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Development a New Carbon Nanocomposite Containing MWCNT as adsorbent for Effective Removal of Cloxacillin

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Abstract

Antibiotics along with their metabolites due to their toxicity and low biodegradability have adverse effects to human and animal health. This work can help to monitor and elimination of the residue of the cloxacillin (Clox) antibiotics in two ways: the first part involves design and fabrication of a new electrochemical nanosensor based on a screen-printed carbon electrode modified with gold nanourchin and graphene oxide for detection and determination of Clox in aqueous media. The second part focuses on the preparation of carbon nanocomposites modified with multi-walled carbon nanotubes (MWCNT/CC) as adsorbent for the removal of Clox from aqueous medium. The MWCNT/CC nanocomposites were made using sol-gel process and then the efficiency of the antibiotic removal was assessed by the designed nanosensor. In Clox removal experiments, the effect of independent variables including pH, exposure time, extent of MWCNTs and amount of adsorbent on the removal of antibiotic as a dependent variable was investigated using response surface methodology. The morphological and physical properties of the suggested adsorbent were explored. The maximum efficiency of Clox removal (97%) was achieved in conditions of using 1.52 g/L of the adsorbent fabricated by 2.9 wt. % of MWCNTs in 0.1 M phosphate buffer solution at pH of 5.0 during 75 minutes. The highest adsorption capacity of the MWCNT/CC was 296 mg/g at optimal conditions.

Keywords: Pharmaceutical Contaminants, MWCNT, Adsorbent, Sensor.

1. Introduction

Cloxacillin (Clox) is a semi-synthetic antibiotic from the class of beta-lactamase-resistant penicillin. This antibiotic is only effective for bacterial infections and does not eliminate viral infections (such as the common cold and the flu) (Elmolla; 2009). Nowadays, excessive antibiotics utilization and subsequently, permeation of these chemicals into the groundwater and surface water resources have led to serious concerns worldwide. Usually, the residues of these drugs, along with their metabolites, enter the environment after digestion and metabolism in the human urine and faeces (Almakki; 2019). However, they may enter the environment via various ways, such as the wastewater streams of the pharmaceutical industries, hospitals and animals. The residues of these compounds due to their toxicity and low biodegradability have adverse effects on human health (Xiong; 2019). The presence of these substances not only causes problems in the process of wastewater treatment and the microbial ecology of surface water, but also results in resistant bacteria domination of other bacteria in the aeration tank of urban wastewater (Szymańska; 2019). The proliferation of antibiotic-resistant bacteria will disturb biological balance and cause unforeseen adverse effects on human and animals. In addition, the presence of antibiotics in wastewater treatment systems may inhibit the activity of sewage bacteria, which can seriously affect the decomposition of organic matter (Hernández; 2019). Due to the potential and actual risk of the pharmaceutical pollutants, awareness the amount of pollution and effective ways to eliminate it can help to preservation of the natural resources and environmental health (Pirsaheb; 2019). In the field of trace antibiotics removal from aqueous, numerous procedures have been recommended so far, such as UV irradiation (Pan; 2019), electrical coagulation (Grehs; 2019), nanofiltration (Lan; 2019), advanced oxidation techniques, such as photolysis (Cuerda-Correa; 2020), Fenton (Wang;2019), electrocatalytic degradation (Misal;2020), biological methods (Kumar; 2019) and adsorption

(Jafari; 2019, Nasseh; 2019). These methods have their own advantages, but they have also disadvantages that make their applications difficult in most cases. For example, secondary pollutants are normally generated in physical methods such as coagulation and centrifugation (Bahrpaima; 2019), and in biological methods it takes a long time and the process efficiency is very low (Crini; 2019). Methods such as chlorination (Chang; 2019), ozonation (Gomes; 2019), advanced oxidation (Anawar; 2019), and nanofiltration (Completo; 2019) are also limited due to their high cost and inefficiency in the presence of antibiotics.

Adsorption is one of the commonly adopted approaches in treatment of water and wastewater that taken into consideration as a suitable method due to its low cost, high flexibility, easy design and handling, non-sensitive and high ability to remove toxic and hazardous substances (Wang; 2019, Esfandiyari; 2017). Various sorbents such as silica (Gounani; 2019), sepiolite (Wu; 2020), zeolite (Souza; 2020), bentonite (El Maataoui; 2019), chitosan (Mahmoud; 2020), activated carbon (Teixeira; 2019), clay (Premarathna; 2019) and agricultural wastes (cotton and sugarcane, corn cob, rice bran and coconut (Cukierman; 2019- Dai; 2020- Hasanzadeh; 2020) have been used to remove antibiotics from aqueous solutions.

Based on the above limitations, the manufacture of adsorbents with high absorption capacity and rapid recovery capability are required for fast and easy separation of pollutants. Nanotechnology with unique properties of nanoscale materials can solve this problem (Malakootian; 2019). One of the prominent features that has led to much attention being paid to the nanomaterials is believed to be their high surface-to-volume ratio. Nanoparticles can have high potential to absorb contaminants from polluted environments due to this eminent feature and other favorable properties (Noronha; 2019). The use of carbon nanotubes today has been widely investigated as a promising solution for the removal of various types of pollutants due to their high surface area, small, hollow and layered structures, flexibility and high elasticity (Xiang; 2019).

Nevertheless, CNTs have been suggested to be separate difficultly because of their high diffusion capability and distribution in aqueous media. Accordingly, the resulting aqueous carbon colloids are able to enter any medium, and annihilate the cell wall via contact with skin or pass into both human and animal food chain (Mohanta; 2019). In order to avoid the dispersion of CNTs and their subsequent separation from aqueous media, various procedures have been offered including filtration (Yang; 2011), using chemicals (Zhang; 2019), magnetization (Masotti; 2013), embedment of CNTs in composite matrix (Kunde; 2019, Chae; 2019).

Hopefully, the carbon allotropes could be easily modified or combined with other materials to increase their absorption capacity and separate (Esfandiyari; 2017). Nanocomposites have better performance than their primary constituents. In the meantime, carbon composites have shown remarkable physical, mechanical, chemical and thermal properties (Yadav; 2019). Due to their structural porosity, these materials are lightweight and have a high specific surface area while maintaining high thermal stability (Ahmadi; 2016).

Electrochemical techniques based on modified electrodes due to their fast response and capability in being online, sensitivity and selectivity in tracing of elements and compounds are more popular than other measurement methods (Shojaei; 2016, Jafari; 2017). Modification or integration of nanoparticles such as graphene, CNTs or gold nanoparticles in the structure of electrodes can contribute to the precision, sensitivity and performance of electrochemical sensors (Jafari; 2021).

