**ADSORPTIVE REMOVAL OF METHYLENE BLUE AND ACID ORANGE 7 BY HEXADECYLTRIMETHYLAMMONIUM BROMIDE MODIFIED RICE HUSK**

Auni Afiqah Kamaru, Nurul Soraya Ahmad Jani, Nik Ahmad Nizam Nik Malek*, Nor Suriani Sani

Department of Biotechnology and Medical Engineering, Faculty of Biosciences and Medical Engineering, Universiti Teknologi Malaysia, 81310 UTM Johor Bahru, Johor, Malaysia

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*Corresponding author
niknizam@fbb.utm.my

**Graphical abstract**

MB adsorbed onto RRH

AO7 adsorbed onto SMRH

**Abstract**

The feasibility of rice husk (RRH) and surfactant modified rice husk (SMRH) to adsorb cationic dye, methylene blue (MB) and acid orange 7 (AO7) from aqueous solution was studied. SMRH was prepared by reacting RRH with different initial concentrations (1.0, 2.5 and 4.0 mM) of cationic surfactant quaternary ammonium compound, hexadecyltrimethylammonium bromide (HDTMABr). RRH and SMRH were characterized using Fourier transform infrared (FTIR) spectroscopy to determine surface functional group and effect of surfactant modification on the structure of RRH. Adsorption studies were performed in a series of batch experiment and effect of initial dye and HDTMABr concentrations on the adsorption capacity of RRH and SMRH were evaluated. The results showed that the removal of MB was higher for RRH compared to SMRH meanwhile AO7 removal was higher for SMRH compared to RRH. Modification of rice husk by cationic surfactant was proven to decrease the adsorption site for MB. On the other hand, the presence of surfactant on SMRH increased the adsorption site and allows more adsorption to occur for AO7. The equilibrium data were better described by Langmuir isotherm with maximum adsorption capacity for MB was 100.0 mg/g and 200.0 mg/g for AO7. In conclusion, the modification of rice husk by HDTMABr decreased the adsorption towards cationic dye but increased the adsorption towards anionic dye.

**Keywords:** Rice husk, surfactant, adsorption, methylene blue, acid orange 7

**Abstrak**

Kebolehlaksanaan sekam padi (RRH) dan sekam padi yang diubahsuai dengan surfaktan (SMRH) untuk menjerap pewarna kationik, metilina biru (MB) dan pewarna anionik, asid jingga 7 (AO7) dalam larutan akueus telah dikaji. SMRH dihasilkan melalui tindak balas sebatian ammonium kuarternari surfaktan kationik, heksadesiltrimethylammonium bromida (HDTMABr) pada kepekatan yang berbeza [1.0, 2.5 dan 4.0 mM]. RRH dan SMRH telah dicirikan dengan menggunakan kaedah spektroskopi inframerah perubahan Fourier (FTIR) bagi mengenal pasti kumpulan berfungsi yang terdapat pada permukaan RRH dan SMRH dan kesan pengubahsuai surfaktan terhadap struktur RRH. Proses penjerapan telah dijalankan secara berkelompok dan kesan kepekatan larutan pewarna dan HDTMABr yang berbeza terhadap kapasiti penjerapan RRH dan SMRH telah dianalisis. Hasil kajian menunjukkan bahawa penyingkiran tertinggi MB adalah dengan menggunakan RRH berbanding SMRH manakala penyingkiran tertinggi AO7 adalah dengan menggunakan SMRH berbanding RRH. Pengubahsuai sekam padi oleh surfaktan kationik telah mengurangkan tapak penjerapan untuk MB. Sebaliknya, kehadiran surfaktan pada SMRH telah meningkatkan tapak dan kadar penjerapan untuk AO7. Data eksperimen berpadanan dengan model Langmuir dengan kapasiti penjerapan maksimum untuk MB adalah 100.0 mg/g dan 200.0 mg/g untuk AO7. Sebagai kesimpulan, pengubahsuai sekam padi oleh HDTMABr telah mengurangkan kapasiti penjerapan pewarna kationik sebaliknya meningkatkan penjerapan pewarna anionik.
1.0 INTRODUCTION

The rise of textile industries in recent centuries has contributed to serious water pollution problem due to the release of dyes into water bodies [1]. For example, in Malaysia, the growth of batik industry in the coast of Peninsular Malaysia and Sarawak producing untreated effluents containing various pollutants including dye [2]. The presence of dyes in water streams threaten natural ecosystem and possess detrimental effects to human being as dyes inhibit photosynthetic activity of aquatic biota as well as highly mutagenic to living things [3,4]. Thus, by considering adverse harmful effects, removal of dyes from natural environment has received a great concern over the past years [5]. The wastewater containing dyes is reported to be the most difficult water to be treated due to the complex molecular structure and high water soluble properties of dyes [6]. Therefore, diverse techniques have been implemented to remove dyes from wastewater including flocculation, sedimentation and filtration [4]. However, all of the aforementioned methods are unable to treat various classes of dyes and inefficient to completely remove dyes from aqueous phase [7]. Conversely, adsorption has emerged as an alternative method as it promised efficient treatment process as well as production of safe treated water [8].

