РАДИОБИОЛОГИЯ, ЭКОЛОГИЯ И ЯДЕРНАЯ МЕДИЦИНА

CARBONIZED WASTE FOR THE CUT-DOWN OF ENVIRONMENTAL POLLUTION WITH HEAVY METALS

K. Gmucová [a], *M. Morvová* [b], *E. Havránek* [c], *J. Kliman* [a],
I. Košinár [b], *D. Kunecová* [b], *A. I. Malakhov* [d],
Yu. S. Anisimov [d], *I. Morva* [b], *I. Siváček* [a],
M. Sýkorová [c], *A. Šatka* [e]

[a] Institute of Physics, Slovak Academy of Sciences, Bratislava, Slovak Republic

[b] Comenius University, Faculty of Mathematics, Physics and Informatics, Bratislava, Slovak Republic

[c] Comenius University, Faculty of Pharmacy, Bratislava, Slovak Republic

[d] Joint Institute for Nuclear Research, Dubna

[e] International Laser Centre, Bratislava, Slovak Republic

Nowadays, an increasing concern about the treatment and disposal of waters contaminated by toxic heavy metals is noticed. The toxic pollutants must be removed from the sewage water which then is fed back into the materials cycle. Any candidate technology should result in reusable by-products. With this in mind, the aim of the present study is to test a low cost procedure for utilization of the carbonized waste, a product of PET (polyethylene terephthalate) bottles pyrolysis on sand bedding, for this purpose. Both the water present in PET bottles waste and combustion exhaust probably contribute to the conversion of carbon char to activated carbon directly within the pyrolysis oven. Preliminary results, obtained for several heavy metal ions under laboratory conditions are presented and discussed. Adsorption of heavy metals on the carbonized PET waste is tested by both the electrochemical methods and X-ray fluorescence spectrometry. A simple desorption procedure for the regeneration of prepared active carbon is proposed.

В настоящее время отмечается возрастающий интерес к очистке воды, загрязненной токсичными тяжелыми металлами. Токсичные загрязнения должны удаляться из сточной воды, снова участвующей в производственном цикле. Любые технологии должны допускать многократное ее использование. Целью настоящего исследования является применение дешевой процедуры утилизации закоксованных отходов продуктов пиролиза бутылок из полиэтилентерефталата (ПЭТ) на подложке из песка. Вода, присутствующая в ПЭТ, и продукты горения способствуют превращению углеродного кокса в активированный углерод непосредственно в пиролизной печи. В настоящей работе представлены и обсуждены предварительные результаты, полученные для нескольких видов ионов тяжелых металлов в лабораторных условиях. Адсорбция тяжелых металлов закоксованными ПЭТ отходами проверена как электрохимическим методом, так и рентгеновской флюоресцентной спектрометрией. Предложена простая процедура десорбции для регенерации и приготовления активного углерода.

INTRODUCTION

Heavy metals as serious pollutants can get into aquatic environments after direct or indirect release from agriculture, industry, and households. An urgent worldwide problem is the soil pollution with heavy metals. Understanding the spatial distribution of pollutants is critical for environmental management and decision-making. The results giving an insight into risk assessment of environmental pollution with various heavy metals [1], have been already published. Cu, Zn, and Cd have been shown to have high risk for environment pollution and human health. Obtained results indicated the potential of agricultural cultivation adjustments in the polluted areas. The influences of urban population on trace metal contamination have been discussed. According to the authors [2], the most studied contaminants in the urban environment are various toxic and potentially toxic trace metals, such as Pb, Cd, Cu, Ni, and Zn. These trace metals are among those in the greatest use commercially and among the most emitted, with toxicological effects on humans who are excessively exposed to them. The use of copper fungicides has led to long-term accumulation of copper in vineyard soils [3], copper is transported to the deeper soils' horizons and can potentially contaminate groundwater [4].

One of the goals of ecotoxicology is to understand the concentration of chemicals by which organisms in the environment are affected. A fast and simple method to assess the relative toxicity of copper in aquatic environment [5] has been proposed. In this work, plasmid DNA assay has been used to detect whether the structure or the shape of plasmid DNA can be changed by the existence of Cu in pure water solutions, and if so, whether there is any dose-response relationship that can be used to quantify the idea of relative toxicity in the field of aquatic environment.

