

Environmental Nanotechnology: Carbon Nanotubes as an Alternative to Reduce Organic Matter in Wetlands

Eusterio H. Acosta Suasnabar, Marcia L. Aquino Soto, Elmer Benites-Alfaro, Jonnatan V. Bañon Arias

Universidad César Vallejo, Campus Los Olivos, Lima, Perú
 eacostas@ucv.edu.pe

Wetlands are a crucial means of life and balance for flora and fauna as they provide a refuge and habitat for many species. However, anthropogenic activities aimed at taking advantage of these wetlands also contribute to their deterioration, with one of the most significant factors being the dumping of wastewater that results in an increase in organic matter in these bodies of water. This research presents an alternative solution to this problem by testing the use of carbon nanotubes with diameters of 20-40 nm and lengths of 10-30 μm to remove organic load from the wetlands located in Ventanilla, Callao – Peru. Using doses of 50, 100, and 150 g of carbon nanotubes, the study evaluated the decrease in the indicator parameters of organic load. The dose of 150 g was found to achieve the most significant reduction, decreasing BOD₅ by 84%, COD by 79%, and nitrogen by 93%. The research demonstrates that carbon nanotubes are efficient in removing organic load from wetland water, and this method can be replicated in other locations to aid in the conservation of these essential ecosystem services.

1. Introduction

The development of new water treatment technologies is necessary with water quality for its re-use and for the protection of the environment. The use of nanomaterials favors the development of more efficient and advanced treatments in water (Chávez-Lizárraga, 2018). The potential solution for wastewater treatment lies in nanotechnology with techniques such as filtration, the use of nanoparticles in catalysis, and desalination. In addition, conventional techniques such as adsorption, flocculation and coagulation can be enhanced (Lu and Astruc 2018). In nanotechnology, material is manipulated on a scale close to the atomic to produce new structures, artifacts, and materials; They are made up of particles with a dimension in the range of 1 -100 nm (Morose, 2010), so nanoparticles can be effectively transported by the flow of water (Zhang, 2003). Carbon nanotubes possess rapid absorption of impurities in aqueous sources and interact with organic molecules through van der Waals force, hydrogen bonding, and hydrophobic interactions, also carbon nanotubes are regenerable adsorbents and could be used up to five absorption cycles without losing efficiency, with efficiency in the separation of heavy metal ions in aqueous solutions. (Rojas et al., 2016).

For the removal of metal ions: Pb (II) and Cr (VI) from wastewater, carbon nanotubes are effective adsorbents, in which they have gained some advantages in recent years due to their highly stable structures, unique properties and excellent removal performances. (Guoqiang et al., 2018), carbon nanotubes (CNTs) have many applications, such as water purification and heavy metal removal from industrial wastewater, due to their adsorption properties, such as chemical, mechanical, and thermal. They are a great contribution in the adsorption of heavy metals in wastewater and solution to environmental problems. (Mubarak et al. 2014).

Carbon nanotube filters have a high removal efficiency of over 90% in wastewater treatment due to their ability to adsorb biological and chemical contaminants. This technology can be used by developing countries as it is a cost-effective treatment technology (Sadia and Zhou, 2016). The development of new water treatment technologies is necessary to improve the quality of water for its reuse and environmental protection. In terms of sustainability, the use of nanotechnology has reported very few environmental problems (Das et al., 2018).

