Enhanced Adsorption of Toxic and Biologically Active Levofloxacin Residuals from Wastewater Using Clay Nanotubes as a Novel Fixed Bed: Column Performance and Optimization

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ABSTRACT: Kaolinite nanotube particles (KNTs) were synthesized by a chemical exfoliation and scrolling process in the existence of sonication waves. The KNT product was identified as a mesoporous material (12 nm in pore diameter) with high surface area (105 m²/g) and promising adsorption affinity for the levofloxacin antibiotic (LVOX) residuals in wastewater. The KNT particles were used as a fixed bed in the continuous adsorption column system for LVOX considering the essential variables. The investigation of the KNT fixed bed in a continuous column for 1800 min verified its suitability to reduce the LVOX content in 9 L of polluted solutions by 80.4%. This was recognized after using the KNT bed of 4 cm in height, a flow rate of 5 mL/min, a pH value of 8, a total flow interval of 1800 min, and an LVOX concentration of 10 mg/L. The regeneration study of the bed declared effective recyclability properties for the KNT particles in the LVOX adsorption column system. The dynamic properties of the KNT bed-based column system were explained based on Thomas, Adams−Bohart, and the Yoon−Nelson kinetic models. The LVOX adsorption reaction by KNTs follows Langmuir behavior with homogeneous and monolayer uptake form. The Gaussian energy (2.05 kJ/mol) and the thermodynamic parameters emphasized physical, spontaneous, and exothermic adsorption reactions for LVOX by KNTs.

1. INTRODUCTION

The wide detection of the biologically active compound as the commonly used antibiotics in the water resources was classified as one of the essential concerns for the water, environmental, and health authorities in the world.1,2 The antibiotics as chemical compounds are vital components in several human medicines as well as veterinary practice, and their discharges into surface or groundwater supplies show hazardous side effects even at very low concentrations.2−4

Levofloxacin is a known type of fluoroquinolone antibiotics that can be used in the treatment of pneumonia as well as immunodeficiency virus in addition to its role as an antibacterial and anti-dysentery agent.5,6 The poor metabolic properties of levofloxacin in the human body resulted in a continuous release of it in its parent form to the environment including water resources.2,5 Levofloxacin as water pollutants was described as a non-biodegradable and toxic dissolved compound of high affinity to form complexes with other dissolved organic compounds or the different species of the metal ions, which affect negatively the ecosystem and human health.7 Additionally, it presents negative impacts on the pathogen resistance of the present microorganisms by forming several species of chemical inhibitors.5

Several synthetic materials were assessed in the decontamination of levofloxacin residuals as goethite,8 biochar,9 cerium-doped ZnO,10 MoS₂/TiO₂,11 and graphene oxide-CdS.12 This...
associated with continuous and strong efforts of other advanced adsorbents that are of high capacities, low cost, and wide availability.\textsuperscript{13} Using natural minerals and rocks as precursors in the production of innovative adsorbent was recommended greatly for the commercial and technical values of such materials in addition to their huge reserves in the world.\textsuperscript{1}

One-dimensional nanostructures as nanorods and nanotubes were introduced as promising adsorbents with high surface area and excellent dispersion properties.\textsuperscript{14,15} Recently, innovative modified forms of clay-based adsorbents as the clay nanotubes and exfoliated clay sheets were studied as highly effective products in water purification systems.\textsuperscript{16,17} The clay nanotubes were synthesized mainly from kaolinite mineral by sonication-induced chemical exfoliation and scrolling processes.\textsuperscript{18,19} Such morphological modifications result in scrolled single or several sheets of kaolinite giving it semicrystalline properties, high surface reactivity, promising surface area, remarkable porous structure, and effective adsorption capacities.\textsuperscript{1,18,20} In our previous studies, we investigate the production of clay nanotubes from kaolinite as a highly effective adsorbent for different species of heavy metals (Zn\textsuperscript{2+} (103 mg/g), Cd\textsuperscript{2+} (116 mg/g), Pb\textsuperscript{2+} (89 mg/g), and Cr\textsuperscript{6+} (91 mg/g)).\textsuperscript{16} This makes the clay nanotubes adsorbents an active point for further studies about their suitability for decontamination of different types of water pollutants, especially the organic and biological types.

Up to our knowledge, no previous studies have been conducted to investigate the production and applying the kaolinite nanotubes in adsorption of the pharmaceutical residuals as levofloxacin from wastewater. Therefore, the present manuscript column adsorption studies for levofloxacin using kaolinite nanotube beds. The studies conducted considering all the commonly evaluated variables for the column studies and the performance of the column were assessed based on the investigated parameters from the breakthrough curves and different kinetic models. The expected nature for the interaction between the antibiotic molecules and the surface of KNTs was followed considering the equilibrium as well as the thermodynamic studies.

