

Azo dye removal from aqueous solution by organic-inorganic hybrid dodecanoic acid modified layered Mg-Al hydrotalcite

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Abstract—Hydrotalcite (HTC), a typical layered compound, is a promising adsorbent for removal of organic pollutants. To partition azo dye from aqueous solution, Mg-Al HTCs intercalated with dodecanoic acid (DA) modifier, DAHTCs, were prepared by ion exchange and calcination-rehydration methods. The structures of HTCs and DAHTCs were characterized by powder XRD and FT-IR techniques. The introduction of DA broadened the spacing of interlayers and provided more space for ion exchange. The effects of pH value, contact time, adsorbent amount, temperature and different intercalated modifiers on the adsorption of azo dye onto HTCs and DAHTCs were determined. The optimum pH of uptake was around 3.0 and all the lower or higher pH values proved to decrease the adsorption properties. The pseudo-second-order model was found to best describe the adsorption dynamics of all adsorbents. Meanwhile, the size and polarity of intercalated modifiers might be crucial for adsorption of azo dye.

Key words: Hydrotalcite, Dodecanoic Acid, Intercalation, Azo Dye, Methyl Orange

INTRODUCTION

Massive amounts of pollutants are discharged into the natural environment every day, causing serious soil, water, and living pollution. The removal of these pollutants is an urgent problem to solve. Dye wastewater, which is mainly derived from the textile industry, consists of many adverse azo organic compounds. These compounds are quite stable and have low biodegradability, even at high temperature, direct light, and chemical treatment. It is desirable to develop effective methods and materials to separate these pollutants.

Adsorption has proven to be a low-cost and efficient technique for treatment of organic pollutants. Clay is considered a promising adsorbent because of its high capacity, inexpensive price, flexible functionality and regeneration. Hydrotalcite (HTC), a typical layered clay, has been widely applied in ion exchange, CO₂ adsorption, catalysis, and materials synthesis, etc. [1-5]. The material (noted as [Mg_{1-x}Al_x(OH)₂]^{x+}) consists of layered brucite [Mg(OH)₂] where some divalent cations (Mg²⁺) are replaced by trivalent cations (Al³⁺) at the centers of octahedral sites of the hydroxide layers. The excess positive charges are compensated by other anions (CO₃²⁻) to maintain charge neutrality. It is interesting to know that the anions in the layers of HTC can be easily exchanged with other anions in aqueous solution. Thus, the removal of charged inorganic and organic ions from aqueous solution by HTC becomes reliable [6-9]. For example, Xu et al. reported phenol and 4-nitrophenol removal from aqueous solution using calcined HTC, MgAl-mixed oxide [7]. Additionally, some inorganic cations (Zn²⁺, Fe³⁺, etc.) and anions (Cl⁻, SO₄²⁻, etc.) have been usually introduced to tailor the structures and properties of HTC [10-12]. Recently, some organic anions have also been intercalated into the layers of HTC to modify the hydrophobic

environment and obtain higher exchangeable capacity for organic pollutants by ion exchange method and calcination-rehydration method [13-16]. Anionic surfactants like dodecylsulfate and dodecyl benzene sulfonate are intercalated into the layers of HTC to prepare novel organic-inorganic hybrid adsorbents, showing excellent adsorption ability for phenols and basic dyes [17-20]. To the best of our knowledge, no investigations have been performed with organic acids as intercalated modifier for HTC in the removal of azo dyes from wastewater.

In the present work, novel organic-inorganic hybrid adsorbents, dodecanoic acid intercalated HTC (DAHTC), were prepared by ion exchange and calcination-rehydration methods. The structures of HTCs and DAHTCs were characterized by powder XRD and FT-IR techniques. The effects of pH value, contact time, adsorbent amount, dye concentration, and temperature on the adsorption of azo dye were determined.

EXPERIMENTAL

1. Reagents

All of the chemical reagents such as Mg(NO₃)₂·6H₂O and Al(NO₃)₃·9H₂O employed were of analytical grade. Dodecanoic acid (DA), myristic acid (MA), hexanedioic acid (HA), terephthalic acid (TPA), and sodium dodecylbenzene sulfonate (SDBS) with a purity of 98% as intercalated modifiers were provided by Alfa Aesar. Pure methyl orange (Sodium *p*-dimethylaminoazobenzene sulfonate, Color Index Number: 13025) obtained from Acros Organics was a typical azo compound, which was used to simulate azo dye in chemical wastewater. Other inorganic/organic reagents were of analytical grade and were used without further purification. The structures of some organic compounds are shown in Fig. 1.

