Development of a Toxic Lead Ionic Sensor Using Carboxyl-Functionalized MWCNTs in Real Water Sample Analyses

Hadi M. Marwani 1,2, Jahir Ahmed 3,4 and Mohammed M. Rahman 1,2,*

1 Chemistry Department, Faculty of Science, King Abdulaziz University, P.O. Box 80203, Jeddah 21589, Saudi Arabia
2 Center of Excellence for Advanced Materials Research (CEAMR), King Abdulaziz University, P.O. Box 80203, Jeddah 21589, Saudi Arabia
3 Promising Centre for Sensors and Electronic Devices (PCSED), Advanced Materials and Nano-Research Centre, Najran University, P.O. Box 1988, Najran 11001, Saudi Arabia
4 Department of Chemistry, Faculty of Science and Arts, Najran University, P.O. Box 1988, Najran 11001, Saudi Arabia
* Correspondence: mmrahman@kau.edu.sa

Abstract: Functional multiwall carbon nanotubes (f-MWCNTs) are of significant interest due to their dispersion ability in the aqueous phase and potential application in environmental, nanotechnology, and biological fields. Herein, we functionalized MWCNTs by a simple acid treatment under ultrasonification, which represented a terminal or side-functional improvement for the fabrication of a toxic lead ion sensor. The f-MWCNTs were characterized in detail by XRD, Raman, XPS, BET, UV/vis, FTIR, and FESEM-coupled XEDS techniques. The analytical performance of the f-MWCNTs was studied for the selective detection of toxic lead ions by inductively coupled plasma-optical emission spectrometry (ICP-OES). The selectivity of the f-MWCNTs was evaluated using several metal ions such as Cd\(^{2+}\), Co\(^{2+}\), Cr\(^{3+}\), Cu\(^{2+}\), Fe\(^{3+}\), Ni\(^{2+}\), Pb\(^{2+}\), and Zn\(^{2+}\) ions. Lastly, the newly designed ionic sensor was successfully employed to selectively detect lead ions in several environmental water samples with reasonable results. This approach introduced a new technique for the selective detection of heavy metal ions using functional carbon nanotubes with ICP-OES for the safety of environmental and healthcare fields on a broad scale.

Keywords: f-MWCNT; lead ions; ICP-OES; selectivity; real samples; environmental safety

1. Introduction

Recently, carbon nanotubes (CNTs) have become an interesting material in fundamental research due to their versatile applications such as miniaturized bio-electronic devices and the detection of carcinogenic metallic ions. Their small dimensions, as well as the extraordinary physical properties of functionalized multiwalled carbon nanotubes (f-MWCNTs), has made them an excellent material for multipurpose applications [1]. Since the discovery of CNTs in 1991, they have been introduced as a new subject in many studies in chemical, physical, sensor, adsorption, and material science fields owing to their unique structural, mechanical, electronic, and electrochemical properties [2–6]. Based on their diameter and chirality, CNTs can electrically behave either as a metal or a semiconductor [7]. Functionalized multiwalled carbon nanotubes (f-MWCNTs) have drawn huge attention in the last few years. Research works regarding the promising application of f-MWCNTs are considered to be crucial. Recent developments in sensitive and effective techniques have become important to monitor toxic metals in the environment. Several analytical techniques have been utilized to determine heavy metals from aqueous systems such as atomic absorption spectrometry [8], inductively coupled plasma-optical emission spectrometry (ICP-OES) [9], anodic stripping voltammetry [10], ion chromatography [11],
and electrochemical methods [12,13]. However, metal ions cannot be directly determined from aqueous systems by these analytical methods, especially with ultra-low levels of metal ions, because of poor sensitivity and selectivity. Consequently, an appropriate separation step is often necessary before the detection of metal ions [14]. Many extraction techniques of the analyte of interest can be implemented before the detection of metal ions with suitable analytical techniques such as liquid–liquid extraction [15], ion exchange [16], co-precipitation [17], cloud point extraction [18], and solid-phase extraction (SPE) [19,20]. Among them, SPE is recognized as the most popular method due to less solvent usage, the disposal costs, and the extraction time in the sample preparation. Due to the attractiveness of SPE in selective analyte extractions, many adsorbents have been used, including alumina [21], C18 [22], molecular imprinted polymers [23], cellulose [24], silica gel [25], activated carbon [26,27], and CNTs [28].

Nanoscale materials have also attracted considerable interest owing to their prospective application in fabricating opto-electronics, electro-analytics, the selective detection of metal ions, opto-electronics, biological devices, nanocomposites, electron-field emission sources for emission exhibits, chemical detections, and surface-enhanced Raman properties [29–31]. They have typical morphological structures that are composed of a number of regular phases, with geometrically controlled metals as well as oxide atoms along the axes. Here, we prepared functionalized multiwalled carbon nanotubes; in the preparation method, there were several advantages such as a low-temperature preparation and an accurate control of the stoichiometry. They were also easy to handle with a one-step reaction and a high porosity as well as a high surface area. The optical, morphological, electrical, and chemical properties of nanoscale carbon nanomaterials are of huge significance from scientific aspects [32–34]. In nanostructure materials, the doped material has a large band gap (E_{bg}), which, in its non-stoichiometric form, exhibits a non-insulating nature. Non-stoichiometry, mostly oxygen vacancies, forms its conducting nature. The formation energy of oxygen vacancies and metal interstitials in metal oxides is very low; thus, these defects eagerly form, resulting in the experimental elevated conductivity of the nanoscale substrates [35,36]. Electrical properties such as the charge carrier concentration and conductivity can further be enhanced by extrinsic transition metallic dopants into the nanomaterials. There are many reports in the literature that highlight the sensing properties of pure and doped/undoped materials [37,38]. However, to date, there are no reports focusing on the adsorption properties of the uptake of metal ions (lead toxic ions) on carboxylic functional carbon nanotubes in the aqueous phase.

Generally, carbon nanoscale materials such as carbon nanotubes (CNTs), graphene (G), fullerene, and carbon nanofibers play a significant role in the detection of analytes for the safety of environmental and healthcare fields. Amongst them, multiwalled carbon nanotubes (MWCNTs) are a promising material for the fabrication of electrochemical sensors in room conditions owing to their large specific surface area, excellent electrical conductivity, rapid electrode kinetics, and high chemical stability [39]. To improve the sensor probe performance (such as the selectivity, long-term stability, linear dynamic range, and sensitivity), composites of two or more materials and the functionalization of carbon nanotubes have been explored for electrode modifications to study the potential synergistic effects. A higher peak current could be obtained through the proper selection of composite components with functionalized carbon materials, compared with each material or unfunctionalized carbon material working alone [40]. Until today, several methods (e.g., hydrothermal, solution, sol–gel, and sono-chemical) have been utilized for the preparation of functional carbon composites.

Therefore, in this work, we devoted ourselves to investigating the analytical ability of f-MWCNTs as the selective extractor of lead ions before detection with ICP-OES. The selectivity of the f-MWCNTs using several metal ions such as Cd²⁺, Co²⁺, Cr³⁺, Cu²⁺, Fe³⁺, Ni²⁺, Pb²⁺, and Zn²⁺ was investigated to study the efficiency of the f-MWCNTs in the selective detection of metal ions. The selectivity study data revealed that the f-MWCNTs showed the most selective behavior toward lead ions than other metal ions. The
adsorption capacity for Pb$^{2+}$ ions was experimentally found to be $\approx 77.12 \text{ mg g}^{-1}$. We also investigated the analytical parameters. The adsorption isotherm results also established that this adsorption process formed a monolayer onto a perfectly homogeneous surface with a finite number of identical sites. For the first time, a new route for the uptake of selective heavy metal ions with functionalized carbon materials with ICP-OES for the safety of environmental and healthcare fields on a broad scale is introduced.

