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Research article

Acid Dye Removal from Wastewaters using Rice Husk Ash Functionalized with Organic Amine Groups as Adsorbent

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Abstract: The use of rice husk ash functionalized with organic amine groups (RHA-NH_2) as an adsorbent for acid dye adsorption from wastewater was studied. The RHA–NH_2 was synthesized successfully via the grafting method using (3-Aminopropyl)-triethoxysilane (APTES) as amine group precursors. The synthesized adsorbents were characterized by using X-ray Powder Diffraction (XRD), Fourier Transform Infrared Spectroscopy (FTIR), N_2 adsorption-desorption analysis, and Scanning Electron Microscopy (SEM). The RHA-NH_2 exhibited an amorphous silica structure and possessed the organic amine group functionalized on the silica surface. The adsorption was studied by using Acid Blue 225 as an acid dye. The amount of acid dye remaining in the aqueous solution was measured by ultraviolet-visible spectrophotometer (UV-Vis). The RHA-NH_2 revealed a higher adsorption capacity (~82 mg/g) than RHA because the amine group enhanced the chemisorption energy.

Keywords: Adsorption; adsorbent; rice husk ash; acid dye, organic amine groups

1. Introduction

Acid dyes are used in many industries, such as textile and dye manufacturing. Water pollution caused by industrial wastewater has become a common problem in many countries [1]. Removing dyes from water is very important since color greatly affects water quality. Even very small concentrations of dyes (less than 1 mg L-1) in water are obvious and unpleasant. Moreover, these dyes also cause health problems such as allergic dermatitis, skin irritation, cancer, and human mutation [2].

Many methods, including physical and chemical technologies and biological processes, have been used to remove colored contaminants from wastewater and reduce environmental problems. The main treatment processes are oxidation [3], coagulation and flocculation [4], membrane separation [5] and adsorption [6]. Among these techniques of dye removal, adsorption is the most convenient and effective due to being less expensive than the others. This process transferred dyes from the water effluent to the adsorbents [7]. Over the past years, several adsorbents have been employed for dye removal, such as metal-organic frameworks (MOFs) [8], zeolite [9], and mesoporous silica [10]. However, those adsorbents are expensive, which results in high operating costs.

Recently, the low-cost adsorbent is interesting for use in adsorption and has a higher usage trend. Rice husk (RH) is an agricultural waste that produces about one-fifth of the world's annual rice production, or around 550 million metric tons [11]. It can be applied for several uses, such as energy production and as an adsorbent. RH has the potential to be accounted as an adsorbent because its main components are carbon and silica. In addition, rice husk ash (RHA) produced by heating rice husk at 700 °C possesses a higher amount of silica content (~84.3%) and has been used as an adsorbent for the removal of pollutants in wastewater such as heavy metals ions [12], and dye [13].

To enhance silica adsorbents' adsorption capacity and selectivity for substances, surface modification is useful by utilizing interactions between adsorbents and adsorbates. Therefore, the modified silica surface has been regarded as an effective adsorbent due to its high surface area, allowing many surface groups to be binding. The amine-functionalized silica (SiO_2-NH_2) has received substantial attention because the amine group positively impacts the performance of the adsorption systems of heavy metals, dyes, and other organic compounds [14-16]. In addition, there has been reported using silica or mesoporous silica modified with amine groups applied as adsorbent to remove the dye in aqueous [17,18]. However, preparing commercial silica or mesoporous silica modified with amine groups as adsorbents is quite complicated and expensive, resulting in high operating costs. Therefore, rice husk ash with high silica content is interesting to modify its surface with amine groups to enhance its adsorption performance and applied as a low-cost adsorbent.

This work aimed to study the use of amine-functionalized rice husk ash (RHA-NH_2) as adsorbents for removing acid dye from wastewater. Advanced analyses examined the textural and structural properties of RHA-NH_2 concerning adsorption. The adsorption performance of RHA–NH_2 for removal of acid dye was evaluated by studying the effects of types of adsorbents and initial concentration of acid dye.

2. Materials and Methods

2.1 Chemicals and reagents

3-Aminopropyltriethoxysilane (3-APTES) was purchased from Aldrich. Dichloromethane, Ethanol, HCl, and NaOH were purchased from RCL Labscan Limited. Acid Blue 225 was of commercial grade and obtained from Dystar Thai LTD. Its chemical structure is shown in Figure 1. All the above materials were used without further purification. Deionized water was used throughout this work.

