Individual and competitive adsorption of phenol and nickel onto multiwalled carbon nanotubes

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ABSTRACT

Individual and competitive adsorption studies were carried out to investigate the removal of phenol and nickel ions by adsorption onto multiwalled carbon nanotubes (MWCNTs). The carbon nanotubes were characterized by different techniques such as X-ray diffraction, scanning electron microscopy, thermal analysis and Fourier transformation infrared spectroscopy. The different experimental conditions affecting the adsorption process were investigated. Kinetics and equilibrium models were tested for fitting the adsorption experimental data. The characterization experimental results proved that the studied adsorbent possess different surface functional groups as well as typical morphological features. The batch experiments revealed that 300 min of contact time was enough to achieve equilibrium for the adsorption of both phenol and nickel at an initial adsorbate concentration of 25 mg/l, an adsorbent dosage of 5 g/l, and a solution pH of 7. The adsorption of phenol and nickel by MWCNTs followed the pseudo-second order kinetic model and the intraparticle diffusion model was quite good in describing the adsorption mechanism. The Langmuir equilibrium model fitted well the experimental data indicating the homogeneity of the adsorbent surface sites. The maximum Langmuir adsorption capacities were found to be 32.23 and 6.09 mg/g, for phenol and Ni ions, respectively. The removal efficiency of MWCNTs for nickel ions or phenol in real wastewater samples at the optimum conditions reached up to 60% and 70%, respectively.

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Introduction

Industrial effluents contribute largely to environmental pollution problem. These effluents contain a variety of organic and inorganic pollutants. Among these pollutants phenol and nickel(II) are frequently encountered together in wastewaters such as from metal plating, dye and painting industries [1,2]. The maximum allowable concentration of nickel in effluents in the United States from the electroplating process wastewater is 4.1 mg/l [3] while that in drinking water should be less than 0.5 mg/l [4]. For phenol, the US Environmental Protection Agency (USEPA) regulations call for lowering its content in wastewater to less than 1 mg/l [5]. As per the World Health Organization regulation, the permissible limit for phenol concentration in potable water is 0.002 mg/l [6].

The presence of nickel ions and phenol in an aqueous environment causes a worldwide concern due to their toxicity...
and carcinogenicity, which may result in damage to various systems of the human body [7].

Various conventional methods were designed and used to remove nickel ions and phenol from aqueous solutions such as adsorption, precipitation and coagulation, ion exchange, filtration, membrane separation, chemical oxidation, sedimentation, and reverse osmosis. Adsorption process is commonly applied because of its ease of application as well as its cost effectiveness [8].

In the recent years, carbon nanotubes have emerged as highly effective adsorbents for wastewater treatment. Carbon nanotubes (CNTs) discovered by Iijima in 1991 [9] are characterized by their unique structural, mechanical, chemical and physical properties [10]. The known ability of CNTs to establish π–π electrostatic interactions and their large surface areas can facilitate the adsorption of many kinds of pollutants from water [11]. CNTs have been proven to be superior adsorbent for removing many kinds of organic and inorganic pollutants [11,12]. CNTs display high distinctive surface areas and symbolize a new kind of adsorbent that offers a good option for removing various pollutants such as Ni(II) metallic ions [13] and phenol [14] from polluted water.

The objective of the present study was to investigate the adsorption capability of multiwalled carbon nanotubes (MWCNTs) for the removal of phenol and nickel ions from their individual and mixed aqueous solutions under different experimental conditions. The effects of contact time, initial pH, adsorbents loading weights, and initial nickel ions and phenol concentrations on the adsorption capacity of MWCNTs were investigated. The kinetics and equilibrium models of nickel and phenol adsorption onto MWCNTs were also studied.

Material and methods

**Multiwalled carbon nanotubes**

MWCNTs were purchased from Nanostructured & Amorphous Materials Inc. (820 Kristi Lane, Los Alamos, NM 87544, USA). The physical properties of the MWCNTs are listed in Table 1.