2. RESULTS AND DISCUSSION

2.1. Characterization of KNTs. The SEM and the HRTEM images were used to confirm the modification of kaolinite mineral from pseudo-hexagonal flakes (Figure 1A) into rolled or folded flakes of tabular forms (Figure 1B). The HRTEM images emphasized the presence of such tabular particles as well as developed nanotubes with the characteristic cylindrical hollow structure (Figure 1C,D). These tubes were
detected with a length from 50 nm to nearly 600 nm, with an outer diameter from 10 to 50 nm, and with an internal diameter within the range from 2 nm to 20 nm (Figure 1C,D).

The previous change in the morphology has a strong impact on the textural features of the materials. The N2 isotherm curve was changed from type II, which identifies the kaolinite flakes, to type IV with H3 hysteresis loop, which identifies the nanoporous materials that have tabular or cylindrical pores (Figure S1). This appeared also in the surface area and the total porosity, which increased from 10 m²/g and 0.052 cm³/g for kaolinite to 105 m²/g and 0.51 cm³/g, respectively, for KNTs. The measured average pore diameter of KNTs is 12 nm, which categorizes it as mesoporous materials (2–50 nm).

The crystallinity of the used precursors and KNTs is demonstrated in Figure 2A. The used kaolinite is a highly crystalline mineral of triclinic crystal system, and this was confirmed by its diffraction peaks especially at 12.33° (001), 24.87° (002), and 26.6° (111) (Figure 2A,A). The kaolinite sample, which was intercalated with DMSO, showed the essential peaks of triclinic kaolinite mineral ((001, 002)) but in misrepresented positions and wider area (Figure 2A,B). Additionally, the basal spacing showed a noticeable increment from their FT-IR spectra (Figure 2B). Si−O−Al, Si−O−Si, Al−OH, and Si−OH were identified as the essential structural groups of kaolinite, and their bands were observed at 456, 680, 912.12, 1020, 1641.23, 3500.20, and 3689.40 cm⁻¹, respectively (Figure 2B.A). The same structural groups were identified for KNTs but with slight shifting for their bands. Such shifting signifies deformation for the structural units of kaolinite layers during the scrolling procedures (Figure 2B,B). Moreover, the predicted complexation between the siloxane groups and the intercalated DMSO and methanol organic molecules by new hydrogen bonds might have a considerable effect on the position of the FT-IR bands.¹

The thermal stability of the synthetic KNTs appears to be similar to that detected for raw kaolinite mineral. The TGA curve of KNTs shows significant stability within the range from 50 °C to about 460 °C (Figure S2). Then, the weight declined strongly from 460 °C to about 580 °C, demonstrating the dehydroxylation of the scrolled kaolinite sheets (Figure S2).

2.2. Column Adsorption Results. 2.2.1. Influence of pH.

The pH effect was studied at batch tests to fix it at its best value for the pumped LVOX solutions. The pH values were varied regularly from pH 2 to pH 10 considering the other controlling variables at 360 min, 25 mg/L, 150 mL, 0.02 g, and 25 °C for the contact time, the LVOX concentration, the studied volume, the KNT dosage, and the reaction temperature, respectively (Figure 3). The experimental affinity of KNTs for LVOX molecules enhanced regularly within the pH range from pH 2 to pH 8 as the LVOX decontamination percentage increased from 20.8% to 88.6%. The conducted experiments at pH above 8 reflected a decrease in the decontamination efficiency to 80.7% and 74.5% at pH 9 and pH 10, respectively (Figure 3).

This related to the speciation properties of LVOX as well as the dominant charges on the reactive surface of KNTs. The speciation studies of the dissolved LVOX reported its existence in three essential forms of positive charge (cationic form related to the protonated piperazinyl group), neutral charge (zwitterionic form), and negative charge (anionic form related to the deprotonated carboxyl group).¹ The cationic form was identified as the essential form within the conditions of pH lower than 5. Beyond pH 5, the LVOX molecules become a zwitterionic form up to pH 8.5, and above that, the molecules become an anionic form.¹ The protonation of the active siloxane groups of KNTs at the high acidic conditions and their deprotonation at the high alkaline conditions make the surface of highly repulsive properties with essential LVOX forms at these conditions.¹ Therefore, the pH range from pH 7 to pH 8 in which the zwitterionic LVOX form show high domination representing the best environments for the adsorption elimination of LVOX by KNTs (Figure 3). The previous explanation for the adsorption behavior of LVOX by KNTs as a function of the adjusted pH was induced by detecting the pH value at zero point charge considering the zeta potential values. The detected pH of zero point charge of KNTs is pH 7.54, which reflects the dominance of the negative charge above this value and the presence of sufficient positive and negative charges within this range to adsorb the zwitterionic forms of LVOX molecules.

