A REVIEW ON APPLICATIONS OF CARBON NANOTUBES AND THEIR MODIFICATIONS FOR DIFFERENT CONTAMINANTS REMOVAL

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ABSTRACT: Industrialization and technology developments have increased the release of hazardous pollutants into the environment. Though many treatment techniques have been developed, persistency and number of pollutants is on increase day by day. In recent years, application of carbon nanotubes in wastewater treatment has gained much interest due to its versatile properties. Carbon nanotubes and its composites have greatly enhanced adsorption efficiency for individual and mixed pollutants removal. In current article, we have summarized the treatment property of carbon nanotubes towards different organic and inorganic pollutants with emphasis on enhancement of treatment efficiency by different surface modifications and nano-composite preparations. This paper enlightens the pathway towards development of more advanced materials for the treatment of variant mixed pollutants.

KEYWORDS: wastewater; carbon nanotubes; surface modification; nano-composites; mixed pollutants

I. INTRODUCTION

As the world is heading towards luxury and comfort through development in technology and industrialization, safety and cleanliness of the environment is being neglected. Though focus on treatment and safeguard of environment has begun, it stands negligible in comparison to destruction of the environment on the other side. Development in the economic demand of the increasing population has polluted every sector of environment [1]. These problems have to be addressed sooner to escape environmental disasters which may substantially eradicate life on earth.

The basic problem today many countries face is availability of clean drinking water [2,3]. Industries generate large amount of organic and inorganic waste, which mixes with the environmental bodies leading to increase in pollutants. There has been increasing concern and more stringent regulation standards pertaining to the discharge and removal of organic and inorganic matter like dyes, heavy metals, due to their toxicity and detriment to living species including humans [4,5]. Research on treatment of water has begun decades back, but with an increase in number of emerging pollutants, conventional methods tend to be non-effective. Thus, an urgent up-gradation and addition of new treatment materials and techniques are required to the available techniques [6].

Carbon nanotubes (CNT's) are one such material belonging to carbon family has been in focus of research. Among different materials like zeolite, silica, carbon (carbon nanotubes, graphene and activated carbon), carbon nanotubes has been of greater interest, due to its distinctive tubular structure, higher mechanical strength, larger specific area and wider electric properties [7]. The overall adsorption capacity of CNT's is higher than activated carbon (AC) due to the higher surface area that helps in interaction with the pollutants [8]. There uniqueness lies in the stronger bonding between the atoms and tubular structure, which can have extreme aspect ratios. Based on the structural variation, CNT's are classified into two types: Single wall carbon nanotubes (SWCNT) and multiwall carbon nanotubes (MWCNT). In SWCNT's a single tubular ring makes up the structure, whereas in MWCNT's there are multiple nested tubes with increasing diameter, held together by interatomic forces among them, providing larger surface area and higher thermal and chemical stability.

Iijima was the first person to discover CNT's in 1991. Multiwall Carbon nanotubes were the first observed CNT's with adjacent tube separation of ∼0.3nm and inner diameter of ∼1nm. In 1993, SWCNT's with smaller diameter were discovered by Iijima, Ichihashi and Bethune et al., independently. Later researchers have developed both structures with different sizes and diameters [9, 10].

Selection of carbon nanotubes for multiple application was due to its extraordinary physical, chemical, mechanical and electric properties [11-13]. In environmental applications, it has shown a wider positive application in treatment of variant pollutants. In the current article, we have reviewed the application of carbon nanotubes for the removal of organic and inorganic pollutant with an emphasizes on adsorption of pollutants with and without structural modifications.

II. CARBON NANOTUBES: ADSORPTIVE TREATMENT

Adsorption is a process of binding or adhesion of molecules on to the surface of a matrix. The nature of binding depends upon the type of bond formed between the two surfaces. In recent years, use of carbon nanotubes as adsorbents has gained much attention, holding uniqueness from others in carbon-adsorptive family. They provide well-defined uniform structure with large surface area and chemical inert surface for physical adsorption. Use of CNT's as adsorbents for organic pollutants and inorganic pollutants like metallic ions has been reported [14,15]. CNT's has different adsorption sites which together increases the site of adsorption: Internal surface of tube, interstitial spaces between the tubes, grooves (bonding location with neighboring tube) and external surface of the tube.

Adsorption of Hazardous Gases

CNT's are widely used in electronic applications as sensitive gas detector, which established a new platform for investigation of CNT's in gas detection and storage. Adsorption of gases can occur on the all inner and outer sites of CNT's. Reports have also proved that adsorption occurs in the pores or on surfaces formed due to aggregation of nanotubes [16-19]. Successful investigations on adsorption of gases were carried out to locate the site and pattern of adsorption. Rols et al. studied the structure of argon gas adsorption on various adsorption sites of SWCNT's bundles using thermodynamics and neutron-diffraction measurements combined with molecular dynamics simulation to determine the structure. Results demonstrated that adsorption proceeded first on inner walls of individual nanotubes and formed one-dimensional Ar chains in the grooves at the outer surfaces of the bundles, followed by adsorption on the axial sites and quasi-hexagonal monolayer on the outer surface of the CNT's [20].

Further, a new possible adsorption site was discovered at the entrance of the channel in a bundle of closed CNT's, which hindered the adsorption process. Theoretical and experimental data suggested that external grooves has quick adsorption with highest adsorption energy (capacity to adsorb) compared to other sites. Experiment conducted upon adsorption of Xenon and Krypton showed that grooves exhibited higher adsorption energy -218meV and -175meV respectively. Whereas in case of methane gas, internal adsorption sites showed higher adsorption energy of 8.44kcal mol^{-1}` and groove site showed 5.8kcal mol^{-1} [17, 21-24]. CNT's can be used for adsorption and storage of atmospheric carbon dioxide (CO_2), a major causative agent for global warming. The level of CO_2 has increased dramatically in the last decade and expected to increase further [25]. Researchers started designing and investigating different novel materials to address the increasing CO_2 levels by possible treatment or capture and storage of emitted CO_2 from industries [26, 27]. Further research indicated that carbon capture and storage is the sustainable technique to face the challenge of increasing CO_2 concentration until the full-fledged development and use of renewable energy [28]. Theoretical investigation showed that CO_2 forms stronger interaction with Boron carbon nanotubes compared to hydrogen, nitrogen and methane. It also concludes that Boron carbon nanotubes could serve as a promising material for CO_2 capture and storage and could further enhance the ability by introduction of negative charges [29]. These studies indicate that, CNT's can be used as a sustainable matrix for capture and storage of variant hazardous gases.

