

Flow Injection Analysis of Indigo Carmine Using Green Coconut (Cocos Nucifera L.) Fiber as a Bioadsorbent

Felipe Zaidan¹, Patricia Antonio de Menezes Freitas²

Escola de Engenharia Mauá, Centro Universitário do Instituto Mauá de Tecnologia, Praça Mauá 1, 09580-900, SP, São Caetano do Sul, SP, Brazil

Abstract— This paper deals with a procedure for preconcentration and determination of indigo carmine in textile industrial effluent. The product of Indigo blue sulphonation, 5,5'-disulfonic indigotin (5,5'-DI) aqueous solution was run through a mini-column packed with green coconut fiber (*Cocos Nucifera L.*) in a flow injection system. The 5,5'-DI was preconcentrated on the sorbent at pH 2 and sample flow rate 3.9 mL min^{-1} and eluted by $\text{HCl } 0.1 \text{ mol L}^{-1}$ to be detected by UV-vis spectrophotometry at 612 nm. An increase of 18.7% in the indigo recovery was observed with fiber washed with albumin and 11.7% in fiber washed with NaOH. A linear response was observed within the range 0.157 to $75.2 \text{ } \mu\text{mol L}^{-1}$, with detection limit, coefficient of variation and sampling rate estimated as $0.0376 \text{ } \mu\text{mol L}^{-1}$ (95% confidence level), 4.5% ($n = 21$) and 101 determinations per hour, respectively. The enrichment factor achieved was 1.64. The proposed method was successfully applied to the determination of 5,5'-disulfonic indigotin in textile industrial effluents.

Keywords— Adsorption, flow-analysis, green coconut, solid-phase extraction, spectrophotometry.

I. INTRODUCTION

The textile industry has a large environmental impact because it generates a significant volume of wastewater, which sometimes is discharged without treatment[1]. Some dyes and organic compounds from these industrial effluents are highly toxic and chemically stable[2,3]. Disodium salt of Indigotin 5,5'-disulphonic acid, FD & C Blue 2 or Acid Blue W (IUPAC name 3,3-dioxo-2,2-bis-indolyden-5,5-disulfonic acid disodium salt) is popularly known as indigo carmine. It is considered as a highly toxic indigoid class of dye[4]. Apart from its use as a textile-coloring agent and additive in pharmaceutical tablets and capsules, indigo carmine is also used for medical diagnosis[5]. Several methods have been reported for quantitative determination of Indigo carmine, including chromatographic[6], voltammetric[7] and spectrophotometric[8,9] ones. New treatment technologies have been developed in order to meet the legal requirements regarding effluent disposal of this dye as well as to reduce the operating costs of such processes[10]. Coconut fiber (*Cocos Nucifera L.*) has been used as a low cost alternative bioadsorbent for the removal of pollutants (dyes and other natural and inorganic substances) from natural waters[11-13]. Also, the retention capacity of several metallic ions in aqueous solutions has been previously reported using coconut fiber as the adsorbent [14-17]. This is a sustainable alternative because of waste reuse. Approximately 60 million tons of coconut were produced worldwide in 2008: 85% in Asia, 8.5% in the Americas, 2.9% in Africa and 3.2% in Oceania[18-20]. Specifically in Brazil, about 1.3 billion coconuts were produced in 2013, producing about 1.5 kg of solid residue per fruit; in general, 80% of this biomass is discarded in the environment[21-24]. The decomposition of coconut generates methane, which is a major greenhouse gas [25-28]. Aiming reuse, the coconut husk can be processed to the condition of fiber, which is composed by cellulose, hemicellulose, lignin, pectin and various minerals[29-32]. This fiber can be used in the preparation of composites, such as bioplastics, natural adsorbents and raw materials for several processes[33-35]. Flow-based systems are an alternative to develop a new analytical procedure that focuses on the reduction of reagent consumption and waste [36,40]. Moreover, flow systems minimize the analyst intervention in chemical analysis, increase the number of samples that can be processed at a time and improves measurements precision[41-45]. Flow injection spectrophotometry has been proposed for determination of indigo carmine dye[8] but the use of coconut fibers as biosorbent for this dye has not been found in the literature. This study aimed the use of coconut fiber as a biosorbent for retention of the organic compound 5,5'-disulfonic indigotin (5,5'-DI), a sulphonated species of Indigo blue dye (Fig. 1). The sorption process was carried out in a flow injection system aiming analyte separation and preconcentration before spectrophotometric determination. In addition, the appropriate conditions for the adsorption and the elution of the 5,5'-DI were determined, as well as the mass of dye retained per mass of green coconut fiber, which can be used for an upscale project to be implemented to recover 5,5'-DI from industries wastewater.

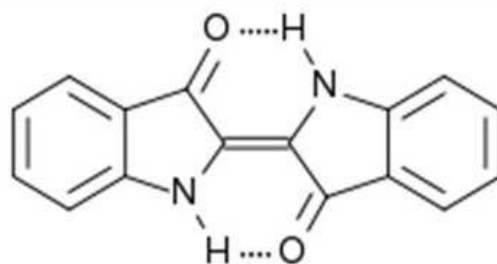


FIGURE 1. CHEMICAL STRUCTURE OF THE REAGENT INDIGO BLUE DYE[12].

