



## Review

# A review on adsorptive removal of oil pollutants (BTEX) from wastewater using carbon nanotubes



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## ABSTRACT

A progressive economic growth and proliferating global population caused adequate provision of clean water as a global issue. The systematic eradication of toxic pollutants from the environment has become a predominant matter from a biological and environmental perspective. Thus, adsorptive removal of hazardous components from wastewater is one of the most captivating strategies for purification technologies. Recently, carbon nanotubes (CNTs) have been reported to be very promising in the adsorption of various stable organic compounds due to their unique properties essential for further surface modification. In order to get the maximum removal of these pollutants, it is mandatory to understand the interaction mechanisms between the sorbent and sorbate. This review summarizes the recent literature on the adsorptive removal of BTEX from wastewater using CNTs. The impact of various factors (sorption sites of CNTs, physical properties of nanotubes, properties of background solution, and surface chemistry of CNTs) on the adsorption of BTEX over CNTs and the plausible interaction mechanisms such as hydrophobic interaction, electrostatic interaction, dispersive/repulsive interactions,  $\pi$ - $\pi$  interactions and hydrogen bonding are critically reviewed. The present review has sorted out numerous prevailing gaps in the available information whilst recognizing a number of encouraging avenues and approaches for the upcoming research thrust.

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## 1. Introduction

Water contamination is a crucial problem that is getting worse with the growing domestic and industrial activities. According to world health organization's report, 62% of the world's population will suffer from water scarcity by 2030 [1]. Moreover, most of the world's waste water (>80%) is discharged in water bodies without proper treatment whereas this figure goes to 95% for the developing countries [2]. This contamination not only affects the quality of water but also endangers marine life. Hence, highly efficient and cost effective technologies for wastewater treatment are urgently required.

This issue must be addressed critically because it directly influences the earth's ecosystem. More than 700 pollutants have been reported in the literature that affects the living organisms and must sustainably minimize the generation of pollutants. Among these pollutants, benzene, toluene, ethylbenzene and isomers of xylene (BTEX) are classified as hazardous pollutants which has a very low water solubility (201 ppm, 50 ppm, 111 ppm, 130 ppm, 106 ppm, 111 ppm for benzene, toluene, ethylbenzene, *o*-xylene, *m*-xylene, *p*-xylene respectively), acute toxicity and genotoxicity [3,4]. They are predominately produced by catalytic reforming, cracking and pyrolysis. Furthermore, the possible key sources of water contamination are accidental gasoline spills and service tanks leakage. Continuous exposure to these hazardous materials may affect the physical system, respiratory system and central nervous system [5,6], and hence it is mandatory to eliminate these mutagenic chemicals from the environment.

Many well established and developed methods namely, liquid extraction, extractive distillation, chemical clarification, membrane filtration, advanced oxidation, photocatalytic oxidation, ion exchange, bubble separation, adsorption, electro dialysis, phytoremediation, reverse osmosis, biofiltration and membrane technology have been employed to remediate the contaminated effluents [7–9]. The removal of these unwanted substances using standard protocols is not economically viable (10\$–450\$ per million litres) as they do not result in appropriate uptake. Nevertheless, novel technologies are continually being developed through constant efforts of researchers. Each of these processes has its own pros and cons; however, adsorption process proves to be one of the most efficient, cost-effective (10\$–200\$ per million litres) and universal protocol (removes soluble/insoluble pollutants with >90–99% efficiency) among the above-mentioned methodologies to purify the effluent at low concentration levels both in laboratory as well as in industrial scale [10,11]. In spite of the remediation of wastewater, adsorption is also used for source reduction, reclamation and other applications. This unit operation removes surface active material by interphase transfer [10,12].

Generally, in order to evaluate an adsorbent various parameters such as adsorption capacity, pore size distribution, the resources needed for its production, regeneration, availability and environmental compatibility are carefully taken into account. Since, the advent of adsorption, activated carbon has been used as a sorbent for the treatment of municipal and wastewater due to the presence of free valencies and efficient sorption capacity. But, unfortunately, the overall cost for activation towards targeted application and regeneration makes a low cost activated carbon, an expensive sorbent [13]. Therefore, low-cost adsorbents such as zeolites, clays, diatomite, lignite, fly ash, coal, sand, natural oxide, industrial waste have attracted much attention towards further research [14,15].

It is clear that among all the available adsorbents, the carbonaceous sorbents present a superior performance due to their profound specific surface area (SSA), well-developed microporosity, pore size distribution, the existence of oxygen-bearing functional groups, the degree of functionalization, stability and regeneration capacity and above all is the complex heterogeneous nature of carbon [16,17]. Recently, an intriguing class of carbon-based adsorbents, carbon nanotubes (CNTs) have emerged and manifested improved efficiency in various research domains, particularly in water treatment applications. The comparison

of characteristics of available adsorbents for the removal of BTEX is summarized in Table 2.

Although zeolites present appropriate surface areas after surface modification and there are various laboratory results about the improved sorption capacity of these zeolites but their industrial utilization has never been filed in literature. One of the possible reasons can be the small particle size (~1  $\mu\text{m}$ ) that make it impractical for industrial application as an adsorbent [18]. Additionally, natural zeolites manifest high adsorption capacities for heavy metals and ammonium but little adsorption for organics, specifically aromatics. Therefore, they are not considered as good adsorbents for aromatic or anionic compounds which may be cation exchange nature and surface hydrophilics [19]. On the other hand, the hydrophilic clays are proved to be ineffective sorbent for the removal of aromatic compounds because of very low sorption capacity and selectivity. But after surface functionalization they present appropriate efficacy of the sorbent. Probably, the competition of water in relation to non-polar compounds to the clay surface, is held responsible for minimization of adsorption efficiency. More importantly, steric constrains of cations attached to the clay framework also affect the overall uptake of organic compounds [20].

Though lignite is the primary source of energy but large amount of fine particles cannot be easily handled, stored and transported. The probable reasons are high moisture content and high reactivity that can cause spontaneous combustion. Other than that, low calorific value, high ash, sulfur and nitrogen contents make them another environmental problem. While, mineral matter in lignite is largely organically bound and inseparable by standard washing techniques. Furthermore, high sodium content contributes to boiler fouling and slagging problems and the quartz content accelerates erosion of furnace burners [21]. Although, activated carbon is a carbonaceous sorbent with large surface areas but the micropores play its role in decreasing the transport velocity of organic compounds. A part from that the irregularly shaped pores increase the diffusion resistance of sorbate thus sorption equilibrium takes longer time duration [22,23].

On the contrary, nanotubes do not present high specific surface areas but the larger pore diameters and enhanced surface chemistry make them prominent candidate for the sorption of organic compounds [24]. Additionally, in order to get maximum sorption capacity, the appropriate surface modification of nanotubes is necessary. Hence, in order to modify CNTs with targeted physiochemical properties towards BTEX adsorption, it is very important to identify the interaction mechanism between BTEX and nanotubes, which is the main ingredient to better understand the sorption process in terms of enhanced adsorption capacity. Thus, it may save the time for experimentation (batch/continuous) and reduce the overall cost of the project.

However, there are discrepancies and contradictions about the dominant interaction mechanism between nanotubes and BTX. As some of the researchers inferred that  $\pi$ - $\pi$  interactions are responsible for increased sorption capacity of CNTs [25–31]. On the contrary, some of them claim that electrostatic dispersions are the dominant interaction mechanism [32–34].

Therefore, this review critically analyze the available literature in terms of the effect of properties of various factors (possible adsorption sites, physical properties and surface chemistry of CNTs), the importance of various types of interactions (electrostatic forces, dispersive/repulsive forces, hydrophobic forces,  $\pi$ - $\pi$  forces and hydrogen bond interaction mechanism), their dominant role under suitable circumstances, kinetics, isotherm, thermodynamics and adsorption-desorption study for the effective removal of BTEX using CNTs.

### 1.1. Background of CNTs

Graphitic carbons are  $sp^2$  hybridized pure elemental carbons including natural and highly ordered pyrolytic graphite and their structure composed of three covalently shared  $\sigma$ -electrons and one delocalized  $\pi$ -electron [35]. Carbon nanotubes are nanometer-scale rolled up sheets

of graphene. These allotropes of carbon appear either in the form of rolled up sheets of graphite held together by Van der Waal interactions (SWCNT) with a very narrow diameter distribution that leads towards the formation of crystalline ropes or as coaxially arranged nested concentric tubes similar to Russian doll-like structure (MWCNT) with inter-layer spacing in the range of 0.342–0.375 nm [36,37].

The diameter of nanotubes varies from 0.8 nm to 100 nm or above while the length of these rolled up graphene sheets lies in the range of nanometers to several centimetres. They are 100 times stronger than stainless steel, as hard as diamond, 1000 times higher current carrying capacity than steel and copper wires and higher thermal conductivity than that of diamond [38]. The bending strength of large-diameter CNTs ( $14.2 \pm 0.8$  GPa) is higher than that of graphite (1 GPa). The high bending strength of CNTs is thought to be related to their increased flexibility [39]. Moreover, carbon nanotubes are being produced by arc discharge [36,40], laser ablation [41] and chemical vapor deposition method [42]. Due to the cage-like symmetric structure of carbon, they exhibit prodigious physical and chemical properties [38,43,44]. The common physical properties of various carbonaceous materials in comparison with CNTs are summarized in Table 1.

Depending upon the morphology i.e., zigzag, armchair and chiral, they are classified as high aspect ratio containing nanomaterials [45]. On the other hand, the market forecast for carbon nanotubes in 2016 was 1740 million dollars, estimated to grow at 16.8% of annual growth rate and if it continues to grow at the same pace, it will exceed 2070.5 million dollars in the period of 2022–2024 [46,47]. The MWCNTs are currently dominating the market with a market share of 95% due to their low prices and diverse applications [47].

The multifaceted applications in different research areas, including composite materials and filters (CNT bicycles, antifouling CNT paint, ceramic filter resistors, fuzzy fibers etc.), contaminant remediation (adsorption, antimicrobial and antiviral agents, semiconducting photocatalyst), environmental sensing (battery operated small-scale sensors, field effect/thin film transistors, conductors, electrostatic discharge shielding), supermolecular functionalization, renewable energy (CNT anodes, symmetrical nano-membranes, in wind harvesting devices, photovoltaic devices, photoelectron chemical cells, proton exchange membrane fuel cells) biotechnology (biosensors for monitoring and detecting microbial ecology and pathogens, drug delivery, catheter coating, low-impedance neural interface electrodes), multifunctional applications (de-icing, lightning strike security, and basic auxiliary checking for aircraft), drive the market development over the conjecture time frame [47–49].

Furthermore, carbon nanotubes are particularly hydrophobic and susceptible to aggregate because they are mediated by strong van der Waals interactions with the long axis. In this manner, they exist in bundles as independent nanotubes [50]. The aggregation of carbon nanotubes normally diminishes their surface areas which results in an increase in pore volumes by the formation of the sorption sites (interstitial channels and peripheral grooves) confined in the entanglements. This process generates new sort of sorption sites, which further take part in overall adsorption [51]. The researchers introduced hydrophobic, mild hydrophilic and hydrophilic sites as general sorption sites [52].

The water molecules compete with the targeted pollutant at the hydrophobic as well as less hydrophilic sorption sites [52,53]. Initially, nanotubes attract BTEX compounds much quickly but the removal

efficiency reduces slowly until saturation media is the aromatic molecules interact strongly at a short inter-planer distance that is mediated by delocalized  $\pi$ -bonds and their planar shape. This is ascribed to the efficient sorption of the BTEX molecules into the internal pores [54]. On the contrary, sorption of aromatic compounds from aqueous solution via activated carbons has been attributed mainly due to electrostatic and dispersive interactions [55]. The oxygen-bearing functional groups on the carbon-based adsorbent, facilitate the specific interactions between aromatic rings (BTEX) and carbon basal plane ( $\pi$  orbital) which ultimately improve the sorption efficiency [56].

The dispersion of CNTs in aqueous media is a critical issue to enhance its efficiency. One of the concrete barrier to exploit different kinds of CNTs for the commercial applications is the entanglement of ropes of the nanotubes. Experimental and computational studies proved that the relationship between the dispersibility of CNT and the nature of its functionalization has not been analyzed comprehensively [57].

