Asian Journal of Chemistry; Vol. 35, No. 9 (2023), 2161-2170

ASIAN JOURNAL OF CHEMISTRY

https://doi.org/10.14233/ajchem.2023.28124

Thermally Activated Natural Clay for the Removal of Pharmaceutical Drug Levofloxacin

Shilpa Yakkerimath[1,2], Raviraj M. Kulkarni[1,2,*], Sanjaykumar V. Divekar[1], Vaibhav R. Chate[2,3] and Bekal Purandara[3]

[1]Department of Chemistry, KLS Gogte Institute of Technology (Autonomous) affiliated to Visvesvaraya Technological University, Udyambag, Belagavi-590008, India

[2]Centre for Nanoscience and Nanotechnology, KLS Gogte Institute of Technology (Autonomous) affiliated to Visvesvaraya Technological University, Udyambag, Belagavi-590008, India

[3]Department of Civil Engineering, KLS Gogte Institute of Technology (Autonomous) affiliated to Visvesvaraya Technological University, Udyambag, Belagavi-590008, India

*Corresponding author: E-mail: ravirajmk@git.edu

Received: 8 June 2023; *Accepted*: 13 July 2023; *Published online*: 31 August 2023; AJC-21359

The adsorption behaviour of natural clay (NC) and thermal activated clay (TAC) mineral of the Panchanganga river flood zone sediment for levofloxacin (a class of fluoroquinolone antibacterial drug) has been studied. The isotherm and kinetic studies were performed using the batch technique. The results showed that TAC has 72.6% removal efficiency comparatively higher than NC, which is 62.8% at 120 min, pH = 7, dosage 0.40 g/L and Initial concentration of 18.69 mg/L. The kinetic and isotherm results indicate the adsorption of levofloxacin on NC and TAC follows Freundlich isotherm suggesting multilayer sorption and chemisorption as a rate-limiting step during the process. A plausible mechanism is proposed for the interaction of NC and TAC with levofloxacin from the results of the adsorption study. The negative free energy change and positive enthalpy change indicated that the adsorption process is spontaneous and endothermic.

Keywords: Levofloxacin, Adsorption, Panchganga river, thermal activated clay, Natural Clay.

INTRODUCTION

An extensive utilization of pharmaceutical drugs has generated substantial concern in recent times owing to the adverse environmental consequences. The presence of a significant number of pharmaceuticals in diverse environmental compartments has resulted in various deleterious effects on the ecosystem; as a result, they are classified as emerging pollutants [1]. Antibiotics are special pharmaceuticals that enter different environmental compartments, especially water bodies through effluents from industries, hospitals and domestic sewage. The rate of consumption of antibiotics has increased around the globe and according to an estimate [2], the annual usage of antibiotics in European countries is between 5000-10,000 tons. Thus, posing antibiotic resistance risk to the environment as well as human health [3]. The presence of various antibiotics in the environment is subject to variation due to differences in their respective half-lives. As a consequence of their prolonged persistence, the pollution levels within the environmental compartment have experienced a significant increase in recent times [4] and no appropriate methods have been employed for the complete removal of these antibiotic contaminants.

Recent investigations have shown that effluents generated from the pharmaceutical industries contains over 250 types of antibiotics [5,6]. Fluoroquinolones are such a class of antibiotics widely used worldwide to treat pneumococcal respiratory and other Gram-positive infections [7]. In recent years, several works have been reported regarding the fate, occurrence and toxicity level of antibiotics in the environmental compartment worldwide [8-10] and many studies revealed a higher concentrations of these antibiotics in the environment posing an ecological risk [11-14]. Therefore, a significant amount of antibiotics enters the water environment because only a fraction of prescribed drugs are used to treat diseases in humans and animals [15-17]. Since, the water treatment plant uses conventional procedure and have no suitable method for removing these antibiotics. Several techniques *viz.* photodegradation, Fenton/photo-Fenton, ozonation, *etc.* are applied for the removal of antibiotics, however, these methods are expensive, involve complex procedures and are not suitable for large-scale municipal water treatment [18,19]. Therefore, adsorption is one of the most convenient methods to adopt because of its low cost, high efficiency and no harmful secondary products during the process the adsorption material can be regenerated for future use and these adsorption materials are nano-based substances, activated carbons, metal oxides, modified polymers, *etc.*, which are expensive and require complex mechanisms to synthesize these materials [20-22]. This study aims to examine the function of natural clay (NC) minerals as a self-purifying natural substance obtained from the Panchganga river flood zone, in the efficient elimination of antibiotic levofloxacin. Additionally, the removal efficiency percentage is compared between NC minerals and thermally treated clay minerals (TAC).

EXPERIMENTAL

Preparation of natural clay and thermally activated clay: The soil samples were collected in polyethylene bags from the Panchganga river flood zone (latitude 16º41′51″N and longitude 74º9′59.4″E), which lies between Kolhapur and Narasoba Wadi area, India (Fig. 1). The raw clay samples were kept in an oven at 100 ºC for 24 h to remove moisture. The dried samples were subjected to grinding and then turned into a fine powder and later sieved using 75 µm mesh. Sieved soil particles (> 75 µm), which dominantly contained natural clay, were heated in a muffle furnace at 400 ºC for 3 h to activate clay particles.

Preparation of levofloxacin solution: Levofloxacin used for the adsorption study was obtained from Aldrich, USA. A stock solution of 1×10^{-3} mol/L was prepared and then aliquot solutions were prepared with different concentrations. The reagents used in this investigation were all of AR grade.

Thermal activated clay (TAC) and natural clay (NC) mineral characterization: The NC and TAC materials structure was investigated using XRD (Cu*K*α irradiating by 154 nm wavelength for 10,000 min^{-1} in 10-90º scan range), morphology and elemental composition of NC and TAC were examined using SEM and EDS, surface area, pore size and pore volume was identified by BET analysis (Belsorb Mini (II) BEL Japan instrument). The presence of functional groups before and after adsorption of both material was examined using FTIR-2000, Perkin-Elmer in the range 4000-400 cm^{-1}, while the zero-point charge (ZPC) of NC and TAC was examined using a Potentiometric mass titration experiment (PMT).

Adsorption studies: The adsorption of levofloxacin on NC and TAC was carried out using the batch experiment with a known amount of adsorbent and adsorbate in an orbital shaker

