# Montmorillonite Nanoparticles in Removal of Textile Dyes from Aqueous Solutions: Study of Kinetics and Thermodynamics

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**ABSTRACT:** *Dyeing wastewaters are one of the most common pollutants that cause many problems for public health and environment due to dermatitis and skin rashes, cancer production, mutagenesis, etc. Thus, treatment of these wastewaters is necessary. The purpose of this study was to investigate the efficiency of montmorillonite nanoparticles as an adsorbent in adsorption process of Reactive Yellow 15 (RY15) and Reactive Yellow 42 (RY42) dyes from aqueous solutions. In this study, montmorillonite nanoparticles were used to remove RY15 and RY42 dyes. The effect of different variables such as pH, contact time, dye concentration and adsorbent dosage was studied. Finally, the effect of process temperature and thermodynamic was studied. Also, pseudo-first and second orders of kinetics were studied. The results showed that 3 is the best pH for the removal of both dyes. As contact time increases to 15 minutes, adsorption capacity increases and then reaches an approximately constant value. Adsorption capacity was also increased with increased dye concentration. By changing the adsorbent dosage from 0.2 to 0.6 g/L, adsorption capacity for RY15 and RY42 was reduced from 142 and 166 to 63 and 59 mg/g, respectively. The results also showed that both dyes had the highest correlation with pseudo-second-order kinetics. The results of analyzing the process thermodynamics and temperature showed that values of ΔH, ΔS and ΔG are negative for both dyes.*

**KEYWORDS:** *Montmorillonite nanoparticles; Adsorption; Reactive Yellow dye; Textile; Wastewater; Kinetic; Thermodynamic.*

## INTRODUCTION

Nowadays, pollution of water resources by dyeing wastewaters is one of the major environmental problems [1]. Different industries such as textile, papermaking, cosmetics, food and leather release dyeing wastewaters into the environment [2-4]. Among these, the textile industry is one of the major industries of the country

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in terms of product variations in raw materials and pollution level [5]. Wastewater of this industry includes chemicals, suspended solids, toxic compounds, and dyestuff, which are one of the most controversial wastewaters [6]. Almost 10-15% of dyes used in the textile industry effluent to be discharged [7]. In terms of chemical structure, dyes have different types such as acidic, alkaline, reactive, dispersing, azo, diazo, anthraquinone-base and metallic dyes [8]. Reactive dyes are water-soluble and anionic dyes. The dyes have easy application techniques and low energy consumption and are largely used in textile industry [9] and due to their high solubility in water and low degradability are one of the most problematic pollutant compounds in the wastewaters of textile industries [5]. Reactive yellow 15 dye (RY15) is highly toxic to living organisms and plants and is one of the widespread contaminants of the environment. Wastewaters containing RY 15, due to their complex heterocyclic structure, stability, difficulty in its degradation, are extremely difficult to treatment [10]. Remazol Yellow FG (RY42) is an azo dye which is a kind of synthesis of dyes is quite important and widely used. More than 27.2% of the textile industry uses Remazol Yellow FG dye [11]. Most of these dyes cause many problems in humans including dermatitis and skin itching. They also accelerate cancer and mutagenicity in humans [12-14]. In addition, the entry of dyeing wastewaters into receiving waters such as lakes and rivers prevents the full passage of light into the water and thereby reduces photosynthesis and water dissolved oxygen and endangers aquatic animals such as fish. Therefore, it is of special necessity to remove dyes from these wastewaters [15, 16].