However, a few modification methods such as mechanical (ultrasonication, milling, calendaring, extrusion, shear mixing), physico-chemical (oxidation, fluorination, cycloaddition, hydrogenation, amidation, esterification, thiolation, silanization and polymer grafting) [58–64] and irradiation ( $\gamma$  and plasma irradiation) [65–67] have been reported to enhance their surface dispersion by introducing modifier molecules [68]. The most commonly used functionalization protocols are physicochemical methods which are broadly classified as covalent (sidewall functionalization & termini functionalization) and non-covalent modifications (van der Waals,  $\pi$ - $\pi$  and hydrophobic interactions). Covalent functionalization involves the attachment of functional groups on the sidewalls or introduction of vacancies on the surface of nanotubes in the forms of defects [45,69]. During this process, nanotubes inevitably lose some of their electrical properties due to the presence of these groups, which in turn results in the disruption of  $sp^2$  hybridization network of CNTs. These functional groups (carboxylate etc.) impart a negative charge on the surface, creating electrostatic stability which is expected to be the mandatory requirement for colloidal dispersion [58].

The extent of modification depends upon the tube diameter, curvature and tortuosity of carbon nanotubes and these properties are dictated by the synthesis conditions of CNTs [24]. The degree of modification may be helpful in designing the tailor fit nanotubes, nevertheless, the detailed information pertaining to this aspect has not been reported extensively. As a matter of fact, FTIR, XPS and Boehm titration can provide the qualitative as well as quantitative information about the extent of modification [68]. In contrast with covalent modification that may result in fragmentation of CNTs (disruption of  $\pi$  electron system), scattering of electrons and phonons, responsible for electrical properties of CNTs, non-covalent functionalization is based on supermolecular complexation using the adsorption forces ( $\pi$ - $\pi$  interactions, van der Waals forces) and conserve the conjugated ( $sp^2$ ) structure and electrical properties of carbon nanotubes [70]. They are classified as exohedral and endohedral functionalization.

The exohedral modification involves the adsorption and wrapping. Former is the most convenient and efficient way of modifying the nanotubes without any disruption in conjugated structure. The surfactants (ionic, nonionic), ionic liquids (amphiphilic cationic surfactant) and polyaromatic moieties have been employed to modify the nanotubes

**Table 1**  
Common physical properties of carbon-based adsorbents [43,44,196].

Carbonaceous material	Specific gravity g/cm <sup>3</sup>	Electrical conductivity S/cm	Electron mobility cm <sup>2</sup> /Vs	Thermal conductivity W/mK	Coefficient of thermal expansion K <sup>-1</sup>	Thermal stability in air °C
Graphite	1.9–2.3	4000	$2 \times 10^4$	298	$-1 \times 10^{-6}$	450–650
Nano fibers	1.8–2.2	–	–	1950	$-1 \times 10^{-6}$	~600
Activated carbon	1.88	–	–	0.1–0.2	$2 \times 10^{-6}$	>600
SWCNT	0.8	$10^2$ – $10^6$	$\sim 10^5$	3000–7000	negligible	>600
MWCNT	1.8	$10^3$ – $10^5$	$10^4$ – $10^5$	>3000	negligible	>600

by electrostatic forces or  $\pi$ - $\pi$  stacking [71]. However, the degree of modification depends on the length of hydrophobic regions that interact with nanotubes and the type of hydrophilic groups of surfactants which stabilize the carbon nanotubes by electrostatic repulsions [72–75].

Moreover, wrapping involves the conjugated polymers (poly(*m*-phenylene vinylene), poly(3-hexylthiophene), poly(*m*-phenylene vinylene)-polystyrene copolymer) etc.), that weaken the inter-tube van der Waal interactions and wrap around the nanotubes by  $\pi$ - $\pi$  interactions [76–78]. On the other hand, an endohedral method of functionalization of carbon nanotubes encapsulate the guest molecules (Au, Ag, Pt, C<sub>60</sub>, DNA etc.) inside the tube. This happens, perhaps due to the presence of sidewalls or localized defects which enables the guest molecules to enter into the cage of the nanotube and ultimately enhance the dispersion [69,79]. Apart from the detailed knowledge of types of CNTs, their properties, geometries, forces involved in sorption mechanisms and types of possible functionalization which enhance the sorption capacity, several other factors that affect the capability of CNTs for adsorption of aromatic compounds (BTEX) are discussed in detail below.

## 1.2. Factors influencing adsorption

### 1.2.1. Possible adsorption sites for nanotube bundles

The adsorption on nanotubes can occur at four possible sites: (1) endohedral cavities (inside the pores with open ends), (2) interstitial channels (between the tubes in the bundle) have the ability to adsorb smaller molecules, (3) external grooves, (4) external surfaces [80]. The endohedral cavities exhibit an exceptional surface area and pore volume for open-ended tubes while for close-ended nanotubes sorption occurs in interstitial channels, external grooves and external surfaces. The studies revealed that the interstitial channels are too strangled ( $\sim 3.4$  Å) so that even a small molecule can hardly enter into it [81]. However, a few years later, studies related to SWCNT exhibited that the molecules can also get adsorbed over the interstitial channels too [82]. The width of interstitial channels depends upon the adjacent nanotube; therefore, some channels are spacious enough to accommodate the pollutants with high molecular size while external grooves are independent of the size of adjoining CNTs with a reported pore width of  $\sim 3.4$  Å [83].

However, many studies exhibited that external curved surfaces of CNTs are the key adsorption sites for aromatic compounds [84,85]. In this aspect, Agnihotri et al. speculated that for narrow nanotubes external surface and grooves are the more attractive available sites for adsorption, due to the reason that the organic compounds attach to the high energy sites more quickly and then occupy the low energy sites, whereas the inner pore sorption demands more dimensional flexibility [32]. However, Bina et al. concluded that the external adsorption sites are the central sites for the sorption of ethylbenzene because the nanotubes, in their aggregates, are inefficient to develop interstitial spaces [86]. On the contrary, Chen et al. inferred that the innermost and outermost surfaces were found to be the most active sorption sites of MWCNT because the interlayer spacing is unable to attract aromatic compounds between coaxial tubes [87]. Similarly, Fujiwara et al. reported that inner pores of nanotubes exhibit a strong affinity for adsorption than that of interstitial channels of tube bundles which could be due to i) the difference in the electronic structure of curvature of graphene sheet; ii) potential difference in carbon atom configuration [88].

During the multilayer adsorption on the external surface of SWCNT, the void space between the bundles got filled up [89]. On the other hand, the impurities (amorphous carbon/metal catalyst) and water cluster formation may also impede the benzene ring to be attached to the inner surface of CNTs [90–92].

Thus, the inner cavities can be blocked by the existence of humic impurities (amorphous carbon, ash content, metal catalyst) or functional

groups [93]. These pores can be opened up by using different treatments, i.e., thermal treatment (563 K) for the removal of humic substances [94] and acid treatment (using hydrochloric acid, nitric acid, hydrogen peroxide and base) to remove metal catalysts (present, if any) from the end of the hydrophobic CNTs [58,95–98]. This unavailability of interstitial sites is either due to no bundle formation [99] or the large organic molecules that are unable to fit into the specific area [100]. Hence, the accessibility of sorption sites of nanotubes essentially depends upon their physical properties and entanglements.

Therefore, different treatment processes have their own impact on the properties of CNTs as explained in Fig. 1. After the purification steps, surface functionalization increases the oxygen content by reducing the surface area. Thus, the reduction in hydrophobicity causes the reduced sorption/uptake of nonpolar hydrocarbons and planar organic compounds due to insufficient interactions. Moreover, the process of graphitization eliminates these oxygen enriched functional groups and diminishes the sorption of polar organic compounds, but the effect is reversed for nonpolar/planar hydrocarbons [98].

Furthermore, Fig. 2 highlights the impact of oxygen content on the sorption of organic compound onto CNT. It reveals that with the increase of oxygen-bearing complexes, the sorption for polar organic compounds increases, whereas inverse behaviour is observed for nonpolar organic compounds. For polar organic compounds, the increased hydrogen bond interactions or electron donor-acceptor interactions are responsible for this behaviour. However, the decrease of sorption with the increase of oxygen-containing complexes is attributed to minimal hydrophobic interactions [98,101].

### 1.2.2. Impact of physical properties of nanotubes on adsorption characteristics

The physical properties of nanotubes play a most vital role in the adsorption of volatile organic compounds. The specific surface area (SSA) of SWCNTs is usually in the range from 150 to 600 m<sup>2</sup>/g [102–109] and 15–300 m<sup>2</sup>/g for MWCNT [109–115]. The values of the SSA of SWCNT have been found in the range of 20–1587 m<sup>2</sup>/g. Similarly, the different values of SSA for MWCNT (e.g. 22.38 m<sup>2</sup>/g to 1670 m<sup>2</sup>/g) have been reported. The lower value of SSA is caused by the presence of high amount of impurities (metal catalyst, amorphous carbon) that make the inner surface unapproachable for the functional groups, which is due to the low purity synthesis process (arc discharge technique) and the high SSA values are the result of high purity synthesis protocol (chemical vapor deposition) used for the process. However, Oleszczuk et al. proposed a positive correlation between the SSA and total pore volume with the sorption capacity of CNTs [116]. Similarly, Zhang et al. also described that the SSA and total pore volume are influential for the sorption of organic contaminants [90]. Additionally, Chin et al. revealed that internal and total surface areas of CNT was enhanced up to 81.98% and 14.7% respectively, while micropore volume increased from 0.05 cm<sup>3</sup>/g to 0.092 cm<sup>3</sup>/g because the oxidizing agent was efficient enough to open up the end caps of CNT and revelation of pores as well [26]. Theoretically, the pore volume of SWCNT ( $0.78 \pm 0.23$  cm<sup>3</sup>/g) was considerably higher as compared to that of MWCNT ( $0.64 \pm 0.39$  cm<sup>3</sup>/g) because the inner pores of MWCNT impeded the available space whereas single-walled carbon nanotubes did not face any hindrance due to the open inner channels. Additionally, the study delineated that for single-walled carbon nanotubes, the accessibility of inner pores affects the pore volume significantly [90]. Nonetheless, to the best of available literature, the aggregation state of CNTs has not yet been correlated with their SSA and pore volume in the aqueous solution. In order to determine the SSA, it is important to consider that whether the ends of nanotubes are opened or remain closed. Some researchers assume that they all are open, while the others presume that they all are closed. However, only the purification and functionalization processes can decide the blockage or opening of the ends of CNTs [104,105,109,117–120].



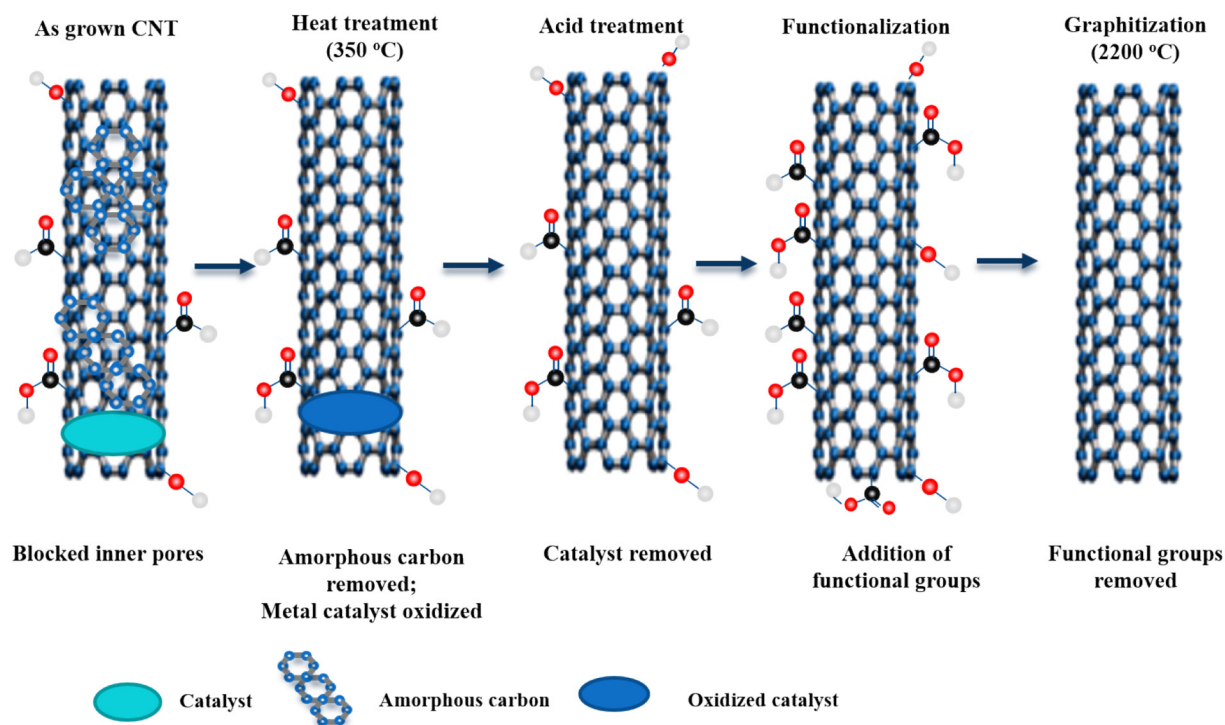


Fig. 1. Adsorption properties as affected by functional group [98].