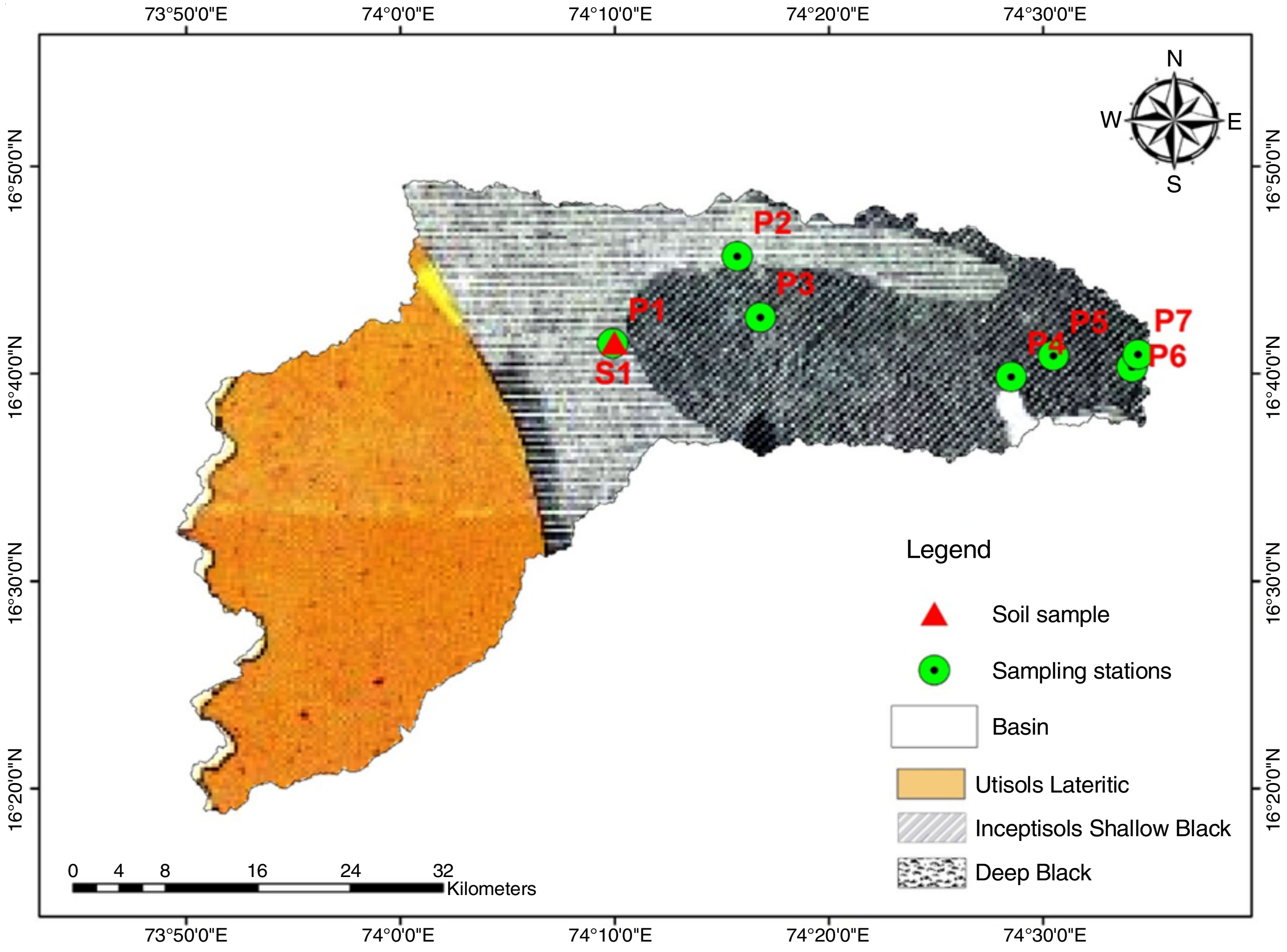

Fig. 1. Clay sample collection point (S1) from Panchganga river catchment

for a time period of 2 h at room temperature (298 K). The solution was centrifuged and examined in UV-visible spectrophotometer at 286 nm (Agilent Cary 60 USA). The uptake percentage of levofloxacin on NC and TAC was calculated by eqn. 1 whereas the adsorption loading (q_e) at equilibrium was calculated from eqn. 2:

$$\text{Uptake (\%)} = \frac{C_I - C_F}{C_I} \times 100 \qquad (1)$$

where C_I = initial concentration (mg L^{-1}); C_F = final concentration (mg L^{-1}).

$$q_e = \frac{C_I - C_E}{W} V \qquad (2)$$

where C_I = initial concentration (mg L^{-1}); C_E = concentration at equilibrium (mg L^{-1}); V = volume of levofloxacin, W = weight of the NC or TAC (g).

RESULTS AND DISCUSSION

XRD studies: XRD spectra of NC and TAC (Fig. 2) showed several peaks. The NC peaks correspond to strong peaks of quartz, 2θ = 20.91º, 26.681º, 40.346º, 50.171º, 68.681º (JCPDS No. 86-1628) followed by cristobalite at 2θ = 21.376º, 36.710º (JCPDA No. 76-1390), rutile at 2θ = 27.820º, 54.186º (JCPDS No. 82-0514), hematite at 2θ = 32.63º, 35.56º, 53.236º (JPDS No. 89-0598) and Al_2O_3 at 2θ = 33.204º, 75.740º (JCPDS No. 78-5510). However in case of TAC, low intensity peaks were observed, which is attributed due to the removal of interlayer hydroxyl groups in clays [23]. The XRD results also revealed the disappearance of some peaks after thermal activation of NC at 400 ºC [24].

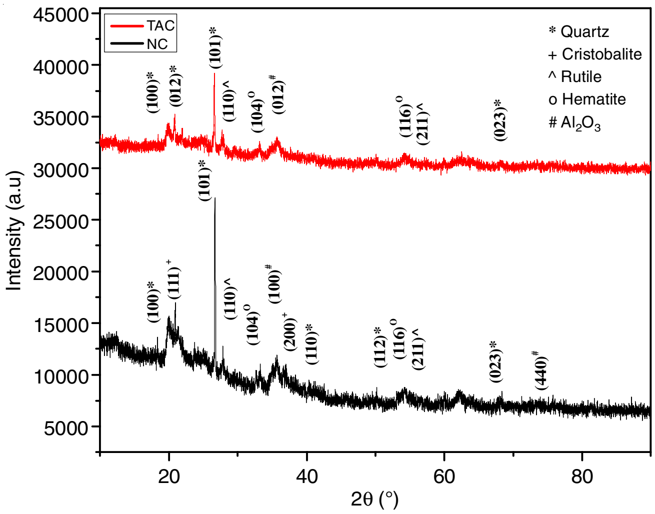

Fig. 2. XRD pattern of natural clay (NC) and thermal activated clay (TAC)

FTIR studies: The functional groups on clay were analyzed from the IR spectrum of NC and TAC further from the analysis; adsorption was confirmed by the characteristic bands illustrated in Fig. 3. The peak observed at 468 cm^{-1} is assigned for Si-O-Al stretching of illite mineral, 536 cm^{-1} is due to Si-O, Si-O-Al stretching band of quartz, 752 cm^{-1} is Si-O-Al vibration in illite, 795 cm^{-1} peak indicates O-H stretching band of a water molecule, 1033.61 cm^{-1} is asymmetric stretching of silanol, intense peak at 1384.87 cm^{-1} is out of plane stretching of Al-O group, a broad peak at 3402.10 and 1637 cm^{-1} of NC confirmed O-H asymmetric stretching and the bending vibration of a water molecule, The O-H asymmetric stretching vibrations observed at 3694 and 3619.35 cm^{-1} indicates kaolinite structure [25,26]. However, after the thermal activation, the O-H asymmetric stretching broad band at 3402 cm^{-1}, a water molecule disappeared and also there is a shift of peaks in TAC due to heating. Further, the characteristic peaks of levofloxacin after adsorption appeared in both NC and TAC at 1532 cm^{-1} is assigned due to asymmetric stretching vibration of the O-C-O of levofloxacin and accordingly enhancement of peak at 1400 cm^{-1} and appearance of new vibration band at 3146 cm^{-1} [27], which confirmed the presence of C-H groups of aromatic rings in levofloxacin [28]. Hence, further the shift of peaks in FTIR spectra substantiates the adsorption of levofloxacin on the NC and TAC.

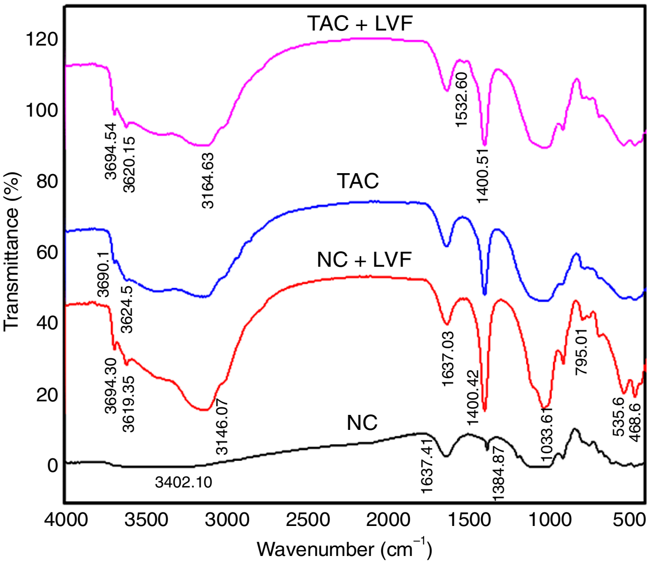

Fig. 3. FTIR spectrum of natural clay (NC), thermal activated clay (TAC), levofloxacin (LVF) adsorbed on natural clay (NC), levofloxacin (LVF) adsorbed on thermal activated clay (TAC)

SEM studies: SEM images revealed the morphological characteristics of clay minerals. Fig. 4a of NC depicts the bulk appearance of the minerals indicating its irregular surfaces having several pores [29]. In Fig. 4b, the TAC particles show micro-aggregates of minerals and irregular appearance of the surface confirms an increase in the pore size of NC after the thermal activation [30]. Images obtained from SEM revealed two types of minerals *i.e.* crystallized illite (in the form of spherical pieces) and quartz minerals (smooth edged form). The composition of minerals was confirmed from the XRD results.