Different methods and processes such as coagulation and flocculation, biological treatment, chemical oxidation, electrochemical treatment, ion exchange, adsorption, membrane processes, etc could be used to remove dyes and organic matters from wastewaters [17-19]. Among these, advanced treatment processes are often expensive and their use is limited [20]. In addition, because dyeing dyes are synthetic are aromatic structured, treatment of such wastewaters is not possible using biological treatment processes [21, 22]. Moreover, due to the low biodegradability of dyes, the common biological wastewater treatment processes are not effective in treating dyeing wastewaters. Thus, dying wastewaters are usually treated by physical and chemical methods [23]. Coagulation and flocculation process produces large amounts of sludge that there are many problems at their disposal [24]. Membrane processes, due to a problem such as high operating costs and re-cleaning the membrane, are less used [25]. Adsorption is one of the common physical methods, which are performed by different adsorbents such as activated carbon [26], bentonite [27] and chitosan [28]. Due to high adsorption capacity and the ability to absorb many compounds, activated carbon has probably the most widespread use in the adsorption process [29, 30], Some limitations and disadvantages including the high cost of preparation, activation, and regeneration have limited its use in the removal of some pollutants [31]. Adsorption process using cheap adsorbents is known as an effective and economical method for the removal of dyes [32, 33]. Therefore, in recent years, many studies have been conducted to find cheap and more efficient adsorbents. Nanoclay is one of the cheapest nanomaterials with properties such as being environmentally non-toxic, high specific surface area and high adsorption capacity [34]. *Öztürk et al.* (2014) showed that raw clay could effectively remove basic yellow 2 dye from the aqueous phase. Removal of dye using clay followed pseudo-first order kinetics and Langmuir isotherm [35]. *Karim et al.* (2009) study on the removal basic red 46 from the aqueous environment using natural clay indicates the effective removal of dye during 20 minutes and at a rate of 54 mg per gram of adsorbent. BET test results showed that the adsorbent surface was equivalent to 42 square meters per gram [36]. In a study entitled "Application of Acaciatortilis Shuck as of Low-cost Adsorbent to Removal of Azo Dyes Reactive Red 198 and Blue 19 from Aqueous Solution", *Jafari Mansoorian et al.* (2014) showed that the highest efficiency of dye removal from dyes solutions in pH 4, 10 min contact time and 2 g/L adsorbate dosage and using mesh 60-100 was for both Reactive Red 198 and Blue 19 [37]. In a study entitled "Removal of methyl violet dye by adsorption onto bentonite with copper ferrite nano-particles", *Hashemian* (2011) showed that the maximum dye removal occurred at a contact time of 15 min and pH = 12. In the absence of copper ferrite nano-particles, the time was increased to 60 minutes [38].

The present study focuses on the removal of RY15 and RY42 dyes from aqueous solutions by montmorillonite nanoparticles. The effect of initial pH,

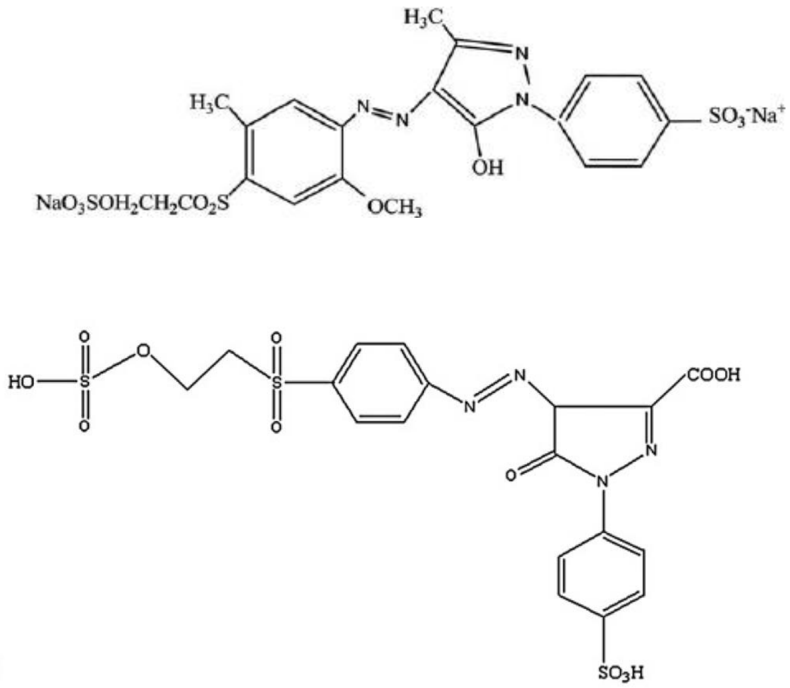


***Fig. 1: Chemical structures of dyes; a) RY15 [10], b) RY42 [39].***

contact time, the concentration of dye, adsorbent dosage, temperature and process thermodynamic was evaluated. In addition, adsorption kinetics were also investigated and analyzed.

