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A review of recovery of metals from industrial waste

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ABSTRACT

Due to rapid industrialization the demand for heavy metals is ever increasing, but the reserves of high-grade ores are diminishing. Therefore there is a need to explore alternative sources of heavy metals. The rapid industrialization generates a variety of industrial wastes. These industrial wastes possess toxic elements such as heavy metals. Improper disposal of these wastes becomes a key factor in metal contamination and thus when leached into atmosphere cause serious environmental problem. These metals exert wide variety of adverse effects on human being. Some of the metals have extremely long biological half-life that essentially makes it a cumulative toxin. Also some metals are carcinogenic in nature. Among the wastes, electronic scraps, medical waste, metal finishing industry waste, spent petroleum catalysts, battery wastes, fly ash etc., are some of the major industrially produced wastes. These solid wastes mostly contain Au, Ag, Ni, Mo, Co, Cu, Zn, and Cr like heavy metals in it. Hence these waste materials which are causing serious environmental problems, can act as potential source for heavy metals. In this sense these industrial wastes can act as artifitial ores. The valuable metals can be recovered from these industrial wastes. There are varieties of methods in use for recovery of heavy metals. These include pyrometallurgical, hydrometallurgical and bio-hydrometallurgical methods. Pyrometallurgical recovery consists of the thermal treatment of ores and metal containing wastes to bring about physical and chemical transformations. This enables recovery of valuable metals. Calcining, roasting, smelting and refining are the pyrometallurgical processes used for metal recovery. The hydrometallurgical recovery uses mainly the leaching process. It involves the use of aqueous solutions containing a lixiviant which is brought into contact with a material containing a valuable metal. Further the metals are concentrated and purified by using precipitation, cementation, solvent extraction and ion exchange. The metals are finally recovered in pure form by using electrolysis and precipitation methods. Biohydrometallurgy is one of the most promising and revolutionary biotechnologies. This technique exploits microbiological processes for recovery of heavy metal ions. In last few decades the concept of microbiological leaching have played a grate role to recover valuable metals from various sulfide minerals or low grade ores. Now the microbiological leaching process has been shifted for its application to recover valuable metals from the different industrial wastes. There are many microrganisms which play important role in recovery of heavy metals from industrial wastes. Among the bacteria Acidithiobacillus ferrooxidans, Acidithiobacillus thiooxidans, Leptospirillum ferrooxidans, and Sulfolobus sp., are well known for the bioleaching activity while Penicillium, and Aspergillus niger are some fungi those help in metal leaching process. The process of recovery makes sense only if the cost of recovery is much less than the value of the precious metal. The restrictions imposed on waste disposal and stringent environmental regulations demand eco-friendly technologies for metal recovery. This paper reports a review of number of industrial processes that generate metal containing waste and the various methods in use for recovery of metals from these wastes. This will help in selection of a proper method for recovery of heavy metals from industrial wastes.

Keywords: Environmental management; Industrial waste; Heavy metals; Pyrometallurgical methods; Hydrometallurgical methods; Bio-hydrometallurgical methods

1. Introduction

Metals play an important part in modern societies and have historically been linked with industrial development and improved living standards [1]. Environmental pollution by heavy metals has accelerated dramatically during the last few decades [2]. These heavy metals are discharged to the environment by several industries, such as mining, metallurgical, electronic, electroplating and metal finishing. Table 1 shows the various types of industrial wastes and the metals present in these wastes.

Table 1.
Various types of hazardous wastes generated by industries and the metals present

Waste type	Metals in waste
Waste batteries	Ni, Cd, Ag
Electronic waste	Cu, Sn, Au, Ag, Ni, Al, Zn
Waste X-ray films	Ag
MSW fly ash	Cu, Zn, Ni, Al, Cr, Pb
Petroleum spent catalyst	Ni, Co, Mo
Metal finishing industrial wastes	Cr, Ni, Cu, Zn, Au, Ag, Cd