**Chemicals**

Analytical grade nickel nitrate (Merck Ltd., Taipei, Taiwan, 96–97% purity) and phenol (Fluka, 99.5%) were employed to prepare the stock solutions containing 1 g L\(^{-1}\) of Ni(II) and phenol, respectively. These stock solutions were further diluted using deionized water to the desired single or mixed nickel and phenol concentrations. HCl and NaOH used to adjust solutions pH were obtained from Sigma–Aldrich Company.

**Adsorbent characterization**

The adsorbent surface functional groups were determined by FTIR analysis, over the range of 500–4000 cm\(^{-1}\) with a resolution of 4 cm\(^{-1}\) using a Nicolet, AVATAR FTIR-370 Csl instrument. The microstructure of the adsorbent was examined using a Scanning electron microscopy (SEM, Quanta 250-FEI). The surface elemental composition analyses were proposed based on X-ray Powder Diffractometer (model ARL X’ TRA 156, Thermo Fisher Scientific Inc, USA). Thermogravimetric analysis of the adsorbent was also carried out using a thermogravimetric analyzer (TGA-Q500). pH was measured using pH meter (ORION model 420A) Thermo Scientific, USA.

**Adsorption experiments**

Batch adsorption studies were carried out at room temperature. The effect of contact time on phenol and nickel removal was investigated by mixing a known volume of phenol and/or nickel solution with a known adsorbent weight in stopped conical flasks for different time intervals (30–900 min). The solution-adsorbent mixtures were stirred at 100 rpm in a shaking water bath at 25 °C. At the end of each time interval the samples were filtered through Whatman No. 50 filter paper (2.7 μm size particle retention) to eliminate any fine particles. In all experiments blank measurements were taken.

The effect of each of the operational parameters affecting phenol and nickel ions adsorption was studied. Batch studies were performed as function of adsorbent dosage ranging from (0.2–1 g), solution pH (2–8) and adsorbate concentrations (5–100 mg/l) in separate experiments.

The concentration of phenol was determined using a double beam UV–vis spectrophotometer (Shimadzu UV-1601 Spectrophotometer, Japan) at 270 nm and nickel ions concentration was measured using an atomic absorption spectrometer (Shimadzu AA-6300) at 232 nm.

 Phenol and nickel removal percentages were determined using equation

\[
\text{Removal} \% = \left( \frac{C_i - C_f}{C_i} \right) \times 100
\]

where \(C_i\) and \(C_f\) are the initial and final concentrations of phenol and nickel (mg/l) in the solution.

Adsorption capacity was calculated using equation

\[
q = \left( \frac{C_i - C_f}{V/W} \right)
\]

where \(q\) is the adsorption capacity (mg g\(^{-1}\)), \(C_i\) is the initial adsorbate concentration in solution (mg/g), \(C_f\) is the equilibrium adsorbate concentration (mg/l), \(V\) is the volume of adsorbate solution (L) and \(W\) is the weight of the adsorbent (g).

The kinetics of phenol and nickel removal from aqueous solution by MWCNTs was studied by applying the pseudo-first-order [15] and pseudo-second-order [16] models. The adsorption mechanism was also investigated using the intra-particle diffusion model [17,18].

The equations describing the three studied models are presented by the following equations:

\[
\ln(q_e - q_t) = \ln q_e - k_1 t
\]
Adsorption of phenol and nickel onto carbon nanotubes

\[ t/q_t = 1/k_2 q_e^2 + t/q \quad (4) \]

\[ q_t = k_0 t^{1/2} + C_{b0} \quad (5) \]

where \( q_e (\text{mg} \text{ g}^{-1}) \) and \( q_t (\text{mg} \text{ g}^{-1}) \) are the amounts of nickel ions (or phenol) adsorbed at equilibrium and at time \( t \), respectively, \( k_1 (\text{min}^{-1}) \) is the pseudo first order rate constant and \( k_2 (\text{g} \text{ mg}^{-1} \text{ min}^{-1}) \) is the rate constant of the second order equation. \( k_0 \) is the intra-particle diffusion parameter, and \( C_{b0} \) is the thickness of the boundary layer at stage \( t \).

