

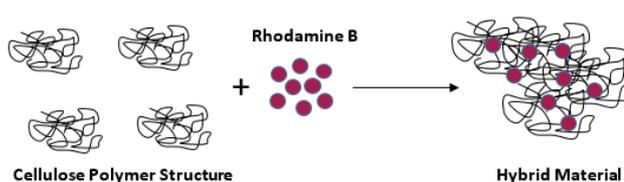
## INVESTIGATION OF A HYBRID MATERIAL AND PHOTOPHYSICAL PROPERTIES OF RHODAMINE B IN AQUEOUS SUSPENSIONS OF CELLULOSIC PARTICLES\*\*

Mehmet KAYA\*

Recep Tayyip Erdoğan University, Science&Arts Faculty, Department of Chemistry, 53100 Rize/TURKEY

Received February 2, 2018

In this work, it was focused on the photophysical properties of Rhodamine B (Rh-B) dye compound in the rice husk (sawdust) suspensions (RHS), as well as the characterization of the hybrid material from Rh-B and rice husk (RH). It was revealed that the type of molecular assembly of Rh-B in RHS was H-aggregation. As regards the results of Fourier transformed infrared (FT-IR) spectroscopic characterization, it can be explained that Rh-B dye molecule adsorbed (or penetrated) on the surface of RH particles via H-bonding alongside electrostatic interactions. It was also demonstrated that the particle size of hybrid materials in a colloidal dispersion was about 250 nm, which is a feasible value for ink applications.



### INTRODUCTION

Most recently, researchers have focused on the interaction between some particles *e.g.* sawdust, clay, polymer, polyelectrolyte<sup>1-4</sup> and dyes for producing novel hybrid materials and detailed understanding of the aggregation ion properties of the dye compounds *e.g.* crystal violet, C.I. Basic Blue 41, thiocyanine and brilliant green, in aqueous suspensions.<sup>5-10</sup> Because of the penetration of dye molecules on the surface of any particle in a suspension, spectral shifts called H- or J- aggregation (molecular self-assembly) in their absorption spectra can be observed.<sup>11</sup> Generally, the aggregation behaviour of dye molecules takes place in the highly concentrated dye aqueous solution. On the contrary, in case of presence of some additives such as sawdust particles, colloidal nanoparticles, clays and polymers, the aggregation and spectral shifts can be observed in the diluted dye solutions.<sup>12</sup>

Some synthetic dyes like Rhodamine B (Rh-B) are well-known for coloring various polymers and plastics and improving the surface properties of some materials.<sup>13</sup> Moreover, Rhodamine-based compounds are used intensely as an adjusting wavelength of electromagnetic radiation in dye lasers due to its perfect photophysical properties, such as high fluorescence quantum yield, long absorption and emission wavelengths extended to visible region and fluorescent labelling reagent<sup>14-16</sup>. Therefore, the last studies have shown that there are a lot of attention in the development of photophysical properties of some types of dyes in different media like suspensions<sup>12,17-20</sup> and solutions.<sup>21-23</sup> Such compounds also offer many advantages like photosensitivity and colour strength<sup>24,25</sup> because of their usage in a variety of applications such as coating, plastics production, printing inks, etc. Considering these advances, numerous materials such as sawdust,<sup>26</sup> clay<sup>25</sup> and polymer<sup>27</sup> have been used to prepare “green” hybrid composites. Rice husk, a low cost and eco-friendly

\* Corresponding author: mehmet.kaya@erdogan.edu.tr

\*\* Supplementary information on <http://web.icf.ro/rrch> or <http://revroum.lev.ro>

sawdust material, is one of the most significant agricultural wastes and is approximately produced in millions of tones per year as a waste.<sup>26</sup> A sawdust/dye hybrid composite can be obtained by treatment of rice husk sawdust with Rh-B. As a result of penetration of dye species into the sawdust particles, the hybrid structure can be formed via H-bonding<sup>28</sup> or electrostatic interaction.<sup>29</sup> In this study, adsorption technique was used as a method for production of rice husk-Rh-B as hybrid pigment composite, we studied preparation, and characterization of a hybrid pigment composite composed of Rhodamine B (Rh-B) dye and rice husk—a low cost material, abundant and gained from Turkey rice plants. Besides, the aggregation behavior of Rh-B in the rice husk (sawdust) aqueous suspensions was investigated. The interaction of Rh-B with the sawdust particles in the aqueous suspensions was investigated by spectroscopic techniques. It was found that the sawdust particles triggered the dye aggregation of Rh-B. In the present work, various techniques such as SEM (scanning electron microscopy), FT-IR (Fourier transformed infrared spectroscopy), Ultraviolet-Visible (UV-VIS) spectrophotometry, steady-state fluorescence spectrofluorophotometry, thermal analysis and particle size analysis of dispersed hybrid materials were used.

## EXPERIMENTAL

### Materials

Rh-B dye purchased from Fluka Company was used without further purification and its chemical formula was presented in Supplementary Fig. S1. Rice husk (RH) is a by-product obtained from rice plant in Turkey. The obtained rice husk was ground to the finest form as preliminary step.

### Preparation of Rice Husk Samples

10.0 g of raw RH sample was washed with deionized water several times to remove the soluble impurities prior to the application of the adsorption procedure, centrifuged, filtered and then dried at 80°C for 12 h. After dried, the RH

product was grained and sieved to 38-106  $\mu\text{m}$  and <400  $\mu\text{m}$  for preparation of hybrid composite and dye suspensions, respectively. The elemental and proximate analysis results of rice husk were given in Table 1.

