



Application of dithiocarbamate-modified starch for dyes removal from aqueous solutions

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ABSTRACT

The present study shows that the dithiocarbamate-modified starch (DTCS) is a commercially promising sorbent for the removal of anionic dyes from aqueous solutions. It is more effective than activated carbon for this purpose. At the appropriate solution pH of 4, kinetic studies indicate that the sorption of the dyes tends to follow pseudo-first-order equation. The sorption equilibrium is best described by the Langmuir–Freundlich isotherm model at 298 K. The capacities for individual dyes follow the sequence acid orange 7 > acid orange 10 > acid red 18 > acid black 1 > acid green 25, which is consistent with the inverse order of molecular size. The negative enthalpy change for the adsorption process confirms the exothermic nature of adsorption, and a free energy change confirms the spontaneity of the process. The FT-IR spectra and thermogravimetric analyses verify the sorption based on starch–NH₂⁺CSSH...⁻O₃S–dye electrostatic attraction. The DTCS can be regenerated from the dye loaded DTCS in a weak basic solution containing sodium sulfate.

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1. Introduction

Textile industries are among the most polluting industries in terms of the volume and the complexity of treatment of its effluents [1]. Wastewaters discharged by textile industries are known to contain large amounts of toxic dyes. Thus, removal of dyes from wastewater before discharging to environment is essential for the protection of health and environment. Some of the techniques used in treatment of wastewater containing dyes are flocculation, coagulation, precipitation, adsorption, electrochemical techniques, membrane filtration, ozonation, and fungal decolorization [2]. Among these techniques, adsorption process for dyes removal is quite unique because it is simple, highly efficient, economic compared with other ways [3]. Moreover, adsorption treatment has been shown a large applicable scale to remove dyes [4]. Proper selection of adsorbent used in the adsorption procedure will produce high-quality treated effluents.

Recently natural polysaccharides have been developed as environmentally friendly materials for removing toxic pollutants from aqueous solutions, and attracted much attention [5]. Among numerous polysaccharides starch is an abundant, inexpensive, renewable and fully biodegradable natural raw material [6]. However, its application in dyes removal is limited due to the low

capacity and stability [7]. To circumvent the problems, in our group, a new class of modified starches has been synthesized and applied as adsorbents for anionic dyes [8–10]. One of the most striking adsorbent is the dithiocarbamate-modified starch (DTCS). The DTCS can effectively adsorb most heavy metals and positive particles [11]. Furthermore, the metal bound DTCS strongly chelates dyes resulting in extensive use of the material [12]. Unfortunately, the DTCS itself is not employed to treat textile wastewater. If its sorption ability for dyes is noteworthy, the DTCS would be applicable to a broad range of wastewater treatments (i.e., textile effluents, metal polluted water and complicated sewage). It will show good business prospects. The focus of this work is to evaluate the dyes adsorption properties of the DTCS. The Langmuir–Freundlich isotherm is used to investigate the sorption mechanism to obtain new insights into the intermolecular interaction between dyes and the DTCS.

2. Materials and methods

2.1. Materials

Maize starch, of food grade quality, was used in this research. Five commercially available dyes were purchased from Shanghai Reagents Company and used without further purification. They are commonly used in China and regarded as typical dye contaminants in the discharged effluent [13,14]. The chemical structures and characteristics of the selected dyes are listed in Table 1.

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Nomenclature

a	parameter in Langmuir isotherm (mmol g^{-1})
b	parameter in Langmuir isotherm (L mmol^{-1})
c_0	dye initial concentration (mmol L^{-1})
c_e	dye equilibrium concentration (mmol L^{-1})
k_1	rate constant of pseudo-first-order (min^{-1})
k_2	rate constant of pseudo-second-order ($\text{g mmol}^{-1} \text{min}^{-1}$)
K_F	parameter in Freundlich isotherm ($\text{mmol}^{1-1/n} \text{L}^{1/n} \text{g}^{-1}$)
K_{LF}	parameter in Langmuir–Freundlich model ($\text{L}^{1/\nu} \text{mmol}^{-1/\nu}$)
m	mass of adsorbent (g)
q_e	amount of dye sorbed at equilibrium (mmol g^{-1})
q_m	maximum adsorption capacity in the Langmuir–Freundlich model (mmol g^{-1})
n	parameter in Freundlich isotherm
q_t	amount of dye sorbed at any time t (mmol g^{-1})
T	temperature (K)
ν	parameter in Langmuir–Freundlich model
ΔG^θ	changes of Gibbs energy (kJ mol^{-1})
ΔH^θ	changes of enthalpy (kJ mol^{-1})
ΔS^θ	changes of entropy ($\text{J mol}^{-1} \text{K}^{-1}$)

