

## Effective NH<sub>2</sub>-grafting on attapulgite surfaces for adsorption of reactive dyes

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### ABSTRACT

The amine moiety has an important function in many applications, including, adsorption, catalysis, electrochemistry, chromatography, and nanocomposite materials. We developed an effective adsorbent for aqueous reactive dye removal by modifying attapulgite with an amino-terminated organosilicon (3-aminopropyltriethoxysilane, APTES). Surface properties of the APTES-modified attapulgite were characterized by the Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), and nitrogen adsorption–desorption. We evaluated the impact of solvent, APTES concentration, water volume, reaction time, and temperature on the surface modification. NH<sub>2</sub>-attapulgite was used to remove reactive dyes in aqueous solution and showed very high adsorption rates of 99.32%, 99.67%, and 96.42% for Reactive Red 3BS, Reactive Blue KE-R and Reactive Black GR, respectively. These powerful dye removal effects were attributed to strong electrostatic interactions between reactive dyes and the grafted NH<sub>2</sub> groups.

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### 1. Introduction

Clay minerals have high surface areas and in recent years they have been widely used for the removal of heavy metal ions [1–3], dyes [4–7], and other organics [8–10] from aqueous solutions. The clay mineral attapulgite (also known as palygoskite), is a form of crystalline hydrated magnesium aluminum silicate mineral that forms unique three-dimensional structures, which has a fibrous morphology with exchangeable cations and reactive –OH groups on its surface. Attapulgite is widely used in adsorbents, drilling fluids, paints, adhesives, and supports, because of its unique structure, and special sorptive, colloidal–rheological and catalytic properties, as well as its low cost and ready availability [11,12].

Attapulgite and activated attapulgite are used intensively as adsorbents for the removal of heavy metal ions and organic contaminants [13–15]. An effective approach for enhancing attapulgite adsorption capacity and selectivity is the surface chemical modification of attapulgite with organic reagents [16], such as, N-methylimidazole [17], 2, 2-bis(hydroxymethyl)-propionic acid [18], octadecyl trimethyl ammonium chloride [19], ammonium citrate tribasic [20], and polyacrylamide [21–23].

We attempted to modify the attapulgite surface with an amine-terminated organosilicon (3-aminopropyltriethoxysilane, APTES)

to create new N-immobilized Lewis basic centers [24] and substantially enhance the attapulgite adsorptive capacity for reactive dyes in aqueous solutions. We evaluated the effects of several reaction variables, including, solvent, APTES concentration, water volume, reaction temperature, and time on the surface modification. The modified attapulgite surface was characterized by Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), and nitrogen adsorption–desorption. The adsorption performance of the modified attapulgite was tested for removal of reactive dyes.

### 2. Materials and methods

#### 2.1. Materials and reagents

The following dyes were obtained from Guangzhou Lifeng Dye Co., China: Reactive Red 3BS: C.I. Reactive Red 195, Reactive Blue KE-R: C.I. Reactive Blue 171 and Reactive Black GR: C.I. Reactive Black 5. The chemical structures of the reactive dyes are shown in Fig. 1. All dyes are known to contain anionic sulfonate groups. Absorbance values of Reactive Red 3BS, Reactive Blue KE-R and Reactive Black GR were recorded at the corresponding maximum wavelength absorbances of 546, 620 and 602 nm, respectively. Attapulgite was supplied by Jiangsu Xuyi Anhalt Non-metallic Mining Ltd., with an average diameter of 200 mesh. APTES was purchased from Shanghai Yaohua Chemical Reagent Co., China. Toluene and anhydrous ethanol were of analytical grade. Distilled water was used in all experiments.

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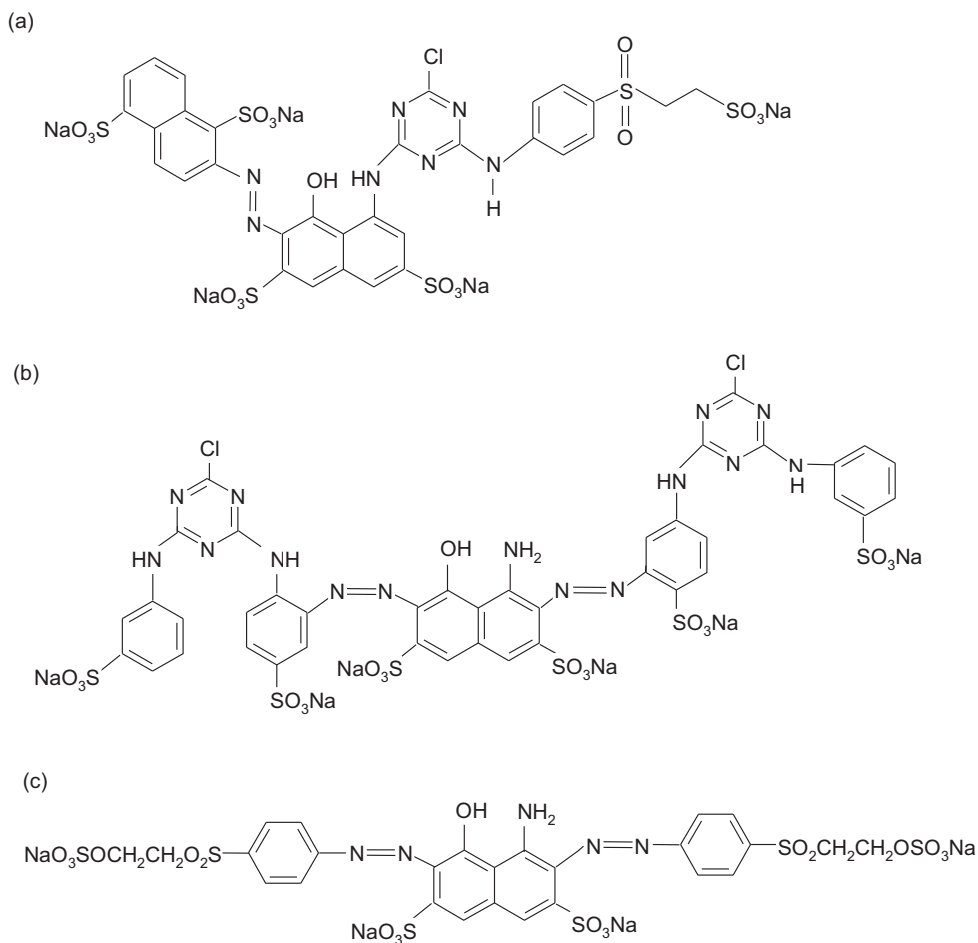