## EXPERIMENTAL SECTION

### *Materials*

In this research, montmorillonite nanoparticles were used as adsorbent which were purchased from Pishgaman Nano Materials Company. RY15 and RY42 dyes were provided by Alvan Sabet Company and maximum adsorption wavelength of the dyes is 420 nm and 430 nm, respectively. Chemical structure of RY15 and RY42 are shown in Fig. 1a and Fig. 1b, respectively. Other chemicals used in these tests were provided by Merck Company.

### *Adsorption experiments*

The study is an applied research which was experimentally conducted in the laboratory of Environmental Health Engineering department of Birjand University of Medical Sciences. Wastewater samples provided by 1000 mg/L synthetic wastewater and parameters such as initial pH (3-11), contact time (2-120 min), initial dye concentration (20 to 60 mg/L), temperature (288, 298, 308 and 323 K) were tested discontinuously during the adsorption process. The volume of solution was 100 mL in all tests and 250 mL glass flasks were used.

*Effect of initial pH on dye adsorption*

At this stage, the effect of pH on RY15 and RY42 dyes removal was examined. For this purpose, initial pH of dyeing solutions (concentration of 40 mg/L) was set in the range of 3 to 11 using HCl and NaOH 1 N (pH-meter Knick, 765 Caliamatic). Then, 0.4 g/L adsorbent was added to the dyeing solutions and was put in contact with the adsorbent on a shaker (Orbital shaker, Mode KS260C) at a stirring speed of 250 rpm. After 60 minutes, the samples were filtered and dye concentration was measured using spectrophotometer (UV/Vis spectrophotometer T80, PG Instrument Ltd).

*Effect of contact time and dye concentration on the efficiency of dye adsorption:*

After determining the optimal pH of dye adsorption, solutions with a dye concentration of 20-60 mg/L were prepared and were put at a contact time of 2-120 minutes with an adsorbent dosage of 0.4 g/L. finally, after the dye adsorption was measured using a spectrophotometer.

*The optimal dosage of adsorbent:*

At this stage, after determining optimal pH, contact time and concentration of dye in previous stages, the test was conducted with five adsorbent of 0.2-0.6 g/L and the dye concentration of solutions were determined like previous stages.

In all stages, equation 1 was used to determine the adsorption capacity (the amount of dye adsorbed from solution per weight unit of adsorbent). In this equation, $q_e$ is adsorption capacity of dye (mg/g), $C_0$ is initial concentration of dye (mg/L), $C_e$ is remaining dye concentration (mg/L), m is adsorbent dosage (g) and $V$ is sample volume (L) [40].

$$qe = \frac{C_0 - Ce}{m} V \tag{1}$$

***Temperature and thermodynamics of adsorption process***

For this stage of the study, all optimized parameters obtained from previous stages such as pH, contact time, adsorbent dosage and dye concentration kept constant and the test was conducted using incubator shaker device (shaking incubator, Model SI-100R, Korea) at temperatures of 288, 298, 308 and 323 K. Then, thermodynamic parameters of adsorption including Gibbs free energy (ΔG°), entropy change (ΔS°) and enthalpy change (ΔH°) were studied. The following equations (Equation (2), (3) and (4)) were used to extract the thermodynamic constants. In these equations, $R$ (8.314 J/mol.K) is universal gas constant, $T$ (K) is absolute temperature and $K_e$ is thermodynamic equilibrium constant [41].

