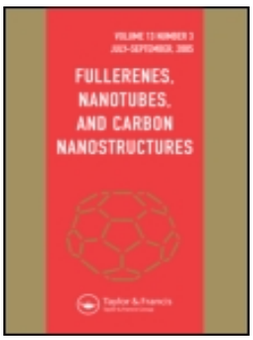

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Amoxicillin Removal from Aqueous Media Using Multi-Walled Carbon Nanotubes

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Multi-walled carbon nanotubes (MWCNT) were used to separate amoxicillin from aqueous media. The parameters affecting amoxicillin adsorption such as pH, temperature, time, interferences of similar molecules, and the amount of adsorbent used were studied. Amoxicillin adsorption using MWCNT was compared to that using Fullerene C60 and activated carbon (AC). The adsorption efficiency of 0.1 and 0.2 g of MWCNT using in a continuous mode were 86.5% and 87.9%, respectively. Evaluation of the adsorbent capacity showed that each gram of MWCNT can absorb 22.9 mg amoxicillin. The effect of pH was studied over the range 2–8 and revealed that adsorption of the amoxicillin at the initial pH of 4.6 was more effective than any other pH. The adsorption of amoxicillin on MWCNT was much greater than Fullerene C60 and AC. Adsorption data showed that they were best fitted to the Langmuir isotherm.

Keywords: amoxicillin, multi-walled carbon nanotubes, adsorption, water

1. Introduction

Environmental pollution as a consequence of technological evolvement has become one of the most crucial problems for the global population. The first reports on the presence of pharmaceuticals in wastewater effluent and surface water were published in the United States in the 1970s (1). Pharmaceuticals such as antibiotics are widely used to treat many infections and are considered as water and waste water pollutants. The presence of antibiotics in pharmaceutical company and hospital waste that flow into surface or underground water has poses two risks. The first is the occurrence of these materials in the environment is in itself a threat and the consequence of environmental contamination is the risk of microorganism resistance which reduces the ability to treat infections (2). Amoxicillin is widely used in human and veterinary medicine and has been isolated in waste water (3), and this compound originating from wastewater treatment plant (WWTP) effluent has reached environmental water bodies (4). Many pharmaceuticals are only partially removed using biological processes in Sewage Treatment Plants and they are consequently often released into surface water (5). The removal of antibiotics from waste water is a great concern regarding the prevention of bacterial resistance and side effects of exposure. Several methods have been reported to remove amoxicillin from aqueous media and include reversed osmosis, use of ion exchange resins (6), ozonation (5), oxidation by Fenton's reagent (7–10), use of micro- and nanoscale iron particles (11), antibiotic removal by biological treatment (12), nanofiltration (13), membrane separation (14), and adsorption processes (15, 16). Adsorption is considered a highly effective means to remove contaminants in water or wastewater even at very low concentrations (<1 mg/L) (15). Depending on the type of adsorbent used this method is simple and applicable for the removal of common substances with low operation cost in comparison to other techniques (17, 18). To our knowledge the use of MWCNT as an adsorbent for amoxicillin removal from aqueous media has not been reported. Therefore, the main aim of this study was to use MWCNT to remove amoxicillin using a batch and/or continuous process.

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Color versions of one or more of the figures in this article can be found online at www.tandfonline.com/lfnn.

2. Materials and Methods

2.1 Chemicals

MWCNT and fullerene C60 (PlasmaChem, GmbH, Germany) were used in this study. The purity of the MWCNT was >95%

and the diameter and length was 10–30 and 1–10 mm, respectively, with 3–15 walls per MWCNT. Commercially available powdered AC was purchased from E. Merck AG (Darmstadt, Germany). In all experiments, ultrapure water (UPW) is used for the preparation and dilution of solutions and was produced using a Milli-Q system (18.2 M, Millipore, Bedford, MA, USA). Amoxicillin trihydrate was purchased from Cosar Pharmaceutical Co. (Karaj, Tehran). Ampicillin, penicillin V K, and cephalexin were kindly donated by Zakaria-Tabriz Pharmaceutical Co. (Tabriz). Hydrochloric acid and sodium hydroxide were used to adjust the pH of the solutions. All other chemicals used in the study were purchased from E. Merck AG (Darmstadt, Germany) and used without further manipulation.

