REMOVAL OF REACTIVE DYE USING RAW SUGARCANE BAGASSE

K.V. Veloo[1,*], F. Adam[2]

[1]Faculty of Agro Based Industry, Universiti Malaysia Kelantan, Jeli Kelantan, Malaysia

[2]School of Chemical Sciences, Universiti Sains Malaysia, Penang, Malaysia

[1]For correspondence; Tel. + (60) 099472171, E-mail: veni.v@umk.edu.my

ABSTRACT: *Agricultural waste, raw sugarcane bagasse was utilized as a low-cost biosorbent for the removal of Reactive Yellow 86 dye from aqueous solution. The effective adsorption parameters such as particles size, initial dye concentration, pH, contact time, biosorbent dosage, and effect of agitation were studied to determine the optimum condition for removal of Reactive Yellow 86 dye from aqueous solution. The optimum condition for removal of Reactive Yellow 86 was observed at initial dye concentration (10.0 mg/L) which was at acidic medium (pH 2.0), 10 minutes of agitation using sugarcane bagasse with particle size of (63-125 µm) and 10.0 mg/L dosage. Results showed that the removal percentage using raw sugarcane bagasse were 95.1%.*

Keywords: Raw sugarcane baggase, reactive dye, adsorption.

1. INTRODUCTION

Synthetic dye have been used widely in manufacturing process industries such as paints, textile, printing inks, pharmaceutical, food, cosmetics, plastics and paper for coloration. Reactive dyes are the largest class of dye used in textile industry due to their high photolytic stabilities, bright shade range and excellent fastness properties [1]. In general, they are azo-based chromophores with different reactive groups such as vinyl sulfone, chlorotriazine and trichloropyrimidine [2, 3].

Disposal dye wastewater which contains significant level of organic contaminants to the environment without efficient treatment has lethal effect on aquatic living and humans by imparting intensive color and toxicity of the dyes [4, 5]. The treatment of this wastewater is a great concern, since it is non-biodegradable, stable to oxidizing agent, water-soluble [6]. Furthermore, the dyes are difficult to be treated owing to their synthetic nature and complex molecular structure [7].

Techniques such as biological, physical, physico-chemical, chemical or combination of those approaches have been reported in literatures to treat coloured wastewater [8, 9]. However, most of these methods have drawbacks and limitations such as high operating cost, incomplete dye removal leading to coloured effluent, high requirement of energy, generation of by-products and sludge that may be more toxic than the starting materials [10, 11, 12]. Adsorption, however, has been found the most promising method to remove the dyes because of simple operation, cost-effectiveness, high efficiency and insensitivity to toxic pollutants and the availability of many adsorbents [13, 14].

In recent years, natural and siliceous materials, agricultural and industrial wastes have been studied extensively as potential alternative low cost adsorbents. A number of low cost materials have been reported for the adsorption of reactive dye such as coconut shell, fly ash, zeolite, silica beads and so on. Sugarcane bagasse can be available in a large quantity product produced by sugar manufacturing. The global sugarcane agricultural industry generated almost 24 million tons of bagasse on dry basis [15].

However, literature review reveals that so far not much effort has been made to study the removal of reactive dyes in particular Reactive Yellow 86 (RY86) in aqueous solution by using raw sugarcane bagasse. Therefore, the aim of this study is to investigate the optimum conditions for removal RY86 in aqueous solution using raw low-cost agricultural waste, sugarcane bagasse in a laboratory scale. A few effective parameters have been studied including particles size, initial dye concentration, pH of dye solution, contact time, dosage and agitation.

