Advances in Nano Research, *Vol. 11, No. 6 (2021) 667-678*
https://doi.org/10.12989/anr.2021.11.6.667

Drug adsorption and anti-microbial activity of functionalized multiwalled carbon nanotubes

Megha Saxena[1], Disha Mittal[2], Richa Boudh[1], Kapinder Kumar[2], Anita K. Verma[2] and Reena Saxena*[1]

[1]*Department of Chemistry, Kirori Mal College, University of Delhi, Delhi 110007, India*
[2]*Nanobiotech Lab, Department of Zoology, Kirori Mal College, University of Delhi, Delhi 110007, India*

(*Received November 23, 2020, Revised October 25, 2021, Accepted October 31, 2021*)

Abstract. Multiwalled carbon nanotubes (MWCNTs) were first oxidized (O-CNTs) to introduce carboxylic group and then further functionalized (F-CNTs) with m-phenylenediamine, which was confirmed by FTIR and SEM. It was used as an effective adsorbent for the adsorptive removal of diclofenac drug from water. Under optimum conditions of pH 6, stirring speed 600 rpm, the maximum adsorption capacity obtained was 532 mg g^{-1} which is superior to the values reported in literature. The adsorption was quite rapid as 25 mg L^{-1} drug solution was adsorbed in only 3 minutes of contact time with 10 mg of adsorbent dose. The adsorption kinetics and isotherms were studied using various models to evaluate the adsorption process. The results showed that the data best fit in kinetics pseudo-second order and Langmuir isotherm model. Furthermore, the oxidized and functionalized MWCNTs were applied on gram-negative Escherichia coli and gram-positive Staphylococcus aureus using agar disc diffusion assay to validate their anti-microbial activity. Results were unique as both oxidized and functionalized MWCNTs were equally active against both *E. coli* and *S. aureus*. The newly synthesized F-CNTs have great potential in water treatment, with their dual action of removing drug and pathogens from water, makes it potential applicant to save environment.
Keywords: adsorption; antimicrobial; diclofenac; functionalized multiwalled carbon nanotubes; m-phenylenediamine

1. Introduction

Pharmaceuticals are produced to save human life from many deadly diseases. However, prolonged presence of a pharmaceutical in water makes it an emerging pollutant which causes hazardous effect on living beings. Since pharmaceutical drugs are generated to affect the target parts of body or cells and are prescribed with precaution about their doses and quantity. Higher or improper dosage of these can cause certain severe side effects or even lead to death. Nowadays, the excessive presence of pharmaceutical drugs in water bodies which could be due to hospital effluents or pharmaceutical industrial waste becomes a serious problem for whole ecosystem (Patel *et al*. 2019). Various pharmaceutical drugs like aspirin, paracetamol, etc., are used in hospitals as first aid or to cure different diseases. Diclofenac sodium is the most popular drug that used as pain killer. The chemical name of Diclofenac is 2-(2, 6-dichloranilino) phenylacetic acid and it is an anti-inflammatory drug which is used to reduce inflammation and help in relieving pain. Diclofenac with its high consumption rate and poor degradation can't be removed completely by simple wastewater treatment plants. So, it easily passes in river water, ground water, etc., which is used for drinking purpose. Its high amount has detrimental effect on human health.

Diclofenac in human body affects kidney attributed to Ischaemia induced by inhibition of prostaglandin synthesis resulting in tubular necrosis. It can cause serious hepatotoxicity (Liver damage). Diclofenac also has adverse effect on aquatic species such as endocrine disruptor in Daphnia magna. It can destroy the eggs of fishes (Lonappan *et al*. 2016). Since the pharmaceutical removal is difficult it became a challenge for researchers to find an effective method for its removal. There are various methods such as membrane filtration (Ouyang *et al*. 2019), electro-coagulation (Ensano *et al*. 2019), oxidation (Kanakaraju *et al*. 2018), photocatalytic degradation (Mestre and Carvalho 2019), adsorption (Ighalo and Adeniyi 2020) etc. which are used to remove the pharmaceuticals from wastewater. Adsorption is the most common method which is low cost, effective and easily combines with wastewater treatment plants. There are various adsorbents like activated carbon (Mansour *et al*. 2018), alumina (Chauhan *et al*. 2020), silica (Barczak *et al*. 2020), cellulose (Raicopol *et al*. 2019) and chitosan (Pereira *et al*. 2020), which shows good removal of pharmaceuticals but suffers certain limitations like low capacity and high cost. Nowadays, nanomaterials like metal oxide nanoparticles, silica nanoparticles, chitosan nano-particles and carbon nanotubes-based nanoparticles are used for pharmaceutical removal (Saxena *et al*. 2020). Carbon nanotubes (CNTs) are the most popular adsorbent due to their large surface area, high adsorption capacity, stability and ease of modification. These inherent unique properties of CNTs offer an exciting platform to enable significant research opportunities (Ebrahimi and Mahmoodi 2018). Surface functionalization of CNTs with different modifying agents or organic moieties improves its hydrophilicity and makes it biocompatible for biomedical applications. Functionalization further facilitates the complex formation capability of CNTs, thereby enhancing its selectivity

*Corresponding author, Professor,
E-mail: rsaxena@kmc.du.ac.in

ISSN: 2287-237X (Print), 2287-2388 (Online)

(Mousavi and Janjani 2018). The Functionalized CNTs have high tendency to form complex with inorganic pollutants such as metal ions (Tiwari *et al*. 2017) as well as with organic pollutants like dyes (Saxena *et al*. 2020) and thus help in their removal from water. The effect of functionalized CNTs on plants was also observed by Dasgupta-Schubert *et al*. (2017), which indicates that functionalization improves the sensitivity of CNTs.

Most pharmaceuticals are water soluble and hence difficult to detect. Various Detection techniques like High pressure liquid chromatography (HPLC), Gas-chromatography-mass spectroscopy (GC-MS), Liquid-chromatography-mass spectroscopy (LC-MS), and UV-visible Spectroscopy (Siddiqui *et al*. 2017, Atole and Rajput 2018) are used for the detection of pharmaceuticals. All these techniques are good in detection of pharmaceuticals but have drawbacks like high operational cost, use of organic solvents, trained user. Among them, UV-visible Spectroscopy is fast, cheap, accurate, reliable and easy to handle technique. It does not require special training to operate.

Apart from organic pollutants which have harmful effect on human beings, the biological pollutants such as bacteria, virus, microbes (pathogens) are also responsible for various kinds of disease in living organisms. There are various nanoparticles like silver (Supraja *et al*. 2018), zinc oxide (Supraja *et al*. 2017a), that show antimicrobial properties and also used in biomedical applications (Supraja *et al*. 2017b). It has also been known that carbon-based nanomaterials exhibit high antimicrobial activity. The surface area and size of carbon nanomaterials are significant parameters affecting their antibacterial activity; that is, increasing the surface area of the nanoparticles by decreasing their size leads to improve their activity for interaction with bacteria. Staphylococcus aureus (*S. aureus*) is a human pathogen that causes both community-acquired and nosocomial infections (Mohanty *et al*. 2007). The range of diseases caused by this bacterium encompasses wounds and soft tissue infections to endocarditis and septic shock. Staphylococci commonly occur on the surface of the skin and at all the natural openings on the human body. Skin infections with *S. aureus* include furuncles, impetigo, cellulites, carbuncles and staphylococcal toxin induced scarlet fever. Lung and airway infections may also result in abscesses in the lung. Bacterial membranes are abundant in the anionic surface phospholipids, have high negative trans membrane potential and lack cholesterol. It has been proposed that aggregation of carbon-based nanomaterials may cause membrane damage in bacteria due to an oxidative stress. It was reported that direct cell contacts with CNTs influenced the cellular membrane integrity, metabolism processes and morphology of Escherichia coli (*E. coli*) (Verma *et al*. 2015). Kang *et al*. (2007) provided the first proof that showed carbon nanotubes have strong antimicrobial activity on *E. coli*. (Dizaj *et al*. 2015). Disc Diffusion Assay is a standardized technique for performing antimicrobial susceptibility, as it has the ability to test multiple antimicrobial agents on each bacterial isolate (Biemer 1973).

In this paper, m-phenylenediamine functionalized MWCNTs have been synthesized and used as an adsorbent for the adsorptive removal of Diclofenac from water as well as to evaluate their biological efficacy by anti-microbial disc diffusion assay. The modifier m-phenylenediamine is used previously as Mg/Al layered double hydroxide-poly (m-phenylenediamine) composite for removal of diclofenac using HPLC-UV technique (Xiong *et al*. 2019). The advantage of using m-phenylenediamine is that, it provides functional groups which facilitates the fast adsorption. So, m-phenylenediamine was used to functionalize MWCNTs (F-CNTs) by a simple synthetic route. The method and detection technique utilized were simple batch method and UV-visible spectrophotometer, which is less expensive than HPLC and also doesn't require hazardous organic solvents. The adsorption capacity obtained is much higher (532 mg g^{-1}) in comparison to other nanoadsorbents reported in literature. The amount of adsorbent used was also quite less (10 mg) which makes the process more economical. As per literature survey, the dual action of proposed F-CNTs, as an adsorbent for removal of diclofenac as well as its antimicrobial activity in water has been reported first time in this paper.

