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Characteristics and Rhodamine B Adsorption Ability of Modified Sepiolites

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Abstract: Sepiolite has been treated with ethanol under isothermal conditions and characterized by XRD, SEM, FT-IR, and BET measurements. The materials showed a typical lamellar structure and fibrous morphology. After treatment of sepiolite, the surface area of the solid is significantly improved while the material structure still remains. Both fresh and treated sepiolites were used as adsorbents for the adsorption of rhodamine B in water. In isothermal conditions, both samples exhibit a good ability to adsorb rhodamine B in water. Experimental results indicate that the adsorption of rhodamine B for sepiolite was fitted to the Langmuir and Freundlich adsorption models. The treated sepiolite showed a higher adsorption capacity than does the fresh sample.

Keywords: Sepiolite, Adsorbent, rhodamine B, Langmuir, Freundlich.

1. Introduction

A vast amount of dyes is annually discharged as effluent mainly by paint and textile industries [1, 2]. The most hazardous issue of the dyes is rather toxic and even carcinogenic to humans and environments as well [3]. Thus, the removal of the industrial dyes is the most global concerning problems nowadays. Because of environmental legislations, industrial concerns are forced to treat dyes in wastewater before discharging into water streams. Most of the commercial dyes are of synthetic organic compounds consisting of aromatic structures that are stable in water [1, 4, 5]. These dyes may be treated by the photodegradation or advanced oxidation process [2, 4]. Photosynthesis was known as a promising way to eliminate these toxic compounds but has a limitation due to inhibition of sunlight penetration; while the advanced oxidation process usually requires to use expensive oxidants such as H_2O_2 [2, 3]. Recently, scientists are therefore focused on the removal of dye from effluent using the adsorption methods, which do not generate secondary harmful substances resulting from the incomplete oxidation of dyes [5-10]. Activated carbon, clays, mesoporous silicas are

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the popular adsorbents for the collection of toxic compounds in water [1, 11]. Thus, there is much interest in the development of new adsorbents for the treatment of industrial wastes.

Sepiolite is a natural hydrated magnesium silicate with a wide range of industrial applications derived mainly from its adsorptive properties. It has a fibrous structure formed by an alteration of blocks and channels that grow up in the fiber direction. Each block is constructed of two tetrahedral silica sheets with a central magnesia sheet. Adsorption ability of sepiolite is related to the presence of active adsorption centers on the external layers. Indeed, oxygen atoms are in the tetrahedral sheet, water molecules are coordinated with the Mg^{2+} ions at the edge of the structure, and silanol groups are formed through the Si—O—Si bonds [12-14]. Thus, sepiolite is widely applied in many fields of adsorption including the removal of metals [15], dyes [5, 16], organic molecules [17]...

The purpose of this work is to examine the adsorption ability of fresh and modified sepiolite in removing rhodamine B from aqueous solution.

2. Experimental Section

2.1. Sepiolite

Sepiolite was purchased from Fuka Chemical Company and used without further purification. For the treated sample, 1.00 g of sepiolite powder was added into a Teflon-lined stainless steel autoclave of 100 ml capacity in which 80 mL of ethanol solution was added. The reaction solution was stirred, sealed and maintained at 80 ^{o}C for 72 h, then air-cooled to room temperature. The precipitate was filtered, and dried in air at 80^{o}C.

Powder X-ray diffraction (XRD) patterns were recorded on a D8 Advance-Bruker instrument using CuK_{α} radiation (λ = 1.59 Å). Scanning Electron Microscopy (SEM) micrograph was shot by a Hitachi S-4500 (Japan) with the magnification of 200,000 times. Fourier transform infrared (FT-IR) spectra were obtained in 4000 – 400 cm^{-1} range on a FT/IR spectrometer (DX-Perkin Elmer, USA).The specific surface areas were calculated by the Brunauer–Emmett–Teller (BET) method, and the pore size distribution and total pore volume were determined by the Brunauer–Joyner–Hallenda (BJH) method using a an Autochem II 2920 (USA).

