar o efeito inibitório do efluente de laboratório na bio-atividade dos microrganismos. Estudos cinéticos conduzidos para as etapas de ENCHIMENTO/REAÇÃO e SEDIMENTAÇÃO mostraram que o efluente é de difícil biodegradabilidade, alcançando uma redução de DQO de 11%.

Palavras chave: efluente de laboratório, reator batelada seqüencial, RBS, precipitação com hidróxido.

Introduction

During the last years, a worldwide understanding of the need of treatment or proper disposal for any type of residues has grown in chemical industries, academic institutions and governmental organs (Amaral *et al*., 2001). The waste, generated during the operations of the Control and Environmental Prevention Laboratory at the *Departamento de Engenharia Química* (Department of Chemical Engineering) of the *Universidade Estadual de Maringá* - Brazil, has been held for many years at the laboratory site, waiting for acceptable disposal modes to be developed. Because of the lack of specific legislation to regulate waste chemicals treatment, this is a common situation in many Brazilian institutions, such as the *Departamento de Química* (Chemistry Department) of the *Universidade Federal do Paraná* (Cunha, 2001).

Waste chemicals from academic laboratories are generated fundamentally by small amounts of different wastes (National Research Council, 1995). These wastes are constituted of a great diversity of substances, including new compounds of unknown toxicity (Micaroni *et al*., 2002). The complex organic and inorganic composition of laboratory wastewaters can make them difficult to treat. As a result, the treatment has been typically via chemical action or incineration (National Research Council, 1995). Regarding the biological process, it is necessary to conduct treatability studies for laboratory wastewaters, since they may contain toxic substances that may cause adverse effects on biological systems. In this work, the feasibility of biological treatment for chemical laboratory wastewater, after hydroxide precipitation, was evaluated, using a sequencing

batch reactor (SBR).

Although the activated sludge process was first developed as a batch system, the configuration was quickly changed to continuous flow. This was due to the high demands on operator time, lack of specialized technological equipment and some operational problems of batch systems, like the clogging of aeration diffusers (Katsogiannis *et al*., 1999). Lately, it is coming back into operation as a result of the availability of suitable solutions for controlling such reactors (Pavšelj *et al*., 2001).

The SBR process carries out functions of equalization, treatment and sedimentation in a time rather than a space sequence (Lim *et al*., 2002). A typical cycle involves five operational phases described as fill, react, settle, decant and idle/waste sludge (Coelho *et al*., 2000). According to Irvine *et al*., *apud* Katsogiannis *et al*. (1999), the SBR is perfectly suited for small wastewater flows (<10 MGD), performing satisfactorily even in larger applications.

Several authors describe the attractive advantages of using SBR over continuous-flow technologies. Fu *et al*. (2001) describe the advantages of using SBR in terms of pollutant removal - the alternating feast and famine conditions in the reactor result in high rates of substrate removal during the reaction phase, and the SBR enables the buildup and retention of biomass in the reactor, thus contributing to improve pollutant removal. Norcross, *apud* Katsogiannis *et al*. (1999), emphasize that the advantages of the SBR, compared to a continuous-flow reactor (CFR), are: flexibility in operation, quiescent or carefully controlled mixing during settling, no need for a separate clarifier and ability to discharge treated wastewater only after effluent limitations have been met. According to Lim *et al*. (2002), the perceived merits of SBR systems include better tolerance towards shock load, good settling due to better control of filamentous growth, simplicity and ease in operation, as well as compact layout.

The objective of this study is to investigate the chemical laboratory wastewater treatment by hydroxide precipitation and biological treatment using sequencing batch reactor (SBR) aiming to conduct preliminary studies on the biodegradability of laboratory wastewater.

