

Removal of Glucocorticoids from Pharmaceutical Wastewater using Modified Clinoptilolite

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Abstract—Glucocorticoids have sparked significant concern by their occurrence in pharmaceutical wastewater and they have been the focus of environmental contaminants in contemporary scientific study. Due to their threat to human health and aquatic life even at a low concentration of nanograms per liter, glucocorticoids need to be removed from pharmaceutical wastewater. Modified clinoptilolite is deemed to be the best adsorbent to remove glucocorticoids from pharmaceutical wastewater. This research study is conducted to investigate modifying agent that will deem clinoptilolite the best suitable adsorbent to remove glucocorticoids from the pharmaceutical wastewater. The purpose of this study is to modify clinoptilolite in order to remove glucocorticoids from the pharmaceutical wastewater using three different modifying agents: amine, acid and organic agent. These chemicals: n-Butyl amine, hydrochloric acid and tetrahydrofuran as amine, acid and organic agent were respectively used to modify clinoptilolite adsorbent. The modified clinoptilolites adsorbent were characterized using Fourier transform infrared spectroscopy (FTIR), X-ray fluorescence (XRF) and Scanning electron microscope (SEM) analytical techniques. The results further showed that using amine, acid and organic as the modifying agents, clinoptilolite attains a higher adsorption capacity. The adsorption isotherms, thermodynamics and kinetics study also attest to the findings stipulated in the above section. Adsorption of glucocorticoids from pharmaceutical wastewater by clinoptilolite modified with n-butyl amine, hydrochloric acid and tetrahydrofuran was confirmed by Freundlich isotherm technique model. The initial modifying agent's concentration of 0.1M for all the chemicals was used as preliminary modification concentration. The optimum conditions show dosage of = 50 g/100 mL; pH = 6; contact time = 24 hours; initial concentration = 10 mg/L and at a room temperature of 25°C to obtain maximum adsorption capacity.

Keywords—Adsorption, clinoptilolite, Glucocorticoids, Pharmaceutical wastewater

I. INTRODUCTION

GLUCOCORTICOIDS (GCs) compounds are hazardous complex organic molecules micro-pollutants exposed in water networks by hospitals, pharmacies and sewage. GCs drugs range from, beclomethasone, betamethasone, budesonide, cortisone, dexamethasone, hydrocortisone,

methylprednisolone, prednisolone, prednisone and triamcinolone. Ecological sustainability is being deepened by new pollutants like pharmaceutical products in the aquatic environment [1]. Pharmaceutically active compounds, which are complex organic molecules with a variety of physicochemical and biological properties enter the aquatic environment through a number of routes, including improper disposal by private households, hospitals, and industrial units or domestic wastewaters containing unused or human excreted drugs [2]. Glucocorticoids (GCs) are one of the most important groups of pharmaceuticals which are widely incorporated in as inflammation treatment in humans and animals [3]. Glucocorticoids lead to some serious health risks such as weakening the immune system and amplifies the risks of suffering from infectious diseases. And due to health risks associated to glucocorticoids in pharmaceutical wastewater, then it is therefore necessary that these micro-pollutants be removed from wastewater to alleviate the health risks they pose to human health and aquatic animals [4]. There are different pharmaceutical wastewater treatment systems such as biological treatment, filtration, chemical coagulation, sedimentation, electrocoagulation, crystallization, and adsorption [5]. But most research have chosen to use an adsorption process because of the complexity of the treatment procedures, high energy consumption, the issue of secondary pollution, and the impossibility of biological approaches due to the hydrophobicity and poor solubility of glucocorticoids [4]. In numerous research investigations, clinoptilolite was employed as an adsorbent. Clinoptilolite is a low-cost material, and they have high potential to be used as adsorbents if modified, and they are even simple to access at a large amount, and worldwide, their presence gives further benefits to be considered as effective materials decreasing in the wastewater treatment process [6]. Clinoptilolites are aluminosilicates hydrated from alkaline earth metals, which are a collection of microporous mineral structures consisting of the phenomenon of SiO₄ and AlO₄ spatial relationships [7]. Modification of clinoptilolite has received noticeable attention from the research community, since modified forms have specific properties and therefore their area of application has been broadening [8].

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II. MATERIALS AND METHODS

Clinoptilolite adsorbent minerals were purchased and supplied by Pratley Minerals South Africa. Three modifying agents; n-Butyl amine ($C_4H_{11}N$, > 99%), Hydrochloric acid (HCl, 32%) and Tetrahydrofuran (C_4H_8O > 99%) were purchased and received from Lab Chem suppliers. Natural clinoptilolite was first washed before modified and all chemicals' concentrations were calculated accordingly as per their assay given on the chemical's labels for solution preparation under room temperature, and the solution was mixed and agitated enough to guarantee even and homogeneous mixture.

A. Modification of clinoptilolite

Preliminary concentrations of 0.1 M $C_4H_{11}N$, 0.1 M HCl, and 0.1 M C_4H_8O were prepared proportionately. The concentration of each modifying agent was converted into grams using molecular weight in order to prepare the solution. The first solution prepared was for n-Butyl amine, using its molecular weight of 73.14 g/mol and concentration of 0.1 mol/L, a weight of 7.31 g/L was determined, and it was weighed on a weight scale before mixing it in a 1L of de-ionized water. The second solution of hydrochloric acid was also prepared using its molecular weight of 36.46 g/mol and initial concentration of 0.1 mol/L, then a weight of 3.65 g/L was calculated and mixed in a 1L of de-ionized water. Third solution of tetrahydrofuran was prepared using its molecular weight of 72.11 g/mol and concentration of 0.1 mol/L, then a weight of 7.21 g/L was found and got mixed in a 1L beaker of de-ionized water. All assorted solutions were put in an incubator and mixed for 30 mins at 200 rpm and a temperature of 25°C so that a uniform mixture can be achieved. Natural clinoptilolite adsorbents of 50 grams×3 samples were soaked in de-ionized water and agitated for 15 mins to get rid of any impurities that may possibly interfere with the modification process of the adsorbents. Finally, 50 grams×3 samples of clinoptilolite adsorbents were mixed in the three separate solutions to administer modification process.

