ҚАЗАҚСТАН РЕСПУБЛИКАСЫ
БІЛІМ ЖӘНЕ ҒЫЛЫМ МИНИСТРЛІГІ

МИНИСТЕРСТВО ОБРАЗОВАНИЯ И НАУКИ
РЕСПУБЛИКИ КАЗАХСТАН

ҚазҰТЗУ ХАБАРШЫСЫ

ВЕСТНИК КазНИТУ

VESTNIK KazNRTU

№4 (128)

АЛМАТЫ 2018 АВГУСТ

Sagitova G.F., Zhumabaev M.Sh., Alibaeva A.B., Mukhametalikyzy S., Syban E.R.

Practical recommendations to development motivation to study chemistry

Summary. In this article the possibility to raise cognitive activity of pupils at chemistry lessons by means of didactic games, as games process stimulates thinking activity, a child feels and creates freely. A didactic game will allow to brightly implement all the principal teaching functions and also to use a complex of informative tasks of interdisciplinary character (the integrated tasks), a set of cards on self-testing of individual achievements and independent increase in level of knowledge and abilities.

Keywords: perspective, teaching chemistry, didactic games, cognitive activity, motivation

УДК 543.33:544.654.2

A.Dalbanbay, B.G. Kemal, A. Dauletbay, M.Kh. Nauryzbayev
(Al Farabi Kazakh National University, Almaty, Kazakhstan
The Center of Physical Chemical Methods of Research and Analysis, Almaty, Kazakhstan
E-mail: amantay.d@gmail.com)

Pb (II) SPECIFICATION ON CARBON PASTE ELECTRODE MODIFIED BY ELECTROCHEMICAL DEPOSITION OF SILVER NANOPARTICLES IN WATER

Abstract. In this work a simple and economical electrode has been developed to detect Pb (II) in water by anodic stripping voltammetry. To achieve a better sensing performance of lead (II) CPE modified with silver nanoparticles by electrodeposition. The carbon paste electrode (CPE) modified with silver nanoparticles (AgNPs) demonstrates high sensitivity in the detection of lead (II) by using anodic stripping square wave voltammetry. For AgNPs modified CPE detection limit of lead was $8{,}03\times10^{-8}$ mol/L.

Keywords: silver nanoparticles, Pb^{2+} detection, carbon paste electrode, electrodeposition

Introduction

Refinement of water from toxic metals is worldwide concern. Toxic heavy metals are hazardous pollutants by their high solubility in the aquatic environments. They can be absorbed by living organisms. When they enter the food, large concentrations of heavy metals may accumulate in the human body. If the metals are ingested beyond the permitted concentration, they can cause serious health disorders. Therefore, detection of toxic heavymetals from aqeuous solution is primaryimportance.

Poisoning with lead in human cause's serious harm to the kidney, liver also nervous and reproductive systems. It also can affect to nephro toxic effects of high exposure level and bone injury for long-term exposure [1,2]. According to Ref. [3], for certain reasons children are more sensitive to the influence of lead than adults. Among to their major consequences are diminished intelligence quotient, effects on the nervous system, impairing of sensory systems, involuntary nervous and kidney functions, and premature births.

The main lead pollution is by automobiles and battery industries[4]. Also, ions of lead generally occur in industrial and agricultural wastewater and acidic leachate from landfill sites in relatively high concentration[1].

Up to know, many of methods have been applied to determine Pb ions. Researchers [5] were developed colorimetric detection technique for Pb^{2+} ions. In living organisms Pb^{2+} ions were detected with sensitive near-infrared fluorescent probe methods. [6] Also, a method was investigated for analysis of Pb ions in aqueous and biologic systems by combining online flow injection and preconcentration with inductively coupled plasma-MS [7]. But these methods need costly apparatus. The most reliable techniques used for the determination of Pb ion is the electrochemical methods, where they have many advantages such as high sensitivity and selectivity with high speed, less cost, relative simplicity and low detection limit. Although, nowadays voltammetric methods have been extensively used.

