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| REVIEW ARTICLE

Carbon Nanotubes as Adsorbents for Heavy Metals: Focus on Arsenic and Hydrargyrum Removal from Water

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| ABSTRACT

Water is the most common and indissoluble substance in the ecosystem. It is really sad that the development of cities, people, and industries has side effects on water resources, as they are getting worse. Heavy metals are mostly found in industries; their toxicity levels are a big challenge. The work details the latest methods employed in the removal of water contaminants with heavy metals, absorption being the technique used. Following the completeness of the literature review for various sorbents that are used to remove heavy metals from wastewater, this article details one of the possible sorbents that can play this role, using carbon nanotubes as a sorbent. Through the test, it has been demonstrated that CNTs have high efficiency, yet some shortcomings have also been shown. It should, additionally, be known that further improvement of desulfurizing agents to make them better at removing heavy metals is needed. This work demonstrates that, in comparison to IL's, which must be supplied by producers, DES's, as an alternative approach, are cheaper, more accessible to use, and much safer for the environment. In other words, the method of adsorption with functionalized CNTs + DESs proved to be the most suitable. The practical diagnostics and conclusions generated from this research should prove valuable to engineers and environmental scientists involved in carbon nanotube applications in environmental remediation.

| KEYWORDS

Water purification, Heavy metal contamination, Adsorption, Deep eutectic solvents, Carbon nanotubes.

| ARTICLE INFORMATION

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1. Introduction

Water is the most important and also required substance for the existence of life on earth. On the other hand, as civilization continued to expand, along with human population growth and industrialization, degradation in water resource quality set in a continuous decline. This has resulted in a situation where about one in four people in the world is not provided with safe drinking

water, a health hazard (Clean Water, 2024). Harmful pollutants such as heavy metals and radioactive nucleating metals also lead to energy focus. These pollutants pose a threat to living beings. In modern times, water purification has now become an issue that is very important and a significant concern to many. Many other ways to purification water have been designed, such as adsorption, reverse osmosis, and precipitation, among others.

2. Methodology

In this study, the literature about the removal of heavy metals using various methods, types of adsorbents, and functionalization agents is discussed, taking into consideration the best combination of an adsorbent and a functionalization agent. It briefly narrates the modelling method used to identify the most effective method of heavy metal removal. In particular, it considers the use of functionalized CNTs for efficient metal removal from water. The specific attention of this research is on the use of F-CNTs (functionalized carbon nanotubes) together with DESs (Deep eutectic solvents) to address the problem of heavy metals elimination. Literature shows that these latter are used in most nanotechnology applications to functionalize carbon nanotubes, which in turn enhances their metal removal capability. Moreover, there are numerous processes that are effective in the removal of heavy metals from water slurry. One of those adsorption processes is discussed in this study, and functionalized carbon nanotubes are employed as adsorbents.

3. Properties of Carbon Nanotubes as Adsorbents

Carbon nanotubes (CNTs) possess diverse adsorption capabilities and unique structures. Its large surface area-to-volume ratio gives CNTs many sites that are suitable for adsorption. This greatness in capturing molecules and ions in either the aqueous or gaseous phases makes CNTs very efficient. Their tunable porosity, diameter, and surface chemistries can give rise to customized adsorption capacities and selectivity denoted by pollutants or the target molecules. In addition to these properties of CNTs, they show superior mechanical performance and stability, which helps them be reused for adsorption applications. Their conduction makes our process of monitoring and regeneration easier, while their combination with functionalization boosts their adsorption performance and functioning efficiency. In short, CNTs can be considered as effective sorbents in one or another environmental restoration, wastewater purification and sensing processes.

3.1 Structure and Properties of Carbon Nanotubes

Carbon nanotubes (CNTs) are nanostructures that are cylindrically organized with rolled graphene sheets and exhibit remarkable mechanical, electrical, and thermal properties. Their structure can be subdivided into single-walled carbon nanotubes (SWCNTs) and multi-walled carbon nanotubes (MWCNTs), the latter consisting of multiple concentric graphene layers covering up the former one-layer carbon framework. CNTs have the highest tensile strength, more than ordinary steel, and other electrical conductivity properties that make them good for various uses like nanoelectronics, composites, and energy storage. Additionally, CNTs display unique optical features that are widely used in nanophotonic sensors. Their superb thermal conductivity provides the thermal management of heat in electronics, which is very vital. The exceptional contribution of this unique blend of structural properties and specific attributes gives CNTs a promising role in different scientific progress.

3.2 Adsorption Mechanisms of CNTs

The carbon nanotubes (CNTs) have excellent nano-adsorption capacities due to their special structure and surface properties. Mechanisms of adsorption of CNTs include physical and chemical adsorption interactions. Such attractive forces, which are key to the adsorption process of CNTs because of their high aspect ratio and the huge surface area, efficiently lead to the physisorption of molecules and nanoparticles. Moreover, the defect sites and functional groups on the specifics of the CNT surface function as a catalyst for chemisorption by means of interactions such as hydrogen bonding, π-π stacking and electrostatic attraction, which makes the absorption of specific molecules or ions more effective. Of particular interest is the innate conductivity of CNTs, which facilitates electron transport and adsorption, thereby assisting in the elimination of pollutants by redox reactions. Thus, particular interaction modes of CNTs make them potentially suitable for such applications as environmental remediation, storage, sensing and catalysis.

3.3 Advantages of CNTs as Adsorbents

Carbon nanotubes (CNTs) offer several advantages as adsorbents: Carbon nanotubes (CNTs) offer several advantages as adsorbents:

High Surface Area: CNTs bring an incredible advantage of much higher surface area compared to volume ratio, which is capable of plenty of adsorption site levels.
Tunable Pore Size: The diameter and length of CNTs can be adjusted without limitations to accommodating liquid or gaseous molecules with the required pore size.
Chemical Stability: CNTs have a high chemical stability feature, so decomposition in harsh conditions is hard to occur, therefore enabling the adsorption process to go a long time.

