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Preparation of SBA-15-PAMAM as a Nano adsorbent for Acid dye removal from aqueous media: Kinetics andThermodynamics Studies

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ABSTRACT: Removal of acid dyes from aqueous media has been effectively regarded and for this aim various methods have been tested. So in this study a new physical modification of mesoporous silica SBA-15 with PAMAM dendrimer as a new modifier and its application for the removal of Acid Red 266(AR266) from aqueous media has been verified. SBA-15, SBA-15-Cl and SBA-15-PAMAM were synthesized and then were characterized by FTIR.Also, the surface morphology of SBA-15 was recognized by transmission electron microscopy (TEM).Also, the effects of pH, adsorbent dosage, contact time, dye concentration and temperature as five important parameters for effective adsorption of acid dye were studied.Pseudo-first order and pseudo-second order kinetics models were analyzed to characterizing of adsorption rate. The calculated thermodynamic parameters represented the exothermic and spontaneous nature of the adsorption process. The results represented, SBA-15-Den can be applied as an affective Nano adsorbent for removal of acid dye from aqueous media.

Keywords: *Acid dye;Adsorption; Kinetic;Nano-adsorbent; Removal; SBA-15-PAMAM; Thermodynamic*

INTRODUCTION

During the past years, several chemical and physical methods have been used to remove dyes from theaqueous media, which is changing in operating cost, usefulness and Environmental effect (Gupta, *et al.*, 2009, Piccin, *et al.*, 2009). Among all thead vised methods, adsorption of dye molecules on theadsorbent can be a very appropriate and low cost process toremove the color from aqueous Medi as (Dotto, *et al.*, 2011, Salehi, *et al.*, 2010). Adsorption has been used particularly for the removal of organic compounds from aqueous media (Kamble, *et al.*, 2008). Zhao, *et al.* in 1998 initiated SBA-15 mesostructured silica, which include of parallel cylindrical pores with axes ordered in a hexagonal unit cell.

Commonly, SBA-15 with pores range from 5 to 30 nm has widerpores than MCM-41, and superior pore volume. Besides, in comparing with other mesostruc-

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(*) Corresponding Author-e-mail: tayebi_h@yahoo.com tured silica materials, SBA-15 has thicker pore walls between 3.1 and 6.4 nm, which supply high hydrothermal stability (Zhao, *et al.*, 1998, Khodakov, *et al.*, 2005), and is appropriate for using in aqueous solutions. Mesoporous silica material SBA-15 has appealed considerations consideration since its discovery (Zhao, *et al.*, 1998). The mesoporous silica materials, with well-behavedstability, have been used in different fields such as separation and adsorption (Tao, *et al.*, 2010) catalysis (Du, *et al.*, 2008), enzyme immobilization (Ikemoto, *et al.*, 2010), itsparticular morphology is significant in various designed usage (Prieto,*et al.*, 2009). The SBA-15is new Nano porous silica with high surface area, hexagonal construction, wide pore size, broad pore wall thickness, andhigh thermal resistance (Badiei,*et al.*, 2011). Dendrimers suggests major chances in molecular design due to their multifunctional properties in molecular design due to their multifunctional attributes such as host-guest chemistry, dendritic catalysts, medical application, etc. (Bosman, *et al.*,1999). In our method for chemical modification of SBA-15, dendrimer is one of the yummy molecules because of its multi functionality. Dendrimers are converting more famous as nanomaterial stabilizersor covering agents. The reason is that they have high loading valenceowing to their Nano hollows. Indendrimers, the nanoparticles can be shaped either in the internalhollowsof the dendrimer or inthe perimeter of the dendrimers. Normally the procurement of nanoparticles within the dendrimers includestwo procedures (Bao, *et al.*,2003, Weir, *et al.*, 2010).

The purpose of the present study is to increase the adsorption valence of SBA-15 for acid dye. Toperform this idea, SBA-15 is properly modified by grafting of 3-chloro propyl tri methoxysilane asthe anionic quality. The SBA-15-Den has not been considerably studied for theremoval of acid dye. The operating convertibles such as: pH, time contact, adsorbent dosage and temperature of process wereselected to consider the adsorption capacity of SBA-15-Den. The kinetic and thermodynamic characteristics were analyzed to define the adsorption manner of produced Nano adsorbent.