2. Experiment

2.1. Materials and Methods

For the experiment, we purchased reagents (reagent grade) of 97% H$_2$SO$_4$, 60% HNO$_3$, 98% Triton X-100, and 30% H$_2$O$_2$ from the Showa Chemical Company (Tokyo, Japan); these were used as received without further purification. We used deionized (DI) distilled water (resistivity $> 18.0$ MΩ cm) to prepare the different solutions. We purchased standard stock solutions of 1000.0 mg L$^{-1}$ Cd$^{2+}$, Co$^{2+}$, Cr$^{3+}$, Cu$^{2+}$, Fe$^{3+}$, Ni$^{2+}$, Pb$^{2+}$, and Zn$^{2+}$ from Sigma-Aldrich (USA). All reagents used in this work were highly pure. We recorded the FTIR spectrum of the f-MWCNTs using a Bruker spectrophotometer. The morphology of the f-MWCNTs was studied by an FESEM instrument (JSM-7600F, Tokyo, Japan). An energy dispersive X-ray analysis (XEDS) was examined for the f-MWCNTs using an FESEM-coupled XEDS from JEOL (Tokyo, Japan). The X-ray photoelectron spectroscopy (XPS) measurements were executed on a Thermo Scientific K-Alpha KA1066 spectrometer (NY, USA) for the f-MWCNTs. In the optical analysis, a monochromatic AlKa X-ray radiation source was used as the excitation source; the beam spot size was kept at 300.0 μm. The spectra were recorded in the fixed analyzer transmission mode, where the pass energy was kept at 200.0 eV. The scanning of the spectra was performed at pressures less than 10–8 Torr. The UV/vis spectrum of the f-MWCNTs was recorded using a Lambda-950 (Perkin Elmer, Berlin, Germany). The ICP-OES investigations were performed using a Perkin Elmer ICP-OES model Optima 4100 DV (NY, USA). The BET analysis for the pore-size distributions and the surface area of the f-MWCNTs for different nitrogen gas loadings was performed with a Quantachrome. The parameters for the BET analysis are given here.

Sample weight: 0.0075 g; outgas time, 4.0 h; analysis gas, N$_2$; pressure tolerance, 0.100/0.100 (ads/des); analysis time, 602.4 min; sample volume, 0.0025 cc; outgas temp, 250.0 °C; bath temp, 77.3 K; equil. time, 60/60 (ads/des); sample density, 0.806 g/cc. DFT: N$_2$ at 77.0 K on carbon (slit pore, NLDFT equilibrium model); release pressure range, 0.0000–1.0000. Adsorbate: nitrogen gas; cross section, 16.200; liquid density, 0.806 g/cc.

We optimized the ICP-OES instrument every day immediately before the measurements. It was operated as per the manufacturer’s recommendations. The ICP-OES spectrometer was used with the following parameters: FR power, 1300 kW; frequency, 27.12 MHz; demountable quartz torch, Ar/Ar/Ar; plasma gas (Ar) flow, 15.0 L min$^{-1}$; auxiliary gas (Ar) flow, 0.2 L min$^{-1}$; nebulizer gas (Ar) flow, 0.8 L min$^{-1}$; nebulizer pressure, 2.4 bar; glass spray chamber according to Scott (Ryton) sample pump flow rate, 1.5 mL min$^{-1}$; integration time, 3 s; replicates, 3; wavelength range of monochromator, 165–460 nm. Selected metal ions were measured at wavelengths of 228.80 nm for Cd(II), 238.90 nm for Co(II), 267.72 nm for Cr(III), 327.39 nm for Cu(II), 259.94 nm for Fe(III), 221.65 nm for Ni(II), 220.35 nm for Pb(II), and 206.20 nm for Zn(II).

2.2. Preparation and Purification of the f-MWCNTs

Generally, carbon nanotubes are pure although a few nanoparticles might be present in the as-procured sample as a by-product. MWCNTs can exist in isolated units or as nanotubes in a bundled arrangement; we did not take any steps to separate them. The refinement of common CNTs is important as most of the CNT applications require a
high-purity material. An acid treatment is the most usual means to purify CNTs and has been recognized as the first step in the numerous purification schemes. A nitric acid treatment is commonly used for removing the metal catalysts and amorphous carbons [41]. Additionally, it also oxidizes the terminal carbon atoms. Sonivating the CNTs in nitric acid opens the terminal carbons [42]; hence, -COOH groups at the ends or the defect sites of CNTs are introduced [43]. We functionalized the MWCNTs with -COOH groups using a nitric acid treatment. Briefly, we ultra-sonically dispersed the MWCNTs in 5.0 M nitric acid for 6.0 min. We then diluted it using a large volume of water and added a little Triton X-100 to enhance the solubility. We continued the sonication process until it became a black solution. Later, we collected the f-MWCNTs by filtration using a 0.2 µm diameter film.

We repeated these steps twice. The evidence for the formation of a functional carboxyl group on the f-MWCNTs was exhibited by FTIR spectroscopy (a broad peak appeared at 1712 cm⁻¹).

2.3. Sample Preparation and Procedure

Stock solutions of Cd²⁺, Co²⁺, Cr³⁺, Cu²⁺, Fe³⁺, Ni²⁺, Pb²⁺, and Zn²⁺ were prepared using 18.2 MΩ·cm DI water and stored at 4.0 °C in a dark place. In the selectivity study of the f-MWCNT system toward different metal ions, we prepared 5.0 mg L⁻¹ of a standard solution for each metal ion and adjusted the pH to 5.0 using an acetate buffer. We mixed 25.0 mg of the f-MWCNTs with each of the standard solutions separately. We used a pH value of 5.0 for all metal ions to avoid precipitation, particularly for Fe³⁺ due to the formation of an Fe(OH)₃ precipitate at higher pH values. To investigate the Pb²⁺ adsorption capacity, standard solutions of 0, 5.0, 10.0, 15.0, 20.0, 25.0, 30.0, 50.0, 70.0, 85.0, 125.0, and 150.0 mg L⁻¹ were also prepared as mentioned above; the pH value was adjusted to 5.0 and separately mixed with 25.0 mg f-MWCNTs. We shook all mixtures for 1.0 h at 150 rpm in ambient conditions. The effect of the contact time on the uptake of the f-MWCNTs for the Pb²⁺ ion was investigated using the same batch conditions but at different equilibrium periods (2.5, 5, 10, 20, 30, 40, 50, and 60 min).

3. Results and Discussion

3.1. Evaluation of the Spectral Analysis

To evaluate the physical activity of the f-MWCNTs, we recorded the optical absorption spectra in the range of 200.0–800.0 nm in ambient conditions. In the UV/vis spectroscopic technique, the outer electrons from the active materials undergo an electronic transition from low to high energy states by absorbing the radiant energy [44,45]. Herein, we used the optical absorption band to estimate the band gap energy ($E_{bg}$) of the f-MWCNTs. It was revealed that the maximum absorption of the radiation occurred at ~316.5 nm (Figure 1a). The $E_{bg}$ was calculated as ~3.9 eV based on the absorption band of the f-MWCNTs using Equation (1):

$$E_{bg} = \frac{1240}{\lambda} \text{ (eV)}$$

where $\lambda$ is the wavelength (~316.5 nm) at which the maximum absorption occurred. The absence of additional peak(s) related to impurities indicated that the functionalization process controlled the crystallinity of the f-MWCNTs [46].