Mechanical Strength: CNTs comprise excellent mechanical strength to withstand higher pressures and shear stress during adsorption, which further enhances their flexibility and durability.
Fast Adsorption Kinetics: The distinct structure of CNTs enables quick adsorption kinetic mode because adsorbate molecules can attain the active sites on carbon tube surfaces with low energetic barriers.
Regenerability: CNTs can be restarted via methods such as thermal or chemical treatments whereby the revival of the catalytic activities is possible, and hence, the multiple cycles of adsorption-desorption can be repeated without a significant decrease in performance.
Versatility: CNTs can be functionalized with particular groups of functionalities or combined with other materials to feature enhanced special adsorption properties and offer increased flexibility of adsorption range width.

4. Heavy Metal (Arsenic and Hydrargyrum) Contamination

The poisonous heavy metals are relatively metalloid and dense with high or extreme potential toxicities (Ungureanu, E. L., & Mustatea, G. 2022). The atomic weight of heavy metals falls between 63.5 and 200.6, and their density is greater than 5 g/cm3 (Singh, J., & Mishra, V. 2020). Heavy metals can, therefore, become sources of contamination under several factors and in diverse situations, such as modern chemical industries, farmers who use pesticides for their fertilizers production, battery manufacture, which produces nickel or cobalt and also incorporates calcium absorbed from lead lunacy shells; assembly Nowadays, different kinds of harmful substances may be found in water resources; they are chromium, nickel, mercury, zinc, and copper (Dahiya, V. 2022). They are toxic, and therefore, unevenly high concentrations bring a lot of danger, regardless of how small they are. The following parts of this section provide a bit more detailed discussion about the most common and inhumane.

4.1 Sources and Health Effects of Arsenic Contamination

Arsenic (As) is known as the deadliest metal among all of the heavy metals. Its toxicity has been a discussed matter for a long time. It is characterized by many ramifications for some of the living species. Arsenic may be a chemical compound that exists in a multitude of different forms and has various levels of toxicity. The impacts of human activities or natural processes can be seen in the arsenic contamination of water sources such as lakes, rivers, groundwater, and drinking water sources. As per the World Health Organization (WHO), the requirement for arsenic in drinking water is less than 10 mmol/L (Weerasundara et al., 2021). Many different types of cancer, like bladder cancer, urinary tract cancer, and skin cancer, are found as a result of exposure to arsenic throughout life, aggravated by the growth factor for proliferation (Ozturk et al., 2022).

4.2 Sources and Health Effects of Hydrargyrum (Mercury) Contamination

Mercury (Hg) is among the most poisonous compounds that can be found in nature. It can be an occurrence associated with either vapor or liquid. Exposure to mercury-led organs of the renal systems, gastrointestinal (GI), and neurologic systems is most affected. In the soil, fresh water and seawater are found these elements. Industrially, mercury can also be seen in some waste processes and products, including wiring device production, various switching systems, fossil fuel processing, and measuring devices (Subeshan et al., 2023). The recommended maximum allowable mercury concentration set by the World Health Organization (WHO) is 1 mg/L because of its serious effects at very low concentrations (Mallongi et al., 2023).

4.3 Regulatory Limits for Arsenic and Mercury in Water

The WHO sets arsenic and mercury standards in drinking water to ensure people's health. The guideline values of the WHO for arsenic in drinking water are 10 µg/L (Frisbie & Mitchell, 2022), representing the health hazards connected with long-term exposure to arsenic, which may cause severe skin lesions, cancer, and heart diseases. The WHO guideline value for mercury is 6 ug/L (Tang et al. 2022) due to the neurological effects as well as other organs, including the developing fetuses and young children. Compliance with these regulatory limits by all parties involved is vital for the sake of public health and also for the assurance of the safety of drinking water globally.

5. Functionalization of Carbon Nanotubes with Deep Eutectic Solvents

CNTs are used in most applications because of their outstanding chemical, physical, and electrical characteristics, which include medical science, environmental engineering, electrical engineering, and material science (Raphey et al., 2019). However, some notable challenges of CNTs are the interactive forces arising due to the carbonic nanostructures that cause them to form agglomerates, thus making manipulation and dispersal quite difficult. The principal active chemical sites on carbon nanotubes are around defective regions like pentagons, which are oriented oppositely to their bodies and consist of pure hexagons, and it is this property that allows CNT to have a high affinity for other substances (Roy et al., 2021). Functionalization of CNT is the most important step for increasing its efficacy. The best possible manner in which this can be accomplished is dependent on the CNTs involved in a particular variable, especially their size, surface nature, and chemical composition. In order to improve CNTs' strength, the addition of functional groups to the surface of CNTs is a necessary step. There are two classes of functionalization: covalent and non-covalent. Side chains, which covalently bind to the CNT skeleton through chemical reactions, are called a linear covalent functionalization type. Covalent functionalization, however, is surface modification via the interaction of functional groups with the

