REMOVAL OF HEAVY METALS FROM THE ENVIRONMENT BY IRON NANOPARTICLES

Dana FIALOVA[1], David HYNEK[1,2], Pavel KOPEL[1,2], Monika KREMPLOVA[1], Vojtech ADAM[1,2] and Rene KIZEK*[1,2]

[1]Department of Chemistry and Biochemistry, Faculty of Agronomy, Mendel University in Brno, Zemedelska 1, 613 00 Brno, Czech Republic
[2]Central European Institute of Technology, Brno University of Technology, Technicka 3058/10, 616 00 Brno, Czech Republic
*kizek@sci.muni.cz

INTRODUCTION

Water is the most important component of living organisms, is necessary for most biochemical reactions within plants and animals, essential for the creation and preservation of life. With a growing population and industrial development the water consumption is rising and at the same time the greater pollution of the water is occurred. Due to development of heavy industry, traffic and construction, the water gets large amounts of heavy metals [1, 2]. Pollution of the aquatic ecosystem by heavy metals is one of the global environmental problems. Among the heavy metals include, in particular cadmium, lead, copper, zinc and mercury. These elements are highly undegradable, capable to accumulate in various tissues of organisms [3, 4]. For the most toxic forms of heavy metals are considered to be the ionic forms, organic compounds of anthropogenic origin and biomethylated organometallic compounds [5]. The accumulation in the human body may cause damage to the structure and function of kidney, bones, central nervous system, hematopoietic disorders, may influence the course of the fundamental biochemical reactions and have adverse reproductive effects [6]. A large number of institutions are interested in new and efficient technologies for the removal of heavy metals from surface and waste water. In recent years, the nanotechnologies recorded a great development in this area. It is usually the use of new and unusual properties of nanomaterials, thus particles size of nanometers to micrometers. Nanotechnologies have applications in various disciplines from medicine through chemical technology to the construction industry [7, 8]. Nanomaterials may have applications even in the isolation and removal of heavy metals from water environment.A very important part in this issue is the detection of metal ions, which should be rapid, sensitive and simple. However, these methods require complex laboratory equipment, expensive chemicals and their availability is very limited. Instead the electrochemical methods can be used (differential pulse voltammetry and/or cyclic voltammetry). These techniques are one of the best for metal detection because of their low detection limits, metal selectivity, high sensitivity, mobility and low cost [14-16].

EXPERIMENTAL PART

Sample preparation: For the analysis of heavy metals and creating calibration data there have used cadmium, lead and copper $Cd(NO_3)_2$, $Pb(NO_3)2$ and $Cu(NO_3)_2$ standards, all purchased from Sigma Aldrich (St. Louis, USA). Samples were diluted to the desired concentration with ACS water (Sigma Aldrich, Wed Louis, USA). For the heavy metals isolation using nanoparticles, the samples were prepared as follows: into the microtube there was weighed 10 mg of Fe_2O_3 nanoparticles (manufactured in Laboratory of metallomics and nanotechnologies), 1 ml of heavy metals solutions at a concentration of 100 μM was added, the tubes were shaken and incubated for specific time (1, 5, 10, 15 and 30 minutes and 1, 3, 6, 12 and 24 hours). After the time interaction, the nanoparticles were anchored in the bottom of the tube using a magnet and all of the solution was pipetted away. Residues of nanoparticles from the supernatant were removed by membrane filtration. At this stage, the samples were subjected to electrochemical analysis.

