# Removal of Reactive Black 5 from wastewater using natural clinoptilolite modified with apolaccase

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ABSTRACT: In this study, a clinoptilolite modified with apolaccase was used to adsorb Reactive Black 5 (RB5) dye from aqueous solution using the batch procedure. The influences of pH, contact time, temperature and absorbent dosage on the adsorption were investigated. The optimum adsorption was obtained at pH = 6, contact time = 60 min, temperature = 25ºC and adsorbent dosages of 1.62 and 1.59 mg/50 mL per gram of clinoptilolite and of apolaccase-modified clinoptilolite (LMC), respectively. The adsorption experimental data fitted both the Langmuir and Freundlich isotherm models well. In addition, pseudo-first-order and pseudo-second-order kinetics were used to study the kinetics of RB5 dye adsorption onto natural clinoptilolite and LMC. Adsorption appears to follow pseudo-second-order kinetics with a high correlation coefficient. Thermodynamic parameters such as changes in the free energy ($\Delta G^{o}$), enthalpy ($\Delta H^{o}$) and entropy ($\Delta S^{o}$) of adsorption were calculated. The thermodynamic parameters indicate that the adsorption of RB5 dye onto LMC was less spontaneous, feasible and endothermic. The LMC can be used as an alternative low-cost adsorbent for the dye removal from aqueous solutions.

Due to the low biodegradation of dyes, conventional biological processes are not very effective for treating a dye-containing wastewater; such wastewaters are usually treated either by physical or chemical processes. However, these processes are very expensive and cannot be used effectively to treat the wide range of dye wastes (Grag *et al.*, 2003; Azhar *et al.*, 2005). Adsorption is an effective method for removing dyes from waste effluents and has advantages over other methods because it is a sludge-free, clean operation that can remove dyes completely, even from the dilute solution. Activated carbon is the most widely used adsorbent as it has an excellent adsorption capacity for organic compounds; however, commercial activated carbon is very expensive. Nowadays, there are alternative, low-cost, commercially available adsorbents that are used for dye removal (Azhar *et al.*, 2005; Wang *et al.*, 2005).

One naturally-occurring adsorbent is zeolite, a silicate with a three-dimensional cage structure, which possesses a permanent negative charge due to isomorphous substitution in its structure that is
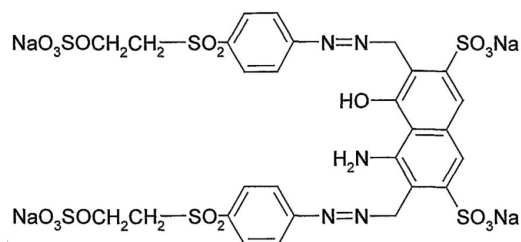
Fig. 1. Chemical structure of RB5.

balanced by exchangeable cations (Weng and Pen, 2007). The use of zeolites as adsorbents for removing heavy-metal ions from aqueous solution has attracted much interest due to their large ion-exchange capacities (Yousef *et al.*, 2011). The existence of large deposits of natural zeolites worldwide offers promise because of their capacity for treating wastewater contaminated with heavy metals at low cost (Ahmaruzzaman, 2008).

*Lactarius volemus*, a species of mushroom in the family Russulaceae, is widely distributed in the area of Erzurum, Turkey. As a mycorrhizal fungus, its fruit bodies grow on the ground at the base of various species of trees in the summer and autumn in broad-leaved forests, either individually or in groups. *Lactarius volemus* produces the enzyme laccase that has innate properties of reactive radical production, which confer antioxidant, antiradical and antimicrobial activities (Ozen *et al.*, 2011;

Nadaroglu & Tasgin, 2013). It uses oxygen, producing water as a by-product, to degrade a range of compounds including phenolic and non-phenolic compounds. It also has the ability to detoxify a range of environmental pollutants (Imran *et al.*, 2012). The present study describes the use of apolaccase-modified-clinoptilolite (LMC) for the removal of Reactive Black 5 (RB5) dye from aqueous solutions. The adsorption of RB5 was investigated as a function of contact time, pH, temperature and adsorbent dose. Adsorption isotherms, kinetic and thermodynamic studies were performed to describe the adsorption process.

## MATERIALS AND METHODS

### Reactive Black 5

Reactive Black 5 (RB5) (Fig. 1) is an anionic dye with full chemical name: tetrasodium 4-amino-5-hydroxy-3,6-*bis*[[4-[[2-(sulfonatooxy)ethyl]sulfonyl] phenyl]azo]naphthalene-2,7-disulfonate and formula $C_{26}H_{21}N_5Na_4O_{19}S_6$, CAS Reg. No. 17095-24-8.

