

## OZONATION AND SOL-GEL METHOD TO OBTAIN Cu/CuO NANOPARTICLES FROM CYANIDATION WASTEWATER

María de Jesús SORIA AGUILAR<sup>1</sup>, Damaris Margarita PUENTE SILLER<sup>1</sup>,  
Francisco Raúl CARRILLO PEDROZA<sup>1\*</sup>, Luis Alfonso GARCÍA CERDA<sup>2</sup> and  
Jesús VELÁZQUEZ SALAZAR<sup>3</sup>

<sup>1</sup> Facultad de Metalurgia, Universidad Autónoma de Coahuila, Carretera 57 K. 4.5, Monclova, Coahuila, México, C.P. 25710

<sup>2</sup> Centro de Investigación en Química Aplicada, Blvd. Enrique Reyna No. 140 Col. Los Pinos, Saltillo, Coahuila, México, C.P. 25253

<sup>3</sup> Department of Physic and Astronomy, University of Texas at San Antonio, One UTSA Circle, San Antonio TX 78249

\*Autor de correspondencia: frrcarrillo@yahoo.com.mx

*(Recibido noviembre 2014; aceptado enero 2015)*

Key words: cyanide, gold mining effluents, nanoparticles, copper

### ABSTRACT

The extraction process of gold and silver by cyanidation generates large amounts of effluent which also contain contaminants such as cyanide and significant metal values such as copper. This paper presents the results of the removal and recovery of copper from ozonation treatment of a residual aqueous cyanide. The residual solution was treated by ozonation-precipitation to obtain a precipitate of copper. From this, copper nanocomposites obtained by Pechini modified sol-gel method were obtained. The compounds obtained were characterized by XRD, showing a dependence of the type of compounds formed over time of ozonation and heat treatment of the gel. The particle size was measured by SEM and calculated by the Scherrer equation, being between 50 and 120 nm.

Palabras clave: cianuro, efluentes de la minería del oro, nanopartículas, cobre

### RESUMEN

El proceso de extracción de oro y plata por cianuración genera grandes cantidades de efluentes que contienen, además de contaminantes como el cianuro, valores importantes de metales, como el cobre. En este trabajo se presentan los resultados de la remoción y recuperación de cobre a partir del tratamiento por ozonización de una solución acuosa residual de cianuración. La solución residual fue tratada por ozonización-precipitación para obtener un precipitado de cobre. A partir de este precipitado se obtuvieron nanocompuestos de cobre por el método de sol-gel modificado de Pechini. Los compuestos obtenidos fueron caracterizados por difracción de rayos X, en los que se observó una dependencia del tipo de compuestos formados con el tiempo de ozonización y el tratamiento térmico del gel. El tamaño de partícula fue medido por microscopía electrónica de barrido y calculado por la ecuación de Scherrer, con un resultado de entre 50 y 120 nm.

## INTRODUCTION

Cyanide has been widely used as an essential material in several industries including textile, plastics, paints, photography, electroplating, agriculture, food, medicine and mining/metallurgy. Because of its high affinity for gold and silver, cyanide is able to selectively dissolve or leach these metals from ores. This is called “cyanidation” process (Habashi 1966, Rubo *et al.* 2006). After gold and silver are extracted from a cyanide solution, wastewater or process solutions may contain three principle types of cyanide compounds: free cyanide, weakly complexed cyanide and strongly complexed cyanide. Cyanide forms ionic complexes with metals (e.g. Fe, Cu, Zn). Stability of cyanide-metal complexes may vary depending on the type of metal. Weak acid dissociable Cu and Zn complexes are relatively unstable (Ministry of Environment Ontario 2013). Cyanide in effluents resulting from gold mining is known to be the prime candidate for treatment. However, according to many studies, ammonia, suspended solids and copper are identified as the most important contaminants in gold mining effluents rather than cyanide (Mudliara *et al.* 2009). Then, gold mining effluents can be an important source of valuable metals.

