



Enhancement of Remazol Brilliant Blue R Adsorption Capacity by using Modified Clinoptilolite

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ABSTRACT

In this study, the adsorption behavior of Remazol Brilliant Blue R (RBBR) from aqueous solution by using raw and modified clinoptilolites were investigated. In the experimental work, raw clinoptilolite (R-CL) was treated with $\text{Zn}(\text{NO}_3)_2$ in ethanol and produced zinc-grafted clinoptilolite (Zn-CL). The adsorption experiments were carried out under different conditions of initial concentration (25-250 mg/L), adsorption time (0-2h), solution pH (2-12), and temperature (300-353 K) to determine optimum conditions for the highest RBBR removal. The influence of these parameters on the adsorption capacity was studied using the batch process. The results indicated that the solution pH was observed to be a key factor of the RBBR adsorption process. The maximum dye adsorption was achieved with Zn-CL adsorbent at pH~6 and the corresponding adsorption capacity was found to be 42.2 mg/g, which was higher than R-CL (12.5 mg/g). Lower adsorption capacity of RBBR was found by Zn-CL between pH 8 and 12 opposite to R-CL which showed a marginal increase in adsorption capacity within the same pH range. The results proved that Zn-CL which is a modified clinoptilolite is an effective adsorbent for the removal of RBBR from aqueous solution.

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INTRODUCTION

Reactive dyes have been extensively used in textile dyeing by which, significant amount of these types of dyes are released into the receiving water without appropriate and efficient treatment [1]. As a result, reoxygenation of water will be retarded due to limited sunlight penetration into the water surface. Nevertheless, reactive dyes are the most common dye employed in textile related industry due to their beneficial characteristics including bright color, water fastness, simple application techniques and low energy consumption. As a matter of fact, most of the dyes used in the industry nowadays carries significant amount of coloring materials that are toxic and harmful to organisms and human well being [2]. Up to 40% of the color is discharged in the effluent from reactive dyeing

operation resulting in a highly colored effluent. They are not easily biodegradable, thus, even after extensive treatment, color may still remain in the effluent [3].

Therefore, there is a need to effectively remove these dyes from wastewater and some of the available methods to remove the dyes including chemical precipitation, adsorption, ion exchange, flotation, membrane filtration, electrochemical treatment and coagulation-flocculation. Until now, adsorption has been the most favourable process than others and this process has become more efficient if low-cost adsorbents are used [4].

Natural zeolites are crystalline hydrated alumina silicates with a framework structure adsorbent. Zeolite normally exhibit pores occupied with, alkali and alkaline earth cations. They are abundant in nature, which can be obtained at low cost. The advantages of high cation-exchange and having the characteristics of molecular sieve properties, natural zeolites have been widely used as adsorbents in separation and purification for many years [5]. Akgül [1] found that the properties

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of zeolite's external surface can be tailored for specific applications through surface functionalization. These modifications can alter physical and chemical properties of the zeolites and the resulting modified zeolite can be used for a variety of applications such as ion-exchange, adsorption, catalysis, etc. [1, 6-7].

In this study, raw clinoptilolite was modified via Zn^{2+} -grafting to prepare a functionalized zeolite material that enhanced adsorptive properties for remazol brilliant blue R (RBBR) in aqueous solution. The dye adsorption capacity of the resulting modified zeolite was evaluated to determine the adsorption characteristics for RBBR.

MATERIALS AND METHODS

Adsorbate

Remazol Brilliant Blue R (RBBR) supplied by Sigma-Aldrich (M) Sdn. Bhd, Malaysia was used as a model organic dye for evaluating the adsorption behavior of the sorbent. The negatively charged dye, RBBR has a chemical formula of $\text{C}_{22}\text{H}_{16}\text{N}_2\text{Na}_2\text{O}_{11}\text{S}_3$ with molecular weight of 626.54 g/mol. The chemical structure of RBBR is shown in Figure 1. Deionized water supplied by USF ELGA water treatment system was used to prepare all the reagents and solutions.