Due to their high toxicity and tendency to accumulate in living organisms, the removal of heavy metals from wastewaters is of critical importance [3]. Therefore the recovery of toxic and/or valuable components from industrial wastes becomes an absolute necessity. There are two important aspects of the problem: one is economy, and the second is the protection of the environment from dispersed toxic compounds, especially compounds of heavy metals. Therefore, studies are being carried out aimed at developing new or modified processes for the separation of metals, mainly from industrial waste by-products [4, 5, 6]. Metals can be recycled nearly indefinitely. Unlike polymer plastics, the properties of metals can be restored fully, though not always easily, regardless of their chemical or physical form. Nevertheless, the ability to recover metals economically after use is largely a function of how they are used initially in the economy and their chemical reactivity. The success of secondary metals markets depends on the cost of retrieving and processing metals embedded in abandoned structures, discarded products, and other waste streams and its relation to primary metal prices [1]. There are several technologies which may be used to recover metals from industrial waste; these are pyrometallurgy, hydrometallurgy, and bio-hydrometallurgy [7, 8, 9].

1.1. Pyrometallurgy

Pyrometallurgical process can be a general solution to recover valuable elements from industrial wastes. Pyrometallurgical processes have proved to be more efficient for the extraction of metals, such as Ti, Zr, Nb, Ta, Mo, etc [10]. Pyrometallurgy employs the thermal treatment to bring about physical and chemical transformations in the materials to enable recovery of valuable metals. The smelting, roasting, converting and refining are the various pyrometallurgical methods used for metal recovery. This process is fast because the physical form of the scrap is not as important as that required in chemical treatments. However, most methods involving thermal processing are quite expensive due to high-energy requirement. Furthermore, this thermal process usually produces polluting emissions and causes the loss of metals from the scrap during combustion [8, 11].

1.2. Hydrometallurgy

Hydrometallurgy is a process in which chemical reactions are carried out in aqueous or organic solutions for the recovery of metals [12]. Typically three general steps are carried out during hydrometallurgical recovery of metals, namely, leaching, solution concentration and purification, and metal recovery. Various reagents have been used in chemical leaching. These include nitric acid, mixtures of nitric, hydrochloric and sulphuric acids, sulphuric acid, nitric acid and hydrogen peroxide, aqua-regia, ferric chloride, thiourea, potassium iso-cyanate, potassium iodide and iodine, iodide–nitrite mixture, thiosulphate and cyanides [7, 13, 14, 15]. In the solution concentration and purification step, the solutions are subjected to separation procedures such as solvent extraction, precipitation, cementation, ion exchange, filtration and distillation to isolate and concentrate the metals of interest [16, 17]. Metal recovery is the final step in a hydro-metallurgical process. The electrolysis, gaseous reduction, and precipitation are the metal recovery processes [18].

1.3. Bio-hydrometallurgy

Over the last 40 years many researchers have investigated the application of biotechnology in mining. To date, several bio-technologies have been exploited commercially in well mechanized, engineered systems that can be categorized under the term bio-hydrometallurgy [19]. Bioleaching has been applied successfully and commercially in biohydrometallurgy for extracting copper and precious metals from low-grade ores and tailings for many years [20]. In biotechnological processes, solubilization of metals is based on the interactions between metals and microorganisms. This technique allows metal recycling by processes similar to that in the natural biogeochemical cycles, and is therefore environmentally friendly, with low cost and low energy requirement [21, 22]. Many studies discovered recovery of metals from various sources such as sludge, fly ashes, sediments, soils, batteries, electronic scraps etc [23-30]. The microbial leaching process, using aerobic sulfur- and iron-oxidizing microorganisms, has been shown to be capable of eluting the heavy metals associated with solids. Heterotrophic bacteria and fungi (*Bacillus sp., Aspergillus niger* and *Penicillium simplicissimum, Saccharomyces cerevisiae, Yarrowia lipolytica)* have been used to mobilize metals. A Sulfolobus-like organism was able to leach gallium arsenide from semi-conductors [9, 31].