Electrochemical determination : The electrochemical analysis of heavy metals were performed by 797 VA STAND in connection with 813 VA Computrace (both Metrohm, Switzerland). For determination there was used a standard electrochemical cell with classical three-electrode system. The hanging mercury drop electrode with drop area of 0.4 mm^2 was used as a working electrode. An Ag/AgCl/ 3M KCl electrode was chosen as reference electrode and platinum as auxiliary one. All samples were deoxygenated by argon (99.999%) prior to measurements. The parameters for differential pulse voltammetry and linear sweep voltammetry were chosen as follows: start potential -1.3 V, end potential 0.2 V, deposition potential -1.3 V, time of accumulation 240 s, purge time 120 s, voltage step 0.025 V, voltage step time 0.2 s, sweep rate 1 V/s. 0.2 M acetate buffer (sodium acetate trihydrate, adjusted at required pH by acetic acid, Sigma Aldrich, St. Louis, USA) was chosen as a supporting electrolyte. The volume of pipetted sample was 15 μl, the volume of electrochemical cell was 2 ml (15 μl of the sample + 1985 μl of electrolyte).

RESULTS

For this study there were used two basic electrochemical methods - differential pulse voltammetry and linear sweep voltammetry. In both methods, it was first optimized the pH of the electrolyte (acetate buffer) and then measured the calibration curves. Fig. 1 shows the dependence of the selected electrolyte pH due to the applied concentration of heavy metal. For cadmium, lead and copper, it is clear that high and stable signal providing an acetate buffer adjusted to pH 5. The same trend was observed in the samples measured by LSV (data not shown). 0.2 M acetate buffer adjusted to pH = 5 was used as the supporting electrolyte for all further measurements. For all the heavy metals there were measured calibration curves (Fig. 1) with a concentration range of 1.56 -2000 μM, all the calibration curves shows the linear trend. For cadmium, the regression equation was y = 1.2697x, coefficient of determination was R^2 = 0.999. Limit of detection (3S/N) was set at 0.208 μM. To lead the regression equation was y = 1.6977x, coefficient of determination was R^2 = 0.980. Limit of detection (3S/N) was set at 0.310 μM. For copper, the regression equation was y = 1.9516x, coefficient of determination was R^2 = 0.996. The limit of detection was set at 0.326 μM. The characteristic peak for cadmium was observed in the potential of -0.645 V, in -0.475 V for lead and for copper in potential -0.030 V. The calibration curves were measured by differential pulse voltammetry.

The calibration curves were measured simile manner by method of linear sweep voltammetry (data not shown). Thanks to lower detection limits there were selected differential pulse voltammetry for further measurement.

The next step was the isolation of heavy metals using iron nanoparticles. Solutions of heavy metals were incubated with the nanoparticles at different time intervals. Fig. 3 presents graphs showing the percentage of heavy metals isolation in the timeline. For all of these heavy metals is clear that after 24 hours of incubation the particles followed 100% of metal from solution, the electrochemical voltammograms contained no signal. In figure 3D there is shown a comparison of adsorption efficiency of 30 minutes and 24 hours, lead ions were adsorbed rapidly to the surface of Fe_2O_3 particles, cadmium ions slowly.