Removal of copper ions from water using adsorbent materials prepared from paper industry waste materials [6] has been reported. The adsorption characteristics of Cu^{2+} and Pb^{2+} ions onto various adsorbent surfaces [7] from aqueous single solution with respect to the changes in the pH of solution, adsorbent composition, contact time, and temperature were investigated. Similarly, low-cost adsorbents from different types of waste ashes and post-consumer PET (PET was melted and blended with ashes) for use in industrial wastewater treatment [8] have been studied. Although the utilization of waste ash for agricultural use as an additive, or starting material for land reclamation, highway construction, water purification, and the production of building materials is important from an economic and environmental perspective, it is limited by heavy metals contained in the ash. Thus, how to utilize waste ash reasonably and safely without causing environmental problems is a major challenge. The carbonization of various types of solid waste has been found as a feasible option for the pretreatment before landfills, as well as for fuel recovery [9].

During the past decades various types of activated carbons have formed a wide group of universal and versatile adsorbents. Their activity is primarily determined by the raw material, as well as by the conditions of preparation. Carbon precursors may be of botanical origin, of mineral origin, or from polymeric materials. The product of simple carbonization, that is pyrolysis of the starting material, with exclusion of air and without addition of chemical agents, is usually a low-active or inactive material — its pores are filled, or at least blocked, by the disorganized carbon. The objective of either the physical or the chemical activation process is to enhance the surface to volume ratio. Such activation processes [10] are often studied. Pyrolysis of lignocellulosic materials in contact with a stream of steam proved to be a promising scheme for the production of activated carbon. The process is a simple one-step

procedure [11] that saves energy and time, performed at moderate temperatures (600–700 °C), and results in a relatively high carbon yield. Moreover, some heavy metals, particularly Pb and Zn, can be volatilized [12] under N_2 pyrolysis at 800 °C. Similarly, cotton stalks have proved to be a promising raw material [13] for the production of activated carbon. The adsorption of hexavalent chromium from aqueous medium by rice husk-based activated carbon was studied [14] as a function of pH, contact time, contact temperature, adsorbate concentration and adsorbent with different pore structure. Adsorption of copper, cobalt, nickel, and lead ions on multiwalled carbon nanotubes has been reported [15]. Low cost adsorbents, such as activated carbon, kaolin, bentonite, blast furnace slag, and fly ash [16] were used to remove the lead and zinc ions from water. A method using direct current to the removal of copper from charcoal (carbonized wood wastes) [17] has been proposed.

Stripping analysis has been widely recognized as a powerful tool for trace metal analysis. Mercury electrodes have been traditionally employed for achieving high reproducibility and sensitivity of the stripping technique. However, because of the toxicity of mercury, new alternative electrode materials are highly desired, particularly for on-site environmental monitoring of trace pollutants. The preparation of Cu/Nafion/Bi electrodes and their application to heavy metal analysis by anodic stripping voltammetry [18] has been reported. Mercury coated platinum microelectrodes were employed for the *in situ* determination, in soils and porewater of sediments, of redox key species of environmental interest. Moreover, thanks to the microelectrode properties, calibrationless procedures [19] for the quantification of the electroactive species have been employed.

In the present work, electrochemical methods together with X-ray fluorescence spectrometry are used to make sure of the capability of the prepared carbonized PET waste to fulfill the above-mentioned requirements on a proper heavy metal adsorbent. The heavy metal concentrations used for the testing of adsorption ability of the carbonized PET waste were set at the boundary values specified by the surface water quality standards.

1. EXPERIMENTAL

Carbonized PET Waste Preparation and Characterization. The PET-bottles waste carbonization inside a high temperature combustion chamber [20] was performed using a direct heating by exhaust gas flow in an oxygen free atmosphere. The carbonization chamber was heated directly using exhaust produced in natural gas oven, sand bedding was used as a subbase for PET bottles. The oven is able to burn 10 m^3 of gas per hour. Ambient air, used as an oxidant, is spontaneously sucked through the vent in the height of burners. This results in almost stoichiometric combustion, with minimal concentration of oxygen in the flue gas. The carbonization zone is placed 10 cm above burners, its total volume is 24 dm^3. The temperature in the combustion zone can reach 975 °C, produced flue gas 950 °C. When the PET waste is heated, first volatile part is evaporated. Subsequently, when the temperature reaches 350 °C the thermal cracking starts. In this process the hydrocarbons with lover chains are released. At 500 °C, smaller hydrocarbons and its radicals are produced, and at 650 °C hydrogen is produced. The PET waste contains certain amount of water, the combustion exhaust contains CO_2. These compounds convert the formed carbon char to activated carbon.