EDS studies: The EDS spectrum of NC and TAC from (Fig. 4a-b) revealed the presence of the elements Si (1.790), Al (1.659), C (0.389), O (0.557), Ca (3.689), Mg (1.256), Fe (6.401), Ti (0.525). The mass % of elements present before and after the thermal activation were C: 25.38 (26.43), O: 49.32 (48.15), Al: 5.58 (5.90); Si: 8.72 (9.23), Ti: 1.87 (0.61), Fe: 8.01 (8.45); Mg: 0.47 (0.57); Ca: 0.47 (0.44); K: 0.18 (0.24).

BET studies: Surface properties of NC and TAC were analyzed by N_2 adsorption and desorption isotherms at nitrogen

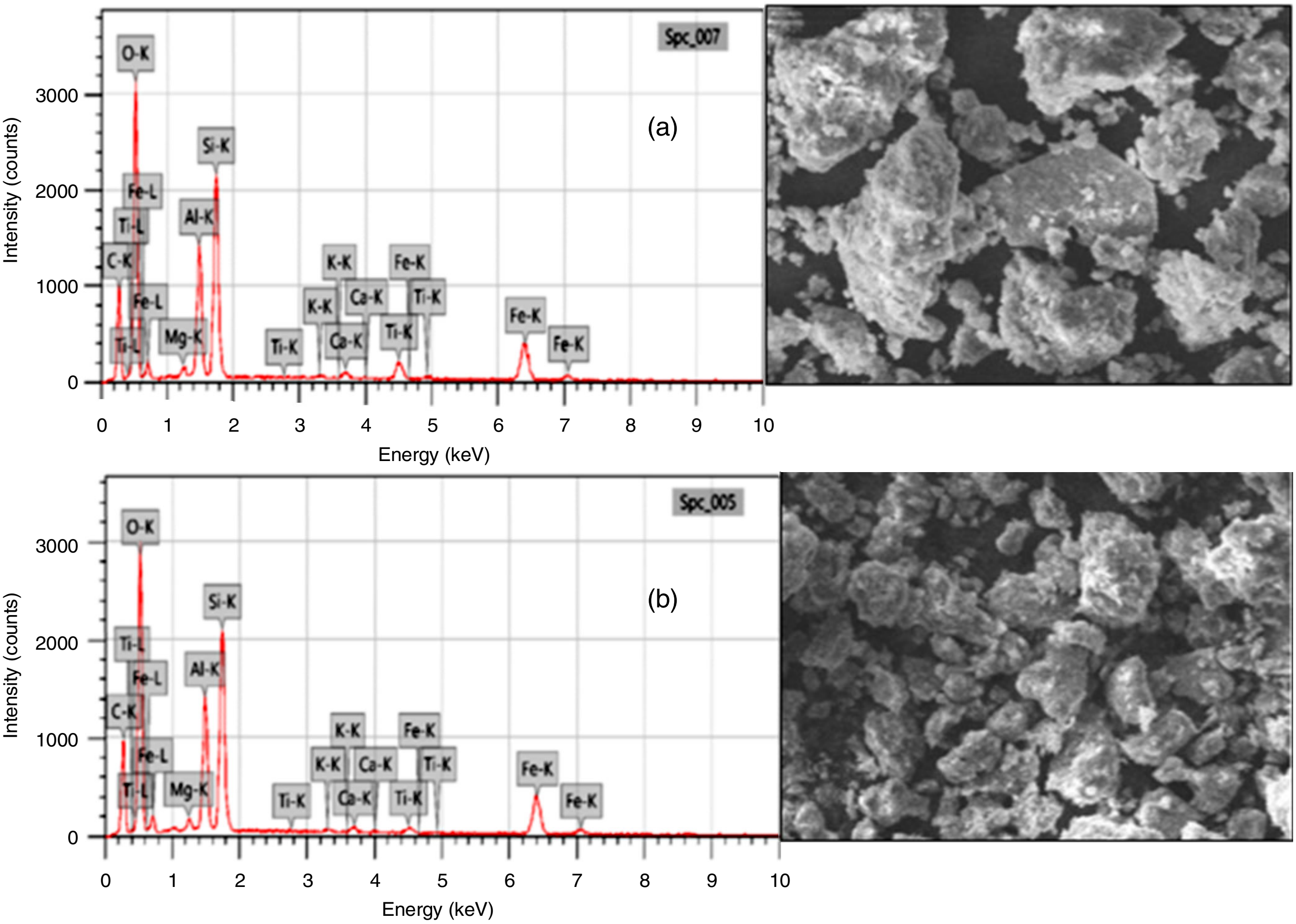

Fig. 4. (a) EDS and SEM images x2000 magnification of natural clay (NC), (b) EDS and SEM images x2000 magnification of thermal activated clay (TAC)

temperature 77 K. Isotherms of both NC and AC showed type IV and H4 type hysteresis loop where the relative partial pressure varied from 0.45 to 0.98 indicating the mesoporous structure of clays [31-33]. Pore size distribution (Table-1) from the BJH method is shown in Figs. 5a-b. Therefore, BET results confirmed the filling of levofloxacin initially in mesoporous

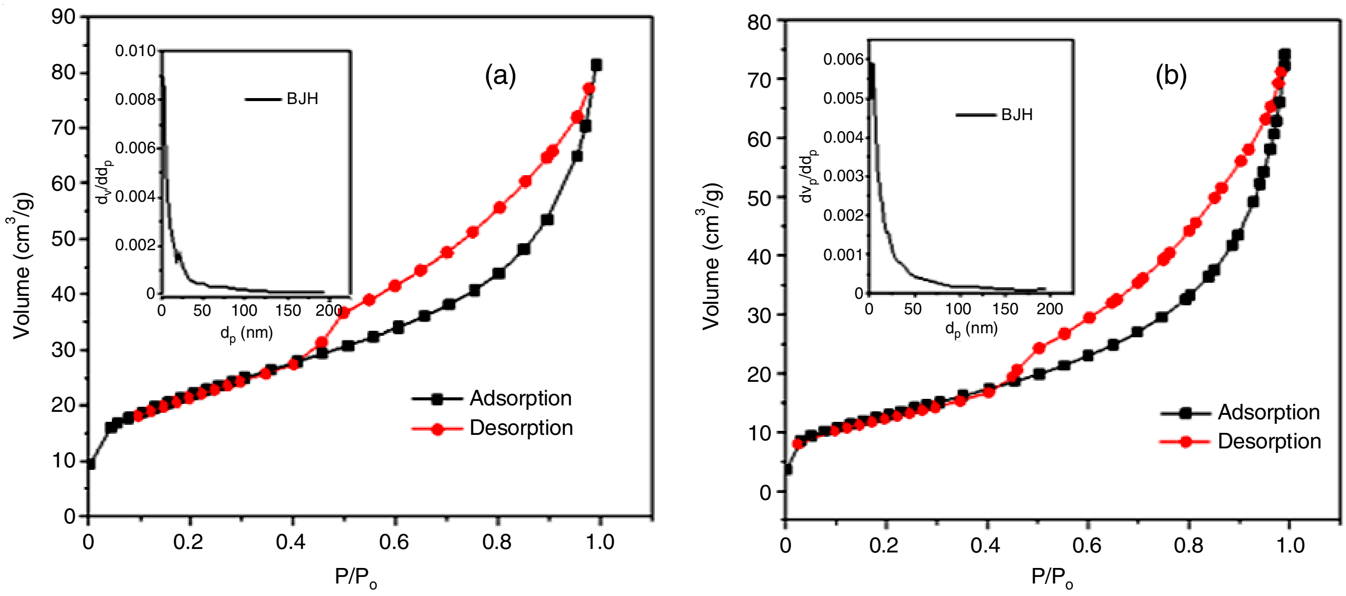

Fig. 5. Nitrogen adsorption/desorption isotherm and BJH pore size distribution of (a) natural clay (NC) and (b) thermal activated clay (TAC)

structure of clays that is followed by adsorption on exterior surface. The surface characteristics of NC and TAC are summarized in Table-1.