Voltammetric methods have been conducted with different electrodes. Carbon paste electrodes (CPEs) are perspective electrochemical sensors of wide workability. **The authors of more recent studies[8–12]have established that c**arbon paste electrodes were sensitive and reliable. Carbon paste electrodes have many possibilities like easily renewable surface, low cost, and have very low background currents[12]. The advantages of applying carbon wax electrodes for electrochemical measurements mostly in voltammetric and polarographic researches, such as improved reproducibility, low residual currents and robust in operation, have been earlier reported[13,14]. The carbon-wax sensor features (sensitivity, pH optimum, electrochemical behavior, storage and operational stability) have been evaluated and compared with a traditionally utilized

CP electrode using paraffin oil as the binding reagent[9].The present paper includes modified carbon paste electrode with improving properties. The deposited AgNPs to carbon paste electrode purposes new possibilities for the development of sensors with developed analytical performance.

Materials and Methods

2.1. Apparatus

Electrochemical measurements were carried out by using a conventional three electrode system. Modified carbon paste electrode acted as the working electrode. A saturated KCl Ag/AgCl electrode and Pt Plate served as reference and counter electrode, respectively. In case of electrodeposition of silver nanoparticles the reference electrode was silver wire. Electrochemical measurements such as CV, SWV and CA were carried out by computer controlled electrochemical workstation Biologic SP-300. All experiments were performed at room temperature, without any purge of inert gaseous. The morphologies of carbon paste electrode surface were obtained by Quanta 200i 3D scanning electron microscope (NNLOT, KazNU).

2.2. ***Reagents***

All chemicals were analytical grade and used without further purification. All solutions were prepared with double-distilled water. Silver nitrate was used to prepare silver nanoparticles and also used to modify carbon paste electrode. Paraffin was used as the pasting agent for the carbon paste electrode and particle size less than 0.1 mm graphite was used for preparing the working electrode. Acetate buffer solution 0.1M, pH = 4.5 prepared by mixing stock standard solutions of acetic acid and sodium acetate.

2.3 Preparation of carbon paste electrode

In the present work, graphite was used to prepare carbon paste electrode. The carbon paste mixture was prepared by thoroughly mixing of 0.08 g powder of graphite with 0.02 g of paraffin wax. Paraffin wax was heated till melting before mixing with the graphite powder. Mixture was packed into a 5 mm diameter insulin syringe of which piston is connected with copper wire for electrical contact. The working surface of the carbon paste electrode was smoothed on a filter paper and sonicated by 5 minute in ultrasonic bath to remove the graphite residue, before each experiment the electrode rinsed with distilled water. The working electrode performance was further improved by the electrochemical deposition of AgNPs in 0.5 mM silver nitrate solution with 0.1 M $NaNO_3$.

2.4 Synthesis of silver nanoparticle

Electrodeposition is a powerful method for the preparation of nanostructured materials[15,16] Silver nanoparticles were synthesized by modified method in reference[17]. The electrodeposition of silver nanoparticles on carbon paste electrodes was performed in a glass cell of 10 ml volume using a standard, three-electrode equipment. Potentiostatic single-pulse technique was used for electrodeposition of silver on carbon paste electrode. The electrolyte is a 0.5mM $AgNO_3$ solution with 0.1M $NaNO_3$ as supporting electrolyte. The pulse parameters are as follows: −0.9 V vs Ag wire for 50 ms, the electrodepostion conducted without stirring. AgNPs modified CP electrode was rinsed with distilled water prior to using in measurements.

3 Results and Discussion

3.1. Characterization of Carbon Paste Electrode modified with AgNPs

The silver nanoparticles were obtained by the potentiostatic electrodeposition method. A sufficiently negative voltage (900 mV vs Ag/AgCl) is used to the electrode which will cause the reduction of metal ions to metal atoms. These metal atoms then clustered to form nanoscopic metal particles on the CP electrode surface. According to this method, the formation of silver nanostructures could be readily realized on the electrical conducting surfaces[18]. The deposition time was varied from 50 ms to 300 ms, the 50 ms deposition time indicate a good result. In order to assert the presence of AgNPs on the surface of CPE, a cyclic voltammetry was performed in 0,1M HNO_3 solution. Scanning range varied from 0 to 0.6 V vs Ag/AgCl. Scanning started from 0 V to more positive direction with 100mV/s scan rate. The cyclic voltammagrams of AgNPs modified CPE and bare CPE are illustrated in Figure 1. At AgNPs/CPE in 0,5V range a pick appeared, this peak supposed an AgNPs stripping peak. In reverse scan a 0,35 V peak corresponds to Ag^+ reduction peak. For comparative studies cyclic voltammetry was conducted with bare CPE, there is no analytical signal was observed. These observations have exhibited the presence of AgNPs.

