



Treatment of textile effluent containing indigo blue dye by a UASB reactor coupled with pottery clay adsorption

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ABSTRACT. This study aimed to evaluate the treatment of a synthetic textile wastewater containing the blue indigo dye in a UASB (upflow anaerobic reactor), on a bench scale, followed by pottery clay adsorption. The system monitoring was verified by the following physical and chemical parameters: pH, alkalinity, volatile acids, COD and removal of color. The adsorption tests using pottery clay (construction debris) as an alternative adsorbent material were performed on a jar test equipment. The results showed satisfactory effectiveness in removing color and organic matter (COD) by the UASB, at the order of 69 and 81.2%, respectively. The color removal using ceramic clay as an alternative adsorbent material was 97% for the concentration of 200 g L⁻¹ of adsorbent, evidencing that the use of pottery clay as adsorbent material had significant and promising results, and may be used as a post-treatment unit for removal of dyes present in textile effluents, and since construction debris currently represents a major environmental problem, its use in wastewater treatment may become an alternative to a proper destination of this waste.

Keywords: UASB reactor, adsorption, Indigo Blue dye, pottery clay.

Tratamento de efluente têxtil sintético contendo corante Azul Índigo em reator UASB, seguido por adsorção em cerâmica de argila

RESUMO. Este trabalho teve como objetivo avaliar o tratamento de um efluente têxtil sintético, contendo o corante Azul Índigo, em um reator UASB (reator anaeróbico de fluxo ascendente), em escala de bancada, seguido por adsorção em cerâmica de argila. O monitoramento do sistema foi verificado pelos seguintes parâmetros físico-químicos: pH, alcalinidade, ácidos voláteis, DQO e remoção de cor verdadeira. Os ensaios de adsorção utilizando cerâmica de argila (entulho da construção civil) como material adsorvente alternativo foram realizados em um aparelho “jar test”. Os resultados obtidos demonstraram eficiência satisfatória na remoção de cor e matéria orgânica (DQO) pelo UASB, da ordem de 69 e 81,2%, respectivamente. A remoção de cor, utilizando a cerâmica de argila como material adsorvente alternativo, foi de 97% para a concentração de 200 g L⁻¹ de adsorvente, constatando-se que, a utilização da cerâmica de argila como material adsorvente apresentou resultados significativos e promissores, podendo esta ser utilizada como unidade de pós-tratamento na remoção de corantes presentes em efluentes têxteis. Como o entulho da construção civil configura-se atualmente em grande problema ambiental, sua utilização no tratamento de efluentes pode se tornar uma alternativa para um destino adequado desse resíduo.

Palavras-chave: reator UASB, adsorção, corante Azul Índigo, cerâmica de argila.

Introduction

The growing concern with the preservation of water resources in the last few years has become evident both by the establishment of environmental standards increasingly restrictive, or by the charges, according to the paying polluter and paying user principles. Pollution and contamination of the water bodies by different human activities have caused several environmental, social, economic and of public health problems.

Besides the economic importance, the textile industries are also recognized by the high consumption

of water and generation of hazardous effluents. Management measures related to the improvement of production techniques, which lead to a lower water consumption, and the treatment and reuse of generated effluents, certainly enable a reduction of environmental impacts. The textile industry is one of the largest producers of liquid effluents. Approximately 80 liters of water are necessary to produce 1 kg of fabric. However, there is reference to values in the order of 150 liters, being 80% of this volume discarded as effluent and only 12% of the total composes the losses by evaporation (HARRELKAS et al., 2009).

The characteristics of these effluents depend on the technology and the industrial processes used and also the types of fibers and chemical products employed, but it is known that the major problems associated with the effluents are related to the high amount of organic load, color, toxicity and salinity (HARRELKAS et al., 2009). Several types of dyes (natural, reactive, acids, cationic, among others) can be used in textile industry, mainly during the dyeing and finishing steps. These substances configure in an important part of the pollution problems, once it is estimated that 50% of the applied quantity to the fabric fibers do not fix to them, subsequently forming the wastewater (HARRELKAS et al., 2009). Besides the toxicity, effluents with high color absorb the light in the receiving bodies, affecting the balance of the aquatic ecosystems (ALINSAFI et al., 2006).

