Preparation and characterization of modified sepiolite for the removal of Acid green 20 from aqueous solutions: isotherm, kinetic and process optimization

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Abstract

In this study, adsorption of Acid green 20 (AG₂₀) by modified sepiolite, hexadecyltrimethylammonium-modified sepiolite (HDTMA-Sep), was optimized using response surface methodology based on a central composite design. Characteristics of natural sepiolite and modified sepiolite can be analyzed by FTIR and XRD techniques. In order to achieve a better comprehension of applicability of adsorbent for removing dyes from colored effluents, isotherm and kinetic studies were also carried out. The maximum dye removal of 78% and 72% for synthetic solutions and real wastewater, respectively, was obtained at the initial dye concentration of 77.1 mg/L, contact time of 24.81 min, solution pH of 6.19 and adsorbent dosage of 1.03 g/L. The kinetic studies revealed that the adsorption process followed pseudo-second-order model. The adsorption data were best fitted to Freundlich model. The result indicated that the contact time and dye concentration have more influence on the removal efficiency rather than pH and amount of adsorbent. The experimental data from this study indicated that the modified sepiolite is an efficient adsorbent for dye removal from aqueous solutions.

Keywords Adsorption · Sepiolite · Response surface methodology · Acid green 20 · Central composite design

Introduction

Dyes are used in various industrials such as textile, tannery, paper, printing, pharmaceutical and plastic (Wang et al. 2015a; Shirsath et al. 2013). These materials are considered as important and harmful pollutants in industrial effluents. Dyes are categorized in different ways including their applications and structures (dos Santos et al. 2007).

Azo dyes are a group of dyes with one or more azo bonds (–N=N–) in their structures which are estimated around 60–70% of all textile used dyes (Thiam et al. 2015; Olya et al. 2015; Dasgupta et al. 2015). Due to their strong stability and high water solubility, treatment of wastewater containing azo dyes is difficult (Dasgupta et al. 2015). Some problems including resistance to aerobic degradation, generation of toxic aromatic amines under anoxic conditions and generation of carcinogenic and mutagenic activities have been reported (Tee et al. 2015; Wang et al. 2015a; Jin et al. 2014; Fan et al. 2015). Therefore, in order to protect the environment and human health, decolorization of these effluents should be considered.

Acid green 20 (AG₂₀) was selected as the non-biodegradable model of azo dyes (Zhang and Zheng 2009). Many

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industries including textile and printing use these dyes in their processes because of light resistance ability, perspiration and wash ability (Zhang and Zheng 2009).

Several techniques including coagulation, ion exchange, filtration, biological treatment, advanced oxidation processes, electrolysis, activated sludge, adsorption and solvent extraction have been proposed to remove dyes from the industrial wastewater (Tee et al. 2015; Zhang et al. 2015; Jin et al. 2014). Due to their chemical structure and potentially carcinogenic effects, conventional physical and chemical methods are not able to remove completely this dye from effluents (Zhou et al. 2012). Among these techniques, adsorption is proven to be effective and economical method for dyes removal from industrial wastewater (Wang et al. 2015a; Elwakeel et al. 2017a, b; Malakootian et al. 2017). Studies showed that several materials, including chitosan (Crini and Badot 2008), fly ash (Mall et al. 2006), activated carbon (Cheng et al. 2015) and natural clays such as bentonite (Tahir and Rauf 2006), montmorillonite (Wang et al. 2004), sepiolite (Doğan et al. 2007) and zeolite (Jin et al. 2014), could be used as an effective adsorbent for the removal of dyes from wastewaters.

Sepiolite (hydrous magnesium silicate) is a zeolite-like clay material with $\text{Si}_{12}\text{O}_{30}\text{Mg}_8(\text{OH})_4(\text{H}_2\text{O})_4 \cdot 8\text{H}_2\text{O}$ formula and characterized by its fibrous morphology that is due to its crystalline structure (Qiu et al. 2013; Marjanović et al. 2013). It presents a structure of needlelike particles which can be explained as composition of talc-like sheets that is made of two sheets of tetrahedral silica and a central octahedral magnesium sheet (Lescano et al. 2014; Lazarević et al. 2012). Because of sorptive, rheological and catalytic properties, this material is extensively used in various industrial applications (Fu et al. 2015; Algoufi et al. 2014). Sepiolite has a higher surface area ($\sim 300 \text{ m}^2/\text{g}$) (Algoufi et al. 2014) than other clay minerals such as Hj clay (Li et al. 2016), Fer-smectite (Li et al. 2015), kaolinite (Üzum et al. 2009) and montmorillonite (Bhowmick et al. 2014).

