International Journal on
"Technical and Physical Problems of Engineering"
(IJTPE)
Published by International Organization of IOTPE

ISSN 2077-3528
IJTPE Journal
www.iotpe.com
ijtpe@iotpe.com

June 2017 | Issue 31 | Volume 9 | Number 2 | Pages 43-48

CHEMICAL-MECHANICAL CLEAR FILTRATION (CMP) OF WASTE WATER USING ELECTRO-COAGULATION METHODS AND SEMI CONDUCTIVE ELEMENTS BASED PRODUCTION

N.M. Hosseinahli [1] M.A. Hasanov [2]

1. Azarbaijan Higher Education and Research Complex, Tabriz, Iran, nhosseinahli@gmail.com
2. Institute of Physics, Azerbaijan National Academy of Sciences, Baku, Azerbaijan, magerram-hasanov@rambler.ru

Abstract- In this paper, the waste water purification, using Mechanical-Chemical pellucid (Clear Filtration), is being discussed. In purification process, method of using large semiconductors was used. In this method, Concentration of suspended solids (SS), Clarity degrees of turbidity (NTU) were calculated. Chemical Oxygen demand (COD) was 500milligram per liter and cupper concentration was 100 milligrams per liter. Experiments have shown that it is possible to reduce concentration rate of cupper, Clear the color of waste water, and reduce COD, considerably by electro-coagulation process. Different phases of electro-coagulation process monitored. Also, Different pairs of electrodes were used in these experiences. Average sizes of particles were 100 nanometers and average size of suspended particles, were 68 to 120 nanometers. Experiments show that Iron-Aluminum electrode pairs produce better results. These pairs are able to eliminate 99 percent of cupper pollutant, with color clarity rate of 96.5 percent. The COD ratio was less than 100 milligrams per liter in standard Debi. Filtered waste water material could be used in different applications.

Keywords: CMP, COD, NTU, Electro-Coagulation-Electrodes, Waste Water.

I. INTRODUCTION

In these experiences, semi conductive industrial production, a very broad array of complex reactions (such as silicates reactions, oxidation, compressed concentration, ionic, photography, rate of discharge, metal surface connection and cleanness of surfaces, are used [1-4].

In process of this experimental production, more than 200 compound and numerous organic and mineral based filters had been used. For cleaning and washing of semiconductors, pure ultra-violet ray had been used [2-4]. After implementation of above mentioned steps, a different type of semi conductive waste water was collected which contained chemical solvents, different types of acids and salts and heavy metals, suspended acidic particles and other compounds [1-4].

Also in process of this experimental production, in order to analyses different steps of CMP and semiconductors, Debi of waste water through water and its quality had been regulated and monitored [5-6].

CMP process was done in continuous IC circuit and in measurement smaller than 0.25 micrometer. Major disadvantage of this system was higher cost of operation compare to method that uses pure ultra violet beam. In our experiment, pure ultra violet beam was calculated and used for only 40% of consumed water in industrial semi conductors' method [11].

Pure ultra violet beam was also used in following steps: post elimination phase of CMP grout removal, cleaning of necessary water for processes, cleaning of metals particles and other accumulated particles on surfaces of semiconductors. Most particles in CMP grout (in controlled PH environment) were of suspended de-oxide of Selsiom, tri-oxide of Aluminum and CeO_2. Also traces of oxidant compounds such as $Fe(NO_3)_3$, Copper Sulfate, H_2O_2, $KmnO_4$, Hydroxide chlorate of aluminum, Additives such as NH_4OH, Inorganic buffers, Acidic agents, different types of activators, corrosion compounds and etc. had been found in.

To eliminate cupper particles smaller than 0.15 micrometer, CMP grout was completely washed and cleaned by various organic and inorganic compounds. More than 100 milligram of cupper particles were collected from inside of larger filters [12-14].

Most of solid matters in waste water came from industrial sources. Elimination of these solid particles (T.S) was one of the primary goals of this research [7]. Ultra-filtration process was used for elimination of very fine particles, such as alumina and silica particles [8].

In order to do addition experiences in filtration of very fine suspended solid particles, by means of Electro-coagulation and chemical coagulation, oxidation and reduction methods, coagulated polymers for different surfaces were prepared and tested. Obtained results shows that, in waste water CMP complex steps with allowances of extra time for completion of process, are more effective in removing very fine suspended particles and CODs [10].

