

Application Progress of Carbon Nanotube Composites in Heavy Metal Ion Treatment

Yuzhe Cao

*School of Material Science and Engineering, Tianjin University, Tianjin, China
1209477300@qq.com*

Abstract: Wastewater from industrial pollution contains a large number of heavy metal ions, which can contaminate drinking water and food when it flows into rivers or leaches into the soil. Because of their persistent and bio-accumulative nature, these metals can continue to concentrate in soils, transferring to crops and, subsequently, to humans. Carbon nanotube materials have a strong adsorption capacity for heavy metal ions, so they have become a new research site in the field of environmental science. In this paper, the principle of adsorption of heavy metal ions by carbon nanotube materials is discussed, and the research progress in recent years is summarized. In the end, this paper concludes that while CNTs are promising in adsorbing heavy metal, there are still issues to be resolved, like enhancing scalability, cutting production costs, and optimising the adsorbent's effectiveness under a range of water conditions. Future research might focus on improving the composite structure even further to boost stability in various environmental settings, improve adsorption efficiency, and leverage cutting-edge techniques like artificial intelligence and machine learning to support future investigations.

Keywords: Heavy metal, carbon nanotube, CNT, composite material

1. Introduction

Water contamination has progressively grown to be a significant issue as cities and industry have developed quickly. In general, there are three types of water pollution: heavy metal pollution, organic matter pollution, and excessive nutrient contamination, primarily from nitrogen and phosphorus [1]. Carbon nanoparticles have maintained their position at the forefront of nanotechnology due to their large pore volumes and high specific surface areas. Particularly, CNTs are widely utilized to remove heavy metals from water, such as Hg(II), Pb(II), Cd(II), etc [2]. This paper discusses the basic knowledge of CNTs, then introduces different kinds of CNTs, including their production, effectiveness, and SEM, TEM, XRD, EDS, etc. are used to analyze the morphology and phase of these new materials. In conclusion, this paper investigates the performance and applications of carbon nanotubes (CNTs) in heavy metal adsorption, providing the water treatment industry with new material options and technical references, which helps to enhance the industry's technological level and competitiveness. As a representative of nanomaterials, the research and application of carbon nanotubes have driven the development of the nanomaterial industry. The findings of this paper can offer technical guidance to related enterprises, promoting the commercial application of carbon nanotubes in the field of water treatment.

2. The adsorption theory of CNTs

Depending on the number of concentric graphene cylinders they contain, CNTs are classified as either single-walled (SWCNTs) or multi-walled (MWCNTs), as shown in Figure 1 [3].

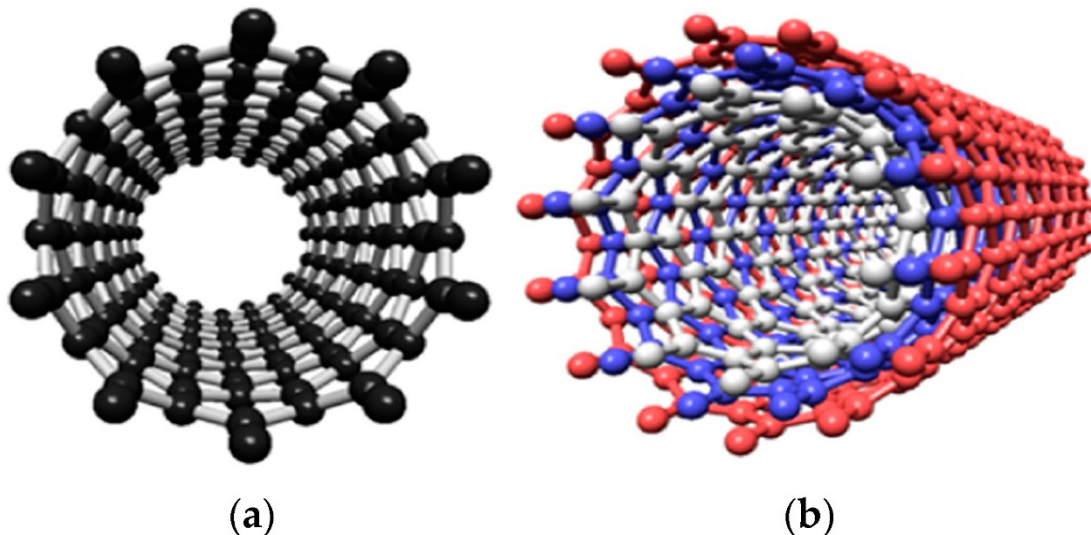


Figure 1: (a) Single-walled carbon nanotubes (SWCNTs); (b) multi-walled carbon nanotubes (MWCNTs)

Because of their atomic-level smoothness, CNTs have a high intermolecular connection, facilitating the fabrication of clusters with low dispersibility. In order to address the shortcomings of CNTs, chemical modification is required since this impact significantly lowers their adsorption efficiency and effective interaction with contaminants. CNTs must be modified into a composite so that other features could be enhanced[4]. This paper presents the synthesis of CNTs by using various modification methods and evaluating their adsorption efficiency for heavy metals.

