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CNTs AS POTENTIAL MATERIAL FOR WASTEWATER PURIFICATION: A REVIEW

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Abstract

Water purification has been identified as a key global concern, due to fast developing of economy which is result of crude oil exploration and production, as well as pharmaceuticals manufacturing. Comparing to other adsorbents carbon nanotubes have proven to be good choice for wastewater treatment of organic pollutants because of their high adsorbtion capacity. This paper presents a review of literature data on the use of carbon nanotubes to the purification of wastewater, which has been one of the most prominent and major areas for their application since their creation and commercial usage.

Keywords*: carbon nanotubes, organic pollutants, wastewater treatment*

1. INTRODUCTION

Pharmaceuticals, personal care products, organic dyes, pesticides, detergents and a typical industrial organic wastes such as phenols, halogens and aromatics are examples of organic pollutants. Worryingly, they are unremitting and persistent in the environment. They are growing more prevalent as industrialization progresses. In comparison to the limited varieties of heavy metals in water, organic contaminants are increasing in number as industrial growth continues. The international environmental accord imposed restrictions on the manufacture, use, and discharge of twelve important persistent organic pollutants [1].

The worldwide distribution of oil and its derivatives generates a significant danger to the environment. There are multiple traditional methods for removing oil from water, but due to several defects and disadvantages, research efforts have centered on identifying such adsorbents that may boost oil adsorption capacities. Oil spills in oceans, seas, lakes, and rivers make up a significant environmental catastrophe [2].

Adsorption is a simple, inexpensive, and efficient method of eliminating hydrocarbons from water. Carbon-based adsorbents, particularly carbon nanotubes (CNTs), are frequently used to separate water and oil. In comparison with other adsorbents, they satisfy all of the requirements for effective oil adsorption [3].

2. REMOVAL OF ORGANIC POLLUTANTS FROM WASTEWATER

Chemical oxidation, adsorption and photocatalytic degradation are the most often used ways for cleaning water from organic contaminants. Most organic pollutants may be successfully oxidized into inorganic carbon (CO_2) via the oxidation process (using O_2, O_3, Cl_2, ClO_2 and H_2O_2), but the potential drawback of this procedure is health risk of incomplete degradation of side products [4]. Compared to oxidation process, with adsorption process doesn't exist risk of secondary potential contamination and it has shown to be the most successful and vital approach for removing contaminants from water at an affordable cost. This process has been applied for wastewater purification for many years owing to its speed, effectiveness and economic benefits. Its efficacy is mostly determined by the type of adsorbent and operating conditions. Active carbons, zeolites, clays and carbon nanomaterials (graphene, graphene oxide, and carbon nanotubes) are the most often utilized adsorbents for the adsorption of organic contaminants in water [5]. Photocatalytic degradation is one of the methods for removing organic contaminants from water that uses the

Fenton process to degrade organic pollutants. TiO_2, TiO_2 and ZnO can be utilized in this method since they have the capacity to break down organic contaminants into little molecules without being hazardous [6].

2.1 Removal of organic pollutants from water using CNTs

Oil products are the most widespread sources of water pollution, coming into contact with water through the release of oil and fuel from land-based plants, tanker spills and accidental leaks during transport. Removal of unleaded gasoline from water is possible using multi-walled carbon nanotubes (MWCNTs) due to a number of favorable properties they possess as adsorbents, such as good hydrophobicity and oleophilicity, capacity and speed of uptake and retention of hydrocarbons. During the experiments, the conditions of actual polluted water were simulated. Dispersions of commercial unleaded gasoline (20 ml) in water (30 ml) were used, which were exposed to varying amounts of MWCNTs (0.2–0.8 g) at room temperature. Obtained results are shown graphically in Figure 1. The highest percentage of unleaded gasoline removed was obtained by using small amounts (0.7 g) of MWCNTs during a very short mixing time (5 min), larger amounts of adsorbent did not improve the efficiency of the process. Small amounts used in the presented experiments, simple regeneration after each application and low costs of the raw materials used for the production of MWCNTs, make this process economical [7].

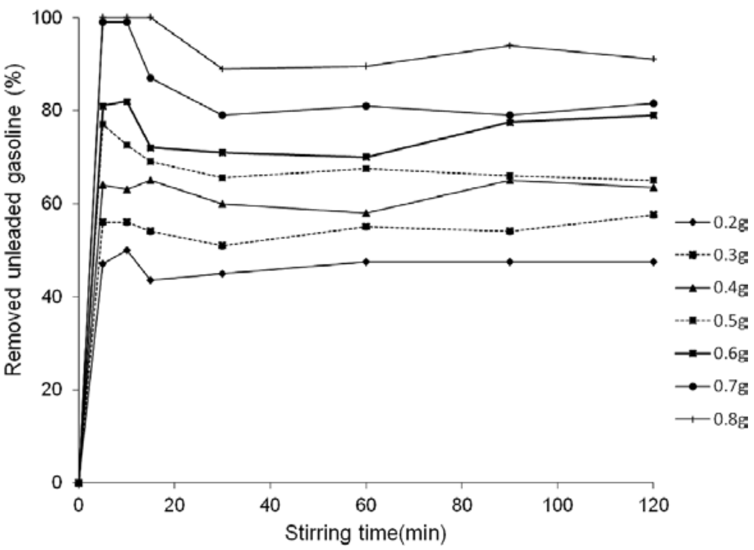

Figure 1 - Removed unleaded gasoline (%) from hydrocarbon / water dispersion as function of mixing time [7]

