Journal of Chemical Health Risks

www.jchr.org

ORIGINAL ARTICLE

Removal of Pharmaceutical Pollutions of Aspirin and Atrazine from Waste Water Using Carbon Nanotubes

Farzaneh Rezaei Ranjbar, Farhad Khamchin Moghadam*

Department of civil Engineering, Mashhad branch, Islamic Azad University, Mashhad Iran

(Received: 5 June 2019 Accepted: 23 November 2019)

KEYWORDS

Initial Concentration;
Contact Time;
Adsorbent Dosage;
Multi-walled Carbon Nanotubes

ABSTRACT: Currently, there is a serious water crisis in the world, which necessitates the purification of polluted water. Nowadays, new methods have been presented for the treatment of contaminated water. In the present study, single- and multi-walled nanotubes were used for adsorption of aspirin and atrazine pharmaceutical pollutions from waste water. In addition, various tests were performed at six levels to evaluate the parameters of effects of the initial concentration of solution, level of nano-absorbent, contact duration, temperature and pH on pharmaceutical pollutions of aspirin and atrazine in two single- and multi-walled carbon nanotubes. Moreover, results of each level of the test were separately shown on diagrams based on the concentration percentage. After the comparison of results, it was demonstrated that in the parameter of effect of the initial concentration of solution, the pharmaceutical pollution of atrazine had the highest adsorption percentage (94.03%) in the presence of multi-walled carbon nanotubes. In terms of the total adsorption percentage of aspirin and atrazine, the highest adsorption percentage was observed in the presence of multi-walled carbon nanotubes.

INTRODUCTION

Today, the modern world is faced with water crisis, and while three-quarters of the planet's surface is filled by water, fresh water is in short supply for use and survival. This crisis has been exacerbated due to drought, water pollution, excessive consumption of water and lack of proper management of water use and treatment. Water contamination is identified as direct or indirect transfer or intrusion of different types of pollutants into the environment by human beings. One of the new methods for treatment of contaminated water is application of nanoparticle technology. Some of the properties of nanoparticles include large surface area relative to large particles and ability to combine with different chemical groups to increase continuity. Generally, carbon nanoparticles are used due to high capacity and selective adsorbents for organic solvents in aqueous solutions. In addition, multi-walled carbon nanoparticles act as better adsorbents of contaminations in aqueous solutions, compared to unstable organic compounds [1].

Due to high potentials, large volumes and sizes, corresponding optical form, as well as electronic and catalytic properties, nanoparticles are used as water purification catalysts and active restorative networks. In the past decade, titanium oxide nanoparticles have emerged as a photocatalyst for water purification [2]. In addition, this type of nanoparticle is exploited as an oxidizing and reviving catalyst for organic and mineral pollutants [3]. Moreover, zero-valent iron nanoparticles and bimetallic

*Corresponding author: f.khamchin@gmail.com (F. Khamchin Moghadam)
DOI: 10.22034/jchr.2020.578325.0

iron nanoparticles are used to reduce redox-active metal ions, such as tetravalent chromium to trivalent chromium, with less toxicity and mobility [4]. Membrane technology, such as ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RS), has emerged as a key part of advanced water treatment and desalination processes [5].

In general, NFs are used to remove organic and biological pollutants, as well as nitrates and arsenic from surface and underground water [6]. Moreover, the ability of NFs in increasing the quality of water in large water distribution systems has been confirmed [7]. The selective feature and diffusivity by UF membrane can increase by elevating the concentration of alumina nanoparticles with iron, manganese and lanthanum [8]. Dendrimer enhanced ultrafiltration (DEUF) has been developed from aqueous solutions to modify metal ions. In addition, use of DEUF and polyamidoamine (PAMAM) dendrimers with core ethylenediamine (EDA) and exogenous NH2 groups has been tested in isolation of divalent copper from aqueous water. In the initial mass, the PAMAM dendrimer copper capacities are much larger and more sensitive compared to the solution pH of linear polymers with amine groups. Separation of dendrimer-copper complex from solution can be easily obtained by UF membrane with molecular weight cut-off (MWC). Moreover, dendrimer containing metal ion can be reproduced by reducing the pH of the solution to four [9, 10].