Many methods have been investigated to cyanide destruction and metal recovery. In this work, ozone is used with this purpose. Ozone, as a strong oxidizing reagent has been used to destroy cyanide. Ozone is generated on-site typically by the silent electrical discharge method. One advantage is the ability of ozone to destroy zinc, copper and nickel cyanide complexes, obtaining metallic hydroxides or oxides precipitates (Mudliara *et al.* 2009). In this context, the present study is focused in obtaining copper oxide nanoparticles from gold mining effluents by a combination of two techniques: ozone oxidation-precipitation and Pechini modified sol-gel method.

Particularly, nanoparticles have been the subject of intense scientific and technological research due to their interesting size-dependent physicochemical and optoelectronic properties, and consequently exciting application potential in many important fields of science and technology as sensors, electrochemical cells, optical devices and catalysts (Kakihana 1996, Ren *et al.* 2009, Theivasanthi and Alagar 2011). Moreover, one of the most important challenges is the comprehensive utilization of waste to obtain metal values using methods and techniques that demand less energy consumption, environmentally friendly and economically favorable (Segal 1997). The oxides of transition metals are an important class of semiconductors,

which have applications in magnetic storage media, solar energy transformation, electronics and catalysis. Among the oxides of transition metals, copper oxide nanoparticles are of special interest as a less expensive alternative (Lanje *et al.* 2010). The research rapidly turned towards amorphous materials based on dispersed CuO due to their better hydrothermal and mechanical stability. Copper-based catalysts have been reported to have a superior performance in hydrogenolysis of glycerol (Huang *et al.* 2009), hydrogen production by methanol (Gadhe and Gupta 2007) and the reduction of nitrogen oxides (NO<sub>x</sub>) with reducing species (hydrocarbon) in high oxidant atmosphere (Bennici *et al.* 2003).

In our study, Pechini modified sol-gel method was used to obtain the nanoparticles. In this method, a solution of metal-organic compounds (such as metal alkoxides) is used to form a gelled material, a network of polymer chains formed by hydrolysis and condensation reactions (Rahaman 2007). This polymeric precursor method is one of the ways of obtaining catalysts with a high degree of dispersion and uniform component distribution (Gvishi 2009). This method was initially intended for the synthesis of oxide ceramics in electronic applications, but later it found wide use in the syntheses of catalytic materials, as copper oxides (Potemkina *et al.* 2010).

## MATERIALS AND METHODS

Industrial gold mining effluents samples (free CN<sup>-</sup>, 700 mg/L; Cu, 626.7 mg/L; Zn, 5.58 mg/L; Fe, 3.16 mg/L; pH, 11; 20 °C) were placed in a type-column ozonation reactor and then oxidized with ozone (produced by L-22 Pacific Ozone generator) in order to remove cyanide. Experiments were performed at constant ozone flow rate of 1 g O<sub>3</sub>/h during different ozonation times. After ozone oxidation and subsequent solid-liquid separation, metallic nanoparticles were synthesized using the sol-gel method. Citric acid (CA) and ethylene glycol (EG) obtained from the ozonized solution were added to the solids (previously dried) using a molar ratio CA:EG of 1:4. Solution was heated in a hot plate at constant agitation to evaporate the excess of water. A dark green transparent gel was obtained after concentrating the solution by slow evaporation. This gel was then dried in air at 140 °C for 24 h, finely ground in an agate mortar, and burnt at temperatures from 400, 600 and 800 °C in air for 15 min in a tube furnace. **Figure 1** shows a schematic experimental setup, indicating where citric acid and ethylene glycol (CA-EG) is added.