### Zeolite

The zeolite sample used in this study was collected from an open-pit mine in the Gordes (Manisa) region of west Anatolia. This region has high-quality zeolites, mainly clinoptilolite (Fig. 2). The zeolite material used as the adsorbent in this
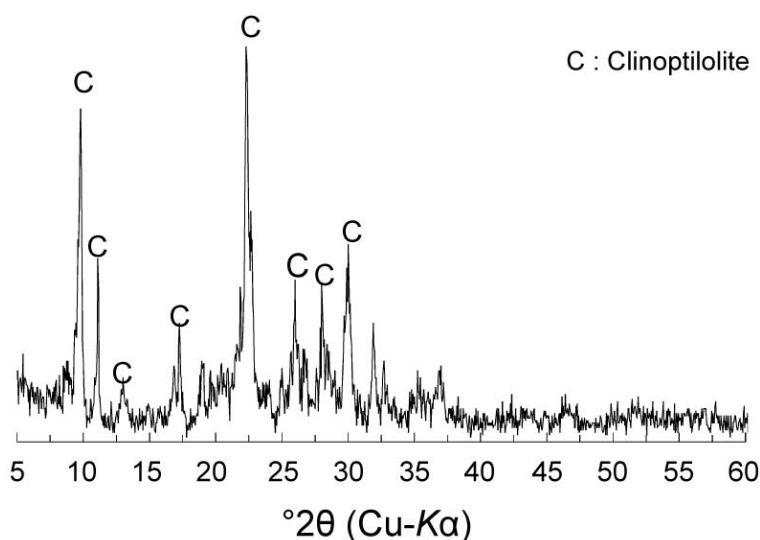


Fig. 2. XRD pattern of the zeolite

study consists mainly of clinoptilolite (85%) with small amounts of feldspar (10%) and clay minerals (5%). The clinoptilolite, identified from its XRD pattern (Fig. 2), displays a range of colours: white, pink, yellow-reddish and transparent. A typical sample had a density of 2.25 g/cm$^3$ with a specific surface area of 40.80 m$^2$/g. The reason for selecting this clinoptilolite as an adsorbent was its relatively moderate specific surface area with its exceptionally high, and selective, ion-exchange capacity (Aydin & Kuleyin, 2011).

## Isolation of the laccase enzyme and purification of the apolaccase enzyme

The laccase enzyme from *Lactarius volemus* (Russulaceae) was purified as described previously (Nadaroglu and Tasgin, 2013). The 1 M KCl extract from *Lactarius volemus* was purified by precipitations with $(NH_4)_2SO_4$ followed by a combination of ion exchange (DEAE-cellulose) and size-exclusion chromatography (Sephacryl S200). The protein content of the chromatographic eluates was measured on an ultraviolet/visible (UV/Vis) spectrophotometer (Epoch Nanodrop Multi-Volume Spectrophotometer System) at 595 nm using the Bradford method (Bradford, 1974). The laccase activity was determined using 2,2′-azino-di-(3-ethylbenzothiazolsulfonate) (ABTS) as a substrate.

The purified laccase (100 mg) was dissolved in pH 7.0 phosphate buffer (5 mL, 0.2 M), containing dipiclonic acid (0.075 M) and dialyzed against the same buffer for 5 h in a dialysis tube. The solution was dialyzed further for 18 h using deionized water, changing the solution 5 to 6 times and then for 5 h against pH 5.0 acetate buffer (0.01 M), which was used for the measurement of activity. A solution of almost pure apoenzyme was obtained (Kazuko 1970; Demir *et al.*, 1993).

## Material characterization

Scanning electron microscopy (SEM) was used to examine the surface of the adsorbents before and after dye adsorption (JEOL JSM-6400 SEM). Energy dispersive X-ray (EDX) analysis was used for qualitative analysis of the clinoptilolite. Before SEM examinations, the surfaces of the samples were coated with a 20 nm layer of gold to obtain a conductive surface and to avoid electrostatic charging during examination.

## Adsorption of apolaccase onto the clinoptilolite

The crushed clinoptilolite was washed thoroughly with distilled water until neutral. The suspension was wet-sieved through a 200-mesh screen; the small amount of the suspension that remained on the sieve was discarded. The solid fraction was washed five times with distilled water following the sequence of mixing, settling and decanting. The final suspension was filtered and the solid residue was dried at 105ºC, ground using a pestle and mortar and passed through a 200-mesh sieve. The clinoptilolite (1 g) was modified with apolaccase by shaking with the apolaccase solution (10 mL) for ~1 h and the reaction mixture was centrifuged at 5000 rpm for 10 min and the separated particles of LMC were stored at 4ºC until use (Zhang *et al.*, 2010).

