Journal of Community Health Research. 2016;5(2): 73-89.

Original Article

Kinetics, Thermodynamics, and Equilibrium Studies on Adsorption of Reactive Red 198 from Textile Wastewater by Coral Limestone as a Natural Sorbent

Mohammad Malakootian[1,2], Somaye Mohammadi[2], Najmeh Amirmahani[1], Zahra Nasiri[3], Alireza Nasiri*[1]

[1] Environmental Health Engineering Research Center, Kerman University of Medical Sciences, Kerman, Iran.

[2] Department of Environmental Health, School of Public Health, Kerman University of Medical Sciences, Kerman, Iran.

[3] Department of Fatemeh Al-zahra, Kerman Educational Organization, Kerman, Iran.

Received: 2016/04/05 **Accepted:** 2016/05/24

Abstract

Introduction: Dyes are among the most hazardous chemicals in industrial wastes due to their toxicity for aquaculture, reduction of light permeability, and in turn development of disorders in photosynthesis process. The current study aimed to investigate the efficiency of coral in removing red reactive 198 from textile dye wastewater was investigated.

Materials & Methods: In this experimental study, the adsorption process was completed performed on a synthetic sample in a batch system Optimal conditions was also performed on the real wastewater of Yazdbaf textile factory. The effects of such parameters as the pH, dye's concentration, contact time, sorbent's dose, and temperature were investigated, following this, adsorption isotherms were determined and then the process was examined kinetically and thermodynamically. Next, the study data was analyzed by SPSS (ver, 21), EXCEL 2007, applying Pearson correlation coefficient.

Results: The optimal conditions in removing the dye included pH=3, an equilibrium contact time of 120 min, 25 mg/L of the dye's concentration, and 3g/100mg of the sorbent's initial value. Under the optimal conditions, the dye's removal efficiency and the maximum adsorption capacity in the synthetic and real wastewater sample of Yazdbaf Company were 97.63%, 8.14 mg/g and 67.78%, 5mg/g respectively. The equilibrium data followed the Langmuir adsorption isotherm with a correlation coefficient of R^2=0.96 and the adsorption's kinetics followed pseudo-second-order model with a correlation coefficient of 1 (R^2=1). The thermodynamic investigations also indicated that the adsorption is of physical process and endothermic.

Conclusion: As the results revealed, the good performance of the coral sorbent in removing dyes in aquatic environments, enjoying suitable density, having quick precipitation properties, not needing activation, and environmental safety of the process can encourage the efficiency of this adsorbent in treatment of dye-containing wastewaters.

Keywords: Adsorption; Coral limestone; Kinetics; Reactive Red 198; Thermodynamics;

***Corresponding author: Tel:**+98 34 3132 5128 **email:** ARNasiri@kmu.ac.ir & Nasiri_a62@yahoo.com

[Downloaded from jhr.ssu.ac.ir on 2025-12-24]

Introduction

Population growth, development of different industries, agriculture, and healthy water deficit in the world have caused consumption waters to gain great significance with respect to their treating, reusing, and recycling. Textile industries lie within important industries in the country [1-3]regarding production variety in their raw materials as well as the level of contamination load, countries. Annually, over 10,000 types of synthetic dye are produced in the world and used extensively in various industries including production of paper and wood pulp, plastic and rubber, leather, cosmetics, and pharmaceuticals as well as metal electroplating, food products[4-6]. According to their chemical structure, dyes are divided into 20-30 different groups, the most important of which are Azo, Anthraquinone, and phthalocyanine[7]. Azo dyes can be mentioned as the largest and most important group of dyes, which have one or several azo groups establishing a connection between their ringstructures [2]. The dyes used in textile industries are divided into three main classes of anion (direct, reactive, acidic), cation (alkaline dyes), and nonionic (disperse dyes) [2]. Reactive dyes are suffocated and water-soluble, their adsorption on biological masses is poor, that cannot be degraded through aerobic methods [8].

Discharge of dye-containing wastewaters into the receiving waters can jeopardize the life of aquaculture through decreasing light permeation levels, reducing the levels of dissolved oxygen, and increasing chemical oxygen demand (COD)[9]. According to the findings of different studies, aromatic compounds of some dyes can develop into production of carcinogenic and mutagenic amine. Further, due to divisibility of minimal values of dye in the water (1mg/L), they are also regarded as an aesthetic contamination [2,9]. Since dyes are degradable, aerobic digestion-resistant, and stable against light, heat, and oxidizer agents, treatment of dye wastewaters seems to be difficult[2].

Various physical, chemical, and biological processes have been used in order to decolorize this type of wastewater including adsorption, precipitation, ion exchange, coagulation and flocculation, advanced oxidation, ozonation, membrane filtration, and liquid-liquid extraction[2, 9-12],among which, adsorption has been used as an effective method of wastewater decolonization due to its easy operation, low capital cost, insensitivity to toxins, and ability in treating concentrated forms of dye[2,10,13]. However, there are some disadvantages as well in this method including the need for chemical modification of the sorbent, lack of destructiveness of the process (the contaminant is not perished), decreased sorbent properties in response to reduction, and reusing [2].

Structurally, Reactive Red 198 belongs to mono-Azo dyes used widely in textile industries in our country [8]Malakootian et al.(2015), investigated removal of methylene blue dye from aquatic environments using activated volatile ash in Zarand Plant (Kerman)in Iran[14]. Dattu et al. (2009), evaluated optical degradation of Reactive Red

[Downloaded from jhr.ssu.ac.ir on 2025-12-24]

198 in India on the level of titanium oxide[15]. Faraji et al. (2010), in Iran examined application of magnetic nanoparticles modified with cation surfactant (cetyltrimethyle ammonium) as a adsorbent for removing reactive dyes of Block 5, Reactive Red 198, and Blue Reactive 21[16]. Esameili et al. (2012), studied degradation of Reactive Red 198 using Aspergillus Flavus Fungus[17]. Debrassi et al. (2012), studied application of chitosan N-loryl particles in removal of Reactive Red 198 in Brazil [18]. In a study by Karimian et al.(2013) in Iran, coral limestone granules and Leca granules were investigated in removal of reactive orange 3R[19]. Shokuhi et al. (2012), examined the removal efficiency of lead and cadmium metals from aquatic environments using coral limestone granules in Iran [20]. In another study by Norouzi et al. (2012), in Iran, arsenate removal was investigated using coral limestone bark as well as coral limestone bark coated with aluminum sulfate were [21]. Furthermore, various studies have been conducted regarding application of nanoparticles as Nano photo catalysts and Nano-sorbents in dye removal processes [22-24].