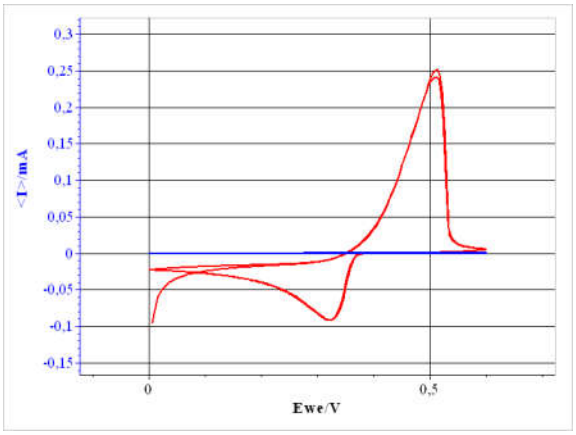

Figure 1. Cyclic voltammogram of CPE in 0,1 M HNO_3, scan rate 100 mVs^{-1}, bare CPE (blue line), CPE modified with AgNPs (red line)

Figure 2 illustrates the SEM image of AgNPs/CPE surface. The nanoparticles obtained by double-pulse method had a wide distribution of sizes, when using a single pulse method, the particles deposited more evenly[19]. According to the figure 2 fewer large particles of Ag are present on the surface and the Ag nanoparticles show a spherical shape, having sizes in the range 20 - 100 nm.

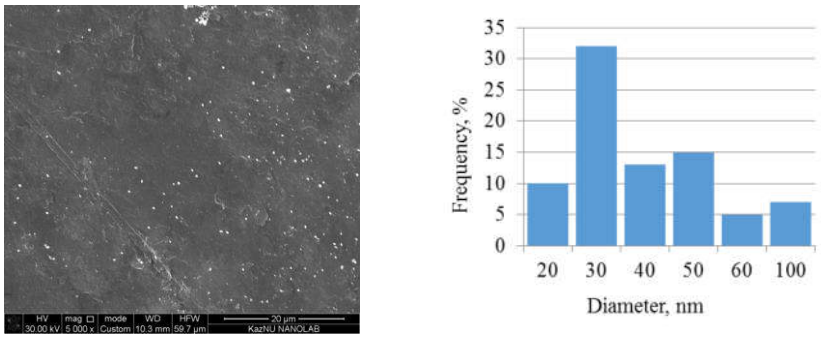

Figure 2. SEM image and particle size distribution histogram for silver particles electrochemical deposited on CPE, t_{dep}=50 ms, E_{dep}= -0,9 V vs Ag/AgCl

Ferro/ferrocyanide redox couple is often used for the evaluation of electrochemical properties of electrode materials[20]. In our work potassium ferricyanide was used to study electrochemical properties of AgNPs/CPE. As shown in Figure 3 a higher current peak in comparison with the bare CPE was appeared at AgNPs/CPE. It demonstrates that deposited AgNPs improved the electrochemical properties of CPE.

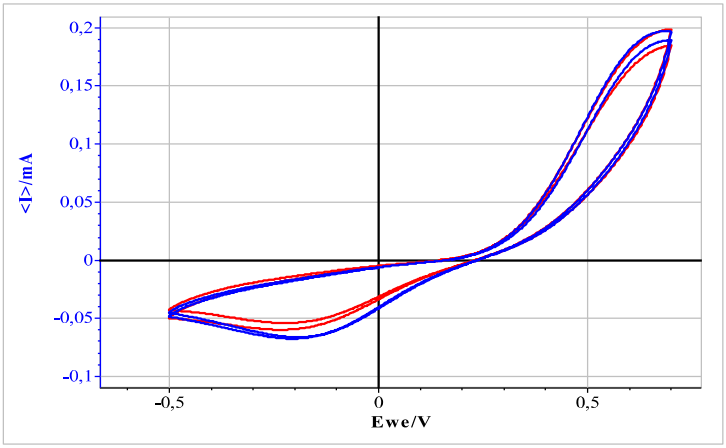

Figure 3. Cyclic voltammetry of 1 mM potassium ferro/ferricyanide (pH 4,5), scan rate 50 mVs^{-1} CPE (red line), CPE modified with AgNPs (blue line)

3.2 Electrochemical detection of Pb^{2+} by SWV

Electrochemical detection of Pb^{2+} ions were performed by anodic stripping square wave voltammetry method. The square wave voltammetry technique has two steps: the first is called as a preconcentration, which involves holding the potential at a sufficiently negative value for a set length of time. The second step is the sweeping of the potential from −1 to 0 V vs Ag/AgCl, which results in the electrochemical oxidation of Pb^0 to Pb^{2+} at the CPE surface, allowing the detection of the Pb concentration in the solution by stripping signals.