2.2 Adsorption of Organic Pollutants

Carbon nanotubes have an efficient adsorption property towards organic pollutant due to its porous membrane with larger surface area and higher binding affinity. Use of CNT's as adsorbents has demonstrated satisfying results compared to other carbon materials such as carbon molecular sieves, activated carbon and bonded silica (C_{18}) [30-32]. CNT's have demonstrated excellent adsorption properties towards various organic pollutants, such as dye, phenols, trichloromethane, benzene, polycyclic aromatic hydrocarbons and dioxins [33-36]. Yao et al. studied the adsorption kinetics of methyl orange from aqueous solution and found to be following pseudo second-order reaction kinetics. Calculated change in Enthalpy (ΔH^0) and Gibbs free energy (ΔG^0) were 19.39kJ/mol and 0.1015kJ/mol respectively, which indicates reaction was endothermic and spontaneous in nature [37]. Similarly adsorption of basic Yellow 28 dye on to MWCNT's-carbon ceramic composite (CCC) followed Freundlich isotherm model with endothermic and spontaneous reaction, exhibiting MWCNT's-CCC as promising adsorbent for dye removal [33]. Molecular dynamics simulation studies on adsorption of benzene, alkylated benzene and alkylated naphthalenes by CNT's indicated them to be suitable material for selective adsorption and shape-selective separation of aromatic molecules with respect to different sizes and different shapes [38].

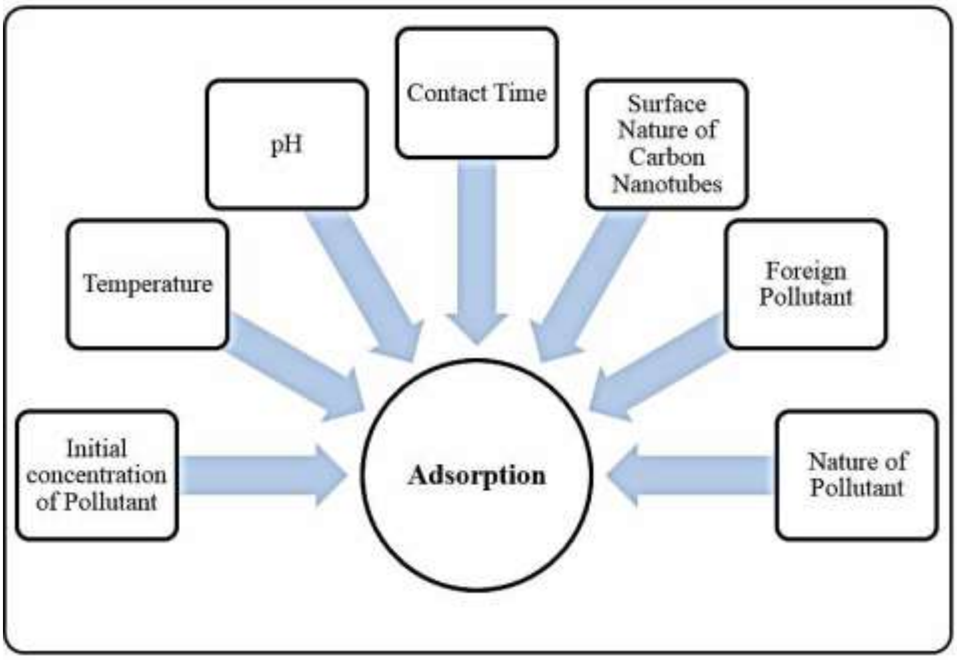
Adsorption mechanism of organic pollutants is unpredictable, depending upon the nature of pollutants (polar or non-polar). The interaction can be due to the hydrogen bonding, electrostatic or hydrophobic interaction and dominant bonding type depends upon the nature of the pollutant [39]. Different factors that affects the adsorption process also has tooptimized to achieve maximum removal. Fig. 1 displays predominant factors that affect the adsorption process. All parameters plays vital role based upon the nature and conditions of adsorbate and adsorbent. Thus, CNT's has shown wider application in the adsorptive treatment of organic pollutants and could be further investigated for enhanced removal. Researchers have developed novel techniques to enhance the efficiency of overall adsorption by surface modification or composite preparation, which has been discussed further.

2.3. Adsorption of Heavy metals:

Heavy metal is one of the predominant pollutant present in waste water and its removal essential in treatment process. The process of metal ions binding onto CNT's is attributed to electrostatic attraction, precipitation and chemical interaction between the ions and the surface functional groups. Among these, chemical interaction is the predominant adsorption mechanism [40-42]. Compared to other carbon adsorbent materials, CNT's has been reported for having greater potential in removing lead, cadmium, zinc, nickel, copper [43-48]. Reports also present the role of functional groups in the adsorption of Pb is important for efficient adsorption [49].

Other than nature of adsorbent, few other parameters also affect the process (Fig1) and mostly pH of the adsorbate solution plays a vital role in adsorption process [50]. Thus, CNT's displays adsorption towards metal ions and additional introduction of functional chargers and composite enhances the treatment efficacy.

Fig. 1: Illustrates various factors that affect the adsorption of Organic and Inorganic pollutants onto CNT's



III. SURFACE MODIFICATION OF CARBON NANOTUBES

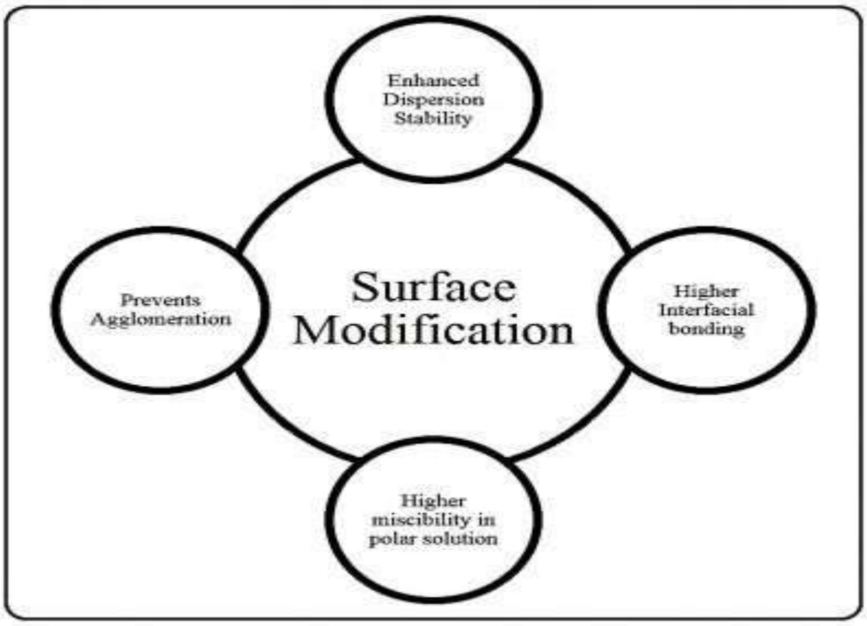
Surface modification is addition of functional group/metal oxide of interest by either mechanical or chemical method such as amine group, chelating agents and other functional groups as shown in Table1, based on the final target application. The modifications largely prevent bundling or agglomeration of CNT's, which could enhance dispersion stability and miscibility in the solution, and improve interfacial bonding with the matrices through stronger chemical or physical interaction. Fig 2 illustrates advantages of surface modification on CNT's. Dispersion stability is a major problem due to the inherent building or entangling nature of CNT's [51, 52]. The interfacial interaction among the CNT's and matrices are weaker which attempts its dissociation from the matrices [53-55]. Modification techniques are chosen based on the target application: mechanical or chemical method.

