

# Effects of Anions on Adsorption of Trace Levels of Cu(II), Pb(II) and Cr(VI) by Amino-Functionalized Multi-Walled Carbon Nanotubes

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*This work studies the adsorption of heavy metal ions (Cu(II), Pb(II) and Cr(VI)) in aqueous solutions on amino-functionalized multiwalled carbon nanotubes (MWCNTs-NH<sub>2</sub>) in the ppb concentration range (50-3000 µg/l) as a function of contact time, initial concentration of heavy metal ions and the presence of four inorganic electrolyte anions (Cl<sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup>, PO<sub>4</sub><sup>3-</sup>). The adsorption of heavy metals from aqueous solution was studied using different kinetic models. The results showed that the adsorption process is best fitted with the pseudo-second-order model indicating that the process is controlled by chemisorptions through electrostatic attraction and chemical interaction/complexation between the metal ions and the surface functional groups of MWCNTs-NH<sub>2</sub>. The intra-particle diffusion model showed that diffusion is slow, but did not govern the rate of the overall adsorption process. The effects of Cl<sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup> and PO<sub>4</sub><sup>3-</sup> anions on the adsorption of Cu(II), Pb(II) and Cr(VI) are variable (improvement, reduction, no impact).*

**Keywords:** nanostructures, surface properties, adsorption, chemisorptions

The contamination of water by heavy metals is a very serious environmental problem. Unlike some organic pollutants, heavy metals are not biodegradable. Therefore, reliable methods are needed to remove heavy metals from environment. Many studies have shown that adsorption is a widely used process for the removal of heavy metals from water, since it is a simple and economically feasible method [1-4].

In water systems the commonly present inorganic electrolyte anions are carbonate (CO<sub>3</sub><sup>2-</sup>), chloride (Cl<sup>-</sup>), sulfate (SO<sub>4</sub><sup>2-</sup>), nitrate (NO<sub>3</sub><sup>-</sup>) and phosphate (H<sub>2</sub>PO<sub>4</sub><sup>-</sup>/HPO<sub>4</sub><sup>2-</sup>) [5-7]. To date, many researchers have dealt with the kinetic studies, adsorption capacities and the effect of pH [2-4, 8-11]. However, the effect of various anions on adsorption of heavy metal ions has not been investigated thoroughly [12-16]. Directly or indirectly, anions can affect metal adsorption (improvement, reduction, no impact) depending on the adsorption system and solution conditions. They also play important roles in the speciation of metal ions and emerging metal-ligand complexes (different sizes, charges and affinities for the adsorbent surface). The metal-ligand complexes may be adsorbed weakly or strongly, or precipitates with metal ions, inhibiting or improving adsorption of metal ions by the presence of the electrolyte anions [15]. Also, anions may react with adsorbent surface, thereby altering the surface electrical properties [12]. Thus, investigation of the influence of inorganic electrolyte anions on heavy metal adsorption is important to assess the adsorption capacity of an adsorbent.

It is well known that carbon nanotubes (CNTs) have very strong adsorption affinity toward many organic [17-19] and inorganic pollutants [11,13,20]. Although MWCNTs possess the potential for heavy metals removal from aqueous solutions [11,13,14] the removal efficiency and

selectivity remain limited due to small reactivity of the sidewalls of CNTs and a small dispersibility [21]. Also, CNTs are very hydrophobic and tend to aggregate in aqueous solution because of high van der Waals interaction forces along the tube outside. Attractive van der Waals forces between carbon surfaces increase the dispersion difficulty [22,23]. Chemical covalent functionalization of CNTs can provide useful polar functional groups onto the CNTs surface which changed the hydrophobic nature of CNTs to hydrophilic one [23]. Surface modifications or the functionalization of different adsorbents is commonly employed to improve adsorption affinity towards metals [3, 24]. The same approach has been used to enhance the dispersion status and adsorption capacities of multiwalled carbon nanotubes (MWCNTs) for heavy metals with oxidation being the most common MWCNTs modifications [2,10,14,25]. The sorption capacity significantly increases after oxidation by HNO<sub>3</sub>, NaOCl and KMnO<sub>4</sub> solutions due to the generation of -COOH, -OH, or -CO groups [22]. The presence of these oxygen atoms also increases the surface charge, which can contribute to electrostatic interaction. Studies that investigated the adsorption of heavy metal ions on amino-functionalized MWCNTs are rare [1,22].

Mostly, available literature refers to the uptake of metal ions in the parts per million concentration range (usually above 100 mg/L) and not for the parts per billion range (ppb), except in a few papers [11,26]. A few years ago the US Environmental Protection Agency (EPA) has expressed an interest for the environmental applications of carbon nanotubes as one of the key areas that needed to be investigated and for monitoring trace levels of heavy metals in the environment [11]. Researches in the area of low concentrations are very significant because of increasingly stringent criteria of quality set by the World Health Organization [27].