III. RESULTS AND DISCUSSIONS

A. XRF Characterization

Table I displays the findings of X-ray fluorescence (XRF) studies for the chemical composition of natural and modified clinoptilolites. The acid alteration caused a change in the native clinoptilolite's. The quantity of Fe_2O_3 , Al_2O_3 , and SiO_2 tetrahedral and octahedral was raised by the acid treatment. Most exchangeable cations in the clinoptilolite's octahedral structure, such as Mg, K, Ca, and Na were reduced. Consequently, there was a decrease in the amount of CaO, MgO, K_2O , and Na_2O contents in the altered clinoptilolites. One noteworthy feature of the Fe^{3+} behavior that is very dependent on Ca^{2+} is that it appears that Fe^{3+} increases in

proportion to the amount of calcium that is removed from the clinoptilolite.

TABLE I
X-RAY FLUORESCENCE (XRF) OF NATURAL AND MODIFIED CLINOPTILOLITES

Component	Natural Clino	Modified Clinoptilolite			
		HCl	n-butyl	Tetra	
MgO	0.4694	MgO	0.4133	0.4099	0.4400
Al_2O_3	12.8103	Al_2O_3	12.4252	12.5431	12.7354
SiO_2	76.4050	SiO_2	75.4652	76.4824	76.1726
P_2O_5	0.0089	P_2O_5	0.0122	0.0000	0.0000
SO_3	0.0137	SO_3	0.0277	0.0182	0.0166
K_2O	5.2652	K_2O	5.4278	5.2114	0.0593
CaO	1.9328	CaO	1.9412	1.8231	5.0501
TiO_2	0.2161	TiO_2	0.2268	0.1958	1.7978
MnO	0.0241	MnO	0.0301	0.0315	0.2260
Fe_2O_3	2.6376	Fe_2O_3	2.8846	2.3494	2.5518
ZnO	0.0073	ZnO	0.0086	0.0070	0.0085
Ga_2O_3	0.0064	Ga_2O_3	0.0000	0.0000	0.0000
Rb_2O	0.0239	Rb_2O	0.0263	0.0242	0.0207
SrO	0.1276	SrO	0.1396	0.1193	0.1219
ZrO_2	0.0410	ZrO_2	0.0431	0.0349	0.0438
Nb_2O_5	0.0106	Nb_2O_5	0.0115	0.0123	0.0120
Na_2O	0.0000	Na_2O	0.7087	0.6193	0.6785
Cl	0.0000	Cl	0.1528	0.0868	0.0593
Cr_2O_3	0.0000	Cr_2O_3	0.0552	0.0316	0.0332

Since acid modification seems to have a significant impact on the K_2O level, the K_2O shows some decrease in its content. The amine alteration did cause a change in the structural chemical composition of the clinoptilolites, leading to an increase in SiO_2 tetrahedral. Nevertheless, Al_2O_3 exhibits a little reduction in its structural composition whereas other amounts were unaffected by the amine treatment. In the octahedral structure of the clinoptilolite, several additional exchangeable cations were either little altered or remained unchanged. As a result, the changed clinoptilolites' concentrations of CaO, MgO, K_2O , and Na_2O showed a little reduction. A rising molecular size non-aromatic heterocyclic amine is shown in the characterization data of the modified clinoptilolite. The clinoptilolites' structural chemical composition and organic modification both contributed to a drop in SiO_2 , with the organic alteration causing an even greater decrease in SiO_2 tetrahedral. Additionally, Al_2O_3 shows a slight loss in its structural makeup, while the organic treatment also caused a decrease in other amounts. Several other exchangeable cations were either slightly altered or modified in the clinoptilolite's octahedral structure. Consequently, a decrease in the concentrations of CaO, MgO, K_2O , and Na_2O in the modified clinoptilolites was observed, which was offset by the adsorption process.

The FTIR spectra (a) have shown the characteristic bands around 3390 and 1631 cm^{-1} that represent the elongation vibration band as the Si-O-Si/Al structure with C=O functional group. At 1013 cm^{-1} , the average decline in

vibration band confirms the ion exchange and modification of clinoptilolite as it bonds to result into OH that eventually display another pitch band at a vibration of 789 cm^{-1} as a deformation confirmation at a band of around 670 cm^{-1} .

