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ADSORPTION OF COPPER, COBALT, AND MANGANESE IONS FROM AQUEOUS SOLUTIONS USING OXIDIZED MULTI-WALLED CARBON NANOTUBES

Adsorption of Cu^{2+} , Co^{2+} , and Mn^{2+} metal ions on oxidized multi-walled carbon nanotubes (O-MWCNTs) was investigated as a function of contact time, pH, sorbent dosage, and initial metal ion concentration. Multi-walled carbon nanotubes (MWCNTs) were oxidized using HNO_3 . All the adsorption experiments were conducted by the batch method. Determination of metal ions was performed by the flame atomic absorption spectrometry. The results showed that the amount of metal ions adsorbed strongly depended on pH. The affinity order of the three adsorbed metal ions by O-MWCNTs was $\text{Cu}^{2+} > \text{Co}^{2+} > \text{Mn}^{2+}$.

1. INTRODUCTION

Environmental pollution is one of the most important problems of today's life [1]. Industrial processes belong to main sources of heavy metals in the environment. In the developing countries, heavy metals are discharged straightly into environment and since these pollutants are non-biodegradable, they remain in the environment [2].

Accumulation of heavy metals in various organs including brain, kidneys, and liver can cause serious illness. Thus, removal of these materials from wastewater is the target of many studies in recent years. MWCNTs show excellent adsorption behavior, because of high surface to volume ratio, light weight, strength, large external surface area, and internal sites in their structures. However, application of these nanoparticles is limited due to their accumulation and stabilized bundles, which result from the van der Waals bonds among the graphene sheets in their structures. This problem can be overcome by surface modification of MWCNTs with various organic molecules [3]. Modification of

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the MWCNTs surface have been reported in various studies for uptake of pollutants such as zinc [4], hexavalent chromium [5], nickel [6], lead [7], copper [8], and phenols [9].

MWCNTs modification by oxidation yields nanotubes with oxygen-containing functional groups such as carboxylic ($-\text{COOH}$), carbonyl ($-\text{C}=\text{O}$), and hydroxyl ($\text{O}-\text{H}$) at both the sidewall and the end of nanoparticles [10]. Presence of these groups leads to better dispersion in water and improves the application of carbon nanotubes; especially as adsorbent of pollutants from the wastewater. In the case of oxidized treatment of MWCNTs, digestion of end caps of MWCNTs makes the inner channels accessible for adsorption of contaminants on the inside walls of the nanotubes.

In this work, surface modification of MWCNTs were conducted using HNO_3 and characterized by scanning electron microscopy (SEM) and Fourier transform infrared (FTIR). The O-MWCNTs were applied for removal of Cu^{2+} , Co^{2+} and Mn^{2+} in water samples. The effects of pH, contact time, sorbent amount, and initial heavy metal concentration on the adsorption process were determined via the batch method. Determination of metal ions was performed by the atomic absorption spectrometry.

2. EXPERIMENTAL

Materials. MWCNTs with 20–30 nm outer diameter and 30 nm length were obtained from Cheap Tubes Inc. (USA). The purity of MWCNTs was more than 95%. All reagents such as concentrated HNO_3 (63%) and metal nitrates were purchased from Merck. Metal stock solutions ($1000 \text{ mg} \cdot \text{dm}^{-3}$) were prepared by dissolving salts in deionized water and then diluted to the required concentrations for standard solutions ($2\text{--}80 \text{ mg} \cdot \text{dm}^{-3}$).

Analytical methods. Concentration of heavy metals was measured by the flame atomic absorption spectrometry (FAAS) using Varian Model spectra AA.200 equipped with a single element hollow cathode (HCL) lamps, deuterium background correction, and air-acetylene. The surface functional groups of MWCNTs were detected by the FTIR spectrometer (EQUINOX 55) from $4000\text{--}400 \text{ cm}^{-1}$. Morphology of oxidized MWCNTs was observed by Tescan VEGA-II scanning electron microscope. pH was adjusted using a Metrohm digital pH meter.