II. EXPERIMENTAL

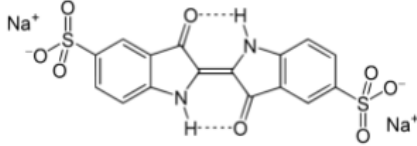
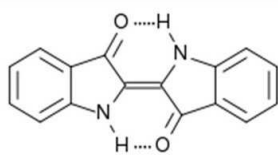
2.1 APPARATUS

The flow system was constructed with a time-controlled sliding-bar injector-commutator (B352, Micronal, Brazil), an Ismatec IPC-8 peristaltic pump equipped with Tygon® tubes for fluid propelling at (1.2; 2.4; 3.0 and 3.9) mL min⁻¹ and polyethylene extension tubes with 0.8 mm i.d. An UV-vis spectrophotometer (Cary E1 Varian) with a 10-mm optical path (80 µL inner volume) quartz flow cell (Hellma) was employed for signal measurements. A SPE mini-column was lab-made by using polyethylene (2-mm diameter, 15-mm long) and it that was filled with bark of green coconut (0.0211-0.0695) g. Measurements of pH were performed with a Metrohm pH-meter Model 827 with a combined glass electrode with the Ag/AgCl reference electrode filled with 3 mol L⁻¹ NaCl solution. Agitation of the mixtures was performed on an Incubator Shaker (Model AL-222-CF, American Lab) with controlled velocity and temperature. All cuvettes, glass and plastic vessels were washed with a 10% HNO₃ (v/v) solution followed by deionized water.

2.2 REAGENTS AND SOLUTIONS

All reagents and solvents were of analytical grade. Deionized water with conductivity > 18 MΩ cm (Milli-Q) was used to prepare the solutions. Indigo blue dye ((3H-indole-3-one2-(1,3-dihydro-3-oxo-2H-indol-2ylidene)-1,2-dihydro) is known in literature as CI Vat Blue or D&C no.6 and is used to dye natural and synthetic fibers. It is a blue crystalline solid with the molecular formula C₁₆H₁₀N₂O₂ (262.27 g mol⁻¹), CAS Number 482-89-3 and a melting point within 300 and 303°C.

TABLE 1
PHYSICAL AND CHEMICAL PROPERTIES OF 5,5'-DI AND INDIGO BLUE.

Property	5,5'-DI	Indigo blue
Commercial name	Indigo carmine	Indigo blue
Alternative name	5,5'-Indigodisulfonic acid sodium salt or indigotine	3H-indole-3-one2-(1,3-dihydro-3-oxo-2H-indol-2ylidene)-1,2-dihydro
Empirical Formula ^a	C ₁₆ H ₈ N ₂ O ₈ S ₂	C ₁₆ H ₁₀ N ₂ O ₂
Molecular structure		
Molecular weight (g mol ⁻¹) ^a	466.36	262.27
Solubility in water (g L ⁻¹), 298 K ^a	10	9.9 × 10 ⁻⁴
Melting point (K)	> 573	663
CAS number	860-22-0	482-89-3
Appearance	Dark blue to violet powder	Dark blue powder
Biodegradability	Biodegradable	Not readily biodegradable
Nature	Acid dye	Vat dye

^aTaken from the manufacturer.

TABLE 2. PHYSICOCHEMICAL PROPERTIES OF GREEN COCONUT ADSORBENT[34, 46].

Physicochemical Property	Green Coconut
Cellulose (%)	23 – 43
Hemicellulose (%)	3 – 12
Lignin (%)	35 – 45
Electrical conductivity (dS m ⁻¹)	1.8
Average diameter (μm)	157
Relationship (C/N)	132
Specific area (m ² g ⁻¹)	362
Dry / Wet density (g cm ⁻³)	1.15 – 1.45

The 5,5'-disulfonic indigotin solution (FD&C Blue No. 2) was prepared as previously described[46]: 1.05 g of the Indigo blue dye (Sigma Aldrich) was added to 35 mL of concentrated H₂SO₄ while stirring. The temperature was kept at 80°C and after cooling, the solution was diluted to 1000 mL with deionized water. Reference solutions were prepared in the range 1.50×10^{-7} a 7.52×10^{-5} mol L⁻¹, at pH 2, by dilution of a 5.19×10^{-3} mol L⁻¹ stock solution. To analyze the dye adsorption in different pH's values, sodium hydroxide 1,0 mol L⁻¹ was added to the stock solution until the aimed pH value was reached. Some of properties of 5,5'-disulfonic indigotin (5,5'-DI) and Indigo Blue are given in Table 1. The wastewater samples were from a textile industry. Samples were sulfonated in the same conditions as in the preparation of 5,5'-DI solution. The coconuts were grown in Paraiba-Brazil and purchased at the local market in Santo Andre-Brazil). The fruits were washed, drilled to remove the water and then cut to remove the pulp. The bark was first ground in a toothed roller mill and then shredded in a hammer mill before placing in an oven at 378 K for at 6 h. Some physicochemical parameters of the obtained material are shown in Table 2. The effect of washing the coconut fiber was evaluated by placing 100 mg samples separately in contact with 10 mL of 40 g L⁻¹ albumin, 0.1 mol L⁻¹ NaOH and 0.1 mol L⁻¹ HNO₃ solutions under constant agitation for 24 hours[46,47].