2.2 Optimization and Validation of the Spectrophotometric Method for Determination of amoxicillin in Aqueous Solutions

The absorption spectrum and absorbance at 228.7 nm were measured using a Perkin-Elmer Lambda 25 model UV–visible spectrophotometer (Perkin-Elmer, USA). A calibration curve was constructed for the concentration range of 5–80 mg/L, calculated on an anhydrous basis and was validated for precision, accuracy, LOD, LOQ, stability of the solutions, and interference from compounds with similar chemical structures such as ampicillin, penicillin V K, and cephalexin. RSD%, error%, and interferences less than 5% are considered appropriate.

2.3 Sorption Studies

Fullerene C60, MWCNT, and AC were used as adsorbent materials. Sorption was studied using batch and continuous methods. All experiments were performed using 20 mL of a 40 mg/L solution of amoxicillin. In all sorption experiments, the samples placed in contact with the adsorbents were filtered for batch experiments and was waste effluent for continuous experiments. The samples were harvested prior to and after exposure to adsorbent to establish the amoxicillin content by spectrophotometry.

2.4 Batch Sorption Studies

For the batch sorption experiments, 0.05 g of each adsorbent was weighed and placed in contact with separate 40 mg/L amoxicillin solutions in UPW. The adsorbents were placed in contact with the amoxicillin solution for 0–40 minutes and samples were tested at 10-minute intervals. The contact between the adsorbent and amoxicillin solution was facilitated by agitation using a shaker at a speed of 150 rpm (Heidolph, Germany). After sampling at the specified time, the absorbance of the solution was measured directly. The amoxicillin removal efficiency was calculated using the expression (1).

$$\mathrm{RE} = \frac{[\mathrm{Amoxicillin(init)}] - [\mathrm{Amoxicillin(fin)}]}{[\mathrm{Amoxicillin(init)}]} \qquad (1)$$

where
RE = removal efficiency,
[Amoxicillin (init)] = initial concentration
[Amoxicillin (fin)] = final concentration.

The amount of amoxicillin adsorbed per unit weight of adsorbent, viz., Amoxicillin (ad) was determined as the ratio of amoxicillin that had been adsorbed and the total weight of solid used initially.

2.5 Continuous Sorption Studies

For the continuous sorption experiments, a 5-mL syringe with an inner diameter of 10 mm and a length of 90 mm was used to create a cartridge to pass through amoxicillin solutions. Two membrane filters (0.45 microns, Sartorius, Germany) were placed in the syringe outlet port. Prior to running the experiment the cartridge was filled with 0.05 g of the appropriate adsorbent that was conditioned by passing ethyl alcohol and deionized water through the cartridge. At this stage, 10 mL of the 40 mg/L amoxicillin solution was passed through the conditioned cartridge. The absorbance of the solution was measured prior to and following solution flow through the cartridge.

2.6 Effect of Adsorbent

Using a batch type experimental approach amoxicillin adsorption was studied with 0.05 g of AC, fullerene C60 or MWCNT following exposure of the material to 20 mL of the 40 mg/L amoxicillin solution. Each experiment was repeated three times to evaluate adsorption efficiency of adsorbents.

2.7 Effect of pH

To evaluate the effect of pH on amoxicillin sorption using a batch approach the initial pH of the amoxicillin solutions was adjusted to 2.0, 4.0, 6.0, and 8.0 using either sodium hydroxide or hydrochloric acid. The pH of the amoxicillin solution without any adjustment was also measured and found to be approximately 4.6.