Sorbent preparation. The sorbent was prepared by treatment of pristine MWCNTs using $3 \text{ mol} \cdot \text{dm}^{-3} \text{ HNO}_3$. At first, 2 g of pristine MWCNTs were suspended in HNO_3 and then sonicated in a water bath for 30 min. The mixture was stirred at $110 \text{ }^\circ\text{C}$ for 48 h. After cooling to the room temperature, the suspension of O-MWCNTs was added to 150 cm^3 of deionized water, and then filtered. Washing the filtrate with deionized water was repeated until the solution became neutral. The adsorbent obtained was overnight mounted in the vacuum oven for complete drying.

Batch method procedure. The adsorption experiments were performed by the batch method. 5–30 mg of O-MWCNTs were added to 10 cm³ of the solution of metal ions in a triangular flask. Adjustment of the initial pH to 3–11 was performed using either 0.1–0.01 mol·dm⁻³ HNO₃ or NaOH. The flasks were shaken on a shaker at 160 rpm at the room temperature. The final mixture obtained was centrifuged at 1600 rpm for 15 min, filtered, and its pH was measured.

Concentrations of residual heavy metal ions in the solution were measured by FAAS. The percentage of metal ions removed (R) by the adsorbent was calculated from [11]:

$$R = \frac{C_0 - C_t}{C_0} \times 100 \quad (1)$$

where C_0 and C_t are the initial concentration and concentration at time t of the metal ions.

3. RESULTS AND DISCUSSION

3.1. CHARACTERIZATION OF O-MWCNTs

SEM images of pristine and O-MWCNTs are displayed in Fig. 1. The pristine MWCNTs have external diameters in the range of 20–30 nm. Many dark impurities can be observed in pristine MWCNTs, which correspond to the amorphous carbon and catalyst residues. It seems that the oxidation process considerably removed the dark particulate impurities.

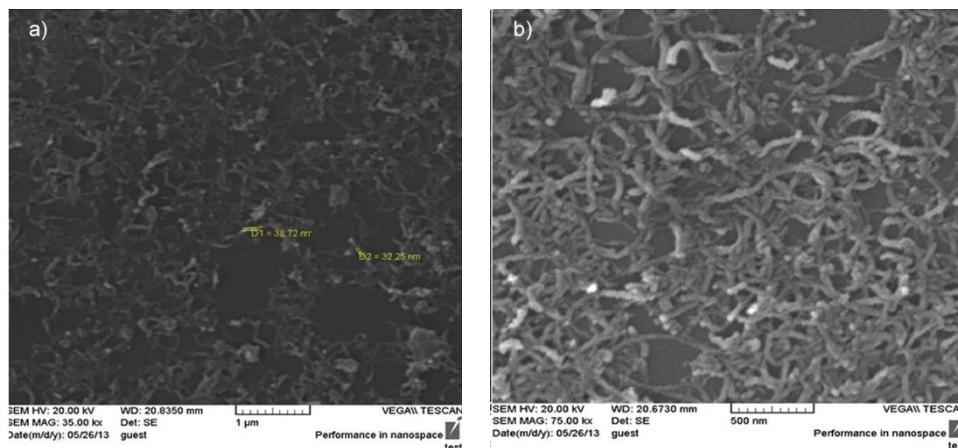


Fig. 1. SEM images of: a) MWCNTs, b) O-MWCNTs

Some aggregations can be detected in these micrographs due to the van der Waals interactions among the carbon nanotubes with different shapes and directions. By comparing the size and shape of nanoparticles, one can find that the acidic modification has no significant effect on the shape and size of MWCNTs and only a smoother surface is obtained.