Fig. 1. Chemical structures of reactive dyes (a) Reactive Red 3BS, (b) Reactive Blue KE-R and (c) Reactive Black GR.

## 2.2. Surface modification of attapulgite

APTES was used to introduce terminal amino groups onto the attapulgite surface. We dispersed 6.0 g of attapulgite (dried at 105 °C) into 100 mL solvent (toluene or anhydrous ethanol) with ultrasound for 10 min. APTES was added dropwise to the mixture with vigorous stirring in volumes of 1.5, 3, 4.5, 6, 7.5, or 9 mL. Water was also added with an H<sub>2</sub>O/APTES volume ratio of 0, 1:5, 1:4, 1:3, 1:2, or 1:1. The mixture was refluxed for 0.5, 1, 1.5, 2, 3, 4, or 5 h at temperatures of 15, 30, 45, 60 or 75 °C. The resulting modified attapulgite was filtered and washed with toluene and anhydrous ethanol to remove unreacted material. The product was dried at 105 °C and sieved until similar-sized particles were collected. The product was stored in a desiccator for adsorption experiments or subsequent analysis. The parameters that could affect the efficacy of the modification were evaluated to determine the optimal conditions for the modification, *i.e.*, APTES volume, water volume, solvent type, reaction time, and temperature.

## 2.3. Surface characterization

The samples were characterized using a Nicolet Corporation AVATAR-360FT-IR spectrophotometer (USA). X-ray diffraction (XRD) analysis was conducted using an ARL corporation ARL/X'TRA with Cu K $\alpha$  radiation, operated at 45 kV and 40 mA over 5° < 2 $\theta$  < 70°. X-ray photoelectron spectroscopy (XPS) analyses were made using an ESCALAB 250 with an Al K $\alpha$  X-ray source. Binding energies (BEs) were calibrated by the C 1s peak at 284.6 eV. The specific surface area of the samples was obtained by

applying the BET method using the Surface Area and Pore Size Analyzer SA3100PLUS (Beckman Coulter Company, USA).

## 2.4. Adsorption experiments

Adsorption experiments were conducted to evaluate the optimal conditions for the NH<sub>2</sub> modification. Adsorption experiments were carried out by dispersing 0.3 g of modified attapulgite products in 100 mL of 100 mg/L aqueous solutions of Reactive Red 3BS, Reactive Blue KE-R, and Reactive Black GR, at 20 °C for 20 min in a shaking thermostatic bath. After adsorption, the supernatant solution was centrifuged at 3000 rpm for 10 min and the dye concentration was measured spectrophotometrically at  $\lambda_{\max}$  of 546, 620 and 602 nm for Reactive Red 3BS, Reactive Blue KE-R, and Reactive Black GR, respectively. All adsorption experiments were conducted in duplicate.

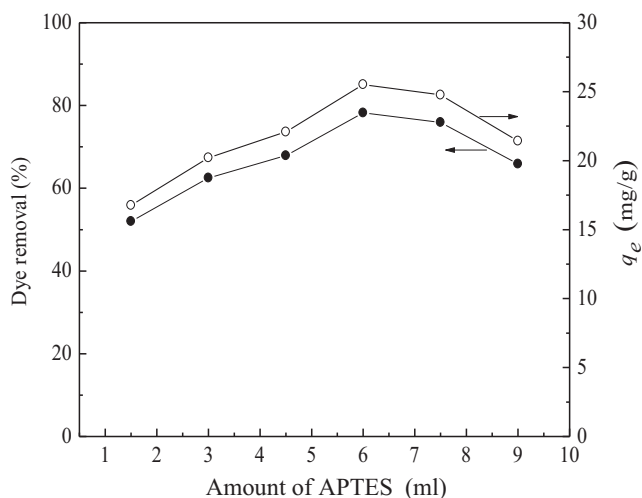
The percentage removal (*R*%) of dye was calculated using the equation:

$$R\% = \frac{100(C_0 - C_e)}{C_0} \quad (1)$$

where *C*<sub>0</sub> and *C*<sub>*e*</sub> are the initial and equilibrium dye concentration, respectively.

The amount of adsorptions at equilibrium, *q<sub>e</sub>* (mg/g), was calculated by:

$$q_e = \frac{(C_0 - C_e)V}{W} \quad (2)$$



**Fig. 2.** Effect of the APTES volume on dye removal and  $q_e$ . (Reaction conditions: 6.0 g attapulgite,  $H_2O/APTES = 1:3$  (v/v), solvent: toluene,  $T = 45^\circ C$ ,  $t = 4$  h).

where  $C_0$  and  $C_e$  (mg/L) are initial and equilibrium dye concentration, respectively.  $V$  (L) is the volume of the solution and  $W$  (g) is the mass of dry sorbent used.