$$\ln Ke = \frac{\Delta S^\circ}{R} - \left(\frac{\Delta H^\circ}{R.T}\right) \tag{2}$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \tag{3}$$

$$\ln Ke = \frac{qe}{Ce} \tag{4}$$

***Adsorption kinetics:***

In this stage, pseudo-first order and pseudo-second-order kinetics were analyzed in five different dye concentrations (20 to 60 mg/L). The equations associated with pseudo-first-order and pseudo-second-order models are as follows (Equations (5) and (6)). In this equations, $q_e$(mg/g) is adsorbed dye at equilibrium, $q_t$ (mg/g) is adsorbed dye at the time t (1/min), $k_1$ is the constant of pseudo-first-order equation and $k_2$ is the constant of pseudo-second-order equation [41].

$$\frac{dq_t}{dt} = K_1\left(q_e - q_t\right) \tag{5}$$

$$\frac{dq_t}{dt} = K_2\left(q_e - q_t\right)^2 \tag{6}$$

## RESULTS AND DISCUSSION

***Characteristics of adsorbent***

The morphological characteristics of montmorillonite nanoparticles surface were investigated by using SEM (Scanning Electron Microscope). Fig. 2. Show the SEM images of the montmorillonite nanoparticles. The images of SEM showed that montmorillonite nanoparticles have suitable surface porosity and uniformity. Also according to SEM images, montmorillonite nanoparticles have layer structure. The thickness of this layer is estimated between 45 to 59 nm.

FT-IR analysis characterizes materials and is especially useful in recognizing inorganic mixtures. FT-IR, as Raman spectroscopy, can provide the molecular and structural information about organic and inorganic materials. Regarding Fig. 3 the band 3622.41 $cm^{-1}$ in the spectrum can be assigned Amide N-H Stretch. The band of 3435.77 $cm^{-1}$ assigned as Amine N-H Stretch. The band of 1639.05 $cm^{-1}$ is related to Alkenyl C=C Stretch. The band of 1035.19 $cm^{-1}$ is related to Si-O stretching, clay minerals. Furthermore, the bands at the range of 680-860 $cm^{-1}$ can be assigned as Aromatic C-H Bending. Also, the band at 529.41 $cm^{-1}$ belongs to Fe-O, $Fe_2O_3$ Si-O-Al stretching. The bands at 468.20 $cm^{-1}$ can be assigned to Si-O-Si bending.

XRD pattern of the montmorillonite nanoparticles show a medium peak at 2Ө=5.97° and also a sharp peak at 2Ө=27.81° that corresponds to the nanostructures of adsorbents **(**Fig. 4).

***Effect of pH***

The results of the effect of pH on RY15 and RY42 dyes adsorption process by montmorillonite nanoparticles indicate that adsorption efficiency is higher in more acidic pH and it declines as pH increases to alkaline values. Fig. 5 shows the effect of pH on RY15 and RY42

