Photodegradation and Absorption Efficiency of Modified Clinoptilolite for Congo Red Dye from Industrial Wastewater

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Abstract—This study is to examine the performance of modified clinoptilolite as an adsorbent and a catalyst for the removal of Congo red dye from industrial wastewater. The experiments were carried out in a batch system to optimise operation variables such as time on a catalyst for photodegradation, adsorbent dosage, particle size, and pH in the adsorption process. 120-minute catalyst has the highest degradation efficiency (90,043%), a dosage of 40 g/100 mL achieves the highest removal (90.654 %) and the smallest particle size of 0.15 mm, shows the highest removal (97.619%). It was found that a pH of 6 resulted in the highest removal effectiveness (98.324%). The adsorption kinetic followed the pseudo-second order equations. Further thermodynamic investigations showed that the adsorption is exothermic and spontaneous process. This study's findings suggested that clinoptilolite could be implemented as a catalyst for the photodegradation and an adsorbent for the removal of Congo red dye from industrial wastewater.

Keywords—Adsorption, Clinoptilolite, Congo Red Dye, Photodegradation and Wastewater.

I. INTRODUCTION

Congo red (CR) dyes are a type of anionic diazo dye derived from benzidine by reacting tetrazotised benzidine with two molecules of napthionic acid [1]. The presence of dyes in water reduces light penetration which can in turn modify the photosynthetic activity. Also, many dyes or their metabolites have toxic effects such as carcinogenic, mutagenic, and teratogenic effects on aquatic life and humans [2]. Dye removal can be accomplished by a variety of processes, including adsorption, ion-exchange, electrochemical treatment, ultrafiltration, photodegradation, and coagulation-flocculation approaches [3]. Among these processes, adsorption is one of the most efficient methods due to its flexibility, simplicity, low-cost, and effectiveness. The CR dyes ion removal from aqueous solution has been studied using different adsorbents such as calcite, pumice, clay, activated carbon and natural zeolites [4]. Many research have focused on the low-cost adsorbent for the removal of dyes. Zeolite have been used to control the pollution due to their ion-exchange capacity, low-cost and availability in many

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deposits. The most common type of zeolite found in nature is clinoptilolite, and it finds widespread application. Natural and modified clinoptilolites are commonly considered one of the best supports due to their unusual structure, homogenous pores and channels, high surface area, high adsorption capacity, low cost, environmentally acceptable nature, and exceptional thermal and mechanical endurance. Modified clinoptilolites are preferred over their natural counterparts because of the high level of purity they offer, as well as the flexibility to alter their properties through a variety of synthesis and post synthesis modification techniques [5, 6]. These modifications can change physicochemical properties of the clinoptilolite and the resulting modified clinoptilolite can be used for a variety of applications such as ion-exchange, adsorption and catalysts. Due to its good adsorption property, it helps in concentrating the pollutants on its surface therefore bringing the pollutants near the microorganism colonies [7]. At the same time, modified clinoptilolite can be used in the photoreactor as a catalyst support, and this ensures integration of adsorption and photocatalysis as well as facilitating post-treatment catalyst recovery [8, 9]. The main objective of this study is to investigate the efficiency of modified clinoptilolite as an adsorbent and catalyst in adsorption and photodegradation processes, respectively for the removal of Congo red dye from industrial wastewater.

II. METHODOLOGY

A. Materials and Chemicals

The Congo red dye was supplied by a textile business in Gauteng, South Africa. The clinoptilolite employed came from Vulture Creek, in the KwaZuluNatal Province, South Africa. pH was adjusted by 0.1 M NaOH and HCl. All the chemicals used in this study were analytical grade reagents from Sigma-Aldrich Corporation.

B. Experimental Procedures

B.1. Preparation of Clinoptilolite
The natural Clinoptilolite was washed in distilled water and HCl then dried in an oven at 110℃ for 24 hours. The clinoptilolite was Crushed at 75 μm for characterizations (SEM and FTIR).

B.2. Modification of Clinoptilolite as catalyst

A solution containing 250 mm of distilled water, 20 g of sodium carbonate (Na_2CO_3), and 20 g of sodium hydroxide (NaOH) were combined with 100 g of naturally occurring clinoptilolite. After that, the mixture was allowed to react on the magnetic stirrer for 24 hours at a speed of 200 revolutions per minute (rpm). This was done after the products had been thoroughly rinsed with distilled water several times and prior to being dried in an oven at a temperature of 110℃ for 2 hours.

B.3. Modification of clinoptilolite as adsorbent

A mixture of 100 g of natural clinoptilolite, 20 g of potassium hydroxide (KOH), and 250 mm of distilled water was combined. After that, the mixture was allowed to react on the magnetic stirrer for 24 hours at a speed of 200 revolutions per minute (rpm). Previously, the products had been washed several times with distilled water before being dried in an oven at a temperature of one hundred and 110℃ for 2 hours.