In addition, sepiolite has low price and produced in large amount (Chao and Chen 2012). Generally, negative surface clay minerals showed little success to adsorb anionic pollutants especially acidic dyes (Jin et al. 2014). Several methods can be used to alter the properties of sepiolite surface (Gök

et al. 2008; Özcan et al. 2006; Wang et al. 2012; Lazarević et al. 2007): modification by the use of surfactant through simple ion-exchange reaction to direct van der Waals interaction between adsorbate and organic surfactant cations is one of them. The surfactant-modified clay entitled “organoclay,” surfactant modification strongly enhanced the transformation of organophobic compound toward organophilic surface, and finally, the adsorption capacity increases (Li and Bowman 2001). In the previous study, hexadecyltrimethylammonium bromide (HDTMA-Br) was used to enhance adsorption capacity related to nitrate, chromate and arsenate (Li and Bowman 2001). Hexadecyltrimethylammonium (HDTMA-Br) bromide, a cationic surfactants with tetra-substituted ammonium with permanently charged quaternary nitrogen and a long straight alkyl (C_{16}) chain that make unique with a high degree of hydrophobicity, is a good candidate for sepiolite modification (Kaboarani and Riedl 2015). HDTMA has good points such as availability, low cost and possibility to be degraded by some microorganism in the environment (Kaboarani and Riedl 2015). Malakootian et al. conducted studies on the removal dyes from aqueous solutions (Malakootian et al. 2015; Malakootian 2016; Malakootian et al. 2013, 2016).

Response surface methodology (RSM) as a reliable statistical method applied to evaluate the interaction effects among parameters with least number of experimental runs (Yolmeh et al. 2014). Thus in this study, RSM based on central composite design (CCD) was used for optimization and estimation of the adsorption process using modified sepiolite to develop a mathematical correlation between the selected parameters including adsorbent dosage, initial dye concentration, contact time and solution pH in AG_{20} removal from aqueous solution and real wastewater.

Experimental

Chemicals

The Acid green 20 (AG_{20}) with purity of $> 87\%$ was purchased from Alvan Sabet Company, Iran. The main properties of AG_{20} are shown in Table 1. Sepiolite (Sep) was

Table 1 The main properties of AG_{20} (Zhang and Zheng 2009)

Name	Chemical structure	Molecular formula	M_w (g/mol)
Acid green 20 (AG_{20})		$\text{C}_{22}\text{H}_{16}\text{N}_6\text{Na}_2\text{O}_7\text{S}_2$	586.51

prepared from Dorkav Mining Company, Iran. The chemical composition of sepiolite (%) was: SiO₂, 55.52; Al₂O₃, 0.4; Fe₂O₃, 0.68; MgO, 16.29; CaO, 1.3; Na₂O, 0.02; K₂O, 0.01; and TiO₂, 0.02. Also, sepiolite has a specific surface area: 179.9 m²/g; pore size: 15–40 nm and pore volume: 0.378 cm³/g (Sharifipour et al. 2015). Hexadecyltrimethylammonium bromide, sodium hydroxide and sulfuric acid were purchased from Merck, Germany. All other chemicals used in this experiments were of analytical grade and used without further purification.

Preparation and characterization of adsorbent (HDTMA-Sep)

Four grams of sepiolite (60-mesh sieve) was added into 100 mL HDTMA solution with the concentration of 2% (wt/wt) and thoroughly shaken at 200 rpm for 48 h, after that the suspension was centrifuged (Hettich, EBA 20, Germany) and the supernatant was separated. In order to remove excess HDTMA, the centrifuged solid was soaked several times in distilled water, and then, the HDTMA-Sep was dried in an oven (UNB-400, Germany) at 120 °C for 6 h. The dried powder was sieved through a 60 mesh. Finally, white powder (HDTMA-Sep) stored in a desiccator until use (Jin et al. 2014).