However, one study showed that CNTs can increase metal uptake and toxicity levels in living cells (Wang et al., 2014). Immobilization of nanoparticles on reactor surfaces or support media can minimize the risk to public and environmental health. This can also reduce nanoparticle aggregation and improve activity (Xiaolei et al., 2013). The separation of organic matter from CNTs presents the mechanism of chemical and physical adsorption (Van der Waals force), including hydrogen bonds and $\pi - \pi$ bonds (Bittner et al., 2003; Yang and Xing, 2010; Peng et al., 2009). In other technologies, such as The Toha system, which is a biofilter, according to Chávez (2017), the treatment of industrial effluents reduced the concentration of organic load by 94% BOD5 and 92% in COD. Likewise, Castro (2017) used 1% aluminum sulfate to reduce the organic load of the Camal municipality effluent through a jar test, determining a removal efficiency of 95.85% in COD and 95.34% in BOD5. Burgos (2015) eliminated organic matter from wastewater through artificial wetlands and reduced it by 60% after 7 days. Moncada (2017) used a slow sand filter for the treatment of effluents from the floriculture industry, removing BOD5 up to 97.14%. Vuppala et al. (2019) carried out a pilot wastewater treatment plant with high concentrations of Chemical Oxygen Demand (COD), Total Organic Carbon (TOC) and phenols, in addition to other pollutants, first with an organic coagulant (chitosan), and then with a photocatalytic step prior to the integrated membrane process. After the photocatalytic process, the concentrations of COD, TOC, and Phenols were reduced by up to 42%, 38%, and 36%, respectively.

Zha et al. (2018) managed to reduce COD using single-walled carbon nanotubes (SWCNTs), multi-walled carbon nanotubes (MWCNTs), and graphitized multi-walled carbon nanotubes (GWCNTs). They obtained an adsorption rate of 210.2 mg/g for graphitized multi-walled nanotubes (the highest adsorption rate) in 360 minutes, while the highest amount of COD adsorption was achieved for single-walled carbon nanotubes (227 0.8mg/g). In addition, they achieved full organic carbon adsorption with an efficiency of 64.5% for SWCNT and 60.0% for MWCNT. In earlier work, Zha et al. (2018) was able to reduce COD from 70 mg/L to 50 mg/L in effluents using activated sludge with ultra-short solids retention time (SRT) (≤ 4 days), but the effluent quality was relatively poor. The effectiveness of the CNT organic matter reduction method is due to its nanometer size, which provides a larger contact surface, hollow structure, and shell shape, making carbon nanotubes (CNTs) excellent adsorbents for removal of organic micropollutants (Ahmad et al., 2019).

Various technologies are available to reduce the organic load in wastewater, including anaerobic processes that use enzyme catalysts to speed up microbiological digestion and reduce BOD5 and COD. Chalen et al. (2017) reported efficiencies of 76.6% and 82%, respectively, using this method. Activated sludge is another methodology, which Mejía-López et al. (2019) used to reduce organic matter with an efficiency of 88% at 60 days. Phytodepuration of rural municipal waste using microalgae with Chlorophyceae and Cyanophyceae in a closed photobioreactor system at the semi-pilot level was also effective in reducing COD, total nitrogen, and total phosphorus, achieving reductions of 50%, 60%, and 50%, respectively, and complying with environmental quality standards, according to Casazza and Rovatti (2019). Finally, the separation processes (ultrafiltration, nanofiltration and reverse osmosis) were carried out and almost all the initial concentrations of COD, TOC and phenols were eliminated. In this context, the objective of the research was to determine the efficiency of the reduction of the organic load in the water of the Ventanilla Wetlands in the Callao region, using carbon nanotubes (NTC).

2. Methodology

2.1 Collection of the water sample to be studied

The sample was obtained from the Ventanilla wetlands, it is located in the district of *Ventanilla*, Province of *Callao*, Peru, it is located between the coordinates 11° 51' 23" - 11° 52' 42" Lat. South and 77° 07' 43" - 77° 09' 32" Long. West. The wetlands area is 275.8 ha.

2.2 Pre-test characterization of the simple

The pre-test characterization of the water was performed using the National protocol for Monitoring the Quality of Surface Water Resources R.J 010-2016-ANA and comparing it with the Supreme Decret N° 004- 2017 MINAN, Category 4 Waters, to determine the level of organic load of the Wetland (MINAM. ECA, 2017).

2.3 Acquisition of the multi-walled carbon nanotubes.

The MWCTNs were purchased from XFNANO, INC laboratory in China, with the characteristics shown in Table 1.

2.4 Sample collection for the final test

The water sample was taken in a container with a capacity of 8 L, following the national protocol for monitoring the quality of surface water resources (ANA, 2016). See Figure 1.