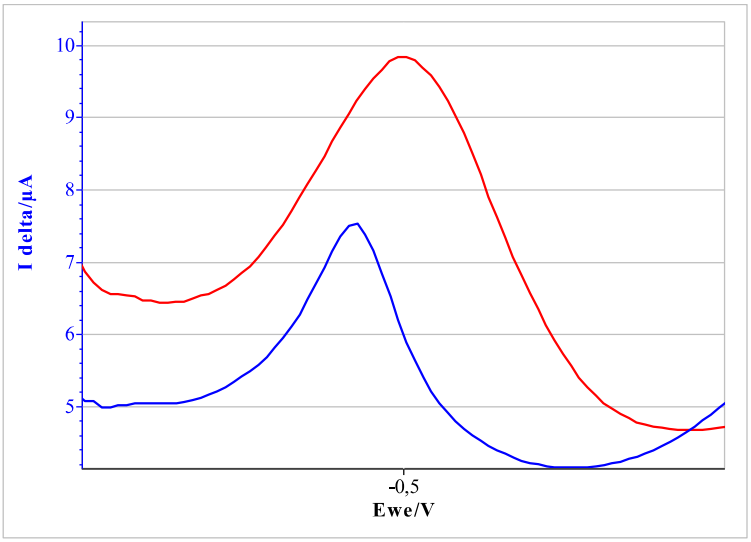

Figure 4. Anodic stripping SWV of 2 ppm Pb (II) by CPE in 0,1 M acetate buffer solution, in the potential range from -1 to 0 V (Ag/AgCl) at a scan rate of 100 mVs^{-1} by using bare electrode CPE (blue line), CPE modified with AgNPs (red line)

In order to study the influence of AgNPs on Pb determination, the SWV was conducted with and without AgNPs on CPE. Figure 4 demonstrates a comparison of SWV results of the bare CPE to the AgNPs/CPE, in the same concentration of Pb (II) (10^{-8} M). The peak area and the potential of current peak are the equal at approximately -0,55 V vs Ag/AgCl for both electrodes, but the magnitude of peak current is 1,5 times larger for the AgNPs/CPE. This demonstrates that the AgNPs/CPE is more sensitive to the Pb (II) reduction than bare CPE.

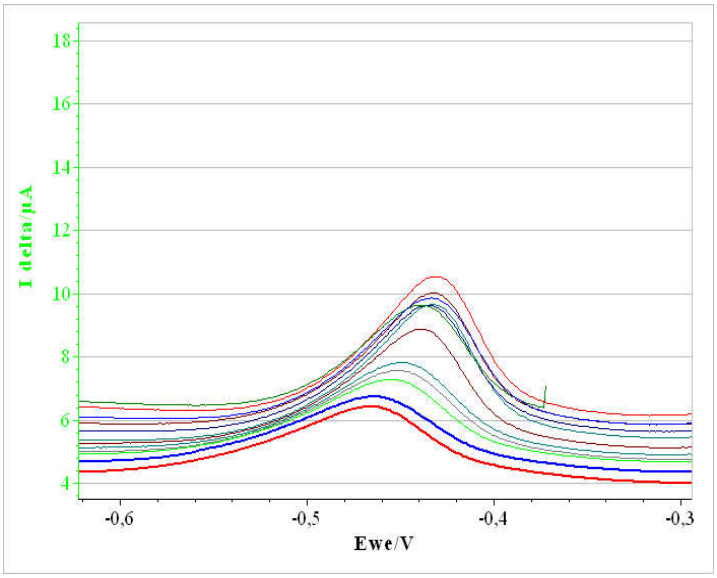

Figure 5. Anodic stripping SWV for increasing levels of Pb (II) in 10^{-8} $molL^{-1}$ by CPE in 0,1 M acetate buffer (pH= 4,5), in the potential range from -1- 0 V (vs. Ag/AgCl) at a scan rate of 100 mVs^{-1}

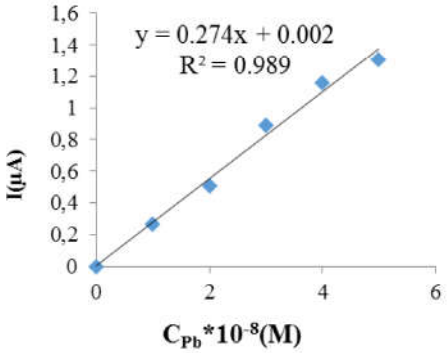

Figure 6. Calibration curve for Pb (II) at a bare CP electrode

Figure 5 and figure demonstrates the SWV results of a bare CP electrode in 10^{-8} molL^{-1} Pb (II) solution. It is shown that by increasing added Pb the stripping is increased gradually. Also, figure 6 demonstrates the calibration curve for Pb(II) at a bare CP electrode.