Adsorption isotherm studies were also carried out using the Langmuir [19] Eq. (6) and Freundlich [20] Eq. (7) isothermal models.

\[ q_e = C_e/q_e = 1/bq_{\text{max}} + C_e/q_{\text{max}} \quad (6) \]

\[ q_e = K_f C_e^{1/n} \quad (7) \]

where \( q_e \) and \( C_e \) represent the adsorbent capacity at equilibrium (\( \text{mg} \text{ g}^{-1} \)) and the concentration of nickel (or phenol) at equilibrium (\( \text{mg/l} \)), respectively. In the Langmuir equation, \( q_{\text{max}} \) is considered the maximum sorption capacity related to the total cover of the surface and \( b \) is associated with sorption energy. From the Freundlich model, \( K_f \) represents the sorption capacity and \( 1/n \) is related to the energy distribution of the sorption sites.

**Competitive adsorption studies**

Following the procedure given by Tang et al. [21]; the competitive adsorption experiments were performed when both adsorbates were adsorbed onto MWCNTs simultaneously. In the competitive adsorption studies, the concentration of Ni(II) and phenol in their mixed solution was varied between 25 and 100 mg/l (for both adsorbates). The competitive studies were performed at the optimum previously achieved operating conditions.

**Results and discussion**

**Characterization**

Generally, the adsorption ability of MWCNTs was known to be attributed to its surface chemical composition and rich surface area [22]. Fig. 1 shows the X-ray diffraction patterns of raw MWCNTs.

From Fig. 1 it can be seen that the diffractogram of raw MWCNTs exhibits the typical peaks at 20 around 26.5° and 42.7°, corresponding to the normal structure of graphite (002) and (100) reflections (Joint Committee for Powder Diffraction Studies (JCPDS) No. 01-0646) respectively [22]. Similar findings were reported by Chen et al. [23], Gupta et al. [24], Oh et al. [25] and Chen & Oh [26].

Scanning electron microscopy (SEM) imaging was also used to characterize the surface morphology of multiwalled carbon nanotubes. Fig. 2 displays the SEM images of raw MWCNTs. It is evident from the figure that the MWCNTs are cylindrical in shape, curved and tangled together [18,27]. The length of the raw MWCNTs is in the range of 5–15 μm.

TG–DTG analysis of the MWCNTs was obtained by heating the samples from 30 to 900 °C at a ramping rate of 10 °C/min under nitrogen gas atmosphere. TGA analysis was performed to estimate the homogeneity of the raw MWCNTs and its thermal stability [27].

Fig. 3 displays the TGA results of raw MWCNTs. It is evident that MWCNTs are considerably stable and show a little weight loss close to 4.37% below 550 °C. Then MWCNTs decomposed in one stage until they are completely decomposed around 720 °C [18,21,27]. The obvious weight loss over the range of 550–720 °C was caused by the oxidation of the nanotubes [28].

Fig. 4 presents the FTIR spectra of (a) raw MWCNTs, (b) phenol-loaded MWCNTs, (c) Ni(II)-loaded MWCNTs and (d) phenol and Ni(II)-loaded MWCNTs. As seen from Fig. 4(a), the spectra of raw MWCNTs exhibit a broad absorption band at around 3423 cm⁻¹ corresponding to (OH) stretching vibration of the surface hydroxyl groups [24,29]. The two observed peaks at 2924 and 2855 cm⁻¹ are somewhat weak and could be attributed to SP3 (C–H) stretching vibration motions [30], originated from the surface of tubes [24] or of the sidewalls [31].

