

Basic and Reactive Dyes Sorption Enhancement of Rice Hull through Chemical Modification

¹Siew-Teng Ong, ²Pei-Sin Keng and ³Chnoong-Kheng Lee

¹Department of Chemical Science, Faculty of Science, University Tunku Abdul Rahman,
Jalan University, Bandar Barat, 31900 Kampar, Perak, Malaysia

²Department of Pharmaceutical Chemistry, International Medical University,
No.126, Jalan 19/155B, Bukit Jalil, 57000 Kuala Lumpur, Malaysia

³Chemical Sciences Division, Academy of Sciences Malaysia, 902-4,
Jalan Tun Ismail, 50480 Kuala Lumpur, Malaysia

Abstract: Problem statement: Many studies have been conducted on the removal of either anionic or cationic dyes. However, as a mixture of dyes does commonly exist together in wastewater, therefore it is of great interest to have a material that can remove both types of dyes. **Approach:** To prepare an inexpensive and efficient sorbent by chemically modifying rice hull for the removal of both basic and reactive dyes. Different chemical modifications were performed on rice hull and a comparison study on the uptake of dyes was carried out. Optimization study was carried out on most promising modified rice hull. Surface morphology of modified rice hull was examined and the functional groups present were determined using FTIR. **Results:** From the results, it appeared that by using EDA modified rice hull, an appreciable amount of both dyes could be sorbed. Varying the EDA/NRH ratios and heating temperatures affected the uptake of BB3 and RO16. The investigated sorbents were non-porous materials, due to the absence of pores and cavities. Sorption-desorption study showed that a complete recovery of BB3 can be obtained using high concentrations of H₂SO₄ and HCl but the desorption experiments of RO16 using NH₃ and NaOH were not successful. **Conclusion:** The modification of rice hull with EDA under the optimum conditions (in a ratio of 1.00 g of NRH to 0.02 mole of EDA in a well stirred water bath at 80°C for 2 h) resulted in the formation of a sorbent (MRH) that could be used successfully to remove Both Basic (BB3) and Reactive dyes (RO16).

Key words: Adsorption, dyes, batch study, column study, surface morphology, wastewater

INTRODUCTION

Removal of color from industrial effluents is a challenging problem in controlling environmental pollution. Textile, pulp and paper, tannery and dye manufacturing are among the most common sources of colored effluents. Various dyes used in the industry are particularly difficult to remove by conventional waste methods as they are stable to light and oxidizing agents and resistant to aerobic digestion (Low *et al.*, 2000). There is thus a need to search for new process that could remove dyes that are commonly used in the industry. Adsorption is one of the noteworthy treatment processes. However activated carbon used as the adsorbent is costly and difficult to regenerate (Tsai *et al.*, 2007). Thus, there has been intensive research exploring the potential of alternative low-cost materials as sorbents for dyes. A number of

investigations have shown that low cost sorbents such as Neem leaf powder, hazelnut shells, rice hull and wood shavings have the potential of being used as alternative sorbent for the removal of dyes from aqueous solutions (Bhattacharyya and Sharma, 2004; Ferrero, 2006; Ong *et al.*, 2007; 2009; Han *et al.*, 2008; Janos *et al.*, 2008).

Various chemical modifications on these materials have been carried out to enhance their sorption capacities and thus usefulness in the treatment of wastewater. However, most of the materials investigated are efficient in binding either cationic or anionic dyes but not both. As they do commonly exist together in wastewater it is of great interest to have a material that can remove both types of dyes.

The present project aims to modify rice hull, an agricultural by-product, to produce a material that could be used as a sorbent for both cationic and anionic dyes.

Corresponding Author: Siew-Teng Ong, Department of Chemical Science, Faculty of Science,
University Tunku Abdul Rahman, Jalan University, Bandar Barat, 31900 Kampar, Perak, Malaysia

In addition the surface morphology of the modified rice hull was examined using scanning electron microscope and atomic force microscopy.