2. Experimental section

2.1 Materials and method

Multiwalled carbon nanotubes and Diclofenac sodium drug was purchased from Sigma Aldrich. Modifier m-phenylenediamine was purchased from Thomas baker. Phosphate buffer of pH 7 was supplied by Merck. HCl and NaOH were also of analytical grade. Ultrapure Milli-Q water was used for solution preparation and dilution. Nutrient agar, nutrient broth, and Gentamycin were purchased from Hi-Media Laboratories Pvt. Ltd. (Mumbai, India). Agar was obtained from SRL, India.

2.2 Instrumentation

The detection of concentration of diclofenac was done using Cary 60 UV-Visible Spectrophotometer Agilent Technologies. The pH of solutions was adjusted with the help of pH Meter model LI-614 ELICO India. The FTIR was recorded on PerkinElmer FT-IR spectrophotometer of Model Spectrum RX-1 with 16 scans, 4 cm^{-1} resolution and in range 400-4000 cm^{-1}). SEM was recorded with model FEI Quanta 200F scanning electron microscope. The ultrapure water used was of Milli-Q Millipore.

2.3 Chemical modification of Multiwalled carbon nanotubes

The chemical modification of MWCNTs was done according to our previously published method (Bajaj *et al*. 2021). Briefly, pristine MWCNTs were added to the solution of concentrated HNO_3: H_2SO_4 (1:3) and ultrasonicated for 2 h to get the oxidized MWCNTs (O-CNTs). Further modification of O-CNTs with m-phenylenediamine was conducted by suspending OCNTs

and m-phenylenediamine in phosphate buffer of pH 7 and mixture was stirred at 45°C for 2 days. Then m-phenylenediamine functionalized MWCNTs (F-CNTs) were filtered, dried and stored in desiccator.

2.4 Adsorption experiment

The adsorption experiment was carried out by first preparing the standard calibration curve of diclofenac at 275 nm using diluted standard solution of diclofenac (1000 mg L^{-1}). In adsorption experiments, first the optimization of parameters like contact time, pH, stirring speed and initial drug concentration was carried out by adding 50 mL of 25 mg L^{-1} diclofenac solution in 100 mL conical flask. Then 10 mg of F-CNTs were added and solution was stirred for 1-10 min. After that the solution was filtered using syringe filter of 0.2 µm pore size. The remaining concentration of diclofenac in filtrate was determined using UV-Visible Spectrophotometer. Under optimum conditions the kinetics and isotherm experiments were performed with 100 mL of different initial drug concentrations (10-100 mg L^{-1}) and 10 mg adsorbent. All experiments were carried out at room temperature.

The adsorption capacity and drug removal efficiency were calculated using Eqs. (1)-(2) given below:

$$\text{Adsorption Capacity, } q_e = \frac{(C_0 - C_e)V}{m} \quad (1)$$

$$\text{Drug removal efficiency, } \% = \frac{(C_0 - C_e)}{C_0} \times 100 \quad (2)$$

Here, q_e is the adsorption capacity (mg g^{-1}), C_o and C_e are initial and equilibrium drug concentrations (mg L^{-1}) respectively, V is the volume of drug solution (L) and m is the amount of adsorbent (g).

2.5 Desorption experiment

The desorption of diclofenac from the surface of F-CNTs was performed as; after adsorption, the drug saturated adsorbent was filtered through Whatman 42 filter paper and dried. After that the drug saturated F-CNTs was treated with 50 mL of various eluents/desorbing agents at 600 rpm stirring speed, 3 min contact time at room temperature. The eluent that gave maximum desorption percentage was further analysed by changing volume and time.

2.6 Antimicrobial disc diffusion assay

2.6.1 Preparation of bacterial culture media

The bacterial culture media was grown according to the modified procedure reported before (Verma *et al*. 2015). An appropriate amount of nutrient broth was dissolved according to manufacturer's instruction. Broth was autoclaved at 121°C, 15 psi pressure for 20 min. Bacterial cultures from mother inoculum was taken in 1:100 ratios and added to the above sterile nutrient broth. The flask was incubated at 37°C overnight in the orbital shaker incubator. The turbidity of media was directly proportional to the growth of the culture.

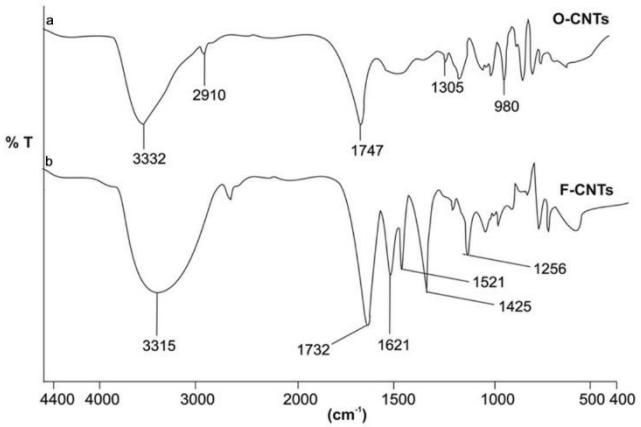

Fig. 1 FTIR spectra of (a) O-CNTs and (b) F-CNTs

Absorbance was measured at 600 nm by a UV spectrophotometer and colony forming unit (CFU/mL) was calculated as a ratio between the optical density and CFU/mL, given below as

$$1 \text{ OD} = 0.8 \times 10^9 \text{ CFU/mL}.$$

2.6.2 Disc diffusion assay

All the glassware and prepared media were autoclaved. *E. coli* (DH5α) and *S. aureus* were used as test bacterial strains representing Gram-negative and Gram-positive bacteria, respectively. The bacterial suspension was grown in nutrient broth at 37°C overnight. The antibacterial susceptibility of modified MWCNTs was evaluated using the Kirby Bauer method. The bacterial cultures were thoroughly mixed with soft agar and poured on a LB agar plate. The plates were then divided into sections and sterile discs of 5 mm diameter were placed on each section loaded with 20 µL of the sample (oxidized MWCNTs (O-CNT), functionalized MWCNTs (F-CNTs), and pristine MWCNTs) dispersed in distilled water, Gentamycin (positive control) and Distilled water (negative control), respectively; The zone of inhibition (ZOI) was measured after incubating the plates were further incubated overnight at 37°C.

3. Results and discussion

3.1 Characterization

The characterization of modified MWCNTs was done using FTIR and SEM analysis.

FTIR: The oxidation and modification of MWCNTs was confirmed by Fourier transform infrared (FTIR) spectroscopy. The peaks at 3332, 2910, 1747, 1305 and 980 cm^{-1} represent O-H, C-H, C=O, C-C, C-O stretching of O-CNTs (Fig. 1(a)). The peaks get shifted and new peaks appeared on modification of O-CNTs with m-phenylenediamine. The peaks at 3315, 1732, 1621, 1425, and 1256 cm^{-1} shows N-H, C=O stretching, N-H bending, C=C stretching, C-N stretching respectively. The specific peak at 1521 cm^{-1} is a characteristic peak of CONH bending