### 3. Results and discussion

#### 3.1. Effects of reaction conditions

##### 3.1.1. Effect of the APTES volume

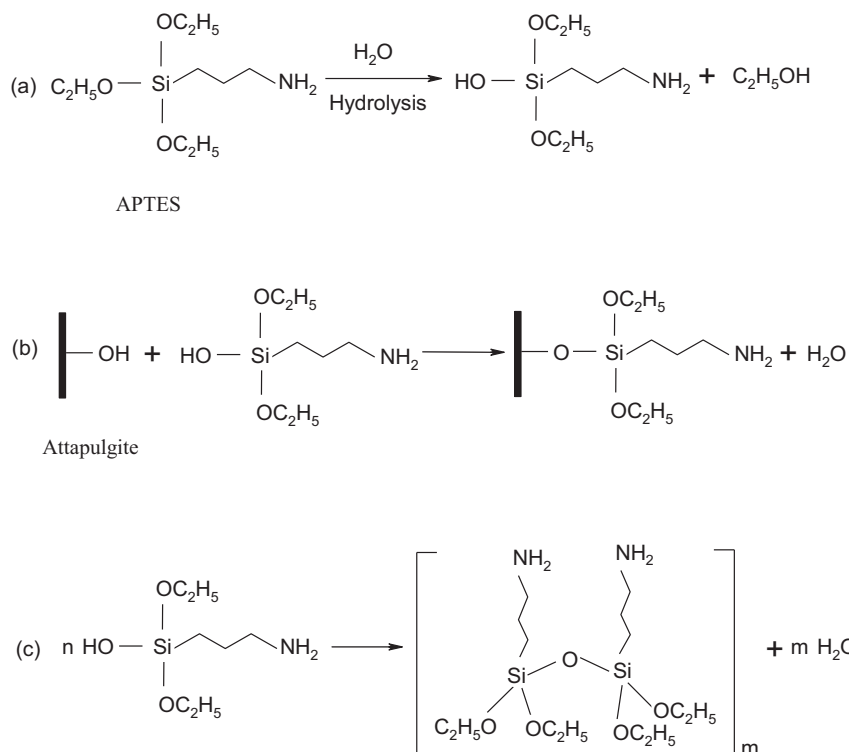
The effect of APTES volume is shown in Fig. 2. Fig. 2 shows that 6 mL of APTES achieved the highest dye removal capacity with modified attapulgite. Dye removal initially increased with the increasing volume of APTES, but it reached a maximum at 6 mL of

APTES and decreased thereafter. A same result has been observed in  $q_e$ . In the presence of water, alkoxy silane is first hydrolyzed to generate active silanol intermediates (Fig. 3a) [25]. Increasing the amount of APTES might mean that more active silanol groups (Si–OH) interacted with the attapulgite surface hydroxyl groups, leading to more active  $-NH_2$  terminal groups on the attapulgite surface (Fig. 3b) [25] and a higher dye removal capacity. However, the presence of excess APTES in the system and the hydrolytic nature of APTES in water, means that any free APTES might be expected to self-polymerize after hydrolysis to form a Si–O–Si backbone (Fig. 3c) [25,26]. This will prevent APTES molecules from further reacting with or binding to the attapulgite surface. Thus, the  $-NH_2$  on the modified attapulgite surface would reduce with an excess of APTES, and lead to a reduced Reactive Red 3BS removal capacity. As a result, 6 mL APTES was selected as the optimal volume for the preparation of modified attapulgite.

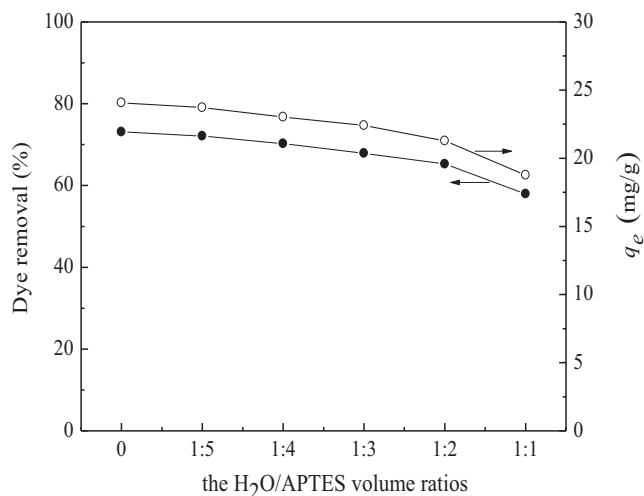
##### 3.1.2. Effect of water volume

Water was identified as a major important parameter in the reaction of APTES with the surface of materials [27]. Water can facilitate the initial hydrolysis of APTES at the material surface, depending on the volume of water present in the system [24]. We prepared amino-functionalized samples by grafting APTES in toluene containing different volumes of water. The water volume corresponded to different ratios of  $H_2O/APTES$ , i.e., 0, 1:5, 1:4, 1:3, 1:2, and 1:1 (v/v).