Functional groups in natural sepiolite (N-Sep) and HDTMA-Sep were determined with Fourier transform infrared spectroscopy (Tensor 27, Bruker, Germany) in the range 4000–400 cm⁻¹. X-ray diffractometer (XPERT, Holland) working at 30 mA and 40 kV using Cu K α radiation source ($\lambda = 1.5418 \text{ \AA}$) at $2\theta = 2-70^\circ$ with counting time of 1.5 s and step size of 0.02 was used to analyze the crystalline phase of natural sepiolite.

Adsorption experiments

Batch adsorption experiments were conducted in various initial concentrations of dye, adsorbent dosage, different contact times and solution pH_s, which at first designed with response surface methodology. AG₂₀ stock solution was prepared by dissolving AG₂₀ into deionized water, and different concentrations of AG₂₀ solution were prepared by proper dilution of AG₂₀ stock solution. The pH values of samples were adjusted with NaOH or H₂SO₄ (0.1 N). All experiments were done in 100-mL beaker containing 50 mL dye solution and shaken at 200 rpm during contact time using mechanical shaker. Suspension was centrifuged at 3700 rpm for 10 min, and then, liquid phase was separated by 0.45- μm filter. The final AG₂₀ concentration was determined by UV–Vis spectrophotometer (Shimadzu, UV-1800, Japan) at wavelength of 606 nm, and according to Eqs. 1 and 2, the removal efficiency (%) and adsorption capacity (q_e), respectively, were calculated:

$$\text{Removal}_{\text{efficiency}}(\%) = \left(\frac{C_0 - C_t}{C_0} \right) \times 100 \quad (1)$$

$$q_e = \left(\frac{C_0 - C_e}{m} \right) \times V \quad (2)$$

where C_0 (mg/L) and C_e (mg/L) are initial and equilibrium concentrations of AG₂₀ in the solution, respectively, and C_t (mg/L) is the concentration of AG₂₀ at time of t (min). V (L) is the volume of AG₂₀ solution, and m is the mass of the adsorbent in grams.

To ensure the accuracy of the result, all experiments were duplicated and mean of values was considered for analysis of the data.

Response surface methodology (RSM)

The experimental design was done based on CCD in software Design-Expert V. 7. 0. 0. Response surface methodology (RSM) is a statistical method that is applied to improve, develop and optimize chemical process (Ye et al. 2016). The main objective of RSM is to optimize the response which is influenced by various independent input parameters (Mandal et al. 2015). RSM based on central composite design (CCD) was used for optimization of AG₂₀ decolorization process. Application of CCD allows estimation of four independent parameters effectiveness, including the initial AG₂₀ concentration, solution pH, adsorbent dosage and contact time on removal percentage. The previous studies have stated that the concentration range of dyes in textile industry wastewater varies between 10 and 200 mg/L (El Haddad et al. 2014). Thus, AG₂₀ concentration of solutions was selected in the range of 10–100 mg/L. In this model, the number of experimental runs was calculated from Eq. 3 (Srivastava et al. 2015):

$$N = 2^n + 2n + x_c \quad (3)$$

where N , n and x_c are the number of experimental runs, the number of variables and the number of central points, respectively.

According to Eq. 3, based on 4 variables and 6 central points, 30 runs were acquired. Five levels of $-\alpha$, -1 , 0 , $+1$ and $+\alpha$ were coded for each variation. On the basis of program setting, the “ α value” was coded as 2. In Table 2, the operational ranges of the input variables as coded level and actual units of measurements are shown.

The quadratic equation for predicting the optimal conditions with RSM based on CCD is shown in Eq. 4 (Azizi et al. 2012; Karimifard and Moghaddam 2016):

$$Y = \beta_0 + \sum_{i=1}^n \beta_i X_i + \sum_{i=1}^n \beta_{ii} X_i^2 + \sum_{i=1}^{n-1} \sum_{j=i+1}^n \beta_{ij} X_i X_j \quad (4)$$

Table 2 Operational range of input variables as coded level and actual units for the adsorption of AG₂₀ onto HDTMA-Sep

No.	Code	Parameters	Parameters level				
			−2 (α)	−1	0	+1	+2(α)
1	A	Contact time (min)	5	28.75	52.5	76.25	100
2	B	Adsorbent dosage (g/L)	0.5	0.88	1.25	1.63	2
3	C	Dye concentration (mg/L)	10	32.5	55	77.5	100
4	D	Solution pH	3	4.5	6	7.5	9

where Y indicates the corresponding response of input variables β_0 , β_i , β_{ij} and β_{ii} symbolizing the constant, the linear, interaction and quadratic regression coefficients, respectively, and X_i and X_j are value of coded independent variables. The validity of the model fitness and significance analysis of variables was evaluated by means of ANOVA.