Pharmaceutical pollutants are among the most important issues of modern life, and their negative effects on the environment and human health are undeniable. Generally, pharmaceutical compounds enter the sewage networks as drug residues through the urine and feces of patients who consume these drugs. Without refining, these pollutants enter the wastewater of refineries with high resistance and find their way into surface waters and rivers [11].

Studies have shown that drugs enter the environment from drug manufacturing factories and in the form of expired drugs, excessively used drugs, and drugs consumed by animals and humans. Drugs used by humans are the main source of contamination. There is a high possibility of the existence of drugs in aquatic resources due to the high solubility of these compounds. Unfortunately, normal water treatment is not able to remove these pollutants. Medications that have a high half-life, especially antibiotics, accumulate, increase resistance in the human body, and cause the mutation of microorganisms, which have dangerous consequences [12].

Considering the importance of this issue, the present study aimed to evaluate the removal of two types of pharmaceutical pollutants (Aspirin and Atrazine) using carbon nanotubes.

The current experiment was carried out to evaluate the removal of two pharmaceutical pollutants of aspirin and atrazine through single- and multi-walled carbon nanotubes. Pharmaceutical contaminants of aspirin and atrazine in polluted water infiltrate into underground water, which leads to the contamination of water resources, endangering human health, and destructing aquatic habitats due to their sustainability in the aquatic environment.

MATERIALS AND METHODS

In this research, removal of two types of pharmaceutical pollutants (i.e., aspirin and atrazine) through single- and multi-walled carbon nanotubes was evaluated.

Examination tools included: 1) a UV device, 2) drugs (Aspirin and Atrazine), 3) distilled water. The test of absorption of pharmaceutical pollutants by single and multiwall carbon nanotubes is explained below. As mentioned before, this test was carried out at six levels of effect of changes in the parameters of temperature, concentration, time and pH on the level of removal of pharmaceutical pollutants. In order to perform the test, a certain amount of solution was prepared with a specific concentration of the desired pollutant, which is called the standard solution. Afterwards, a particular amount of adsorbent was poured into the solution. After the absorption of some of the contaminants by nano adsorbents (carbon nanotubes), the filtration process was carried out on the standard solution in order to assess the concentration of the new solution that contains the remaining amount of adsorbent.

A UV-VIS spectroscopy was used to determine the number of residual contaminants in the solution and evaluate the amount of absorbed material. In this process, the sample was exposed to light from the bulb of the device, and absorption occurred due to exposure to UV rays. Applying the Beer–Lambert law, the amount of absorption of the desired pollutant was read from the device. Following that, the percentage of pollutant absorption was estimated using the equation below. The results are presented in the diagram.

$$R=(C/C0)*100$$

In this equation, the parameters are defined as follows:

R: adsorption efficiency

C: solution concentration

C0: initial concentration of solution

RESULTS AND DISCUSSION

Results obtained from these tests are presented below:

Effect of the Initial Concentration of Solution

The effect of initial concentrations of the solution was assessed using different initial concentrations in case of fixed level of adsorbent followed by estimation of level of adsorption of each pollutant (aspirin and atrazine) for various initial concentrations in the presence of single- and multi-walled carbon nanotubes. Following that, the adsorption efficiency was calculated for each of the adsorbed amount using the equation below. In addition, the related diagram was drawn for single- and multi-walled carbon nanotubes.