2.2.2. Influence of KNT Bed Height.

The influence of KNT bed thickness on the performance of its column system during
the decontamination of LVOX was followed within the studied range from 1 to 4 cm at pH 8, an LVOX concentration of 20 mg/L, and a flow rate of 5 mL/min for 1800 min. As presented in Figure 4A, using the KNT bed at higher heights induced significantly the performance of the column and its lifetime. This was observed in the systematic increment in the breakthrough time intervals by 720, 960, 1140, and 1260 min in the existence of KNT bed of 1, 2, 3, and 4 cm in height, respectively (Figure 4A and Table 1). Additionally, the saturation interval extended by 1440, 1560, 1680, and 1800 min.

![Figure 4](https://dx.doi.org/10.1021/acsomega.0c03785)

**Table 1. Mathematical Parameters of the Breakthrough Curves during the Adsorption of LVOX Molecules by the KNT Bed in a Continuous Column System**

| KNT bed | Bed height (cm) | flow rate (mL/min) | conc. (mg/mL) | \( C_{ad} \) (mg/L) | \( q_{a,d} \) (mg/g) | \( M_{total} \) (mg) | \( R, \% \) | \( t_b \) (min) | \( t_s \) (min) | \( V_{eff} \) (mL) |
|---------|-----------------|--------------------|---------------|----------------------|-----------------|------------------|----------|----------------|----------------|----------------|
| Bed height | 1 | 5 | 20 | 368.6 | 1136.7 | 757.6 | 2790 | 40.73 | 720 | 1440 | 7200 |
| | 2 | 5 | 20 | 405.9 | 1310.7 | 436.9 | 2790 | 46.97 | 960 | 1560 | 7800 |
| | 3 | 5 | 20 | 449.4 | 1540 | 342.3 | 2790 | 55.2 | 1140 | 1680 | 8400 |
| | 4 | 5 | 2 | 494.4 | 1670.6 | 278.4 | 2790 | 59.9 | 1260 | 1800 | 9000 |
| Flow rate | 4 | 5 | 20 | 494.4 | 1670.6 | 278.4 | 2790 | 59.9 | 1260 | 1800 | 9000 |
| | 4 | 10 | 20 | 458.44 | 3079.7 | 513.3 | 5616 | 54.8 | 1080 | 1740 | 17,400 |
| | 4 | 15 | 20 | 393.3 | 3712.9 | 618.8 | 8370 | 44.36 | 900 | 1560 | 23,400 |
| | 4 | 20 | 20 | 298.6 | 4683.6 | 780.6 | 11,160 | 41.96 | 600 | 1260 | 25,200 |
| LVOX concentration | 4 | 5 | 10 | 266.8 | 1121.2 | 186.9 | 1395 | 80.4 | 1440 | 9000 |
| | 4 | 5 | 20 | 494.4 | 1670.6 | 278.4 | 2790 | 59.9 | 1260 | 1800 | 9000 |
| | 4 | 5 | 30 | 676.23 | 2479.2 | 413.2 | 4185 | 59.24 | 1020 | 1680 | 8400 |
| | 4 | 5 | 40 | 722.24 | 2656.3 | 442.7 | 5580 | 47.6 | 780 | 1500 | 7500 |
| Regeneration cycles | cycle 1 | 4 | 5 | 10 | 266.8 | 1121.2 | 186.9 | 1395 | 80.4 | 1440 | 9000 |
| | cycle 2 | 4 | 5 | 10 | 247.86 | 971.4 | 161.9 | 1395 | 69.6 | 1320 | 1740 | 8700 |
| | cycle 3 | 4 | 5 | 10 | 201.96 | 664.5 | 110.75 | 1395 | 47.6 | 900 | 1560 | 7800 |
| | cycle 4 | 4 | 5 | 10 | 162.48 | 433.3 | 72.2 | 1395 | 31 | 780 | 1200 | 6000 |
| | cycle 5 | 4 | 5 | 10 | 125.48 | 267.4 | 44.57 | 1395 | 19.2 | 540 | 960 | 4800 |
The regular increase in the LVOX concentration from 10 to 40 mg/L induced the totally adsorbed quantities in the KNT bed by 1121.2, 1670.6, 2479.2, and 2556.3 mg for the studied concentrations in order (Figure 4C and Table 1). This also reflected in the increment in the LVOX equilibrium capacities of KNT bed by 186.9, 278.4, 413, and 442.7 mg/g for LVOX concentrations of 10, 20, 30, and 40 mg/L, respectively (Figure 4C and Table 1). Such enhancement in the quantities of LVOX, which were retention within the KNT bed, has no impact in inducing the final removal percentages. The removal percentages of LVOX by the KNT bed diminished by 80.4%, 59.9%, 59.24%, and 47.6% with increasing the tested concentrations by 10, 20, 30, and 40 mg/L, respectively (Figure 4C and Table 1). This declared the role of the higher LVOX concentrations in increasing the concentrations gradients and lowering the mass transfer resistance within the bed, which in turn causes fast saturation of the available sites by the LVOX molecules.