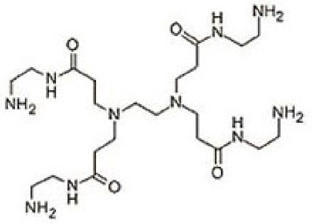

Fig. 1.Thechemical structure of dendrimers PAMAM (chemical formula $C_{22}H_{48}N_{10}O_4$, Mw = 517 g/mol, G_0)

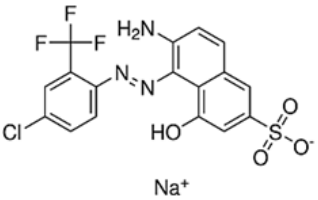

Fig. 2.The chemical structure of utilized Acid Red 266

MATERIALS AND METHODS

Materials

Block copolymer surfactant Pluronic-123 withmolecular weight (Mw = 15800 g/mol) was purchased from Sigma-Aldrich.3-chloro propyl tri-methoxy-silane was provided from Merck (Germany). PAMAM dendrimer (Generation Zero) was provided from the (Sigma-Aldrich, USA) and were selected as the adsorbents (Fig. 1). AcidRed 266 was supplied by Dystar Co. (Fig.2). All used solvents and materials were analytical graded and purchased from Merck Company.

Chemical modification of SBA-15-Den

SBA-15was synthesized by the procedure reclaimed by (Boettcher, *et al.*, 2007).So, the amount of (4g) block copolymer surfactant Pluronic-123 was mixed with 125 cm^3 HCL (1.9M) inaqueous media. The solution was homogenized at a temperature of 40ºC and the monotonous and homogeneous solution was stirred by stirring consistently and continuously. Then, the amount of (8.58 g) TEOS was added to thesolution and was stirred for 20 h. The provided mixture was located for 24 hours at 100°C in apoly ethylenecontainer. The resulting solution was dried, filtered and calcined at 550°Cfor 10 hours. The amount of (10 g) SBA-15 and (10 ml) 3-chloro-propyl tri-methoxysilane was mixed with 15 ml toluene and was mixed by magnetic magnet and stirred for 15 minutes at room temperature and reflux for 24 hours. The result solution was cooled and filtered and orderly was washed by 30 ml toluene.

The result product was dried under low pressure for 8 hours at 100°C to produce SBA-15-Cl (Matos, *et al.*, 2001, Marino, *et al.*, 2003).SBA-15-Cl was modified by PAMAMdendrimer by addition of (5.16 g) of PAMAM dendrimer to (1 g) of chloro- mesoporous silicaand dispersed in (50 ml) of dry toluene. Then themixture was refluxed at 70-80°C under stirring for 24 h, and thenthe synthesized material was filtered, washed with toluene, ethanol and diethyl ether, and dried for 8 h at 70°C to produced SBA-15-PAMAM (Weber and Morris, 1963).

Methods of characterization

To better identify structural properties, identification tests were performed. Analytical techniques such as Fourier transform infrared (FTIR) and transmission electron microscopy (TEM) were applied.

Adsorption procedure

The dye adsorption quantification were performed by blending various amounts of SBA-15-PAMAM (0.01–0.1 g) for AR266 including of dye solution (40 ppm) at different pH0 (2–12) in a shaker brooder (Heidolph).The pH of the solution was controlled by increasing a little value of H_2SO_4 or NaOH. At the termination of the adsorption tests, the solution specimens were centrifuged at 4000 rpm for 20 min and then the dye concentration was controlled applying Eq. (1). Aspectrophotometer (UV-Vis T80$^+$) to control the concentration of AR266 in solution was used. The measurements in maximum wavelength (λ_{max}) of dye (AR266:524 nm) were carried out.

$$\text{Dye removal}(\%) = \left[\frac{C_0 - C}{C_0}\right] \times 100 \quad (1)$$

Where C_0 and C are respectively initial dye concentration (mg/L) and dye concentration (mg/L) at time t.