## Dye adsorption procedure

The clinoptilolite and the LMC were used for the study of RB5 removal from aqueous solution. A calibration curve in the range 0−40 ng/cm$^3$ of aqueous RB5 was produced on a UV/Vis spectrophotometer (PG Instruments T80 spectrophotometer) at $\lambda$ = 597 nm using serial dilutions of the stock solution. Adsorption of the RB5 from a synthetic wastewater was measured by stirring (500 rpm) the clinoptilolite or LMC (1 g) at 303±1 K in flasks containing the RB5 dye solution (50 mL, 1mg/mL). Small samples (2 mL) were pipetted from the flasks periodically for the timed experiments and centrifuged at 5000 rpm for 10 min. The supernatant solutions were filtered through 0.45 μm filters and the concentration of the RB5 measured.

The amounts of dye adsorbed onto the clinoptilolite or LMC ($q_e$, mg/g) were calculated from the equation:

$$q_e = ((C_o - C_e) \times V)/m \qquad (1)$$

where: $C_o$ and $C_e$ are the initial and equilibrium concentrations of dye in solution (mg/L); $V$ is the volume of solution (L) and $m$ is the mass of the adsorbent (g).

For all other experiments, where the effect of factors such as pH, temperature, amount of sorbent and adsorption isotherms were determined, a standard equilibration time of 60 min was used.

## RESULTS AND DISCUSSION

### Characterization by SEM

The SEM images of LMC (Fig. 3a) and dye-loaded LMC (Fig. 3b) are shown. The LMC displays a rough and porous surface, which is one of the factors responsible for the large adsorption capacity. After adsorption of the RB5, the surface appears to have become smoother (Fig. 3b), suggesting that the adsorption of the RB5 changes the surface morphology of the adsorbent (Nadaroglu *et al.*, 2015).

### Adsorption studies

*Effect of pH*. The pH of the solution is an important factor in the adsorption process as it affects the surface charge of the adsorbent, the degree of ionization of the dye and the specificity of the adsorbate (Imamoglu & Tekir, 2008). In order to establish the influence of pH on the adsorption of the dye, batch equilibrium studies were carried out at pH 3−8 and the results are presented in Fig. 4. The pH affected the adsorption of RB5 onto clinoptilolite and LMC significantly at low concentrations. Maximum dye removal was observed at pH 6 for both clinoptilolite and LMC adsorbents.

LMC removed RB5 almost completely from the wastewater. Moreover, LMC was a more efficient adsorbent than the original clinoptilolite. Large adsorption rates for RB5 were observed at acidic pH values on clinoptilolite and LM-clinoptilolite. It has been suggested that $H^+$ ions in the positively charged surface interacted with dye molecules thereby increasing the amount of adsorbed dye (Demirbas *et al.*, 2008; El-Sayed *et al.*, 2011).

*Effect of contact time*. The contact time between adsorbent and adsorbate species is significant for the removal of pollutants from water and wastewater by means of adsorption at a particular temperature and pH. Fast removal of dye pollutants and rapid establishment of equilibrium signifies the efficiency of the adsorbent for its use in wastewater treatment (Anbia & Ghaffari, 2011). In this study, the effect of contact time on the removal of RB5 onto LMC was investigated over 6 h and the results are shown in Fig. 5. The adsorption capacity of the clinoptilolite and LMC for the RB5 dye increased considerably during the initial adsorption stage and then continued to increase at a relatively slow rate with contact time until equilibrium was established after 60 min. This suggests that a large number of sites were available for adsorption at the initial stage, then after a period of time, the remaining sites were less accessible due to repulsive forces between the solute molecules on the solid and the bulk phase (Bazrafshan *et al.*, 2012). The maximum adsorption efficiency of RB5 dye, at a contact time of 60 min, was 1.623 and 1.792 mg/g for the clinoptilolite and the LMC, respectively.

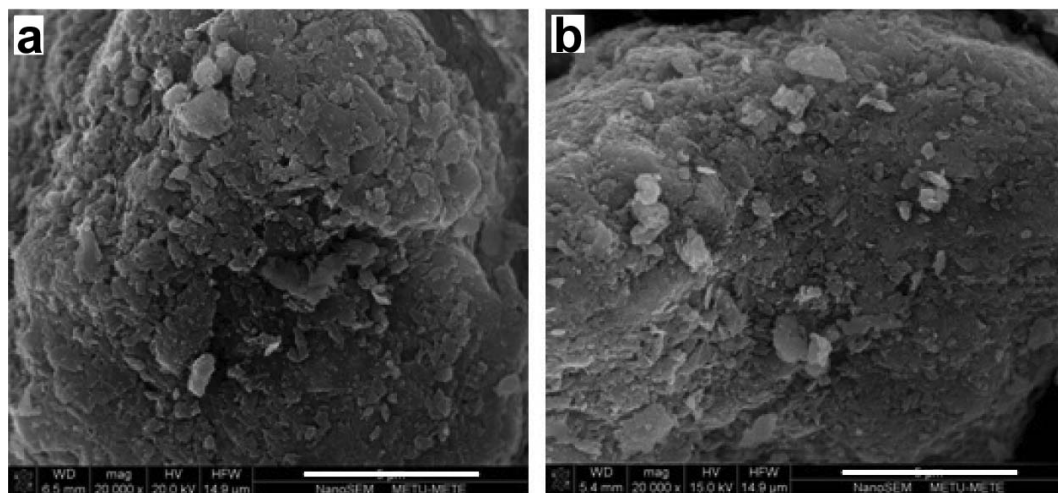*Effect of temperature*. Temperature affects the adsorption rate by modifying the molecular