2.2.4. Influence of LVOX Concentration. The influence of the LVOX concentration in the effluents on the performance of the KNT bed-based column system was followed within a studied range from 5 to 40 mg/L at pH 8, an LVOX concentration of 20 mg/L, and a KNT bed of 4 cm in height for 1800 min (Figure 4B). The obtained breakthrough curves reflected a strong role for the flow rate in controlling the performance of the column during the adsorption of LVOX as well as its lifetime (Figure 4B and Table 1). This was observed in the recognizable declination in the breakthrough time intervals by 1260, 1080, 900, and 600 min with pumping the LVOX solutions at flow rates of 5, 10, 15, and 20 mL/min, respectively. Additionally, the saturation interval reduced from 1800, 1740, 1560, and 1260 min at the same adjusted flow rates in order (Figure 4B and Table 1).

However, the breakthrough parameters verified a significant increase in the volumes of the treated LVOX solutions with accelerating their flow rates, and the results demonstrated an extensive decline in both totally adsorbed LVOX in the KNT bed and the final removal percentages. The higher flow rates resulted in a low residence time for the LVOX molecules in contact with the KNT particles. This reduces the uptake chances of the LVOX molecules by the active receptors of KNTs, which in turn affect negatively the final capacity of the bed and the performance of its column system. The total retention of LVOX by the KNT bed at flow rates of 5, 10, 15, and 20 mL/min are 1670.6, 3079.7, 3712.9, and 4386.6 mg, respectively. This also associated with an obvious enhancement in the final removal percentages by 59.9%, 54.8%, 44.3%, and 41.9% for previously tested flow rates in order (Figure 4B and Table 1).

2.3. Modeling of the KNT Column System. Three common kinetic models (Thomas, Adams–Bohart, and Yoon–Nelson) were assessed to the dynamic behavior of the KNT bed. The investigation of such models assists strongly in following the performance of the KNT-based column and its breakthrough adsorption properties. The parameters of the Adams–Bohart as well as the Yoon–Nelson models used widely to predict the breakthrough activities of the KNT bed and its adsorption behavior for LVOX during the initial stages of the reactions. These models are highly effective in addressing the performance of the KNT bed based on the capacity of the KNT bed, the saturation concentration of LVOX, and the time interval for 50% breakthrough value.

The KNT adsorption results for LVOX were representative equations of the models from eqs 1 to 3 for the three models in order:

\[
\ln \left( \frac{C_s}{C_i} - 1 \right) = \frac{K_{15} q M}{F} - K_{15} C_f
\]
2.3.1. Thomas Model. Thomas model as a descriptive model for the kinetic of the KNT bed suggested that the retention of the LVOX molecules within the KNT column system follows the behavior of the systems that are second-order kinetic properties. Additionally, it refers to the presence of reversible uptake reactions of Langmuir equilibrium properties without an effective role for the dispersion axial and without limitations for the internal and/or external diffusion for the LVOX molecules.\(^2\),\(^3\)

The presented fitting results considering the studied variables of bed height, flow rate, and LVOX concentration reflected excellent agreement between the adsorption properties of KNT bed and the model (Figure 5A–C and Table 2). The mathematical parameters of this model demonstrated strong declination in the LVOX equilibration capacity of the KNT bed by using a bed of higher height from 1 to 4 cm. On the other hand, the capacity of the KNT bed increased systematically by applying higher flow rates and with testing higher LVOX concentrations (Table 2).

\[
\ln \left( \frac{C_t}{C_0} \right) = K_{AB}C_0t - K_{AB}N_o \frac{Z}{U_0} \\
\ln \left( \frac{C_t}{C_0 - C_t} \right) = K_{YN}t - \tau K_{YN}
\]

\[(2)\] 
\[(3)\]

2.3.2. Adams–Bohart Model. This model shows valuable significances in predicting the transport properties of the LVOX molecules with the KNT-based column system. This model suggested stepping isotherm properties for the uptake of LVOX molecules by the KNT bed with constant uptake capacity.\(^3\) The LVOX within the KNT bed show strong agreement with the Adams–Bohart model achieving significant determination coefficient values (\(R^2\)) for all the assessed experimental variables (bed height, flow rate, and LVOX concentration) (Figure 5D–F and Table 2). The values of the saturation concentrations \(N_o\) declined significantly with using the KNT bed with higher thicknesses (from 1 to 4 cm).