For non-crucial situation, inner linear control of filtrations and separation of particles is use and tested. Also, exchange of ions between different particles, were studied [12]. Positive results in elimination of ultra-fine cupper and acidic particles from CMP grout were obtained from above filtration method [13].

Another experimental method for elimination of cupper particles, using coagulating agent with combination of above mentioned experiences, were done and positive results in elimination of cupper ions and acidic particles were obtained. Experiences show that largest percentage of elimination of pollutants, were achieved by using semiconductors method. Exiting CMP liquid contains a large portion of compound materials (measurable in 500 COD milligram per liter unit).

Elimination of Organic materials and Filtration of waste water using CMP is not possible on the same time. For Filtration of waste water from different sources such as waste water from human consumption, from fish nurseries. From textile factories, restaurants and from cities waste water department, using electro-coagulating method is preferred method [14-24]. This method can be used for filtration of Phenol [25] and other activating agents in industrial waste water materials.

In this research, Electro-coagulation method of purification and filtration, with emphasis on reduction of suspended acidic particles and reduction on cupper concentration, were discussed. General steps of Electro-coagulation method in pre and post CMP conditions and also necessary steps and their quality were discussed too.

II. EXPERIMENTS

Waste water samples CMPs were processed using semiconductors. All related properties such as natures of contained particles, concentration ratio and also different grouts of CMP were categorized. Different steps of experiments were planned too. Quality of water in Waste water CMP, Color tonality (NTU), COD factor, PH factor and conductivity were measured by known methods [27].

It worth mentioning that Spectrometer machines and other hi tech machines were used to determine quality of water after electro-coagulation process. To determine amount of fine acidic suspended particles in COD of waste water material Zeta Potential Algorithm was used through different steps of electro-coagulation process (Figure 1).

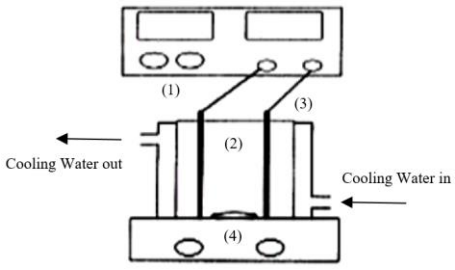

Figure 1. Electro-coagulation exams system

Basically, this machine is composed of a glass of water (one-liter capacity) inside a reactor with Iron and Aluminum bars in Titanium jars are put inside it (sizes of jars are 20cmL×3cmW and there are 5 different even anode and cathode electrodes hanging in there from altitude of 12 centimeters). Water temperature inside glass is same as external cover of glass. Separation and replacement happened in altitude of 8 centimeters of bars. Effecting surface was measured 72 cm^2. Inducing voltages was fixed at 30 Volts.

In whole process time, an electric mixer with 100rpm speed was used. For concentrations of 25 to 50 milligram per liter, separation of compounds and ions happened nicely. To increase conductivity, NaCl was added to water which accelerate filtration process. Each 10 minutes a sample was collected and whole electro-coagulation process lasted 2 hours. All samples, either outside of container or inside it were analyzed. Traditionally, filtration time of 30 minutes deemed adequate for waste water CMP treatments.

III. DISCUSSIONS

A. A Few Properties of Waste Water CMP

Table 1 shows an average composition of particles in waste water CMP water from large industrial semiconductor (taken for experiments. Gray or milky color of waste water is an indicator of cupper ions and fine suspended acidic particles. On average it contains 4000 to 5000 milligrams of solid materials (T.S) and 0.1 to 0.4 milligrams of not very important suspended solids per liter (S.S). Average size of particles were100 nanometer and this size scale were used in calculations of concentration of solids in waste water (T.S). All collected acidic fine particles were collected from drying of waste water samples in electrical kilns [27].

Experiments were done on 120,000 milligrams of solids per liter (T.S) in CMP grout as Table 1 (lesser than total waste water CMP). All semiconductors' part was kept clean in duration of experiments. One very noticeable observation was higher concentration of COD in waste water CMP compare to grout of original matter (clearly be seen in mixing process and as indicator of existence of organic materials). Elimination of COD is more essential than elimination of cupper and suspended fine acidic material.