2. Synthesis and Characterization of HTC and DAHTC

51.2 g (0.20 mol) Mg(NO₃)₂·6H₂O and 37.5 g (0.10 mol) Al(NO₃)₃·

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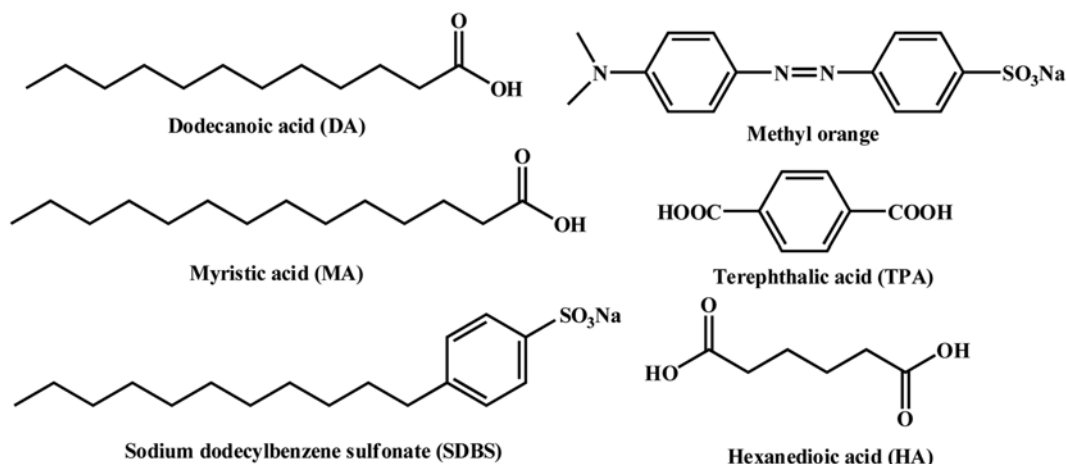


Fig. 1. The structures of some organic compounds.

$6\text{H}_2\text{O}$ were dissolved into 140 cm^3 distilled water to prepare solution A. Solution B was prepared by dissolving 28.0 g (0.625 mol) NaOH and 20.0 g (0.1886 mol) Na_2CO_3 into 200 cm^3 distilled water. Solution A was added slowly into the solution B under shaking at 308 K . Then, the mixture was crystallized at a heating condition of 338 K for 18 hours. After being cooled to room temperature, it was filtered under vacuum, washed with distilled water, dried under vacuum overnight, and the resultant white solid was ground to obtain sample HTC-1. After being calcined in air at 773 K for 24 hours, sample HTC-2 was obtained.

2.3 g HTC-1 and 2.5 g (0.0124 mol) dodecanoic acid were dispersed homogeneously in the ethylene glycol (EG) solution under vigorous stirring, respectively. Then the two parts of solutions were mixed and stirred vigorously at 423 K for 1 hour. The residue was filtered, washed three times with distilled water, and dried under vacuum at 343 K for 24 hours. The solid was ground to obtain a novel dodecanoic acid modified layered Mg-Al hydrotalcite (noted as DAHTC-1). Sample DAHTC-2 was prepared using the same method by intercalating dodecanoic acid into HTC-2.

All samples were characterized by powder X-ray diffraction (PXRD, Rigaku DP-D1, Japan) technique and Fourier transform infrared (FT-IR, Nicolet 605XB, USA) spectra. PXRD patterns were obtained by using Ni-filtered $\text{Cu K}\alpha$ radiation. Data were collected by step scanning within the 2θ range of 5 to 40° . The FT-IR spectra were recorded using the KBr self supported pellet technique.

3. Batch Adsorption Experiments of HTC and DAHTC

All distribution coefficients were measured by batch adsorption experiments. The pH value in aqueous solution was in the range of 2 to 13. A given amount of adsorbent was contacted with 100 cm^3 of 5 ppm azo dye aqueous solution in a 500 cm^3 ground glass-stoppered flask. It was shaken mechanically for a desired contact time. After being filtrated by a funnel, the concentrations of azo dye were determined with a UV-Vis spectrometer (Varian Cary-50, USA) at absorption wave of 490 nm . The removal ratio (R) and adsorption capacity (q) of the azo dye onto the adsorbents were calculated as follows:

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

$$q(\text{mg/g}) = \frac{(C_0 - C_e) \times V}{W} \quad (2)$$

where C_0 and C_e represent the initial and equilibrium concentrations of azo dye in aqueous phase, respectively. W and V are the weight of dry adsorbents and the volume of aqueous phase used in the experiments.