2.3 FLOW DIAGRAM AND PROCEDURE

The diagram of the FIA-SPE system is shown in Fig. 2. The resting times of the sliding-bar commutator in the loading and elution positions were both set at 60s. In the position shown, sample or 5,5'-DI reference solutions (3.74×10^{-5} mol L⁻¹) were pumped through the mini-column - the dye was adsorbed by the fiber and the remaining solution was discharged to waste. When the commutator was switched to the elution mode, 1.0 mol L⁻¹ HCl solution percolated the column and the eluate was carried towards the flow cell for spectrophotometric measurements at 612 nm, which is the 5,5'-DI absorption maximum[46,47]. Measurements were based on peak height and taken in triplicate.

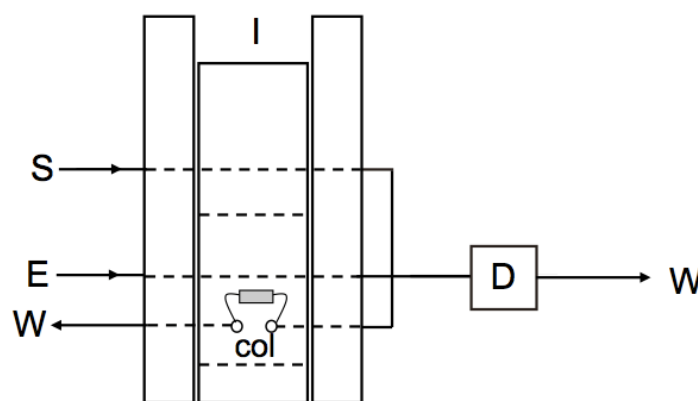


FIGURE 2. FLOW DIAGRAM OF THE SYSTEM FOR 5,5'-DI determination. I: sliding-bar injector, S: sample (2.4 mL min⁻¹), E: eluent (3.0 mL min⁻¹), col: mini-column (2-mm diameter, 15-mm long, filled with green coconut fiber), D: spectrophotometer (612 nm) and W: waste.

III. RESULTS AND DISCUSSIONS

3.1 SYSTEM OPTIMIZATION

Chemical and flow variables were investigated aiming at better sensitivity and repeatability, including sorbent mass, eluent type and its concentration and flow rate, loading and elution times and sample flow rate. The amount of the solid coconut fiber is a very important parameter for the adsorption of 5,5'-DI and two different masses of adsorbent were evaluated with the FIA-SPE system (Fig. 3). With the initial mass of 0.0695 g, perturbations by Schlieren effect[48-50] were evidenced (Fig. 3a). This is due to the change of the acid concentration when the column is inserted into the eluent and may affect precision and accuracy of the measurements. For the mass of 0.0211 g, this effect was not observed, because the column was shorter (25 mm, instead of 75 mm) then resulting in lower dead volume (Fig. 3b). Therefore, a column with 0.0211 g of coconut was used in further studies. Nitric and hydrochloric acids (1.0 mol L^{-1}) were evaluated for elution of 5,5'-DI retained in the column, with different retention (30 and 60)s and elution (10 to 60)s times. Elution was more efficient with HCl in all retention and elution times studied, and therefore it was recommended for the subsequent experiments. The effect of eluent concentration is shown in Fig. 4.

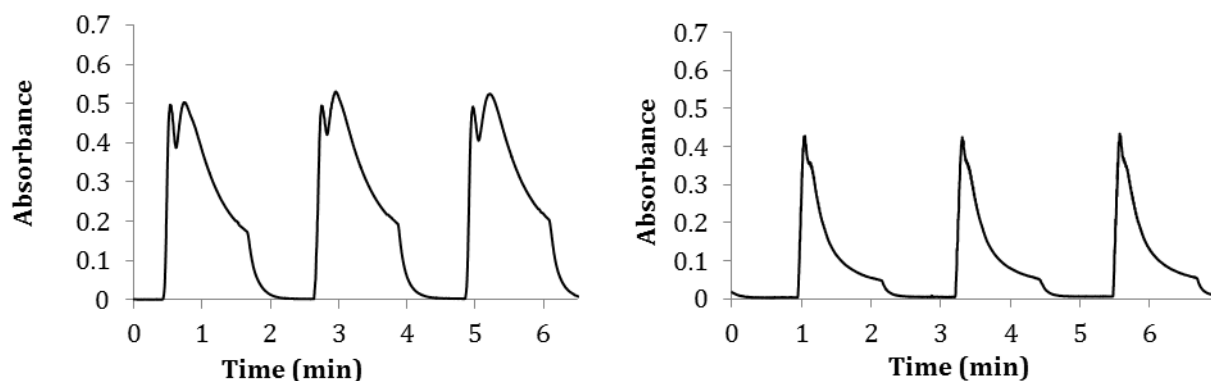


Figure 3. EFFECT OF THE COCONUT FIBER MASS IN THE MINI-COLUMN: (a) 0.0695 g and (b) 0.0211 g using 5,5'-DI solution $3.76 \times 10^{-5} \text{ mol L}^{-1}$.