The morphology of the prepared activated carbon was investigated by a field-emission gun scanning electron microscope (FESEM LEO-1550) using an in-lens and Everhart–Thomley detectors of secondary electrons (Fig. 1).

X-ray fluorescence spectrometry was used for the determination of elements with $Z > 18$. This method [21] is based on the interaction of primary radiation with the analyzed matter and on the measurement of the intensity of radiation emitted by the component to be determined. ^{238}Pu radioisotope source (AMERSHAM) ($A = 1100$ MBq, $E = 12-22$ keV, $T_{1/2} = 86.4$ y) and X-ray tube ECLIPSE III (AMPTEK) with Ag-anode ($U = 15$ kV, $I = 40$ μA) have been used for the excitation. The energy emitted by the elements has been detected by a solid state detector Si/Li with active area 20 mm^2 and 50 μm Be window (energy resolution 170 eV at 5.9 keV). The data from the detector have been recorded with the acquisition
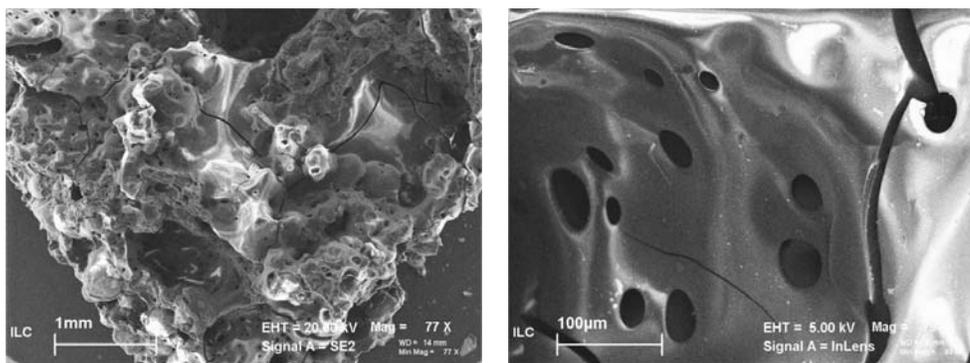
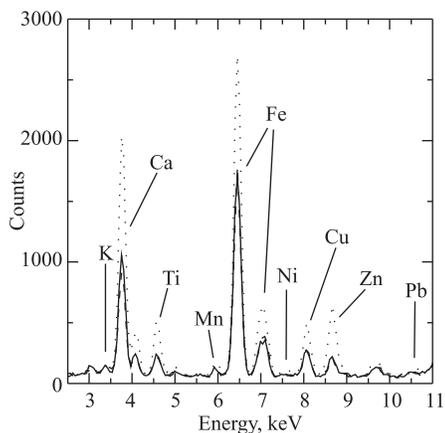Fig. 1. Typical scanning electron microscopy image of the used carbonized PET waste

Fig. 2. Amplitude spectrum of characteristic radiation of elements excited by ^{238}Pu, carbonized PET waste: solid line — as prepared; dashed line — falling fraction; dotted line — floating fraction
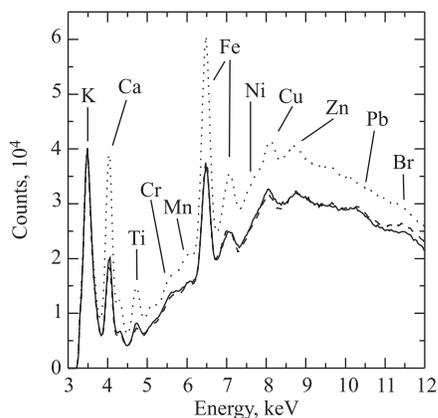
Fig. 3. Amplitude spectrum of characteristic radiation of elements excited by the X-ray tube, carbonized PET waste: solid line — as prepared; dashed line — falling fraction; dotted line — floating fraction

systems ORTEC® and PMCA (AMPTEK). Acquisition time was 2000 s. The sensitivity of $1 \cdot 10^{-6}$ g/g has been obtained for the analyzed copper. Quantitative analysis has been performed using the standard addition method. The samples have been prepared as follows. The carbonized PET waste was grinded, mixed with benzoic acid (ratio 1:1), homogenized and pelletized to a defined shape (with a surface density ~ 0.075 g/cm^2) at the pressure of 10 MPa.

