Air pollution Analysis: Nickel paste on Multi-walled carbon nanotubes as novel adsorbent for the mercury removal from air

Ali Ebrahimi a,* and Ahmad Salarifar b

a,* Occupational Health Engineering Department, School of Public Health, Qom University of Medical Sciences, Qom, Iran.

b Environmental Engineering, Faculty of Natural Resources, Islamic Azad University, Bandar Abbas Branch, Bandar Abbas, Iran

ARTICLE INFO:
Received 13 Jul 2019
Revised from 17 Aug 2019
Accepted 2 Sep 2019
Available online 28 Sep 2019

ABSTRACT
Mercury as a hazardous material can be released in air and caused renal failure and CNS problem in humans. In this study, mercury vapor removed from air based on nickel-coated on multi-walled carbon nanotubes (Ni-MWCNTs) as a novel sorbent at room temperature. By procedure, amalgamation of mercury with Ni-MWCNTs was achieved by solid-gas phase removal method (SGPR). In bench scale set up, the mercury vapor generated and mixed with purified air with electro air cleaner and moved to sorbent at optimized flow rate. After thermal desorption of Ni-MWCNTs at 200 °C, the mercury vapor flowed to quartz glass cell with argon gas and determined by cold vapor atomic absorption spectrometer technique (CV-AAS). In optimized conditions, 25 mg of Ni-MWCNTs and MWCNTs with different size from 30-100 nm was used and the adsorption capacity of sorbents was obtained 194 mg g⁻¹ and 64 mg g⁻¹, respectively. The efficient recovery was obtained at optimized conditions such as, temperature of 25-40 and flow rate of 200 mL min⁻¹. Due to results, the surface of Ni-MWCNTs had good potential for removal of mercury vapor from the air and can be used as a low cost and efficient sorbent in industrial workplace.

1. Introduction
Mercury was ranked as a hazardous material for human health and animals such black fish and extra concentration cause dangers disease in human body [1,2]. Mercury is a toxic element and has no essential biological function in human body and normal range was reported less than 20 µg L⁻¹ and 2 µg L⁻¹ in urine and blood serum, respectively by ACGIH. Organic and inorganic mercury occurs in fishes, foods, vegetables, waters and air [3].

It is emitted to the atmosphere from chlor-alkali factory, sea, chemical process, coal, oil combustion for energy generation, and metal mining. The contribution of industrial sources for mercury and other heavy metals emissions to the atmosphere, rivers and fish and humans [4]. Human exposure to mercury evaluated and studied in occupational and environmental health [5]. Mercury generated from chemicals, petrochemical and electrical industries [6]. The mercury exposure caused many health problems in human body such as, central nervous system defects, erythrism, arrhythmias, cardiomyopathies, and kidney damage. Necrotizing
bronchitis and pneumonitis arising from inhalation of mercury vapor can result in respiratory failure [5, 6]. Mercury is listed and suggested as one of the hazardous air pollutants in the 1990 and recently many methods was used for mercury removal from air [7]. The air sampling and analysis methods was used for mercury determination by the national institute for occupational safety and health (NIOSH) and the occupational safety and health administration (OSHA), respectively(NIOSH 6009). The main disadvantages of these methods related to interference by other metal compounds and organic mercury in air. the sample tube be The fragile of sample tube, low adsorption capacity, impurities and contamination of reagents used for sample preparation, the use of nitric acid and hydrochloric acid, as well as being time consuming, the mercury loss during sample preparation, operator skills and the costs of solid sorbent tubes caused to consider as a weak procedure [8, 9]. Many Nano carbon compound such as carbon nanotubes (MWCNTs, SWCNTs), graphene and mesoporous silica nanoparticles (MSN) was syntheses and used as a sorbent for removal of mercury from air. Carbon nanotubes are unique wall porous structures with nanometer diameter and can be simply removed mercury from air with two type’s single walled carbon nanotubes (SWNTs) and multiple walled carbon nanotubes (MWNTs) [16]. MWCNT and SWCNT were used in many published papers for mercury removal from air/gas. Adsorption of mercury was achieved by montmorillonite powder modified with Copper Compounds or amorphous of MoS₂ pasted on TiO₂ was used for removal metals from gas/air. Also, the bimetallic sorbents such as Pd–Fe and catalytic compounds such as Ce–Mn/TiO₂ applied for Hg⁰ removal in air [10-15]. In fact, CNTs with chemical and physical properties have good potentially in many applications such as, nanotechnology, electronics, optics, water, chemistry, environment and other fields of materials science [16-20]. Low diameter (nm), low weight, thermal conductivity and high surface area, thermal resistance, high tensile strength and a very high Young modulus caused to introduce as novel adsorbent in many science [21-22]. Also, these compounds also have been used for absorb the gases and metal cations and volatile organic compounds [23-27]. The carbon nanotubes have a good repeatability in high temperature, So, CNTs introduce a favorite sorbent for mercury removal from air by thermal desorption method [28, 29]. Also, the health effect of exposure to solvents, acids and other chemical methods were reduced by proposed method. Recently, different instruments coupled with techniques was reported for mercury analysis by researchers, activated carbon from mixed recyclable waste modified by phosphonium-based ionic liquid (IL-ACMRW) based on Inductively Coupled Plasma- mass spectroscopy (ICP-Ms) was used for mercury removal from wastewater. Inductively coupled plasma atomic emission spectroscopy (ICP OES), high-performance liquid chromatography coupled hydride generation atomic absorption spectrometry (HPLC-HG-AAS), hydride generation atomic absorption spectrometry (HG-AAS), hydride generation atomic absorption spectrometry coupled mercury concentration (HG-AAS-MC3000). In this work, Ni-MWCNTs and MWCNTs was removed the mercury vapor from air due to their unique physicochemical properties. Strong chemical interactions between Ni and Hg⁰ (Hg→Ni-MWCNTs) caused to increase removal efficiency of sorbent by SGPR. The reusable of Ni-MWCNTs can be considered as a cost effective sorbent.