The Raman spectroscopic technique is a versatile tool to characterize CNTs. All allotropes of carbon (such as fullerens, CNTs, amorphous carbon, and polycrystalline carbon) are Raman-active [47]. The position, width, and relative intensity of the bands are modified based on the types of carbon [48–51]. The tangential mode (TM) in the range of 1400–1700 cm⁻¹ provides information regarding the electronic properties. The D-band that appears at 1361 cm⁻¹ provides information regarding the disordered carbon. The D-band to TM band ratio is a qualitative measure for the formation of undesirable forms of carbon [52,53]. Herein, we used a 788 nm (semiconductor sapphire laser) excitation. This provided the most direct evidence of the f-MWCNTs directly observed from the Raman spectrum. In the Raman spectrum of the f-MWCNTs (and as shown in Figure 1b), the
G-band at 1599 cm\(^{-1}\) appeared from the graphitic sheet structures \([54,55]\) and the D-band at 1361 cm\(^{-1}\) correlated with the defects in MWCNTs \([54,55]\). Therefore, we concluded that there was no change in the physical structure of the MWCNTs during the functionalization process except for the opened ends.

We also recorded the FTIR spectrum of the f-MWCNTs to identify the different functional groups attached to the f-MWCNT surface \([56–58]\). FTIR spectroscopy has been extensively used in the structural determination of molecules. Figure 1c shows comparative FTIR data for the refluxed samples. As observed in the prepared sample, there was a signal with a small C-C stretch (1598 cm\(^{-1}\)). With the acid treatment, a number of new peaks appeared. The bands due to the C=O stretch were prominently seen at 1712 cm\(^{-1}\) for the carboxylated MWCNTs. The sample refluxed in 3:1 H\(_2\)SO\(_4\):HNO\(_3\) acid for 6–7 h showed a distinct band at 1712 cm\(^{-1}\), which could be assigned to the acid carbonyl-stretching mode (Figure 1c). Another band exhibited in this functionalized sample was at 3396 cm\(^{-1}\), which was characteristic of O-H stretches. C-C vibrations occurred due to internal defects and the O-H vibration was associated with the amorphous carbon because amorphous carbon easily forms a bond with atmospheric air. However, the intensity of this O-H peak was relatively lower and showed that a lesser amount of amorphous carbon formed during the growth \([59]\). The peak at 1598 cm\(^{-1}\) could be associated with the stretching of the carbon

Figure 1. Typical (a) UV/vis, (b) Raman, and (c) FTIR spectra of the f-MWCNTs.
nanotube backbone [60]. Thus, the evidence for the formation of a functional carboxyl group (with a peak at 1712 cm\(^{-1}\)) on the MWCNTs was investigated by FTIR spectroscopy.

3.2. Evaluation of the Structural and Morphological Analysis

As in recent articles [61,62], the diffraction patterns of the wall of the f-MWCNTs also displayed a peak of 26.1° at 2\(\theta\) as shown in Figure 2a. This peak could be related to the (002) lattice plane [48,52]. The XRD pattern of the f-MWCNTs was similar to that of the pristine MWCNTs [53]. Therefore, we concluded that the f-MWCNTs still possessed the same cylindrical-walled structure and inter-planner spacing as the pristine MWCNTs even after the functionalization process. Hence, the structural property of the f-MWCNTs remained the same even after the acid treatment, as confirmed by the previous XRD investigation [63]. The diameter of the f-MWCNTs was also calculated using the Scherrer Equation [64–67]:

\[
D = \frac{0.9\lambda}{\beta\cos \theta}
\]

where \(\lambda\) is the wavelength of X-ray radiation and \(\beta\) is the full width at half maximum (FWHM) of the peaks at the diffracting angle \(\theta\). The average diameter of the f-MWCNTs was obtained as \(~11.2\ nm\).

![Figure 2. Typical (a) powder XRD and (b,c) low to high magnified FESEM images of the f-MWCNTs.](image-url)
High-resolution FESEM images of the f-MWCNTs (low and higher magnification) are presented in Figure 2b,c. The FESEM images revealed that aggregated functional materials existed in tube shapes. The average diameter of the f-MWCNTs was estimated to be 5.0 to 20.0 nm, which was close to ~11.9 nm. The FESEM images showed that the f-MWCNTs had a regular tube shape with high-density material. Therefore, the nitric acid treatment of the MWCNTs caused severe etching on the graphitic surface, producing shorter tubes with a huge number of disordered sites [68]. The analysis of the FESEM images of the f-MWCNTs allowed a trustworthy length measurement of the nanotubes; these measured values were between 5.0 and 20.0 nm, identical to those for pristine MWCNTs according to the literature [69].

3.3. Evaluation of the Elemental Analysis

The XEDS investigation confirmed the existence of C and O elements in the f-MWCNTs, as shown in Figure 3a. The weight percent compositions of C and O were 94.55% and 5.45%, respectively. The XEDS spectrum and corresponding elemental analysis data are presented in Figure 3b. The absence of any other extra peaks in the XEDS spectrum confirmed the purity of the f-MWCNTs. After the functionalization of the MWCNTs, the as-obtained final product—f-MWCNTs—contained an oxygen element in the nanotubes, which confirmed the formation of carboxylic groups (-COOH) in the carbon nanotubes.

![Typical XEDS measurements for the f-MWCNTs](image)

**Figure 3.** Typical XEDS measurements for the f-MWCNTs: (a) selected area for the XEDS measurements; (b) XEDS spectrum with elemental compositions.
3.4. Evaluation of the Binding Energy Analysis

XPS investigations were performed to further confirm the elemental compositions and chemical states of the different elements present in the f-MWCNTs. Figure 4a shows the spin–orbit peak of the C1s binding energy that appeared at around 285.1 eV, which was well-matched with the literature [48,52,53,70]. The asymmetric XPS peak for O1s appeared at 532.7 eV, as shown in Figure 4b, and confirmed the existence of oxygen in the f-MWCNTs [71–74]. The full-scan XPS spectrum of the f-MWCNTs, as shown in Figure 4c, clearly showed two distinct peaks for C1s and O1s. Therefore, we concluded that the f-MWCNTs contained only two different elements; this was also supported by the XRD, Raman, and FTIR investigations.

![Typical XPS spectra showing the binding energy (B.E.) for (a) C1s level, (b) O1s level, and (c) f-MWCNT level acquired from MgKα1 radiation.](image)

3.5. Evaluation of the BET Analysis

The Brunauer–Emmett–Teller (BET) theory explains the physical adsorption of nitrogen gas on mesoporous functionalized carbon nanotubes and thus measures the specific surface area of f-MWCNTs. The average pore diameter and specific surface area (BET: surface area and pore volume) were measured for the f-MWCNTs using a Quantachrome NOVA 1000 (NY, USA). To observe whether any changes to the physical structure of the f-MWCNTs occurred, we investigated the specific surface area (adsorption/desorption...
isotherms) and the pore-size distribution using a multipoint BET analysis. Figure 5a shows that the specific surface area of the f-MWCNTs was 222.450 m$^2$/g and Figure 5b shows the pore-size distribution. This high surface area originated from the formation of nanopores accessible to nitrogen gas, leading to an amplified capacitance of the f-MWCNTs. The experimental results showed that changes in the conditions during the acid treatment of MWCNTs greatly affected the specific surface area and pore-size distribution of the f-MWCNTs, as displayed in Figure 5 (adsorption/desorption isotherms in Figure 5a and size distribution plot in Figure 5b).

![Figure 5](image_url)

**Figure 5.** BET analysis: (a) surface area and (b) pore-size distribution of the f-MWCNTs for different nitrogen gas loadings.