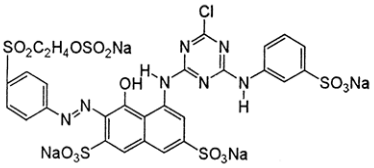
The present study conducted aimed to investigate the removal efficiency of Reactive Red 198 dye compound from aquatic environments using coral limestone as a natural sorbent. Considering the review of the relevant studies, this sorbent has not been used in removal of this dye from real samples of wastewater of YAZDBAF Textile factory yet. In this study, the effects of various factors including the solution's pH, initial concentration of the dye, the sorbent's dose, contact time, and the process temperature were investigated in order to optimize the dye removal process. The kinetics and thermodynamics of the adsorption process were also examined. Following examination of the optimal conditions, the efficiency of this sorbent in removing Reactive Red 198 from real wastewater sample of YAZDBAF textile factory was also explored.

Materials and Methods

The study is of experimental type conducted in environmental health engineering research center in Kerman University of medical sciences. This study was first carried out on a synthetic solution, and then following optimal conditions, it was performed on a real wastewater sample of Yazdbaf textile factory.

In addition, Reactive Red 198 dye was supplied by Sabet Alvan Company. The properties of this dye are provided in Table 1.

Table 1. The properties of Reactive Red 198 dye

C.I number	Name	λ_{max}(nm)	MW (g/mol)	Formula	Type	Chemical Structure
18221	Remazol Red 133	518	967.5	$C_{27}H_{18}C_1N_7Na_4O_{15}S_5$	Mono Azo	

[Downloaded from jhr.ssu.ac.ir on 2025-12-24]

The coral limestone sorbent was prepared from the marine coral remnants of lime coasts of Kish Island located in Persian Gulf, represented in Fig. 1.

Fig. 1. The picture of the coral limestone used as sorbent

In order to prepare the studied sorbent, first the corals were crushed into smaller pieces in a mortar. Following washing with deionized water, to remove debris and purify them, the corals were placed in an oven for 12 hours at 105°C so that their moisture were removed. Followed by the sorbent drying, the samples were crushed using mill and then sieved by a No 4 sieve. They were then kept in a closed-lid dish to be used for the experiments. In order to investigate the physical and chemical structure of the sorbent, FTIR spectrum of the sorbent was prepared through Fourier-transform infrared spectrophotometer (TENSOR27). Similarly, XRD spectrum and SEM image of the sorbent were taken by X-ray diffraction device (X' Pert Pro MPD) and scanning electron microscopy (JEO1JSM-5410), respectively. Across all stages of the experiment, the pH was adjust educing HCl 0.1*N* and sodium hydroxide 0.1*N*solutions. To determine the concentration of dye in the samples, UV-VIS spectrophotometer (UV-1800, SHIMADZU Co.) was applied at the wavelength of 518 nm. In all the experiments, pH was measured by a pH-meter (Hanna 211).

Stock solution of the desired dye was prepared with a concentration of 1000 mg/L. Concentrations of 5, 10, 25, 50, 75, and 100 mg/L of the stock solution were developed for plotting the standard curve. To determine the unknown concentrations of dye, this curve was employed. In fact, all the experiments were carried out in 200mL beakers. The sample volume was 100 mL and its concentration was 25 mg/L. The factors influencing the adsorption process included pH (3, 5, 7, 9, 11, and 13), contact time (30, 60, 90, 120, 150, and 180 min), initial concentration of the dye (5, 10, 25, 50, 75, and 100 mg/L), the amount of the sorbent (1, 2, 3, 4, 5, and 6 g), and the temperature (5, 10, 15, 25, and 35°C). During the reaction, the contents of the container were stirred using a magnetic stirrer at around 600 rpm. Once the reaction was finished, it was then centrifuged for 10 min at 3000 rpm. Thereafter, the concentration of the remaining dye was measured using a spectrophotometer of the wavelength of 518 nm. To ensure the correctness of the results, all the experiments were replicated three times, whereby the mean score of the obtained values was calculated. On the whole, 90experimentswere investigated.

In order to determine the effectiveness of different parameters on removal yield of the Reactive Red 198 by the studied sorbent, the process efficiency at each stage of the experiment was obtained by equation 1.

$$\%\mathbf{Removal} = \mathbf{C_0 - C_t/C_t \times 100} \qquad \text{(Eq.1)}$$

[Downloaded from jhr.ssu.ac.ir on 2025-12-24]

Where, C_0 and C_t, respectively, represent the initial concentration of the dye and dye concentration at time of t per mg/L, respectively.

In order to study adsorption isotherms, Langmuir and Freundlich isotherms models were investigated. Following examination of the optimal conditions, the efficiency of this sorbent was examined in removal of Reactive Red 198 from real wastewater sample of Yazdbaf textile factory, followed by calculation of the removal efficiency. The obtained optimal conditions were also applied to the real sample of Yazdbaf textile factory; the physiochemical properties of which are provided in Table 2. The data analysis was performed by SPSS software (ver21), EXCEL 2007, followed by determination of significance level using Pearson test and Regression analysis.

Table 2. The physiochemical properties of the wastewater sample of Yazdbaf textile factory

EC (µs/cm)	**Dye Conc. at 518 nm** (mg/L)	**TSS** (mg/L)	**Turbidity** (NTU)	**COD** (mg/L)
4840	22	2200	640	1600

Results

The Physiochemical Structure of the Sorbent

The results obtained from XRD and FTIR analysis along with SEM image of the sorbent are represented in Figs. 2-4.

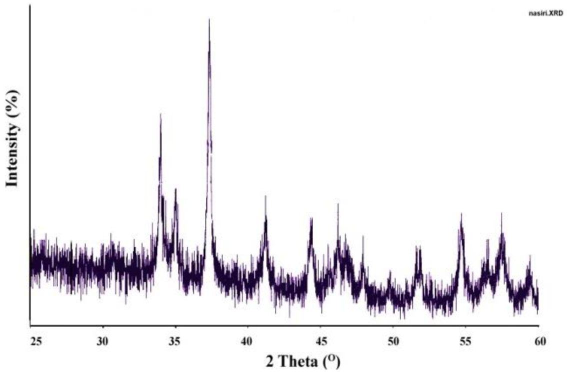


Fig. 2. The results obtained from XRD analysis of the coral sorbent

The results obtained from XRD analysis of the coral sorbent are depicted in Fig. 2. The sharp peak observed at 2θ of around 37°can be attributed to Aragonite mineral (calcium carbonate) which shows am orphic phase of the sorbent. Calcium carbonate ($CaCO_3$) is regarded as the major constituent compound of the sorbent[25,26].