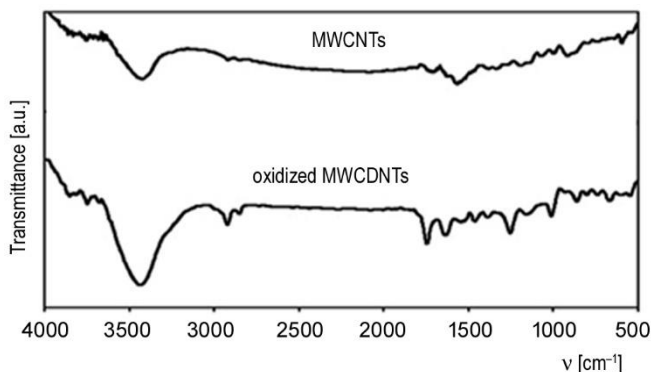


Fig. 2. FTIR spectra of MWCNT and O-MWCNT

FTIR spectra for the pristine MWCNTs and O-MWCNTs are presented in Fig. 2. The pristine MWCNTs exhibited the band at 3420 cm^{-1} , which is related to O–H vibrations, and could be caused by water adsorption on MWCNTs. The FTIR spectra showed that after the nitric acid treatment, many functional groups appeared on the surface of nanoparticles. The presence of O–H (3420 cm^{-1}), C=O (1730 cm^{-1}), and C–O (1210 cm^{-1}) stretching vibrations in the FTIR spectra of O-MWCNTs confirms that oxidation of the MWCNTs was successfully done [12].

3.2. EFFECT OF pH ON METAL REMOVAL EFFICIENCY

The interaction between heavy metal ions and O-MWCNTs can be influenced by pH. Heavy metal ions and charge of the adsorbent surface are controlled by this parameter [13, 14]. It is well known that at pH values below the point of zero charge (pH_{pzc}), the surface charge is mainly positive while at $\text{pH} > \text{pH}_{\text{pzc}}$, the surface charge is predominantly negative. In acidic solutions, the low adsorption of metal ions on O-MWCNTs can be attributed to competition between H^+ and metal ions on the same sorption sites. It is clear that metal ion species in deionized water could be in forms of M^{2+} , $\text{M}(\text{OH})^+$, $\text{M}(\text{OH})_2$, and $\text{M}(\text{OH})^{3-}$ [15]. Figure 3 shows the dependence of percentage removal, of metal ions adsorbed onto the O-MWCNTs on pH. As can be seen, removal of Cu^{2+} , Co^{2+} , and Mn^{2+} quickly increases at higher pH. To avoid the interference of precipitation and adsorption, experiments were done at $\text{pH} = 5.7\text{--}6$. In this range, most metal ions in the solution are in the cation form and no precipitation occurs in the solution. Adsorption of heavy metal ions on O-MWCNTs can be explained by three mechanisms: Firstly, cation exchange reaction between H^+ of carboxylic groups and metal ions, secondly,

formation of surface complex, and finally entrance of metal ions to the inner channel of MWCNTs. In order to clarify the reaction mechanism, the final pH of the solution was measured in each experiment. It was found that pH of the solutions decreased at the end of the experiments (equilibrium state). For example, the pH value for the solution of metal ions decreased by 0.5–0.7. This decrease can be explained by ion exchange between H^+ ions of the carboxylic groups and metal cations in the solution. However, carboxyl and hydroxyl functional groups on the surface of O-MWCNTs can form complex with metal ions or hydroxyl metal cations, which is not negligible. Adsorption of metal ions on O-MWCNTs is a complicated process, which is the other mechanism probably participating in the removal process.

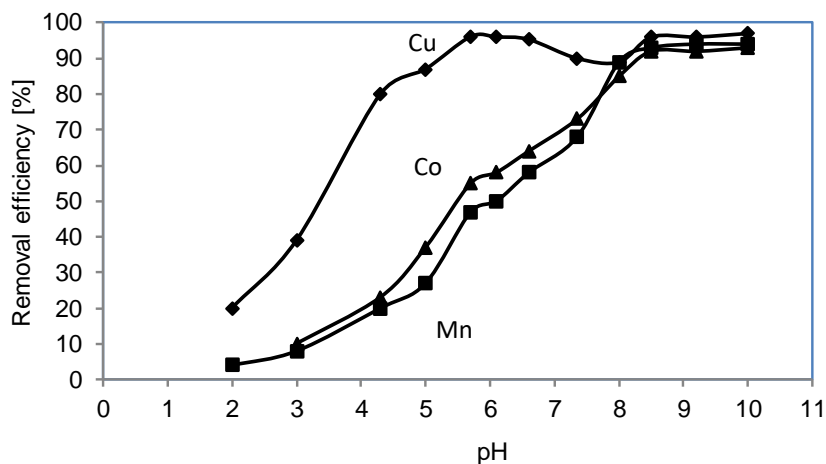


Fig. 3. Dependences of percentage removal of Cu^{2+} , Mn^{2+} , and Co^{2+} ions on pH