Kinetic studies

In this study, experimental data were modeled by the pseudo-first-order and pseudo-second-order model equation. The pseudo-first-order model presumes that the rate of change of the solute adsorption for the whole range of contact time may cause to change in the adsorption capacity (Eq. 5) (Wang et al. 2015b; Kumar and Tamilarasan 2013):

$$\log(q_e - q_t) = \log q_e - \frac{K_1}{2.303} t \quad (5)$$

where K_1 (1/min) is adsorption rate constant of the pseudo-first order, q_e (mg/g) is the amount of adsorbed AG₂₀ at equilibrium and q_t (mg/g) is the amount of AG₂₀ adsorbed on at any time.

Pseudo-second-order model supposed that the rate-limiting step includes resembles over in the whole adsorption processes and chemical forces of attraction. Equation 6 shows the linear form of the pseudo-second-order model (Kumar and Tamilarasan 2013; Wang et al. 2015b):

$$\frac{t}{q} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} t \quad (6)$$

where K_2 (g/mg min) is adsorption rate constant of the pseudo-second-order equation and q_e (mg/g) is the amount of adsorbed AG₂₀ at equilibrium.

Adsorption isotherm studies

Isotherm study was conducted to clarify the distribution behavior of dye between solid and liquid phases at constant temperature and equilibrium. In this study, two isotherm models, Freundlich and Langmuir, were used. The Freundlich isotherm is applied based on the hypothesis that the sorption process was comprised of a heterogeneously layer.

Freundlich equation (Eq. 7) in the linearized form is (Anari-Anaraki and Nezamzadeh-Ejehieh 2015):

$$\log q_e = \log k_f + \frac{1}{n_f} \log C_e \quad (7)$$

where q_e (mg/g) is the equilibrium capacity, C_e (mg/L) is an equilibrium concentration of the adsorbate in liquid phase, K_f ((mg/g)(L/mg)^{1/n}) is a constant associated related to the adsorption capacity of the adsorbent and $1/n$ is intensity of adsorption.

Value of $1/n$ between 0 and 1 verified the adsorption intensity or surface heterogeneity and values lower than 1 show a normal Freundlich isotherm, while values higher than one show cooperative adsorption (Ghaedi and Kokhdan 2015).

The Langmuir isotherm proposes that the adsorption continues in a monolayer onto homogeneous surface. Langmuir equation (Eq. 8) in the linearized form is as follows (Kumar and Tamilarasan 2013):

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{K_L q_m} \quad (8)$$

where q_e (mg/g) and C_e (mg/L) are the equilibrium capacity and concentration, respectively. q_m (mg/g) is the maximum quantity of adsorbed dye per unit mass of sorbent at complete monolayer on the surface bound, and K_L (L/mg) is a constant associated with the attraction of the binding sites.

Results and discussion

FTIR analysis

Functionality present at the adsorbent surface was detected by FTIR spectra between 4000 and 400 cm^{−1}. The variation of functional groups is shown in Fig. 1. The band at 3686.56 cm^{−1} that assigns to stretching (ν OH) vibration of hydroxyl group (belong to Mg₃OH) attached to octahedral Mg ions placed in the inner blocks of N-Sep and HDTMA-Sep (Bakhtiary et al. 2013). The broadband at 3435.51 cm^{−1} attributed to H₂O was observed at bare and treated sepiolite (Madejová 2003). The spectrum of HDTMA-Sep shows a pair of bands at 2857.21 and 2928.37 cm^{−1}. These two