Even though, many researchers reported the range of diameters of single-walled carbon nanotubes as 0.8 nm to 2 nm, while in another study it is claimed to be in the range of 10–20 nm [121]. However, for MWCNT, the reported studies showed much higher inner (2–15 nm) and outer diameter (4–200 nm). Thus, the outer diameter of MWCNT is dependent upon the distance between the number of concentric walls of nanotubes [24]. Moreover, the reported length of SWCNT and MWCNT are in the range of 0.4–50  $\mu\text{m}$  and 0.3–500  $\mu\text{m}$  respectively [25,32,122–124]. Su et al. explained that the higher sorption of organic compounds essentially depends upon the larger pore diameter with average pore volume [125]. However, in most of the studies, the porosity of CNT is not considered to explain the phenomenon of high uptake/adsorption [98].

It is also reported that the reduction in diameter of nanotubes increases the curvature, that in turn enhances the number of multilayers [99], and further facilitates higher adsorption [80,93,126] and improves the separation efficiency of a binary mixture [127]. But, Gotovac et al. exhibited an increase in adsorption capacity with slight increment in

diameter for molecules with ring structure (e.g. benzene), because the planar geometry enhances the contact with the adsorbent [94]. These two contradictory results need further investigation. Therefore, it is well established that the specific surface area, porosity and diameter of nanotubes, alone are not sufficient enough for explaining the complete adsorption characteristics of CNT towards BTEX.

On the contrary, ionic strength and pH of background solution are the key factors governing the sorption capacity which largely depend upon the ionization ability of BTEX and interaction mechanisms between targeted aromatic compounds and nanotubes. The variation in pH values affects the protonation or deprotonation state of the functional groups over the exterior surface of nanotubes. The removal of hydrogen cation ( $\text{H}^+$ ) from acidic groups increases the charge density of these groups, which in turn either establishes repulsive forces or enrich the  $\pi$ - $\pi$  electron donor acceptor (EDA) interactions between aromatic moieties and nanotubes. Besides, water cluster formation and reduction in hydrogen bond are the two plausible mechanisms which also take part in increasing repulsive or donor-acceptor interactions by decreasing the hydrophobicity and sorption affinity respectively [27,30,33,94,98,128–134].

The possible mechanisms and their contribution to the variation in pH values are illustrated in Fig. 3. For  $\text{pH} < \text{pK}_a$  the decrease in pH causes the sorption capacity to be decreased, because of weak electrostatic repulsions, whereas for  $\text{pK}_a < \text{pH}$ , the significant electrostatic interactions influence the adsorption positively. Similarly, adsorption coefficient decreases with decreasing pH for  $\text{pH} < \text{pH}_{zpc}$  ( $\text{pH}$  at zero point charge) and increasing pH (for  $\text{pH} > \text{pH}_{zpc}$ ). However, for the cases where at  $\text{pH} \approx \text{pH}_{zpc}$  different sorption mechanisms are intended to contribute to overall sorption process [101,128].

Several ideas/concepts are reported by the researchers for determining the influence of variation of pH on the sorption capacity [101]. Peterson et al. concluded that at a solution with a  $\text{pH} < 4$ , electrostatic forces are weak, whereas, for the solution of  $\text{pH} \geq 6$ , strong electrostatic forces are observed that ultimately influenced the sorption [135]. However, Zhang et al. proposed different equations to identify the contribution of interaction parameters at the pH range of 1.5–12 for the oxidized

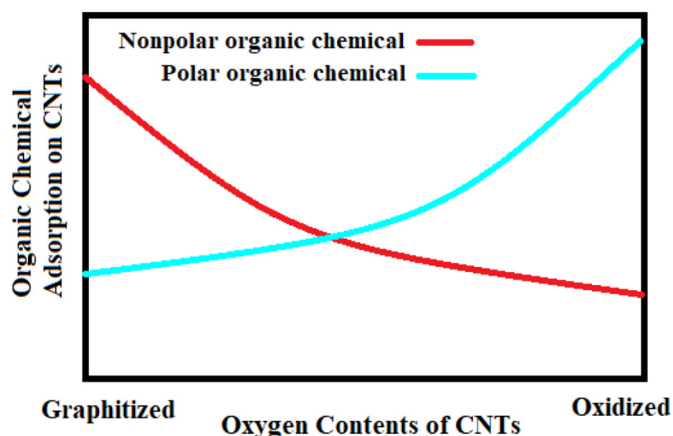


Fig. 2. Impact of oxygen content on the sorption of organic compound onto CNT [98].

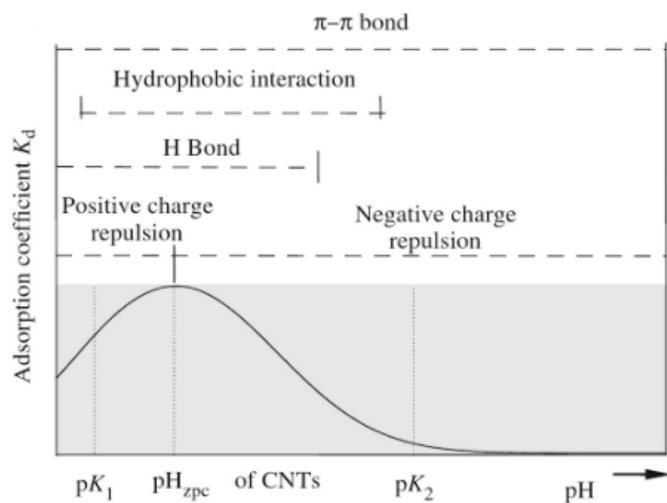


Fig. 3. Plausible adsorption mechanism at different pH values [101,128].

and graphitized CNTs [136], and reported that at neutral pH, the adsorbent is pre-eminent to contribute over 80% of overall adsorption.

$$K_d = K_d^- \delta^- + K_d^0 \delta^0 + K_d^+ \delta^+ \quad \text{pH} < 3.5 \quad (1)$$

$$K_d = K_d^+ \delta^+ + K_d^0 \delta^0 \quad \text{pH} > 3.5 \quad (2)$$

$$K_d = K_d^0 \delta^0 \quad \text{pH} = 1.5 - 12 \quad (3)$$

where  $K_d$  = overall sorption coefficient,  $K_d^-$  = sorption coefficient of cationic adsorbent,  $K_d^0$  = sorption coefficient of neutral adsorbent,  $K_d^+$  = sorption coefficient of anionic adsorbent,  $\delta^-$  = Percentage of cationic adsorbent,  $\delta^0$  = Percentage of neutral adsorbent,  $\delta^+$  = Percentage of anionic adsorbent

The hydrophobic forces between aromatic ring structure and nanotubes are increased due to salting out effect [128,137]. The reports on the impact of ionic strength on the sorption of aromatic ring structure using nanotubes are scarce and hence there exists a large research avenue for future investigations. However, Chen et al. reported an insignificant effect of ionic strength on the adsorption of aromatic compounds and concluded that there is no difference in ionic and nonionic organic compounds via ionic strength test [129].

Furthermore, Pourzamani et al. proposed that contact time is also a governing factor in attaining the improved efficiency of adsorbent and reported that at optimum contact time (20 min), 98.6% of benzene was removed [138].

### 1.2.3. Impact of surface characteristics of CNTs on adsorption

Apart from the physical properties, the surface chemistry of CNTs is one of the key factors in dictating the sorption capacity. The surface oxidation enhances the specific surface area (SSA) of MWCNT whereas a decrease in SSA has been reported for SWCNT when functionalized by ozonolysis [139]. This treatment coupled with hydrogen peroxide also results in reduced SSA. It is, perhaps associated with the hydrogen bonding that causes the entanglements of nanotubes which subsequently blocks the pores of graphitic structure. However, the SSA of ozonolyzed CNTs has improved by acidic treatment followed by thermal treatment [102,139]. However, a few researchers indicated that the oxidation of SWCNT is associated with some bottlenecks (pore blockage and distortion of tubes) therefore resulting in a decrease in the specific surface area either due to harsh oxidation conditions or use of concentrated acids [102,107,118,140]. As a matter of fact, the removal of impurities damages the nanotubes, which further generates more impurities in the form of carbon shells, fullerene and graphitic particles etc. [102,107,118,140]. The provided rationale speculates that the enhanced

surface oxygen complexes lead to a diminishing sorption of aromatic moieties [51,90,141–144]. These oxygen bearing complexes on the surface of CNTs either cause the more energetic water cluster formation that leads towards the reduction of the specific surface area or these contents localize the  $\pi$  electrons which in turn weaken the  $\pi$ - $\pi$  interactions between the graphitic layer structure and planar shape aromatic moieties [142,145,146]. The characteristics of CNTs before and after surface modification and the dominant interaction mechanisms involved for the successful adsorption of BTEX are summarized in Table 2.

It is apparent from the data (Table 2) that till date, the oxidation is used as the successful surface modification method for the removal of BTEX. Although several oxidizing agents (individually and in combined form) were used but the complete removal is not achieved. Moreover, most often, the pretreatments cause the opening of ends of nanotubes due to chemisorption [147]. Thus, the carbon atoms of the nanotube, react with water and oxides of carbon, (in the presence of air) that may result in the production of oxygen content over the surface of carbon nanotubes [148]. However, the relation between the percentage contribution of oxygen-bearing complexes and the molar ratios of aromatic rings of nanotubes (Fig. 4) showed that the  $\pi$  polarity of ring structure on CNT decreases sharply with an increase in surface acidic groups. Hence, it can be concluded that in order to enhance the surface aromaticity of nanotubes and interactions, the excessive functional groups impart negative impact on the sorption capacity of CNTs [52,149].

Moreover, there are several types of interaction forces that are active at three different interfaces during the process of adsorption. These forces may change with the variation in energy of interaction as summarized in Table 3 [150]. The adsorbate-adsorbent interaction depends upon the polarizability which in turn affect the size of the targeted pollutant [98]. These interactions exist in all types of physical or chemical forces. Additionally, the adsorbate-water interactions depend on the solubility of adsorbate which is the indicator of sorption strength or magnitude of sorption force and solubility has an inverse relation with sorption strength [24]. The adsorbent-water interactions are attributed to the fact that how many water molecules removed from the sorbent surface. These adsorbate-water and adsorbent-water interactions do not exist at higher interaction energy as adsorbate makes a strong covalent bond with the surface functional groups or charged surface groups attract the opposite charges or repel the negative charges. Thus, the targeted pollutants bound by chemisorption can't accumulate at more than one molecular layer because of shorter bond length between adsorbent surface and adsorbate [150]. Most of the researchers claimed that the dominant interaction mechanism is  $\pi$ - $\pi$  interaction at neutral pH whereas, Chen et al., Chin et al. and Yu et al. reported that sorption capacity increase at acidic pH with  $\pi$ - $\pi$  dispersion. However, solution chemistry plays a vital role in determining the mechanism. Without considering it, we may not propose the plausible interaction mechanism. In this review a comprehensive detail is provided that how solution chemistry affects the interactions and how to determine the right dominant mechanism to avoid future perplexities [26,28,151].