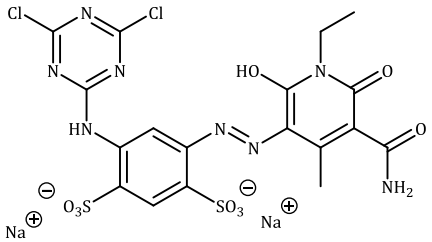

Fig.1: Chemical structure of Reactive Yellow 86 dye

2. EXPERIMENTAL DETAILES

2.1. Solutions and reagents

The textile dye, Reactive Yellow 86 (RY86; 61951-86-8; $C_{18}H_{14}Cl_2N_8Na_2O_9S_2$; 667.37 g/mol) was purchased from MP Biomedicals and used without further purification. The chemical structure of RY86 is given in Figure 1. Sodium hydroxide (NaOH) and hydrochloric acid (HCl) (25%, w/w) was purchased from Merck and Sigma Aldrich, respectively. Distilled water was used to prepare all the solution.

The working solutions of RY86 were prepared by diluting the dye stock solution with distilled water to the desired concentrations. Both stock and working solutions were freshly prepared each time prior to use. The pH adjustments of the solutions were made with aliquots of HCl/NaOH (0.1-0.01M). The pH of the solutions was measured using a Hanna HI 8424 set pH meter.

2.2. Sugarcane bagasse biosorbent preparation

Sugarcane bagasse (SCB) was collected from a local market in Jeli, Kelantan. It was washed with distilled water to remove ash components and sugars. Then it was cut to reduce the length and oven dried at 60°C for 24 hours. The dried SCB were ground and sieved through siever with aperture size of 63 µm, 125 µm, 150 µm, 250 µm, 300 µm, 425 µm and 500 µm. The particles size ranges of 63-125 µm, 125-150 µm, 150-250 µm, 250-300 µm, 300-425 µm, were collected and stored in an airtight glass container for further use.

2.3. Characterization of bagasse

The SCB biosorbent was characterized by FTIR using a Shimadzu FTIR, model 8300 (Kyoto, Japan) in the range of 4000–400 cm^{-1}. The sample was prepared as KBr pellet under high pressure.

SCB biosorbent before and after adsorption of RY86 were also analyzed by JEOL JMT 300 scanning electron microscopy (SEM) to study the morphological and surface characteristics.

2.4. Adsorption studies

Batch adsorption experiments were conducted in 250 mL conical flasks containing 100 mL aqueous solution with known RY86 concentration (5.0-60.0 mg/L) and the required amount of biosorbent (0.5-3.0 g). The pH of RY86 solutions was adjusted by HCl/NaOH (0.1-0.01M), ranged from 1.0 to 10.0. All the experiments were carried out at room temperature for 24 hours to ensure that adsorption equilibrium was attained. To separate liquid and solid phases, the mixtures were filtered.

The residual concentration of the dye remaining in the solution was determined using UV-Visible spectrophotometer Spectroquant® Pharo 300 at a maximum absorbance wavelength of 417 nm.

The experiment was carried out by varying the particles size, amount of biosorbent (0.5-3.0 g/L), initial concentration of RY86 solution (5.0-60.0 mg/L) and pH (1–10) at different time intervals. The effect of agitation was also studied.

The percentages of RY86 removal was calculated using the following equation:

$$\text{Dye removal } (\%) = \frac{C_0 - C_t}{C_0} \times 100 \qquad (1)$$

Where C_0 is dye initial concentration; and C_t, dye concentration at time t.

3. RESULTS AND DISCUSSION

3.1. Characterization of biosorbent

FTIR technique was used to examine the surface groups of raw SCB biosorbent and to identify the groups responsible for the RY86 adsorption. Figure 2 showed the broad bands at around 3338 cm^{-1} and 2897 cm^{-1} are assigned to OH groups and C-H stretching, respectively [16]. Meanwhile, the peak at 1731 cm^{-1} is assigned to the carboxylic group of bagasse [17]. Carboxylic groups are believed to play a very important role for dye adsorption [18]. The peaks at 1604 cm^{-1} and 1514 cm^{-1} are due to aromatic skeletal vibration of lignin [19, 20]. The intense peak at 1033 cm^{-1} is associated with the C-O bond stretching of cellulose.