Several trace elements (K, Ca, Ti, Mn, Fe, Cu, Zn, and Pb) have been identified in the prepared samples (Figs. 2, 3). We suppose that these elements originate from the drink residue, used coloring agents (from the etiquettes of PET bottles) and construction materials of the pyrolysis oven released at high temperatures. The carbonized PET waste consists of two fractions — a majority of the crushed carbonized PET waste fall down to the bottom after filling it into the adsorption tank, while a small fraction floats on the water surface. Both the fractions were analyzed separately, too (Figs. 2, 3). Markedly higher intensities of the characteristic radiation of elements were obtained for the floating fraction.

2. ELECTROCHEMICAL METHODS USED FOR THE ADSORPTION STUDIES

The used electrochemical analyser [22] was developed in our laboratory. Its main advantage consists in an enhanced sensitivity to the kinetics of the redox reaction taking place at the electrode surface, which makes it an applicable candidate in sensing. The transient current flowing in response to a potential step through the electrochemical cell is integrated and processed by the time-domain filter, while scanning the applied potential. As an alternative to the typical scheme of differential pulse voltammetry (sampling the transient current just before and at the end of the excitation pulse), the transient charge is sampled in the interval between subsequent excitation pulses at three different events within the entire transient response. Such a filtering scheme is capable of eliminating both the constant and linear components in the transient charge, which results in a significant suppression of both the steady-state and capacitive contributions of the transient current with respect to the diffusion current contribution. Moreover, each measurement period is preceded by a single measurement of the steady-state current with the excitation pulse being switched off. In such a way, during the single potential scan both the steady-state voltammetric wave and the double-step voltcoulometry signal are obtained. The ratio of the maximum of measured voltcoulometric signal to the corresponding limiting current multiplied by the sampling delay can serve not only as a tool for discriminating deviations of the kinetics from the ideal Cottrell value [23], but also provide an information about the suitability of either voltcoulometry or voltammetry for the detection of chosen species with a chosen type of the working electrode.

The experiments were performed in the electrochemical cell kept at room temperature and equipped with a carbon fibre microelectrode as a working electrode and an Ag–AgCl wire as a reference electrode. The working electrode was formed of a glass micropipette with up to eight carbon fibers (diameter of each fiber being approximately 7–8 μm). The pipette tip (diameter 100–150 μm) was filled with paraffin wax to prevent liquid from seeping inside around the carbon fibers. The exposed surfaces of the filaments were treated electrochemically before starting the experiments. First, a cathodic potential of -0.8 V was applied for 20 s, followed by a triangular waveform of 0 to $+3$ V for 5 s; finally, an anodic potential of $+1.5$ V was applied for 5 s. Seeing that the diameter of such electrode is smaller than the diffusion

length for the time scale of a typical electrochemical experiment, its response need not be predicted by the Cottrell equation. Therefore, the kinetics sensitive voltcoulometry should be a good choice for our study.

3. MATERIALS AND REAGENTS

Bidistilled water of pH $= 6.67$ was used (without any deareating procedure) to prepare unsupported aqueous heavy metal solutions (using certified reference materials of concentration 0.999 g/L, matrix 2% HNO_3, purchased from SMU Bratislava). Benzoic acid (LACHEMA Brno) was used for the pelletization of carbonized PET waste. Hydrochloric acid was used for the hydrogen adsorption study.

4. RESULTS AND DISCUSSION

Environmental issue such as the water pollution has a very high profile with both the government and public. Accurate measurements play a vital role in gauging the scale of pollution and in the development of strategies to mitigate its short- and long-term impacts.
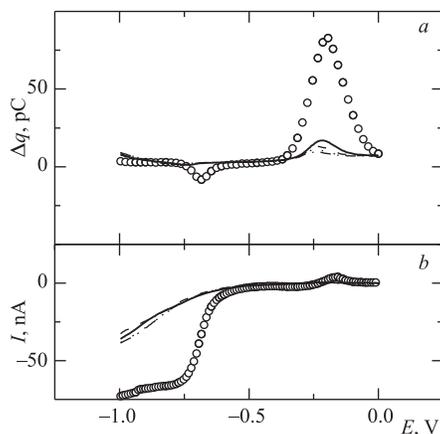