### Preparation of Rh-B/Rice Husk Hybrid Composite

The hybrid dye composite was prepared by adding 0.5 g rice husk to 10.0 mL of aqueous solution containing concentrated (0.5 g/L) Rh-B. The resulted suspension was placed into plastic tube and then stirred robustly for 60 min (the sorption equilibrium time) at 25°C in a thermostatic shaker. Afterwards, the suspension was centrifuged at 6000 rpm, decanted, filtered and then dried at 80°C for 24 h. Photographs of hybrid (RH/Rh-B) and raw RH materials were shown in Supplementary Fig. S2.

### Preparation of dye/rice husk suspensions

50.0 mg Powdered RH with a particle size of <400  $\mu\text{m}$  was suspended in 10.0 mL of deionized water in order to prepare a suspension and stirred for 24 h. The solvent of a certain volume of Rh-B from stock solution ( $1.0 \times 10^{-3}$  M in ethanol) added to plastic tubes was evaporated with nitrogen gas purging until removal of solvent was completely evaporated by purging nitrogen gas and then 5.0 mL Rice Husk suspension was added into the tubes. The final concentrations of Rh-B in the aqueous suspensions were adjusted as  $1.0 \times 10^{-6}$ ,  $2.5 \times 10^{-6}$ ,  $5.0 \times 10^{-6}$ ,  $1.0 \times 10^{-5}$ ,  $2.5 \times 10^{-5}$  and  $5.0 \times 10^{-5}$  mol.L<sup>-1</sup>. While deviations from Lambert-Beer law at higher concentrations of Rh-B ( $> 5.0 \times 10^{-5}$  M) were observed, consistent data could not be obtained at lower concentrations ( $< 1.0 \times 10^{-6}$  M).

### Instrumental Characterization

Perkin-Elmer (Model Lambda 35) spectrophotometer was used to record the absorption spectra of the samples. Steady-state fluorescence spectra were measured using Agilent Cary Eclipse G9800A Spectrofluorophotometer. FTIR spectra were recorded in the region of 4000-650 cm<sup>-1</sup> on a Spectrum-100 FTIR spectrometer at a resolution of 4 cm<sup>-1</sup>. The thermogravimetric analyses were performed by a SII A6 6300 TG instrument in an air atmosphere (heating rate: 10°C min<sup>-1</sup>, platinum crucibles, mass~10 mg and temperature range: 20-1000°C). Elemental Analysis was performed using Leco Truspec Micro elemental analyzer. SEM analysis was carried out using JEOL JSM 6610 instrument equipped with EDS analyzer. Particle size of the obtained dye/sawdust (Rh-B/RH) nanocomposite in the suspensions was measured by Malvern Zetasizer Nano ZSP particle size analyzer.

Table 1

Elemental and Proximate Analysis of Rice Husk Sawdust

Elemental Analysis		Proximate Analysis	
Component	Weight (%)	Component	Weight (%)
C	55.45	Moisture	5.70
O	36.24		
N	0.71	Ash	13.82
S	0.19		
H	7.41	Combustibles	80.48

## RESULTS AND DISCUSSION

### Photophysical Properties of Rh-B in Rice Husk Suspensions

It is significant for material chemistry that photophysical behaviors of dye compounds are handily tuned by some additives materials such as sawdust, clay, etc.<sup>12</sup> In this study, the spectral changes and aggregation behaviour of the Rh-B molecule in RH (sawdust) aqueous suspensions were examined compared with those in deionized water. As it is seen in Fig. 1a), it appears that the

wavelength maxima of the absorption (at 552 nm) and fluorescence emission (at 575 nm) spectra are close to each other. The fluorescent dyes like Rh-B with high quantum yield and small Stokes shift can emit the energy of the absorbed radiation without much loss.<sup>30</sup> Besides, it is clear in fig. 1b that Rh-B ( $1.0 \times 10^{-6}$  M) in RH suspension is aggregated and the absorption band maximum (547 nm) shifts to blue called as “hypsochromic shift” or “H-aggregation”.<sup>31,32</sup> It can be deduced that Rh-B molecule is aggregated at even the most diluted concentration in the RH aqueous suspension.

