GRAPHENE-MODIFIED CARBON NANOPARTICLES FOR HEAVY METAL BINDING

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INTRODUCTION

The goal of many research institutions is fast and cheap removal of heavy metals from the environment. In the industry an intensive development of nanomaterials is remarkable. Nanomaterials differ from classic materials in their large surface area, chemical stability and resistance to external influences. These materials have the ability to effectively separate heavy metal ions from the environment by the adsorption on its surface. Into these materials, the carbon based adsorbents can be included, eg graphene. Graphene is a material formed from a single layer of carbon atoms [1,2]. The monolayer structure provides unique electrical and mechanical properties. Several methods of the preparation are known. The most common is the oxidation of graphite oxide to graphene. The next step after isolation of heavy metals is their detection. Electrochemical methods are providing excellent properties for detection of metals. These methods have low detection limits with sufficient selectivity for the metal, low cost, high sensitivity and potential for miniaturization. In this experiment, we focused on application of carbon-based nanomaterials, such as graphene, expanded carbon and multi-wall nanotubes for isolation of heavy metals from the environment [3,4].

EXPERIMENTAL PART

Preparation of graphene: Graphite oxide (GO) was prepared from graphite flakes (Sigma Aldrich) by the Hummers method. Graphene (GR) was prepared by reduction of GO by hydrazine. Hydrazine (4 ml, 35 %) and NH_3 (32 ml, 25 %) were added with stirring to the suspension of GO in 300 ml of water. The mixture was heated on a water bath for 1 h and after cooling collected on the frit and washed several times with water and finally methanol. Graphene was dried at 40 ºC . In the second step of the experiment the samples of carbon and cadmium were prepared. 10 mg of carbon nanomaterials (graphene, MWCNT and expanded carbon) was mixed with 1 ml cadmium ions solution (100 µM), (rotary shaker Multi RS - 60 Biosan, 25 rpm, 20 °C to interact for 1, 3, 6, 12 and 24 hours) [4,5,6].

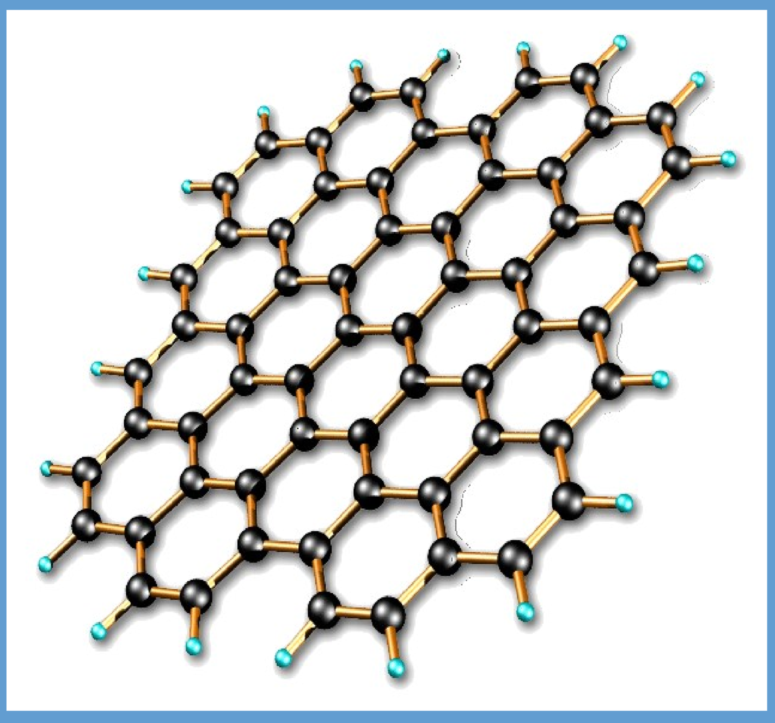

Fig. 1 The structure of graphene

After the interaction the samples were first centrifuged at FVL – 2400N, Combi - Spin, BIOSAN 10 min, the supernatant was removed and filtered (Syringe Filter MicroPure, RC, 0.45 micron, 25 mm). The effectiveness of graphene and MWCNT adsorbents mixture was tested. The graphene was applied in different mass ratios from 0 to 50 mass percent .The total sample weight was 10 mg. Preparation procedure differed only in the time of interaction (two times of interaction: 1 and 24 hours). Determination of cadmium by differential pulse voltammetry were performed with 797 VA Computrace instrument connected to 813 Compact Autosampler (Metrohm, Switzerland), using a standard cell with three electrodes [1].

