ORIGINAL PAPER

Adsorption Isotherms for Bleaching Soybean Oil with Activated Attapulgite

Yuanfa Liu · Jianhua Huang · Xingguo Wang

Abstract Activated attapulgite was characterized and used as bleaching clay (adsorbent) for soybean oil. Adsorption isotherms for bleaching soybean oil were determined to investigate the applicability of the Langmuir and Freundlich equations and to elucidate the adsorption characteristics of oil on activated attapulgite. The Freundlich model was found to provide a better fit with the experimental data than the Langmuir model. The larger Freundlich constant, K_F at higher temperature indicated more effective adsorption. The heat evolved for oil bleaching increased as the levels of activated attapulgite increased from 0.5 to 3%, due to the increase in adsorptive sites with increasing attapulgite levels as well as multilayer adsorption driven by van der Waals' forces at smaller amounts of adsorbents. There are enough adsorptive sites with 3% attapulgite to adsorb the pigments associated with soybean oil bleaching. The amount of attapulgite has no effect on ΔH_a when it is >3%, and ΔH_a is about 32 kJ/mol.

Keywords Soybean oil · Attapulgite · Bleaching · Adsorption isotherms

Introduction

Bleaching is an important edible oil refining process. A number of factors affect the performance of the bleaching procedure, among which the bleaching adsorbent plays a central role. Activated clay is preferred to other adsorbents such as activated carbon- and silica-based products due to its relatively high performance and low cost. After bleaching the oil becomes brighter, less colored and more stable. Researchers have recently become interested in the importance and the complexity of the edible oil bleaching process [1–3].

There are seven major clay groups and at least 33 different specific clay minerals used as adsorbents for oil bleaching [4]. Bentonite is the bleaching clay most commonly used and studied in the oil industry. However, there are other clays that are not well documented in the literature. Attapulgite is a chain-layer magnesium–aluminum silicate mineral that has desirable properties such as high porosity and large specific surface area, it has been used as an absorbent by various industries [5–7]. However, other than our reported work [8] little has been reported on the use of attapulgite as bleaching oil. Acid activation is typically employed to modify the surface area, pore size distribution and surface acidity of clay-based adsorbents, thus increasing the adsorptive powers of natural clays [9]. Because bentonite requires a relatively intensive acid treatment to achieve adequate activity, extensive leaching takes place during the activation process. Excess residual acid and acidic salts formed during activation must be washed off and separated from the product by filtration, and the resulting leachate waste stream must be treated or otherwise disposed of in an environmentally acceptable manner. In contrast, attapulgite is highly susceptible to acid, and hence consumes substantially less acid and time in the acid activation step. Consequently, residual acid levels are so low that subsequent washing and filtration are in many cases unnecessary [10, 11]. Attapulgite is normally heated at a

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relatively low temperature after acid activation to attain greater adsorption ability. Due to its clearly advantageous processing characteristics, attapulgite is widely used in the oil bleaching process and plays a significant commercial role as a bleaching clay in China.

Adsorption equilibrium is the most fundamental property of the adsorbate–adsorbent interaction. Therefore, the theoretical and empirical models that describe reversible adsorption have been developed on the basis of a thermodynamic equilibrium [12]. The Langmuir and Freundlich equations, shown below, are models that are widely used to describe vegetable oil bleaching by adsorption:

Freundlich: $q_e = KC^{1/n} \leftrightarrow \log q_e = \log K + 1/n \log C$ (1)

Langmuir:

$$\frac{q}{q_{max}} = \frac{K'C}{1 + K'C} \leftrightarrow \frac{1}{q} = \frac{1}{q_{max}} + \frac{1}{K'q_{max}}\frac{1}{C} \leftrightarrow \frac{C}{q}$$
$$= \frac{C}{q_{max}} + \frac{1}{K'q_{max}}$$ (2)

where C is the residual concentration of the substance in the solution at equilibrium, q_e is the amount of substance adsorbed per mass of adsorbent at equilibrium, q_{max} is the adsorbate surface concentration when all available adsorption sites are occupied, the maximal concentration of solid-phase solute, K and n are Freundlich constants, and K' is the Langmuir constant.

For the oil bleaching process, the Freundlich and Langmuir equations are always expressed as Eqs. 3 and 4, which are derived from Eqs. 1 and 2 [12]:

Freundlich: $\log \frac{X}{m} = \log K + N \log C$ (3)

Langmuir: $\frac{C}{X/m} = \frac{1}{a} + \left(\frac{b}{a}\right)C$ (4)

where X is the amount of substance adsorbed, m is the amount of adsorbent, K and N are Freundlich constants, and a and b are Langmuir constants.