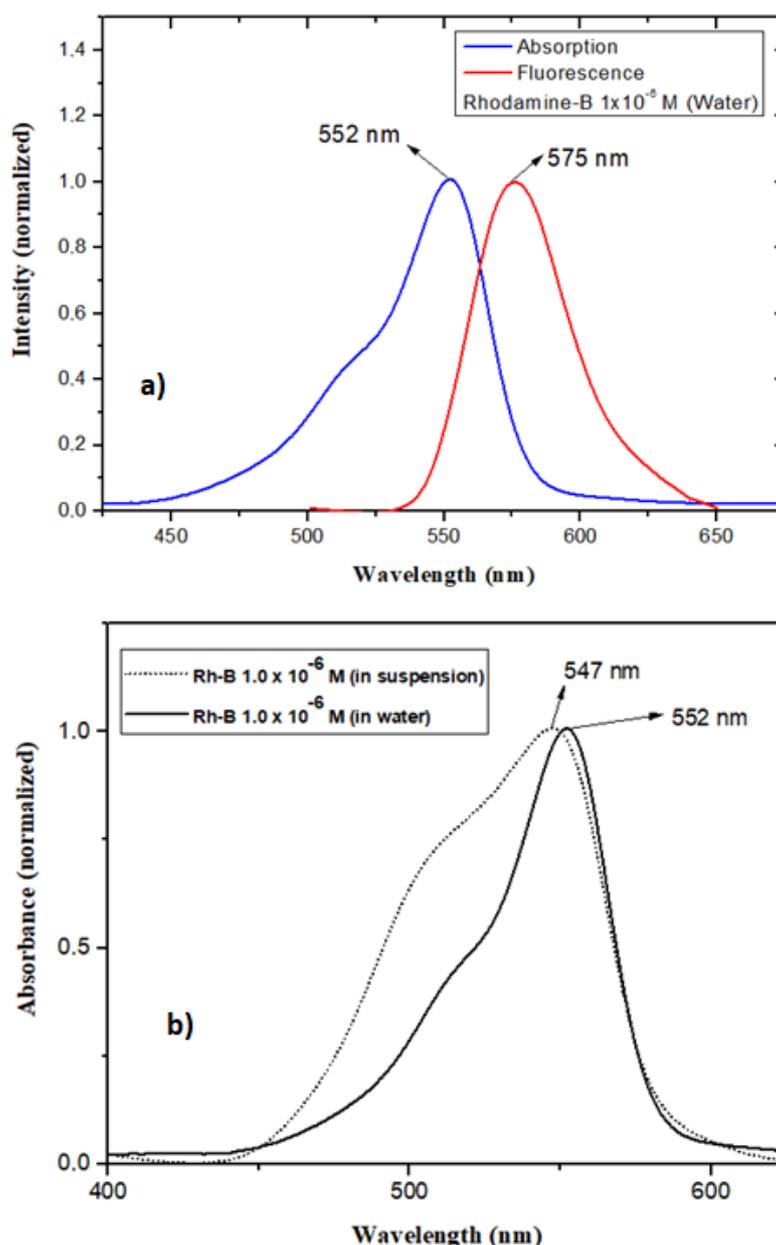


Fig. 1 – (a) The absorption and emission spectra of Rh-B in water and (b) the absorption spectra of Rh-B recorded in aqueous solution and rice husk suspension.

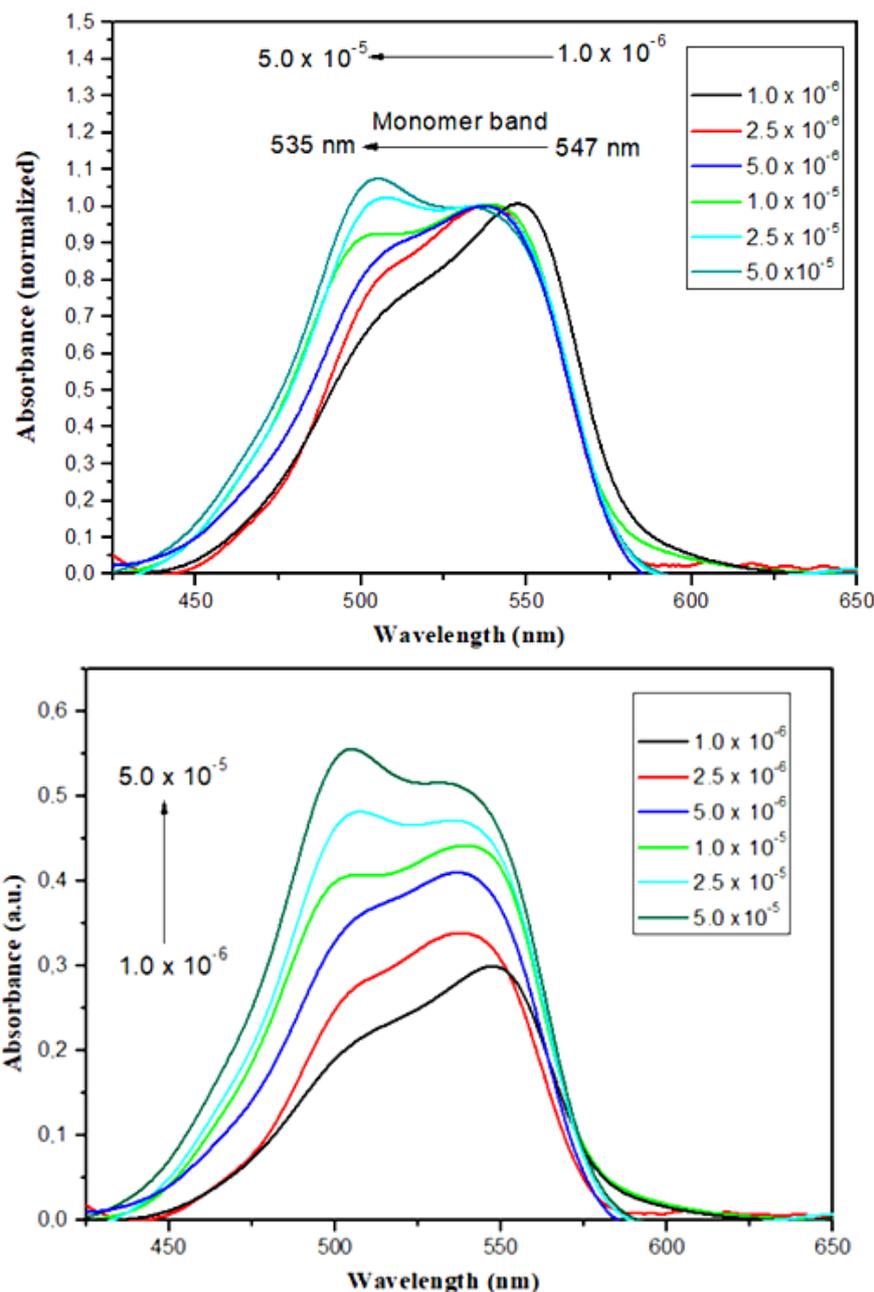


Fig. 2 – (a) The concentration-dependence of absorption spectra of Rh-B in aqueous rice husk suspension and (b) the same spectra normalized at the monomer band.