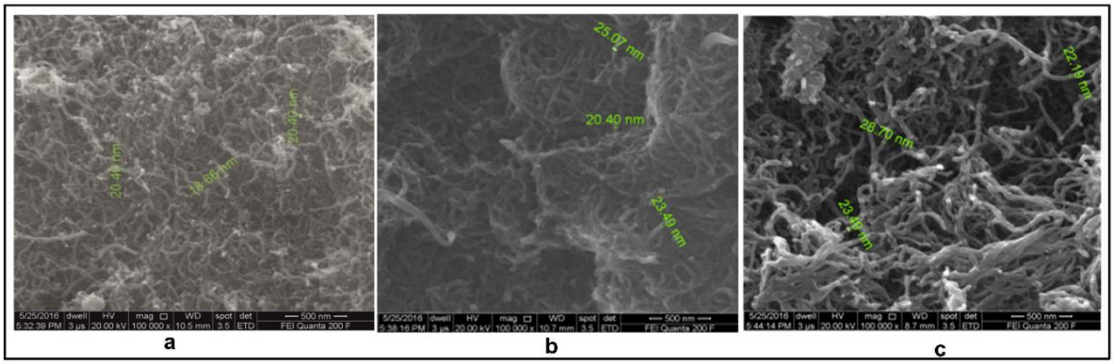

Fig. 2 SEM image of (a) pristine MWCNTs; (b) O-CNTs and (c) F-CNTs

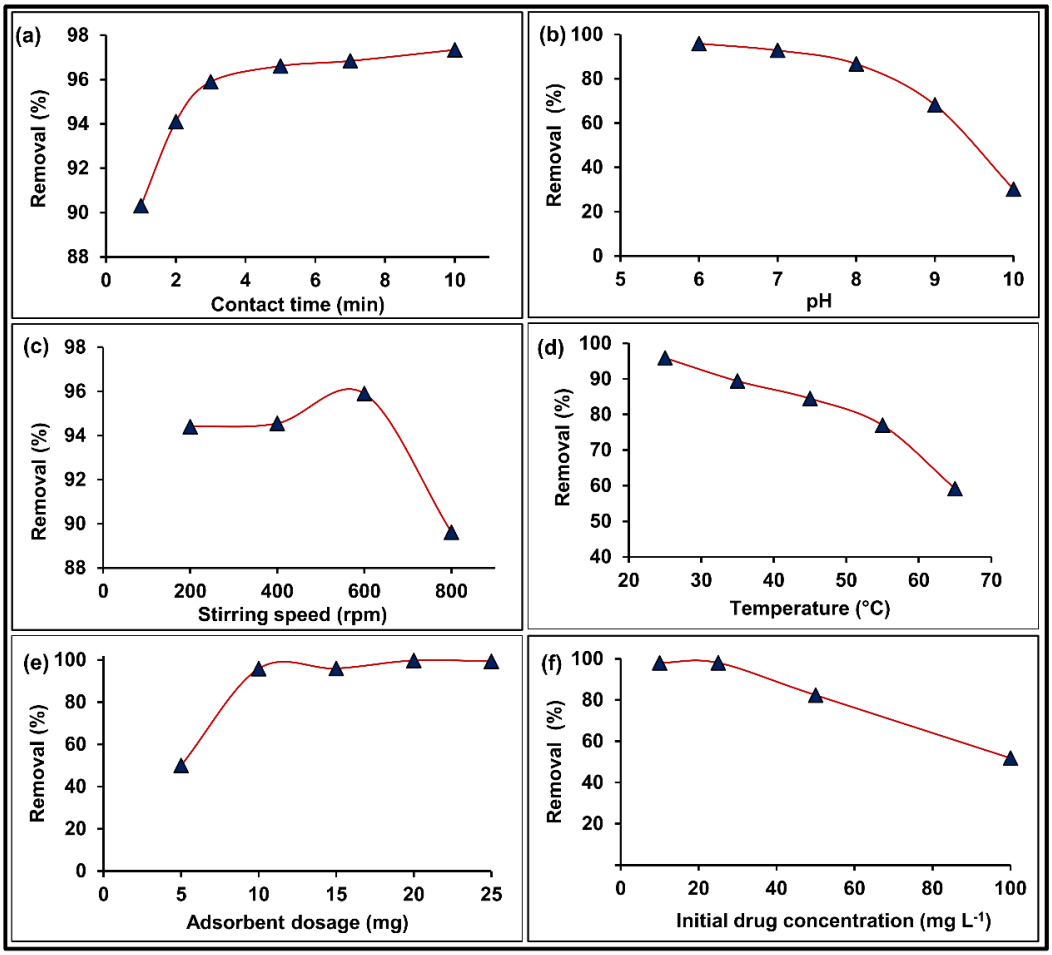

Fig. 3 The effect of (a) contact time; (b) pH; (c) stirring speed; (d) temperature; (e) adsorbent dosage and (f) initial drug concentration

which appeared due amide bond formation between -COOH group of O-CNTs and NH_2 group of m-phenylenediamine (Fig. 1(b)) (Bajaj *et al*. 2021).

SEM: The structure and morphology of O-CNTs and F-CNTs was confirmed by scanning electron microscopy (SEM). As shown in Figs. 2(a)-2(c) the diameter of carbon nanotubes increases and get thicker on functionalization with -COOH group in O-CNTs and with m-phenylenediamine group in F-CNTs. This can also be verified with the size as in pristine (18-20 nm), O-CNTs (20-25 nm) and F-CNTs (22-28 nm).

3.2 Optimization of adsorption parameters

Optimization of adsorption parameters was done to check the effect of various parameters which influences the adsorption. The optimization was necessary to get the maximum result in minimum time and chemicals.

3.2.1 Effect of contact time

The effect of contact time was studied from 1-10 min. The result obtained shown in Fig. 3(a), revealed that the adsorption of Diclofenac was very fast and >95% got

adsorbed within 3 min. After 3 min the increase was gradual and become constant as equilibrium reached. The study was continued till 10 min.

3.2.2 Effect of pH

The effect of pH was studied from 6-10 and it was found that the maximum adsorption occurred at pH 6 and after that it decreases as shown in Fig. 3(b). The pH was studied from 6 onward because before pH 6 the diclofenac solution became turbid due to formation of water insoluble non-dissociated acid. The reason for decrease in drug removal efficiency with increasing pH is the generation of negative charge on the surface of adsorbent and repulsive interaction occurs (Barczak *et al*. 2018).

3.2.3 Effect of stirring speed

It is the important parameter as the stirring speed decides the interaction of adsorbent with drug. The result in Fig. 3(c), shows that as the stirring speed increases from 200-600 rpm the drug removal efficiency increases from 94.4 to 95.9 %, which is due to the faster approach of drug molecules towards the adsorbent. On further increase in stirring speed decreases the efficiency (89.6 %) as it starts hindering the interaction.

3.2.4 Effect of temperature

Temperature is an important parameter in the adsorption process. The effect of temperature on adsorption of diclofenac on F-CNTs was studied in range of 25°C to 65°C as shown in Fig. 3(d). The result indicated that the increase in temperature had a negative effect on adsorption of diclofenac as the drug removal percentage decreases from 95.9% to 59.2% as temperature increased from 25°C to 65°C. This shows that the adsorption of diclofenac on F-CNTs is exothermic in nature. Since maximum adsorption was obtained at 25°C, it was chosen as an optimum temperature.

3.2.5 Effect of amount of adsorbent

The adsorbent dose has also significant effect on adsorption process. The adsorbent dose study was carried out in range of 5 mg-25 mg as shown in Fig. 3(e). The result indicated that initially the percentage removal increases from 50 % to 95.9 % as adsorbent dose increased from 5 mg to 10 mg which was due to the reason that more amount of adsorbent provides more surface area for adsorption and thus more will be the adsorption or greater will be the percent removal. Further increase in adsorbent dosage from 15 mg to 25 mg the percentage removal reached >99 % due to more vacant sites as provided by more amount. Since, 10 mg showed >95% adsorption, it was chosen as an optimum amount of the adsorbent (Wan *et al*. 2021).

3.2.6 Effect of initial drug concentration

The effect of initial drug concentration was studied from 10-100 mg L^{-1}. It can be seen clearly in Fig. 3(f) that as the initial concentration of drug increases from 10 to 100 mg L^{-1} the drug removal efficiency decreases from 98.0 to 51.8 %. The decrease was obvious as all the vacant sites on adsorbent surface get exhausted as the concentration of drug increases.

However, the adsorption capacity increases from 99.6 to 532.0 mg g^{-1} with increase in initial concentration of drug from 10-100 mg L^{-1}.

3.3 Adsorption kinetics

The kinetics of adsorption of diclofenac on F-CNTs was studied using different models such as, pseudo first order, pseudo second order, intraparticle diffusion and fractional power models as given by Eqs. (3)-(6) respectively.

(i) Pseudo first order model

$$In(q_e - q_t) = Inq_e - K_1 t \quad (3)$$

Here, the terms q_e and q_t represents adsorption capacity at equilibrium and time t. K_1 is the rate constant of pseudo first order model.

(ii) Pseudo second order model

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} t \quad (4)$$

The term K_2 is the rate constant of pseudo second order model.

(iii) Intraparticle diffusion model

$$q_t = K_P t^{1/2} + C \quad (5)$$

The term K_p is rate constant of intraparticle diffusion, C is a constant that shows thickness of the boundary layer. The adsorption is said to be intraparticle diffusion controlled if the plot between q_t and $t^{½}$ is a straight line and passes through the origin.

(iv) Fractional power model

$$logq_t = logK + v\ log\ t \quad (6)$$

The terms k and v are constants of fractional power model and their value can be obtained from slope and intercept. The fractional power model represents diffusion control process and said to be fit well if the value of v is less than 1 (Wang and Guo 2020).