Figure 5. Fitting of the KNT bed adsorption results with (A) Thomas kinetic model as a function of the KNT bed height, (B) Thomas kinetic model as a function of the flow rates, (C) Thomas kinetic model as a function of the LVOX concentration, (D) Adams–Bohart model as a function of the KNT bed height, (E) Adams–Bohart model as a function of the flow rate, (F) Adams–Bohart model as a function of LVOX concentration, (G) Yoon–Nelson model as a function of the KNT bed height, (H) Yoon–Nelson model as a function of the flow rate, and (I) Yoon–Nelson model as a function of the LVOX concentration.
LOVX concentration

Flow rate

considering the concentration at a certain value.25 This
LVOMolecules as well as their adsorbed reactions
and the predicted maximum LOVX uptake capacity in mg/g.
concentration in mg/L, the LOVX uptake capacity in mg/g,
the breakthrough properties of the KNT bed.24 The properties
model assigns the LOVX uptake rates related essentially to
emphasizes the agreement with the Yoon
25 adjusting the essential e
within the LOVX range from 25 to 300 mg/L and after
byeqs 4, 5, and 6, respectively:

\[ q_e = \frac{q_{\text{max}} b C_o}{(1 + b C_o)} \]  
\[ q_e = K_F C^{1/n} \]  
\[ q_e = q_{\text{m}} e^{-\beta \phi} \]

where \( C_o, q_{\text{m}}, \) and \( q_{\text{max}} \) symbols are the remaining LOVX concentration in mg/L, the LOVX uptake capacity in mg/g, and the predicted maximum LOVX uptake capacity in mg/g.

Table 2. Theoretical Mathematical Parameters of the Studied Kinetic Models for the Fixed Bed Column Systems

| parameters | Thomas model | Adams–Bohart model | Yoon–Nelson model |
|------------|--------------|---------------------|------------------|
| height (cm) | flow rate (mL/min) | concentration (mg/L) | \( R^2 \) | \( K_{T0} \) ((L/h·mg)/(10^4)) | \( q_{\text{m}} \) (mg/g) | \( R^2 \) | \( K_{A0} \) (L/g·min) | \( N_{b0} \) (mg/L) | \( R^2 \) | \( K_{YN} \) (min^{-1}) | \( t \) (min) |
| Bed height | | | | | | | | | | | |
| 1 | 5 | 20 | 0.98 | 2.87 \times 10^{-4} | 76.92 | 0.91 | 1.75 \times 10^{-4} | 12061.7 | 0.98 | 0.0057 | 1151.9 |
| 2 | 5 | 20 | 0.98 | 3.75 \times 10^{-4} | 41.05 | 0.93 | 2.23 \times 10^{-4} | 62123 | 0.98 | 0.0075 | 1230 |
| 3 | 5 | 20 | 0.97 | 3.85 \times 10^{-4} | 30.35 | 0.96 | 2.46 \times 10^{-4} | 4340.23 | 0.97 | 0.0077 | 1364 |
| 4 | 5 | 20 | 0.98 | 3.65 \times 10^{-4} | 25.33 | 0.98 | 2.7 \times 10^{-4} | 3399.2 | 0.98 | 0.0073 | 1519.6 |
| Flow rate | | | | | | | | | | | |
| 4 | 5 | 20 | 0.98 | 3.65 \times 10^{-4} | 25.33 | 0.98 | 2.7 \times 10^{-4} | 3399.2 | 0.98 | 0.0073 | 1519.6 |
| 4 | 10 | 20 | 0.97 | 3.095 \times 10^{-4} | 46.6 | 0.96 | 2.095 \times 10^{-4} | 66220.5 | 0.97 | 0.0062 | 1398.1 |
| 4 | 15 | 20 | 0.98 | 3.55 \times 10^{-4} | 60.14 | 0.89 | 2.055 \times 10^{-4} | 9229.2 | 0.98 | 0.0071 | 1202.8 |
| 4 | 20 | 20 | 0.98 | 4.22 \times 10^{-4} | 60.5 | 0.85 | 1.8 \times 10^{-4} | 11290.2 | 0.98 | 0.0084 | 906.52 |
| LOVX concentration | | | | | | | | | | | |
| 4 | 5 | 10 | 0.99 | 6.83 \times 10^{-4} | 15.28 | 0.98 | 6.39 \times 10^{-4} | 1876.9 | 0.99 | 0.0068 | 1834.1 |
| 4 | 5 | 20 | 0.98 | 3.65 \times 10^{-4} | 25.33 | 0.98 | 2.7 \times 10^{-4} | 3399.2 | 0.98 | 0.0073 | 1519.6 |
| 4 | 5 | 30 | 0.95 | 1.72 \times 10^{-4} | 32.43 | 0.98 | 1.216 \times 10^{-4} | 4664.2 | 0.95 | 0.0051 | 1297.5 |
| 4 | 5 | 40 | 0.96 | 1.58 \times 10^{-4} | 30.5 | 0.93 | 8.25 \times 10^{-5} | 5185.14 | 0.96 | 0.0063 | 914.04 |