The concentration-dependent absorption spectra obtained in the concentration range of  $1.0 \times 10^{-6}$  M to  $5.0 \times 10^{-5}$  M were exhibited in fig. 2a and b. The absorption spectrum of Rh-B with two peaks located at 507 nm (H-aggregate band) and 547 nm (Monomer band) at the lowest concentration ( $1.0 \times 10^{-6}$  M) was revealed in Fig. 2a. On the other hand, it was seen in Fig. 2b that the band intensity and tendency of H-aggregation gradually increased and the absorption spectra continued shifting to blue (to lower wavelength-535 nm-monomer band), when Rh-B concentration ascended up to

$5.0 \times 10^{-5}$  M. It can be attributed that the interaction between Rh-B and RH is probably intermolecular H-bonding because RH, a sawdust, is mainly composed of cellulose derivatives (cellulose, hemicellulose) and lignin.<sup>28, 33-37</sup> This phenomenon induces the high aggregation tendency of Rh-B in the rice husk aqueous suspensions, with high concentration of Rh-B localized via H-bonding on the surface of rice husk particles. This interaction between cellulose and Rh-B molecule was depicted in Supplementary Fig. S3.

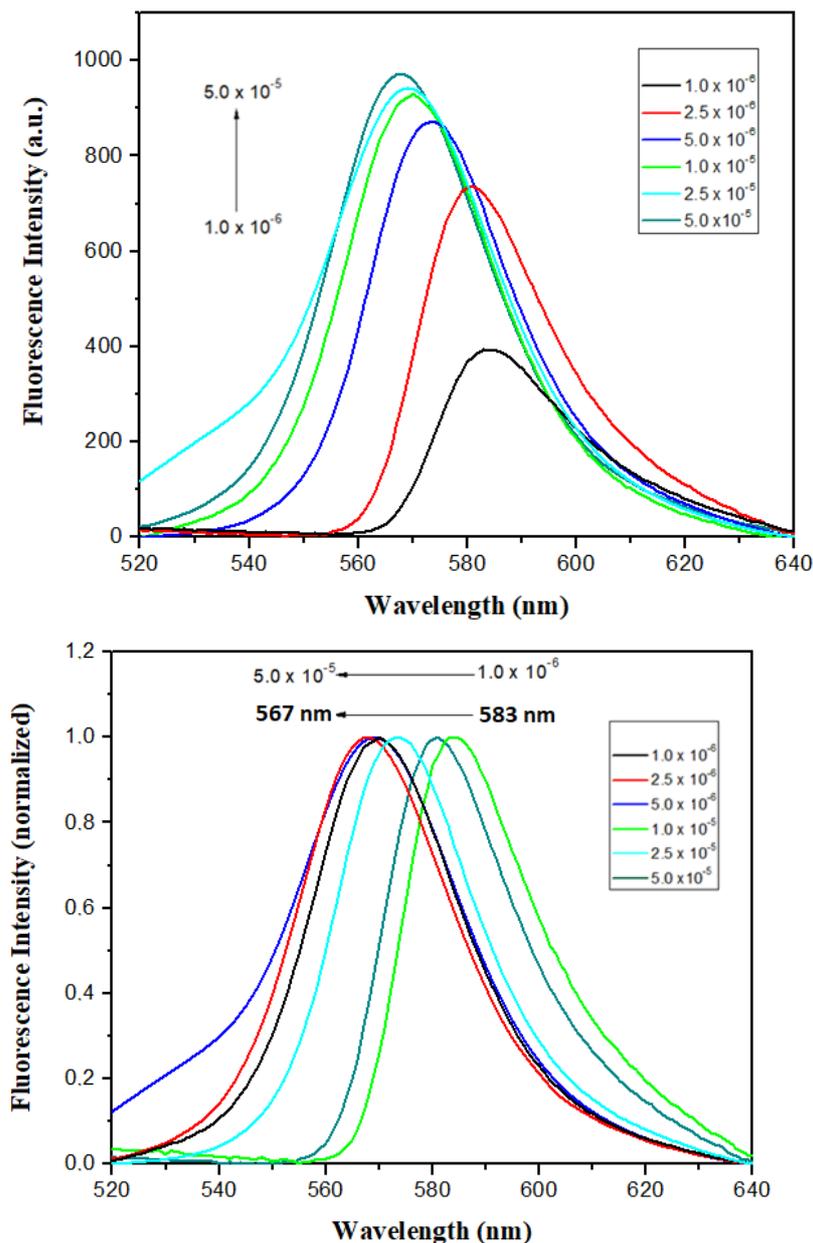


Fig. 3 – (a) The concentration-dependence of fluorescence spectra of Rh-B in aqueous rice husk suspension and (b) the same spectra normalized to unity.