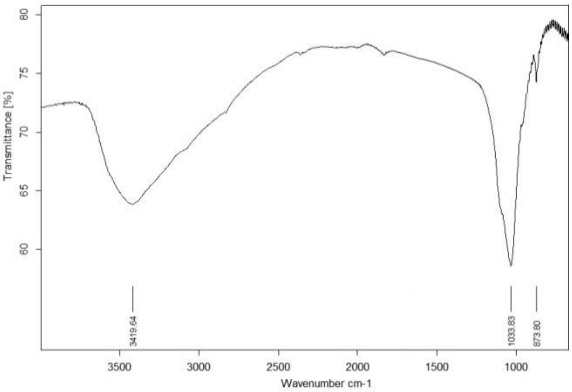


Fig. 3. FTIR spectrum of the coral used as the sorbent

The results obtained from FTIR spectrum of the coral sorbent are demonstrated in Fig. 3. As it can be seen, FTIR spectrum was

[Downloaded from jhr.ssu.ac.ir on 2025-12-24]

examined within 1000-4000 cm^{-1}. The sharp adsorption band observed at 1033 cm^{-1} is related to stretching vibrations of carbonate compound in the chemical structure of the coral sorbent. The wide adsorption band seen at 3419 cm^{-1} is associated with hydroxyl functional group, representing water and the moisture absorbed onto the sorbent [25].

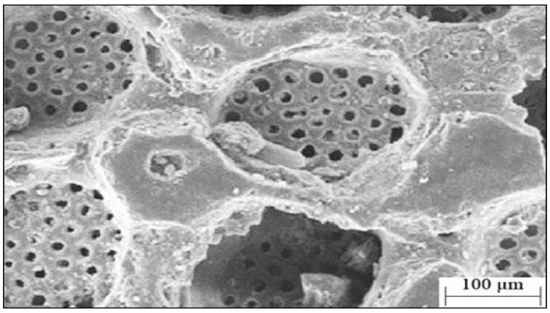


Fig. 4. SEM image of coral used as the sorbent

The results obtained from SEM image of coral is shown in Fig. 4. Asit is observed, the sorbent enjoys a porous and suitable structure for the adsorption process.

The Effect of Solution's pH

In order to investigate the effect of pH in Reactive Red 198 removal using the coral sorbent, 100 ml of dye solution with an initial concentration of 25 mg/L at pHs of 3, 5, 7, 9, 11, and 13, within 120 minutes, and temperature of 25°C was exposed to 3 g of sorbent, whose results are provided in Diagram 1.

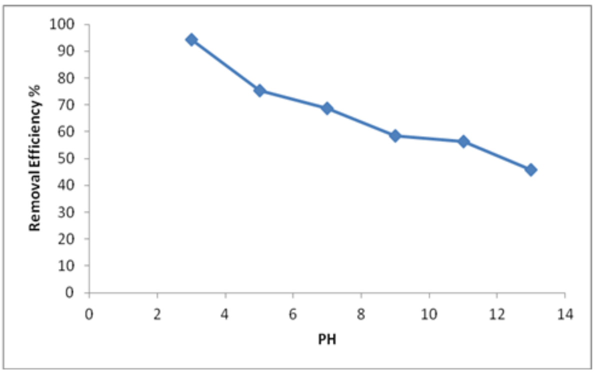


Diagram 1. The effect ofpHon dye removal efficiency (3 g of sorbent, 100 ml of dye solution with a concentration of 25 mg/L, contact time of 120 min, 25°C)

The Effect of Contact Time

Removal of Reactive Red 198 dye using coral at contact times of 30, 60, 90, 120, 150, and 180 minutes was investigated at pH=3, for initial concentration of 25 mg/L of the dye, and 3 g of the sorbent at 25°C. As the study results are demonstrated in Fig. 2., with the increase in the contact time, the removal efficiency also grows. Nevertheless, having reached an equilibrium time (120 min), the removal efficiency became almost constant. The statistical examination revealed that the relationship between the contact time and the removal efficiency along with the relationship between contact time and the adsorption capacity were demonstrated to be significant (P_v=0.013).

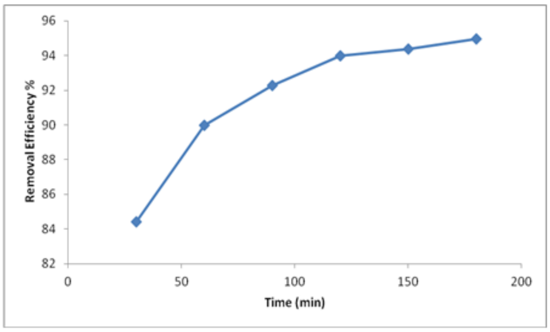


Diagram 2. The effect of contact time on dye removal efficiency (3 g of sorbent, 100 ml of dye solution with a concentration of 25 mg/L, pH=3, 25°C)

The Effect of the Sorbent's Dose

Effect of initial sorbent dose was investigated by varying its dose from 1 to 6 g in 100 mL of dye solution. This experiment was conducted at pH=3, initial

[Downloaded from jhr.ssu.ac.ir on 2025-12-24]

dye concentration= 25mg/L and balance time=120 min. Diagram 3 shows that increasing the adsorbent dose increased the dye removal from 62.22% to 98.58%.Considering the results, 3 g of sorbent in 100 ml of dye solution was determined as the optimal sorbent value. As the statistical analysis demonstrated, the relationship between the sorbent's dose and the sorbent's capacity (P_v=0.006) along with the relationship between the sorbent's dose and the removal efficiency (P_v=0.032) was demonstrated to be statistically significant.