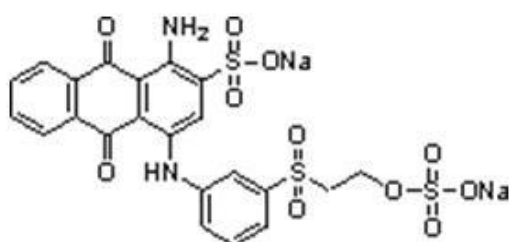


Figure 1. The chemical structure of RBBR

Adsorbent preparation and modifications

Natural zeolite, clinoptilolite, sample was obtained from Malaysia Agricultural Research and Development Institute (MARDI) which mainly supplied to farmers as fertilizer to increase crops yield. Preparation of raw clinoptilolite (R-CL) was done by washing the clinoptilolite using deionized water to remove all dust or other impurities and to maintain the natural pH of the clinoptilolite. Next, the clinoptilolite was dried in an oven for 24 hour at 373.15 K to remove moisture. In order to obtain modified form, the R-CL was treated with $\text{Zn}(\text{NO}_3)_2$ in ethanol at 333 K. The treatment was carried out by adding 1.0 g R-CL into a $\text{Zn}(\text{NO}_3)_2$ (0.3 g) solution in ethanol (15 mL). The concentration of $\text{Zn}(\text{NO}_3)_2$ was 0.1 mol/L with 99.9% purity. The mixture was treated in an oil bath at 333 K for 6 h. Then, the zeolite sample was separated by filtration, washed with ethanol to remove excess salt and dried at

353 K for 24 h. The resulting Zn^{2+} -grafted sample is designated as Zn-CL.

Characterization

Fourier transform infrared (FTIR) analysis was applied to determine the surface functional groups, using FTIR spectroscope (FTIR-2000, Perkin Elmer), where the spectra were recorded from 4000 to 450 cm^{-1} . The BET surface area, total pore volume and average pore size of the R-CL and Zn-CL were measured using ASAP 2020 Micrometrics instrument by Brunauer–Emmett–Teller (BET) method.

Adsorption studies

Batch equilibrium studies were carried out by adding a 0.5g of R-CL and Zn-CL each into 250 mL Erlenmeyer flasks containing 200 mL of different initial concentrations (25-250 mg/L) of dye solution. The flasks were agitated in an isothermal water-bath shaker at 120 rpm and different solution temperature (300-350 K) for 24 h until equilibrium was reached. The pH was adjusted by adding a few drops of diluted 0.1M NaOH or 0.1M HCl and was measured using a pH meter (Model Delta 320, Mettler Toledo, Switzerland). The dye concentrations before and after treatment were measured using UV-Visible spectrophotometer (Model Shimadzu UV-1800, Japan) at 590 nm. The amount of equilibrium adsorption, q_e (mg/g), was calculated by:

$$q_e = \frac{C_o - C_e}{W} \quad (1)$$

where C_o and C_e (mg/L) are the liquid-phase concentrations of RBBR at initial and at equilibrium, respectively. V is the volume of the solution (L) and W is the mass of dry adsorbent used (g).

Batch kinetic studies

The procedure of kinetic adsorption tests was identical to that of batch equilibrium tests, however the aqueous samples were taken at present time intervals. The concentrations of RBBR were similarly measures. The RBBR uptake at any time, q_t (mg/g), was calculated by:

Combustion rate: Burning time is obtained by observing the mass changes recorded on mechanical balance and also by using stop watch. It is the time for the biomass combustion to be completed. With known amount of total burnt briquette and burning time, average combustion rate can be calculated using the following formula [12].

$$q_t = \frac{(C_o - C_t) V}{W} \quad (2)$$

where C_t (mg/L) is the liquid-phase concentration of RBBR at any time, t (h).