## 2. Adsorption mechanisms of BTEX onto CNTs

The structural properties allow the attraction towards the surface of nanotubes and the repulsion from the aqueous solution for the adsorption of BTEX. The hydrophobic forces are the pre-eminent repulsive forces that remove BTEX from aqueous solution onto the CNT surface. The interacting forces during adsorption process at all three interfaces are summarized in Table 3 [150]. These are accompanied either by the protonation condition of ionizable ring structure or with the size and polarity of this molecule. Nonetheless, Van der Waals interactions are the dominant mechanism of all the interactions and their intensity relies on the electric charge, polarizability and molecular size. These forces emerge from the affinity of electron-rich and electron-deficient regions of uncharged molecules. However, in cases, where dipole-dipole forces,

**Table 2**

Summary of characteristics of common adsorbents (pristine/modified) for the removal of BTEX from aqueous solution.

Adsorbent	Pollutant	Pristine/modified	Surface area ( $S_{\text{BET}}$ ) (m <sup>2</sup> /g)	Pore volume (cm <sup>3</sup> /g)/basal spacing $d_{001}$ (nm) <sup>a</sup>	Pore diameter (nm)	Adsorption capacity $Q_m$ (mg/g)	Conditions	Dominant interaction
Zeolites								
SBA-15 [197]	Toluene	Pristine	594	0.85	7	9.1	–	Strong surface interaction
MCM-41 [197]	Toluene	Al-MCM-41	1310	0.66	2	33.6	–	Strong surface interaction
SBA-15 [198]	Benzene	Phenyl group	611	0.99	5.2	0.650 <sup>a</sup>	–	Strong $\pi$ - $\pi$ interactions
MCM-41 [199]	BTX	Pluronic 123 (P123)	484.03	0.814	7.49	B: 0.68 T: 0.66 o-x: 0.63 p-x: 0.62 B: 150.42 T: 152.41 E: 162.21 m, p-x: 175.32 o-x: 164.57	28 ± 2 °C	Van der Waals interaction
NaY zeolite [200]	BTEX	Hexadecyltrimethylammonium (HDTMA)	650.3	–	–	B:38 <sup>a</sup> T: 25 E: 12 B: 0.15 <sup>a</sup> T: 0.25 p-x: 0.38	T: 28 ± 1 °C No pH adjustment	Chemical interactions
NaY zeolite [201]	BET	Octadecyltrichlorosilane (OTS)	498	0.218	1.9	B: 0.12 <sup>a</sup> T: 0.18 p-x: 0.43	T: 25 °C	–
Powdered mesoporous silica (PMPS) [202]	BTX	Octyl surfactant	41	0.071	2.3	B: 145.6 T: 748.8 p-x: 413.9 B: 485.5 T: 854.4 p-x: 587.4 B: 0.032 T: 0.050 o-X: 0.147 p-X: 0.129	T: 20 °C	–
Granular mesoporous silica (GMPS) [202]	BTX	Octyl surfactant	255	0.147	2.4	B: 3.467 T: 6.251 E: 2.631 X: 6.818 B: 3.814 T: 5.065 E: 2.997 X: 6.236	T: 20 °C	–
Na-P1 zeolite [203]	BTX	Pristine	–	–	–	B: 160 T: 155 o-X: 170 B: 1.1 T: 7.0 p-X: 5.0 B: 28 T: 27	T: 20 °C	–
Na-P1 zeolite [203]	BTX	Hexadecyltrimethylammonium (HDTMA)	–	–	–	B: 21 T: 16	T: 20 °C	–
Na-P1 zeolite [204]	BTX	NaOH	75.59	0.149	7.39	B: 0.28 T: 0.31 o-X: 0.09 T: 2.7 <sup>b</sup> E: 3.5 p-X: 2.9 o-X: 2.5 m-X: 3.0	T: 20 °C	–
Na-X zeolite [205]	BTEX	Hexadecyltrimethylammonium (HDTMA)	282.6	0.235	–	B: 3.58	–	–
clinoptilolite (Cp) [205]	BTEX	Hexadecyltrimethylammonium (HDTMA)	30.31	0.123	–	B: 21 T: 16	–	–
Clays								
Smectite [206]	BTX	Trimethylammonium (TMA)	206	0.13 <sup>*</sup>	–	B: 160 T: 155 o-X: 170 B: 1.1 T: 7.0 p-X: 5.0 B: 28 T: 27	T: 20 °C	Weak interactions
Na-MMT [207]	BTEX	methylphenylpyridinium (MPPyr)	36	1.36 <sup>*</sup>	–	B: 21 T: 16	–	–
Na-MMT [208]	BT	Benzyltrimethyltetradecylammonium (BDTDA)/Benzyltrimethylammonium (BTMA)/Hyamine	803	0.38 <sup>*</sup>	–	B: 0.28 T: 0.31 o-X: 0.09 T: 2.7 <sup>b</sup> E: 3.5 p-X: 2.9 o-X: 2.5 m-X: 3.0	T: 20 °C pH: 7.2	–
Sericite mica [208]	BT	Benzyltrimethyltetradecylammonium (BDTDA)/Benzyltrimethylammonium (BTMA)/Hyamine	14	–	–	B: 0.28 T: 0.31 o-X: 0.09 T: 2.7 <sup>b</sup> E: 3.5 p-X: 2.9 o-X: 2.5 m-X: 3.0	T: 20 °C pH: 7.7	–
Bentonite [209]	BTX	Pristine	700	–	–	B: 0.28 T: 0.31 o-X: 0.09 T: 2.7 <sup>b</sup> E: 3.5 p-X: 2.9 o-X: 2.5 m-X: 3.0	T: 20 °C	$\pi$ - $\pi$ interactions
Organo bentonite [210]	TEX	cetyltrimethylammonium bromide (CTMAB)	740	–	–	B: 3.58	–	Van der Waals interactions
Na-MMT [211]	BTEX	Poly ethylene glycol (PEG)	27.8	–	–	B: 3.58	T: 25 °C pH: 7	–

(continued on next page)

Table 2 (continued)

Adsorbent	Pollutant	Pristine/modified	Surface area ( $S_{BET}$ ) (m <sup>2</sup> /g)	Pore volume (cm <sup>3</sup> /g)/basal spacing $d_{001}$ (nm)*	Pore diameter (nm)	Adsorption capacity $Q_m$ (mg/g)	Conditions	Dominant interaction
Semectite organoclay [212]	BTEX	hexadecyltrimethylammonium chloride (HDTMACI)	61.66	0.22*	–	T:4.2 E:5.18 X:5.98 B:2.04 T: 1.27 E:6.67 m, X:3.83 p-X:2.09 410	T: 23.85 °C pH:9	–
Na-smectite [213]	Toluene	hexadecyltrimethylammonium bromide (HDTMAB)	59.87	0.40*	40.17	–	pH:6	–
Porous clay heterostructures (PCH) [214]	Toluene	Cetyltrimethyl ammonium bromide (CTAB), dodecylamine (DDA)	728	0.16	2.40	101.1	T: 25 ± 2 °C pH: 3	–
MMT [215]	Benzene	1-hexyl-3-methyl imadazolium chloride	–	–	–	588.32	T: 25 °C pH: 8	–
Diatomite [216]	BTEX	Pristine	38.40	0.0504	52.52 <sup>c</sup>	B: –0.08 <sup>d</sup> T: –0.710 E:0.478 p-X: 0.460 o-X: 0.325	T: 20 °C ± 1 pH: 7	–
Diatomite [216]	BTEX	Thermal treatment (750 °C)	43.30	0.0601	55.49 <sup>c</sup>	B: –0.015 <sup>d</sup> T: –0.040 E:-0.081 p-X: –0.091 o-X: –0.042	T: 20 °C ± 1 pH: 7.5	–
Diatomite [217]	BTEX	Pristine	13.04	0.02398	73.580 <sup>c</sup>	B: 0.0004 <sup>a,b</sup> T:0.0004 E:0.0004 m, p-X: 0.0009 o-X: 0.0004	T: 25 °C	–
Diatomite [217]	BTEX	HCl (lake water)	9.4	0.0150	47.815 <sup>c</sup>	B: 0.0004 <sup>a,b</sup> T: 0.0005 E: 0.0006 m, p-X: 0.0007 o-X: 0.0009	T: 25 °C pH: 7.76	–
Diatomite [217]	BTEX	HCl (sea water)	9.4	0.0150	47.815 <sup>c</sup>	B: 0.0005 <sup>a,b</sup> T: 0.0005 E: 0.0005 m, p-X: 0.0009 o-X: 0.0005	T: 25 °C pH: 8.06	–
Lignite [21]	BTEX	Pristine	11.40	0.0156	54.780 <sup>e</sup>	B: 0.0016 <sup>a,b</sup> T: 0.0014 E: 0.0013 m, p-X:0.0022 o-X: 0.0013	T: 20 °C pH: 5.39	–
Lignite [21]	BTEX	Thermal treatment (750 °C)	95.19	0.0908	38.139 <sup>e</sup>	B: 0.0348 <sup>a,b</sup> T:0.0343 E:0.0320 m, p-X: 0.0594 o-X: 0.0351	T: 20 °C pH: 10.79	–
Activated carbon ACF (phenolic resin-coated glass fiber) [218]	BTEX	HNO <sub>3</sub>	483	0.176	–	B: 66 T: 85 EB: 237 X: 185	T: 25 °C pH: 7	–
AC (date pits) [219]	BTEX	H <sub>3</sub> PO <sub>4</sub>	800	0.58	13.9A radius	B <sub>DP</sub> : 8.8 T <sub>DP</sub> : 5.0 E <sub>DP</sub> : 5.6 X <sub>DP</sub> : 6.2	pH: 7.8 T: 25 °C	π-π donor acceptor interactions



Table 2 (continued)

Adsorbent	Pollutant	Pristine/modified	Surface area ( $S_{BET}$ ) ( $m^2/g$ )	Pore volume ( $cm^3/g$ )/basal spacing $d_{001}$ (nm) <sup>a</sup>	Pore diameter (nm)	Adsorption capacity $Q_m$ (mg/g)	Conditions	Dominant interaction
AC (cotton stalks) [219]	BTEX	H <sub>3</sub> PO <sub>4</sub>	1183	1.055	17.9A radius	B <sub>CS</sub> : 3 T <sub>CS</sub> : 6.7 E <sub>CS</sub> : 8.7 X <sub>CS</sub> : 9.3	pH: 7.8; T: 25 °C	$\pi$ - $\pi$ donor acceptor interactions
AC (peach stones) [219]	BTEX	H <sub>3</sub> PO <sub>4</sub>	1346	0.935	13.9A radius	B <sub>PS</sub> : 3 T <sub>PS</sub> : 6.5 E <sub>PS</sub> : 8.3 X <sub>PS</sub> : 8.7	pH: 7.8 T: 25 °C	$\pi$ - $\pi$ donor acceptor interactions
AC (almond shells) [219]	BTEX	H <sub>3</sub> PO <sub>4</sub>	1279	1.011	15.6A radius	B <sub>AS</sub> : 1.3 T <sub>AS</sub> : 5 E <sub>AS</sub> : 6.5 X <sub>AS</sub> : 7.4	pH: 7.8 T: 25 °C	$\pi$ - $\pi$ donor acceptor interactions
AC (olive stones) [219]	BTEX	H <sub>3</sub> PO <sub>4</sub>	848	0.632	14.9A radius	B <sub>OS</sub> : 8.3 T <sub>OS</sub> : 5.8 E <sub>OS</sub> : 6.6 X <sub>OS</sub> : 7.2	pH: 7.8 T: 25 °C	$\pi$ - $\pi$ donor acceptor interactions
AC (rice husk) [219]	BTEX	H <sub>3</sub> PO <sub>4</sub>	956.5	0.726	12.1A radius	B: 4.76 T: 5.5 E: 6.75 X: 7.33	T: 25 °C pH: 6.5	$\pi$ - $\pi$ donor acceptor interactions
AC (coal based) [56]	BT	HNO <sub>3</sub>	938.36	0.351	–	B: 150.43 T: 157.07	T: 30 °C pH: 7	Dispersive interactions
AC (coal) [56]	BT	Pristine	877.82	0.342	–	B: 219.42 T: 230.53	T: 30 °C pH: 7	Dispersive interactions
AC (coal based) [56]	BT	Thermal treatment (800 °C)	863.66	0.339	–	B: 268.97 T: 279.16	T: 30 °C pH: 7	Dispersive interactions
AC [220]	BT	KOH	3216	1.59	2.16	B: 860 T: 1200	T: 25 °C pH: 7	–
AC [21]	BTEX	Pristine	1371	0.7606	22.188 <sup>c</sup>	B: 0.4934 E: 0.5129 m <sub>n</sub> p-X: 0.8341 o-X: 0.4781	T: 20 °C pH: 7	–
AC (coconut shell) [221]	BTX	Pristine	724	0.39	21.35 <sup>c</sup>	B: 114.77 T: 125.09 o-X: 141.30 365	T: 30 °C pH: 6.4	–
AC (rice husk) [222]	Benzene	H <sub>3</sub> PO <sub>4</sub>	–	–	–	B: 5.47 T: 5.53 X: 5.19	T: 25 °C pH: 6.5	$\pi$ - $\pi$ interactions
AC (date-palm pits) [223]	BTX	FeCl <sub>3</sub>	893.780	–	–	B: 5.47 T: 5.53 X: 5.19	T: 20 °C ± 1 pH: 10	–
AC (banana trunk) [224]	Benzene	Pristine	–	–	–	197.108	T: 30 °C pH: 7	No interactions between adsorbent and adsorbate
AC (banana trunk) [224]	Benzene	Mercurized and CTAB loaded. (M-CTAB-BT) Mercurized-Cetyltrimethylammonium bromide (m-CTAB)	–	–	–	373.081	T: 30 °C pH: 7	No interactions between adsorbent and adsorbate
Ordered mesoporous carbon [22]	Benzene	HCl/HF	1762	1.54	5	17.34 <sup>a</sup>	T: 25 °C pH: 7	$\pi$ - $\pi$ interactions
Ordered mesoporous carbon [225]	BTEX	Citric acid	1276 ± 6	1.79 ± 0.01	5.99 ± 0.01	B: 5.1 ± 1.4 T: 18.2 ± 3.1 E: 31.7 ± 2.4 X: 46.0 ± 2.1 ± ± ±	T: 25 °C pH: 7	–
Carbon nanotubes SWCNT [87]	Benzene/Toluene	60% NaOCl	370	–	–	B: 60.1 T: 103.2	T: 25 °C pH: 3	$\pi$ - $\pi$ donor acceptor interactions