Since absorbance measurements are taken in all experiments for the bleaching process, the amount of pigment adsorbed (X) and the residual amount at equilibrium (X_e) can be obtained from Eqs. 5 and 6 as follows:

$$X = \frac{A_0 - A_e}{A_0}$$ (5)

$$X_e = \frac{A_e}{A_0}$$ (6)

where A_0 is the absorbance of the neutralized oil at 475 nm and A_e is the absorbance of the oil at equilibrium at 475 nm. Thus, by writing X_e instead of the residual

concentration of substance in the solution at equilibrium, C, Eqs. 3 and 4 can be rearranged as follows [13, 14]:

$$\log(X/m) = K + N \log X_e$$ (7)

$$\frac{X_e}{X/m} = \frac{1}{a} + \left(\frac{b}{a}\right)X_e$$ (8)

K and N are the Freundlich constants related to adsorption capacity and adsorption intensity, and a and b are the Langmuir constants. K is a constant for the system related to bonding energy, which can be defined as an adsorption or distribution coefficient describing the amount of adsorbate adsorbed onto attapulgite for the unit equilibrium concentration. N is related to the magnitude of the adsorption driving force and to the adsorbent site energy distribution [15]. Both of the parameters K and N can be calculated by plotting $\log(X/m)$ versus $\log X_e$. The values of K and N can be obtained from the intercept on the y-axis and the slope of the linear line.

In this paper, we characterize the natural attapulgite and its activated product, determine the applicability of the Langmuir and Freundlich equations to adsorption isotherms for bleaching soybean oil with activated attapulgite,

natural attapulgite (20000×)
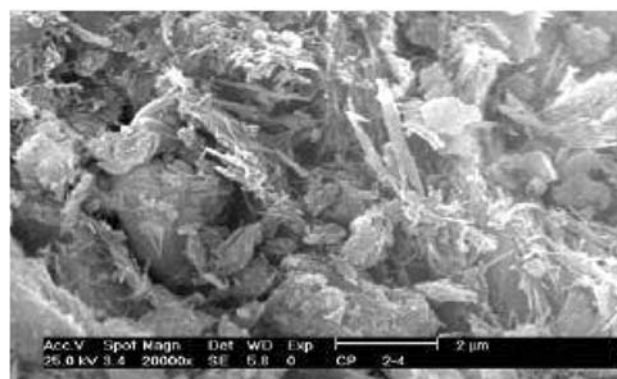
activated attapulgite (20000×)

Fig. 1 SEM of natural attapulgite and its final activated product

and elucidate the forces between the adsorbent and the adsorbate by calculating the heat evolved during the bleaching process.
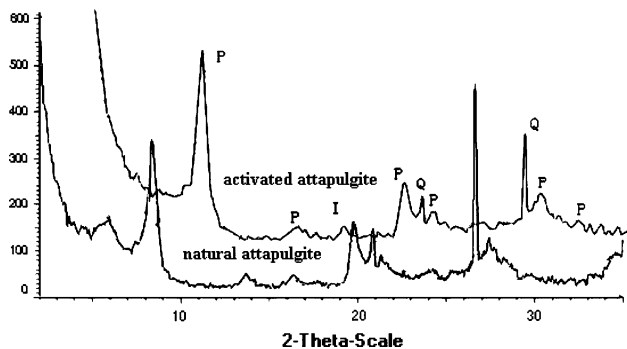