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The objectives of this study were to: 1) investigate the adsorption efficiency of MWCNTs-NH<sub>2</sub> for removal of trace levels of Cu(II), Pb(II) and Cr(VI) ions in the presence of various inorganic electrolyte anions (Cl<sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup> and PO<sub>4</sub><sup>3-</sup>), 2) to identify different types of interactions between selected heavy metal ions, various anions and MWCNTs-NH<sub>2</sub>, and 3) to suggest adsorption mechanism of heavy metals onto MWCNTs-NH<sub>2</sub> in the presence of inorganic electrolyte anions.

## Experimental part

### Materials

MWCNTs were synthesized from catalytic chemical vapor deposition process (CCVD) over Co, Fe and Ni containing conventional and sol-gel silica-aluminas [28]. The amino-functionalization of multiwalled carbon nanotubes was done according to the method of Wang et al. [29]. All chemicals used in the experiments were analytical-grade (Sigma-Aldrich). Stock solutions of heavy metals (1000 mg/L) were prepared by dissolution of copper (II) sulphate, lead (II) acetate and potassium dichromate in deionized water. Stock solutions were further diluted with deionized water to the required metal ion concentration for the adsorption experiments. To investigate the adsorption efficiency of MWCNTs-NH<sub>2</sub> in the presence of various inorganic electrolyte anions, calcium chloride, sodium nitrate, magnesium sulfate and potassium dihydrogen phosphate were added in the stock to prepare work solutions which have the same concentration of anions (0.01 M), but different ionic strength. Solution of 0.1 M HCl was used for pH adjustment.

### Characterization of adsorbent

The BET (Brunauer-Emmett-Teller) specific surface area (SSA) and pore specific volume were determined by nitrogen adsorption/desorption at 77 K by the Autosorb iQ Surface Area Analyzer (Quantochrome Instruments, USA). Mesopore volumes were calculated using the adsorption branch of N<sub>2</sub> desorption isotherms based on BJH (Barrett-Joyner-Halenda) model. A micropore volume of MWCNTs-NH<sub>2</sub> was calculated using the t-test method. Fourier transform infrared spectroscopy (FTIR) of MWCNTs-NH<sub>2</sub> was performed using a Nexus 670 infrared spectrophotometer (Thermo Nicolet, USA). For FTIR determinations, samples were prepared by mixing and homogenizing with spectroscopic KBr in the form of pellets. The pH value at the point of zero charge (pH<sub>pzc</sub>) of the sample was measured using the pH mass titration method [30].

### Adsorption experiments

All measurements were run in triplicate at room temperature (20±2 °C) at pH 4.5 and only the average value is reported. All experiments were performed in glass vials with a screw cap having Teflon-lined silicon septum covered with silver foil. Head space in the glass vials was kept at minimum.

### Kinetic studies

The initial concentrations were 920 µg/L for Cu(II), 870 µg/L for Pb(II) and 440 µg/L for Cr(VI). The procedure was as follows: 1-5 mg of the adsorbent was weighed in 40 mL glass vials and was added appropriate volume of deionized water. Mass ratio of the adsorbent and deionized water was adjusted in order to obtain the percentage of adsorption between 20-80 %. To enhance dispersion of MWCNTs-NH<sub>2</sub> in deionized water, glass vials were placed in the ultrasonic bath for 30 min to obtain a homogeneous

suspension. A certain volume of heavy metal stock solution was spiked and vials were continuously shaking for 2, 10, 30, 45, 60, 240, 1440, 2880, 4320 and 5760 min. The suspensions were then filtered through a 0.22 µm membrane filter and residual metal ion concentrations in the filtrates were determined by atomic absorption spectrophotometer (AAS) (Perkin Elmer AAnalyst 700).

### Adsorption isotherms and effect of anions

All adsorption experiments were performed according to the batch method. The background solution was 0.01 M solution of Cl<sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup> and H<sub>2</sub>PO<sub>4</sub><sup>-</sup>/HPO<sub>4</sub><sup>2-</sup> ions in deionized water (single ion system). Initial concentration of heavy metal ions in suspension ranged from 50 to 3000 µg/L. The amount of MWCNTs-NH<sub>2</sub> ranged from 1-5 mg to correspond to a sample/solution ratio that resulted in 20-80% uptake of solute. The procedure was as follows: glass vials containing premeasured adsorbent and background solution were agitated in an ultrasonic bath for 30 min before a certain volume of stock solution of heavy metal ion was spiked and equilibrated at room temperature by continuous shaking for 48 h. The equilibration period of 48 h was based on a preliminary kinetics experiment which was performed over 96 h. The initial pH of background solution was 4.5, while the pH of the suspension after reaching equilibrium was in the range 4.3-4.5. After 48 h, suspensions were filtered through a 0.22 µm membrane filter and equilibrium metal ion concentrations were analyzed by AAS. To determine the initial concentration of heavy metal for each isotherm point and to account for heavy metal losses other than adsorption to the adsorbent, two control flasks without any MWCNTs-NH<sub>2</sub> were prepared and treated in exactly the same way. The recoveries of the initial concentrations of heavy metal were in the range of recoveries for applied analytical methods.