TABLE-1
SURFACE CHARACTERISTICS PROPERTIES (BET) OF NATURAL CLAY (NC) AND THERMALLY ACTIVATED CLAY (TAC)

Clays	Surface area (m^2 g^{-1})	Total pore volume (cm^3 g^{-1})	Pore diameter (nm)
NC	78.253	0.1252	6.3989
TAC	65.815	0.1132	9.4925

Zero-point charge (ZPC): The potentiometric mass titration (PMT) was employed to calculate clay's zero point charge [34]. In this method, an aqueous suspension of different masses of clay particles 0.1 g, 0.5 g and 1 g taken in a different conical flasks along with 10 mL (0.0652 M) of NaCl and the same amount of 0.25 M NaOH was equilibrated for 20 h then titrated against 0.25 M HCl corresponding change in pH is measured using pH meter and the intersection point of the three various masses were plotted against pH, at pH 5 all the curves have common intersection point, therefore, pH = 5 is the ZPC of clay sample used for the study. Therefore, at pH 5 the charges on the clay particle are neutral.

Optimization of parameters affecting adsorption: In the adsorption of levofloxacin by NC and TAC all parameters have distinct impacts on the adsorption mechanism such as adsorbent loading, contact time, pH and initial concentration of levofloxacin solution.

Effect of contact time: The contact time variation required for the adsorption of levofloxacin on NC and TAC (0.04 g/L) was examined at pH = 7 and temperature 298 K (100 mL of levofloxacin solution). Fig. 6a showed an initial rapid uptake percentage of levofloxacin from both NC and TAC due to the greater number of vacant sites available for adsorption. It was also observed that adsorption reaches equilibrium at 150 min for both adsorbents [35].

Effect of loading: The levofloxacin percentage uptake was examined by varying the amount of NC and TAC 0.02, 0.040, 0.06, 0.08, 0.10 and 0.12 g with 100 mL of 50 μmol/L levofloxacin at constant pH = 7 at 298 K. Fig. 6b indicates a direct relationship between adsorbent loading and removal % and the maximum adsorption was achieved at 0.04 g for both adsorbents. It is further observed that an increase in loading was steady due to the equilibrium of the adsorbent and levofloxacin solution. The results also indicated that the increased adsorbent amount means an increase in the number of available active sites for adsorption. In addition, the adsorption is higher for TAC compared to NC mainly due to an increase in pore size (after calcination at 400 °C) as the dehydration of the interlayer -OH occurs in the clay. Apart from that the binding force between clay and levofloxacin enhances the adsorption [36].

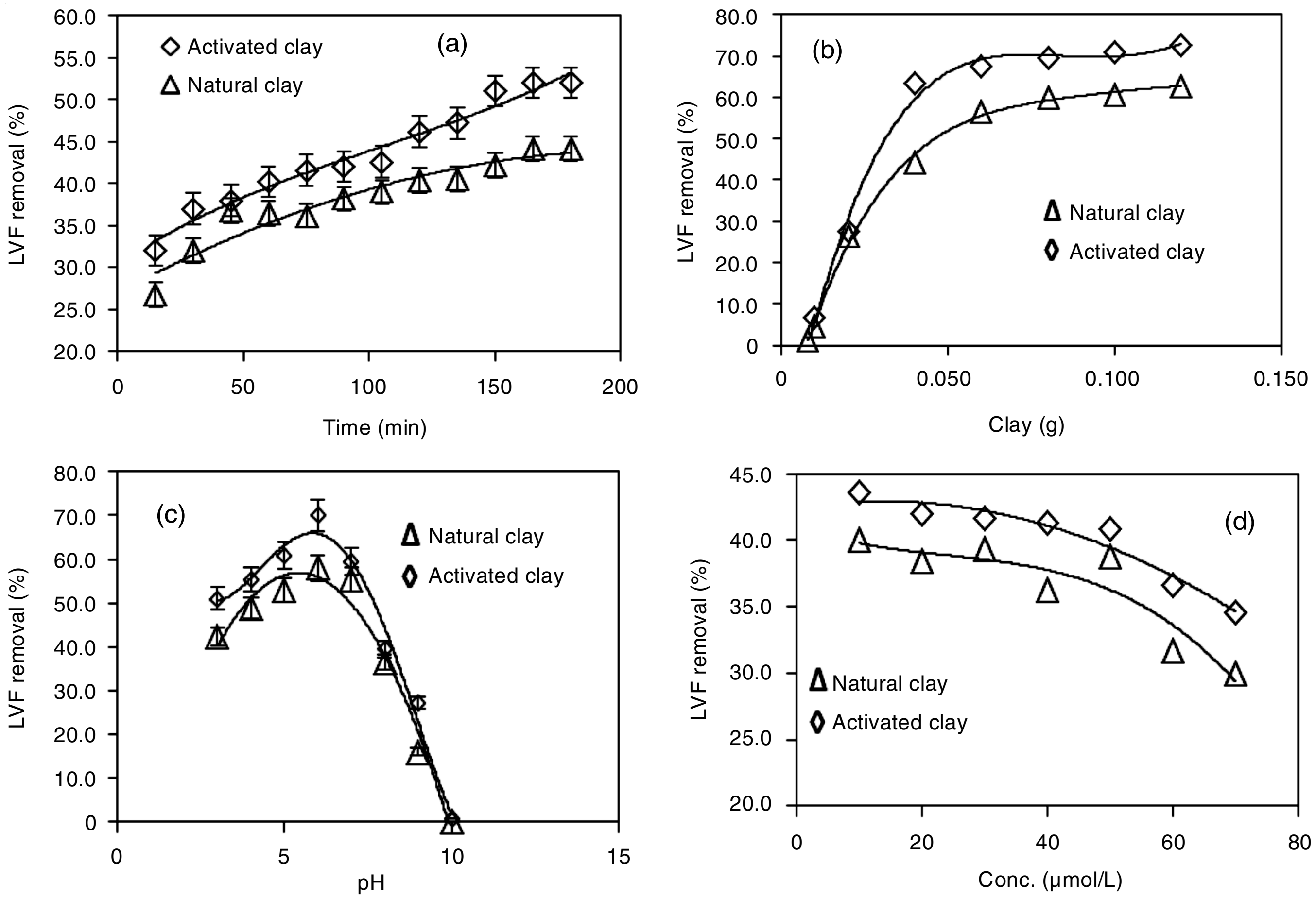

Fig. 6. Effect of (a) contact time, (b) NC and TAC loading, (c) pH, (d) initial concentration

Effect of pH: The levofloxacin solution's pH directly influences the surface charge and adsorption efficiency. Therefore, the pH value was varied between 3 and 10 using acetate, phosphate and borate buffer keeping other factors constant to estimate the maximum removal efficiency. Initially, from pH 3 to 6, an increase in removal% was observed (Fig. 6c) and a further increase in pH 7-10 showed a decrease in the removal percentage. A closer examination of clay's speciation indicates that the neutral species are dominant when pH is between 6 and 8, whereas, positive levofloxacin is dominant at $pH < 6$ and negative at $pH > 8$ [37,38]. The zero-point charge of NC and TAC was 5. Hence, both clays possess a positive charge below pH_{ZPC} and are negatively charged above pH_{ZPC}. Therefore, pH at 3 and 9, showed a declining trend of adsorption due to the repulsive interaction of charges, whereas at pH = 6, maximum adsorption was observed due to attractive interactions of opposite charges. And it is, therefore, confirmed that the chemical interactions between levofloxacin and functional groups of clay plays a crucial role in adsorption phenomenon.