Fig. 2 XRD spectra of the natural, acid-activated product and the final activated product. *P*, attapulgite; *I*, illite; *Q*, quartz
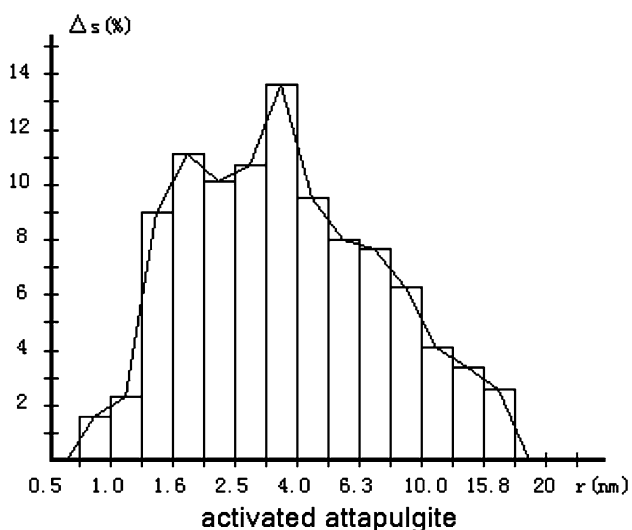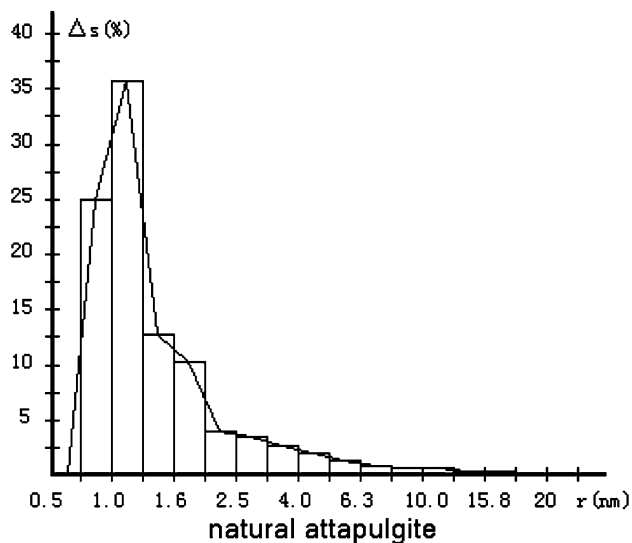

natural attapulgite

activated attapulgite

Fig. 3 Pore size distributions of the natural attapulgite and the final activated attapulgite product

Materials and Methods

Materials and Characterization

Alkali-refined soybean oil was supplied by East-Ocean Cereals & Oils Co. Ltd. (Zhang Jia-Gang, China), and natural attapulgite clay was supplied by OilBetter Clay Material Co. (China). Attapulgite clay (150 g) was treated with 1N HCl (50 ml) for 3 h and then heated at 473 K (200 °C) for 12 h to get the activated attapulgite product. Preliminary investigations showed that there was no difference between the properties of oils bleached by the activated clays with and without washing. All other chemicals were of analytical grade.

Scanning electron microscope (SEM) analyses of the surfaces of natural attapulgite and its final activated products were performed with an XL-30 SEM (Philips, Eindhoven, The Netherlands). The surface area and pore size distribution of the adsorbents was obtained from the N_2/77 K adsorption isotherms by applying the BET method using an ST-2000B surface area and pore size analyzer (Beijing Puqi Institute of Analysis, China). Basal spacing was determined using a Bruker D8S AXS X-ray diffractometer (Karlsruhe, Germany). The attapulgite samples were prepared and characterized in triplicate.

Oil Bleaching Process

Alkali-refined soybean oil (36 g) was stirred and heated to a constant temperature [353 K (80 °C), 368 K (95 °C), 383 K (100 °C)] within 5 min at 18 mmHg in a three-necked flask. When the desired temperature was reached, the final activated attapulgite clay was added to the heated
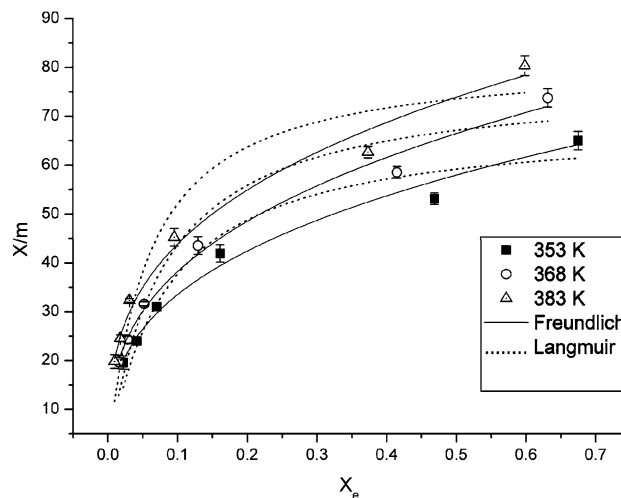

Fig. 4 Adsorption isotherm of oil bleaching (stirred at 250 rpm, vacuum pressure at 40 mbar, heated at 110 ± 1 for 40 min) by activated attapulgite. X/m, the relative amount of pigment adsorbed on the adsorbent; X_e, the residual relative amount of pigment at equilibrium

Table 1 Freundlich constants and Langmuir constants for oil bleaching at different temperatures