3.3. REGENERATION OF SORBENT

Desorption of the metal ions loaded was carried out at $pH < 3$. For the desorption study of O-MWCNTs, adsorption experiments were conducted at initial metal ions concentration of $30 \text{ mg} \cdot \text{dm}^{-3}$ (similar to the batch experiment). Then the sorbent was kept at 50°C for 2 h and then added to deionized water at $pH < 3$ (using HNO_3). Removal of metal ions from O-MWCNTs was determined using FAAS. After regeneration of the sorbent, O-MWCNTs were washed with deionized water and used in further tests. Adsorption/desorption cycles were repeated and the efficiency of heavy metal desorption amounted to $97 \pm 3\%$, $95.8 \pm 2\%$, and $96.8 \pm 3\%$ for Cu^{2+} , Mn^{2+} , and Co^{2+} , respectively.

3.4. CONTACT TIME STUDIES

Contact time is a reflection of the adsorption rate, which determines the time required for perfect adsorption. Effect of contact time was monitored by the batch method

in 15 min steps and the concentration of each heavy metal ion in the solution was measured by FAAS in each step. In Figure 4, percentage removal of heavy metal ions from the aqueous solution by O-MWCNTs is shown as a function of the contact time. As can be seen, after 60 min of contact, removal of heavy metals remained fixed; thus, for all the experiments contact time of 60 min was considered.

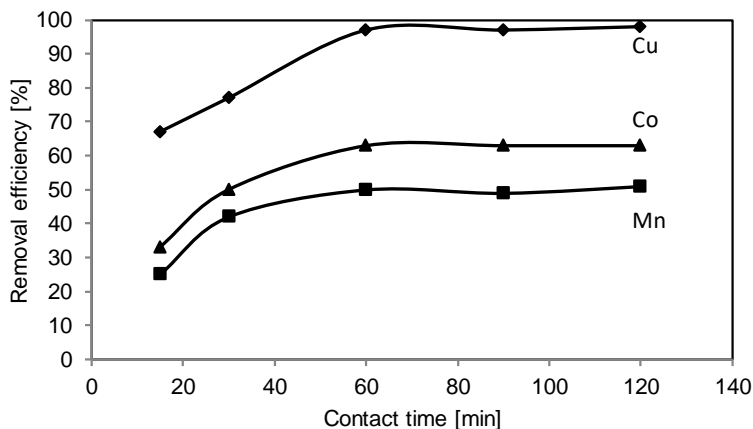


Fig. 4. Time dependences of percentage removal of Cu^{2+} , Mn^{2+} , and Co^{2+} ions

3.5. EFFECT OF SORBENT AMOUNT ON METAL REMOVAL EFFICIENCY

The influence of adsorbent amount on the efficiency of removal of heavy metals from the aqueous solution was investigated by increasing the sorbent amount in the range of 5–30 mg under optimal values for other variables. The efficiency of removal of heavy metal ions increased with the increase of adsorbent, as shown in Fig. 5.

Adsorption of heavy metal ions on O-MWCNTs reached the maximum value with sorbent dosage of 10 mg. This phenomenon can be explained by increase in the binding sites on higher amounts of the adsorbent. In other words, high adsorbent amount provided more adsorption sites for attachment of metal ions and this accessibility greatly improve the adsorption of metal ions.

3.6. ADSORPTION CAPACITY

The amount of sorbent required for analyte extraction from the solution was determined by sorption capacity. For this purpose, a suspension of 10 mg of O-MWCNTs in 10 cm^3 of heavy metal solution under the initial conditions ($2\text{--}60 \text{ mg}\cdot\text{dm}^{-3}$ and pH 5.7–6) was prepared. After 60 min of shaking, the liquid phase was separated from the solid phase and residual metal ion concentrations were measured by FAAS. The amount of adsorbed cations (Q in $\text{mg}\cdot\text{g}^{-1}$) was plotted in function of the initial concentration (C_0 in $\text{mg}\cdot\text{dm}^{-3}$) in Fig. 6.