Material and methods

Laboratory effluent characterization

All chemical analysis residues generated in the laboratory during the period of September/2001 to April/2002 were retained in clearly marked containers and their sources were defined in a notebook record. Later on, they were combined and characterized through physicochemical analysis in terms of to pH, chemical oxygen demand (COD), total phenols, real and apparent colors, turbidity, sulfate and metal content (Cu, Fe, Zn, Al, Co, Cr, Mn, Mg, K and Ca).

Experimental system

Preliminary studies on biodegradation process were conducted on a bench-scale cylindrical aerobic sequencing batch reactor (SBR) with a working volume of 2.3L. The biological reactor was equipped with a variable speed stirrer and an aquarium air pump, and it was operated at room temperature. The sludge for seeding was collected from a conventional activated sludge unit at a local treatment plant of a gelatin industry.

First, chemical precipitation using sodium hydroxide (~30% w/v) at pH=8.0 was performed with the combined wastewaters, obtained as described previously. The supernatant was then taken and combined with domestic wastewater, obtained from a local wastewater treatment plant. The reactor was fed with this mixture of laboratory and domestic wastewater, in order to establish a viable biomass and minimize the potential toxic effects from the laboratory wastewater.

Initially, 2L of the seed and 1.3L of the combined wastewater (50% v/v of domestic wastewater and 50% v/v laboratory effluent diluted at effluent/distilled water ratio of 1:4) with an average COD concentration of approximately 900mg O_2/L and pH of 7.8 were fed into the reactor. The contents were gently agitated by a mixer, keeping the biomass in suspension, and aerated for 20h per cycle. After every cycle, the contents were allowed to settle for 3.5h, the supernatant was decanted, and the reactor was refilled. After 25 days operating, the proportion of domestic wastewater was increased to 70%, to minimize the toxic effects of laboratory wastewater on microorganisms, reaching an average of COD concentration of 450mg O_2/L and pH 7.7. The operation continued until the reactor attained a steady-state, approximately after 45 days operating, reaching a working volume of 2.3L composed of 30% sludge and 70% wastewater. Stable operation of the SBR was determined by monitoring effluent soluble COD and effluent volatile suspended solids (VSS). Once the reactor had attained steady state, its performances in terms of soluble COD, pH, volatile suspended solids and counted bacteria in solid plates (total culturable) were monitored for further 35 days. In addition, all colonies having different

morphologies were selected from the nutrient agar (total culturable) and classified according to their cellular morphologies. These bacteria were spread on agar plates (Nutrient Agar) and allowed to grow for a period of 72h. The solid media containing the cultures were then sliced in small pieces and added to the sludge at the 43rd day to re-inoculate the reactor.

At the 75th day of operation, kinetic studies were performed to investigate the effluent biodegradability during the FILL/REACT and SETTLE periods in a cycle in terms of soluble COD and VSS. Mixed liquor samples were collected at 1-hour intervals from the SBR, as soon as the REACT period had begun. The sample was allowed to settle for 45min, the sludge was returned to the reactor and the supernatant was then analyzed for COD and VSS.

Analytical methods

Measurements of COD, VSS, sulfate and pH followed Standard Methods (APHA, 1998). Total phenols were measured according to the colorimetric method of Folin-Ciocaulteu reagent described by Scalbert *et al*. (1989). Real and apparent colors and turbidity were measured by an analytical method developed by HACH Company. Metal concentrations (Cu, Fe, Zn, Al, Co, Cr, Mg, Ca, K and Mn) were determined in the filtrate by atomic absorption spectroscopy (Varian SpectrAA - 10 Plus).

Microbial enumeration

Measurements of changes in sludge during SBR operation followed the pour plate method according to APHA (1998). Agar plates were divided in three equal parts and samples of 25μL of homogenized sludge and their dilutions in saline solution (0.85%) were inoculated in each area in three replicates. The solid media employed for total culturable enumeration was Nutrient Agar, obtained from Difco Laboratories (Detroit, MI). All plates were incubated at 37°C for 24-48h and the colonies were counted soon after the incubation period. Colonies were classified according to their cellular morphologies by brightfield microscopy of Gram-stained preparations. The number of organisms per oil immersion field was reported as rare (<1), few/occasional (1-4), moderate (5-10), and many (>10).