D. Preparation of Congo Red Dye

The preparation of solutions required the use of distilled water. The anionic dye known as Congo red (CR) was procured from Sigma Chemical Co., SA in an analytical purity form, and the substance did not require any further purification before being use. To prepare the stock solution, the dye was weighed accurately and then dissolved in distilled water at a concentration of 0.1 mg L^{-1}. In order to get the working solutions, you need to dilute the dye stock solution until it reaches the concentration wanted. To adjust the acidity of the solutions, either 0.10 mol. L^{-1} solutions of sodium hydroxide or hydrochloric acid were utilized, and a pH meter with a Digimed Model DM 20 was used to measure the solutions' pH levels.

E. Adsorption

To gaining a deeper comprehension of the adsorption behaviour of the composite particles, a batch experiment was carried out. In order to optimize the adsorbent dose, an explicitly defined amount of material was swirled for 2 hours in a shaker incubator using 100 mL of dye concentration at 32℃. This allowed the adsorbent dose to be optimized. Other parameters that were tweaked include the size and pH. The dye concentration in the supernatant was measured with a UV−Vis Spectrophotometer at a wavelength of maximum absorption of 497 nm to get an accurate reading. The primary investigation was carried out using adsorbent doses ranging from 10−40 g, particle sizes ranging from 0.15−2 mm, and pH levels ranging from 2−12 in order to investigate the adsorption properties that guarantee the maximum amount of dye adsorption. The adsorption capacity of the material was determined by using (2), whereas the percentage of dye that was taken up by the material was determined by using (1).

$$\% \ CR \ adsorbed = \frac{(C_i - C_f)}{C_i} \ X \ 100 \qquad (1)$$

Adsorption capacity:

$$(q_e) \quad = \quad V\frac{(C_i - C_f)}{M} \quad X \quad 100$$

(2)

where C_i is the initial concentration of CR dye in milligrams per liter (mg L^{-1}), C_f is the final concentration of CR dye (mg L^{-1}), V is the volume of solution and M is the weight of the adsorbent used.

F. Photodegradation

The batch approach was used in order to determine the photocatalytic degradation of CR that was caused by modified clinoptilolite. The powdered CR dye was dissolved in the distilled water, and the resulting solution had a concentration of 100 mg of CR per liter. The concentration of the CR stock solution varied from 10 mgL^{-1} all the way up to 50 mgL^{-1}. The photocatalytic degradation of CR was carried out in the shaker incubator in the presence of light at a constant pH 12. The contact period ranged from 30 to 120 mins, and the dosage of clinoptilolite catalyst was 20 g/100 mL. The experiment was carried out multiple times with all three variables in order to validate the results. The average CR degradation percentage is calculated by (3):

$$\% \ CR \ degradation = \frac{(C_i - C_f)}{C_i} \ X \ 100 \qquad (3)$$

where C_i and C_f are initial and final absorbance values respectively.
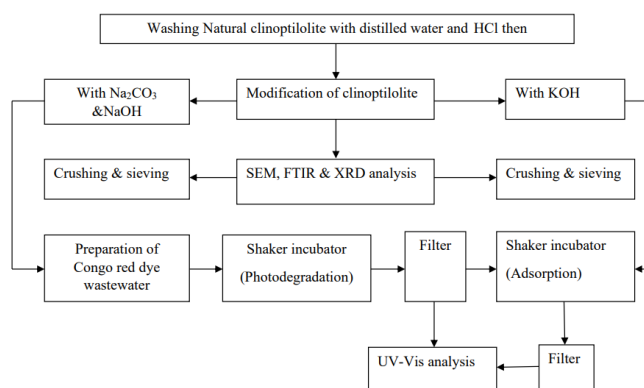
G. Experimental set up

Fig. 1 Experimental procedure

III. RESULTS AND METHODOLOGY

A. Surface characterization (SEM)

SEM analysis was used to determine the microstructure of natural and modified clinoptilolites. The microstructure of natural and modified catalysts was also determined using SEM. Figures 2a and 2b show scanning electron micrographs of natural and modified catalysts, respectively. The natural catalyst is made up of large and tiny globular particles that