MATERIALS AND METHODS

Sorbates: The cationic dye BB3 (CI = 51004, 40% dye content Sigma) and anionic dye RO16 (CI = 17757, 50% dye content Aldrich) were used without further purification. Concentrations of dye solutions prepared were calculated taking the dye content into consideration. Standard dye solutions of 2000 mg L⁻¹ were prepared as stock solutions and subsequently diluted when necessary.

Sorbents: For the present study, various sorbents are prepared as follows.

Natural rice hull: Rice hull was obtained from a rice mill and washed thoroughly with water to ensure the removal of dust and ash. Rice hull was then rinsed several times with distilled water and dried overnight in an oven at 50°C. The dried rice hull was then ground to pass through a 1 mm sieve and labeled as Natural Rice Hull (NRH).

Base treated rice hull: Base modification was carried out by treating 2 g of NRH with 40 mL of 0.1 M sodium hydroxide (NaOH). The mixture was shaken at 300 rpm for 1 h room temperature (26±2°C). It was then filtered and washed with distilled water until neutral and labeled as Base treated Rice Hull (BRH).

Hydrochloric acid treated rice hull: The modification was carried out by stirring 5 g of NRH in 100 mL of 1.0 M hydrochloric acid (HCl) for 1 h at room temperature. The treated rice hull was washed with distilled water until neutral and dried overnight at 50°C. The final product was labeled as Acid treated Rice Hull (ARH).

Quaternized rice hull: Quaternization was carried out according to the method reported by Laszlo (1996) with minor modification. About 5 g of NRH in 6.25 mL of 5 M NaOH solution was left at room temperature for 30 min. At the end of this incubation period, 3-chloro-2-hydroxypropyl trimethyl-ammonium chloride solution (C₆H₁₅Cl₂NO, 65% w/w in water) with pH adjusted to 5.3 was added to the mixture. It was left in the oven at 60-70°C for 4 h with intermittent stirring. The reaction mixture was rinsed with distilled water and finally suspended in dilute HCl at pH 2 for 30 min. The resulting product was subsequently washed

with distilled water until pH 5. After drying at 50°C overnight in the oven, it was termed Quaternized Rice Hull (QRH).

Citric acid treated rice hull: NRH was mixed with citric acid in a ratio of 1.0 g NRH to 7.0 mL of 1.2 M citric acid. The mixture was placed in the oven at 50°C overnight and subsequently heated at 140°C for 90 min. The reaction product was washed with distilled water until neutral and dried overnight in the oven at 50°C. The final product was labeled as Citric Acid treated Rice Hull (CARH).

Nitrilotriacetic acid treated rice hull: Rice hull was modified in a ratio of 1.0 g of NRH to 7 mL of nitrilotriacetic acid. The reaction mixture was dried overnight at 50°C. The material was subsequently heated at 140°C for 2 h. Modified rice hull was then washed with distilled water until neutral and dried at 50°C overnight. The modified rice hull was labeled as Nitrilotriacetic acid treated Rice Hull (NTA-RH).

Ethylenediamine modified rice hull: Modification was carried out by treating NRH with Ethylenediamine (EDA). The reaction mixture was kept in a water bath at 80°C for 2 h with intermittent stirring. Optimum conditions for the treatment using EDA were determined by varying the temperature of water bath (60-90°C) and the ratio of EDA (0.02-0.08 mole) to 1.00 g of rice hull. The reaction product was washed with distilled water until neutral, dried overnight in the oven at 50°C and labeled as EDA Modified Rice Hull (MRH).