Fig. 4 shows that the maximum dye removal occurred in the absence of water and it was only slightly affected by the amount of water at ratios between 0 and 1:4. However, the dye removal decreased from 70.23% with a  $H_2O/APTES$  ratio of 1:4 to 57.94% at a ratio of 1:1. When water was absent from the system, observations were in agreement with APTES binding directly to the hydroxyl group on the surface of the attapulgite. However, excess water in the system promotes the polymerization of APTES in the solvent



**Fig. 3.** Reaction schemes between APTES and hydroxyl groups of attapulgite surface in the presence of water (a) the reaction of APTES hydrolysis, (b) the reaction between silanol intermediates (Si–OH) and hydroxyl groups of attapulgite surface and (c) the reaction of silanol intermediates self-polymerization.

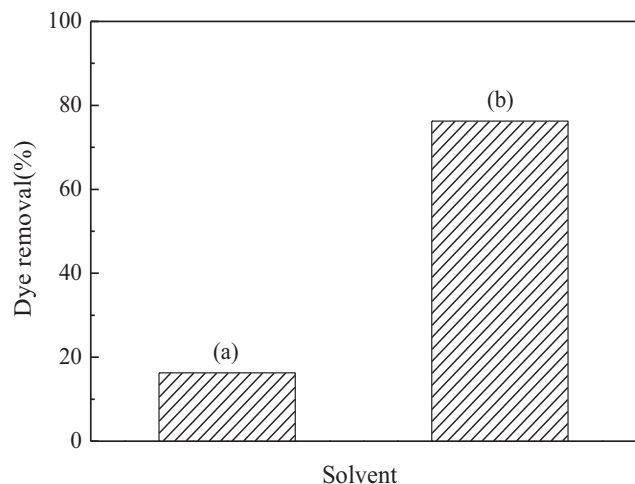


**Fig. 4.** Effect of water volume on dye removal and  $q_e$ . (Reaction conditions: 6.0 g attapulgite, 6 mL APTES, solvent: toluene,  $T = 45^\circ\text{C}$ ,  $t = 4$  h.)

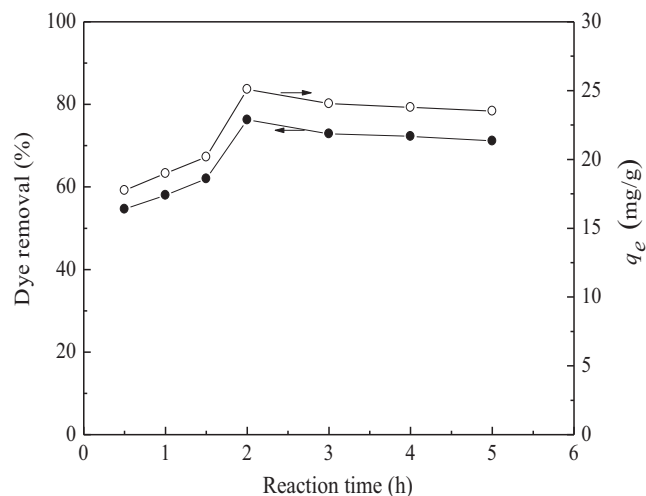
phase, which prevents APTES molecules from further reacting with, or binding to, the attapulgite surface [24]. For this reason, the dye removal decreased when H<sub>2</sub>O/APTES the ratio was higher than 1:1. The presence of water would lead to uncontrolled levels of APTES polymerization. Polymerization may be avoided by omitting water from the system [28]. And  $q_e$  has the same trend with the dye removal. To avoid hydrolysis and polymerization of aminosilanes, all subsequent silanization reactions were performed in the absence of water.

### 3.1.3. Effect of the solvent

The type of solvent used as a reaction medium during APTES modification is known to influence interactions between APTES molecules and the surface of the attapulgite. Attapulgite surface modification reactions were performed at  $45^\circ\text{C}$  using two different types of polar organic solvents one protic (ethanol) and one aprotic (toluene). Fig. 5 shows the difference between using ethanol and toluene as solvents. Dye removal was higher in the reaction medium of toluene compared with anhydrous ethanol. The main difference between ethanol and toluene, as solvents used in silanization of the attapulgite, is the protic character of ethanol, which might mean it competes with silane for surface hydroxyl groups by H-bonding. A favorable solvent–surface interaction



**Fig. 5.** Effect of the solvent on dye removal. (a) Anhydrous ethanol and (b) toluene. (Reaction conditions: 6.0 g attapulgite, 6 mL APTES,  $T = 45^\circ\text{C}$ ,  $t = 4$  h.)



**Fig. 6.** Effect of reaction time on dye removal and  $q_e$ . (Reaction conditions: 6.0 g attapulgite, 6 mL APTES, solvent: toluene,  $T = 45^\circ\text{C}$ .)

could create a strongly bound solvent layer around the attapulgite, which might have hindered APTES modification [29]. This is likely not the case in toluene-mediated reactions. This observation reflects similar results obtained with surface modification of magnetic nanoparticles [29]. In the following experiments, we selected toluene as the organic medium for the modification.

### 3.1.4. Effect of reaction time

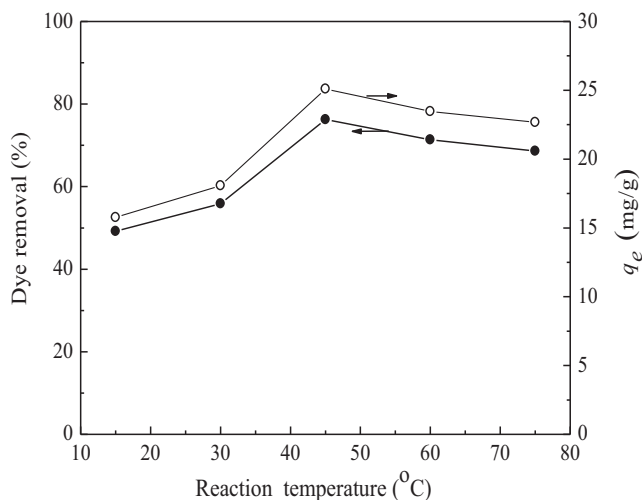
Fig. 6 shows that the optimal reaction time for the APTES modification was around 2 h. Increasing the reaction time did not improve dye removal and  $q_e$  with modified attapulgite. A reaction time of 2 h was adequate for silylation, so the following experiments were conducted with a 2 h reaction time.