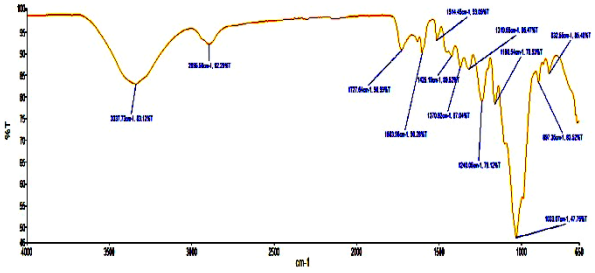

Fig. 2: FTIR spectrum of raw sugarcane

The morphology of raw sugarcane bagasse before and after adsorption was observed using scanning electron microscopy (SEM) technique. Based on SEM image obtained, a number of pores can be observed clearly on the surface of raw SCB before adsorption (Fig. 3a) and have been occupied by RY86 after adsorption (Fig. 3b) occurred. This shows that the raw sugarcane bagasses are capable to be utilised as biosorbent.

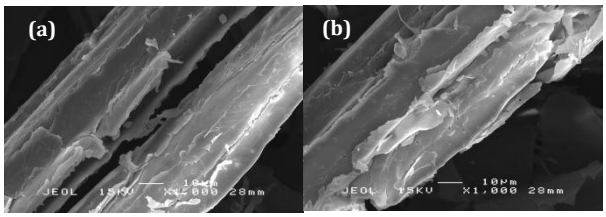

Fig. 3: SEM migrographs of SCB (a) before and (b) after adsorption of RY86 at 1000 magnification.

3.2. Effect of particles size

The effect of particle size of SCB biosorbent on the adsorption was studied at 27°C with 40.0 mg/L of dye solution (pH5) and 0.5 g/L biosorbent. According to Fig. 4, the removal of RY86 using small particles sizes of SCB biosorbent (63-125 µm) was higher than larger particles sizes of SCB biosorbent (125-150 µm, 150-250 µm, 250-300 µm, 300-425 µm, 425-500 µm. This is due to the fact that lower particles size would yield higher surface area and therefore lead to high dye removal percentage [21, 22]. Therefore, the SCB biosorbent with particles sizes in the range of 63 to 125 µm were selected as optimized parameter and used for further experiments.

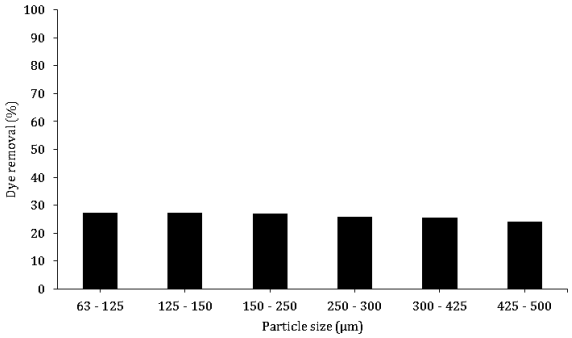

Fig. 4: Effect of particles size on RY86 adsorption

3.3. Effect of initial dye concentration

The effect of initial dye concentration on equilibrium was observed by mixing 0.5 g/L of SCB biosorbent with 100 mL of dye solutions (pH 5) of varying initial concentrations (5.0-60.0 mg/L) at 27°C. Figure 5 showed that the RY86 dye removal increased to 25.3% at 10.0 mg/L of RY86 dye before slightly decreased at 20.0 mg/L of dye solution. However, the increasing initial dye concentration over 20.0 mg/L had no significant effect on RY86 dye removal.

This is due to the when the concentration of initial dye concentration increases, the higher mass transfer driving force will occur, resulting to higher adsorption of RY86 dye. The initial dye concentration provides an important driving force to overcome all mass transfer resistances of the RY86

dye between the aqueous solution of RY86 dye and solid phase of the biosorbent [23].

