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 contain 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 concentration 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 16°41′51″N and longitude 74°9′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 °C 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 °C 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 (CuKα irradiating by 154 nm wavelength for 10,000 min⁻¹ in 10-90° 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.
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:

\[
\text{Uptake} (\%) = \frac{C_i - C_e}{C_i} \times 100 \tag{1}
\]

where \(C_i\) = initial concentration (mg L\(^{-1}\)); \(C_f\) = final concentration (mg L\(^{-1}\)).

\[
q_e = \frac{C_i - C_e}{W} \tag{2}
\]

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, \(2\theta = 20.91^\circ, 26.68^\circ, 40.34^\circ, 50.17^\circ, 68.68^\circ\) (JCPDS No. 86-1628) followed by cristobalite at \(2\theta = 21.37^\circ, 36.71^\circ\) (JCPDA No. 76-1390), rutile at \(2\theta = 27.82^\circ, 54.18^\circ\) (JCPDS No. 82-0514), hematite at \(2\theta = 32.63^\circ, 35.56^\circ, 53.23^\circ\) (JPDs No. 89-0598) and \(\text{Al}_2\text{O}_3\) at \(2\theta = 33.20^\circ, 75.74^\circ\) (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 °C [24].

**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.

**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 (0.44); 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.
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...
structure of clays that is followed by adsorption on exterior surface. The surface characteristics of NC and TAC are summarized in Table-1.

<table>
<thead>
<tr>
<th>Clays</th>
<th>Surface area (m² g⁻¹)</th>
<th>Total pore volume (cm³ g⁻¹)</th>
<th>Pore diameter (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NC</td>
<td>78.253</td>
<td>0.1252</td>
<td>6.3989</td>
</tr>
<tr>
<td>TAC</td>
<td>65.815</td>
<td>0.1132</td>
<td>9.4925</td>
</tr>
</tbody>
</table>

**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 ºC) 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](image-url)
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 pHZPC and are negatively charged above pHZPC. 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 concentrations 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 is a mixed type of Langmuir and Freundlich isotherm as a 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].

The isotherm model parameters and correlation coefficient R² values are summarized in Table-2. The results of the analysis substantiate that the R² value of Freundlich fits well compared to the Langmuir and Redlich-Peterson model [42]. However, the corresponding β < 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].

$$
\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{K_{L} q_m}
$$  \hspace{1cm} (3)

$$\log q_e = \log K_f + \frac{1}{n_f} \log C_e
$$  \hspace{1cm} (4)

$$q_e = \frac{A_{c_e}}{1 + BC_c^\beta}
$$  \hspace{1cm} (5)

Table-2: Adsorption Isotherm Model parameters and correlation coefficient R² for natural clay (NC) and thermally activated clay (TAC).

<table>
<thead>
<tr>
<th>Clay</th>
<th>Langmuir isotherm model</th>
<th>Freundlich isotherm model</th>
<th>Redlich-Peterson isotherm model</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>K_l (L/mg)</td>
<td>q_m (mg/g)</td>
<td>R²</td>
</tr>
<tr>
<td>NC</td>
<td>0.04169</td>
<td>46.900</td>
<td>0.991</td>
</tr>
<tr>
<td>TAC</td>
<td>0.043175</td>
<td>54.2338</td>
<td>0.8633</td>
</tr>
</tbody>
</table>

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

Adsorption thermodynamics: The thermodynamic parameters $\Delta G^0$, $\Delta H^0$, $\Delta S^0$ were calculated using the van’t Hoff equation and the results are summarized in Table-4. Negative $\Delta G^0$ indicates the adsorption process is feasible and spontaneous. Positive $\Delta H^0$ values vary between -20 and 40 KJ/mol confirms the process as endothermic and physical adsorption [49-51]. Positive $\Delta S^0$ 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 with electron rich nitrogen and fluorine 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 3: Adsorption Kinetics Models Parameters of Natural Clay (NC) and Thermally Activated Clay (TAC)