The abundance of agricultural wastes has attracted interest of researchers in utilizing these natural resources as an adsorbent in treating wastewater containing dyes. Hence, in this study, rice husk, an agricultural wastes being produced abundantly in Malaysia [9] and approximately 100 million tonnes annually in developing countries [10] was selected as studies adsorbent. The major components of rice husk are cellulose, hemicelluloses, lignin, silica and ash [11]. The hydroxyl group in cellulose and lignin tend to release hydrogen ion in aqueous solution which results in the formation of negatively charged surface [12]. The application of raw rice husk as an adsorbent in wastewater treatment process is only beneficial to adsorb cationic dye but not its counterpart. Therefore, it is necessary to modify the surface of rice husk prior to adsorption process in order to enhance its adsorption affinity towards anionic dye.

Bhatnagar and Sillanpaa [13] proposed that surface modification is able to enhance the affinity of raw agricultural wastes towards anionic dye while according to Namasingam and Sureshkumar [14], cationic surfactant is the best modifying agent for the aforesaid purpose. This is due to the presence of positively charged head group of surfactant that is able to attract anionic compound. Therefore, the major aim of this paper is to report the surface modification of rice husk with cationic surfactant, hexadecyltrimethylammonium bromide (HDTMABr) and to evaluate the influence of surface modification on the adsorption capacity of rice husk towards methylene blue (MB) and acid orange 7 (AO7) which are cationic and anionic dye, respectively. The parameters that affect the adsorption process including initial dye concentration, surfactant concentration and types of dyes were evaluated. Models to fit the adsorption equilibrium data were formulated.

2.0 EXPERIMENTAL

2.1 Preparation of Raw and Surfactant Modified Rice Husk

Rice husk was provided by Provet Group of Companies Sdn. Bhd., Serdang, Selangor, Malaysia. The rice husk was washed with distilled water, sundried for 8 hours and subsequently dried in an oven at 80 °C for 24 hours. The dried rice husk was crushed and ground into fine powder. The resulting powder was sieved to constant size using #40 American Society for Testing Materials (ASTM) sieve. The rice husk powder less than 425 µm was used as adsorbent in the adsorption study and abbreviated as raw rice husk (RRH).

Three different concentrations of HDTMABr solution (1.0, 2.5 and 4.0 mM) were prepared by dissolving the appropriate amount of HDTMABr in distilled water. The surfactant modified rice husk (SMRH) was prepared by reacting RRH with HDTMABr in the ratio of 10:1 (RRH:HDTMABr, w/v) under constant stirring for 10 minutes at room temperature. The resulting SMRH was filtered and dried in an oven at 90 °C for 24 hours. The remaining filtrate was kept for the determination on the amount of surfactant adsorbed onto RRH. The dried SMRH modified using 1.0, 2.5 and 4.0 mM of HDTMABr solution were abbreviated as 1.0 SMRH, 2.5 SMRH and 4.0 SMRH, respectively.

2.2 Determination of Surfactant Adsorbed

The procedure for the determination of surfactant adsorbed onto RRH was performed as described by Scott [15]. Initially, 25 mL distilled water, 5 mL sulfuric acid (2 M), 10 mL chloroform and 2 mL acid orange 7 (1 mM) were mixed and shaken in separating funnel. Then, 1 mL HDTMABr filtrate was added to the previous mixture and shaken vigorously. The chloroform layer was extracted and analyzed using visible
spectrophotometer (model NANOCOLOR® VIS, Macherey Nagel, Germany) at λ_{487\text{nm}}. The amount of HDTMABr adsorbed onto RRH, \( q_{\text{ads}} \) (mmol/kg) was calculated using the following equation:

\[
q_{\text{ads}} = \frac{(q_i - q_e)V}{W}
\]

where \( q_i \) and \( q_e \) (mmol/L) are concentration of HDTMABr solution before and after adsorption process, respectively. \( V \) (L) is the volume of HDTMABr solution and \( W \) (kg) is weight of RRH sample.