2.2. Adsorption of rhodamine B

Rhodamine B was used as a model dye purchasing from Sigma-Aldrich. Adsorption of rhodamine B was carried out by a batch technique to obtain equilibrium data. For isotherm studies, adsorption experiments were carried out by adding 50 mg of the sepiolite sample to 40 mL of rhodamine B solution of varying concentrations in a series of 100 mL flasks. Each flask was filled with 50 mL of a dye solution of varying concentrations. The flask was shaken for 60 minutes and then decanted for another 60 minutes to reach equilibrium. The suspension was filtered and the concentration of the dye in the filtrated solution was spectrophotometrically analyzed using a CARY 100 UV-VIS Spectrophotometer. The measurements were made at the wavelength of λ= 553 nm. Blank tests containing no dye were used for each series of experiments.

3. Results and Discussion

3.1 Catalyst Characterization

The phase structure of sepiolites was examined by X-ray diffraction method. Figure 1 shows the XRD pattern of both fresh and modified samples. The 2-theta values observed at 2-theta of 7.3, 19.8, 20.6, 23.8, 26.7, 28.0, 34.9, 36.8 and 39.9° were matched with the data of JCPDS Card No. 00-013-0595 in the library [13, 17]. It is noted the most peak intensity at 2-theta of 7.34° indexed to the (110) plane is usually used as an indication of the state of crystallinity in the sepiolite. Since this reflection line was the most intense feature in the diffraction pattern of sepiolite after treatment indicating no structural changes and a high crystallinity of the treated sepiolite [13, 14].

Surface properties and chemical bonding behavior of the sepiolite are investigated using FT-IR technique. Figure 2A represents the IR spectrum of fresh sepiolite with the band of the triple bridge group of trioctahedral Mg_3OH at 3576 cm^{-1} and the broaden signal of the structurally bound water at 34330 cm^{-1}. The OH-bending mode at 1678 cm^{-1} is associated with water molecules in channels [14]. A set of bands at 1215, 1026 and 976 cm^{-1} is assigned to the Si-O lattice vibrations. In other context, the basal plane of the tetrahedral units exhibits the Si-O-Si plane vibrations at 1014 and 474 cm^{-1} and Mg_3OH bending vibration at 647 cm^{-1} [5, 12, 14].

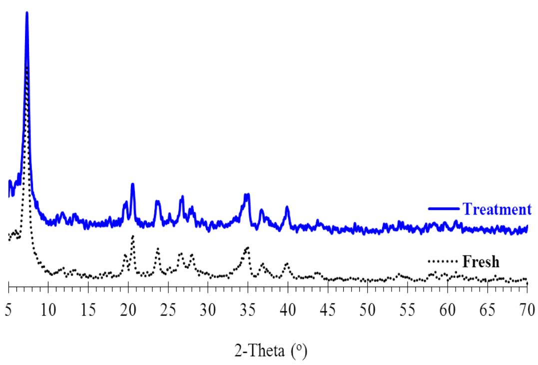


Figure 1. XRD patterns for fresh and treated sepiolite sample.

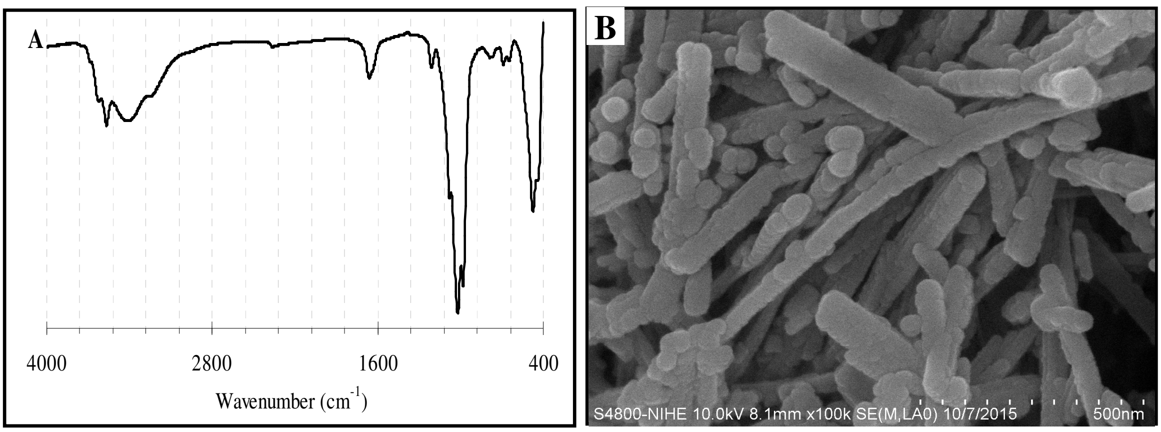
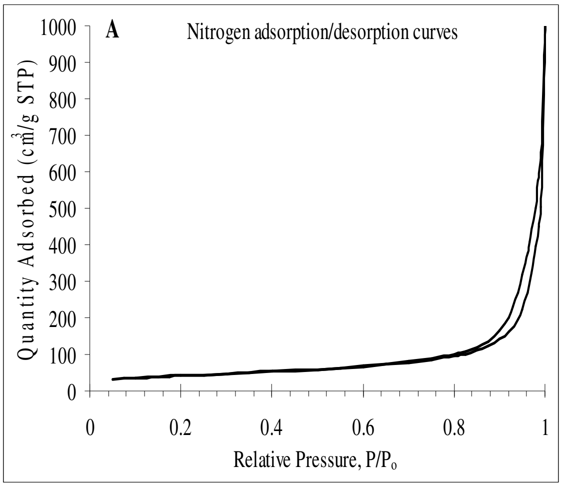