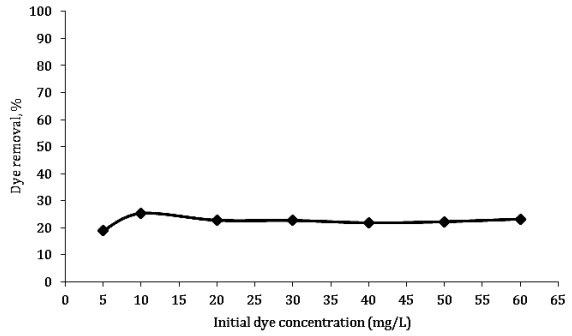

Fig. 5: Effect of initial dye concentration on RY86

3.4. Effect of pH solution

pH is an important factor for biosorption processes, as it affects both the chemical properties of dyes and the active sites on the biosorbent surface. The effect of pH on dye adsorption was investigated at 27°C with 10.0 mg/L dye solution and 0.5 g/L biosorbent, pH ranged from 1.0-10.0. Figure 6 showed that a considerable difference was observed for the effect of pH solution on the dye using the biosorbent. The percentage of RY86 removal increased from 72.3% (pH 1) to 83.9% (pH 2) before decreasing markedly to 35.0% (pH 4.0), and kept decreasing gradually to 22.5% (pH 10.0). SCB is a lignocellulose material which contain mainly carboxyl and hydroxyl group, and its surface charge will have some dependence on the solution properties [24]. The anionic RY86 dye has two sulfonate groups which present negative charges even in highly acidic solutions due to their pKa values lower than zero [25].

Therefore, the increasing dye removal at low pH is because of the electrostatic attraction force between the positively charged biosorbent and negatively charged RY86 ions increased, as the pH increased from 1.0 to 2.0. (i.e. Dye-SO_3Na → Dye-SO_3^- + Na^+). When the pH value further increased, the number of negatively charged active sites on the biosorbent increased as well, which lead to an electrostatic repulsion between the biosorbent and anionic dyes [26]. Therefore, pH 2.0 was selected as optimised pH.

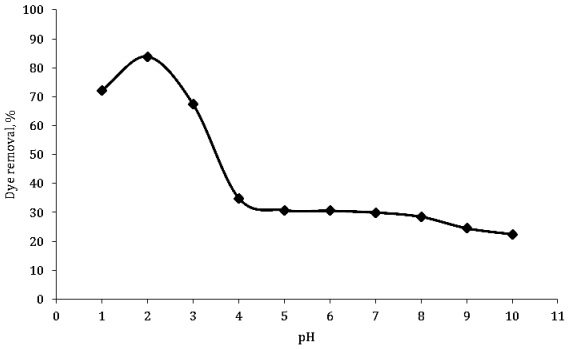

Fig. 6: Effect of solution pH on RY86 adsorption

3.5. Effect of contact time

Figure 7 shows the effect of contact time towards dye removal percentage (%). It showed that RY86 dye was removed rapidly within the first 4 hours and slightly increased at 8 hours up to 83.1%. After 8 hours, the trend became nearly constant.

A rapid increase at the beginning of adsorption occured because of the presence of large number of unoccupied active sites for adsorption of RY 86 dye and after the constant trend after 8 hours is due to saturation of absorption sites on biosorbent. Therefore, there is no significant change in dye removal efficiency [5]. As a result, 8 hours selected as a optimum contact time.