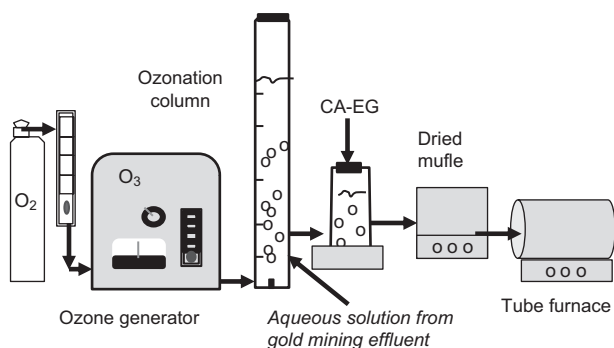


Fig. 1. Schematic experimental setup. Citric acid (CA) and ethylene glycol (EG)

The heat-treated samples were characterized by X-ray diffraction (XRD) in a Siemens D-5000 diffractometer operated at 25 mA and 35 kV. Experiments were carried out in the  $2\theta$  range of 20 to 55° at a step size of 0.02 degrees. Characterization by scanning electron microscopy (SEM) with energy dispersive scanning (EDS) was done in a Hitachi S-5500 microscope operated from 10.2 to 10.5 A and 20 KV.

## RESULTS AND DISCUSSION

Figure 2 shows the results of X-ray diffraction obtained in samples ozonized during 6, 11 and 25 min and finally heat treated in air at 400 °C for 15 min. Characteristic peaks of ZnO are observed for all of the oxidation times in the cyanide solution investigated. The presence of metallic Cu is observed in samples obtained at ozonation time values of 11 and 25 min. These results suggest that the ozonation time in cyanide solutions has a significant effect on the resulting species-type causing variations in the peaks intensities of the species present in samples synthesized by sol-gel. Nevertheless, the final species depended on the heat treatment conditions.

The reactions occurring during treatment are explained below. The ozonation of cyanide solution occurs according to the following reaction. Gibb's free energy at 20 °C was calculated from Outokumpu, HSC Chemistry® for Windows 2002 software (Roine 2002):

Oxidation of free cyanide,  $\text{CN}^-$ :



Oxidation of metal cyanide complex:

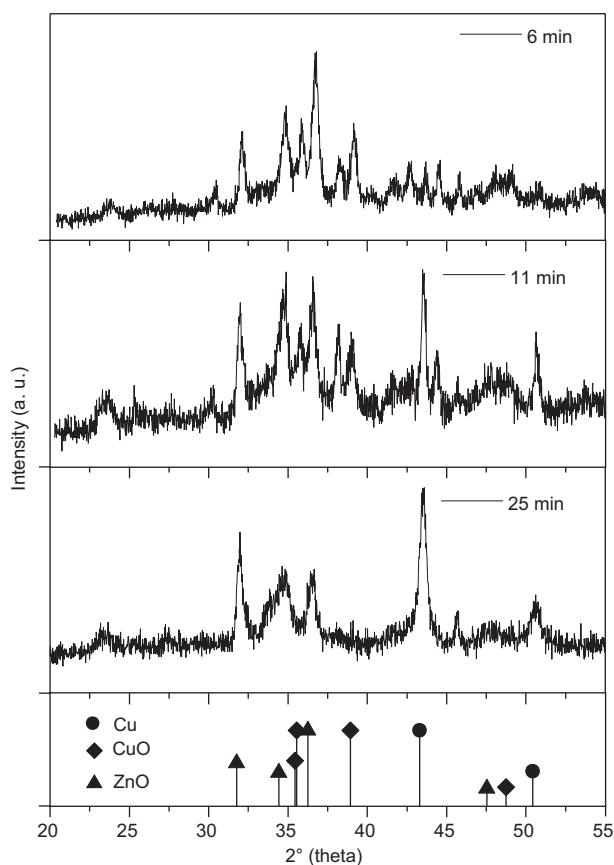
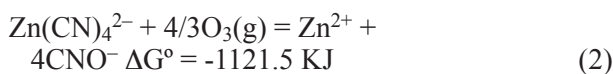
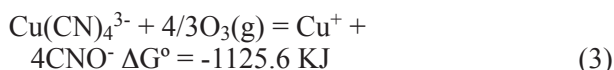
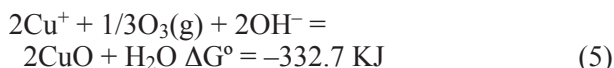
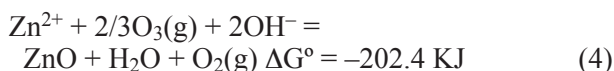