(continued on next page)

Table 2 (continued)

Adsorbent	Pollutant	Pristine/modified	Surface area ( $S_{\text{BET}}$ ) ( $\text{m}^2/\text{g}$ )	Pore volume ( $\text{cm}^3/\text{g}$ )/basal spacing $d_{001}$ (nm)*	Pore diameter (nm)	Adsorption capacity $Q_m$ (mg/g)	Conditions	Dominant interaction
MWCNT [87]	Benzene	60% NaOCl	148	–	–	36.2	T: 25 °C pH: 3	$\pi$ - $\pi$ donor acceptor interactions
SWCNT [26]	<i>p</i> -Xylene	Pristine	247.6	0.050	–	77.5	T: 25 °C pH: 5	$\pi$ - $\pi$ interactions
SWCNT [26]	<i>o</i> -Xylene/ <i>p</i> -Xylene	HNO <sub>3</sub>	284	0.092	–	<i>o</i> -X: 115 <i>p</i> -X: 85.5	T: 25 °C pH: 5	$\pi$ - $\pi$ interactions
SWCNT [27]	BTEX	30% NaOCl	Micropore: 133.33 Mesopore: 194.08	Micropore: 0.0382 Mesopore: 1.1100	Micropore: 0.30 Mesopore: 23.75	B: 212.6 T: 172 E: 180 X: 170	T: 25 °C pH: 7	$\pi$ - $\pi$ electron donor acceptor interactions
SWCNT [27]	BTEX	HCl	Micropore: 96.74 Mesopore: 271.20	Micropore: 0.0361 Mesopore: 1.4790	Micropore: 0.33 Mesopore: 22.72	B: 45 T: 60 E: 50 X: 148	T: 25 °C pH: 7	$\pi$ - $\pi$ electron donor acceptor interactions
SWCNT [27]	BTEX	HNO <sub>3</sub>	Micropore: 78.47 Mesopore: 165.24	Micropore: 0.0223 Mesopore: 1.1599	Micropore: 0.34 Mesopore: 28.87	B: 105.7 T: 160.8 E: 153.1 X: 108.9	T: 25 °C pH: 7	$\pi$ - $\pi$ electron donor acceptor interactions
SWCNT [27]	BTEX	H <sub>2</sub> SO <sub>4</sub>	Micropore: 86.47 Mesopore: 237.83	Micropore: 0.0367 Mesopore: 1.9710	Micropore: 0.32 Mesopore: 34.00	B: 42.6 T: 36.7 E: 143.6 X: 78.4	T: 25 °C pH: 7	$\pi$ - $\pi$ electron donor acceptor interactions
SWCNT [27]	BTEX	Pristine	Micropore: 310.75 Mesopore: 231.89	Micropore: 0.0784 Mesopore: 0.3710	Micropore: 0.25 Mesopore: 23.54	B: 18.1 T: 80.1 E: 81.1 X: 147.8	T: 25 °C pH: 7	$\pi$ - $\pi$ electron donor acceptor interactions
CNT [33]	BTEX	30% NaOCl	88.56	0.024	–	B: 247.87 T: 279.81 E: 342.67 P-X: 413.77	T: 25 °C pH: 7	Electrostatic interactions
SWCNT [86]	Ethylbenzene	NaOCl	24.5	–	–	9.98	T: 25 °C pH: 7	Dispersive interactions
MWCNT [86]	Ethylbenzene	NaOCl	37.6	–	–	9.2	T: 25 °C pH: 7	Dispersive interactions
HCNT [86]	Ethylbenzene	NaOCl	40.7	–	–	9.9	T: 25 °C pH: 7	Dispersive interactions
MWCNT [28]	TEX	2% NaOCl	471	0.64	5.4	T: 44.90 E: 61.12 m-X: 62.82	T: 25 °C pH under 7	$\pi$ - $\pi$ electron donor acceptor interactions
MWCNT [28]	TEX	3.2% NaOCl	381	0.58	6.0	T: 99.47 E: 115.63 m-X: 112.19	T: 25 °C pH under 7	$\pi$ - $\pi$ electron donor acceptor interactions
MWCNT [28]	TEX	4.7% NaOCl	382	0.58	6.0	T: 59.48 E: 79.15 m-X: 100.45	T: 25 °C pH under 7	$\pi$ - $\pi$ electron donor acceptor interactions
MWCNT [28]	TEX	5.9% NaOCl	327	0.49	5.9	T: 31.28 E: 40.18 m-X: 48.73	T: 25 °C pH under 7	$\pi$ - $\pi$ electron donor acceptor interactions
SWCNT [29]	Benzene/ Toluene	Pristine	273.64	0.73	13.06	B: 9.95 T: 9.97	T: 10 °C pH: 7	$\pi$ - $\pi$ electron donor acceptor interactions
HCNT (MWCNT-SiO <sub>2</sub> ) [29]	Benzene/ Toluene	Pristine	198.93	0.62	12.02	B: 9.98 T: 9.96	T: 10 °C pH: 7	$\pi$ - $\pi$ electron donor acceptor interactions
MWCNT [29]	Benzene/ Toluene	Pristine	132.42	0.58	13.57	B: 9.97 T: 9.95	T: 10 °C pH: 7	$\pi$ - $\pi$ electron donor acceptor interactions
MWCNT [226]	Benzene	Pristine	–	–	–	182.6	T: 25 °C pH: 7	$\pi$ - $\pi$ electron donor acceptor interactions
MWCNT [226]	Benzene	NaOCl	–	–	–	187.7	T: 25 °C pH: 7	$\pi$ - $\pi$ electron donor acceptor interactions
MWCNT [226]	Benzene	CaOCl	–	–	–	188.6	T: 25 °C pH: 5	$\pi$ - $\pi$ electron donor acceptor interactions
MWCNT [28]	TEX	Pristine	471	0.64	5.4	T: 44.90 E: 61.16 p-X: 76.15	T: 20 °C pH: 7	$\pi$ - $\pi$ interactions

Table 2 (continued)

Adsorbent	Pollutant	Pristine/modified	Surface area ( $S_{\text{BET}}$ ) ( $\text{m}^2/\text{g}$ )	Pore volume ( $\text{cm}^3/\text{g}$ )/basal spacing $d_{001}$ (nm) <sup>a</sup>	Pore diameter (nm)	Adsorption capacity $Q_{\text{m}}$ (mg/g)	Conditions	Dominant interaction
MWCNT [28]	TEX	HNO <sub>3</sub> /3% NaOCl	381	0.58	6	m-X: 76.86 o-X: 61.86 T: 99.47 E: 115.63 p-X: 56.17	T: 20 °C pH: 7	$\pi$ - $\pi$ interactions
MWCNT [28]	TEX	HNO <sub>3</sub> /15% NaOCl	327	0.49	5.9	m-X: 112.19 o-X: 75.27 T: 31.28 E: 38.40 p-X: 44.60	T: 20 °C pH: 7	$\pi$ - $\pi$ interactions
MWCNT [227]	TEX	HNO <sub>3</sub> /30% NaOCl	382	0.58	6	m-X: 48.58 o-X: 44.42 T: 59.48 E: 85.49 p-X: 103.40	T: 20 °C pH: 7	$\pi$ - $\pi$ interactions
MWCNT [28]	TEX	KOH	534.6	–	20–30	m-X: 109.78 o-X: 97.39 T: 99.52 E: 339.37	T: 10 °C pH: 6	Chemical interactions
MWCNT [228]	Xylene	Pristine	132.4	13.21	10	m-X: 278.28 o-X: 9.2	T: 25 °C pH: 8	Electrostatic dispersions
MWCNT [228]	Xylene	SiO <sub>2</sub>	273.6	–	–	m-X: 9.8	T: 25 °C pH: 8	Electrostatic dispersions
SWCNT [30]	BTEX	Pristine	–	–	1–2	B: 9.98 T: 9.98 E: 9.98 X: 9.98	T: 10 °C pH: 7	$\pi$ - $\pi$ electron donor acceptor interactions
MWCNT [30]	BTEX	Pristine	–	–	10	B: 9.8 T: 9.8 E: 9.9 X: 9.9	T: 10 °C pH: 7	$\pi$ - $\pi$ electron donor acceptor interactions
HCNT [30]	BTEX	SiO <sub>2</sub>	–	–	–	B: 9.97 T: 9.8 E: 9.8 X: 9.8	T: 10 °C pH: 7	$\pi$ - $\pi$ electron donor acceptor interactions
SWCNT [138]	Benzene	FeCl <sub>2</sub> ·4H <sub>2</sub> O/FeCl <sub>3</sub> ·6H <sub>2</sub> O/NH <sub>3</sub>	303.2	0.85	14.1	m-X: 193.1	T: 25 °C pH: 7	$\pi$ - $\pi$ dispersions
MWCNT [190]	TEX	Pristine	113.5	–	11.03	T: 23.28 E: 92.71 m-X: 70.58 o-X: 44.18 p-X: 44.15	T: 20 °C pH: 6	$\pi$ - $\pi$ interactions
MWCNT [190]	TEX	KOH	662.1	–	2.26	T: 63.34 EB: 249.44 m-X: 227.05 o-X: 138.04 p-X: 105.59	T: 20 °C pH: 6	$\pi$ - $\pi$ interactions
MWCNT [229]	Benzene	Ozone (80%)/NaOCl (30%)	–	–	–	m-X: 16.6	T: 25 °C pH: 5	$\pi$ - $\pi$ electron donor acceptor interactions
MWCNT [191]	Toluene/Xylene	Pristine	138	0.61	33.4	T: 127.94 p-X: 219.51	T: 25 °C pH 7	–
MWCNT [191]	Toluene/Xylene	Fe <sub>2</sub> O <sub>3</sub>	216	0.96	37.0	T: 381.18 p-X: 458.52	T: 25 °C pH 7	–
SWCNT [230]	Xylene	FeCl <sub>2</sub> ·4H <sub>2</sub> O/FeCl <sub>3</sub> ·6H <sub>2</sub> O/NH <sub>3</sub>	187.34	0.64	12.12	50	T: 25 °C pH 8	Electrostatic interactions

<sup>a</sup> : mmol/g.<sup>b</sup> :  $q_e$  (equilibrium adsorption).<sup>c</sup> : Pore radius ( $\text{Å}$ ).<sup>d</sup> : mmol/Kg.<sup>e</sup> : Pore radius (nm).

dipole-induced-dipole forces, donor-acceptor interactions and hydrogen bond interactions exist, these nonspecific interactions are not solely the principal factor for improved adsorption of BTEX [24,98,152]. Besides, some studies designate the polarizability of benzene ring structure on carbon surface as a principal factor that

plays a vital role in enhancing the sorption efficiency. Keeping in view, the strong hydrophobicity, polarizability and exceptional surface area of nanotubes, they are the ideal class of carbon-based adsorbents for the removal of organic compounds from aqueous solution [25].