2. Experimental
2.1. Material and Methods
All reagents such as, Sodium borohydride, nitric acid, sodium hydroxide and hydrochloric acid were prepared from Sigma Aldrich. Mercury standard solutions were prepared from a stock solution of 1000 mg L⁻¹ in 1% ultra-pure nitric acid. Working standard solutions were freshly prepared by dilution of stock and intermediate standards. Sodium borohydride (NaBH₄) prepared fresh daily. 3.0 g of NaBH₄ and 3.0 g of sodium hydroxide (NaOH) were mixed and diluted by deionized water (DW) up to 500mL. Deionized water obtained from a
water purification system (Millipore, Bedford, MA, USA) was used for preparing all solutions. All containers (quartz crucibles, plastic tubes) were cleaned with detergent and treated successively by the hydrochloric acid and rinsed with deionized water. Argon was used as the pure gas (99.99%). The present research is an experimental study and it includes stages such as preparation of the various concentrations of mercury vapor, adsorption of mercury vapor in various concentration, time, temperature optimized as well as retention time of adsorbed mercury by multi-walled carbon nanotubes. The atomic absorption spectrometer (GBC) Model (AAS–932 Puls) with cold vapor technique (CV-AAS/HG3000) has been used for the analysis of samples. Instrumental parameters for cold vapor atomic absorption spectrometry are shown in Table 1. The mercury concentrations were prepared from 1 µgL⁻¹ to 50 µgL⁻¹. The Ni-MWCNTs (25 mg) as solid phase was used and placed in a glass tube with length of 5 cm and the internal and external diameters of 5 and 8 mm respectively. Then, end-capping with some silica/cotton was performed to prevention of humidity. MWCNTs were provided by Nano department of RIPI, Tehran. Also, all solutions and materials were purchased from Merck, Germany.

2.2. Synthesis of nickel coated on MWCNTs
The Ni-MWCNTs has prepared as follows, 2.0 g of the pure MWCNTs was added to 50 mL of DW with 0.25 g of Sodium sulfosuccinate esters (NaO₃SCH(CO₂R’)CH₂CO₂R) as a surfactant by low heating at 300 rpm stirring speed. The nickel nitrate (0.5 g) was added to the Final solution without heat in 200 rpm stirring speed. Then, ammonia solution (2 mL) was added to solution and diluted with DW up to 200 mL with stirring in 20 min at 300 rpm speed. Then finally, 10 mL of formalin slowly was added for five minutes as a reducing agent. The synthesis of Ni-MWCNTs nanoparticles was obtained by increasing the speed of Stirring after addition formalin for 10 min (800 rpm). The extra formalin and ammonia on Ni-MWCNTs cleaned by DW washing after filtration by Whatman filter. In addition, oxidation of the Ni-MWCNTs nanoparticles was prevented by washing with Ethanol.