The small band at around 1650 cm⁻¹ could be attributed to the presence of COO, C=O stretching mode of functional groups on the surface of raw MWCNTs and can also indicate the bending vibration of adsorbed water or arising from the
The absorption of atmospheric CO$_2$ on the surface of MWCNTs [24]. The peaks between 1000 and 1380 cm$^{-1}$ can be attributed to C=O stretching of COOH and O=H bending modes of alcoholic, phenolic and carboxylic groups [29]. In addition, sharp band at 1380 cm$^{-1}$ confirmed the existence of a C=O bond on raw MWCNTs, reinforcing the interaction with carboxylate groups [22].

The changes in the surface functional groups of raw MWCNTs after adsorption of phenol and nickel ions were also confirmed by FTIR spectra through the changes in the positions of some the peaks as well as the appearance of some new peaks.

The stretching band of C=C at 1420 cm$^{-1}$ on raw MWCNTs got split into 1419 and 1461 cm$^{-1}$ when both phenol and nickel ions were individually adsorbed and was shifted to 1456 cm$^{-1}$ when they were simultaneously adsorbed.

Fig. 4(b–d) displays new peaks in the range of around 2340–2360 cm$^{-1}$ that were absent in the spectra of raw MWCNTs. These peaks can be related to O=H stretch.
from strong H-bonded—COOH [30]. These peaks at 2340–
2360 cm⁻¹ could also be assigned to CO₂ that was absorbed
during the realization of the FTIR spectra.

The emerging peaks at wave numbers 1742 and 1740 cm⁻¹
are associated with C=O (carbonyl groups) stretching mode
of carboxylic acid in case the Ni(II) is adsorbed alone or
together with phenol, respectively [22].

The new peaks around 400–870 cm⁻¹ in case of Ni(II)-
adsorbed MWCNTs and phenol and Ni(II)-adsorbed
MWCNTs were assigned to the strong bonding between the
metal ions and the nanotube through oxygen-containing
functional groups [32]. The new absorption peaks at ~400–
870 cm⁻¹ in Fig. 4(c and d) were attributed to Ni−O stretch,
suggesting the formation of nickel oxides on the surface of
MWCNTs.

FTIR spectra showed that raw MWCNTs are mainly com-
posed of polymeric OH groups, CH₂ and COO groups. Accord-
ing to Machado et al. [33] these functional groups (OH, COOH,
C=O, etc.) played an important role in adsorption due to their
electrochemical properties. These oxygen-containing func-
tional groups can provide numerous adsorption sites and thus
increase the adsorption capacity for phenol molecules and
nickel ions [29].

**Effect of contact time and adsorption kinetics**

The effect of contact time on the removal percentage of phenol
and Ni(II) by adsorption onto MWCNTs was studied at differ-
tent time intervals (from 30 to 900 min) at room temperature
(Fig. 5). The other experimental factors were kept constant
at an initial phenol and Ni(II) concentration of 25 mg/l, an
adsorbent dosage of 5 g/l, and at a solution pH = 7. The
results showed that the removal of both adsorbates increased
gradually until equilibrium was reached after 300 min. Thus
this contact time was used in subsequent experiments.

The adsorption kinetic data of phenol and nickel ions onto
MWCNTs were analyzed using three different kinetic models:
the Lagergren pseudo-first-order model [15], the pseudo-
second-order model [16] and Weber and Morris intra-particle
diffusion model [17,18] represented by Eqs. (3)–(5); respectively.

The linear plots of log (qe−qt) versus t for different concen-
trations of nickel ions (or phenol) are shown in Fig. 6. The
obtained values of k₁, calculated qₑ values and determination
coefficients $R^2$ for adsorption of nickel ions (or phenol) on
MWCNTs are given in Table 2.

The Lagergren model’s $R^2$ value for adsorption of phenol
was found to be relatively high >0.94 and the experimental
$qₑ$ value was found to be in good agreement with that calcu-
lated $qₑ$ value obtained from the linear Lagergren plots.