3.1 Mechanical modification:

Mechanical modification is a technique of applying external pressure on to the particle to disperse it in the solution. Low dispersion property of CNT's is targeted by an external force, which may involve exposure to reactant gases or dispersing agents. Resultant particle is easily dispersible with modified surface functional groups. Ball milling, ultra- sonication and mechanical stirring is the most predominantly used technique [56, 57]. Surfactant is added to enhance the dispersion ability and change the adsorbent surface nature to cationic or anionic [58].

In Ball milling method, the high-energy balls hits the surface of the CNT's creating localized energy states [59]. Combination of ball milling with exposure to reactant gases, ultra-sonication and mechanical stirring on functionalized CNT's with surfactant treatment are also reported [60, 61]. Ultra-sonication and mechanical stirring is a method of external pressure application onto the CNT's for better dispersion in solution. The dispersion rate depends upon the energy applied and the surface nature of CNT's, which is enhanced by the effect of surface modifications [62]. Amine functionalized and composites with non-modified CNT's showed better dispersion, whereas hydroxylated showed poor dispersion [61]. Surfactants rises the adsorption by forming hydrophilic region across CNT's and thus increases the contact angle with metal ions. It also tends CNT's to attract charge specific metallic ions. Anionic surfactant favoring cationic metals and cationic surfactants favoring anionic metal adsorption [63].

Fig. 2: Major advantages of surface modification on CNT's



3.2 Chemical Modification

Chemical modification is a process of addition of molecule, chelating agent or any other functional group over the CNT's surface (Table1 and Fig3) to enhance the interaction and stability of the surface with the pollutants [64]. Modification is usually carried with the functional group containing lone pair electron and through sharing of electron forming an efficient bond [65]. Treatment by chelating agents bonded upon CNT's was tested but with the growing need of advanced adsorbent material, researchers developed methods of functional group addition on to the surface of CNT's. Among all the possible functional groups (Fig 3), addition of oxide and amine group gained higher interest due to many advantages.

3.2.1 Addition of chelating agent:

Chelating agent is a chemical molecule, which aids in formation of bond with toxic metallic ions and thus favors the detoxification. Chelating agents are added onto the surface of CNT's with Vander Waals forces and ionic interaction between the hydrogen bonding. Other than adsorption property, they are also used in determination of metallic ions. Table 3 enlists examples tested for adsorption and determination of metallic ions. The major disadvantages in the usage of chelating agent, it often leaks affecting the reusability [65]. Further to enhance the reusability and develop a material for treatment of mixed pollutant both organic and inorganic (in case of chelating agents, it is metal-ion specific) modification by addition of chemical molecule is widely adopted.

Table1: List of various chelating agents and their application in towards treatment of metallic ions

Chelating agent	Metallic Ions	References
5-(4′-dimethylaminobenzyliden)-rhodanine (DMABRH)	Au(III)	[66]
N,*N*′-bis(2-hydroxybenzylidene)-2,2′(aminophenylthio)ethane (NBHAE)	Mn(II), Au(II)	[67]
di-(2-ethyl hexyl phosphoric acid) + tri-n-octyl phosphine oxide (D2EHPA+TOPO)	Zn(II), Ni(II), Cu(II)	[68]
1-(2-pyridylazo)-2-naphthol (PAN)	Co(II), Zn(II), Pb(II), Cd(II), Ni(II)	[69, 70]

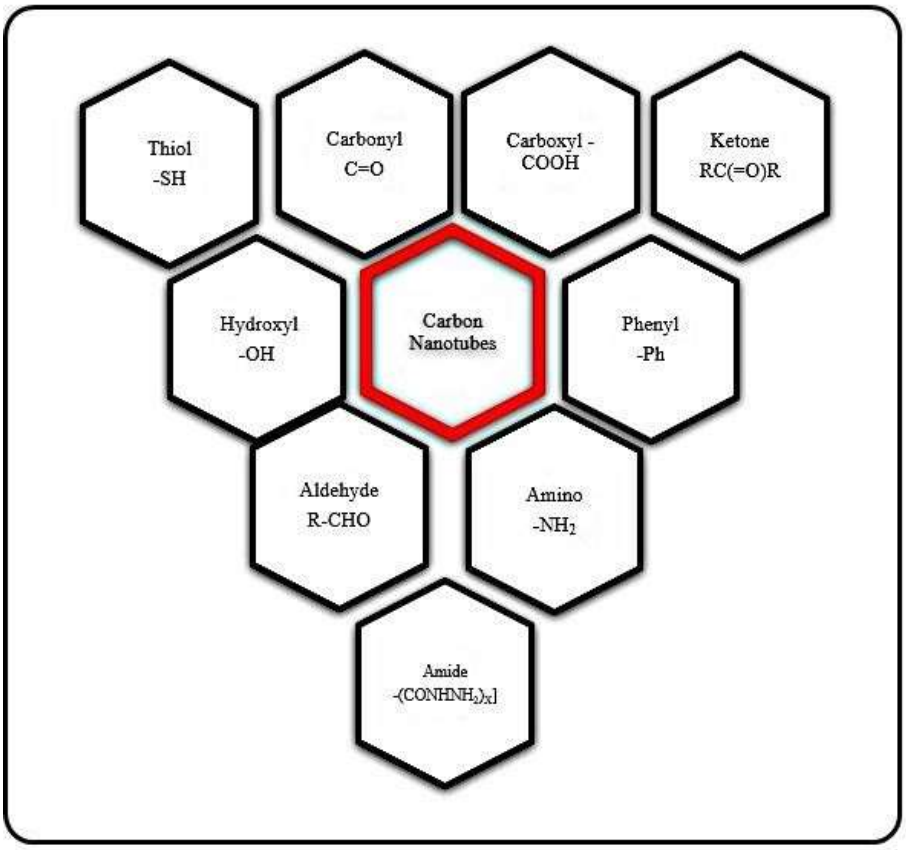
3.2.2. Oxidation

Carbon nanotube modification by oxidation involves addition of oxygen groups like carboxylic, carbonyl, hydroxyl, nitro and other groups (Fig 3) onto the CNT's. Addition of desired modifier has to performed under mixing condition as it supports in opening of tube caps, formation of holes, addition of oxygen containing functional group, exfoliation of CNT's and easy dispensability [65]. Use of oxidized CNT's in biological and environmental applications with satisfying results has been reported [71-74]. Similarly, Multi- oxidation of CNT's by intercalating agent (H_2So_4) and oxidants ($KMnO_4$ and $NaNO_3$) created porous layer and bonding of large amount of oxygen containing groups on CNT's that enhanced dispersion in water without surfactant addition [75]. The carbon nanotube's surface becomes more deprotonated and causes electrostatic interaction between metallic ions and oxidized CNT's [76]. Adsorption affinity of metallic ions towards oxidized MWCNT's at varying pH 7.0-9.0 showed that Cu(II) has greater affinity and Mn(II) has lowest affinity. The affinity of order is as follows: Cu(II) > Pb(II) > Zn(II) > Co(II) > Ni(II) > Cd(II) > Mn(II) [77].