Fig. 2. X-ray diffraction patterns from samples oxidized in different ozonation times, synthesized by sol-gel and a heat treatment of 400 °C under air atmosphere



**Precipitation.** Due to high pH solution ( $\text{pH} > 10$ ), the metal ions could precipitate as hydroxide once the oxidation time for all free cyanide and cyanide complexes is reached. However, metal ions can precipitate as oxides due to continuous addition of ozone, according to the following equations:



In the case of copper (major presence), the oxides precipitation can be confirmed by the precipitates colorations: during ozonation a first blue precipitate appears. Later the precipitate turns to brown and finally to dark color. These colors emerge according to copper transformations: of copper (I) hydroxide

(blue) to copper (I) oxide (brown) and, finally, copper (II) oxide (dark) due to continuous ozonation.

In the sample with the shortest ozone injection time (6 min), the presence of copper is not detected by XRD because the oxidation of cyanide solution starts with the decomposition of the most weak metal cyanide complex, in this case  $\text{Zn}(\text{CN})_4^{2-}$  (stability constant,  $\log K_{25^\circ\text{C}} = 19.6$ ; Smith and Martel 1976, Gerhardt 1987). Apparently, in the first six minutes of the ozone oxidation treatment, the time is not sufficient to obtain a significant amount of the copper cyanide complex by decomposition. Only zinc is precipitated and quickly oxidized by ozone. On the other hand, the intensity of peaks for metallic Cu is higher in samples with longer oxidation times (11 and 25 min). The latter is due to the decomposition of a higher amount of copper cyanide complex,  $\text{Cu}(\text{CN})_4^{3-}$  ( $\log K_{25^\circ\text{C}} = 23.1$ ; Smith and Martel 1976, Gerhardt 1987) and copper oxide precipitation, according to equations 3 and 5.

Afterwards these precipitates are dissolved, reduced or complexed to form poly-chelates between the C=O ligands of citric acid (CA) and metal ions. In the Pechini method (Bennici *et al.* 2003), the chelate undergoes polyesterification while heating with a polyfunctional alcohol like ethylene glycol (EG). In the modified Pechini method (combination of the traditional Pechini and the citrate method) the chelating process takes place during the evaporation of the precursor solution containing metallic salts and CA-EG. Furthermore, air heating produces a dark viscous resin and a rigid transparent vitreous gel.

The presence of Cu in metallic state observed in **figure 2** at 11 and 25 min during the heat treatment at 400 °C indicates that heat treatment temperature is insufficient to complete the combustion of organic matter (from citric acid and ethylene glycol). Then, the reducing atmosphere generated during the heat treatment at 400 °C is sufficient to the reduction of copper oxide at copper zero-valent, according to equation 6. However, these conditions are not thermodynamically sufficient to reduce the ZnO, as indicated in equation 7:



The average particle size calculated from the data of XRD (sample treated with 25 min ozonation and heat treatment at 400 °C and 15 min) using the Scherrer equation varies from 20 to 90 nm. Scherrer

equation is represented by the following equation (Monshi *et al.* 2012):

$$D = K\lambda/\beta\cos\theta \quad (8)$$

In Scherrer's formula,  $D$  = mean particle diameter,  $K$  is the shape factor ( $K = 0.9$ ),  $\lambda$  is the x-ray wavelength ( $\lambda = 0.15417 \text{ nm}$ ),  $\beta$  is the line broadening (full width) at half the maximum intensity (FWHM) in X-ray spectrum (radians), and  $\theta$  is the Bragg angle.

**Figure 3** shows a SEM photomicrography of sample treated with 25 min ozonation and heat treatment of 400 °C for 15 min, where spherical particles have a size between 50 and 130 nm. The EDS analysis obtained in a specific particle (**Table I**) and the respective qualitative elemental mapping confirm that particles consist mainly of a mixture of particles of Cu metallic and Cu oxides. Cu particles are deposited in organic material (from CA-EG partially burned). This result is in accordance with the initial chemical analysis and with the XRD results: the synthesized nanoparticles obtained at 400 °C heat treatment are predominantly Cu metallic.