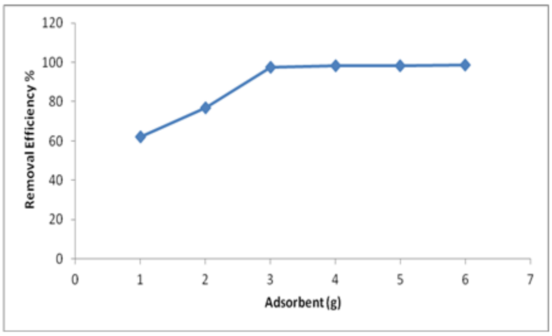


Diagram 3. The effect of sorbent's dose on dye removal efficiency (100 ml of dye solution with a concentration of 25 mg/L, pH=3, contact time of 120 min, 25°C)

The Effect of the Initial Concentration of the Dye

At this stage, 100 mL of the dye solution with concentrations of 5, 10, 25, 50, 75, and 100 mg/L were subjected to pH=3 for 120 minutes in contact with 3 g of the sorbent at 25°C. As it can be observed from Diagram 4, with the increase in the dye's initial concentration from 5 mg/L to 100 mg/L, the removal efficiency declined from 94.83% to 59.5%. Statistically, a significant relationship was detected between the removal efficiency and the dye concentration (P_v=0.002). On the other hand, with the increase in the initial concentration of the dye from 5 mg/L to 100 mg/L, the adsorption capacity of the sorbent increased from 1.58 to 19.83 mg/g. The adsorption capacity demonstrated a significant relationship with the dye's initial concentration (P_v=0.000).

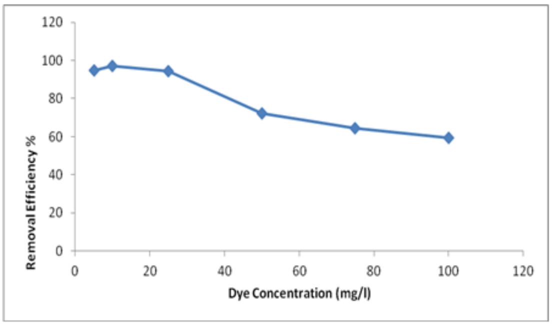


Diagram 4. The effect of initial concentration of the dye on dye removal efficiency (3 g of sorbent, 100 ml of dye solution, contact time of 120 min, pH=3, 25°C)

The Effect of Temperature

An increase in the temperature from 5 to 30°C in 100 ml of dye solution with a concentration of 25 mg/L, 3 g of the sorbent, equilibrium contact time of 120 minutes and pH=3, removal efficiency increased.

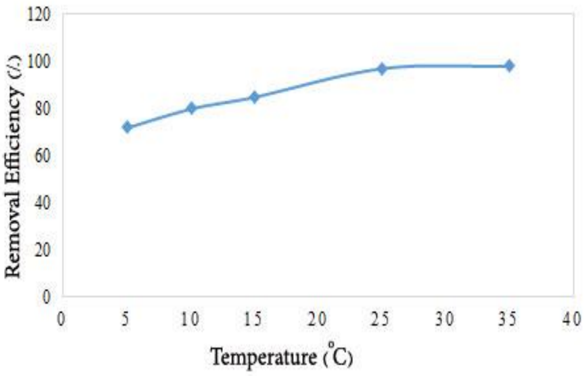


Diagram 5. The effect of temperature on dye removal efficiency (3 g of sorbent, 100 ml of dye solution, contact time of 120 min, pH=3)

Discussion

[Downloaded from jhr.ssu.ac.ir on 2025-12-24]

The results indicated that as pH increased from 3 to 13, removal efficiency declined from 94.18% to 45.76%. Therefore, the pH of 3 was considered as the optimal pH. The statistical analysis indicated that in the adsorption process, pH has a significant relationship with the removal efficiency (P_v=0.001). The solution's pH, superficial charge of the sorbent, ionization degree of different contaminants, and separation of functional groups influencing the active sites of the sorbent playing an important role in the adsorption process[27]. Considering the anionic nature of the investigated dye, reduction of the pH solution, and elevation of the concentration of positive ions of hydrogen result in the accumulation of these positive ions onto the sorbent's surface, thereby increasing the attractive electrostatic force between the sorbent molecules and the negative dyed molecules and, leading to increased removal efficiency. However, under alkaline conditions, the competition between negative ions of hydroxyl and negatively charged molecules diminishes the removal efficiency. According to the results of a study conducted by Karimian et al. (2013) in Iran who used coral limestone granule and Leca granule in removing Reactive orange 3R dye, the greatest efficiency was achieved at the pH of 2. The reason was reported to be due to the surface bombardment of Leca and coral limestone sorbents by the positive hydrogen ions establishing electrostatic bond between the positive surface of sorbents and the negative molecules of the dye[19]. Furthermore, according to a study carried out by Norouzi et al.,(2012) in Iran, aiming at removing arsenate using coral limestone bark and coral limestone bark coated with aluminum sulfate, acidic pH provided the best conditions for absorbing arsenate by coral limestone bark coated with aluminum sulfate. The reason was demonstrated to be elevation of the attraction force between the arsenate (negatively charged compound) and aluminum within this pH range[21]. Shokouhi et al. (2012), investigated removal of lead and cadmium using coral limestone granules from aquatic environments in Iran. They found that as the pH increased in alkaline conditions, the removal efficiency increased and the optimal pH was calculated as 10. It was also reported that under these conditions, chemical precipitation of lead and cadmium metals influences the removal of these metals [20].

With the increase in the contact time from 30 to 180 minutes, removal efficiency and adsorption capacity increased from 84.42 to 94.95% and 7.03 to 7.91 mg/g, respectively, where they became almost constant after reaching the equilibrium time (120 min). In the early stages of adsorption, a large number of sorbent's superficial sites were available for the dye adsorption. Due to this, over 84% of the removal efficiency was achieved during the first 30 minutes. Following a contact time of 120 min, the changes in the efficiency of dye removal were trivial, suggesting that the sorbent became almost saturated during this period and the changes in dye adsorption did not show any significant increase the initial stages of contact time. If we lengthen the

[Downloaded from jhr.ssu.ac.ir on 2025-12-24]

contact time further, due to the low efficiency, dye removal will not be economical and thus the sorbent should be recovered or replaced. The findings of the current study are consistent with studies of Karimian, (optimal contact time of 180 min)[19], Shokouhi and Bazrafshan (equilibrium time of 60 min) [20,29], Zazouli (equilibrium time of 45 min) [27]. The findings of all the mentioned studies revealed reported very minor changes after reaching the removal efficiency equilibrium, confirming the results of the current study and current research.