3.2.3. Amination:

In this technique, amine group is added on to the surface of material by a donor chemical or biological source. Major advantage of addition of amine group is to create stronger interaction between CNT's and surface polymers. Reports have showed that amine treated CNT's had enhanced interfacial bonding with the plasma resin [78]. Combined effect of oxidation and amination upon MWCNT's interaction with epoxy resin showed overall enhancement of dispersion and minimal agglomeration, with stronger interaction towards resin [79].

Fig. 3: Illustrates various functional groups which can be linked on to the surface of Carbon Nanotubes



IV. CARBON NANOTUBE COMPOSITE

The term composite defines the material, which is designed with combination of different materials. Materials of similar properties or different properties can be combined to form a composite. The driving force towards the development of composite material was to achieve a single composite material, which can enhance the rate of reaction and employed for multiple environmental applications. Based on specific application such as organic pollutant degradation, a catalyst is added to the composite, whereas for treatment of inorganic pollutants like metallicions composite with magnetic oxides or metal oxides along with chemical functional groups are used as composite [80]. Composite materials have unique adsorption and condensation property, which facilitates degradation of organic compounds. Literature reports that it exhibits superior properties under different environmental stimuli (pH, temperature and mechanical or bio/chemical stress) [81, 82]. In recent years, textiles combined with nanomaterials have been in use for potential applications in wearable displays, power storage and bio monitoring. The CNT-coated cotton fabrics reported for greater hydrophobicity with improved physical property and enhanced conductivity [18, 83, 84]. Thus exhibiting a possible CNT composite with versatile materials, paving way for its multidirectional usage in environmental applications.

4.1 Composite preparation methods:

Composite is a combination of two or more materials held together by strong bonding by physical interaction or chemical bonding. There are different methods in use for preparation of composites. Fig 4 displays commonly used methods for preparation of composite for catalysis and adsorption. Among which sol-gel and co-precipitation method is most widely followed for its proven reliability and stability. Many reports on successful use of these methods in composite preparation over other methods has been reported [33, 85-87].

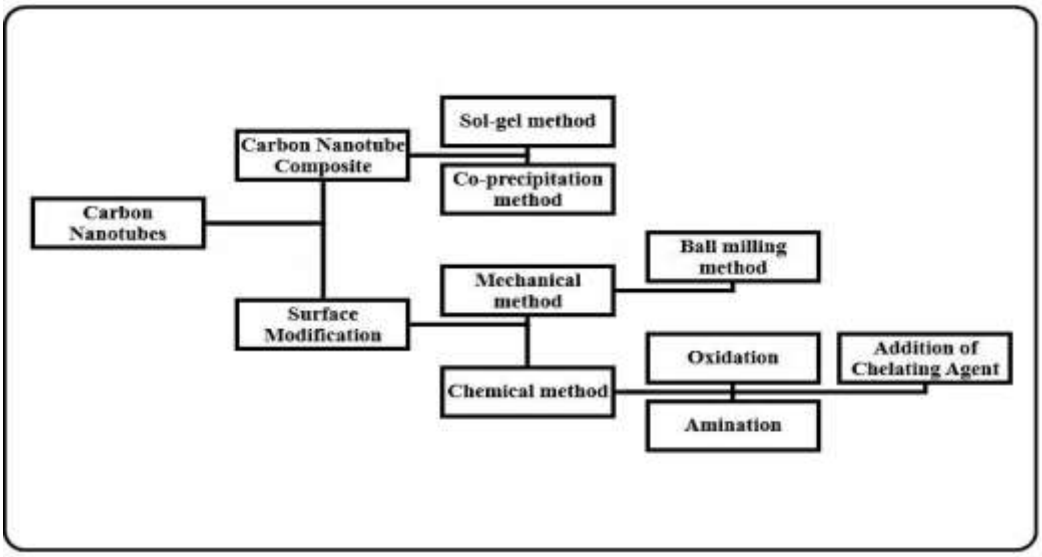
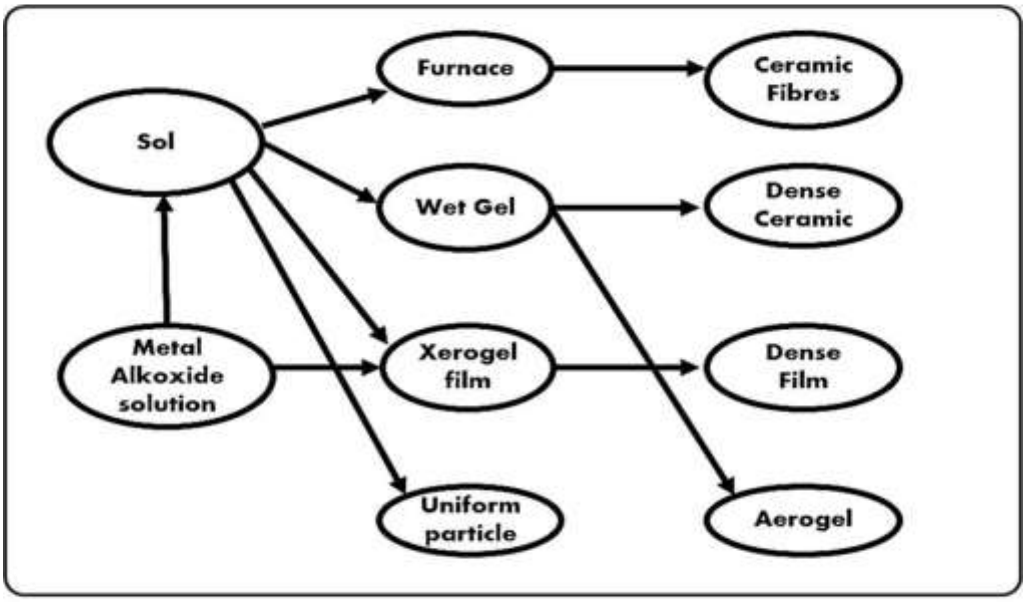


Fig. 4: Outlay of commonly used reliable techniques for surface modification and carbon nanotube composite preparation by various mechanical and chemical methods

4.1.1. Sol-gel method:

Sol-gel method involves metal alkoxides or metal chlorides for preparation of solvated metal precursor (*sol*) as displayed in Fig 5. Precursor (*sol*) is hydrolyzed and polycondensed to form a colloid (*gel*). Reaction is continued until a solid mass is obtained and then further subjected to calcination at 800^{0}C [88]. Fig 5 also displays other possible routes for obtaining dense ceramic, dense film and aerogel.