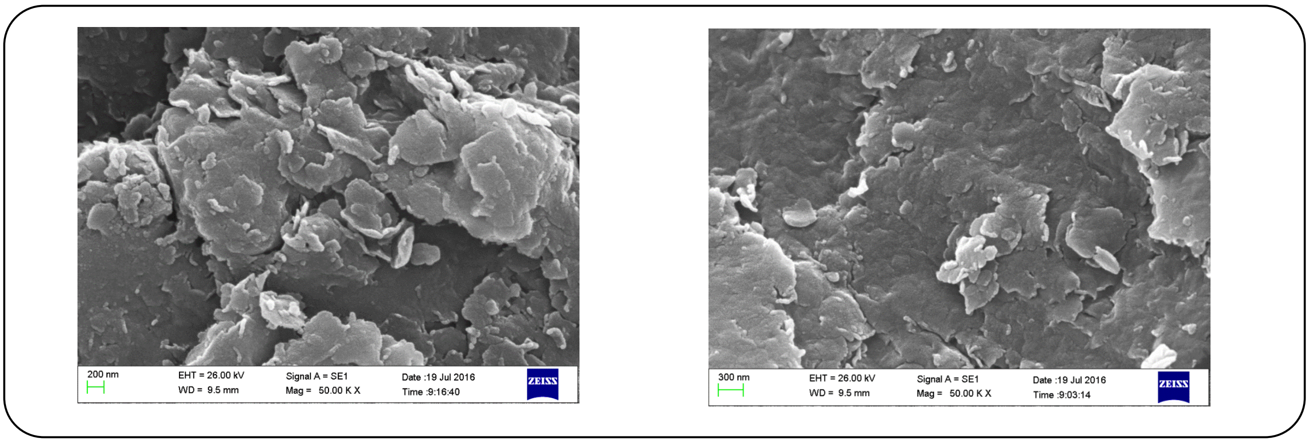


***Fig. 2: SEM of the montmorillonite nanoparticles.***

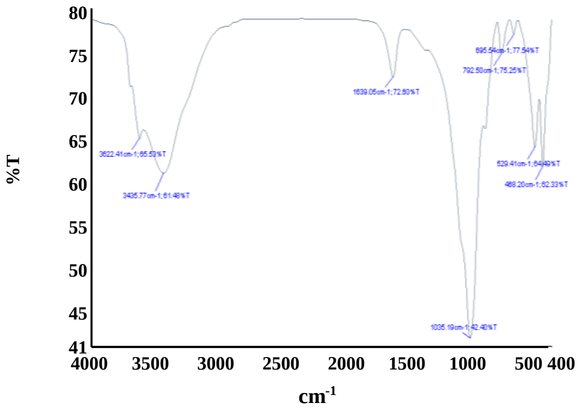


***Fig. 3: FT-IR Spectra of the montmorillonite nanoparticles.***

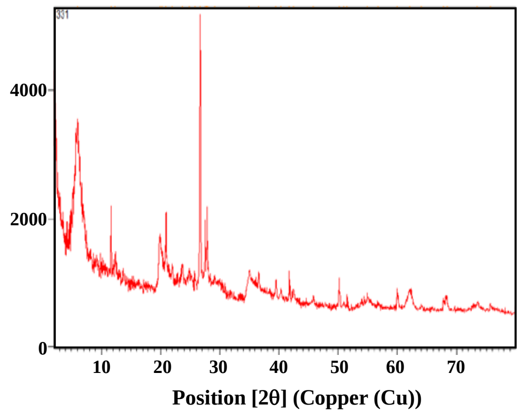


***Fig. 4: XRD pattern of the montmorillonite nanoparticles.***

adsorption process. As shown in this Fig., the maximum dye adsorption for both dyes (RY15 and RY42) was observed at pH=3, which the associated adsorption capacities were 64 mg/g and 75 mg/g, respectively. Thus, the rest of tests were conducted at this pH.

The results of the effect of pH on the efficiency of RY42 and RY15 dyes removal indicated that the highest rate of adsorption occurred at pH=3 and adsorption capacity was higher at acidic pH. The maximum adsorption capacity in this pH for RY15 and RY42 is 64 and 75 mg/g, respectively. Solution pH has an important role in adsorption capacity, which is due to its impact on an adsorbent surface charge, ionization degree of different pollutants and molecular structure of dye [42]. At alkaline pH, probably because of the abundance of hydroxyl radicals, a repulsive force is created between dye and adsorbent surface, both of which are negatively charged, and this may be the reason for lower adsorption at alkaline pH [43]. The results are depicted in Fig. 5 Similar results by *Gong et al* have been obtained in this regard In this study, the powdered peanut hull to remove anionic dyes (amaranth, sunset yellow and fast green FCF) from synthetic wastewater were used and it was found that the dye removal efficiency decreased by increasing of pH and the most suitable pH for the dyes, pH = 2 [44].

### *Effect of contact time and dye concentration:*

Figs. 6 and 7 show the effect of contact time and dye concentration on the efficiency of dye removal. As shown in these Figs., with increasing contact time and dye concentration, adsorption capacity increases and the maximum dye adsorption occurs at the early stages and then reaches a fixed amount. Based on the results of these Figs., the maximum adsorption of RY15 and RY42 is 109 and 98 mg/g, respectively.