In this study, aiming to utilization of the exclusive features of MWCNTs in the adsorption of medicinal pollutants from water as well as resolving the problem of their dispersion in aqueous solutions, a novel MWCNTs-containing carbon nanocomposite has been designed and manufactured using silane polymers (sol-gel method). Optimization of antibiotic removal conditions by adsorption requires investigation of the effect of numerous experimental factors

on the efficiency of the removal process. Response surface method (RSM) is a statistical technique by which through systematically performing a limited number of experiments, in addition to obtaining information on the effect of experimental variables on the response, one can also predict optimal operating conditions (Etemadifar; 2014). So far, RSM has been used to optimize the removal conditions of some antibiotics by adsorption (Okoli; 2019, Pirsaeheb; 2019, Sarker; 2019).

In order to, detection and determination of trace Clox antibiotic in aqueous media during adsorption on carbon nanocomposite, a new electrochemical nanosensor was fabricated by immobilizing gold nanourchins (GNU) and graphene oxide (GO) nanolayer on screen-printed carbon electrode (SPCE) surface. This can expand the electron transfer rate and lead to availability of more Clox in the redox reaction due to agglomeration and catalytic activity of GNU and GO (Jafari; 2021). Also, RSM was applied to optimize the Clox removal from synthetic solutions polluted with Clox using MWCNTs modified carbon composite. For this purpose, the central composite design (CCD), which is one of the most widely used response surface designs, was implemented for assessing of effect of operational parameters such as MWCNTs amount for preparation of carbon composite, adsorbent dose, pH and contact time on the removal efficiency. The results of the CCD implementation were used to estimate the contribution of experimental factors and their interactions in response as well as to determine the optimal conditions. The kinetics and isothermal data of the adsorption of Clox antibiotic on MWCNTs/carbon composite (MWCNT/CC) surface were analyzed.

2. Experimental

2.1. Chemicals and devices

In the present experimental study, Cloxacillin (98% purity, Scheme S1) antibiotic was purchased from Sigma-Aldrich (USA). Potassium trimethoxysilane, methanol, phosphoric acid

and sodium hydroxide were obtained from Merck (Germany) and MWCNTs were received from NanoLab Co. (USA). Double-distilled water was used in all experiments to prepare aqueous solutions. The graphene oxide (GO, 3.0 mg/mL) dispersion and gold nanourchins (GNU, 30 $\mu\text{g/mL}$ in H_2O) were obtained from the Sigma-Aldrich (USA) to make an electrochemical nanosensor for the quantity of Clox.

Phosphoric acid and sodium hydroxide were used to adjust the pH of the solutions and a 827 model pH meter (Metrohm Autolab, Netherland) was applied for determination of solution pH. The stirring of aqueous samples was performed using Fartest magnetic stirrer (Model HPM 700, Farzaneh Arman Co., Ltd, Iran) and carbon composite as adsorbent powder was centrifuged by Eppendorf centrifuge device (MiniSpin, Germany). The concentration of Clox was determined using a potentiostat/galvanostat M101 $\mu\text{Autolab}$ type III model instrument (Metrohm Autolab, Netherland) attached to a designed electrochemical nanosensor by differential pulse voltammetry (DPV).

2.2. Detection of Clox

In the present research, an electrochemical nanosensor prepared by modifying a SPCE with GO/GNU nanocomposite layer in order to detect Clox. By a micropipette, a drop of 2.0 μL of aqueous GO dispersion (4.0 mg/mL) with pH = 7.0 was deposited on the electrode surface and then dried in a moist chamber (scheme 2). Afterwards, the electrode was washed with distilled water and a drop of 1.0 μL of GNU dispersion (0.1 mg/mL) was placed on the electrode surface. The procedure of preparing the modified sensor are illustrated in scheme S2.

In the DPV measurements of Clox, the electrochemical response of the designed sensor versus increment of Clox concentration in the solution was first assessed. Accordingly, several solutions containing certain concentrations of Clox were prepared and then analytical signal of the modified electrode were recorded in the prepared solutions by DPV. Next, a linear diagram of the electrochemical response of the designed sensor, namely, the oxidation current of Clox

at the electrode surface, was depicted against the concentration of Clox. The obtained diagram was used to calculate the concentration of Clox in subsequent experiments.

In order to determine Clox concentration in the removal trials using prepared nanocomposites, at specified intervals, 5.0 mL samples from the solution that had been in contact with the adsorbent composite was transferred directly to the electrochemical cell and the response of the designed nanosensor was recorded. The residual concentration of Clox in solution was then calculated using the above-mentioned diagram.

2.3. Fabrication of the suggested adsorbent nanocomposite

In this study, the suggested adsorbent, namely, carbon nanocomposite, based on graphite modified with MWCNTs (MWCNT/CC) was made using a sol-gel process at room temperature according to previous studies (Esfandiyari, 2017). In brief, 20.0 μ L potassium trimethoxysilane was added to 4.0 mL of ethanol/water solution (9:1) (v/v) (preparation of sol). The pH of the obtained solution was adjusted at 4.5 with the aid of 0.1 M HCl solution. Afterwards, the solution was stirred for 90 minutes using magnetic stirrer in order to hydrolyze the silanol compound. Subsequently, the color of the mixture became milky because of the hydrolysis of the silane compound and the silane network formation (formation of gel). A given volume of sol-gel mixture was then added to a specified homogenous mixture of MWCNTs/graphite with a certain weight ratio. A carbon paste was consequently formed, which was left at ambient temperature in order to evaporate the solvents. The dried paste was then posited for extra 2 h in an oven at 50 °C to be transformed into the carbon composite (MWCNT/CC), which was used as an adsorbent in the later stages.

2.4. Optimization of Clox removal

In order to achieve the highest antibiotic removal rate from aqueous solutions using the prepared carbon nanocomposites, independent variables including pH (2.0-11.0), contact time

(20-120 min), MWCNTs' content in the carbon nanocomposite (0.1-5.0 wt%) and amount of adsorbent (MWCNT/CC) in aqueous solutions (0.2-1.0 g/L) was chosen and their effect on antibiotic removal rate was investigated. Antibiotic removal conditions were optimized by using the carbon nanocomposites based on response surface statistical method and a mathematical model was developed to predict Clox removal from the aqueous solutions. In fact, with the aid of this statistical method and with the least number of experiments, the simultaneous effect of all four independent variables and their interactions on antibiotic removal rate were studied thoroughly. The experimental design, statistical analysis of the obtained data and the mathematical modeling were performed using Design of Expert V.11 software package. Via introducing the variables and their studied range into the software (Table 1), 30 tests were proposed in order to optimize the removal efficiency, which are summarized in Table 2 together with their respective results.