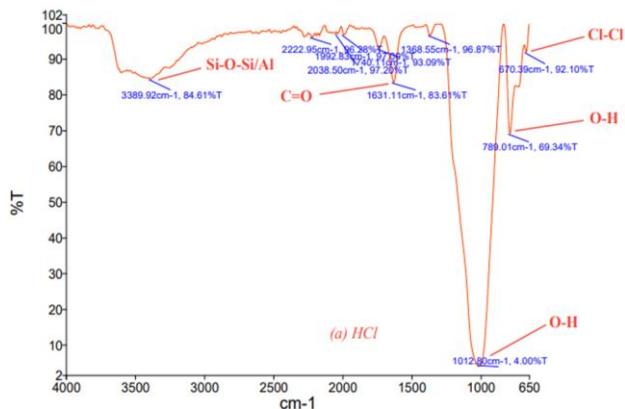


Fig. 1 FTIR spectra of hydrochloric acid as modifying agent

The Cl-Cl functional group's vibration shear is in the band at around 1450 cm^{-1} . The bending vibration of Si-O-Al and Si-O-Si is responsible for the peak at 670 cm^{-1} in Figure 1, whereas the stretching vibration of Si-O is responsible for the peak at 1369 cm^{-1} . The distinctive band around 1369 cm^{-1} , which corresponds to the Cl-Cl of the acidic group, confirms that the peak at 631 cm^{-1} is characteristic of the carboxyl (C=O) elongation vibration band [9]. The OH functional group is responsible for the peak that occurs between 1012 and 789 cm^{-1} . At 1740 cm^{-1} , the asymmetric vibration of Si-O-Si was observed. It is thought that the peak at 2223 cm^{-1} is caused by zeolitic water. The peak at 1013 cm^{-1} is due to the bending and stretching vibration of hydroxyl groups O-H, whereas the peak at 789 cm^{-1} is related to free hydrogenation water and intermolecular hydrogen bonding (zeolitic water). The alkyl molecule's skeleton deformation vibration is responsible for the peak at 1013 cm^{-1} in the FTIR spectrum shown in Figure 1. The C=O stretching vibration and Cl-Cl bending vibration modes are responsible for the peaks at 1631 and 1361 cm^{-1} , respectively. The cause of the peak at 2223 cm^{-1} is Si-O-Si/Al and Si-O-Si. Peaks at 670 cm^{-1} and 92 % transmittance are ascribed to stretching vibrations with Cl-Cl and C=O values. The O-H stretching vibration at 1012 cm^{-1} , which is more intense than the O-H at 789 cm^{-1} , is responsible for the comparatively broad peak at 670 cm^{-1} . This is because intramolecule molecular hydrogen bonding will be preferred for the structural pattern of the modified clinoptilolite. Since an ion exchanger or adsorbent may retain some of its characteristics after modification, the major peak at 2223 cm^{-1} for both the original and modified clinoptilolite was seen [10]. The vibration of Cl-Cl is said to be symmetrical and asymmetrical at peaks at 670 and 1631 cm^{-1} . The stretching vibrations of Cl-Cl and C=O are responsible for the peaks in the 1631 and 670 cm^{-1} range, while the bending and stretching vibration of O-H is responsible for the peak at 1012 cm^{-1} . The

intensity of the modified clinoptilolite increased between 2223 and 1368 cm^{-1} . This provides proof of the alteration. The peaks in the 1739 and 1669 cm^{-1} range in Figure 2 are caused by the stretching vibrations of the C=O and N group, whereas the peak at 1016 cm^{-1} is caused by the bending and stretching vibration of O-H.

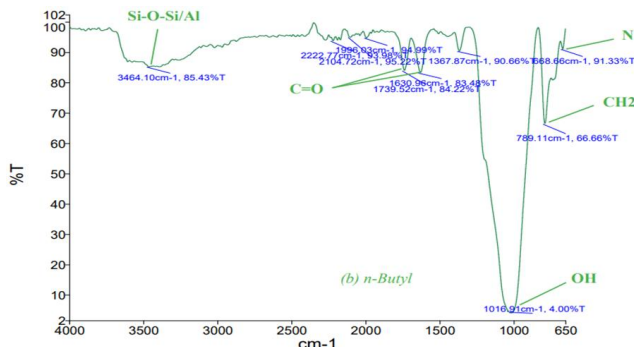


Fig. 2 FTIR spectra of n-butyl amine as modifying agent

The relatively large peak at 7368 cm^{-1} is caused by the O-H stretching vibration at 1017 cm^{-1} , which is more powerful than the H-C-H at 789 cm^{-1} , which is familiar to the peak of clinoptilolite-acid modification in Figure 1. The modified clinoptilolite showed an increase in intensity between 3464 and 1739 cm^{-1} . This offers evidence of the modification. The hydroxyl molecule's skeleton deformation vibration is responsible for the peak at 1017 cm^{-1} in the FTIR spectrum shown in Figure 2. The C=O stretching vibration was twice bending vibration modes that are responsible for the peaks at 1630 and 1739 cm^{-1} , respectively. The cause of the peak at 3464 cm^{-1} is Si-O-Si/Al and Si-O-Si. Peaks at 7669 cm^{-1} and 91 % transmittance are ascribed to stretching vibrations with N group and CH₂.

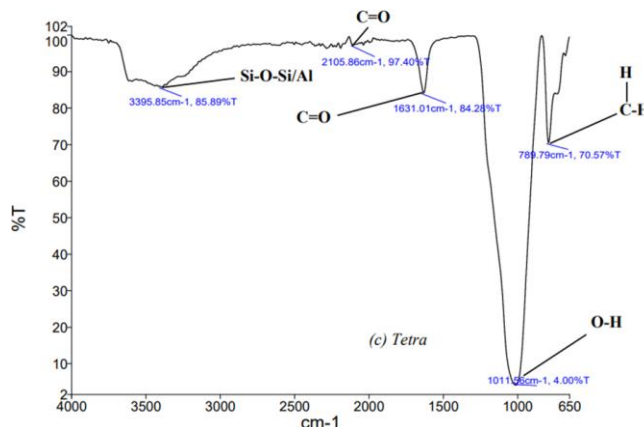


Fig. 3 FTIR spectra of tetrahydrofuran as modifying agent

At 3396 cm^{-1} , the asymmetric vibration of Si-O-Si/Al was observed in Figure 3. It is thought that the peak at 2106 cm^{-1} is accounted for water contained in clinoptilolite tuff. The peak at 1631 cm^{-1} is due to the bending and stretching vibration of carboxyl group C=O, whereas the peak at 790 cm^{-1}

¹ is related to free carbon chain and intermolecular hydrogen bonding. The ion exchange of adsorbent with the modifying agent seem to keep part of its properties and characteristics after the modification occurrence, the minor peak above 790 cm^{-1} of carbon group confirms the authenticity and the original structure reformation just after the modification process of clinoptilolite was seen. The vibration of H-C-H is still accounted to as a symmetrical and asymmetrical at peaks above 790 cm^{-1} . The distinctive band beyond 3396 cm^{-1} , which corresponds to the bands above H-C-H of the organic group compound, attests to the peak at 2106 cm^{-1} as the characteristic of the carboxyl (C=O) elongation vibration band. The OH functional group is responsible for the peak that occurs at a band vibration of 1012 cm^{-1} similar to that in Figure 1 for acid as the modifying agent [11].