The "AZO" dyes, for example, systematically investigated by the scientific community, produce aromatic carcinogenic amines, and were banned by the textile sector in 2003, following the recommendation of the European Community.

Several alternatives of treatment for these effluents were reported in literature. It is worth highlighting that, in full scale, an isolated unit hardly will fulfill the restricted levels of discharge required by the law, being necessary the development of systems that integrate generally several unities. In these cases, the main characteristic is the complementation between the strengths and the weaknesses points of each component, allowing more effective results.

In this way, according to Assadi and Jahangirib (2001), for textile effluents, additionally to the biological treatment, the physical and chemical methods are also used to remove coloring substances.

The anaerobic biological processes (HAROUN; IDRIS, 2009; SANTOS et al., 2004) have been prioritized, in relation to the aerobics (ALINSAFI et al., 2006), due to the advantages such as lower sludge generation, lower energy demand and lower operational costs, but the studies that consider the anaerobic/aerobic association also had been carried out (KAPDAN; ALPARSLAN, 2005).

The chemical methods usually involve coagulation followed by precipitation and chemical sludge oxidation and the physical methods involve mainly the adsorption on activated carbon (SIRIANUNTAPIBOON et al., 2007) and at lower scale, the membranes technology.

The various types of coal are widely used in adsorption operations. The vegetable coal, for example, is obtained from the burning of wood, i.e., derives from an activity that also implies in environmental degradation.

Considering that the coal burning is somehow inevitable, at least in India, due to power generation plants, Rao and Rao (2006) have studied the treatment of textile effluent by adsorption together with the ashes generated in the process, comparing the results with the activated carbon, obtaining similar color removals of 96 and 98.5%, respectively. However, this initiative can be considered even a "palliative" and the search for alternative adsorbent materials, also derived from less aggressive activities, become a need of researches related to the subject.

The building rubble of building industry is perhaps the most heterogeneous among the industrial wastes. It is made up of remains of practically all-building materials (mortar, sand, ceramic, concrete, wood, metal, paper, plastic, stone, brick, ink, among others) and its chemical composition is bound to the composition of each one of its constituents.

Given the above, this study analyzed the treatment of a synthetic textile effluent, through a UASB reactor followed by an adsorption unit, in which it was investigated the activated carbon and the pottery clay as adsorbent materials to verify the removal of organic material (COD) and color.

Material and methods

Synthetic textile wastewater

The basis of the wastewater used in the study was chosen due to the simplicity to prepare large volumes. Freire et al. (2008) used the same synthetic wastewater (without adding indigo dyes) for the performance and the fluid-dynamic analyses, respectively, in an Anaerobic Fluidized Bed Reactor (AFBR).

The composition of the synthetic textile effluent used is presented in the Table 1, with the values based on a concentration of organic material in terms of COD in the order of 1,000 mg L⁻¹. For different concentrations of COD from the stipulated, it was added the reactants in the desired proportion.