Table 1

Table 2

At optimum conditions, 152 mg of carbon nanocomposites (MWCNT/CC) containing 2.9 wt % of MWCNTs was added to 100 mL of 0.1 M phosphate buffer (pH = 5.0) containing 10.0 ppm Clox (10.0 μ M) and stirred using a magnetic stirrer for 75 minutes at a speed of 500 rpm, in order to create a balance between the composite adsorbent and the Clox solution. The solution was then centrifuged for 10 minutes at 5000 rpm to remove the carbon nanocomposite. Residual Clox in the solution was measured using a designed nanosensor by DPV. All experiments were repeated three times in order to increase the reliability and accuracy of the results, and the mean of the results was then reported. The efficiency of antibiotic removal (Clox Re) by carbon nanocomposite was calculated using the following equation:

$$Clox\ Re\ (\%) = \frac{C_0 - C_t}{C_0} * 100 \quad \text{Eq. (1)}$$

In this equation C_0 is the initial concentration of Clox and C_t is the actual antibiotic concentration in solution (after contact time of t min). In addition, the adsorption capacity of carbon nanocomposite (Q) particles (mg of Clox absorbed per gram of nanocomposite) was calculated using the following equation:

$$Q = \frac{(C_0 - C_t)V}{m} \quad \text{Eq. (2)}$$

where, V is solution volume (L) and m is used mass of the nanocomposite (g).

2.5. Modeling of adsorption kinetics and isotherms

At this stage, experiments were performed by equilibrating 152 mg of adsorbent (MWCNT/CC) containing 2.9 % wt. MWCNTs in 100 mL Erlenmeyer flasks containing 10.0 ppm (100 mg/L) Clox solution at pH of 5.0. The mixture was shaken on a magnetic stirrer at 500 rpm by keeping temperature constant (25 °C). At intervals of 5 - 120 min, the residual Clox concentration was measured after sampling and separating of the adsorbent (based on Section 2-2).

Also, to investigate the equilibrium adsorption of Clox on sorbent, solutions with different initial concentrations of antibiotic; 30, 50, 80, 100, 120 and 150 mg/L were prepared at pH = 5.0 and after adding 152 mg of carbon nanocomposites containing 2.9 wt% MWCNTs, solutions were placed on magnetic stirrer for 1 hour (equilibrium time). The concentration of residual Clox in the solution was also measured using the designed nanosensor in Section 2-2. Langmuir and Freundlich isotherms were used to analyze the equilibrium data and pseudo-first-order and pseudo-second-order models were also used to investigate the kinetics of the adsorption process. The constants of the adsorption kinetics and isotherm data were extracted to interpret the results, capacity, type and energy of the adsorption process.

2.6. Study of structural properties of adsorbent

Morphology of carbon composites containing MWCNTs was observed using a Mira 3-XMU model field emission scanning electron microscope (Tescan, Japan). N₂ adsorption/desorption isotherms at 77 °C were utilized to determine pore diameter, porosity and total pore volume of the prepared carbon composites using a Belsorp analyzer (BEL Inc., Japan). The Brunauer-Emmett-Teller (BET) method was also applied in order to ascertain specific surface area of the composites. Also, the zero-charge point (pH_{pzc}) of the prepared adsorbent was determined using a Zetasizer 2000 model Zeta-meter instrument (Malvern, UK).

3. Results and discussion

3.1. Characterization of the developed nanosensor

Figs. S1A and S1B show SEM images of the surface of SPCE modified with GO and GNU/GO, respectively. As shown in Fig. (S1A), the surface of SPCE is roughened as a result of modification with GO, plate structure of which can be seen on the electrode surface. After immobilization of the GNU on the GO modified SPCE (Fig S1B), the effective electrode surface is increased, and therefore, their presence is anticipated to improve the electron transfer rate from the electrode surface, therewith enhancing the electrode sensitivity to Clox molecules. These results are consistent with the results of Sangili et al (2020) for surface modification of electrodes with graphene oxide / gold nanoparticles to increase surface area and improve electron transfer rate.

3.2. Characterization of carbon nanocomposites modified with multi-walled carbon nanotubes (MWCNT-CC)

The FESEM images of morphology of the carbon composite lacking MWCNTs (Fig 1A) and carbon nanocomposite containing MWCNT (fig 1B) are shown in Figure 1. As can be seen, the addition of MWCNT to the carbon composite has created numerous holes and porous

structure in the carbon composite. This porous structure will be very effective in the adsorption process of antibiotics in aqueous.

TEM image taken from the carbon nanocomposites containing MWCNTs is exhibited in Fig. 1C. A bundle of carbon nanotubes outed from the surface of carbon nanocomposites is seen in the image. The presence of the nanotubes on the surface, ends of which are located inside the carbon matrix, significantly providing the nanocomposite's porosity, resulting in enlargement of the surface area and active sites essential for Clox adsorption. Similar findings have been reported on adsorbent containing CNTs by other researchers (Hudaib; 2018, Pourzamani; 2018).

Figure 1D shows the surface element analysis and elemental distribution (mapping) of the carbon nanocomposite modified with MWCNTs. Carbon, which is the main constituent of the porous structure of the designed composite in the present work, accounts for the highest percentage (79.8%) and silicon and oxygen, which belong to the silane precursor for the preparation of sol-gel solution, are found to be less abundant on the surface of the carbon nanocomposite.

Fig 1.

The adsorption–desorption isothermal curves of unmodified carbon composite and carbon nanocomposites modified with MWCNTs are shown in Fig. 2. The curves show that the incorporation of carbon nanotubes in the carbon composite structure has increased the volume of adsorbed nitrogen gas sharply in the relative pressure region of 0.7 to 0.9, which may be attributed to the capillary density inside the structure of the nanocomposite as well, decisively confirmed their mesoporous features (Sharifpour; 2020).

The calculations of the specific surface area, pore diameter and total pore volume were performed using BET method, the results of which are presented in Table 3. As the results of this table show, the texture properties of the nanocomposites have been greatly improved via

the addition of MWCNTs to the carbon matrix. It can be deduced that specific surface area and pore diameter of the nanocomposites grew more than 4-fold because of using carbon nanotubes. The opening of the pore diameter can help more absorption of the antibiotic molecules onto the surface of the nanocomposite, thus, enhancing their removal from aqueous solutions.

Table 3.