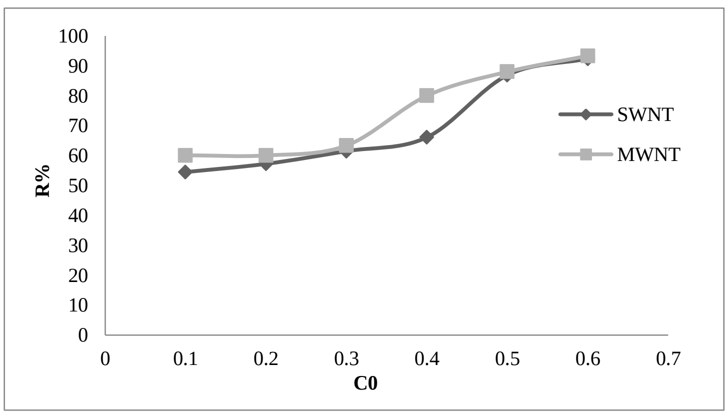

Figure 1. Evaluation of the effect of initial solution concentration on level of aspirin adsorption in the presence of a single-walled carbon nanotube and multi-walled carbon nanotube.

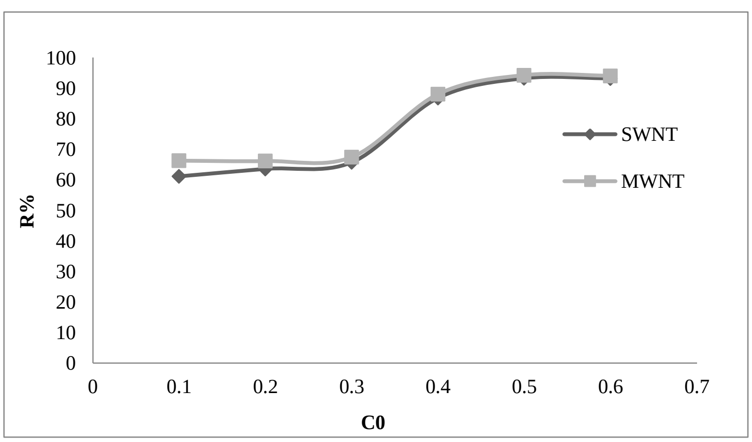

Figure 2. Evaluation of the effect of the initial solution concentration on level of atrazin adsorption in the presence of a single-walled carbon nanotube and multi-walled carbon nanotube.

According to diagrams 1 and 2, increased initial solution concentration led to a higher aspirin and atrazine adsorption percentage in case of fixed concentrations of the single- and multi-walled carbon nanotubes. With regard to the adsorption efficiency, multi-walled carbon nanotubes had a more efficient performance in adsorption of atrazin, compared to single-walled carbon nanotubes.

Effect of Nano-adsorbent Amount

In another level of the tests, the parameter of the effect of nano-adsorbent amount (W) on adsorption level of pollutants was evaluated while considering a fixed initial solution concentration. After the test, the adsorbed amounts of the pollutants by single- and multi-walled carbon nanotubes were obtained, followed by estimation of adsorption percentage of pharmaceutical pollutants by single- and multi-walled carbon nanotubes for a specific concentration of adsorbent, if the initial concentration of the solution was fixed. The resulting data are presented in the following table.

Table 1. Percentage of adsorption of pollutants by single-wall carbon nanotubes for a certain concentration of adsorbent if the initial concentration of the solution.

W	Aspirin	Atrazin
0.1	3.272	4.34
0.25	11.72	13.14
0.43	21.05	22.48
0.55	38.38	42.48
0.67	54.38	58.34
0.89	83.72	84.08

Table 2. Percentage of adsorption of pollutants by multi-wall carbon nanotubes for a certain concentration of adsorbent if constant initial concentration

W	Aspirin	Atrazin
0.1	6.38	7.14
0.25	14.38	15.94
0.43	23.72	25.28
0.55	41.05	45.28
0.67	57.05	61.14
0.89	86.38	86.88

After the comparison of the tables 1 and 2, it was concluded that increased concentration of nano-adsorbent led to a higher adsorption level of aspirin and atrazin in case of fixed initial solution concentration. In addition, concentration of nano-adsorbent above 0.6 mg/L was associated with a higher efficiency in adsorption. With regard to the adsorption efficiency, it was demonstrated that multi-walled carbon nanotubes had a better performance in adsorbing atrazin, compared to single-walled carbon nanotubes.