In order to produce a hydrophobic adsorbent, the MWCNTs surface can be modified using the microemulsion method (MEMWCNT) without changing their structure. The results of UV spectrophotometric analysis showed that MEMWCNTs are more effective for adsorbing toluene from the toluene-water mixture (90%) compared to untreated MWCNTs (77%). Using kerosene as a model hydrocarbon, the efficiency of its adsorption from water in the presence of MWCNTs was compared with MEMWCNTs. From 35%, which was adsorbed by MWCNT, using MEMWCNT this value increased to 96%. The adsorption capacities of MEMWCNTs are higher than those of MWCNTs for all hydrocarbon models and range from 6.07 to 5.68 g/g, while the adsorption capacity of MWCNTs is in the range of 2.48–4.64 g/g. The experimental results proved that MEMWCNTs are good hydrocarbon adsorbents, and that the surface modification of MWCNTs by the microemulsion method had a beneficial effect on the hydrophobic properties of MWCNTs [8].

Aromatic amines and phenols are considered the most common pollutants found in water bodies. Their presence in the aquatic ecosystem causes an imbalance, because the food chain is disrupted, which further causes the death of many aquatic organisms. The removal of aniline by MWCNTs is performed in two steps. First, aniline molecules diffuse from the aqueous solution to the outer surface of the MWCNTs, and then the aniline molecules diffuse through the MWCNTs. The highest removal efficiency of toluene, ethylbenzene and xylene isomers was observed with MWCNTs oxidized by 3% NaOCl. The presence of oxygen-containing groups caused less pore damage. The removal increased with longer contact time, while it decreased with increasing reaction temperature [9].

Various pharmaceutical and personal care products (PPCPs) have been detected in groundwater, rivers and lakes. For the removal of ibuprofen and triclosan from synthetic water, single-walled CNTs (SWCNTs) showed the highest efficiency compared to MWCNTs and oxidized MWCNTs. Due to their large specific surface area (~1020 m^2/g) SWCNTs are often used to remove pharmaceuticals from water. Adsorption of diclofenac on MWCNTs was 41.4 mg/g in clean water and 22.3 mg/g in wastewater. According to the research results, oxidized MWCNTs can improve tetracycline adsorption due to the introduction of COOH and C–O groups on the MWCNTs surface. Oxidized MWCNTs show a greater ability to adsorb other drugs, such as ciprofloxacin, due to improved hydrophilicity and dispersibility. Pore size is the rate-determining step, and the introduction of ionic liquid into CNTs resulted in an improvement in the hydrophobicity of CNTs, which allows for more interactions between the adsorbent and the adsorbate [9].

CNTs have the ability for successful adsorption of dye molecules from wastewater. Methylene blue was removed from wastewater using carpet-like vertical arrays of CNTs connected to porous carbon foam surfaces by coating with a silicon dioxide buffer layer. The amount of CNTs on the foam and adsorption capacity of hybrid CNTs are directly related. The maximum adsorption capacity for methylene blue using CNT arrays is around 43.5 mg/g, which is more than what can be accomplished with a variety of other methylene blue adsorbents [10].

3. CONCLUSION

The contamination of the planet by countless harmful compounds, both from manufactured and natural sources is continual. Numerous harmful substances have been released into the environment as a result of rapid industrial development and population increase. Without properly evaluating the threats to the environment and impacts on human health, many new compounds are utilized. Based on previous experiments, CNTs have proven to be excellent adsorbents for organic dyes, oil, pharmaceutical products and pesticides. Before implementing on a large-scale, a risk evaluation for the environment and human health should be made, since nanomaterials frequently have hazardous effects on aquatic creatures when used in large amounts.

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REFERENCES

[1] A. Ojha, D. Tiwary, Contamination of Water, Academic Press, Cambridge, 2021, p.237-250.
[2] B. Zhang, E. Matchinski, B. Chen, X. Ye, L. Jing, K. Lee, World Seas: an Environmental Evaluation (Second Edition) Volume III: Ecological Issues and Environmental Impacts, Elsevier Ltd., Amsterdam, 2019, p.391-406.

[1] T. A. Abdullah, T. Juzsakova, S. A. Hafad, R. T. Rasheed, N. Al‑Jammal, M. A. Mallah, A. D. Salman, P. C. Le, E. Domokos, M. Aldulaimi, Clean Technol. Environ. Policy, 24 (2) (2022) 519-541.
[2] M. Panizza, G. Cerisola, Chem. Rev., 109 (12) (2009) 6541-6569.
[3] M. N. Rashed, Org. Pollut.- Monit. Risk Treat., IntechOpen, London, 2013, p.167–194.
[4] P. K. Pandis, C. Kalogirou, E. Kanellou, C. Vaitsis, M. G. Savvidou, G. Sourkouni, A. A. Zorpas, C. Argirusis, ChemEngineering, 6 (1) 8 (2022).
[5] D. Lico, D. Vuono, C. Siciliano, J. B. Nagy, P. De Luca, J. Environ. Manage., 237 (5) (2019) 636-643.
[6] N. Al-Jammal, T. A. Abdullah, T. Juzsakova, B. Zsirka, I. Cretescu, V. Vágvölgyi, V. Sebestyén, C. Le Phuoc, R. T. Rasheed, E. Domokos, Functionalized carbon nanotubes for hydrocarbon removal from water, J. Environ. Chem. Eng., 8 (2) (2020) 103570.
[7] K. M. Lee, C. P. P. Wong, T. L. Tan, C. W. Lai, Mater. Sci. Eng., 236-237 B (2018) 61-69.
[8] H. Vijwani, M. N. Nadagouda, V. Namboodiri, S. M. Mukhopadhyay, Chem. Eng. J., 268 (2015) 197-207.