These results may be used as indication for the applicability
of Lagergren equation to phenol adsorption on MWCNTs.
Thus it can be concluded that the adsorption of phenol
on MWCNTs follows the Lagergren first order kinetics and the
process depends on both the solution concentration and the
number of available adsorption sites [34].

On the other hand, the line obtained for adsorption of
Ni(II) showed a poor fitting with relatively low $R^2$ value
(≤0.81) and notable variances between the experimental and
theoretical amount of nickel ions. The obtained results indicate
that the pseudo-first-order equation was not appropriate for
describing the adsorption of the target nickel ions by
MWCNTs.

In many adsorption processes, the Lagergren pseudo-first-
order equation did not fit well the whole range of contact time
and was generally applicable over the initial stage (20–30 min)
of the adsorption processes [35]. Kinetic data were further
treated with the pseudo-second-order kinetic model [36].

For many adsorbate–adsorbent systems, where both physical
and chemical adsorption occurs, the adsorption data are
well correlated by the pseudo-second-order equation [37].
The integral form of the model represented by Eq. (4) predicts
that the ratio of the time/adsorbed amount should be a linear
function of time [38].

By applying the pseudo-second-order rate equation to the
experimental data for the adsorption of phenol and Ni(II)
Fig. 7 was obtained.
The pseudo-second-order rate equation parameters calculated from the slope and intercept of the plot of \((t/q_t)\) vs. \((t)\) are presented in Table 2. It is clear from the data that all of the experimental data had good determination coefficient values \((R^2)\), which indicates the suitability of the pseudo-second-order rate equation for the description of the adsorption of the target metal ions and phenol from aqueous solutions by MWCNTs.

The amounts of phenol and nickel ions adsorbed per unit mass of MWCNTs at equilibrium \((q_e)\), calculated from the slope of the plot of \(t/q_t\) vs. \(t\), were in good agreement with experimental values. The above results suggested that the pseudo-second order adsorption mechanism was prevalent for the adsorption phenol and Ni(II) by MWCNTs [36,39].

Also, according to Wu et al. [40] the pseudo-second-order model was suitable for the adsorption of low molecular weight adsorbate on smaller adsorbent particles, which could explain for its applicability in this study. The suitability of the pseudo-second-order rate equation for the adsorption of phenol and Ni(II) by MWCNTs agreed well with many previous studies [18,41].

The similar phenomena have also been observed in the adsorption of phenol on activated carbons prepared from beet pulp [42], plum kernels [43] and rattan sawdust [44]. Also, the pseudo-second-order rate equation was reported to fit the kinetics of Ni(II) sorption onto sphagnum moss peat [39], Azaadirachta indica (leaf powder) [45] and meranti sawdust [46].

The mechanism by which phenol and Ni(II) are adsorbed from aqueous solutions by MWCNTs was investigated using the intra-particle diffusion model. Since neither the pseudo-first-order nor the pseudo-second-order kinetic models can identify the diffusion mechanism, the kinetic results were then analyzed by using the intra-particle diffusion model to determine the diffusion mechanism. A Plot between \((q_t)\) versus \((t^{1/2})\) representing the intra-particle diffusion model is given in Fig. 8.

The values of \(k_{(i)}\) and \(C_{(b(i))}\) can be calculated from the slope and intercept, respectively, and the results are tabulated in Table 3. From Table 3 it can be observed that high determination coefficient values \((R^2 > 0.95)\) were obtained for the intra-particle diffusion model suggesting the applicability of the model for describing the adsorption of phenol and Ni(II) onto MWCNTs.

### Table 2

| Adsorbate | First-order kinetic model | Pseudo-second-order model |
|-----------|---------------------------|---------------------------|
|           | \(k_1\) (min\(^{-1}\))  | \(q_{(e)}\) (mg/g) | \(R^2\) | \(\Delta q\) | \(k_2\) (g/mg min) | \(q_{(e)\text{calc}}\) (mg/g) | \(R^2\) | \(\Delta q\) |
| Phenol    | 0.005                     | 3.72                      | 0.939 | 0.640 | 3.03 \times 10^{-3} | 4.10 | 0.994 | 0.26 | 4.36 |
| Ni(II)    | 0.01                      | 7.41                      | 0.805 | -3.290 | 5.5 \times 10^{-5} | 4.29 | 0.963 | 0.17 | 4.12 |

Fig. 7  Pseudo-second order kinetics for the adsorption of (a) phenol and (b) Ni(II) onto MWCNTs.

