Evaluation of a pilot plant for a secondary treatment of mining effluents

Yfantis N.[1], Yfantis A.[2*], Gazea V.[3]

[1]Technical Director, Sychem S.A, Mesogion Avenue 518, Agia Paraskevi, 153 42 Athens

[2]Managing Director, Sychem S.A, Mesogion Avenue 518, Agia Paraskevi, 153 42 Athens

[3]Environmental Manager, Hellas Gold S.A., Stratoni 63082, Chalkidiki

*corresponding author: Yfantis N.

e-mail: n.yfantis@sychem.gr

Abstract Mining effluents can often contain heavy metals such as Lead (Pb), Zinc (Zn), Iron (Fe), Manganese (Mn), Cadmium (Cd), Arsenic (As) and if left untreated can cause damage to the local aquatic environment. In this study we demonstrate the operation of a 9 m^3/h pilot unit (PU) installed in Greece. It consists of a pH regulation and oxidation stage, followed by filtration to a catalytic multimedia filter, activated carbon filter and a reverse osmosis (RO) unit. PU is fed by the existing pretreatment installation outlet. Our results prove that PU installing improved the water quality of water discharge, so that the final concentrations of dissolved metals to be even lower than the legislation limits for potable water. The removal of Fe, Mn and Zn was 97 – 100 %, As, Cd and Pb was 80 – 93 %. Operational data demonstrated very good removal efficiency of the Filtration Stage so that RO stage can be omitted. PU successful application enables design to be applied covering the complete installation needs. The operation of PU is simple, automatic, and constant. It is environmentally friendly and economically viable in terms of fixed and operational cost.

Keywords: Mine, Effluents, Heavy, Metals, Filtration

1. Introduction

Mining effluent takes up a very large proportion of the total volume of waste produced in the European Union (EU) (approximately 30% in 2012) [DeSouza *et al.*, 2017; COM (2016) 553, final; Acheampong *et al.*, 2014]. The presence of heavy metals such as Lead (Pb), Zinc (Zn), Iron (Fe), Manganese (Mn), Cadmium (Cd) and Arsenic (As) are of major concern due to their non-biodegradability. Instead they accumulate in the living organisms of the local environments causing severe health problems in animals, plants and humans such as cancer, kidney failure, metabolic acidosis, oral ulcer and renal failure [Bernard *et al.*, 2013].

The main methods used for the heavy metal removal from wastewater are precipitation, reduction, ion-exchange, and adsorption [Karniba *et al.*, 2014]. Membrane processes have also showed great promise due to their efficiency [Ricci *et al.*, 2015]. Coagulation and flocculation followed by sedimentation and filtration is used as well. Other methods are flotation and electrochemical treatment [Acheampong *et al.*, 2014; Fenglian *et al.*, 2011].

In our study, the effluent produced at the mining site "Olympias" of Hellas Gold S.A was examined. Wastewater is discharged due to the treatment of the gold bearing arseniferous pyrite concentrate [Stefanakis and Kontopoulos, 1989] and it is directed to an existing wastewater treatment plant which consists of primary physicochemical processes.

The scope of our pilot unit (PU) was the further enhancement of heavy metals removal after the primary treatment in order for it to meet even lower limits than those enforced by the environmental permit. In order to do so, we designed a process that was based on the oxidation of heavy metals with modified catalytic sand filters (CSF) and activated carbon filters (ACF).

The choice of the CSF and ACF as a main processing step was based on their particular effectiveness for removing heavy metals [Aguayo *et al.*, 2017; Ibrahim *et al.*, 2016; Tounsadia *et al.*, 2016; Bernard *et al.*, 2013]. Its main advantages compared to other process are: 1) Minimum amount of discharge 2) Very limited use of chemicals. 3) Small installation space requirement, 4) Low electricity consumption 5) Absence of any odor.

The operation of the installation is simple, automatic and constant, requiring minimum time for daily check. It is financially attractive in terms of fixed (CAPEX) and operating cost (OPEX) especially considering that the CSF-ACF Filtration stage can be used alone in order to achieve very good heavy metal removal efficiency. Reverse Osmosis (RO) is used as a final optional polishing treatment after the activated carbon filtration stage.

2. Material and methods

The existing WWTP at "Olympias" site consists of a primary treatment stage where the removal of turbidity and bulk contaminants is achieved by adding lime emulsifier. The PU was installed as a secondary treatment stage and during its monitoring the metal concentrations of the collected samples were determined by ICP (Induced Current Plasma).