2.2. Techniques

UV–vis spectra were measured on Perkin Elmer Lambda 35 Spectrometer. Thermogravimetric analysis was performed with STA 409 PC/4/H Lux at a heating rate of 10°C per minute under

N_2 atmosphere. Fourier transform infrared spectra (FT-IR) were recorded on a PE Spectrum One spectrometer with KBr pellets in the $4000\text{--}450 \text{ cm}^{-1}$ region.

2.3. Preparation of dithiocarbamate-modified starch (DTCS)

The ethylenediamine modified starch (CAS) was first synthesized as our previous report [15]. Then 10 g dried CAS further reacted with 5 mL CS_2 in alkaline solution. The mixture was warmed up to 40°C . After 12 h, the precipitation was separated and washed with deionized water, dilute HCl solution, dilute NaOH solution and acetone in sequence. The acquired DTCS was kept in a vacuum oven for 1 day and stored in desiccators. The procedure was depicted in Fig. 1.

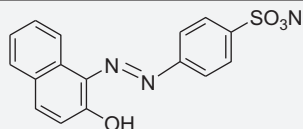
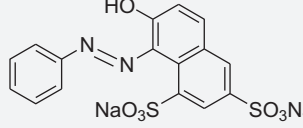
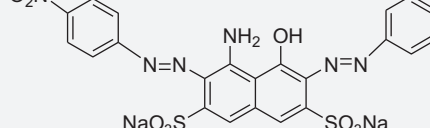
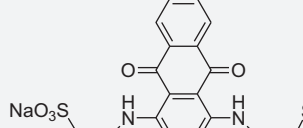
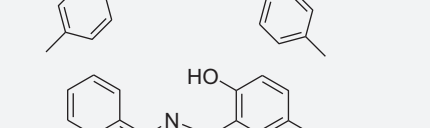
2.4. Concentration measurement calibration

To determine the dye concentration in the solution, a calibration curve was first obtained using the UV–vis spectrophotometer. The maximum absorbance of each dye was confirmed by scanning the dye aqueous solution over the spectral range of $200\text{--}800 \text{ nm}$. A series of dye solutions with various concentrations were used for the measurement of a calibration curve. A linear relationship between the absorbance (at the wavelength of maximum absorbance, λ_{max}) and the dye concentration was obtained.

2.5. Sorption and desorption experiments

The effect of solution pH on the adsorption of the investigated dyes onto DTCS was investigated at $25 \pm 1^\circ\text{C}$. A 0.100 g of dry DTCS samples were placed in a series of 100 mL flasks containing 50 mL of dye stock solution with concentration of 800 mg L^{-1} . The desired

Table 1
Characteristics and structures of the adsorbates used in this study.

Generic name	Abbreviation	C.I.	Class and Fw	λ_{max} (nm)	Structure
Acid orange 7	A07	15,510	Monoazo 350.3	485	
Acid orange 10	A010	16,230	Monoazo 452.4	475	
Acid black 1	AB1	20,470	Diazo 616.5	618	
Acid green 25	AG25	61,570	Anthraquinone 622.6	642	
Acid red 18	AR18	16,255	Monoazo 604.5	506	

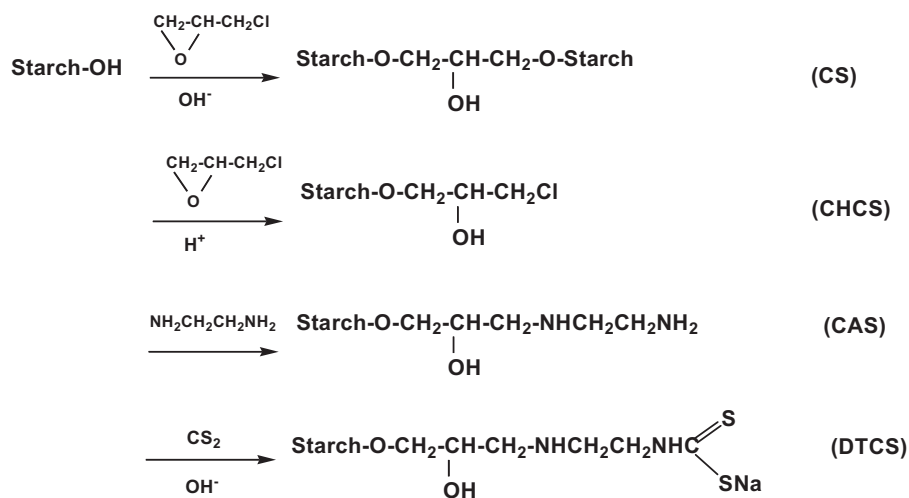


Fig. 1. Synthesis of dithiocarbamate-modified starch (DTCS).