### 3.1.5. Effect of reaction temperature

The rate of APTES modification of the attapulgite surface depends on the reaction temperature. An increase in temperature is broadly accompanied by an increase in the reaction rate. However, steric crowding and particle aggregation may also be promoted, which could lead to an opposite effect [29]. A detailed study was undertaken to determine the effect of temperature on APTES modification of attapulgite. The relationships of dye removal,  $q_e$  and reaction temperature are given in Fig. 7. When the reaction occurred under variable temperatures (15, 30, 45, 60 or  $75^\circ\text{C}$ ), the percentage removal of dye and  $q_e$  by the modified attapulgite first increased with increasing temperature, then reached a maximum value at  $45^\circ\text{C}$ , before decreasing slightly with further increases in temperature. At elevated temperature, the kinetics of the APTES system is accelerated by increasing the mobility of APTES in the toluene phase [25] and an increase in interactions between APTES molecules and the attapulgite surface hydroxyl groups, thereby facilitating APTES binding to the attapulgite surface. However, measurements did not show that a higher temperature led to increased dye removal and  $q_e$ . A similar trend was reported for the effect of reaction temperature on Hg adsorption capacity by APTES modified activated carbon [24].

## 3.2. Characterization

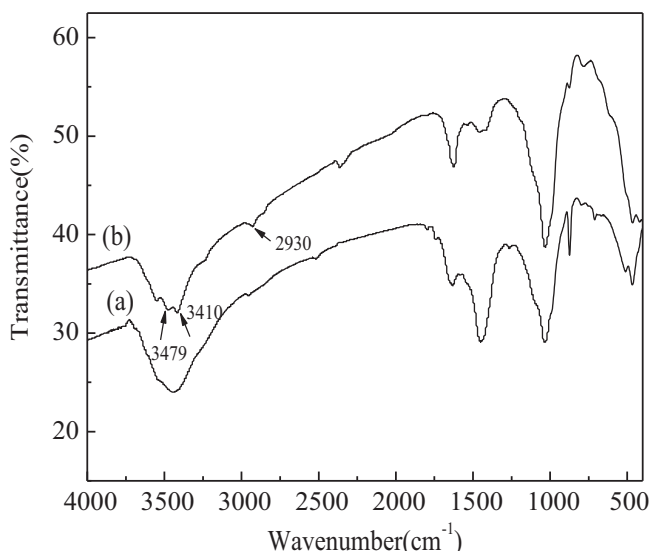
We used FTIR, XRD and XPS to confirm the successful grafting of APTES onto the attapulgite surface, and to provide further information on the reaction mechanism between APTES and attapulgite.



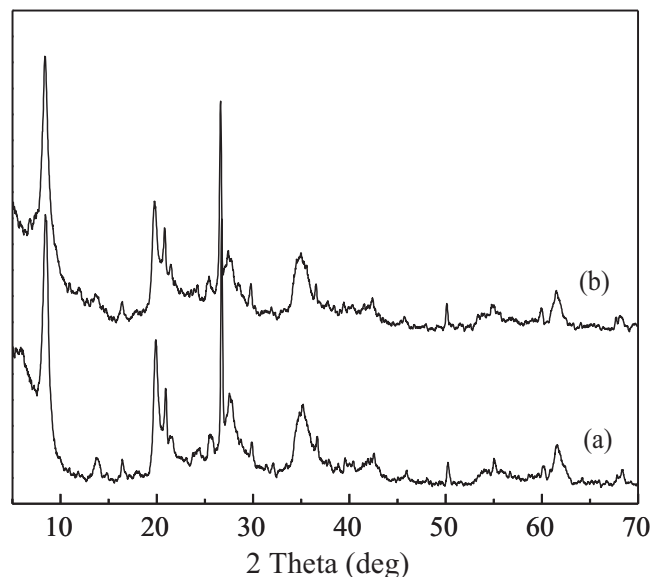
**Fig. 7.** Effect of reaction temperature on dye removal and  $q_e$ . (Reaction conditions: 6.0 g attapulgite, 6 mL APTES, solvent: toluene,  $t = 2$  h.)

### 3.2.1. Fourier transform infrared spectroscopy

The successful modification of attapulgite with APTES was confirmed by FTIR. The FTIR spectra of the attapulgite and modified attapulgite are shown in Fig. 8. The new bands at 3479 and 3410  $\text{cm}^{-1}$  of the modified attapulgite (Fig. 8b) indicate the symmetric and asymmetric stretching vibrations of the free amine  $-\text{NH}_2$ , showing the presence of an aminopropyl functional group. The absorption band at 2930  $\text{cm}^{-1}$  in Fig. 8b corresponds to the C–H stretching vibration of the  $\text{CH}_2$  groups of APTES. The peak intensity at about 1450  $\text{cm}^{-1}$  in the FTIR spectrum (Fig. 8a) of the unmodified attapulgite decreased in the spectrum (Fig. 8b) of the modified attapulgite, which corresponds to the hydroxyl bending of structural  $\text{OH}_2$  and zeolitic  $\text{H}_2\text{O}$ . This indicates that APTES molecules have been grafted to attapulgite via reaction with the structure hydroxyl of attapulgite. The absorption band at 880  $\text{cm}^{-1}$  in Fig. 8a may be assigned to the stretching vibrations of Si–O bond. Comparing the attapulgite and modified attapulgite, the peak at 880  $\text{cm}^{-1}$  in Fig. 8a has disappeared in Fig. 8b. It indicates the structures of Si–O have been destroyed partly that may be contributed to reaction between APTES and attapulgite [20,30–32].