Fig. 4. Voltcoulometric (*a*) and voltammetric (*b*) signals of 1 mM HCl adsorbed on carbonized waste (CW); solid line — 0.5 wt% of CW; dashed line — 1 wt% of CW; dotted line — 1.5 wt% of CW; dash-dotted line — 2 wt% of CW, and open dots — 1 mM HCl

To demonstrate the power of carbonized PET waste to prevent the environmental pollution by heavy metals, we have tested electrochemically the amount of copper ions in aqueous solutions adsorbed on various types of carbonized waste. The prepared solutions were stabilized with the nitric acid, and the competing adsorption of hydrogen and copper was studied, too.

As a first step, the hydrogen adsorption from 1 mM hydrochloric acid solution was studied electrochemically. The changes in the H^+ electrochemical signals due to the presence of a given amount of carbonized waste were recorded to obtain information on its adsorption onto the carbonized waste. Results obtained for the carbonized waste amount in the prepared analyte, which varied from 0.5 to 2 wt% are shown in Fig. 4. The hydrogen oxidation is envisioned as the peak at ~ -0.7 V on the voltcoulometric signal record, and as the respective steady-state wave — on the voltammetric signal record. The signal coming from another species present in the prepared analyte is observed for activation potential ~ -0.2 V. It can be ascribed to the oxidation of lead ions present as the impurity in HCl (for 1mM HCl the concentration of Pb^{2+} is lower than 5 ppb). The signal from hydrogen was completely removed for all the used amounts of carbonized waste, and the presence of lead in the analyte was dramatically reduced. That means that the carbonized waste could
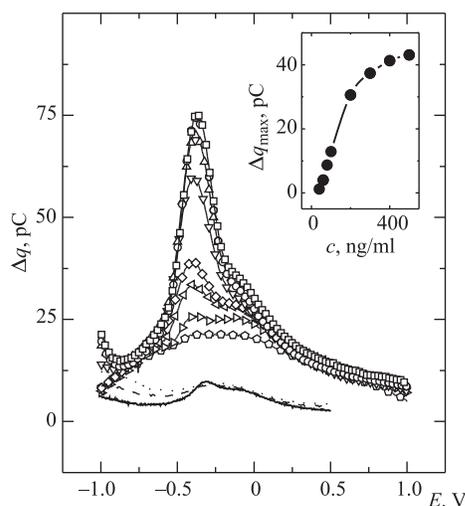
Fig. 5. Voltcoulometric signals of Cu^{2+} solutions (as prepared) — 40 ng/ml (pentagon), 60 ng/ml (right triangle), 80 ng/ml (left triangle), 100 ng/ml (diamond), 200 ng/ml (down triangle), 300 ng/ml (up triangle), 400 ng/ml (circle), and 500 ng/ml (square); calibration curve as the inset. Voltcoulometric signals obtained after the Cu^{2+} (500 ng/ml) adsorption on 0.05 wt% of the crushed carbonized waste (CW) (solid line), on 0.25 wt% of the crushed CW (dashed line), and on 0.5 wt% of the crushed CW (dotted line)

serve as a filter capable of modifying the pH of acid rain. Concerning the lead adsorption, it must be noted that voltcoulometry cannot be used without calibration for a simple estimation of concentration changes as it is kinetically sensitive and the respective calibration curve is nonlinear. However, this method provides other advantages in the monitoring of environmental pollution with heavy metals. As calculated for the obtained signals of 1 mM HCl solution, the ratio of the maximum of measured voltcoulometric signal to the corresponding limiting current multiplied by the sampling delay for lead and hydrogen is 1.34, and 0.01, respectively. We can conclude that voltcoulometry is a better choice for the lead (and the other heavy metals, too) detection, its detection limits for heavy metals on the carbon fibre microelectrode are lower than those relevant for voltammetry.

Two typical features appear in voltcoulometric signal as a consequence of the three-channel filtering scheme, connected with the low-order terms suppression (i.e., constant, 1st, and 2nd order in the respective polynomial expansion). The first one is that the apparent activation potential (i.e., the maximum of voltcoulometric peak) differs from the tabular one, it is shifted in the potential scale due to the used filtering scheme. The second one is the nonlinearity of a calibration curve. Calibration measurements performed for the copper solutions of the concentration range from tens to hundreds ng/ml are shown in Fig. 5, the respective calibration curve is depicted as the inset. Linear part was obtained only within the concentration range 40–200 ng/ml.