Effect of initial levofloxacin concentration: The impact of variation in initial concentration of levofloxacin on removal % is shown in Fig. 6d. It shows a decrease in removal efficiency as initial concentration increases. This is due to the saturation of all available active sites of a fixed amount of clay for adsorption. As the active sites available on clay particles are limited (0.04 g/L), an increase of levofloxacin concentration does not get sufficient active sites for adsorption and therefore, the efficiency of removal did not increase [39,40].

Isotherms studies: The levofloxacin adsorptions on NC and TAC under equilibrium conditions were studied using Langmuir (eqn. 3), Freundlich (eqn. 4) and Redlich-Peterson (eqn. 5) isotherms. Langmuir isotherm explains the monolayer formation of levofloxacin on clays by homogeneous distribution. The Freundlich isotherm assumes multilayer adsorption of levofloxacin on the heterogeneous surface of clays. Redlich-Peterson isotherm is a mixed type of Langmuir and Freundlich isotherm was used to understand the exact mechanism of the adsorption of levofloxacin on clays [41].

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{K_L q_m} \tag{3}$$

$$\log q_e = \log K_f + \frac{1}{n_f} \log C_e \tag{4}$$

$$q_e = \frac{A_{rC_e}}{1 + BC_e^{\beta}} \tag{5}$$

The isotherm model parameters and correlation coefficient R^2 values are summarized in Table-2. The results of the analysis substantiate that the R^2 value of Freundlich fits well compared to the Langmuir and Redlich-Peterson model [42]. However, the corresponding $\beta < 1$ obtained from the Redlich-Peterson model suggests the adsorption phenomenon follows the Freundlich model compared to Langmuir isotherm (Fig. 7). This clearly implies the occurrence of heterogeneous sites due to which the multi-layer adsorption process is favoured as indicated by the Freundlich model [43,44].

Kinetic studies: An adsorption kinetic study was performed to understand the mechanism and rate-controlling steps followed in the reaction process. In present work, pseudo-first-order (eqn. 6), pseudo-second-order (eqn. 7), Ritchies-second-order (eqn. 8) and intraparticle diffusion (eqn. 9) models were analyzed and shown in Fig. 8a-d. The pseudo-first-order explains the rate of the adsorption process directly depends on the number of available active sites. According to the pseudo-second-order model chemical interaction of functional groups between adsorbates and adsorbents is responsible for the adsorption mechanism and the kinetics also assumes the filling of adsorption sites on clays is directly proportional to the square of a number of unfilled sites [45]. Ritchies-second-order assumes the NC and TAC as homogenous material and adsorption occurs through the filling of one site for successive adsorption and the intraparticle diffusion model is used to comprehend the rate-determining step during adsorption [46].

$$\log(q_e - q_t) = \log q_e - \left(\frac{k_1}{2.303}\right)t \tag{6}$$

TABLE-2

ADSORPTION ISOTHERM MODEL PARAMETERS FOR NATURAL CLAY (NC) AND THERMALLY ACTIVATED CLAY (TAC)

Clay	Langmuir isotherm model				Freundlich isotherm model			Redlich-Peterson isotherm model		
	K_L (L/mg)	q_m (mg/g)	R_L	R^2	n_f	K_f (L/mg)	R^2	β	A_r (L/g)	R^2
NC	0.04169	46.900	0.991	0.8021	1.23165	2.093	0.9674	0.212	2.129	0.7995
TAC	0.043175	54.2338	0.8633	0.9437	1.24011	2.519	0.9935	0.205	5.778	0.8047

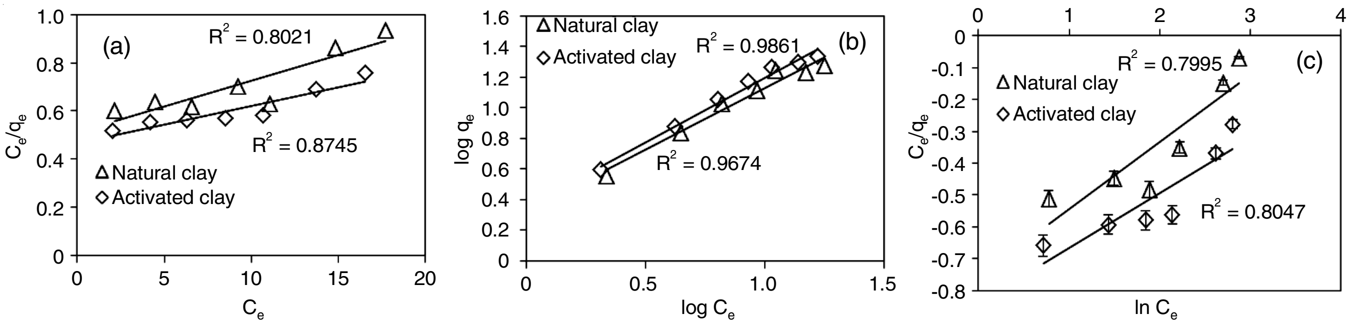

Fig. 7. Isotherm models plots (a) Langmuir Model (b) Freundlich model (c) Redlich-Peterson model

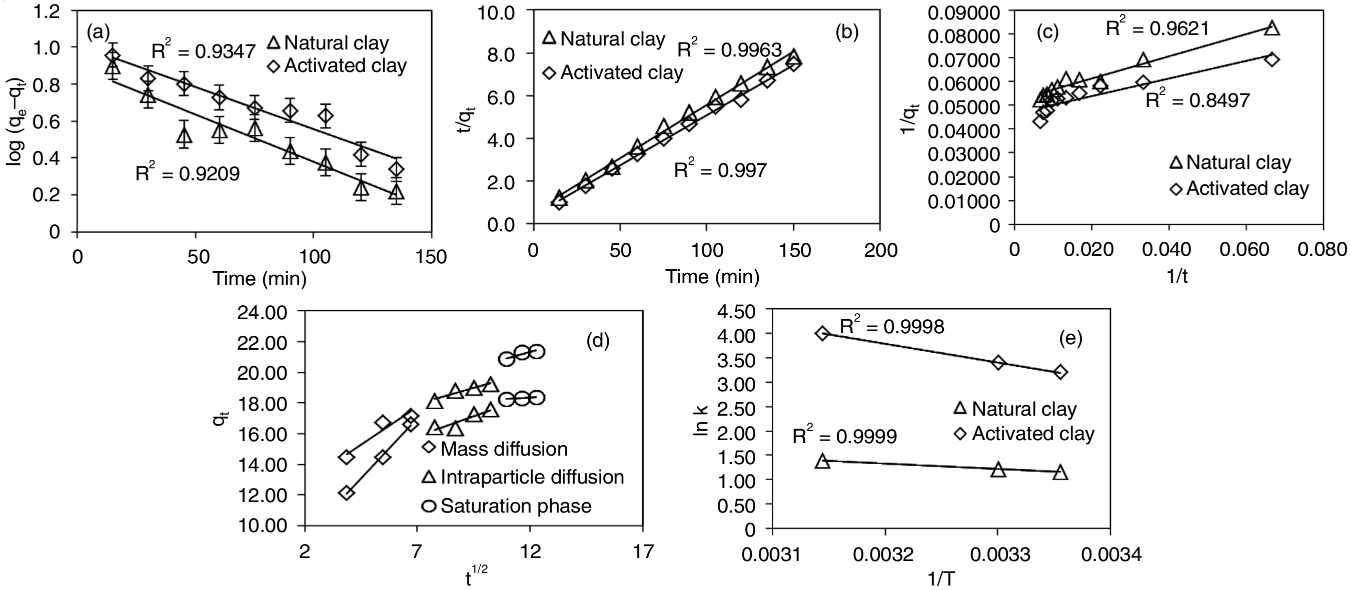

Fig. 8. Kinetic models plots (a) pseudo-first-order, (b) pseudo-second-order, (c) Ritchie's-second-order, (d) Intra-particle diffusion (IPD), (e) Plot of ln k *vs.* 1/T adsorption of levofloxacin (LVF) on natural clay (NC) and thermal activated clay (TAC)

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} - \frac{1}{q_e} t \tag{7}$$

$$\frac{1}{q_t} = \frac{1}{k_r q_e t} + \frac{1}{q_e} \tag{8}$$

$$q_t = k_{idp} t^{1/2} + A \tag{9}$$

The correlation coefficient (R^2) values and all kinetic parameters are summarized in Table-3. The R^2 value obtained by pseudo-second-order is higher compared to pseudo-first-order and Ritchies-second-order. The experimentally obtained and calculated q_e values were compared. It is found that these are in good agreement with the pseudo-second-order model indicating adsorption of levofloxacin on both NC and TAC which are followed by chemical sorption and physisorption [47,48]. The above results are further substantiated by intra-particle diffusion curves (Fig. 8d) indicating more than one mechanism involved in adsorption.