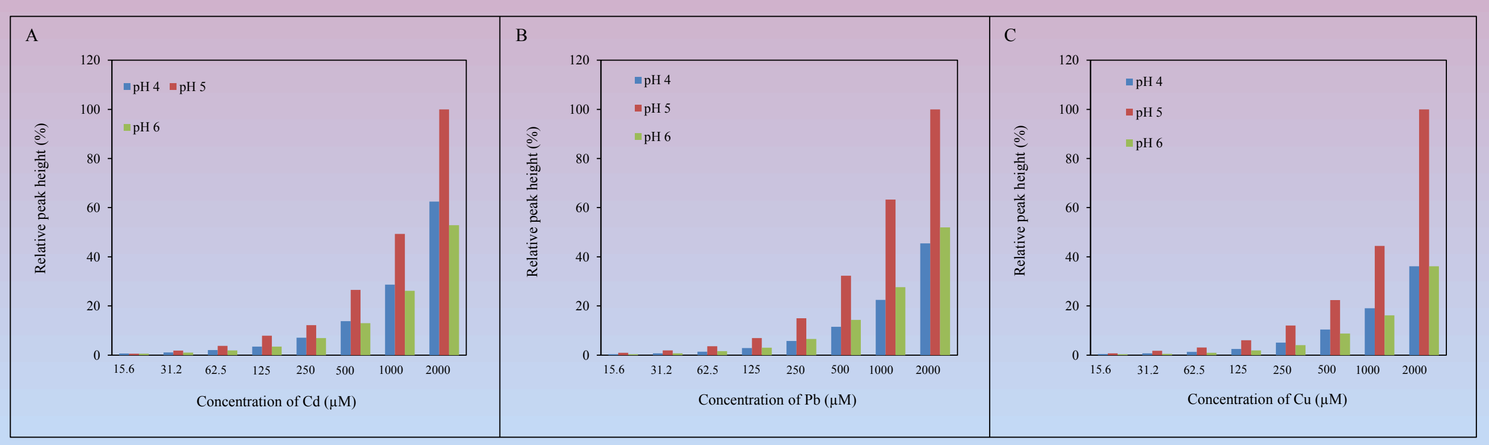

Fig.1: Optimization of supporting electrolyte pH for (A) cadmium, (B) lead, (C) copper. 0.2 M acetate buffer was used as an electrolyte; the determination method was difference pulse voltammetry

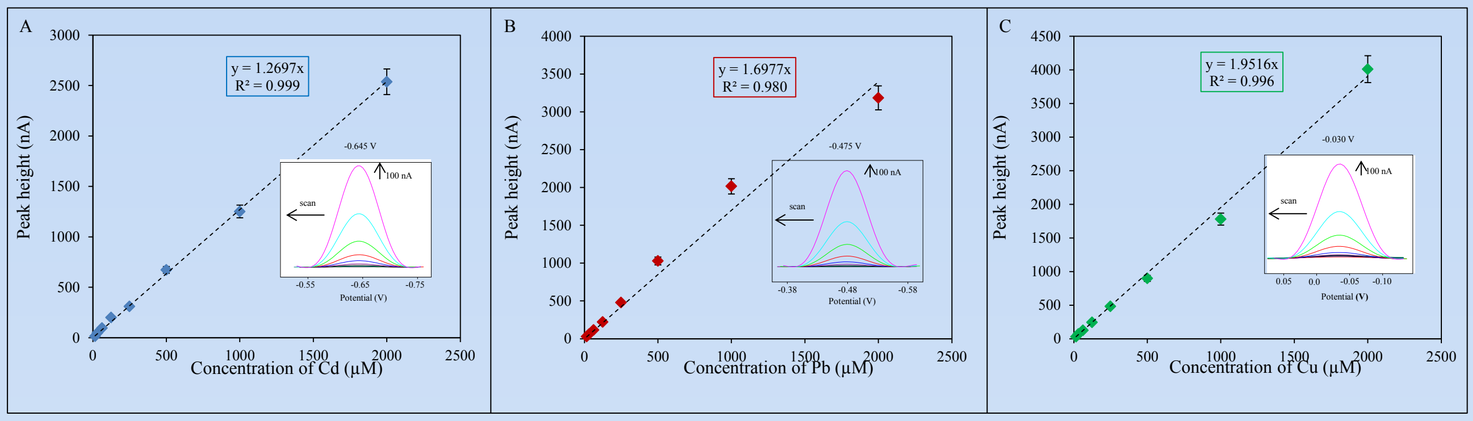

Fig. 2: Calibration curves for (A) cadmium, (B) lead and (C) copper. The concentration range was 1,56-2000 μM, the method was DPV, 0.2 M acetate buffer pH=5 was used as a supporting electrolyte