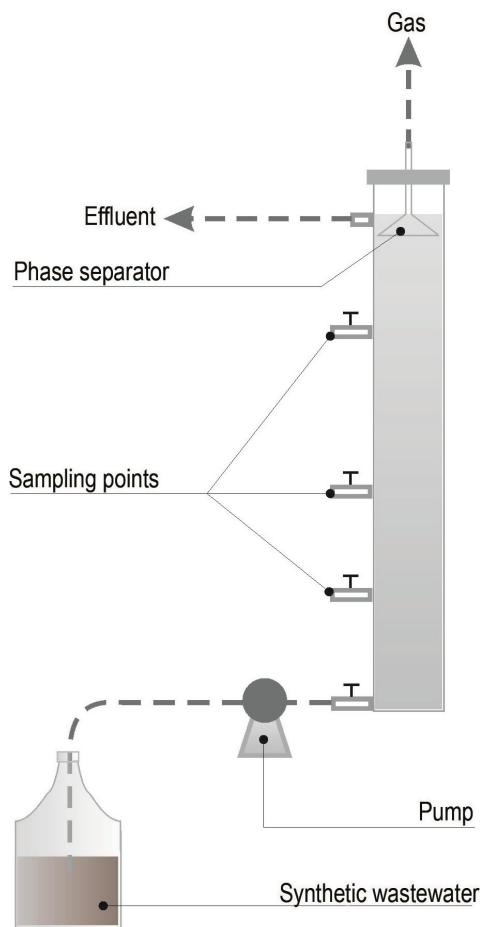
UASB Reactor

The bench-scale upflow anaerobic sludge blanket reactor (UASB) used in the study, as illustrated in the Figure 1, was built in acrylic with volume of 1 L, height of 55 cm and diameter of 4.8 cm. The reactor has three sampling points along its height, for biomass sampling. Initially, the reactor was operated with flowrate of 2.5 L day⁻¹ and, subsequently, with more optimized results, with flowrate of 4.5 L day⁻¹, corresponding to HRT of 5.3h, at room temperature.

Table 1. Composition of the synthetic textile wastewater.

Compound	Concentration (mg L ⁻¹)
Glucose	1,000
Urea	62.5
Nickel sulfate	0.5
Ferrous sulfate	2.5
Ferric chloride	0.25
Cobalt chloride	0.04
Selenium oxide	0.035
Monobasic potassium phosphate	42.5
Potassium phosphate dibasic	10.85
Sodium phosphate dibasic	16.7
Sodium bicarbonate	1,000
Indigo Blue Dye	300

The monitoring of the reactor performance treating the textile effluent was verified by the following physical and chemical parameters: pH, total alkalinity, volatile acids, COD and color removal.

**Figure 1.** UASB reactor scheme.

The UASB reactor was inoculated with sludge of an anaerobic reactor (AFBR) from the wastewater treatment plant of the city of Umuarama, Paraná State. The inoculation process through the already "formed" biomass was adopted to accelerate the obtainment of satisfactory results in the removal of

organic material, once the starting periods without inoculation are quite long (FREIRE et al., 2008).

Indigo blue dye

The dye used with the wastewater was the synthetic Blue Indigo, purchased at specialized commerce. After an adaptation period of the biomass to the new conditions (30 days), the dye was added to the affluent solution of the UASB reactor in the concentration of 300 mg L⁻¹. The indigo dye concentration and the ratio between the applied concentration and the respective value of color were determined in preliminary tests and literature review.

Adsorbent materials

As adsorbent materials, in the present study were used, the activated carbon (testimony material) and the pottery clay (building industry material). The activated carbon is a material employed widely in adsorption processes of several classes of dyes. Its viability not only as an effective adsorbent, but also as a support media of biological reactors, mainly of fluidized bed reactors, is systematically presented in literature.

In general are used coals of vegetable origin, being activated with CO₂, water vapor or phosphoric acid.

The vegetable coal, for example, is obtained from the burning of wood, an activity that implies in environmental degradation, and the search for alternative adsorbent materials, derived from less aggressive activities, becomes a need of researches related to the subject.

Certainly, the choice of pottery clay as an adsorbent material obeyed to a more speculative character. By the fact of the clay in its different forms (bentonite, vermiculite, illite, among others) is a material with proved adsorbent potential, it is assumed that the pottery, for being formed from the burning of clay at 600°C also manifest such characteristics.

Thus, the parcel of the building industry rubble formed by this material (mainly bricks, ceramic tiles and roof tiles) can be reused in adsorption operations.