Fig. 3. SEM images of LMC (a) and LMC loaded with RB5 dye (b). Scale bars 5 μm.
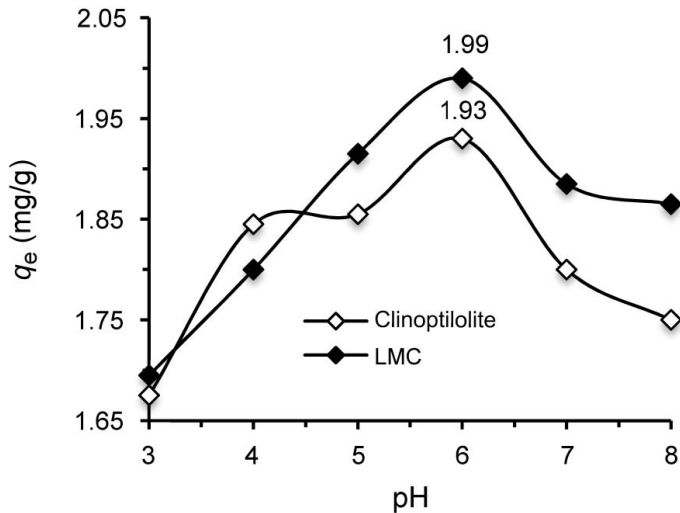
F<small>IG</small>. 4. Adsorption of RB5 on clinoptilolite and LMC at different pH values (RB5 concentration: 1 mg/mL, adsorbent dose: 1 g/50 mL, stirring speed: 500 rpm, temperature: 303±1 K), time: 60 min (see Fig. 5).

interactions and the solubility of the adsorbate (Kanawade & Gaikwad, 2011; Setshedi *et al.*, 2012). In order to study the effect of temperature on the adsorption of RB5 onto the clinoptilolite and the LMC, batch adsorption experiments were carried out over the range 20−80ºC (Fig. 6) for 60 min. Maximum adsorption of RB5 dye was observed at 40ºC for clinoptilolite (1.613 mg/mL) and ~25ºC (1.602 mg/mL) for LMC.

*Effect of adsorbent dosage*. The adsorbent dose determines the capacity of adsorbent for a given initial concentration of dye solution (Mosallanejad & Arami, 2012). The effect of adsorbent dose on the dye removal is shown in Fig. 7. Initially, dye adsorption was very fast and then equilibrium was reached slowly. The maximum RB5 removal attained with an adsorbent dose of 1 g/50 mL was 1.59 and 1.82 mg/g for the clinoptilolite and the
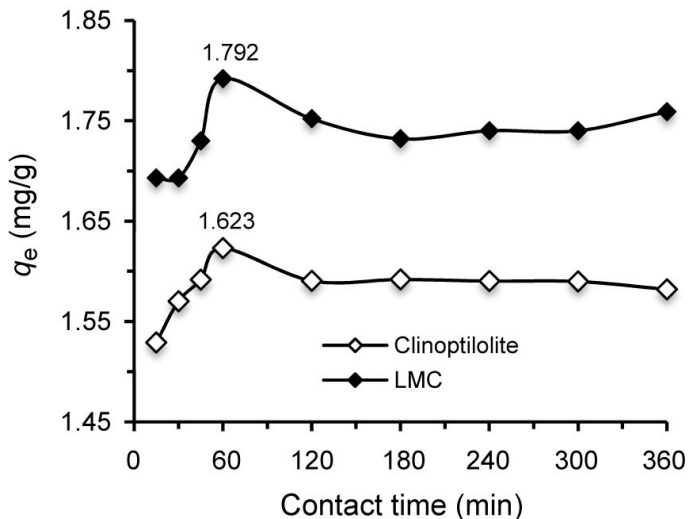