Effect of contact time

In this section, the effect of contact time on adsorption percentage of pollutants by the nano-adsorbent was evaluated. In this test, the adsorption percentages of pharmaceutical pollutants of aspirin and atrazine by single- and multi-walled carbon nanotubes with fixed absorbent and primary concentrations were evaluated at different times. The obtained results were presented in a diagram based on the adsorption percentage for aspirin pollutant, one time in the presence of a single-walled carbon nanotube and another time with a multi-walled carbon nanotube. The same process was carried out for atrazine pollutant based on the contact time.

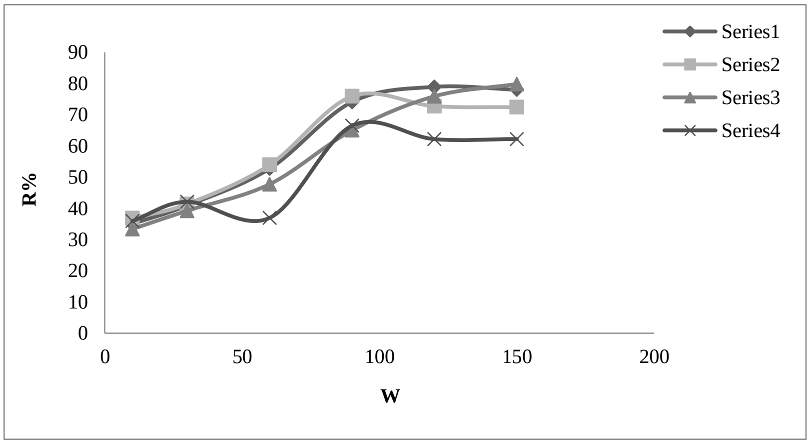

Figure 3. The effect of time passage on adsorption of drug pollutants in the presence of single-wall and multi-wall carbon nanotubes.

After the comparison of diagram, it was concluded that increased contact time of solution with nano-adsorbent led to an elevated percentage of adsorption in case of fixed initial and nano-adsorbent concentrations for adsorbing aspirin and atrazine. However, with regard to the adsorbent efficiency up to 90 minutes, the multi-walled carbon nanotube had a higher adsorption percentage, compared to the single-walled nanotube. However, the single-walled nanotube had a higher adsorption percentage after 120 minutes and was then fixed at a certain level.

Evaluation of temperature effect

At this level of the test, the level of adsorption of pharmaceutical aspirin and atrazine pollutants was assessed one time with single-walled carbon nanotube and another time with multi-walled carbon nanotube at various temperatures with fixed adsorbent (w=1) and initial (c=0.7) concentrations and contact time (t=90). Results related to each different temperature are presented in a tables based on the adsorption percentage for each pollutant using the single- and multi-walled carbon nanotubes separately.

Table 3. Evaluation of the effect of temperature on the adsorption percentage of aspirin and atrazin in the presence of a single-walled carbon nanotube.

T	Aspirin	Atrazin
25	70	68.57
35	75.71	78.57
45	71.42	70

Table 4. Evaluation of the effect of temperature on the adsoprtion percentage of aspirin and atrazin in the presence of a multi-walled carbon nanotube.

T	Aspirin	Atrazin
25	78.57	81.42
35	77.14	80
45	70	68.57

After comparing the tables 3 and 4, it was concluded that multi-walled carbon nanotubes had a higher aspirin and atrazin adsorption percentage, compared to single-walled carbon nanotube, in the presence of increased temperature of the solution, fixed initial and nano-adsorbent concentrations and contact time of 90 minutes (with regard to the adsorption efficiency up to 35°C), which was then reduced, reaching 25°C.

Effect of pH

In this level of the test, the effect of various pH levels on adsorption percentage of aspirin and atrazine was evaluated one time with single-walled carbon nanotube and another time with multi-walled carbon nanotube in case of fixed adsorbent concentration (W=1), contact time (t=90) and temperature (T=25°C).