Figure 2. FI-IR spectrum (A) and SEM micrograph (B) of fresh sepiolite sample.

Since sepiolite IR spectrum indicates the presence of octahedral Mg–(OH) groups and, coordination water, SEM technique would provide the morphology of sepiolite. Figure 2B shows the fibrous morphology of sepiolite. It is observed a more randomly oriented structure resulting from mixing of the fiber bundles, which leads to form a large external surface area. An average length of fibers is about 500 nm for fresh sepiolite. The diameter of these fibers is about 50-70 nm.

The disordered arrangements of such nanofibers make the material become more porosity. Indeed, nitrogen sorption measurement reveals the shape of the isotherm close to a type II isotherm with a hysteresis loop type H_3 (IUPAC). The average pore radius was estimated from the BET surface area and total pore volume assuming an open-ended cylindrical pore model without pore networks (Fig. 3) [18]. The BET surface area (143.8 m^2/g) of the fresh sepiolite is much lower than that (220.1 m^2/g) of the modified sepiolite. The average pore size of the fresh sepiolite estimated from the BJH (Barret–Joymer–Halenda) method is 9.15 nm and another pore width is around 39.4 nm. Another pore size distribution position is in the broad range of 20-120 nm. These large pores results from the inter-aggregation of uniform fibers [13,16]. Furthermore, Figure 3 also indicates that the isothermal curve is likely plateau in the relative pressure range of 0-0.5 and the pore size distribution curve turns up at the initial stage (< 2 nm), which both also indicate the presence of micropores in the sepiolite [13, 14, 18]. Thus, we are expected that the sepiolite with high porosity would be excellent candidate adsorbent for the collection of dyes.



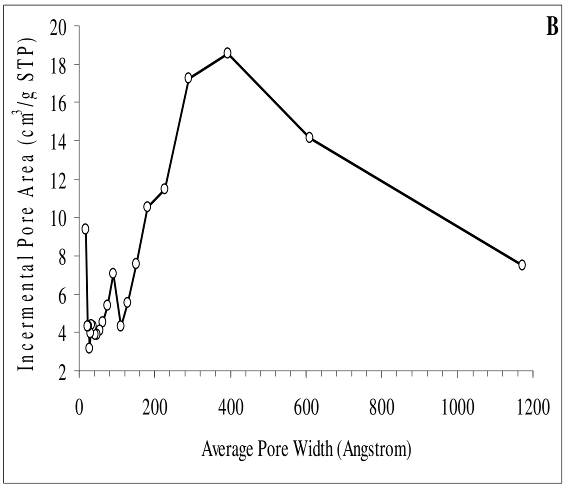


Figure 3. Nitrogen adsorption/desorption isotherm (A) and BJH pore size distribution (B) of sepiolite.