2. Metal recovery from wastes

2.1. Fly ashes

Fly ashes can be considered as renewable secondary sources for the recovery of heavy metals [9]. These fly ashes are usually

classified as hazardous material due to their high content of toxic metals and soluble components. Fly ash contains a number of toxic trace elements like Si, Al, Fe, Cd, Mn, B, As, Hg [32]. Therefore, fly ashes have to be deposited in specialized landfills [33]. However, groundwater pollution from landfill leachate is of concern, as are gas emissions. Furthermore, any toxic products present in the original waste will remain in unknown, uncontrolled form in the landfill [34]. To avoid this number of methods has been suggested to stabilize fly ash in order to reduce leaching. Also, some of the metal elements (e.g. Al and Zn) are present in concentrations that would allow an economic recovery. From this viewpoint, the fly ash may indeed be considered as an artificial ore [35]. Conventionally, thermal treatment, chloride evaporation [36] and chemical leaching [28] are used in the detoxification or decontamination of incineration fly ash. Iretskaya et al. [34] developed a phosphate chemical treatment followed by a thermal treatment. The phosphate treatment is an aqueous sol-gel process which produces agglomerated fly ash particles and extracted chlorides. The thermal treatment consists, after drying at 60°C, in calcining the fly ash agglomerates in air at 900°C. The most widespread leaching method is acidic leaching using strong mineral acids as many metal compounds have high solubility at low pH. However, due to the alkalinity of the ash large amounts of acid are needed [37, 38]. To overcome this problem Fedje et al. [39] investigated some alternative leaching media (EDTA, ammonium nitrate, ammonium chloride and a number of organic acids). They found that the use of mineral acids and EDTA mobilized many elements, especially Cu, Zn and Pb, whereas the organic acids generally were not very effective as leaching agents for metals. Leaching using NH_4NO_3 was especially effective for the release of Cu. Their results show that washing of MSW filter ash with alternative leaching agents is a possible way to remove hazardous metals from MSW fly ash. Unfortunately, these techniques suffer from the main disadvantage of high-energy requirement, as well as the liability of hazardous chemical usage during the treatment [26].

Bioleaching using a fungal microorganism producing gluconic acid or citric acid, sulfur-oxidizing bacterium (SOB) producing sulfuric acid or iron-oxidizing bacterium (IOB) oxidizing a reduced metal compound, has been reported as a promising technology for recovering valuable metals from fly ash [40]. Brombacher et al. [41] developed a laboratory-scale leaching plant (LSLP) for the processing of fly ash from municipal waste incineration. They used pure cultures of a sulfur-oxidizing bacterium (SOB) and an iron-oxidizing bacterium (IOB) and a mixed culture. The leaching efficiencies obtained for the metal, Zn, were up to 81%, and the leaching efficiencies for Al were up to 52%. Highly toxic Cd was completely solubilized (100%), and the leaching efficiencies for Cu, Ni, and Cr were 89, 64, and 12%, respectively. Ishigaki et al. [40] also used pure cultures of a sulfur-oxidizing bacterium (SOB) and an iron-oxidizing bacterium (IOB) and a mixed culture for bioleaching of fly ash. They found that in the recovery of the valuable metals from fly ash, bioleaching using a mixed culture of SOB and IOB was a promising technology. In another study *Aspergillus niger* was used for recovery of metals from fly ash. Xu and Ting [42] used the modified Gompertz model for the growth of the fungus. Since the metals present in the fly ash are toxic and inhibit microbial growth, an inhibition kinetic model using the generalized Monod growth kinetics was evaluated. They showed that an increase in metal concentration leached with a concomitant increase in the citric acid production at various pulp densities. Several other researchers have showed role of bacteria and fungi in recovery of metals from fly ash [9,24,35,43]. As compared to pyro and hydrometallurgical methods, bioleaching is cleaner and consumes less energy [40].