**Fig. 8.** FTIR spectrum of (a) attapulgite and (b) modified attapulgite.



**Fig. 9.** X-ray diffraction patterns of (a) attapulgite and (b) modified attapulgite.

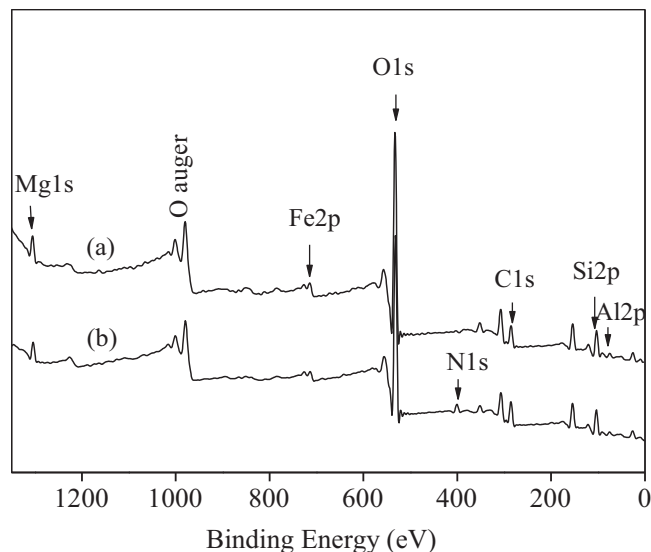
These observations clearly indicate that the surface modification of attapulgite was achieved by APTES.

### 3.2.2. X-ray characterization

XRD patterns of the attapulgite and the modified attapulgite are shown in Fig. 9. There was no change in the XRD patterns of the attapulgite after surface modifications with APTES. Thus, APTES was grafted onto the surface of the clay, but it did not change the crystal structure of attapulgite.

### 3.2.3. X-ray photoelectron spectroscopy

The full XPS spectra (Fig. 10a) were used to verify elements present on the surface of particles and their bonding states, including, Al 2p, Si 2p, Fe 2p, Mg 1s, C 1s, and O 1s. We found no N 1s in attapulgite. The appearance of peaks at about 400 eV in the amino-functionalized attapulgite sample (Fig. 10) was attributed to nitrogen from the APTES amine groups, thereby confirming the successful grafting of APTES onto attapulgite. The same result was obtained with FTIR.



**Fig. 10.** Typical wide-scan XPS spectra of (a) attapulgite and (b) modified attapulgite.

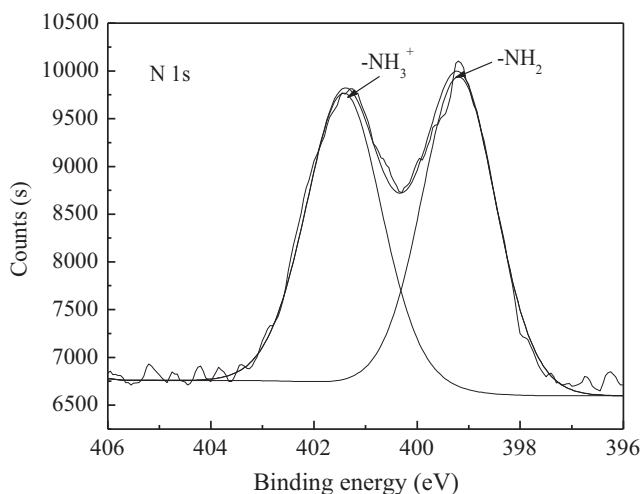


Fig. 11. N 1s XPS spectra of modified attapulgite.

High resolution XPS spectra provided evidence for the modification mechanism, specifically N 1s in modified attapulgite. Fig. 11 shows the N 1s peak deconvoluted into two different nitrogen species that occur in different binding states. One species can be located at 399.19 eV (51.5%) binding energy, and the other at 401.42 eV (48.5%). The standard binding energy for a free amine group ( $\text{-NH}_2$ ) falls in the region of 399–401 eV, whereas the protonated amine ( $\text{-NH}_3^+$ ) has a higher binding energy of 1.5 eV above the free amine groups [33]. Thus, the peak at 399.19 eV was assigned to the free amine groups, whereas the peak at 401.42 eV was attributed to protonated amine groups [34,35]. This is due to the flip mechanism of the APTES molecule when it interacts with the attapulgite surface during the silylation process. These reactions were described in previous reports [36,37]. The amine may enter into a hydrogen bonding interaction with a surface hydroxyl group of the attapulgite (Fig. 12a), or the basic amine function may abstract a proton from a hydroxyl group and form an ionic bond (Fig. 12b). This latter type of interaction is much more stable than the first. The hydrogen-bonded molecules may self-catalyze the condensation of the silicon side of the silane molecule, and a covalent siloxane bond is formed (Fig. 12c). Upon condensation of the silicon side, the amine group loses its interaction with the attapulgite surface and the amine points away from the surface. The higher number of ethoxy groups on the APTES molecule leads to a much faster stabilization. Thus, the aminosilane molecule turns from the original amine-down position to an amine-up position (Fig. 12d). This is known as the flip mechanism. There was a contribution of 48.5% of the protonated form, which may indicate that not all the original amine-down position are flipped by condensation and that both forms are present.