RESULTS AND DISCUSSION

Characterization

FTIR spectra of R-CL and Zn-CL are shown in Figure 2. The characteristic infrared signals for Si–O–Al asymmetrical stretching (1034 cm^{-1}), Si–O bending (469 cm^{-1}), O–Si–O bending (606 cm^{-1}), Si–O asymmetric stretching (1207 cm^{-1}) and O–Si–O symmetric stretching (796 cm^{-1}) are present in both R-CL and Zn-CL. The peaks at 518 and 764 cm^{-1} are attributed to “pore opening” vibration and to symmetric stretching of free SiO_4 , were appeared and similar to the result obtained by Akgül [1]. The FTIR spectra also exhibit typical bands of the bridging OH groups in $\equiv\text{Al}-\text{OH}-\text{Si}\equiv$ groups at 3640 cm^{-1} and the vibration of the bonds $\text{O}-\text{H}\cdots\text{O}$ at 3374 cm^{-1} [8]. Furthermore, it can be seen that the aforementioned bands such as 3300 and 1600 cm^{-1} still appear but exhibit increased intensity for Zn-CL. The above changes confirm the increment in the hydroxyl groups since the absorption band at 3400 cm^{-1} arises from stretching vibrations of O–H bonds. This is due to the formation of additional Brønsted acidsites (new hydroxyl groups) by the incorporation of Zn^{2+} into the clinoptilolite [9]. It also indicated that Zn^{2+} grafting improved the surface activity of the clinoptilolite.

The physical properties derived from N_2 adsorption–desorption data are summarized in Table 1. After the clinoptilolite was grafting with Zn^{2+} , the BET surface area was increased from 13.5 to $21.3\text{ m}^2/\text{g}$ due to the formation of surface cracks and defects as a result of the collapse of pore structure during Zn^{2+} -grafting in ethanol. The BET surface area of modified clinoptilolite (Zn-CL) obtained in this study was comparable with those of Akgul, [1] ($24.6\text{ m}^2/\text{g}$ for $\text{Fe}(\text{NO}_3)_3$ -modified zeolite), of Salgado-Gómez et al. [10] ($11.93\text{ m}^2/\text{g}$ for NaCl-modified zeolite-rich tuff), and of Lin et al. [11] ($60.83\text{ m}^2/\text{g}$ for NaCl-modified zeolites).

However, pore volume and mean pore diameter of the Zn-CL was decreased as compared to R-CL which is attributed to an increase in the microporosity. As

reported earlier, solvent extraction can result an increase in the microporosity due to some causes, such as the opening of side pockets, removal of some impurities occluded within the clinoptilolite pores [12, 13].

TABLE 1. Physical properties of the zeolite sample.

Zeolite	Surface area (m^2/g)	Total pore volume (cc/g)	Mean pore diameter (\AA)
R-CL	13.5	0.042	32.6
Zn-CL	21.3	0.039	30.8

Effect of the adsorbent dosage

The effect of adsorbent dosage on adsorption of RBBR onto R-CL and Zn-CL is illustrated in Figure 3. As can be seen, the adsorption uptakes of RBBR increased from 4.2 to 14.1 mg/g and from 11.5 to 30.4 mg/g for R-CL and Zn-CL, respectively for an increase in Zn-CL dose from 0.2 to 0.5 g . This was due to contribution of the increasing sorbent surface area and availability of more adsorption sites. However, the adsorption uptakes decreased after 0.5 g . This may be due to the decrease in total adsorption surface area available to RBBR resulting from overlapping or aggregation of adsorption sites [14].