Fig. 1 FTIR spectra of N-Sep and HDTMA-Sep

bands were assigned to the symmetrical and asymmetrical CH_2 -stretching vibration (Rožić and Miljanić 2011). The observed bands at about 1208.76 and 1078.85 cm^{-1} are attributed to the Si–O vibrations (Xu and Boyd 1995). The deep band at 1019.15 cm^{-1} shows the stretching of Si–O in the Si–O–Si group of the tetrahedral sheet (Li and Bowman 1997). The observed peak at 694.40 cm^{-1} corresponds to the bending vibration of Mg_3OH for bare and treated sepiolite (Xu and Boyd 1995). The band at 470.87 cm^{-1} assigned to Si–O–Si bending vibration of both sepiolite (Rožić and Miljanić 2011; Li and Bowman 1997). As shown in Fig. 1,

no real shift occurred in observed peaks, but their intensity was dramatically changed after HDTMA treatment.

XRD analysis

The X-ray diffractogram is depicted in Fig. 2. The diffractogram showing a sharp reflection peak at $2\theta = 7.223$ (12.1 Å) is a sepiolite characteristic peak (Li and Bowman 1997; Bakhtiary et al. 2013). According to the studies of Bakhtiary et al. (2013) (Bakhtiary et al. 2013), Liu et al. (2014) (Liu et al. 2014), Gajowiak et al. (2013) (Gajowiak

Fig. 2 X-ray diffraction of N-Sep

et al. 2013) and Ozcan and Gok (2012) (Özcan and Gök 2012), structure of the modified clay with cationic surfactants does not have considerable difference with the bare one. It can be concluded that HDTM⁺ cations attach to the edge of sepiolite and cannot enter the internal pores of sepiolite.

Finding of CCD

An empirical relationship in terms of coded factors from RSM based on CCD obtained for AG₂₀ removal based on quadratic model is shown in Eq. 9:

$$\text{Removal} = 78.50 + 2.65A + 1.33B + 1.97C + 0.6D - 0.77BC - 0.79CD - 3.13A^2 - 1.30B^2 - 2.50C^2 \quad (9)$$

Based on this equation, the effects of each factor and their interaction on the response can be understood. The positive and negative signs in this equation are used to indicate synergistic and antagonistic effects, respectively. The experimental design and AG₂₀ removal percentage are shown in Table 3.

The statistical adequacy of the model is tested using analysis of variance (ANOVA). ANOVA is a statistical method which applied to subdivide the whole variation in a set of data into constituent parts related to particular sources of variation for the aim of testing hypothesis about the parameters of the model (Subramaniam and Pon-nusamy 2015).

Table 4 shows the regression parameters of ANOVA for the predicted quadratic model. The *F* value of 50.24 and *P* value of regression less than 0.05 implied that the model is statistically significant. Also, *R*-squared (*R*²) for the quadratic model was 0.9832.

The *P* value of lack of fit (0.5997) is more than 0.05 which demonstrates that lack of fit was not significant and the model was significant. The value of “Adequate precision” more than 4 (> 4) is favor (Ezechi et al. 2015; Zinatizadeh et al. 2006), and for the present study, the value of 23.960 was obtained as “Adequate precision” which is preferred.

According to the above-mentioned reasons obtained from ANOVA, the quadratic model is statistically significant and can explain the relationship between the response and variable adequately.

Based on Table 4 and consideration of two columns “Source” and “Sum of square,” Fig. 3 is designed. In this Fig. 3, the percent of contribution off our parameters including A (contact time), B (adsorbent dosage), C (dye concentration) and D (pH) in the dye removal efficiency is shown. According to this figure, among these parameters, A and C have more influence on the removal efficiency rather than other two parameters (B and D).

Table 3 Experimental design and dye removal percentage through the adsorption AG₂₀ onto HDTMA-Sep