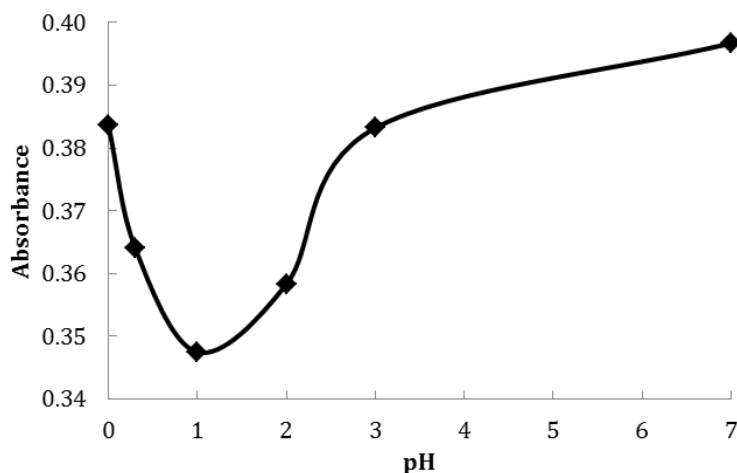


FIGURE 4. INFLUENCE OF THE ELUENT pH ON THE ABSORBANCE.

It was observed that at pH 1 defines the borderline between two different phenomena. In pH values higher than 1.0 the elution is not so effective, and the readings of absorbance were attributed mainly to the interstitial solution. From 0.1 mol L^{-1} , higher HCl concentrations yielded better elution. However, as an increase of 10 times on the concentration led to only 9.4% increase on the absorbance readings, 0.1 mol L^{-1} was selected as eluent to minimize reagent consumption. This same phenomena was observed in literature [51-53]. Elution efficiency increased with the flow-rate (Fig. 5), which indicates that the process is fast and the result is a consequence of a narrow zone obtained with higher flow-rates. As an increase of from 3.0 mL min^{-1} to 3.9 mL min^{-1} resulted in an only 8.7% higher absorbance reading, the former value was selected for further

experiments. The loading time and sample flow-rate define the amount of 5,5'-DI that flow through the column. Three preconcentration times were studied, (20, 30 and 40)s, leading to (120, 89 and 72) measures per hour, respectively. Since there was no more than 3% variation between the three times analyzed, which indicates the saturation of the column, the lower was recommended since it would imply in a higher sample rate (120 samples processed per hour), without affecting the dye adsorption.

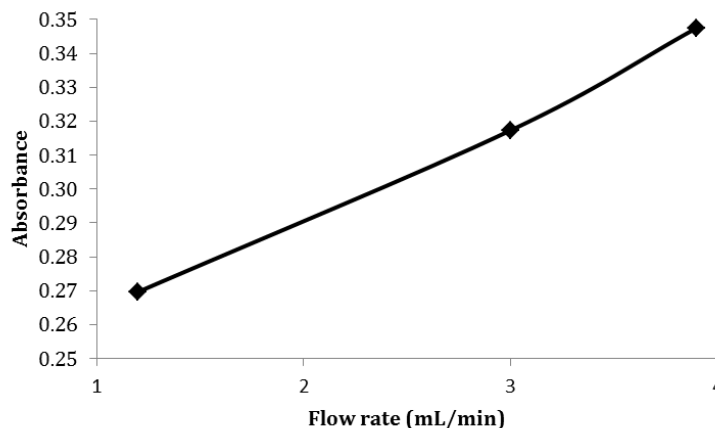


FIGURE 5. EFFECT OF THE FLOW-RATES OF THE ELUENT HCL 0.1 mol L⁻¹.

To study the elution time, for three minutes the system was kept in the preconcentration mode, to ensure that the coconut fiber sites of adsorption were absolutely saturated. After that, elution with 0.1 mol L⁻¹ HCl was carried out for 4 min with simultaneous absorbance reading. It was observed that elution occurred during the first 15s, which was the elution time recommended (sampling rate 104 h⁻¹). Three different sample flow rates were studied. It was observed that the absorbance readings increased linearly with the flow-rates (Fig. 6), because of the higher analyte mass flowing to the column. This also means that the column was not completely saturated at the higher sample flow-rates. Therefore, the 3.9 mL min⁻¹, which was the higher flow rate studied, was recommended.