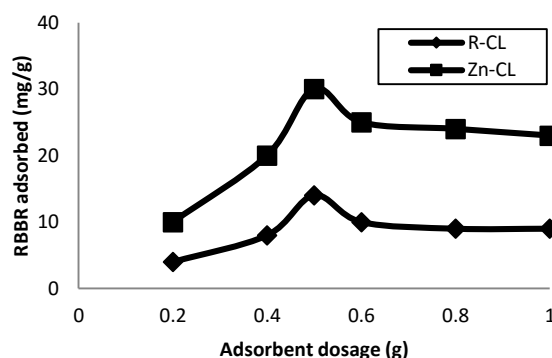


Figure 3. Effect of the adsorbent dosage on RBBR adsorption (dye concentration=100 ppm, pH 6.5, adsorption time= 1.0 h)

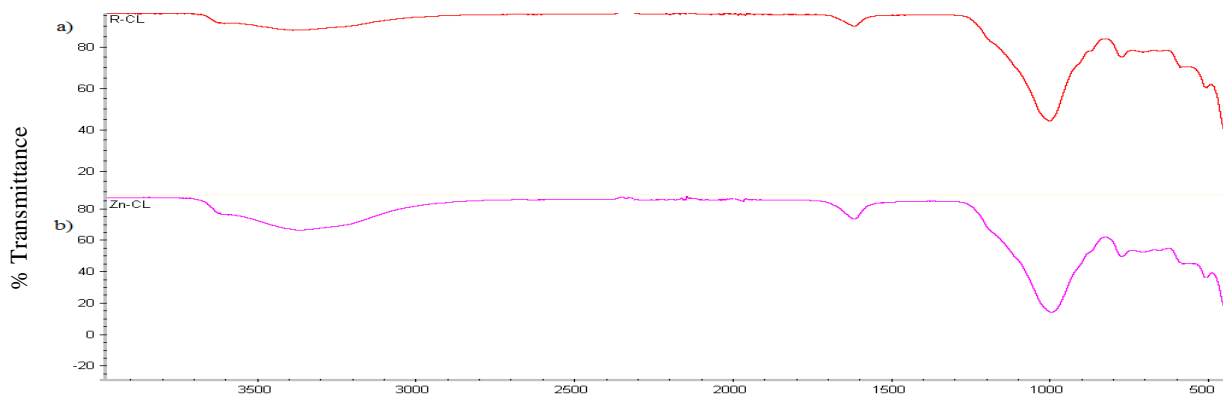


Figure 2. FTIR spectra of (a) R-CL and (b) Zn-CL zeolite sample

Effect of the initial dye concentration

Figure 4 illustrates the adsorption of RBBR for different initial concentration of RBBR between 25 and 250 mg/L at 300 K as a function of contact time on R-CL and Zn-CL. As the initial dye concentration increases from 25 to 250 mg/L, the adsorption uptakes of RBBR at equilibrium were found to increase from 4.2 to 17.5 mg/g and from 12.5 to 42.2 mg/g for R-CL and Zn-CL, respectively. The q_e values increased with the increase of initial RBBR concentration up to the equilibrium concentration values. This was because, when the initial concentration increases, the mass gradient between the solution and adsorbent increases, which made it act as a driving force for the transfer of dye molecules from bulk solution to the particle surface [15]. If the number of RBBR molecule in the unit volume increases, the number of ions competing for the available sites on the surface of zeolite was high, hence, resulting in higher RBBR adsorption capacity. It can be seen from Figure 4 that for both zeolites, the amount of RBBR adsorbed increased with time and reached a constant value which no more RBBR can be removed from the solutions. This behavior was due to availability of surface sites on the zeolites presence during initial phase of adsorption process. After a lapse of time, the remaining surface sites have been occupied and difficult to be occupied anymore due to the repulsion forces exerted between the solute molecules of the solid and bulk phases [16]. It is demonstrated in Figure 3 that Zn²⁺-grafting has increased RBBR adsorption with higher adsorption capacity than R-CL. The maximum adsorption capacities of R-CL and Zn-CL were found as 12.5 and 42.2 mg/g, respectively at room temperature. The reason for the difference can be attributed to the marked change in the surface activity as a result of Zn²⁺-grafting process, as can be seen in Figure 2. In fact, the amount of accessible active sites for adsorption increases after modification due to the increases of surface area as presented in Table 1.