Investigation of the sorbent's mass and determination of the sorbent's optimal mass used in adsorption processes are among the most important issues that should be taken into consideration. In the current study, with the increase in the value of sorbent, the removal efficiency improved, whereas adsorption capacity decreased. By the increase of the adsorption level, a larger surface of the sorbent came into contact with the dye solution. In other words, the specific area of the sorbent in the solution increases. However, as the amount of sorbent rises, the level of adsorption per unit of the sorbent's mass or the adsorption capacity declines. Intra-particle reactions including compression due to increased levels of sorbent and not using all active points of the sorbent's surface can be the reasons of decreased adsorption capacity, resulting in diminished superficial area of the sorbent and increased bonded distance between the sorbent and the absorbed compound[19,30].Karimian et al investigated removal of Reactive orange 3R dye by using coral limestone granules and Leca granules and concluded that the optimal level of the sorbent was 10 g/L[19]. Shokouhi et al., reported the optimal level of 1 and 8 g/L for removing of lead and cadmium metals by using coral limestone granules respectively[20]. In other study performed by Norouzi et al., the optimum dosage of coral limestone bark and coral limestone bark coated with aluminum sulfate for removing of arsenate was reported 5 g/L[21]. In addition, similar results have been reported by Ghaneian et al. (2011),who investigated the efficiency of squid's bone powder in removing Reactive red 198 (optimal value of the sorbent was 2 g/100 mL). At last, Asilian et al.(2010),regarded took into account the application of the sludge obtained from coagulation process of water treatment plant in absorbing Reactive red 198 (optimal level of the sorbent was 2 g/L)[31]. Thus, the present study reached the same results as the literature.

The initial concentration of the dye provides a considerable driving force to overcome the resistance resulted from mass transfer of the dye between the solid and liquid phases. This is indeed one of the factors that influences adsorption levels[29]. In this study, an increase in the dye's concentration diminished removal efficiency, while the dye's adsorption capacity grew. With the increase in the initial concentration of the dye, at a constant sorbent's mass, the active surface extent available for adsorption remains constant, but the number of contaminants ’moles present in the reaction environment increases, thereby reducing the removal efficiency. On the other hand, with the increase in the initial

[Downloaded from jhr.ssu.ac.ir on 2025-12-24]

concentration of the dye, the force of mass transfer grows which overcomes the force resisting adsorption. This results in development of a considerable driving force to transfer the contaminant from liquid phase to the interface of the sorbent and the liquid, and causing increased adsorption capacity. In this regard, similar results have been obtained by Ghaneian et al. in 2010, 2011, and 2012 in Iran. They investigated removing Reactive red 198 dye using titanium dioxide nanoparticles, squid's bone powder, and pomegranate kernel powder, respectively. Likewise, Asilian et al. (2010) achieved similar results), who studied removal of Reactive red 198 dye through adsorption on the sludge resulting from coagulation process of water treatment plant, [30-33].

According to the results shown in Diagram 5, with the increase in temperature, removal efficiency increased from 72% at 5°C to 98% at 35°C. As the removal efficiency at 25°C, also the ambient temperature, and the difference in removal efficiency with 35°C were very low, the temperature of 25°C was considered as the optimal temperature. Thus, increased temperature can lead the level of adsorption to increase, suggesting endotherm city of the adsorption process of Reactive red 198 onto the coral limestone sorbent. Yazdani et al. (2012), used Feldspar mineral sorbent in removing caution dyes of Basic Blue 41 and Basic Red 18. The results obtained from their study indicated that the dye removal efficiency increased with temperature, which seems to be congruent with the results obtained from the present study[37]. Jahed et al.(2015) used active carbon in removing methylene blue dye. They found the process to be endothermic and spontaneous, which is in accordance with the results of the present study[39].

Studying the Adsorption Isotherm Models

In this study, the adsorption isotherm models of Langmuir and Freundlich were investigated. Eq. (2) represents the Freundlich isotherm model.

$$\mathbf{Log\ q_e = Log\ K_f + 1/n\ Log\ C_e} \qquad \text{(Eq.2)}$$

Where q_e is the amount of the dye absorbed per mass unit of the sorbent (mg/g), C_e is the equilibrium concentration of the dye in the solution (mg/L), and K_f and n are Freundlich constant sobtained through plotting log $q_e$vs log C_e.

Equation 3 represents Langmuir isotherm model:

$$\mathbf{C_e/q_e = 1/bq_m + C_e/q_m} \qquad \text{(Eq.3)}$$

Where q_e is the amount of the dye absorbed per mass unit of the sorbent (mg/g), C_e is the equilibrium concentration of the dye in the solution (mg/L), q_m is the maximum value of the absorbed compound onto the sorbent at the equivalence time (the maximum adsorption capacity) (mg/g), and b is the Langmuir constant, obtained by plotting C_e/q_e vs C_e.

As can be seen in Diagram 6, the best-fitted model to explain the adsorption of RR198 by the sea coral was the Langmuir model (of R^2=0.962). These results are in line with the Freundlich model adsorption isotherm with a correlation coefficient of 0.904.

[Downloaded from jhr.ssu.ac.ir on 2025-12-24]

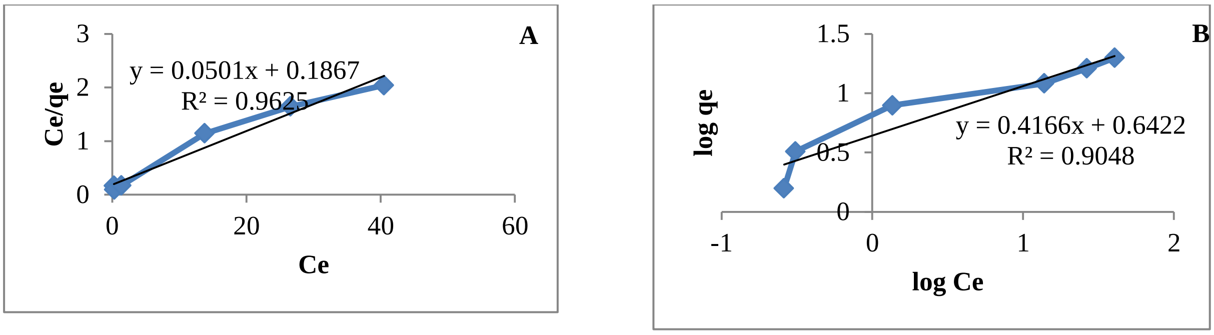


Diagram 6. The adsorption isotherm models a) Freundlich adsorption isotherm, b) Langmuir adsorption isotherm (3 g of the sorbent, 100 ml of the dye solution with concentrations of 5, 10, 25, 50, 75, and 100 mg/L, pH=3, and contact time of 120 min)

The parameters resulting from the adsorption isotherm models are provided in Table 3.

