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APLLICATION OF NANOMATERIALS IN WATER TREATMENT FROM MANGANESE

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Abstract

Wastewater treatment is of crucial importance for the growing global water scarcity. Mining and processing industries generate wastewater containing toxic elements discharged into rivers and lakes. One of these highly toxic elements polluting water is manganese. The possibility for manganese removal from synthetic wastewater by using carbon nanotubes as an adsorbent has been examined. Carbon nanotubes have promising potential for water purification due to their tunable and distinctive physical and chemical characteristics. It was found that up to 99% purification effect is achieved at low concentrations of manganese ions in water.

***Keywords**: carbon nanotubes, water treatment, manganese, electrical conductivity*

1. INTRODUCTION

Water scarcity and water quality regulation is a major challenge for sustainable development [1]. Contaminated water has a major impact on public health, and it is expected that nearly 800 million people worldwide will soon lack access to good quality water for domestic use [2, 3]. The European Water Framework Directive 2000/60/EC [4] aims at a more sustainable use of water resources, encouraging technological development towards systems for treatment of all water, especially industrial wastewater. Goal 6, which is a key target in the United Nations 2030 Agenda [5], concerns sustainable management of water resources, which is consistent with circular economy strategies. Most of the industrially polluted water are characterized by a low pH and a high content of dissolved metals, such as copper, iron, manganese, etc.

Manganese is a naturally occurring element found in rocks, soil, water, and food [6]. In humans and animals, this trace element plays a role in bone mineralization, energy balance, metabolic regulation, and cellular defense [7]. On the other hand, in high concentrations, manganese is very toxic and can lead to a permanent neurological disorder known as manganism with symptoms that include tremors, difficulty walking and facial muscle spasms, irritability, aggressiveness and hallucinations, among others. Traditional water purification techniques, including filtration, distillation, coagulation-flocculation, biofiltration, and reverse osmosis, fail to remove all heavy metal ions from contaminated water. These methods are not sufficient to provide good quality water, which enforces the search for new energy-saving technologies for this purpose [9].

The application of nanomaterials (NM) in water purification is of utmost importance for the rapid removal of contaminants through adsorption or decomposition processes. Nanotechnology seems to offer promising applications in the field of water purification and remediation [10].

The interest in using carbon nanotubes in wastewater treatment is due to their exceptional properties such as larger surface area, higher binding capacity, higher chemical and thermal stability, and hollow structure, which also determines the possibility of their interaction with pollutants. The aim of this work is to investigate the possibility of effective treatment of manganese-contaminated wastewater.

2. EXPERIMENTAL

The laboratory studies were conducted with model aqueous solutions containing manganese, imitating the concentrations of this metal in wastewater from various industries. Multi-walled carbon nanotubes, representing carbon atoms arranged in the form of a hexagonal lattice in cylindrical macromolecules with the trade name - “A.R.T. NANO P”, were used. The carbon nanotubes used in this study were supplied by ARTMONBAT AD. The nanotubes were produced by the so-called chemical vapor deposition method, at the company's production facility in the Republic of Bulgaria. The equipment for the synthesis of the nanotubes was entirely designed and patented by the company. In the experimental work, model aqueous solutions were used, obtained after dissolving appropriate amounts of $MnSO_4$ in distilled water. The metal concentrations were determined using ICP spectrometer with inductively coupled plasma model-VARIAN VISTA-MPX. The electrical conductivity of the aqueous solutions was measured using a μS-tester. The removal efficiency (%) was calcualted as follows:

$$RE = \frac{(C_o - C_e)}{C_o} * 100 \quad (1)$$

Where C_o and C_e are the initial and equilibrium ions concentrations (mg/L).

The equilibrium capacity (q_e, mg/g) of the CNTs was calcualted as follows:

$$q_e = \frac{(C_o - C_e)V}{m} \quad (2)$$

Where V is the volume of solution (L), and m is the mass of the adsorbent (g).

The adsorption equilibrium for the Mn^{2+} removal was studied using 50 mL model solutions, containing manganese in concentrations between 10 and 300 mg/L, pH 4.6, contacting with 2.5 g of CNTs. Shaking was carried out for 24 hours at 200 rpm using DIAB SK-0180-Pro shaker. Then samples were taken, filtered through blue ribbon filter paper to remove adsorbent particles and analyzed. The obtained results were described by Langmuir, BET and Toth equilibrium models (Table 1).

Table 1. Isotherm models used for experimental results interpretation.