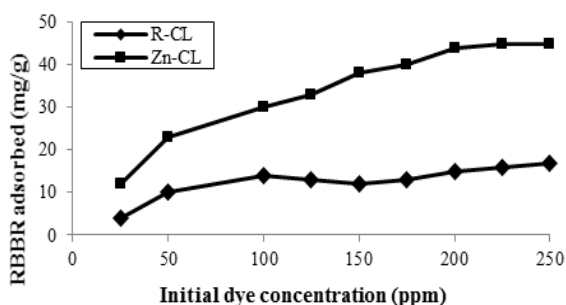


Figure 4. Effect of initial RBBR concentration on RBBR adsorption (adsorption time = 1.0 h, pH 6.5, temperature = 300K)

Effect of pH

An important influencing factor for dye adsorption has been referred to pH since it will affect the surface binding sites of the adsorbent and the degree of ionization of the dye in solution [17]. Therefore, in order to find a suitable pH for the effective adsorption of RBBR dyes by the zeolite samples, experiments were performed over a pH range of 2-12 while other parameters were fixed constant and the results showed in Figure 5 indicated different binding patterns for both adsorbents. As shown in Figure 5, the adsorption capacity of RBBR for Zn-CL increased from pH 2 to 6 before it decreased gradually until pH 7. The adsorption capacity remains fairly constant thereafter until pH 8. After pH 8 there was a gradual decrease in the amount of RBBR adsorbed until it reached pH 12. The high adsorption capacity of the RBBR solution at acidic pH could be attributed to the electrostatic interactions between the positively charged of the adsorbent and the negatively charged RBBR dye anions [18]. The presence of high concentration of H⁺ can increase the positive charge on the surface of Zn-CL by protonating the negatively charged sites (M-O⁻) and hydroxyl groups (M-OH) and forming M-OH²⁺ (M: Si or Zn) as the solution pH reduces [1]. The adsorption at alkaline pH can be affected by the presence of excess OH⁻ ions competing with the dye anions for the adsorption sites which explained the increasing electrostatic repulsion between the anionic dye adsorbate species and negatively charged adsorbent surfaces. As for the R-CL, the adsorption capacity increase from pH 2 to 7 and then remained constant in between pH 7 to 12. At alkaline pH, the negatively charged surface of adsorbent normally will not favor the adsorption of anionic dye due to the electrostatic repulsion. However, in this study, the amount of RBBR adsorbed was still significant even in alkaline condition. This phenomenon probably due to chemical interaction between the anionic dye and the adsorbent [19,20].

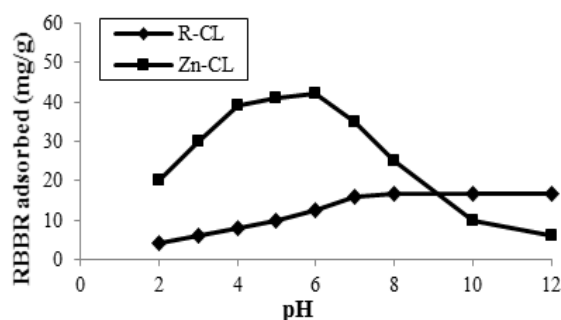


Figure 5. Effect of pH on RBBR adsorption (dye concentration = 100ppm, adsorption time= 1.0h temperature = 300K)

Effect of contact time

As can be seen from Figure 6, the adsorption intensity of RBBR was higher for Zn-CL compared to R-CL. Initially, the adsorption of RBBR was rapid and reached equilibrium in ~60 min. This phenomenon was due to the fact that a large number of surface sites are available for adsorption at the initial stages and after a lapse of time, the remaining surface sites are difficult to be occupied because of repulsion between the solute molecules of the solid and bulk phases [16]. The amount of adsorbed dye did not show significant change after 60 min. Therefore, it can be concluded that the adsorption time of around 60 min was sufficient to reach the equilibrium state. In fact, it can be observed that Zn-CL was a high affinity clinoptilolite adsorbent compared to R-CL due to high RBBR removal in a short adsorption equilibrium time. Besides, the adsorption curves were observed relatively smooth and continuous that led to equilibrium which was due to the monolayer coverage of dye on the surface of both zeolites [22].