### AAS measurements

Total solution metal concentrations were determined using flame and electrothermal atomic absorption spectrometry (AAS) (AAnalyst 700, Perkin Elmer) according to the EPA 7000b and EPA7010 protocol.

### Data analysis

To explore possible adsorption mechanisms and to identify rate-controlling steps three models were applied: the pseudo-first-order [31], the pseudo-second-order [32] and intra-particle diffusion [32]. The relationship between adsorbed Cu(II), Pb(II) and Cr(VI) ions and its concentration in solution under equilibrium conditions is described by the widely used Freundlich isotherm model.

## Results and discussions

### Adsorbent properties

The main characteristics of investigated MWCNTs-NH<sub>2</sub> are given in table 1. The results of the t-test method showed that the studied adsorbent does not contain micropores. The adsorbent is mesoporous based on the average pore diameter of 14.6 nm. pH<sub>pzc</sub> was 8.

The FTIR spectra of MWCNTs-NH<sub>2</sub> (fig. 1) showed greater numbers of bands that originate from the functional groups of the primary amine. The bands at 1630 cm<sup>-1</sup> and 1587 cm<sup>-1</sup> were assigned to bending vibrations of the N-H group. The presence of bands at 1117 cm<sup>-1</sup> and 1052 cm<sup>-1</sup> correspond to C-N bond stretching. The band at 3427 cm<sup>-1</sup> is attributed to the stretching vibration of the O-H group and may be due to water adsorbed mainly on the KBr and MWCNTs-NH<sub>2</sub>. This band overlaps the band that arises from the N-H stretching vibration, which should be located at

**Table 1**  
SPECIFIC SURFACE AREA (SSA), PORE VOLUMES AND POINT OF ZERO CHARGE OF MWCNTs-NH<sub>2</sub>

Adsorbent	SSA, (m <sup>2</sup> /g)	Average pore diameter-BET, (nm)	Micropore t-test, (cm <sup>3</sup> /g)	BJH pore volume, (cm <sup>3</sup> /g)	pH <sub>PZC</sub>
MWCNTs-NH <sub>2</sub>	181.9	14.64	0	1.310	8

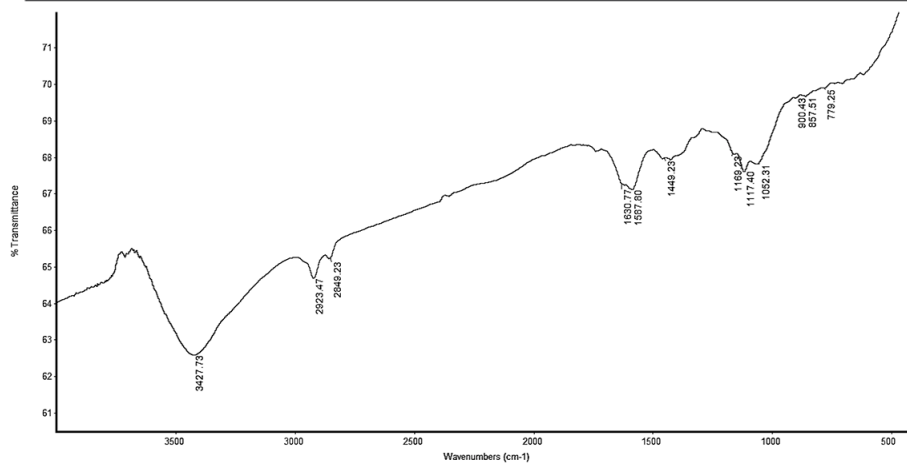


Fig. 1. The FTIR spectra of MWCNTs-NH<sub>2</sub>

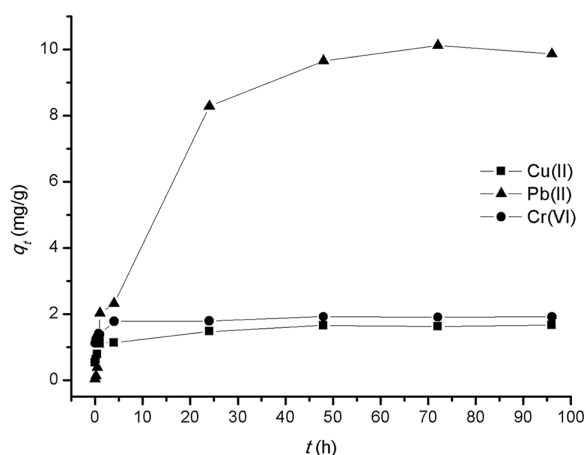


Fig. 2. The amount of adsorbed Cu(II), Pb(II) and Cr(VI) ions by MWCNTs-NH<sub>2</sub> as a function of contact time