Figure 6. Fitting of the LOVX uptake results by KNTs with different isotherm models.

\[ K_q, n, b, \) and \( \beta \) symbols are the constants of the Freundlich model that related to the LOVX uptake capacity, Freundlich model that related to the LOVX uptake intensity, Langmuir model, and D-R model, respectively. The \( \epsilon \) and \( q_{\text{m}} \) symbols of the D-R model are the Polanyi potential and the predicted maximum LOVX uptake capacity, respectively. The results are highly descriptive by the Langmuir isotherm hypothesis rather than by Freundlich’s assumption considering both the determination coefficient \( (R^2) \) and the chi-squared \( (\chi^2) \) (Figure 6 and Table 3). Therefore, the adsorbed LOVX molecules by KNTs are of monolayer form and adsorbed by homogeneously distributed sites on its surface achieving a \( q_{\text{max}} \) of 442 mg/g.16 Additionally, the theoretically estimated RL values demonstrated favorable reactions between the KNTs and the adsorbed LOVX molecules (Table 3).

The D-R isotherm results show significant indications about the type of operating reactions as well as the theoretical capacity of KNTs for the LOVX pollutants (Figure 6). The Gaussian energy for the adsorption reaction of LOVX by KNTs is 2.05 kJ/mol, which signifies physical adsorption reactions13 (Figure 6 and Table 3). Moreover, the predicted LVOX \( q_{\text{max}} \) for KNTs as a parameter from the model is 408 mg/g.

2.4.2. Thermodynamic Properties. The thermodynamic evaluation for the LVOX adsorption reactions by KNTs was
accomplished considering the batch adsorption results of different tests at different operative temperature values (25–45 °C). The controlling variables were studied at 360 min, 25 mg/L, 150 mL, 0.02 g, 25 °C, and pH 8 for the contact time, the LVOX concentration, the studied volume, the KNT dosage, the reaction temperature, and pH, respectively. The essential parameters that control the thermodynamic properties for the reaction between KNTs and LVOX molecules are the enthalpy (∆H°), the entropy (∆S°), and the Gibbs free energy (∆G°). The values of ∆H°, as well as ∆S°, were appraised as a theoretical parameter for the linear fitting of LVOX data with van’t Hoff formula (eq 7) (Figure 7 and Table 3). The Langmuir constant (K_L) value was calculated directly from eq 8 where the used K_L constant value refers to the ratio between the LVOX uptake capacity by KNTs and its equilibrium concentration. Additionally, the theoretical values of ∆G° were calculated from eq 9 directly (Table 3):

\[
\ln(K_L) = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT}
\]  

\[K_L = K_D \times 55.5\]  

\[\Delta G^0 = -RT \ln K_L\]  

The negative sign of the enthalpy and enthalpy verified uptake of LVOX by KNTs by exothermic reaction and the randomness of this reaction reduced systematically with conducting the tests at high operative temperature values (Table 3).33 The assessed free energy (∆G°) at all the considered temperature values is of negative sign, i.e., the uptake reaction of LVOX by KNTs display spontaneous, favorable, and feasible properties.33 The recognized values of both entropy and free energy are related to physical adsorption reactions, which induce the isotherm studies.34

\[\Delta G^0 = -RT \ln K_L\]  

2.5. Adsorption Mechanism. The synthetic KNTs as an adsorbent are composed of highly active scrolled sheets of kaolinite. Therefore, they are characterized by high dominance and exposed active siloxane groups (Si–OH and Al–OH).35 These groups are highly active groups and with very high affinity to complex with different dissolved ions and molecules or attract with them by electrostatic attraction, known as outer surface complexation and inner surface complexation processes.35 The chemical complexation between the drug molecules and KNT functional groups involved the formation of hydrogen bonding between the siloxane groups or the basal oxygen of the KNT sheets and the carboxylic acid groups of LVOX 36. On the other hand, the electrostatic attraction between the ionized species of LVOX and the charged binding sites of KNT surfaces induced the formation of the complexes under the effect of the Coulombic forces of the silicate layers.35 Other studies demonstrated an essential role for the predicted intercalation of the multilayered kaolinite scrolls by the LVOX molecules.36

2.6. Comparison Study. The LVOX uptake capacity by KNTs was compared with reported capacities from some studied adsorbents in the literature as the natural kaolinite without modifications, natural and synthetic zeolite, porous silica, activated charcoal, and silica/iron oxide composite (Table S1). The presented capacities in the table demonstrated the excellent adsorption capacity of KNTs for LVOX as toxic and biological active water pollutants as compared to different types of synthetic and natural materials.

