

# The temperatures effects on treatment of heavy metals with zinc oxide nano tubes from industrial wastewater

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**Abstract.** Nanomaterials have been gaining increasing interest in the area of environmental remediation mainly due to their enhanced surface and also other specific changes in their physical, chemical and biological properties that develop due to size effects. In this work, the treatment efficiency of industrial wastewater by using Zinc Oxide Nano tubes ZnONTs, is investigated. The response of adsorption characteristics of some divalent metal ions of heavy metal contaminants of industrial wastewater such as Cadmium, Lead, and Copper towards adsorption behavior of ZnONTs at different temperatures (25, 30, 40, 50, 60, 70°C) is studied. Results show that the adsorption capacity of all tested heavy metal increase in a proportional-like trend with the increase of temperature and reaches its highest value; around 70% for Pb at 70°C as compared to Co and Cu which are about 60%, and 50%, respectively at the same temperature. By tracing these technological advances to the physicochemical properties of ZnONTs, the present research outlines the opportunities and limitations to further capitalization of these unique properties for sustainable industrial wastewater management.

## 1. Introduction

Nanotechnology refers broadly to using materials structures with nanoscale dimensions, usually ranging from 1 to 100 nanometres (nm). The basic structures of nanotechnology include nanoparticles or nanocrystals, Nano layers, and Nano-tubes. Nanostructures, such as silicon nanowires that detect pH, carbon nanotubes, small organic molecules, and biomolecules are examples of nanoscale materials, devices, and circuits that could be used for pollutant sensing, prevention, and treatment [1].

Water contamination is one of the major problems which the world is facing today, and is not only effect environment and human health, but it has also impacts on economic and social costs. Nanotechnology has also proved to be one of the finest and advanced ways for wastewater treatment. There are various reasons behind the success of nanotechnology and scientists are still working on further enhancement of its usage. Various classes of nanomaterials are also proved to be efficient for water treatment like nanostructured catalytic membranes, nano sorbents, nano catalysts, bioactive nanoparticles, biomimetic membrane metal-containing nanoparticles, carbonaceous nanomaterials, zeolites, dendrimers and molecularly imprinted polymers [2].

Nanoparticles have a great potential to be used in wastewater treatment. Its unique characteristic of having high surface area can be used efficiently for removing toxic metal ions, disease-causing microbes, organic and inorganic solutes from water. On the other hand, the nanoparticles have very high absorbing, interacting and reacting capabilities due to its small size with a high proportion of



atoms at the surface. Nanoparticles have the great advantage of treating water in depths and any location which is generally left out by other conventional technologies. Since water treatment using nanoparticles has high technology demand, its usage cost should be managed according to existing competition in the market [3].

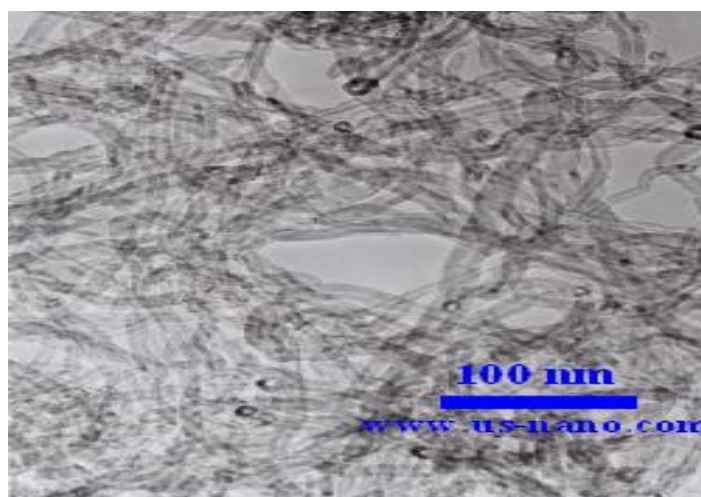
The effects of heavy metals such as lead, mercury, copper, zinc, and cadmium in water have been a major preoccupation for many years because of their toxicity towards human health. Several processes have been used and developed over the years to remove metal ions, such as chemical precipitation, reverse osmosis, electrolytic recovery, ion exchange or adsorption [4, 5].