By comparing the sensitivity of AgNPs/CPE and a bare CPE to the Pb (II) reduction reaction, Pb(II) calibration curves AgNPs/CPE electrode were obtained. The SWV and calibration curve are demonstrated on figure 7 and 8, respectively.

According to calibration curves that were demonstrated in figure 6 and figure 8 the linear regression equation was drawn for both electrodes. As calculation show, I_{pc} = -0,384μA with a correlation coefficient of 0.993 for AgNPs/CPE is 1.5 time higher than CPE, which is indicate I_{pc} = -0,274 μA. Limit of detection for AgNPs/CPE was also 1.5 time higher than CPE. The calculated results were 8,03x10^{-8} and 11,9x10^{-8} mol/L for AgNPs/CPE and CPE.

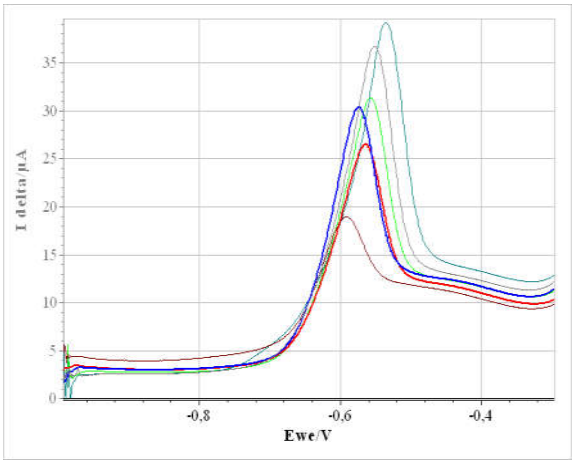

Figure 6. Anodic stripping square wave voltammograms for increasing levels of Pb (II) in 10^{-7} molL^{-1} by AgNPs/CPE in 0,1 M acetate buffer (pH= 4,5), in the potential range from -1 to 0 V (vs. Ag/AgCl) at a scan rate of 100 mVs^{-1}

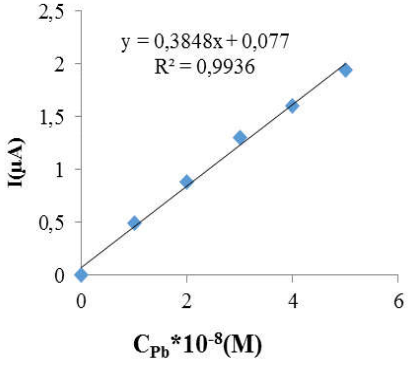

Figure 7. Calibration curve for Pb(II) at a AgNPs/CPE

The reproducibility of AgNPs/CPE was calculated by performing 7 measurements of same standard solutions (10^{-8} $molL^{-1}$) of Pb (II). Relative standard deviation (RSD %) was 4,5% for Pb(II).

3.3 Real samples

To evaluate the reliability of the method for the detection of Pb(II) in real samples, was used tap water for preparation of solutions. The detection of Pb(II) in the samples was performed by AgNPs/CPE using standard addition method. The Pb (II) was diluted 6,0 times with tap water solution. Then these solutions were analyzed with SWV. The data given in Table 1 demonstrate satisfactory results. The proposed method could be effectively used for detection of Pb(II) and other metals in sample analysis.

Table 1. **Determination of Pb (II) in tap water using AgNPs/CPE**

Sample	Added (ppb)	Found (ppb)	Recovery (%)
1	10	9,13	92%

Conclusion

In this work, solid carbon paste electrode was prepared and modified with AgNPs by electrochemical method, were microscopically and electrochemically characterized and considered for application to the determination of Pb(II).