<table>
<thead>
<tr>
<th>Adsorption kinetic model</th>
<th>Parameters</th>
<th>NC</th>
<th>TAC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pseudo-first-order kinetic model</td>
<td>$K_1$ (min$^{-1}$)</td>
<td>0.01608</td>
<td>0.01309</td>
</tr>
<tr>
<td></td>
<td>$q_e$ (cal) (mg/g)</td>
<td>23.5</td>
<td>20.0</td>
</tr>
<tr>
<td></td>
<td>$q_e$ (exp) (mg/g)</td>
<td>13.99</td>
<td>8.36</td>
</tr>
<tr>
<td></td>
<td>$R^2$</td>
<td>0.9347</td>
<td>0.9209</td>
</tr>
<tr>
<td>Pseudo-second-order kinetic model</td>
<td>$K_2$ (min$^{-1}$)</td>
<td>0.09665</td>
<td>0.11499</td>
</tr>
<tr>
<td></td>
<td>$q_e$ (cal) (mg/g)</td>
<td>23.5</td>
<td>20.0</td>
</tr>
<tr>
<td></td>
<td>$q_e$ (exp) (mg/g)</td>
<td>23.82</td>
<td>20.02</td>
</tr>
<tr>
<td></td>
<td>$R^2$</td>
<td>0.9904</td>
<td>0.997</td>
</tr>
<tr>
<td>Ritchie’s-second-order kinetic model</td>
<td>$K_t$ (min$^{-1}$)</td>
<td>0.01716</td>
<td>0.0245</td>
</tr>
<tr>
<td></td>
<td>$q_e$ (cal) (mg/g)</td>
<td>23.5</td>
<td>20.0</td>
</tr>
<tr>
<td></td>
<td>$q_e$ (exp) (mg/g)</td>
<td>21.42</td>
<td>19.30</td>
</tr>
<tr>
<td></td>
<td>$R^2$</td>
<td>0.9649</td>
<td>0.8497</td>
</tr>
<tr>
<td>Intra particle diffusion</td>
<td>$k_d$</td>
<td>0.67869</td>
<td>0.79151</td>
</tr>
<tr>
<td></td>
<td>$A$</td>
<td>10.678</td>
<td>11.821</td>
</tr>
</tbody>
</table>

### Table 4: Thermodynamic Parameters of Levofloxacin Adsorption on NC and TAC

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>$\Delta G^0$ (kJ/mol)</th>
<th>$\Delta H^0$ (kJ/mol)</th>
<th>$\Delta S^0$ (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>25 °C</td>
<td>35 °C</td>
<td>45 °C</td>
<td></td>
</tr>
<tr>
<td>NC</td>
<td>-2.8818</td>
<td>-3.0829</td>
<td>-3.6652</td>
</tr>
<tr>
<td>TAC</td>
<td>-3.8342</td>
<td>-4.714</td>
<td>-5.1067</td>
</tr>
</tbody>
</table>
levofloxacin form bond with negative surface of clay due to the electrostatic attraction in neutral/mild acidic 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

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**TABLE-5**

**COMPARISON OF ADSORPTION CAPACITIES OF NC AND TAC WITH DIFFERENT ADSORBENTS FOR THE REMOVAL OF LEVOFLOXACIN**

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Adsorbate (pollutant)</th>
<th>Loading (g)</th>
<th>Initial concentration (mg/L)</th>
<th>Adsorption capacity qₑ (mg/g)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Iron-pillared montmorillonite</td>
<td>Levofloxacin</td>
<td>0.025</td>
<td>20-100</td>
<td>48.6</td>
<td>[55]</td>
</tr>
<tr>
<td>SBA-15 mesoporous silica + ZnO</td>
<td>Ciprofloxacin</td>
<td>0.04</td>
<td>2.5-25</td>
<td>SBA-15-13.04</td>
<td>[56]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>ZnO – 32.58</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>ZnO-SBA-15(5%)-19.89</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>ZnO-SBA-15(10%)-28.78</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>ZnO-SBA-15(20%)-32.28</td>
<td></td>
</tr>
<tr>
<td>Magnetic carbon nanocomposite</td>
<td>Levofloxacin</td>
<td>0.04</td>
<td>20-40</td>
<td>20.75</td>
<td>[57]</td>
</tr>
<tr>
<td>CuFe₃O₄/Montmorillonite-K10</td>
<td>Levofloxacin</td>
<td>0.2</td>
<td>100</td>
<td>35.8</td>
<td>[58]</td>
</tr>
<tr>
<td>Biochar/MgFe₂O₄</td>
<td>Levofloxacin</td>
<td>0.03</td>
<td>100</td>
<td>45.1</td>
<td>[59]</td>
</tr>
<tr>
<td>1) Copper oxide nanoparticle (CuONP)</td>
<td>Levofloxacin</td>
<td>0.01</td>
<td>10-50</td>
<td>CuONP-0.125</td>
<td>[60]</td>
</tr>
<tr>
<td>2) Zero-valent iron nanoparticles (nZVI)</td>
<td></td>
<td></td>
<td></td>
<td>nZVI-0.127</td>
<td></td>
</tr>
<tr>
<td>1) Natural clay (NC)</td>
<td>Levofloxacin</td>
<td>0.04</td>
<td>1.86-18.69</td>
<td>NC -46.90</td>
<td>Present study</td>
</tr>
<tr>
<td>2) Thermal activated clay (TAC)</td>
<td></td>
<td></td>
<td></td>
<td>TAC -54.23</td>
<td></td>
</tr>
</tbody>
</table>
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° value suggests that adsorption of levofloxacin on NC/TAC is feasible and spontaneously occurring process whereas the AH° 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.

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