The selectivity investigations for the f-MWCNT phase toward different metal ions were performed using the batch adsorption method. The selectivity was also investigated using the distribution coefficient ($K_d$), which could be calculated by Equation (3) [75]:

$$K_d = \frac{(C_o - C_e)}{C_e} \times \frac{V}{m}$$

where $C_o$ and $C_e$ are the initial and final concentrations before and after filtration with the f-MWCNTs, respectively, $V$ is the volume (mL), and $m$ is the weight of the f-MWCNTs.
3.6. Lead Ion Detection Using f-MWCNTs with ICP-OES (Static Adsorption Method)

3.6.1. Selectivity Study of the f-MWCNTs

The selectivity investigations for the f-MWCNT phase toward different metal ions were performed using the batch adsorption method. The selectivity was also investigated using the distribution coefficient \(K_d\) for the f-MWCNT phase, which could be calculated by Equation (3) [75]:

\[
K_d = \left( \frac{C_o - C_e}{C_o} \right) \times \frac{V}{m}
\]

where \(C_o\) and \(C_e\) are the initial and final concentrations before and after filtration with the f-MWCNTs, respectively, \(V\) is the volume (mL), and \(m\) is the weight of the f-MWCNT phase (g). Table 1 shows the calculated \(K_d\) values for all metal ions, which revealed that the \(\text{Pb}^{2+}\) ion had a greater \(K_d\) value than the other metal ions. A scheme representing the \(\text{Pb}^{2+}\) ion adsorption onto the surface of the f-MWCNTs with comparative schemes using real FESEM images is displayed in Figure 6, which shows the FESEM images of the f-MWCNTs before (Figure 6(a,a1)) and after (Figure 6(b,b1)) the adsorption of the \(\text{Pb}^{2+}\) ions. The FESEM image of the f-MWCNTs again revealed an aggregated tube-shaped morphology with a high density. A dwindle image was observed after the \(\text{Pb}^{2+}\) adsorption onto the f-MWCNT surface and the edges of the tubes were not clearly visible (Figure 6(b1)). We also proposed that approximately all the \(\text{Pb}^{2+}\) ions adsorbed onto the aggregated functional nanotubes were composed of a large surface area. The lead ions were adsorbed onto the functional as well as the defect sites of the f-MWCNTs. With the ICP-OES method, the detection responses of the \(\text{Pb}^{2+}\) ions using the f-MWCNTs were clearly demonstrated; these are presented in Figure 6c.

| Metal Ion | \(q_e\) (mg g\(^{-1}\)) | \(K_d\) (mL g\(^{-1}\)) |
|-----------|-----------------|--------------|
| \(\text{Pb}^{2+}\) | 4.99 | 7.13 \times 10^5 |
| \(\text{Cd}^{2+}\) | 3.74 | 2.97 \times 10^3 |
| \(\text{Cr}^{3+}\) | 3.69 | 2.81 \times 10^3 |
| \(\text{Cu}^{2+}\) | 3.49 | 2.31 \times 10^3 |
| \(\text{Fe}^{3+}\) | 3.27 | 1.89 \times 10^3 |
| \(\text{Zn}^{2+}\) | 2.93 | 1.42 \times 10^3 |
| \(\text{Co}^{2+}\) | 2.63 | 1.11 \times 10^3 |
| \(\text{Ni}^{2+}\) | 0.91 | 2.22 \times 10^2 |

Therefore, based on the above results, we concluded that the selectivity of the f-MWCNT phase toward the \(\text{Pb}^{2+}\) ions was greater than all other metal ions. Thus, the f-MWCNT phase could selectively detect \(\text{Pb}^{2+}\) ions, providing that the mechanism of adsorption was an electrostatic attraction or a complex formation.

3.6.2. Static Adsorption Capacity of the f-MWCNTs

To estimate the uptake capacity of the \(\text{Pb}^{2+}\) ions onto the f-MWCNT phase, 25.0 mL \(\text{Pb}^{2+}\) ion samples with varying concentrations (0–150.0 mgL\(^{-1}\)) were adjusted to pH 5.0 and separately mixed with 25.0 mg of the f-MWCNTs. These mixtures were mechanically shaken for 1.0 h in ambient conditions. The static adsorption capacity was calculated using Equation (4):

\[
q_e = \frac{(C_o - C_e)V}{m}
\]

where \(q_e\) is the adsorbed \(\text{Pb}^{2+}\) ions onto the f-MWCNT phase (mg g\(^{-1}\)); \(C_o\) and \(C_e\) represent the initial and equilibrium concentrations of the \(\text{Pb}^{2+}\) ions (mgL\(^{-1}\)), respectively; \(V\) refers
to the volume (L); and \( m \) is the weight of the \( f \)-MWCNT phase (g). Figure 7 displays the \( \text{Pb}^{2+} \) ion adsorption profile and the calibration curve based on the experimental adsorption isotherms. The adsorption capacity and sensitivity of the \( f \)-MWCNTs in the \( \text{Pb}^{2+} \) ion detection reached 77.12 mg g\(^{-1}\) and 0.8513 L g\(^{-1}\), respectively, which were comparable with the literature regarding \( \text{Pb}^{2+} \) ion detection by other methods (32.75 [76], 49.9 [77], 54.48 [78], 82.66 [79], 90.25 [80], 97.08 [81], and 114.05 mg g\(^{-1}\) [82]) (Table 2). The linear dynamic range from the calibration plot was obtained as 0 to 85.0 mg L\(^{-1}\).

Figure 6. Schematic representation and FESEM images of (a) before and (b) after \( \text{Pb}^{2+} \) adsorption on the \( f \)-MWCNTs. (c) \( \text{Pb}^{2+} \) ion detection with the ICP-OES method using the functionalized MWCNTs.

Figure 7. (a) Adsorption profile and (b) calibration curve (for sensitivity) of \( \text{Pb}^{2+} \) ions in 25.0 mg of the \( f \)-MWCNT phase in relation to the concentration at pH 5.0 and 25.0 °C.
Table 2. Comparative study of lead metal ion uptake capacity with ICP-OES using various nanocomposite materials.

| Materials            | Methods | Detection Limit | Adsorption Capacity | References |
|----------------------|---------|-----------------|---------------------|------------|
| MWCNTs–5-ASA         | ICP-OES | 0.25 ng mL⁻¹    | 32.75 mg g⁻¹        | [76]       |
| AC–EDA               | ICP-OES | 0.17 ng mL⁻¹    | -                   | [77]       |
| EDA–MWCNTs           | ICP-OES | 0.35 ng mL⁻¹    | -                   | [78]       |
| CuO–ZnO NCs          | ICP-OES | -               | 82.66 mg g⁻¹        | [79]       |
| SG-1,10-PhenanNTf₂   | ICP-OES | -               | 5.89 mg g⁻¹         | [80]       |
| MWCNTs               | ICP-OES | -               | 97.08 mg g⁻¹        | [81]       |
| Co₃O₄–TiO₂ NPs       | ICP-OES | -               | 114.05 mg g⁻¹       | [82]       |

3.6.3. Adsorption Isotherm Models of the f-MWCNTs

The experimental results for the adsorption of Pb²⁺ ions onto the f-MWCNT phase were studied by common models to interpret the equilibrium isotherm data. The Langmuir equation is effective in monolayer sorption onto a completely homogeneous surface with a finite number of identical sites and a negligible interaction between the adsorbed molecules. The Langmuir adsorption isotherm model is presented by Equation (5) [83]:

\[ \frac{C_e}{q_e} = \left( \frac{C_o}{Q_o} \right) + \frac{1}{Q_o b} \]  

where \( C_e \) is the equilibrium concentrations of the Pb²⁺ ions (mgmL⁻¹) and \( q_e \) is the adsorbed Pb²⁺ ions by the f-MWCNTs (mgg⁻¹). The symbols \( Q_o \) and \( b \) refer to the Langmuir constants related to the adsorption capacity (mgg⁻¹) and energy of adsorption (Lmg⁻¹), respectively. These constants can be calculated using the linear plot of \( C_e/q_e \) vs. \( C_e \), where the slope and intercept are equal to \( 1/Q_o \) and \( 1/Q_o b \), respectively. The important features of the Langmuir adsorption isotherm model can be expressed using an equilibrium parameter \( (R_L) \), where \( R_L = \frac{1}{1 + bC_o} \). Here, \( b \) is the Langmuir constant that specifies the nature of adsorption and the shape of the isotherm; \( C_o \) refers to the initial concentration of the analytes. The \( R_L \) value offers information regarding the type of adsorption isotherm; its value lies between 0 and 1, suggesting an encouraging adsorption [84].