### 3.2.4. Nitrogen adsorption

Nitrogen adsorption–desorption isotherms for raw and amino-functionalized attapulgite (Fig. 13) resulted in type II isotherms, according to the IUPAC classification, with a hysteresis loop that indicated the presence of a large proportion of mesopores and macropores [11,38]. The shape of the hysteresis loops was of type H3, which is associated with plate-like particles or slit-shaped pores [39]. Isotherm type was the same for both attapulgite and modified attapulgite.

The surface area (calculated by application of the BET equation) increased as the treatment progressed. Raw attapulgite had a surface area of 152.66  $\text{m}^2/\text{g}$ . Samples treated with APTES has surface areas of c. 62.409  $\text{m}^2/\text{g}$ . The smaller  $S_{\text{BET}}$  of amino-functionalized attapulgite was a consequence of aggregation during silylation [11].

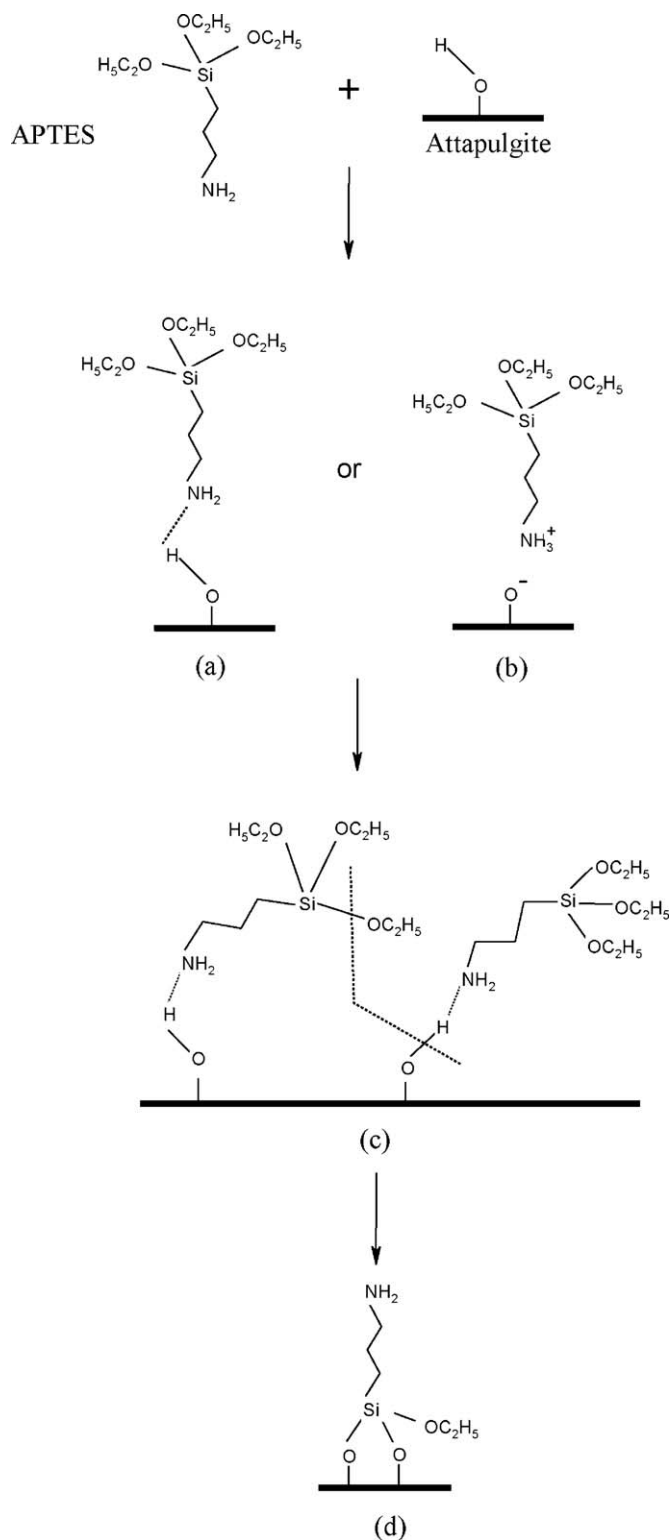


Fig. 12. Various interaction types between attapulgite surface and APTES in the absence of water (a) hydrogen bonding, (b) proton transfer, (c) condensation to siloxane and (d) amine-up position.