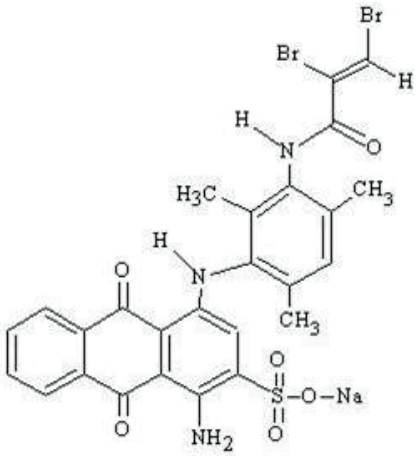

Figure 1. Chemical structure of Acid Blue 225

2.2 Preparation of RHA and RHA-NH_2

The rice husk was immersed in DI water, 1M HCl for 4 h, at a 40 g husk/L ratio. The husks were washed repeatedly with DI water and then dried in an oven at 110 °C for 2 days. Samples of rice husks were converted into adsorbent-rice husk ash (RHA) by heat-treating using ceramic crucibles at 700 °C for 6 h in a muffle furnace. The heated rice husks were crushed to obtain an approximate diameter of < 2mm.

The organic amine functionalized rice husk ash (RHA-NH_2) was prepared by mixing 5 g of RHA with 100 mL of dried toluene. The mixture was refluxed under a nitrogen atmosphere for two hours, and then 4 g of 3-aminopropyltriethoxysilane (3-APTES) was slowly added by a dropper. The mixture was refluxed again for 24 h. The solid was filtered, rinsed with ethanol and dichloromethane 3 times, and then dried at room temperature.

2.3 Characterization of adsorbents

The structures of RHA and RHA-NH_2 materials were analyzed by powder X-ray diffraction (XRD). The XRD analysis was performed on a Bruker D8 Advance X-ray diffractometer with Cu Kα radiation operated at 40 kV and 40 mA. The functional groups of these samples were analyzed FTIR. The FTIR spectra were obtained from a Spectrum 2000 FTIR spectrometer (Perkin-Elmer) with the usual KBr pellet method. The spectral range was chosen from 4000 to 400 cm^{-1}. N_2 adsorption-desorption measurements were carried out at 196 °C using a BEL Japan BELSORP-mini II instrument to determine the material's textural characteristics. SEM analyzed the morphology of these adsorbents. The SEM analysis was carried out using a scanning electron microscope (Model JEOL JEM-2010) at an electron acceleration voltage of 20 kV. Before scanning, the samples were coated with a thin layer of gold using a sputter coater to make them conductive.

2.4 Adsorption study

The adsorption of acid blue 225 over RHA and RHA-NH_2 was investigated in a batch system by adapting from the previous report of Mansoor *et al.* [18]. All batch experiments were carried out in 125 mL glass-stoppered Erlenmeyer flasks containing a fixed amount of adsorbent with 25 mL dye solution at a known initial concentration. The flasks were agitated at a constant speed of 150 rpm for one hour in an incubator shaker at 313 K. The initial dye concentrations were 20, 40, 60, 80, and 100 mg L^{-1}. The solid/liquid ratio was 0.025 g mL^{-1}. The residual amount of dye in each flask was investigated using a UV/VIS spectrophotometer (Model Hitachi-U2001). The amount of dye adsorbed per unit adsorbent (mg dye per g adsorbent) was calculated according to a mass balance on the dye concentration using Eq. (1):

$$q_e = \frac{(C_i - C_e)V}{m} \quad (1)$$

Where C_i is the initial dye concentration (mg L^{-1}), C_e is the equilibrium dye concentration in solution (mg L^{-1}), V is the volume of the solution (L), and m is the weight of adsorbent in g. All the experiments were performed in duplicate, and the average value from the results was taken.

3. Results and Discussion

3.1 Characterization of adsorbents

X-ray patterns for RHA and RHA-NH_2 materials are presented in Figure 2. The XRD patterns of these two materials displayed a broad peak at a diffraction angle (2θ) between 15-30° and a sharp peak at 27°, corresponding to amorphous silica and crystalline silica in quartz form, respectively [11]. However, the RHA-NH_2 materials exhibited a few lower XRD intensities (2θ= 27°) than primary RHA due to functionalized organic amine on RHA surfaces, resulting in a silica structure disorder.