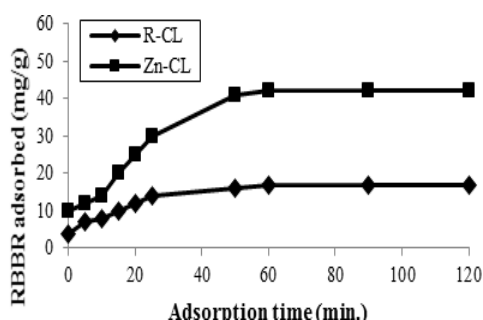


Figure 6. Effect of contact time on RBBR adsorption (dye concentration = 100ppm, pH=6.5, temperature = 300K)

Effect of temperature

The effect of solution temperature on RBBR removal adsorption capacity of the Zn-CL was studied by varying the solution temperature from 300-353 K, while other parameter were fixed constant as shown in Figure 7. From Figure 7, RBBR adsorption capacity was found to increase with increasing solution temperature from 300 to 333 K, showing the endothermic nature of adsorption process. This phenomenon was due to the increased in the mobility of the dye with increasing temperature whereby an increasing number of molecules required sufficient energy to enable an interaction with active sites at the surface [22]. Besides, the endothermic reaction during RBBR adsorption might also due to the increase in chemical interaction between the adsorbate and surface functionalities of adsorbent [23]. Marginal reduction in the adsorption capacity beyond 333 K might be associated to the weakening of bonds between dye molecules and active

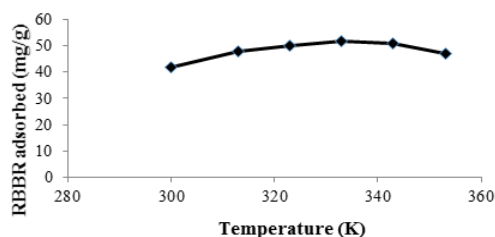


Figure 7. Effect of the temperature on RBBR adsorption (dye concentration of 100 ppm, pH 6.5, adsorption time= 1.0 h)

sites of the adsorbents at high temperatures and also between adjacent dye molecules on the sorbed phase [16].

Adsorption isotherms

Langmuir model is based on the assumption that adsorption energy is constant and independent of surface coverage. The maximum adsorption occurs when the surface is covered by a monolayer of adsorbate [24]. The linear form of Langmuir isotherm equation is given as:

$$\frac{C_e}{q_e} = \frac{1}{Q_o K_L} + \frac{1}{Q_o} C_e \quad (3)$$

where C_e (mg/L) is the equilibrium concentration of the RBBR dye, q_e (mg/g) is the amount of RBBR adsorbed per unit mass of adsorbent. Q_o (mg/g) and K_L (L/mg) are Langmuir constants related to adsorption capacity and rate of adsorption, respectively.

Freundlich model is based on sorption on a heterogeneous surface of varied affinities [25]. The logarithmic form of Freundlich was given as:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (4)$$

where K_F and n are Freundlich constants with n as a measure of the deviation of the model from linearity of the adsorption and K_F (mg/g (L/mg)^{1/n}) indicates the adsorption capacity of the adsorbent. In general, $n > 1$ suggests that adsorbate is favourably adsorbed on the adsorbent. The higher the n value the stronger the adsorption intensity.