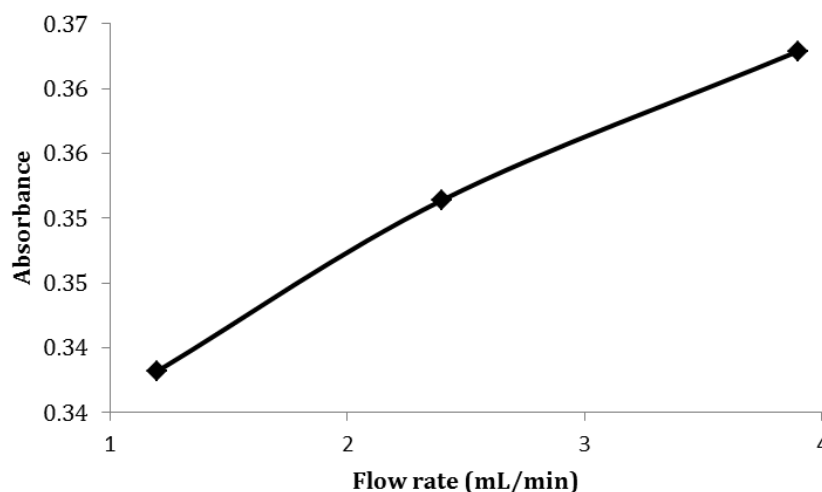


FIGURE 6. EFFECT SAMPLE FLOW RATE ON THE ABSORBANCE SIGNAL

3.2 ANALYTICAL FEATURES

The flow system was submitted to a repeatability study for 30 complete preconcentration and elution cycles, yielding a coefficient of variation of 2.03%, without significant baseline drift. This is an indicative of the long-term stability of the flow system. The sampling rate was estimated at 101 samples per hour. Under optimized conditions and with a 20 s loading time, a linear response range was observed in the 1.50×10^{-7} mol L⁻¹ to 7.52×10^{-5} mol L⁻¹ range, described by the equation

$A = 9314 \times [5,5'\text{-DI}] + 0.0032$ ($r^2 = 0.999$), in which A corresponds to the absorbance and C is the molar 5,5'-DI concentration. The detection limit was estimated at $3.76 \times 10^{-8} \text{ mol L}^{-1}$. From the results obtained without SPE, an enrichment factor of 1.64 was estimated. This value can be considered low in comparison with the results usually obtained in FIA-SPE - usually enrichment factors around 4 are achieved[48-50]. This is due to the mass of the coconut fiber and the relatively low loading time. Most studies are realized with adsorbent masses of around 0.1 g, which result in higher sample amounts adsorbed, and thus higher absorbance readings. With the calibration curve it's also possible to determine the mass of 5,5'-DI retained per mass of coconut fiber, which can be used for an upscale project of an industrial treatment column. The mass of dye retained and then eluted is 368 μg of 5,5'-DI per gram of coconut fiber. That means that 61% of the dye was recovered. The breakthrough volume is an important flow parameter that represents the maximum sample volume that can be adsorbed in the minicolumn without hindering of the analyte retention[54]. In other words, it allows a theoretical recovery of 100%. The breakthrough volume was estimated as $(1.87 \pm 0.02) \text{ mL}$ by graphic analysis of the FIAGram. The effect of pH on dye samples was studied aiming to know if it's possible to realize readings and analyses without pH adjustment. $3.76 \times 10^{-5} \text{ mol L}^{-1}$ 5,5'-DI samples in pH's values ranging from 1 to 12 were submitted in the flow system. It was observed that system behaved similarly with samples with pH values ranging from 2 to 9 (Table 3). For pH 12 the behavior was completely different, and it can be explained by the change of the dye's color to green at about pH 11.5.

TABLE 3
INFLUENCE OF pH VALUES ON DYE SAMPLES ABSORPTION ($[5,5'\text{-DI}] = 3.76 \times 10^{-5} \text{ mol L}^{-1}$).

pH	Reading in 612 nm	Absorbance in the flow cell	Relative Absorbance
2	0.701	0.3234 ± 0.0006	0.4613 ± 0.0008
5	0.734	0.356 ± 0.001	0.485 ± 0.002
7	0.728	0.369 ± 0.003	0.507 ± 0.004
9	0.731	0.371 ± 0.007	0.507 ± 0.009
12	0.068	0.0539 ± 0.0003	0.793 ± 0.005

In order to study the effect of the fiber washing, three minicolumns were prepared with coconut fiber washed with nitric acid, sodium hydroxide and albumin. The results are presented in Table 3. Washing with nitric acid did not affect fiber adsorptivity. On the other hand, sodium hydroxide presented an increase of 11.7% in absorbance reading compared to the natural fiber. Albumin presented an even higher increase of absorbance reading (18.7%). In the case of albumin, the dye mass retained and then eluted is 437 μg of Indigo per gram of coconut fiber. That means that 72% of the Indigo is recovered, compared to the 61% obtained when fiber is not washed. Finally, wastewater from textile industry was studied. While on the conditions analyzed before it was possible to retain 437 μg of Indigo per gram of coconut fiber, in the sulfonated wastewater it was possible to obtain 453 μg of Indigo from sulfonated wastewater per gram of coconut fiber, therefore there was a gain of 3.7% when compared to analytical samples and a recovery of 75% of the Indigo in the sample. This result show that it might be possible to adapt the FIA system presented in this study to wastewater recovery, which should be studied in further researches.

IV. CONCLUSION

The FIA-SPE method[55] developed and described in this paper provides a simple and efficient procedure for the preconcentration and determination of indigo blue. The lowest 5,5'-DI concentration analyzed was $3.76 \times 10^{-8} \text{ mol L}^{-1}$. It was possible to achieve a sampling rate of 101 samples per hour with a relative standard deviation of 2.03%. In the wastewater analysis, from textile industry, it was possible to recover 75% of 5,5'-DI. There is also a potential to apply this kind of retrieval in textile industries that use dyes with similar physicochemical characteristics, such as Indigo Blue, in jeans industry. This kind of process could be an alternative to biological treatment, which is also often applied to the wastewater treatment[41,42].