Thereafter, the comparison of the copper adsorption from 1000 ng/ml copper solution stabilized with the nitric acid on various types of crushed carbonized waste (carbonized PET bottles, carbonized oats) and graphite was performed. After the preparation of copper solutions given amount of carbonized waste was put into them, immixtured, and immediately filtered. Obtained data are shown in Fig. 6. After the one-hour adsorption on the same amount of carbonized waste no copper signals were measured. Since the prepared solutions were stabilized in acidic media, the competitive adsorption of hydrogen and copper was studied, too. Evolution of pH during the adsorption from prepared solutions is shown in Figs. 7, 8.

Furthermore, the X-ray fluorescence spectrometry has been used to confirm the presence of copper in the crushed carbonized PET waste after its exposition to the copper solution
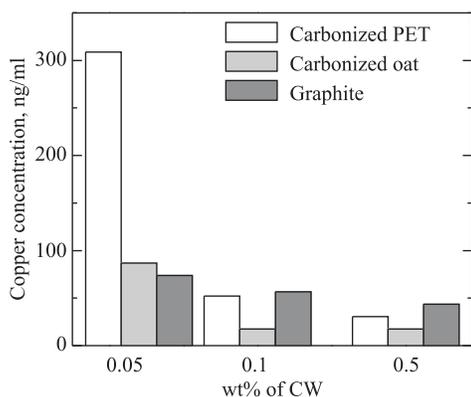
Fig. 6. Comparison of the copper adsorption from 1000 ng/ml solution stabilized with the nitric acid on various types of carbonized waste and graphite, y axis represents the copper amount in the analyte after the adsorption process
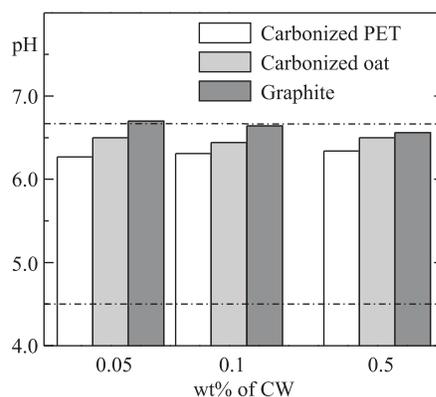

Fig. 7. Competitive adsorption of hydrogen, pH evolution during the copper adsorption from solution stabilized with the nitric acid — measurement performed immediately. The dash-dotted lines are set at the pH of formal copper solution, and pH of the water used for the solution preparation
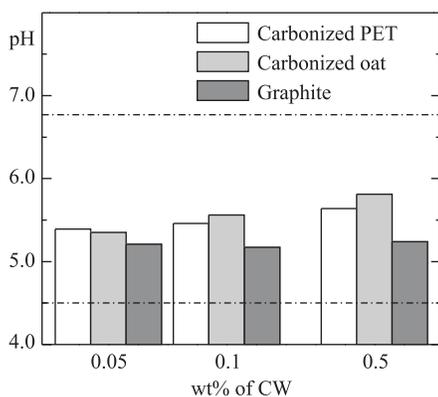

Fig. 8. Competitive adsorption of hydrogen, pH evolution during the copper adsorption from solution stabilized with the nitric acid — measurement performed after 1 h adsorption. The dash-dotted lines are set at the pH of formal copper solution, and pH of the water used for the solution preparation
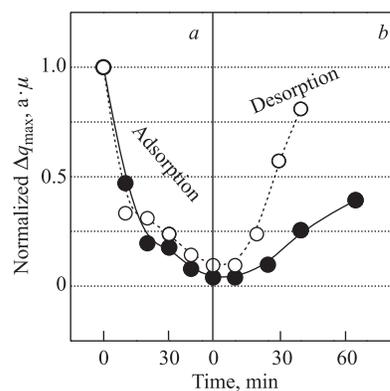

Fig. 9. Signal evolution for the «field assisted» adsorption (a) and desorption (b) for copper (open dots) and mercury (full dots) solutions

(500 ng/ml of Cu^{2+}) and subsequent filtration and exsiccation. The obtained results revealed that after 45 min 75% of the total copper amount was adsorbed on the carbonized PET waste, which is in good accordance with the data obtained using electrochemical methods.