Qualitative identification of functional groups was accomplished by FT-IR spectroscopy. Figure 3 shows the FT-IR spectrum of RHA and organic amine functionalized RHA materials over the 4000-400 cm^{-1} range. A broad band in the range of 3700-3010 cm^{-1} was seen, which can be attributed to the framework of Si-OH group interaction with the defect sites and adsorbed water molecules. The Si-OH peak appeared at about 3172 cm^{-1}. The asymmetric stretching vibrations of Si-O-Si were observed by the absorption bands at 1110 cm^{-1}. The functionalized RHA with amine groups (Figure 3b) generally shows a broad NH_2 stretching at 3424 cm^{-1}, an N-H deformation peak at 1628 cm^{-1}, and C-H stretching of methyl groups at 3064 cm^{-1} [16]. Moreover, the RHA-NH_2 exhibited decreasing peak intensity at 3172 cm^{-1}, implying the loss of surface silanol groups. These results confirmed that the organic amine functionalized on the RHA structure by replacing silanol groups, as seen in the synthesis pathway in Figure 4.

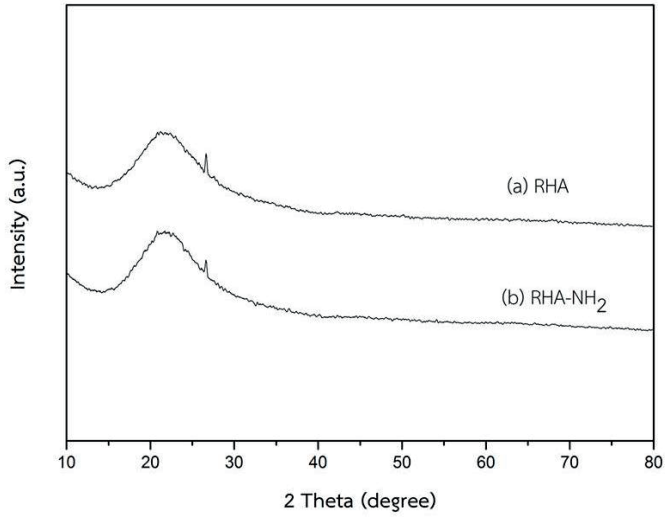

Figure 2. XRD pattern of (a) RHA and (b) RHA-NH_2

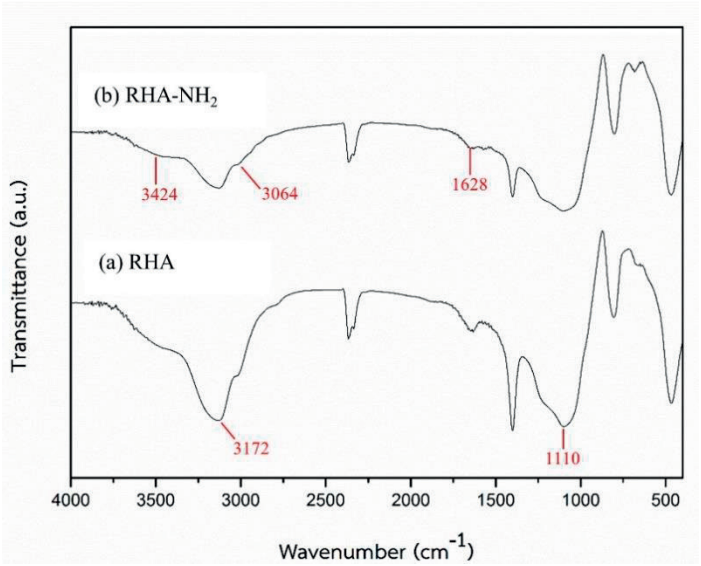

Figure 3. FT-IR spectra of (a) RHA and (b) RHA-NH_2

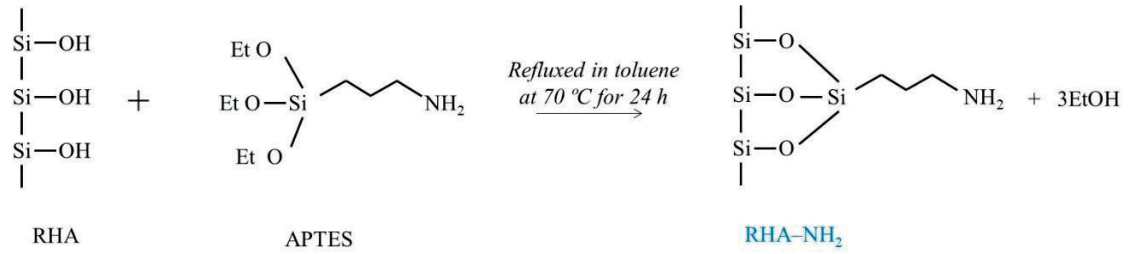

Figure 4. Functionalized with organic amine groups, the replacement of silanol groups on the RHA surface [11].