Overall, it can be stated that due to utilization of sol-gel method and the addition of MWCNTs for construction of carbon nanocomposite, the surface area, total pore volume, and average pore size of the active carbon treated with sol gel (composite without MWCNT) have increased dramatically. This may indicate the more porous structure of the composite surface (Esfandiyari; 2017). Although, mixing of MWCNT with AC using sol gel importantly decreased the adsorption/purification ability and surface area of the MWCNT; but CNTs can be easily separated after adsorption with the help of a paper filter.

To evaluated the surface charge of carbon nanocomposites modified with MWCNTs, the isoelectric point (a certain value of pH at which the net electric charge point is equal to zero) were determined via measurement of zeta potential in the pH range of 2-10. The results are shown in Fig S2. The adsorbent's isoelectric point prepared was measured to be 5.4. This means that the surface charge of carbon nanocomposites at values below 5.4 is positive due to the protonation of functional groups such as hydroxyl on the surface of nanocomposites or oxygen at silanol network and conditions are provided for the adsorption of antibiotic anionic molecules in solution. The surface charge of the composite at $\text{pH} \geq \text{pH}_{\text{pzc}}$ ($\text{pH} > 5.4$) is negative due to the removal of the proton from the negatively charged hydroxyl groups and creates a repulsive force between the antibiotic molecules (negative surface charge) and the adsorbent surface (.

3.3. FTIR study

To probe the occurrence of the adsorption of antibiotic molecules on the functionalized groups of adsorbent FTIR spectroscopy were performed. FTIR spectra of prepared MWCNT/CC, as well as MWCNT/CC after the Clox adsorption process are presented in Fig 3 and Table S1.

In the FTIR spectrum of MWCNT/CC, a characteristic absorption peak at 1143 cm^{-1} is evident corresponding to COO group, and a broad absorption peak is seen at $3357\text{--}3502\text{ cm}^{-1}$, which are assigned to O-H stretching vibrations in the structure of the adsorbent nanocomposite. In the FTIR spectrum of the nanocomposites after the adsorption process of Clox, the characteristic peaks of Clox, i.e. 3502 , 3357 , 1764 , 1604 , 1504 , 1419 , 1334 and 773 cm^{-1} are present (Schneider; 2018), which confirm the adsorption of Clox molecules onto the MWCNT/CC surface.

Fig 3.

3.4. Detection of Clox using the modified electrode

Electrochemical response of three types of SPCEs, namely, bare SPCE, GO-modified SPCE and GNU/GO/SPCE, to Clox was assessed by cyclic voltammetry (CV) technique, the results of which are shown in Fig. 4A. In this figure, the voltammograms are plotted in 0.1 M phosphate-buffered solution in the presence of 0.1 mM Clox. In the presence of Clox the bare SPCE shows an oxidation peak at 0.79 V with a current of around 0.4 nA (curve a). Nonetheless, the current decreases by 0.05 nA after immobilization of GO on the electrode surface, and the oxidation peak exhibits a partial shift to more positive potentials (curve b). One can infer that the modification of the electrochemical sensors by GO reduces surface conductivity or, equivalently, GO reduces electron transfer rate. After immobilization of GNU on the surface of GO-modified SPCE, the oxidation current of Clox is observed to be increased at the electrode surface and the oxidation peak demonstrates a shift to lower potentials. Thus, one can deduce that the desirable properties of GNU, especially their outstanding conductivity,

play an important role in elevation of the surface conductivity and enhancing the electron transfer at the electrode surface (Jafari; 2021).

In order to evaluate the validity of the modification steps of the electrode, analytical responses of the modified and bare SPCEs, as electroactive probes, to $K_3 [Fe (CN)_6]$ (1.0 mM) were determined, the results of which are demonstrated in Fig. 4B. A perspicuous reversible CV peak pair at 0.27 V is observed in the CV responses of the bare SPCE probe (curve a). Nevertheless, it is seen that the modification of the SPCE with GO alleviated the reversible CV peak pair of the probe. (curve b). Moreover, the reduction and oxidation potentials of the probe is seen to be shifted to more positive and negative values, respectively. The presence of a negative charge on GO, which exerts a repellent force to the negatively charged $[Fe (CN)_6]^{3-/4-}$, as well as the formation of an isolating layer by the GO, which hinders the $[Fe (CN)_6]^{3-/4-}$ ions from approaching to the electrode surface can be regarded as the reasons of the observed phenomenon. Accordingly, the oxidation and reduction processes of the probe occur more difficultly.

It has been discerned that GO, as a semiconductor, has a reducing effect on electricity, but, some other researchers presume electrocatalytic effects of GO to be more prominent (Dehghani; 2018, Azimzadeh; 2016, Jafari; 2018). The curve c in Fig 9, demonstrates significant augmentation of both cathodic and anodic partial currents of the probe after the modification of GO/SPCE with GNU. This can be attributed to various factors including substantial growth of the effective surface area of the electrode in the presence of the conductive nanoparticles as well as the outstanding electrical conductivity and the eminent electron transfer coefficient of gold (Hajihosseini; 2016, Aghili; 2017). As a result, the oxidation and reduction of the probe happens readily in the presence of GNU on the surface of the electrode.

The behavior of the designed sensor was investigated at different Clox concentrations to appraise the sufficiency and performance of the sensor in Clox detection. Therefore, a GNU/GO-modified SPCE was prepared according to the mentioned procedure and then situated in a phosphorus solution (0.1 M) at pH of 7.0 in the presence of various concentrations of Clox. Afterwards, DPVs of the sensor as operant electrodes were plotted for a three-electrode set-up.

The results of the changes of the oxidation current of Clox on the surface of the GNU/GO/SPCE versus concentration of Clox in Fig. 4C show that there is a linear relationship at a relatively wide concentration range (20.0–950.0 nM) between the concentration of Clox and its oxidation current on the surface of the designed sensor. The following equation was used to evaluate the performance of the modified electrode to determine the detection limit of Clox (Zare; 2005):

$$C_m = 3s_{bl}/m \quad \text{Eq (3)}$$

where, s_{bl} represents the standard deviation of the measured currents for the GNU/GO modified SPCE in Clox-free solutions. Based on the slope of the diagram ($0.2867 \mu\text{A nM}^{-1}$), the detection limit of the developed sensor for determination of Clox is 8.0 nM.

In order to verify the feasibility of the developed method for Clox analyses in aqueous, the determination of Clox in solutions containing different amounts this antibiotic was carried out using the prepared electrochemical sensor. The recoveries of the spiked Clox, based on three-parallel detections, are listed in Table 4. The values of recoveries are found to be from 90.9 to 109.0 %, and % RSD ranged from 1.4 to 6.2 %. As well, performance of the developed sensor was compared with HPLC, summarized in Table 4. This shows that the suggested sensor has a proper potential for the determination of Clox in aqueous samples, which was comparable to results obtained with HPLC.