F<small>IG</small>. 5. Effect of contact time on adsorption of RB5 by the clinoptilolite and LMC (initial RB5 concentration: 1 mg/mL, adsorbent dose: 1 g/50 mL, stirring speed: 500 rpm, temperature: 303±1 K).
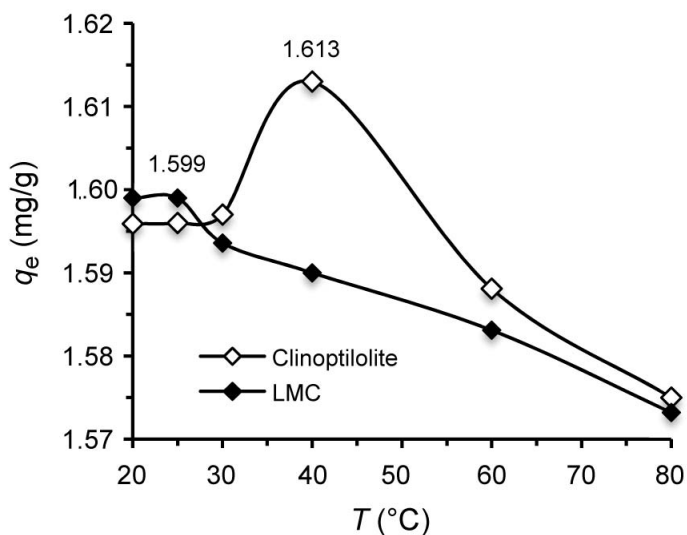
FIG. 6. Effect of temperature, *T*, on RB5 dye adsorption by the original clinoptilolite and LMC (initial RB5 concentration: 1 mg/mL, adsorbent dose: 1 g/50 mL, stirring speed: 500 rpm, time: 60 min)

LMC, respectively. Adsorption of RB5 increased with an increasing amount of mesoporous adsorbent and remained almost constant up to a certain limit. This can be attributed to the increased adsorbent surface area and the availability of additional adsorption sites (Garg *et al.*, 2004; Mall *et al.*, 2005; Anbia & Ghaffari, 2011).

*Adsorption isotherms*

*Langmuir adsorption isotherm model*. The Langmuir isotherm assumes that adsorption occurs at specific homogenous sites on the adsorbent. The linear form of the Langmuir isotherm equation is:
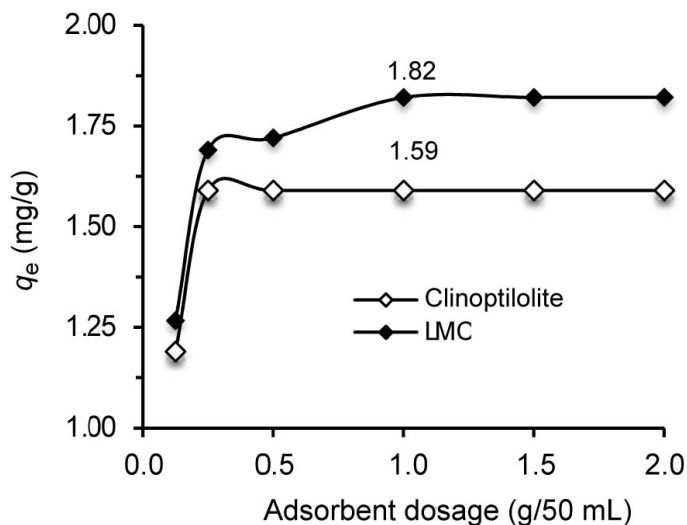
$$q_e = \frac{q_{max} bC}{1 + bC} \qquad (2)$$



FIG. 7. Influence of adsorbent dosage on the adsorption of RB5 dye on clinoptilolite and LMC (initial dye concentration: 1 mg/mL, stirring speed: 500 rpm, temperature: 303±1 K, time 60 min)
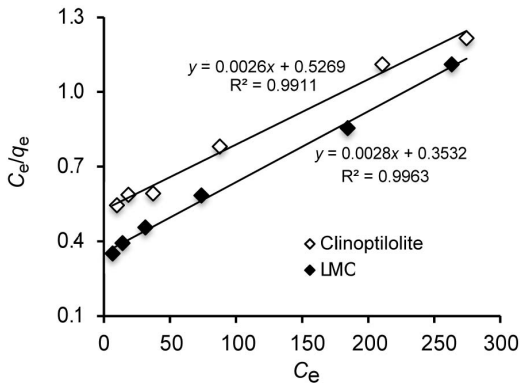
FIG. 8. Langmuir isotherm model for the adsorption of RB5 on the natural clinoptilolite and the LMC.
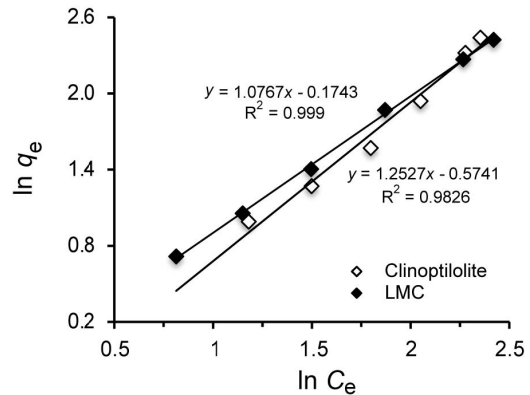