PU has three main stages:

2.1. Pre-treatment Stage

The pretreatment step consists of: a. Chlorination; Chlorination causes oxidation to iron, manganese and heavy metal ions, which are converted into insoluble compounds and precipitate. Chlorination is applied by injecting a sodium hypochlorite (NaOCl) 12% solution at the inlet pipe of the aeration tank. b. pH adjustment; After chlorination follows a pH adjustment step in order to create an alkaline environment in the feedwater, which improves the efficiency of the CSF filters. Adjustment of pH is achieved by injecting a 50% caustic soda (NaOH) solution at the inlet of the aeration tank. c. Aeration (oxygenation); In the aeration tank, mining wastewater goes through an aeration stage, to aid oxidation for removal of precipitated iron, manganese and heavy metals. The typical aeration technique consists of a forced air flow, using blowers and diffusers to generate small air bubbles which improve the water-air contact.

2.2. Filtration Stage

In this step filtration of the water is achieved by means of CSFs and ACFs. a. Catalytic sand filters; After the aeration tank, the water travels towards the CSFs which retain various suspended particles, turbidity, Fe, Mn, and substances harmful to the treatment so that the Silt Density Index (SDI) becomes less than 5. Water flows (at a suitable speed) through carefully pre-selected layers for the retention of contaminants on the surface of these materials. Filter layers are of different granulometry of quartz gravel, silica sand, pyrolusite (mainly consisting of manganese dioxide, MnO_2) and anthracite. The method used for Fe and Mn removal from the water is a natural process which is based on oxidation by air (as mentioned above) combined with the use of chemicals commonly used in the treatment of drinking water, which is an advantage compared to the other processing methods.

b. Activated carbon filters; After the CSFs water passes through the ACFs, as a second filtration/adsorption stage for the removal of the remaining manganese and iron which passed through the CSFs and heavy metals such as arsenic, lead, zinc, chromium and cadmium. Activated Carbon quality has been selected in order to maximize ACF efficiency.

2.3. Polishing Stage - Reverse Osmosis

In reverse osmosis (RO), the water is fed to semi-permeable membranes. RO has been designed as an optional process in order to ensure that even at the most challenging operational parameters permeate water will remain below the required limit.

RO is suitable for removing very low concentrations of metals. In any case RO process requires a good pretreatment stage in order to operate without fouling as the water treated is wastewater. It has been designed to operate at 75% recovery ratio.

3. Results & Discussion

The metal concentrations of the collected samples were determined by ICP (Induced Current Plasma).

Initially the pre-treatment step included oxidation only by aeration but the Mn removal was not up to the desired limits. It has been observed that the process was more efficient when the dissolved metals in the effluent stream were oxidized by NaOCl dosing and the pH was regulated. In Fig.1-6, concentration reduction of Mn, As, Cd, Zn, Pb, Fe after the filtration, the RO stage of the PU and after the introduction of NaOCl and NaOH to the pre-treatment is shown. In most cases, metal concentration limits achieved project’s requirements only by the implementation of filtration stage.

RO polishing helped in the rare cases when the filtration effluent reached or slightly exceeded target limits for the metals concentration.

More specifically, RO unit was able to minimize the effluent concentrations of Mn and As but the impact on Cd, Zn, Pb and Fe was negligible. This was anticipated since their concentration was in the ppb range where RO is not very effective.