It is known that H-aggregates are non-fluorescent and decrease the fluorescent intensity of dye molecules.<sup>38</sup> Hereby, it can be taken into consideration that the RH particles have a fluorescence quenching effect and a comprehensive understanding of this effect is important with regard to fluorescence applications for dye compounds. In order to determine fluorescence behavior of Rh-B in the RH suspensions, the fluorescence spectra were recorded with the excitation wavelength of 500 nm (Fig. 3a and b). From Fig. 3a and b, it is apparent that an increase in the fluorescence intensity with concentration rise of Rh-B in the suspensions and a hypsochro-

mic shift (567 nm←583 nm) were observed. However, the rate of increase in the fluorescence intensity slowed down at higher concentrations owing to the predominance of non-fluorescent H-aggregate species in comparison with the fluorescent monomer.

### Characterization of Hybrid Material

#### SEM Analysis

The SEM photographs of hybrid materials (RH/Rh-B) and raw (RH) were given in fig. 4a and b, respectively. It is clearly seen in fig. 4a and b

that while the hybrid materials had a larger particle size, the raw materials were much smaller in particle size. This is because the dye molecules penetrated into the cellulose structure in RH by H-bonding. Considering fig. 4a and b, it is also observed that both samples are rough and irregular in shape (fibrous and particles). A schematic demonstration of hybrid material formation of RH and Rh-B is given in Supplementary Fig. S4.

#### *FT-IR Analysis*

In order to analyze functional groups presented on the structure and type of interaction between

studied species, FT-IR spectroscopic method was used in this work. As seen from fig.5a and b, the peaks located at  $3326\text{ cm}^{-1}$  and  $3332\text{ cm}^{-1}$  (broad bands) assigned to the OH groups and the peaks at  $2892\text{ cm}^{-1}$  and  $2908\text{ cm}^{-1}$  ascribed to C-H stretching vibrations were observed, respectively. Based on that, it was appear that the intensity of OH band for hybrid material dramatically decreased by comparison with raw material. Thereby, it can be stated this circumstance supports the possibility of interaction via H-bonding.

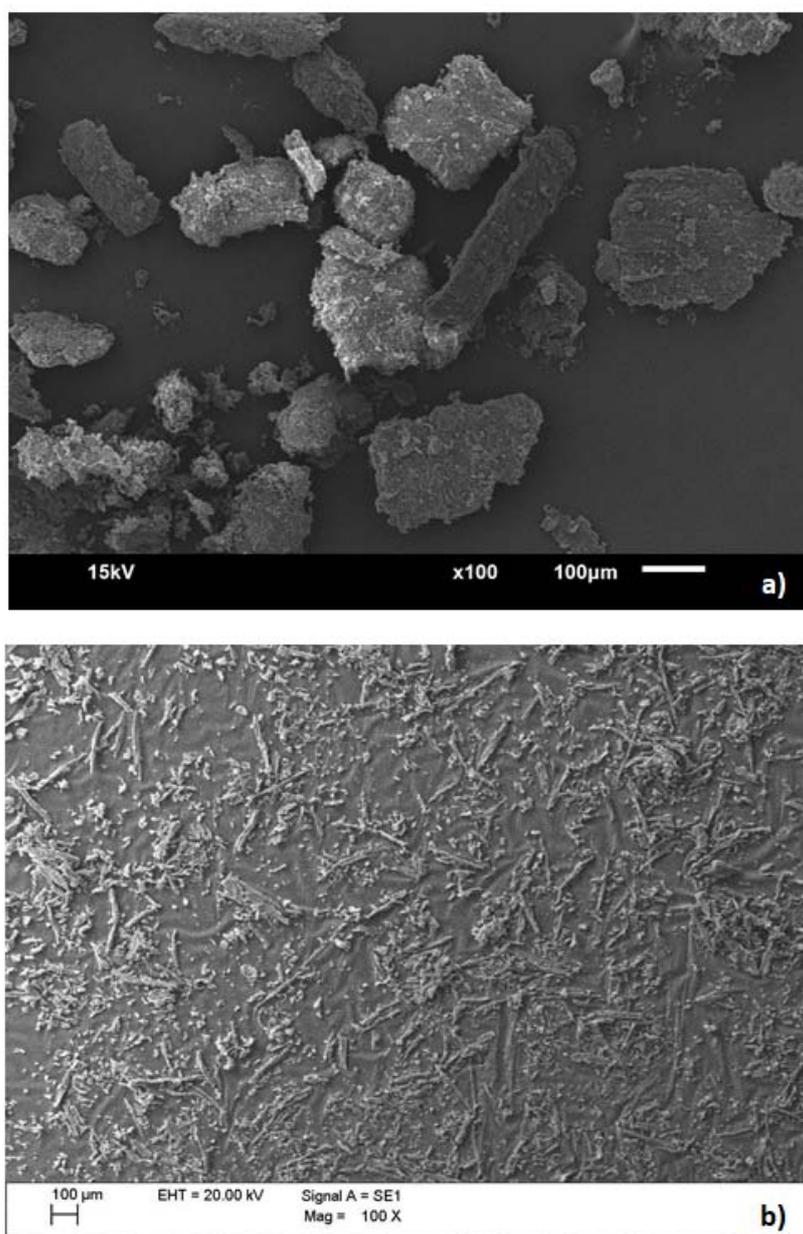


Fig. 4 – (a) SEM images of Hybrid (Rh-B/RH) and (b) Raw RH Materials .