Results and discussion

The major chemical analysis and activities that generated the laboratory wastewater during the period of September/2001 to April/2002 were COD, total phenols, polysaccharides, protein, phosphate, sulfide, sample preparation and standards for atomic absorption, solutions standardization and enzymatic activity. The main characteristics of combined wastewater produced by the chemical laboratory during the period of study are listed in Tables 1 and 2.

Table 1. Main characteristics of combined wastewater from the chemical laboratory.

pH	Apparent color (Pt/Co)	Real color (Pt/Co)	Turbidity (NTU)	Sulfate (g/L)	COD (mg O_2/L)	Total phenols (mg/L)
< 1	13800	980	4340	268	2537	52.3

Table 2. Metal concentrations (mg/L) on combined wastewater from the chemical laboratory.

Fe	Cr	Cu	Zn	Co	Al	Na	Mn	Mg	Ca	K
142	225	1.3	0.5	0.8	54	3763	0.5	3.8	71	437

Chemical precipitation is applicable to the treatment of aqueous hazardous wastes containing toxic constituents that may be converted to an insoluble form. This includes wastes containing the metals arsenic, barium, cadmium, chromium, copper, lead, mercury, nickel, selenium, silver, thallium and zinc (Jefferson *et al*., 2001). Hydroxide precipitation using sodium hydroxide at pH=8.0 was performed with the combined wastewater. A 31% COD reduction was observed and also a reduction on most of the metals concentration, as can be seen in Tables 3 and 4. Further studies on the solubilities of several metal hydroxides on the basis of jar tests with the combined wastewater are being carried out to optimize the precipitation and produce the best effluent quality.

Table 3. Main characteristics of the combined wastewater after chemical precipitation.

pH	Apparent color (Pt/Co)	Real color (Pt/Co)	Turbidity (NTU)	Sulfate (g/L)	COD (mg O_2/L)	Total phenols (mg/L)
8	6600	5950	18	85	793	14.9

Table 4. Metal concentrations (mg/L) on the combined wastewater after chemical precipitation.

Fe	Cr	Cu	Zn	Co	Al	Na	Mn	Mg	Ca	K
3.1	8.4	0.7	0.0	0.8	0.1	62331	0.0	2.6	53.9	333

The COD and VSS concentration during the SBR operation is shown in Figures 1 and 2. In order to establish a viable biomass and minimize potential toxic effects from the laboratory wastewater, the reactor was fed with a mixture of laboratory and domestic wastewater. Initially (phase "a") a proportion of 50% domestic wastewater and 50% diluted laboratory wastewater (1:4 effluent/distilled

water ratio) was used, with an average COD concentration of 900mg O_2/L and pH 7.8.

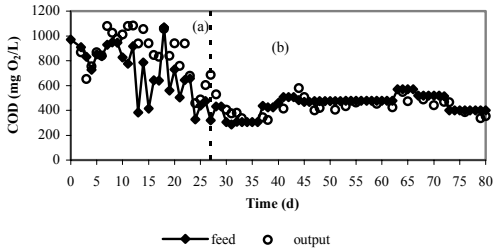

Figure 1. Soluble COD concentration during the SBR operation: (a) feed: 50% v/v of domestic wastewater and 50% v/v diluted laboratory effluent; (b) feed: 70% v/v of domestic wastewater and 30% v/v diluted laboratory effluent.

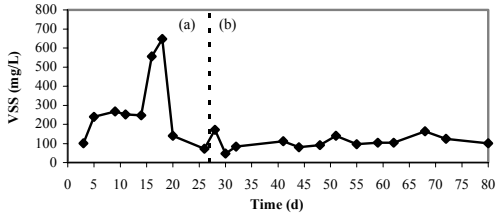

Figure 2. VSS concentration during the SBR operation: (a) feed: 50% v/v of domestic wastewater and 50% v/v diluted laboratory effluent; (b) feed: 70% v/v of domestic wastewater and 30% v/v diluted laboratory effluent.