### Adsorption kinetics

The amount of metal ions adsorbed ( $q_t$ ) per unit mass of MWCNTs-NH<sub>2</sub> in function of contact time is presented in Figure 2. Data show that all systems reached equilibrium within 48 h.

In the case of porous or nanomaterials, adsorption of heavy metal ions onto a solid surface generally follows four steps: (1) transport of the metal ions from the bulk solution to the boundary film surrounding the adsorbent (bulk diffusion), (2) transfer through the liquid film attached to the solid surface (film diffusion), (3) diffusion in the internal structure of the adsorbent (intra-particle diffusion), and (4) interactions with the surface atoms leading to chemisorption or physisorption. The slowest step will determine the overall rate of the adsorption process. It is usually assumed that the first and fourth steps are rapid and therefore do not limit the rate of the adsorption process. Therefore, film diffusion and intra-particle diffusion are the possible rate-controlling steps [9,16].

To identify the rate-controlling mechanisms during the adsorption of Cu(II), Pb(II) and Cr(VI) on MWCNTs-NH<sub>2</sub> three models were applied. The results obtained for pseudo-first and pseudo-second-order models are summarized in table 2.

the same position. The bands around 2932-2958 cm<sup>-1</sup> originate from the valent vibrations of -CH<sub>2</sub> and -CH<sub>3</sub> groups. The band at 1450 cm<sup>-1</sup> is assigned to the deformation of the C-H bond which is very characteristic and proves the presence of -CH<sub>3</sub> group. Bands at 900 cm<sup>-1</sup> and 857 cm<sup>-1</sup> were due to the out of plane NH<sub>2</sub> bending mode.

**Table 2**  
PARAMETERS OF THE PSEUDO-FIRST AND PSEUDO-SECOND-ORDER MODELS FOR Cu(II), Pb(II), Cr(VI) IONS ADSORBED ONTO MWCNTs-NH<sub>2</sub> at pH 4.5

Metal ion	pH	$q_{e,exp}$ (mg/g)	Pseudo-first-order*			Pseudo-second-order**		
			$q_{e,cal}$ (mg/g)	$k_1 \cdot 10^{-4}$ (1/min)	$R^2$	$q_{e,cal}$ (mg/g)	$k_2 \cdot 10^{-3}$ (g/(mg min))	$R^2$
Cu(II)	4.5	1.67	2.96	6.11	0.8516	1.66	11.6	0.9989
Pb(II)		9.90	8.66	10.3	0.9775	10.1	0.242	0.9871
Cr(VI)		1.92	1.85	8.47	0.7170	1.91	24.7	0.9998

\*  $q_{e,exp}$  – the amount of adsorbate adsorbed per unit mass of adsorbent (mg/g) at equilibrium,  $q_{e,cal}$  – the calculated values of adsorbate adsorbed per unit mass of adsorbent (mg/g),  $k_1$  – pseudo-first-order adsorption rate constant (1/min),  $R^2$  – correlation coefficient

\*\*  $k_2$  – pseudo-second-order adsorption rate constant (g/(mg min))



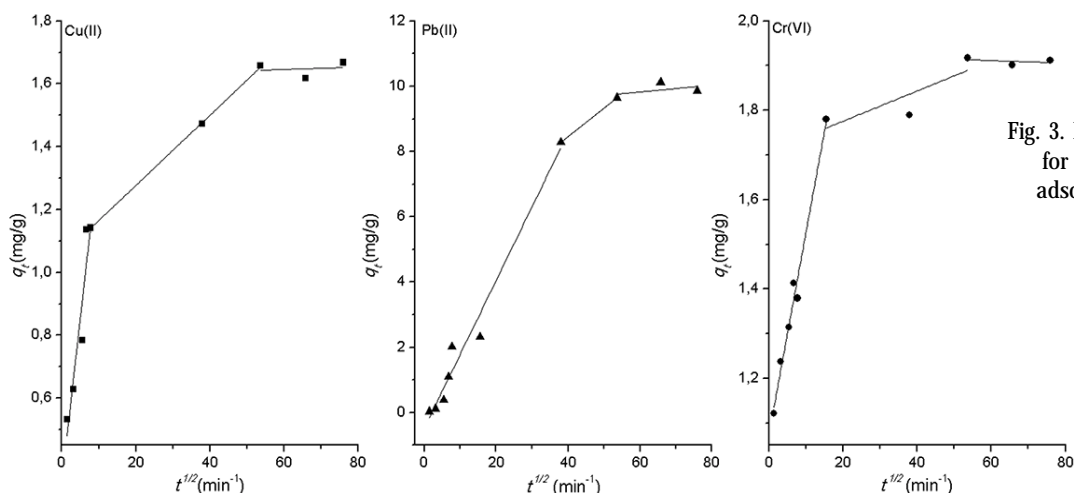


Fig. 3. Intra-particle diffusion plots for Cu(II), Pb(II) and Cr(VI) adsorbed onto MWCNTs-NH<sub>2</sub>