2.3 Characterization of RRH and SMRH

The samples of RRH and SMRH were characterized by Fourier transform infrared (FTIR) spectroscopy (model Nicolet is5, Thermo Fischer Scientific, USA) using attenuated total reflectance (ATR) method. The FTIR spectra were recorded using OMNIC software at spectral range of 400 to 4000 cm\(^{-1}\).

The sample of RRH was characterized using scanning electron microscope (SEM) (model JSM-6390 LV, JOEL, Malaysia) at an electron acceleration voltage of 10 kV. Prior to scanning, RRH was coated with a thin layer of platinum using autofine coater to make the sample electrical conductive.

2.4 Adsorption Study

The adsorption of MB and AO7 was conducted at different initial MB and AO7 concentration ranging from 5 to 1000 mg/L. The MB and AO7 stock solutions were prepared by dissolving 1000 mg of respected dye in 1000 mL distilled water. The subsequent working solutions were prepared by diluting the stock solution with distilled water to the desired concentration. The batch adsorption study was performed at room temperature where 250 mg of RRH and SMRH was added to 25 mL MB or AO7 solution and shaken at 200 rpm for 2 hours. The concentration of MB and AO7 before and after adsorption was determined using visible spectrophotometer (model NANOCOLOR® VIS, Macherey Nagel, Germany) at \( \lambda_{661\text{nm}} \) and \( \lambda_{487\text{nm}} \), respectively. The amount of MB and AO7 adsorption at equilibrium, \( q_e \) (mg/g) was calculated using the following equation:

\[
q_e = \frac{bQ_oC_e}{1 + bC_e}
\]

where \( q_e \) (mg/g) and \( C_e \) (mg/L) are the amount of adsorbed dye per unit of adsorbent and concentration of adsorbed dye at equilibrium, respectively. \( Q_o \) (mg/g) is the maximum amount of dye per unit mass of adsorbent to form complete monolayer coverage on the surface of adsorbent and \( b \) is Langmuir constant related to the affinity of binding site. The Freundlich isotherm model is expressed as:

\[
q_e = K_f C_e^n
\]

where \( K_f \) and \( n \) are Freundlich constant with \( K_f \) (mg/g) is the maximum adsorption capacity of adsorbent and \( n \) is an indicator on the favorability of adsorption process.

3.0 RESULTS AND DISCUSSION

3.1 Adsorption of Surfactant on RRH

The modification of RRH by cationic surfactant was done in three concentrations of HDTMABr which were 1.0, 2.5 and 4.0 mM. The amount of HDTMABr adsorbed onto RRH at different HDTMABr initial concentrations is presented in Figure 1. It can be observed from Figure 1 that the amount of HDTMABr adsorbed onto RRH increased with the increased in initial concentration of HDTMABr solution. As the concentration of HDTMABr increased from 1.0 to 4.0 mmolkg\(^{-1}\), which was four times increments, the amount of HDTMABr adsorbed increased quadruple which was from 37.28 to 161.89 mmolkg\(^{-1}\). Therefore, it can be concluded that the amount of HDTMABr adsorbed onto RRH was in the same proportion and dependent to the initial concentration of HDTMABr solution. From this observation, it was expected that HDTMABr was successfully introduced into the structure of RRH.
3.2 Characterization of RRH and SMRH

The FTIR spectroscopy was used to determine the functional groups present in raw and modified rice husk. The FTIR spectra of RRH and SMRH are presented in Figure 2. From Figure 2, broads and intense band ranging from 3300 to 3400 cm\(^{-1}\) in all samples was due to -OH stretching vibration. The peaks centred at 2919 cm\(^{-1}\) was attributed to -CH stretching vibration while band around 1631 to 1737 cm\(^{-1}\) represents C=O stretching correspond to ester and carboxylic group from hemicelluloses [16,17]. The peaks around 1546 to 1652 cm\(^{-1}\) and 1375 to 1430 cm\(^{-1}\) were ascribed as C=C stretching of alkenes and C-O-H bending, respectively [18]. The sharp and narrow peak appeared at 1050 to 1300 cm\(^{-1}\) was corresponding to C-O stretching vibration.

The results from FTIR spectroscopy indicate that there were no obvious peaks changes between RRH and SMRH except for the increased in C-H stretching intensity from RRH to 4.0 SMRH. This is due to the increased in aliphatic carbon content of HDTMABr across the samples. This observation is in line with the previous studies reported on the modification of agricultural wastes using cationic surfactant [19,20]. The overall FTIR spectra of RRH and SMRH demonstrated that surface modification did not change the structure of rice husk substantially.

