Peculiarities of $\text{XO}_4^{2-}$ ($\text{X} = \text{Cr, Mo, W}$) Oxide Molecular Anions Adsorption on the Surface of Carbon Nanostructures

V. Borysiuk$^1$, S. Nedilko$^1$, Yu. Hizhnyi$^1$, A. Shyichuk$^{2, 3}$

$^1$Taras Shevchenko National University of Kyiv, Volodymyrska Street 64/13, 01601 Kyiv, Ukraine
$^2$Adam Mickiewicz University, Department of Rare Earth, Faculty of Chemistry, Umultowska 89b, 61-614 Poznań, Poland
$^3$University of Wrocław, Faculty of Chemistry, Joliot-Curie 14, 50-383 Wrocław, Poland

Chemical functionalization of carbon nanostructures (single-walled carbon nanotubes (SWCNT), graphene sheets, etc.) can modify their physical and chemical properties, leading to the improvement of their performance for specific applications. Carbon nanostructured materials are intensively studied at present as materials for efficient removal and storage of various toxic molecules. Pollution of heavy metals in industrial wastewater has been causing worldwide concern. The main sources of heavy metals are the wastewaters from modern chemical industries. Some studies have already indicated that functionalized CNTs are a promising for the removal of toxic heavy metals traces from water wastes [1]. Theoretical modeling of such molecular adsorption on the CNTs surfaces is a powerful tool what allows to predict some important properties of materials perspective for mentioned use. Adsorption of many kinds of molecules on CNTs of various structures have been considered so far in such computational studies and high predictive power of this theoretical method is now generally accepted.

In this work we studied adsorption characteristics of the $\text{XO}_4^{2-}$ ($\text{X} = \text{Cr, Mo, W}$) molecular oxyanions on the surfaces of pure and N/B-doped SWCNTs, MWCNTs and graphene sheets. DFT-based geometry-optimized calculations of the electronic structures of carbon nanostructures with adsorbed oxyanions were carried out by Gaussian 09 program package [2].

Binding energies, relaxed geometries, charge states of the adsorbates and the electronic wavefunction profiles were calculated and analyzed. Taken results are supplemented by calculations of the $\text{XO}_4^{2-}$ oxyanions adsorption on B/N-doped graphene sheets which are considered as model approximation for large-diameter CNTs. Effects of water solvent on studied adsorption surfaces are considered in a model of polarizable continuum.

Calculation results were discussed in view of potential application of the CNT-based materials as efficient adsorbents of toxic oxides of hexavalent metals. Adsorption mechanism was illustrated by dependence of the binding energy on tube-molecule distance of $\text{XO}_4^{2-}$ ($\text{X} = \text{Cr, Mo, W}$) molecular oxyanions. Optical characteristics of $\text{XO}_4^{2-}$ ($\text{X} = \text{Cr, Mo, W}$) anions adsorbed on the surface of carbon nanostructures, such as oscillator strengths of electronic transitions and absorption spectra were calculated. These results were used for verification of computational approach by experimental data.