RESULTS AND DISCUSSIONS

1. Characterization of HTC and DAHTC

PXRD patterns for the four samples of HTC-1, HTC-2, DAHTC-1, and DAHTC-2 are illustrated in Fig. 2. HTC-1 shows three sharp characteristic peaks at 11.6° (003), 23.3° (006), and 29.3° (009), indicating it is a well-defined hydrotalcite-like compound. The inter-layer spacing of 0.76 nm for HTC-1 coincides with other previous results [4,6]. After being calcined, the characteristic peaks of HTC disappear and larger diffraction angles appear, which confirms that CO_3^{2-} is removed from the interlayer and Al and Mg mixed oxides are yielded during calcination process.

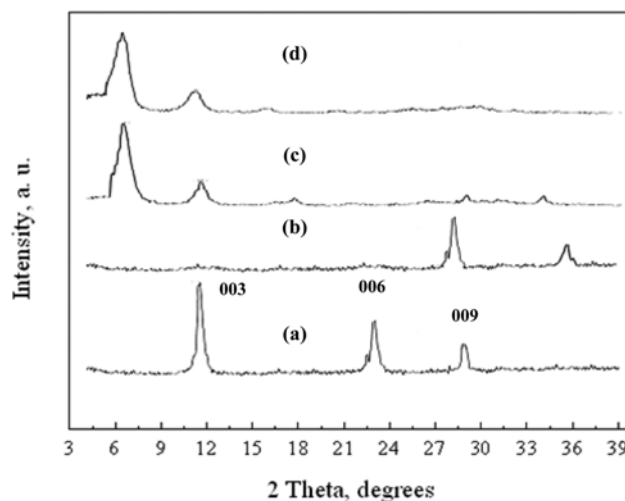


Fig. 2. PXRD patterns of (a) HTC-1, (b) HTC-2, (c) DAHTC-1, and (d) DAHTC-2.

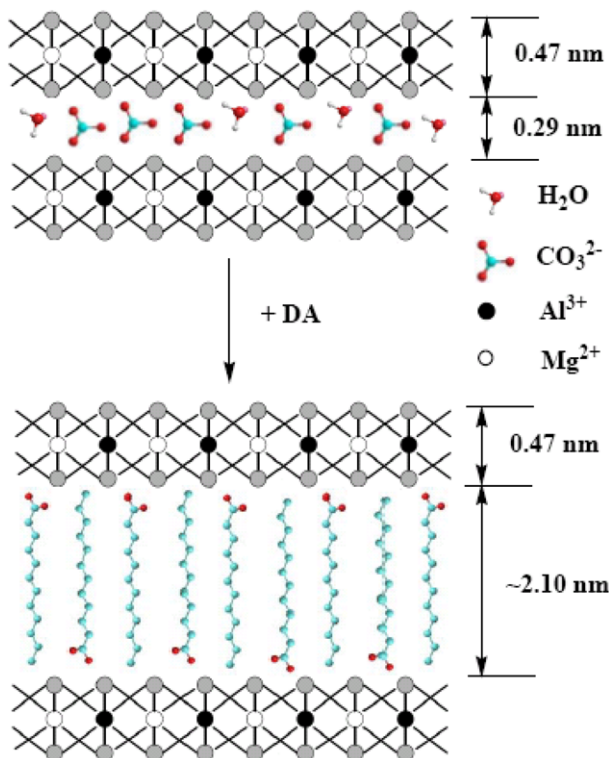


Fig. 3. The schematic illustration of the intercalation orientation.