2.3. Experimental Procedure
In bench scale set up, the air was purified with electro air cleaner (EAC, Canada, model EAHEPA600M-3) by HEPA. The HEPA act for efficient removing particles under 300 nm (99.97%) from air. Then, the pure air of EAC passed through polyethylene tubes and entered to polyethylene bag (1 Li) by a SKC pump. All of the gas lines were PE tubes and those that enter to PE bag were covered with heating jackets capable of controlling the temperature at 50 °C to prevent water vapor and mercury vapor from condensing. In SGPR, trace of elemental mercury vapor in air was prepared by aqueous standard solution of mercury (1-50 µgL⁻¹). The aqueous standard solutions entered to hydride generator system and mercury vapor generated in a continuous flow rate. The system was designed by a peristaltic pump that can be pumped standard solutions of mercury, tin chloride as reducing agent and ionized water into a mixer continuously. Peristaltic pump rotation rate was 1.5 rounds per second or 90 rpm. The solution mixed thoroughly in reaction tube and then pushed into a liquid–gas separator where the mercury vapor is separated from the liquid using an inert carrier gas. The mercury vapor mixed with pure air and flowed to Ni-MWCNT by flow rate 100-300 ml min⁻¹. After adsorption mercury by Ni-MWCNTs, the remained air stored in polyethylene bag 1(1 L). The air into air bag was determined by CV-AAS and MC3000

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lamp Current</td>
<td>5 mA</td>
</tr>
<tr>
<td>Wavelength</td>
<td>253.7 nm</td>
</tr>
<tr>
<td>Band pass</td>
<td>0.5 nm</td>
</tr>
<tr>
<td>Flame Conditions</td>
<td>Cold vapor</td>
</tr>
<tr>
<td>Lamp</td>
<td>HCL</td>
</tr>
<tr>
<td>Argon gas pressure</td>
<td>400 k Pa</td>
</tr>
<tr>
<td>Gas flow to the mixer block</td>
<td>100 mL/min</td>
</tr>
<tr>
<td>Gas flow to the separator</td>
<td>35 mL/min</td>
</tr>
</tbody>
</table>

Table 1. Conditions of cold vapor atomic absorption spectrometry (CV-AAS) for mercury
(gold trap). After thermal desorption of MWCNT, the mercury vapor flowed with Ar gas and stored in another bag (bag 2, 1L) and mercury determined by CV-AAS and MC 3000. The pilot plan for mercury removal from air was shown in Figure 1.

### 3. Results and Discussion

#### 3.1. Scanning electron microscopy images from carbon nanotubes

The scanning electron microscopy (SEM) and Transmission electron microscopy (TEM) images of MWCNT and Ni-MWCNTs was shown in Figures 2 and 3, respectively. Elemental analysis conditions showed that Ni-MWCNTs included 8% nickel and 90% carbon. Mercury was removed by sorbent 0.55% by Ni-MWCNTs (Table 2).

#### 3.2. Adsorption efficiency for different amounts of MWCNTs

The adsorption efficiency with 25 mg of Ni-MWCNTs and MWCNTs was examined for 0.01-0.1 µg of mercury concentration by SGPR. According to the results, the adsorption efficiency for Ni-MWCNTs was more than 95% as compared...
to MWCNTs (less than 70%). Also the RSD had different value from 5 to 8%. The results showed that the good recoveries for mercury removal by two sorbents were achieved in low and high mercury concentration (Table 3).

3.3. Adsorption capacity of Ni- MWCNTs and MWCNTs

In batch system, 10 mg L⁻¹ of mercury standard solution (Merck) selected and injected in closed special glass (CSG) after put into Ni- MWCNTs

Table 2. Energy Dispersive X-Ray Analysis of Ni-MWCNTs (EDX) for mercury removal

<table>
<thead>
<tr>
<th>Elt</th>
<th>Line</th>
<th>Int</th>
<th>Error</th>
<th>K</th>
<th>Kr</th>
<th>W%</th>
<th>A%</th>
<th>ZAF</th>
<th>Ox%</th>
<th>Pk/Bg</th>
<th>Class</th>
<th>LConf</th>
<th>HConf</th>
<th>Cat#</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>Ka</td>
<td>676.1</td>
<td>80.3865</td>
<td>0.4213</td>
<td>0.2945</td>
<td>48.21</td>
<td>90.22</td>
<td>0.6107</td>
<td>0.00</td>
<td>37.86</td>
<td>A</td>
<td>47.66</td>
<td>48.76</td>
<td>0.00</td>
</tr>
<tr>
<td>Ni</td>
<td>La</td>
<td>1269.7</td>
<td>6.5990</td>
<td>0.4792</td>
<td>0.3350</td>
<td>41.14</td>
<td>8.57</td>
<td>0.8142</td>
<td>0.00</td>
<td>26.05</td>
<td>A</td>
<td>40.79</td>
<td>41.48</td>
<td>0.00</td>
</tr>
<tr>
<td>Au</td>
<td>La</td>
<td>7.0</td>
<td>0.5642</td>
<td>0.0839</td>
<td>0.0586</td>
<td>9.29</td>
<td>1.06</td>
<td>0.6307</td>
<td>0.00</td>
<td>2.41</td>
<td>B</td>
<td>8.25</td>
<td>10.34</td>
<td>0.00</td>
</tr>
<tr>
<td>Hg</td>
<td>Ma</td>
<td>47.1</td>
<td>6.5990</td>
<td>0.0157</td>
<td>0.0110</td>
<td>1.36</td>
<td>0.55</td>
<td>0.8077</td>
<td>0.00</td>
<td>3.20</td>
<td>B</td>
<td>1.30</td>
<td>1.42</td>
<td>0.00</td>
</tr>
</tbody>
</table>