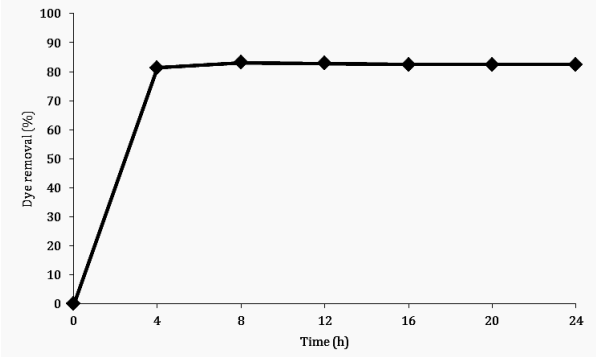

Fig. 7: Effect of contact time on RY86 adsorption

3.6. Effect of biosorbent dosage

The study of biosorbent dosage of SCB for removal of the RY86 from aqueous solution was carried out at different biosorbent dosages (0.5-3.0 g /L) using a 10.0 mg/L of dye solution (pH 2.0). According to Fig. 8, the increasing of biosorbent dosage from 0.5 g/L to 1.5 g/L significantly increased the RY86 dye removal from 87.2% to 92.9%. However, a further increase in biosorbent dosage over 1.5 g/L, RY86 removal remained almost constant.

The increased in dye removal is because of more biosorption active site available to interact with the dye molecules as the biosorbent dosage increased [27]. In contrast, the low dye removal was observed when dosage over 1.5 g/L was used might due to the saturation of adsorption sites and hence cannot further adsorb the dye molecules. Therefore, biosorbent dosage 1.5 g/L was selected as optimum dosage.

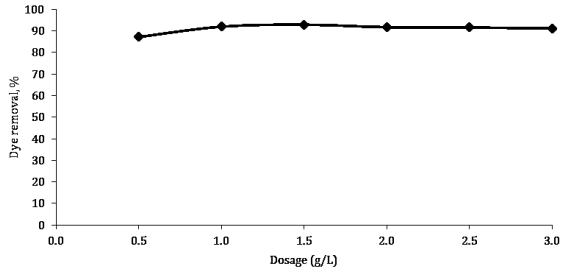

Fig. 8: Effect of biosorbent dosage on RY86

3.7. Effect of agitation

The effect of agitation on RY86 dye removal was observed by stirring the mixture of 1.5 g/L of SCB biosorbent in 100 mL of 10.0 mg/L of dye solution (pH 2.0) on a rotary orbital shaker at 120 rpm.

Fig. 9 showed that a rapid initial adsorption (90.5%) was observed at 1 minute and increased gradually until reached the equilibrium at 10 minute (95.0%). It was cleared that increasing time over 10 min had no significant effect on RY86 adsorption. This observation can be explained by the saturation of absorption sites on biosorbent [5]. According to Fig. 7, the equilibrium of RY86 adsorption reached at 8 hours. However, the equilibrium can be achieved at 10 minutes when the agitation was applied to the adsorption system. In this case, the adsorption efficiency increased due to increasing kinetic energy between RY86 molecules and the biosorbents particles [28].

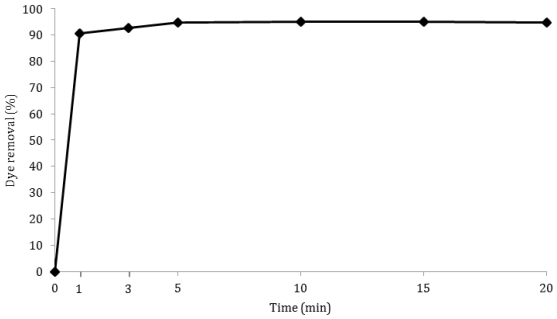

Fig. 9: Effect of agitation on RY86 adsorption

4. CONCLUSIONS

Raw sugarcane bagasse was successfully used as biosorbent for removal of RY86 dye. The experiment was carried out by varying the particles size, amount of biosorbent (0.5-3.0 g/L), initial concentration of RY86 solution (5.0-60.0 mg/L) and pH (1–10) at different time intervals. The effect of agitation was also studied. The optimum condition for removal of Reactive Yellow 86 was observed at initial dye concentration (10.0 mg/L) was at acidic medium (pH 2.0), with 10 minutes of agitation using sugarcane bagasse with particle size (63-125 μm) and 10.0 mg/L dosage. Results showed that the removal percentage using raw sugarcane bagasse were 95.1%.

ACKNOWLEDGMENT

KV Veloo would like to express gratitude to RAGS funding.