The experimental isotherm data were the best fit with the Langmuir equation (Figure 8a) based on the least squares fit, confirming the validity of the Langmuir adsorption isotherm model for this adsorption process. This revealed that the adsorption process in this study was primarily a monolayer formation onto a homogeneous adsorbent surface. Langmuir constants \( Q_o \) and \( b \) were obtained as 77.30 mgg⁻¹ and 0.57 Lmg⁻¹, respectively. The regression coefficient for the Langmuir model was obtained as \( R^2 = 0.9970 \) during the Pb²⁺ ion adsorption onto the f-MWCNTs. Furthermore, the calculated Pb²⁺ ion adsorption capacity (77.30 mgg⁻¹) obtained from the Langmuir equation was consistent with that of the experimental isotherm study (77.12 mgg⁻¹). The \( R_L \) value of the Pb²⁺ ion adsorption onto the f-MWCNTs was 0.01, suggesting a very favorable adsorption process based on the Langmuir classical adsorption isotherm model.

3.6.4. Effect of the Shaking Time

The effect of the contact time was examined to confirm the applicability of the f-MWCNTs to the selective adsorption of Pb²⁺ ions and to estimate the time required to establish the equilibrium. A batch process was employed for varying contact times (2.5 to 60.0 min) using a fixed concentration of 125.0 mgL⁻¹ Pb²⁺ ions, as illustrated in Figure 8b. A close investigation, as presented in Figure 8b, demonstrated that the adsorption of Pb²⁺ ions onto the f-MWCNT phase was significantly improved with the increasing contact time. Over 65.0 mgg⁻¹ Pb²⁺ ions were adsorbed onto the f-MWCNTs in just 10 min of the equilibrium period. The loading capacity of the Pb²⁺ ions was also raised to
more than 72.0 mg g\(^{-1}\) after 30 min until the maximum adsorption of the Pb\(^{2+}\) ions onto the f-MWCNTs was reached after 60 min. Therefore, we concluded that the equilibrium kinetics for the adsorption of Pb\(^{2+}\) ions onto the f-MWCNT phase were very fast.

Figure 8. (a) Langmuir adsorption isotherm model; (b) effect of the shaking time on adsorption; (c) pseudo-second-order adsorption kinetic model of Pb\(^{2+}\) ion adsorption upon the 25.0 mg f-MWCNT phase at pH 5.0 and 25.0 °C. Adsorption experiments were performed using varying concentrations (0–150.0 mg L\(^{-1}\)) of Pb\(^{2+}\) ions under static conditions.

3.6.5. Kinetic Model Analysis

To obtain the kinetic adsorption parameters, we investigated several kinetic models. Kinetic models were used to check how properly they fitted with the experimental data, where the regression coefficient (\(R^2\)) was a measure of agreement between the experimental data and the models. The kinetics for pseudo-second-order adsorption were presented by Equation (6):

\[
\frac{t}{q_t} = \frac{1}{v_o} + \left(\frac{1}{q_e}\right)t
\]

where \(v_o = k_2q_e^2\) denotes the initial adsorption rate (mg g\(^{-1}\) min\(^{-1}\)); \(k_2\) (g mg\(^{-1}\) min\(^{-1}\)) represents the rate constant of the adsorption; \(q_e\) (mg g\(^{-1}\)) is the amount of metal ions adsorbed at the equilibrium; and \(q_t\) (mg g\(^{-1}\)) refers to the amount of metal ions on the
adsorbent surface at any time \( t \) (min). The parameters \( q_e \) and \( v_o \) could be obtained from the slope and intercept of a plot of \( t/\dot{q}_t \) vs. \( t \), respectively [85].

The adsorption kinetics data were well-matched with the pseudo-second-order model, suggesting that the kinetics of Pb\(^{2+}\) ion adsorption onto the f-MWCNTs obeyed pseudo-second-order kinetics (Figure 8c). The \( R^2 \) value (0.998) also supported that the pseudo-second-order model was better than other kinetic models. Parameters \( v_o, q_e, \) and \( k_2 \) were calculated as 47.84 mg g\(^{-1}\) min\(^{-1}\), 78.29 mg g\(^{-1}\), and 0.01 g mg\(^{-1}\) min\(^{-1}\), respectively. The value of \( q_e \) was consistent with the results of the adsorption isotherms, supporting the validity of the Langmuir adsorption isotherm model. In this approach, we found the highest results to the lead ion uptake were with the ICP-OES technique with carboxylic functional MWCNTs compared with other nanostructure materials [86–96].

3.6.6. Real Sample Analysis

To confirm the applicability of this proposed method, the f-MWCNTs were employed to determine the Pb\(^{2+}\) ions from real water samples. A standard addition method was used to verify the precision of the Pb\(^{2+}\) ion extraction from four different water samples such as drinking water, lake water, seawater, and tap water collected from Jeddah in Saudi Arabia. The percent extraction of the different amounts of Pb\(^{2+}\) ions (1.0, 5.0, and 10.0 mg L\(^{-1}\)) using real water samples were determined (Table 3). The recovery test results showed that the extraction of Pb\(^{2+}\) ions from spiked water samples was acceptable and thus revealed that this method was suitable for analyzing real samples.

Table 3. Determination of Pb\(^{2+}\) at different concentrations in real water samples using 25.0 mg of f-MWCNTs (\( N = 3 \)).

| Samples       | Added (mg L\(^{-1}\)) | Not Adsorbed (mg L\(^{-1}\)) | Extraction (%) |
|---------------|-----------------------|-----------------------------|---------------|
| Tap water     | 1                     | 0.02                        | 98.10         |
|               | 5                     | 0.15                        | 96.94         |
|               | 10                    | 0.45                        | 95.49         |
| Lake water    | 1                     | 0.03                        | 96.90         |
|               | 5                     | 0.20                        | 95.92         |
|               | 10                    | 0.62                        | 93.84         |
| Seawater      | 1                     | 0.04                        | 96.40         |
|               | 5                     | 0.21                        | 95.70         |
|               | 10                    | 0.82                        | 91.85         |
| Drinking Water| 1                     | 0.01                        | 99.20         |
|               | 5                     | 0.10                        | 97.96         |
|               | 10                    | 0.31                        | 96.95         |

4. Conclusions

Herein, we functionalized MWCNTs by an acidic treatment. The as-obtained f-MWCNTs were characterized by XRD, BET, FESEM, XPS, XEDS, UV/vis, and FTIR spectroscopy. The detailed crystalline and morphological evaluations of XRD and FESEM demonstrated that the f-MWCNTs were almost tube-shaped, with carboxylic functional groups with typical average diameters of ~11.2 nm. The specific surface area was also investigated by a BET analysis and was found to be 222.45 m\(^2\)/g by using the physical adsorption of nitrogen gases. The analytical efficiency of the f-MWCNT phase for the selective adsorption and detection of Pb\(^{2+}\) ions in an aqueous solution was studied. The Pb\(^{2+}\) ion static uptake capacity of 77.12 mg g\(^{-1}\) with f-MWCNTs adsorbent in aqueous media was reasonable. The sensitivity and linear dynamic ranges of the f-MWCNTs as a lead sensor were calculated from a calibration plot and were 0.8513 Lg\(^{-1}\) and 0–85.0 mg L\(^{-1}\), respectively. This proposed method provided reasonable results for the selective detection of toxic lead ions from spiked real water samples. Therefore, the method may be recognized as an efficient route in the selective detection of lead ions from complex matrices.
Author Contributions: Methodology, H.M.M. and J.A.; Formal analysis, J.A. and M.M.R.; Investigation, M.M.R.; Resources, H.M.M.; Data curation, H.M.M.; Writing—original draft, M.M.R.; Writing—review & editing, H.M.M. and J.A.; Funding acquisition, H.M.M. All authors have read and agreed to the published version of the manuscript.