**Table 3**  
INTRA-PARTICLE DIFFUSION COEFFICIENTS FOR Cu(II), Pb(II), Cr(VI) ADSORBED ON MWCNTs-NH<sub>2</sub> AT pH 4.5

Ion	pH	$k_{id}$ (mg/(g min <sup>1/2</sup> ))	$C_i$	$R^2$
Cu(II)	4.5	0.104	0.334	0.8792
Pb(II)		0.226	0.481	0.9695
Cr(VI)		0.0454	1.07	0.9801

$k_{id}$  (mg/(g min<sup>1/2</sup>)) – intra-particle diffusion coefficient and  $C_i$  is proportional to the extent of boundary layer thickness

Comparing the correlation coefficient ( $R^2$ ) values, pseudo-second-order model for the adsorption of Cu(II), Pb(II) and Cr(VI) of MWCNTs-NH<sub>2</sub> fitted well. In addition, the amount of metal ions adsorbed per unit mass of MWCNTs-NH<sub>2</sub> at equilibrium ( $q_{e,exp}$ ) were in good agreement with calculated values ( $q_{e,cal}$ ) for pseudo-second-order kinetics model. The suitability of the pseudo-second-order model agreed well with literature data [2,33,34].

The diffusion mechanism is explored using the intra-particle diffusion model [32,35]. When intra-particle diffusion plays significant role in the adsorption process, the graph of  $q_t$  vs.  $t^{1/2}$  should yield a straight line passing through the origin. The  $q_t$ - $t^{1/2}$  plots for the experimental data obtained in this study are given in figure 3, while the intra-particle diffusion values and the coefficient related to the extent of boundary layer thickness are presented in table 3.

The straight lines did not pass through the origin whereas three linear sections can be identified in the plots: the first corresponds to external mass transfer, the second to a gradual adsorption stage, where the intra-particle diffusion is the controlling step, and the third to a final equilibrium stage where the intra-particle diffusion starts to decelerate due to extremely low solute concentrations in the solution and due to a slower phase of metal intra-particle diffusion within MWCNTs-NH<sub>2</sub> pores as well as the interstitial canals found within the cell agglomerate of the given adsorbent [9,16]. In each case, the nonzero intercepts of the plots were a clear indication that although intra-particle diffusion is slow, it was not the slowest of the rate processes that determine the overall adsorption process. The intra-particle diffusion plots suggest that the Cu(II), Pb(II) and Cr(VI) diffusion in the boundary film (film diffusion) controls the adsorption rate, while the interaction of metal ions with MWCNTs-NH<sub>2</sub> surface remains the most significant process. The similar results have been presented in the literature [9,16,24].

#### Adsorption mechanism

The dominant reaction that may take place at solid solution interface indicate the formation of surface complexes of  $M^{2+}$  with amino groups. The repulsive electrostatic interactions are expected to be present and responsible for lower efficiency of  $M^{2+}$  ion binding at pH 4.5 [24,36]. Also, it is known that Cu(II) usually form inner-sphere complexes [8].  $HCrO_4^-$  prevails in acid solutions (pH 0.9-6.5), while  $CrO_4^{2-}$  is predominant in an alkaline medium [37]. Electrostatic attraction between  $HCrO_4^-$  and  $-NH_3^+$  is expected in acid solution [2,11,13]. Results obtained in this study agreed with the available scientific literature [2, 11, 38, 39].

#### Adsorption under equilibrium conditions

The isotherm experiments were carried out at different initial Cu(II), Pb(II) and Cr(VI) concentrations (50-3000  $\mu$ g/L) in deionized water at pH 4.5 for 48h. The effects of 0.01 M  $Cl^-$ ,  $SO_4^{2-}$ ,  $NO_3^-$  and  $PO_4^{3-}$  anions on the adsorption isotherm were also investigated under the same conditions. The Freundlich adsorption isotherms obtained using the non-linearized method are shown in figure 4, and the adsorption parameters are listed in table 4.