RESULTS

The aim of our study was the synthesis of graphene to isolate cadmium from solution using adsorbents, such as graphene, expanded carbon and multiwall carbon nanotubes. Effects of adsorption of these three forms of carbon were compared with each other. Efficiency of adsorption of cadmium is summarized in Fig. 2. The figure 2 shows that the graphene has clearly the best ability to adsorb the heavy metal. After 1 hour interaction only 1 % of cadmium was detected in the supernatant that corresponded to 99 % efficiency of graphene to adsorb cadmium. The MWCNT effect was lower, after 1 hour only 30 % of cadmium was adsorbed and after 24 hours 50 % of cadmium was removed from the solution. The ability of the expanded carbon to adsorb cadmium is very small (only 10 % in 24 hours).

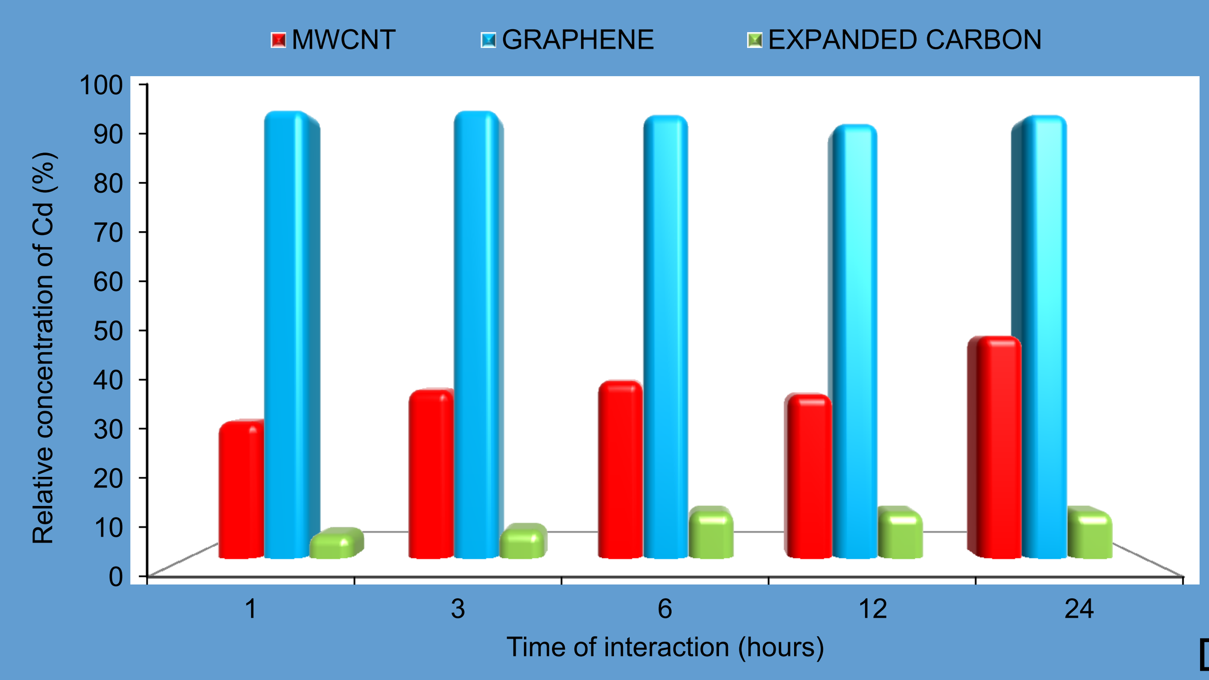

Fig. 2. The amount of bound cadmium ions on various adsorbents. Time dependence (1; 3; 6; 12; 24 hours) of cadmium binding to (red), multi-walled carbon nanotubes, (blue) graphene, (green) expanded carbon. All values were related to the applied concentration of cadmium (100 µM). Determination of cadmium by electrochemical method differential pulse voltammetry.