pH was controlled using 2 mol L^{-1} HCl and 2 mol L^{-1} NaOH. The contents of the flasks were equilibrated on a thermostatic shaker for 12 h. The residual concentration of the dye was determined spectrophotometrically at λ_{max} of each dye.

In experiments of batch kinetic adsorption, a mixture of DTCS (0.100 g) and 75 mL $2.0 \times 10^{-3} \text{ mol L}^{-1}$ dye solution were agitated with a water bath. The pH was kept constant (pH 4.0) throughout kinetic studies. The concentration of each dye was measured at different time intervals up to 24 h. Each data point was obtained from an individual flask.

For equilibrium sorption studies, sorption of individual dyes from aqueous solutions (varied from 400 mg L^{-1} to 1500 mg L^{-1}) was investigated in batch experiments at pH value of 4. The reproducibility of the sorption experiments results was verified in duplicate. The amount of individual dyes sorbed onto unit mass of DTCS (sorption capacity, mmol g^{-1}) was calculated from:

$$q_e m = (c_0 - c_e)V \quad (1)$$

where q_e is the dye concentration in the solid phase (adsorbent) at equilibrium (mmol g^{-1}), m is the mass of DTCS used (g), c_0 is the initial dye concentration in the liquid phase (mmol L^{-1}), c_e is the dye concentration in the liquid phase at equilibrium (mmol L^{-1}), and V is the total volume of solution used (L). The models of the isotherms were fitted to equilibrium data using a nonlinear method, with the nonlinear fitting facilities of the Microcal Origin 7.0 Software.

The dyes release experiments were carried out after an initial incubation time of 24 h under conditions described above. When DTCS samples were saturated with individual dyes, they were separated out and placed in 50 mL of Na_2SO_4 solutions having a 0.25 mol L^{-1} concentration at pH 8. After shaken for 24 h at $25 \pm 1^\circ \text{C}$, the concentrations of free dyes in solutions were measured.

3. Results and discussion

3.1. Effect of pH and sorption mechanism

The pH of the aqueous solution is an important controlling parameter in the dyes sorption processes. The influence of pH on the adsorption capacity was observed over a pH range of 4–8. It is known that the dyes molecules are stable in the pH range. The wavelength of maximum absorbance of each dye does not shift in the pH range investigated. As can be seen from Fig. 2, the capacity of DTCS for each dye is pH dependent. With the increase of pH value, the adsorption capacity for each dye decreases dramatically.

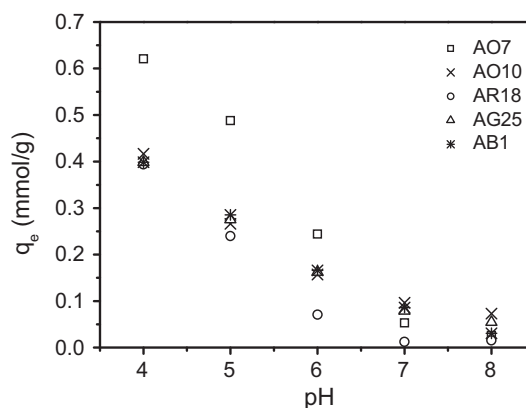
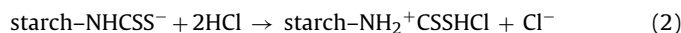
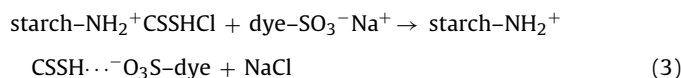


Fig. 2. Effect of pH value on adsorption of the dyes onto DTCS.