The plots of contact time of diclofenac adsorption on F-CNTs, pseudo first order, second order, intraparticle diffusion and fractional power models are given in Figs. 4(a)-4(e). The kinetics parameters calculated from the plots are given in Table 1. The result reveals that the kinetics of diclofenac sodium adsorption on F-CNTs followed pseudo second order model as the value of correlation coefficient (R^2) is 0.99 for both 50 and 100 mg L^{-1} drug solution. It can also be confirmed by the value of calculated adsorption capacity (q_{cal}) which is in close agreement with experimental value (q_{exp}). The intraparticle model showed multilinear plot which indicates that the adsorption is not controlled by intraparticle diffusion only but other processes are also involved (Hu *et al*. 2017). The poor R^2 value of fractional model also indicates that it is not adequate model to explain adsorption process (Turner *et al*. 2015). These results conclude that the adsorption of diclofenac on F-CNTs is a chemisorption process in which adsorption efficiency is directly proportional to number of available vacant sites on the surface of nanoadsorbent.

Table 1 Kinetic parameters of pseudo first order, second order, Intraparticle diffusion and fractional power models

Pseudo first order model				
Initial drug concentration (mg L^{-1})	q_{exp} (mg g^{-1})	q_{cal} (mg g^{-1})	K_1 (min^{-1})	R^2
50	411.0	242.1	0.0739	0.9534
100	532.0	336.3	0.0576	0.9756
Pseudo second order model				
Initial drug concentration (mg L^{-1})	q_{exp} (mg g^{-1})	q_{cal} (mg g^{-1})	K_2 (g mg^{-1} min)	R^2
50	411.0	416.7	0.0009	0.9980
100	532.0	526.3	0.0005	0.9954
Intraparticle diffusion model						
Initial drug concentration (mg L^{-1})	K_{p1} (mg g^{-1} $min^{1/2}$)	C_1 (mg g^{-1})	R_1^2	K_{p2} (mg g^{-1} $min^{1/2}$)	C_2 (mg g^{-1})	R_2^2
50	75.837	54.88	0.9332	9.0171	330.97	0.9106
100	90.789	59.11	0.9373	18.629	353.41	0.9523
Fractional power model				
Initial drug concentration (mg L^{-1})	v (min^{-1})	k (mg g^{-1})	kv (mg $g^{-1}min^{-1}$)	R^2
50	0.2279	168.38	38.37	0.9415
100	0.2601	184.29	47.93	0.9515

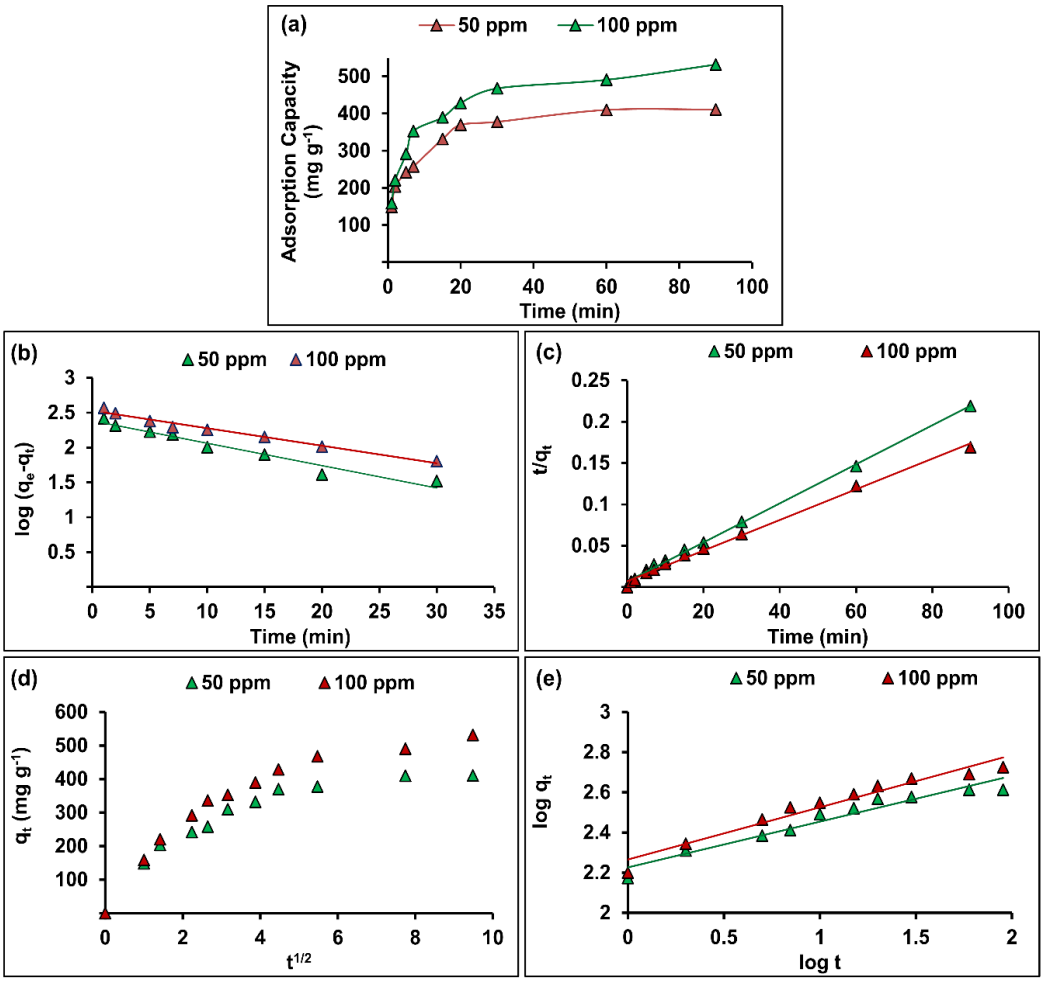

Fig. 4 Kinetics of (a) diclofenac with F-CNTs; (b) pseudo first order; (c) pseudo second order; (d) intraparticle diffusion and (e) fractional power model

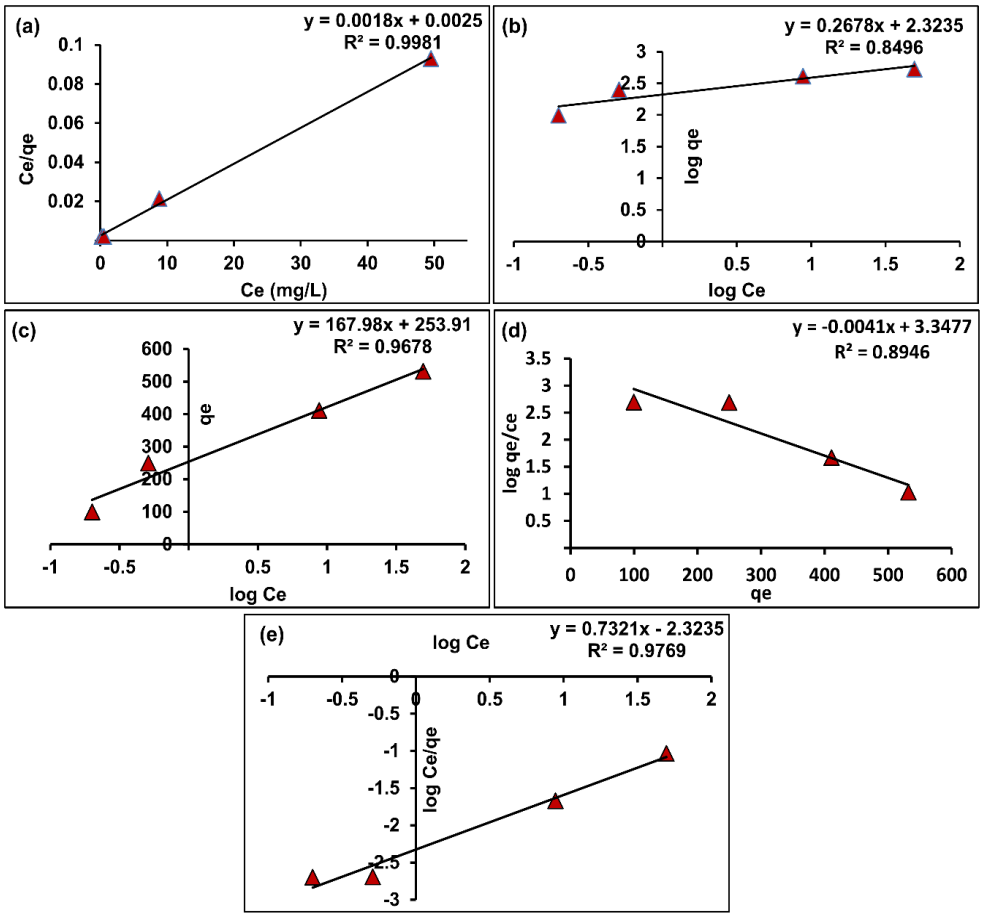

Fig. 5 Adsorption Isotherm models (a) Langmuir; (b) Freundlich; (c) Temkin; (d) Elovich and (e) Redlich Peterson for adsorption on F-CNTs

3.4 Adsorption isotherm

The adsorption isotherm can be explained using different models like Langmuir, Freundlich, Temkin, Elovich and Redlich Peterson isotherm. The isotherm models Langmuir and Freundlich reveal the pattern of adsorption whether it is monolayer or multilayer. The Temkin model shows that heat of adsorption decreases linearly as the adsorption takes place. The Elovich model assumes that there is an exponential increase in adsorption sites as adsorption takes place and denotes the multilayer adsorption. The Redlich Peterson model is the combination of the Langmuir and the Freundlich models and helps in differentiation between homogeneous and heterogeneous system. The adsorption isotherm was studied using these five models which are expressed by Eqs. (7)-(12) respectively.