3. Application of modified CNTs in adsorption of heavy metal in the water

By searching different kinds of CNTs, it has been found that polymer CNTs, N(Ag)-doped CNTs, and magnetic CNTs are most commonly researched. And their constitute, efficiency will be discussed as follows.

3.1. Polymer carbon nanotubes

Chang, P. et al. used a hybrid hydrogel composed of CNTs, sodium alginate (SA), and polyacrylic acid (PAA) produced by free radical polymerisation to examine the removal effectiveness of Cu^{2+} from wastewater. Batch adsorption studies were used to examine the adsorption performance for Cu^{2+} while taking the pH, dose, beginning concentration, and contact duration into account. For the elimination of Cu^{2+} , pH 5.0, 500 mg/L of adsorbent, and 360 minutes of contact time were ideal. The adsorption was best represented by the Freundlich isotherm, which had a saturation capacity of 358.52 mg/g, according to isotherm studies. This study highlights the high efficiency and environmental friendliness of CNT@SA/PAA composites for Cu^{2+} removal from wastewater, providing a promising approach for water treatment [5].

J. F. Amaku and R. Taziwa prepared a novel adsorbent from multi-wall carbon nanotubes (MWCNTs) and Citrus sinensis juice extract-modified MWCNTs (OJMW). The results showed that the nanotubes exhibited good surface area, pore size, functional groups, and robust stability under

high-temperature conditions. Optimal Cr(VI) adsorption efficiency for MWCNTs and OJMW was attained with 3 h exposure duration, 0.05 g sorbent loading, and pH 2 in the aqueous medium. The monolayer adsorption capabilities ($q_{\max}$) of MWCNTs and OJMW at 298 K were 44.72 and 12.26 g, in turn, suggesting that the spontaneous adsorption behaviors were observed with practical applicability. The adsorption-desorption tests demonstrated OJMW's strong capacity for regeneration [6].

El-Aassar, M. R., et al. described the creation and testing of sodium alginate-Poly (acrylonitrile-co-styrene)/Carbon Nanotubes (SA-M*Poly (AN-co-ST)/CNTs) composite beads, which exhibited a very efficient capability to remove Fe(II) ions from effluent-receiving systems. The poly(acrylonitrile-co-styrene) copolymer was modified and functionalised with carboxylic acid groups to create the composite. Then, sodium alginate and carbon nanotubes (CNTs) were combined to make strong gel beads. With an equilibrium adsorption capacity of 85 mg/g, batch adsorption tests demonstrated that the highest Fe(II) removal effectiveness reached 90% under ideal circumstances of pH = 3.0, 80 min of exposure period, and a sorbent mass of 40 mg. Additionally, this composite demonstrated excellent reusability, retaining 80% of its adsorption capability following five rounds of regeneration [7].

Esmaeili Chermahini, M., et al. created a high-performance and regenerable magnetic adsorbent by functionalising dopamine with ethylenediaminetetraacetic dianhydride and forming a polymer coating on magnetic carbon nanotubes (EDTA@PD-CNT/Fe₃O₄). Aqueous-phase Pb(II) and Cd(II) ions were efficiently captured by the synthesized material. By adjusting important variables such pH, adsorbent dose, contact duration, and ion concentration, the uptake capacity showed substantial improvement. Studies of adsorption thermodynamics confirmed the thermodynamically favored and heat-absorbing nature of the process, with the magnetic nanocomposite showing superior affinity for Pb²⁺ over Cd²⁺ [8].

3.2. N(Ag)-doped carbon nanotubes

Cheng, S., et al. produced magnetic nitrogen-doped carbon nanotubes in a single pot utilising synthetic polymer waste as raw material in conjunction with urea and Fe(NO₃)₃ for Cr(VI) decontamination in industry effluents. The magnetic N-CNTs exhibited substantial nitrogen incorporation, as confirmed by the characterization data (EDS and SEM). With an adsorption capacity of 27.47 mg/g, the presence of the nitrogen group and iron carbide helped remove hexavalent chromium ions by complexation and reduction. Waste plastic was used to create magnetic nitrogen-doped carbon nanotubes, which were then used to extract hexavalent chromium ions from aqueous streams [9].