Table 1. Average compositions of particles in waste water materials and CMP grout

Parameters	CMP Slurry	CMP Wastewater
pH	10.2	6-8.7
TS (mg/l)	124,100	4000-5000
SS (mg/l)	0.2	0.1-0.4
Copper Concentration (mg/l)	-	45-120
Oxide Particle Size (nm)	100	100
Conductivity (µs/cm)	-	450-470
COD (mg/l)	98	210-480
BOD/COD	NM	0.11-0.15
Color	Milky	Milky

B. Different Phase of Electro-Coagulation & Observations

Figures 2(a) and 2(b), and also distribution of zeta potential, show properties of fine suspended materials before and after Electro-coagulation. In Figure 2(a) size of fine suspended oxidized particles in CMP of main waste water (in both side of curve) are between 68 to 120 nanometer (average size is 100 nanometer).

Paper filters were used for measuring concentration of suspended solids (S.S) and maximum size of 159 nanometers was obtained. These particles were collected and disregarded before grout analyzes process. In different experiments, total volume of solids (T.S) were not fixed

and varied in each experiment and their sizes varied from 49 to 141 micrometers, as shown in Figure 2(b). Average size was 16.76 and most of them were larger than 11.3 micrometer. Quality of concentrating device was very high and removal time was less than 30 minutes. All collecting steps of experiences were meticulously monitored [28].

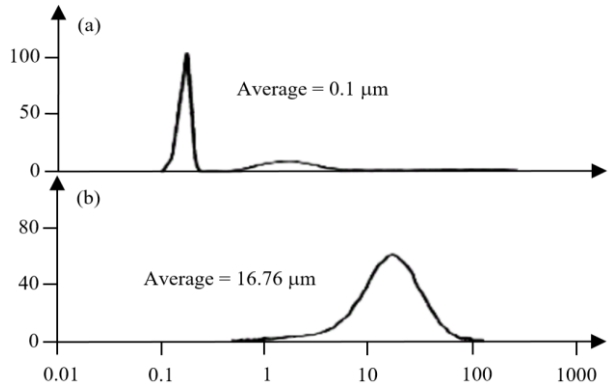

Figure 2. Distribution of Zeta potentials before and after electro-coagulation

Figure 3 shows experiment mechanism for zeta potential and suspended fine acidic particles during filtration process. In this experiment, for first 30 minutes Zeta potential were stable and around 49 mille-volts. In this time span, Collective particles were accumulated in continuous manner. This potential after 80 minutes was decreased to 15 mV. Results were how the researched expected to be and after with constant increase of zeta potential, accumulation rate increased too [28]. In these experiments, different semi conductors' surfaces used and best results were obtained from even electrodes in different steps of electro-coagulation [29].

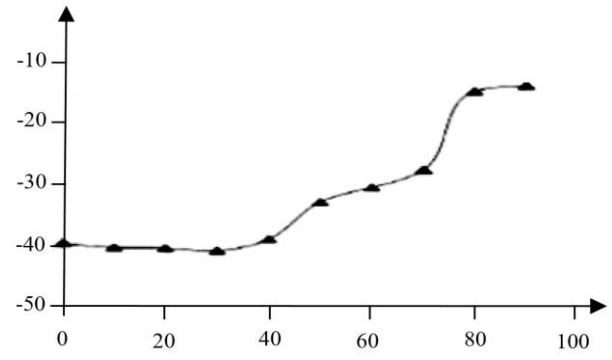

Figure 3. Change of duration of accumulation of particles in electro-coagulation, using even pair of Iran and Aluminum electrodes

Aluminum and Iran electrodes combines with Titanium plates were main electric parts. The five different solutions were prepared. And best responding solution, to act with even pair electrodes, was chosen. Figures 4(a) and 4(b) shows elimination rate of COD and also clearing rate of color (NTU) in differ pairs of anodic and cathode electrodes. Direct and indirect oxidation processes were responsible for elimination of COD. Decomposition of organic matters happened in different phases of electro-coagulation process.

Figure 4(a) shows different span of elimination of COD for selected electrode pairs. Namely: for Al-Fe pair = 75.3%, for Al-Al pair = 88.4%, and very limited and not useful for Fe-Al, Fe-Fe, Ti/Fe pairs

Reduction on waste water COD in standard Debi were, between 100 milligram to 288 milligram per liter. Figure 4(b) shows that color clearing, for all pairs of electrodes, were same. In most functionally limited pair (Iran electrode as anodic electrode) was about 60% (NTU).