Total culturable in the sludge for seeding was enumerated at the order of 10^6 CFU/mL. Cellular morphologies, determined by brightfield microscopy of Gram-stained preparations of the sludge samples, showed a diversity of microorganisms that contained gram-negative spirilla (rare), gram-positive bacilli (many), chain disposed gram-positive coccus-bacilli (few), gram-negative bacilli (many) and chain disposed short gram-positive bacilli (few). The presence of protozoa was also observed.

During the acclimation period, a constant drop was observed on the counting of bacteria (Figure 3). In order to minimize the toxic effects of laboratory wastewater on microorganisms, the proportion of domestic wastewater was increased to 70% (phase "b"); with an average COD concentration of 450mg O_2/L, SSV concentration of about 72mg/L and pH 7.7. At this point, all colonies having a different morphology were selected from the nutrient agar (total culturable). Cellular morphologies, determined by brightfield microscopy of Gram-stained preparations, showed that the microorganisms found in the sludge contained gram-positive bacilli (predominant), chain disposed gram-positive coccus-bacilli, gram-negative bacilli and chain disposed short gram-positive bacilli. These bacteria were used then to re-inoculate the reactor at the 43rd day.

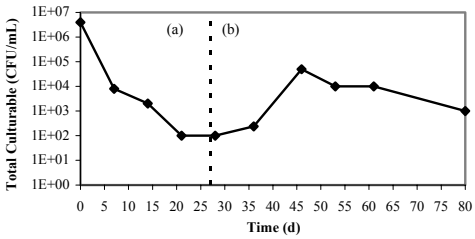

Figure 3. Bacterial counting during the SBR operation: (a) feed: 50% v/v of domestic wastewater and 50% v/v diluted laboratory effluent; (b) feed: 70% v/v of domestic wastewater and 30% v/v diluted laboratory effluent.

During the treatment the pH was relatively unchanged. In phase "b", the effluent presented a COD:N:P ratio of about 13:10:1 and C:N:P ratio of about 4:10:1. According to Metcalf and Eddy apud Jefferson *et al*. (2001), for assuring a good bacterial growth it is necessary to have a correct mixture of nutrients containing COD:N:P in the ratio of 100:20:1. Thus, there was a low organic matter content in the mixed wastewater, although domestic wastewater was added to it.

Initially, the sludge volume index (SVI) of the sludge for seeding was 95mL/g. After the acclimation period (approximately 45 days), it was observed that the SVI of the sludge decreased to 69mL/g. After the reactors had attained the steady state (45 days operating), a low removal efficiency of COD was observed, with an average of 10% after the SETTLE period.

At the 75th day of operation, kinetic studies were performed in the SBR, to investigate the effluent biodegradability during the FILL/REACT and SETTLE periods in a cycle, in terms of soluble COD and VSS (Figures 4 and 5). At the end of the SETTLE period, an 11% removal efficiency of COD was observed, showing that the effluent is of difficult biodegradability, probably because of the laboratory wastewater toxic effects.

Although the reactor apparently attained steady-state, in terms of COD and VSS values (Figures 1 and 2), low organic matter removal efficiency and low VSS concentration were observed. Furthermore, at the end of 80 days operating a difficulty to enumerate the microorganisms was observed; thus, it was not possible to perform identification tests for the detection of enteric bacteria/non fermenters/gram-negative. This was probably due to the low concentration of viable cells found in the

treatment.

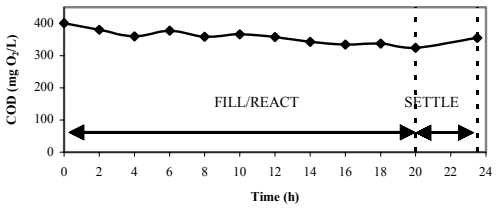

Figure 4. Soluble COD concentration during FILL/REACT and SETTLE periods at the 75th day of operation.