Table 3. The parameters of Langmuir and Freundlich isotherms for removing Reactive red 198 dye by the coral limestone sorbent

Isotherm	**Parameters**		
Langmuir	q_m	b	R^2
	19.96	0.268	0.962
Freundlich	n	K_F	R^2
	2.4	4.387	0.904

The isotherm equations of adsorption describe the way reaction takes place between the absorbed compound and the sorbent. In other words, under conditions in which both phases are at equilibrium, isotherm equation represents the relationship between the dye concentration in the solution and the amount of the dye absorbed onto the sorbent's surface[29]. the current The results of this study, which via investigates the adsorption isotherm models of Langmuir and Freundlich, were obtained from adsorption of Reactive red 198 on the sea coral and showed better out comes with Langmuir's model with a correlation coefficient of 0.962 than with Freundlich's. The Langmuir isotherm model seems to demonstrate identical results in regard with monolayer adsorption onto a surface containing a limited number of adsorption sites reflected in some other studies [29];Similar observations were reported for the adsorption of Reactive orange 3R dye on coral limestone granule and Leca granule[19], arsen at on coral limestone bark and coral limestone bark coated with aluminum sulfate[21] and RR198 on sludge obtained from coagulation in water

[Downloaded from jhr.ssu.ac.ir on 2025-12-24]

treatment plant[31], TiO_2[15] and magnetic nanoparticles coated with cetyltrimethyle ammonium bromide[16].

Studying the Kinetics of Adsorption

In order to evaluate the adsorption kinetics of Reactive red 198, the obtained data were put into pseudo-first-order kinetic (Eq. 4) and pseudo-second-order kinetic (Eq. 5) equations.

$$\mathbf{Log\ (q_e\text{-}q_t) = Logq_e - K_1t} \qquad \text{(Eq.4)}$$

$$\mathbf{t/q_t = 1/K_2q_e^2 + t/q_e} \qquad \text{(Eq.5)}$$

Where, q_e is the sorbent's adsorption capacity at the time of equilibrium (mg/g), q_t is the sorbent's adsorption capacity at the time of t (mg/g), and k_1 and k_2 are constant values. The results obtained from investigating the pseudo-first and pseudo-second-order kinetic equations are mentioned in Table 4.

Table 4. Pseudo-first and pseudo-second-order kinetic parameters for adsorption of Reactive red 198 onto the coral limestone sorbent

Adsorption kinetic	**Parameters**	
Pseudo-first order	K_1	$\mathbf{R^2}$
	0.0902	**0.66**
pseudo-second order	K_2	$\mathbf{R^2}$
	0.0256	**1**

According to the results obtained from kinetic investigation of the studied dye adsorption in Table 4, the process follows pseudo-second-order kinetics with a correlation coefficient of $R^2=1$. These results seem to bear econgruent with the findings of other studies such as Karimian et al. (2013), regarding removal of Reactive orange 3R using coral limestone granule and Leca granule [19], Norouzi et al.(2012), aiming to removing arsenate using coral limestone bark and coral limestone bark coated with aluminum sulfate [21], and Faraji et al.(2010), regarding investigation of magnetic nanoparticles coated with cetyltrimethyl ammonium bromide [16] as an efficient sorbent in removing reactive dyes from textile industries wastewater.

Thermodynamic Investigation of the Adsorption Process

In thermodynamic investigation of adsorption process, determination of three thermodynamic quantities including; standard enthalpy of adsorption (ΔH^o), standard Gibb's free energy of adsorption (ΔG^o), and standard entropy of adsorption (ΔS^o) is of significance. These parameters can be obtained according to equation6, through the dependence of the K_s thermodynamic equilibrium constant on temperature.

$$\mathbf{\Delta G^o = -RTLnK_s} \qquad \text{(Eq.6)}$$

In this relation, ΔG^o is Gibbs free energy, R is the constant of gases (8.314 J.mol/K), T is Kelvin temperature, and K_s represents distribution coefficient of the adsorption

[Downloaded from jhr.ssu.ac.ir on 2025-12-24]

process. K_s is calculated according to equation 7.

$$K_s = C_e/C_t \qquad \text{(Eq.7)}$$

K_s shows the relationship between the amount of the dissolved and adsorbed compound onto the sorbent (C_e) and the amount of the compound dissolved in the solution (C_t) at the time of equilibrium. The values of changes in the standard enthalpy (ΔH^o) and standard entropy (ΔS^o) can be obtained by Want-Hoof equation according to Relation 8 [32,33].

$$\mathrm{Ln}K_s = -\Delta H^o/R\ (1/T) + \Delta S^o/R \qquad \text{(Eq.8)}$$

The standard enthalpy and entropy change values of adsorption can be calculated using equation 8. The results obtained from thermodynamic investigation of the adsorption process of reactive red 198 onto the coral limestone sorbent are tabulated in Table 5.

Table 5. Thermodynamic data of adsorption of Reactive red 198 onto the coral limestone

Temp. (**^oK**)	**ΔG** (**KJ/mol**)	**ΔH^o** (**KJ/mol**)	**ΔS^o** (**J/mol.K**)
278	-3.24	71.82	**0.27**
283	-4.59		
288	-5.94		
298	-8.64		

According to the obtained results, the value of Gibbs free energy is negative, suggesting spontaneity of the adsorption process. Furthermore, elevation of the absolute value of the changes of Gibbs free energy or elevation of temperature indicates that the reaction takes place more easily at higher temperatures. Further, ΔG^o can determine the chemical or physical nature of the adsorption process. Generally, the changes of Gibbs free energy for physical adsorption ranges between zero to-20 KJ/mol, whereas the value of changes in the Gibbs free energy for chemical adsorption varies between -80 to-400 KJ/mol[34].