Fig. 5: Different routes in Sol-gel method of composite preparation to achieve various physical structures of composites



Use of CNT's for preparation of composite by sol-gel technique has gained much popularity due to its multiple advantages. Textile based composite with special properties such as anti-wrinkle finishing, dye fastness, UV-radiation protection, incorporation of antimicrobial function and formation of organic-inorganic coating at room temperature are reported in many findings [89, 90]. Esfandiyari et al. reported that MWCNT's – carbon ceramic composite had a special surface area of (SSA) 20.7m^2/g and pore volume (PV) 4.75 cm^3/g much higher than the only carbon ceramic composite (SSA =13.71 m^2/g and PV=3.15 m^3/g). It could be attributed to the fixation of MWCNT's upon the surface of carbon ceramic composite by Sol-gel method [33]. MWCNT's coated upon hydrophobic conductive cotton fabrics using sol-gel method showed water contact angle of 146^0 and surface resistance 40kΩ cm^{-2} [91]. Thus, sol-gel method exhibited usage in wider applications and a promising linker of CNT's with other metals.

Co-precipitation method:

Co-precipitation methods involves formation of desired composite, with simultaneous doping of material on to the surface of adsorbent material, followed by thermal decomposition. Optimization on particle size with doped molecules is also reported [92]. As CNT's have higher sorption capacity and high surface area, it is one of the best surface materials chosen for composite formation [48]. Table 2 displays few of the novel composites designed for environmental applications. Composites remain stable for longer period up to 200 cycles [93].

Table 2: List of various CNT composites used in Treatment of various pollutants

Composite	Application	Reference
Ceria nanoparticles and Carbon nanotube	Adsorption for Cr(VI)	[93]
Manganese oxide and Carbon Nanotube	Adsorbent for Pb(II) and Cd(II)	[48]
CNT - Carbon ceramic composite	Adsorption of Cationic dye	[33]

Carbon Nanotube and Xerogel as support for Platinum catalyst	Treatment of Aqueous aniline solution by catalytic wet air oxidation	[95]
Nanocomposite	Adsorption of Ni(II),	[93]

CNT's composite formed with catalyst are also employed for organic pollutant breakdown. The catalyst present in composite helps in catalysis of organic pollutant, simultaneously CNT's surface helps in adsorption of pollutant, enhancing the overall removal efficiency. Platinum catalyst supported upon CNT's with the support of Xerogel (Table2) was tested for the treatment

of aqueous aniline solution which showed significant activity [95]. For efficient removal of metallic pollutants, composite with magnetic oxides were developed. Magnetic oxides are doped upon CNT's to form composite for metal removal application (Table 2), which do not require packing into column or on a stationery surface. These magnetic oxides composites exhibits magnetic attraction property towards metals in mixed pollutants [96]. Composites suspended into the solution with metallic pollutant can be recovered using an external magnetic support, indicating metal oxide composite to have major applications in the field of environment and could further be enhanced or altered as per target application.

V. CONCLUSION

Carbon Nanotubes stands novel with its wider applications in environmental treatment. Use of CNT's in pollutant treatment process as adsorbent has shown significantly satisfactorily results with the presence of its unique properties which caters the need of higher adsorption. It has excellent rate of adsorption towards toxic gases, organic and inorganic pollutants. Surface modification (oxidation and amination) has increased the efficiency of binding towards the pollutants. Use of CNT's with other adsorptive material as a composite has completely upgraded the properties of CNT's, with increased adsorptive and catalytic property. Surface modification and composite preparation of CNT's needs more better understanding towards physical and chemical interaction among the materials, regeneration of materials, increasing the stability of the composite. Adsorption of Gas requires much more intense study towards the adsorption pattern of various gases, there binding affinity and hold time for longer storage to face the challenges of increasing CO_2 concentration. CNT's could prove to be the futuristic weapon against all the environmental challenges.

VI. REFERENCES

[1] Yuwono, E., Jennerjahn, T. C., Nordhaus, I., Riyanto, E. A., Sastranegara, M. H., & Pribadi, R. (2007). Ecological status of Segara Anakan, Indonesia: a mangrove-fringed lagoon affected by human activities. *Asian Journal of Water, Environment and Pollution*, *4*(1), 61-70.
[2] Gleick, P. H. (1998). The human right to water. *Water policy*, *1*(5), 487-503.
[3] Gadgil, A. (1998). Drinking water in developing countries. *Annual review of energy and the environment*, *23*(1), 253-286.
[4] Li, Y. H., Wang, S., Luan, Z., Ding, J., Xu, C., & Wu, D. (2003). Adsorption of cadmium (II) from aqueous solution by surface oxidized carbon nanotubes. *Carbon*, *41*(5), 1057-1062.
[5] Lu, C., & Su, F. (2007). Adsorption of natural organic matter by carbon nanotubes. *Separation and Purification Technology*, *58*(1), 113-121.
[6] Sun, F., Chen, J., Tong, Q., & Zeng, S. (2008). Managing the performance risk of conventional waterworks in compliance with the natural organic matter regulation. Water research, 42(1-2), 229-237.