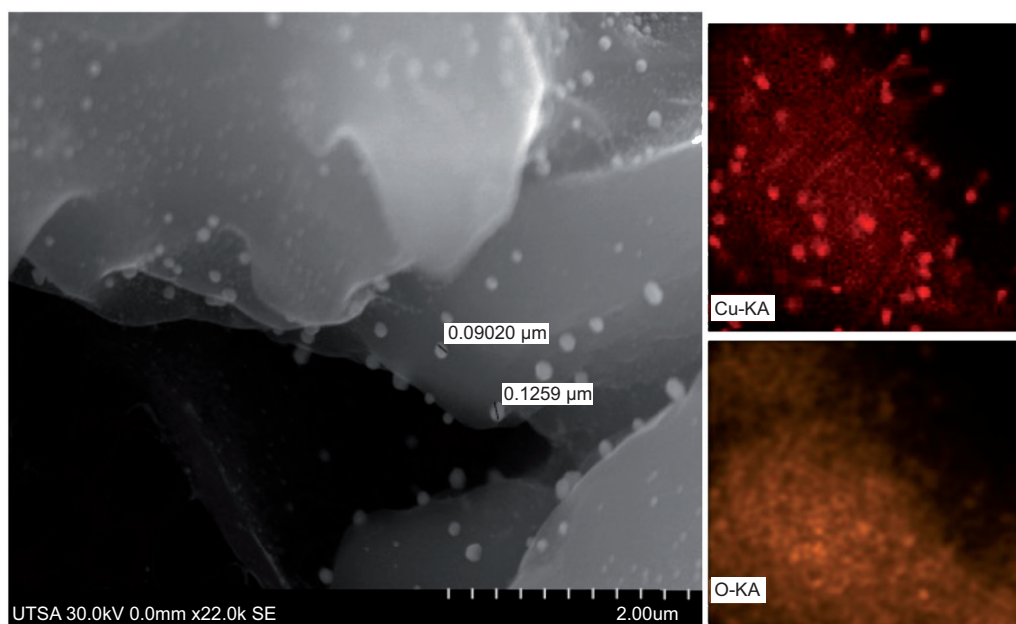
When the heat treatment is performed at 800 °C all organic matter is consumed and the oxygen presence (air atmosphere in chamber furnace) is sufficient to oxidize the copper (**Fig. 4**). Furthermore, the intensity of peaks corresponding to CuO increases, while those of metallic Cu phase disappear.

Then, ozonation time is important to obtain sufficient metal values and to destroy the dangerous cyanide, making safe the subsequent sol-gel process. Obviously, the gold mining effluent sample used in this work is rich in copper, while the other metals (Zn, Fe) are present in very low amounts. However, the knowledge of the chemical reactions of complexes oxidation, stability constants and oxidation-reduction reactions during air dried and heat treatment permits to set up adequate operation conditions to obtain metal (or metal oxides), micro or nanoparticles selectively.

## CONCLUSIONS

According to the experimental results, an oxidation treatment with ozone at alkaline pH allows the oxidation of cyanide in the cyanide solution used in this work. The  $\text{pH} > 10$ , cyanide and Cu amounts in the industrial gold mining effluent indicate that Cu is present in cyanide complexes  $\text{Cu}(\text{CN})_4^{3-}$ . Zinc is also in solution as  $\text{Zn}(\text{CN})_4^{2-}$ . During the oxidation with ozone, both cyanide complexes are oxidized to