Funding: Deanship of Scientific Research (DSR) at King Abdulaziz University, Jeddah, under grant no. G: 058-130-1443.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Data will be available upon reasonable request.

Acknowledgments: This project was funded by the Deanship of Scientific Research (DSR) at King Abdulaziz University, Jeddah, under grant no. G: 058-130-1443. The authors acknowledge with thanks the DSR for technical and financial support.

Conflicts of Interest: The authors declare no conflict of interest.

References
1. Iijima, S. Helical microtubules of graphitic carbon. *Nature* **1991**, *354*, 56–58. [CrossRef]
2. Ahmed, J.; Rakib, R.H.; Rahman, M.M.; Asiri, A.M.; Siddiquey, I.A.; Islam, S.M.M.; Hasnat, M.A. Electrocatalytic Oxidation of 4-Aminophenol Molecules at the Surface of an FeS$_2$/Carbon Nanotube Modified Glassy Carbon Electrode in Aqueous Medium. *ChemPlusChem* **2019**, *84*, 175–182. [CrossRef] [PubMed]
3. Baughman, R.H.; Zakhidov, A.A.; Heer, W.A. Carbon Nanotubes—The Route towards Applications. *Science* **2002**, *297*, 787–792. [CrossRef]
4. Rahman, M.M.; Ahmed, J.; Asiri, A.M.; Siddiquey, I.A.; Hasnat, M.A. Development of highly-sensitive hydrazine sensor based on facile CoS$_2$-CNT nanocomposites. *RSC Adv.* **2016**, *6*, 90470–90479. [CrossRef]
5. Rahman, M.M.; Ahmed, J.; Asiri, A.M.; Siddiquey, I.A.; Hasnat, M.A. Development of 4-methoxyphenol chemical sensor based on NiS$_2$-CNT nanocomposites. *J. Taiwan Inst. Chem. Engr.* **2016**, *64*, 157–165. [CrossRef]
6. Rahman, M.M.; Ahmed, J.; Asiri, A.M. glassy carbon electrode modified with γ-Ce$_2$S$_3$-decorated CNT nanocomposites for uric acid sensor development: A real sample analysis. *RSC Adv.* **2017**, *7*, 14649–14659. [CrossRef]
7. Kim, P.; Odom, T.W.; Huang, J.-L.; Lieber, C.M. Electronic Density of States of Atomically Resolved Single-Walled Carbon Nanotubes: Van Hove Singularities and End States. *Phys. Rev. Lett.* **1999**, *82*, 1225–1228. [CrossRef]
8. Mohammadi, S.Z.; Afzali, D.; Pourtalebi, D. Flame atomic absorption spectrometric determination of trace amounts of lead, cadmium and nickel in different matrixes after solid phase extraction on modified multiwalled carbon nanotubes. *Cent. Eur. J. Chem.* **2010**, *8*, 662–668. [CrossRef]
9. Li, Y.; Hu, B. Cloud point extraction with/without chelating agent on-line coupled with inductively coupled plasma optical emission spectrometry for the determination of trace rare earth elements in biological samples. *J. Hazard. Mater.* **2010**, *174*, 534–540. [CrossRef]
10. Bonfil, Y.; Kirowa-Eisner, E. Determination of nanomolar concentrations of lead and cadmium by anodic-stripping voltammetry at the silver electrode. *Anal. Chim. Acta* **2002**, *457*, 285–296. [CrossRef]
11. Tanikkul, S.; Jakmunee, J.; Lapanantnoppakhun, S.; Rayanakorn, M.; Sooksamiti, P.; Synovec, R.E.; Christian, G.D.; Grudpan, K. Flow injection invalse mini-column pretreatment combined with ion chromatography for cadmium, lead and zinc determination. *Talanta* **2004**, *64*, 1241–1246. [CrossRef] [PubMed]
12. Katowah, D.F.; Hussein, M.A.; Alam, M.M.; Ismail, S.H.; Osman, O.I.; Sobahi, T.R.; Asiri, A.M.; Ahmed, J.; Rahman, M.M. Designed network of ternary core-shell PPCOT/NiFe$_2$O$_4$/C-SWCNTs nanocomposites. A Selective Fe$^{3+}$ ionic sensor. *J. Alloys Compd.* **2020**, *834*, 155020. [CrossRef] [PubMed]
13. Aqlan, F.M.; Alam, M.M.; Al-Bogami, A.S.; Saleh, T.S.; Wani, M.Y.; Al-Farga, A.; Asiri, A.M.; Karim, M.R.; Ahmed, J.; Fazal, M.A.; et al. Efficient electro-chemical sensor for sensitive Cd$^{2+}$ detection based on novel in-situ synthesized hydrazonoyl bromide (HB). *J. Mol. Struct.* **2021**, *1231*, 129690. [CrossRef]
14. Pyrzynska, K. Recent developments in the determination of gold by atomic spectrometry techniques. *Spectrochim. Acta Part B* **2005**, *60*, 1316–1322. [CrossRef]
15. Yamaguchi, N.S.; Sekine, T. Solvent extraction of copper (i) and (ii) as thiocyanate complexes with tetrabutylammonium ions into chloroform and with trioctylphosphine oxide into hexane. *Anal. Sci.* **1997**, *13*, 903–911.
16. Tao, G.H.; Fang, Z. Dual stage preconcentration system for flame atomic absorption spectrometry using flow injection on-line ion-exchange followed by solvent extraction. *J. Anal. Chem.* **1998**, *360*, 156–160. [CrossRef]
17. Soylak, M.; Erdogan, N.D. Copper (ii)–rubeanic acid coprecipitation system for separation–preconcentration of trace metal ions in environmental samples for their flame atomic absorption spectrometric determinations. *J. Hazard. Mater.* **2006**, *137*, 1035–1041. [CrossRef]
18. Manzoori, J.L.; Abdolmohammad-Zadeh, H.; Amjadi, M. Simplified cloud point extraction for the preconcentration of ultra-trace amounts of gold prior to determination by electrothermal atomic absorption spectrometry. *Mikrochim. Acta* 2007, 159, 71–78. [CrossRef]

19. Ahmed, S.A. Alumina physically loaded by thiosemicarbazide for selective preconcentration of mercury (ii) ion from natural water samples. *J. Hazard. Mater.* 2006, 156, 521–529. [CrossRef]

20. Montero Alvarez, A.; Estévez Alvarez, J.R.; Padilla Alvarez, R. Heavy metal analysis of rainwaters: A comparison of txf and asv analytical capabilities. *J. Radioanal. Nucl. Chem. Artic.* 2007, 273, 427–433. [CrossRef]

21. Al-Anghi, Y.M.; Kadi, M.; Ismail, I.M.; Gabal, M.A. Effect of alumina incorporation on restricting grain growth of nanocrystalline tin (iv) oxide. *Open Chem.* 2010, 8, 331–340. [CrossRef]