According to the results demonstrated in Table 5, ΔG^o values range between zero to-20 KJ/mol, suggesting that the adsorption process is physical. ΔG^o values have been investigated across all temperatures and a negative value between -3.24 to-8.64 KJ/mol has been obtained, showing spontaneity of the adsorption process [35]. Physical adsorption takes place when the Van der Waals intermolecular attraction force of the Reactive Red 198 dye compound and the coral sorbent are greater than the intermolecular force among the dye molecules themselves. Physical adsorption can be monolayer or multilayer, and occurs very quickly. In contrast, chemical adsorption is the result of chemical bonds development between the sorbent and absorbed compound. According to the results mentioned in Table 5, the value of ΔH^o standard enthalpy is positive and equal to 71.82 KJ/mol, suggesting endothermic city of the Reactive Red 198 adsorption process onto the coral limestone sorbent. As the results

[Downloaded from jhr.ssu.ac.ir on 2025-12-24]

obtained from temperature investigation indicated, an increase in temperature was observed to lead the level of adsorption to increase as well, increased, which is congruent with the results of ΔH^o). The positive value of the changes in standard entropy (ΔS^o) is equal to 0.27 J/mol. K, suggesting the tendency of the dye to the sorbent. It also signifies that entropy increases at the interface of the sorbent and absorbed compound during the adsorption process [36]. The results obtained from thermodynamic investigation of the adsorption process of Reactive Red 198 onto the coral limestone sorbent were in accordance with the results obtained by Yazdani et al.(2012)),[37], Ramavandi et al.(2014)),[38], and Jahed et al.(2015) in Iran [39].

Based on the conducted experiments and optimal conditions achieved, the process of removing Reactive Red 198 dye from the real wastewater sample of Yazdbaf textile factory was also investigated. The removal efficiency of the dye in the real sample and synthetic sample were obtained as 67.78 % and 97.63%, respectively. Presence of interfering factors in the wastewater sample can be mentioned as the reason of the reduction in removal efficiency in Yazdbaf textile factory wastewater relative to synthetic wastewater.

Conclusion

As the findings of the present study revealed and considering the properties of coral limestone sorbent including suitable density, quick precipitation ability, availability and inexpensiveness, no need for activation, and environmental safety of the process, the sea coral appears to be suitable low cost and efficient sorbent in treatment of dying waste waters. Furthermore, by considering the mentioned points this sorbent, its application recommended in the wastewater of other industries can be investigated in future studies. Furthermore, its resorption and reusability should also be taken into consideration for the further research.

Acknowledgment

This study was conducted under the supervision of environmental health engineering research Center at Kerman University of medical sciences as well as the support of Vice Chancellor for Research and Technology of this university. Hereby, we would like to appreciate their assistance and support which highly facilitated conductance of this research.

References

1. Dalvand A, Gholami M, Joneidi A, et al. Investigation of Electro chemical Coagulation Process Efficiency for Removal of Reactive Red 198 from Colored Wastewater. Journal of Science and Technology of Color. 2009;3:97-105 [Persian]
2. Nidheesh P.V, Gandhimathi R, Ramesh S.T. Degradation of dyes from aqueous solution by Fenton processes: a review .Environmental Science and Pollution Research.2013;20(4):2099-2132

[Downloaded from jhr.ssu.ac.ir on 2025-12-24]

3. Alidadi H, Karimian H, Bazrafshan E, et al. A Survey on Dye Removal from Colored Textile Wastewater Using Multi-walled Carbon Nanotubes and Palm Ash as a Natural Adsorbent. Journal of Research in Environmental Health. 2015;1(1):10-19 [Persian]
4. Daneshvar N, Khataee A, Rasoulifard M.H, et al. Removal of Organic Dyes from Industrial Wastewaters Using UV/H_2O_2,UV/H_2O_2/Fe (II), UV/H_2O_2/Fe (III).Processes water and wastewater. 2007;61:34-42 [Persian]
5. Maleki A, Rezaee R. Toxicity Reduction of Reactive Black 5 and Disperse Orange 25 by Advanced Oxidation Processes. Journal of Science and Technology of Color. 2009;3:17-23 [Persian]
6. Moussavi S, Emamjomeh M, Ehrampoush M, et al. Removal of Acid Orange 7 Dye from Synthetic Textile Wastewater by Single-Walled Carbon Nanotubes: Adsorption Studies, Isotherms and Kinetics. Journal of Rafsanjan University of Medical Sciences.2014;12:907-918 [Persian]
7. Dos Santos A.B, Cervantes F.J, Van Lier J.B. Review paper on current technologies for decolourisation of textile wastewaters: perspectives for anaerobic biotechnology. Bioresource Technology. 2007;98(12):2369-2385
8. MoradiPasand L, Ayati B. Study of reactive blue 171 dye degradation in hybrid system of UV/H_2O_2&SBAR, Iran. J. Health & Environ. 2013;6(3):393-406 [Persian]
9. Tan K.A, Morad N,Teng T.T, et al. Removal of cationic dye by magnetic nanoparticle (Fe3O4) impregnated onto activated maize cob powder and kinetic study of dye waste adsorption. APCBEE Procedia. 2012;1:83-89
10. Badruddoza A, Hazel G.S.S, Hidajat K, et al. Synthesis of carboxymethyl-β-cyclodextrin conjugated magnetic nano-adsorbent for removal of methylene blue. Colloids and Surfaces A: Physicochemical and Engineering Aspects. 2010;367(1-3):85-95
11. Bellir K, Bouziane I.S, Boutamine Z, et al. Sorption study of a basic dye "Gentian violet" from aqueous solutions using activated bentonite. 2012;18:924-933
12. Chowdhury S, Chakraborty S, Saha P.D. Response surface optimization of a dynamic dye adsorption process: a case study of crystal violet adsorption onto NaOH-modified rice husk. Environmental Science and Pollution Research. 2013;20(3):1698-1705
13. Zazouli M.A, Balarak D, Mahdavi Y. Effect of Azolla filiculoides on removal of reactive red 198 in aqueous solution. Journal of Advances in Environmental Health Research. 2013;1(1):44-50
14. Malakootian M, Rezaei S, Nasiri A, et al. Removal of Methylene Blue Dye from Aqueous Solutions Using Activated Fly Ash from Zarand Power Plant in Kerman. Journal ofwater and wastewater. 2015;3:62-71 [Persian]
15. Dutta S, Parsons S.A, Bhattacharjee C, et al. Kinetic study of adsorption and photo-decolorization of Reactive Red 198 on TiO_2 surface. Chemical Engineering Journal. 2009;155(3):674-679
16. Faraji M, Yamini Y, Tahmasebi E, et al. Cetyltrimethylammonium bromide-coated magnetite nanoparticles as highly efficient adsorbent for rapid removal of reactive dyes from the textile companies' wastewaters. Journal of the Iranian Chemical Society. 2010;7:130-44
17. Esmaeili A, Kalantari M. Bioremoval of an azo textile dye, Reactive Red 198, by Aspergillus flavus. World Journal of Microbiology and Biotechnology. 2012;28(3):1125-1131