walls of CNTs (Gao et al., 2023). The variety of successful functionalization methods of CNTs have obviously been used in different applications. The most significant of these functionalization methods is using chlorine (Cl) for sidewall soluble dichlorocarbene reactions. 2% carbon atoms out of 100 saturations influenced the structure of the electronic band in a very wonderful manner (Yang et al., 2018). Oxidation processes are probably the most widely used ones in the functionalization of organic compounds. After this, the acidification is done by refluxing them in an acid solution, such as sulfuric acid, nitric acids, or a mixture of them (Saleh, T. A. 2011). The second method, oxidation, involves the use of strong oxidants such as KMnO4 (Wang et al., 2023). Although carboxylic groups result from the oxidative method of CNTs, it is possible to find a significantly good number of functional groups, which in turn can offer room for more functionalization and applications (Rathinavel et al., 2021). The most active functional groups on carbon nanotubes (CNTs) include the carboxyl (-COOH) or the hydroxyl (-OH) groups. Furthermore, functional group attachment can equally influence the hydrophobic characteristic of CNTs through a more hydrophilic part positioned on the surface of the CNTs, as the polar groups on the CNT surface make CNTs able to disperse in the organic solvents (Poorsargol et al., 2020). It was also studied, but in our case, nucleophilic and alkyl amine derivatives were studied for SWCNTs as well. The octadecy1 amine branching synthesized from the acid functionality exhibits the solubility of SWCNTs (Hamon et al., 1999). Lots of other methods for the treatment of CNTs have been utilized, for example, biomolecules, arylation and alkylation, esterification (Khan, A., & Alamry, K. A. 2022), polymer grafting, thiolation (Díez-Pascual, A. M. 2021) and salination (Barrejón, M., & Prato, M. 2022). In recent times, ionic liquids (ILs) have caught enough attention as environment-friendly solvents because of their deep qualities. Ionic liquids combination as a functional tool in nanotechnology was first mentioned by Hammond, O. S., & Mudring, A. V. (2022). The MWCNT anion of IL, which makes an exchanger salt with the anion of MWCNT, was found in points of solubility of organic solvents and water (Matandabuzo, M., & Ajibade, P. A. 2018). ILs have been vindicated as solvents and strong acids as functionalizers. Compared to the case of using organic solvents, which result in the deactivation of the original CNTs, these functions can be characterized as non-destructive reactions (Aslam et al., 2021). Nonetheless, as for the pollutants they can emit, ILs will also experience some limits. Lastly, bagasse-based biomaterials have a few limitations, including low cost and waste disposal. (Maloney et al., 2023) Hence, the renewed research focus should be on searching for a novel, superior excipient. This part of the article aims to find an alternative to the yellow deep eutectic solvents, DESs, through which we can obtain a material that is a green solvent, biodegradable, economical, and requires less complex synthesis.

5.1 Introduction to Deep Eutectic Solvents (DES)

Abbott et al. (2003) unveil DES as an IL's alternative. Almost invariably, the components of DESs are two or even more mixtures of compounds with a lower melting point than either of the respective compounds, according to Abdelquader et al. (2023). They are created using hydrogen-bond-donor (HBD) adsorption on the surface of the solid salt. DESs can be developed using various salts (Stephens, N. M., & Smith, E. A. 2022). DES can be divided into three types: Class A ionic liquids consisting of an ionized salt and an electrolyte, which are the group descriptors. Fig. 1 demonstrates the DES formulation as explained: the combination of choline chloride and urea. The formula of the Class B DESs is a metal salt and an ionized form of the salt, e.g., zinc chloride and choline chloride (Ramón et al., 2020). Besides classes A and B, class C is also more complex. It is generated from the mixture of ammonium salts, urea, and carbohydrates in different measures. An example is choline chloride, the main reason for the difference between d-glucose and d-fructose (Istasse, T. 2021).

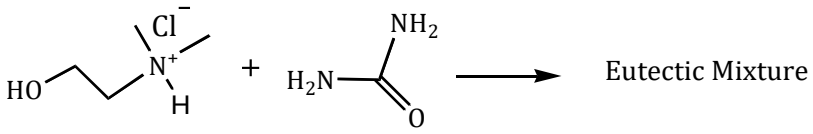


Fig. 1. ChCl: U eutectic mixture.

Water content and the physicochemical properties of DESs mimic those of conventional ILs. Therefore, both ILs and DESs give out liquids of high viscosity, based on the same starting products, and are low boiling point and non-flammable. The DESs can be regarded as the subsequent generation of the ILs (Afonso et al., 2023). This concerns non-toxic or low toxicity categories, lower costs, and higher economic and environmental sustainability, as shown by Zou et al. (2021). Moreover, the ingredients of DESs are bare and easy to provide and synthesize on a large scale (Svigelj et al., 2021). The key point is that the DES syntheses are done by straightforwardly mixing the components, and consequently, all that other hassle (in the production and waste disposal) is ignored.

5.2 Functionalization Techniques of CNTs with DES

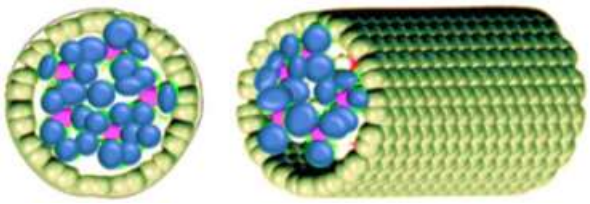
The mechanization of CNTs with DES is not a single-step method; rather, it is a multiple-step process that aims to change the CNT surface properties for distinct purposes. The CNTs used for reinforcing are mixed with the DES first to produce a stable single-phase suspension. This occurs due to the DES unevenness, and hence, its interaction with the CNT surface occurs, and the incorporation of functional groups through either chemical reactions or physical adsorption occurs subsequently. The use of DES and the type of functional groups is a tricky task, so the final properties of the modified CNTs depend on the use of particular DES

and functional groups. Further cleaning steps, such as centrifugation or filtration, are regularly performed to take off DES and unreacted nogroups, and eventually, those CNTs will be obtained that are adequately soluble, readily dispersible, and specifically compatible with certain matrices or applications. This interfacing approach presents a quite flexible and suitable way for designing functional CNTs properties to treat various industrial and scientific matters.