2.2. Ni-Cd batteries

Usually Ni-Cd batteries are treated separately. There are two important reasons for this, the presence of cadmium that promotes some difficulties in the recovering of mercury and zinc by distillation, and the metallurgical difficulties associated with the separation of nickel and iron [44]. Various pyrometallurgical processes are employed for the recycling of Ni-Cd batteries. In one process cadmium is evaporated in open furnace, and the cadmium is recovered in the form of cadmium oxide powder. In the other process, cadmium is distilled in a closed furnace, in a controlled atmosphere, obtaining metallic cadmium powder and a high-content nickel alloy [45, 46]. Battery chlorination is one more process for the recycling of Ni-Cd batteries. In this process, the battery is put in contact with chlorine or hydrochloric acid and there is the formation of cadmium chloride, but Ni and Co remain stable in the initial process [47]. There are some studies which investigated the fundamentals of spent Ni-Cd batteries recycling through vacuum metallurgy separation (VMS) and magnetic separation (MS). The vacuum metallurgy does not need secondary off-gas or wastewater treatment. Due to this VMS have the advantages of high efficiency and better environmental properties [48, 49, 50]. The acid or base leaching of spent Ni-Cd batteries is carried out during hydrometallurgical recycling [51]. Toegepast-Natuurwetenschappelijk Onderzoek process concentrated Ni and Cd in the fine fraction. The fine fraction is then leached in 6N HCl acid that is also used to wash the coarse fraction. Liquid/solid ratio is 10/1, and the temperature is kept at 90°C [52]. Also the reports are available for solvent extraction of cadmium and nickel [53, 54, 55]. Some studies reported the recovery of Ni and Cd, by electrodeposition technique. Experiments have been carried out to leach out the positive and negative active materials and current collector by the strong acids, followed by Cd metal recovery by a electrodeposition technique [56, 57].

Bioleaching is one of the few techniques applicable for the recovery of the toxic metals from hazardous spent batteries. Its principle is the microbial production of sulphuric acid and simultaneous leaching of metals [58]. Cerruti et al. [23] used this principle for indirect dissolution of spent Ni-Cd batteries. In another study a novel continuous flow two-step leaching system was introduced to dissolve heavy metals in batteries. It consists of an acidifying reactor which was used to culture indigenous thiobacilli and a leaching reactor which was used to leach metals from spent batteries. They used ferrous ions and elemental sulfur as substrate for the growth of indigenous thiobacilli in sewage sludge [59]. The hydraulic retention time (HRT) of the bio-sulphuric acid in the leaching reactor is an important parameter represents the time that the medium being in contact with the battery material. Zhao et al. [60] investigated the leaching efficiency and leaching behavior of the three heavy metals Ni, Cd and Co of battery in different HRT. They found that if the HRT was too short, the electrode materials of batteries cannot be dissolved sufficiently.

While if it was too long, bigger volume of leaching reactor was needed and the pH decreased slowly. Recently in our lab we used ferric sulfate dehydrate for recovery of metals from spent Ni-Cd batteries. The 88 and 84% of nickel and cadmium were recovered respectively under the optimal experimental condition in 4 days (This study is under consideration to another journal). These results indicate that the use of chemical method is advantageous over bioleaching processes. Table 2 shows time required for metal extraction from spent Ni-Cd battery and microorganisms used in various studies.

Table 2.
Time required for metal extraction from spent Ni-Cd battery and microorganisms used in various studies

Reference	Metal content (%)		Microorganism used	Time of extraction (Days)
	Nickel	Cadmium		
Cerruti et al., [23]	96.50	100	*At. ferrooxidans*	93
Zhu et al., [58]	66.10	100	Indigenous acidophilic thiobacilli in sewage sludge	50
Zhao et al., [59]	100	100	Indigenous acidophilic thiobacilli in sewage sludge	16
Zhao et al., [60]	100	100	Indigenous acidophilic thiobacilli in sewage sludge	40
Velgosova et al., [61]	--	84	*At. ferrooxidans*, & *At. thiooxidans*	28

The metal dissolution by using ferric sulfate required considerably less time as compared to bioleaching processes. Hence this could be an economic and effective alternative for recycling spent and discarded batteries.

2.3. Plating and deposition industry

In metal plating process several deposition and finishing operations are carried out in combination. Wastewaters from metal finishing industries contain contaminants such as heavy metals, organic substances, cyanides, and suspended solids. These contaminants are present at levels which are hazardous to environment [62]. Precipitation is the technique of choice for the removal of dissolved heavy metals from wastewaters of metal finishing industries. This might involve several steps: (i) Cr reduction (from the hexavalent to trivalent state) in acidic conditions (ii) pH neutralisation (pH near to 8.5) (iii) coagulation and flocculation [63].