RESULTS AND DISCUSSIONS

Chemical characterization

FTIR analysis used to determine the presence offunctional groups in the chemical structure of SBA-15, SBA-15-Cl, and SBA-15-PAMAM (Fig.6). The conjunction of organic groups in the SBA-15 frame work was stabilized by FT-IR spectra (Fig. 1-(a)). A broad absorption band at 3450 cm^{-1} for the unmodified SBA-15 sample is attributed to the –OH stretching vibrations of silanol groups and water molecules adsorbed.In three plots, the bands around 805 and 1091 cm^{-1} was seen are devoted to the typical symmetric and asymmetric stretching of Si-O-Si owing to condensed silica network. The broad peak around 3436, 3411 cm^{-1} was assigned to O-H stretching vibration of SiO-H and HO-H of adsorbed water. In Fig. (1-(b)), the bands at 1434 and 1464 cm^{-1} dedicating to the -CH_2 bending vibration, while the peaks at 2851 and 2958 cm^{-1} were attributed to C-H stretching vibrations in the methylene groups of the aliphatic chain, showing the anchoring CPTMS on the silica surface. The absorption band at 1556 cm^{-1} which obviously overlapped with bending vibration of adsorbed H_2O was related to N-H bending vibration of -NH_2 groups. Moreover, the peaks at 2923 and 3080 cm^{-1} were assigned to C-H stretching vibrations of the methylene groups. Therefore, the FT-IR results affirmed the conjunctions of functional groups on the SBA-15 silica surface (Badiei, *et al.*, 2011).

Morphology of synthesized SBA-15 was characterized by TEM equipment. Fig. 2 exhibits TEM image with the electron beam parallel to the direction of main channels of SBA-15. The SBA-15 shows hexagonal well-ordered mesoporous structure which already found by (Cheng,*et al.*, 2006).

Adsorption studies

Effect of initial pH on the dyes removal

PH is animportant factor on dye adsorption and it couldaffect the adsorbent characteristics andalsoadsorbatespecialization, mainlyin instances of thedye adsorption (Kim,*et al.*, 2005, Badiei,*et al.*, 2011).As seen in Fig. 3, the decrease of initial pH was beneficial forincreasing the dye removal, which several reasons can beascribed to this tendency.Decreasing the pH value causes to raise in quantity of theamino end groups of PAMAM dendrimer, consequently, the adsorption behaviorimproves.Adsorption processes, mostly through the formationof covalent bonds between the amine end groups of dendrimer (PAMAM) and the anionic groups of AR266. The increase in the cationicamine groups is the important cause in ad-

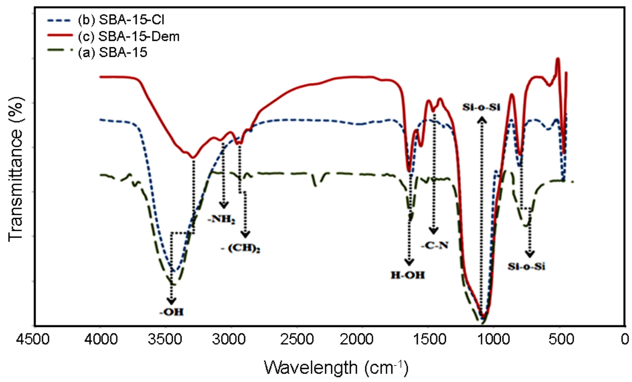

Fig. 1. FTIR spectra of (a) SBA-15 (b) SBA-15-Cl (c) SBA-15-PAMAM

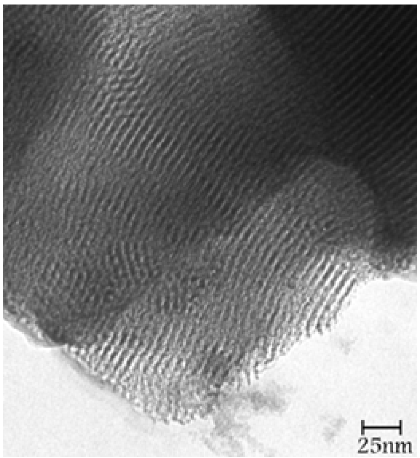

Fig. 2. TEM Image of SBA-15

sorption improvement of AR266 (Kyzas, *et al.*, 2008, Crini, *et al.*, 2008).