22. Pei, S.; Fang, Z. Flame atomic absorption spectrometric determination of silver in geological materials using a flow-injection system with on-line preconcentration by coprecipitation with diethylthithio-carbamate. *Anal. Chim. Acta* 1994, 294, 185–193. [CrossRef]

23. Cho, H.J.; Myung, S.-W. Determination of cadmium, chromium and lead in polymers by icp-oes using a high pressure asher (hpa). *Bull. Korean Chem. Soc.* 2011, 32, 489–497. [CrossRef]

24. de Castro, G.R.; de Alcântara, I.L.; dos Santos Roldan, P.; de Fátima Bozano, D.; de Magalhães Padilha, P.; de Oliveira Florentino, A.; Rocha, J.C. Synthesis, characterization and determination of the metal ions adsorption capacity of cellulose modified with p-amino benzenoic groups. *J. Mater. Res.* 2004, 7, 329–334. [CrossRef]

25. Liu, Y.; Guo, L.; Zhe, L.; Sun, X.; Chen, J. Removal of cr (iii, vi) by quaternary ammonium and quaternary phosphonium ionic liquids functionalized silica materials. *Chem. Eng. J.* 2010, 158, 108–114. [CrossRef]

26. Marwani, H.M.; Albishri, H.M.; Soliman, E.M.; Jalal, T.A. Selective Adsorption and Determination of Hexavalent Chromium in Water Samples by Chemically Modified Activated Carbon with Tris(hydroxymethyl)aminomethane. *J. Dispers. Sci. Technol.* 2012, 33, 549–555. [CrossRef]

27. Marwani, H.M.; Albishri, H.M.; Jalal, T.A.; Soliman, E.M. Activated carbon immobilized dithizone phase for selective adsorption and determination of gold (iii). *Desali. Water Treat.* 2012, 45, 128–135. [CrossRef]

28. Biparva, P.; Hadjmohammadi, M.R. Selective Separation/Preconcentration of Silver Ion in Water by Multiwalled Carbon Nanotubes Microcolumn as a Sorbent. *Clean-Sol Air Water* 2011, 39, 1081–1086. [CrossRef]

29. Pearton, J.S.; Heo, W.H.; Ivill, M.; Norton, D.P.; Steiner, T. Dilute magnetic semiconducting oxides. *Semicond. Sci. Technol.* 2004, 19, R59. [CrossRef]

30. Morales, J.; Sánchez, L.; Martín, F.; Ramos-Barrado, J.R.; Sánchez, M. Nanostructured CuO thin film electrodes prepared by spray pyrolysis: A simple method for enhancing the electrochemical performance of CuO in lithium cells. *Electrochimica Acta* 2004, 49, 4589–4597. [CrossRef]

31. Rahman, M.M.; Khan, S.B.; Marwani, H.M.; Asiri, A.M.; Alamry, K.A.; Rub, M.A.; Khan, A.A.P.; Qusti, A.H. Low dimensional Ni-ZnO nanoparticles as marker of toxic lead ions for environmental remediation. *J. Adv. Mat.* 2014, 5, 1071–1078. [CrossRef]

32. Prato, A.; Zambonin, F.; Ramos-Barrado, J.R.; Sánchez, M. Nanostructured CuO thin film electrodes prepared by spray pyrolysis: A simple method for enhancing the electrochemical performance of CuO in lithium cells. *Electrochimica Acta* 2004, 49, 4589–4597. [CrossRef]

33. Raula, M.; Rashid, H.; Paira, T.K.; Dinda, E.; Mandal, T.K. Ascorbate-Assisted Growth of Hierarchical ZnO Nanostructures: Sphere, Spindle, and Flower and Their Catalytic Properties. *Nanotechnology* 2010, 21, 255706. [CrossRef]

34. Vacca, R.; Goze, C.; Azzar, R.; Michiolet, V.; Journet, C.; Bernier, P. Purification procedure of carbon nanotubes. *Synth. Met.* 1999, 103, 2492–2493. [CrossRef]

35. Dujardin, E.; Ebbesen, T.W.; Krishnan, A.; Treacy, M.M. Wetting of Single Shell Carbon Nanotubes. *J. Adv. Mat.* 1998, 10, 1472–1475. [CrossRef]

36. Protsailo, L.F.; Fawcett, W.R. Electrochemical Impedance Spectroscopy at Alkanethiol-Coated Gold in Propylene Carbonate. *Langmuir* 2002, 18, 8933–8941. [CrossRef]
44. Ahmed, J.; Rahman, M.M.; Siddiquey, I.A.; Asiri, A.M.; Hasnat, M.A. Efficient Bisphenol-A detection based on the ternary metal oxide (TMO) composite by electrochemical approaches. *Electrochimica Acta* 2017, 246, 597–605. [CrossRef]
45. Ahmed, J.; Rahman, M.M.; Siddiquey, I.A.; Asiri, A.M.; Hasnat, M.A. Efficient hydroquinone sensor based on zinc, strontium and nickel based ternary metal oxide (TMO) composites by differential pulse voltammetry. *Sensors Actuators B Chem.* 2018, 256, 383–392. [CrossRef]
46. Du, N.; Zhang, H.; Wu, P.; Yu, J.; Yang, D. A General Approach for Uniform Coating of a Metal Layer on MWCNTs via Layer-by-Layer Assembly. *J. Phys. Chem. C* 2009, 113, 17387–17391. [CrossRef]
47. Zhang, H-B.; Lin, G-D.; Zhou, Z-H.; Dong, X.; Chen, T. Raman spectra of MWCNTs and MWCNT-based H₂-adsorbing system. *Carbon* 2002, 40, 2429–2436. [CrossRef]
48. Shah, S.S.A.; Najam, T.; Javed, M.S.; Rahman, M.M.; Tsiakaras, P. Novel Mn-/Co-Nx moieties captured in N-doped carbon nanotubes for enhanced oxygen reduction activity and stability in acidic and alkaline media. *ACS Appl. Mater. Interfaces* 2021, 13, 23191–23200. [CrossRef]
49. Rahman, M.M.; Alam, M.M.; Alamry, K.A. Sensitive and selective m-Tolylhydrazine sensor development based on CdO nanoparticles decorated multi-walled carbon nanotubes. *J. Ind. Eng. Chem.* 2019, 77, 309–316. [CrossRef]
50. Rahman, M.M.; Hussein, M.A.; Alamry, K.A.; Al-Shery, F.M.; Asiri, A.M. Polyaniiline/graphene/carbon nanotubes composites for sensing strongly alkaline environment. *Nano-Struct. Nano-Objects* 2018, 15, 63–74. [CrossRef]
51. Arepalli, S.; Nikolaev, P.; Gorelik, O.; Hadijev, V.; Holmes, W.; Files, B.; Yowell, L. Catalytic Effect of Dopants on Microstructure and Performance of MCMB-derived Carbonaceous Lamination. *Carbon* 2004, 42, 1983–1989.
52. Rahman, M.M.; Balkhoyor, H.B.; Asiri, A.M. Phenolic sensor development based on chromium oxide-decorated carbon nanotubes for environmental safety. *J. Environ. Manag.* 2017, 188, 228–237. [CrossRef] [PubMed]
53. He, X.; Xu, X.; Bo, G.; Yan, Y. Studies on the effects of different multiwalled carbon nanotube functionalization techniques on the properties of bio-based hybrid non-isocyanate polyurethane. *RSC Adv.* 2020, 10, 2180–2190. [CrossRef] [PubMed]
54. Ferrari, A.C.; Robertson, J. Interpretation of Raman spectra of disordered and amorphous carbon. *Phys. Rev. B* 2000, 61, 14095–14107. [CrossRef]
55. Basca, W.S.; Ugarte, D.; Chatelain, A. High-resolution electron microscopy and inelastic light scattering of purified multishelled carbon nanotubes. *Phys. Rev. B* 1994, 50, 15473.
56. Basca, W.S.; Ugarte, D.; Chatelain, A. High-resolution electron microscopy and inelastic light scattering of purified multishelled carbon nanotubes. *Phys. Rev. B* 1994, 50, 15473.