Experimental procedure

Initially, the synthetic wastewater was prepared to present COD of about 500 mg L⁻¹. The synthetic textile effluent was stored in a 50 liter-container and transported to the UASB reactor through solenoid dosing pump (Prominent). The reactor feeding was initially performed with extremely reduced flowrates, aiming the adaptation of the biomass

(inoculum sludge) to the provided substrate. After passing through the UASB, the wastewater was collected in an output reservoir.

During the first days, only the UASB reactor was put into operation. This strategy is due to distinct reasons. The idea is that, besides respecting the time limits of biomass adaptation to the synthetic wastewater, the input parameters should be varied in such a way to reach more optimized operational conditions.

Also, the physical operations and the chemical processes of treatment usually present much faster responses than the biological processes, not requiring in this way, the same time of operation. Completed the period of the UASB operational optimization, a volume of the reactor effluent was accumulated for the conduction of the tests in the adsorption unit.

The adsorption tests were performed in "Jar test" equipment (Nova Ética, model 218-6LDB), capable of 6 simultaneous tests. The two adsorbent materials used (activated carbon and pottery clay) were selected by the sieving, particles with about 2 mm of diameter.

Before the tests, the activated carbon was oven dried at $60 \pm 2^\circ\text{C}$ for 12h and the pottery clay for 24h at $103 \pm 2^\circ\text{C}$. Both the analyzed adsorbents were submitted to an effluent with the same characteristics to obtain greater reproducibility of the results.

For each adsorbent, four simultaneous batch tests were performed for the pre-determined masses of 70, 100, 150 and 200 g of adsorbent in contact with 1 liter of effluent in each container.

The jars (2.5 liters capacity) were submitted to a constant rotation speed of 120 rpm and the total test duration of 6h. Aliquots of the effluent were withdrawn every 120 minutes (stirring switched off temporarily) for the reading of color removal.

The samples of each container were centrifuged for 5 minutes at 2500 rpm in centrifuge MTD III PLUS to separate the solid part of the supernatant. For the color removal estimation, readings of initial and final absorbance were performed in the UASB reactor and in the adsorption tests in a spectrophotometer 600 PLUS – FEMTO with wavelength of 560 nm.

All the analyses were performed at the Pollution and Sanitation Laboratory of the DTC/UEM. The methodologies of analyses and the procedures for collection and preservation of samples followed the patterns described in the *Standard Methods for the Examination of Water and Wastewater* (APHA; AWWA; WEF, 2005).

Results and discussion

UASB reactor performance

The monitoring results of the reactor performance on the removal and the removal efficiency of COD are illustrated in Figures 2 and 3, respectively.

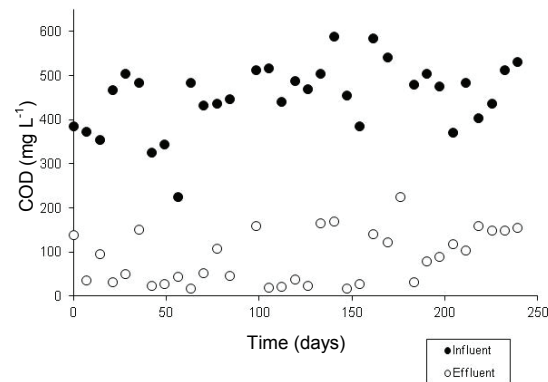


Figure 2. Temporal variation of influent and effluent COD values in the UASB.

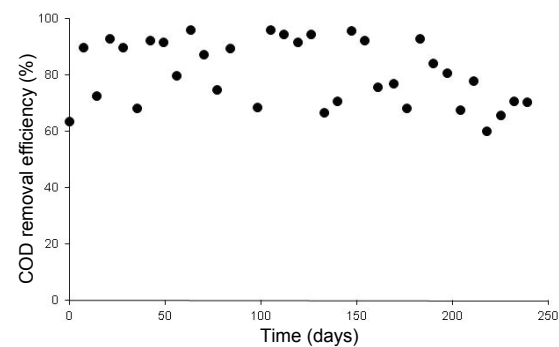


Figure 3. COD removal efficiency in the UASB reactor.