FIG. 9. Freundlich isotherm model for the adsorption of RB5 on the natural clinoptilolite and the LMC

where: $q_{max}$ (mg/g) is the maximum adsorption capacity and b (dm$^3$/mg) is a constant that indicates the affinity of the binding sites. They are determined from the linear form of equation 2:

$$\frac{C_e}{q_e} = \frac{1}{bq_{max}} + \frac{C_e}{q_{max}} \quad (3)$$

Dye concentration varied from 25 mg/L to 500 mg/L. The values of $q_{max}$ and b were calculated from the slope and the intercept of the plot of $C_e$ *vs.* $C_e/q_e$ (Fig. 8) and the Langmuir parameters are presented in Table 1. The isotherm was linear throughout the entire concentration range studied and showed high coefficients of determination ($R^2 = 0.9911$ and 0.9963 for clinoptilolite and LMC, respectively), suggesting that the Langmuir model fits the data adequately in both cases.

*Freundlich adsorption isotherm model.* The Freundlich isotherm model is an empirical relationship describing the adsorption of solutes from a liquid to a solid surface that assumes that adsorption sites with different adsorption energies are involved.

It is described by the following equation:

$$q_{max} = K_F C_e^{1/n} \quad (4)$$

where $K_F$ is the empirical Freundlich constants related to the sorption capacity of the adsorbent (mg/g) and *n* is the energy of adsorption. They can be calculated from the linear form of equation 4:

$$\ln q_e = \ln K_F + 1/n \ln C_e \quad (5)$$

The values of $K_F$ and n were calculated from the intercept and slope of the Freundlich plot (Fig. 9). The calculated values of the Freundlich parameters are listed in Table 1. The corresponding $R^2$ for the adsorption of RB5 onto clinoptilolite and LMC adsorbents were 0.9826 and 0.9990, respectively, showing that the Freundlich model fits the data adequately in both cases. The Langmuir and Freundlich isotherm models describe the equilibrium adsorption of RB5 onto the clinoptilolite and the LMC sufficiently, suggesting that the adsorption process is monolayer coverage of the dye on the surface of both materials (Zhou *et al.*, 2014).

TABLE 1. The Langmuir and the Freundlich constants for the adsorption isotherms

| Langmuir constants | —— Langmuir adsorption model —— Clinoptilolite | LMC | Freundlich constants | — Freundlich adsorption model — Clinoptilolite | LMC |
|---|---|---|---|---|---|
| $q_{max}$ (mg/g) | 500 | 500 | $K_F$(mg/g) | 0.241 | 0.759 |
| b (L/mg) | 263 | 176.5 | n | 0.799 | 0.930 |
| $R^2$ | 10.9910 | 0.9860 | $R^2$ | 0.9826 | 0.9990 |

## Adsorption kinetic models

*The pseudo-first-order kinetic model.* The linear form of the pseudo-first-order kinetic model can be written as (Kobiraj *et al.*, 2012):

$$\frac{1}{q_t} = \frac{k_1}{q_e t} + \frac{1}{q_e} \qquad (6)$$

where $k_1$ is the pseudo-first-order rate constant $(min^{-1})$ and $q_t$ and $q_e$ are the amounts of dye adsorbed at time $t$ and at equilibrium (mg/g). At different dye concentrations, the correlation coefficients and the $k_1$ values were calculated for dye adsorption from the linear plots of $\ln(q_e - q_t)$ *vs.* $t$ for the original clinoptilolite and LMC (Fig. 10). For the pseudo-first-order model, the coefficients of determination $(R^2)$ for clinoptilolite and LMC adsorbents ranged from 0.9284 to 0.9741 and from 0.9543 to 0.9956, respectively (Table 2). The large $R^2$ values suggest that the pseudo-first-order model describes the removal of RB5 by both clinoptilolite and LMC adequately.