The Scanning electron microscopy (SEM) has been used in the characterization of natural and modified clinoptilolite to determine the change in the morphological structure of the clinoptilolite for adsorption, and the SEM image of clinoptilolite modified with hydrochloric acid is shown in Figures 4 (a) and (b). The SEM images of natural and modified clinoptilolite powder were studied before adsorption. The SEM image shows a great deal of difference between the natural and modified clinoptilolite and the natural clinoptilolite resemble the presence of bigger globular particles with irregular shapes. However, after the hydrochloric acid applied as modifying agent there are cavities of different forms, shapes and sizes. Additionally, a few larger pores between the particles could be viewed onto natural clinoptilolite as validation of ion exchange capacity. HCl modified clinoptilolite SEM image (b) in Figures 4 (a) and (b) further exposes a matured-developed and tiny glassy spherical particle with outer surface which is full of cavities as a conformation of modification that took place [12].

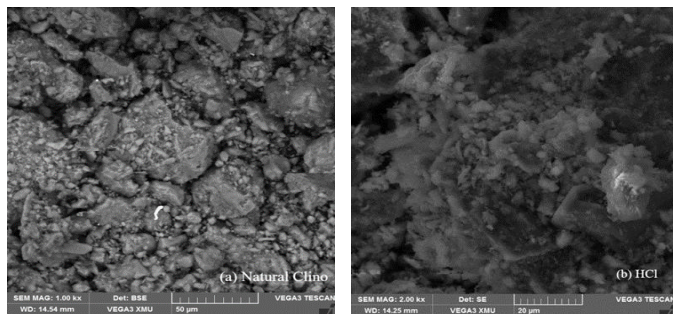


Figure 4. SEM image of natural clinoptilolite (a) and modified clinoptilolite (b) with hydrochloric acid (HCl)

SEM analytical technique has been utilized to determine the change in the morphological structure of the clinoptilolite compared to that which was modified. The SEM image of natural clinoptilolite and modified clinoptilolite with n-butyl amine are presented here in Figure 5 (a) and (c), respectively. The SEM image of natural clinoptilolite identifies the

presence of bigger globular particles with irregular shapes. After modification, cavities of different shapes and sizes had larger pores between the particles that can be observed in Figure 5 (c). The image reveals a well-developed and small glassy spherical particle, with an external surface which is full of cavities. This suggests that the clinoptilolite alteration was accomplished satisfactorily. This modification's primary goal was to boost the clinoptilolite's surface ion exchange capacity prior to allowing for the appropriate removal of GC ions by selective glucocorticoid ion adsorption [13].

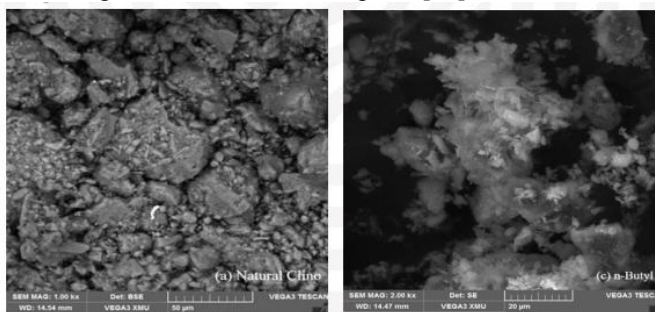


Fig. 5 SEM image of natural clinoptilolite (a) and clinoptilolite modified (c) with n-butyl amine (n-Butyl)

SEM image in Figure 6 portray natural and tetrahydrofuran as organic modifying agent, and the exchange capability is visible due to its porosity characterization which is based on the presence of open pores, and that is related to properties such as permeability and surface area of the porous structure that is suitable for adsorption and removal of glucocorticoids from wastewater. The SEM further image indicates the presence of bigger particles with irregular shapes. Figures 6 (a) and (b) additionally show the cavities of different shapes and sizes, whereby even larger pores between the particles could be observed, which will be pivotal for structural ion exchange permeating. High porosity cavities confer a favourable adsorption of glucocorticoids ions [14]. The imagery reflects granules that enhance and optimize the surface area of the composite for adsorption, and that is adequate for effective adsorption of glucocorticoids. A clear change seen regarding surface morphology is also visible emanating from a potential of ion exchange and adsorption.

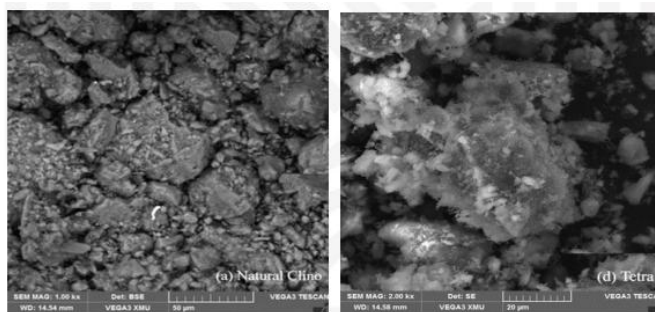


Fig. 6 SEM image of natural and modified clinoptilolite with tetrahydrofuran (THF)

However, the congested cracks and pores on the surface of a tetrahydrofuran modified clinoptilolite stimulate increase of contact for adsorption and eventually lead to cracks diffusion during the adsorption process. The SEM image indicates morphology that alters as the tetrahydrofuran modifying agent concentration picks up and concurrently, multiple cavities and pores are observed [15].

B. The effect of initial concentration for the removal efficiency

The effect of the initial concentration of prednisone and cortisone glucocorticoids were studied at a concentration range from 10-50 mg/L according to their strengths [16]. And other conditions were specified as follows; pH 6, dosage of 50 g, agitation time of 24 hours at a temperature of 25°C. Figure 7(A) depicts a possible increase in prednisone and cortisone removal % at initial concentrations range of 10-50 mg/L. This is because of altered zeolite clinoptilolite complexation mechanisms and the equilibrium character of ion exchange. Le Chatelier's principle states that when prednisone and cortisone concentration rise in the solution phase, equilibrium advances and dissolved prednisone and cortisone are removed more effectively. This pattern persists until the maximum concentration of 50 mg/L is attained before the decrease; the reason for prednisone decline might be the modified clinoptilolite's active sites being saturated [17].