### 3.3. Reactive dye adsorption

The amino-functionalized attapulgite exhibited a unique affinity for reactive dyes. Fig. 14 shows the reactive dyes removal rates of simulated wastewater adsorbed by attapulgite and  $\text{NH}_2$ -attapulgite. The removal rates of  $\text{NH}_2$ -attapulgite as an

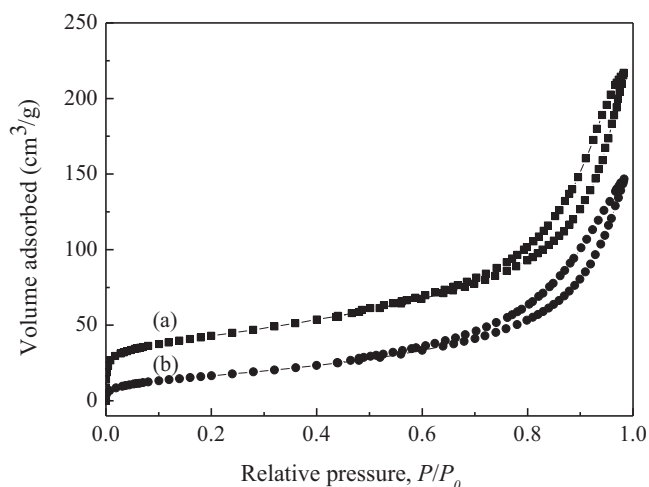


Fig. 13.  $N_2$  adsorption-desorption isotherms of (a) attapulgite and (b) modified attapulgite.

adsorbent for Reactive Red 3BS, Reactive Blue KE-R, and Reactive Black GR were 99.32%, 99.67%, and 96.42%, respectively. The  $NH_2$ -attapulgite adsorbent efficiently removed Reactive Red 3BS, Reactive Blue KE-R, and Reactive Black GR. In comparison, the removal rates for the raw attapulgite adsorbent with Reactive Red 3BS, Reactive Blue KE-R, and Reactive Black GR were 1.16%, 3.30%, and 2.88%, respectively, under the same conditions. Therefore, the changes in the dyes removal rate must be attributable to the electrostatic attraction between reactive dyes and the grafted amino groups. The amine groups ( $-NH_2$ ) of the modified attapulgite can be protonated and exist in the positively charged form ( $-NH_3^+$ ) in aqueous solution. On the other hand, the reactive dyes can dissociate into the negatively charged sulfonate groups ( $DSO_3^-$ ) in the aqueous solution. And in that case reactive dye adsorption would most likely occur by attractive electrostatic interactions between the positively charged adsorption sites ( $-NH_3^+$ ) and negatively charged dye anions ( $DSO_3^-$ ) [40,41]. Thus, modified attapulgite adsorbs reactive dye more effectively than nonmodified, raw attapulgite. This indicates that surface modification by the APTES significantly enhanced the capacity of attapulgite for the adsorption of reactive dyes from aqueous solution.

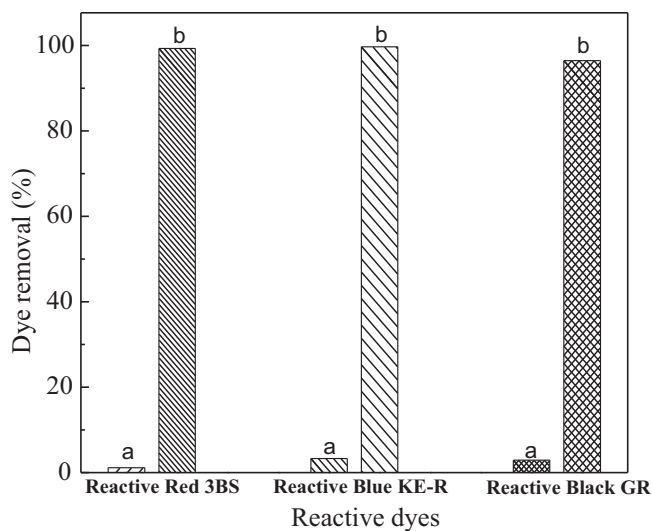


Fig. 14. Comparison of dye removal for attapulgite and modified attapulgite (a) attapulgite and (b) modified attapulgite. (Adsorption conditions: 6g/L adsorbent, 100 mL 100 mg/L dye aqueous solutions.)

Table 1  
Reactive Red 3BS adsorption capacity for the different materials in the literature.

Adsorbent	Reactive Red 3BS adsorption capacity (mg/g)	Reference
Clinoptilolite	3.186	[42]
<i>Pinus sylvestris</i> L.	8.425	[43]
TiO <sub>2</sub> nanoparticles	87	[44]
Wheat bran	103.4	[45]
Amino-functionalized attapulgite	34.235	This work

#### 3.4. Comparison of amino-functionalized attapulgite with other adsorbents

Several studies have been conducted using various types of adsorbents for reactive dyes adsorption. The maximum capacity of Reactive Red 3BS adsorbed on the optimum amino-functionalized attapulgite was 34.235 mg/g [40]. Table 1 presents a comparison of the adsorption capacity of the results. It can be seen from the table that amino-functionalized attapulgite shows the comparable adsorption capacity with respect to other adsorbents, revealing that modified attapulgite is suitable for the removal of reactive dyes from aqueous solutions. Therefore, considering the economic advantage and the adsorption capacity, modified attapulgite is a very potential adsorbent for reactive dyes.

#### 4. Conclusion

This study modified the attapulgite surface with an amine-terminated organosilicon (3-aminopropyltriethoxysilane, APTES) and created new N-immobilized Lewis basic centers, which substantially enhanced the attapulgite adsorptive capacity for reactive dyes from aqueous solutions. The optimal conditions for surface modification of attapulgite were achieved using 6 mL APTES (relative to 6.0 g attapulgite) with toluene as the solvent, and the reaction was conducted at 45 °C for 2 h. This optimal silanization of the attapulgite was successfully used to remove reactive dyes from aqueous solution. The modified attapulgite showed much greater efficiency in the adsorption of reactive dyes from aqueous solution than unmodified attapulgite. This approach could be extended to the activation of other material surfaces with other functional groups. Functionalization of clays with organosilanes provides a method for to changing the surface properties of materials and extends the possible applications of this field.

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