*The pseudo-second-order kinetic model.* The linear form of the pseudo-second-order kinetic model is (Kobiraj *et al.*, 2012):

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \qquad (7)$$

where $k_2$ is the equilibrium rate constant of the pseudo-second-order model (g mol$^{-1}$ min$^{-1}$). This equation has been applied to the present study. At different dye concentrations, the correlation coefficients, $q_e$ and $k_2$ for dye adsorption on the
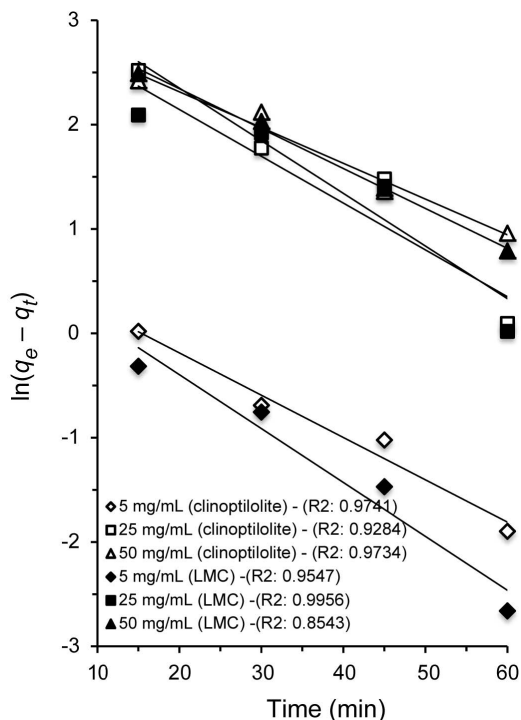


FIG. 10. Pseudo-first-order model for RB5 adsorption onto the clinoptilolite and the LMC at different concentrations.

clinoptilolite and the LMC were calculated from the linear plots of $t/q_t$ *vs.* $t$ (Fig. 11). For the pseudo-second-order models, the coefficient of determination $(R^2)$ values range from 0.9709 to 0.9970 and from 0.9905 to 0.9966 for the natural

TABLE 2. Kinetic parameters for the adsorption of RB5 on clinoptilolite and LMC.

| Initial RB5 concentration (mg/dm$^3$) | $q_e$-exp (mg/g) | Pseudo-first-order rate equation | | | Pseudo-second-order rate equation | | |
|---|---|---|---|---|---|---|---|
| | | $k_1$ | $q_e$-cal (mg/g) | $R^2$ | $k_2$ | $q_e$-cal (mg/g) | $R^2$ |
| Zeolite adsorbent | | | | | | | |
| 5 | 2.48 | 0.040 | 1.86 | 0.9741 | 0.025 | 2.86 | 0.9970 |
| 25 | 14.60 | 0.030 | 20.09 | 0.9284 | 0.00174 | 18.87 | 0.8793 |
| 50 | 21.50 | 0.034 | 28.79 | 0.9734 | 0.0012 | 28.57 | 0.9709 |
| LMC adsorbent | | | | | | | |
| 5 | 2.48 | 0.051 | 1.89 | 0.9547 | 0.036 | 2.78 | 0.9959 |
| 25 | 16.60 | 0.038 | 20.95 | 0.9956 | 0.0015 | 22.20 | 0.9905 |
| 50 | 24.40 | 0.044 | 22.42 | 0.8543 | 0.00134 | 31.25 | 0.9966 |
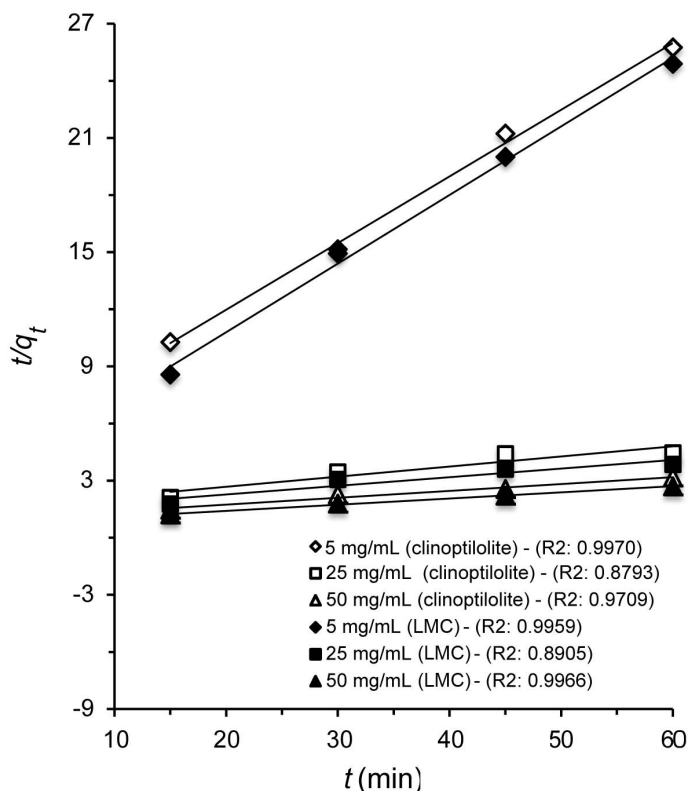
FIG. 11. Pseudo-second-order reaction for RB5 dye adsorption onto the clinoptilolite and the LMC adsorbents at different concentrations.

clinoptilolite and the LMC adsorbents, respectively. The large $R^2$ values suggest that the pseudo-second-order model also describes the removal of RB5 by natural clinoptilolite and LMC adequately.