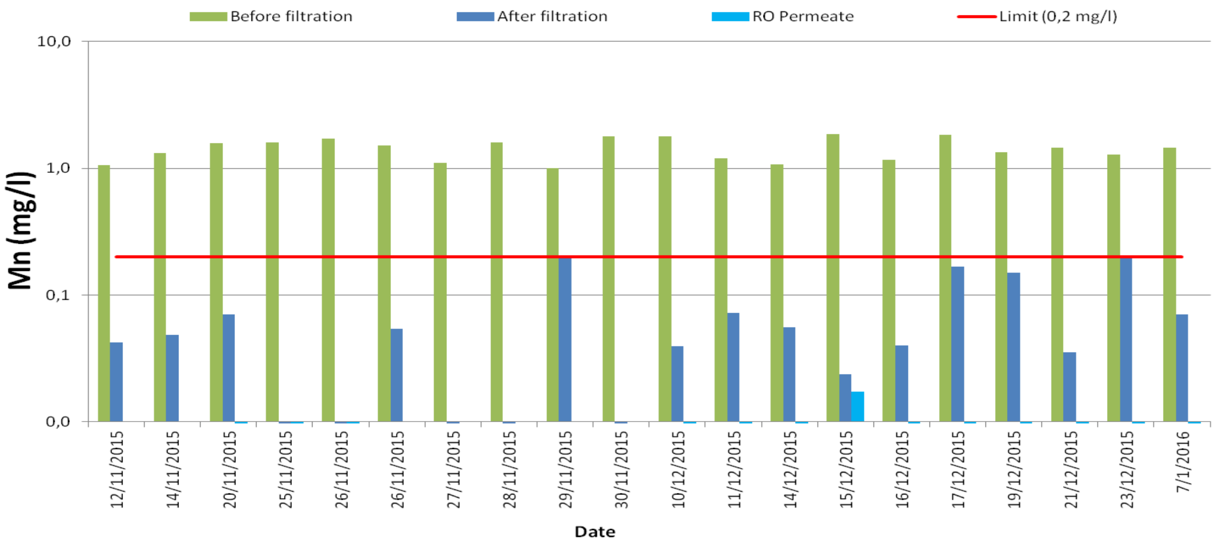

Figure 1: Monitoring of Manganese removal during pre-treatment, filtration and reverse osmosis treatment stages.

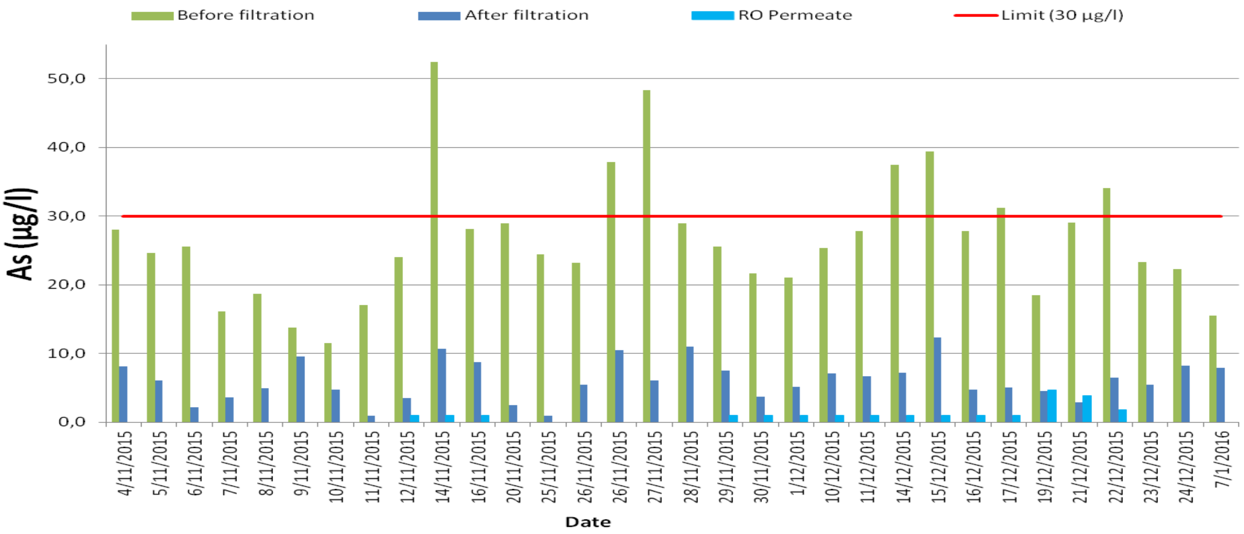

Figure 2: Monitoring of Arsenic removal during pre-treatment, filtration and reverse osmosis treatment stages.