In the period of the UASB reactor operation that treats the synthetic textile effluent, it was obtained mean affluent COD of 461.24 mg L^{-1} with standard deviation of 88.51 mg L^{-1} , obtaining input values of COD similar to the initial values stipulated (500 mg L^{-1}). The mean effluent COD for the same period was 88.41 mg L^{-1} , showing considerable removal of the organic matter (Figure 2).

Analyzing the Figure 3, it was verified that the mean removal efficiency of COD in the UASB throughout the observation period was 81.2%, with peaks up to 96.4%.

In the Figures 4, 5 and 6 are presented the values of pH, alkalinity and volatile acids, respectively, obtained from the reactor performance monitoring.

The mean values of affluent and effluent pH in the UASB reactor (Figure 4) were 7.6 and 8.0, respectively, indicating the consumption of acids and alkalinity generation in the biochemical reactions inside the UASB.

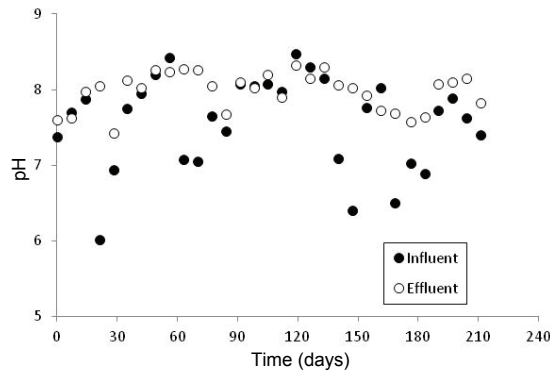


Figure 4. Temporal variation of influent and effluent pH values of the UASB.

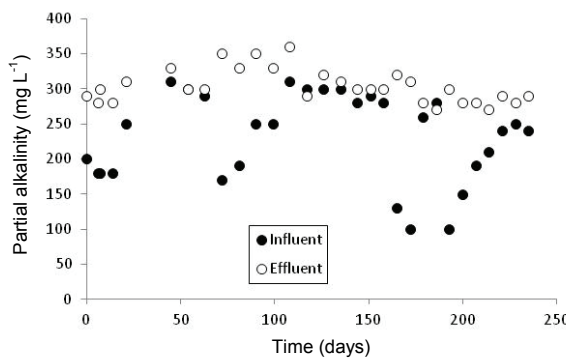


Figure 5. Temporal variation of influent and effluent values of partial alkalinity of the UASB.

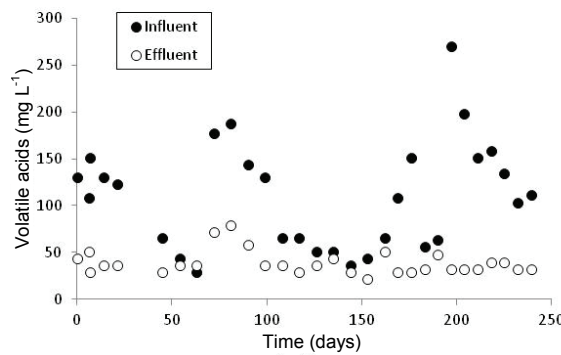


Figure 6. Temporal variation of influent and effluent volatile acids values of the UASB.

The alkalinity generation throughout the anaerobic process is a good indicative of stability. The higher values in the effluent (mean value of $307 \pm 23 \text{ mg L}^{-1}$) than in the affluent ($225 \pm 56 \text{ mg L}^{-1}$) represented the efficiency in the removal of volatile acids from the system.

Adsorption units performance

Activated carbon

The data obtained by means of the readings of color removal, and the final efficiency of removal for the adsorption tests using the activated carbon as

adsorbent, in the masses of 70, 100, 150 and 200 g are presented in Table 2.