The $R^2$ values of the pseudo-second-order model are closer to unity and the calculated $q_e$ values computed from the pseudo-second-order equation show very good agreement with experimental values. This indicates that the pseudo-second-order kinetic model is more suitable for the adsorption of RB5 dye onto the natural clinoptilolite and LMC adsorbents.

*Adsorption thermodynamics*

The thermodynamic properties of adsorption must be considered to decide whether the process is spontaneous or not (Hong *et al.*, 2009). In the present study, the adsorption capacity increased with increasing temperature from 293 to 303 K. The changes in free energy ($\Delta G^\circ$, kJ/mol), enthalpy ($\Delta H^\circ$, kJ/mol) and entropy ($\Delta S^\circ$, J/K mol) were

determined from the following equations (Chakravarty *et al.*, 2008):

$$K_L = C_s/C_e \qquad (8)$$

$$\Delta G^\circ = -RT \ln K_L \qquad (9)$$

$$\ln K_L = \left(\frac{\Delta S^\circ}{R}\right) + \left(\frac{\Delta H^\circ}{RT}\right) \qquad (10)$$

where $K_L$ is the equilibrium constant, $C_s$ is the concentration of the solid phase at equilibrium (mg/L), $C_e$ is the concentration of the liquid phase at equilibrium (mg/L), $T$ is the temperature (K) and R is the gas constant. The influence of temperature on the thermodynamics of RB5 adsorption by clinoptilolite and LMC adsorbents is illustrated in Fig. 12, while the thermodynamic parameters are listed in Table 3.

The $\Delta G^\circ$ values were positive, indicating that the adsorption of RB5 was not spontaneous over the
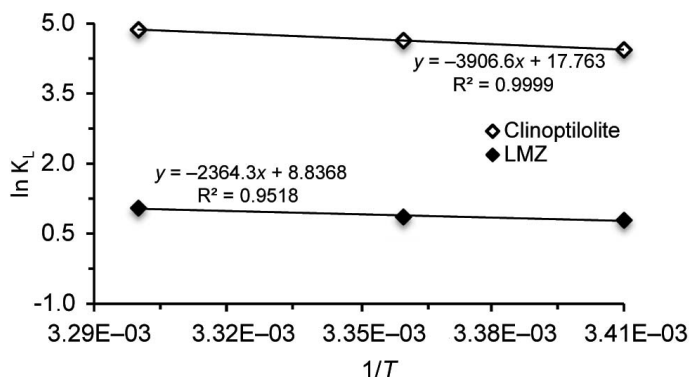
FIG. 12. Influence of temperature on the thermodynamics of adsorption of the RB5 dye

range of temperatures studied. The positive value of $\Delta G^o$ suggests that the adsorption requires energy to convert reactants into products (Deniz & Saygideger, 2010). The positive values of $\Delta H^o$ confirm the endothermic nature of the adsorption further and the positive $\Delta S^o$ values suggest an increase in adsorbate concentration in the solid−liquid interface thereby indicating an increase in adsorption onto the solid phase and confirming an increased randomness at the solid−liquid interface during adsorption. This is the normal consequence of the physical adsorption process, which takes place through electrostatic interactions (Fatih *et al.*, 2014).

## CONCLUSIONS

In the present study, the adsorption of RB5 dye by clinoptilolite and LMC from aqueous solution was investigated in batch mode. The equilibrium data fit the Langmuir isotherm model better, with a larger $R^2$ value, than the fit to the Freundlich isotherm model. The sorption process was best described by the pseudo-second-order kinetic model. The thermodynamic parameters $\Delta G^o$, $\Delta H^o$ and $\Delta S^o$ indicate non-spontaneous, endothermic adsorption of RB5 dye onto the clinoptilolite from aqueous solutions. The results of the present investigation indicate that LCM, a low-cost adsorbent could be employed as an alternative to commercial adsorbents for the removal of RB5 from aqueous solutions.

TABLE 3. Thermodynamic parameters for the adsorption of RB5 on the natural clinoptilolite and the LMC.

| Temperature (K) | – Thermodynamic parameters – | | |
| --- | --- | --- | --- |
| | $\Delta G^o$ (kJ mol$^{-1}$) | $\Delta H^o$ (kJ mol$^{-1}$) | $\Delta S^o$ (J mol$^{-1}$) |
| Clinoptilolite adsorbent | | | |
| 293 | 1329.44 | | |
| 298 | 1352.12 | 25.718 | 116.70 |
| 303 | 1374.80 | | |
| LMC adsorbent | | | |
| 293 | 1891.00 | | |
| 298 | 1923.30 | 10.643 | 68.67 |
| 303 | 1955.55 | | |

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