2.5 Jar Test

The jar test (See Figure 2) was carried out with three samples of 2 L each, adding 50 g, 100 g and 150 g of MWCNTs, with the operating conditions indicated in Table 2.

Table 1: Characteristics of carbon nanotubes. SEM of XPQ044 industrial grade MWCNTs

Characteristics	Value
Name	Multi-walled carbon nanotubes
Standard quality	Industrial
Purity	> 95 %
Length	10 - 30 μm
Diameter	20 - 40 nm
Elaboration method	Chemical Vapor Deposition (CVD).

Font: XFNANO, INC



Figure 1: Sample collection



Figure 2: Test jars, UCV laboratory

Table 2: Operating conditions in the treatment by means of "Jar test"

Sample number	Agitation time (min)	Velocity agitation (RPM)	Sedimentation Time (min)
1	2	190	30
2	15	70	30
3	30	40	30

The standard methods to calculate the main parameters were:

- Biochemical Oxygen Demand (BOD5): SMEWW-APHA-AWWA-WEF Part 5210 B, 23rd Ed.2017.
- Chemical Oxygen Demand (COD): APHA-AWWA-WEF (2012) 5220 B.
- Total nitrogen: Kjeldahl method.

3. Results and discussions

3.1 Physicochemical parameters before treatment with CNT

The initial results of the analysis of the water from the *Ventanilla* wetlands presented values of BOD5 (28 mg/L), total nitrogen (3.18 mg/L) and electrical conductivity (20780 $\mu\text{s}/\text{cm}$), values that exceeded the environmental regulations corresponding to the environmental quality standards of Peru (DS. 004 - 2017. MINAN, category 4 for lakes and lagoons), See Table 3.

Table 3: Initial parameters of the water samples from the *Ventanilla* wetlands

Parameter	Unit	Result	ECA: DS.004-2017- MINAN	Variation
Biochemical Oxygen Demand (BOD5)	mg/L	28.00	5	exceeds
Chemical Oxygen Demand (COD)	mg/L	45.00	valueless	-
Total Nitrogen	mg/L	3.18	0.315	exceeds
turbidity	NTU	9.70	valueless	-
Hydrogen potential. pH	-	7.60	6.5 – 9.0	Not exceed
Electric conductivity	$\mu\text{s}/\text{cm}$	20780	1000	exceeds

The results of the initial parameters of water from the *Ventanilla* Wetlands, shown in Table 3, indicate that this source of water requires treatment to reach the standard quality according to the environmental regulations of Peru.

3.2 Physicochemical parameters after treatment with different doses of CNT

Biochemical Oxygen Demand (BOD5): After the treatment of the water sample, it was found that using the 150 g dose, the most optimal value of 4.25 mg/L is reached, which is less than 5 mg/L (ECA), fulfilling the environmental regulations of Peru; this means a reduction of 84.82%, see Table 4.

Table 4: BOD5 in water from wetlands treated with three different doses of CNT.

Parameter	Sample number	Treatment with 50 g			Treatment with 100 g			Treatment with 150 g		
		Initial	Final	Variation (%)	Initial	Final	Variation (%)	Initial	Final	Variation (%)
BOD5	1	28	8.26	70.5	28	6.43	77.04	28	4.25	84.82
	2	28	7.14	74.5	28	6.57	76.54	28	4.35	84.46
	3	28	7.14	74.5	28	6.48	76.86	28	4.44	84.14

Chemical Oxygen Demand (COD): Wetland water after treated with NTC, it was found that using the 150 g dose, this parameter reaches the best value of 9.41 mg/L, which is equivalent to 79.09% reduction; quite important value, see Table 5.

Table 5: COD of wetland water treated with three different doses of CNT.