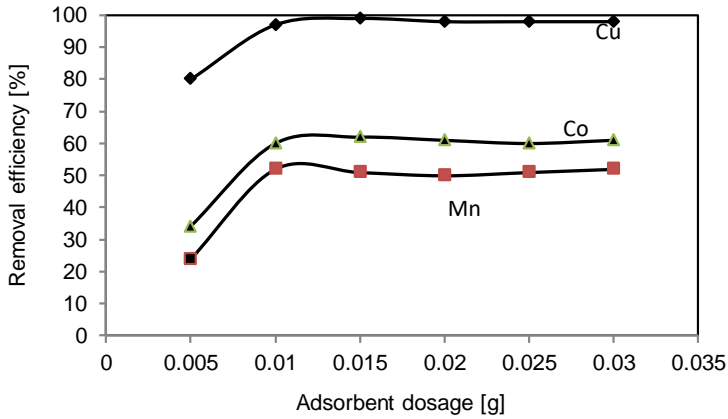


Fig. 5. Dependences of percentage removal of Cu^{2+} , Mn^{2+} , and Co^{2+} ions on sorbent dosage

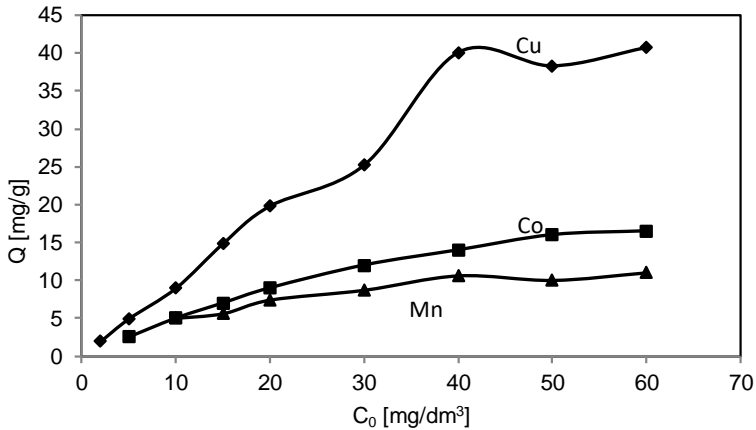


Fig. 6. Adsorption capacity Q of Cu^{2+} , Mn^{2+} , and Co^{2+} ions on O-MWCNT

Q was calculated according to the following equation [12]:

$$Q = \frac{(C_0 - C_e) V}{M} \quad (2)$$

where C_e is the equilibrium concentration of metal ions in $\text{mg} \cdot \text{dm}^{-3}$, M – the adsorbent weight in g, and V is the volume of metal ion solutions in dm^3 . As can be seen, Cu^{2+} ions show the highest adsorption in comparison to Co^{2+} and Mn^{2+} . The main reason for this trend is higher electronegativity of Cu. In other words, higher electronegativity of a metal ion represents its higher attraction for electrons and attraction for negative charges plays a major role in the adsorption phenomenon.

3.7. ADSORPTION ISOTHERM

The Langmuir and Freundlich models were used for modeling the adsorption isotherms [16]. According to the Langmuir equation (the most extensively used), adsorption is monolayer and all adsorbed molecules have equal energy. The Langmuir equation is:

$$q_e = \frac{bq_m C_e}{1 + bC_e} \quad (3)$$

where C_e and q_e are metal ion concentrations in the liquid and solid phases, respectively, q_m is the maximum amount of metal ion adsorbed, and b is the Langmuir constant that indicates the affinity of binding sites on the adsorbent surface. In the linear form, the Langmuir isotherm equation is:

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{bq_m} \quad (4)$$

q_m and b values may be calculated from the intercept and slope of $1/q_e$ vs. $1/C_e$.

The Freundlich model is usually adopted for adsorption from liquid phase on heterogeneous surfaces (like O-MWCNTs). The Freundlich model is:

$$q_e = K_f C_e^{1/n} \quad (5)$$

where K_f and n are the Freundlich constants related to the capacity and power of adsorption, respectively. The linear form of the Freundlich isotherm is given as:

$$\ln q_e = \ln K_f + \frac{1}{n} \ln C_e \quad (6)$$

This model shows that the ratio of the adsorbed metal ion content onto the adsorbent to the concentration of metal ion in the solution varies in function of metal ion concentration. The adsorption isotherms of heavy metal ions on O-MWCNTs at pH in the range of 5.7–6 are shown in Fig. 7.