5.3 Advantages of DES Functionalization

Soon after, the ILs found their first application in nanotechnology at room temperature (Arumugam et al., 2018) for two probable ways of utilization: they synthesized Pd-biscarbene mixtures and stabilized the clusters. Given the crucial role that both studies and papers play in the hair loss industry, noticeable and breakthrough patents about using ILE in nanotechnology were soon published and presented for further research fulfillment. Lately, hard disk drives (DESs) have been adopted in many fields of nanotechnologies and in other applications in place of ILs. Obviously, the nanomaterials' limitation is their tendency to aggregate. Humanize: In this context, perfect dispersion is a critical determinant of nanomaterials offering out their best potential, and, therefore, creating environments that offer it is of importance. Zeta potential for good stability should be more than 40 mV, in accordance with ASTM standards by Lunardi et al. (2021). The objective has been defined, and DES can be undertaken as a dispersant environment for the synthesis of nanoparticles. For instance, Hassan et al. (2022) studied the use of ChCl: He as an organic template (structure-directing agent) and for reducing the ions of gold (reaction media for the synthesis of gold nanoparticles). The DES acrylic acid: To demonstrate the application of this green DES in the synthesis process, the microporous poly (acrylic acid)-carbon nanotube mixture was prepared, and the results revealed that nanocomposite environmental and biological application production could be improved using green DES in this way (Tran et al., 2022). Meanwhile, we tested the use of ChCl: Use tris (hydroxymethyl) propane DES (trimethylolpropane triacrylate) as a curing agent for the epoxy resin production while GNP/DES epoxy resin has been made. This is proof that the presence of DES supports the improvement of epoxy composites. Following Azzouzet al. (2023), DESs are excellent candidates for improving the potential for electrochemistry when combined with nanomaterials investigated the use of ChCl: urea is used as providing counterions for quercetin detection that help substantiate the fact that an MWCNT electrode is more and less demanding for usage than an IL-CNT mixture. Another study implements uniform Pt nanoflowers produced with DESs by using both electro-chemical and tackled-oriented fabrication methods (Maniam et al., 2022), which is also known to have higher stability and electrocatalytic activity. The DES ChCl: ZnCl, as shown below-inset of Fig. 2-encapsulated into SWCNTs with equal Zn: Cl M ratio, is demonstrated. The procedure was conducted under thermal conditions of SWCNTs being decapped, and it was adopted together with many characterization issues (Onyancha et al., 2022). DSs have also been employed profusely in other areas of applications such as alimentation, industries, and medicines (Gu and Tu, 2011). broke up a new strategy for both thermochromic exhibiting and metal complexes. This involved the use of two DESs, ChCl: ethylene Glycol and ChCl: urea, a photochemical technique that allows them to dissolve a whole range of metal chlorides. NiCl2 + 6H2O turned out to be the most efficient and reliable thermochromic dye in the temperature range of 25 to 150 °C. Ultimately, the researchers concluded this would have an impact on the future creation of high-grade thermochromic materials for easier manufacturing. DESs are also the platform for the fabrication of functionalized graphene (Deng et al., 2023). We analyzed different types of DESs, which we used to see how the graphene surface behaves under their application. The result of this study was that the DES functionalization had shown tremendous applause, particularly in improving the performance of graphene-based sensors, mainly due to the nature of the functional groups that were formed when the functionalization interaction happened. Carbon nanotubes (CNTs) have become the best material for the removal of a battalion of pollutants from water because of their unique properties (Viltres et al., 2021). Moreover, the implementation of CNTs is a tricky undertaking thanks to problems like lack of solubility, complicated manipulation, and polymerization. DESs constitute cheaper alternatives to lipophobic ionic liquids (ILs) that have analogue properties with ILs, according to a reference (Hunt, 2019), among others. DESs also have the following benefits over traditional ILs: they are made up of liquid crystal components that have many different physical properties; DESs are able to be used at varying mole ratios; they are quickly manufactured; and they cost less as compared to the mixtures they come from.

Fig. 2. DES encapsulated SWCNT.



5.4 Applications of DES

Patents and research on synthesizing and using DESs are proliferating currently, which indicates that DES can play an increasingly important role as an environmentally friendly solvent in the near future. DESs were originally created with the purpose of solvent design for industrial applications in electrodeposition and electroplating (Prabhune, A., & Dey, R. 2023). The first role of electrode-supporting substrates was to be used as metallic media to be electroplated, and thus, various types of metallic electroplating

media were studied. DESs have, in addition, extended the whole production process and purification via biodiesel production. Likewise (Šalić et al. 2020) gained a new approach, which is supported by DES (Different types of solutes) for the separation of glycerol from biodiesel. Spurred by the awareness of high CO2 and CH3 emissions to the sky, advanced research on the innovations of absorption and differentiation of these gases has significantly increased in recent years. In addition to the ILs' ability to dissociate CO2 is the Dess' competence, too (Pourvahabi et al., 2023). Lee and co-researchers conducted an experiment using a urea and ChCl mixture and different molar ratios, pressures, and temperatures in a test mode (Lee et al., 2020). Also, there are various advantages of DESs in gas storage, such as the presence of coordinatively unsaturated segments that are suggested for gas storage and porosity creation that increase the gas storage capacity (Perovic et al., 2020). Li et al. (2023) examined the use of ChCl: In sorbent-based systems, glycerol is used to adsorb SO2 with different molar ratios, pressures, and temperatures. On the other hand, in their work proper, Vaičekauskienė et al. (2023) investigated the role of DESs in pore architectures´ composition, thus showing the link between gas adsorption and CO2 content by using two DES-based topological carbon monoliths. The carbon forcing strength of DES has been found to have good selectivity and a broad adsorption capacity for CO2 (Petrovic et al., 2021). To conclude, the DESs (Design of Experiments) were developed for enzymes with lots of such studies. The employment of DESs is the first try regarding enzymatic catalysis in DESs by Bjelić et al. (2022). Besides these, surface area and lipase-catalyzed reactions are to be explored (Cavalcante et al., 2021).