Parameter	Sample number	Treatment with 50 g			Treatment with 100 g			Treatment with 150 g		
		Initial	Final	Variation (%)	Initial	Final	Variation (%)	Initial	Final	Variation (%)
Chemical Oxygen Demand (COD)	1	45	15.18	66.27	45	12.07	73.18	45	9.54	78.80
	2	45	14.06	68.76	45	12.04	73.24	45	9.47	78.96
	3	45	14.01	68.87	45	12.11	73.09	45	9.41	79.09

Total Nitrogen: This parameter in treated wetland water reaches values of 0.295 mg/L (90.72% reduction) and 0.229 mg/L (92.80% reduction) that are within the regulated environmental quality standard, which is 0.315 mg/L, using doses of 100 and 150 mg/L of CNT respectively, see table 6.

Table 6: Total nitrogen in wetland water after treatment with three different doses of CNT

Parameter	Sample number	Treatment with 50 g			Treatment with 100 g			Treatment with 150 g		
		Initial	Final	Variation (%)	Initial	Final	Variation (%)	Initial	Final	Variation (%)
Total Nitrogen (mg/L)	1	3.18	1.06	66.67	3.18	0.298	90.63	3.18	0.235	92.61
	2	3.18	1.01	68.24	3.18	0.295	90.72	3.18	0.233	92.67
	3	3.18	1.03	67.61	3.18	0.295	90.72	3.18	0.229	92.80

Other parameters: Presented in Table 7 the values found for temperature, pH and electrical conductivity for the treatment of the three samples. It is found that the temperature did not suffer significant variation, as for the pH, it remains around the neutral and the electrical conductivity presents an increase due to the fact that the carbon nanotubes show a high electrical potential, a micro and macroscopic structure and various functional chemical groups (Li, C., Yang, J., Zhang, L. et al, 2021).

Table 7: Other physicochemical parameters before and after treatment with NTC

Parameter	Sample number	Treatment with 50 g		Treatment with 100 g		Treatment with 150 g	
		Initial	Final	Initial	Final	Initial	Final
Temperature (°C)	1	24	24.7	24	24.3	24	24.3
Hydrogen Potential (pH)	2	7.6	7.44	7.6	7.18	7.6	7.21
Electrical conductivity ($\mu\text{s}/\text{cm}$)	3	20.78	29.34	20.78	29.39	20.78	29.28

In this research, multi-walled carbon nanotubes (MWCNTs) were used to remove organic load from water samples from the *Ventanilla* wetlands based on the reduction of COD, BOD₅, and NT as indicators of the organic load present. After treatment with MWCNTs, the samples of water from *Ventanilla* wetlands reduced the BOD₅ contents from 28 to 4.25 mg/L, reduced the COD contents from 45 to 9.41 mg/L, and reduced the total nitrogen from 3.18 to 0.229 mg/L. These reductions fulfill the aim of the research to reduce the organic load as an effect of treatment with MWCNTs. The major mechanisms by which CNTs adsorb organic compounds differ depending on the polar properties of the compound of interest (Pan and Xing, 2008), and several possible interactions between organics and CNTs have been proposed. Hydrophobic interactions, π - π stacking interactions, Van der Waals forces, electrostatic interactions, and hydrogen bonding interactions might act individually or simultaneously (Jin-Gang et al., 2014). Adsorption of contaminants by CNTs occurs at four possible types of sites such as outer and inner grooves and interstitial channels, and the inner region of CNTs is less adsorptive (Aslam et al., 2021). In organic compounds, the polar aromatic substituents possess superior adsorption affinity to CNTs relative to the nonpolar substituents with the same aromatic structure, and this phenomenon is attributed to the π - π electron donor-acceptor interaction between the aromatic molecules and the CNTs (Awad et al., 2020). MWCNTs usually contribute more pore volumes of inner sites than SWCNTs. These mechanisms of adsorption is assumed to have happened during the treatment of water samples from *Ventanilla* wetlands with MWCNTs. The organic loads interacted with MWCNTs through hydrophobic interactions, π - π stacking interactions, van der Waals forces, electrostatic interactions, and hydrogen bonding interactions, as reported in different research previously.