N_2 adsorption-desorption analysis, as shown in Table 1, determined the textural properties of synthesized materials. Based on its textural properties, RHA is suitable for adsorption due to its highly specific surface area, pore diameter, and pore volume. After the surface of RHA with amino silane was modified, the surface area, pore diameter, and pore volume were reduced compared to pristine RHA. It was probably due to the agglomeration of silica particles after modification of the RHA surface with amino silane. Additionally, the RHA-NH_2 materials exhibited an increase in CHN contents (Table 1). These results suggested that the aminosilane had been incorporated into the pore structure of RHA.

Table 1 Physicochemical properties of the adsorbents

Sample [a]	S_{BET} [b]	D_p [c]	V_t [d]	CHN contents [e]		
	(m^2 g^{-1})	(nm)	(cm^3 g^{-1})	% C	% H	% N
RHA	136	3.71	0.34	0.22 ± 0.01	0.22 ± 0.01	0.08 ± 0.01
RHA-NH_2	44	3.28	0.20	1.63 ± 0.14	0.42 ± 0.04	0.55 ± 0.04

[a] Dried samples
[b] BET surface area
[c] Pore diameter calculated using BJH method
[d] Total pore volume
[e] Determined by CHNS analyzer

SEM analyzed the surface morphology of RHA and RHA-NH2 adsorbents. The micrographs in Figures 5a and c represented the RHA surface in different magnifications. From the SEM images of the RHA adsorbent, it was found that hardly any residual fiber could be observed on its surface. It has been shown that the preparation of silica adsorbent from RHA that had been treated with strong acid and calcination at 700 °C should result in high-purity silica consistent with the CHN result (Table 1). In addition, the prepared adsorbent showed amorphous silica morphology consistent with the XRD result (Figure 2). Moreover, it revealed the agglomeration of silica particles and the surface roughness. However, as seen in Figure 5b and d, the morphology of RHA-NH_2 was quite similar to that of pristine RHA.

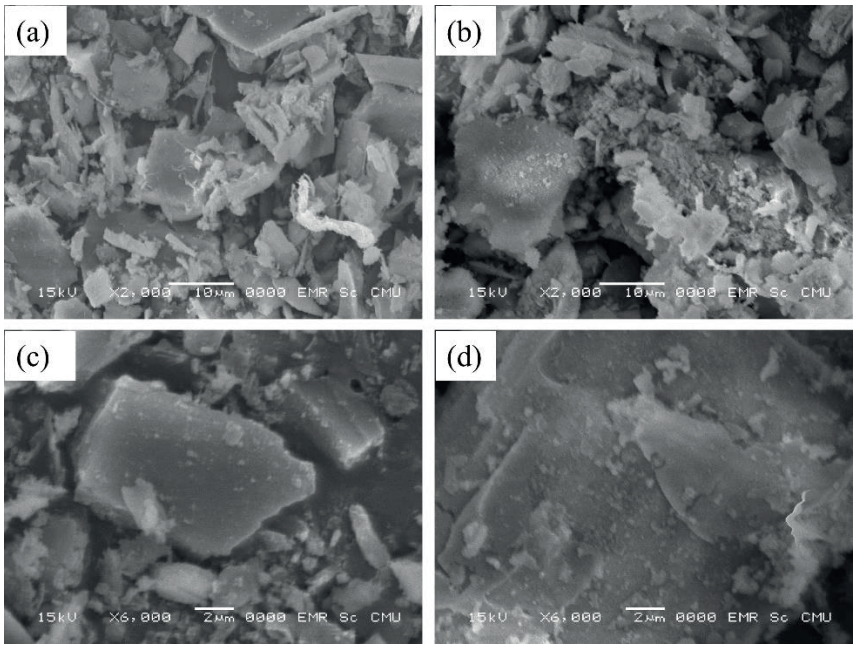

Figure 5. SEM image of (a, c) RHA and (b, d) RHA-NH_2 at a magnification of 2000x and 6000x, respectively.

3.2 Adsorption study

To evaluate the prepared adsorbents' efficacy, the acid dye's equilibrium adsorption was studied as a function of equilibrium concentration. The adsorption isotherms of acid dye on the RHA and RHA-NH_2 adsorbents are shown in Figure 6. By increasing the initial concentration of acid blue 225 from 20 to 100 mg L^{-1}, the adsorption capacity of both adsorbents grew dramatically with a steep slope, resulting in an enhanced rate of adsorption. However, the adsorption order regarding the amount adsorbed (mg/g adsorbent) on the adsorbents is RHA-NH_2 > RHA. The results of this study were consistent with the study of Apichat *et al.*, which reported on the removal of humic acid in wastewater by comparing the RHA and RHA-NH_2 adsorbents [11].