Both DAHTC-1 and DAHTC-2 have three characteristic peaks of HTC, which indicates the initial structure of HTC remains undestroyed after being intercalated with DA. However, the peaks of DAHTC-1 and DAHTC-2 shift to lower diffraction angles and exhibit relatively broader and smaller intensity. The introduction of DA broadens the interlayer spacing of HTC, making the interlayer spacings of DAHTC-1 and DAHTC-2 be 2.55 and 2.57 nm, respectively. The CO_3^{2-} in the interlayer is substituted by DA anion through ion exchange mechanism. Considering the thickness of 0.47 nm for the host layer, the gallery heights are 2.08 and 2.10 nm for DAHTC-1 and DAHTC-2, respectively, which are very similar with the length of DA anion. Thus, the DA anions should be arranged perpendicularly to the brucite-like layers [21]. The schematic illustration of the intercalation orientation is shown in Fig. 3. It is worthy to note that calcined HTC-2 can rehydrate and incorporate anions to rebuild the initial hydrotalcite structure, which is defined as the memory effect of HTC. That's why the DAHTC-2 material holds the initial structure of HTC. The relevant synthetic reactions are shown in Eqs. (3) and (4).

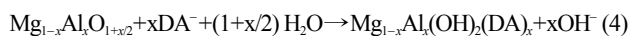


Fig. 4 shows the FT-IR spectra of HTC-1, HTC-2, DAHTC-1, and DAHTC-2. A broad band in the range of 3,600–3,400 cm^{-1} is observed in Figs. 4(b), (c) to (d), which is attributed to the stretching vibration of hydroxyl groups and water molecules from the interlayer. Such broad peak in Fig. 4(a) is not obvious because of the decomposition of HTC at calcined temperature. It is known that HTC-1 contains CO_3^{2-} in the interlayer, so the characteristic absorp-

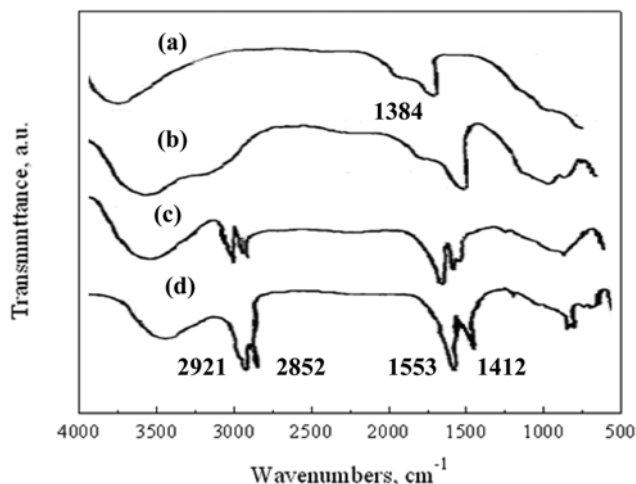


Fig. 4. FT-IR spectra of (a) HTC-2, (b) HTC-1, (c) DAHTC-1, and (d) DAHTC-2.

tion peak at 1,384 cm^{-1} is ascribed to stretching vibration of CO_3^{2-} , whose intensity in HTC-2 becomes lower, indicative of the decomposition of HTC. Some new absorption peaks at 2,921, 2,852, 1,553 and 1,412 cm^{-1} , corresponding to the stretching vibration of C-H in methyl, C-H in methylene, C=O, and C-O in carboxyl group, respectively, appear after being intercalated with DA modifiers. Other bands between 500 and 800 cm^{-1} are possibly attributed to the bonding vibration of M-O and M-O-M (M=Mg, Al). The differences between these FT-IR spectra show that the DA modifiers are successfully intercalated into the interlayer of HTC.

2. Effect of pH Value

The pH value plays an important role in the adsorption of azo dye, which seriously affects the dissolution of HTC and the speciation of methyl orange. To investigate the adsorption behavior of HTC and DAHTC towards azo dye, the effect of pH value in the range of 2 to 13 was studied at azo dye concentration of 5.0 ppm, phase ratio of 0.05 g/100 cm^3 , contact time of 180 mins.