3. CONCLUSIONS

Kaolinite nanotube particles were synthesized by sonication-induced chemical scrolling for natural kaolinite flakes and characterize as an innovative fixed bed in the decontamination of LVOX residuals. The synthetic types display mesoporous properties (12 nm in pore diameter) and promising surface area (105 m²/g). The continuous fixed-bed column study for 1800 min verified the applicability of the KNT bed to remove 80.4% of the present LVOX molecules in the treated effluent with a total purified volume of more than 9 L. This removal percentage was recognized after using the KNT bed of 4 cm in height, a flow rate of 5 mL/min, a pH value of 8, a total flow interval of 1800 min, and an LVOX concentration of 10 mg/L. The dynamic properties of the KNT bed-based column system were explained based on Thomas, Adams–Bohart, and the

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Table 3. Estimated Equilibrium and Thermodynamic Parameters for the Uptake of LVOX by KNTs

| model       | parameters | LVOX |
|-------------|------------|------|
| Isotherm models |            |      |
| Langmuir    | q_{max} (mg/g) | 442.4 |
|             | b (L/mg)     | 0.0068 |
|             | R^2          | 0.98  |
|             | R_L          | 1.14  |
|             | LVOX         | 0.33–0.85 |
| Freundlich  | 1/n         | 0.29  |
|             | K_F (mg/g)   | 83.45 |
|             | R^2          | 0.85  |
| D-R model   | β (mol²/kf²) | 0.118 |
|             | q_{max} (mg/g) | 408  |
|             | R^2          | 0.88  |
|             | R_L          | 2.14  |
|             | LVOX         | 2.05  |
| Thermodynamic parameters | ΔG° (kJ mol⁻¹) | 298.15 K -20.03 |
|             | 303.15 K -19.92 |
|             | 308.15 K -19.38 |
|             | 313.15 K -18.74 |
|             | 318.15 K -18.66 |
|             | 323.15 K -18.67 |
|             | ΔH° (kJ mol⁻¹) | -39.23 |
|             | ΔS° (J K⁻¹ mol⁻¹) | -64.38 |

Figure 7. Fitting of the LVOX adsorption data by KNTs at different temperature values with the van’t Hoff formula.
Yoon–Nelson kinetic models. The Langmuir isotherm properties and thermodynamic studies emphasized physical adsorption reactions of spontaneous nature, exothermic type, and monolayer form with a theoretical $q_{\text{max}}$ of 442.4 mg/g.

4. EXPERIMENTAL WORK

4.1. Materials. The natural kaolinite mineral was delivered directly as a powder from the Central Metallurgical Research & Development Institute in Egypt. NaOH pellets, methanol, dimethyl sulfoxide (DMSO), and surfactant of cetyltrimethylammonium bromide (CTAB) (Sigma-Aldrich, Egypt) were of high purity grade and used in the scrolling steps without any physical or chemical purification. Levofoxacin antibiotic (LVOX) of $C_{18}H_{20}N_{3}O_{4}F$ chemical structure and more than 98% chemical purity (Sigma-Aldrich, Egypt) was used in the adsorption tests.

4.2. Synthesis of Kaolinite Nanotubes (KNTs). The essential procedures, which were followed during the synthesis of KNTs, were completed based on Abukhadra et al.16 First, 15 g of the ground kaolinite particles were mixed for 24 h with about 50 mL of diluted DMSO (80%) forming hybrid kaolinite layers intercalated with DMSO molecules. Then, the resulted DMSO hybrid kaolinite particles were washed with methanol for five runs and each washing run consumed about 20 min. This step resulted in replacing of the DMSO molecules by methanol molecules producing methoxy kaolinite. After that, the methoxy kaolinite particles were mixed for 48 h with a previously prepared CTAB solution (50 mL) to ensure effective expansion for the layered units from each other. The exfoliation process was endorsed by the ultrasonic waves after adjusting the power at 240 W. The sonication treatment continued for another 48 h causing rolling of the layered units into nanotubes. Finally, the product was washed carefully with methanol followed by distilled water and dried to be used in the adsorption studies.