4. Conclusions

Carbon nanotubes have been shown to be effective in reducing the organic load in the waters of the *Ventanilla* Wetlands. The appropriate amount of multi-walled carbon nanotubes for the removal of organic load was found to be 150 g, with a maximum removal capacity of 84.82% for BOD₅, 79.09% for COD, and 92.80% for total nitrogen. These values are within the standards of environmental quality for surface waters such as lagoons and lakes. The results obtained confirm that the use of CNTs is a viable and easy-to-implement methodology for addressing the issue of high organic load in surface water and facilitating its recovery.

Acknowledgements

The authors would like to thank the Vicerrectorado de Investigación of the Universidad César Vallejo for financial support for the publication of this research.

References

- Ahmad J., Naeem S., Ahmad M., Usman A. R. A., Al-Wabel M.I., 2019, A critical review on organic micropollutants contamination in wastewater and removal through carbon nanotubes. *Journal of Environmental Management*, 246, 214-228.
- ANA. National Water Authority. Headquarters Resolution No. 010-2016-ANA. National protocol for monitoring the quality of surface water resources, 2016. www.ana.gob.pe/publicaciones/protocolo-nacional-para-el-monitoreo-de-la-calidad-de-los-recursos-hidricos-0.
- Aslam, M. M.-A., Kuo, H.-W., Den, W., Usman, M., Sultan, M., & Ashraf, H. (2021). Functionalized Carbon Nanotubes (CNTs) for Water and Wastewater Treatment: Preparation to Application. *Sustainability*, 13(10), 5717. MDPI AG. Retrieved from <http://dx.doi.org/10.3390/su13105717>
- Awad, A. M., Jalab, R., Benamor, A., Nasser, M. S., Ba-Abbad, M. M., El-Naas, M., & Mohammad, A. W. (2020). Adsorption of organic pollutants by nanomaterial-based adsorbents: An overview. *Journal of Molecular Liquids*, 301, 112335.