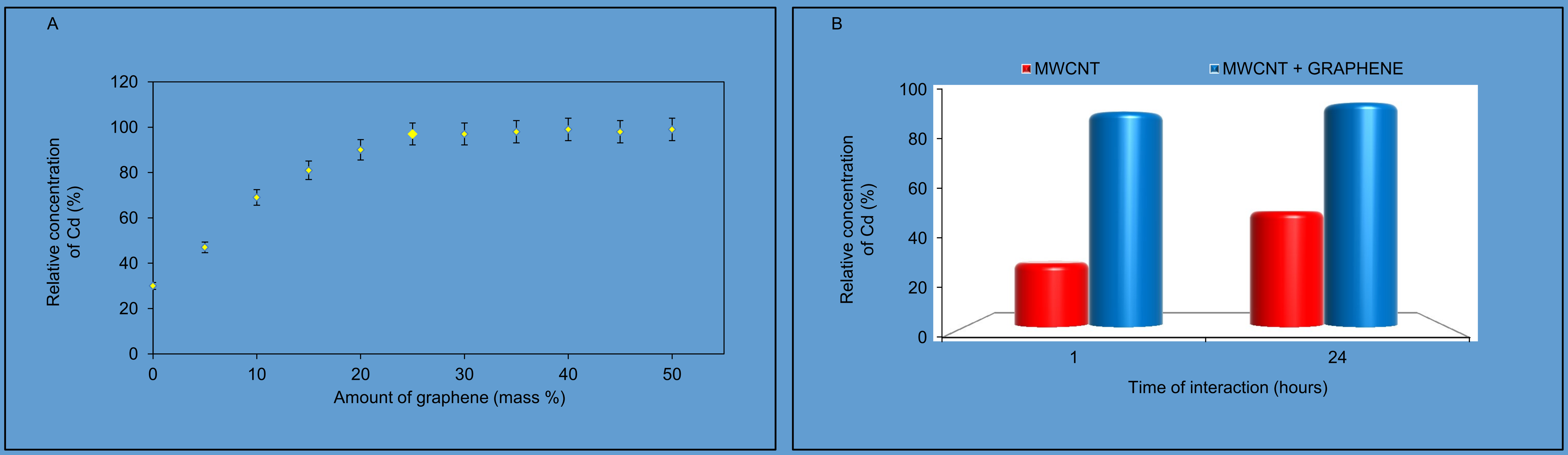

Fig. 3. (A) The dependence of cadmium (100 µM) adsorption efficiency on graphene addition to MWCNT (time of interaction 1 and 24 hours). **(B)** Comparison of the effectiveness of cadmium adsorption on the surface of MWCNTs and MWCNTs containing graphene (75:25 mass %). All values were related to the applied concentration of cadmium.