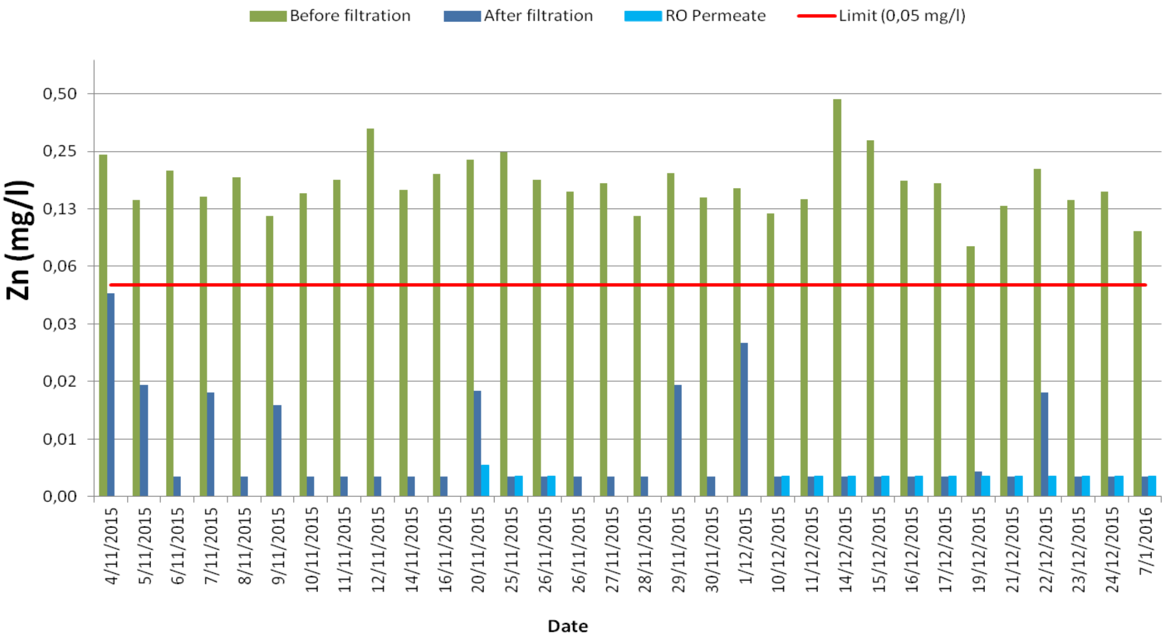

Figure 3: Monitoring of Cadmium removal during pre-treatment, filtration and reverse osmosis treatment stages.

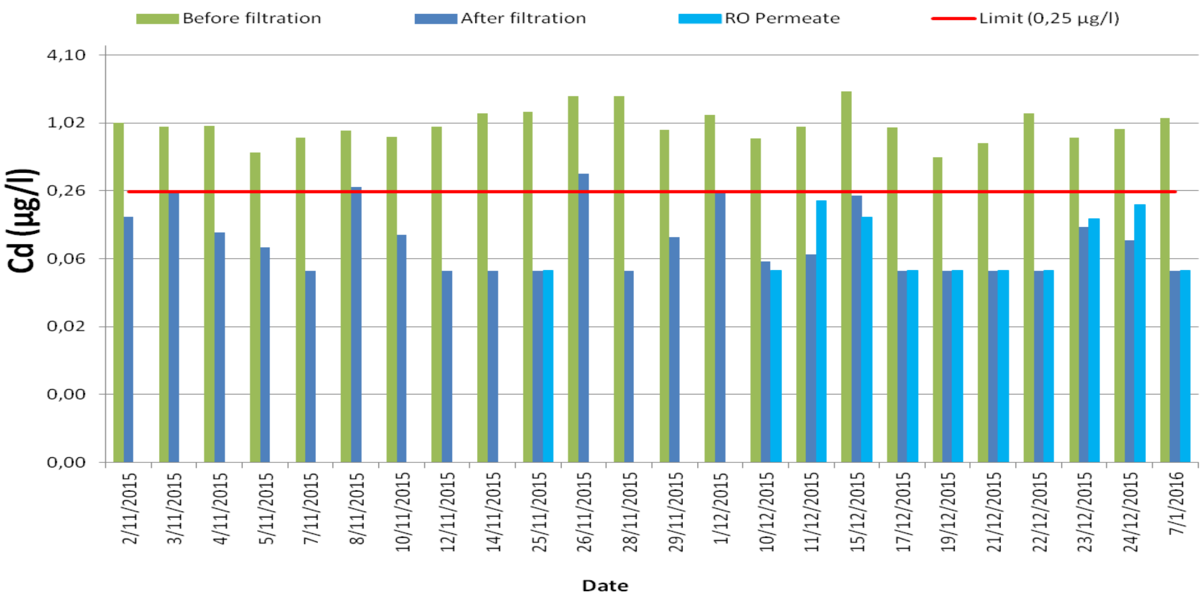

Figure 4: Monitoring of Zinc removal during pre-treatment, filtration and reverse osmosis treatment stages.