The increasing acceptance of biological processes for the treatment of refractory mining concentrates should be considered as a positive move both in terms of process flow sheet development and its commitment to the environment [64]. Electroplating sludge is poisonous for most bacteria [65], and so biological processes have been actively researched. Wang and Shen [66] studied bacterial reduction of Cr. In another study Suzuki et al. [67] demonstrated that the bacteria effectively eliminated Cu and Cr from electroplating waste. Yan et al. [68] used two bacterial species, *Thiobacillus ferrooxidans* and *Thiobacillus thiooxidans* to investigate the bioleaching characteristics of heavy metals from electroplating sludge.

2.4. Electronic waste

Electronic equipments are being produced in huge amounts nowadays [69]. Studies by Bertram et al. [70] suggest that wastes from electrical and electronic equipment (WEEE) are the fastest growing waste category; this finding emphasizes the need for efficient WEEE recycling strategies. Pyrometallurgical processing, including incineration, smelting in a plasma arc furnace or blast furnace, melting and reactions in a gas phase at high temperatures has become a traditional method to recover non-ferrous metals as well as precious metals from electronic waste [22]. Veldbuizen and Sippel [71] reported the Noranda process. Materials entering the reactor are immersed in a molten metal bath (1250°C), which is churned by a mixture of supercharged air. The resulting of agitated oxidation zone converts impurities including iron, lead and zinc into oxides which become fixed in a silica-based slag. The copper matte containing precious metals is removed and transferred to the converters. The copper is refined in anode furnaces and cast into anodes with purity of 99.1%. The remaining 0.9% contains the precious metals including gold, silver, platinum and palladium, which are recovered by electrorefining. In the past two decades, extensive research has been carried out on recovery of metals from electronic scraps by hydrometallurgical techniques. The main steps in hydrometallurgical processing consist of a series of acid or caustic leaches of solid material [22]. Barakat [72] successfully recovered lead, tin, and indium from alloy wire electronic scrap through acid/alkali leaching. Lee et al. [73] investigated the recovery of valuable metals and the regeneration of the expended PCB nitric acid etching solutions. Nitric acid was selectively extracted from the expended etching solution using tributylphosphate (TBP), whereas a pure nitric acid solution was extracted using distilled water. After nitric acid extraction, pure copper metal was obtained through electrowinning, and tin ions were precipitated by adjusting the pH of the solution with $Pb(OH)_2$. Lead, with a purity of 99%, was obtained by cementation with an iron powder. In another study Veit et al. [74] used printed circuit boards for metal recovery. They used two step processes. In the first stage, mechanical processing was used, followed by size and magnetic and electrostatic separation. A fraction concentrated in metals and another fraction containing polymers and ceramics were obtained. In the second stage, the fraction concentrated in metals was dissolved with aqua-regia or sulfuric acid and treated in an electrochemical process to recover the metals separately, especially copper.

Recently some studies with microorganisms have been conducted to explore biotreatment of electronic waste. These studies were conducted with mesophilic chemolithotrophic (*Acidithiobacillus ferrooxidans* and *Acidithiobacillus thiooxidans*) or cyanogenic bacteria (*Chromobacterium violaceum*) [24, 75]. The rates of bioleaching of metals from ores by moderate thermophiles have been demonstrated to be higher than mesophiles and in another case even higher than extreme thermophiles [76]. Considering this Ilyas et al. [69] used moderately thermophilic

strains of acidophilic chemolithotrophic and acidophilic bacteria for recovery of metals from electronic scrap. In some reports effects of two acidophiles *Acidithiobacillus ferrooxidans* and *Acidithiobacillus thiooxidans* on metal recovery from PCBs was studied. They found that mixed culture of acidophiles showed the highest metals bioleaching capacity [77, 78]. Also heterotrophic bacteria and fungi (*Bacillus* sp., *Saccharomyces cerelisiae*, *Yarrowia lipolytica)* have been used to mobilize Pb, Cu, and Sn from printed circuit boards [79].