6. Remediation methods for heavy metal removal

Various techniques have been applied to remove heavy metals from water. For instance, primarily oxidation as well as reverse osmosis, ion exchange, precipitation, occultation, flocculation and photocatalysis. On the other hand, every one of these approaches has some shortcomings. Take the precipitation method as an example; it causes harmful waste, while such waste requires even more treatment on its own. The limitation of the otherwise efficient ion exchange method is the lack of recyclability. Membrane filtration is constrained by several issues, which it faces in the process of generation: costs and getting rid of waste materials. The flocculation and coagulation method has an issue in the amount of sludge produced, while the photocatalytic technique takes a long time to operate. Electrodialysis is a spot-on technique, though it has such flaws as high consumption of electricity and power costs. In addition, heavy metals in soil may need some treatments that utilize certain techniques for their removal. Due to the various disadvantages inherent in the above discussed methods, new alternative approaches and technologies must be developed. In this study, the adsorption technique is selected since it proves to be more effective than other conventional techniques for the removal of heavy metal ion contamination from water, even in cases of low concentration. The readily availability of adsorbents, opportunities for treatment regeneration work and finally employment simplicity make this technique superior to others. The next subsection presents additional information on adsorption techniques.

6.1 The adsorption methods for the heavy metal's removal

The adsorption method is preferably applicable for the removal of heavy metal ions due to its low cost, low energy consumption, and the availability of synthetic materials, which make different types of adsorbents. The adsorption method refers to the process of attaching soluble liquids and gases to the surface of an adsorbent. The adsorption process is predominantly divided into two types. Physisorption refers to the sorption process, where an absorbent and adsorbate (the component that is to be absorbed) are held together by the van der Waals force. In contrast, chemisorption happens when the molecules of the adsorbate are adsorbed on the surface of the adsorbent through strong chemical bonding (Huber et al., 2019). The adsorption quality is determined by the adsorption capacity, which depends on the characteristics of the surface and its interaction with specific pollutants to be captured. For instance, surface charge, surface area, and functional groups may induce varied activity in different types of contaminants. For example, many kinds of adsorbents such as modified chitosan, manganese oxides, peanut hulls, peat; sewage sludge ash granular biomass fly ash extracellular polymeric substances; landfill clay and activated carbon have been utilized to remove heavy metals (Gomesa et al., 2022). On the other hand, these adsorbents have some limitations, including low adsorption capacity, poor elimination efforts, and low efficiency in removing heavy metals. Therefore, there is a need to try to look for other superior adsorbents. The nanotechnology revolution creates a new area for development in innovative adsorption methods. In general, carbon nanotubes (CNTs) have magnificent chemical and physical properties, making them superior adsorbents (Hoang et al., 2022). They are poor adsorbents in themselves, but by introducing a fresh, functional group to their surface, they become excellent selectively and sensitively towards heavy metals, thereby enabling them to quite adopt the latter considerably. In fact, CNTs have to be coated with a material substance of another kind in order to work efficiently as a reaction to multifaceted pollutants (Jain et al., 2022).

6.2 Adsorption of heavy metals by functionalized CNTs

The first electronic publication of carbon nanotubes was done by Iijima (1991). They are nanometer-scale structures made up of a combination of one or more graphene sheets twisted to form cylindrical shapes that measure over 20 mm long and less than about 100 nm in diameter (Aligayev et al., 2022). There are two types of carbon nanotubes: The multi-walled carbon nanotubes (MWCNTs) have more than one graphene sheet, whereas single-wall carbon nanotubes (SWCNTs) contain only one graphene sheet. Fig. 3 provides sketches of SWCNTs and MWCNTs, as shown in Fig. 4 below:

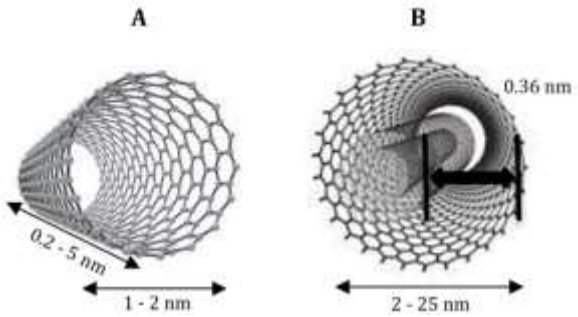


Fig. 3. The structure of SWCNTs and MWCNTs.