The experimental data for each heavy metal was fitted to the models considered. The parameters calculated for the models and the correlation coefficients are reported in Table 1.

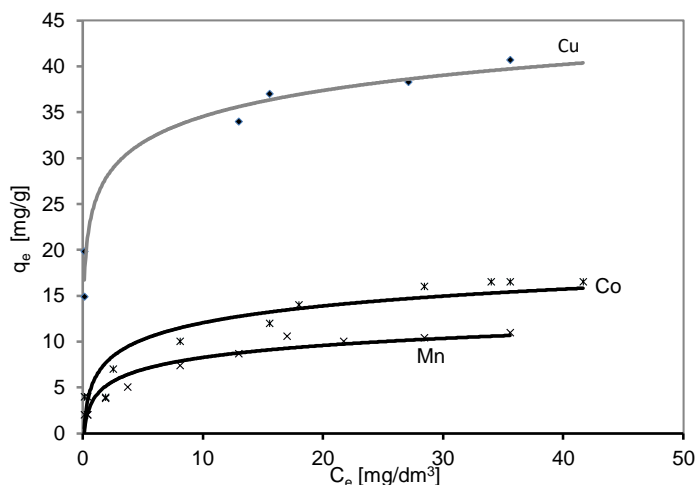


Fig. 7. Adsorption isotherm of Cu^{2+} , Mn^{2+} , and Co^{2+} ions on O-MWCNT

Table 1

Langmuir and Freundlich isotherm parameters for adsorption of metal ions onto O-MWCNTs

Metal ion	Freundlich model			Langmuir model		
	K_f	n	r^2	b	q_{\max} [mg/g]	r^2
Cu^{2+}	15	3.19	0.841	2.04	53	0.989
Co^{2+}	4.9	1.66	0.986	0.047	26.3	0.998
Mn^{2+}	2.29	2.45	0.985	0.080	13.33	0.955

The correlation coefficients for the Langmuir model in the cases of Cu^{2+} , Co^{2+} and Mn^{2+} are higher than those of the Freundlich model. This model better demonstrates the adsorption behavior of Cu^{2+} , Co^{2+} , and Mn^{2+} on O-MWCNTs and can be concluded that the adsorption is in the monolayer form. In addition, the values obtained for n from the isotherm models were larger than unity, which indicates desirable adsorption on O-MWCNTs. The maximum adsorption capacities based on the Langmuir equation were 53, 26.3, and 13.33 $\text{mg}\cdot\text{g}^{-1}$ for Cu^{2+} , Co^{2+} and Mn^{2+} , respectively, indicating good adsorption capacities for this sorbent.

4. CONCLUSIONS

O-MWCNTs were prepared with the ability to remove heavy metal ions (Cu^{2+} , Mn^{2+} , Co^{2+}) from wastewater by an efficient surface modification method. Oxidation of

MWCNTs was conducted with nitric acid to produce oxygen-containing functional groups via covalently bound (such as $-\text{COOH}$, $-\text{OH}$, $-\text{CO}$) on the surfaces of MWCNTs. Surface modification of MWCNTs with nitric acid enhances their adsorption capacity for heavy metal ions and generates a fine sorbent for removal of heavy metal ions in wastewater. The main reason for adsorption of heavy metal ions on the surface of the O-MWCNTs originates from ion exchange reaction mechanism. pH has the main role in adsorption process and the amount of heavy metal adsorbed onto the O-MWCNTs was increased as pH increased. The quantity of adsorbed Cu^{2+} , Co^{2+} , and Mn^{2+} on the O-MWCNTs was determined in the following order $\text{Cu}^{2+} > \text{Co}^{2+} > \text{Mn}^{2+}$. This trend is consistent with higher electronegativity and first stability constant of ion hydroxide.

The Langmuir isotherm model agrees well with the equilibrium experimental data for each heavy metal ion. Regarding the Langmuir equation, the maximum adsorption capacity values for Cu^{2+} , Co^{2+} , and Mn^{2+} were 53, 26.3 and 13.33 mg/g, respectively.

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