2.5. Spent catalyst

Spent hydro-processing catalysts, the major solid wastes of petro-chemical industries, contain various hazardous components, such as Al, V, Mo, Co, Ni and Fe, as well as nonmetallic elements such as elemental sulfur, carbon and oils that are potentially hazardous to the environment [80]. However, such waste materials containing high metal concentrations can serve as secondary raw materials. A variety of processing approaches for recovering metals from the spent catalysts has been proposed [81]. The metal values present in spent catalyst can be recovered through pyrometallurgical or hydrometallurgical routes. Techniques such as direct smelting, calcination and smelting, chlorination and salt roasting are applied for metal recovery from spent hydro-processing catalysts [82, 83]. Also many reagents, such as NaOH, H_2SO_4, NH_3, $(NH_4)_2SO_4$ and oxalic acid with H_2O_2 and $Fe(NO_3)_2$, have been tested [84, 85, 86]. Mulak et al. [87] investigated the leaching efficiency of Mo, Ni, V and Al from the spent catalyst in oxalic acid solution with hydrogen peroxide addition. They also studied the effects of oxalic acid and hydrogen peroxide concentrations and the stirring speed on the rate of metal leaching. They found that addition of hydrogen peroxide to oxalic acid up to 3.0 M concentration enhanced leaching of metals remarkably.

Bio-hydrometallurgical approaches appear to offer good prospects for recovering valuable metals from spent petroleum catalyst [19]. *Acidithiobacillus thiooxidans* was used by Briand et al. [88] to treat a spent vanadium phosphorus catalyst. Bosio et al. [89] also used *Acidithiobacillus thiooxidans* for the treatment of the spent nickel catalyst generated during the hydrogenation of vegetable oil. Zeng and Cheng [90] recently reviewed applications of the bioleaching process to recovering metal values from spent petroleum catalyst. Some reports described bioleaching procedures applied to the recovery of metals from spent refinery catalysts by means of iron/sulfur oxidizing bacteria [19, 80, 91]. Gholami et al. [92] studied the toxicity of heavy metals present in waste catalyst to bacteria. Also they optimized variables, such as pH, temperature, particle size, pulp density, and speed of rotation for metal extraction. The use of *Aspergillus niger* for the bioleaching of spent refinery processing catalysts has also been reported [93, 94]. This fungus produces organic acids such as citric, oxalic, malic and gluconic acids. Acidolysis is the principal mechanism in bioleaching of metals by *Aspergillus niger* [95].

2.6. Button cell batteries

In recent years, recycling of small silver oxide primary cells has attracted much attention. This is important mainly with respect to environmental aspects in addition to the savings [96]. These cells have a high capacity per unit weight, a long operating life and are currently used in hearing aids, digital thermometers, insulin pumps, portable medical monitors, hospital pagers, watches, toys and calculators, among others [97]. These silver oxide cells becomes a waste after their life is over. Recycling procedures are needed to prevent any environmental impact from these wastes and to recover the value inherent in the scrap [96]. There are a few battery recycling plants around the world that apply their own recycling processes to recover valuable components from spent batteries or to facilitate environmentally friendly disposal [98]. The spent silver oxide batteries are processed by smelting in which the impurities are removed as slag to leave a residue for silver recovery [99]. In another method, spent batteries are disassembled into anode and cathode parts, and the valuable materials are recovered [100]. A method based on a cementation technique has been reported [101] where silver is recovered by the addition of copper sulfate solution after nitric acid leaching. Sathaiyan et al. [102] described smelting and electrolytic methods for silver recovery from battery waste. They found that acid leaching of waste batteries and precipitation of silver as silver chloride followed by smelting at 1000°C yields a silver recovery of about 83%. They also applied an electrolytic route as an alternative to the smelting operation. In another study Aktas [96] investigated a hydrometallurgical process for silver recovery from spent silver oxide button cells. They studied the effects of acid concentration, reaction temperature, reaction time and shaking rate on the silver dissolution. They used potassium chloride solution and zinc powder for selective precipitation of silver. In a recent study in our lab we showed the use of *Acidithiobacillus ferrooxidans* culture supernatant for recovery of silver from spent silver oxide button cells (This study is under consideration to another journal).