Table 3. Recovery of adsorption for different concentration of mercury from low to high range (n=10; Mean SD of results ± 0.0032)

<table>
<thead>
<tr>
<th>Pilot concentrations (µg)</th>
<th>Found</th>
<th>desorption</th>
<th>RSD%</th>
<th>Recovery (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>25 mg of Ni-MWCNTs</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.01</td>
<td>0.00944</td>
<td>0.67</td>
<td>94.4</td>
<td></td>
</tr>
<tr>
<td>0.02</td>
<td>0.0195</td>
<td>0.52</td>
<td>97.5</td>
<td></td>
</tr>
<tr>
<td>0.03</td>
<td>0.0286</td>
<td>0.73</td>
<td>95.3</td>
<td></td>
</tr>
<tr>
<td>0.05</td>
<td>0.0487</td>
<td>0.81</td>
<td>97.4</td>
<td></td>
</tr>
<tr>
<td>0.1</td>
<td>0.0976</td>
<td>0.76</td>
<td>97.6</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>25 mg of MWCNTs</th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>0.01</td>
<td>0.00654</td>
<td>0.74</td>
<td>65.4</td>
<td></td>
</tr>
<tr>
<td>0.02</td>
<td>0.0148</td>
<td>0.63</td>
<td>74.0</td>
<td></td>
</tr>
<tr>
<td>0.03</td>
<td>0.0206</td>
<td>0.73</td>
<td>68.6</td>
<td></td>
</tr>
<tr>
<td>0.05</td>
<td>0.0388</td>
<td>0.54</td>
<td>77.6</td>
<td></td>
</tr>
<tr>
<td>0.1</td>
<td>0.0683</td>
<td>0.59</td>
<td>68.3</td>
<td></td>
</tr>
</tbody>
</table>

Fig. 3. SEM (L) and TEM (R) images of Nickel coated on multi-walled carbon nanotubes
and MWCNTs as sorbents in CSG. After heating, the temperature increased up to 80 °C for 10 min. The mercury was vaporized and absorbed on sorbents. The results showed us, the absorption capacity (AC) of Ni- MWCNTs and MWCNTs for mercury removal was obtained 194.7 mg g⁻¹ and 64.4 mg g⁻¹, respectively (Fig. 4). In temperature of 50°C for 10 min, AC was decreased about 8% but after 20 min AC was similar to proposed procedure.

3.4: Determine the optimum time and temperature for desorption

For optimization of temperature, the rate of desorption at different temperatures was studied by SGPR. The maximum of desorption rates on the Ni-MWCNTs was achieved in 160-250°C. So, 200°C was selected as an optimum temperature for desorption point by Ni-MWCNT. Based on the optimum temperature and after several experiments, the results showed that the best time

![Graph showing absorption capacity (AC) of mercury vapor in Ni-MWCNTs and MWCNTs (n=10).](image1)

![Graph showing the effect of time desorption of Ni-MWCNTs and MWCNTs by SGPR (n=10).](image2)
for desorption high efficiency was about 2.33 min with average desorption efficiency equals to 94.5 - 98.2% by peak area mode (Fig. 5).

3.5. Adsorption/desorption efficiency
Removal efficiency and linear regression between the mean values of the mass adsorption and desorption by Ni-MWCNTs and MWCNTs have been shown in Figure 6. The mercury concentration (0.02-0.1 mg L⁻¹) was used for calculating of removal efficiency by proposed procedure. Based on Figure 6 the removal efficiency of Ni-MWCNTs (25 mg) was more than MWCNTs (25 mg) as compared to adsorption/desorption procedure for mercury removal from air by 200 ml min⁻¹.