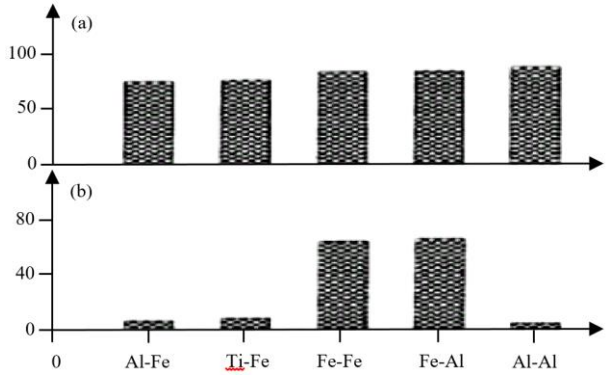

Figure 4. Elimination of COD and Clearing of color of waste water using different electrodes

In all steps of electro-coagulation, $Fe(OH)_2$ used and accumulations happened. In Figure 5(a) elimination of cupper by all pairs of electrodes with very satisfactory result, up to 98% has shown (100% elimination with Aluminum anodic electrodes). Concentration of cupper in starting point was 79 milligrams per liter and in final phase was one milligram per liter in standard Debi for industrial waste water. The main place for absorbing cupper ions is surface of plate. Then, these cupper muds make sediments in the container.

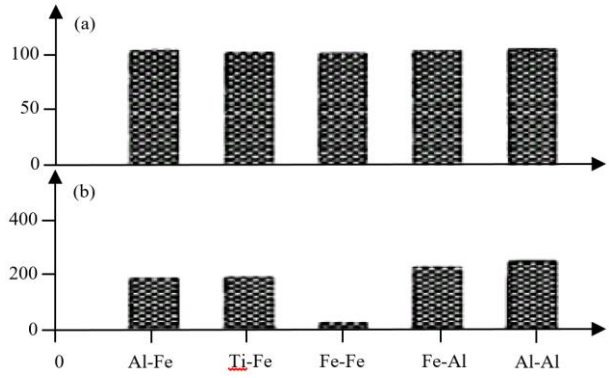

Figure 5. Amount of eliminated cupper and amount of produces ooze using different electrodes

Allocated time for, all electro-coagulation experiments, were 30 minutes and amount of sediment slims and its volume were main indicators for quality of electro-coagulation process. Figure 5(a) shows that electrode pair of Fe-Fe in waste waters CMP, produces only 18 milliliter of slime per each liter. For other four pairs, this amount was 160 to 216 milliliter per each liter. Size of particles produced, using Fe-Fe electrodes, were on average 18.2 micrometer, which is smaller than sizes of

particles produce by other four pairs of electrodes (Figure 2(b)). It worth mentioning that slim from Fe-Fe electrodes was darker more concentrated and for some finer solid particles (S.S), separation process took more than 30 minutes (Figure 5(b)). Experiments showed that electrode pair of Al/Fe is electrode pair of choice for better results.

Process and different steps of electro-coagulation and chemical coagulation for direct and indirect oxidations are well known process [21-22]. In these processes, direct oxidation is located on anodic side. This oxidation is activated by indirect oxidation of pollutant and its properties are in direct proportion with chemical coagulation process [2-21]. It showed conductivity value of less than 500 Ms, using semi conductors' method (Table 1).

As we can see in this table, conductivity properties are main cause of electro-coagulation process. Amount of electrolytes are not optimal in this case and main reason for electro-coagulation process is higher degree of KNO_3 in electrolyte. NaCl is suggested and used for further experiments. Figures 6(a) and 6(b) shows elimination of COD and Clearing degree, respectfully, for period of less than an hour 50 milligrams per liter and for time span of 80 to 90 minutes, it turbidity (NTU) to less than 25 milligrams per liter. Figure 6(a) shows following results: 1) Elimination of COD with concentration of 25 milligrams per liter of (NaCl) in 30 minutes is 65%, 2) same in 40 minutes was 73.3%, same with concentration of 50 milligrams in 30 minutes = 65%, same without use of NaCl in 120 minutes was 63%.