The results indicate that the adsorption affinity of MWCNTs-NH<sub>2</sub> decreases in the following order Cu > Pb > Cr in the presence of  $Cl^-$  and  $PO_4^{3-}$  ions, while in the presence of  $NO_3^-$  and  $SO_4^{2-}$  the following order is Cu > Cr > Pb. Pb(II) has the bigger ionic radius and higher electronegativity than the Cu(II) [8], which lead to its lower adsorption since metal ions with smaller ionic radius penetrate more easily through the boundary layer. Deviation of  $n$  values from 1 indicates a non-linear adsorption that takes place on heterogeneous surfaces. The  $n$  values are smaller than 1, which indicates favorable adsorption of heavy metal ions, except for Cu(II) in the presence of  $Cl^-$ ,  $NO_3^-$  and  $PO_4^{3-}$ . The obtained  $K_f$  values for MWCNTs-NH<sub>2</sub> are in accordance with the literature data [13].

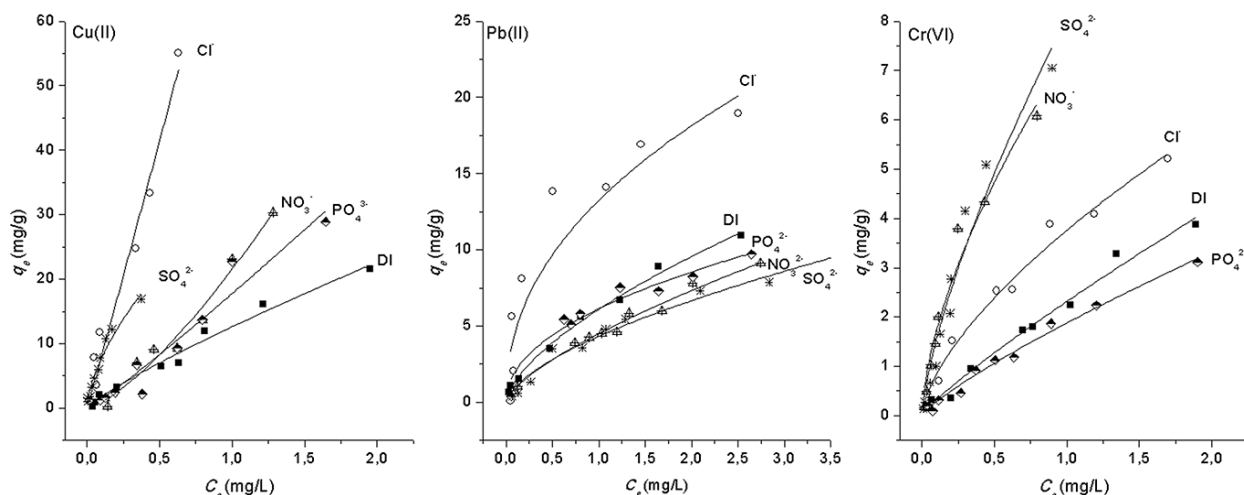


Fig. 4. The Freundlich isotherms for adsorption of Cu(II), Pb(II) and Cr(VI) on MWCNTs-NH<sub>2</sub> at pH 4.5 in deionised water (DI) and in 0.01 M aqueous solutions of respected anions

**Table 4**

FREUNDLICH ISOTHERM PARAMETERS FOR Cu(II), Pb(II) AND Cr(VI) ADSORPTION ON MWCNTs-NH<sub>2</sub> AT pH 4.5 IN DEIONISED WATER (DI) AND IN 0.01 M AQUEOUS SOLUTIONS OF RESPECTED ANIONS

Metal ion	anion	Freundlich parameters*		
		$K_F$ (mg/g)/(mg/L) <sup>n</sup>	$n$	$R^2$
Cu(II)	DI	12.6	0.84	0.982
	Cl <sup>-</sup>	83.6	1.01	0.966
	NO <sub>3</sub> <sup>-</sup>	21.6	1.37	0.970
	SO <sub>4</sub> <sup>2-</sup>	33.1	0.63	0.962
	PO <sub>4</sub> <sup>3-</sup>	17.8	1.09	0.935
Pb(II)	DI	6.13	0.64	0.993
	Cl <sup>-</sup>	13.27	0.46	0.903
	NO <sub>3</sub> <sup>-</sup>	4.51	0.70	0.984
	SO <sub>4</sub> <sup>2-</sup>	4.34	0.63	0.976
	PO <sub>4</sub> <sup>3-</sup>	6.14	0.48	0.945
Cr(VI)	DI	2.28	0.92	0.991
	Cl <sup>-</sup>	3.79	0.66	0.981
	NO <sub>3</sub> <sup>-</sup>	7.27	0.62	0.973
	SO <sub>4</sub> <sup>2-</sup>	8.11	0.72	0.958
	PO <sub>4</sub> <sup>3-</sup>	1.89	0.82	0.987

\*  $q_e$  – equilibrium adsorption uptake of heavy metal ions (mg/g),  $C_e$  – equilibrium aqueous concentration of heavy metal ions (mg/L),  $K_F$  – Freundlich constant related to the affinity of the adsorbate to the adsorbent ((mg/g)/(L /mg)<sup>n</sup>),  $n$  – site energy heterogeneity factor indicating isotherm nonlinearity (dimensionless)

#### Effect of anions

The influence of background electrolyte anions on heavy metals removal in 0.01 M solutions of Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup> and PO<sub>4</sub><sup>3-</sup> is presented in figure 5.