In addition, based on their two-dimensional sheets, CNTs are divided into three types: zigzag, armchair, and chiral nanotubes. The zigzag, illustrated in Fig. 4a, exhibits a hexagonal pattern around the body of the tubule (Fiyadh et al., 2019). The armchair form, shown in Fig. 4b, includes one or two cyclohexane conformers, with the carbon atom also tracing a hexagonal pattern as it travels around the body of the tubule base. The third type of chiral CNTs in Fig. 4c is one that consists of a configuration with helical carbon atoms forming a circular structure. The word chiral refers to 'handedness' and, thus, the opposite of chirality, which means that this tube can twist in any direction. In relation to chirality, SWCNTs exhibit shapes that resemble the existence of zigzag and armchair forms (Hu, Z. 2022). All these forms are also typical for transportation within SWCNTs. It also possesses a set of graphene cylinders. Through TEM, it is possible to obtain an inter-shell spacing that ranges from 0.335 nm to just 0.34 nm, complemented by a declining exterior tube diameter. The highest allowance and lowest diameter are in the high cover, which causes some undesirable stress, followed by a decreasing diameter from within the CNT shell (Choudhary et al., 2022). Ru proved that the interlayer spacing mean value is 0.3444 ± 0.001 nm and also established that CNTs are larger by a few percent than bulk graphite crystals (Tan, X., & Wang, X. 2022). There is a gap between different layers that is denoted by d = 3.39 Å, the value of which was calculated theoretically, and it is greater than that observed for graphite. The spacing of d=3.4Å was experimentally determined using a TEM image for MWCNTs (Seef Saadi, F. 2019). This particular CNT structure is, therefore, magical because it produces awesome properties on the chemical and physical sides. Since two-dimensional graphite, CNT, has bonding between the sp2 directions of carbon atoms, it is one of the strongest materials on Earth (Armano, A., & Agnello, S. 2019). Their studies clearly showed that the strength and Young's modulus of CNTs are 10–100 times higher than steel, respectively. The specific heat capacity and the thermal conductivity of CNTs have been estimated through phonons, as discussed by Wang et al. (2004). At the same time, 8-350 K for SWCNTs and 4-300 K for MWCNTs were mentioned by (Ahmad, M., & Silva, S. R. P. 2020). Furthermore, research showed that CNTs have much higher electrical conductivity than many other materials (Bulmer et al., 2021). Such high conductivity is associated with the hexagonal ring geometry along the tubular frontier regardless of whether it is a semiconductor or a metal. The semiconducting and metallic characteristics of the narrow gap SWCNTs are determined through their chiral vectors (n, m), which are two integers. The semi-conducting and metallic state is possible by m and n variation, but there are multiple or three differences between the same results under CNT's metallic properties. Additionally, it is possible to zigzag the nanotube with a number of chiralities so as to form a heterojunction that can allow for numerous sub-nanoscale components of the device (of electronics) from various nanoscale molecular arrangements (Abbas et al., 2023).

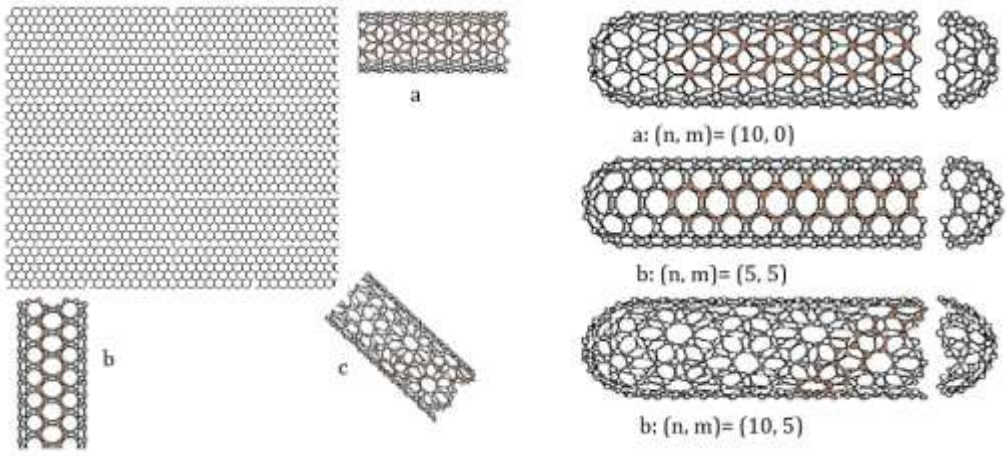


Fig. 4. Patterns of CNT. (a) Zigzag SWCNTs, (b) Armchair SWCNTs, (c) Chiral SWCNTs.

7. Adsorption Performance of DES Functionalized CNTs for Arsenic Removal

The precipitation of arsenic (As) from water is more of a science than that of other heavy metals, and the adsorption technique is one of many practiced for this purpose. Nonetheless, there is not much research that focuses on using CNT as an adsorption medium to remove As, even though there are numerous studies for other heavy metals (Sezer, N., & Koç, M. 2019). The determination of carbon nanotube oxidizing with HNO3 acid and H2SO4 mixture by means of sonication for 3 h at 40 ◦C temperature has been presented. The oxidized MWCNTs were suspended in EDA with (1[Bis(dimethylamino)methylene]-1H-1,2,3-triazolo[4,5-b]pyridinium3-oxidhexafluorophosphate) and methanol currently as the coupling agents by sonication for 4 h at 40. The maximum adsorption ability of the Oxidized MWCNTs became 12 mg/g, and the adsorption process can be perfectly described by the Freundlich model (Šolić et al., 2021). According to works cited before there is some censor from the arsenic to metals oxides differing from the interaction bases (Ayub et al., 2022). For instance, a " Fe–MWCNT" composite was elaborated by Tugirumubano et al. (2021) in order to remove arsenic (As3+). The most important feature occurs at the pH 7–8 range, where the content is equal to 84.8%, and the adsorption model works according to the Langmuir isotherm and the pseudo-second order reaction kinetics process (Ezzati et al., 2020).

7.1 Adsorption Mechanisms of Arsenic on DES-CNTs

The mechanisms of the adsorption of arsenic by DES-functionalized carbon nanotubes (CNTs) are multidimensional and consist of several intertwined processes. DES-CNTs (designed carbon nanotube structures) benefit from the large surface area and a multitude of surface functional groups that bind to arsenic species in water effectively. These interactions mainly consist of chemisorption, electrostatic adsorption, and micropore compounding. Chemisorption is the formation of an olefin or a weaker covalent bond between arsenic species and moieties on the DES-CNT surface, such as hydroxyl (-OH), carboxyl (-COOH), carboxyl (-COOH) and amine (-NH2) groups. The attraction between positive arsenate As(V) species and negative functional groups of DES-CNTs takes place due to electrostatic attraction, particularly pH. Firstly, surface complexation constitutes the development of inner-sphere complexes between arsenic ions and surface functional groups by means of coordination bonds. The unfamiliar properties of DES-CNTs are associated with these adsorption mechanisms, which ensure that it is very effective as an agent for arsenic removal from water, making the technology suitable for water purification.