Carbon Nanotubes (CNTs), a new form of carbon, are attracting researchers' great interest due to their exceptional mechanical properties [6], unique electrical property [7], high chemical stability and large specific surface area since their discovery [8]. Their hollow and layered Nano-sized structures make them a good candidate as adsorbents. Recently, Multi-Wall Carbon Nanotubes MWCNTs have been characterized as efficient adsorbents with a capacity that surpasses that of activated carbon [9, 10]. Considerable attention has focused on adsorption by CNTs of contaminants such as dioxin [11],  $\text{Zn}^{2+}$  [12],  $\text{Pb}^{2+}$  [13],  $\text{Cd}^{2+}$ ,  $\text{Cu}^{2+}$  [14], trihalomethanes [15], cadmium [16], and Ni(II) [17]. The hexagonal arrays of carbon atoms in graphite sheets of CNTs surface have strong interactions with other molecules or atoms. The study of adsorption properties of carbon nanotubes is important in both fundamental and practical point of view.

In this work, the analytical potential of MWCNTs as an adsorbent at different temperatures for elements removal such as the oil, Total Suspended Solids TSS, Chemical Oxygen Demand COD and Total Heavy Metal THM concentrations on the adsorption behavior towards MWCNTs from wastewater of Al- Dora refinery had been studied. Apart of this study, the additional ion concentrations of the selective heavy metal like Cu, Pb, and Co from the industrial wastewater of Al-Dora refinery and on the adsorption behavior was examined.

## 2. Materials and Method

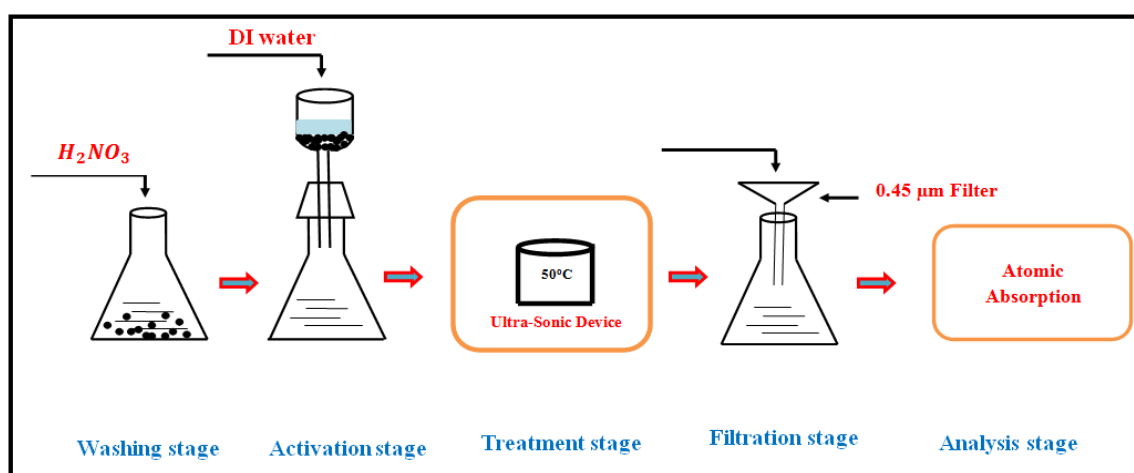
Wastewater from Al- Dora refinery have been treated using MWCNTs, purity > 95%, outside diameter OD: 5-15 nm, inside diameter ID: 3-5 nm, length: ~50  $\mu\text{m}$ . Figure (1) shows the TEM image of as-grown carbon nanotubes.



**Figure 1.** TEM image of as-grown carbon nanotubes (US Research Nanomaterials Inc., USA).

In this work, one gram of activating MWCNTs was soaked in 50 mL of  $\text{HNO}_3$  for 12 h at room temperature. The samples were washed with deionized water until the neutral ( $\text{pH}=7$ ), as well as the solution, was filtered through a 0.45 $\mu\text{m}$  membrane filter [13].

In adsorption experiments, 50 mg of MWCNTs were mixed with 10 mL of wastewater from Al-Dora refinery under ultra-sonication technique. Removal of heavy metal ions and organic compounds from Al-Dora refinery wastewater was investigated. On the other hand, the adsorption behavior from wastewater solution with different heavy metal ions concentrations removal includes Cu, Pb, and Co was examined by Atomic Absorption Spectrometry (AAS, Nova 400; Analytic Jena, Germany). The nanomaterials suspension was sonicated at different temperatures such as 25, 30, 40, 50, 60, 70°C for 1 h using a bath sonicator to ensure homogeneous nano-particle dispersion. After the suspensions were sonicated for 1 h at room temperature, they were filtered through 0.45µm membrane filters. Finally, the amounts of metal ions adsorbed on MWCNTs were measured and calculated as the difference between initial and final concentration by an atomic absorption spectrophotometer as well as the oil content, NO<sub>3</sub>, NO<sub>2</sub>, THM, COD and TSS concentrations were tested by HORIBA/ Japan, UV/visible spectrophotometer (Cecil/ UK), gas chromatography (GC, DANI/ Italy), (Dr 5000 color meter/Hatch) and Weighted method respectively. Figure 2 shows the schematic diagram of treatment process by MWCNTs.