Table 2 summarizes all the constants and correlation coefficient, R^2 values obtained from the two isotherm models applied for adsorption of RBBR dye on the Zn-CL. On the basis of the R^2 , Langmuir isotherm seemed to represent the equilibrium adsorption data with better fit as compared to the other isotherms. This implies that RBBR adsorption onto Zn-CL is more like a monolayer adsorption process with uniform distribution of energetic

TABLE 2. Langmuir, Freundlich and Temkin isotherm parameters for the adsorption of RBBR dye onto Zn-CL at different temperatures.

Isotherm	Isotherm constants
Langmuir isotherm	
Q_o (mg/g)	49.65
K_L (L/mg)	0.026
R^2	0.996
Freundlich	
K_F (mg/g) (L/mg) ^{1/n}	1.954
n	2.331
R^2	0.936

adsorption sites on its surface. The value of n is greater than unity, suggesting that RBBR dye was favourably adsorbed by Zn-CL.

Adsorption kinetics

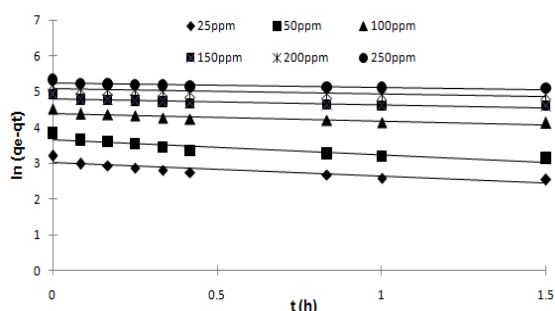
In order to analyze the adsorption kinetics of RBBR dye on Zn-CL, two kinetic models; pseudo-first-order and pseudo-second-order kinetic were applied for the experimental data.

Pseudo-first-order kinetic model

The pseudo-first-order kinetic model found by Lagergren and Svenska [26] was widely used to predict sorption kinetic and was defined as:

$$\ln(q_e - q_t) = \ln(q_e - k_1 t) \quad (5)$$

where q_e and q_t (mg/g) are the amounts of adsorbate adsorbed at equilibrium and at any time, t (h), respectively and k_1 (1/h) is the adsorption rate constant. The linear plot of $\ln(q_e - q_t)$ versus t gives a slope of k_1 and intercept of $\ln q_e$ as shown in Figure 8. The values of k_1 and R^2 obtained from the plots for adsorption of RBBR

**Figure 8.** Pseudo-first-order kinetic plot for the adsorption of RBBR dye onto Zn-CL at 303K

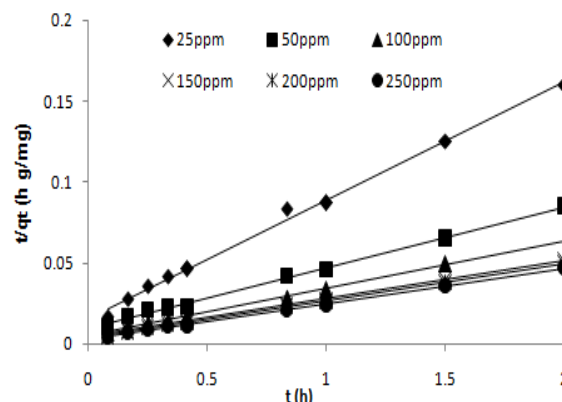
dye on the adsorbent at 303K are reported in Table 3. It was observed that the R^2 values obtained for the pseudo-first-order model did not show a consistent trend. Besides, the experimental q_e values did not agree with the calculated values obtained from the linear plots. This shows that the adsorption of RBBR dye on the adsorbent does not follow a pseudo-first-order kinetic model.

Pseudo-second-order kinetic model

The pseudo-second-order equation by Ho and Mckay [27] predicts the behaviour over the whole range of adsorption and is expressed as:

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

where k_2 (g/mg h) is the rate constant of second-order adsorption. The linear plot of t/q_t versus t gave $1/q_e$ as the slope and $1/k_2 q_e^2$ as the intercept. Figure 9 shows a good agreement between the experimental and the calculated q_e values. From Table 3, all the R^2 values obtained from the pseudo-second-order model were close to unity, indicating that the adsorption of RBBR dye on Zn-CL fitted well into this model.