have random forms and a little amount of space between them. On the other hand, the modified catalyst is made up of similarly random globular particles, but there is a much larger amount of space between them. The modification has resulted in the image displaying highly developed and minute spherical particles that are glassy and have an external surface that is cavity-filled.
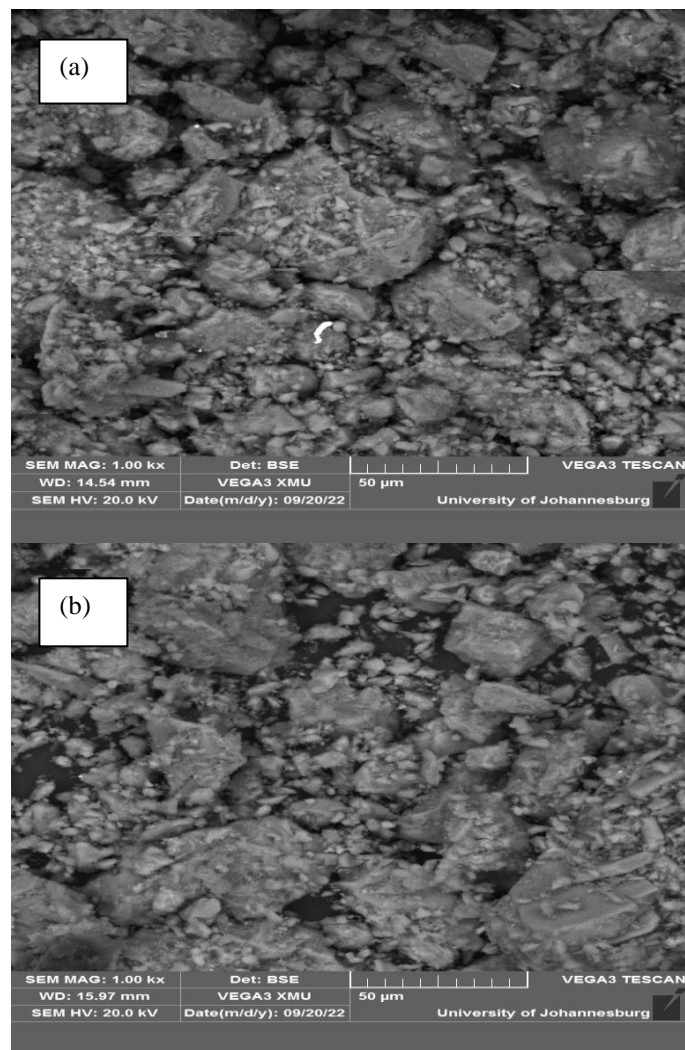

Fig. 2 SEM of Natural (a) and Modified (b) Clinoptilolite (photodegradation).

SEM was also used to examine the natural and synthetic adsorbents to learn more about their microstructure. Figures 3c and 3d show SEM images of natural and modified adsorbent, respectively; the former contains large and small globular particles with random forms and small space between them, while the latter contains similarly random globular particles but large space between them and white deposits, indicating the presence of KOH.
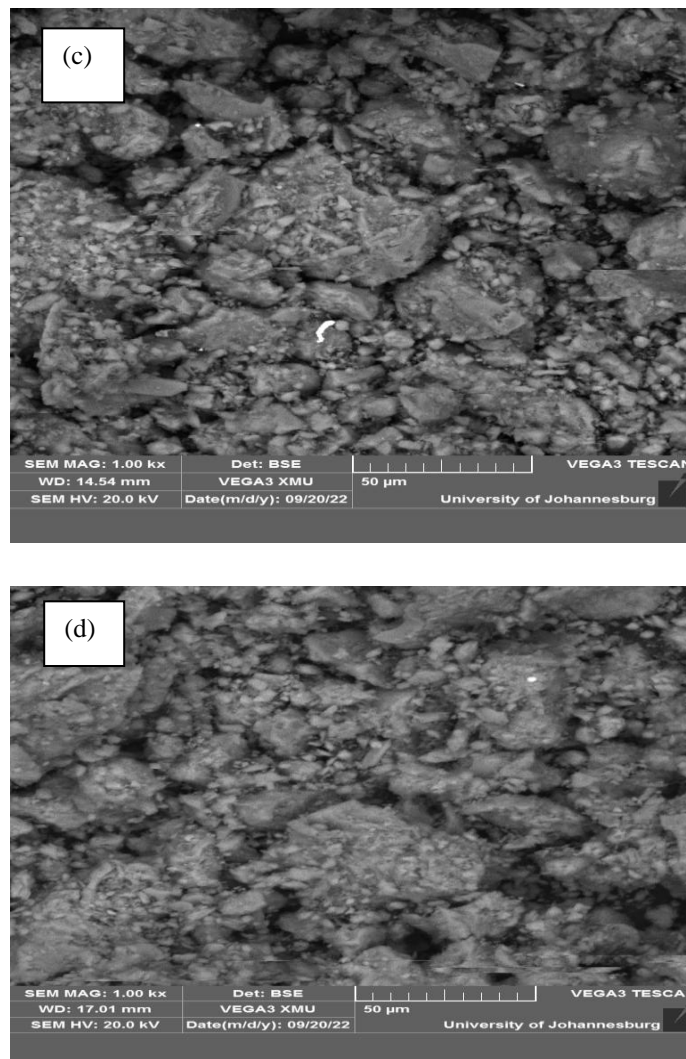