[Downloaded from jhr.ssu.ac.ir on 2025-12-24]

18. Debrassi A, Baccarin T, Demarchi C.A, et al. Adsorption of Remazol Red 198 onto magnetic N-lauryl chitosan particles: equilibrium, kinetics, reuse and factorial design. Environmental Science and Pollution Research. 2012;19:1594-604
19. Karimian K, Shookohi M.R, Samadi M.T, et al. A Comparative Study of Removal Efficiency for Reactive Orange 3R from Aqueous Solution Using Coral Limestone Granule and LECA Granule. Journal of Salamat and Behdasht. 2013;4(3):217-231[Persian]
20. Shookohi R, Ehsani H.R, Tarlaniazar M. Efficiency Survey of Cd and Pb Removal from Aqueous Environment Using Coral Limestone Granule. Journal of Environmental Technology and Science. 2012; 16(1):109-121 [Persian]
21. Nourozi R, Samadi M.T, Mehdinejad M.H, et al. Investigation Comparison of Coral Limestone and Aluminium Sulfat-Coated Coral Limestone as an Adsorbent in Arsenic(V) removal of aqueous solution: Equilibrium and Kinetic Study. Journal of Health and Environment. 2012;5(4):479-488 [Persian]
22. Minaii Zangi Z, Ganjidoust H, Ayati B. Photocatalytic Degradation of Dye Using Dopping Titanium Dioxide Nanoparticles and its Kinetic Study. Journal of Color Science and Technology. 2014;8:203-211 [Persian]
23. Falah-Shojaei A, Shams-Nateri A, Ghomashpasand M. Synthesis and Characterization of C-TiO_2@Fe_3O_4 Magnetic Nanoparticles for Degradation Direct Blue 71 Under Visible Light Irradiation. Journal of Color Science and Technology. 2015;8:339-346[Persian]
24. Allahgholian A, Mehrizad A, Gharbani P. Adsorption of Methylene Blue Dye from Aqueous Solutions onto Modified Nano-TiO_2. Journal of Color Science and Technology. 2015;9(1):35-43
25. Kamba A.S, Ismail M, Ibrahim T.A.T, et al. Synthesis and Characterisation of Calcium Carbonate Aragonite Nanocrystals from Cockle Shell Powder (Anadara granosa).Journal of Nanomaterials. 2013;2013:1-9
26. Rahman M.A, Jochen H, Ryuichi S. X-Ray Diffraction Is a Promising Tool to Characterize Coral Skeletons, Advances in Materials Physics and Chemistry. 2013;3:120-125
27. Zazouli M.A, Balarak D, Mahdavi Y, et al. Adsorption rate of 198 reactive red dye from aqueous solutions by using activated red mud. Iranian journal of health sciences. 2013;1(1):63-43
28. Ghaneian M.T, Ehrampoush M.T, Ghanizadeh G, et al. Study of Eggshell Performance as a Natural Sorbent for the Removal of Reactive Red 198 Dye from Aqueous Solution. Journal of Toloee Behdasht. 2011;10(1):70-81 [Persian]
29. Bazrafshan E, Mostafapour F.K, Barikbin B. Decolorization of Reactive Red 198 by means ofpistachio-nut shell ash. journal of Birjand University of Medical Science. 2012;19(3):266-276[Persian]
30. Ghaneian M.T, Ehrampoush M.H, Dehvari m, et al. A Survey of the Efficacy of Cuttle Fish Bone Powder in the Removal of Reactive Red 198 dye from Aqueous Solution. Journal of Tolue Behdasht. 2011;10(3-4):127-138 [Persian]
31. Asilian H, Mousavi G, Mahmoodi M. Adsorption of Reactive Red 198 Azo Dye fromAqueous Solution onto theWaste Coagulation Sludge of theWater Treatment Plants. Journal of Health and Science. 2010;3(1);93-102 [Persian]

[Downloaded from jhr.ssu.ac.ir on 2025-12-24]

32. Ghaneian M.T, Dehvari M, Taghavi M, et al. Application of Pomegranate Seed Powder in the removal of Reactive Red 198 dye from aqueous solutions. journalof Health Science of Jondi Shapour. 2012;4(3):45-55 [Persian]
33. Ghaneian M.T, Ehrampoush M.H, Rahimi S, et al. Adsorption of Reactive Red 198 Dye on TiO_2 Nano-particle from Synthetic Wastewater. Journal of Toloee Behdasht. 2010;9(4):59-70 [Persian]
34. Greluk M, Hubicki Z. Kinetics, isotherm and thermodynamic studies of Reactive Black 5 removal by acid acrylic resins. Chemical Engineering Journal. 2010;162:919-926
35. Moradi O, Zare K, Monajjemi M, et al. The studies of equilibrium and thermodynamic adsorption of Pb(II), Cd(II) and Cu(II) Ions from aqueous solution onto SWCNTs and SWCNT–COOH surfaces. Fuller. Nanotub. Car. 2010;18(3):285-302
36. Rodrigues L.A,Alvarez-Mendes M.O, Thim G.P, et al. Phenol removal from aqueous solution by activated carbon produced from avocado kernel seeds, Chemical Engineering Journal, 2011;174(1):49-57
37. Yazdani M, Arami M, Bahrami H. Textile Dyes Removal from Single and Binary Systems Using Inorganic Adsorbent, Journal of Color Science and Technology. 2012;6:153-164 [Persian]
38. Ramavandi B, Leili M. Efficiency of Shrimp Shell to Remove Methylene Blue from Aqueous Solutions, Journal of health. 2014;5(4);310-325 [Persian]
39. Jahed B, Shaker Khatibi M, Baghapoor M.A, et al. The application of activated carbon produced from used newspaper in the removal of methylene blue dye from aqueous solution: isotherm, kinetic and thermodynamic study, Modares Civil Engineering Journal. 2015;14(4):1-9 [Persian]

[Downloaded from jhr.ssu.ac.ir on 2025-12-24]