Moreover, RHA-NH_2 exhibited the highest adsorption capacity of the acid dye at 82 mg/g, which is 8 times greater than that of the RHA adsorbent. However, the RHA-NH_2**.** However, the RHA-NH_2 adsorbent showed a lower acid dye adsorption capacity than that of amine-functionalized mesoporous silica (~5-6 times), which was previously reported by Mansoor *et al.* [18]. Since the S_{BET} of RHA-NH_2 was lower than that of amine-functionalized mesoporous silica (~1,092 $m^2\ g^{-1}$), a low amount of organic amine functionalized onto the RHA surface was produced.

In general, the adsorption capacity depends on the chemical and physical properties of the surface of the adsorbent. The RHA with a pure silica surface does not provide strong adsorption sites to interact strongly with acid dyes. The hydroxyl groups on the silica surface fail to induce strong interactions with acid dyes. The adsorption capacity of acid dyes by RHA was enhanced through functionalization with amine groups. The higher adsorption capacity of RHA-NH_2 may be explained to proceed via electrostatic interaction and hydrogen bond formation between the surface of the adsorbent and acid dyes. The sulfonate groups of the acid dye were dissociated and converted to anionic ions in the aqueous solution. Also, in the presence of H^+, the amine groups of RHA-NH_2 become protonated. Then, electrostatic attraction could occur between the positively charged protonated amino groups on the silica surface ($–NH_3^+$) and the negatively charged sulfonate groups ($–SO_3^-$) of the acid dyes. Besides, a simulation of interactions between RHA-NH_2 and acid blue 225 is shown in Figure 7.

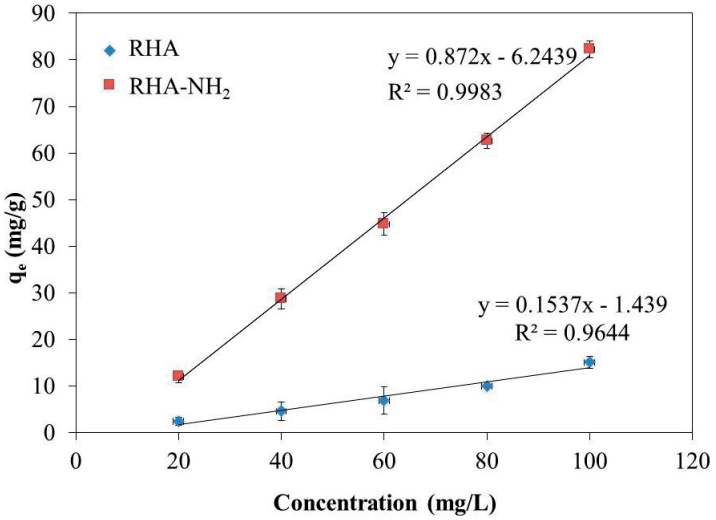

Figure 6. Adsorption isotherm for Acid Blue 225 adsorption on RHA and RHA-NH_2 (solid/liquid ratio = 0.025 g mL^{-1}, agitation speed = 150 rpm, time 60 min, temperature = 40 °C)

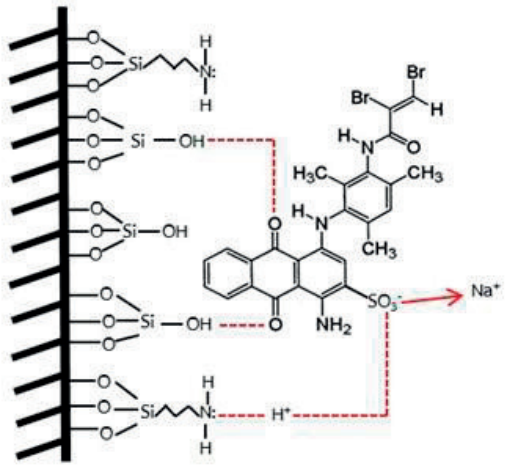

Figure 7. Interactions between Acid blue 225 and RHA-NH_2

4. Conclusions

The adsorption performances of acid dye by rice hush ash (RHA) and organic amine-functionalized rice husk ash (RHA-NH_2) materials were studied in the present work. The RHA-NH_2 could be prepared via the grafting method with 3-APTES. The characteristic results indicated that the RHA-NH_2 exhibited structural properties and morphology similar to pristine RHA. However, the textural properties of RHA-NH_2 were lower than that of RHA adsorbent. In addition, the obtained results showed that the acid dye adsorption capacity of RHA-NH_2 > RHA adsorbent (~ 8 times). Since the adsorption capacity of acid dye by the RHA-NH_2 was enhanced through functionalization with amine groups. Furthermore, the RHA-NH_2 adsorbent exhibited the highest adsorption capacity of the acid blue 225 at 82 mg/g.

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