Fig. 3 SEM of Natural (c) and Modified (d) Clinoptilolite (Adsorption)

B. Surface characterization (FTIR)

FTIR analysis was used to determine the bonds and the groups functional of natural and modified clinoptilolite. Figure 4 presents the FTIR of both the natural and modified clinoptilolite, which exhibits peaks at 439 and 441 cm^{-1} due to bond vibration modes (SiO_4). The bond of ($Si-O-Si$) and ($Si-O-Al$) in natural Clinoptilolite accounted for the peak identified at ($1016-1800$ cm^{-1}), however the bonds ($Si-O-Na$) at 1020 cm^{-1} modified Clinoptilolite raised the transmittance %, due to the asymmetric vibration of. It has been determined that the stretching and bending vibration of the hydroxyl (OH) group is responsible for the persistent peak that can be found in modified clinoptilolite as natural Clinoptilolite is at around 3800 cm^{-1}.

Figure 5 presents the FTIR of both the natural and modified clinoptilolite, which exhibits peaks at 439 and 443 cm^{-1} due to bond vibration modes (SiO_4). The bond of ($Si-O-Si$) and ($Si-O-Al$) in natural Clinoptilolite accounted for the peak identified at ($1016-1800$ cm^{-1}), however the bonds ($Si-O-K$) at 1024 cm^{-1} modified Clinoptilolite raised the transmittance % and Adsorbed water in clinoptilolite, due to

the asymmetric vibration of clinoptilolite. It has been determined that the stretching and bending vibration of the hydroxyl (OH) group is responsible for the persistent peak that can be found in modified clinoptilolite as natural Clinoptilolite is at around 3800 cm^{-1}.
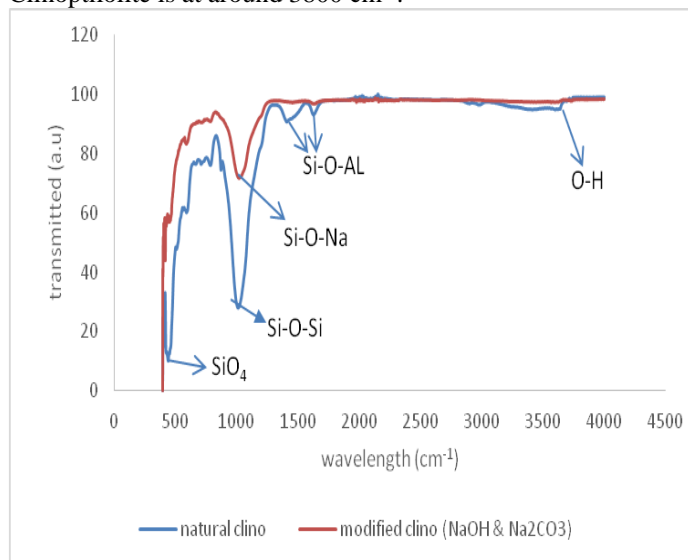

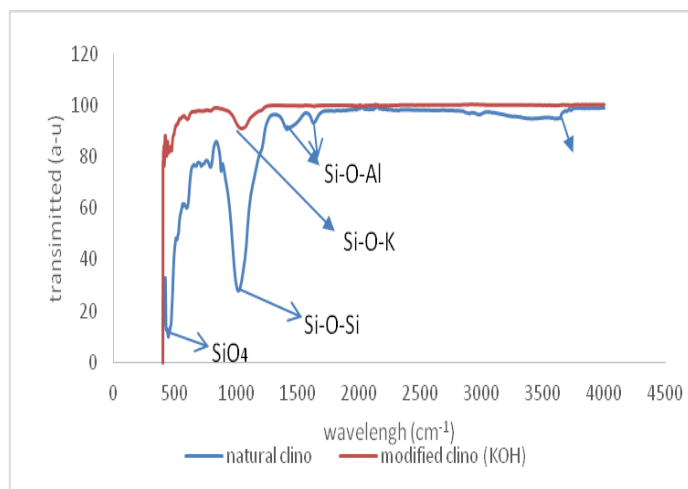Fig. 4 FTIR of Natural and Modified Clinoptilolite (Catalyst)

Fig. 5 FTIR of Natural and Modified Clinoptilolite (Adsorbent)