**Figure 9.** Pseudo-second-order kinetic plot for the adsorption of RBBR dye onto Zn-CL at 303K

CONCLUSIONS

The present investigation showed that modified clinoptilolite, Zn-CL was a promising adsorbent to be used in the removal of RBBR from aqueous solution. Better adsorption capacity obtained for Zn-CL (42.2 mg/g) compared to R-CL (12.5 mg/g) was mainly attributed to the formation of new hydroxyl groups by

TABLE 3. Pseudo-first-order and pseudo-second-order kinetic model parameters for the adsorption of RBBR dye onto Zn-Cl at 303K.

C _o (mg/L)	q _{exp} (mg/g)	Pseudo-first-order kinetic model			Pseudo-second-order kinetic model		
		q _{ei} (mg/g)	k ₁ (1/h)	R ²	q _{e2} (mg/g)	k ₂ (g/mg h)	R ²
25	12.85	20.07	0.38	0.806	13.71	0.33	0.996
50	23.52	38.38	0.42	0.819	26.56	0.15	0.997
100	30.70	80.99	0.23	0.802	34.44	0.17	0.997
150	38.56	122.02	0.18	0.736	42.70	0.13	0.996
200	40.15	158.38	0.14	0.698	43.92	0.14	0.998
250	42.20	186.10	0.12	0.641	45.54	0.17	0.997

the incorporation of Zn²⁺ as well as the increase of high surface area. Adsorption of RBBR was found to increase with increase in contact time and RBBR initial concentration. The maximum adsorption capacity of RBBR was obtained at pH~6 and was favourable in endothermic nature. The result demonstrated that Zn-CL could be economically feasible to be applied in industrial wastewater treatment due to its high capacity, local availability and low cost.

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Persian Abstract

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چکیده

در این پژوهش، رفتار جذب رمازول آبی درخشان-R (رمازول بریلینت بلو آر) از محلول آبی با استفاده از کلینوپتیلولیت‌های خام و اصلاح شده بررسی شد. در بررسی تجربی، کلینوپتیلولیت خام (R-CL) با $Zn(NO_3)_2$ در اتانول اصلاح گردیده و کلینوپتیلولیت با پیوند روی (Zn-CL) تشکیل شد. آزمایشات جذب برای تعیین شرایط بهینه به منظور بیشترین میزان حذف RBBR، در شرایط گوناگونی از غلظت اولیه (بیست و پنج تا دویست و پنجاه میلی گرم بر لیتر)، زمان جذب (صفر تا دو ساعت)، pH محلول (دو تا دوازده) و دما (سیصد تا سیصد و پنجاه کلوین) انجام گرفت. اثر این پارامترها در ظرفیت جذب طی یک فرآیند ناپیوسته بررسی گردید که نتایج حاصل از آن نشان می‌دهد، pH محلول عاملی کلیدی در فرآیند جذب RBBR می‌باشد. حداکثر مقدار جذب رنگ توسط جاذب روی-کلینوپتیلولیت (Zn-CL) در pH حدود شش بدست آمد و ظرفیت جذب مربوطه چهل و دو و دو دهم میلی گرم بر گرم محاسبه شد که این مقدار نسبت به جاذب R-CL با ظرفیت جذب دوازده و نیم میلی گرم بر گرم بالاتر بود. برخلاف R-CL که افزایش محدودی در ظرفیت جذب در محدوده pH هشت الی دوازده از خود نشان داد، ظرفیت جذب پائین تری از RBBR توسط Zn-CL در بازه pH مشابه، مشاهده گردید. نتایج کار نشان می‌دهد که می‌توان Zn-CL، که کلینوپتیلولیتی اصلاح شده است، را به عنوان یک جاذب موثر برای حذف RBBR از محلول آبی تلقی نمود.