3.2. Absorption studies

The equilibrium adsorption of rhodamine B on sepiolites was examined at room temperature and the results are shown Figure 4A and 5A. In the present work, the adsorption capacity of rhodamine B molecules adsorbed per gram adsorbent (mg/g) was calculated using the equation $q_e = \frac{(C_o - C_e)V}{m}$, where q_e is the equilibrium concentration of rhodamine B on the adsorbent (mg/g), C_o the initial concentration of the rhodamine B solution (mg/L), C_e the equilibrium concentration of the rhodamine B solution (mg/L), m the mass of adsorbent (g), V the volume of rhodamine B solution (L). The adsorption isotherm indicates how the adsorption molecules distribute between the liquid phase and the solid phase when the adsorption process approaches an equilibrium state [5, 17, 20]. The analysis of the isotherm data by fitting them to different isotherm models is an important step to find the suitable model [21-23]. There are several isotherm equations available for analyzing experimental adsorption equilibrium data. In this study, the equilibrium experimental data for adsorbed rhodamine B on sepiolite sample were analyzed using the Langmuir and Freundlich models.

a) Langmuir isotherm model: Langmuir adsorption model can be represented as the equation: $C_e/q_e = C_e/q_{max} + 1/K_L q_{max}$, where C_e is the equilibrium concentration of RhB dye (mg/L), qe is the quantity of RhB dye adsorbed onto the adsorbent at equilibrium (mg/g), q_{max} is the maximum monolayer adsorption capacity of adsorbent (mg/g) and K_L is the Langmuir adsorption constant (L/mg) (Fig. 4). The plot of C_e/q_e against C_e gives a straight line with a slope and intercept of $1/q_{max}$ and $1/q_{max}K_L$ respectively (Fig. 4B). From these data, the maximal adsorption quantity and the Langmuir adsorption constant for each sample were calculated in Table 1.

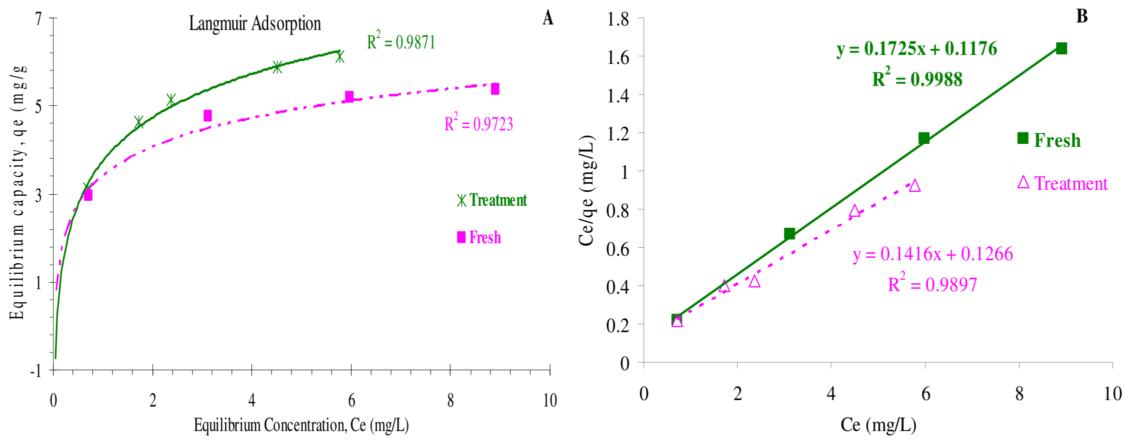


Figure 4. Variation of equilibrium amount adsorbed, *q*, with equilibrium dye concentration according to Langmuir model.

b) Freundlich isotherm model: Freundlich adsorption model can be represented as the equation: $\log q_e = \log K_F + (1/n)\log C_e$, where q_e is the quantity of RhB adsorbed at equilibrium (mg/g), C_e is the concentration (mg/L) of RhB in solution at equilibrium; K_F and *n* are Freundlich constants incorporating the factors affecting the adsorption capacity and adsorption intensity, respectively (Fig. 5). The plot of log q_e against log C_e gives a linear graph with slope 1/n and intercept log K_F from which *n* and K_F can be calculated respectively in Figure 5B and Table 1.