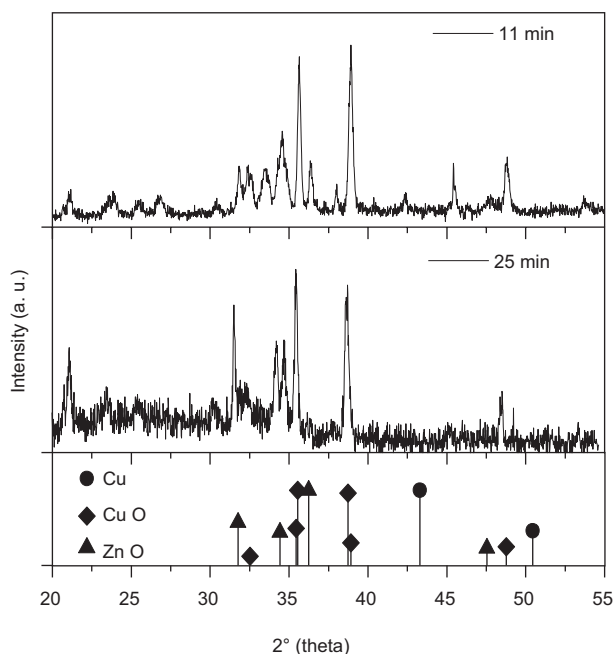
**Fig. 3.** Scanning electron microscopy photomicrograph and mapping of sample treated with 25 min ozonation, synthesized by sol-gel and heat treatment at 400 °C for 15 min. Area with white lines in the micrograph corresponds to the energy dispersive scanning analysis from **Table I**. Cu-KA = Cu-Kalpha, O-KA = OK alpha (principal energy level, KeV)

**TABLE I.** ENERGY DISPERSIVE SCANNING ANALYSIS (CORRESPONDING TO **FIG. 3**) FOR SAMPLE TREATED WITH 25 MIN OZONATION, SYNTHESIZED BY SOL-GEL AND HEAT TREATMENT AT 400 °C FOR 15 MIN

Element	C norm (wt. %)	Error (wt. %)
Cu	75.04	0.9
O	24.96	1.7
Total	100	

CuO and ZnO, respectively. Iron, another element in the effluent, forms a strong cyanide complex that is not easily destroyed by ozone. Precipitates obtained from oxidized solutions are subsequently complexed with citric acid and ethylene glycol to obtain a sol-gel, which is thermally treated.

From effluent chemical analysis, the amount of Cu is about 100 times higher than zinc. This implies a greater number of XRD peaks associated with Cu or CuO. The presence of metallic Cu in samples thermally treated in air at 400 °C is justified by the incomplete combustion of polymeric material that generates a reducing atmosphere. When the heat treatment is performed at 800 °C, all polymeric material is consumed and the presence of oxygen (air atmosphere in chamber furnace) is enough to oxidize the Cu. Furthermore, the intensity of peaks



**Fig. 4.** X-ray diffraction patterns from samples oxidized in different ozonation times, synthesized by sol-gel and a heat treatment of 800 °C under air atmosphere

corresponding to CuO increases, while those of metallic Cu phase disappear as the temperature is increased at 800 °C. Although the diffraction results indicate the presence of ZnO, its quantity is smaller than 1 % w/w.

SEM results confirm the presence of Cu as metal or in oxidized state, although a major control is necessary to obtain small size nanoparticles. As conclusion, at 400 °C and 800 °C, relative good pure Cu metallic and CuO nanoparticles, respectively, could be obtained from ozonated Cu-rich gold mining effluents by the Pechini modified sol-gel method.

This preliminary work shows the possibility of using industrial wastewater as low-cost raw material to obtain high-value compounds, as metallic and oxide metal nanoparticles. In this case, the combination of the two methods, (ozonation and sol-gel synthesis), represents a low-cost alternative for obtaining nanoparticles from industrial gold mining effluents.

### ACKNOWLEDGMENTS

The authors would like to thank the International Center for Nanotechnology and Advanced Materials - Kleberg Advanced Microscopy Center - at the University of Texas, San Antonio (ICNAM-UTSA) for their technical assistance with the SEM characterization.