TABLE-3
ADSORPTION KINETICS MODELS PARAMETERS OF NATURAL CLAY (NC) AND THERMALLY ACTIVATED CLAY (TAC)

Adsorption kinetic model	Parameters	NC	TAC
Pseudo-first-order kinetic model	K_1 (min^{-1})	0.01608	0.01309
	q_e (cal) (mg/g)	23.5	20.0
	q_e (exp) (mg/g)	13.99	8.36
	R^2	0.9347	0.9209
Pseudo-second-order kinetic model	K_2 (min^{-1})	0.09665	0.11499
	q_e (cal) (mg/g)	23.5	20.0
	q_e (exp) (mg/g)	23.82	20.02
	R^2	0.9904	0.997
Ritchie's-second-order kinetic model	K_r (min^{-1})	0.01716	0.0245
	q_e (cal) (mg/g)	23.5	20.0
	q_e (exp) (mg/g)	21.42	19.30
	R^2	0.9649	0.8497
Intra particle diffusion	k_{id}	0.67869	0.79151
	A	10.678	11.8212

Adsorption thermodynamics: The thermodynamic parameters *viz.* ΔG°, ΔH°, ΔS° were calculated using the van't Hoff equation and the results are summarized in Table-4. Negative ΔG° indicates the adsorption process is feasible and spontaneous. Positive ΔH° values vary between -20 and 40 KJ/mol confirms the process as endothermic and physical adsorption [49-51]. Positive ΔS° indicate the affinity of NC and TAC towards the adsorption of levofloxacin, which could be attributed to the increased randomness.

Adsorption mechanism: The adsorption of antibiotic levofloxacin on NC and TAC follows a complex phenomenon since clay is composed of an aluminum silicate base called silanol and aluminol. Fig. 9 shows the interaction and bonding of various ions between clay and levofloxacin. Accordingly, the negatively charged surface helps the chemical interaction with cationic levofloxacin [52]. Iron present in the clay minerals also form coordinate bond withelectron rich nitrogen and oxygen present in levofloxacin. Positively charged levofloxacin undergo ion exchange with Ca^{2+} and Mg^{2+} ions. The -OH groups on the clay surface form hydrogen bonding with nitrogen and flourine groups of levofloxacin. However, positive piperazine ring in

TABLE-4
THERMODYNAMIC PARAMETERS OF LEVOFLOXACIN ADSORPTION ON NC AND TAC

Adsorbent	ΔG° (kJ/mol)			ΔH° (kJ/mol)	ΔS° (kJ/mol)
	25 °C	35 °C	45 °C		
NC	-2.8818	-3.0829	-3.6652	8.7662	0.03909
TAC	-3.8342	-4.4714	-5.1067	13.6554	0.059172

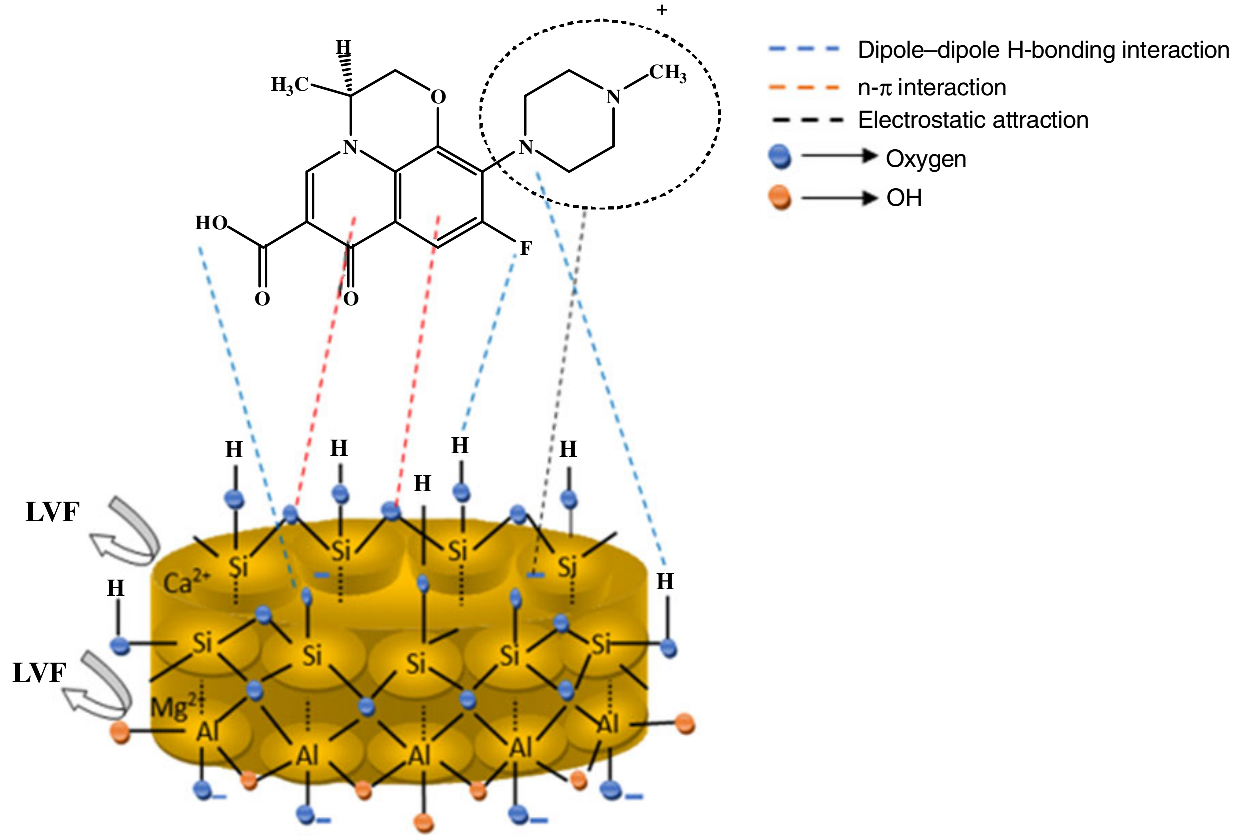

Fig. 9. Plausible mechanism of adsorption of levofloxacin (LVF) on natural clay (NC) and thermal activated clay (TAC)

levofloxacin form bond with negative surface of clay due to the electrostatic attraction in neutral/mild acdic condition whereas, the aromatic ring of levofloxacin form interaction with lone pair electrons of oxygen molecule in clay minerals [53,54].

Comparison study: The adsorption capacities of NC and TAC were compared with different adsorbents for the removal of levofloxacin in water and wastewater systems. It was observed that the removal efficiency for NC and TAC is much higher than other adsorbents. Table-5 shows that natural and thermal activated clays have high adsorption capacity compared to some modified montmorillonite clays, nanocomposites, carbon-based material like biochar and synthetic materials. Therefore, the study substantiates the importance of NC/TAC, without any advance modification they can be used as better adsorbents in removal of harmful pharmaceutical drug from the polluted water.