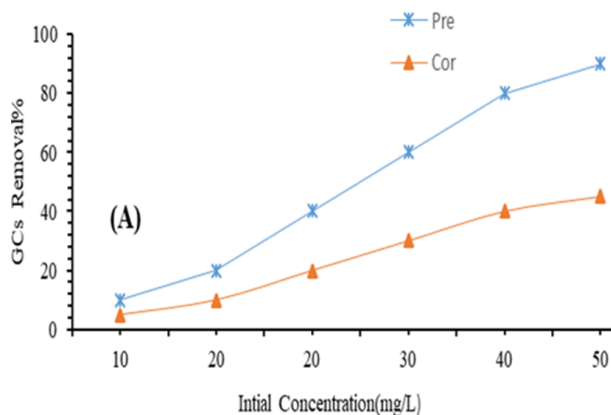


Fig. 7A Effect of initial concentration on the removal of prednisone and cortisone

C. The effect of pH

The impact of pH on the proportion of prednisone ions adsorbed by modified clinoptilolite is depicted in Figure 8(B). The outcome showed that the medium's pH has a significant impact on the elimination of prednisone and cortisone glucocorticoids from solution. In an acidic medium, the adsorption was minimal, but as the pH of the solution rose, it increased. One significant factor influencing the prednisone and cortisone elimination process is the pH of the mixture. Prednisone and cortisone glucocorticoids were removed, with a pH range of 1 to 6 being examined. The agitation period was

24 hours, and the starting concentration, clinoptilolite dosage, and temperature were maintained at 10 mg/L, 50 g, and 25°C, respectively. Figure 8(B) displays the findings from the tests that were carried out. Prednisone and cortisone removal onto modified clinoptilolite was significantly impacted by the pH solution; the maximum removal efficiency was noted at a pH of 6. This demonstrates effective glucocorticoid elimination. Due to the impact of hydroxyl anions in precipitating clinoptilolite cations at a high pH and the completion of proton ion in highly acidic media with glucocorticoids cations [18]. The surface of modified clinoptilolites takes on a negative charge when the pH reaches 6. Therefore, it would be assumed that prednisone would be removed at a greater rate as electrostatic repulsion decreased. Prednisone cations can precipitate as hydroxide at higher pH values, which lowers the prednisone and cortisone glucocorticoids concentration in solution. This is also because the elimination of glucocorticoids by modified clinoptilolite is equilibrium-based [19].

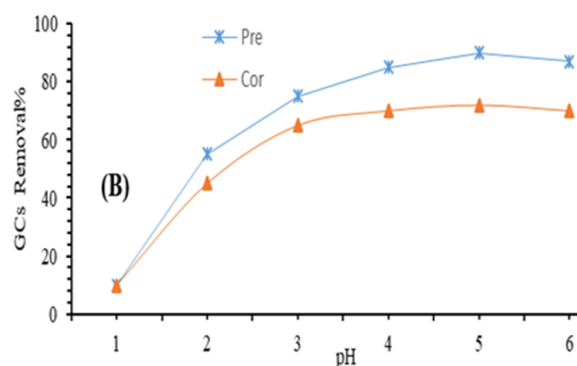


Fig. 7B Effect of pH on the removal of prednisone and cortisone

D. The effect of adsorbent dosage of clinoptilolite

Because dosage affects the modified clinoptilolite's capacity at the beginning concentration, it is a crucial parameter in the ion exchange process [20]. The elimination of prednisone and cortisone glucocorticoids were investigated using modified clinoptilolite weighing between 10 and 50 g. After a 24-hour incubation period, the starting concentration, pH, and temperature were maintained at 10 mg/L, 6 pH, and 25°C, respectively. The dosage of modified clinoptilolite was raised from 10 to 50 g, as indicated in Figure 9(C). As ion exchange and adsorption occur, the removal percentage rises, and the proportion of prednisone and cortisone glucocorticoids removed increases as the dosage of modified clinoptilolite is increased. This is because the enhanced clinoptilolite's increased active site makes adsorption more advantageous for the elimination of prednisone. At 50 g, the greatest removal percentage was seen along with a significant glucocorticoid removal % of 89 and 87% for prednisone and cortisone, respectively.

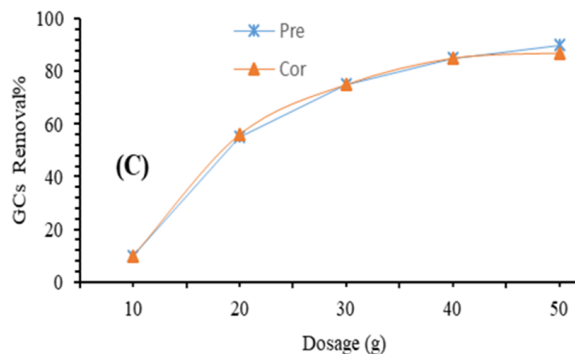


Fig. 7C Effect of dosage on the removal of prednisone and cortisone

Freundlich, Dubinin-Radushkevich and Temkin—were used to study the adsorption isotherms of prednisone and cortisone ions on modified clinoptilolite [21]. The experimental data from this work were fitted using these models. Prednisone (PDN) and cortisone (CTS) adsorption isotherms were investigated at 50 g of adsorbent mass at 276, 318, 333, and 348 K with solution pH 7. Different ratios of 3:1 was used. Figures 8, 9, 10 and 11 (A, B, C, D, E, F, G, and H) show the results from the linear Langmuir and Freundlich isotherms plot from the adsorption of prednisone and cortisone ions onto modified clinoptilolite.