### REFERENCES

- Bennici S., Gervasini A. and Ragaini V. (2003). Preparation of highly dispersed CuO catalysts on oxide supports for de-NO<sub>x</sub> reactions. *Ultrasonics Sonochem.* 10, 61-64.
- Gadhe J. and Gupta B. (2007). Hydrogen production by methanol reforming in supercritical water: Catalysis by in-situ-generated copper nanoparticles. *Int. J. Hydrogen. Energ.* 32, 13, 2374-2381.
- Gerhardts W. (1987). *Ullman's encyclopedia of industrial chemistry*, 5th edition, VCH, Weinheim, Germany, 639 pp.
- Gvishi R. (2009). Fast sol-gel technology: from fabrication to applications. *J. Sol-Gel Sci. Technol.* 50, 241-253.
- Habashi F. (1966). The theory of cyanidation. *Transactions of the mineralogical society of AIME.* 235, 236-239.
- Huang Z., Cui F., Kang H., Chen J. and Xia C. (2009). Characterization and catalytic properties of the CuO/SiO<sub>2</sub> catalysts prepared by precipitation-gel method in the hydrogenolysis of glycerol to 1,2-propanediol: Effect of residual sodium. *App. Catal. A.* 366, 288-298.
- Kakihana M. (1996). Sol-gel preparation of high temperature superconducting oxides. *J. Sol-Gel Sci. Technol.* 6, 7-55.
- Lanje A., Sharma S., Pode R. and Ningthoujam R. (2010). Synthesis and optical characterization of copper oxide nanoparticles. *Adv. Appl. Sci. Res.* 1, 2, 36-40.
- Ministry of Environment Ontario (2013). Safe drinking water act, 2002 and amendment in 2006 [online]. [http://www.ontario.ca/laws/statute/02s32\\_06/06/2014](http://www.ontario.ca/laws/statute/02s32_06/06/2014).
- Monshi A., Foroughi M. and Monshi M. (2012). Modified scherrer equation to estimate more accurately nanocrystallite size using XRD. *World J. of Nano Sci. and Eng.* 2, 154-160.
- Mudliara R., Umareb S.S., Ramtekea D.S. and Wate S.R. (2009). Energy efficient—Advanced oxidation process for treatment of cyanide containing automobile industry wastewater. *J. Hazard. Mater.* 164, 1474-1479.
- Potemkina D., Snytnikova P., Pakharukova V., Semina G., Moroza E. and Sobyana V. (2010). Copper-cerium oxide catalysts prepared by the Pechini method for CO removal from hydrogen containing mixtures. *Kinet. Catal.* 51, 1, 119-125.
- Rahaman M. (2007). *Ceramic processing*, CRC Press. Boca Raton, Florida, USA, 388 pp.
- Ren G., Hu D., Cheng E., Vargas-Reus M., Reip P. and Allaker R. (2009). Characterization of copper oxide nanoparticles for antimicrobial applications. *Int. J. Antimicrob. Agents.* 33, 6, 587-590.
- Roine A. (2002). Outokumpu, HSC chemistry® for windows (2002). Chemical reaction and equilibrium software with extensive thermochemical database. Outokumpu Research Oy. Finland.
- Rubo A., Kellens, R., Reddy J., Steier N. and Hasenpusch W. (2006). Alkali metal cyanides, in *Ullmann's encyclopedia of industrial chemistry*, Wiley-VCH, Weinheim, Germany [online]. [http://onlinelibrary.wiley.com/doi/10.1002/14356007.i01\\_i01/abstract](http://onlinelibrary.wiley.com/doi/10.1002/14356007.i01_i01/abstract)
- Segal D. (1997). Chemical synthesis of ceramic materials. *J. Mater. Chem.* 7, 1297-1305.
- Smith R. M. and Martel A. E. (1976). Critical stability constants, volume 4: Inorganic complexes. Plenum Press, New York, USA, 469 pp.
- Theivasanthi T. and Alagar M. (2011). Nano sized copper particles by electrolytic synthesis and characterizations. *Int. J. Phys. Sci.* 6, 3662-3671.