Fig. 5 shows the adsorption of azo dye onto HTC-1, DAHTC-1,

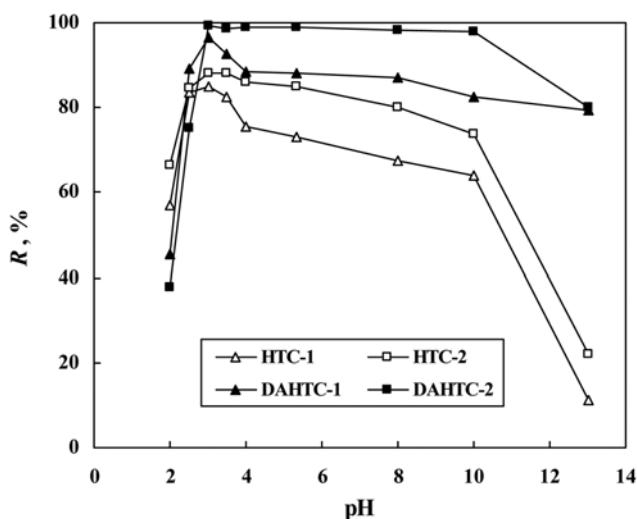


Fig. 5. Adsorption of azo dye onto HTC-1, DAHTC-1, HTC-2, and DAHTC-2 as a function of pH value at 293 K.

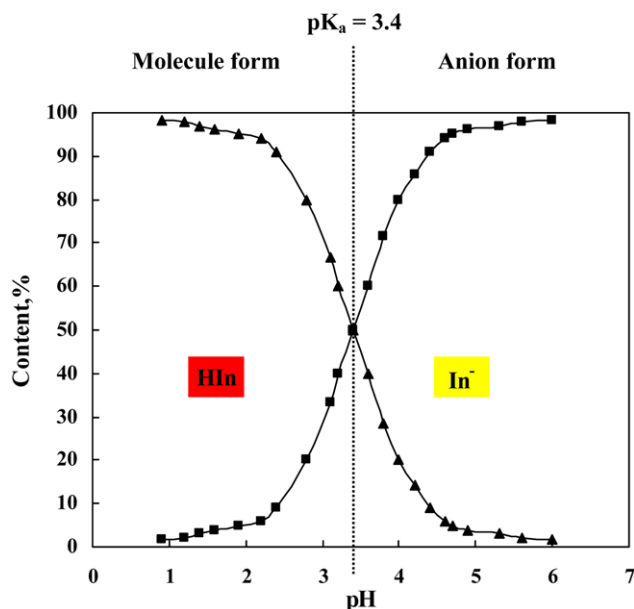
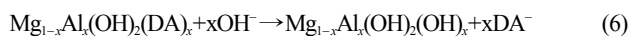
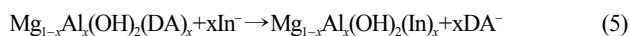


Fig. 6. Speciation of methyl orange at various pH values.

HTC-2, and DAHTC-2 as a function of pH value. The uptakes of azo dye increase with an increase of pH value for all samples at low pH. When the pH value continues to increase, the removal ratios (R) of azo dye reach an optimum at $\text{pH}=3.0$ and decrease at higher pH value. The removal percentages of azo dye for DA-modified HTCs are larger than those of initial HTCs, especially at higher pH values. Such improved adsorption properties should be attributed to the intercalated reagents. The presence of DA modifiers broadens the interlayer spacing and increases the hydrophobic nature of HTC, which is beneficial for the ion exchange of azo dye. In addition, calcined (DA)HTCs exhibit more favorable adsorption for azo dyes than uncalcined (DA)HTCs. The amazing memory effect of HTC may be a good explanation for that.

According to Fig. 6, we know that the dissociation constant ($\text{p}K_a$) of methyl orange is around 3.4 [22]. Thus, the methyl orange mainly shows molecule form (HIn) at $\text{pH}<3.4$ and anion form (In^-) at $\text{pH}>3.4$. The molecule form is too difficult to exchange with the anions in the interlayer of HTCs and DAHTCs, which is why the removal ratios of azo dye are small at low pH value. Additionally, higher acidity increases the dissolution of Mg and Al from the adsorbents, which destroys the structures of HTCs and DAHTCs. At basic environment, OH^- anions participate in the competitive adsorption against In^- anions, making the decrease of azo dye adsorbed onto HTCs and DAHTCs. The relevant reactions are presented as follows:



3. Effect of Contact Time

In partitioning of azo dye from aqueous solution, the quick adsorption and desorption dynamics are usually required. To understand the adsorption equilibrium, the uptake of azo dye onto HTC-1, DAHTC-1, HTC-2, and DAHTC-2 as a function of contact time was investigated at azo dye concentration of 5.0 ppm, phase ratio of 0.05 g/100 cm³, pH value of 3.0. The result is shown in Fig. 7.