(i) Langmuir isotherm model

$$\frac{C_e}{q_e} = \frac{1}{q_{max}\, K_L} + \frac{1}{q_{max}}\, C_e \tag{7}$$

The terms q_{max} represents the maximum adsorption capacity. C_e and q_e represents the final equilibrium concentration and capacity. The K_L is Langmuir constants.

$$R_L = \frac{1}{(1 + K_L\, C_0)} \tag{8}$$

The other important factor in the Langmuir isotherm model is R_L. If value of R_L lies between 0 to 1 it shows favourable adsorption. If it's more than 1 it shows unfavourable adsorption.

(ii) Freundlich isotherm model

$$log q_e = log K_F + \frac{1}{n}\, log C_e \tag{9}$$

K_F is the Freundlich constant and 1/n is adsorption intensity. The value of 1/n determines whether the adsorption is favourable ($0 < 1/n < 1$), unfavourable $1/n > 1$ and irreversible ($1/n = 1$).

(iii) Temkin isotherm

$$q_e = 2.303\, (B\, log K_T + B\, log C_e) \tag{10}$$

K_T and B are constants which can be calculated from the slope and intercepts of plots of q_e *versus* log C_e. K_T is the binding energy constant and B is also a constant represents heat of adsorption.

(iv) Elovich isotherm

$$log\, \frac{q_e}{C_e} = log K_e\, q_m - \frac{q_e}{2.303\, q_m} \tag{11}$$

K_e is the Elovich constant and q_m represents the Elovich maximum adsorption capacity.

(v) Redlich-Peterson isotherm

$$log\ \frac{C_e}{q_e} = \beta\ log C_e - log A \quad (12)$$

The term A and β are constants, which can be obtained from the intercept and slope of plot between log C_e/q_e versus log C_e. The value of β generally lies between 0 and 1. If the value of β is close to unity it shows that the adsorption favours Langmuir and if it is approaching 0 which means adsorption follows Freundlich (Al-Ghouti and Da'ana 2020, Ayawei *et al*. 2017).

The isotherm parameters are given in Table 2 and plots of Langmuir, Freundlich, Temkin, Elovich and Redlich Peterson are given in Figs. 5(a)-5(e). The model which can be used to describe adsorption process can be decided using the value of correlation coefficient R^2. The best fit of various models based on their correlation coefficient (R^2) are Langmuir > Redlich Peterson > Temkin > Elovich > Freundlich. The plot of Langmuir is a straight line and the value of $R^2 > 0.99$ which means the adsorption is monolayer. The calculated value of adsorption capacity is also in favour of Langmuir model. The other parameter like the value of R_L also lies between 0 and 1 which indicates favourable adsorption (Leone *et al*. 2018). The value of 1/n is 0.2678 which is between 0 and 1, also indicates favourable adsorption.

The value of β in Redlich Peterson model is also 0.7321 which is close to 1 which also favours Langmuir model. The poor R^2 value of Freundlich and Elovich model suggests that the adsorption was not multilayer. Hence it can be concluded that the adsorption of diclofenac on F-CNTs followed Langmuir model and is monolayer.

3.5 Adsorption mechanism

The possible interaction between diclofenac and nanoadsorbent can be explained on the basis of different types of possible forces like π-π interaction and H-bonding as shown in Fig. 6. The π-π interaction can be possible as CNTs have many π-electrons due to sp^2 hybridized carbon atoms and the modifier m-phenylenediamine has aromatic ring structure which contains multiple π-bonds. The diclofenac also has aromatic ring which has π-bonds so it can interact with both CNTs and modifier. H-bonding is also possible between oxygen carrying carboxyl group of diclofenac and H atoms of nanoadsorbent (Liang *et al*. 2019).

3.6 Desorption study

The choice of desorbing agent/eluent is important for rapid desorption. The desorption of adsorbed diclofenac on F-CNTs was carried out by different eluents or desorbing agents as shown in Fig. 7. The adsorption of 50 mL diclofenac was carried out in 3 min. of contact time at 600 rpm stirring speed. Under similar conditions, the desorption experiments were performed using 50 mL of eluent, stirred at 600 rpm for 3 min. Initially, deionized water was taken as eluent and as the results shown in Fig. 7 indicated the desorption percent was only 5.91 %. After that 0.1 mol L^{-1} HCl was used that showed even less desorption, i.e., 3.05 %, which confirmed that the acids are not an option for the

Table 2 Adsorption Isotherm model parameters

Isotherm model	Parameters	Values
Langmuir model	q_{exp} (mg g^{-1})	532.0
	q_{max} (mg g^{-1})	555.6
	K_L	0.7199
	R_L	0.0137
	R^2	0.9981
Freundlich model	K_F	210.6
	R^2	0.8496
	1/n	0.2678
Temkin model	B	72.94
	K_T	32.51
	R^2	0.9678
Elovich model	q_m	106.38
	K_e	1.075
	R^2	0.8946
Redlich Peterson model	A	210.6
	β	0.7321
	R^2	0.9769

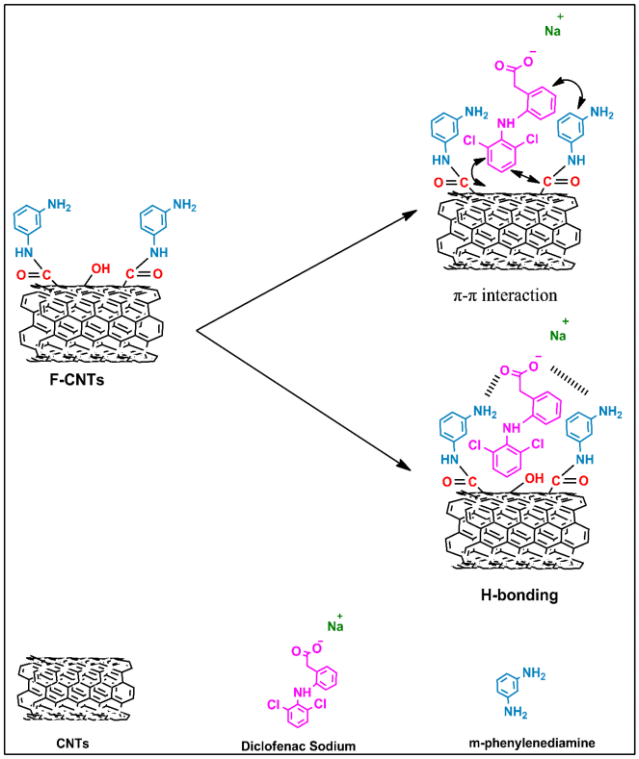

Fig. 6 Possible mechanism of Interaction between Diclofenac and F-CNTs

desorption of diclofenac. After that a series of eluents such as ethanol, methanol, acetonitrile, 0.1 mol L^{-1} NaOH were applied and it was observed that the maximum desorption was obtained from 0.1 mol L^{-1} NaOH, i.e., 52.39 %. Since single eluents were not sufficient for complete desorption of diclofenac, combination of two eluents were used. The combination of ethanol and water in ratio 1:1 v/v gave only