C. Photodegradation dynamics
C. 1. Effect of Photodegradation time

TABLE I
PHOTODEGRADATION TIME

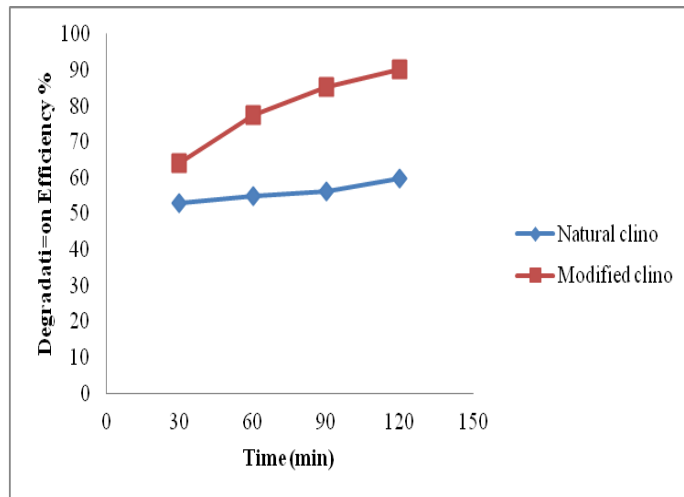| Time (min)	Natural clinoptilolite		Modified clinoptilolite	
	(ppm)	Degradation Efficiency (DE) (%)	(ppm)	Degradation Efficiency (DE) (%)
30	47.178	59.880	36.003	63.997
60	44.943	56.057	22.709	77.291
90	43.943	55.057	14.569	85.431
120	40.120	52.822	9.957	90.043

Fig. 6: Degradation efficiency Vs time

The effect of contact time on the photodegradation of CR dye was investigated from 30 to 120 mins (Figure 6). The best variables were determined to be a dye concentration of 100 mgL^{-1} and a catalyst dosage of 20 g/100 mL. The percentage of deterioration that took place increased from 63.997 to 90.043% as the contact time increased. After 120 mins, it reached a steady state; hence, this amount of time was utilized as the equilibrium time for the process of deterioration. This is due to the fact that the CR that is located on the surface of the catalyst degrades at a rapid rate. After this, the ions have to diffuse slowly in order to reach the microspores, which are located in an area where the degradation sites are more difficult to reach. This is what causes the observed phenomenon.

D. Adsorption dynamics
D. 1. Effect of adsorbent dose

TABLE II
ADSORPTION TABLE FOR THE DOSAGE

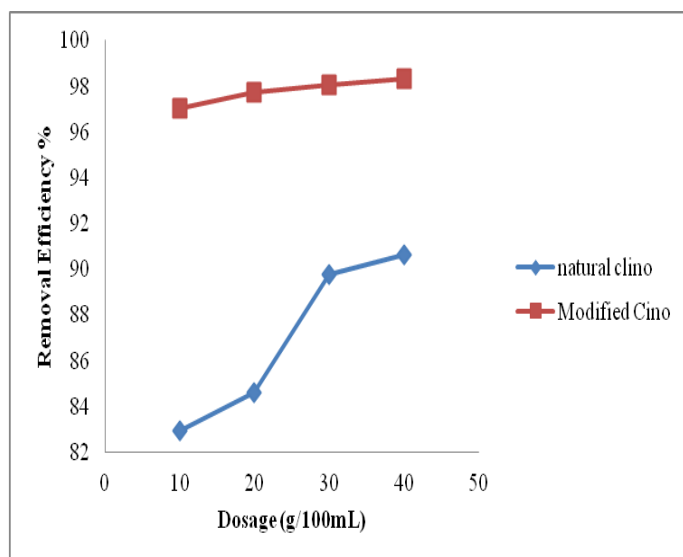| Dosage (g/100 mL)	Natural clinoptilolite		Modified clinoptilolite	
	(ppm)	Removal Efficiency (RE) (%)	(ppm)	Removal Efficiency (RE) (%)
10	17.086	82.914	2.946	97.054
20	15.416	84.584	2.287	97.713
30	10.216	89.784	1.958	98.042
40	9.346	90.654	1.676	98.324

Fig 7 Removal efficiency % Vs Dosage (Adsorption)

In order to determine the percentage of Congo red dye that was removed, the dose of clinoptilolite was changed from 10 to 40 g while the concentration and volume remained constant. It is correct that a greater quantity of adsorbent results in a greater number of sites that are available for adsorption (a larger surface area), which in turn results in a greater percentage of the dye being removed. According to the findings, which are presented in Fig. 7, an increase in the adsorbent dose resulted in an improvement in the composite material's ability to absorb the contaminant. At a dose of 40 g, the removal efficiency was found to be at its highest, and increasing the dose beyond that point had no discernible effect or brought about an increase in removal efficiency.