ACKNOWLEDGEMENTS

FAPESP, CNPq and CEUN-IMT.

Professor Dr. Fábio Rodrigo Piovezani Rocha – CENA/USP

REFERENCES

- [1] R. M. Dallago, A. Smaniotto, L. C. A de Oliveira, Solid waste from tanneries as adsorbent for the removal of dyes in aqueous medium. *Quim. Nova*, vol. 28, pp. 433-437, 2005.
- [2] M. Sequin-Frey, The chemistry of plant and animal dyes, *Journal of Chemical Education*, vol. 58, pp. 301-307, 1981
- [3] A. Bayer and V. Drewson, Darstellung von indigblau aus orthonitrobenzaldehyd, *Berichte der Deutschen Chemischen Gesellschaft*, vol. 15, pp. 2856-2864, 1982.
- [4] A. Mittal, J. Mittal, L. Kurup, Batch and bulk removal of hazardous dye, indigo carmine from wastewater through adsorption, *Journal of Hazardous Materials*, vol. 137, pp. 591-602, 2006.
- [5] C. L. Jenkins, Textile dyes are potential hazards, *Journal of environmental health*, vol. 40, pp. 7-12, 1978.
- [6] J. G. Huddleston, H. D. Willauer, K. R. Boaz, R. D. Roger, Separation and recovery of food coloring dyes using aqueous biphasic extraction chromatographic resins, *Journal of Chromatography*, vol. 711, pp. 237-244, 1998.
- [7] N. Barka, A. Assabane, A. Nounah, Y. A. Ichou, Photocatalytic degradation of indigo carmine in aqueous solution by TiO₂-coated non-woven fibres, *Journal of Hazardous Materials*, vol. 152, pp. 1054-1059, 2008.
- [8] J. J. Berzas, J. R. Flores, M. J. V. Llerena, N. R. Farinas, Spectrophotometric resolution of ternary mixtures of Tartrazine, Patent Blue V and Indigo Carmine in commercial products, *Analytica Chimica Acta*, vol. 391, pp. 353-364, 1999.
- [9] H. L. Zheng, W. Q. Xiong, Y. K. Gong, D. J. Peng, L. C. Li, Catalytic spectrophotometric determination of trace aluminum with indigo carmine, *Spectrochimica Acta Part A*, vol. 66, pp. 1243-1247, 2007.
- [10] D. W. Boykin, A Convenient Apparatus for small-scale dyeing with indigo, *Journal of Chemical Education*, vol. 75, pp. 769-770, 1998.
- [11] N. Sriccia, M. C. Hawley, M. Misra, Characterization of natural fiber surfaces and natural fiber composites, *Composites Part A: Applied Science and Manufacturing*, vol. 39, pp. 1632-1637, 2008.
- [12] N. Meksi, M. Kechida, F. Mhenni, Cotton dyeing by indigo with borohydride process: Effect of some experimental conditions on indigo reduction and dyeing quality. *Chemical Engineering Journal*, vol. 131, pp. 187-193, 2007.
- [13] F. W. Sousa, S. A. Moreira, A. G. Oliveira, J. P. Ribeiro, M. F. Rosa, D. Keukelereire, R. F. Nascimento, Green coconut shells applied as adsorbent for removal of toxic metal ions using fixed-bed column technology, *Journal of Environmental Management*, vol. 91, pp. 1634-1640, 2010.
- [14] S. A. Umoren, M. M. Solomon, U. M. Eduok, I. B. Obot, A. U. Israel, Inhibition of mild steel corrosion in H₂SO₄ solution by coconut coir dust extract obtained from different solvent systems and synergistic effect of iodide ions: Ethanol and acetone extracts, *Journal of Environmental Chemical Engineering*, vol. 2(2), pp. 1048-1060, 2014.