Temperature	Freundlich constants[a]			Langmuir constants[b]		
	$1/n$	K_F	R^{2c}	a	b ($\times 10^{-3}$)	R^{2c}
353 K (80 °C)	0.341 ± 0.014	1.87 ± 0.09	0.9889	69.0 ± 2.9	82.8 ± 4.1	0.9833
368 K (95 °C)	0.344 ± 0.010	1.93 ± 0.06	0.9937	77.5 ± 2.1	77.5 ± 2.7	0.9784
383 K (100 °C)	0.322 ± 0.009	1.97 ± 0.07	0.9900	82.0 ± 2.0	57.4 ± 1.9	0.9776

[a] Freundlich isotherm equation: $\log (X/m) = K + N \log X_e$

[b] Langmuir isotherm equation: $\frac{X_e}{X/m} = \frac{1}{a} + \left(\frac{b}{a}\right) X_e$

[c] Correlation coefficient

oil, and the mixture stirred with a mechanical stirrer at a constant speed (250 rpm). After bleaching for 40 min, the mixture was rapidly cooled to 303 K (30 °C) under vacuum, and then filtered through a Buchner funnel. The A_e and A_0 values were measured with a UV spectrophotometer [UV-2000 Visible; Unico (Shanghai, China) Instruments Co., Ltd.] at 475 nm to determine the relative amount (X) and the residual relative amount at equilibrium (X_e) calculated according to Eqs. 5 and 6. The filtered oil was diluted with hexane as needed to ensure absorbance values of 0.1–0.8. Each experiment was repeated three times.

Results and Discussion

Characterization of Natural Attapulgite and its Activated Product

The natural and activated attapulgite were characterized three times to determine changes from the activating process. The morphologies of the natural and activated attapulgite products as observed by SEM are shown in Fig. 1. SEM examination revealed that the surface morphology of activated attapulgite is different from that of the natural attapulgite, which showed loose aggregates with porous structure. After activation, the fibers were accumulated and shortened bundles consisting of many fibers and some circular aggregates of clay fibers were found. As a result of variations caused by the activation process of attapulgite, the pore spaces of the attapulgite consisted of smaller pores between the individual fibers and larger pores between the bundles of fibers.

Figure 2 shows the XRD patterns of natural attapulgite and the final activated attapulgite product. The interlayer distance of the peak observed at $2\theta = 8.61°$ ($d_{110} = 1.03$ nm) was attributed to the basal space of the attapulgite framework. The peaks at $2\theta = 13.971°$, 16.572°, 19.88° and 21.064° represented the Si–O–Si crystalline layers of the attapulgite. Quartz impurities were also found, as shown by its most intense peak situated at $2\theta = 26.881°(d = 0.33$ nm) and its peak at

$2\theta = 20.8°$. The amount of different samples for basal spacing determination was not a constant. To determine the content of each component, a comparison was made between the intensities of the peaks. After activation, the peaks corresponding to the attapulgite framework ($2\theta = 8.61°$) showed much higher intensities than those corresponding to the quartz. Low acid activation dissolved the carbonate in the natural attapulgite but the quartz impurities were not dissolved by the acid. Based on the ratios of the intensities of the peaks for attapulgite and quartz, it was clear that there was a higher content of attapulgite in the activated product than in the natural attapulgite, indicating that the low acid activation didn't dissolve the attapulgite.

The pore size distribution of the attapulgite clay was changed during the activating process, as shown in Fig. 3. More mesopores and fewer micropores of attapulgite were found after the activation process. The activated attapulgite product exhibited a wider pore distribution (1.2–18 nm), whereas natural attapulgite had more micropores that were smaller than 1.5 nm. The surface areas of the natural attapulgite and the activated attapulgite product were also evaluated in order to characterize the change in the surface area during the activating process. The surface areas of the natural attapulgite and the activated attapulgite product
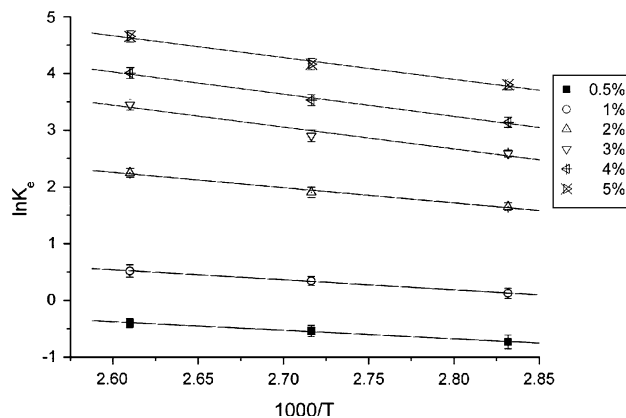