Aliyu, S., et al. investigated the use of pristine carbon nanotubes and Ag-functionalized CNT nanocomposites as nanocapture agent in batch adsorption to mitigate contamination in aquaculture wastewater. A Fe–Ni/kaolin catalytic system was employed in a chemical vapor deposition (CVD) process to synthesize pristine carbon nanotubes, which subsequently underwent acid purification, alongside their silver-modified counterparts prepared through nanoparticle functionalization. CNTs, both unpurified and pure, were crystalline, tube-shaped, and highly porous; Ag-CNTs had a larger surface area (1068 m²/g) than P-CNTs (268.40 m²/g). The adsorption behaviour of P-CNTs and Ag-CNTs to extract Fe, Mn, and Zn from fish pond effluent as a function of temperature, adsorbent dose, and contact duration was examined using the batch adsorption procedure. Thus, it was shown that employing Ag-doped CNTs to remove heavy metals from aquatic effluent is successful in aquaculture [10].

Jiang, J., et al. suggested an uncomplicated technique for creating a new Janus photothermal membrane by fusing a hydrophilic nylon membrane with water-repellent nitrogenous CNTs encapsulating cobalt nanoparticles (Co@C/CNT). This allowed for the simultaneous realisation of

multiple optical absorption pathways and asymmetric surface wettability. After ten cycles, the Janus Co@C/NCNT evaporator retained its solar water evaporation rate of nearly $1.6 \text{ kg m}^{-2} \text{ h}^{-1}$ and evaporation efficiency of almost 90% under single sun irradiation. Meanwhile, the Janus evaporator has an exceptional removal efficiency and structural integrity retention, making it suitable for the practical purification of a variety of simulated wastewater, including dyeing wastewater and heavy metal wastewater [11].

3.3. Magnetic carbon nanotubes

Wang, L., et al. coated multiwalled carbon nanotubes with magnetic nanoparticles to create magnetic multiwalled carbon nanotubes (MMWCNTs), which had a particle diameter of roughly 30 nm and a large number of surface active sites. More than 95% of the Cr(VI) was removed. The MMWCNTs were desorbable using the deep eutectic solvent (DES), a green solvent with significant hydrogen bonding, and the desorption rate was higher than 90%. The adsorbent retained a high capacity even after five cycles of adsorption and regeneration. To sum up, these innovative MMWCNTs have demonstrated multifunctional remediation capabilities for aqueous contaminants, with particular efficacy in hexavalent chromium-laden wastewater elimination since they are effective adsorbents when combined with DES desorption [12].

Zhang, M. created a magnetic nanocomposite of carbon nanotubes (CNTs), starch, and Fe_3O_4 to remove lead (Pb^{2+}) and cadmium (Cd^{2+}) ions from water. The nanocomposite's magnetic saturation and BET area values were 28.36 emu/g and $54.18 \text{ m}^2/\text{g}$, respectively. Over 98% of Pb^{2+} and Cd^{2+} were removed at 25°C , 50 min of detoxification, 10 mg/L of metal, 1 g/L of composite mass, and pH 6 (for Pb^{2+}) and 7 (for Cd^{2+}). The Langmuir model was followed by the adsorption process data, which had q_m factors of $50.36 \text{ mg/g(Pb}^{2+}\text{)}$ and $44.72 \text{ mg/g(Cd}^{2+}\text{)}$. The results shown that the intended adsorbent can effectively clean aqueous solutions containing heavy metals by absorbing and desorbing Pb^{2+} and Cd^{2+} [13].

Grazhulene, S. S., et al. used carbon nanotubes (CNTs), a magnetic nano-sorbent made of CNTs and magnetic nanoparticles (CNT@MNP), and activated carbon (AC) to study the adsorption of noble metals and toxic ions from aqueous solutions. With a capacity increase of around 1.5–2 times, CNT-based adsorbents were shown to have an advantage over AC. The shape of carbon nanotubes (CNTs) grown on iron subgroup catalysts—nickel (CNT(Ni)), cobalt (CNT(Co)), and iron (CNT(Fe))—determines the contaminant loading capacity of the produced magnetic adsorbent. In magnetic solid-phase extraction, CNT@MNP outperformed conventional carbon adsorbents, successfully separating the solid and liquid phases [14].

4. Conclusion

This paper mainly discusses the typical theory and application of CNTs to decontaminate water with heavy metal. It concluded that although there are disadvantages of CNTs, they are promising materials for improving our environment in the future with further research. Unfortunately, this paper failed to reproduce all the experiment results of all the applications mentioned so the validity of all the newly-developed materials remains doubtful. On top of that, the exact adsorption theory of different materials is also not discussed in detail. Based on the research mentioned before, these new materials of CNTs have shown better performance, like stronger resistance to harsh environments, higher working efficiency, lower cost, etc. Future studies can further unlock the potential of CNTs in water treatment by utilizing machine learning or artificial intelligence to optimize the design and application of CNT-based materials for specific pollutants, or by developing cost-effective and scalable production methods for CNTs to facilitate their widespread use.

