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Determination of the Role of Different Surface Functional Groups on EDA Modified Rice Hull in the Sorption of Dyes

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The effectiveness of using ethylenediamine modified rice hull to remove basic blue 3 and reactive orange 16 dyes from aqueous solution was carried out. In order to determine the role of the surface functional groups of rice hull in the sorption of dyes, these surface functional groups were subjected to different chemical modifications. Results indicate that carboxyl group was the major functional group involved in the sorption of basic blue 3, whereas for the binding of reactive orange 16 occurs through the interaction with amino groups.

Key Words: Surface functional groups, Sorption, Modified rice husk, Dyes.

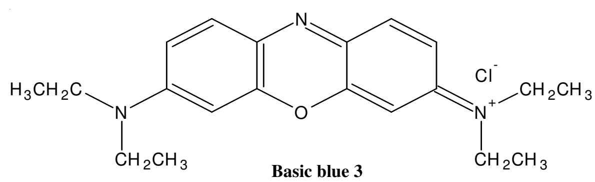
INTRODUCTION

Textile industry has long been one of the largest water users and major polluters as the discharge contains various waste constituents. Textile wastes are generally coloured, highly alkaline, high in biochemical oxygen demand (BOD) and suspended solids and high in temperature. Consequently water contamination originated from the dyeing and finishing in textile industry has become a major concern. There is thus a need to search for new and economical process that could remove dyes that are commonly used in the industry. Some dye-adsorbent systems which have demonstrated commercial potential include coconut husk[1], neem leaf powder[2], castor seed shell[3], hazelnut shell and sawdust[4], spent tea leaves[5] and sugarcane bagasse[6,7].

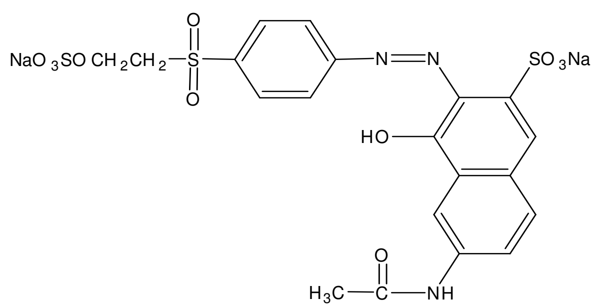
Previous work in our laboratory has shown that modification of rice hull using different chemical agents yielded material capable of removing different types of dyes either singly or binary[8-10]. In this paper, the role of different functional groups on the sorbent in the sorption of dyes was identified through different chemical modifications.

EXPERIMENTAL

Sorbates: The cationic dye basic blue 3 (Fig. 1) (C.I. = 51004, 40 % dye content) and anionic dye reactive orange 16 (Fig. 1) (C.I. = 17757, 50 % dye content) were used as the sorbates in this study without further purification. All dye powders were purchased from Sigma-Aldrich Pte. Ltd. (United States of America). Concentrations of dye solutions prepared were calculated taking the dye content into consideration. Standard dye solutions of 2000 mg/L were prepared as stock solutions and subsequently diluted when necessary.



Basic blue 3



Reactive orange 16

Fig. 1. Chemical structures of dyes

Sorbents: Rice hull was collected and washed several times to ensure the removal of dust and ash. It was subsequently rinsed several times with distilled water and dried overnight in an oven at 50 ºC. The dried rice hull was ground to pass through a 1 mm sieve and labeled as natural rice hull (NRH). Ethylenediamine modified rice hull (MRH) was prepared by treating natural rice hull with ethylenediamine in a ratio of 1.00 g rice hull to 0.02 mol of ethylenediamine in a well-stirred water bath at 80 ºC for 2 h.

Other chemical modifications of surface functional Groups: Both natural rice hull and modified rice hull were subjected to esterification, amination and acetylation reactions in order to elucidate the role of different surface functional groups on the sorption of dyes.

All the sorption experiments were performed by agitating 0.05 g of sorbent in 20 mL of 100 mg/L dye solution in a centrifuge tube at 150 rpm on an orbital shaker for 8 h at room temperature (25 ± 2 ºC) unless otherwise stated. All experiments were conducted in duplicates and the results stated are the means. Controls without sorbent were simultaneously carried out to ascertain that sorption was due to sorbent and not the wall of the centrifuge tube. The percentage of dye uptake was calculated using the following equation:

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

where, C_o is the initial concentration and C_t the concentrations at time t.