- [15] R. O. Cristóvão, A. P. M. Tavares, A. I. Brígida, J. M. Loureiro, R. A. R. Boaventura, E. A. Macedo, M. A. Z. Coelho, Immobilization of commercial laccase onto green coconut fiber by adsorption and its application for reactive textile dyes degradation, *Journal of Molecular Catalysis B: Enzymatic*, vol. 72(1-2), pp. 6-12, 2011.
- [16] S. Shrestha, G. Son, S. H. Lee, T. G. Lee, Isotherm and thermodynamic studies of Zn (II) adsorption on lignite and coconut shell-based activated carbonfiber, *Chemosphere*, vol. 92(8), pp.1053-1061, 2013.
- [17] A. C. A. de Lima, R. F. Nascimento, F. F. de Sousa, J. M. Filho, A. C. Oliveira, Modified coconut shell fibers: A green and economical sorbent for removal of anions from aqueous solution, *Chemical Engineering Journal*, vol. 185-186, pp. 274-284, 2012.
- [18] O. A. Carrijo, R. S. Liz, N. Makishima, Fibra da casca do coco verde como substrato agrícola, *Horticultura Brasileira*, vol. 20, pp. 533-535, 2002.
- [19] S. Ouyang, S. Xu, N. Song, S. Jiao, Coconut shell-based carbon adsorbents for ventilation air methane enrichment, *Fuel*, vol. 113, pp. 420-425, 2013.
- [20] U. J. Etim, S. A. Umoren, U. M. Eduok, Coconut coir dust as a low cost adsorbent for the removal of cationic dye from aqueous solution, *Journal of Saudi Chemical Society*, In Press, Corrected Proof, Available online 12 October 2012.
- [21] Embrapa Agroindústria, <http://www.ceinfo.cnpat.embrapa.br>; accessed in November 2015.
- [22] G. H. Pino, L. M. S. de Mesquita, M. L. Torem, G. A. S. Pinto, Biosorption of cadmium by green coconut Shell powder. *Minerals Engineering*, vol. 19, pp. 380-387, 2006.
- [23] G. O. Santos and L. F. F. da Silva, Os significados do lixo para garis e catadores de Fortaleza (CE, Brasil). *Ciência & Saúde Coletiva*, vol. 16, pp. 3413-3419, 2011.
- [24] M. F. Rosa, F. C. Bezerra, D. Correia, F. J. S. Santos, F. A. P. Abreu, A. A. L. Furtado, Utilização da casca de coco como substrato agrícola, *Embrapa Agroindústria Tropical*, vol. 52, pp. 22-26, 2002.
- [25] I. A. Santana, E. P. Ribeiro, A. M. Iguti, Evaluation of green coconut (*Cocos nucifera* L.) pulp for use as milk, fat and emulsifier replacer in ice cream, *Procedia Food Science*, vol. 1, pp. 1447-1553, 2011.
- [26] V. K. Gupta, R. Jain, M. Shrivastava, Adsorptive removal of Cyanosine from wastewater using coconut husks, *Journal of Colloid and Interface Science*, vol. 347 (2), pp. 309-314, 2010.
- [27] S. A. A. Santana, A. P. Vieira, E. C. da Silva Filho, J. C. P. Melo, C. Airoidi, Immobilization of ethylenesulfide on babassu coconut epicarp and mesocarp for divalent cation sorption, *Journal of Hazardous Materials*, vol.174(1-3), pp. 714-719, 2010.
- [28] E. Gallego, F.J. Roca, J.F. Perales, X. Guardino, Experimental evaluation of VOC removal efficiency of a coconut shell activated carbon filter for indoor air quality enhancement, *Building and Environment*, vol. 67, pp. 14-25, 2013.
- [29] A. I. S. Brígida, V. M. A. Calado, L. R. B. Gonçalves, M. A. Z. Coelho, Effect of chemical treatments on properties of green coconut fiber, *Carbohydrate Polymers*, vol. 79, pp. 832-838, 2010.