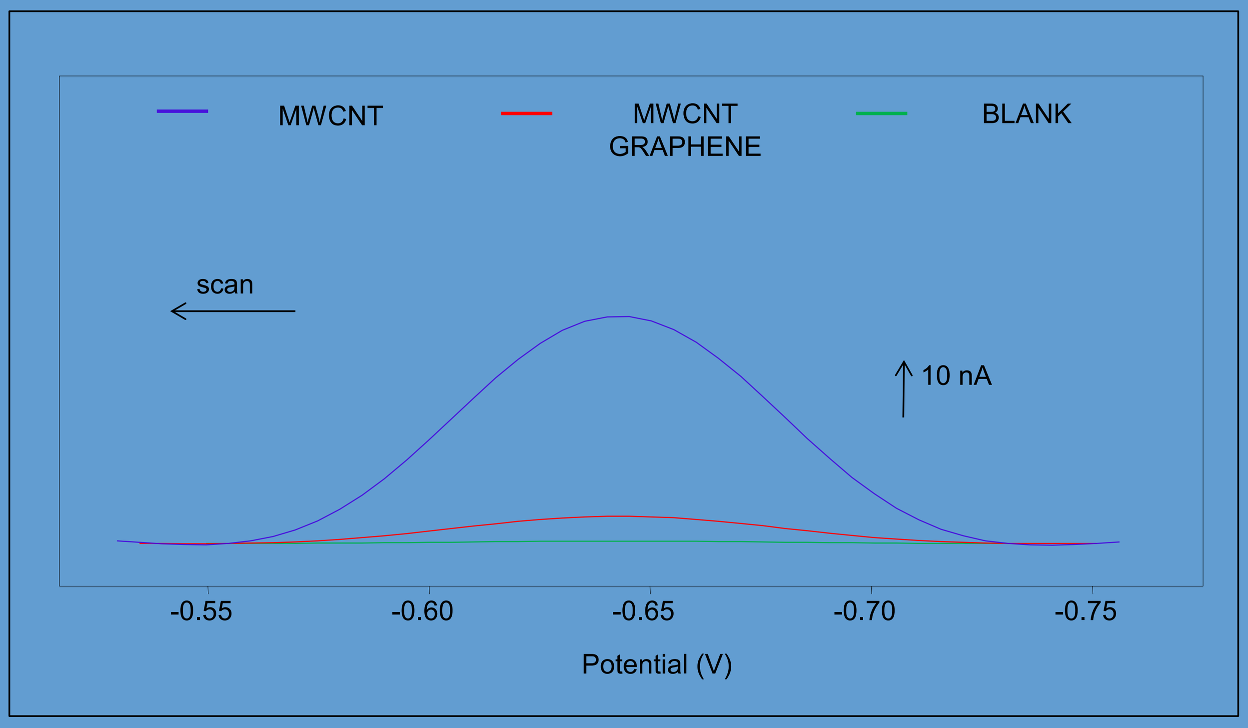

Fig. 4. Electrochemical voltammograms of remaining cadmium ions (after adsorption of cadmium from solution to the mwcnt/mwcnt + graphene) for the time of interaction 24hours. The blue line is for MWCNTs. The red line is for MWCNTs mixed with graphene.

RESULTS

Due to the high adsorption ability of graphene the MWCNTs were mixed by graphene to improve its adsorption properties. From Fig. 3A it can be seen that the addition of graphene considerably increases the adsorption of cadmium. The graph shows that the additions of graphene gradually increase the efficiency of cadmium adsorption. The maximum adsorption is achieved in the amount of 25 mass % of graphene addition (red point in graph). With further increase of graphene addition the absorption efficiency is constant. Samples were measured after one hour interaction. Fig. 3B shows the difference in the cadmium adsorption efficiency by pure MWCNTs and MWCNTs with the graphene addition in time intervals of 1 and 24 hours. For pure MWCNTs the adsorption efficiency after 1 hour was 30 % and after 24 hours was increased to 50 %. With graphene addition the efficiency of adsorption increased after 1 h to 95 % and 24 to 99 %. Real voltammograms of remaining cadmium ions after adsorption in applied cadmium solution see on fig 4.

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CONCLUSION

It is generally known that the adsorption of metal on carbon or its forms is based on the principle of physical adsorption, which is caused by Van der Waals forces, which are relatively weak.

In our study, we confirmed that the adsorption of metal ions on different forms of carbon differs significantly. We found, the graphene addition to MWCNTs increased the adsorption efficiency of cadmium due to enlargement the MWCNTs surface. The graphene was evaluated as the most effective adsorbent that could be used for application in industrial field for example the decontamination of wastewater.

ACKNOWLEDGEMENT

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