Run	A	B	C	D	Removal%
1	52.50	1.25	55.00	6.00	80
2	76.25	1.63	77.50	4.50	79
3	100	1.25	55.00	6.00	70
4	28.75	0.88	32.50	7.50	67
5	28.75	1.63	77.50	4.50	70
6	28.75	1.63	32.50	4.50	67
7	28.75	1.63	77.50	7.50	70
8	52.50	1.25	55.00	6.00	79
9	76.25	1.63	32.50	4.50	73
10	28.75	0.88	77.50	4.50	70
11	52.50	1.25	55.00	6.00	77
12	28.75	1.63	32.50	7.50	70
13	52.50	1.25	55.00	6.00	79
14	52.50	2.00	55.00	6.00	76
15	52.50	1.25	55.00	9.00	75
16	52.50	1.25	55.00	6.00	78
17	28.75	0.88	77.50	7.50	70
18	52.50	0.50	55.00	6.00	73
19	76.25	1.63	32.50	7.50	76
20	76.25	0.88	77.50	4.50	76
21	52.50	1.25	10.00	6.00	65
22	28.75	0.88	32.50	4.50	64
23	52.50	1.25	55.00	3.00	77
24	76.25	0.88	32.50	4.50	68
25	76.25	0.88	32.50	7.50	75
26	52.50	1.25	55.00	6.00	78
27	5.00	1.25	55.00	6.00	62
28	76.25	1.63	77.50	7.50	77.5
29	52.50	1.25	100	6.00	72
30	76.25	0.88	77.50	7.50	76

A = time (min); B = M (g/L); C = C (mg/L); D = pH

Optimized values of parameters

The primary objective of the present study was the determination of the optimum condition for examined parameters, including the initial AG₂₀ concentration, contact time, pH of the solution and adsorbent dosage. The optimal condition was acquired at the initial AG₂₀ concentration of 77.1 mg/L, contact time of 24.81 min, pH of 6.19 and adsorbent dosage of 1.03 g/L with the predicted removal efficiency of 78. The verification experiment was resulted in the removal efficiency of 78.5 which is in agreement with predicted result. Also, the AG₂₀ adsorption capacity at optimum conditions obtained 58 mg AG₂₀ per gram of modified sepiolite. Similar result has been reported by Marjanovic et al. (2013) in the case of chromium (VI) adsorption onto functionalized acid-activated sepiolite (Marjanovic et al. 2013). By comparison,

Table 4 ANOVA result for quadratic model terms

Source	SS	DF	MS	F value	P value	
Model	700.55	14	50.04	50.24	<0.0001	Significant
A-time	151.30	1	151.30	151.91	<0.0001	
B-M	25.41	1	25.41	25.52	0.0003	
C-C	83.39	1	83.39	83.72	<0.0001	
D-pH	5.19	1	5.19	5.21	0.0414	
AB	4.59	1	4.59	4.61	0.0530	
AC	4.59	1	4.59	4.61	0.0530	
AD	0.28	1	0.28	0.28	0.6059	
BC	8.03	1	8.03	8.06	0.0149	
BD	0.026	1	0.026	0.027	0.8732	
CD	8.58	1	8.58	8.61	0.0125	
A ²	256.25	1	256.25	257.28	<0.0001	
B ²	24.25	1	24.25	24.35	0.0003	
C ²	164.09	1	164.09	164.75	0.0001	
D ²	0.093	1	0.093	0.093	0.7654	
Residual	11.59	12	1			
Lack of fit	6.45	7	0.92	0.84	0.5997	Not significant
Pure error	5.50	5	1.1			
Core total	712.50	26

Fig. 3 Contribution percentage of parameters in removal efficiency

the adsorption capacity of modified sepiolite (58 mg/g) was higher than the adsorption capacity of HDTMA-coated zeolite (38.96 mg/g) (Jin et al. 2014) and calcium-rich sepiolite (32 mg/g) (Yin et al. 2011). Thereby, it can be stated that HDTMA-Sep is an efficient adsorbent for the removal of AG₂₀.

In order to assess the applicability of HDTMA-Sep for the removal of AG₂₀ from real wastewater, an experiment under optimal condition with spiked amount of 77 mg/L of AG₂₀ was conducted on textile wastewater. The main characteristics of the used wastewater are shown in Table 5. The results showed that HDTMA-Sep has a great tendency toward dye and the removal efficiency of 72 was obtained. Little difference between the removal efficiency in aqueous solution and real wastewater showed good tendency of modified sepiolite

Table 5 Main parameters of textile wastewater

Wastewater	Unit	Value
AG ₂₀	mg/L	77
pH	–	10
Temperature	°C	21
Turbidity	NTU	640
EC	μS/cm	4840
COD	mg/L	1600

toward dyes even in the presence of organic and inorganic matter that exist in real wastewater.