The effect of pH on the sorption of each dye onto DTCS can be interpreted with the help of surface charge of the sorbent in acidic/basic medium. In acidic medium, positive surface charge is developed due to protonation of dithiocarbamate which increases with the increase in H^+ (decrease in pH):



Then the anionic dyes can be adsorbed via the electrostatic attraction:



That is why sorption of negatively charged dyes is expected to increase with decreasing pH. In basic medium, base abstracts the H^+ of dithiocarbamate group, which makes the surface of DTCS negative. Due to electrostatic repulsion, the sorption ability decreases with increase in pH and almost negligible sorption occurs at pH 8. The sorption efficiency for each dye decreased about 85% from pH 4 to 8. The capacity for each dye is below 0.06 mmol g^{-1} at the pH value of 8. It suggests that the adsorption is controlled by a strong ionic attraction. The other driven forces, such as hydrogen bonding and hydrophobic force, are much weak.

3.2. Effect of contact time and sorption kinetics

From a mechanistic point of view to interpret the kinetic experimental data, prediction of the rate-limiting step is an important

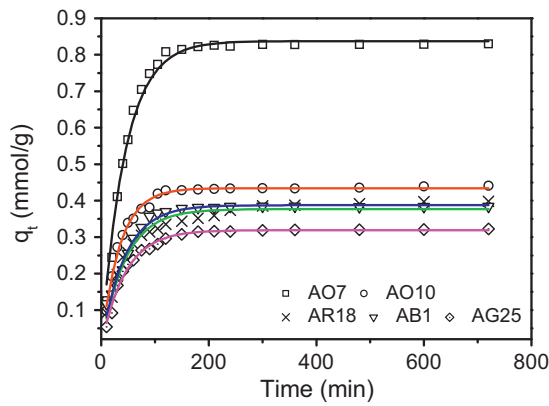


Fig. 3. Adsorption kinetic data fitted to the pseudo-first-order equation. Lines represent modeled results using the pseudo-first-order equation.

factor to be considered in the sorption process. The pseudo-first-order [16] and pseudo-second-order equations [17] were used in this work. The pseudo-first-order rate expression is generally expressed as follows:

$$q_t = q_e(1 - e^{-k_1 t}) \quad (4)$$

The pseudo-second-order equation is also based on the sorption capacity of the solid phase. If the rate of sorption is a second-order mechanism, the pseudo-second-order equation is expressed as

$$q_t = \frac{k_2 q_e^2 t}{1 + k_2 q_e t} \quad (5)$$

where q_t is the amount of dye on the sorbent (mmol g^{-1}) at any time t (min), q_e is the amount of dye adsorbed at equilibrium (mmol g^{-1}), k_1 is the rate constant of pseudo-first-order adsorption (min^{-1}) and k_2 is the rate constant of pseudo-second-order adsorption ($\text{g mmol}^{-1} \text{min}^{-1}$). The first-order rate constant k_1 and the calculated q_e values were determined, respectively (Fig. 3). Commonly, in most studied adsorption systems, the pseudo-first-order equation does not fit well over the entire adsorption period and is generally applicable over the first 20–30 min of the sorption process. Such time-limited application of the pseudo-first-order model was previously mentioned in the related scientific literature [18,19]. However, in our case, there is a high match between pseudo-first-order equation and the experimental results for the five dyes. In addition, as shown in Table 2, the pseudo-first-order predicted $q_{e,\text{cal}}$ of all dyes are the most agreeing values with the experimental data ($q_{e,\text{experiments}}$). Although the pseudo-second-order equation gives satisfying correlation coefficients R^2 values (Fig. 4 and Table 2), the $q_{e,\text{cal}}$ obtained from the model did not fit well with $q_{e,\text{experiments}}$. According to the kinetic modeling results, the pseudo-first-order model shows the best fit to the experimental data related to the biosorption of used dyes onto DTCS. The adsorption processes for the five dyes have two stages. The first is a smoothly increase stage which lasts for about 60 min where 70% of dye removal occurs followed by a slower stage extends to 5 h achieving equilibrium. The sorption rate is

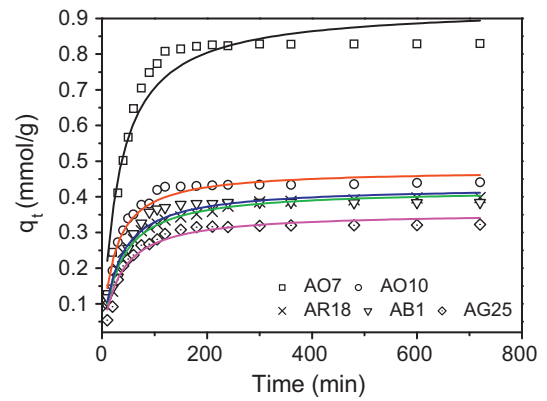


Fig. 4. Adsorption kinetic data fitted to the pseudo-second-order equation. Lines represent modeled results using the pseudo-second-order equation.

not related with the properties of dyes, i.e., molecular size and charges.