2.8 Effect of Time

To optimize the duration of water treatment for efficient removal of amoxicillin sorption experiments were conducted up to 120 minutes and samples were evaluated following exposure for 2, 10, 20, 30, 40, 60, and 120 minutes.

2.9 Effect of Temperature

Adsorption experiments were performed at 30, 40, and 50°C to establish the kinetics of adsorption of amoxicillin to the MWCNT.

2.10 Amount of Adsorbent

Different amounts of MWCNT of 0.05, 0.1, and 0.2 g of adsorbent were used in batch sorption experiments with 20 mL of 40 mg/L of amoxicillin solutions in an attempt to optimize the amount of adsorbent that would be required for use.

2.11 Effect of Interfering Agents on Adsorption Efficiency

As amoxicillin is not the only antibiotic that may be present in waste water the effect of ampicillin, penicillin, and cephalexin, compounds that have similar chemical structures to amoxicillin, on sorption of amoxicillin were investigated. Mixed solutions containing amoxicillin and the aforementioned antibiotics alone or in combination at a final concentration of 40 mg/L were treated in the batch system to establish if any effect on adsorption could be identified.

2.12 Adsorption Capacity Measurements and Desorption

The continuous system was used to assess the amoxicillin removal capacity of the system. For this purpose two amounts of adsorbent of 0.05 and 0.1 g of MWCNT were used. In each experiment 20 mL of 40 mg/L amoxicillin were passed through the cartridge column until the sorbent was saturated. The quotient of the total amount of amoxicillin removed by the sorbent (mg) and mass of adsorbent (g) was used to calculate amoxicillin removal capacity of the system. To evaluate the desorption of amoxicillin from MWCNT and establish whether the material can be reused, sodium hydroxide 0.1 N, hydrochloric acid, and distilled water were used to study the desorption of amoxicillin.

2.13 Sorption Isotherm

The sorption data were fitted to the Langmuir, Freundlich, and Dubinin–Radushkevitch (D–R) equations to establish the sorption isotherm of amoxicillin removal by MWCNT. Data generated using the batch system data were used for this purpose.

3. Results and Discussion

3.1 Amoxicillin Analysis

Spectrophotometric method validation parameters for the analysis of amoxicillin in aqueous media are summarized in Table 1. The data reveal that the parameters are in the acceptable range and the method is reliable for the determination of amoxicillin for all studies.

Table 1. Validation data for the spectrophotometric determination of amoxicillin in aqueous media

Parameters	Amoxicillin ($\lambda = 228.7$ nm)
Concentration range (mg/L)	5–80
$Y = aX+b$	Abs. = 0.0236Conc. - 0.027
Correlation coefficient	0.9999
Standard error of the slope	0.011
Standard error of the intercept	0.512
P value for correlation coefficient	0.0001
Within day CV%	3.5
Between day CV%	2.1
Limit of detection(mg/L)	0.2
Limit of quantitation (mg/L)	0.4
Recovery (%)	98.9
Stability of the solutions at ambient temperature	Not less than 500 hrs

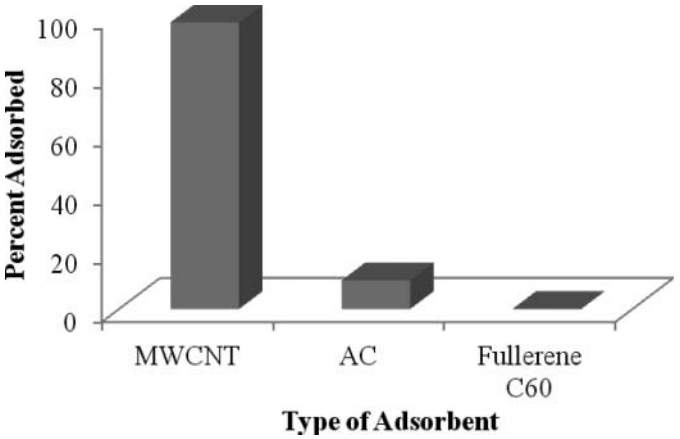

Fig. 1. Percent of amoxicillin adsorbed on different adsorbents.