References

- [1] Z. Zeng, W.-G. Luo, Z. Wang, and F.-C. Yi, "Water Pollution and Its Causes in the Tuojiang River Basin, China: An Artificial Neural Network Analysis," *Sustainability*, vol. 13, no. 2, Jan 2021, Art no. 792, doi: 10.3390/su13020792.
- [2] J. Xu et al., "A review of functionalized carbon nanotubes and graphene for heavy metal adsorption from water: Preparation, application, and mechanism," *Chemosphere*, vol. 195, pp. 351-364, Mar 2018, doi: 10.1016/j.chemosphere.2017.12.061.
- [3] Y.-J. Yim, Y.-H. Yoon, S.-H. Kim, J.-H. Lee, D.-C. Chung, and B.-J. Kim, "Carbon Nanotube/Polymer Composites for Functional Applications," *Polymers*, Review vol. 17, no. 1, Jan 2025, Art no. 119, doi: 10.3390/polym17010119.
- [4] B. Yuan, S. Zhang, D. Ren, and X. Zhang, "Research Progress on the Removal of Heavy Metals in Water and Soil by Modified Carbon Nanotubes: a Review," *Water Air and Soil Pollution*, Review vol. 235, no. 6, Jun 2024, Art no. 418, doi: 10.1007/s11270-024-07238-7.
- [5] P. Chang et al., "Eco-Friendly Carbon Nanotubes Reinforced with Sodium Alginate/Polyacrylic Acid for Enhanced Adsorption of Copper Ions: Kinetics, Isotherm, and Mechanism Adsorption Studies," *Molecules*, vol. 29, no. 19, Oct 2024, Art no. 4518, doi: 10.3390/molecules29194518.
- [6] J. F. Amaku and R. Taziwa, "Aqueous removal of Cr(VI) by Citrus sinensis juice-coated multi-walled carbon nanotubes," *Chemical Papers*, vol. 78, no. 9, pp. 5415-5431, Jun 2024, doi: 10.1007/s11696-024-03481-8.
- [7] M. R. El-Aassar et al., "Development and characterization of sodium alginate beads incorporating functionalized poly(acrylonitrile-co-styrene)/ carbon nanotubes for effective Fe(II) ion adsorption from aqueous solutions," *International Journal of Biological Macromolecules*, vol. 283, Dec 2024, Art no. 137947, doi: 10.1016/j.ijbiomac.2024.137947.
- [8] M. Esmaeili Chermahini, M. Ghiaci, A. Najafi Chermahini, and M. Shirvani, "Fabrication of a novel magnetic carbon nanotube coated with polydopamine modified with EDTA for removing Cd²⁺ and Pb²⁺ ions from an aqueous solution," *Heliyon*, vol. 10, no. 19, pp. e38780-e38780, 2024-Oct-15 2024, doi: 10.1016/j.heliyon.2024.e38780.
- [9] S. Cheng, X. Zeng, and P. Liu, "One-step synthesis of magnetic N-doped carbon nanotubes derived from waste plastics for effective Cr(VI) removal," *Arabian Journal of Chemistry*, vol. 17, no. 10, Oct 2024, Art no. 105956, doi: 10.1016/j.arabjc.2024.105956.
- [10] S. Aliyu, A. S. Ambali, T. J. Oladejo, S. Mustapha, T. C. Egbosiuba, and S. O. Bada, "Development of Ag-doped on multi-walled carbon nanotubes for the treatment of fish pond effluent," *Regional Studies in Marine Science*, vol. 58, Feb 2023, Art no. 102797, doi: 10.1016/j.rsma.2022.102797.
- [11] J. Jiang, H. Jiang, Y. Xu, M. Chen, and L. Ai, "Janus Co@C/NCNT photothermal membrane with multiple optical absorption for highly efficient solar water evaporation and wastewater purification," *Colloids and Surfaces A-Physicochemical and Engineering Aspects*, vol. 647, Aug 20 2022, Art no. 128960, doi: 10.1016/j.colsurfa.2022.128960.
- [12] L. Wang et al., "Efficient removal of Chromium(VI) from wastewater based on magnetic multiwalled carbon nanotubes coupled with deep eutectic solvents," *Chemosphere*, vol. 362, pp. 142732-142732, 2024-Aug 2024, doi: 10.1016/j.chemosphere.2024.142732.
- [13] M. Zhang, "Lead and cadmium decontamination from water media by CNT/Starch/Fe₃O₄, as reclaimable magnetic nanocomposite," *Biomass Conversion and Biorefinery*, ; Early Access 2024, doi: 10.1007/s13399-024-05594-2.
- [14] S. S. Grazhulene, N. I. Zolotareva, and I. I. Hodos, "Efficiency of Adsorbents Containing Various Carbon Allotropes, Including Modified Carbon Nanotubes," *Journal of Analytical Chemistry*, vol. 79, no. 10, pp. 1399-1407, Oct 2024, doi: 10.1134/s106193482470076x.