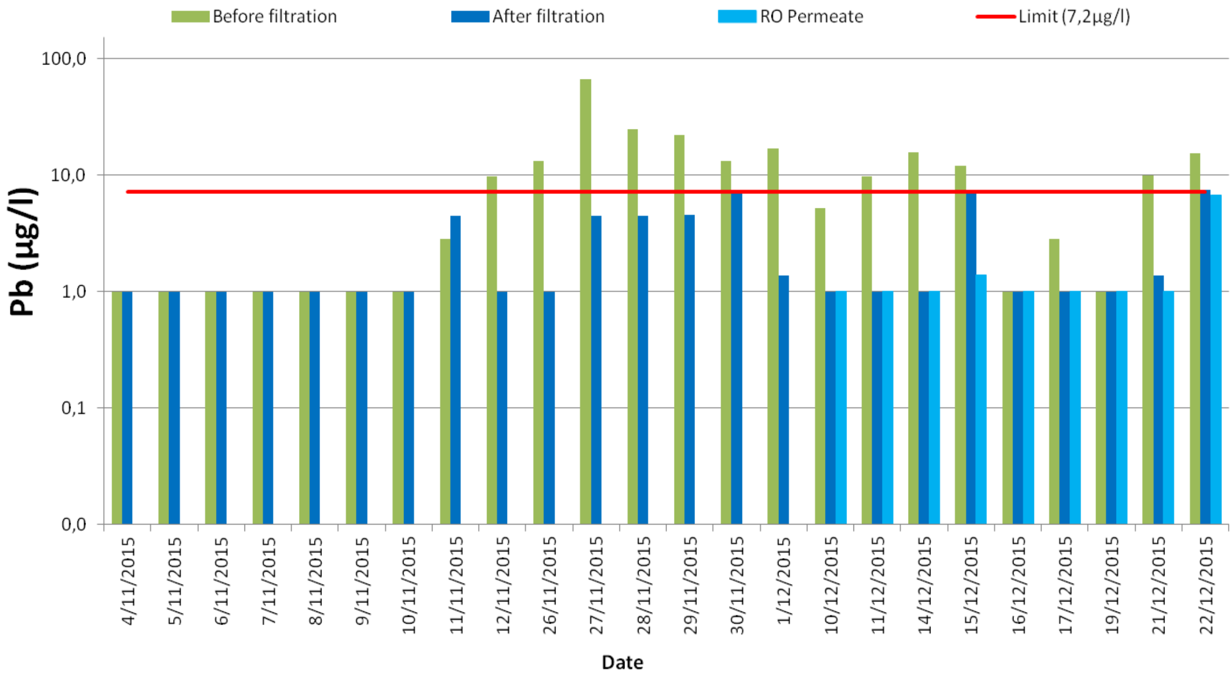

Figure 5: Monitoring of Lead removal during pre-treatment, filtration and reverse osmosis treatment stages.

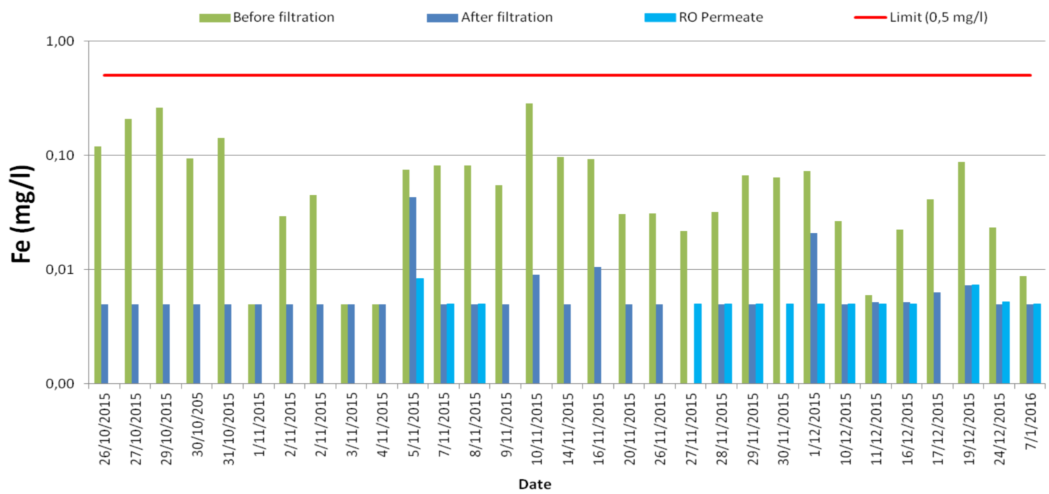

Figure 6: Monitoring of Iron removal during pre-treatment, filtration and reverse osmosis treatment stages.