The carbon paste electrode (CPE) modified with silver nanoparticles (AgNPs) demonstrates high sensitivity in the detection of lead (II) by using anodic stripping square wave voltammetry. For AgNPs modified CPE detection limit of lead was $8{,}03\times10^{-8}$ mol/L.

REFERENCES

[1] Huang Z. et al. Adsorption of lead (II) ions from aqueous solution on low-temperature exfoliated graphene nanosheets // Langmuir. 2011. № Ii. P. 7558–7562.

[2] Fauziah S. et al. Adsorption of Lead (II) Ions in Aqueous Solution Using Selected Agro-Waste // ARPN J. Eng. Appl. Sci. 2015. Vol. 10, № 1. P. 297–300.

[3] Miranda A. et al. World ' s largest Science , Technology & Medicine Open Access book publisher Solid Waste in Agricultural Soils : An Approach Based on Environmental Principles , Human Health , and Food // Solid waste managment in rural areas. 2017. P. 8–102.

[4] Ge Y., Song Q., Li Z. A Mannich base biosorbent derived from alkaline lignin for lead removal from aqueous solution // J. Ind. Eng. Chem. The Korean Society of Industrial and Engineering Chemistry, 2015. Vol. 23. P. 228–234.

[5] Chai F. et al. Colorimetric Detection of Pb^{2+} Using Glutathione Functionalized Gold Nanoparticles // ACS Appl. Mater. Interfaces. 2010. Vol. 2, № 5. P. 1466–1470.

[6] Bi J. et al. Near-infrared fluorescent probe for sensitive detection of Pb(II) ions in living cells // Inorganica Chim. Acta. 2017. Vol. 468, № Ii. P. 140–145.

[7] Wang S. et al. Determination of V, Cr, Cu, As, and Pb ions in water and biological samples by combining ICP-MS with online preconcentration using impregnated resin // J. AOAC Int. 2015. Vol. 98, № 1. P. 218–224.

[8] Cheraghi S., Taher M.A., Fazelirad H. Voltammetric sensing of thallium at a carbon paste electrode modified with a crown ether // Microchim. Acta. 2013. Vol. 180, № 11–12. P. 1157–1163.

[9] Okamoto Y., Gorton L. Amperometric peroxide sensor based on horseradish peroxidase and toluidine blue O -acrylamide polymer in carbon paste // Anal. Chim. Acta. 1998. Vol. 373. P. 241–251.

[10] Abbaspour a, Moosavi S.M.M. Chemically modified carbon paste electrode for determination of copper(II) by potentiometric method. // Talanta. 2002. Vol. 56, № 1. P. 91–96.

[11] Manjunatha J.G. et al. Simultaneous voltammetric measurement of ascorbic acid and dopamine at poly (vanillin) modified carbon paste electrode: A cyclic voltammetric study // Der Pharma Chem. 2012. Vol. 4, № 6. P. 2489–2497.

[12] Mersal G.A.M. Experimental and Computational Studies on the Electrochemical Oxidation of Caffeine at Pseudo Carbon Paste Electrode and Its Voltammetric Determination in Different Real Samples // Food Anal. Methods. 2012. Vol. 5, № 3. P. 520–529.

[13] Gligor D., Maicaneanu A., Walcarius A. Iron-enriched natural zeolite modified carbon paste electrode for H2O2detection // Electrochim. Acta. Elsevier Ltd, 2010. Vol. 55, № 12. P. 4050–4056.

[14] He J.B. et al. Voltammetry and spectroelectrochemistry of solid indigo dispersed in carbon paste // Electrochim. Acta. Elsevier Ltd, 2010. Vol. 55, № 17. P. 4845–4850.

[15] Plieth W. et al. Electrochemical preparation of silver and gold nanoparticles: Characterization by confocal and surface enhanced Raman microscopy // Surf. Sci. 2006. Vol. 8, № 1–3. P. 1197–1203.

[16] Wu S. et al. Electrodeposition of silver-DNA hybrid nanoparticles for electrochemical sensing of hydrogen peroxide and glucose // Electrochem. commun. 2006. Vol. 8, № 8. P. 1197–1203.

[17] Ueda M. et al. Double-pulse technique as an electrochemical tool for controlling the preparation of metallic nanoparticles // Electrochim. Acta. 2002. Vol. 48, № 4. P. 377–386.

[18] Shang L. et al. Electrochemical Preparation of Silver Nanostructure on the Planar Surface for Application

in Metal-Enhanced Fluorescence Electrochemical Preparation of Silver Nanostructure on the Planar Surface for Application in Metal-Enhanced Fluorescence. 2007. P. 10780–10784.