72. Subhan, A.; Saha, P.C.; Sumon, S.A.; Ahmed, J.; Asiri, A.M.; Rahman, M.M.; Al-Mamun, M. Enhanced photocatalytic activity and ultra-sensitive benzaldehyde sensing performance of a SnO$_2$-ZnO-TiO$_2$ nanomaterial. *RSC Adv.* **2018**, *8*, 33048–33058. [CrossRef] [PubMed]

73. Puglia, C.; Bennich, P.; Hasselström, J.; Brühwiler, P.; Nilsson, A.; Li, Z.; Rudolf, P.; Mårtensson, N. XPS and XAS study of oxygen coadsorbed with a dispersed phase of K on graphite. *Surf. Sci.* **2001**, *488*, 1–6. [CrossRef]

74. Rahman, M.M.; Ahmed, J.; Asiri, A.M. Thiourea sensor development based on hydrothermally prepared CMO nanoparticles for environmental safety. *Biosens. Bioelectron.* **2018**, *99*, 586–592. [CrossRef] [PubMed]

75. Soliman, E.M.; Marwani, H.M.; Albishri, H.M. Novel solid-phase extractor based on functionalization of multi-walled carbon nanotubes with 5-aminosalicylic acid for preconcentration of Pb (II) in water samples prior to determination by ICP-OES. *Environ. Monit. Assess.* **2013**, *185*, 10269–10280. [CrossRef] [PubMed]

76. Li, Z.; Chang, X.; Zhou, X.; Ni, R.; Hu, Z.; Li, R. Chemically-modified activated carbon with ethylenediamine for selective solid-phase extraction and preconcentration of metal ions. *Anal. Chem. Acta* **2009**, *632*, 272–277. [CrossRef] [PubMed]

77. Soliman, E.M.; Marwani, H.M.; Albishri, H.M. Novel solid-phase extractor based on functionalization of multi-walled carbon nanotubes with 5-aminosalicylic acid for preconcentration of Pb (II) in water samples prior to determination by ICP-OES. *Environ. Monit. Assess.* **2013**, *185*, 10269–10280. [CrossRef] [PubMed]

78. Li, Y.-H.; Ding, J.; Luan, Z.; Di, Z.; Zhou, Y.; Xu, C.; Wu, D.; Wei, B. Competitive adsorption of Pb$^{2+}$, Cu$^{2+}$ and Cd$^{2+}$ ions from aqueous solutions by multiwalled carbon nanotubes. *Carbon* **2003**, *41*, 2787–2792. [CrossRef] [PubMed]

79. Khan, A.; Marwani, H.M.; Asiri, A.M.; Rahman, M.M.; Marwani, H.M.; Alam, M.M.; Asiri, A.M.; Rahman, M.M. SDBS-functionalized MWCNT/poly(o-toluidine) nanocomposite for selective adsorption of lead ions from aqueous solutions by multiwalled carbon nanotubes. *Carbon* **2003**, *41*, 2787–2792. [CrossRef] [PubMed]

80. Subhan, A.; Saha, P.C.; Sumon, S.A.; Ahmed, J.; Asiri, A.M.; Rahman, M.M.; Al-Mamun, M. Enhanced photocatalytic activity and ultra-sensitive benzaldehyde sensing performance of a SnO$_2$-ZnO-TiO$_2$ nanomaterial. *RSC Adv.* **2018**, *8*, 33048–33058. [CrossRef] [PubMed]

81. Langmuir, I. The constitution and fundamental properties of solids and liquids. *J. Disp. Sci. Technol.* **2015**, *34*, 117–124. [CrossRef]

82. Rahman, M.M.; Khan, S.B.; Asiri, A.M.; Marwani, H.M.; Qusti, A.H. Selective detection of toxic Pb (ii) ions based on wet-chemically prepared nanosheets integrated CuO-ZnO nanocomposites. *Compos. Part B Eng.* **2013**, *54*, 215–223. [CrossRef]

83. Rahman, M.M.; Khan, S.B.; Asiri, A.M.; Marwani, H.M.; Qusti, A.H. Selective detection of toxic Pb (ii) ions based on wet-chemically prepared nanosheets integrated CuO-ZnO nanocomposites. *Compos. Part B Eng.* **2013**, *54*, 215–223. [CrossRef]

84. Han, D.M.; Fang, G.Z.; Yan, X.P. Preparation and evaluation of a molecularly imprinted sol-gel material for on-line solid-phase extraction coupled with high performance liquid chromatography for the determination of trace pentachlorophenol in water samples. *J. Chromatogr. A* **2005**, *1100*, 131–136. [CrossRef]

85. Ho, Y.-S. Second-order kinetic model for the sorption of cadmium onto tree fern: A comparison of linear and non-linear methods. *Water Res.* **2006**, *40*, 110–125. [CrossRef]

86. Khan, A.A.P.; Khan, A.; Alam, M.M.; Asiri, A.M.; Uddin, J.; Rahman, M.M. SDBS-functionalized MWCNT/poly(o-toluidine) nanocomposites for Lead ionic sensor development for the environmental remediation in real sample matrices. *Int. J. Environ. Sci. Technol.* **2019**, *16*, 182, 958–963. [CrossRef] [PubMed]

87. Khan, A.A.P.; Bazan, G.C.; Alhogbi, B.G.; Marwani, H.M.; Khan, A.; Alam, M.M.; Asiri, A.M.; Rahman, M.M. Nanocomposite cross-linked conjugated polyelectrolyte/MWCNT/poly(pyrrrole) for enhanced Mg$^{2+}$ ion sensing and environmental remediation in real samples. *J. Mater. Res. Technol.* **2020**, *9*, 9667–9674. [CrossRef]

88. Khan, A.A.P.; Khan, A.; Alam, M.M.; Asiri, A.M.; Oves, M. Lead sensors development and antimicrobial activities based on graphene oxide/carbon nanotube/poly(O-toluidine) nanocomposite. *Int. J. Biol. Macromol.* **2019**, *121*, 104585. [CrossRef] [PubMed]

89. Khan, A.A.P.; Khan, A.; Asiri, A.M.; Rahman, M.M. Surfactant-assisted graphene oxide/methyl-aniline nanocomposites for Lead ionic sensor development for the environmental remediation in real sample matrices. *Int. J. Environ. Sci. Technol.* **2019**, *16*, 8461–8470. [CrossRef]

90. Ghann, W.; Harris, T.; Kabir, D.; Kang, H.; Jiru, M.; Rahman, M.M.; Ali, M.M.; Uddin, J. Lipoic Acid Decorated Gold Nanoparticles and Their Application in the Detection of Lead Ions. *J. Nanomed. Nanotechnol.* **2019**, *10*, 539. [CrossRef] [PubMed]

91. Aqlan, F.M.; Alam, M.M.; Asiri, A.M.; Zayed, M.E.M.; Al-Zahrani, F.A.M.; El-Shishtawy, R.M.; Uddin, J.; Rahman, M.M. Fabrication of selective and sensitive Pb$^{2+}$ detection by 2,2′-(1,2-phenylenebis(azaneylidenedibis(methaneylidenedi))diphenol by electrochemical approach for environmental remediation. *J. Mol. Liq.* **2019**, *281*, 401–406. [CrossRef]