D.2. Effect of adsorbent size

TABLE III
ADSORBED SITES TABLE

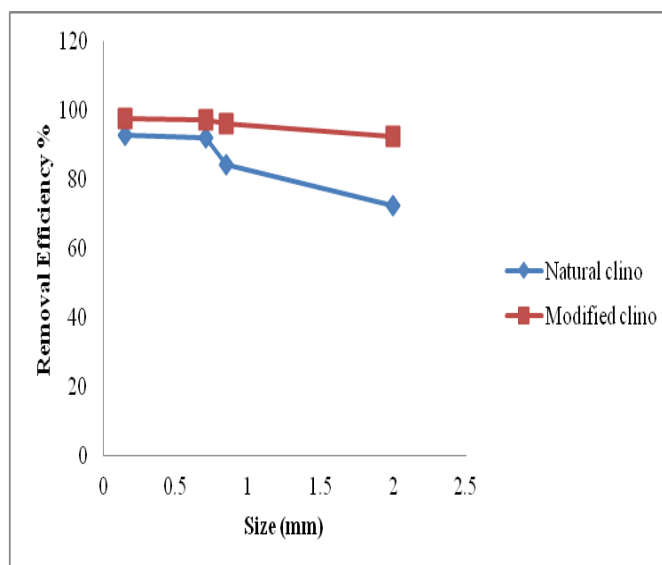| Size (mm)	Natural clinoptilolite		Modified clinoptilolite	
	(ppm)	Removal Efficiency (RE) (%)	(ppm)	Removal Efficiency (RE) (%)
0.15	7.110	92.890	2.381	97.619
0.71	7.793	92.207	2.734	97.266
0.85	13.510	84.490	3.887	96.113
2	27.462	72.538	7.557	92.443

Fig. 8 Congo red dye removal efficiency Vs sizes graph.

When the particle size and the amount of adsorbent (20 g) are optimized, there is a reduction in removal efficiency that ranges from 97.619 to 92.443%. The link between the size of the particles and the amount of Congo red that was taken out is illustrated in Figure 8. According to the data presented in the figure, the adsorbent lost some of its capacity to remove Congo red as the particle size increased. When it came to removal, a clinoptilolite particle size of 0.15 mm was found to be the most effective. As a direct consequence of this finding, subsequent investigations will make use of particles measuring 0.15 mm in size. It is likely that this result was brought about by the fact that smaller particle sizes allowed for a greater number of adsorption sites to be available on the adsorbent, which allowed Congo Red to be adsorbed onto it.

D.3. Effect of pH

TABLE IV
ADSORBED pH TABLE

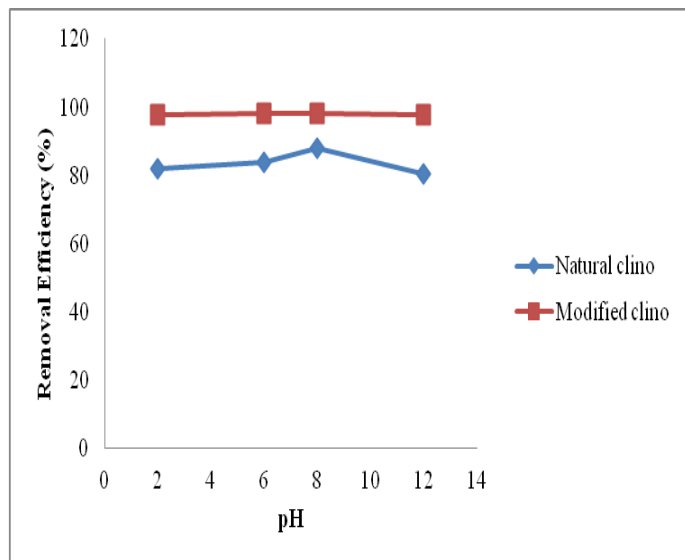| pH	Natural clinoptilolite		Modified clinoptilolite	
	(ppm)	Removal Efficiency (RE) (%)	(ppm)	Removal Efficiency (RE) (%)
2	18.1	81.9	2.33	97.7
6	16.2	83.8	1.68	98.3
8	12.1	87.9	1.98	98.0
12	10.4	80.6	2.19	97.8

Fig. 9 Congo red dye removal efficiency Vs pH graph.

The optimal dosage of adsorbent was 20 g, and the pH of a CR solution (100 mg L^{-1}) was adjusted from 2 to 12. The diagram illustrates the impact of pH on CR's ability to remove contaminants (Figure9). According to the data, lowering the pH from 12 to 2 resulted in a greater percentage of waste being removed (97.7% to 98.3%), with the greatest amount of waste being removed at pH 2. The ionic nature of CR, a dipolar dye, is dependent on the pH of the medium. There is a strong electrostatic attraction between the positively charged molecules of CR and the negatively charged of KOH clinoptilolite surface, which explains why the removal efficiency is higher at a lower pH. The dye is in a cationic form in acidic solutions (at lower pH), so this explains why the removal efficiency is higher. Dye adsorption is greatly inhibited in basic solutions (those with a higher pH) because of the substantial electrostatic repulsion between the negatively charged adsorbent surface and the dye molecules, which are anions in basic media.