5. REFERENCES

1.K. Murugesan, A. Dhamija, I. H. Nam, Y. M. Kim, and Y. S. Chang., "Decolourization of reactive black 5 by laccase: Optimization by response surface methodology," *Dyes and Pigments*, **vol. 75**: 176-184 (2007).

2.K. Vijayaraghavan, and Y. S Yun., "Biosorption of C.I. Reactive Black 5 from aqueous solution using acid-treated biomass of brown seaweed Laminaria sp," *Dyes and Pigments*, **vol. 76**: 726-732 (2008).

3.M. Greluk, and Z. Hubicki., "Kinetics, isotherm and thermodynamic studies of Reactive Black 5 removal by acid acrylic resins," *Chemical Engineering Journal*, **vol. 162**: 919-926 (2010).

4.H. Katsumata, S. Koike, S. Kaneco, T. Suzuki, and K. Ohta., "Degradation of Reactive Yellow 86 with photo-Fenton process driven by solar light," *J. of Env. Sci*, **vol. 22**: 1455-1461 (2010).

5.O. Duman, S. Tunç, B. Bozoğlan, K. and T. G. Polat., "Removal of triphenylmethane and reactive azo dyes from aqueous solution by magneticcarbon nanotube-κ-carrageenan-Fe nanocomposite," *J. of Alloys & Compounds*, **vol. 687**: 370-383 (2016).

6.P. D. Saha, S. Chakraborty, and S. Chowdhury., " Batch and continuous (fixed-bed column) biosorption of crystal violet by Artocarpus heterophyllus (jackfruit) leaf powder," *Col. and Surfaces B: Bioint*, **vol. 92**: 262-270 (2012).

7.Y. S. Ho, T. H. Chiang, and Y. M. Hsueh., "Removal of basic dye from aqueous solution using tree fern as a biosorbent," *Process Biochemistry*, **vol. 40**: 119-124 (2005).

8.D. Suteu, G. Biliuta, L. Rusu, S. Coseri, and G. Nacu., "Cellulose cellets as new type of adsorbent for the removal of dyes from aqueous media," *Env. Eng. and Management. J*, **vol. 14**: 525-532 (2015).

9.A. Yadav, S. Mukherji, and A. Garg., "Removal of chemical oxygen demand and color from simulated textile wastewater using a combination of chemical/physicochemical processes," *Industrial and Eng. Chem. Research*, **vol. 52**: 10063-10071 (2013).

10.C. A. Basar, A. Karagunduz, A. Cakici and B. Keskinler., "Removal of surfactants by powdered activated carbon and microfiltration," *Water Research*, **vol. 38**: 2117-2124 (2004).

11.A. Bogner, P. H. Jouneau, G. Thollet, D. Basset, & C. Gauthier, "A history of scanning electron microscopy developments: Towards "wet-STEM" imaging," *Micron*, **vol. 38**: 390-401 (2007).

12.N. Nishiyama, T. Zheng, Y. Yamane, Y. Egashira, and K. Ueyama., "Microporous carbons prepared from cationic surfactant-resorcinol/ formaldehyde composites," *Carbon*, **vol. 43**: 269-274 (2005).

13.O. Duman, S. Tunç, and T. G. Polat., "Determination of adsorptive properties of expanded vermiculite for the removal of C. I. Basic Red 9 from aqueous solution: Kinetic, isotherm and thermodynamic studies," *Applied Clay Science*, **vol. 109-110**: 22-32 (2015).

14.M. Arami, N. Y. Limaee, and N. M. Mahmoodi., "Investigation on the adsorption capability of egg shell membrane towards model textile dyes," *Chemosphere*, **vol. 65**: 1999-2008 (2006).

15.W.A. Pippo, and C. A. Luengo, C. A., "Sugarcane energy use: Accounting of feedstock energy considering current agro-industrial trends and their feasibility," *Inter. J. of Energy and Env. Eng*, **vol. 4**: 1-13 (2013).