3.3. Adsorption equilibrium and characterizations

To optimize the design of an adsorption system for the adsorption of adsorbates, it is important to establish the most appropriate correlation for the equilibrium curves. Various isotherm equations like those of Langmuir [20], Freundlich [21], and Langmuir–Freundlich isotherms [22] were tested in this work. In the Langmuir theory, the basic assumption is that the sorption takes place at specific homogeneous sites within the adsorbent. This equation can be written as follows:

$$q_e = \frac{abc_e}{1 + bc_e} \quad (6)$$

Eq. (7) is the well-known Freundlich isotherm, which describes heterogeneous systems, i.e., surfaces with nonenergetically equivalent sites.

$$q_e = K_F c_e^{1/n} \quad (7)$$

Another useful equation is the Langmuir–Freundlich isotherm, which includes three parameters. This isotherm is based on the generalized Langmuir and generalized exponential isotherms and is the most promising extension of the Langmuir and Freundlich isotherms. The Langmuir–Freundlich isotherm is expressed as

$$q_e = \frac{q_m (K_{LF} c_e)^\nu}{1 + (K_{LF} c_e)^\nu} \quad (8)$$

where a and b are the Langmuir isotherm parameters, K_F is the Freundlich constant being indicative of the extent of sorption, $1/n$ is the heterogeneity factor being an indicator of sorption effectiveness, q_m is the maximum adsorption (mmol g^{-1}), K_{LF} is the Langmuir–Freundlich constant $\text{L}^{1/\nu} \text{mmol}^{-1/\nu}$ and ν is the Langmuir–Freundlich heterogeneity constant.

The results of the experimental data are shown in Table 3, in Langmuir model the coefficient (R^2) of adsorption for the smaller

Table 2
Parameters of kinetic models for dyes adsorption on DTCS.

Dye	Pseudo-first-order			Pseudo-second-order			$q_{e,\text{experiments}}$ (mmol g^{-1})
	k_1 (min^{-1})	$q_{e,\text{cal}}$ (mmol g^{-1})	R^2	k_2 ($\text{g mmol}^{-1} \text{min}^{-1}$)	$q_{e,\text{cal}}$ (mmol g^{-1})	R^2	
AO7	0.023	0.837	0.989	0.035	0.934	0.926	0.828
AO10	0.028	0.434	0.992	0.091	0.476	0.951	0.439
AG25	0.022	0.319	0.988	0.086	0.356	0.957	0.321
AB1	0.023	0.387	0.981	0.077	0.429	0.932	0.383
AR18	0.023	0.377	0.973	0.072	0.473	0.951	0.397

Table 3
Parameters of Langmuir and Freundlich isotherms for the dyes adsorption onto DTCS.

Dye	Langmuir isotherm			Freundlich isotherm		
	a (mmol g ⁻¹)	b (L mmol ⁻¹)	R^2	K_F (mmol ^{1-1/n} L ^{1/n} g ⁻¹)	$1/n$	R^2
AO7	0.803	58.41	0.988	0.774	0.066	0.812
AO10	0.434	15.98	0.958	0.399	0.085	0.926
AG25	0.323	246.94	0.842	0.322	0.023	0.975
AB1	0.387	150.76	0.829	0.388	0.053	0.939
AR18	0.406	55.62	0.880	0.401	0.076	0.908

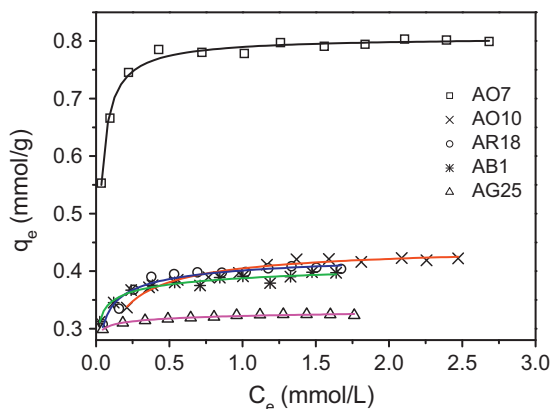


Fig. 5. Adsorption isotherms fitted to Langmuir–Freundlich equation (the real lines).

dyes AO7 and AO10 are satisfied, but those for AG25, AB1 and AR18 are markedly low. When the Freundlich isotherm is applied, there is particularly good agreement with the equilibrium data for the adsorption of the largest molecule, AG25.