Comparison study: The comparison study on the uptake of dyes by various modified rice hulls was carried out at room temperature (25±2°C) by mixing 0.05 g of sorbent with 20.0 mL of dye solution in a centrifuge tube and shaken on an orbital shaker at 150 revolutions min⁻¹ (rpm) for 4 h unless otherwise stated. The reaction mixture was then centrifuged at 3000 rpm for phase separation. All the batch experiments were carried out in duplicate and the results given are the means with a Relative Standard Deviation (RSD) of less than 5%. Control experiments without sorbent was carried out to ascertain that the sorption was by the sorbent and not the wall of the container. The percentage of dye uptake (% uptake) was calculated using the following equation:

$$\text{Uptake (\%)} = \frac{C_o - C_t}{C_o} \times 100 \quad (1)$$

Where:

C_o = The initial dye concentration

C_t = The dye concentration (mg L⁻¹) at any time

To study the sorption-desorption process, the BB3 loaded column was eluted with 0.1 and 0.5 M of acid solutions (HCl and H₂SO₄), respectively, at a flow rate of 1 mL⁻¹ min. As for RO16, after the sorption process, the RO16 loaded column was eluted with 0.05-0.5 M of NaOH. Fifty fractions of eluants were collected at the flow rate of 1 mL min⁻¹ and analyzed for their dye concentrations. The eluted column was then washed thoroughly with distilled water to remove excess acid before being used for the next sorption/desorption cycle.

Techniques: The dye concentrations were analyzed using a Perkin Elmer Lambda 35 UV-vis spectrophotometer. All measurements were made at the wavelength corresponding to maximum absorption; for BB3, λ_{max} = 654 nm and for RO16, λ_{max} = 494 nm. The functional groups of NRH and MRH were determined using Perkin-Elmer FTIR, 1725X at the wave number range of 400-4000 cm⁻¹. The sample disk was prepared by mixing the dried biosorbent with KBr. The mixture was then ground and compressed into a pellet before it was analyzed to obtain the spectrum. The surface morphology of NRH and MRH was studied using SEM which is equipped with energy dispersive X-ray Spectrometer (SEM-EDX)-JEOL JSM-6400 and the AFM (Quesant Q-Scope 250) which is a stylus-type instrument that scanned in raster fashion across the sample.

RESULTS

The comparative uptakes of single BB3 and RO16 by various sorbents are shown in Table 1. The optimization of modification was carried out by varying the amount of EDA used and treatment temperature. The effects of EDA/NRH ratios and heating temperatures on the uptake of BB3 and RO16 are shown in Table 2. The infrared spectra of NRH and MRH are as shown in Fig. 1. Surface morphology of

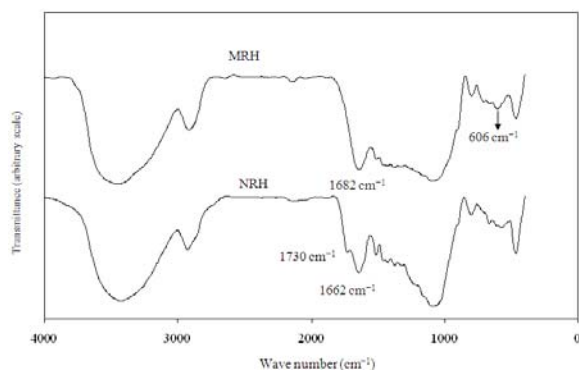


Fig. 1: Infrared spectra of NRH and MRH

the sorbents studied using SEM and contact mode of AFM are presented in Fig. 2-4. Desorption characteristics of BB3 from single dye solution using H₂SO₄ and HCl at different concentrations are shown in Fig. 5 and 6, respectively.

Table 1: Uptake of dyes by chemically modified rice hull

Sorbent	Uptake (%)	
	BB3	RO16
NRH	24.44	0.37
BRH	15.01	5.97
ARH	0.52	15.37
QRH	1.11	10.78
CARH	26.45	0.76
NTA-RH	14.18	0.15
MRH	9.53	32.44

Condition: 0.05 g of sorbent was shaken with 20 mL of dye solution (100 mg L⁻¹) at an agitation rate of 150 rpm for 4 h at room temperature