Summary of results obtained for PET carbonized waste (CW) used as a heavy metal adsorbent; c_a — maximal concentration of given heavy metal species allowed in groundwater. Both the ability to be adsorbed and the possibility of backward desorption in the prototype equipment designed for the regeneration of the carbonized PET waste, are rated

Species	c_a, μg/l	Ability to be adsorbed	Possibility of desorption
Ag^{2+}	5	Yes	Yes
Cd^{2+}	5	Yes	No
Cu^{2+}	20	Yes	Yes
Hg^{2+}	0.2	Yes	Yes
Zn^{2+}	100	Yes	Yes

With the aim to find a method for the adsorbent regeneration, i.e., to reach the reverse desorption of metallic ions adsorbed on carbonized waste, a «field assisted» adsorption/desorption process was tested. In the course of these experiments selected solutions (500 ng/ml of Cu^{2+}, 150 ng/ml of Hg^{2+}) were put into the experimental equipment designed for this purpose. First, the adsorption onto the carbonized waste ($+0.5$ wt% of the prepared sample) situated near the negatively charged (-6 V) electrode was carried out for a given time. The volcoulometric signals were recorded after the selected time periods of the adsorption process duration. Then, the electrode system was repolarized to $+6$ V, and desorption from the carbonized waste back to the solution started. Again, the volcoulometric signals were recorded after the selected time periods of the desorption process duration. The obtained typical behaviour for both the copper and mercury is demonstrated in Fig. 9. A fast decay of the maximum signal during the adsorption was followed with a slower one, which tends to a limit value for the given amount of carbonized waste and the given concentration of metallic ions. The efficiency of desorption process up to 75% for both the copper and mercury has been reached after 30 and 60 min, respectively. Of course, validity of these findings is limited to the performed experiment. For real conditions of high-volume tanks and uncrushed carbonized PET waste, the regeneration process need to be carefully set up considering environmental, safety, and economical terms. However, the possibility to regenerate the carbonized PET waste has been proved in this work, which makes it a practical candidate for the proposed usage.

Finally, more heavy metal pollutants have been tested. Maximal concentrations of heavy metal species allowed in groundwater, the ability of such concentration of a given heavy metal to be adsorbed on 0.5 wt% (relating to the contaminated water sample weight) of carbonized PET waste under laboratory conditions, and the possibility to reactivate the carbonized PET waste by the backward desorption, are summarized in the Table.

CONCLUSIONS

As is well known, the factors that influence the performance of active carbon in water are: the type of compound to be removed, the concentration of the compound, the presence of other organic compounds, which will compete for the available adsorption sites, and the pH of the waste stream. Heavy metal adsorption is typically influenced by pH, because a change of pH can lead to a change of the metal species valency. Moreover, organic and inorganic compunds are adsorbed on active carbon in a very different manner. While organic

compounds are mostly adsorbed by physical adsorption, the adsorption of heavy metals is predominantly chemical. In such a two-component system, both the physical and chemical adsorptions take place, but the first one is more expressive. Therefore, the presence of organic compounds should markedly affect the heavy metal adsorption. In the present study, tentative experiments have been performed to test the adsorption ability of the prepared PET carbonized waste to heavy metals. Organic compounds have been excluded at the moment. Howewer, we expect that the obtained results have proved the potential of prepared carbonized waste as a material matching properties necessary for scumboards, and it can be useful in the prevention of the environmental pollution with heavy metals.

As a consequence of performed studies the following conclusions can be drawn:

— PET carbonized waste with notable adsorption ability towards heavy metals has been prepared and characterized. The amount of heavy metals in the virgin carbonized PET waste has been determined with X-ray fluorescence spectrometry. This material could serve as a filter capable of modifying the pH of acid rain, too.

— The used voltcoulometric method has been shown to provide several advantages in heavy metal pollution monitoring. The kinetics sensitive properties of this method contribute, as compared to typical steady-state voltammetry, for a better discrimination in the spectrum and better detection limit of electrochemical signals coming from heavy metal redox reactions measured on carbon fibre microelectrode.

— A prototype of a small experimental setup has been designed for the regeneration of the used carbonized PET waste. We suppose that in future scum boards made from carbonized waste can be regenerated in electrochemical bath, where heavy metals should be subsequently chemically inactivated or used as a by-product (e.g., for galvanizing).

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