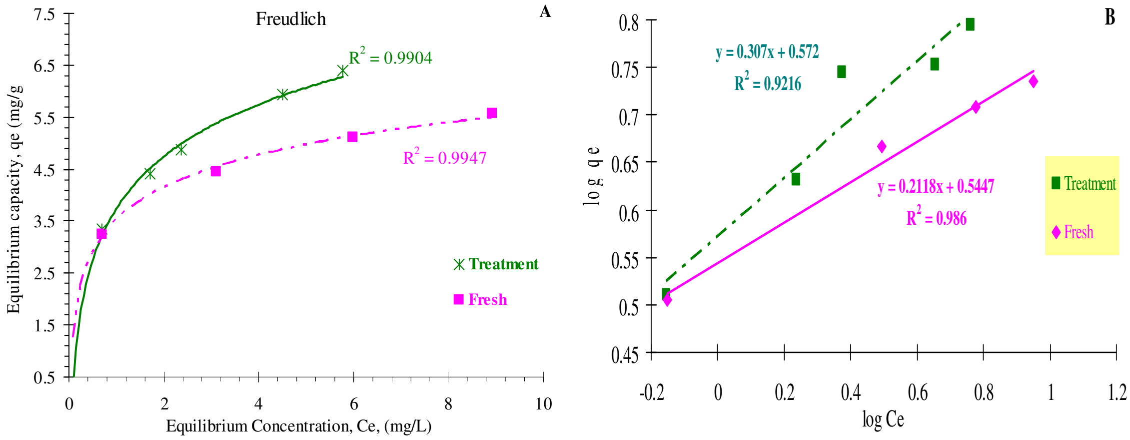


Figure 5. Freundlich isotherm (A) and plots of log q_e against log Ce (B) according to Freundlich model

As seen in Figure 4 and 5, both the Langmuir and Freundlich models were adopted to describe the equilibrium data via a linear regression. The Langmuir model is shown to be more suitable for the equilibrium data since $R^2 > 0.99$ (Fig. 4B and 5B) [5,6]. The results indicated that sepiolite would be good adsorbent or catalyst support for the removal treatment of organic dyes [1, 16, 17, 24]. The adsorption capacity of the modified sepiolite is higher than that of fresh sample. The treatment of sepiolite gives rise to the removals of impurities on the surface.

Table 1: Parameters from the Langmuir and Freundlich adsorption isotherm models

Adsorbents	Langmuir Model		Freundlich model	
	q_{max} (mg/g)	K_L (mg/L)	n	K_F
Fresh sepiolite	5.979	1.467	4.721	3.508
Treated sepiolite	7.062	1.118	3.257	3.732

4. Conclusions

Sepiolite was modified by the hydrothermal treatment in autoclave with ethanol. This treatment provides the possibility to obtain a higher surface area without destruction of sepiolite structure. This situation leads to the preparation of materials with higher surface area and nanofibers. Both fresh and treated samples are potential adsorbents of rhodamine B in water, but the treated sepiolite gave a higher adsorption capacity. The q_{max} for the treated sample is 7.061 mg/g according to Langmuir adsorption. The adsorption of rhodamine B on sepiolite was found to fit with the Langmuir and Freundlich model adsorption models.

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Đặc trưng và khả năng hấp phụ rhodamine B của sepiolite biến tính

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Tóm tắt: Sepiolite được xử lý bằng etanol dưới điều kiện đẳng nhiệt và được đặc trưng bằng các phương pháp vật lý như XRD, SEM, FT-IR và BET. Vật liệu sepiolite có cấu trúc lớp. Sau khi xử lí, diện tích bề mặt của mẫu sepiolite tăng lên đáng kể trong khi cấu trúc vật liệu vẫn được giữ nguyên. Cả mẫu sepiolite ban đầu và mẫu biến tính đều là chất hấp phụ tốt đối với quá trình hấp phụ rhodamine B trong nước. Kết quả thực nghiệm cho thấy sự hấp phụ rhodamine B trên sepiolite phù hợp với mô hình hấp phụ đẳng nhiệt Langmuir và Freundlich. Mẫu sepiolite biến tính có tải trọng hấp phụ cao hơn so với mẫu sepiolite ban đầu.

Từ khóa: Sepiolite, chất hấp phụ, rhodamine B, Langmuir, Freundlich.