[7] Natarajan, T. S., Lee, J. Y., Bajaj, H. C., Jo, W. K., & Tayade, R. J. (2017). Synthesis of multiwall carbon nanotubes/TiO2 nanotube composites with enhanced photocatalytic decomposition efficiency. Catalysis Today, 282, 13-23.
[8] Long, R. Q., & Yang, R. T. (2001). Carbon nanotubes as superior sorbent for dioxin removal. Journal of the American Chemical Society, 123(9), 2058-2059.
[9] Iijima, S. (1991). Helical microtubules of graphitic carbon. nature, 354(6348), 56-58.
[10] Iijima, S., & Ichihashi, T. (1993). Single-shell carbon nanotubes of 1-nm diameter. nature, 363(6430), 603-605.
[11] Ajayan, P. M. (1999). Nanotubes from carbon. Chemical reviews, 99(7), 1787-1800.
[12] Dai, L., & Mau, A. W. (2001). Controlled synthesis and modification of carbon nanotubes and C60: carbon nanostructures for advanced polymeric composite materials. Advanced Materials, 13(12-13), 899-913.
[13] Terrones, M. (2003). Science and technology of the twenty-first century: synthesis, properties, and applications of carbon nanotubes. Annual review of materials research, 33(1), 419-501.
[14] Carrales-Alvarado, D. H., Leyva-Ramos, R., Rodríguez-Ramos, I., Mendoza-Mendoza, E., & Moral-Rodríguez, A. E. (2020). Adsorption capacity of different types of carbon nanotubes towards metronidazole and dimetridazole antibiotics from aqueous solutions: effect of morphology and surface chemistry. Environmental Science and Pollution Research, 1-15.
[15] Alguacil, F. J., & López, F. A. (2020). On the Active Adsorption of Chromium (III) from Alkaline Solutions Using Multiwalled Carbon Nanotubes. Applied Sciences, 10(1), 36.
[16] Agnihotri, S., Mota, J. P., Rostam-Abadi, M., & Rood, M. J. (2005). Structural characterization of single-walled carbon nanotube bundles by experiment and molecular simulation. Langmuir, 21(3), 896-904.
[17] Calbi, M. M., & Riccardo, J. L. (2005). Energy barriers at the ends of carbon nanotube bundles: effects on interstitial adsorption kinetics. Physical review letters, 94(24), 246103.
[18] Kong, J., Franklin, N. R., Zhou, C., Chapline, M. G., Peng, S., Cho, K., & Dai, H. (2000). Nanotube molecular wires as chemical sensors. science, 287(5453), 622-625.
[19] Novak, J. P., Snow, E. S., Houser, E. J., Park, D., Stepnowski, J. L., & McGill, R. A. (2003). Nerve agent detection using networks of single-walled carbon nanotubes. Applied physics letters, 83(19), 4026-4028.
[20] Rols, S., Johnson, M. R., Zeppenfeld, P., Bienfait, M., Vilches, O. E., & Schneble, J. (2005). Argon adsorption in open-ended single-wall carbon nanotubes. Physical Review B, 71(15), 155411.
[21] Agrawal, B. K., Agrawal, S., Singh, S., & Srivastava, R. (2006). Ab initio study of curvature effects on the physical properties of CH4-doped nanotubes and nanoropes. Journal of Physics: Condensed Matter, 18(19), 4649.
[22] Denis, P. A. (2008). Methane adsorption inside and outside pristine and N-doped single wall carbon nanotubes. Chemical Physics, 353(1-3), 79-86.
[23] Rawat, D. S., Calbi, M. M., & Migone, A. D. (2007). Equilibration time: kinetics of gas adsorption on closed-and open-ended single-walled carbon nanotubes. The Journal of Physical Chemistry C, 111(35), 12980-12986.
[24] Stan, G., Bojan, M. J., Curtarolo, S., Gatica, S. M., & Cole, M. W. (2000). Uptake of gases in bundles of carbon nanotubes. Physical Review B, 62(3), 2173.
[25] Keith, D. W. (2009). Why capture CO2 from the atmosphere?. Science, 325(5948), 1654-1655.
[26] Bae, Y. S., & Snurr, R. Q. (2011). Development and evaluation of porous materials for carbon dioxide separation and capture. Angewandte Chemie International Edition, 50(49), 11586-11596.
[27] D'Alessandro, D. M., Smit, B., & Long, J. R. (2010). Carbon dioxide capture: prospects for new materials. Angewandte Chemie International Edition, 49(35), 6058-6082.
[28] Haszeldine, R. S. (2009). Carbon capture and storage: how green can black be?. Science, 325(5948), 1647-1652.
[29] Sun, Q., Wang, M., Li, Z., Ma, Y., & Du, A. (2013). CO2 capture and gas separation on boron carbon nanotubes. Chemical Physics Letters, 575, 59-66.
[30] Lu, C., & Su, F. (2007). Adsorption of natural organic matter by carbon nanotubes. Separation and Purification Technology, 58(1), 113-121.
[31] Vinu, A., Hossain, K. Z., Kumar, G. S., & Ariga, K. (2006). Adsorption of L-histidine over mesoporous carbon molecular sieves. Carbon, 44(3), 530-536.
[32] Shih, Y. H., & Gschwend, P. M. (2009). Evaluating activated carbon− water sorption coefficients of organic compounds using a linear solvation energy relationship approach and sorbate chemical activities. Environmental science & technology, 43(3), 851-857.
[33] Esfandiyari, T., Nasirizadeh, N., Ehrampoosh, M. H., & Tabatabaee, M. (2017). Characterization and absorption studies of cationic dye on multi walled carbon nanotube–carbon ceramic composite. Journal of Industrial and Engineering Chemistry, 46, 35-43.
[34] Long, R. Q., & Yang, R. T. (2001). Carbon nanotubes as superior sorbent for dioxin removal. Journal of the American Chemical Society, 123(9), 2058-2059.