E. Adsorption kinetics

Kinetic models allow for a quantitative knowledge of the adsorption process [10]. These kinetic models are useful for characterizing the adsorption mechanism. The present investigation used pseudo first order and pseudo second order kinetic models to examine the mechanism of congo red dye adsorption and photodecomposition by the composite. Equation (4), which is implied by the term "pseudo first order kinetic model," is as follows:

$$ln\ (qe\text{-}qt) = ln\ (qe) - K_1 t \tag{4}$$

where qe (mg/g) and qt (mg/g) are the adsorbent quantities at equilibrium and time t, and k1 (min^{-1}) is the first-order adsorption rate constant. When [ln (qe - q)] is plotted against time, a straight-line results, from which we may calculate the slope (in min^{-1}) and intercept (in mg/g) to get the value of K_1. It can be seen that the adsorption of dye onto the composite is not of the first order due to the lower value of the correlation

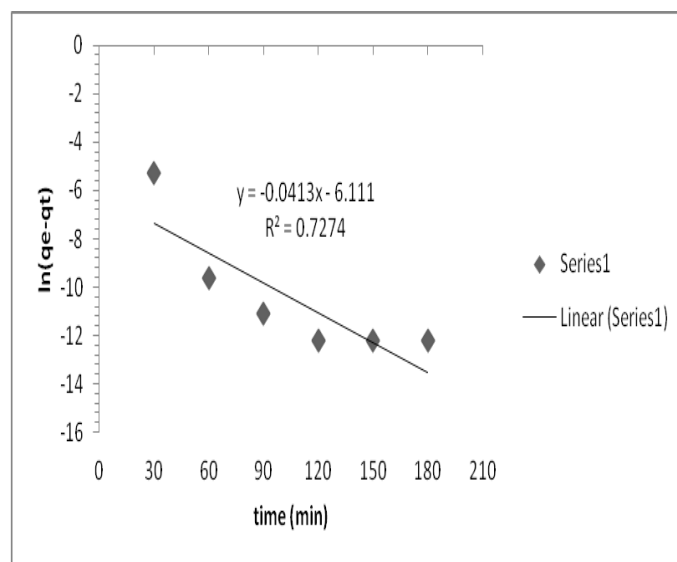coefficient and the mismatch between the estimated and experimental value of qe.

Fig. 10 Pseudo-first order linear kinetic plot for Congo Red Dye adsorption

The pseudo-second order model can be expressed in the form of equation:

$$\frac{t}{q_t} = \frac{1}{K_2\,q_t^2} + \frac{t}{q_e} \tag{5}$$

The amounts of adsorbent (mg/g) at equilibrium and time t are denoted by qe and qt, respectively; K_2 is the pseudo-second-order rate constant.
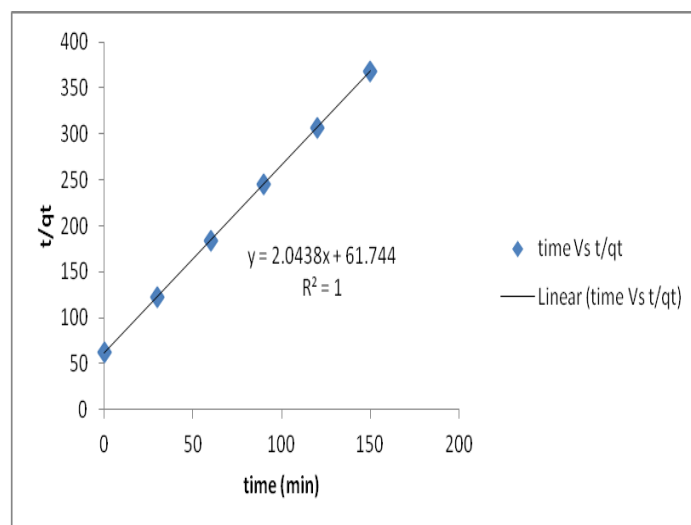

Fig. 11 Pseudo-second-order linear kinetic plot for Congo red dye adsorption.

Pseudo-second order linearity in the kinetic pattern [t/qt vs. t] is depicted (Fig. 10). By calculating the intercept and slope of the linear curve, we can determine the value of the second

order rate constant, k_2 (g mg^{-1} min^{-1}), and the equilibrium constant, qe (mg/g). It is likely that the adsorption process is second order kinetics, as indicated by the high value of the correlation coefficient and the agreement between the calculated (obtained from the graph) and experimental value of qe.