RESULTS AND DISCUSSION

Sorption mechanisms: In this study, when amination of natural rice hull was carried out using ethylenediamine, the proposed reaction shown below is postulated to take place:

$$S_h\text{-COOH} + H_2NCH_2CH_2NH_2 \rightarrow S_h\text{-COHNCH}_2CH_2NH_2 + H_2O \quad (1)$$

where, S_h represents the surface of rice hull.

The modification process to produce modified rice hull was believed to involve carboxyl groups on the rice hull. Upon reacting natural rice hull with ethylenediamine, the resultant hull contained primary amide and primary amines.

Chemical modifications of surface functional groups: The results of amination and esterification on surface functional groups of natural rice hull and modified rice hull are summarized in Fig. 2. The carboxyl groups in natural rice hull were esterified (E-NRH) using acidic methanol method to study the role of carboxyl groups in the sorption process of dyes. If the binding of the dye molecules occurs through the interaction with the carboxyl groups, this type of modification will render the carboxyl groups unavailable for the binding and result in a reduction in the sorption of the dyes. The general reaction scheme of the treatment involved[11]:

$$RCOOH + CH_3OH \xrightarrow{H^+} RCOOCH_3 + H_2O \quad (2)$$

The esterified natural rice hull exhibited a decrease of 10.0 and 12.1 % in basic blue 3 uptake in single and binary dye solutions, respectively. This indicates that carboxyl group was the major functional group involved in the sorption of basic blue 3. Similar phenomenon was reported in the adsorption of cationic dye by peanut hull[11]. Upon esterification of the hull, a rapid decrease in the adsorption of cationic dyes

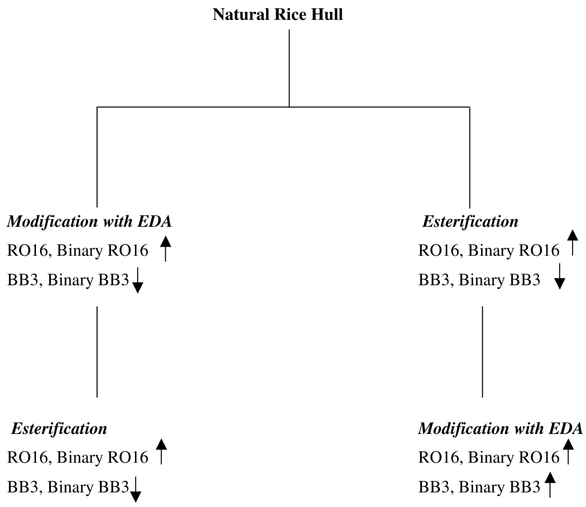


Fig. 2. Effect of the sequence of amination and esterification of natural rice hull on the sorption of BB3 and RO16 (↑ = uptake increased, ↓ = uptake decreased)

was observed. This clearly indicated that carboxyl groups played a dominant role in the adsorption of cationic dyes.

On the other hand, for the sorption of reactive orange 16 in both single and binary dye solutions, an increase was observed after esterification reaction. The increase in the reactive orange 16 uptake can be explained by the removal of the negative charge of carboxyl group through esterification; this reduced the overall surface negative charges and thus increased the sorption of anions.

The results of dye sorption from single and binary dye solutions onto modified rice hull and esterified modified rice hull (E-MRH) showed the same trend as in esterified natural rice hull (Fig. 3). However, in this case, in addition to the esterification of the COOH group, another possible explanation for the increased sorption of reactive orange 16 is that protonation of the amine groups occurred. This situation enhanced the uptake of negatively charged species but inhibited the sorption of the positively charged species.