Table5. Evaluation of the effect of pH on aspirin adsorption percentage in the presence of a single-walled carbon nanotube.

pH	Aspirin	R%
3	0.15	30
7	0.32	64
10	0.2	40

Table6. Evaluation of the effect of pH on aspirin adsorption percentage in the presence of a multi-walled carbon nanotube.

pH	Aspirin	R%
3	0.18	36
7	0.39	78
10	0.24	48

After the comparison of tables 5 and 6, it was concluded that increasing the solution pH led to a higher aspirin adsorption percentage in single-walled nanotubes, compared to multi-walled nanotubes, in case of having stable initial solution and nano-adsorbent concentrations, contact time of 90 minutes and temperature of 25°C with regard to adsorbent efficiency up to pH=7. However, this adsorption percentage reduced after that, which means that the highest adsorption occurred at pH=7.

Table 7. Evaluation of the effect of pH on atrazine adsorption level in the presence of a single-walled carbon nanotube.

pH	Atrazin	R%
3	0.19	38
7	0.37	74
10	0.19	38

Table 8 . Evaluation of the effect of pH on atrazine adsorption level in the presence of a multi-walled carbon nanotube.

pH	Atrazin	R%
3	0.19	42
7	0.37	76
10	0.19	46

Comparison of tables 7 and 8 demonstrated that increased pH of solution resulted in a higher atrazine adsorption percentage by multi-walled carbon nanotubes, compared to single-walled carbon nanotubes, in case of fixed initial solution and nano-adsorbent concentrations, contact time of 90 minutes and temperature of 25°C with regard to adsorption efficiency up to pH=7. However, the adsorption level decreased after that, which could be interpreted as the occurrence of highest adsorption at pH=7.

CONCLUSIONS

After the evaluation of performed tests and diagrams on adsorption level of aspirin and atrazine in water and sewage contaminated with these pollutants, samples were collected and standard solutions with specific volumes and concentrations were created for single- and multi-walled carbon nanotubes in order to evaluate the parameters of initial concentration of solution with nano-adsorbent and contact time with nano-adsorbent, temperature and pH of solution. Results are presented, as follows:

In case of having fixed concentration of nano-adsorbent and contact time, the adsorption percentage of aspirin increased by elevated initial concentration of solution, where multi-walled carbon nanotubes had a higher efficiency in adsorbing aspirin, compared to single-walled carbon nanotubes. On the other hand, there was an increase in adsorption of aspirin in the presence of elevated concentration of nano-adsorbent if there was fixed initial concentration of solution and contact time. In this regard, multi-walled carbon nanotubes had a better performance in absorbing aspirin, compared to single-walled carbon nanotubes.

In case of fixed initial concentration of solution and nano-adsorbent concentration, the adsorption percentage of aspirin increased by elevated concentration of nano-adsorbent. In addition, the optimal contact time (where the highest percentage of adsorption occurred) was 90 minutes, after which the adsorption percentage decreased. In this respect, multi-walled carbon nanotubes had a higher efficiency in adsorbing aspirin, compared to single-walled carbon nanotubes. Having fixed initial solution and nano-adsorbent concentration, contact time of 90 minutes, and increased temperature, there was an increase in aspirin adsorption percentage, where the highest level of adsorption occurred at 35°C, after which the adsorption percentage was reduced. In this regard, multi-walled carbon nanotubes had a better performance regarding aspirin adsorption, compared to single-walled carbon nanotubes.

In case of fixed initial solution and nano-adsorbent concentrations, contact time of 20 minutes and temperature of 25°C, aspirin adsorption percentage increased by elevated pH level, where the highest adsorption percentage occurred at pH=7 and decreased after that. In this respect, multi-walled carbon nanotubes had a higher efficiency in adsorbing aspirin, compared to single-walled carbon nanotubes. Having fixed initial solution concentration and contact time, the percentage of atrazine adsorption increased with elevated concentration of nano-adsorbent, where multi-walled carbon nanotubes had a better performance regarding atrazine adsorption level, compared to single-walled carbon nanotubes.