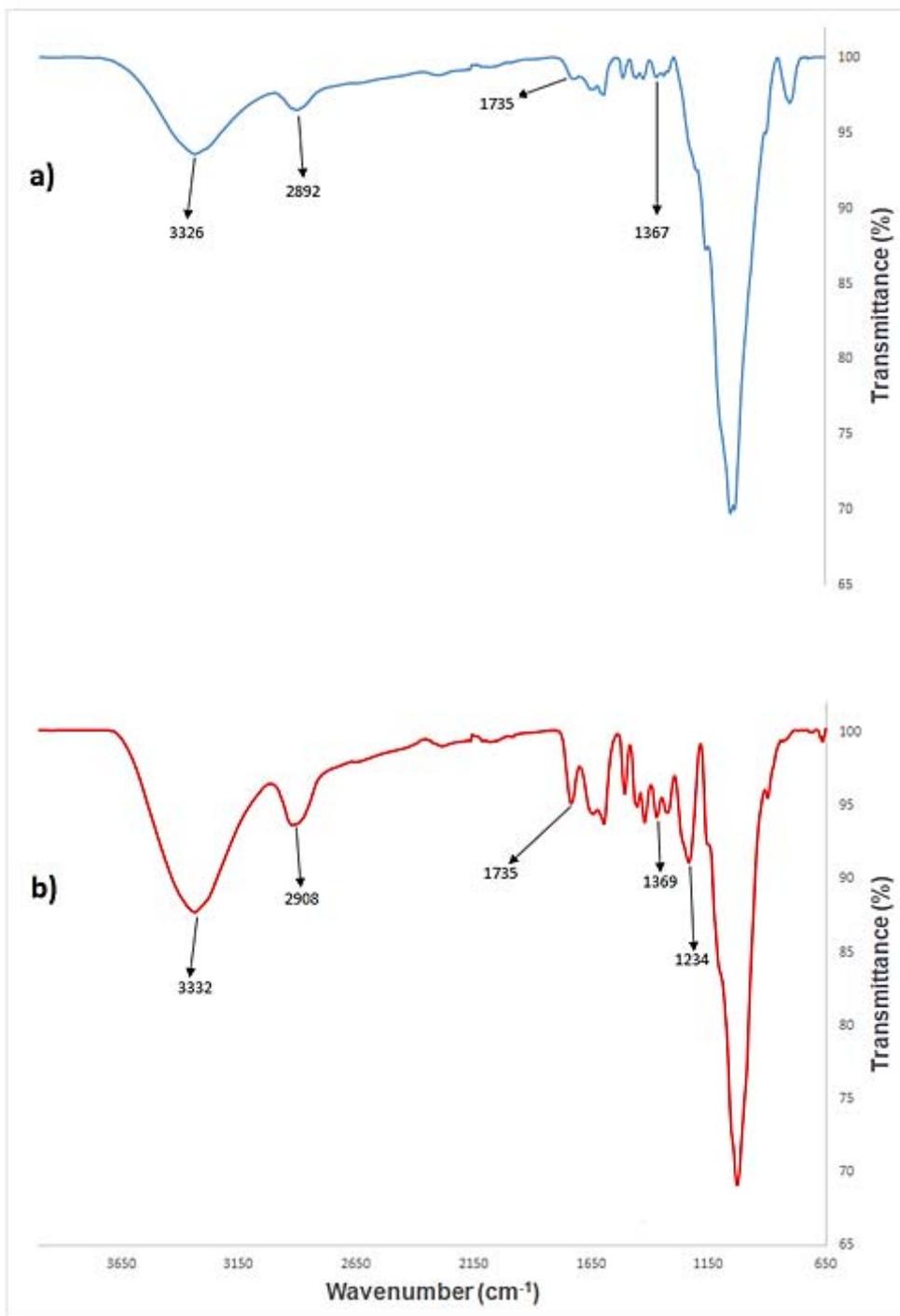


Fig. 5 – FT-IR spectra of (a) hybrid and (b) raw material.

### ***Particle Size Analysis***

Particle size analysis was performed using dynamic light scattering (DLS) method. A large part of hybrid dye materials, pigments and ink products exist in particulate. The particle size distribution of these materials provides determination of their availability, functionality, processability and quality. The pigment or colour hybrid particles must yield a

colloidal dispersion in printing ink applications<sup>42</sup>. This means that the particles suspended in a medium have diameters within 1-1000 nm. According to the results of particle size distribution whose median value is about 250 nm, it can be seen that the hybrid particles formed a colloidal dispersion and can be used for ink applications see Supplementary Fig. S5.