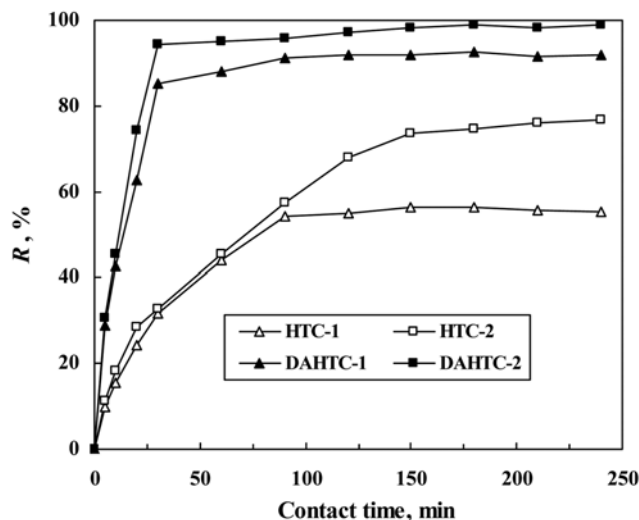


Fig. 7. Adsorption of azo dye onto HTC-1, DAHTC-1, HTC-2, and DAHTC-2 as a function of contact time at 293 K.

As can be seen, the adsorption dynamics of azo dye onto DAHTC-1 and DAHTC-2 are very quick. Both of them reach adsorption equilibrium at about 30 mins. But the equilibrium time for HTC-1 and HTC-2 needs about 150 mins. It shows that the introduction of DA extends the interlayer of HTC, which provides large space and quick ion exchange.

To understand the adsorption dynamic mechanism, it assumes that the reaction orders with respect to the contact time are first-order and pseudo-second-order [23,24], respectively. The mathematic models are expressed as follows:

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \quad (7)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} - \frac{t}{q_e} \quad (8)$$

Where q_e and q_t represent the amount of azo dye adsorbed at equilibrium and any time, k_1 and k_2 are rate constants for first-order

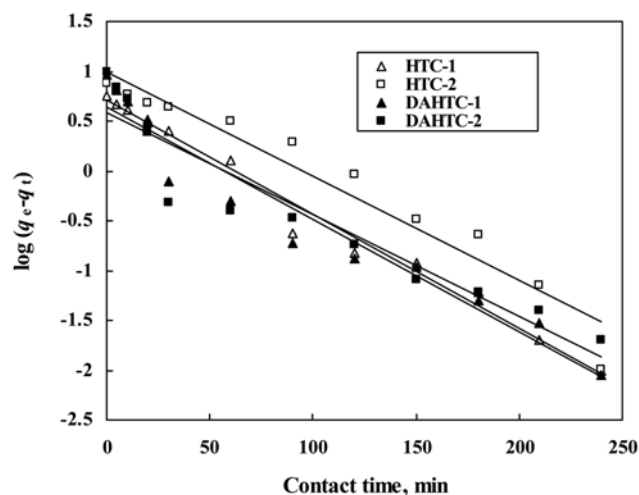


Fig. 8. First-order plot for azo dye removal from aqueous with HTC-1, DAHTC-1, HTC-2, and DAHTC-2.

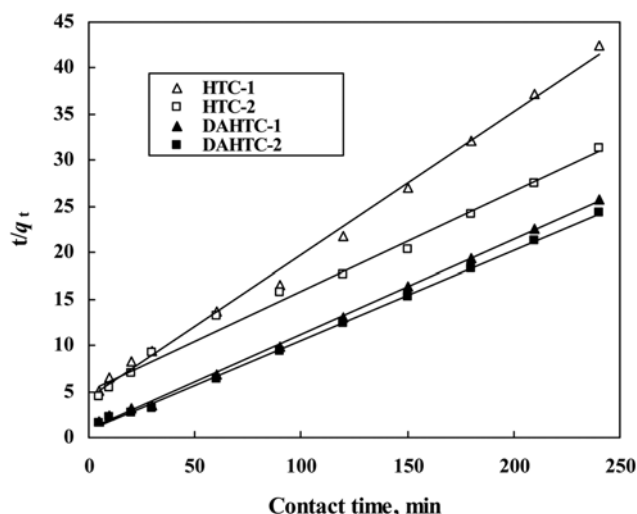


Fig. 9. Pseudo-second-order plot for azo dye removal from aqueous with HTC-1, DAHTC-1, HTC-2, and DAHTC-2.

model and pseudo-second-order model, respectively.