Table 1: % Removal of heavy metals at maximum effluent concentrations of the existing pretreatment installation by Pilot Unit.

[1]European Directive 98/83/EC, and Greek Legislation JMD Y2/2600/2001,GG 630 / B `/ 26.4.2007," Quality of water intended for human consumption".

Heavy Metal	Max Effluent Concentration	Concentration after filtration	Removal [%]	Project Target	Limit for Potable Water[1]
Pb [ppb]	66,34	4,5	≈93%	7,2	10
Zn [ppm]	0,467	<0,005	≈100%	0,05	-
Fe [ppm]	0,286	0,009	≈97%	0,5	0,2
Mn [ppm]	1,863	0,024	≈99%	0,2	0,05
Cd [ppb]	1,96	0,23	≈88%	0,25	5
As [ppb]	52,42	10,70	≈80%	30	10

Table 1 shows the removal efficiency in percentage of the PU compared to the maximum heavy metal concentrations. The PU effluent met project limit targets which are similar to potable water limits.

4. Conclusions

The PU is based on the oxidation of heavy metals with modified catalytic sand filters and activated carbon filters. The process is very effective with proper pH and Redox regulation and it has been demonstrated that it can effectively reduce the concentration of specific heavy metals below the permissible levels requested. The removal ratio for most of the contaminants is marginal and non-cost effective when RO is applied as polishing stage. The pilot plant provided clear evidence that: 1) The removal of Fe, Mn and Zn is excellent from 97 – 100 %.

2) The removal of As, Cd and Pb is very good from 80 – 93%.

Acknowledgement

Authors wish to acknowledge Mr. Christos Charisiadis contribution to this paper and thank Hellas Gold SA for their trust and support for this project.

Note: The PU has been designed, installed and operated by SYCHEM S.A

References

Acheampong M.A., Len P.N.L. (2014), Treatment of gold mining effluent in pilot fixed bed sorption system, *Hydrometallurgy*, 141

Aguayo I.A-Villarreal, Bonilla A.-Petriciolet, Muñiz R-Valencia (2017), Preparation of activated carbons from pecan nutshell and their application in the antagonistic adsorption of heavy metal ions, *Journal of Molecular Liquids*, **230**

Bernard E, Jimoh A. and .Odigure J.O (2013), Heavy Metals Removal from Industrial Wastewater by Activated Carbon Prepared from Coconut Shell, *Research Journal of Chemical Sciences*, **3**(8)]

DeSouza E.S., Texeira R.A, DaCosta H.S.C., Oliveira F.Jr., Melo L.C.A, Faial K.C.F, Fernandes A.R (2017), Assessment of risk to human health from simultaneous exposure to multiple contaminants in an artisanal gold mine in Serra Pelada, Pará, Brazil, *Science of the Total Environment,* **576**

European Commission (2016), Report from the commission to the European parliament, the council, the European economic and social committee and the committee of the regions, on the implementation of Directive 2006/21/EC on the management of waste from extractive industries and amending Directive 2004/35/EC, COM 553 Final

Fenglian F., Wang Q (2011), Removal of heavy metal ions from wastewaters: A review, *Journal of Environmental Management,* **92**

Ibrahim W.M. ,Hassan A.F, Azab Yahia A. (2016), Biosorption of toxic heavy metals from aqueous solution by Ulva lactuca activated carbon, *Egyptian journal of basic and applied sciences,* **3**

Karniba M, Kabbanib A., Holaila H, Olamaa Z, (2014), Heavy Metals Removal Using Activated Carbon, Silica and Silica Activated Carbon Composite, *Energy Procedia*, **50**

Ricci B.C, Ferreira C.D., Aguiar A.O, Amaral M.C.S (2015), Integration of nanofiltration and reverse osmosis for metal separation and sulfuric acid recovery from gold mining effluent, *Separation and Purification Technolog*y, **154**

Stefanakis M. and Kontopoulos A., (1989), Environmental aspects of METVA SA Gold Metallurgy, *Proceeding of conference on Protection of Environment in mining, metallurgy and material technology,* Athens, National Technical University of Athens

Tounsadia H., Khalidib A., Machrouhia A., Farnanea M., Elmoubarkia R., Elhalila A., Sadiqa M., Barkaa N. (2016), Highly efficient activated carbon from Glebionis coronaria L. biomass: Optimization of preparation conditions and heavy metals removal using experimental design approach, *Journal of Environmental Chemical Engineering*, **4 (**4), Part A