Isotherm	Non-linear expression	Plot
Langmuir	$q_e = \frac{q_m K_L C_e}{1 + K_L C_e}$	q_e vs. C_e
BET	$q_e = \frac{q_{mBET} K_{BET1} C_e}{(1 - K_{BET2} C_e)(1 - K_{BET2} C_e + K_{BET1} C_e)}$	
Toth	$q_e = \frac{K_T C_e}{(a_T + C_e^z)^{1/z}}$	

3. RESULTS AND DISCUSSION

The structure of the CNTs used in the experimental work (Figure 1) was determined using an X-ray diffractometer (PANalytical Empyrean) and a computed X-ray microtomograph (Bruker SkyScan 1272). The specification of the nanotubes is presented in Table 2, and the SEM image is shown in Figure 2. The SEM image in Figure 2 shows a network of thin nanotubes, with a distinct fibrous structure. They appear to be highly intertwined, which is typical for CNTs, especially when they are short and multi-walled. The magnification in the upper right corner shows the diameter of one of the tubes, which is approximately 20 nm. The tubes are randomly oriented with non-directional growth. The structure of the material is complemented by the XRD result (Figure 1). The main peak is around 2θ ≈ 26°, which is a characteristic peak for the (002) plane of a graphite-like structure, which is associated with well-ordered carbon layers (π-π stacking). In nanotubes (especially multi-walled) this peak is a strong indicator of crystallinity along the c-axis. Weaker peaks are observed in the range of ~42°–44° and 54°–55°, which corresponds to (100) and (004) of graphite, further confirming the presence of crystalline carbon. Table 2 summarizes the results of the CNTs studies presented by the manufacturer.

Table 2. Nanotubes charachteristics.

Condition	Powdered
Type	Polyhedral
Length	≥ 2 μm
Diameter	10-40 nm
Number of walls	10-20
Specific surface area	55 m^2/g
Carbon content	≥ 90 wt.%
Bulk density	0.2 g/cm^3
True (pycnometric) density	2.2 g/cm^3
Ash content	7 wt.%

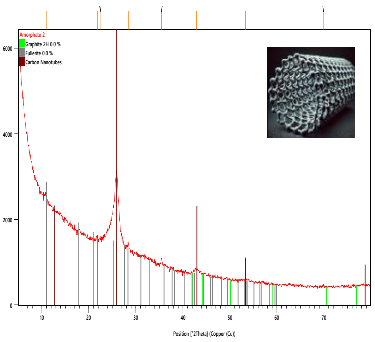

Figure 1. XRD pattern of CNTs.

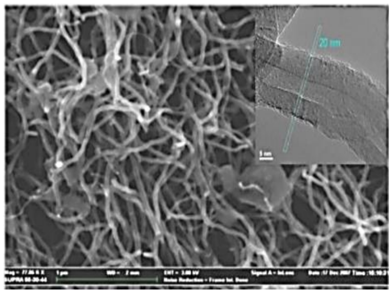

Figure 2. SEM of CNTs.

Figure 3 and Figure 4 present the relationships between the initial concentration of manganese ion, the removal efficiency, and the adsorption capacity, respectively. The results show that as manganese ion concentration increases, the removal efficiency drops significantly (Figure 3). This is likely due to the limited number of active sites on the nanotube surface, as indicated by its specific surface area (55 m²/g).

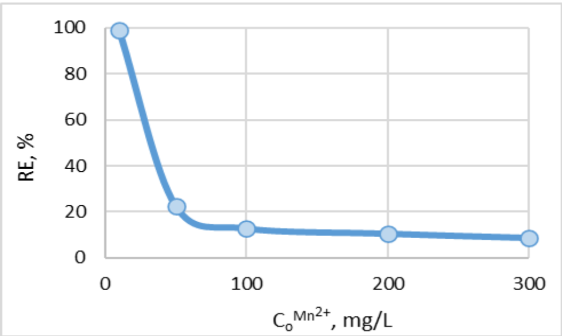

Figure 3. Dependence between the initial concentration of the element and the removal efficiency.

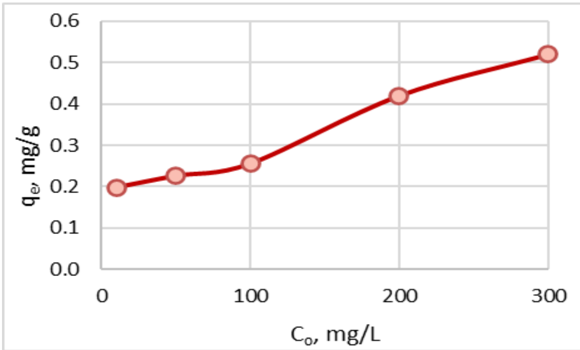

Figure 4. Adsorption capacity of the carbon nanotubes.