**Figure 2.** The schematic diagram of treatment process by MWCNTs.

### 3. Results and discussion

The chemical and thermal treatment processing could have a great impact on the adsorption capability of MWCNTs for metal ions removal because the performance of carbon materials is mainly determined by the nature and concentration of the surface functional groups. Gas phase oxidation of activated carbon increases mainly the concentration of hydroxyl and carbonyl surface groups, while oxidation in the liquid phase increase particularly the content of carboxylic acids [12]. Oxidation of MWCNTs with nitric acid is an effective method to remove the amorphous carbon, carbon black and carbon particles introduced by their preparation process [11]. It is known that oxidation of carbon surface can offer not only a more hydrophilic surface structure but also a larger number of oxygen-containing functional groups, which increase the ion-exchange capability of carbon material. Nitric acid treatment reduced these groups and additionally creates the new acidic groups, which dominate the surface charge of the carbon nanotubes. Furthermore, it has been reported that the as-grown MWCNTs have weak adsorption capability compared with activated MWCNTs by concentrated nitric acid; so our experiments were carried out only under acidic condition [10].

Samples of wastewater from Al-Dora refinery have been characterized and treated by using activated MWCNTs. Table 1 shows the results of the treatment process for removal elements such as the oil, NO<sub>3</sub>, NO<sub>2</sub>, THM, COD, and TSS from wastewater of Al-Dora refinery at different temperatures. The percentage removal for these elements was calculated from equation (1).

$$\% \text{removal} = \frac{C_i - C_f}{C_i} \times 100 \quad (1)$$

where  $C_i$  and  $C_f$  are the concentrations before and after treatment ( $\text{mg/L}$ ) of the contaminants in the solution. It can be seen from table 1 the percentage removal of contaminated wastewater from the oil and THMs were 100%. In addition, the effect of some metals ions concentrations such as lead, copper, and cadmium on the adsorption behavior of the syntheses wastewater was studied. The initial metal concentration was increased from 5 to 25  $\text{mg/L}$ , while pH of all solutions was fixed at 7 also the temperatures were fixed at 50 °C. It could be seen that the removal of heavy metals by activated CNTs of Pb and Co was higher than Cu depend on the surface charge of the adsorbent, the degree of ionization, and speciation of the adsorbate [10, 11]. The percentage removal was found [17, 12] to increase gradually with increasing pH and reaches an optimum value of (pH 7.0) for Pb(II), Cu(II), and for Hg(II). As mentioned above, our study assumes that the process tends towards neutral pH (7) under all conditions. The metal concentration of the syntheses solutions was determined by atomic absorption spectrophotometer. The adsorption capacity  $q$  ( $\text{mg/g}$  CNTs) was obtained as follows:

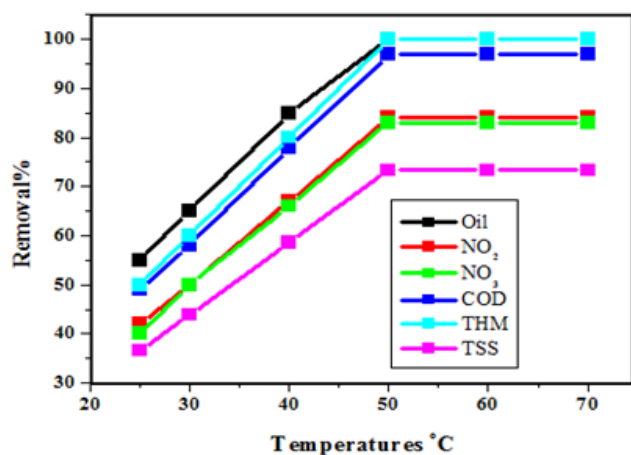
$$q = [(C_i - C_f)V / m] \quad (2)$$

where  $C_i$  and  $C_f$  are the initial and final concentrations ( $\text{mg/L}$ ) of the metal ion in the syntheses solution, respectively, ( $V$ ) the volume of metal ion solution and ( $m$ ) is the weight of MWCNTs.