7.2 Factors Influencing Arsenic Adsorption Efficiency

Arsenic sorption by deep eutectic solvent (DES) functionalized carbon nanotubes (CNTs) depends on a number of variable properties such as pH, temperature, initial arsenic concentration, contact time, and the presence of competing anions. pH is really important for two reasons: pH affects the zeta potential of DES-CNT and forms arsenic species in solution, subsequently leading to quick adsorption kinetics and equilibrium. As a rule, the arsenic adsorption rate increases with decreased pH because positively charged arsenic compounds are attracted by negatively charged functional groups on DES-CNTs. Temperature has an impact on the kinetics of adsorption since high temperature leads to faster rates of adsorption. Firstly, the initial arsenic concentration and the contact time are a controlling factor in the mass transfer of arsenic onto DES-CNTs, and typically, with higher initial concentrations and longer contact times, the adsorption capacity tends to be higher. Furthermore, Divalent cations like phosphate and sulfate are able to outcompete DES-CNTs adsorption of arsenic by competing sorption mechanisms. The optimization and knowledge of these factors are paramount for achieving the DES-CNTs' best performance in water treatment processes.

8. Adsorption Performance of DES Functionalized CNTs for Mercury Removal

Removing mercury (Hg) from water is vital so as to safeguard clean drinking waterbodies. Through the application of conventional methods such as photoreduction, coagulation, membrane separation, reverse osmosis, ion exchange, precipitation, and solvent extraction (Fei et al., 2023), lower Hg concentrations in water may be achieved. Nonetheless, various methods of production have the flip side, which necessitates either a large quantity of chemicals, a high amount of energy consumption, or both. Alternative methods for Hg elimination are therefore imperative. The adsorption technology showed better results than the other conventional technologies. This is why it has been the subject of much study, and researchers agree on this kind of technology. (Goci et al., 2023) Here, the chapter deals with the use of CNTs as adsorbents in the removal of mercury, which provides insight into the methods used to mitigate this type of pollution.

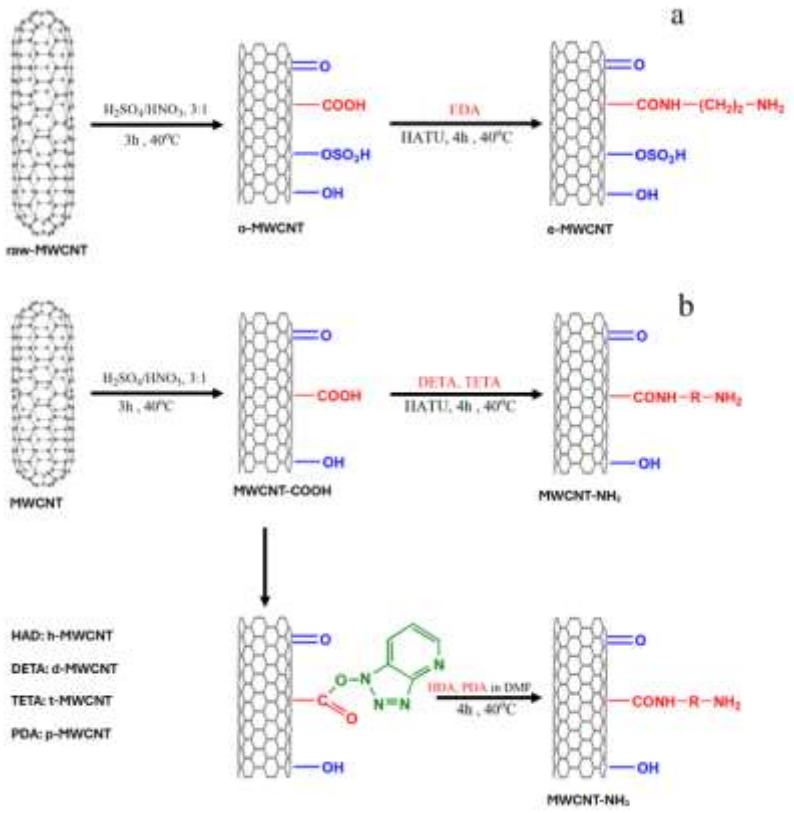


Fig. 5. Functionalization of MWCNTs by amino groups and the abbreviations.

SWCNTs functionalized with amino thiol through a study regarding the application of CNTs in the removal of Hg2+ demonstrated an adsorption efficiency was up to 91% with only 5-fold of the fuel usage (Emenike et al., 2023). The triethoxysilane (MPTS) offered its support for the increased hydrophilicity of the CNTs/Fe3O4 surface, which improved the sorption capacity of the nanocomposites by combining the shapes. Further, the nanocomposites could remove Hg2+. PS It exhibited 65.52 mg/g adsorption capacity for Hg2+ in solution acidified to pH 6.5. The adsorptive capacity increases with the pH values, which reach the optimal of 6.5 mg/g, resolving pH values competition between the Hg and metal ions and the tendency of these ions to hydrate M(OH)2 (Mamidi et al., 2022). (He et al., 2023) conducted research on the geometrical effects of non-oxidized MWCNTs. The results showed that there are no significant differences in the performance of the following structures: oxidized and non-oxidized MWCNTs. The other Kauret al. (2018) research article described the synthesis of MWCNTs with KMnO4/H2SO4 and MWCNTs with HNO3. If we consider fitted curves, the pseudo second order model delivered the best results, and the underlying mechanism of adsorption was primarily that of chemisorption (Alayan, 2018). In addition, the Langmuir equation comes out with the ordered set of isotherms models of MWCNTs, in which the adsorption capacity of the functionalized MWCNTs became higher than that of pristine MWCNTs (Saxena et al., 2020). SMWCNTs containing sulfur were subsequently tried out (Ravi Kumar et al., 2022) against the removal of Hg2+ from water, with a maximum adsorption capacity of 72.8 mg/g and a good fitting with the Langmuir adsorption equation (Kumar et al., 2006).