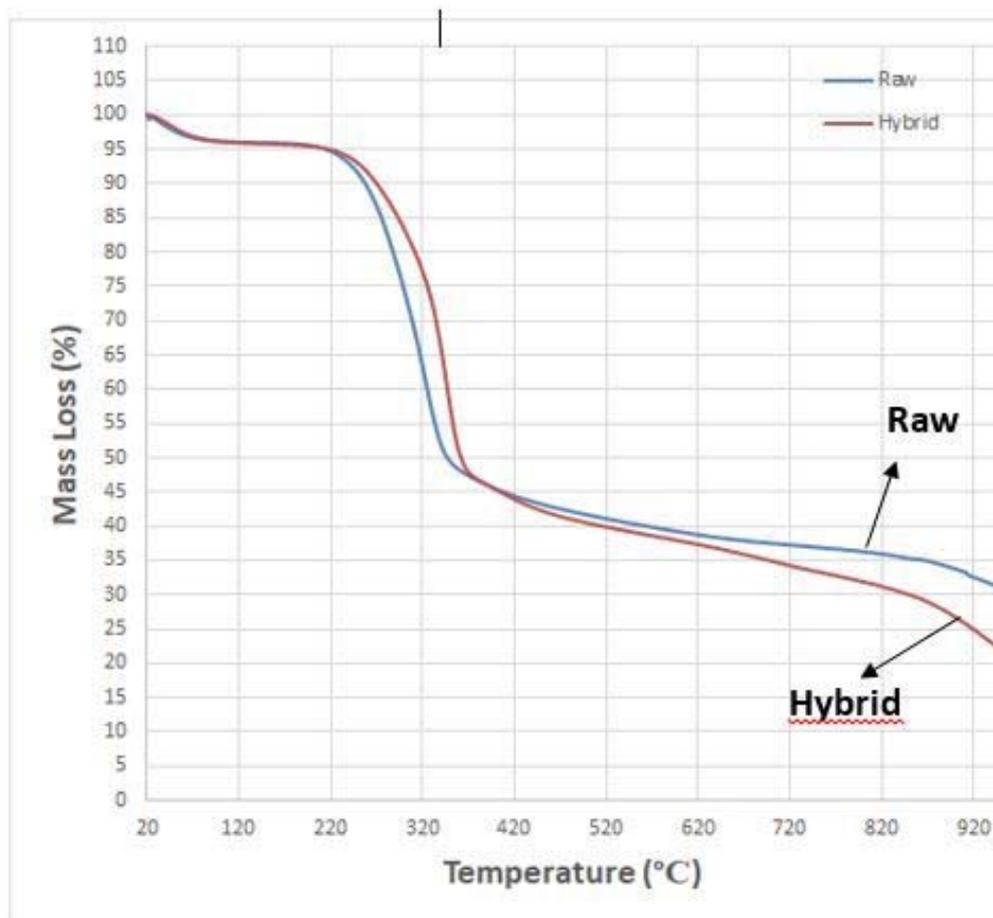


Fig. 6 – Thermogravimetric analysis of raw and hybrid materials.

### Thermal Analysis

TG analysis, one of the most used techniques in materials world, was used in order to determine thermal behaviour of the present sawdust substantially composed of cellulose, hemicelluloses and lignin, each of which exhibits a different behavior related to thermal degradation. The TG curves of hybrid and raw materials, which were recorded at a heating rate of 10.0°C/min, are shown in fig. 6. As can be seen, the initial mass loss starts at almost the temperature up to 100°C which can be attributed to moisture, with an approximately corresponding mass loss of 5.70%.<sup>43</sup> This is followed by a great weight loss where the decomposition of rice husk sawdust biomass and Rh-B takes place with maximum rate between 250°C and 375°C. In this degradation stage, the weight loss is by reason of the thermal decomposition of the wood component: hemicelluloses are degraded mainly between 200°C and 300°C, cellulose in the range of 275-400°C, and lignin in 250-500°C.<sup>44</sup> Furthermore, it can be understood

from fig. 6 that Rh-B penetrated into the rice husk sawdust does not change significantly the thermal stability of both samples.

### CONCLUSION

In summary, it was disclosed that the interaction of Rh-B with RH in the aqueous suspension affected the photophysical properties of Rh-B as a function of dye concentration. This interaction also caused the formation of H-aggregate of Rh-B in aqueous suspensions. The penetration process of Rh-B into the RH particles from aqueous suspensions was examined in detail and confirmed by FTIR, SEM and UV-Vis absorption spectroscopic techniques. A hybrid material was successfully obtained from Rh-B and RH and its characterization was also performed by the techniques aforementioned. It has been predicted the present hybrid material will provide insight into the developments on the design, production and utility of such types of systems.

*Acknowledgment:* The author thanks the Research Fund of Recep Tayyip Erdoğan University, Department of Chemistry for the financial support of this work.