Fig. 5 Plot of ln X_e versus 1,000/T

Table 2 Thermodynamic parameters for soybean oil bleaching with different amounts of activated attapulgite

Amount of adsorbent (%)	0.5	1.0	2.0	3.0	4.0	5.0
ΔH_a (kJ/mol)	12.47 ± 0.88	14.72 ± 0.61	22.42 ± 2.41	32.07 ± 5.85	32.53 ± 2.56	31.89 ± 2.48
ΔS (J/mol K)	29.28 ± 2.39	42.76 ± 1.66	77.06 ± 6.57	112.0 ± 15.92	118.1 ± 6.96	121.7 ± 9.46

Thermodynamic parameters were determined using the following equation: $\ln K_e = -\frac{\Delta H_a}{RT} + \frac{\Delta S}{R}$

were 288 ± 9 m^2/g and 183 ± 7 m^2/g, respectively. The pore size distribution of the attapulgite was more important than the surface area for oil bleaching. The more pores of size 0.8–3.2 nm, the more effectively the oil was bleached [8]. Obviously, changing the pore distribution during the activation process of attapulgite is useful for oil bleaching.

Adsorption Isotherms

The pigments in the oil were decreased dramatically after bleaching with the activated attapulgite; the highly effective adsorption was caused by its high surface area, its appropriate pore size distribution, and its surface acidity [9]. Oxidation may be another reason for the reduction of the red color [16, 17]. Figure 4 shows the adsorption isotherm plots of oil bleached by activated attapulgite at three different temperatures. X_e (the residual relative amount of pigment at equilibrium) values decreased with increasing temperature, indicating that the bleaching process is endothermic. The Freundlich isotherm model was based on the assumption that adsorption is dependent on the energy of the adsorption sites, while the Langmuir isotherm model assumes a homogeneous surface. The experimental isotherm data fit the Freundlich equation (Eq. 7) better than the Langmuir equation (Eq. 8), when the experimental data was fitted to the two models. Similarly, the Freundlich equation was found to be more applicable than the Langmuir equation for the adsorption of carotene on attapulgite in rapeseed and soybean oil bleaching [18]. The parameters of the fitted curves are summarized in Table 1. The parameters of the Freundlich equation, K and N, are relative indicators of adsorption capacity and energy of adsorption, respectively. The term N expresses the affinity between the adsorbate and the adsorbents. As seen from Table 1, the value of N ranged between 0.1 and 1, indicating a favorable adsorption. The larger K values at higher temperatures indicated more effective adsorption [19].

Thermodynamic Parameters of Adsorption

The thermodynamic parameters can be calculated by the following van't Hoff equilibrium equation:

$$\ln K_e = -\frac{\Delta H_a}{RT} + \frac{\Delta S}{R} \qquad (9)$$

where T is the temperature, ΔH_a is the enthalpy of adsorption, ΔS is the entropy of adsorption, and R and K_e are constants. The equilibrium constant, K_e, was obtained from the equation $K_e = (A_0 - A_e)/A_e$.

ΔH_a and ΔS were calculated from the slope and the intercept of the van't Hoff equilibrium by plotting of $\ln K_e$ versus $1/T$ (Fig. 5). Table 2 represents the thermodynamic parameters for soybean oil bleaching by activated attapulgite. Obviously, the bleaching of soybean oil by activated attapulgite is entropically driven. The positive values of enthalpy indicate that the oil bleaching process is endothermic. The energy of adsorption of different forces. In this study, the enthalpy of soybean oil bleaching (ΔH_a) increases with the addition of adsorbent (from 0.5 to 3.0%) because of the increase in the number of activation adsorption sites with increasing amount of adsorbent. Multilayer adsorption, which occurs at small amounts of adsorbent, is a physical process involving van der Waals' forces. Thus, the heat evolved during adsorption was lower when the amount of adsorbent was 0.5–2%. Further increasing the attapulgite amount has no effect on ΔH_a when the amount of attapulgite is more than 3%, and ΔH_a is about 32 kJ/mol. The protonated S–OH$_2$ structure of activated attapulgite can serve as an effective binding site that permits the attachment of pigments in the soybean oil [20]. The use of 3% attapulgite is sufficient to adsorb the pigments for the soybean oil bleaching. The positive values of entropy suggest increased randomness at the solid–solution interface during the oil bleaching process.

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