The number of cationic sites increases as the pH ofthe system decreases. Cationic sites on the SBA-15-PAMAM are preferred to theadsorption of acid dyes because of the electrostatic adsorption.As the results, the general mechanism of adsorption ofacid dyes onto SBA-15-Den can be described in terms of Eqs. (2–4):

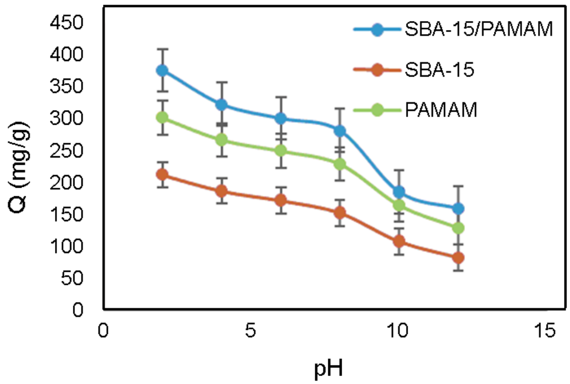

Fig. 3. Effect of pH on acid dye removal (100 ml of 40 mg/l acid dye, time = 2 h, T=25°C and the amount of adsorbent = 30 mg)

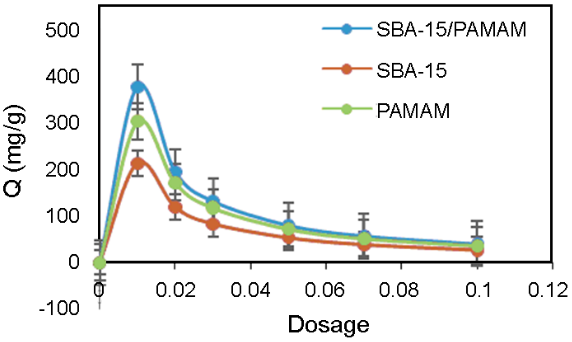

Fig. 4. Effect of SBA-15, SBA-15-Cl, SBA-15-PAMAM adsorbent amount on AR266 adsorption (100 ml of acid dye solution with 40 mg/l concentration at 25°C and pH= 2)

$$\mathrm{SBA-15-Den-NH_2 \leftrightarrow SBA-15-DeN-NH_2^{+}} \quad (2)$$

$$\mathrm{Dye-SO_4 \leftrightarrow Dye-SO_3^{-} + H^{+}} \quad (3)$$

$$\mathrm{SBA-15-Den-NH_3^{+} + Dye-SO_3^{-} \leftrightarrow SBA-15-Den-NH_3^{+}-SO_3Dye} \quad (4)$$

Effect of adsorbent dosage on the dyes removal

The effect of adsorbent SBA-15-PAMAM amount was investigated ranging from 0.01 to 0.1g at pH= 2 in 100 ml solutions with 40 mg/l AR266 concentration. The obtained results are presented in Fig.4. By increasing adsorbent dosage to 0.1 g, removal efficiency would enhance as expected. At 0.03 g value, the maximum efficiency is about 94%. However, further addition of adsorbent does not affect removal efficiency probably due to adsorbent particles aggregation (Arshadi, 2015, Kakavandi, 2014). Therefore, 0.3 g/l of nanoadsorbent is demonstrated as optimum adsorbent quantity to AR266 removal in this study.