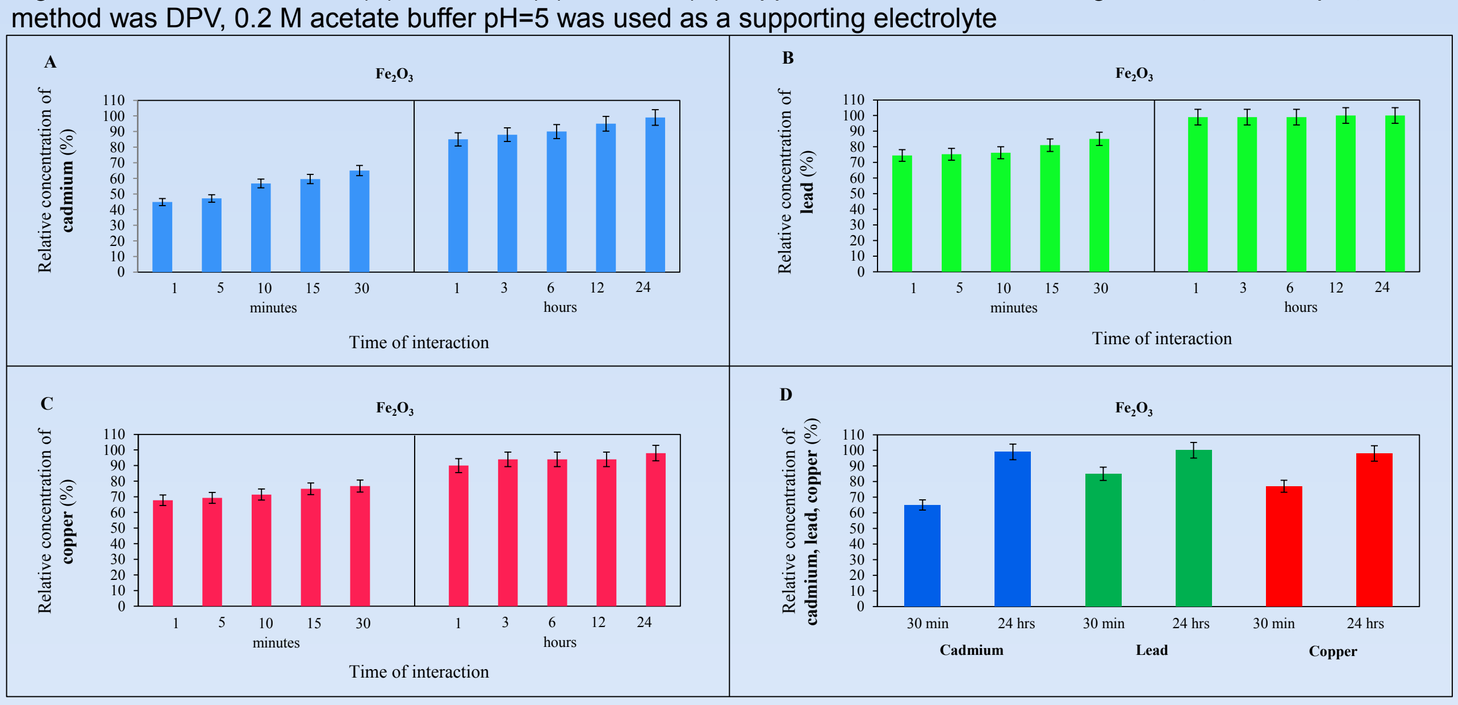

Fig. 3: Time interaction of heavy metals with iron nanoparticles, (A) for cadmium, (B) for lead and (C) for copper. In part D there is a comparison of adsorption efficiency after 30 minutes and 24 hours interaction for all applied heavy metals

CONCLUSION

Pollution of the aquatic ecosystem by heavy metals is one of the global environmental problems. The paper suggests the isolation of heavy metals in surface and waste water. There were used the basic heavy metals cadmium, lead and copper, which have been isolated from aqueous solutions using iron nanoparticles Fe_2O_3. It was found that after 24 hours of interaction, the surface of the nanoparticles adsorbed 100% applied concentration of all the heavy metals. This method can be used as an alternative technology in wastewater treatment.

ACKNOWLEDGEMENT

Financial support from NanoBioMetalNet CZ.1.07/2.4.00/31.0023 *is greatly acknowledged.*