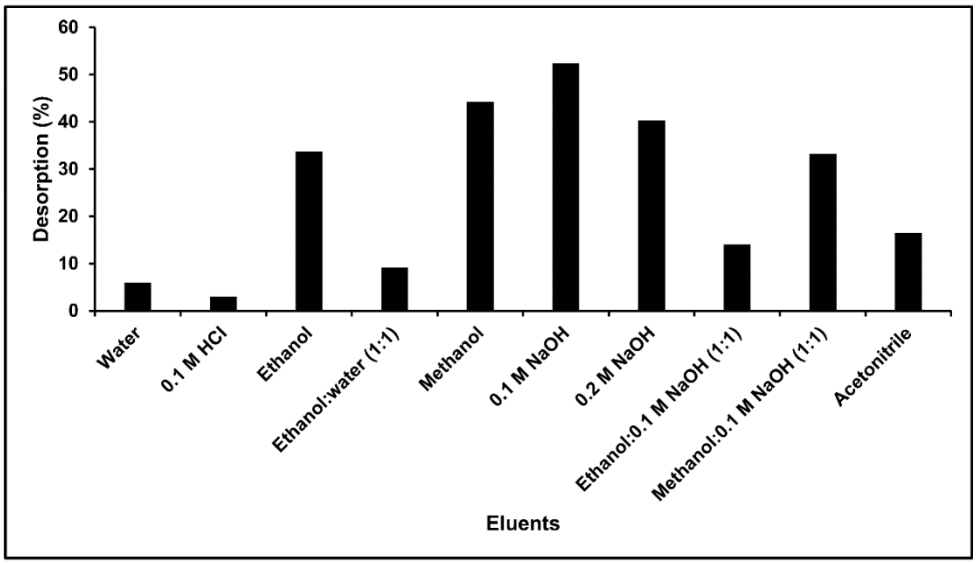

Fig. 7 Desorption efficiency of eluents for the desorption of diclofenac from F-CNTs

9.15 %. Since the maximum desorption obtained from 0.1 mol L^{-1} NaOH, therefore its combination with ethanol, methanol was tried and the result of ethanol and 0.1 mol L^{-1} NaOH (1:1, v/v) showed 14.1 % desorption, while the combination of methanol and 0.1 mol L^{-1} NaOH showed better desorbed of 33.19 %. Since, none of the above-mentioned desorbing agents were capable of complete desorption of diclofenac, different approach was taken into consideration, i.e., effect of other parameters such as volume of eluent, concentration of eluent and time of desorption.

3.6.1 Effect of volume, concentration of desorbing agent and time on desorption

To further verify the effect of volume, concentration and time on desorption of diclofenac, the desorbing agent which gave the maximum desorption percent in 3 min, i.e., 0.1 mol L^{-1} NaOH was chosen. Initially the concentration of NaOH was increased to 0.2 mol L^{-1} but the desorption percentage decreased to 40.24 %. Then the volume of 0.1 mol L^{-1} NaOH was doubled to 100 mL, but the desorption percent decreased drastically to 20.6 %. Then the time was first increased to 30 min and decreased to 1 min 30 seconds but no significant difference was observed. Hence it can be concluded from the above discussions that the adsorption of diclofenac on F-CNTs was through strong and irreversible chemical bonds. Since most of the sites on adsorbent surface were covered with diclofenac its reuse was difficult to achieve. Similar observations of the desorption of diclofenac using different eluents/desorbing agents were reported in literature by many researchers (Liu *et al*. 2017, Hu *et al*. 2019).

3.7 Antimicrobial activity

The antimicrobial activity of the MWCNTs against both gram negative *E. coli* and gram-positive *S. aureus* is summarized in Table 3. The results of the disc diffusion assay indicate higher antimicrobial activity of O-CNTs at all concentrations, when compared to F-CNTs. No ZOI was observed in case of pristine MWCNTs (Fig. 8).

These findings can be explained on the basis of the interaction of the pristine and modified MWCNTs with the cell wall of the bacteria. The O-CNTs and F-CNTs are polar in nature as compared to pristine MWCNTs. It has been proposed that aggregation of carbon-based nanomaterials may cause membrane damage in bacteria due to an oxidative stress. It was reported that direct cell contacts with CNTs influenced the cellular membrane integrity, metabolism processes and morphology of *E. coli*. (Dizaj *et al*. 2015, Biemer 1973, Rawat *et al*. 2014). We infer that the pronounced polarity and presence of functional groups allows both O-CNTs and F-CNTs to show increased antimicrobial activity. It can be predicted that the functional groups further increase their affinity for adsorption of bacteria. The higher antimicrobial activity of O-CNTs towards both *E. coli* and *S. aureus* could be attributed to intercalation of the carboxyl groups with the bacteria, causing structural damage and oxidative stress, (Rawat *et al*. 2014) eventually leading to death (Fig. 8). The F-CNTs showed reduced activity towards both gram positive and negative bacteria. The F-CNTs were unable to penetrate the thick wall of gram-positive bacteria, hence exhibited reduced activity when compared to gram negative bacteria. But the enhanced antimicrobial activity observed at 140 mg mL^{-1} could probably be attributed to the availability of higher amide groups reacting with cell wall of the gram-positive bacteria.

3.8 Comparison with other adsorbents

The efficiency of any adsorbent depends on its structure and adsorption capacity. The comparison of F-CNTs with various other nanoadsorbents in terms of adsorption capacity along with experimental conditions like pH and amount of adsorbent is given in Table 4. The result showed that adsorption capacity of F-CNTs for diclofenac was 532 mg g^{-1} which is quite better than the other nanoadsorbents

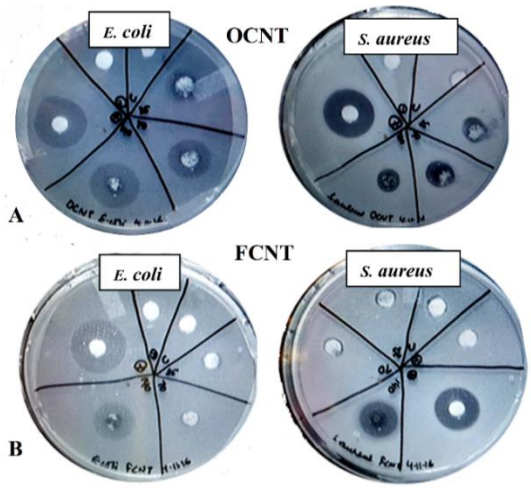

Fig. 8 Antimicrobial activity of (A) O-CNTs of various concentrations against *E.coli* and *S.aureus* (B) F-CNTs of various concentrations against E.coli and *S.aureus*

Table 3 ZOI of O-CNTs and F-CNTs at different concentrations against *E. coli* and *S. aureus*

Solid Phase Extractant	Sample	Zone of Inhibition (mm)	
		E.coli	*S.aureus*
–	Positive (Gentamycin)	7	8
	Negative (Water)	Nil	Nil
	Pristine MWCNTs	Nil	Nil
O-CNTs	35 mg mL^{-1}	1	2
	70 mg mL^{-1}	1	5
	140 mg mL^{-1}	**4**	**6**
F-CNTs	35 mg mL^{-1}	1	1
	70 mg mL^{-1}	1	1
	140 mg mL^{-1}	5	4

reported in Table 4. The amount of F-CNTs used is 0.2 g L^{-1} which is the least in comparison to other nanomaterials. The reason for high adsorption capacity is the presence of modifier m-phenylenediamine as with pristine MWCNTs the adsorption capacity was only 8.5 mg g^{-1}. The modification improves the capacity as can be seen amino-functionalized cellulose nanocrystals/chitosan and amine functionalized chitosan coated magnetic nanoparticles with capacity of 444.44 and 469.48 mg g^{-1} respectively.

4. Conclusions

• The proposed functionalized nanomaterial showed fast drug adsorption >95 % in 3 min of contact time and high adsorption capacity, 532 mg g^{-1}, which is much higher in comparison to other reported Nanomaterials.

• The kinetic study was performed on pseudo first order, second order, intraparticle diffusion and fractional power models and the results revealed that the data fits well in pseudo second order kinetic model with $R^2 > 0.99$. This indicates that adsorption is chemisorption.

Table 4 Comparison of adsorption capacity of m-phenylenediamine-CNTs for Diclofenac with other nanoadsorbents

Adsorbents	Amount of adsorbent (g L^{-1})	pH	Adsorption Capacity (mg g^{-1})	Ref.
MWCNTs	5.0	7.0	8.50	(Gil *et al*. 2018)
Activated carbon impregnated iron oxide nanoparticles	2.4	7.0	81.66	(Silveira *et al*. 2020)
Graphene oxide magnetic nanocomposite	0.74	4.0	32.40	(Van Tran *et al*. 2020)
Amino-functionalized cellulose nanocrystals/ chitosan	1.0	4.5	444.44	(Hu *et al*. 2019)
Amine-functionalized chitosan coated magnetic nanoparticles	0.4	4.5	469.48	(Liang *et al*. 2019)
Poly(methacrylic acid)/Montmorillonite Hydrogel Nanocomposite	1.4	2.0	152.86	(Khan *et al*. 2020)
Titanate nanosheet–pozzolan nanocomposite	1.5	7.0	90.52	(Wamba *et al*. 2019)
F-CNTs	***0.2***	***6.0***	***532.0***	***This study***

• The isotherm study was done on Langmuir, Freundlich, Temkin, Elovich and Redlich Peterson models. The data obtained showed best fitting in Langmuir model which means monolayer adsorption. The value of R_L which is less than unity also indicated favourable adsorption. The result was further supported by the factor β of Redlich Peterson model, whose value is 0.7321 which also favours Langmuir isotherm.