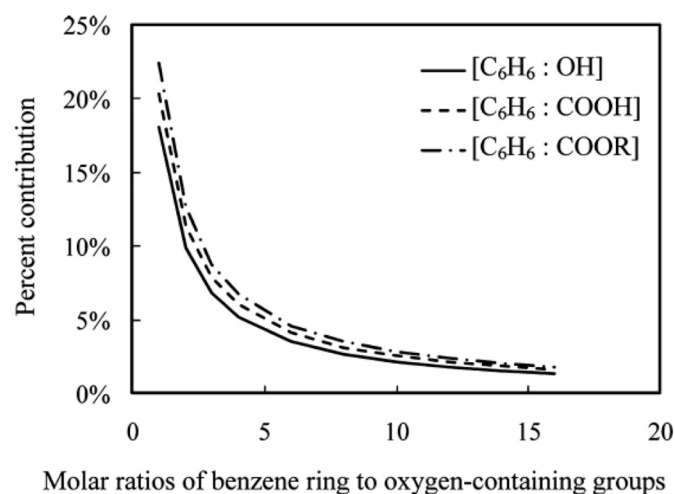


Fig. 4. Relationship between molar ratios of functional groups vs the percentage contribution [52].

Therefore, five possible interactions, namely, i) electrostatic interactions (between the charges of ionizable adsorbate and charged surfaces of adsorbent), ii) hydrophobic interactions (between hydrophobic surfaces of CNT and BTEX), iii)  $\pi$ - $\pi$  interactions (between the resonating  $\pi$  electrons of adsorbent (CNT) and the  $\pi$  electrons of adsorbent (CNT)), iv) hydrogen bonding (between adsorbate (BTEX) with (hydrogen bonding donor) functional groups and graphitic structure of CNT (hydrogen bonding acceptor) and covalent interactions (between BTEX and CNTs, only in the situation, when CNTs are functionalized via amidation, carboxylation and free radical chemistry etc.) are considered as responsible for the enhanced adsorption of BTEX on CNT surface. These forces, their intensities, and contribution to the adsorption phenomenon are dependent on the properties of both aromatic moieties and CNTs [101,153–156]. The current review deals only with the identification of possible mechanisms rather than their relative contribution in the given environmental conditions.

### 2.1. Electrostatic interactions

The electrostatic interactions (also known as coulombic interactions) which at atomic level are interpreted as 'electric', have been utilized to explain the decrease of sorption capacity with the increase of solution pH. The electrostatic interactions depend upon the nature of the charge on BTEX and nanotubes and ionic strength of the solution. The conditions of electrostatic interactions during the adsorption of weak acids and bases are summarized in Table 4. The opposite charge on the surface of concerned moieties causes electrostatic attraction whereas the same charges are known to cause the electrostatic repulsions [157]. Additionally, Jankowska et al. concluded that the interactions of negatively charged oxygen bearing functional groups on the surface of sorbents and positively charged  $\pi$  electrons of ring structures

that cause the strong electrostatic interactions through which the sorption capacity was increased [158].

Moreover, these interactions are largely influenced by the pH of the solution. As the pH increases, the aromatic moieties dissociate into anions rendering the surface of nanotubes significantly negative, ultimately causing the increase in adsorption capacity. However, the decrease in adsorption capacity is associated with electrostatic repulsions [157,159]. But some studies reported that the solution pH has an insignificant role in the enhancement of BTEX removal [27]. Furthermore, Su et al. divulged that nanotubes modified with NaOCl showed high stability for the removal of BTEX at a pH range of 3–12 [33]. Based on their experiments on *o*-xylene and *p*-xylene removal by SWCNT, Chin et al. found no effect of solution pH on the sorption capacity of nanotubes [26]. Hence, these interactions (attractive/repulsive), in fact, strongly depend upon the pH that ultimately influences the sorption capacity and contradictory results should be probed in the future studies. Since the dissociation of BTEX in the aqueous solution is governed not only by electrostatic interactions but also by the decrease in hydrophobic interactions and formation of hydrogen bonds. Thus, it can be interpreted that these interaction mechanisms control the sorption process simultaneously.

### 2.2. Dispersive/repulsive interactions

These Van der Waal (nonspecific) forces contribute to overall interactions between adsorbent and adsorbate, especially when the dominant forces that interact with an aromatic ring and basal planes of carbon framework [152]. It is evident from the literature that the oxygen-bearing groups over the surface of CNT localize the electrons in basal planes to form partial positive charge in those areas (Fig. 5) [160].

On the contrary, the functional groups attached to a benzene ring (toluene, xylene isomers, ethylbenzene) can also influence the interactions by activating or deactivating the ring structure. The activating group (electron donors) devises partial negative charge while deactivating group (electron acceptors) create a partial positive charge over the ring structure. Moreover, methyl and ethyl groups are the activating groups which develop partial negative charge over the benzene ring. These  $sp^3$  hybridized alkyl groups have less electronegative character as compared to that of  $sp^2$  hybridized carbon of benzene ring. Thus, electron density flows from alkyl group to aromatic ring [161]. These interactions (attractions/repulsions) are, in fact, strongly pH dependent and should be analyzed in detail for future research in order to evade contradictory results.

Additionally, electron density increases at ortho and para position of the benzene ring. Thus, the adsorption capacity for these isomers of xylene is observed to be much higher than that of *m*-xylene due to this hyper conjugative resonance that makes these positions more susceptible to electrophilic attack. However, the intensity of these dispersive/repulsive interactions is influenced by the molecular size, available electrons per molecule and polarizability of adsorbent, regardless of the properties of the potential aromatic compound to be attracted [24]. Bina et al. inferred that the activating group ( $-C_2H_5$ ) of

Table 3  
Summary of the interacting forces at all three interfaces [150].

Interactions	Approx. Energy of interaction (KJ/mol)	Interface		
		Adsorbate/adsorbate	Adsorbate/Aqueous	Aqueous/Adsorbent
Coulombic repulsion	>42	Yes	No	NO
Coulombic attraction	>42	Yes	No	NO
Covalent bonding	>42	Yes	No	NO
Ionic-dipole attraction	<8	Yes	Yes	Yes
Dipole-dipole attraction	<8	Yes	Yes	Yes
Dipole-induced dipole attraction	<8	Yes	Yes	Yes
Hydrogen bonding	8–42	Yes	Yes	Yes
Van der Waals attraction	8–42	Yes	Yes	Yes



**Table 4**  
Summary of conditions for electrostatic interaction for the adsorption of weak acids and bases [231].

Adsorbate character	Relative positions of $pH_{pzc}$ & $pK_a$	pH range	Adsorbate charge	Adsorbent surface charge	Resultant electrostatic interaction
Acidic	$pH_{pzc} < pK_a$	$pH > pK_a$	Negative	Negative	Repulsion
	$pH_{pzc} > pK_a$	$pK_a < pH < pH_{pzc}$	Negative	Positive	Attraction
	$pH_{pzc} > pK_a$	$pH > pH_{pzc}$	Negative	Negative	Repulsion
Basic	$pH_{pzc} < pK_a$	$pH < pK_a$	Positive	Positive	Repulsion
		$pH_{pzc} < pH < pK_a$	Positive	Negative	Attraction
		$pH < pH_{pzc}$	Positive	Positive	Repulsion

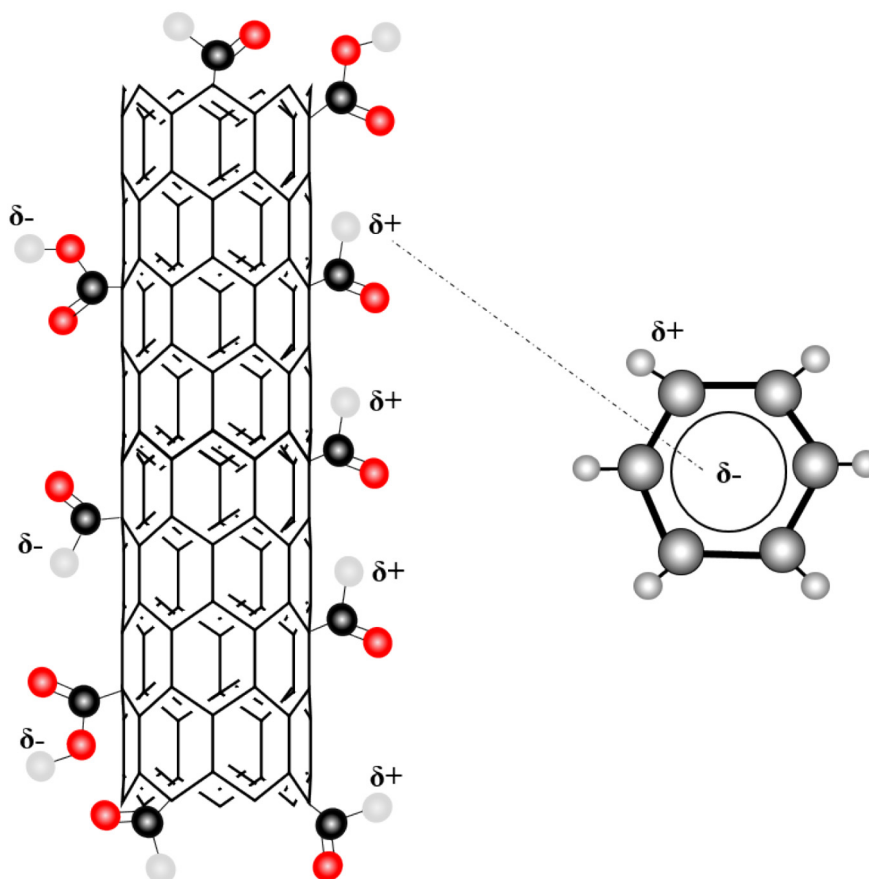
ethylbenzene attracted the negatively charged basal planes of single-walled carbon nanotubes. Thus, the predominant mechanism responsible for increased sorption is dispersive interactions [55,56,86].

### 2.3. Hydrophobic forces

Hydrophobic partitioning describes not only the strong attraction between aromatic moieties and hydrophobic carbon surfaces but also the behaviour of aromatic compounds. Hydrophobic bonding occurs exclusively with water molecules that are bonded together by hydrogen bonds to form the characteristic structure [157]. There are certain other factors that affect the sorption process as molecular size of BTEX (it controls the access of pores on graphitic surface (B, 78 g < T, 92 g < E, X, 106 g)), solubility of targeted pollutant in the aqueous solution (it governs the hydrophobic interactions (B, 1790 mg/l > T, 530 mg/l > E, 152 mg/l > X, insoluble)), boiling point of hazardous aromatic compound (B, 80.18 °C < T, 110.78 °C < E, 136.2 °C < X, 144.8 °C) and pka of background solution (it determines the dissociation of BTEX that may explain the type of interaction mechanism) [27,154,162,163]. The driving forces that push these planar shaped ring structures (BTEX) towards graphitic carbon surface are the entropic forces (as enthalpic

forces have negligible impact in overall process) with the weak dipole-dipole and dispersive interactions. These compounds partition themselves homogeneously in hydrophobic regions of carbon surface. Thus, partitioning increases with the increase of  $K_{OW}$  (partitioning coefficient) and decrease in water solubility of aromatic compounds. However,  $K_{OW}$  ( $\log K_{OW}$  values for B:2.13, T: 2.69, EB: 3.15, o-X: 3.77, m-X: 3.20, p-X: 3.15) increases for the compounds having low dipole moment (B:0.0001D, T:0.31D, EB: 0.58D, o-X: 0.45D, m-X: 0.31D, p-X: 0.00D) and high polarizability [28,84,164,165]. The Fig. 6 shows that with an increase in polarity of the ring structure, the sorption capacity increases. Moreover, the hydrophobic interactions are higher for polar organic compounds leading to high sorption capacity, whereas, opposite trend is found for non-polar organic compounds [101].