- [30] M. J. John and S. Thomas, Biofibres and biocomposites, *Carbohydrate Polymers*, vol. 71, pp. 343-364, 2008.
- [31] M. G. Lomelí-Ramírez, S. G. Kestur, R. do Manríquez-González, S. Iwakiri, G. B. de Muniz, T. S. Flores-Sahagun, Bio-composites of cassava starch-green coconut fiber: Part II—Structure and properties, *Carbohydrate Polymers*, vol. 102, pp. 576-583, 2014.
- [32] S. Hemsri, K. Grieco, A. D. Asandei, R. S. Parnas, Wheat gluten composites reinforced with coconut fiber, *Composites Part A: Applied Science and Manufacturing*, vol. 43(7), pp. 1160-1168, 2012.
- [33] K. O. Chaves, C. R. L. Monteiro, C. R. Muniz, R. B. Gomes, H. L. B. Buarque, Adsorção de indigo carmin em biomassas mortas de *aspergillus niger*, *Engenharia Sanitária e Ambiental*, vol. 13, pp. 351-355, 2008.
- [34] N. H. Phan, S. Rio, C. Faur, L. L. Coq, P. L. Cloirec, T. H. Nguyen, Production of fibrous activated carbons from natural cellulose (jute, coconut) fibers for water treatment applications, *Carbon*, vol. 44(12), pp. 2569-2577, 2006.
- [35] M. V. Sureshkumar, C. Namasivayam, Adsorption behavior of Direct Red 12B and Rhodamine B from water onto surfactant-modified coconut coir pith, *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, vol. 317(1-3), pp. 277-283, 2008.
- [36] W. R. Melchert, B. F. Reis, F. R. P. Rocha, Green chemistry and the evolution of flow analysis. A review, *Anal. Chim. Acta*, vol. 714, pp. 8-19, 2012.
- [37] W. R. Melchert and F. R. P. Rocha, A green analytical procedure for flow-injection determination of nitrate in natural waters, *Talanta*, vol. 65, pp. 461-465, 2005.
- [38] M. Surma, W. Wiczowski, E. Cieřlik, H. Zieliński, Method development for the determination of PFOA and PFOS in honey based on the dispersive Solid Phase Extraction (d-SPE) with micro-UHPLC–MS/MS system, *Microchemical Journal*, vol. 121, pp. 150-156, 2015.
- [39] A. D. Batista, C. F. Nascimento, W. R. Merchert, F. R. P. Rocha, Expanding the separation capability of sequential injection chromatography: Determination of melamine in milk exploiting micellar medium and on-line sample preparation, *Microchemical Journal*, vol. 117, pp. 106-110, 2014.
- [40] W. R. Merchert, C. M. C. Infante, F. R. P. Rocha, Development and critical comparison of greener flow procedures for nitrite determination in natural waters, *Microchemical Journal*, vol. 85 (2), pp. 209-213, 2007.
- [41] B. S. Gentle, P. S. Ellis, M. R. Grace, I. D. McKelvie, Flow analysis methods for the direct ultra-violet spectrophotometric measurement of nitrate and total nitrogen in freshwaters, *Analytica Chimica Acta*, vol. 704(1-2), pp. 116-122, 2011.
- [42] L. H. G. Coelho, W. R. Merchert, F. R. Rocha, F. R. P. Rocha, I. G. R. Gutz, Versatile microanalytical system with porous polypropylene capillary membrane for calibration gas generation and trace gaseous pollutants sampling applied to the analysis of formaldehyde, formic acid, acetic acid and ammonia in outdoor air, *Talanta*, vol. 83(1), pp. 84-92, 2010.
- [43] G. C. S. de Souza, P. A. B. da Silva, D. M. da S. Leotério, A. P. S. Paim, A. F. Lavorante, A multicommuted flow system for fast screening/sequential spectrophotometric determination of dichromate, salicylic acid, hydrogen peroxide and starch in milk samples, *Food Control*, vol. 46, pp. 127-135, 2014.
- [44] S. Tontrong, S. Khonyoung, J. Jakmunee, Flow injection spectrophotometry using natural reagent from *Morinda citrifolia* root for determination of aluminium in tea, *Food Chemistry*, vol. 132 (1), pp. 624-629, 2012.
- [45] H. M. Al-Saidi, M. A. Abdel-Fadeel, A. Z. El-Sonbati, A. A. El-Bindary, Determination of bismuth in different samples by dispersive liquid–liquid microextraction coupled with microvolume β -correction spectrophotometry, *Journal of Molecular Liquids*, vol. 212, pp. 635-640, 2015.
- [46] L. F. Zeferino, I. Gaubeur, M. E. V. Suárez-Ilha, P. A. M. Freitas, Adsorption of 5,5'-disulfonicindigotin (5,5'-DI) onto green coconut fiber (*Cocos nucifera* L.): Kinetic and Isotherms, *Journal of Encapsulation and Adsorption Sciences*, vol. 4, pp. 37-52, 2014.
- [47] C. A. Leal, O. R. S. da Rocha, M. M. M. B. Duarte, M. da Motta, R. F. Dantas, N. M. L. Filho, V. L. da Silva, Evaluation of the adsorption process of remazol black b dye in liquid effluents by green coconut mesocarp, *Afinidad: Revista de química teórica y aplicada*, vol. 67, pp. 136-142, 2010.
- [48] F. R. P. Rocha and J. A. Nóbrega, Efeito Schlieren em sistemas de análise por injeção em fluxo, *Química Nova*, vol. 19, pp. 636-640, 1995.
- [49] C. Su, J. Bai, Measurement of the neutral plane of an internal fire whirl using the background-oriented Schlieren technique for a vertical shaft model of a high-rise building, *Measurement*, vol. 78, pp. 151-167, 2016.
- [50] S. S. M. P. Vidigal, A. O. S. S. Rangel, A reagentless flow injection system for the quantification of ethanol in beverages based on the Schlieren effect measurement, *Microchemical Journal*, vol. 121, pp. 107-111, 2015.
- [51] P. H. G. D. Diniz, K. D. T. de Melo, Y. N. M. F., A. de A. Gomes, E. C. L. do Nascimento, S. R. B. dos Santos, L. F. de Almeida, M. C. U. de Araújo, Flow injection photometric determination of NaCl, KCl and glucose in injectable drugs exploiting Schlieren signals, *Journal of Pharmaceutical and Biomedical Analysis*, vol. 62, pp. 172-176, 2012.
- [52] M. P. Rodríguez, H. R. P., Leonardo Pezza, Simple and clean determination of tetracyclines by flow injection analysis, *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, vol. 153, pp. 386-392, 2016.
- [53] P. Salazar, M. Martín, J. L. González-Mora, A. R. González-Elipse, Application of Prussian Blue electrodes for amperometric detection of free chlorine in water samples using Flow Injection Analysis, *Talanta*, vol. 146(1), pp. 410-416, 2016.
- [54] M. Kanamori-Kataoka, Y. Seto, Measurement of breakthrough volumes of volatile chemical warfare agents on a poly(2,6-diphenylphenylene oxide)-based adsorbent and application to thermal desorption–gas chromatography/mass spectrometric analysis, *Journal of Chromatography A*, vol. 1410, pp. 19-27, 2015.
- [55] M.F. El-Shahat, N. Burham, S. M. Abdel Azeem, Flow injection analysis–solid phase extraction (FIA-SPE) method for preconcentration and determination of trace amounts of penicillins using methylene blue grafted polyurethane foam, *Journal of Hazardous Materials*, vol. 177(1-3), pp. 1054-1060, 2010.