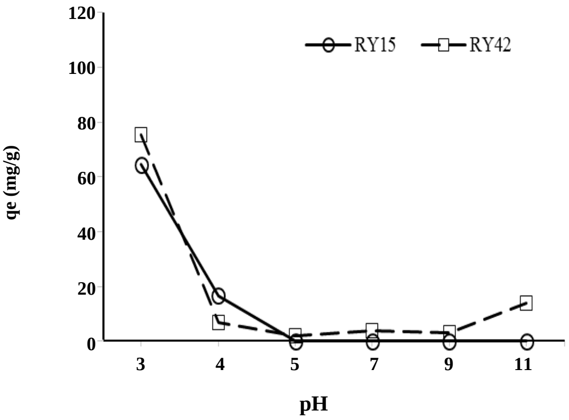


***Fig. 5: Effect of pH on the efficiency of RY15 and RY42 dyes removal by montmorillonite nanoparticles***

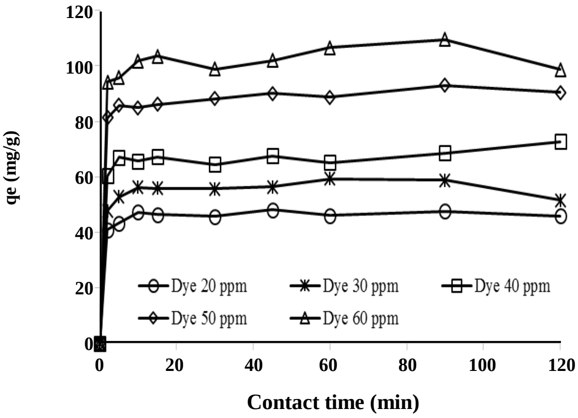


***Fig. 6: Effect of contact time and dye concentration on the efficiency of RY15 dye removal by montmorillonite nanoparticles.***

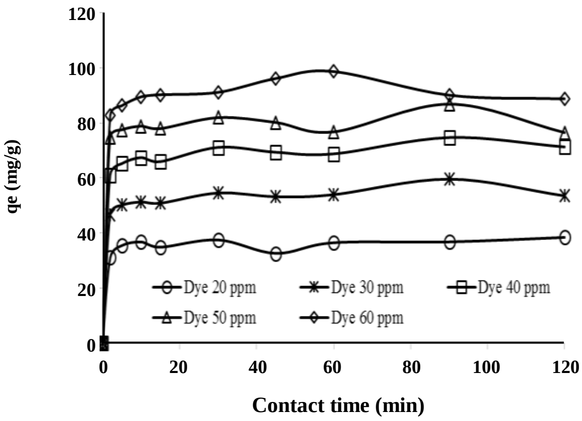


***Fig. 7: Effect of contact time and dye concentration on the efficiency of RY42 dye removal by montmorillonite nanoparticles.***

As shown in Figs. 6 and 7, with increased contact time, RY15 and RY42 adsorption capacity increases for all dye concentrations. The trend is upward until contact time of 15 minutes and then almost reaches equilibrium and no significant increase is found in adsorption capacity. Thus, it can be concluded that increased adsorption rate in earlier times could be due to the surface area and many empty places on the adsorbent surface, bypassing the time which, these places are gradually occupied by dye molecules, and increased repulsive forces between adsorbed dye molecules onto the adsorbent surface has also decreased dye adsorption [45]. Another reason for this is that adsorbents have a limited number of sites, which are saturated as dye concentration increases, and this is why dye adsorption is very fast at first [23]. The results of this research are consistent with *Arami et al*. [46]. Another study conducted by *Ai et al*. entitled removal of methylene blue by magnetite loaded multi-wall carbon, show that dye removal increased by increasing the time and reaches equilibrium after 120 minutes. The reason is that in the early stages, absorbent more empty sites available and after a time the site is occupied. Also, access to the remaining empty sites due to the repulsive forces between dye molecules and solution becomes more difficult [42].