Additionally, these oxygen contents have a strong impact on the electronic density of carbon nanotubes which in turn alters the dispersion between the carbon surface and the ring structure of aromatic compounds. For example, the hydrophobic oxygen bearing complexes at the edges of the nanotubes withdraw electrons from the ring structures of BTEX by hydrophobic interactions. The hydrophobicity of graphitic layers can be probed by quantifying their contact angle, inverse gas chromatography and water adsorption. Thus, Fig. 7 describes the



**Fig. 5.** Proposed schematic diagram of van der Waal interactions between oxidized CNT and benzene ring.

relationship between adsorption coefficient and partition coefficient of ring structure on nanotubes and no explicit relationship was observed between them which further proves that hydrophobic forces are not the only governing interactions that influence the sorption capacity.

#### 2.4. $\pi$ - $\pi$ interactions

Many studies have concluded that sorption of aromatic moieties by un-functionalized nanotubes is due to the  $\pi$ - $\pi$  stacking [166,167]. The oxygen-containing functional groups (acidic nature) on the graphitic surface remove the electrons from the low electron regions, generating positive holes in the conducting band of the surface of carbon which may cause weaker interactions between  $\pi$  electrons of nanotubes and  $\pi$  electrons of the pollutant (Fig. 8) [146]. Mattson et al. elucidated that the uptake of the aromatic ring is influenced by the carbonyl group on the edges of the surface of carbon, however, the lower uptake of pollutant is associated with the conversion of the carbonyl group to the carboxylic group after surface oxidation of graphitic layers [168]. It was also reported that as the planar shaped ring structure approaches to the basal planes of carbon, the functional groups of aromatic compounds either activate or deactivate the ring by pushing or attracting  $\pi$  electrons from it [152]. It is interesting to note that, if the variation in pH plays no significant impact on the sorption, then the  $\pi$ - $\pi$  electron donor-acceptor mechanism (the carboxylic oxygen as the electron-donor and the ring structure as the electron-acceptor) is held responsible for the removal of BTEX by CNTs [33].

In their study, Chin et al. found that the methyl groups on a ring structure of xylene acts as an electron donor but the difference comes with the variation of isomers as the functional groups on *o*-xylene and *p*-xylene propel the electrons towards same side and centre of the aromatic ring structure [26]. The electron distribution in *p*-xylene and the hybridization of  $\pi$  electrons for pairing up to form a chemical bond between the nanotubes and para positioned ring structure are in minimal disordered form. Therefore, the sorption capacity of single-walled carbon nanotubes is a bit higher for *p*-xylene than that of *o*-xylene [25,169].

The reported literature also reveals that the  $\pi$  electron density of the planar shaped ring influences the rich and poor  $\pi$  electrons region that eventually affects the sorption capacity [84,90,141]. Chin et al. also reported that the sorption capacity of single-walled carbon nanotubes for *o*-xylene, increased up to 60% after surface modification, which can be attributed to the  $\pi$ - $\pi$  dispersion forces between  $\pi$  electrons of  $sp^2$  hybridized carbon atoms and the ortho-positioned methyl substituted ring structure. Since the electron donor substitution on xylene propel the electron towards benzene ring, which further enhances the electron density of  $\pi$  electrons, leading to the creation of larger quadrupoles on the ring structure in which the electron rich moieties act as electron

donors that eventually lead to an increased attraction between nanotubes and *o*-xylene [26]. However, the removal of electron density from the benzene ring can make the quadrupole less favourable, rendering ring structure as  $\pi$  acceptors [170–172]. They explained that the sorption of isomers of xylene is influenced by the position of its substitution groups (the methyl group) which impart repulsion interactions on the electron density of xylene [26].

Nonetheless, the studies also reported that the Mattson's mechanism of adsorption seems confusing due to the reason that, the oxidation of  $sp^2$  hybridized graphitic layers not only increase the  $-\text{COO}-$  groups but also the concentration of  $-\text{C=O}$  groups as well [152,154,166]. Hence, the  $\pi$ - $\pi$  donor-acceptor interaction is not the only governing mechanism in the sorption process, there are other possible mechanisms as well that contribute simultaneously to the process of adsorption.

#### 2.5. Hydrogen bonding

Hydrogen bond interactions are the type of non-covalent attractions between an electronegative atom and a hydrogen atom [129]. It was first proposed by Coughlin et al. Most of the studies related to CNT sorption have accentuated the influence of hydrogen bond interactions to the overall adsorption [159,169,173,174]. Furthermore, when hydrogen bonding is the governing mechanism, increase in sorption capacity is anticipated with a decrease in pH. In this scenario, oxygen complexes ( $-\text{COO}^-$ ) are protonated on the surface of nanotubes as hydrogen bond donors [152,175]. These functional groups form hydrogen bonds with hydrogen bond accepting aromatic moieties (Fig. 9). However, the water molecules preferentially bound to the surface oxygen groups by hydrogen bonds. The idea of this competition suggests that the graphitic surface with higher oxygen bearing functionalities will have higher sorption capacity [176].

The surface oxygen complexes usually form H-bonds with the water molecules of background solution (water cluster formation effect) minimizing the access of hydrophobic ring structure to the hydrophobic surface of nanotubes [154]. Likewise, Lin et al. and Oleszczuk et al. reported that hydrogen bonding might be insignificant in the case where no comparative increase in adsorption capacity is observed with the increase of hydroxyl groups ( $-\text{OH}$ ); although the reason behind this could be that they had a very low oxygen and hydrogen content for adsorption on carbon nanotubes [116,169]. It is believed that at lower pH values, the transition from  $-\text{COO}-$  to  $-\text{COOH}$  on the surface of nanotubes occurs which are the strong hydrogen bond donor functional groups. When it comes in contact with hydrogen bond acceptor, non-polar aromatic compounds (BTEX) in aqueous solution, results in enhanced sorption capacity [25]. However, the binding energies of hydrogen bonds are quite weaker than  $\pi$ - $\pi$  electron donor-acceptor interactions, signifying that these aromatic moieties (BTEX) may effortlessly be desorbed and retrieved for re-manoeuvring [177–179].

The binding energies of hydrophobic interactions are reported to be  $\leq 4 \text{ kJ mol}^{-1}$  that is larger than that of Van der Waals forces. Since there is no single independent interaction mechanism that may hold responsible for the sorption of organic pollutants like BTEX, therefore it is believed that these forces operate simultaneously. These binding energies enhance the conformations of aromatic moieties and assist in the attachment process with  $sp^2$  hybridized carbon surface [180–182]. Sutton et al. reported that weak hydrophobic forces and hydrogen bonding facilitate the ring structure to assemble itself with the carbon surface thus, it stabilizes the super molecular complex structures [180]. The determination of the extent to which these interactions contribute is an enthralling challenge for future research.

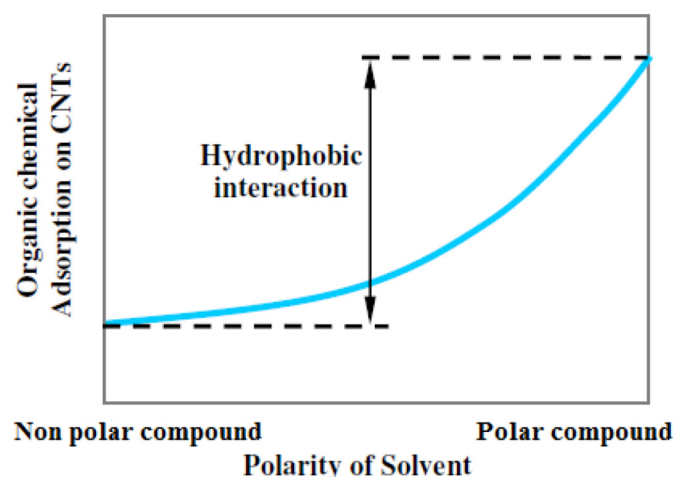


Fig. 6. Impact of polarity on sorption of organic compounds [52].

### 3. Quantitative determination of interaction mechanism

The aforementioned mechanisms can be probed quantitatively through FTIR and XPS that have become surplus investigative tools to

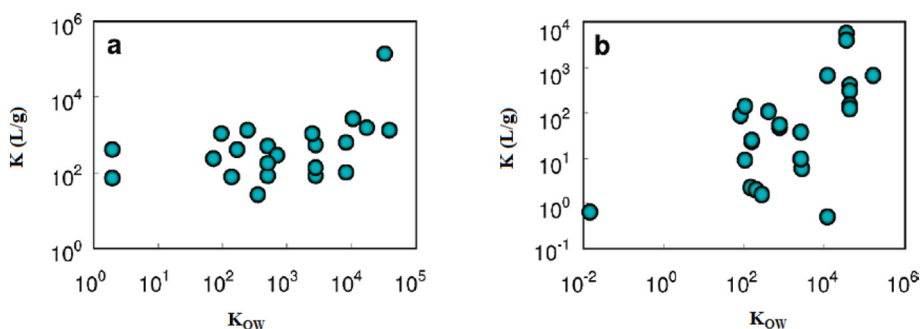


Fig. 7. Relationship between  $K_{ow}$  (partition coefficient) and  $K$  adsorption coefficient [98].

further probe the details of adsorbed pollutant over the surface of adsorbent [183]. Notably, the peak shift of  $\text{—C=C—}$  bonds in FTIR to higher wavenumber after sorption, demonstrates the presence of  $\pi$ - $\pi$  interactions between adsorbent and aromatic ring structure [146,157], whereas, the upshift of  $\text{—C—O—}$  bonds confirms the contribution of  $n$ - $\pi$  interactions which incorporates the interface interactions of electron donor surface of graphene layers and electron acceptor (planar shaped) aromatic ring [168,184]. Moreover, the FTIR analysis of also explains the contribution of hydrogen bonding which is attributed to the upshift of  $\text{—OH}$  group after adsorption [185,186]. X-ray photoelectron spectroscopy expounds the probable adsorption mechanisms. C1 energy spectrum represents  $\text{C—C}$ ,  $\text{C=C}$ ,  $\text{C—H}$ ,  $\text{C=O}$ ,  $\text{C=O}$  and  $\text{O—C=O}$  groups, whereas, corresponding spectra of O1 indicates the acidic functional groups over the surface of the carbon. The increase of peak intensity in C1 spectra after adsorption confirms that aromatic moieties are adsorbed over the surface of adsorbent through  $\pi$ - $\pi$  interaction. However, the elevated peak of the hydroxyl group in O1 energy spectra suggests a strong hydrogen bonding interaction between the two groups [187].

#### 4. Kinetic and thermodynamic studies of sorption

Adsorption kinetics is one of the governing component that establishes the solute uptake rate which in turn determines the kinetic performance of a sorbent by ascertaining the residence time for completion of a sorption reaction [188]. Moreover, isotherm study presents the perception of the sorption mechanism and the degree of affinity of the sorbents whereas thermodynamic parameters effectively anticipate the nature of the adsorption process [189]. In their study Yu

et al. reported the impact of oxygen content on the performance of MWCNT by varying the concentration of oxidizing agent from 2% to 5.2%. The kinetic curve showed that the amount of oxidized CNT was adsorbed by a slow diffusion from external sites to internal sites of oxidized CNT and equilibrium was reached within 6 h. It is found that the pseudo-second-order model fitted all the adsorption data, demonstrating that the chemical interactions are possibly involved in the sorption processes and the sorption capacity increases with the number of active sites on oxidized sorbent. The experimental data conformed to Langmuir isotherm model in the following order  $E > X > T$  which is related to decrease in water solubility, increase in molecular weight and boiling point of potential adsorbates. The negative values of  $\Delta H^\circ$  and  $\Delta G^\circ$  indicated that the sorption process is exothermic and spontaneous in nature [28]. Similar results have been presented by Yu et al. for TEX sorption onto KOH activated MWCNT [190]. In addition to this Abbas et al. exhibited the effective removal of toluene and xylene by iron nanoparticles modified MWCNT. They presented that the experimental data conformed to pseudo 2nd order model and Langmuir isotherm model. It is observed that the values of rate constants were higher for *p*-xylene than that for toluene, which can be attributed to low solubility and higher hydrophobicity of *p*-xylene [191].