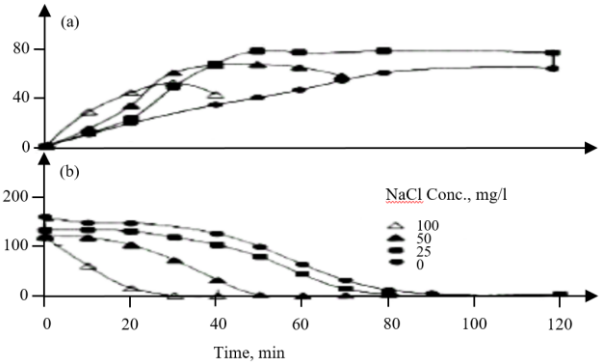

Figure 6. Effect of using NaCl in elimination of COD and Clearing ratio of turbidity, using pair of aluminum and Iran electrodes

Figure 7(a) shows, 98% of cupper elimination in 60 minutes with 25 milligrams of NaCl inside. Figure 7(b) shows elimination of Cu for NaCl, 10 milligrams per liter in 90 minutes is excellent. In all experiments, applied voltage was 30volts. All experiments show that severity of power has direct effect on whole process.

Figures 8(a) and 8(b) show effect of voltage on elimination of copper and clearing of slim (NTU). Figure 8(a) shows 99% copper reduction was achieved by applying 10, 20, 30 volts of electricity for 40, 50, 90 minutes respectfully. Degree of clearing of slim (NTU) for above mentioned voltages were 3.5, 6.3, 6.3, respectfully (Figure 8(b)).

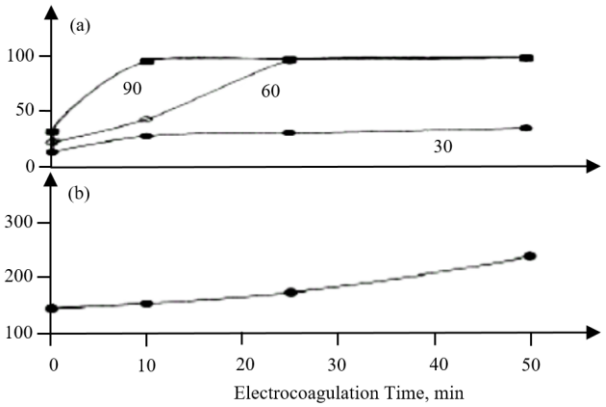

Figure 7. Effect of using NaCl in elimination of Cu and Clearing ratio of sludge produce, using pair of aluminum and Iran electrodes

So using voltage range of 20 to 30 recommended. For voltages of 10, 20, 30 and currency of 0.18, 0.11 and 0.06 resulting in 99% elimination of cupper, power of entering currency were 0.9, 1.83 and 3.6 W, respectfully.

Figure 9 shows that voltage source of 30 V and time spam of 40 minutes is effective in 99% elimination of cupper contents. Entering currency of 3.6 vats and exiting currency of 10 W can only result on only 0.9% point of cupper reduction. To achieve desired reduction of 99%, time span must increase to 90 minutes. For average industrial filtration voltage of 20 is recommended.

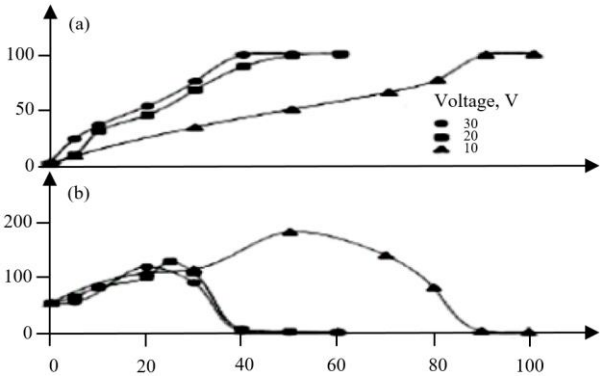

Figure 8. Voltage effect on elimination of cupper and on clearing percentage of waste water color using Iron-Aluminum electrodes

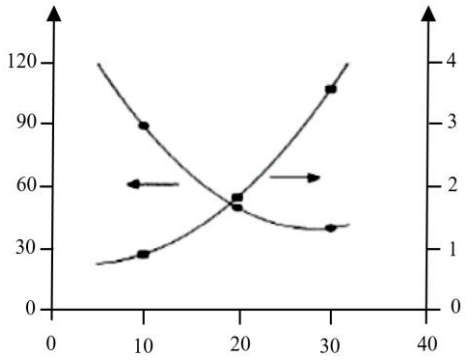

Figure 9. Elimination of cupper in electro-coagulation process using Iron-Aluminum electrodes

IV. RESULTS

In this research waste water CMP using semiconductors and electro-coagulation method, for elimination of cupper particles and also elimination of suspended acidic particles, is analyzed through different experiments. The following conclusions are achieved:

A. Waste water CMP is done on 400 milligrams per liter of solids (T.S) and concentration of 500 milligrams per liter of COD. Average sizes of suspended acidic particles were 100 nanometers and average size of particles, in general, were 68 to 120 nanometers.