Effect of contact time and temperature on the dyes removal

Adsorption of AR266 using SBA-15-PAMAM adsorbent as a function of contact time was investigated in three different temperatures at 25, 35 and 45°C. The obtained results were demonstrated in Fig. 5. It can be observed that at initial stage of adsorption, AR266 removal has faster rate due to more active sites accessibility and then gradually slower rate until the equilibrium is achieved at 60 min when adsorption sites be-

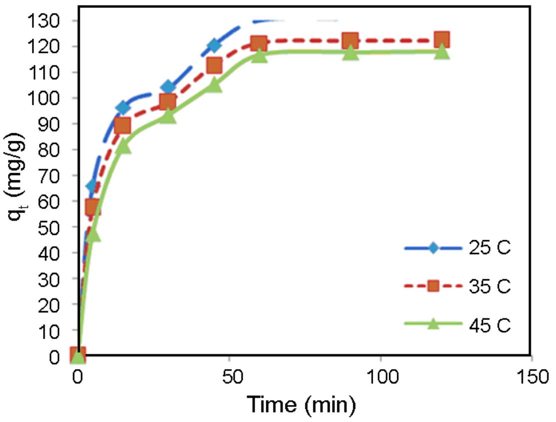

Fig. 5. Effect of AR266 adsorption vs dye concentration at various temperature 25, 35,45°C (100 ml acid dye solution with 40 mg/l concentration, 30 mg of SBA-15-PAMAM at pH= 2)

come filled out (Giannelis, 1998). As shown in Fig. 5, amount of adsorbate per unit mass of adsorbent at time t (mg/g), qt, increases by decreasing temperature from 45 to 25°C indicating exothermic nature of adsorption process as discussed later. However, the simple, safe and tech-economical way is to perform experiments at room temperature without considerable decrease of adsorption efficiency (Fig. 5) (Giannelis, 1998).

Adsorption Kinetic

Various model scan beusedto describe them echanism of absorption of absorbent material on thesolute. To consider the mechanism of absorption, sorption constants determined using the Pseudo-first-order Lagrange equation (Ho and McKay, 1999), equation of the Pseudo-second-order (Langergren, *et al.*, 1998, Ho, 1995). The Pseudo-first-order equation inlinear form (5) is as follows:

$$\log\left(q_e - q_t\right) = 1\log\left(q_e\right) - \log\left(\frac{k_1}{2.303}\right)\mathrm{t} \tag{5}$$

Ask$_1$, q$_1$, q$_e$ are the amount of dye adsorbed at equilibrium (mg/g) and the amount of dye absorbed by thetimet (mg/g) and kinetic equilibrium rate constant of the Pseudo-first-order (1/min), respectively. The k$_1$ and q$_e$ values calculated from the slope and intercept of the plot of ln (q$_e$-q$_t$) against t (Fig.6). The k$_1$, qeand R^2 values are listed in Table 1.

Linear correlation between Log (q$_e$-q$_t$) and time(t) in a pH0 of 2 can represent by kinetic H$_0$ & Mackay, s Pseudo-second-order:

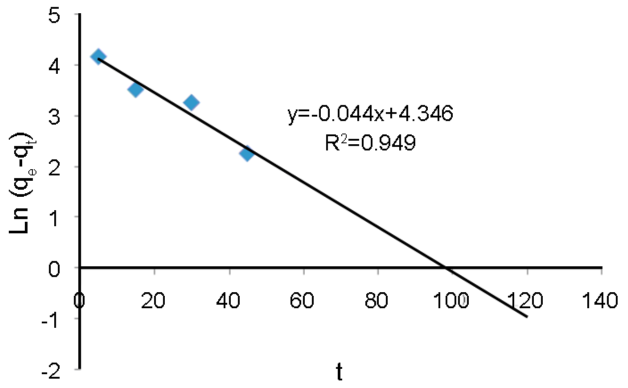

Fig. 6. Pseudo first order kinetics for AR266 adsorption on SBA-15-PAMAM

$$\frac{t}{q_t} = \frac{1}{q_e^2 k_2} + \left(\frac{1}{q_e}\right)t \tag{6}$$

q$_e$ is amount of dye adsorbed atequilibrium (mg/g) and K$_2$ is equilibrium rate constantin the Pseudo-Second-Order (g/mg. min) equation. Linear size between t/q$_t$ and contact time (t) is the kinetic of the Pseudo-Second-Order. Dye adsorption kinetics study and Kinetic absorption rates for Pseudo-Second-Orderwerewell-correlated. The k$_2$ (mg.g^{-1} min^{-1}) and q$_e$ can be calculated from the slope and intercept of the plot of t/q$_t$ against t (Fig. 7). The values of k$_2$, q$_e$ and R^2 are listed in Table 1.