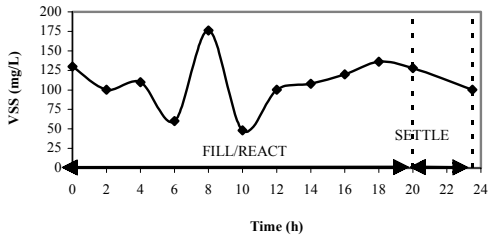

Figure 5. VSS concentration during FILL/REACT and SETTLE periods at the 75th day of operation.

Conclusion

A low removal efficiency of COD during the biological experiment was observed. Based on the preliminary results, the biological treatment cannot be used in a stand-alone basis to treat laboratory wastewaters. Physicochemical or chemical treatments must be performed prior to biological treatment, to achieve lower toxicity levels and extent the biodegradability of the effluent. Further studies must be carried out to test the toxicity effect of laboratory wastewaters on biological systems.

Acknowledgement

The support provided by Capes and by the Universidade Estadual de Maringá is gratefully acknowledged.

References

AMARAL, S. T. *et al*. Relato de uma experiência: recuperação e cadastramento de resíduos dos laboratórios de graduação do Instituto de Química da Universidade Federal do Rio Grande do Sul. *Química Nova*., São Paulo, v. 24, n. 3, p. 419-423, 2001.

APHA - AMERICAN PUBLIC HEALTH ASSOCIATION. *Standard Methods for the Examination of Water and Wastewater*. 20. ed. Washington: AWWA, WPCF, 1998.

COELHO, M. A. Z. *et al*. Optimization of a Sequencing Batch Reactor for biological nitrogen removal. *Water Res.*, Kidlington, v. 34, n. 10, p. 2809-2817, 2000.

CUNHA, C. J. O programa de gerenciamento dos resíduos laboratoriais do Departamento de Química da UFPR. *Química Nova*, São Paulo, v. 24, n. 3, p. 424-427, 2001.

FU, L.Y. *et al*. Treatment of dyeing wastewater in two SBR systems. *Process Biochem.*, Kidlington, v. 36, n. 11, p. 1111-1118, 2001.

JEFFERSON, B. *et al*. Nutrient addition to enhance biological treatment of greywater. *Water Res.*, Kidlington, v. 35, n. 11, p. 2702-2710, 2001.

KATSOGIANNIS, A. N. *et al*. Adaptive optimization of a nitrifying sequencing batch reactor. *Water Res.*, Kidlington, v. 33, n. 17, p. 3569-3576, 1999.

LIM, P. E. *et al*. Simultaneous adsorption and biodegradation processes in sequencing batch reactor (SBR) for treating copper and cadmium-containing wastewater. *Water Res.*, Kidlington, v. 36, p. 667-675, 2002.

MICARONI, R. C. C. M. *et al*. *Gestão de Resíduos em Laboratórios de Ensino do Instituto de Química da UNICAMP*. [S.1.: s.n.], 2002. Disponível em <http://www.sbq.org.br/ranteriores/23/resumos/0517-1/>, Acesso em: 09 jul. 2002.

NATIONAL RESEARCH COUNCIL (U.S.). *Prudent Practices in the Laboratory Handling and Disposal of Chemicals*. Washington: National Academy Press, 1995.

PAVŠELJ, N. *et al*. Experimental design of an optimal phase duration control strategy used in batch biological wastewater treatment. *ISA Trans.*, Kidlington, v. 40, n. 1, p. 41-56, 2001.

SCALBERT, A. *et al*. Tannins in wood: comparison of different estimation methods. *J. Agric. Food Chem*., Washington, DC, v. 37, p. 1324-1329, 1989.

Received on May 29, 2003.
Accepted on October 22, 2003.