- Bittner E. W., Smith, M. R., Bockrath B. C., 2003, Characterization of the surfaces of single-walled carbon nanotubes using alcohols and hydrocarbons: a pulse adsorption technique. *Carbon* 41, 1231–1239.
- Burgos V., 2015, Evaluation of constructed wetlands planted with ornamental species in the elimination of organic matter, nutrients and pathogenic contaminants from wastewater of rural origin. Thesis, University of Concepción, Chile. (Spain).
- Casazza A. A., Rovatti M., 2019, Treatments of Wastewater in Rural Communities using a Pilot Plant Photobioreactor, *Chemical Engineering Transactions*, 74, 343-348.
- Castro M., 2017, Reduction of the organic load of the effluent of the municipal slaughterhouse El Porvenir through treatment with aluminum sulfate at 1%. Thesis, César Vallejo University, Peru, (Spain).
- Chalen J., Peñafiel M., Saltos A., 2017, Elimination of organic and inorganic matter present in the wastewater of a fruit pulp industry using an enzymatic catalyst. *Domain of Sciences (Spain)*, 3(3), 362-376.
- Chávez J., 2017, Efficiency of a biofilter in the reduction of organic load of an industrial effluent in the city of Celendín. Thesis, National University of Cajamarca, Peru, (Spain).
- Chávez-Lizárraga G., 2018, Nanotechnology an alternative for wastewater treatment: Advances, Advantages and Disadvantages. *Journal of the Selva Andina Research Society*, 9(1), 52-61.
- Das, R., Leo, B.F. & Murphy, F., 2018, The Toxic Truth About Carbon Nanotubes in Water Purification: a Perspective View. *Nanoscale Res Lett* 13, 183.
- Guoqiang Y, Yang L., Jiang G, Manisha P., Adarsh B., Xifan W., Bin Q., Clayton J., Suying W., Zhanhu G., Evan K., 2018, Carbon nanotubes, graphene, and their derivatives for heavy metal removal. *Adv Compos Hybrid Mater* 1, 56 – 78.
- Jin-Gang Yu, Xiu-Hui Zhao, Hua Yang, Xiao-Hong Chen, Qiaoqin Yang, Lin-Yan Yu, Jian-Hui Jiang, Xiao-Qing Chen, 2014, Aqueous adsorption and removal of organic contaminants by carbon nanotubes, *Science of The Total Environment*, Volumes 482–483, Pages 241-251, ISSN 0048-9697,
- Li, C., Yang, J., Zhang, L., Li, S., Yuan, Y., Xiao X., Fan X., Song C., 2021, Carbon-based membrane materials and applications in water and wastewater treatment: a review, *Environ Chem Lett* 19, 1457–1475.
- Lu F., Astruc D., 2018, Nanomaterials for removal of toxic elements from water. *Coord Chem Rev* 2018, 35(6), 147-164.
- MINAM - Ministry of the Environment," Supreme Decree No. 004-2017-MINAM: Environmental Quality Standards (ECA) for Water, 2017. www.minam.gob.pe/wpcontent/uploads/2017/06/DS-004-2017-MINAM.pdf.
- Mejía - López A., Cabrera M., Carrillo Y., 2019, Removal of organic contaminants present in domestic wastewater using a laboratory-scale prototype. *La Granja: Life Sciences Magazine (Spain)*, 26(2), 72 - 83.
- Moncada R., 2017, Efficiency of the slow sand filter treatment in the removal of organic load in effluents from the Flores Barranco market, 2017. Thesis, Cesar Vallejo University, Peru, (Spain).
- Morose G., 2010, The 5 principles of Design for Safer Nanotechnology. *J Clean Prod* 2010, 18(3), 285-289.
- Mubarak N. M., Sahu J. N., Abdullah E. C., Jayakumar N. S., 2014, Removal of Heavy Metals from Wastewater Using Carbon Nanotubes, *Separation and Purification Reviews*, 43(4), 311-338.
- Pan B, Xing B. 2008, Adsorption mechanisms of organic chemicals on carbon nanotubes. *Environ Sci. Technol*, 42:9005–13.
- Peng X. J., Jia J. J., Luan, Z. K., 2009, Application of carbon nanotubes in the field of water treatment materials. *Progress in Chemistry*. 21, 1987–1992.
- Rojas-Challa, Y., Méndez, F. J., Rondón, W., Rojas de Astudillo, L., 2016, Lead removal from aqueous sources using carbon nanotubes. *Advances in Chemistry (Spain)*, 11(2), 87-98.
- Sadia J. A., Zhou Z., 2016, Electrochemical carbon nanotube filters for water and wastewater treatment. *Nanotechnology Reviews*, 5(1), 41-50.
- Vuppala S., Cianfrinia C., Stoller M., 2019, Pre-Treatment Processes Optimization for the Purification of Olive Mill Wastewater through a Pilot-Scale Membrane Plant, *Chemical Engineering Transactions*, 73, 271-276
- Wang, C., Wei, Z., Feng, M., Wang, L. and Wang, Z., 2014, The effects of hydroxylated multiwalled carbon nanotubes on the toxicity of nickel to *Daphnia magna* under different pH levels. *Environ Toxicol Chem*, 33: 2522-2528.
- Xiaolei Qu, Jonathon Brame, Qilin Li, and Pedro J. J. Alvarez, 2013, Nanotechnology for a Safe and Sustainable Water Supply: Enabling Integrated Water Treatment and Reuse. *Accounts of Chemical Research*, 46 (3), 834-843.
- XFNANO, Jiangsu XFNANO Materials Tech Co., Ltda. SEM of XFQ044 industrial grade MWCNTs, Multiple Wall Carbon Nanotube 20-40 nm, 2019. www.en.xfnano.com.
- Zha Y., Wang Y., Liu S., Yang Y., Jiang H., Zhang Y., Qi L., Wang H., 2018, Adsorption characteristics of organics in the effluent of ultra-short SRT wastewater treatment by single-walled, multi-walled, and graphitized multi-walled carbon nanotubes. *Scientific reports* 8, 17245
- Zhang W., 2003, Nanoscale Iron Particles for Environmental Remediation. An Overview. *Journal of Nanoparticle Research* 5, 323 – 332.