Incorporating the Langmuir equation and Freundlich equation, the Langmuir–Freundlich isotherm was used to fit the experimental data. The adsorption isotherms based on this model are shown in Fig. 5, and the parameters are listed in Table 4. The Langmuir–Freundlich isotherm clearly provides satisfactory fits for the five dyes. The capacity of DTCS for each dye follows the sequence AO7 > AO10 > AR18 > AB1 > AG25. Obviously, the capacity is not controlled by the number of negative charge on the dye molecule and structures of the dyes. However, the adsorption capacity sequence (AO7 > AO10 > AR18 > AB1 > AG25) is inverse to the order of molecular size (AO7 < AO10 < AR18 < AB1 < AG25). The results suggest that the dyes molecules lay down adsorbent surface. A bigger dye molecule occupies more specific surface area of DTCS, resulting in the decrease of adsorption capacity. The behavior of DTCS is very similar to chitosan [23]. The capacities of DTCS for the dyes are higher than those of activated carbon (0.72 mmol g⁻¹ for AO7 and 0.25 mmol g⁻¹ for AG25) [24,25].

FT-IR spectra were used to investigate dye adsorbing to DTCS. The different FT-IR spectra of DTCS before and after the adsorption of the dyes are shown in Fig. 6. After adsorption of the dyes, the strong and broad peaks at 3400 cm⁻¹ caused by νO–H and νN–H vibration did not move significantly. The peak at 1645 cm⁻¹ assigned to δN–H bent vibration shift to 1639 cm⁻¹, it proved that amino group become protonated and bond with

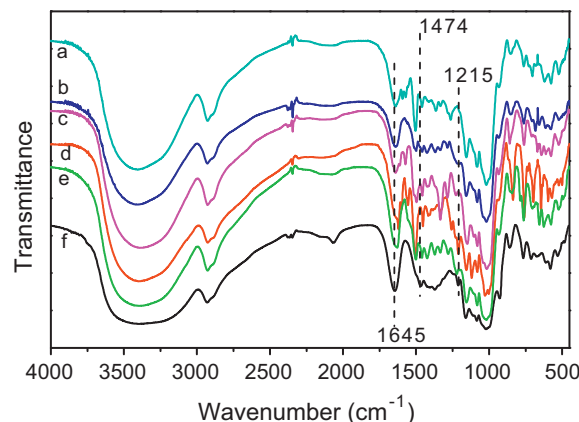


Fig. 6. FT-IR spectra of DTCS before and after adsorption of dyestuffs: (a) DTCS-AG25; (b) DTCS-AR18; (c) DTCS-AB1; (d) DTCS-AO7; (e) DTCS-AO10; and (f) DTCS.

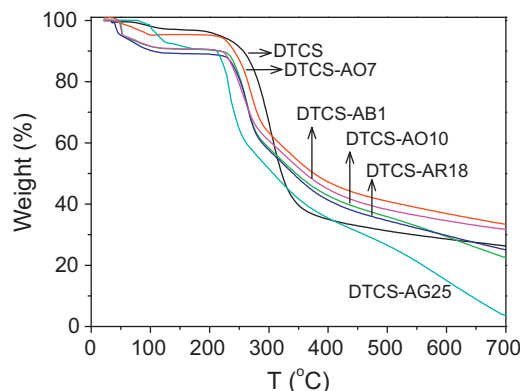


Fig. 7. TGA curves of DTCS and dye loaded DTCS.

dyes by electrostatic force [26]. The peaks at 1474 cm⁻¹ ν(S–C–N) and 1215 cm⁻¹ ν(S–C–N) of DTCS moved to 1500 cm⁻¹, and 1225 cm⁻¹, respectively [27]. Four peaks at about 1556, 1420, 1332 and 1280 cm⁻¹ appear showing the characteristic νC=C vibration of aromatic rings. The typical vibration of νSO₂ is clearly observed at the about 1119 cm⁻¹ [28]. These data verify the starch–NH₂⁺CSH⁺–O₃S–dye electrostatic attraction and the dyes effectively adsorb to DTCS.