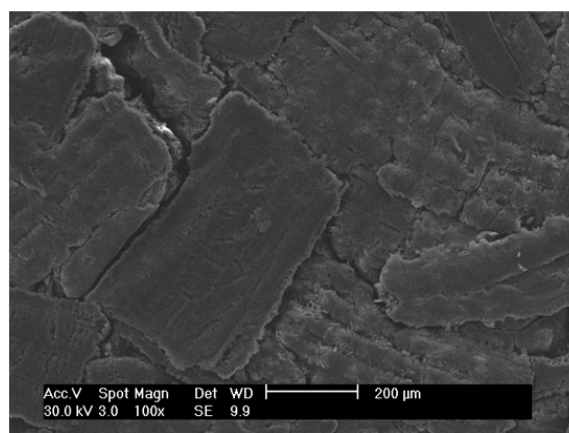


Fig. 2: SEM micrograph of NRH

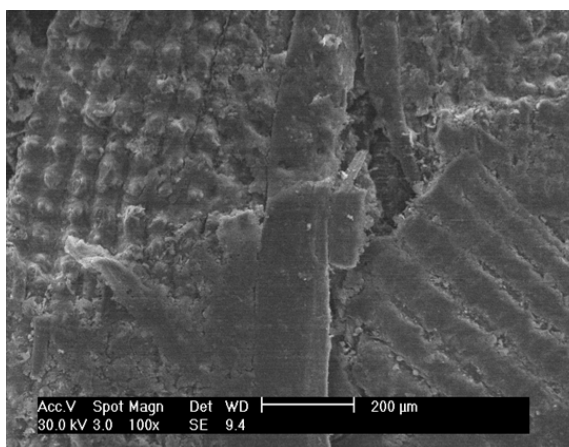


Fig. 3: SEM micrograph of MRH

Table 2: Uptake of dyes by MRH at various treatment temperatures and EDA concentrations for 2 h

Ratio of EDA (mole): 1 g rice hull	Uptake (%)							
	Basic blue 3				Reactive orange 16			
	Treatment temperature (°C)							
	60	70	80	90	60	70	80	90
1 g rice hull	28.39	26.86	25.42	22.99	50.83	56.74	63.44	64.23
0.015	28.24	26.16	24.56	22.18	55.44	58.68	60.08	63.77
0.02	28.71	26.31	24.64	22.07	55.92	57.95	64.23	63.87
0.025	28.04	24.32	22.91	22.40	52.19	57.61	64.06	63.77
0.03	28.14	24.12	22.01	21.01	51.67	56.03	59.25	60.20
0.04	25.45	22.30	20.91	20.30	49.82	54.67	55.87	45.80

Condition: 0.1 g of sorbent was shaken with 20 mL dye solution (100 mg L^{-1}) at an agitation rate of 150 rpm for 4 h at room temperature