#### Effect of Cl<sup>-</sup>

The results showed that the presence of Cl<sup>-</sup> increased adsorption of the Pb(II) and Cu(II) by 25-30%, while adsorption of Cr(VI) slightly decreased by about 3%. At pH

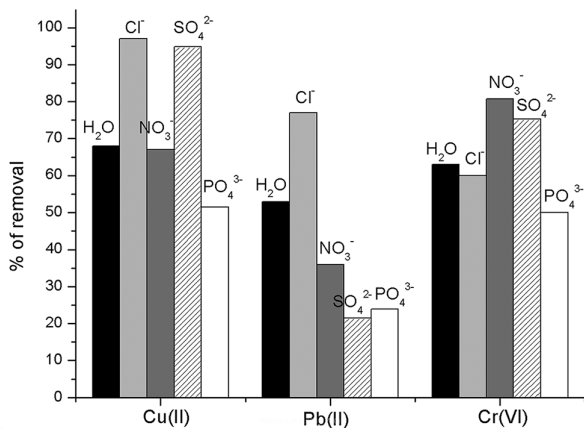


Fig. 5. The influence of background electrolyte anions on Cu(II), Pb(II) and Cr(VI) on removal efficiency by adsorption on MWCNTs-NH<sub>2</sub> at pH 4.5

< 6 dominant forms are Cu<sup>2+</sup> and Pb<sup>2+</sup> [40]. Presence of Cl<sup>-</sup> anions reduces the electrostatic repulsion between Cu<sup>2+</sup> and Pb<sup>2+</sup> and positively charged MWCNTs-NH<sub>2</sub> surface, thus increasing adsorption capacity. Also, it is known that Cu(II) usually form inner-sphere complexes [8]. In the presence of Cl<sup>-</sup> ions, Pb<sup>2+</sup> form complexes in the form PbX<sup>+</sup>, PbX<sub>3</sub><sup>-</sup> etc. [41], and may interact with surface of MWCNTs-NH<sub>2</sub> which also leads to increased adsorption. Similar results are obtained by Hu et al. [12]. In the case of Cr(VI), the presence of Cl<sup>-</sup> slightly reduced the Cr(VI) uptake possibly because smaller Cl<sup>-</sup> ion penetrates more easily through the boundary layer than HCrO<sub>4</sub><sup>-</sup> (radius of Cl<sup>-</sup> and HCrO<sub>4</sub><sup>-</sup> is 0.180 and 0.230 nm, respectively). Di Natale et al. [42] have shown that chloride has displayed a potential to hinder the adsorption of Cr(VI) on adsorbents like activated carbon. In addition, Pillay et al. [11] suggested that the nanotube surface has a greater affinity for the chloride and sulphate ions than for the dichromate ions

#### Effect of NO<sub>3</sub><sup>-</sup>

In the presence of NO<sub>3</sub><sup>-</sup>, no significant changes in Cu(II) adsorption onto MWCNTs-NH<sub>2</sub> was observed. For Pb(II) adsorption, NO<sub>3</sub><sup>-</sup> had a negative effect, while in the case of Cr(VI), NO<sub>3</sub><sup>-</sup> had positive effect. Kosa et al. [8] obtained the same results for Cu(II). Negative effect of NO<sub>3</sub><sup>-</sup> for Pb(II) adsorption onto MWCNTs-NH<sub>2</sub>, can be explained by the fact that at pH 4.5 predominant form is Pb<sup>2+</sup> and therefore negatively charged NO<sub>3</sub><sup>-</sup> ions are adsorbed easier on positively charged surface of MWCNTs-NH<sub>2</sub>. The obtained results are in opposite with previously described in the literature, where is shown that the effect of NO<sub>3</sub><sup>-</sup> on Pb(II) sorption is very weak and negligible in the case of oxidized-MWCNTs [10]. In the case of Cr(VI), NO<sub>3</sub><sup>-</sup> had positive effect as found in literature [8,43].