Conclusion

The current study presents as a significant revelation in terms of the adsorption process on the natural clay (NC) and thermally activated clay (TAC). The Panchganga river which receives large quantities of effluents from various industries present in the catchment area (between Kolhapur and Narasoba

TABLE-5
COMPARISON OF ADSORPTION CAPACITIES OF NC AND TAC WITH DIFFERENT ADSORBENTS FOR THE REMOVAL OF LEVOFLOXACIN

Adsorbent	Adsorbate (pollutant)	Loading (g)	Initial concentration (mg/L)	Adsorption capacity q_e (mg/g)	Ref.
Iron-pillared montmorillonite	Levofloxacin	0.025	20-100	48.6	[55]
SBA-15 mesoporous silica + ZnO	Ciprofloxacin	0.04	2.5-25	SBA-15-13.04 ZnO – 32.58 ZnO-SBA-15(5%)-19.89 ZnO-SBA-15(10%)-28.78 ZnO-SBA-15(20%)-32.28	[56]
Magnetic carbon nanocomposite	Levofloxacin	0.04	20-40	20.75	[57]
$CuFe_2O_4$/Montmorillonite-K10	Levofloxacin	0.2	100	35.8	[58]
Biochar/$MgFe_2O_4$	Levofloxacin	0.03	100	45.1	[59]
1) Copper oxide nanoparticle (CuONP) 2) Zero-valent iron nanoparticles (nZVI)	Levofloxacin	0.01	10-50	CuONP-0.125 nZVI-0.127	[60]
1) Natural clay (NC) 2) Thermal activated clay (TAC)	Levofloxacin	0.04	1.86-18.69	NC -46.90 TAC -54.23	Present study

Wadi) inspite of higher discharge of chemical contaminants, the accumulation of such ions is found to be relatively lower. The results of adsorption experiments revealed that the optimum conditions required for the maximum removal was 62.8% for NC and 72.6% for TAC at 120 min of contact time, pH = 7, 298 K, with NC and TAC loading of 0.40 g/L and 18.69 mg/L of levofloxacin concentration. The kinetics and isotherm results revealed that adsorption follow Freundlich isotherm indicating a multilayer process and also follows the pseudo-second-order kinetic model indicating chemisorption as the initial rate-limiting step, further from the intra-particle diffusion model confirms that the mechanism of adsorption of levofloxacin on NC and TAC proceeds through more than one mechanism. From the thermodynamic parameters, ΔG^o value suggests that adsorption of levofloxacin and NC/TAC is feasible and spontaneously occurring process whereas the ΔH° value suggests the process is endothermic. Hence, it is possible to understand the importance of the clays as self-purifying material in environment for the removal of harmful antibiotics.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

REFERENCES

1. Z. Bing, Y. Qinqin and B. Jun, *Environ. Sci. Technol.*, **44**, 5693 (2010); https://doi.org/10.1021/es9035368
2. M.N. Alnajrani and O.A. Alsager, *Sci. Rep.*, **10**, 794 (2020); https://doi.org/10.1038/s41598-020-57616-4
3. N. Hanna, P. Sun, Q. Sun, X. Li, X. Yang, X. Ji, H. Zou, J. Ottoson, L.E. Nilsson, B. Berglund, O.J. Dyar, A.J. Tamhankar and C. Stålsby Lundborg, *Environ. Int.*, **114**, 131 (2018); https://doi.org/10.1016/j.envint.2018.02.003
4. A. Karlo, A. Ziembiñska-Buczyñska, M. Pilarczyk and J. Surmacz-Górska, *Ecol. Chem. Eng. S*, **22**, 425 (2015); https://doi.org/10.1515/eces-2015-0024
5. M.T.M.H. Hamad and M.E. El-Sesy, *Bioresour. Bioprocess.*, **10**, 1 (2023); https://doi.org/10.1186/s40643-022-00616-1
6. S. Rodriguez-Mozaz, I. Vaz-Moreira, S. Varela Della Giustina, M. Llorca, D. Barceló, S. Schubert, T.U. Berendonk, I. Michael-Kordatou, D. Fatta-Kassinos, J.L. Martinez, C. Elpers, I. Henriques, T. Jaeger, T. Schwartz, E. Paulshus, K. O'Sullivan, K.M.M. Pärnänen, M. Virta, T.T. Do, F. Walsh and C.M. Manaia, *Environ. Int.*, **140**, 105733 (2020); https://doi.org/10.1016/j.envint.2020.105733
7. P. Ball, *J. Antimicrob. Chemother.*, **46(suppl_3)**, 17 (2000); https://doi.org/10.1093/oxfordjournals.jac.a020889
8. S.K. Kurunthachalam, *Hydrol. Curr. Res.*, **03**, 5 (2012); https://doi.org/10.4172/2157-7587.1000e103
9. V. Singh and S. Suthar, *Chemosphere*, **268**, 129331 (2021); https://doi.org/10.1016/j.chemosphere.2020.129331
10. P.K. Mutiyar and A.K. Mittal, *Environ. Sci. Pollut. Res. Int.*, **21**, 7723 (2014); https://doi.org/10.1007/s11356-014-2702-5
11. E. Castrignanò, A.M. Kannan, E.J. Feil and B. Kasprzyk-Hordern, *Chemosphere*, **206**, 376 (2018); https://doi.org/10.1016/j.chemosphere.2018.05.005
12. M.J. Benotti, R.A. Trenholm, B.J. Vanderford, J.C. Holady, B.D. Stanford and S.A. Snyder, *Environ. Sci. Technol.*, **43**, 597 (2009); https://doi.org/10.1021/es801845a
13. O.Golovko, V. Kumar, G. Fedorova, T. Randak and R. Grabic, *Chemosphere*, **111**, 418 (2014); https://doi.org/10.1016/j.chemosphere.2014.03.132
14. J.A. Rivera-Jaimes, C. Postigo, R.M. Melgoza-Alemán, J. Aceña, D. Barceló and M.L. de Alda, *Sci. Total Environ.*, **613–614**, 1263 (2018); https://doi.org/10.1016/j.scitotenv.2017.09.134
15. E. Felis, J. Kalka, A. Sochacki, K. Kowalska, S. Bajkacz, M. Harnisz and E. Korzeniewska, *Eur. J. Pharmacol.*, **866**, 172813 (2020); https://doi.org/10.1016/j.ejphar.2019.172813
16. J. Lyu, L. Yang, L. Zhang, B. Ye and L. Wang, *Environ. Pollut.*, **266**, 115147 (2020); https://doi.org/10.1016/j.envpol.2020.115147
17. X.L. Yang, Q. Wang, T. Li, H. Xu and H.L. Song, *Bioresour. Technol.*, **348**, 126752 (2022); https://doi.org/10.1016/j.biortech.2022.126752
18. S.M. Abegunde, K.S. Idowu, O.M. Adejuwon and T. Adeyemi-Adejolu, *Resour. Environ. Sustainab.*, **1**, 100001 (2020); https://doi.org/10.1016/j.resenv.2020.100001
19. B.L. Phoon, C.C. Ong, M.S. Mohamed Saheed, P.-L. Show, J.-S. Chang, T.C. Ling, S.S. Lam and J.C. Juan, *J. Hazard. Mater.*, **400**, 122961 (2020); https://doi.org/10.1016/j.jhazmat.2020.122961
20. G. Bayramoglu, G. Kunduzcu and M.Y. Arica, *Polym. Eng. Sci.*, **60**, 192 (2020); https://doi.org/10.1002/pen.25272
21. W.R.D.N. Sousa, A.R. Oliveira, J.F. Cruz Filho, T.C.M. Dantas, A.G.D. Santos, V.P.S. Caldeira and G.E. Luz Jr., *Water Air Soil Pollut.*, **229**, 125 (2018); https://doi.org/10.1007/s11270-018-3778-1
22. A.R. Rahmani, H. Rezaei-Vahidian, H. Almasi and F. Donyagard, *Environ. Process.*, **4**, 563 (2017); https://doi.org/10.1007/s40710-017-0251-x
23. M. Dhakal, N. Duwal, N.M. Adhikari, S. Joshi and J. Bhattarai, *J. Nepal Chem. Soc.*, **42**, 80 (2021); https://doi.org/10.3126/jncs.v42i1.35338
24. F. Moodi, A.A. Ramezanianpour and A.S. Safavizadeh, *Sci. Iran.*, **18**, 906 (2011); https://doi.org/10.1016/j.scient.2011.07.011
25. S. Wu, M. He, M. Yang and B. Peng, *Crystals*, **12**, 907 (2022); https://doi.org/10.3390/cryst12070907
26. E.A. Ashour and M.A. Tony, *SN Appl. Sci.*, *SN Appl. Sci.*, **2**, 2162 (2020); https://doi.org/10.1007/s42452-020-03971-w
27. Y. Liu, C. Dong, H. Wei, W. Yuan and K. Li, *Appl. Clay Sci.*, **118**, 301 (2015); https://doi.org/10.1016/j.clay.2015.10.010
28. N.S. Randhawa, N.N. Das and R.K. Jana, *Desalination Water Treat.*, **52**, 4197 (2014); https://doi.org/10.1080/19443994.2013.801324
29. O. Sakin Omer, M.A. Hussein, B.H.M. Hussein and A. Mgaidi, *Arab. J. Chem.*, **11**, 615 (2018); https://doi.org/10.1016/j.arabjc.2017.10.007
30. A.D. Pekdemir, Y. Sarýkaya and M. Önal, *J. Therm. Anal. Calorim.*, **123**, 767 (2016); https://doi.org/10.1007/s10973-015-4866-8
31. A.H. Jawad, A.S. Abdulhameed and M.S. Mastuli, *J. Taibah Univ. Sci.*, **14**, 305 (2020); https://doi.org/10.1080/16583655.2020.1736767
32. A. Mahandrimanana, *Int. J. Mater. Chem.*, **10**, 1 (2020).
33. M. Thommes, K. Kaneko, A.V. Neimark, J.P. Olivier, F. Rodriguez-Reinoso, J. Rouquerol and K.S.W. Sing, *Pure Appl. Chem.*, **87**, 1051 (2015); https://doi.org/10.1515/pac-2014-1117
34. U. Farooq, M.T. Tweheyo, J. Sjöblom and G. Øye, *J. Dispers. Sci. Technol.*, **32**, 519 (2011); https://doi.org/10.1080/01932691003756936
35. E.A. Moawed, N. Burham and M.F. El-Shahat, *J. Assoc. Arab Univ. Basic Appl. Sci.*, **14**, 60 (2013); https://doi.org/10.1016/j.jaubas.2012.09.004
36. R. Rejeb, G. Antonissen, M. De Boevre, C. Detavernier, M. Van de Velde, S. De Saeger, R. Ducatelle, M. Hadj Ayed and A. Ghorbal, *Toxins*, **11**, 602 (2019); https://doi.org/10.3390/toxins11100602
37. M.S. Gudaganatti, M.S. Hanagadakar, R.M. Kulkarni, R.S. Malladi and R.K. Nagarale, *Prog. React. Kinet. Mech.*, **37**, 366 (2012); https://doi.org/10.3184/146867812X13440034591571