Fig. 8  Intra-particle diffusion mechanism for the adsorption of (a) phenol and (b) Ni (II) onto MWCNTs.
As seen from Fig. 8, multi-linear plots with two linear portions were obtained for the adsorption of phenol and Ni(II) from aqueous solution onto MWCNTs. The initial or first stage may be attributed to the effect of boundary layer (external mass transfer) diffusion, i.e. surface adsorption while the second stage may also be due to intra-particle diffusion effects [47].

The nonzero intercepts of the plots in each case were a clear indication that the rate-controlling process is not only due to the intra-particle diffusion some other mechanism along with intra-particle diffusion is also involved in the adsorption process [48].

Effect of pH

The solution pH affects both the surface charge of the adsorbent and the degree of ionization and speciation of the adsorbate [8]. In the present study the pH was varied between of 2 to 8 and higher pH values were omitted to avoid hydroxide precipitation of nickel ions. The other experimental parameters were kept constant e.g. contact time (300 min), adsorbent dosage (5 g/l) and adsorbate concentration (25 mg/l). Fig. 9 illustrates the effect of solution pH on the removal of nickel ions and phenol from their solutions. It was found that the removal percentage of Ni(II) increased as the solution pH increased due to the increase in the electrostatic attractive forces between OH– and Ni²⁺ [8].

According to Chen et al. [23] as pH increases, the adsorbent functional groups are progressively deprotonated, forming negative oxidized MWCNTs charge. The attractive forces between the anionic surface sites and cationic metal ions easily result in the formation of metal–ligand complexes.

It is known that divalent metal ions (M²⁺) can be present in deionized water in the forms of M²⁺, M(OH)⁺, M(OH)₂⁺, M(OH)₃⁻, etc. [11,13]. At a pH ≤ 8, the predominant nickel species is always Ni²⁺. Thus, the fact that more Ni²⁺ sorption took place at a higher pH could be attributed to a decrease in competition between H⁺ and Ni²⁺ at the same sorption site of MWCNTs. Furthermore, the surface of MWCNTs is more negatively charged at a higher pH, which causes a more electrostatic attraction of Ni²⁺.

From Fig. 9 it can be also noticed that the removal of phenol by MWCNTs increased by increasing the solution pH from 2 to 7 and decreased thereafter. At pH 7 the maximum removal of phenol by MWCNTs, was found to be approximately 87.5%. The dependence of phenol removal on the solution pH could be explained in term of both the adsorbent surface charge and the adsorbate species present in solution.

From Fig. 10 it can be concluded that the MWCNTs have a pHPZC equal to 6 and the adsorbent surface charge is positive at pH < 6 whereas at pH > 6 the surface charge is negative. On the other hand the pKa value of phenol is 9.99 hence below this pH phenol is considered a neutral molecule and above this value is found as anionic species [14]. Thus at low pH values the surface charge is positive and the H⁺ ion concentration in solution is high, therefore competition between H⁺ and phenol species could occur [14] which cause a low adsorption of phenol by MWCNTs. At pH 7 where the maximum phenol removal was achieved, the adsorbent surface is negatively charged and neutral phenol species are present in solution. Therefore, there is no repulsion between phenol and the adsorbent, and their interaction can happen in a free way through π electrons [14].

Based on the above results, pH value of 7 was kept constant in the subsequent experiments to ensure maximum removal of both phenol and nickel ions.