The scanning electron microscopy was performed to observe the surface texture properties of raw rice husk that might facilitate the adsorption of HDTMABr, MB and AO7 onto RRH. The SEM micrograph of RRH is presented in Figure 3. The RRH exhibited uneven rough surface with porous structure. The presence of pores provided the larger surface area that allow the adsorption of HDTMABr and MB into lignocellulosic structure and further interact with the available surface functional groups [3].

The adsorption isotherm described the distribution of adsorbate between solid-liquid interphase as the adsorption process reached equilibrium. The adsorption capacity of RRH and SMRH towards MB and AO7 were determined through adsorption isotherm study. The isotherm graph for the adsorption of MB and AO7 are presented in Figure 4 and 5, respectively. From Figure 4 and 5, it can be observed that the adsorption of MB and AO7 for all samples was rapid at the initial stage of adsorption (lower concentration of MB and AO7), subsequently proceeded at slower rate and finally reached constant removal rate as equilibrium achieved. This is because, at lower concentration, all dyes molecules available in the solution were interact with functional groups in RRH and SMRH adsorption sites which further lead to the rapid adsorption rate. However, RRH and SMRH have limited number of binding sites which become saturated after certain period. Therefore, constant adsorption rate was observed as initial MB and AO7 concentration increased [21].
In order to further understand the adsorption behavior of MB and AO7 by RRH and SMRH, the adsorption isotherm data were fitted into Langmuir and Freundlich isotherm models. The values of adsorption isotherm parameters for both models are listed in Table 1. By comparing the correlation coefficient ($R^2$), the experimental data were better described by Langmuir in comparison to Freundlich isotherm model. The maximum uptake of MB and AO7 according to this model was 100.0 and 200.0 mg/g, respectively. The conformation of adsorption data into Langmuir isotherm indicates the monolayer adsorption of MB and AO7 onto homogenous surface of RRH and SMRH whereby all adsorption sites have equal affinity towards MB and AO7 molecules [22].

The comparison of MB and AO7 adsorption by RRH and SMRH is presented in Figure 6. From Figure 6, the highest and lowest adsorption of MB by RRH and 4.0 SMRH, respectively and the MB removal followed the trend of RRH > 1.0 SMRH > 2.5 SMRH > 4.0 SMRH. However, the highest and lowest adsorption of AO7 was by 4.0 SMRH and RRH, respectively and the removal of AO7 followed the trend of 4.0 SMRH > 2.5 SMRH > 1.0 SMRH > RRH. It was observed that RRH and SMRH showed different adsorption behavior towards MB and AO7 where MB was highly adsorbed by RRH while AO7 was by 4.0 SMRH.

The overall results from this study revealed that surface modification process influenced the adsorption affinity of RRH towards anionic dye. The critical micelle concentration (CMC) of surfactant is key important factor in the surface modification process. The CMC of HDTMABr is 0.93 mM [23]. At concentration below CMC, HDTMABr molecules exist as monomer in the solution and adsorbed on the surface of rice husk in a monolayer form. However, as concentration increased above CMC, HDTMABr molecules rearranged on surface of rice husk to form HDTMABr bilayer. This result in surface charge reversal from negative to positive potential due to the positively charged head group of HDTMABr was directed towards the bulk of AO7 solution. Therefore, in this study, the concentration of HDTMABr used to modify the surface of rice husk was slightly higher than the CMC value of the corresponding surfactant. The positively charged SMRH was highly attracted to adsorb AO7 rather than MB. The 4.0 SMRH exhibited highest adsorption capacity towards AO7. This is due to the presence of higher amount of HDTMABr bilayer on the outer surface of rice husk which allows more uptake of AO7 by the surface of rice husk which allows more uptake of AO7.

**Figure 5 Adsorption isotherm of AO7 by RRH and SMRH**

4.0 CONCLUSION

The batch adsorption of MB and AO7 by RRH and SMRH was evaluated. The modification of RRH with cationic surfactant, HDTMABr was able to reverse the surface charge from negative to positive potential and subsequently enhanced the adsorption affinity of SMRH towards AO7. The adsorptions for both dyes were fitted into Langmuir isotherm model with the maximum adsorption of MB and AO7 was 100.0 and 200.0 mg/g, respectively. Therefore, the raw and surfactant modified rice husk can be applied as effective adsorbent to treat wastewater containing different types of dyes.

**Figure 6 Maximum adsorption capacity values of MB and AO7 adsorption by RRH and SMRH**