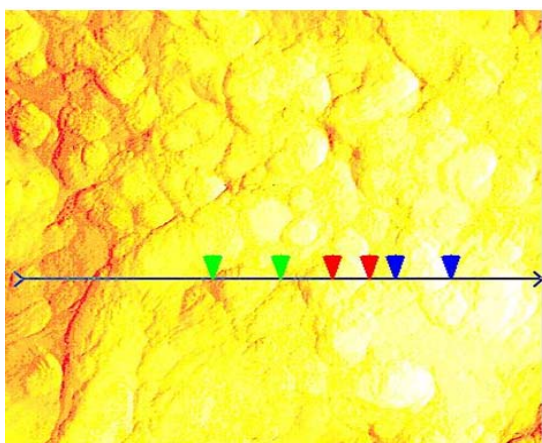


Fig. 4: AFM image of MRH with transect line for cross-sectional analysis

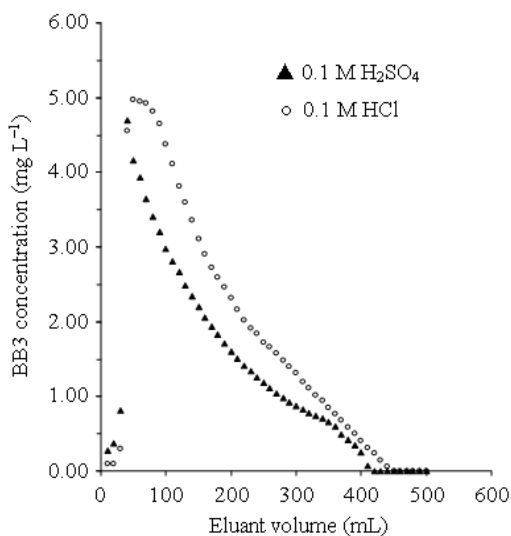


Fig. 5: Elution process of BB3 from single dye solutions in MRH column using 0.5 M H₂SO₄ and 0.5 M HCl

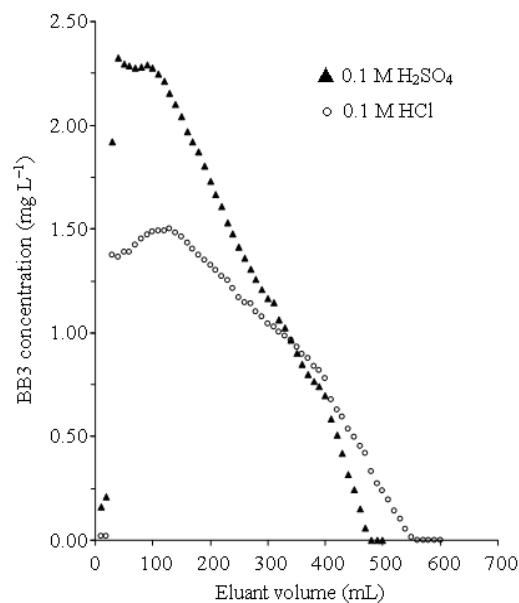


Fig. 6: Elution process of BB3 from single dye solutions in MRH column using 0.1 M H₂SO₄ and 0.1 M HCl

DISCUSSION

Comparison study on the dyes uptake: From the results, it appears that by using MRH as a sorbent, an appreciable amount of both dyes could be sorbed. Since the objective of this study is to find a material that can remove both types of dyes simultaneously, subsequent studies were carried out using MRH.

Optimization of modification of rice hull using ethylenediamine: The results show that sorption of BB3 decreased with increasing reaction temperature while the sorption of RO16 showed the opposite trend. Increasing reaction temperature would probably enhance the introduction of amine groups which are responsible for

the sorption of anionic species onto the rice hull. Amination involved carboxyl groups on the rice hull, thereby decrease the availability of carboxyl groups that binds BB3.

Varying EDA/NRH ratio indicates that sorption of BB3 and RO16 generally increased as the ratio increased and then decreased. This can be related to the more alkaline condition that brings about changes in the rice hull structure, thus resulting in lower sorption capability. Bai and Abraham (2001) reported that excess alkali treatment caused drastic effects like swelling of biomass, probably due to polymer chain breakage thereby hindered the operational stability. In this study, modification was therefore optimized at treating rice hull with EDA in a ratio of 1.00 g rice hull to 0.02 mole of EDA in a well stirred water bath at 80°C for 2 h.

Fourier-transform infrared spectroscopy: Generally, the functional groups present in NRH and MRH cannot be clearly differentiated. Absorption in the region 3200-3600 cm^{-1} is from OH stretching vibrations. The absorption of the OH group does not usually appear as a sharp peak, instead a broad band is observed because the vibrational mode is complicated by hydrogen bonding. The modification of NRH using EDA yields primary amine groups on MRH. Therefore, peaks in the region of 3444 cm^{-1} in MRH could be indicative of both N-H stretching (3000-3600 cm^{-1}) and OH that occur at almost the same region. The presence of N-H bands plus an unusually low value for the C=O (stretch occurs at approximately 1680-1630 cm^{-1}) would suggest the presence of an amide functional group. Primary amides also show a broad band from 750-600 cm^{-1} . Thus, the absorption band shown at 1682 and 606 cm^{-1} in MRH spectra may be attributed to amide functional groups. The absorption band of 1730 cm^{-1} observed in infrared spectra of NRH is due to C=O group of carboxylic acid. Both NRH and MRH illustrate a similar peak around 2900 cm^{-1} and this is owing to C-H stretching.