E. Isotherm studies

Three distinct adsorption isotherm models—Langmuir,

TABLE II
GLUCOCORTICOIDS ADSORPTION ISOTHERMS ON MODIFIED CLINOPTILOLITES

	pH	Isotherm model		303K	318K	333K	348K
PDN	5	D-R	q _m	10.263	2.909	2.909	0.450
			E	5.49	3.32	2.58	1.57
			R ²	0.6779	0.7484	0.8156	0.902
		Langmuir	K _L	0.0333	0.0228	0.0192	0.01464
			q _m	5.848	2.9326	2.2075	0.7734
			R ²	0.877	0.798	0.816	0.850
	Freundlich	n	0.833	0.492	0.383	0.189	
		K _L	1.89x10 ³	5.39x10 ⁴	8.29x10 ⁵	7.07x10 ⁰	
		R ²	0.8905				
	CTS	D-R	q _m	8.103	0.9068	0.9597	0.9709
			E	4.26	2.755	1.847	5.317
			R ²	0.7123	2.4	2.06	1.3
Langmuir		K _L	0.0277	0.7957	0.9206	0.7332	
		q _m	4.7169	0.0188	0.0172	0.0139	
		R ²	0.861	1.9802	1.8939	0.7559	
Freundlich	n	0.677	0.8211	0.9067	0.9186		
	K _L	5.91X10 ³	0.357	0.305	0.172		
	R ²	0.894	1.51x10 ⁶	1.29x10 ⁷	8.7x10 ¹¹		
PDN	7	D-R	q _m	2.305			0.971
			E	5.49	0.906	0.958	3.179
			R ²	0.8351	2.126	2.091	1.44
		Langmuir	K _L	0.0389	3.25	2.16	0.8918
			q _m	7.6923	0.7543	0.8997	0.0139
			R ²	0.950	0.0229	0.0175	0.6494
	Freundlich	n	0.932	2.7174	1.9084	0.855	
		K _F	1.1x10 ³	0.796	0.93	0.168	
		R ²	0.954	0.482	0.307	1.4x10 ¹²	
	CTS	D-R	q _m	15.341	6.3x10 ⁴	1.1x10 ⁷	0.936
			E	7.91	0.887	0.971	1.089
			R ²	0.7881	5.949	4.637	1.86
Langmuir		K _L	0.0519	3.79	3.07	0.9062	
		q _m	10.989	0.7965	0.9113	0.0157	
		R ²	0.872	0.0263	0.0228	1.328	
Freundlich	n	1.311	3.8168	3.7453	0.873		
	K _F	3.7x10 ²	0.844	0.949	0.248		
	R ²	0.941	0.641	0.489	3.4x10 ⁵		
			8.1x10 ³	6.4x10 ⁴	0.948		
			0.964	0.969			

Based on the elevated correlation coefficient R² values for both glucocorticoids ions in Table II, it can be inferred that the Freundlich isotherm has yielded a satisfactory match for the experimental data. At 303K, the modified clinoptilolite's

monolayer adsorption capacities for prednisone and cortisone are 5.848 and 10.989 mg/L, respectively. Multilayer adsorption on heterogeneous surfaces is the foundation of the Freundlich isotherm [6]. Figures 8, 9, 10 and 11 (A, B, C, D, E, F, G, and H) show the results from the linear isotherms plot

for the adsorption of prednisone and cortisone onto modified clinoptilolite.

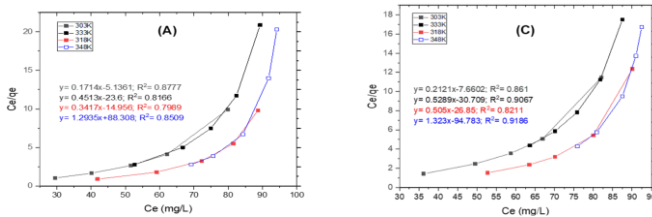


Fig. 8 Langmuir isotherm for (a) prednisone and (c) cortisone

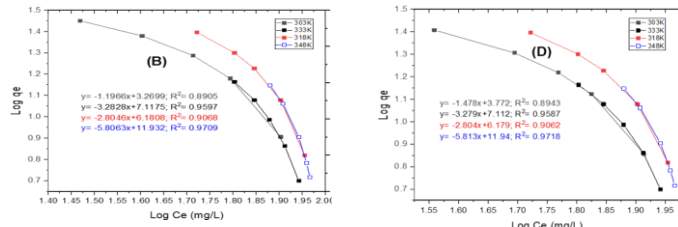


Fig. 9 Freundlich isotherm for (b) prednisone and (d) cortisone

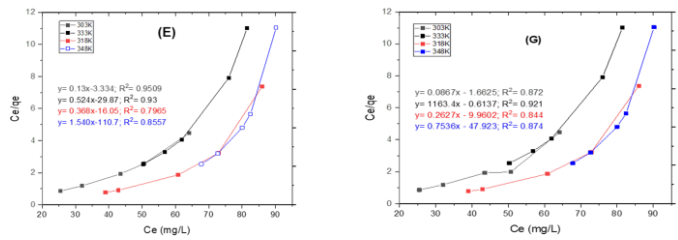


Fig. 10 Langmuir isotherm for (E) prednisone and (G) cortisone

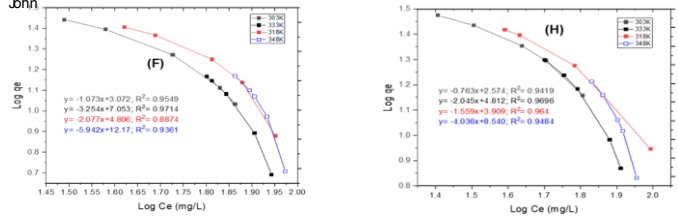


Fig. 11 Freundlich isotherm for (F) and (H) cortisone

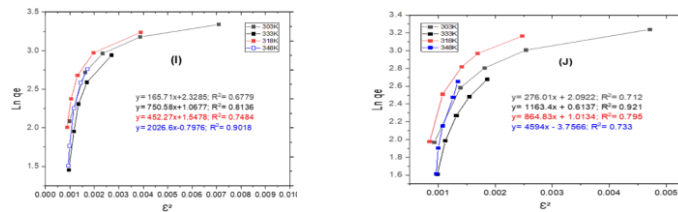


Fig. 12 D-R isotherm for (I) prednisone and cortisone (J) at pH 5

The data are shown in Table II. Prednisone and cortisone ions are favorably adsorbed by modified clinoptilolite, as demonstrated by the value of "n" between 1 and 10, which indicates a good affinity and adsorption. According to Table II, the prednisone and cortisone ions at pH 7 have Freundlich constants of 0.833 and 1.311, respectively. For all temperature values at pH 5 and 7, the values of E (Energy) derived from D-R models [Table II] were less than 8 kJ/mol ($E < 8$ kJ/mol).