Nevertheless, sorption of BTEX by nanotubes is primarily, a process that significantly influenced by temperature. Using thermodynamic principles, Yu et al. concluded that the adsorption of TEX (toluene, ethylbenzene and *m*-xylene) on CNTs decreases by increasing the temperature [142]. Additionally, Su et al. indicated that the increase in temperature results in faster sorption kinetics which results in enhanced diffusion rate. Apart from this, Gibbs free energy, change in enthalpy and entropy encapsulate the information about the spontaneous/

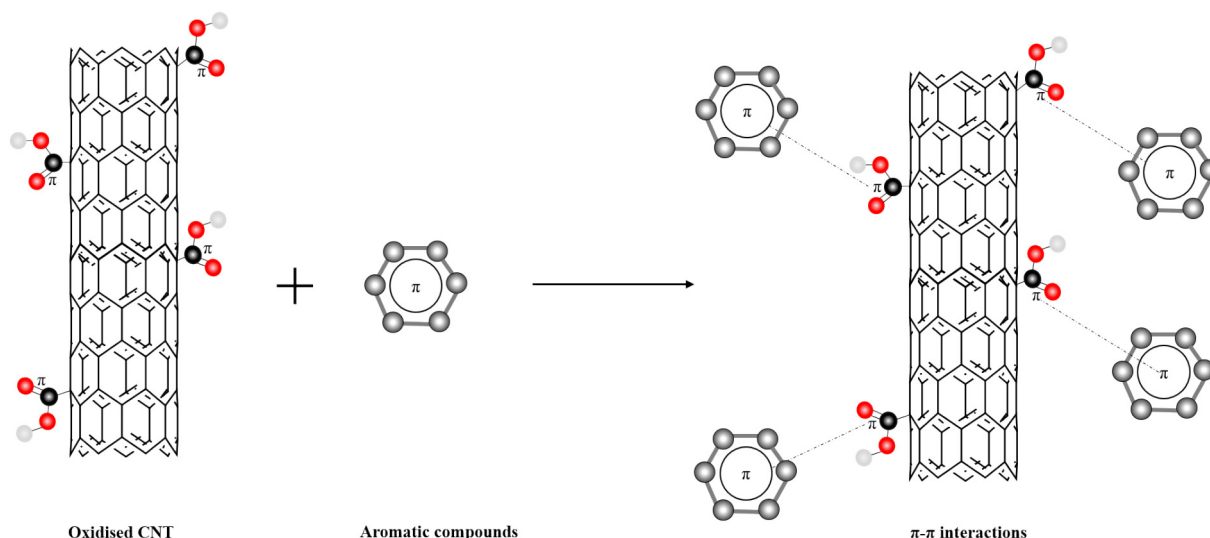


Fig. 8. Pictorial representation of  $\pi$ - $\pi$  interactions between oxidized CNT and aromatic ring structure [27].

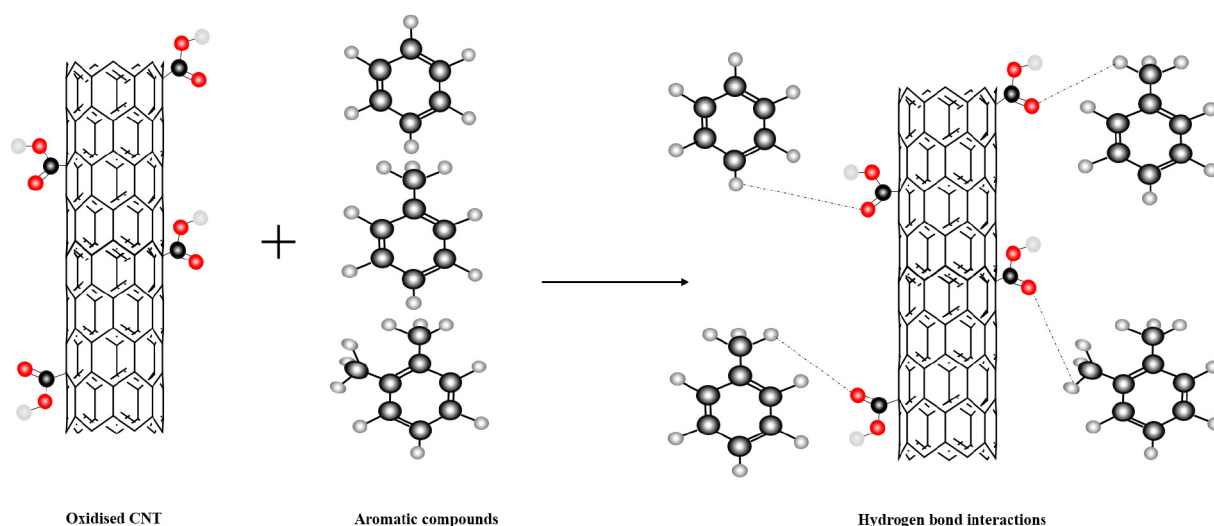


Fig. 9. Pictorial representation of hydrogen bond formation between oxidized CNT and aromatic ring structure.

nonspontaneous sorption, exothermic/endergonic reaction and ordered/disordered system respectively [125]. Some researchers reported that the adsorption of organic compounds by CNTs is an exothermic process and an increase in temperature results in the corresponding decrease in sorption capacity [190,192,193]. On the contrary, some of them reported that the endothermic reactions are followed and thus, the enhanced temperature results in the increased sorption capacity. This endothermic behaviour is because of electrostatic attraction between the nanotubes and targeted pollutants [24,194]. Nonetheless, the solubility of BTEX causes the strong interaction between water molecules and aromatic moieties, resulting in the decreased orderliness of the system [24]. Thus, it can be deduced from the thermodynamic analysis that sorption process is largely governed by the nature of the pre-eminent adsorption mechanism.

Additionally, adsorption-desorption study of a sorbent is essential to design a process for industrial application. Pourzamani et al. showed that by employing thermal treatment ( $105 \pm 2$  °C), xylene can be effectively desorbed from SWCNT and better performing SWCNT can be obtained after one adsorption-desorption cycle [195]. Similarly Bina et al. indicated that the unit cost of nanotubes could be reduced by employing adsorption-desorption cycles at higher temperature ( $105 \pm 2$  °C) for the removal of BTEX. Moreover, CNTs cannot form closed interstitial spaces in their aggregates therefore all of the adsorbed BTEX is released by the temperature [30].

Furthermore, Yu et al. performed three successive cycles of adsorption and desorption of TEX at 20 °C and 40 °C. During the adsorption cycle the porous structure of modified MWCNT was swelled. This structure was distorted (irreversible pore deformation) during the desorption process which in turn formed metastable states in mesopores of KOH-MWCNT. During the adsorption-desorption cycles the bundles of sorbent were rearranged to accommodate TEX inside the structure. Hence, the structural morphologies of the micro and nano pores were not the same as before. They quantitatively measured the extent of adsorption-desorption of TEX and inferred that the true hysteresis existed in the modified MWCNT in the following order  $p\text{-X} > o\text{-X} > m\text{-X} > T > E$  (at 20 °C) and  $o\text{-X} > T > p\text{-X} > m\text{-X} > E$  (40 °C) [190]. Thus, it can be concluded that the kinetics, isotherm, thermodynamics, adsorption-desorption studies are imperative to make nanotube as a potential sorbent for environmental applications.

## 5. Future perspectives

- I. Since, cytotoxicity of CNTs is not clearly understood therefore, risk assessment and environmental impacts of these

nanomaterials should be properly investigated. These nanotubes will come out to be more effective if they are engineered with appropriate green materials. This green functionalization will help in improving the ultimate sorption capacity by changing the surface chemistry of graphitic structure. This may be a fruitful contribution to the ongoing research in nanotechnology. This will lead us towards a new era of green nanotubes for the abatement of hazardous pollutants.

- II. Volatility of BTEX is another concern that is poorly addressed in literature. Although the quantitative analysis of volatility of hydrophobic compounds is reported extensively but the techniques to reduce the volatility of the targeted pollutants in order to prevent the air pollution, is still lacking.
- III. It is evident that the excessive functional groups hamper the sorption capacity therefore, it is mandatory to probe the ways to control the extent of modification. Thus, in order to improve the performance of sorbent, it is necessary that the degree of modification should be quantitatively analyzed.
- IV. The computational tools helped in understanding the synergistic effects and behavior of CNTs in adsorption but the detailed perception of the interaction mechanism at molecular level is still lacking. Additionally, there is no analytical tool to estimate the extent of contribution of these interaction mechanisms. This may provide the robust solution to many challenges in waste water treatment.
- V. Additionally, the chirality of nanotubes is another omnipotent factor that influences the sorption of BTEX profoundly. However, unfortunately, no experimental/theoretical work has been reported, attributing to this perspective. Thus, the adsorption mechanisms for BTEX at different chirality of carbon nanotubes will pave the way for more detailed and inquisitive research in nanotechnology.

## 6. Conclusion

Adsorption is an economical and widely practised unit operation for wastewater treatment from hazardous contaminants (benzene, toluene, ethylbenzene and xylene). This unit operation removes a hydrophobic fraction of surface active materials by interphase transfer. Since, most of the research work is done for batch mode therefore, the long term performance of this technology is mostly unknown. Moreover, the development of advanced adsorptive material is highly desirable to cope with the current limitations (small pore size/pore volume of adsorbents) or to maximize the adsorption capacity by imparting



functionalities to the adsorbents to give particular interaction with adsorbates.

Likewise, a class of intriguing carbonaceous materials, i.e., CNTs, carbon nanotubes have ended the quest for adsorbents with superior performance due to their high specific surface area, tunable microporosity, facile functionalization, degree of modification, the frequency of regeneration and above all complex heterogeneous nature of carbon. In spite of aforementioned properties, cost and cytotoxicity are two major issues that need to be addressed. However, the recent developments paved the way for the mass production of high quality nanotubes at low cost. Additionally, regeneration of these nanomaterials can further improve the cost effectiveness.

The change in surface properties (surface functionalization) of nanotubes results in a change in their physical properties which in turn affect the sorption efficacy. As a result of this variability in surface characteristics, both variations (increase/decrease) in sorption are reported in the literature. However, it is reported that the extreme oxidation of non-polar organic compounds leads to the decrease in sorption capacity of nanotubes due to water cluster formation effect. The presence of oxygen contents on the surface of nanotubes results in enhanced hydrogen bond interaction and electron donor-acceptor interactions, which are ultimately responsible for improved sorption.

The important mechanisms of interactions for selective adsorption/separation of hazardous contaminants include hydrophobic interactions, electrostatic interactions,  $\pi$ - $\pi$  interactions and hydrogen bonding. Moreover, the development and design of safe materials for adsorption will be accelerated through a fundamental understanding of the interaction mechanisms. For example, suitable CNTs may be designed for water purification by utilizing the plausible mechanisms of adsorption. It is evident that all the interactions are influenced not only by the characteristics of carbon nanotubes and properties of BTEX but also via solution chemistry.

An interesting fact reported in the literature is that, if variation in pH plays no significant impact on sorption, then the  $\pi$ - $\pi$  electron donor-acceptor mechanism (the carboxylic oxygen as the electron-donor and the ring structure as the electron-acceptor) is held responsible for the removal of BTEX by CNTs. But most of the researchers (Table 2) reported that  $\pi$ - $\pi$  interaction is the dominant mechanism at pH lower than 7 and in some cases higher than 7 which is contradictory to the fact that the increase in solution pH is associated with strong electrostatic attractions. This increase in solution pH enhances the hydrophilicity (reduced hydrophobicity) and in turn, increases the sorption capacity. However, at pH lower than 7, electrostatic repulsions are the dominant interaction mechanism rather than  $\pi$ - $\pi$  interaction. Nevertheless, when hydrogen bonding is the governing mechanism, increase in sorption capacity is anticipated with a decreased pH values of background solution.

Overall, these reports indicate that the hydrophobicity itself may not explain the adsorption affinity of BTEX on CNTs, and the accessibility of BTEX to different regions of CNT bundles and pores which are considered as important aspects for the adsorption of these aromatic compounds. The present review has sorted out numerous prevailing gaps in the information whilst recognizing a number of encouraging avenues and approaches for the upcoming research thrust. The prevailing uncertainties regarding the in-depth understanding of interaction mechanisms between adsorbate and adsorbent in the upcoming years seem to warrant continued research efforts in the field of adsorption.

This concise literature review provides an explicit compilation of the reported interaction mechanisms for adsorption of BTEX over CNTs, since the fundamental understanding of adsorbate-adsorbent interactions is necessary to design and develop a more rationale multi functionality process/material for future applications.

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