However, the adsorption capacity increases with higher initial concentrations (Figure 4). Figure 5 present the experimental equilibrium data of the manganese ions sorption on carbon nanotubes, and the applied three isotherm models: Langmuir, BET, and Toth. The calculated isotherm model parameters for the investigated system, as well as the values of the error functions are presented in Table 3. The non-linear regression is the most effective method for selecting the best-fitting isotherm. As shown in Figure 5 and supported by the high R^2 value (close to 1) and the low error function values in Table 3, the Toth model provides the best fit for the adsorption data.

Table 3. Values of the equilibrium model parameters and error functions.

System	Manganese ions – Carbon nanotubes			
Equilibrium model	Model parameters		Error function	
Langmuir	q_m	0.356	R^2	0.650
	K_L	12.327	SSE	0.058
			MSE	0.014
			RMSE	0.120
BET	q_{mBET}	-0.189	R^2	0.858
	K_{BET1}	-0.321	SSE	0.038
	K_{BET2}	-0.327	MSE	0.013
			RMSE	0.113
Toth	K_T	0.059	R^2	0.987
	a_T	-0.308	SSE	0.002
	z	0.491	MSE	0.001
			RMSE	0.027

The Toth isotherm is a modified form of the Langmuir model that improves prediction accuracy by accounting for sub-monolayer coverage, which means that less than a full single layer of adsorbate molecules has formed on the surface of the adsorbent - not all sites are filled and the surface is only partially covered.

This often occurs at low adsorbate concentrations or when adsorbate molecules are unevenly distributed due to surface heterogeneity or weak interactions. It means that the nanotubes surface needs to be modified to better metal ions removal.

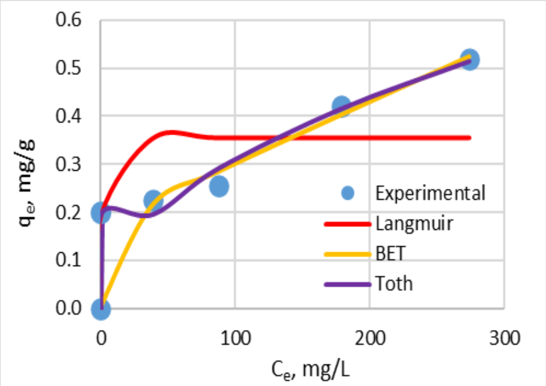

Figure 5. Experimental and model isotherms of the manganese ions sorption on carbon nanotubes.

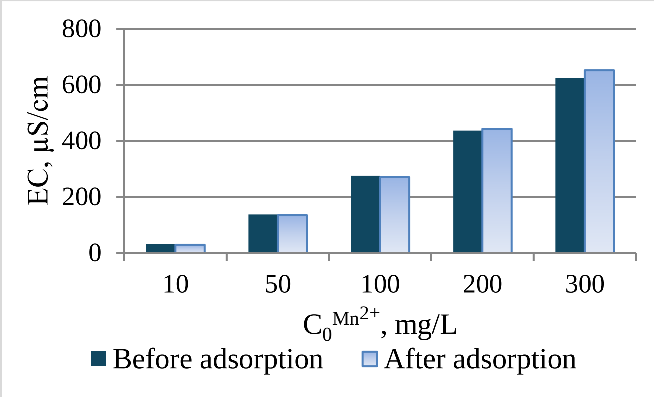

Figure 6. Comparison of electroconductivity of samples before and after adsorption

The Langmuir model describes chemical adsorption, and the BET model-physical adsorption. The R^2 in Langmuir model is low, which probably means that there is no chemical interaction between adsorbate molecules and the surface of the adsorbent.
Figure 6 presents the results of the electrical conductivity measurements of the five solutions with concentration variations from 10 to 300 mg/L. At low concentrations (10-100 mg/L), the electrical conductivity decreases after adsorption, suggesting that the Mn^{2+} ions are retained by the nanotubes and removed from the solution.
At higher concentrations (200-300 mg/L) the electrical conductivity increases after adsorption, meaning that the nanotubes are unable to adsorb Mn^{2+} and the metal ions remain in solution.
If the tubes are functionalized (e.g. by oxidation), they can acquire a negative charge, which increases the electrostatic attraction of the positively charged Mn^{2+} ions. Surface modification of nanotubes is the subject of further research.

4. CONCLUSION

It can be summarized that at low manganese concentrations, carbon nanotubes effectively adsorb metal ions, leading to a decrease in the solution's electrical conductivity. At higher concentrations, adsorption decreases - likely due to surface heterogeneity or weak interactions, and conductivity rises. Enhancing the adsorption capacity requires surface modification of the nanotubes.

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