F. Thermodynamic studies

To analyze the potential and nature of the adsorption process, the thermodynamic parameters Gibbs free energy change ($\Delta G°$), enthalpy change ($\Delta H°$), and entropy change ($\Delta S°$) were calculated. To determine $\Delta H°$ and $\Delta S°$, we plotted ln Kd against *1/T* and utilized the slope and intercept to get $\Delta H°$ and $\Delta S°$. So long as we stick to the formula. To determine the change in Gibbs free energy ($\Delta G°$), we used equation.

$$\Delta G° = -RTlnKd \tag{6}$$

$$\Delta G° = \Delta H^o - \Delta S^o T \tag{7}$$

Taking advantages of Eqs (6) and (7), the Van't Hoff equation can be written as:

$$ln\ K_c = \Delta S^o/R - \Delta H^o/RT \tag{8}$$

where K_c is the equilibrium constant, which is the ratio of the equilibrium concentration of the dye ions on adsorbent to the equilibrium concentration of the dye ions in solution. R is the ideal gas constant (8.324 J/ mol.K) and *T* (K) is the adsorption temperature. $\Delta G°$ (kJ/mol) at different temperatures were evaluated from Eq. (6)/ Plot of ln Kc versus 1/T should give a linear line, where ΔH^o (kJ/mol) and ΔS^o (kJ/mol.K) can be calculated from the slope and intercept of van't Hoff plots.
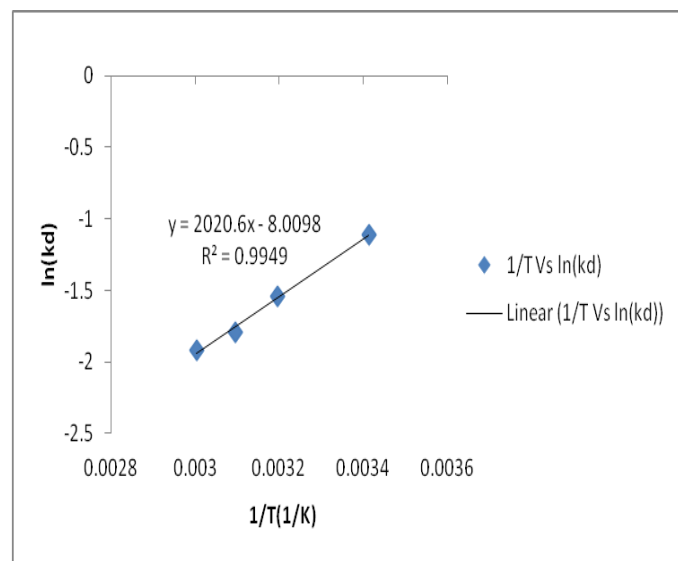

Fig. 12 Thermodynamic linear plot for Congo Red Dye adsorption.

The results in Fig. 12 and Table vi show that the adsorption process is thermodynamically stable. The negative values of ΔH^o which revealed that the adsorption is exothermic and likely to be dominated by physical processes in nature involving weak forces of attraction. The $\Delta G°$ for physisorption is in a range of -20,000 to 0 J/mol and the chemisorption varies between -80.000 and -400.000 J/mol. [11]. The overall $\Delta G°$ of the modified clinoptilolite is negative values at the temperature range studied. The positive value of ΔS^o of modified clinoptilolite suggest a decrease in randomness at solid/solution interface and no significant changes occur in the internal structure of the adsorbent through the adsorption.

TABLE VI
THERMODYNAMIC PARAMETERS OF DYE ADSORPTION

Temp. (K)	283	313	323	333
1/T (1/K)	0.0034	0.0032	0.0031	0.0030
Kd	0.3290	0.2140	0.1670	0.1470
ln (kd)	-1.1100	-1.5440	-1.790	-1.920
ΔG^o (J/mol)	-2704.82	- 4016.69	- 4807.74	- 5314.55
ΔH^o (J/mol)	-16794.28			
ΔS^o (J/mol.K)	66.593			

IV. CONCLUSION

In the present study, the effectiveness of modified clinoptilolite regarding photodegradation and adsorption of Congo red dye in industrial wastewater has been investigated in this batch experiment. SEM and FTIR were used to successfully modify and characterize clinoptilolites. Natural clinoptilolite is shown to be ineffective at removing Congo red dye when compared to the modified form. The results of a study on photodegradation show that longer exposure duration (120 mins) results in a higher removal efficiency of 90.043%. The highest clearance efficiency, 90,654%, is shown at a dosage of 40 g/ 100 mL. The highest efficiency (97.61%) was achieved with a very small particle size (0.15 mm). The optimal pH for removal is 6, where it reaches 98.324%. With the kinetic approach, the second order was maintained at $R^2 =$ 1. The negative values of ΔG^o show the spontaneous process and the negative of ΔH^o indicate that the CR dye adsorption is an exothermic process.

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