[35] Shen, X. E., Shan, X. Q., Dong, D. M., Hua, X. Y., & Owens, G. (2009). Kinetics and thermodynamics of sorption of nitroaromatic compounds to as-grown and oxidized multiwalled carbon nanotubes. Journal of colloid and interface science, 330(1), 1-8.
[36] Tournus, F., & Charlier, J. C. (2005). Ab initio study of benzene adsorption on carbon nanotubes. Physical Review B, 71(16), 165421.
[37] Yao, Y., Bing, H., Feifei, X., & Xiaofeng, C. (2011). Equilibrium and kinetic studies of methyl orange adsorption on multiwalled carbon nanotubes. Chemical Engineering Journal, 170(1), 82-89.
[38] Takaba, H., Katagiri, M., Kubo, M., Vetrivel, R., & Miyamoto, A. (1995). Molecular design of carbon nanotubes for the separation of molecules. Microporous materials, 3(4-5), 449-455.
[39] Pan, B., & Xing, B. (2008). Adsorption mechanisms of organic chemicals on carbon nanotubes. Environmental science & technology, 42(24), 9005-9013.
[40] Lu, C., & Chiu, H. (2006). Adsorption of zinc (II) from water with purified carbon nanotubes. Chemical Engineering Science, 61(4), 1138-1145.
[41] Lu, C., Chiu, H., & Liu, C. (2006). Removal of zinc (II) from aqueous solution by purified carbon nanotubes: kinetics and equilibrium studies. Industrial & engineering chemistry research, 45(8), 2850-2855.
[42] Yim, W. L., & Liu, Z. F. (2004). A reexamination of the chemisorption and desorption of ozone on the exterior of a (5, 5) single-walled carbon nanotube. Chemical physics letters, 398(4-6), 297-303.
[43] Chen, C., & Wang, X. (2006). Adsorption of Ni (II) from aqueous solution using oxidized multiwall carbon nanotubes. Industrial & Engineering Chemistry Research, 45(26), 9144-9149.
[44] Gao, Z., Bandosz, T. J., Zhao, Z., Han, M., Liang, C., & Qiu, J. (2008). Investigation of the role of surface chemistry and accessibility of cadmium adsorption sites on open-surface carbonaceous materials. Langmuir, 24(20), 11701-11710.
[45] Kandah, M. I., & Meunier, J. L. (2007). Removal of nickel ions from water by multi-walled carbon nanotubes. Journal of hazardous materials, 146(1-2), 283-288.
[46] Li, Y. H., Zhu, Y., Zhao, Y., Wu, D., & Luan, Z. (2006). Different morphologies of carbon nanotubes effect on the lead removal from aqueous solution. Diamond and Related Materials, 15(1), 90-94.
[47] Muyibi, S. A., Ambali, A. R., & Eissa, G. S. (2008). Development-induced water pollution in Malaysia: policy implications from an econometric analysis. Water Policy, 10(2), 193-206.
[48] Wang, S. G., Gong, W. X., Liu, X. W., Yao, Y. W., Gao, B. Y., & Yue, Q. Y. (2007). Removal of lead (II) from aqueous solution by adsorption onto manganese oxide-coated carbon nanotubes. Separation and Purification Technology, 58(1), 17-23.
[49] Wang, H., Zhou, A., Peng, F., Yu, H., & Yang, J. (2007). Mechanism study on adsorption of acidified multiwalled carbon nanotubes to Pb (II). Journal of Colloid and Interface Science, 316(2), 277-283.
[50] Li, Y. H., Luan, Z., Xiao, X., Zhou, X., Xu, C., Wu, D., & Wei, B. (2003). Removal of Cu2+ ions from aqueous solutions by carbon nanotubes. Adsorption Science & Technology, 21(5), 475-485.
[51] Hammel, E., Tang, X., Trampert, M., Schmitt, T., Mauthner, K., Eder, A., & Pötschke, P. (2004). Carbon nanofibers for composite applications. Carbon, 42(5-6), 1153-1158.
[52] Song, Y. S., & Youn, J. R. (2005). Influence of dispersion states of carbon nanotubes on physical properties of epoxy nanocomposites. Carbon, 43(7), 1378-1385.
[53] Gong, X., Liu, J., Baskaran, S., Voise, R. D., & Young, J. S. (2000). Surfactant-assisted processing of carbon nanotube/polymer composites. Chemistry of materials, 12(4), 1049-1052.
[54] Liu, T., Phang, I. Y., Shen, L., Chow, S. Y., & Zhang, W. D. (2004). Morphology and mechanical properties of multiwalled carbon nanotubes reinforced nylon-6 composites. Macromolecules, 37(19), 7214-7222.
[55] Xie, X. L., Mai, Y. W., & Zhou, X. P. (2005). Dispersion and alignment of carbon nanotubes in polymer matrix: a review. Materials science and engineering: R: Reports, 49(4), 89-112.
[56] Pragatheeswaran, A., Ravi, R., & Bakshi, S. R. (2019). Microstructural and morphological changes during ball milling of Copper-Silver-Graphite flake mixtures. Advanced Powder Technology, 30(11), 2759-2767.
[57] Hanizam, H., Salleh, M. S., Omar, M. Z., & Sulong, A. B. (2019). Optimisation of mechanical stir casting parameters for fabrication of carbon nanotubes–aluminium alloy composite through Taguchi method. Journal of Materials Research and Technology, 8(2), 2223-2231.
[58] Sumdani, M. G., Islam, M. R., Yahaya, A. N. A., & Isa, N. (2019). Acid-Based Surfactant-Aided Dispersion of Multi-Walled Carbon Nanotubes in Epoxy-Based Nanocomposites. Polymer Engineering & Science, 59(s2), E80-E87.
[59] Kónya, Z., Vesselenyi, I., Niesz, K., Kukovecz, A., Demortier, A., Fonseca, A., ... & Osváth, Z. (2002). Large scale production of short functionalized carbon nanotubes. Chemical Physics Letters, 360(5-6), 429-435.
[60] Kim, S. W., Kim, T., Kim, Y. S., Choi, H. S., Lim, H. J., Yang, S. J., & Park, C. R. (2012). Surface modifications for the effective dispersion of carbon nanotubes in solvents and polymers. Carbon, 50(1), 3-33.

[61] Wladyka-Przybylak, M., Wesolek, D., Gieparda, W., Boczkowska, A., & Ciecierska, E. (2011). Functionalization effect on physico-mechanical properties of multi-walled carbon nanotubes/epoxy composites. Polymers for Advanced Technologies, 22(1), 48-59.

[62] Wang, Y., Wang, J., Morimoto, S., Melvin, G. J. H., Zhao, R., Hashimoto, Y., & Terrones, M. (2019). Nitrogen-doped porous carbon monoliths from molecular-level dispersion of carbon nanotubes into polyacrylonitrile (PAN) and the effect of carbonization process for supercapacitors. Carbon, 143, 776-785.

[63] Li, J., Chen, S., Sheng, G., Hu, J., Tan, X., & Wang, X. (2011). Effect of surfactants on Pb (II) adsorption from aqueous solutions using oxidized multiwall carbon nanotubes. Chemical Engineering Journal, 166(2), 551-558.

[64] Rahimi, K., Riahi, S., Abbasi, M., & Fakhroueian, Z. (2019). Modification of multi-walled carbon nanotubes by 1, 3-diaminopropane to increase CO2 adsorption capacity. Journal of environmental management, 242, 81-89.

[65] Sitko, R., Zawisza, B., & Malicka, E. (2012). Modification of carbon nanotubes for preconcentration, separation and determination of trace-metal ions. TrAC Trends in Analytical Chemistry, 37, 22-31. Afzali, D., Ghaseminezhad, S., & Taher, M. A. (2010). Separation and preconcentration of trace amounts of gold (III) ions using modified multiwalled carbon nanotube sorbent prior to flame atomic absorption spectrometry determination. Journal of AOAC International, 93(4), 1287-1292.

[66] Afzali, D., Ghaseminezhad, S., & Taher, M. A. (2010). Separation and preconcentration of trace amounts of gold (III) ions using modified multiwalled carbon nanotube sorbent prior to flame atomic absorption spectrometry determination. Journal of AOAC International, 93(4), 1287-1292.

[67] Shamspur, T., & Mostafavi, A. (2009). Application of modified multiwalled carbon nanotubes as a sorbent for simultaneous separation and preconcentration trace amounts of Au (III) and Mn (II). Journal of Hazardous Materials, 168(2-3), 1548-1553.

[68] Vellaichamy, S., & Palanivelu, K. (2011). Preconcentration and separation of copper, nickel and zinc in aqueous samples by flame atomic absorption spectrometry after column solid-phase extraction onto MWCNTs impregnated with D2EHPA-TOPO mixture. Journal of hazardous materials, 185(2-3), 1131-1139.

[69] Afzali, D., & Mostafavi, A. (2008). Potential of modified multiwalled carbon nanotubes with 1-(2-pyridylazo)-2-naphtol as a new solid sorbent for the preconcentration of trace amounts of cobalt (II) ion. Analytical Sciences, 24(9), 1135-1139.