8.1 Adsorption Mechanisms of Mercury on DES-CNTs

The adsorption mechanisms of mercury on DES-CNTs can be described by several key processes. To begin, the chemical interaction of the functional group in the deep eutectic solvent with the carbon nanotube surface provides Lewis's acid-base interactions,

electrostatic attractions, and complexation as the active sites for mercury adsorption. These interferences result in the binding of mercury ions onto the DES-CNTs surface. Moreover, the larger surface area and pores of carbon nanotubes lead to faster diffusion of mercury ions to the active sites, contributing to mercury removal. Moreover, the π-π interactions that take place between the conjugated carbon atoms of CNTs and mercury molecules aid the process of adsorption. In the overall picture of chemical interactions, surface morphology and π- π stacking interactions are major factors that favor the adsorption of mercury onto DES-functionalized carbon nanotubes, resulting in the effective removal of mercury from water.

8.2 Factors Influencing Mercury Adsorption Efficiency

Mercury adsorption on CNTs modified by DES has several influencing factors. These factors consist of the inherent characteristics of the adsorbent material and extra circumstances of the surroundings. The specific intrinsic factors include the DES-CNTs surface area and porosity, which provide more active sites and increase the rate of mercury adsorption. The surface chemistry and functional groups of DES-CNTs are concerned; they are the main ones determining the affinity and selectivity of mercury binding. Moreover, mercury concentration and chemical speciation in the aqueous solution that acts as the adsorbate also change the adsorption efficiency, thereby increasing the efficiency at a higher concentration. In addition to external pressure such as pH, temperature and ionic strength, the surface charge of DES-CNTs and the speciation of mercury ions can be altered. Elucidating the role of these factors underlines the importance of creating and using DES-functionalized CNTs and developing efficient water treatment methods.

9. Comparison DES Functionalized Carbon Nanotubes with Other Adsorbents

DES functionalized carbon nanotubes (CNTs) present a compelling alternative to traditional adsorbents due to their unique combination of properties. Compared to activated carbon and other conventional adsorbents, DES functionalized CNTs offer superior adsorption capacities owing to their high surface area and abundant functional groups, enabling efficient removal of various pollutants from aqueous solutions. Additionally, their tunable surface chemistry allows for tailored adsorption selectivity, enhancing their applicability to specific contaminants. Furthermore, DES functionalized CNTs exhibit excellent reusability and stability, minimizing operational costs and environmental impact. Overall, DES functionalized CNTs represent a promising class of adsorbents poised to address challenges in water treatment and environmental remediation with enhanced efficiency and versatility.

Table 1. Comparison of DES Functionalized CNT with traditional adsorbents and other nanomaterials.

Aspects	**DES Functionalized CNT**	**Traditional Adsorbents**	**Other Nanomaterials**	**Ref.**
Adsorption Capacity	High	Moderate to High	Moderate to High	(Ibrahim, 2019)
Regeneration Efficiency	Good	Moderate to Good	Moderate	(Rahmati, 2021)
Surface Area	Large	Variable	High	(Ibrahim, 2019)
Ease of Functionalization	Moderate	Limited	Limited	(AlOmar, 2017)
Application Range	Versatile	Limited	Versatile	(AlOmar, 2017)
Commercial Availability	Limited	Widely Available	Limited	(Duarte, 2022)

10. Challenges and Future Perspectives

Carbon nanotubes (CNTs) have sparked much excitement within the field of environmental spillover technology due to their superior physical, chemical, and electrical features. These days, they are often utilized in making things, including medicine, the environment, electronics, and materials. Tailoring CNs with appropriate surfaces and surface charges would certainly lead to an impressive development in the adsorption of heavy metals when they are functioning with the proper functionalization agent, which is very effective for the conversion of wastewater into clean water for reuse. The deep eutectic solvents (DESs) are a mixture of at least two compounds with a melting point below that of the single component. The nature of DESs is such that they are very easy to produce, are composed of commonly available materials, do not cause serious health problems, and overall have a relatively low environmental impact. The application of DES as a CNT functionalization agent is seen as a way to make it more effective. Though such studies are needed for more DESs to be tested for different ratios, there is hope that functional CNTs can be fabricated with them. On the other hand, the process of adsorption has numerous parameters that cannot be modelled using traditional methods. Future investigations into more competent modelling methods for such processes could be pursued, such as any artificial neural network applications (ANNs).

11. Conclusion

CNTs perform a fair role in the arena of water pollution (eco-environment remediation) and especially in the sphere of addressing increasingly fast-growing problems. To be fair, more efficient technology for separating harmful materials like heavy metals from wastewater may also be considered a huge win in terms of human health. This work has reviewed and examined (a) the historical background of heavy metals in water and their effects on living organisms; (b) remediation techniques that remove heavy metals, with such techniques as adsorption being the emphasis point; (c) the utilization of functionalized CNTs as adsorbents to take away the particularly harmful metals from water, with the primary aim being the removal of arsenic and mercury; DES Functionalization of CNTs is not only more effective and easily controlled but also turns out to be less harmful to the environment compared to Il's. They are also easy to synthesize, the materials that the processes need are easy to access, and the waste production is very low, or no waste at all. On the other hand, this study reveals that there is a necessity for determining and selecting multiple DEMs to make the CNTs able to adsorb different heavy metals more effectively. Various combinations of HBA and salt in different proportions are commonly used to assemble DES onto CNTs. The process of configuring the components and the rates at the optimum level of absorption becomes a challenge. Another issue is that there must be finding of the precise modelling tools in order to reproduce exactly this intricate adsorption process, which is responsible for heavy metals removal by water using carbon nanotubes functionalized with different functional groups.

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