• The adsorption capacity calculated by both pseudo second order kinetic and Langmuir model is in close agreement with experimental value.

• Furthermore, both, the O-CNTs and F-CNTs exhibit mild antibacterial activity towards gram positive and gram-negative bacteria. The antimicrobial activity may be due to preventive effects occurring in the presence of COOH groups on the surface, and the redox activity of the carbonyl (C=O) group. The F-CNTs have too may surface groups that may actually inhibit catalytic activity because of steric hindrance as exhibited by reduced antimicrobial activity. In O-CNTs, the prevalence of COOH groups could possibly enhance the activity. The increased electro-chemical activity at the C=O sites incudes the electronic transfer generally depending on acid-base properties. The COOH and OH groups have electron-donating properties, i.e., capable of distributing the oxygen functional groups resulting in enhanced reactivity.

• The desorption of diclofenac from the surface of F-CNTs was also performed using various desorbing agents such as methanol, ethanol, acetonitrile, NaOH, etc. The results showed that the maximum desorption was obtained using 0.1 mol L^{-1} NaOH. However, it was difficult to achieve the complete desorption due to strong and irreversible chemical interaction between diclofenac and F-CNTs.

• Such modified nanoadsorbents have great potential in

water treatment, with their dual action of removing diclofenac drug and pathogens from water samples. Since, functionalized MWCNTs showed antimicrobial activity and also has high tendency to adsorb drug it can be used in drug delivery applications.

Acknowledgments

The authors are thankful to University of Delhi Innovation Project KMC 302 and Science and Engineering Research Board (SR/S1/IC-64/2012), Delhi, India for the financial support. The authors would also like to thank University Science Instrumentation Centre (USIC), University of Delhi, for providing instrumentation facility.

References

Al-Ghouti, M.A. and Da'ana, D.A. (2020), "Guidelines for the use and interpretation of adsorption isotherm models: A review" *J. Hazard. Mater.*, **393**, 122383. https://doi.org/10.1016/j.jhazmat.2020.122383.

Atole, D.M. and Rajput, H.H. (2018), "Ultraviolet spectroscopy and its pharmaceutical applications-a brief review", *Asian. J. Pharm. Clin. Res.*, **11**(2), 59-66. https://doi.org/10.22159/ajpcr.2018.v11i2.21361.

Ayawei, N., Ebelegi, A.N. and Wankasi, D. (2017), "Modelling and interpretation of adsorption isotherms", *J. Chem.*, 3039817. https://doi.org/10.1155/2017/3039817.

Bajaj, S., Jain, V., Sharma, N., Tiwari, S. and Saxena, R. (2021), "Efficient lead preconcentration using two chemically functionalized carbon nanotubes in hyphenated flow injection-flame atomic absorption spectrometry system", *J. Chromatogr. A*, **1638**, 461888. https://doi.org/10.1016/j.chroma.2021.461888.

Barczak, M., Dobrowolski, R., Borowski, P. and Giannakoudakis, D.A. (2020), "Pyridine-, thiol and amine-functionalized mesoporous silicas for adsorptive removal of pharmaceuticals", *Micropor. Mesopor. Mat.*, **299**, 110132. https://doi.org/10.1016/j.micromeso.2020.110132.

Barczak, M. Wierzbicka, M. and Borowski, P. (2018), "Sorption of diclofenac onto functionalized mesoporous silicas: Experimental and theoretical investigations", *Micropor. Mesopor. Mater.*, **264**, 254-264. https://doi.org/10.1016/j.micromeso.2018.01.013.

Biemer, J.J. (1973), "Antimicrobial susceptibility testing by the Kirby-Bauer disc diffusion method", *Ann. Clin. Lab. Sci.*, **3**, 135.

Chauhan, M., Saini, V.K. and Suthar, S. (2020), "Removal of pharmaceuticals and personal care products (PPCPs) from water by adsorption on aluminium pillared clay", *J. Porous. Mat.*, **27**, 383-393. https://doi.org/10.1007/s10934-019-00817-8.

Dasgupta-Schubert, N., Tiwari, D.K., Francis, E.R., Torres, P.M., Villaseñor, L.M. and Mora, C.V. (2017), "Plant responses to nano and micro structured carbon allotropes: Water imbibition by maize seeds upon exposure to multiwalled carbon nanotubes and activated carbon", *Adv. Nano Res.*, **5**(3), 245-251. http://doi.org/10.12989/anr.2017.5.3.245.

Dizaj, S.M., Mennati, A., Jafari, S., Khezri K. and Adibkia, K. (2015), "Antimicrobial activity of carbon-based nanoparticles", *Adv. Pharm. Bull.*, **5**(1), 19-23. https://doi.org/10.5681/apb.2015.003.

Ebrahimi, F. and Mahmoodi, F. (2018), "Vibration analysis of carbon nanotubes with multiple cracks in thermal environment", *Adv. Nano Res.*, **6**(1), 57-80. https://doi.org/10.12989/anr.2018.6.1.057.

Ensano, B.M.B., Borea, L., Naddeo, V., Belgiorno, V., de Luna, M.D.G., Balakrishnan, M. and Ballesteros Jr, F.C. (2019), "Applicability of the electro coagulation process in treating real municipal wastewater containing pharmaceutical active compounds", *J. Hazard. Mater.*, **361**, 367-373. https://doi.org/10.1016/j.jhazmat.2018.07.093.

Gil, A., Santamaría, L. and Korili, S.A. (2018), "Removal of caffeine and diclofenac from aqueous solution by adsorption on multiwalled carbon nanotubes", *Colloid Interf. Sci. Commun.*, **22**, 25-28. https://doi.org/10.1016/j.colcom.2017.11.007.

Hu, D., Jiang, R., Wang, N., Xu, H., Wang, Y.G. and Ouyang, X.K. (2019), "Adsorption of diclofenac sodium on bilayer amino-functionalized cellulose nanocrystals/chitosan composite", *J. Hazard. Mater.*, **369**, 483-493. https://doi.org/10.1016/j.jhazmat.2019.02.057.

Hu, X., Cheng, Z., Sun, Z. and Zhu, H. (2017), "Adsorption of diclofenac and triclosan in aqueous solution by purified multi-walled carbon nanotubes", *Pol. J. Environ. Stud.*, **26**(1). https://doi.org/10.15244/pjoes/63885.

Ighalo, J.O. and Adeniyi, A.G. (2020), "Mitigation of Diclofenac pollution in aqueous media by adsorption", *Chem. Bio. Eng. Rev.*,**7**(2), 50-64. https://doi.org/10.1002/cben.201900020.

Kanakaraju, D., Glass, B.D. and Oelgemöller, M. (2018), "Advanced oxidation process-mediated removal of pharmaceuticals from water: A review", *J. Environ. Manage.*, **219**, 189-207. https://doi.org/10.1016/j.jenvman.2018.04.103.

Kang, S., Pinault, M., Pfefferle, L.D. and Elimelech, M. (2007), "Single-walled carbon nanotubes exhibit strong antimicrobial activity", *Langmuir*, **23**(17), 8670-8673. https://doi.org/10.1021/la701067r.

Khan, S.A., Siddiqui, M.F. and Khan, T.A. (2020), "Synthesis of poly (methacrylic acid)/montmorillonite hydrogel nanocomposite for efficient adsorption of amoxicillin and diclofenac from aqueous Environment: kinetic, isotherm, reusability, and thermodynamic investigations", *ACS Omega*, **5**(6), 2843-2855. https://doi.org/10.1021/acsomega.9b03617.

Leone, V.O., Pereira, M.C., Aquino, S.F., Oliveira, L.C.A., Corrêa, S., Ramalho, T.C., Gurgel L.V.A. and Silva, A.C. (2018), "Adsorption of diclofenac on a magnetic adsorbent based on maghemite: Experimental and theoretical studies", *New J. Chem.*, **42**(1), 437-449. https://doi.org/10.1039/C7NJ03214E.

Liang, X.X., Omer, A.M., Hu, Z.H., Wang, Y.G., Yu, D. and Ouyang, X.K. (2019), "Efficient adsorption of diclofenac sodium from aqueous solutions using magnetic amine-functionalized chitosan", *Chemosphere*, **217**, 270-278. https://doi.org/10.1016/j.chemosphere.2018.11.023.