Table 2. Absorbance values and final efficiency of color removal obtained in the adsorption test, using activated carbon for the masses of 70, 100, 150 and 200 g.

Time (min.)	M1 70 g	M2 100 g	M3 150 g	M4 200 g
0	0.249	0.249	0.249	0.249
120	0.011	0.012	0.011	0.003
240	0.004	0.008	0.003	0.002
360	0.003	0.001	0.001	0.001
Ef. (%)	99.0	99.6	99.6	99.6

The results in the Table 2 pointed out that the activated carbon used in the adsorption tests presented great efficiency in the removal of the Blue Indigo dye for the four masses analyzed of adsorbent. The efficiencies obtained for the masses of 70, 100, 150 and 200 g were 99.0, 99.6, 99.6 and 99.6%, respectively.

For the three last masses of analyzed carbon, it was obtained the same values of color removal (Figure 7), indicating removal stabilization by using 100 g of the adsorbent.

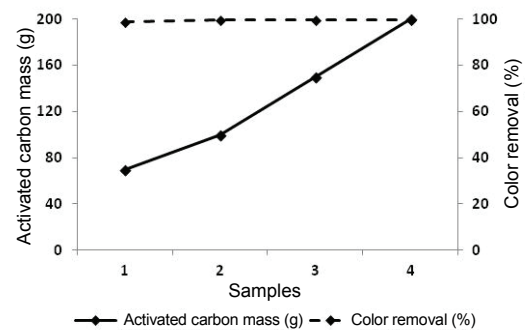


Figure 7. Color removal using activated carbon for the masses of 70, 100, 150 and 200 g.

Pottery Clay

The Table 3 lists the absorbance results obtained with the adsorption tests in pottery clay and the final efficiency of color removal for the four masses analyzed.

The color removal using different masses of ceramic clay is shown in the Figure 8.

Analyzing the data of the Table 3 and Figure 8, it was observed that the largest amounts of clay have also provided higher efficiencies, being the highest (97%) obtained from the test with 200 g.

A shortcoming verified in these tests was the detachment of material from the adsorbent to the solution, material that even after centrifugation was not completely removed, undermining the absorbance readings, being performed previous washing of adsorbent (before the drying), to eliminate the finest particles, minimizing this problem.

Table 3. Absorbance values and final efficiency of color removal obtained in the adsorption test using pottery clay for the masses of 70, 100, 150 and 200 g.

Time (min.)	M1 70 g	M2 100 g	M3 150 g	M4 200 g
0	0.222	0.222	0.222	0.222
120	0.167	0.130	0.153	0.128
240	0.128	0.119	0.062	0.075
360	0.097	0.073	0.041	0.006
Ef. (%)	56	67	82	97

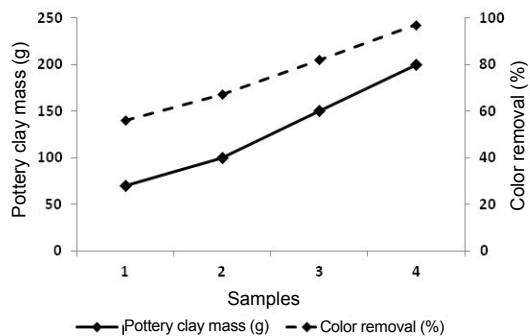


Figure 8. Color removal using pottery clay for the masses of 70, 100, 150 and 200 g.

Conclusion

The mean efficiencies of COD and color removal were 81.2 and 69%, respectively. The reactor presented stability, even with increasing flowrate and dye concentration.

The activated carbon and the pottery clay removed 99.6 and 97.0% of color, respectively, for 200 g of adsorbent.

Greater amount of adsorbent masses in the batch tests promoted higher efficiencies of color removal.

The results indicated the potential of the pottery clay as adsorbent under the studied conditions, representing an alternative for its adequate disposal, with benefits for the field of effluents treatment.

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