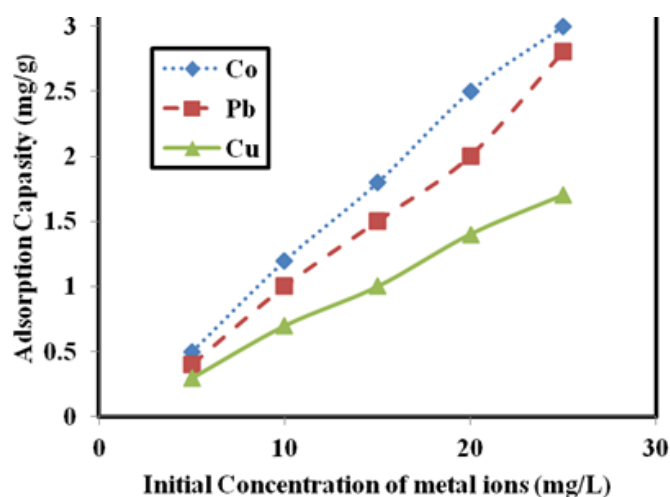
**Table 1.** The removal elements by MWCNTs from wastewater of Al-Dora refinery.

Temperatures C°	Removal %					
	Oil	NO <sub>2</sub>	NO <sub>3</sub>	COD	THM	TSS
25	55	42	40	49	50	36.6
30	65	50	50	58	60	43.9
40	80	67	66	78	80	58.6
50	100	84	83	97	100	73.3
60	100	84	83	97	100	73.3
70	100	84	83	97	100	73.3

On the other hand, the adsorption capacity is an important factor because it determines how much sorbent is required for quantitative enrichment of the analyzed from a given solution. Figure 4 shows the adsorption capacity of Co, Cu, and Pb at their initial concentration range of 5–25  $\text{mg/L}$  with activated MWCNTs at 50 °C. It could be seen from Figure 4, the Co ions are more favorably adsorbed on MWCNTs and the adsorption capacity of Co was 3  $\text{mg/g}$  at an equilibrium concentration of 250  $\text{mg/L}$ , while the adsorption capacity for Pb and Cu were 2.8 and 1.7  $\text{mg/g}$ , respectively, as shown in table 2. Under the condition (pH7), the adsorption capabilities of CNTs for these three heavy metal ions are in the order of Co>Pb>Cu. Also, the mean removal efficiencies of 60% for Co, 56% for Pb, and 35% for Cu elements had been observed. Thus, a carbon nanotube has good adsorption properties and high capacity for Co and can be applied for the pre-concentration and purification of these elements in aqueous solutions containing other metals.



**Figure 3.** The removal elements by MWCNTs from wastewater of Al-Dora refinery at different temperatures.



**Figure 4.** The effect of the metal ions initial concentration on the equilibrium adsorption capacity at 50°C.

**Table 2.** The initial concentration of heavy metal ions with the adsorption capacity (q) of Co, Pb, and Cu at 50°C.

Initial concentration of heavy metals ions (mg/L)	Adsorption capacity of Co q(mg/g)	Adsorption capacity of Pb q(mg/g)	Adsorption capacity of Cu q(mg/g)
5	0.5	0.4	0.3
10	1.2	1.0	0.7
15	1.8	1.5	1.0
20	2.4	2.0	1.4
25	3.0	2.8	1.7

#### 4. Conclusions and Recommendation

In this study, the removal of elements from Al- Dora refinery by using MWCNTs at different temperatures was investigated. The MWCNTs show exceptional adsorption capability for heavy metal ions removal such as of Co, Pb, and Cu from wastewater of Al- Dora refinery after oxidized with nitric acid. Also, the adsorption capacity for Pb and Cu were 2.8 and 1.7 mg/g, respectively. On the other hand, the high removal of oil content, THM, COD, and TSS by CNTs at 50 °C had been observed. It has been shown that activation of the MWCNTs with  $\text{HNO}_3$  an enhanced adsorption capacity for heavy metal ions and may offer a better solution for the removal of organic pollutants in water. These results suggest that MWCNTs have great potential applications in environmental protection. Nanotechnologies have made great improvements for handling water contamination problems and will clearly make further advancements in future. Nanotechnology-based treatment has offered very effective, efficient, durable and eco-friendly approaches.

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