Liu, T., Xie, Z., Zhang, Y., Fan, J. and Liu, Q. (2017), "Preparation of cationic polymeric nanoparticles as an effective adsorbent for removing diclofenac sodium from water", *Rsc Adv.*, **7**(61), 38279-38286. https://doi.org/10.1039/C7RA06730E.

Lonappan, L., Brar, S.K., Das, R.K., Verma, M. and Surampalli, R.Y. (2016), "Diclofenac and its transformation products: Environmental occurrence and toxicity-a review", *Environ. Int.*, **96**, 127-138. https://doi.org/10.1016/j.envint.2016.09.014.

Mansour, F., Al-Hindi, M., Yahfoufi, R., Ayoub, G.M. and Ahmad, M.N. (2018), "The use of activated carbon for the removal of pharmaceuticals from aqueous solutions: A review", *Rev. Environ. Sci. Biotechnol.*, **17**, 109-145. https://doi.org/10.1007/s11157-0179456-8.

Mestre, A.S. and Carvalho, A.P. (2019), "Photocatalytic degradation of pharmaceuticals carbamazepine, diclofenac, and sulfamethoxazole by semiconductor and carbon materials: A review", *Molecules*, **24**(20), 3702. https://doi.org/10.3390/molecules24203702.

Mohanty, B., Verma, A.K., Claessonand P. and Bohidar, H.B. (2007), "Physical and anti-microbial characteristics of carbon nanoparticles prepared from lamp soot", *Nanotechnology*,

18(44), 445102. https://doi.org/10.1088/0957-4484/18/44/445102.
Mousavi, S.A. and Janjani, H. (2018), "Antibiotics adsorption from aqueous solutions using carbon nanotubes: Asystematic review", *Toxin Rev*., **39**(2), 87-98. https://doi.org/10.1080/15569543.2018.1483405.
Ouyang, Z., Huang, Z., Tang, X., Xiong, C., Tang, M. and Lu, Y. (2019), "A dually charged nanofiltration membrane by pH-responsive polydopamine for pharmaceuticals and personal care products removal", *Sep. Purif. Technol*., **211**, 90-97. https://doi.org/10.1016/j.seppur.2018.09.059.
Patel, M., Kumar, R., Kishore, K., Mlsna, T., Pittman Jr, C.U. and Mohan, D. (2019), "Pharmaceuticals of emerging concern in aquatic systems: Chemistry, occurrence, effects, and removal methods", *Chem. Rev*., **119**(6), 3510-3673. https://doi.org/10.1021/acs.chemrev.8b00299.
Pereira, M.B.B., França, D.B., Araújo, R.C., Silva Filho, E.C., Rigaud, B., Fonseca, M.G. and Jaber, M. (2020), "Amino hydroxyapatite/chitosan hybrids reticulated with glutaraldehyde at different pH values and their use for diclofenac removal", *Carbohydr. Polym*., **236**, 116036. https://doi.org/10.1016/j.carbpol.2020.116036.
Raicopol, M.D., Andronescu, C., Voicu, S.I., Vasile, E. and Pandele, A.M. (2019), "Cellulose acetate/layered double hydroxide adsorptive membranes for efficient removal of pharmaceutical environmental contaminants", *Carbohydr. Polym*., **214**, 204-212. https://doi.org/10.1016/j.carbpol.2019.03.042.
Rawat, K., Agarwal, S., Tyagi, A., Verma A.K. and Bohidar, H.B. (2014), "Aspect ratio dependent cytotoxicity and antimicrobial properties of nanoclay", *Appl. Biochem. Biotechnol*., **174**(3), 936-44. https://doi.org/10.1007/s12010-014-0983-2.
Saxena, R., Saxena, M. and Lochab, A. (2020), "Recent progress in nanomaterials for adsorptive removal of organic contaminants from wastewater", *Chem. Select*, **5**(1), 335-353. https://doi.org/10.1002/slct.201903542.
Saxena, M., Sharma, N. and Saxena, R. (2020), "Highly efficient and rapid removal of a toxic dye: adsorption kinetics, isotherm, and mechanism studies on functionalized multiwalled carbon nanotubes", *Surf. Interface*, **21**, 100639. https://doi.org/10.1016/j.surfin.2020.100639.
Siddiqui, M.R., AlOthman, Z.A. and Rahman, N. (2017), "Analytical techniques in pharmaceutical analysis: A review", *Arab. J. Chem*., **10**(1), 1409-1421. https://doi.org/10.1016/j.arabjc.2013.04.016.
Silveira, C., Shimabuku-Biadola, Q.L., Silva, M.F., Vieira, M.F. and Bergamasco, R. (2020), "Development of an activated carbon impregnation process with iron oxide nanoparticles by green synthesis for diclofenac adsorption", *Environ. Sci. Pollut. Res*., **27**(6), 6088-6102. https://doi.org/10.1007/s11356-019-07329-7.
Supraja, N., Avinash, B. and Prasad, T.N.V.K.V. (2017a), "Antimicrobial efficacy and safety analysis of zinc oxide nanoparticles against water borne pathogens", *Adv. Nano Res*., **5**(2), 127-140. https://doi.org/10.12989/anr.2017.5.2.127.
Supraja, N., Avinash, B. and Prasad, T.N.V.K.V. (2017b), "*Nelumbo nucifera* extracts mediated synthesis of silver nanoparticles for the potential applications in medicine and environmental remediation", *Adv. Nano Res*., **5**(4), 373-392. https://doi.org/10.12989/anr.2017.5.4.373.
Supraja, N., Dhivya, J., Prasad, T.N.V.K.V., and David, E. (2018), "Synthesis, characterization and dose dependent antimicrobial and anticancerous efficacy of phycogenic (Sargassum muticum) silver nanoparticles against Breast Cancer Cells (MCF 7) cell line", *Adv. Nano Res*., **6**(2), 183-200. https://doi.org/10.12989/anr.2018.6.2.183.
Tiwari, S., Sharma, N. and Saxena, R. (2017), "Functionalized carbon nanotubes in online speciation of chromium in real water samples using hyphenated FI-FAAS", *New J. Chem*., **41**(12), 5034-5039. https://doi.org/10.1039/C7NJ01253E.
Turner, B.D., Henley, B.J., Sleap, S.B. and Sloan, S.W. (2015), "Kinetic model selection and the Hill model in geochemistry", *Int. J. Environ. Sci. Technol*., **12**(8), 2545-2558. https://doi.org/10.1007/s13762-014-0662-4.
Van Tran, T., Nguyen, D.T.C., Le, H.T., Vo, D.V.N., Nanda, S. and Nguyen, T.D. (2020), "Optimization, equilibrium, adsorption behavior and role of surface functional groups on graphene oxide-based nanocomposite towards diclofenac drug", *J. Environ. Sci*., **93**, 137-150. https://doi.org/10.1016/j.jes.2020.02.007.
Verma, A.K., Dey, A., Dasgupta, A., Kumar, V. and Tyagi, A. (2015), "Evaluation of the of antibacterial efficacy of polyvinylpyrrolidone (PVP) and tri-sodium citrate (TSC) silver nanoparticles", *Int. Nano Lett*., **5**(4), 223-230. https://doi.org/10.1007/s40089-015-0159-2.
Wamba, A.G., Ndi, S.K., Lima, E.C., Kayem, J.G., Thue, P.S., Costa, T.M., Quevedo, A.B. Benvenutti, E.V. and Machado, F.M. (2019), "Preparation, characterization of titanate nanosheet–pozzolan nanocomposite and its use as an adsorbent for removal of diclofenac from simulated hospital effluents", *J. Taiwan Inst. Chem. Eng*., **102**, 321-329. https://doi.org/10.1016/j.jtice.2019.05.001.
Wan, K., Huang, L., Yan, J., Ma, B., Huang, X., Luo, Z., Zhang, H. and Xiao, T. (2021), "Removal of fluoride from industrial wastewater by using different adsorbents: A review", *Sci. Total Environ*., **773**, 145535. https://doi.org/10.1016/j.scitotenv.2021.145535.
Wang, J. and Guo, X. (2020), "Adsorption kinetic models: Physical meanings, applications, and solving methods", *J. Hazard. Mater*., **390**, 122156. https://doi.org/10.1016/j.jhazmat.2020.122156.
Xiong, T., Yuan, X., Wang, H., Wu, Z., Jiang, L., Leng, L., Xi, K., Cao, X. and Zeng, G. (2019), "Highly efficient removal of diclofenac sodium from medical wastewater by Mg/Al layered double hydroxide-poly (m-phenylenediamine) composite", *Chem. Eng. J*., **366**, 83-91. https://doi.org/10.1016/j.cej.2019.02.069.

JL