Table 4

3.5. Statistical modeling and validation

The conditions of preparation and utilization of carbon nanocomposites with maximum removal efficiency were optimized based on response surface method and a mathematical model were modeled using the results to predict the amount of Clox removal using MWCNT/CC.

Statistical analysis of variance was applied to assess the significance and appropriateness of the proposed model by DOE software. Using the CCD and regression analysis of the data, the extracted model coefficients for the removal of Clox by the prepared nanocomposite are presented as coded values in Table 5 based on the variables of solution pH (A), the contact time of adsorbent with antibiotics solution (B), amount of MWCNTs for fabrication of the nanocomposite (C) and amount of carbon composite as adsorbent (D).

The analysis of variances (ANOVA) statistics for the achieved model was checked. As well, model compatibility and statistical significance were considered using the regained values for correlation coefficients (R^2). The proposed model can be considered to be statistically appropriate at 95% confidence level due to the p-value less than 0.0001 in the ANOVA table (Rahmati; 2021).

In order to analyze the statistical significance of all the expressions in the polynomial equation with 95% confidence level the F test was used. The F value obtained by this method represents the ratio of mean squares corresponding to the regression model and the errors, which equals to 15.93. This is an indication of that the factors represent sufficiently variations of the data from their mean value and the factors effects in presented model are correct and true. On the other hand, differences in the experiments are sufficiently high, and the impact of errors is very low, therefore selected intervals of independent parameters are appropriate (Leili; 2020).

The reported F values for each factor as well as analysis of variance of the data indicate that the encoded factors A, B, C and D are independent variables affecting the removal efficiency of Clox by suggested carbon nanocomposites. In addition, the coefficients of interaction

variables such as AB, AD, BC and CD and A^2 and C^2 are also significant. The results indicate that A^2 , C^2 , D and BC are the most influential factors on Clox removal efficiency and the amount of MWCNTs (C), the contact time (B) and solution pH stand next.

Table 5.

DOE software based on statistical modeling and data analysis gives a quasi-empirical equation for prediction of the Clox removal efficiency under the influence of the four parameters:

$$\text{Clox Re (\%)} = 87.87 - 0.308A - 3.115B + 4.285C + 9.041D + 5.36AB - 1.157AC + 4.835AD + 10.117BC - 2.15BD + 7.98CD - 21.18A^2 - 6.031B^2 - 18.926C^2 - 3.32D^2 \quad (\text{Eq. 4})$$

3.6. The effect of operational parameters on Clox removal

In this study, the RSM was used to determine the optimal conditions for removal of Clox using MWCNT/CC with maximum efficiency. In fact, with the help of this statistical method and with the least number of experiments, the simultaneous effects of all four parameters and their interactions on the antibiotic removal efficiency were studied comprehensively (Etemadifar; 2014). The results of this experiment are presented in Table 2. Also, Figure 5A shows changes in Clox removal efficiency as a function of solution pH and contact time of the carbon nanocomposite with the solution when the MWCNTs and the adsorbent amounts were fixed at 3.21% wt. and 1.31 g/L, respectively. It can be seen that by increasing pH in the range of 4.0 - 6.0, the removal efficiency of Clox using MWCNT/CC rises gently, but at higher pH values (6.1-10.0), the removal rate of Clox declines steeply.

The pH of the solution is an important factor determining the amount of contaminant adsorbed on the adsorbent (Shirgholami; 2017). It can be interpreted that the carboxylic groups (-COOH) in the Clox molecule transform to carboxylate (-COO-) in mildly acidic solutions and become anionic species. On the other hand, the pH_{pzc} of MWCNT/CC was to be 5.4. Since, all adsorbents have positive charge at pH below pH_{pzc} and negative at higher pH_{pzc} , in an aqueous

environment with a pH between 2.8 and 5.4, the electrostatic attraction forces between the opposite charges of the negatively charged functional groups at Clox and the positively charges on carbon nanocomposites are the cause of the adsorption mechanism. In addition, by increasing the pH values to 6.1 and above, regarding the fact that the functional groups of antibiotics as well as the carbon nanocomposite are both negatively charged, rate of absorption of Clox by the adsorbent is significantly diminished. Therefore, it is recommended to use mild acidic to neutral pH (about 6.0) to remove this antibiotic with a developed adsorbent.

Alternatively, it is shown that with extending the contact time of the nanocomposites with the solution containing Clox in the range of 20 to 75 minutes, the antibiotic removal efficiency enhances from 25% to 55%. The contact time of Clox molecules and adsorbent is another important factor affecting the adsorption process. There is a direct relationship between the contact time, adsorption capacity and removal efficiency. As there is a high availability of adsorption sites for antibiotic molecules in the early stages, the absorption of Clox is very quick. However, most adsorbent sites are occupied over time and reach to an equilibrium, hence, the removal process becomes slower. In fact, upon reaching equilibrium the adsorbent surface is saturated by Clox molecules and the adsorbent will not be able to absorb more Clox molecules. Similar outcomes have been described by Saha et al. So, it is clear from the graph that in 75 minutes, a considerable amount of antibiotic is absorbed and then reaches a nearly constant value.

The adsorption capacity of all used adsorbents increases with increasing time until a constant value is reached at a given time and an equilibrium is established. This means that rate of adsorption and desorption of Clox on the adsorbent surface is approximately equal. At this moment, the amount of absorbed Clox is dynamically in equilibrium with the amount of Clox desorbed.

The results of effect of variations of the MWCNTs and the carbon nanocomposite amount on removal efficiency of Clox is shown graphically in Figure 5B. In this figure, the contact time and the pH of the solution are assumed to be constant at 67 min and 5.0; and amounts of MWCNTs and the nanocomposite change in the ranges of 0.5-4.5 % wt. and 0.1 -2.0 g/L, respectively. As can be seen in the figure, by increasing the amount of MWCNTs from 0.5 to 2.5 % wt., the antibiotic removal efficiency increases from almost 25 to more than 65%, but higher amounts of MWCNTs do not have positive effect on the removal efficiency.