B. Iron and Aluminum electrodes show better ions separation quality for cupper ions (99% reduction) and COD. They act better than other pairs in reduction of slime and ooze (96% clarity).

C. Adding 25 milliliter of Sodium Chloride is a very useful step in reduction of suspended particles and cupper ions. It is also useful in clearing waste water color.

D. Using ten-minute span and 20 V power source is recommended. For lab experiment power source should be in range or 10 to 30 Volts.

REFERENCES

[1] A. Afkhami, M. Saber Tehrani, H. Bagheri, "Simultaneous Removal of Heavy Metal Ions in Wastewater Samples Using Nano-Alumina Modified with 2.4-Dinitrophenylhydrazine", Journal of Hazardous Materials, Vol. 181, pp. 836-844, 2010.

[2] J. Aguado, J.M. Arsuaga, A. Arencibia, M. Lindo, V. Gascon, "Aqueous Heavy Metals Removal by Adsorption on Amine-Functionalized Mesoporous Silica", Journal of Hazardous Materials, Vol. 163, pp. 213-221, 2009.

[3] C.K. Ahn, D. Park, S.H. Woo, J.M. Park, "Removal of cationic Heavy Metal from Aqueous Solution by Activated Carbon Impregnated with Anionic Surfactants", Journal of Hazardous Materials, Vol. 164, 1pp. 130-1136, 2009.

[4] O. Can, D. Balkose, S. Ulku, "Batch and Column Studies on Heavy Metal Removal Using a Local Zeolitic Tuff", Desalination, Vol. 259, pp. 17-21, 2010.

[5] G.E. McGuire, "Semiconductor Materials and Process Technology Handbook", Noyes Publications, Westwood, New Jersey, 1988, C.L. Lai, S.H. Lin, Chemical Engineering Journal, Vol. 95, pp. 205-211, 2003.

[6] W. Kern, "Handbook of Semiconductor Wafer Cleaning Technology", Noyes Publications, Westwood, New Jersey,1993.

[7] D.G. Giles, R.C. Loehr, "Waste Generation and Minimization in Semiconductor Industry", J. Environ. Eng., ASCE120, pp. 72-86, 1994.

[8] P.V. Zant, "Microchip Fabrication", Third Ed., McGraw-Hill, New York, 2000.

[9] J.M. Steigerwald, S.P. Murarka, R.J. Guttmann, "Chemical Mechanical Planarization of Semiconductor Materials", Wiley, New York, 1997.

[10] S.H. Li, R.O. Miller, "Chemical Mechanical Polishing in Semiconductor Processing", Academic Press, San Diego, CA, 2000.

[11] S. Browne, V. Krygier, J. O'Sullivan, E.L. Sandstrom, "Treating Wastewater from CMP Using Ultrafiltration", MICRO, pp. 78-86, March 1999.

[12] B.M. Belongia, P.D. Haworth, J.C. Baygents, S. Raghvan, "Treatment of Alumina and Silica Chemical Mechanical Polishing Waste by Electrodecantation and Electrocoagulation", J. Electrochem. Soc., Vol. 146, pp. 4124-4130, 1999.

[13] J.H. Golden, R. Small, L. Pagan, C. Shang, S. Raghavan, "Evaluating and Treating CMP Wastewater", Semicond. Int., Vol. 23, No. 6, pp. 92-103, 2000.

[14] S. Browne, J. Maze, B. Head, "Assessing a System for CMP Waste Minimization and Recycling", MICRO, pp. 74-84, March 2000.

[15] G. Corlett, "Targeting Water Reuse for Chemical Mechanical Polishing", Solid State Technol., Vol. 43, No. 6, pp. 182-187, 2000.

[16] D. James, D. Campbell, N. Thuy, D. Brady, "A Process for Efficient Treatment of Cu CMP Wastewater", Semicond. Int., Vol. 23, No. 5, pp. 21-29, 2000.