3.6. Repeatability and retention time
The retention time evaluated for 0.02-0.1 mg of mercury concentration for Ni-MWCNTs and MWCNTs in different temperature. For calculation of retention time, the two ends of sorbents tube with Ni-MWCNTs and MWCNTs were kept at zero 0°C and 25°C. After various times, carbon nanotubes were desorbed in optimum conditions (200°C and 10 min) and then, this procedure followed in different times (1-5 weeks). The results showed us, the main mass of mercury in sorbent tubes was similar to primary mercury concentration after 3 weeks by desorption procedures (0°C). But, in room temperature, only Ni-MWCNTs were stable mass after 1 week. So, Ni-MWCNTs is suitable sorbent for mercury removal from air and saving in room temperature. The adsorption / desorption procedure for Ni-MWCNTs and MWCNTs was repeated based on proposed method and after flashing point, 25 and 27 usage times was achieved as an optimum point for Ni-MWCNTs and MWCNTs, respectively.

3.7. Discussions
According to the results, Ni-MWCNTs were able to absorb mercury from air by SGPR. The atomic absorption spectrometer (GBC) Model (AAS–932 PulS) with cold vapor technique (HG3000) was used for determination of mercury in air, liquid and gas. Previous studies have been researched to attract mercury vapor in gas/air [23-27]. In this study, the Ni-MWCNTs with average diameter of (less than 100 nm) were used to form a stationary phase (sorbent) of glass tubes containing a length of 10 cm, internal diameter of 4cm and external diameter of 6 cm [8, 9]. Shirkhanloo et al. used silver nanoparticles in glassy balls. They showed that silver nanoparticles (AgNPs) had good removal efficiency for mercury from air but it was more expensive as compared to our study.
Also silver nanoparticles can be oxidizing by air, so storage is very hard in room temperature as compared to Ni-MWCNTs [7]. The average absorption rate and absorption capacity (AC) of mercury mass in different concentrations was increased by increasing the mass of nanotubes. In this study, the adsorption capacity of mercury for the Ni-MWCNTs (Ni→Hg) was obtained 194 mg g\(^{-1}\) which was higher than other published methods (less than 170 mg g\(^{-1}\)) and MWCNTs (64 mg g\(^{-1}\)). This amount is more than the adsorption capacity of sorbents such as activated carbon. [30]. According to results in optimized conditions, it seems that the factors such as, concentration of mercury in air, the mass of sorbents, air flow rate, surface area, temperature, and type of the adsorbent affected on the adsorption efficiency of mercury from air up to 80%. Also, the other parameters such as layout of the sorbent tube, length, diameter, \(O_2\) and \(H_2O\) in air, had low affected less than 20%. The optimum point for concentration and temperature desorption was obtained 1-50 \(\mu gL^{-1}\) and 200 \(^{\circ}\)C, respectively. In other studies that designed on the activated carbon, graphene and carbon nanotubes, similar to proposed method [31, 32]. After one month, the retention time of mercury on Ni-MWCNTs, at temperature of 0\(^{\circ}\)C was obtained 98.8% ± 1.05 was near to initial concentration amount. Many papers were used CNTs sorbents for removal mercury from air. The adsorption capacity of Ni-MWCNTs was higher than other sorbents such as MWCNTs, activated carbon and graphene which was previously reported.

4. Conclusions

In present work, a novel sorbent based on Ni-MWCNTs was used for mercury removal from air by SGPR. By proposed procedure, the Ni-MWCNTs were synthesized and put on quartz glass cell. By laboratory bench scale set up, mercury generated in chamber and flowed to sorbent and by amalgamation procedure mercury removed from artificial pure air. After optimizing conditions, the adsorption and desorption point for Ni-MWCNTs was obtained 20-45\(^{\circ}\)C and 200\(^{\circ}\)C, respectively.

The results showed us, the efficiency of mercury removal from air was more than 95% and less than 65% for Ni-MWCNTs and MWCNTs, respectively. The removal recovery was decreased less than 5 % in present of \(O_2\) and \(H_2O\) by SGPR method. So, the Ni-MWCNTs introduced as novel sorbent with high efficiency for mercury removal from air in flow rate of 200 mL min\(^{-1}\) which was acted by physical and chemical adsorption mechanism.

5. Acknowledgements

This study was supported by Iranian petroleum industry health research institute and RIPI.

6. References


[9] Occupational Safety and Health Administration (OSHA), Air contaminants, 29 CFR
Air pollution analysis  
Ali Ebrahimi et al  