16.R. Kumar, G. Mago, V. Balan, and C. E. Wyman., "Physical and chemical characterizations of corn stover and poplar solids resulting from leading pretreatment technologies," *Biorec. Tech*, **vol. 100**: 3948-3962 (2009).

17.Y. Xing, D. Liu, and L. P. Zhang., "Enhanced adsorption of Methylene Blue by EDTAD-modified sugarcane bagasse and photocatalytic regeneration of the adsorbent," *Desalination*, **vol. 259**: 187-191 (2010).

18.A. Srinivasan, A. and T. Viraraghavan., "Decolorization of dye wastewaters by biosorbents," *A review. J. of Env. Management*, **vol. 91**: 1915-1929 (2010).

19.X. Zhao, F. Peng, K. Cheng, and D. Liu., "Enhancement of the enzymatic digestibility of sugarcane bagasse by alkali-peracetic acid pretreatment," *Enz. and Microb. Tec*h, **vol. 44**: 17-23 (2009).

20.Y. Liu., "Is the free energy change of adsorption correctly calculated?" *J. of Chem. and Eng. Data,* **vol. 54**: 1981-1985 (2009).

21.S. Kara, C. Aydiner, E. Demirbas, M. Kobya, and N. Dizge., "Modeling the effects of adsorbent dose and particles size on the adsorption of reactive textile dyes by fly ash," *Desalination*, **vol. 212**: 282-293 (2007).

22.L. D. T.Prola, E. Acayanka, E. C. Lima, C. S. Umpierres, J. C. P. Vaghetti, W.O. Santos, S. Laminsi, and P. T. Djifon., "Comparison of Jatropha curcas shells in natural form and treated by non-thermal plasma as biosorbents for removal of Reactive Red 120 textile dye from aqueous solution," *Ind. Crops and Products*, **vol. 46**: 328-340 (2013).

23.B. H. Hameed, D. K. Mahmoud, and A. L. Ahmad., "Equilibrium modeling and kinetic studies on the adsorption of basic dye by a low-cost adsorbent: Coconut (Cocos nucifera) bunch waste," *J. of Hazardous Materials*, **vol. 158**: 65-72 (2008).

24.M. X. Wang, Q. L. Zhang, and S. J. Yao., "A novel biosorbent formed of marine-derived Penicillium janthinellum mycelial pellets for removing dyes from dye-containing wastewater," *Chem. Eng. J,* **vol. 259**: 837-844 (2015).

25.E. C. Lima, B. Royer, J. C. P. Vaghetti, N. M. Simon, B.M Da Cunha, F.A. Pavan, E. V. R. Benvenutti, Cataluña-Veses, and C. Airoldi., "Application of Brazilian pine-fruit shell as a biosorbent to removal of reactive red 194 textile dye from aqueous solution. Kinetics and equilibrium study," *J. of Hazar. Mater,* **vol. 155**: 536-550 (2008 b).

26.C. Namasivayam, and D. Kavitha., "Removal of Congo Red from water by adsorption onto activated carbon prepared from coir pith, an agricultural solid waste," *Dyes and Pigments*, **vol. 54:** 47-58 (2002).

27.E. C. Lima, B. Royer, J. C. P. Vaghetti, N. M. Simon, B.M Da Cunha, F.A. Pavan, E. V. R. Benvenutti, Cataluña-Veses, and C. Airoldi., "Application of Brazilian pine-fruit shell as a biosorbent to removal of reactive red 194 textile dye from aqueous solution: Kinetics and equilibrium study," *J. of Hazard. Mater,* **vol. 155**: 536-550 (2008 a).

28.B. A. Fil, K. Z. Karcioglu, R. Boncukcuoglu, and A. E. Yilmaz., "Removal of cationic dye (basic red 18) from aqueous solution using natural Turkish clay," *Global Nest Journal,* **vol. 15**: 529-541(2013).