Adsorption thermodynamics

Thermodynamic analysis is used to determine the nature and mechanism of adsorption process. ΔG, ΔH and ΔS amounts are estimated from equations 7 and 8 to describe thermodynamic behavior of adsorbate:

$$\Delta G = -RT\ln K_d \tag{7}$$

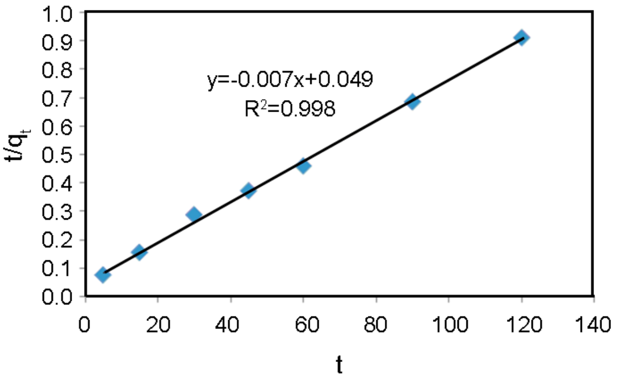

Fig.7. Pseudo second order kinetics for AR266 adsorption on SBA-15-PAMAM

Table 1. The kineticc on stants for Pseudo-First-Order and Pseudo-First-Order model of process parameters.

Pseudo-first order			**Pseudo-second order**		
$(q_e)_{cal.}$(mg/g)	**$(K_1$** (1/min	**R_1^2**	**$((q_e)_{cal.}$**(mg/g	**K_2**(mg/g.min	**R_2^2**
77.239	0.0441	0.949	138.89	0.0011	0.998

Table 2.Thermodynamic parameters of AR266 adsorbed by SBA-15-PAMAM Nano-adsorbent.

ΔH (KJ/mol)	**ΔS** (J/mol^{0}K)	**ΔG** (KJ/mol)			**R^2**
		298^{0}K	308^{0}K	318^{0}K	
- 4.985	1.659	-5.479	-5.496	-5.512	0.9952

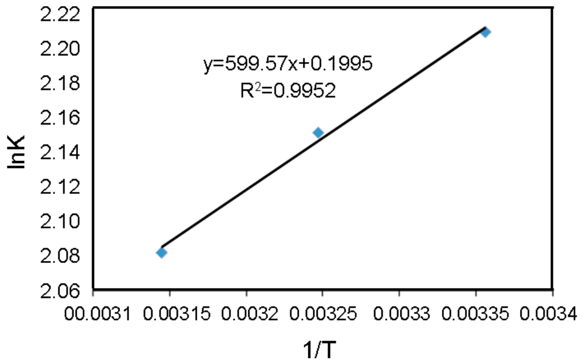

Fig. 8. The thermodynamic Plot for AR266 adsorption on SBA-15-PAMAM

$$\ln K_d = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \qquad (8)$$

Where, ΔH (J/mol) and ΔS (J/mol.K) are prognosticated from slope and intercept of data plotting of ln (k_d) versus 1/T (Fig. 8). The thermodynamic parameters are represented in Table 2.

The negative ΔG values emphasizes the reflex nature of AR266 dye adsorption. The ΔG values are in the range -20 to 0 kJ/mol which shows dye adsorption is a physisorption process (Boujaady, *et al.*, 2014). Besides, negative values of ΔH for AR266 dye indicate its exothermic nature. The positive value of ΔS represents the reversible adsorption of AR266 by SBA- 15-PAMAM Nano-adsorbent.

CONCLUSIONS

In the present study, SBA-15-PAMAM Nano adsorbent was synthesized, characterized and applied for AR266 adsorption from aqueous media. Optimal conditions of AR266 removal was obtained at pH= 2, contact time of 60 min and absorbent dosage of 0.3 g/l at 25°C. AR266 adsorption followed the pseudo-second order kinetic model. Results showed that SBA-15-PAMAM nanoadsorbent is an appropriate adsorbent for AR266 removal from aqueous media.

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