In addition, when there was fixed initial solution and nano-adsorbent concentrations, increased concentration of nano-adsorbent was associated with a higher adsorption percentage of atrazine, where the optimal contact time (for having the highest adsorption level) was 90 minutes and adsorption decreased after that. In this respect, multi-walled carbon nanotubes had a better performance in terms of atrazine adsorption level, compared to single-walled carbon nanotubes. On the other hand, atrazine adsorption percentage increased in the presence of elevated temperature where there were fixed initial solution and nano-adsorbent concentrations and contact time of 90 minutes. The highest adsorption percentage occurred at 35°C and was reduced after that, where the multi-walled carbon nanotubes had a higher efficiency in adsorbing atrazine, compared to single-walled carbon nanotubes.

In case of fixed initial solution and nano-adsorbent concentrations, contact time of 20 minutes and temperature of 25°C, there was an increase in atrazine adsorption percentage in the presence of elevated pH level, where the highest adsorption percentage occurred at pH=7 and was reduced after that. In this regard, multi-walled carbon nanotubes had a better performance regarding atrazine adsorption, compared to single-walled carbon nanotubes. In conclusion, multi-walled carbon nanotubes had a better performance in adsorbing pharmaceutical pollutants, compared to single-walled carbon nanotubes.

ACKNOWLEDGEMENTS

I would like to express my sincere gratitude to my advisor Prof. M.R Bozorgmehr for related research, for his patience, motivation, and immense knowledge. His guidance helped me in all the time.

REFERENCES

1. Li Y.H., Ding J., Luan Z.K., Di Z.C., Zhu Y.F., Xu C.L., Wu D.H., Wei B.Q., 2003. Competitive adsorption of Pb^{2+},Cu^{2+} and Cd^{2+} ions from aqueous solutions by multiwalled carbon nanotubes. Carbon. 41(14), 2787–2792.

2. Obare S.O. Meyer G.J., 2004. Nanostructured materials for environmental remediation of organic contaminants in water. J Environ Sci Health A. 39(10), 2549–2582.

3. Chitose N., Ueta S., Yamamoto T.A., 2003. Radiolysis of aqueous phenol solutions with nanoparticles. 1. Phenol degradation and TOC removal in solutions containing TiO_2 induced by UV, gamma-ray and electron beams. Chemosphere. 50(8), 1007–1013.

4. Zhang W. X., 2003. Nanoscale iron particles for environmental remediation. J Nanopart Res. 5, 323–332.

5. US Bureau of Reclamation and Sandia National Laboratories, 2003. Desalination and water purification technology roadmap—a report of the executive committee. Water Purification. 341Research and Development Program Report No 95, US Department of Interior, Bureau of Reclamation, January 2003.

6. Vander Bruggen B., Vandecasteele C., 2003. Removal of pollutants from surface water and groundwater by nanofiltration overview of possible applications in the drinkingwater industry. Environ Pollut. 122, 435–445.

7. Peltier S., Cotte E., Gatel D., Herremans L., Cavard J., 2003. Nanofiltration improvements of water quality in a large distribution system. Water Sci Tech Water Supply. 3, 193–200.

8. DeFriend K.A., Wiesner M.R., Barron A.R., 2003. Alumina and aluminate ultrafiltration membranes derived from alumina nanoparticles. J Membr Sci. 224(1–2), 11–28.

9. Diallo M.S., Christie S., Swaminathan P., Balogh L., Shi X., Um W., Papelis C., Goddard III W.A., Johnson Jr. J.H., 2004. Dendritic chelating agents 1. Cu(II) binding to ethylene diamine core poly (amidoamine) dendrimers in aqueous solutions. Langmuir. 20, 2640–2651.

10. Diallo M.S., 2004. Water treatment by dendrimer enhanced filtration. US Patent Pending. Unpublished.

11. Olubukola O., Olugbake Olubusola A., Famudehin Kehinde F., 2010. Evaluation of use of antibiotic without prescription among young adults. African Journal of pharmacy and pharmacology. 4(10), 760-2.

12. Sayadi M.H., 2010. Contamination of soil industrial area. Lambert Academic Publishing, Germany. pp. 156.