[19] Fox C.M. Electrochemical Synthesis of Silver Nanoparticles for Applications in Nitrate Detection , Catalysis and Antibacterial Activity. Maynooth university, 2014. 281 p.

[20] Ju H. et al. Electrochemistry of Cytochrome c Immobilized on Colloidal Gold Modified Carbon Paste Electrodes and Its Electrocatalytic Activity // Electroanalysis. 2002. Vol. 14, № 2. P. 141–147.

Далбанбай А., Кемал Б.Ғ., Дәулетбай А., Наурызбаев М.К.

Судағы Pb (II)-ын квадрат толқындық вольтамперметрия әдісімен анодтық еріту арқылы күмістің нанобөлшектерімен модифицирленген көміртек пасталық электродта анықтау

Түйіндеме. Қорғасынды (II) анықтау аналитикалық химияда маңызды мәселелердің бірі болып табылады. Қорғасын металымен улану адам өмірі үшін қауіп тудырады. Бұл мақалада Pb (II) анықтау әдісі келтірілген. Көміртек пасталы электродты модифицирлеуде үшін электротұндырылған күмістің нанобөлшектері пайдаланылды. Моддифицирленген электрод ағын суының құрамындағы Pb (II) анықтау кезінде жоғары сезімталдықты көрсетті.

Кілт сөздер: күміс нанобөлшектері, Pb^{2+}анықтау, көміртек пасталы электрод, электртұндыру

Далбанбай А., Кемал Б.Г., Даулетбай А., Наурызбаев М.К.

Определение Pb (II) на угольно − пастовом электроде, модифицированном электрохимическим осаждением серебряными наночастицами

Резюме.Определение свинца (II) является важной проблемой в аналитической химии. Потому что отравление свинцом вызывает серьезную болезнь для жизни человека. Эта статья демонстрирует метод обнаружения Pb (II) в воде. Для модификации CPE использовались AgNPs. Модифицированный электрод показал высокую чувствительность при определении содержания свинца (II) в водопроводной воде.

Ключевые слова: наночастицы серебра, Pb^{2+} определение, угольно− пастовый электрод, электроосаждение

УДК 662.765

M.R. Shautenov, V.V. Peregudov, A.N. Aitulova, N.A. Imangaliyev
(Kazakh National Research Technical University named after K.I. Satpayev, Almaty, Kazakhstan.
TOO "KRIC-NTK" (Stepnogorsk, Akmola region)
E-mail: shautenov_m@mail.ru , pereval1946@mail.ru , asselaitulova@gmail.com,
boevoe_sambo2015@mail.ru)

RESEARCH ON THE RECOVERY OF USEFUL COMPONENTS FROM ASH AND SLAG WASTES

Abstract: At present, when the reserves of ore minerals exhaust, the man-made materials are required to be processed, say the ash combustion of the Ekibastuz coal. Every year, from 25 to 38 million tons is generated as a result of coal combustion and the ash accumulation consistent with the natural processes. Processing of these man-made materials and acquisition of valuable components out of them contributes to eliminate the high technogenic pressure of mining processing facilities of industrial districts on the ecologically vulnerable natural systems and local population. By the way, the technogenic technology is being developed in a modern technology.

Key words: ash and slag, wastes, technogenic raw material, ash dump, gravity concentration, free gold, spheromagnetite.

М.Р. Шаутенов, В.В. Перегудов, А.Н. Айтулова, Н.А. Иманғалиев
(Казахский национальный исследовательский технический университет имени К.И.Сатпаева, Алматы, Казахстан. ТОО «КРИЦ – НТК» (г. Степногорск, Акмолинская обл.)

ИССЛЕДОВАНИЕ ПО ИЗВЛЕЧЕНИЮ ПОЛЕЗНЫХ КОМПОНЕНТОВ ИЗ ЗОЛОШЛАКОВЫХ ОТХОДОВ

Аннотация: В настоящее время, с истощением запасов рудного минерального сырья, появляется необходимость переработки техногенного сырья, например, золы сжигания Экибастузских углей. Каждый год при сжигании углей образуется от 25 до 38 млн. т золы и по своим масштабам накопление золы сопоставимо с природными процессами. Переработка данного вида техногенного сырья наряду с получением из них полезных компонентов, дает возможность

Physico-mathematical sciences

Chemical and metallurgical sciences