## REFERENCES

- C. P. Ma, G. Y. Xie, X. Q. Zhang, L. T. Yang, Y. Li, H. L. Liu, K. Wang and Y. Wei, *Dyes Pigm.*, **2017**, *139*, 672-680.
- M. Miranda, C. A. Strassert, L. E. Dicelio and E. S. Roman, *ACS App. Mater. Inter.*, **2010**, *2*, 1556-1560.
- D. X. Liang, J. Li and G. S. Pang, *J. Mater. Sci.*, **2016**, *51*, 5412-5420.
- T. A. Khan and M. Nazir, M., *Environ. Prog. Sustain.*, **2015**, *34*, 1444-1454.
- J. W. Davis, M. S. Kahl, and T. D. Golden, *J. Appl. Polym. Sci.*, **2014**, *131* 40141.
- D. Bhattacharjee, S. A. Hussain, S. Chakraborty and R. A. Schoonheydt, *Spectrochim. Acta A.*, **2010**, *77*, 232-237.
- M. Roulia and A. A. Vassiliadis, *Micropor. Mesopor. Mat.*, **2009**, *122*, 13-19.
- N. Miyamoto, R. Kawai, K. Kuroda and M. Ogawa, *Appl. Clay Sci.*, **2000**, *16*, 161-170.
- A. A. Azzaz, S. Jellali, R. Souissi, K. Ergaieg and L. Bousselmi, *Environ. Sci. Pollut. R.*, **2017**, *24*, 18240-18256.
- M. N. Sahmoune and A. R. Yeddou, *Desalin. Water Treat.*, **2016**, *57*, 24019-24034.
- M. H. Habibi, A. Hassanzadeh and A. Zeini-Isfahani, *Dyes Pigm.*, **2006**, *69*, 111-117.
- M. R. Rostami, M. Kaya, B. Gur, Y. Onganer and K. Meral, *Appl. Surf. Sci.*, **2015**, *359*, 897-904.
- M. Kaya, M. Y. Onganer and A. Tabak, *J. Phys.. Chem.. Solids*, **2015**, *78*, 95-100.
- M. J. Snare, F. E. Treloar, K. P. Ghiggino and P. J. Thistlethwaite, *J. Photochem.*, **1982**, *18*, 335-346.
- M. Sameiro, and T. Goncalves, *Chem. Rev.*, **2009**, *109*, 190-212.
- J. X. Liu, Z. J. Diwu, W. Y. Leung, Y. X. Lu, B. Patch, and R. P. Haugland, *Tetrahedron Lett.*, **2003**, *44*, 4355-4359.
- A. M. Senol, O. Metin, M. Acar, Y. Onganer and K. Meral, *J. Mol. Struct.*, **2016**, *1103*, 212-216.
- M. Kaya, K. Meral and Y. Onganer, *J. Mol. Struct.*, **2015**, *1083*, 101-105.
- E. H. Hill, Y. Zhang and D. G. Whitten, *J. Colloid Interf. Sci.*, **2015**, *449*, 347-356.
- S. Salleres, F. L. Arbeloa, V. Martinez, T. Arbeloa and I. L. Arbeloa, *J. Colloid Interf. Sci.*, **2008**, *321*, 212-219.
- Y. S. Marfin, O. S. Vodyanova, D. A. Merkushev, S. D. Usoltsev and V. O. Kurzin, *J. Fluoresc.*, **2016**, *26*, 1975-1985.
- T. Bayraktutan, K. Meral and Y. Onganer, *J. Lumin.*, **2014**, *145*, 925-929.
- D. S. Pellosi, B. M. Esteveao, J. Semensato, D. Severino, M. S. Baptista, M. J. Politi, N. Hioka and W. Caetano, *J. Photoch. Photobio. A.*, **2012**, *247*, 8-15.
- G. Rytwo, *Sci. World J.*, **2012**, 1-7.
- E. Baez, N. Quazi, I. Ivanov and S. N. Bhattacharya, S. N., *Adv. Powder Technol.*, **2009**, *20*, 267-272.
- N. M. Ahmed, W. M. Abd El-Gawad, M. G. Mohamed, and A. A. Elshami, *Prog. Org. Coat* **2016**, *101*, 309-321.
- Y. Q. Li, S. G. Mei, Y. J. Byon, J. L. Wang, and G. L. Zhang, *ACS. Sustain Chem. Eng.*, **2014**, *2*, 318-321.
- A. Pielesz, A. Weselucha-Birczynska, H. S. Freeman, and A. Wlochowicz, *Cellulose* **2005**, *12*, 497-506.
- G. C. Panda, S. K. Das and A. K. Guha, *J. Hazard. Mater.*, **2009**, *164*, 374-379.
- R. F. Kubin, and A. N. Fletcher, *J. Lumin.*, **1982**, *27*, 455-462.
- K. K. Rohatgi, *J. Mol. Spectrosc.*, **1968**, *27*, 545-548.
- M. A. Behnajady, N. Modirshahla, S. B. Tabrizi, and S. Molanee, *J. Hazard. Mater.*, **2008**, *152*, 381-386.
- S. L. Yang, M. S. Wu and C. Y. Wu, *Energy*, **2014**, *66*, 162-171.
- A. D. G. Gouvea, P. F. Trugilo, J. L. Colodette, J. T. Lima, J. R. M. da Silva and J. L. Gomide, *Rev. Arvore*, **2009**, *33*, 1175-1185.
- B. Kurek, and F. Gaudard, *J. Agr. Food Chem.*, **2000**, *48*, 3058-3062.
- N. Phaiboonsilpa, M. Ogura, K. Yamauchi, H. Rabemanolontsoa, and S. Saka, *Ind. Crop. Prod.*, **2013**, *49*, 484-491.
- M. Carrier, A. Loppinet-Serani, D. Denux, J. M. Lasnier, F. Ham-Pichavant, F. Cansell, and C. Aymonier, *Biomass Bioenerg.*, **2011**, *35*, 298-307.
- M. Saha, A. Shil, S. A. Hussain, and D. Bhattacharjee, *J. Photochem. Photobiol. A.*, **2017**, *348*, 199-208.
- E. Manaila, M. D. Stelescu, G. Craciun, and D. Ighigeanu, *Materials*, **2016**, *9*, 503.
- M. Schwanninger, J. C. Rodrigues, H. Pereira, and B. Hinterstoisser, *Vib. Spectrosc.*, **2004**, *36*, 23-40.
- J. P. M. Lommerse, S. L. Price, and R. Taylor, *J. Comput. Chem.*, **1997**, *18*, 757-774.
- M. A. Mulla, H. N. Yow, H. Zhang, O. J. Cayre and S. Biggs, S., "Colloid Particles in Ink Formulations", in "Fundamentals of Inkjet Printing", Wiley-VCH Verlag GmbH & Co. KGaA, **2016**, p. 141-168.
- A. Plis, M. Kotyczka-Morańska, M. Koczyński, and G. Łabojko, *J. Therm. Anal. Calorim.*, **2016**, *125*, 1357-1371.
- M. Zanoaga, F. Tanasa, and Y. Mamunya, *Cell Chem. Technol.*, **2016**, *50*, 637-648.