This indicates that Yanniotis and Blahovec [22] identified a physical adsorption process. Where the concentration is 2 mg, the pH is 5, the dose is 50 g, the contact duration is 60 minutes, and the T is 303, 318, 333, and 348 K.

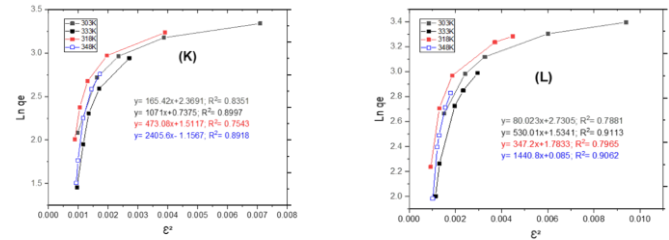


Fig. 13 D-R isotherm of (K) cortisone and (L) at pH 7

The Temkin model relies on the heat of glucocorticoid ion adsorption. It is thought that there is a linear relationship between the ions of glucocorticoids and clinoptilolite. C_e is the equilibrium concentration of glucocorticoid ions (mg/L), T is the temperature (K), R is the universal gas constant (8.314 Jmol/K), and D and B are Temkin isotherm constants linked to the equilibrium adsorption constant and adsorption intensity, respectively. The slope intercept of the plot of q_e vs $\ln C_e$ yields constant B. Calculations of these parameters involved plotting the relationship between q_e and $\ln C_e$ as presented in Table III.

TABLE III
TEMKIN ISOTHERM PROPERTIES OF GLUCOCORTICIODS

		298K	308K	318K	328K
Prednisone	B	21.62	20.952	14.835	10.513
	R ²	0.916	0.920	0.929	0.939
Cortisone	B	11.22	9.872	6.721	5.355
	R ²	0.915	0.925	0.917	0.908

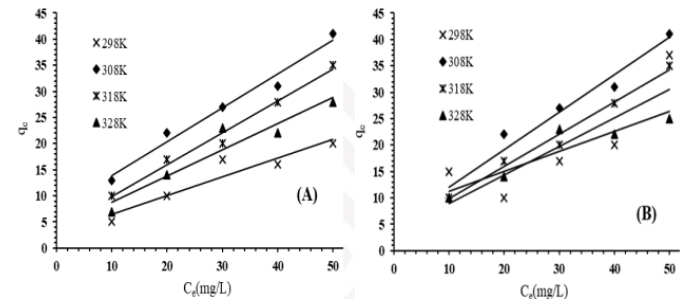


Fig. 14 Temkin isotherm for prednisone (A) and cortisone (B)

The regression coefficient (R^2) values indicate the dominance of Temkin's model. Similarly, the R^2 (%) for the Freundlich isotherm stands at approximately 92% underscoring its significant role in determining adsorption mechanisms. According to these isotherms, micellar surfaces exhibit both favourability and physical activity in adsorption. As seen in Table III, Figures 14 (A) and (B), the Temkin model was plotted at various temperatures. The findings suggest that the Temkin model's correlation coefficient values are not entirely appropriate and applicable for the study of

glucocorticoid adsorption using modified clinoptilolite, but instead most studies incorporate Temkin model in the thermodynamics study [23].

F. Kinetics studies

Adsorption kinetics research can provide important insights into the sorption reaction's mechanisms and reaction pathways, which are crucial for the efficient application of wastewater treatment technologies. The regression coefficient, or R², values for both glucocorticoids' ions in Table III demonstrated a satisfactory match to the adsorption process. Table IV displays the calculated kinetic parameters. According to the pseudo-first-order, or Lagergren, model, the number of vacant sites and the rate of adsorption site occupancy are related. At pH 5, 6, 7, and 9 at 298 K, the kinetic characteristics of the adsorption process were examined in a batch adsorption study. The first-order Lagergren model was fitted to the data. The pseudo-order and pseudo-second-order models were fitted to the experimental data of the adsorption kinetics in this work.

TABLE IV

KINETIC MODEL PARAMETERS RELATED TO THE PROCESS OF ADSORPTION

		First order			
Prednisone	pH	5	6	7	8
	q _e Cal	25.235	25.339	29.854	33.729
	k ₁	2.073	3.224	2.994	3.455
	R ²	0.846	0.977	0.966	0.906
Cortisone	q _e Cal	34.483	66.667	43.478	500
	k ₁	3.876	1.402	3.809	1.356
	R ²	0.981	0.989	0.912	0.961
			Second order		
Prednisone	q _e Cal	25.351	27.861	32.211	24.889
	K ₂	2.994	2.533	4.376	2.994
	R ²	0.471	0.968	0.895	0.714
	Cortisone	q _e Cal	58.824	50	38.462
K ₂		1.119	2.296	9.927	1.066
R ²		0.782	0.971	0.857	0.956

Table IV contains the values of k₂ and q_e, which were determined using the linear plot of t/q_t vs. t.