The linear relationship of the first-order model and pseudo-second-order model are plotted in Figs. 8 and 9. The calculated parameters are shown in Table 1. Compared with the first-order model, the pseudo-second-order model exhibits good linear correlation. The regression coefficients of all adsorbents are higher than 0.99, which shows the pseudo-second-order model is more suitable for azo dye adsorbed onto these adsorbents. The rate constants (k_2) of DA-modified HTCs are larger than those of unmodified HTCs, indicative of quicker adsorption dynamics. The calculated equilibrium adsorption capacities of HTC-1, DAHTC-1, HTC-2, and DAHTC-2 are 6.460, 9.718, 9.276, and 10.277, respectively.

4. Effect of Adsorbent Amount

Fig. 10 shows the effect of adsorbent weight on the adsorption of HTCs and DAHTCs towards azo dye. The adsorption experiments were performed at azo dye concentration of 5.0 ppm, aqueous volume of 100 cm³, pH value of 3.0, and contact time of 180 mins. With respect to all samples, the removal ratios of azo dye increase with an increase of adsorbent amounts. When the weight of adsorbent increases to 0.05 g, the removal of azo dye onto DAHTC-1 and DAHTC-2 is almost completed. However, more adsorbent amounts for HTC-1 and HTC-2 are needed to fully separate azo dyes from aqueous solution. The uptakes of azo dye onto modified HTCs are larger than those of unmodified HTCs across the weight of adsorbents. These results indicate the introduction of DA modifiers can enhance the removal of azo dye and decrease the using amount of

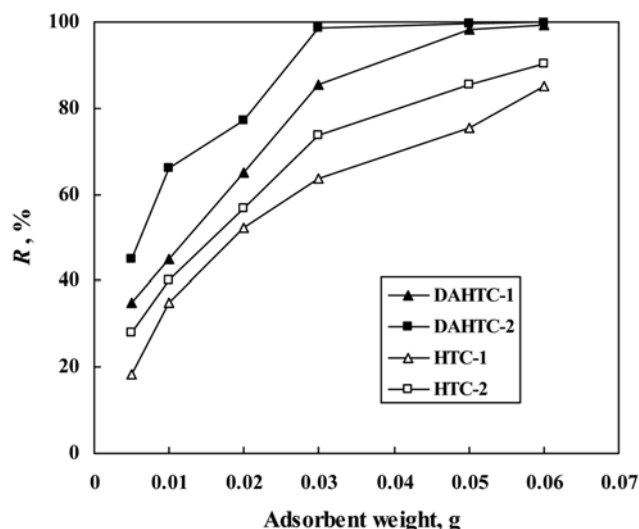


Fig. 10. Adsorption of azo dye onto HTC-1, DAHTC-1, HTC-2, and DAHTC-2 as a function of adsorbent weight at 293 K.

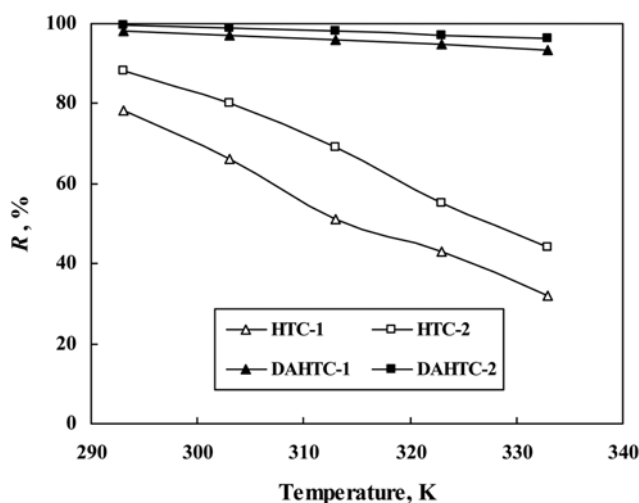


Fig. 11. Adsorption of azo dye onto HTC-1, DAHTC-1, HTC-2, and DAHTC-2 as a function of temperature.

adsorbents.