Kinetic studies

The kinetics studies were done at optimum condition including various concentrations of AG₂₀ (10–100 mg/L), pH: 6.19, adsorbent dosage of 1.03 g/L and contact time equal to 24.81 min. The plots of kinetic studies are presented in Fig. 4. The kinetic parameters are shown in Table 6. According to this table, pseudo-second-order kinetic model has the higher determination coefficient in comparison with the pseudo-first-order kinetic model ($R^2 = 0.9284$), which showed that adsorption process was controlled by chemisorption (Zheng et al. 2015; Zhu et al. 2013). So the adsorption AG₂₀ onto HDTMA-Sep follows pseudo-second-order kinetic model. The results of Ozcan (Özcan et al. 2006), Jin et al. (Jin et al. 2014) and Zheng et al. (Zheng et al. 2015) were in agreement with the finding of this study. By comparison, the rate constant

Fig. 4 The plots of pseudo-first-order model (a) and pseudo-second-order model (b)

Table 6 Result of AG₂₀ kinetic onto HDTMA-Sep

Model	Parameter	Value
Pseudo-first-order	$K_1(\text{min}^{-1})$	0.005
	$q_e(\text{mg/g})$	0.10
	R^2	0.7553
Pseudo-second-order	$K_2(\text{g/mg.min})$	0.15
	$q_e(\text{mg/g})$	0.95
	R^2	0.9284

of pseudo-second order of modified sepiolite (0.15 g/mg min) was better than the constant rate of HDTMA-zeolite (5.5×10^{-3} g/mg min) (Jin et al. 2014), DTMA-bentonite (6.32×10^{-4} g/mg min) (Özcan et al. 2004) and DTMA-sepiolite (1.23×10^{-1} g/mg min) (Gök et al. 2008).

Adsorption isotherm studies

The adsorption isotherm studies were conducted in different concentrations of HDTMA-Sep (0.5–2 g/L), solution pH of 6.19, dye concentration of 77.1 mg/L and contact time equal to 6 h. The plots of adsorption isotherm studies are depicted in Fig. 5. The parameters obtained from the two isotherm models are represented in Table 7. According to Table 7, Freundlich isotherm provided better determination coefficient value ($R^2 = 0.906$) in comparison with Langmuir isotherm. Based on Table 7, the value of $1/n = 0.413$ suggests that the Freundlich isotherm is normal. Almost, similar studies were in consistent with the results of the current study. Esmaeli et al. (2013) investigated sorption of AB1 onto brown macroalgae, and they were reported that AB1 adsorption was better described by the Freundlich model (Esmaeli et al. 2013). Also, Hao et al. (2014) studied adsorption of acid dyes by hydroxyl-aluminum pillared bentonite,

Fig. 5 The plots of Freundlich isotherm (a) and Langmuir isotherm (b)

Table 7 Result of AG₂₀ adsorption isotherm onto HDTMA-Sep

Isotherm	Parameter	Value
Langmuir	Q_m (mg/g)	63.29
	K_L (L/mg)	1.75
	R^2	0.875
Freundlich	$1/n$	0.413
	k_f ((mg/g)(L/mg) ^{1/n})	38.71
	R^2	0.906

and they were reported the Freundlich isotherm as fitted model (Hao et al. 2014).

Interactive effects of parameters

Result of RSM and the corresponding contour plots as the functions of two parameters (pH of solution, dye concentration, contact time and adsorbent dosage) on the adsorption of AG₂₀ onto HDTM-Sep are presented in Fig. 6.

The relationship between adsorbent and dye concentration on the efficiency of the Acid green 20 removal is shown in Fig. 6a. The enhancement of dye removal with increasing adsorbent concentration can be attributed to the fact that increasing amount of adsorbent provides more binding sites (increased surface area) for the adsorption of dye molecules onto the adsorbent, leading to increase in interaction between adsorbent and dye molecules. Hao et al. (2014) prepared hydroxyl-aluminum pillared bentonite, and they were reported that the enhancement of adsorbent dosage leads to increase in the dye removal efficiency (Hao et al. 2014).