#### Effect of SO<sub>4</sub><sup>2-</sup>

The presence of SO<sub>4</sub><sup>2-</sup> increased Cu(II) adsorption by 30%, Cr(VI) adsorption by about 10% and decreased Pb(II) adsorption by 25%. There are several mechanisms that could explain the enhancement of Cu(II) adsorption in the presence of SO<sub>4</sub><sup>2-</sup>. The first includes potential formation of neutral complex CuSO<sub>4</sub> that could be adsorbed more easily by the positively charged MWCNTs-NH<sub>2</sub> [12,13,40]. Another possible mechanism proposed by Lam et al. [44] showed that the SO<sub>4</sub><sup>2-</sup> anion affects the adsorption by interacting with the dissolved copper to form [CuSO<sub>4</sub>]<sup>0</sup> species, coadsorbed with Cu<sup>2+</sup> to form stable complexes.

In the presence of SO<sub>4</sub><sup>2-</sup>, Pb(II) adsorption was decreased. Characterization of the chemical speciation of higher-charged systems such as Pb<sup>2+</sup>-SO<sub>4</sub><sup>2-</sup> is complicated by a number of factors and the formation of solvent-

separated (outer sphere) complexes. While some M<sup>2+</sup>/SO<sub>4</sub><sup>2-</sup> systems form higher-order complexes others appear not to. The existence of Pb(SO<sub>4</sub>)<sub>2</sub><sup>2-</sup> is controversial [45-47]. Double charged SO<sub>4</sub><sup>2-</sup> anion might be attracted more to the positively charged surface of the MWCNTs-NH<sub>2</sub> adsorbent than Pb(II) ions. However, this effect was not observed in our study thus giving no evidence on Pb(SO<sub>4</sub>)<sub>2</sub><sup>2-</sup> formation.

In the case of Cr(VI), SO<sub>4</sub><sup>2-</sup> has a slight positive effect on its removal. Due to the similar configuration of chromate and sulfate anions, it is expected that sulfate anions competes for adsorption sites with chromate anions. On the other side, due to slightly smaller radius of HCrO<sub>4</sub><sup>-</sup> compared to SO<sub>4</sub><sup>2-</sup> (0.230 nm and 0.242 nm, respectively), HCrO<sub>4</sub><sup>-</sup> could penetrate more easily through boundary layer. Possible explanation of the results obtained in this study gave Venditti et al. [37] who demonstrated that CrO<sub>4</sub><sup>2-</sup> could be selectively removed in the presence of SO<sub>4</sub><sup>2-</sup>. This effect is explained by the difference in hydration energy of HCrO<sub>4</sub><sup>-</sup> and SO<sub>4</sub><sup>2-</sup>. Namely, the hydration energy for sulphate (1080 kJ/mol) is much higher than the energy of hydration for HCrO<sub>4</sub><sup>-</sup> (184 kJ/mol) which causes that sulphate ions are more bonded to water molecules than the chromate ions, resulting in a practically selective removal of the chromate anions from solution. Misaelides et al. [43] and Ayuso [48] have shown that the presence of SO<sub>4</sub><sup>2-</sup> reduced the Cr(VI) uptake. However, other authors observed no significant effects of SO<sub>4</sub><sup>2-</sup> on the adsorption of Cr(VI) [49].

#### Effect of PO<sub>4</sub><sup>3-</sup>

Phosphates reduced the adsorption of all metals investigated. The obtained results for Cr(VI) are in accordance with studies of Chowdhury et al. [49] who observed decrease up to 90% of Cr(VI) adsorption onto mixed magnetite and maghemite nanoparticles from aqueous solution and have shown that chromium uptake decreased with increasing phosphate concentration. Li et al. [50] have shown that phosphate reduced Cu(II) adsorption on hematite across a wide pH and cation concentration ranges. Phosphate can occupy the inner-sphere adsorption sites (=FeOH) on the mineral surface, decreasing the inner-sphere adsorption sites for heavy metals. Opposite results, enhanced adsorption for Cu(II) and Pb(II) have been obtained by some authors [12, 51].

## Conclusions

The data presented in this work has shown that MWCNTs-NH<sub>2</sub> can efficiently adsorb ppb levels of Cu(II), Pb(II) and Cr(VI) ions from aqueous solutions in the presence of Cl<sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup> and PO<sub>4</sub><sup>3-</sup>. The results showed that removal of heavy metal ions could be strongly affected by the presence of background electrolyte anions. The process complies with the pseudo-second-order kinetic model. Although intra-particle diffusion is slow, it was not the slowest of the rate processes that determine the overall order. The main adsorption mechanisms of Cr(VI) and divalent metal ions onto MWCNTs-NH<sub>2</sub> are electrostatic attraction and chemical interaction/complexing between the metal ions and the surface functional groups of MWCNTs. This research has contributed to a better understanding of the influence of background anions on the adsorption of heavy metals in aqueous solutions, which is very important for application in water treatments.

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