3.2 Optimization of Adsorption and Desorption

The adsorption of amoxicillin to AC, Fullrene C60 and MWCT revealed that Fullerene C60 had no tendency to adsorb amoxicillin from aqueous solutions with <1% adsorbed after 40 minutes exposure whereas MWCNT had the highest adsorption capacity for amoxicillin with >90% removed from solution after 40 minutes exposure. The adsorption capacity of AC had been approximately 10% after 40 minutes exposure (Fig. 1).

The effect of pH on the adsorption of amoxicillin is shown in Fig. 2. A solution of amoxicillin has a pH of 4.6 and it can be seen that the lowest percent adsorption of 83.8% was observed at a pH of 2 and for all other pH tested the percent adsorbed was > 93%. Therefore, if the pH ranged between 4 and 8, there would be little or no effect on the adsorption of amoxicillin.

Studies to establish the amount of amoxicillin adsorbed at different times reveals that adsorption increases over up to 40 minutes, after which there is little change in adsorption and the curve of adsorption reaches a plateau. Consequently, 40 minutes was selected as the appropriate exposure time for all following experiments. A major challenge was to optimize the temperature to be used since temperatures other than ambient consume energy. The effect of temperature on

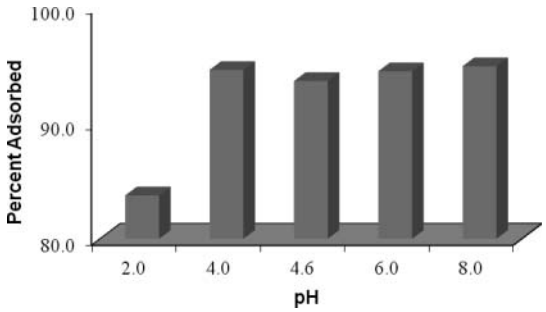

Fig. 2. Percent of amoxicillin adsorbed on MWCNT at different pH.

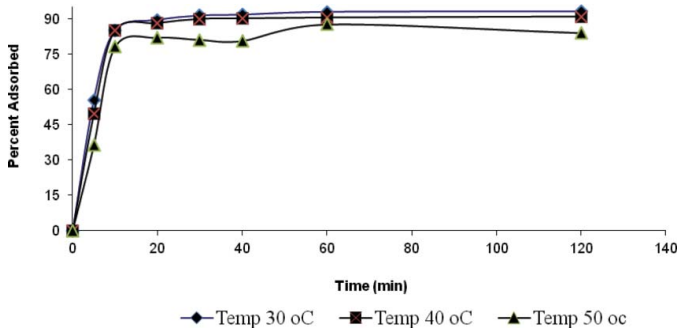

Fig. 3. Amoxicillin adsorbed to MWCNT following exposure to 30, 40, and 50°C up to 120 min.

adsorption of amoxicillin is shown in Fig. 3 and reveals that increasing temperatures result in somewhat decrease in the amount of amoxicillin adsorbed which may be related to the higher kinetic energy of the molecules and less tendency to interact with adsorbent. However in the range of 30–50°C decrease does not appear to be significant and the amount of amoxicillin adsorbed is acceptable at ambient temperatures in comparison to higher temperatures.

The effect of amoxicillin concentration on the percent adsorbed to MWCNT reveals that in the concentration range of 10–60 mg/L, after 40 minutes, there appears to be a negligible effect of concentration on the percent drug adsorbed. This suggests that using 0.05 g MWCNT to remove amoxicillin from 20 mL is adequate as there are many receptor sites on the adsorbent material and saturation of the material by amoxicillin would be unlikely.