The interactive effect of contact time and adsorbent dosage on dye removal is presented in Fig. 6b. It is observed that with increasing contact time and adsorbent dosage, the removal efficiency of dye increased. One of the important parameters that affect wastewater treatment process is contact time (Deniz and Saygideger 2010). Increasing dye removal with increasing contact time can be related to abundant availability of adsorption site for dye molecules, which increase the chance of successful bond of dye molecules onto surface of adsorbent. Özcan et al. (2006) used natural sepiolite as adsorbent for the removal of Acid blue 193 (AB193), and they were reported that amount of AB193 adsorption increased with increasing the contact time (Özcan et al. 2006). Also, Gök et al. (2008) studied adsorption of naphthalene onto organosepiolite, and they were reported similar result (Gök et al. 2008).

The function of pH of the solution and adsorbent concentration onto adsorption process is shown in Fig. 6c. It is observed that with increasing solution pH_s, the AG₂₀ removal was increased. The enhancement of AG₂₀ removal can be related to the isoelectric points of the sepiolite (pH_{IEP} = 6.6) (Xi et al. 2010a, b). At the pH_{IEP}, in the

Fig. 6 2D counter plots showing the interactive effect of **a** adsorbent dosage and dye concentration, **b** contact time and adsorbent dosage, **c** adsorbent dosage and pH

surface of sepiolite, the number of positive and negative charges is equal (Lee and Kim 2002). With the increase in solution pH, the surface of sepiolite is more negatively charged, and electrostatic interaction between AG₂₀ molecules and negatively charged of the sepiolite becomes strong, and thereby, the removal efficiency enhanced. Han et al. (2014) investigated the adsorption of methylene blue (MB) onto natural sepiolite at various pH_s and found that with increasing pH of solution, the more MB is adsorbed (Han et al. 2014). Similar finding has been reported by Qiu

et al. (2013) in the adsorption of Sr (II) by sepiolite fibers (Qiu et al. 2013).

AG₂₀ adsorption mechanisms

The main adsorption mechanisms include chemisorption and physisorption (Yagub et al. 2014). Chemisorption is characterized by strong intraparticle bonds between an exchange of electrons and molecules. This sorption is stable and irreversible. Physisorption such as dipole–dipole, hydrogen bonds and π - π interaction is characterized by weak intraparticle bonds between adsorbent and adsorbate. Physisorption is deemed to be unstable and reversible sorption (Yagub et al. 2014).

Surfactants with a high degree of hydrophobicity enhanced the adsorption capacity of clays as an effective adsorbent for the removal of organic compounds from aqueous solutions (Jin et al. 2014; Bakhtiary et al. 2013; Oyanedel-Craver et al. 2007). The results of FTIR and XRD indicated that HDTMA cations attached to the surface of sepiolite (not to the internal pores of sepiolite). Thus, HDTMA cations on the surface of sepiolite provided sites for the electrostatic attraction between the positive charge surface of HDTMA-Sep and anionic molecules of AG₂₀. Also, the proposed interaction AG₂₀ adsorption mechanism is the partitioning of the AG₂₀ through hydrophobic bonding of alkyl chains of HDTMA (van der Waals interaction).

The maximum adsorption capacity of AG₂₀ at optimal conditions was achieved 31 and 58 mg/g for natural sepiolite and modified sepiolite, respectively. It can be said that enhancement of adsorption capacity (~27 (mg/g) increment) related to the influence of attachment of surfactant cations on the surface of sepiolite. Thus, it can be concluded that the AG₂₀ adsorption mechanisms include both the electrostatic and van der Waals interactions.

Conclusions

In this study, natural sepiolite was modified with hexadecyltrimethylammonium bromide (HDTMA-Br) to adsorb a textile dye from aqueous solution. An initial dye concentration of 77.1 mg/L, pH 6.19, adsorbent dosage 1.03 g/L and contact time 24.81 min resulted in the maximum dye removal of 78% for synthetic solutions, which confirmed by confirmatory experiment. Under this condition, 72% removal AG₂₀ from real wastewater was achieved. The result of isotherm study showed that the process was best fitted with Freundlich model. The data obtained from kinetic study exhibited that adsorption process can be better described by pseudo-second-order model. The AG₂₀ adsorption mechanisms were electrostatic and van der Waals interactions. The result indicated that contact time and dye concentration have

more influence on the removal efficiency rather than pH and amount of adsorbent. It was proved that modified form of sepiolite is an efficient adsorbent for dye removal from aqueous solution.

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