In order to investigate the effect of initial dye concentration on adsorption process, different concentrations of 20, 30, 40, 50 and 60 mg/L were studied. As shown in Figs. 6 and 7, with increased dye concentration, adsorption capacity increases for both RY15 and RY42 dyes. At the equilibrium time (15 minutes) with increasing concentration of 20 to 60 mg/L of dye, the adsorption capacity increased from 46 to 103 mg/g and from 34 to 90 mg/g, for RY15 and RY42, respectively. Increasing the concentration of dye molecules increases the dye concentration gradient and collisions between adsorbent and dye molecules, which increases the dye adsorption by adsorbent and adsorption capacity [47]. In this regard, the findings of *Eren et al.* are accordance with the results of this study. In this study adsorption of Reactive Black 5 by Powdered Activated Carbon (PAC) and Afsin-Elbistan fly was evaluated. The result of the mentioned research show when the initial concentration of dye increased from 5 mg/L to 100 mg/L, the adsorption capacity of PAC increased from 7 mg/g to 49 mg/g, and also, the adsorption capacity of fly ash increased from 0.9 mg/g to 7 mg/g. [31].

***Table 1: Thermodynamic parameters of RY15 and RY42 dyes adsorption by montmorillonite nanoparticles.***

| T(K) | RY15 | | | | RY42 | | | |
|---|---|---|---|---|---|---|---|---|
| | ΔG (kJ/mol) | ΔH (kJ/mol) | ΔS (J/mol.K) | $R^2$ | ΔG (kJ/mol) | ΔH (kJ/mol) | ΔS (J/mol.K) | $R^2$ |
| 288 | -3.93 | -12.55 | -29.90 | 0.85 | -4.38 | -30.09 | -88.28 | 0.79 |
| 298 | -3.71 | | | | -4.42 | | | |
| 308 | -3.73 | | | | -4.06 | | | |
| 323 | -2.60 | | | | -0.49 | | | |

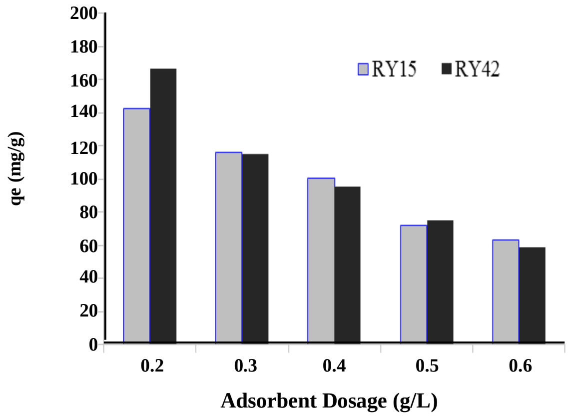


***Fig. 8: Effect of adsorbent dosage on the efficiency of RY15 and RY42 dyes removal by montmorillonite nanoparticles.***

### *Effect of adsorbent dosage*

The results of the study show that for both RY15 and RY42 dyes, adsorption capacity has declined with increasing amount adsorbent. The results are shown in Fig. 8. As shown in this Fig., as adsorbent dosage increases from 0.2 to 0.6 g/L, adsorption capacity declines from 142 to 63 mg/g and 166 to 59 mg/g for both RY15 and RY42 dyes, respectively.

Increased efficiency of dye adsorption with adsorbent dosage could be associated with an increase in adsorbent surface and number of active sites available for interaction between the adsorbent and pollutant [48]. Similarly, reduced adsorption capacity may be because by increasing the adsorbent dosage, some active sites of adsorbent remain non-saturated and, as a result, the total adsorption capacity is not used which this decreases the pollutant (dye) adsorption per unit mass [49]. In this regard, similar results were obtained by *Yang et al.* [50].