5. Effect of Temperature

Temperature plays a vital role in most adsorption processes. The effect of temperature on the adsorption of azo dye onto HTC-1, DAHTC-1, HTC-2, and DAHTC-2 was investigated at azo dye concentration of 5.0 ppm, phase ratio of 0.05 g/100 cm³, pH value of

Table 1. The parameters of first-order model and pseudo-second-order model for azo dye removal with HTC-1, DAHTC-1, HTC-2, and DAHTC-2

Adsorbent	First-order model			Pseudo-second-order model		
	k_1, min^{-1}	$q_e, \text{mg/g}$	R^2	$k_2, \text{g/mg/min}$	$q_e, \text{mg/g}$	R^2
HTC-1	0.0262	5.073	0.986	0.0055	6.460	0.996
HTC-2	0.0240	9.802	0.948	0.0023	9.276	0.991
DAHTC-1	0.0260	4.360	0.941	0.0117	9.718	0.999
DAHTC-2	0.0235	3.837	0.901	0.0123	10.277	0.999

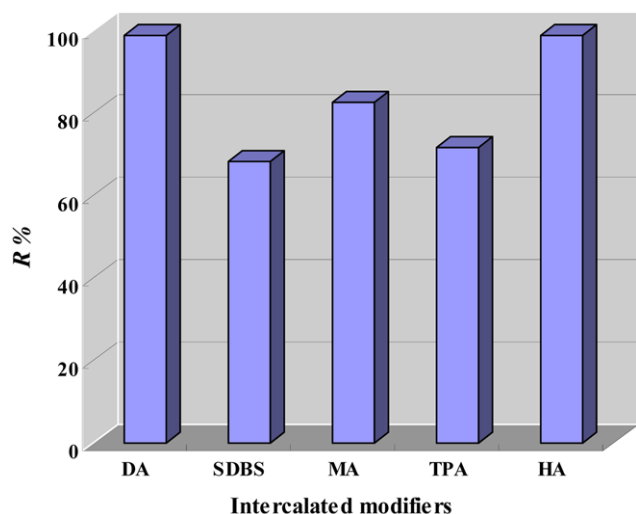


Fig. 12. Effect of intercalated modifiers on the adsorption of azo dye onto the calcined HTC.

3.0, and contact time of 180 mins. As shown in Fig. 11, the HTCs modified with DA exhibit high resistance to temperature and keep high removal ratio of azo dye even at 333 K. On contrary, the uptakes of azo dye onto unmodified HTCs decrease with an increase of temperature, which reflects that HTC-1 and HTC-2 may be unstable at high temperature.

6. Effect of Modifiers on the Adsorption

Anionic surfactants, such as sodium dodecyl sulfate (SDS) and sodium dodecyl benzene sulfonate (SDBS), were reported to modify HTC as intercalated reagents in the previous literature [17-20]. And the adsorption results showed that different removal ratios of organic pollutants were obtained using different modifiers. To investigate the effect of different intercalated modifiers on the adsorption of azo dye, five organic compounds are introduced. The results are shown in Fig. 12.

In this work, the removal ratio of azo dye onto calcined HTC modified with SDBS is 68.2%, which is higher than the 41% reported by Ouali et al. [17]. Furthermore, when using organic acids as intercalated modifiers, high uptakes of azo dye can be obtained. The removal percentage is 98.9% for DA modifier. The uptakes of azo dye onto HTC modified with more hydrophobic organic acids (MA and TPA) are slightly lower. However, a more hydrophilic dicarboxylic acid, HA, can obtain a similar high removal ratio (98.8%) of azo dye with DA. The possible reasons for different removal ratios of azo dye using different modifiers are presented as follows: (1) The hydrophobic and hydrophilic properties of intercalated modifiers; (2) The molecule size of intercalated modifiers; (3) Similar sizes of intercalated modifiers and organic pollutants; and (4) More negative charges for intercalated modifiers.

CONCLUSIONS

To remove azo dye from aqueous solution, novel Mg-Al HTCs modified with DA were prepared and characterized by PXRD and FT-IR. The DA modifiers were successfully introduced into the interlayer of HTCs and the spacing of interlayer was broadened to the

length of DA, providing much space for ion exchange. The adsorption properties of modified HTCs and unmodified HTCs were determined by batch adsorption experiments. The optimum conditions for adsorption of azo dye were at pH value of 3.0, contact time of 180 min, adsorbent amount of 0.05 g, and temperature of 293 K. A pseudo-second-order model proved best to describe the adsorption dynamics of all adsorbents. HTCs modified with different intercalated reagents were found to have different adsorption properties of azo dye, which was helpful to design novel adsorbents for targeted guests by tuning the size and polarity of modifiers.

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