After the dyes adsorbing to the DTCS, the thermal stability of DTCS lowered. As shown in Fig. 7, all the DTCS–dye curves

Table 4
Parameters of Langmuir–Freundlich isotherms for anionic dyes adsorption onto DTCS.

Dye	q_m mmol g ⁻¹	$K_{LF} L^{1/\nu}$ mmol ^{-1/\nu}	ν	R^2
AO7	0.807	63.43	0.910	0.990
AO10	0.451	23.44	0.684	0.978
AG25	0.359	127643.89	0.183	0.983
AB1	0.443	780.68	0.275	0.977
AR18	0.449	105.12	0.475	0.969

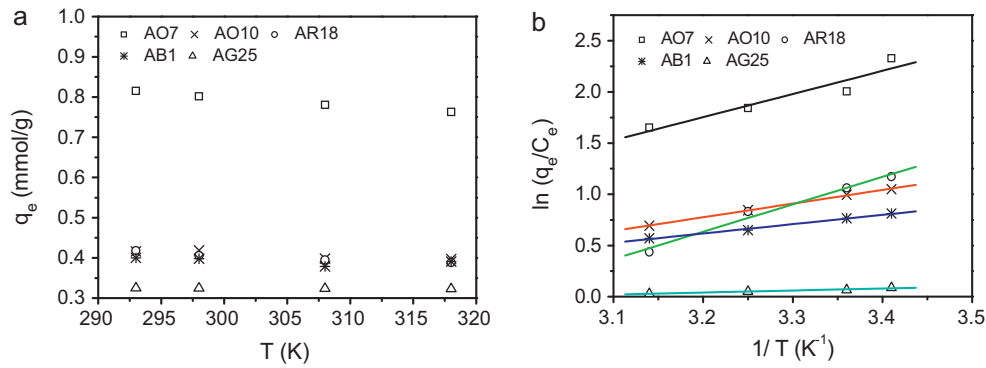


Fig. 8. Effect of temperature on adsorption (a) and plot of Van't Hoff equation for adsorption of dyes on DTCS (b).

appear similar in shape. At least four weight loss stages can be distinguished from the TGA curves. For DTCS, weight loss in the 60–150 °C attributed to the release of adsorbed water, following in the 220–300 °C range, weight loss is due to the breakdown of the dithiocarbamate and partial hydroxyl groups [29,30]. After adsorption occurred, complex of the anionic dye with DTCS (DTCS–dye) was formed. The decomposition temperature of DTCS–dye lowered to 200–210 °C. Furthermore, the DTCS–dye shows a fast decomposition rate than that of DTCS within 300 °C. It can be attributed to the formation of $-\text{NH}_2^+\text{CSSH}\cdots\text{O}_3\text{S}-$ complex, which ruins initial surface structure of DTCS. It induces fast decomposition of dithiocarbamate groups.

3.4. Thermodynamics

To further probe the adsorption of anionic dyes onto DTCS, the thermodynamic parameters of the adsorption were determined by applying Van't Hoff equation (Fig. 8b):

$$\log\left(\frac{q_e}{C_e}\right) = -\frac{\Delta H^\theta}{2.303RT} + \frac{\Delta S^\theta}{2.303R} \quad (9)$$

The calculated values of ΔH^θ (the changes of apparent enthalpy) and ΔS^θ (the changes of entropy) are reported in Table 5. The changes of Gibbs energy (ΔG^θ) can be obtained by using equation:

$$\Delta G^\theta = \Delta H^\theta - T\Delta S^\theta \quad (10)$$

The negative values of ΔH^θ indicate that adsorption process is exothermic. The data given in Table 5 shows that $|\Delta H^\theta| > |T\Delta S^\theta|$ for both dyes at all temperatures. This indicates that the adsorption process is dominated by enthalpic rather than entropic changes. The results show that all the adsorption capacities of the five dyes

are higher at relatively low temperature (Fig. 8a). In fact, the heat adsorbed does enforce the decomposition of $-\text{NH}_2^+\text{CSSH}\cdots\text{O}_3\text{S}-$ complex and increase the solubility of the dye. The observations are in accordance with the equilibrium and thermogravimetric studies. In addition, the negative values of ΔG^θ (Table 5) indicate that the adsorption of both dyes is spontaneous. In many cases, the change in Gibbs energy for physisorption is between -20 and 0 kJ mol^{-1} , but chemisorption is in a range of -80 to -400 kJ mol^{-1} [31,32]. The values of ΔG^θ obtained in this study are within the ranges of -20 to 0 kJ mol^{-1} , indicating that physisorption is the dominating mechanism.