38. B.Yao, X. Chen. K. Zhou, Z. Luo, P. Li, Z. Yang, Y. Zhou, *Biochar*, **4**, 31 (2022); https://doi.org/10.1007/s42773-022-00158-x
39. N. Hodzic, A. Dozic, I. Sestan and H. Alihodzic, *Int. J. Res. Appl. Sci. Biotechnol.*, **7**, 1 (2020); https://doi.org/10.31033/ijrasb.7.1.1
40. M.I. Khan, M.S. Hasan, K.A. Bhatti, H. Rizvi, A. Wahab, Shafique-ur Rehman, M.J. Afzal, A. Nazneen, M.F. Khan, A. Nazir and M. Iqbal, *Mater. Res. Express*, **7**, 015061 (2020); https://doi.org/10.1088/2053-1591/ab66f7
41. N. Ayawei, A.N. Ebelegi and D. Wankasi, *J. Chem.*, **2017**, 3039817 (2017); https://doi.org/10.1155/2017/3039817
42. K.S. Obayomi, J.O. Bello, J.S. Nnoruka, A.A. Adediran and P.O. Olajide, *Cogent Eng.*, **6**, 1687274 (2019); https://doi.org/10.1080/23311916.2019.1687274
43. M. Auta and B.H. Hameed, *Chem. Eng. J.*, **171**, 502 (2011); https://doi.org/10.1016/j.cej.2011.04.017
44. C.M. Grisales-Cifuentes, E.A. Serna-Galvis, J. Porras, E. Florez, R.A. Torres-Palma and N. Acelas, *Bioresour. Technol.*, **326**, 124753 (2021); https://doi.org/10.1016/j.biortech.2021.124753
45. M.H. Al-Jabari, S. Sulaiman, S. Ali, R. Barakat, A. Mubarak and S.A. Khan, *J. Mol. Liq.*, **291**, 111249 (2019); https://doi.org/10.1016/j.molliq.2019.111249
46. W.S.W. Ngah and M.A.K.M. Hanafiah, *Biochem. Eng. J.*, **39**, 521 (2008); https://doi.org/10.1016/j.bej.2007.11.006
47. M. Saeed, M. Munir, M. Nafees, S.S.A. Shah, H. Ullah and A. Waseem, *Micropor. Mesopor. Mater.*, **291**, 109697 (2020); https://doi.org/10.1016/j.micromeso.2019.109697
48. N. Wahab, M. Saeed, M. Ibrahim, A. Munir, M. Saleem, M. Zahra and A. Waseem, *Front. Chem.*, **7**, 654 (2019); https://doi.org/10.3389/fchem.2019.00654
49. H.K. Boparai, M. Joseph and D.M. O'Carroll, *J. Hazard. Mater*., **186**, 458 (2011); https://doi.org/10.1016/j.jhazmat.2010.11.029
50. S. Raghav and D. Kumar, *J. Chem. Eng. Data*, **63**, 1682 (2018); https://doi.org/10.1021/acs.jced.8b00024
51. G.A. Corrêa-Ribeiro, D.S. Araújo-Silva, C.C. dos Santos, A. Pires- Vieira, C.W. Brito Bezerra, A.A. Tanaka and S.A. Abreu-Santana, *Polímeros*, **27**, 16 (2017); https://doi.org/10.1590/0104-1428.2386
52. M. Wei, X. Wang, K. Zhou and R. Yang, *Chemosphere*, **311**, 136878 (2023); https://doi.org/10.1016/j.chemosphere.2022.136878
53. W.K. Wakejo, B.T. Meshasha, J.W. Kang and Y. Chebude, *Adsorpt. Sci. Technol.*, **2022**, 2699530 (2022); https://doi.org/10.1155/2022/2699530
54. S. Martin, A. Shchukarev, K. Hanna and J.F. Boily, *Environ. Sci. Technol.*, **49**, 12197 (2015); https://doi.org/10.1021/acs.est.5b02851
55. Y. Liu, C. Dong, H. Wei, W. Yuan and K. Li, *Appl Clay Sci.*, **118**, 301 (2015); https://doi.org/10.1016/j.clay.2015.10.010
56. W.R.D.N. Sousa, A.R. Oliveria, J.F.C. Filho, T.C.M. Dantas, A.G.D. Santos, V.P.S. Caldeira and G.E. Luz Jr., *Water Air Soil Pollut.*, **229**, (2018); https://doi.org/10.1007/s11270-018-3778-1
57. A. Ullah, M. Zahoor, S. Alam, R. Ullah, A.S. Alqahtani and H.M. Mahmood, *Biomed. Res. Int.*, **2019**, 5276841 (2019); https://doi.org/10.1155/2019/5276841
58. J. Yang, M. Huang, S. Wang, X. Mao, Y. Hu and X. Chen, *Water*, **12**, 3583 (2020); https://doi.org/10.3390/w12123583
59. B. Yao, Z. Luo, S. Du, J. Yang, D. Zhi and Y. Zhou, *Bioresour. Technol*., **340**, 125698 (2021); https://doi.org/10.1016/j.biortech.2021.125698
60. M.T.M.H. Hamad and M.E. El-Sesy, *Bioresour. Bioprocess*, **10**, 1 (2023); https://doi.org/10.1186/s40643-022-00616-1