On the other side of this three-dimensional diagram, it is shown effect of MWCNT/CC concentration on the removal rate of antibiotic from the solution. It is observed that Clox absorption onto the adsorbent and consequently removal of the antibiotic from the aqueous medium enhances with relatively constant slope through elevating the amount of MWCNT/CC from 0.5 g/L to 1.45 g/L. Then, by increasing the adsorbent concentration to about 2.0 g/L, the removal efficiency levels out. It can be stated that the adsorbent surface has active sites for the adsorption of the suspended matter. Therefore, raising the amount of the consumed adsorbent augments number of active adsorption sites and ultimately, elevates removal efficiency (Tao; 2020). The enhancement of the process efficiency at lower values of the adsorbent is more rapid, but beyond a certain concentration of the adsorbent (1.52 g/L), the removal efficiency does not increase significantly and the adsorption process reaches equilibrium. This amount of adsorbent is considered as the optimum and economical dose of adsorbent.

The main objective of the optimization is to determine the optimum values of the variables to obtain the highest Clox removal efficiency using MWCNT/CC and with the aid of the model obtained from experimental data. The DOE software predicted that the highest removal efficiency of Clox (97%) is achieved at 1.52 g/L of the carbon nanocomposites modified by 2.9 % wt of MWCNTs in 0.1 M phosphate buffer solution at pH of 5.0 containing 10.0 μM of

Clox in 75 min. These conditions were used in subsequent tests, including adsorption kinetics and equilibrium.

3.7. Removal efficiency of the Clox and adsorption capacity of the developed adsorbent

In order to evaluate the adsorption capacity of MWCNT/CC for removal of Clox, solutions with certain concentrations of the antibiotic (50, 100 and 150 ppm) were prepared. Then, 76 mg (1.52 g/L) of carbon nanocomposite modified with 2.9 % wt MWCNTs was added to 50.0 mL of 0.1 M phosphate buffer solution with pH = 5.0 containing Clox. The removal process was performed on the magnetic stirrer for a period of 100 minutes, which is slightly longer than the optimum time. After separating the nanocomposite from the solution, the concentration of Clox remaining in the solution was determined using a designed nanosensor by DPV. Efficiency of the antibiotic removal by the carbon nanocomposite and adsorption capacity (Q) of the carbon nanocomposite particles were calculated using equations 1 and 2, respectively.

Figure S3 shows kinetic data for removal of Clox from the aqueous medium, as percentage of its initial value, at different initial concentration of the antibiotic. It is seen that the percentage of Clox removal reaches to a same value of around 97% for all three Clox concentrations in 70 minutes. However, the initial rate of the antibiotic removal diminishes with increasing concentration of Clox. This may be interpreted in terms of constant number of adsorption sites on the carbon nanocomposite, which hinders proportional increase of the removal rate with rising initial Clox concentration. It should be noted that the removal data presented in Fig S3 are relative values with respect to initial Clox concentrations. This trend is in agreement with published data for adsorption process in similar studies (Esfandiyari; 2017, Jia; 2019).

The results of the kinetic measurement of adsorption of Clox by the carbon nanocomposite particles at different initial concentrations of the antibiotic are presented in Fig S4. According to the graph, the amount of Clox adsorption on the carbon nanocomposite particles reaches to the same value of 295 mg/g, for all three Clox concentrations at the end of the test. Nonetheless,

the period, over which this value is attained is shorter for the two highest concentrations. Furthermore, initial adsorption rate is observed to be enhanced with increasing initial concentration of Clox, which can be attributed to the increased probability of collision between the adsorbent and the adsorbate (Tao; 2020, Sharifpour; 2020).

The regeneration and reuse is one main parameters for adsorbents in order to investigate the stability of the synthesized composites. The stability of MWCNT/CC was considered reusability in six sequential reuse at constant parameters with 1.52 g/ L adsorbent prepared with 2.9 % wt MWCNT, 50 mg/L Clox, pH of 5.0, 75 minutes. The suggested adsorbents were separated from the treated solution after each treatment by whatman cellulosic filter paper and washed using ultrapure water, dried and reused for consequent train (Fig.6). As shown in Fig. 6, six successive Clox-removal yields were found in % 95.5, 90.7, 86.5, 78.1, 70.1, and % 67.8 respectively. The achieved data in Fig. 6 exhibit the reusability of MWCNT/CC adsorbents for treatment of water polluted with Clox antibiotic. In similar studies stated that agglomeration of some of the particles may be results in the decrease of the reusability efficiency (Ghaedi; 2013). The comparison between specifications of some adsorbents for removal of antibiotics are listed in Table 6. The collected data in this table display The capacity and characteristics of the proposed adsorbent are comparable to other adsorbents used to remove antibiotics. Although the surface area of the proposed composite is less than that of multi-walled carbon nanotubes, the important point in this composite is the manufacturing method and the easy method of separating the adsorbent from the aqueous solution. The making method of this nanocomposite, i.e. sol gel procedure is easy and cheap, low temperature technique and low-risk procedures. It is able also to achieve uniform and small sized powders with sol gel method.

Regards to advantages of electrochemistry include easy to use and fast training, easy way to construction and or modifying of electrodes, excellent detection limits, with small analyte volumes, easy miniaturization, good selectivity, accuracy and speed of analysis; performance

of electrochemical sensors is such that it can compete with conventional methods of antibiotic detection such as HPLC, EIS, GC-MS and so on (table 6). In this study; Clox detection sensor was fabricated using only 2 microliters of gold nanoparticles, 4 microliters of graphene oxide, and an inexpensive screen printed carbon electrode. Although the mentioned methods have high accuracy, sensitivity and selectivity, but their use requires expensive equipment and experienced labor. They also have a high analysis time and suffer from complicated and complex sample preparation steps and in some cases low sensitivity and selectivity.

Table 6

3.8. Kinetics of the antibiotic adsorption

Rate constant of the absorption of Clox on MWCNT/CC was determined through curve fitting of the obtained kinetic data to pseudo-first-order and pseudo-second-order kinetic models and the most suitable model was specified (Igberase; 2019). The results of data fitting, factors and correlation coefficients for the kinetic models are presented in Table 7. Comparison of the correlation coefficients obtained from the study of adsorption kinetics shows that highest determination coefficient (R^2) was achieved for the pseudo-second order model, 0.997, which verified that experimental data process of Clox adsorption follows pseudo-second-order kinetic model than pseudo-first-order model. Hereupon, we advise the dominant process in the adsorption of Clox on MWCNT/CC is physical but the occurrence of a little chemical adsorptions might be the key feature in controlling step. (Herrera-González; 2019, Zheng; 2019).

Table 7.

3.9. Equilibrium adsorption study

In order to analyze the results obtained through adsorption studies and their isotherms at equilibrium, two common and widely used models of the Langmuir and Freundlich equations were applied. The coefficients and constants of each of the Langmuir and Freundlich equations are illustrated in Table 8. The data presented in table show that the adsorption process best fitted with Langmuir isotherm model and reveals the Clox absorption on the surface of the MWCNT/CC is monolayer.