3.5. Desorption and reproducibility of the adsorption capacity

Studies on dye desorption from the dye saturated DTCS (DTCS–dye) contribute to well understanding the interaction mechanism and repeatedly utilize adsorbent. Fig. 9 emphasizes the desorption of each dye from DTCS–dye in $0.2500 \text{ mol L}^{-1}$ sodium sulfate solution at pH 8. The sorption mechanism is mainly based on electrostatic attraction. In weak basic solution, dithiocarbamate of DTCS changed into anion and lost the ability of binding dyes, resulted in desorption of dyes. The desorption efficiencies of five dyes achieve 80%. For AG25, the effect of molecule size on desorption is most striking. The amount of AG25 loaded on DTCS decreases about 92% in the presence of sodium sulfate. Only a little decrease of the adsorption efficiency was seen in the second use, and the regenerated DTCS retains its dyes uptake capacity of 90.6% after twice use cycles (available online in the supplemental materials). Therefore, the high adsorption capacity and good reproducibility make the DTCS had a significant potential for removing anionic dyes from aqueous solutions.

Table 5

Thermodynamic values at various temperatures for the dyes adsorbed onto DTCS.

T	ΔG^θ (kJ mol^{-1})	ΔH^θ (kJ mol^{-1})	ΔS^θ ($\text{J mol}^{-1} \text{K}^{-1}$)	ΔG^θ (kJ mol^{-1})	ΔH^θ (kJ mol^{-1})	ΔS^θ ($\text{J mol}^{-1} \text{K}^{-1}$)
AO7				AO10		
293 K	-5.45	-18.83	-45.66	-2.59	-11.09	-29.02
298 K	-5.22			-2.44		
308 K	-4.77			-2.15		
318 K	-4.31			-1.86		
AR18				AB1		
293 K	-2.93	-22.27	-65.98	-1.97	-7.57	-19.11
298 K	-2.61			-1.88		
308 K	-1.95			-1.68		
318 K	-1.29			-1.49		
AG25						
293 K	-4.88	-4.88	-4.88			
298 K						
308 K						
318 K						

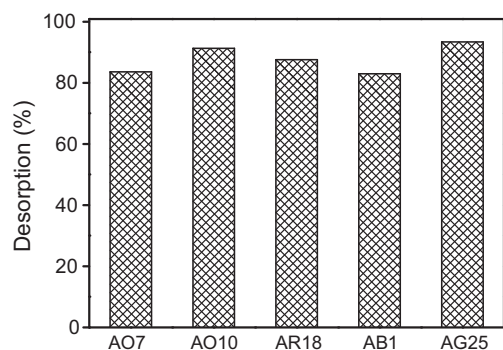


Fig. 9. Desorption of dyes from the dyes loaded DTCS in a $0.2500 \text{ mol L}^{-1}$ at pH 8.

4. Conclusions

A batch system was applied to study the adsorption of five anionic dyes from aqueous solutions by dithiocarbamate-modified starch. The adsorption with respect to the pH and temperature were investigated. It is found that the capacity of DTCS for each dye is pH dependent, and the adsorption is governed by electrostatic attraction. At the suitable pH 4, two kinetic models, that is, pseudo-first- and pseudo-second-order, were tested to investigate the adsorption process. The kinetic parameters of the models were calculated and discussed. The results suggest that the best fit model is the pseudo-first-order equation. The Langmuir, Freundlich and Langmuir–Freundlich adsorption models were applied to describe the equilibrium isotherms and isotherm constants were determined. The Langmuir–Freundlich model agrees very well with experimental data and the maximum adsorption capacity sequence is $\text{AO7} > \text{AO10} > \text{AR18} > \text{AB1} > \text{AG25}$. Thermodynamic parameters such as change in free energy (ΔG^θ), enthalpy (ΔH^θ), entropy (ΔS^θ) were also determined. The adsorption mechanism is shown to be the electrostatic interactions between the dye and DTCS. The desorption data shows that the removal percent of dye from the dye loaded DTCS is over 80% in Na_2SO_4 solutions at pH 8, 25°C . The desorbed DTCS can be reused to adsorb the dye.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jhazmat.2011.01.104.

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