Equilibrium modeling

Equilibrium study on adsorption provides information on the adsorbent capacity. In the present study, Langmuir and Freundlich sorption isotherm models were used to determine
the model that best fits the experimental data of nickel and phenol adsorption onto MWCNTs.

The constants of the Langmuir and Freundlich models for nickel and phenol adsorption onto MWCNTs were obtained from the plots presented in Figs. 11 and 12 and their values are summarized in Table 4. It was observed that the Langmuir isotherm better described the adsorption of phenol with the higher determination coefficient $R^2$ close to 1 (0.990), suggesting that homogeneous sorption on the surfaces of MWCNTs occurred. These results were consistent with many previous works where the Langmuir isotherm was more suitable than the Freundlich isotherm for the adsorption of phenol on various adsorbent, as activated carbons [49], dried aerobic activated sludge [1], Schizophyllum commune fungus [50], activated carbon prepared from biomass material [44] and activated carbon produced from avocado kernel seeds [51].

Also, adsorption data for Ni(II) were better fitted with the Langmuir isotherm (0.983), from which it could be assumed that the adsorbed Ni(II) formed monolayer coverage on the adsorbent surface and all adsorption sites were equal with uniform adsorption energies without any interaction between the adsorbed molecules. Similar results have also been observed by earlier researchers [23,29].

The value of constant $b$, which is related to free energy of sorption, in the Langmuir isotherm played an important role to simulate the concentration at which the phenol amount is bound and indicates the affinity for the binding of phenol. A high $b$ value indicates a high affinity [1]. The $b$ values of phenol and Ni(II) are 3.17 and 2.82 (L mg$^{-1}$), respectively, which indicates that the bonding of phenol on MWCNTs is much stronger than that of Ni(II).

**Simultaneous adsorption between phenol and Ni(II)**

Competitive adsorption of phenol and Ni(II) was evaluated when both adsorbates were adsorbed simultaneously on MWCNTs (Fig. 13).

![Simultaneous adsorption](image)

**Table 4** Langmuir and Freundlich parameters for phenol and Ni(II) adsorption by MWCNTs.

| Adsorbate | Lagmuir model | Freundlich model |
|-----------|----------------|------------------|
|           | $q_{max}$ (mg g$^{-1}$) | $b$ (L mg$^{-1}$) | $R^2$ | $K_f$ | $n$ | $R^2$ |
| Phenol    | 32.25          | 3.17             | 0.990 | 1.11  | 1.76 | 0.896 |
| Ni (II)   | 6.09           | 2.82             | 0.983 | 1.07  | 4.48 | 0.871 |

![Langmuir isotherm](image)

**Fig. 11** Langmuir isotherm for the adsorption of phenol and Ni(II) onto MWCNTs (pH:7; biomass weight: 0.25 g/50 mL; shaking speed: 100 rpm; temp.: 25 °C).

![Freundlich isotherm](image)

**Fig. 12** Freundlich isotherm for the adsorption of phenol and Ni(II) onto MWCNTs (pH:7; biomass weight: 0.25 g/50 mL; shaking speed: 100 rpm; temp.: 25 °C).

![Simultaneous adsorption](image)

**Fig. 13** Simultaneous adsorption of phenol and Ni(II) by MWCNTs.
The results showed that increasing the concentration of nickel from 25 mg/l to 50 mg/l resulted in about 51% decrease in phenol removal. This can be attributed to the formation of inner-sphere and outer-sphere complexes of Ni(II) through carboxylic groups and hydration on the surfaces of MWCNTs and the existence of small and compact metal cation hydration shells on metal chelates indirectly competed with phenol for sorption sites through squeezing, occupying and shielding part of the MWCNTs hydrophilic and hydrophobic sites [52].

It was also noticed that although the increase in phenol concentration from 25 to 50 mg/l resulted in small reduction in nickel removal but further increase in phenol concentration resulted in 69% reduction in nickel adsorption. These results suggest that the presence of either one of the adsorbates (Ni(II) or phenol) in the solution had a suppression effect on the other adsorbate sorption. This can be ascribed to the occurrence of a direct competition between phenol and Ni(II) for certain adsorption sites on MWCNTs [52]. Similar findings were reported by Aksu and Apmar [1] for the adsorption of phenol and nickel ions by dried activated sludge.