The effect of the amount of adsorbent on the percent adsorption reveals that increasing the amount of adsorbent in the system will result in an increase the percent amoxicillin removed from the solutions which is however, not significant. This effect may be related to the concentration and volume of amoxicillin solution used to investigate the effect of amount of adsorbent on the efficiency of the system. Apparently, the absolute amount of amoxicillin that was used in comparison to the receptor sites available for adsorption is extremely low.

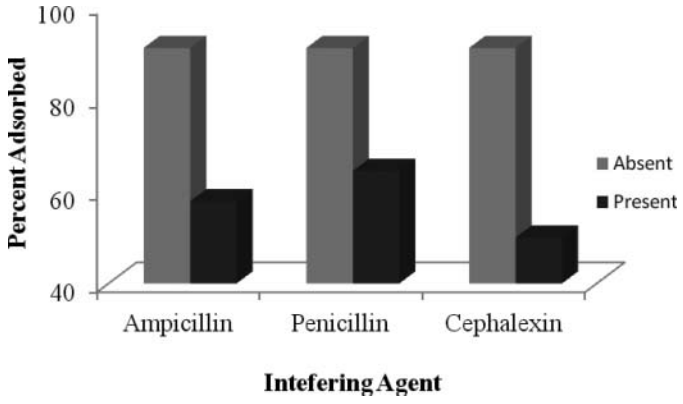

Fig. 4. Adsorption of amoxicillin to MWCNT with and without the presence of ampicillin, penicillin, and cephalexin.

Table 2. Isothermal model equation constants for amoxicillin removal by MWCNT

Model	Parameters		
Langmuir	b (L/mol)	q_{max} (mol/g)	R^2
	2.50e-5	6.42e-5	0.9994
Freundlich	KF (mol1-nLn/g)	n	R^2
	0.0030	0.3749	0.918
D–R	β (mol2/kJ2)	q_{max} (mol/g)	R^2
	2.00e-7	3.95e-4	0.9361

The results of saturation capacity measurements indicate that each gram of MWCNT can adsorb approximately 22.9 mg of amoxicillin when using optimum conditions.

The effect of the presence of interfering agents with a similar chemical structure to amoxicillin on amoxicillin adsorption to MWCNT is depicted in the Fig. 4.

As shown in Fig. 4, all interfering agents lowered the percent amoxicillin adsorbed by MWCNT and cephalexin appears to have the greatest effect. This indicates that the binding sites on the MWCNT have an affinity for chemicals with the same backbone structure and that the removal of amoxicillin may be reduced by the presence of the interfering agents. However this finding to remove antibiotics from wastewater may be of great value, but in the case of selective removal may be a trouble.

To determine the mechanism of adsorption of amoxicillin to MWCNT, the data generated using a batch approach was fitted to three isotherm models including Langmuir, Freundlich, and D–R. The Langmuir isotherm, which is regarded as the most applicable isotherm, is commonly applied in solid/liquid systems to describe saturated monolayer sorption(19). The Freundlich isotherm, which is based on sorption to a heterogeneous surface, is the earliest known relationship that describes sorption equilibrium (20) and the D–R isotherm model is valid at low concentration ranges and can be used to describe sorption onto both homogeneous and heterogeneous surfaces (21). The results of data modeling are listed in Table 2.

The results show that the data were best fitted to the Langmuir isotherm and therefore it can be concluded that adsorption of amoxicillin to MWCNT is monolayer in nature. The results revealed that amoxicillin desorption rates are faster in a basic environment than in either acidic or neutral environments.

4. Conclusions

Antibiotic removal from aqueous media is an important public health consideration to protect people from developing resistance to safe antibacterials and also to protect the environment from contamination by excess chemicals. The data from studies reported in this manuscript suggest that MWCNT have a greater capacity to remove amoxicillin from aqueous environments that either AC or Fullerene C60. The removal of amoxicillin can be accomplished under ordinary conditions and MWCNT can be regenerated using

acidic or alkaline solutions. A simple and effective means to remove antibiotic contamination in aqueous solutions has been reported and may be applied to improve water quality for reuse and to remove unwanted contamination from the environment.

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