[17] G.A. Kruilik, K. Kramasz, J.H. Golden, R.J. Small, C. Shang, L. Ragan, "Copper CMP Wastewater Chemistry and Treatment", Ultrapure Water, Vol. 18, No. 10, pp. 29-35, 2001.

[18] E.L. Vik, D.A. Carlson, A.S. Ekum, E.T. Gjessing, "Electrocoagulation of Potable Water", Water Res., Vol. 18, pp. 1355-1360, 1984.

[19] N. Mameri, A.R. Yeddou, H. Lounici, D. Belhocine, H. Grib, B.Bariou, "Defluoridation of Septentrional Sahara Water of North Africa by Electrocoagulation Process Using Bipolar Aluminum Electrodes", Water Res., Vol. 32, pp. 1604-1612, 1998.

[20] S.H. Lin, C.L. Wu, "Electrochemical Removal of Nitrite and Ammonia for Aquaculture", Water Res., Vol. 30, pp. 715-722, 1996.

[21] S.H. Lin, C.F. Peng, "Continuous Treatment of Textile Wastewater by Combined Coagulation", Water Res., Vol. 30, pp. 587-592, 1996.

[22] S.H. Lin, M.L. Chen, "Treatment of Textile Wastewater by Chemical Methods for Reuse", Water Res. 31, pp. 868-876, 1997.

[23] E.R. Ramirez, "Physicochemical Treatment of Rendering Wastewater by Electrocoagulation", 36th Purdue Industrial Waste Conference, Lafayette, Indiana, 1981.

[24] S.H. Lin, C.T. Shyu, M.C. Sun, "Saline Wastewater Treatment by Electrochemical Method", Water Res., Vol. 32, pp. 1059-1067, 1998.

[25] S.H. Lin, C.C. Chang, "Treatment of Landfill Leachate by Combined Electro-Fenton Oxidation and Sequencing Batch Reactor Method", Water Res., Vol. 34, pp. 4243-4249, 2000.

[26] G.H. Chen, X.M. Chen, P.L. Yue, "Electrocoagulation and Electro-Flotation of Restaurant Wastewater", J. Environ. Eng., ASCE, Vol. 126, pp. 858-863, 2000.

[27] A. Biwyk, "Electrocoagulation of Biologically Treated Sewage", 35th Purdue Industrial Waste Conference, Lafayette, Indiana, 1980.

[28] M.F. Pouet, A. Grasmick, "Urban Wastewater Treatment by Electrocoagulation and Flotation", Water Res., Vol. 31, No. 3-4, pp. 275-283, 1995.

[29] Y.M. Awad, N.S. Abuzaid, "The Influence of Residence Time on the Anodic Oxidation of Phenol", Sep. Purif. Technol., Vol. 18, pp. 227-236, 2000.
[30] G.A. Ciorba, C. Radovan, I. Vlaicu, L. Pitulice, "Correlation between Organic Component and Electrode Material: Consequences on Removal of Surfactants from Wastewater", Electrochem. Acta, Vol. 46, pp. 297-303, 2000.

BIOGRAPHY

Nasrin M. Hosseinahli was born in Tabriz, Iran, 1966. She received B.Sc. degree in Chemistry Form University of Tabriz (Tabriz, Iran) in 1990 and M.Sc. degree in Energy from Abbaspour University (Tehran, Iran) in 2002. She is the academic member of Water and Environment Department at Azarbaijan Higher Education and Research Complex (Tabriz, Iran). She has published many papers in the above mentioned fields.

Maharram A. Hasanov was born in Baku, Azerbaijan on May 9, 1956. He graduated (B.Sc.) from Azerbaijan State University (Baku, Azerbaijan) in 1975 and got diploma (M.Sc.) in Physics, from Leningrad Institute for High Molecular Compounds (Leningrad, Russia) in 1992 and diploma of candidate of sciences (Ph.D.). He works as scientific officer, senior scientific officer, leading scientific officer in High Voltages Physics and Engineering Laboratory, Azerbaijan National Academy of Science (Baku, Azerbaijan). His areas of interests are in electrophysics, high voltage physics and technology, applications of electrical fields and discharges for the polymeric and composite materials modification, X-ray analysis of the polymeric structure, electro physical processes in the polymeric dielectrics. He has more than 50 scientific published articles, 5 patents, participation in more than 7 international conferences, symposiums and seminars on electrical engineering, high voltages physics and engineering, electrical power engineering, and solid state physics.