As well, the criterion of $1/n$ was obtained between 0 and 1, hence, it be able to said that the adsorbent surface is inhomogeneous (Ponnuchamy; 2020). This point out that the Freundlich model can also be applied to expression the adsorption model of the Clox on MWCNT/CC. Several studies have informed usage of both Freundlich and Langmuir isotherms for interpreting of the adsorption (Nandwani; 2019, Liu; 2016). Conversely, as it is seen in Table 8, correlation coefficient (R^2) of Langmuir model is greater compared with Freundlich isotherm, accordingly, Langmuir model is an ideal model for expression of behavior of Clox adsorption on MWCNT/CC. According to Langmuir model, the capacity of Clox adsorption on MWCNT/CC was considered to be 296 mg/g.

Table 8

3.10. Thermodynamic studies

The Clox sorption behaviors at different concentrations onto MWCNT-CC were critically surveyed at 298, 308, 318 and 328 K, respectively. Accordingly, ΔS° and ΔH° can be obtained from the intercept and slope of the plot of $\ln K$ against reciprocal of absolute temperature, respectively (Fig S5) (Esfandiyari; 2017, Ye; 2019). The calculated thermodynamic parameters are illustrated in Table 9. It is seen that the both ΔH° and ΔS° values are positive. The positive ΔH° value, i.e. 3.046 kJ/mol, indicates that the adsorption process of Clox onto MWCNT-Carbon composite is endothermic (Boukhalfa; 2019). This supports that removal efficiency of Clox on the adsorbent is also enhanced by increasing the temperature. This may be due to the

increasing of molecular motions of the antibiotic in solution and increment of probability collision of the molecules with the adsorption sites on the adsorbent (Ghaedi; 2013).

On the other hand, the positive ΔS° value, i.e. 0.0686 kJ/molK, represents enhancement of the stochastic of the adsorption of Clox antibiotic at adsorbent-adsorbate interface. Furthermore, the adsorption process is confirmed to be spontaneous because of the negative ΔG° values. It is also seen that ΔG° value enhances with elevation of temperature, which reveals higher favorability of the Clox adsorption onto MWCNT-CC surface at low temperatures (Rocky; 2019).

Table 9.

4. Conclusion

In this study, a carbon nanocomposite was prepared using a sol-gel procedure and its capability as an adsorbent for Clox removal from aqueous solutions was studied. Moreover, for detection of Clox in such solutions, an electrochemical nanosensor was designed via modification of SPCEs with GO and GNU. The nanosensor was shown to be able to detect Clox in the concentration range of 20.0-950 nM with a quantitative detection limit of 8.0 nM. The surface structure and elemental analysis of the designed nanocomposite were investigated and the results showed presence of carbon, oxygen and silicon elements in the adsorbent structure with a of porous structure. MWCNTs were also observed on the adsorbent surface. The isoelectric point of the adsorbent, was shown to be 5.4, which was measured using zeta potential analysis. The operational conditions affecting the antibiotic removal process by the aid of the prepared nanocomposites such as solution pH, amount of carbon nanocomposite as adsorbent, amount of carbon nanotubes in fabrication of the nanocomposite, and contact time were optimized using response surface methodology. The results of the statistical analysis and ANOVA showed that square of pH have the most effect on the adsorption of Clox. Effects of square of

MWCNTs amount and adsorbent concentration are in the next order, respectively. The optimum conditions for separation of antibiotics from aqueous solutions were pH = 5.0, contact time of 75 min, concentration of 1.52 g/L of carbon nanocomposite modified with 2.9% wt of MWCNTs. Maximum removal of the antibiotic was predicted to be 97 % in optimum conditions by DOE and the actual value of 95.35 % was measured in the laboratory. Thermodynamics and kinetics of adsorption of Clox on MWCNT/CC were also studied. The adsorption behavior of the antibiotic at equilibrium and the adsorption kinetics were shown to be in accordance with the Langmuir isotherm and pseudo-second order model, respectively. Furthermore, the maximum adsorption capacity of the nanocomposite was determined to be 296 mg/g. Determination of removal efficiencies proved that the nanocomposite is able to reduce the amount of the antibiotic content in aqueous media from 100 ppm to less than 5 ppm.

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Compliance with Ethical Standards

Conflict of Interest The authors declare that they have no conflict of interest.

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Authors' contributions

Amir-Mohammad Golkarieh: Material preparation and data collection;

Navid Nasirizadeh: Conceptualization, Supervision;

Reza Jahanmardi: Writing- Reviewing and Editing;

Saied Jafari: Data collection and analysis;

Mohammad Dehghani: Data analysis and first draft of the manuscript;

All authors commented on previous versions of the manuscript.

All authors read and approved the final manuscript.

Data Availability

The data that support the findings of this study are available from the corresponding author [N. Nasirizadeh] upon reasonable request

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Figure Caption:

Fig. 1. FESEM images of the A) carbon composite without MWCNTs and B) carbon nanocomposite containing MWCNTs, C) TEM image and D) Elemental analysis and mapping diagram of carbon nanocomposites containing MWCNTs.

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Fig. 6. Cycle stability of MWCNT/CC during 6 cycle for Clox adsorbent.

Fig. 1.

Fig. 2.

Fig. 3.

Fig. 4.

Fig. 5.

Fig. 6.

Table 1 Experimental range and levels of the independent variables.

Parameters	Unit	Symbol	Levels				
			$-\alpha$	-1	0	1	α
pH	-	A	2	4.25	6.5	8.75	11
Time	Min	B	20	45	70	95	120
MWCNT	Wt%	C	0.1	1.325	2.55	3.775	5
MWCNT-CC	g/L	D	0.1	0.33	0.55	0.75	1

Table 2- Experimental design based on Central Composite design (CCD) used in the present study.