Scanning electron microscopy: From the SEM micrographs, it is observed that there was little difference between NRH and MRH surface morphology. This is because modification using EDA involved only the introduction of amine groups on the surface of rice hull but the fibrous network of the rice hull was retained. It is also clear that all the investigated sorbents are non-porous materials, due to the absence of pores and cavities.

Atomic force microscope: The surface morphology of MRH (Fig. 4) measured using the contact mode by

AFM on a 20×20 μm^2 area was carried out to provide information on the cross-section analysis, bearing analysis and roughness analysis. Both NRH and MRH exhibit spherical like structures and the section analysis obtained through the selection of the transect line across the sample shows that the grain size in NRH has a broad distribution ranging from 0.718-2.364 μm whereas MRH exhibits a smaller range, 1.370-2.085 μm . The AFM image when analyzed in terms of average surface roughness (R_a), increases from 169.5 nm (NRH) to 330.0 nm in MRH. This is most probably caused by the eruption during EDA modification.

Sorption and desorption: In regeneration, the choice of eluant should be considered in terms of desorption efficiency and preservation of biocapacity of the sorbent. In order to evaluate the feasibility of using MRH for multiple sorption cycles, sorption and desorption processes were carried out. The results show that a complete recovery of BB3 can be obtained using high concentrations of H_2SO_4 and HCl (Fig. 5). With 0.1 M H_2SO_4 and HCl only 46.5 and 30% recovery, respectively can be achieved (Fig. 6). In general, the extent of BB3 desorption increases with the increase in the strength of acids from 0.1-0.5 M. Besides, faster desorption was noted in the case of H_2SO_4 . This can be related to the stronger acidity of H_2SO_4 ($\text{pK}_a = -10$) compared to HCl ($\text{pK}_a = -7$). The stronger acid has a greater tendency to give up its proton. The introduction of acids into BB3 loaded column protonates the functional groups that are responsible for the binding of BB3 thereby displacing BB3. However, desorption of BB3 carried out with acid solutions introduces negative effect on the reuse of the MRH column. The MRH column cannot be reused, probably due to the saturation of the binding sites with H^+ ions during the desorption process. Calace *et al.* (2003) found that HCl can be used in the recovery of Cu^{2+} and Cd^{2+} from paper mill sludge column but the eluting process caused the sorbing sites to be saturated with hydrogen ions, thus hindered it from repeated usage.

The desorption experiments of RO16 using NH_3 and NaOH were not successful. This can be related to the strong electrostatic attraction between RO16 and sorbent as well as the occurrence of dipole-dipole interaction. From the dye structure of RO16, it is clear that it consists of many polar groups. Thus, the attraction between these polar groups should be taken into consideration as the dipole-dipole interaction increases with an increase in the polarity of the molecule.

CONCLUSION

The present study shows that modification of rice hull with EDA under the optimum conditions (in a

ratio of 1.00 g of NRH to 0.02 mole of EDA in a well stirred water bath at 80°C for 2 h) resulted in the formation of a sorbent (MRH) that could be used successfully to remove Both Basic (BB3) and Reactive dyes (RO16). The functional groups present before and after modifications cannot be clearly distinguished through the infrared spectra obtained and this could be due to the limitations in the sensitivity of the instrument. The surface morphology of the sorbent was studied using SEM and AFM. Results show that all the investigated sorbents are non-porous materials. In sorption-desorption study, a complete recovery of BB3 can be obtained by eluting the saturated column with 0.5 M H₂SO₄ and 0.5 M HCl but the column cannot be reused. The desorption of RO16 using NaOH and NH₃ was not successful and this could be due to the strong electrostatic attractions as well as the occurrence of hydrogen bonding.

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