[70] Tajik, S., & Taher, M, A. (2011). A new sorbent of modified MWCNTs for column preconcentration of ultra-trace amounts of zinc in biological and water samples. Desalination; 278(57-64). doi:10.1016/j.desal.2011.05.002

[71] Barbosa, A. F., Segatelli, M. G., Pereira, A. C., de Santana Santos, A., Kubota, L. T., Luccas, P. O., & Tarley, C. R. T. (2007). Solid-phase extraction system for Pb (II) ions enrichment based on multiwall carbon nanotubes coupled on-line to flame atomic absorption spectrometry. Talanta, 71(4), 1512-1519.

[72] Costa, H. H. V., de Fátima Lima, G., Nacano, L. R., & Tarley, C. R. T. (2011). Preconcentration/cleanup studies of tin from environmental water samples by oxidized multiwall carbon nanotubes packed column and its determination by ETAAS. Water, Air, & Soil Pollution, 217(1-4), 557-565.

[73] El-Sheikh, A. H., Al-Degs, Y. S., Al-As' ad, R. M., & Sweileh, J. A. (2011). Effect of oxidation and geometrical dimensions of carbon nanotubes on Hg (II) sorption and preconcentration from real waters. Desalination, 270(1-3), 214-220.

[74] Yuan, C. G., Zhang, Y., Wang, S., & Chang, A. (2011). Separation and preconcentration of palladium using modified multi-walled carbon nanotubes without chelating agent. Microchimica acta, 173(3-4), 361-367.

[75] Wang, N., Pandit, S., Ye, L., Edwards, M., Mokkapati, V. R. S. S., Murugesan, M., ... & Liu, J. (2017). Efficient surface modification of carbon nanotubes for fabricating high performance CNT based hybrid nanostructures. Carbon, 111, 402-410.

[76] Li, Y. H., Ding, J., Luan, Z., Di, Z., Zhu, Y., Xu, C., ... & Wei, B. (2003). Competitive adsorption of Pb2+, Cu2+ and Cd2+ ions from aqueous solutions by multiwalled carbon nanotubes. Carbon, 41(14), 2787-2792.

[77] Stafiej, A., & Pyrzynska, K. (2008). Solid phase extraction of metal ions using carbon nanotubes. Microchemical Journal, 89(1), 29-33.

[78] Kim, J. A., Seong, D. G., Kang, T. J., & Youn, J. R. (2006). Effects of surface modification on rheological and mechanical properties of CNT/epoxy composites. Carbon, 44(10), 1898-1905.

[79] Gojny, F. H., Nastalczyk, J., Roslaniec, Z., & Schulte, K. (2003). Surface modified multi-walled carbon nanotubes in CNT/epoxy-composites. Chemical physics letters, 370(5-6), 820-824.

[80] Fan, L., Zhou, A., Zhong, L., Zhang, Z., & Liu, Y. (2019). Selective and effective adsorption of Hg (II) from aqueous solution over wide pH range by thiol functionalized magnetic carbon nanotubes. Chemosphere, 226, 405-412.

[81] Baughman, R. H., Zakhidov, A. A., & De Heer, W. A. (2002). Carbon nanotubes--the route toward applications. science, 297(5582), 787-792.

[82] Park, S., & Jayaraman, S. (2003). Smart textiles: Wearable electronic systems. MRS bulletin, 28(8), 585-591.
[83] Lukowicz, P., Kirstein, T., & Tröster, G. (2004). Wearable systems for health care applications. Methods of information in medicine, 43(03), 232-238.
[84] Mahltig, B., & Textor, T. (2006). Combination of silica sol and dyes on textiles. Journal of sol-gel science and technology, 39(2), 111-118.
[85] Deng, J. H., Zhang, X. R., Zeng, G. M., Gong, J. L., Niu, Q. Y., & Liang, J. (2013). Simultaneous removal of Cd (II) and ionic dyes from aqueous solution using magnetic graphene oxide nanocomposite as an adsorbent. Chemical Engineering Journal, 226, 189-200.
[86] Huang, J., Zheng, Y., Luo, L., Feng, Y., Zhang, C., Wang, X., & Liu, X. (2016). Facile preparation of highly hydrophilic, recyclable high-performance polyimide adsorbents for the removal of heavy metal ions. Journal of hazardous materials, 306, 210-219.
[87] Jose, M., Kumari, M., Karunakaran, R., & Shukla, S. (2015). Methylene blue adsorption from aqueous solutions using undoped and silver-doped nanotubes of anatase-titania synthesized via modified hydrothermal method. Journal of Sol-Gel Science and Technology, 75(3), 541-550.
[88] Hench, L. L., & West, J. K. (1990). The sol-gel process. Chemical reviews, 90(1), 33-72.
[89] Alongi, J., Ciobanu, M., Tata, J., Carosio, F., & Malucelli, G. (2011). Thermal stability and flame retardancy of polyester, cotton, and relative blend textile fabrics subjected to sol–gel treatments. Journal of Applied Polymer Science, 119(4), 1961-1969.
[90] Abidi, N., Hequet, E., Tarimala, S., & Dai, L. L. (2007). Cotton fabric surface modification for improved UV radiation protection using sol–gel process. Journal of Applied Polymer Science, 104(1), 111-117.
[91] Nasirizadeh, N., Dehghani, M., & Yazdanshenas, M. E. (2015). Preparation of hydrophobic and conductive cotton fabrics using multi-wall carbon nanotubes by the sol–gel method. Journal of Sol-Gel Science and Technology, 73(1), 14-21.
[92] Cushing, B. L., Kolesnichenko, V. L., & O'Connor, C. J. (2004). Recent advances in the liquid-phase syntheses of inorganic nanoparticles. Chemical reviews, 104(9), 3893-3946.
[93] Amais, R. S., Ribeiro, J. S., Segatelli, M. G., Yoshida, I. V., Luccas, P. O., & Tarley, C. R. (2007). Assessment of nanocomposite alumina supported on multi-wall carbon nanotubes as sorbent for on-line nickel preconcentration in water samples. Separation and Purification Technology, 58(1), 122-128.
[94] Di, Z. C., Ding, J., Peng, X. J., Li, Y. H., Luan, Z. K., & Liang, J. (2006). Chromium adsorption by aligned carbon nanotubes supported ceria nanoparticles. Chemosphere, 62(5), 861-865.
[95] Gomes, H. T., Samant, P. V., Serp, P., Kalck, P., Figueiredo, J. L., & Faria, J. L. (2004). Carbon nanotubes and xerogels as supports of well-dispersed Pt catalysts for environmental applications. Applied Catalysis B: Environmental, 54(3), 175-182.
[96] Wang, X., Zhao, Z., Qu, J., Wang, Z., & Qiu, J. (2010). Fabrication and characterization of magnetic Fe3O4–CNT composites. Journal of Physics and Chemistry of Solids, 71(4), 673-676.