Run	A:pH	B: time (min)	C:MWCNT (%wt)	D: MWCNT/CC (g/L)	Clox Removal (%)
1	6.5	70	2.55	1.05	87
2	6.5	70	2.55	2	94
3	4.25	45	1.325	1.525	45
4	6.5	20	2.55	1.05	82
5	8.75	95	3.775	0.575	27
6	6.5	70	2.55	1.05	80
7	6.5	120	2.55	1.05	50
8	8.75	95	1.325	0.575	21
9	4.25	45	1.325	0.575	43
10	8.75	95	1.325	1.525	29
11	6.5	70	2.55	0.1	58
12	11	70	2.55	1.05	13
13	6.5	70	2.55	1.05	84
14	4.25	95	1.325	1.525	18
15	8.75	45	3.775	1.525	43
16	4.25	95	3.775	1.525	45
17	8.75	95	3.775	1.525	90
18	6.5	70	2.55	1.05	88
19	8.75	45	3.775	0.575	20
20	6.5	70	2.55	1.05	96
21	6.5	70	0.1	1.05	15.2
22	4.25	45	3.775	1.525	64
23	8.75	45	1.325	1.525	42
24	4.25	95	1.325	0.575	20
25	8.75	45	1.325	0.575	35
26	6.5	70	5	1.05	24
27	4.25	95	3.775	0.575	45
28	6.5	70	2.55	1.05	86
29	4.25	45	3.775	0.58	18
30	2	70	2.55	1.05	9

Table 3. Textural properties obtained by N₂ adsorption/desorption studies.

Parameter	Technique	CC	MWCNT/CC
BET surface area (m ² /g)	BET ^a	7.285	31.377
Pore volume (cm ³ /g)	BJH adsorption ^b	0.017	0.307
Pore diameter (Å)	BJH adsorption ^b	9.671	39.215

^a Computed in the P/P₀ range of 0.05–0.50.

^b BJH (Barrett Joyner Halenda) cumulative adsorption pore volume for pores in range of 0 and 50.0 Å diameter.

Table 4. Determination of Clox in spiked aqueous, proposed sensor and HPLC method.

No. Sample	Proposed sensor				HPLC		
	added (nM)	Founded (nM)	Recovery (%)	RSD (%)	Founded (nM)	Recovery (%)	RSD (%)
1	25	24.59	98.36	3.1	25.40	101.6	0.059
2	50	51.08	102.16	1.7	49.97	99.94	0.135
3	75	74.90	99.86	2.6	75.09	100.12	0.031
4	100	101.47	101.47	2.15	100.85	100.85	0.112

*No. of measurements n=3, ** According to USP 40- NF 35

Table 5- Results of Analysis of Variance of Modeling the Clox Removal Using MWCNT/CC.

	Sum of		Mean	<i>F</i>	p-value	
Source	Squares	df	Square	Value	Prob > F	
Model	25742.13	14	1838.723	15.93835	< 0.0001	significant
A-pH	2281.969	1	2281.969	19.78048	< 0.0001	
B-time	3693.802	1	3693.802	32.01847	< 0.0001	
C-MWCNT	3901.605	1	3901.605	33.81975	< 0.0001	
D-MWCNT/CC	5422.985	1	5422.985	47.00731	< 0.0001	
AB	3921.19	1	3921.19	33.98951	< 0.0001	
AC	944.3286	1	944.3286	8.185594	0.6727	
AD	3835.016	1	3835.016	33.24254	0.0919	
BC	5098.671	1	5098.671	44.19611	0.0019	
BD	1227.58	1	1227.58	10.64087	0.4359	
CD	4480.821	1	4480.821	38.84049	< 0.0001	
A^2	12312.72	1	12312.72	106.7286	< 0.0001	
B^2	997.8857	1	997.8857	8.649836	0.0101	
C^2	9828.36	1	9828.36	85.19383	< 0.0001	
D^2	302.9624	1	302.9624	2.626128	0.1259	
Residual	1730.471	15	115.3647			
Lack of Fit	1519.743	10	151.9743	3.605939	0.848	not significant
Pure Error	210.7278	5	42.14555			
Cor Total	27472.6	29				

Table 6. Comparison of performance of the suggested adsorbent and proposed method for study of the antibiotic removal.

adsorbent	analyte	Adsorbent Specify			Detection method			Ref
		BET surface	Qmax	LOD	Linear range	Method	Recovery	
MWCNT/CC	Clox	31.377	295	8.0 nM	20-950	DPV	98.3-101	This work
PPy-PA6-NFs	Clox	-	-	2.0 ng/mL	5.0-250 ng/mL	CE-DAD	84.2–96.4	Li; 2019
MIP	Clox		280	36 nM	110-750	DPV	98 -100	Jafari; 2019
SWCNT/CC	Clox	105.64	476	1.6	5.0-775.0	DPV		Golkarieh; 2021
MWCNT	TCN	221.9	253.38	-	-	HPLC	-	Babaei; 2016
	TCN	60.17	364.3			UV spectrophotometer	-	Xiong; 2018
MWCNT/MIL-53(Fe)	OTC	60.17	325.5			UV spectrophotometer	-	Xiong; 2018
	CTC	60.17	180.6			UV spectrophotometer		Xiong; 2018
-	Clox	-	-	8–14 ng/L	-	HPLC/MS/MS	83.9–95.9	Cha, 2006
-	Clox	-	-	0.1	0.1-100	EIS	-	Burmańczuk; 2017
-	Clox	-	-	-	30-65	HPLC	-	Najlaoui; 2019

CE-DAD: capillary electrophoresis with a diode array detector (CE-DAD), TCN: tetracycline hydrochloride, OTC: oxytetracycline hydrochloride, CTC: chlortetracycline hydrochloride (CTC)

Table 7. Kinetic parameters for Clox adsorption on MWCNT/CC

q_{max} (exp.) (mg/g)	Pseudo-first order			Pseudo-second order		
	$Ln (q_e - q_t) = Lnq_e - k_1 t$			$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$		
	$k_1 \text{ min}^{-1}$	q_e (calc.) mg/g	R^2	$k_2 \text{ min}^{-1}$	q_e (calc.) mg/g	R^2
296	0.0230	285.5	0.971	0.003	295.7	0.997

Table 8 Isotherm parameters for Clox adsorption on MWCNT/CC.

Isotherm Model	Langmuir			Freundlich		
Linear equation	$C_e/q_e = (1/bq_{\max}) + (1/q_{\max}) C_e$			$\text{Log } q_e = \text{Log } K_F + (1/n) \log C_e$		
	$q_{\max}$	K_L	R^2	K_F	N	R^2
	296.8	0.142	0.993	0.874	1.275	0.981

Table 9: Thermodynamic parameters for the adsorption of Clox on MWCNT-CC

C_e (mg/L)	ΔH^0 (kJ/mol)	ΔS^0 (kJ/molK)	ΔG^0 (kJ/mol)			
	$\ln K = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT}$		$\Delta G^0 = -RT \ln K, K = \frac{q_e}{C_e}$			
		-	298	308	318	328
100	3.046	0.0686	-1.684	-1.338	-0.482	-0.259

R: universal gas constant (8.314 Jmol⁻¹K⁻¹), T: absolute temperature (K), K: distribution coefficient.

Figures

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