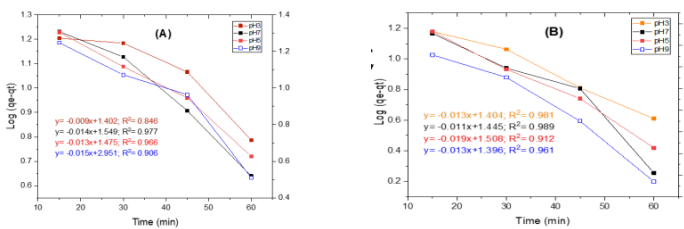


Fig. 15 Pseudo-first-order for (A) prednisone and (B) cortisone glucocorticoid

Further evidence that this model did not yield a satisfactory match to the experimental data for both glucocorticoids in Figure 11 (A, B, C and D) came from the poor R² values produced by the pseudo-second-order equation. This shows

that the sorption of prednisone and cortisone ions onto modified clinoptilolite is not primarily mediated by chemisorption. At pH 5 and 7, it was found that both glucocorticoids' ions matched the pseudo-first-order Figure 16 (A) and (B).

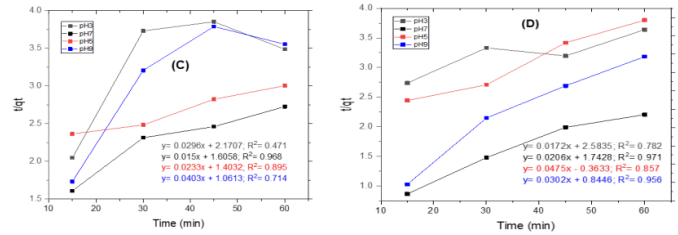


Fig. 16 Pseudo-second-order for (C) prednisone and (D) cortisone glucocorticoid

G. Thermodynamic studies

Figure 17 shows the plot of ln K_d versus 1/T for the reduction of glucocorticoids (prednisone and cortisone) onto modified clinoptilolite. The thermodynamic studies were shown in Table V. The enthalpy change (ΔH°) measured at 298, 303, 313, 318, and 328 K for glucocorticoids was negative, indicating an exothermic process for the adsorption of glucocorticoids (prednisone and cortisone) ions onto modified clinoptilolite. Positive values for glucocorticoids suggest an endothermic process. The favourable and spontaneous adsorption process onto modified clinoptilolite is indicated by the negative (ΔG°) values at different temperatures. Yousef et al. [24] found a similar finding. Furthermore, as indicated in Table V, the impact of temperature on the elimination of glucocorticoids (prednisone and cortisone) was investigated at temperatures of 303, 318, and 333K.

TABLE V
THERMODYNAMIC PARAMETERS

		K _D	ΔG° (kJ/mol)	ΔH° (kJ/mol)	ΔS° (J/mol.K)	
Prednisone	pH 5	303	1.046	-0.114		
		318	1.803	-1.558		
		333	3.287	-3.294	32.732	108.082
		348	5.617	-4.993		
Cortisone		303	1.419	-0.881		
		318	2.785	-2.708		
		333	4.368	-4.082	32.499	110.161
		348	7.873	-5.970		
Prednisone	pH 7	303	1.118	-0.281		
		318	1.796	-1.547		
		333	3.056	-3.092	34.212	112.987
		348	6.759	-5.529		
Cortisone		303	0.856	-0.393		
		318	1.598	-1.240		
		333	2.530	-2.570	34.229	111.324
		348	5.264	-4.405		

The values of ΔH° and ΔS° obtained from the Von't Hoff straight line equation in Figure 17 represent the slope and intercept of the ln K_d vs 1/T. The fact that both

glucocorticoids' ions' ΔG° values were negative almost at all temperatures suggests that the adsorption process was spontaneous. Additionally, it was shown that when temperature rises, the change in free energy increases, indicating that adsorption is not facilitated by higher temperatures [7].

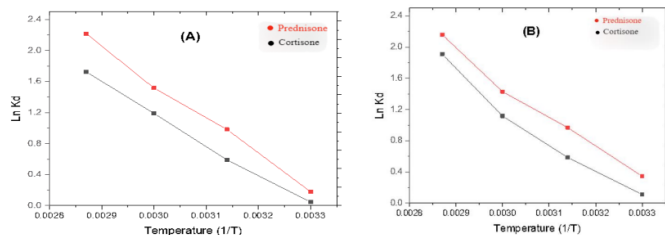


Fig. 17 Van't Hoff plot for adsorption of prednisone and cortisone at (A) pH 5 and (B) pH 7

IV. CONCLUSION

The primary aim of this research was to thoroughly investigate the effectiveness of clinoptilolite modified with amine, acid, and organic chemicals in the removal of glucocorticoids from pharmaceutical wastewater. The four critical factors considered in this study included pH, initial concentration of glucocorticoids, dosage of clinoptilolite, and the starting concentration of the wastewater. The results indicated that the modifications enhanced the material's properties, making it more effective for the targeted application. FTIR analysis revealed a bathochromic shift, which is indicative of changes in the electronic environment of the modified clinoptilolite, suggesting that new chemical bonds and functionalities were formed during the modification process. The consistent presence of carboxyl (C=O) bands at varying transmittance levels further supported this observation, highlighting the potential for increased interaction with glucocorticoids. SEM images illustrated a significant improvement in the surface morphology of the modified clinoptilolite, showcasing a porous structure that is likely to enhance adsorption capacity by providing more active sites for glucocorticoid binding. The study also found that increasing the pH of the solution, particularly at levels of 5 and 7, positively influenced the removal efficiency of glucocorticoids. The experimental results demonstrated high percentage reductions of glucocorticoids, achieving reductions ranging from 0% to 75% within a maximum duration of 120 minutes at a controlled temperature of 30°C, utilizing a clinoptilolite to glucocorticoid ratio of 3:1. Furthermore, the equilibrium data obtained from the adsorption experiments were well-described by the Freundlich isotherm model across various temperatures, indicating a heterogeneous adsorption process. The kinetic data were effectively modeled using the pseudo-first-order kinetic model, which suggests the adsorption of glucocorticoids.

DATA AVAILABILITY STATEMENT

The data presented in this study are available on request.

CONFLICTS OF INTEREST

We declare no conflict of interest.

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