### *Effect of temperature and thermodynamics*

The results of thermodynamics of RY15 and RY42 dyes adsorption process by montmorillonite nanoparticles are presented in Table 1. In this stage, dyeing solution with a concentration of 60 mg/L, pH=3, the adsorbent dosage of 0.2 g/L and contact time of 15 minutes was put at temperatures of 288, 298, 308 and 323 K.

The results of thermodynamic analysis and its related parameters are presented in Table 1. In this study, the numerical value of ΔH parameter for RY15 and RY42 is -12.55 and -30.09, respectively. The negative values of this parameter indicate exothermic reaction for both dyes. A negative value of ΔG indicates that dye adsorption by the studied adsorbent is a spontaneous reaction and positive value of this parameter indicates that the process is possible but non-spontaneous [16]. The value of ΔS is negative which means that the dye molecules at the solid-liquid interface are more organized than those in the bulk solution phase [51].

### *Adsorption kinetics*

Kinetic parameters of RY15 and RY42 adsorption process by montmorillonite nanoparticles are shown in Table 2. The results of adsorption kinetic equations showed that both RY15 and RY42 had the highest correlation with pseudo-second-order kinetics.

Parameters of pseudo-first-order and pseudo-second-order kinetic models are calculated and presented in Table 2. According to these results, adsorption of both RY15 and RY42 dyes follows the pseudo-second-order kinetics. The results of *Sheikh Mohammadi et al.* (2013) on the removal of acid yellow 36 dye by Pinecone have reported that this model is suitable to describe the data obtained from adsorption kinetics experiments [52].

***Table 2: Kinetic constants calculations for adsorption of RY15 and RY42 onto montmorillonite nanoparticles.***

| Dye | $C_0$ (mg/L) | Pseudo-first-order | | | Pseudo-second-order | | | qe,exp(mg/g) |
|---|---|---|---|---|---|---|---|---|
| | | $K_1$ (min-1) | qe, cal (mg/g) | $R^2$ | $K_2$ (g/mg min) | qe,cal(mg/g) | $R^2$ | |
| RY15 | 22 | 0.00 | 2.81 | 0.03 | 0.83 | 46.57 | 1.00 | 49.12 |
| | 31 | 0.00 | 3.88 | 0.01 | 0.02 | 54.09 | 0.99 | 60.29 |
| | 41 | 0.01 | 6.98 | 0.14 | 0.01 | 71.16 | 1.00 | 73.79 |
| | 54 | 0.01 | 6.22 | 0.16 | 0.02 | 91.45 | 1.00 | 94.03 |
| | 62 | 0.00 | 8.76 | 0.03 | 0.02 | 102.54 | 0.99 | 110.51 |
| RY42 | 19 | 0.01 | 3.68 | 0.14 | 0.02 | 37.83 | 0.99 | 39.46 |
| | 31 | 0.01 | 6.76 | 0.05 | 0.03 | 55.51 | 0.99 | 60.62 |
| | 42 | 0.01 | 6.73 | 0.11 | 0.02 | 72.39 | 1.00 | 75.70 |
| | 52 | 0.00 | 6.48 | 0.01 | 0.06 | 79.36 | 0.99 | 87.83 |
| | 63 | 0.00 | 6.08 | 0.00 | 0.02 | 90.12 | 1.00 | 99.67 |

## CONCLUSIONS

The result of this study showed that by increasing the pH from 3 to 11, adsorption capacity is reduced, which the associated adsorption capacities for RY15 and RY42 were 64 mg/g and 75 mg/g, respectively. The maximum efficiency of dye removal is at acidic pH for both dyes. Moreover, the adsorption capacity increases with increased initial dye concentration and increased contact time. The maximum adsorption was in the first 15 minutes, so 15 minutes was considered as the optimal adsorption time. The results of the study also showed that $q_e$ is reduced by increasing the adsorbent dosage, so that for the RY15 this amount reduced from 142 to 63 mg/g and for RY42 from 166 to 59 mg/g. The reaction kinetics was described by pseudo-second-order equation. This study shows that, due to low cost and high availability of montmorillonite nanoparticles, this adsorbent can be effective to remove RY15 and RY42 dyes.

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