### Comparison with other adsorbents

The sorption capacities of phenol and Ni(II) on MWCNTs were compared with other previously adsorbents reported in the literature as given in Table 5.

It was noticed that in most cases MWCNTs had higher removal efficiency for both phenol and Ni(II) in our experiments than in case of many other adsorbents, which could be attributed to its relatively larger specific surface area. Despite this, a major advantage of being effectively and conveniently separated from solution and considerably higher uptake capacity than many other adsorbents made MWCNTs a promising and excellent adsorbent to remove phenol and Ni(II) simultaneously in terms of potential application in wastewater treatment.

### Real industrial effluent treatment

In order to evaluate the efficiency of MWCNTs for phenol and nickel removal from wastewater samples, an optimized procedure was used to conduct an experiment with real industrial effluents of chemicals and engineering companies in Abu-Zabal industrial area in Egypt. The removal efficiency of MWCNTs for nickel ions or phenol in wastewater samples at the optimum conditions reached up to 60% and 70%, respectively. It can be concluded that there was a slight decrease in the removal percentages of phenol and nickel by MWCNTs in real effluents compared to synthetic water. This waive in the removal efficiency can be attributed to the matrix composition of the real effluents which are likely to contain other pollutants that can compete with phenol and nickel to the MWCNTs adsorption sites.

### Conclusions

The multiwalled carbon nanotubes used in the present study have been proven to have higher adsorption capacities for the removal of phenol and nickel ions from aqueous solutions. The optimum conditions for the adsorption process were found to be 300 min for contact time, a solution pH equal to 7 and adsorbent dose of 5 g/L. The kinetics of the adsorption was described by the pseudo-second-order model and the isothermal Langmuir model was the best to describe the equilibrium of both adsorbates. The competitive adsorption results revealed that lower adsorption capacities as compared to the individual adsorption results. Comparing the present study results with the results of other adsorbents collected from literature. The desorption of both adsorbates from MWCNTs reached up to 75% using NaOH (1 M) indicating the possibility of the adsorbent reusability.

It can be concluded that the multiwalled carbon nanotubes offer a new and highly effective adsorbent that can be applied to wastewater treatment systems.

### Conflict of interest

The authors have declared no conflict of interest.

### Compliance with Ethics Requirements

This article does not contain any studies with human or animal subjects.

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**Table 5** Maximum sorption capacities of phenol and nickel ions with MWCNTs and other sorbents.

| Sorbents                     | Maximum sorption capacities ($q_{\text{max}}$) (mg g$^{-1}$) | References |
|------------------------------|-------------------------------------------------------------|------------|
| Phenol                       | Ni (II)                                                     | References |
| MWCNTs                       | 32.25                                                       | Present work |
| MWCNTs                       | 6.09                                                        | 53         |
| PHHEMA microbead modified Cibacron blue | 8.30                                                        | 54         |
| PHHEMA microbead modified alkali blue 6B | 13.60                                                       | 55         |
| Samla coal                   | 13.30                                                       | 56         |
| Natural coal                 | 18.80                                                       | 57         |
| Activated coal               | 1.48                                                        | 58         |
| Kaolinite                    | 1.67                                                        | 59         |
| Chitosan                     | 2.40                                                        | 60         |
| Chabazite                    | 4.50                                                        | 61         |
| Chabazite–phillipsite        | 0.56                                                        | 62         |
| Activated carbon (AC) cloths: CS 1501 | 5.80                                                        | 63         |
| Grapefruit peel              | 46.13                                                       | 64         |
| Treated algae                | 40.9                                                        | 65         |

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The authors have declared no conflict of interest. This article does not contain any studies with human or animal subjects.
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