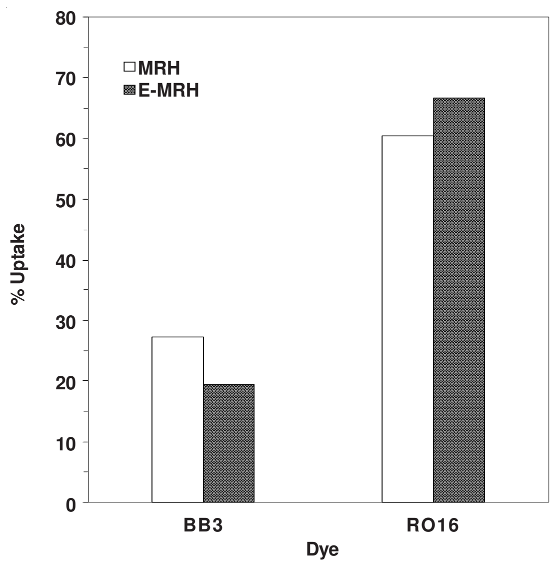


Fig. 3. Uptakes of basic blue 3 (BB3) and reactive orange 16 (RO16) by modified rice hull and esterified modified rice hull from binary dye solutions

When esterified natural rice hull was further modified by using ethylenediamine, an enhancement was observed in the sorption of both dyes. Aminated esterified natural rice hull in single dye solution showed a two-fold and fifteen-fold increase in the sorption of basic blue 3 and reactive orange 16, respectively compared to esterified natural rice hull. As in binary dye solution, a two-fold and five-fold increase in the sorption of basic blue 3 and reactive orange 16 was observed for the aminated esterified natural rice hull compared to esterified natural rice hull. This can be related to the poor and good leaving group characteristics of a molecule. As the OCH_3 group in esterified natural rice hull is a better leaving group compared to -OH group, this leads to a slightly greater extent of the amination process, thus resulting in higher uptake of dyes. The proposed reaction is shown as below:

$$S_h\text{-}CO(OCH_3) + H_2NCH_2CH_2NH_2 \rightarrow S_h\text{-}COHNCH_2CH_2NH_2 + CH_3OH \quad (3)$$

Acetylation of amino groups: Acetylation reaction reduces the number of positively charged sites on the biomass surface, therefore a reduction in the adsorption of negatively charged species would be anticipated[12]. The general reaction scheme of this treatment is:

$$RNH_2 + (CH_3CO)_2O \rightarrow RNHCOCH_3 + CH_3COOH \quad (4)$$

In order to elucidate the role of amine groups on the sorption of dyes, acetylation of the amine groups of the biosorbent was carried out. The proposed reaction is assumed to be as below:

$$S_h\text{-}COHNCH_2CH_2NH_2 + 2ClCH_2COONa \rightarrow S_h\text{-}COHNCH_2CH_2N(CH_2COOH)_2 + 2NaCl \quad (5)$$

The results show a decline in the uptake of reactive orange 16 in both single and binary dye solutions by the acetylated modified rice hull (A-MRH). This supports the postulate that sorption of reactive orange 16 by modified rice hull occurred through the interaction with amine groups. Similar result was reported in the uptake of Cr (VI), whereby upon acetylation, a reduction in Cr (VI) uptake was observed. The decrease in the uptake following acetylation was due to the involvement of -NH group in Cr (VI) binding[12].

The introduction of additional carboxyl groups on the acetylated modified rice hull (eqn. 5), explains the enhancement shown in basic blue 3 uptake, irrespective of single or binary dye solution. In order to show that the enhancement of basic blue 3 sorption was due to carboxyl groups, acidic methanol esterification of the chloroacetate modified modified rice hull was carried out. The esterified acetylated modified rice hull exhibited a decrease of about 12.4 % and 14.4 % in basic blue 3 uptake from single and binary dye solutions, respectively. This clearly indicates that the enhancement of basic blue 3 sorption is due to chloroacetate carboxyl groups. The proposed esterification reaction is shown as below:

$$S_h\text{-}COHNCH_2CH_2N(CH_2COOH)_2 + 2CH_3OH \rightarrow S_h\text{-}CO\text{-}HNCH_2CH_2N(CH_2COOCH_3)_2 + 2H_2O \quad (6)$$

Conclusion

The results from chemical modification of surface functional groups indicate that carboxyl groups were the major functional groups involved in the sorption of cationic species whereas sorption of anionic species occurred through the interaction with amine groups.

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