4.3. Characterization. The crystallinity of KNTs as well as their precursor materials was determined by a PANalytical X-ray diffractometer (Empyrean) within a scanning range from 5° to 70°. The morphological SEM images were captured by a scanning electron microscope (Gemini, Zeiss-Ultra SS) at 30 kV as the applied accelerating voltage. The internal features were assessed using the TEM images from a transmission electron microscope (JEOL-JEM2100) at about 200 kV as an adjusted acceleration voltage. The structural chemical groups were studied by a Fourier transform infrared spectrometer (FTIR-8400S; Shimadzu) within the examined frequency range from 400 to 4000 cm$^{-1}$. The average pore diameter as well as the surface area were measured based on the plotted N$_2$ adsorption/desorption isotherm curve using a Beckman Coulter SA3100 surface area analyzer after treating the data using the BJH and BET methods. The detection of the remaining LVOX molecules in the treated samples was accomplished using an HPLC system (Merck/Hitachi).

4.4. Fixed-Bed Column Adsorption of LVOX. The column adsorption of LVOX in the presence of KNT bed was accomplished in a prepared column system composed of a borosilicate cylinder that is 15 cm in length and 2 cm in internal diameter. The KNT bed was packed within two layers of upper polyethylene wool and lower plastic mesh to avoid the expected leaching of the used KNT particles during the pumping of the polluted water through the column. The flow rates of the pumped LVOX solution in the column were controlled using a peristaltic digital pump. The efficiency of the KNT bed was followed by chemical detection for the LVOX in the treated samples after regular flow intervals of 60 min using the HPLC system (Merck/Hitachi). This was carried out as triplicate experiments, and all the plotted data were studied in its average values with a standard deviation of less than 4.75.

The reported breakthrough time intervals and the exhausting time intervals in addition to the general shapes of the curves were used to study the performance of the KNT column considering the breakthrough point at an LVOX removal percentage of 10% and the exhausted or the saturation point at 95% as the LVOX removal percentage. Additionally, the other mathematical parameters of the KNT fixed-bed column such as the total volumes of the treated LVOX solutions ($V_{\text{eff}}$ (mL)), the adsorption capacity of the KNT bed ($C_{\text{ad}}$ (mg/g)), the total LVOX molecules adsorbed by KNT bed ($q_{\text{total}}$ (mg/g)), the total LVOX molecules passed into the column during the total flow period ($M_{\text{total}}$ (mg/g)), the equilibrium LVOX adsorption capacity ($q_{\text{eq}}$ (mg/g)), and the total LVOX removal percentage ($R_{\%}$) were calculated from eqs 1 to 6:

\begin{equation}
V_{\text{eff}} = Q \times t_{\text{total}}
\end{equation}

\begin{equation}
C_{\text{ad}} = C_{0} - C_{\text{eff}}
\end{equation}

\begin{equation}
q_{\text{total}}(\text{mg}) = \frac{QA}{1000} = \frac{Q}{1000} \int_{0}^{t_{\text{total}}-t_{\text{total}}} C_{\text{ad}}\,dt
\end{equation}

\begin{equation}
= \frac{Q}{1000} \int_{0}^{t_{\text{total}}} (C_{0} - C_{t})\,dt
\end{equation}

\begin{equation}
M_{\text{total}}(\text{mg}) = \frac{C_{0}Qh_{\text{total}}}{1000}
\end{equation}

\begin{equation}
q_{\text{eq}}(\text{mg/g}) = \frac{q_{\text{total}}}{X}
\end{equation}

\begin{equation}
\text{total removal, } \% (R_{\%}) = \frac{q_{\text{total}}}{M_{\text{total}}} \times 100
\end{equation}

The $C_{0}$ and $C_{\text{eff}}$ symbols refer to LVOX starting concentrations and the remaining LVOX concentrations, respectively. The $Q$, $A$, $t_{\text{total}}$, and $X$ symbols are the indicator symbols of the volumetric flow rate (mL/min), the measured areas of the breakthrough curves, the total time for the flow of the LVOX solutions in min, and the quantities of the packed KNT particles in g, respectively.

4.5. Regeneration of KNT Beds. The regeneration of the KNT bed to be reused several times in the decontamination of LVOX in a continuous column system was performed for five runs. The used KNT particles in the bed were rinsed using NaOH solution diluted with distilled water (2.5%), which was pumped into the column at a flow rate of 1.5 mL/min and this was reduplicated three times. After that, the column was addressed in a series of LVOX removal runs to investigate the recyclability properties of the KNT bed in the continuous column system. All the recyclability tests were carried out at the pre-identified best conditions from the experimental inspection of the main variables.
**ASSOCIATED CONTENT**

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.0c03785.

The nitrogen adsorption/desorption isotherm curves of the synthetic kaolinite nanotubes (KNTs) (Figure S1), the TGA curves of KNTs (Figure S2), and comparison between the uptake capacity of the used KNTs and other adsorbents in the literature (Table S1) (PDF)

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Notes

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