2.7. Medical waste

Radiographic film is a polyester sheet coated on both sides by radioactive material, which is sensitive to light. It is used for industrial purposes, medical and dental services for some investigations. Approximately 2 billion radiographs are taken around the world each year, including chest X-rays, mammograms, CT scans, etc. Traditionally, 94-98% of X-ray films are used in medical services [103]. In these radiographic films silver salt is used due to its high photosensitivity [104]. The amount of silver varies between 1.5% and 2.0% by weight [105]. During the usage of light sensitive materials, about 80% of the silver enters the fixing bath and the remainder (about 20%) remains in the films [106]. Various studies have been carried out over a long period of time to recover the silver from wastes radiographic film. Two typical ways to recover silver from used radiographic films are combustion technology and the acid leaching process. The used film is incinerated at high temperatures in the combustion process and silver is recovered from ash by smelting and refining processes [107]. In the acid leaching process, used film is submerged into a strong acid solution [108]. Nakiboglu et al. [105] developed a novel, simple, fast, and cheap method for recovering the silver from waste X-ray photographic films with NaOH stripping. Another study presents hydrometallurgical

recovery of silver from exposed X-ray films. In this process hydrometallurgical separation of inorganic component of films from polymer substratum was carried out by leaching with oxalic acid solution. Advantages of this method are production of silver in metallic form directly from leaching process with no side-products and possibility of recycling of leaching agents [109].

Though burning the films directly is a conventional method used at present for the recovery of silver, but it generates undesirable foul smell. The polyester film on which cannot be recovered and this method causes environmental pollution. The use of chemical methods for stripping the gelatin-silver layer cause environmental hazards. Also these methods are either time consuming or very expensive. Therefore there is a need to develop cost effective and environmentally friendly methods to recover silver from X-ray/photographic waste. This can be achieved by applying enzyme based methods [105, 110]. The emulsion layer on X-ray film contains silver and gelatin. Gelatin is a protein which contains a large number of glycine, proline and 4-hydroxyproline residues. It is possible to break down the gelatin layer using proteases and release the silver [105, 111]. Nakiboglu et al. [105] reported use of enzyme extract obtained from *Bacillus subtilis* ATCC 6633 for silver recovery from the waste X-ray films. The enzymatic hydrolysis of the gelatin layers on the X-ray film enables not only the recovery of the silver, but also the polyester base which can be recycled. Hence in recent years, enzymatic methods using microbial proteases are being explored as alternatives to the burning and oxidation methods of silver recovery from photographic/X-ray films [105, 111, 112, 113]. Most of the proteases used so far for silver recovery are of bacterial origin. Shankar et al. [110] used fungal alkaline protease for recovery of silver. They obtained alkaline protease from *Conidiobolus coronatus*.

3. Conclusions

Pyrometallurgy, hydrometallurgy, and bio-hydrometallurgy have their own merits and demerits. There could be various technical, economic and environmental reasons for choosing one process over the other. Developing inexpensive extraction processes to remove heavy metals from industrial waste is the need of the day. Various pyrometallurgical and hydrometallurgical methods are in use for extraction of heavy metals from industrial waste. However, in spite of high extraction efficiencies, the practical application of these processes on a larger scale has its own limitations, as these require huge investments on leaching reagents and operations. Also these processes themselves create secondary pollution. Considering this bio-hydrometallurgical recovery of heavy metals from industrial waste appears to be an attractive treatment technique. Almost without exception, microbial extraction procedures are more environment friendly, while giving high extraction yields in excess of 90%. In future, new strains have to be identified to improve the metal recovery from solid waste. The bio-hydrometallurgical processes are still at the laboratory scale. There is a need to advance commercial application of bio-hydrometallurgical processes.

References

[1] I. Wernick, N.J. Themelis, Recycling Metals for the Environment, Annual Reviews Energy and Environment 23 (1998) 465-497.

[2] S. Naaz, S.N. Pandey, Effects of industrial waste water on heavy metal accumulation, growth and biochemical responses of lettuce (Lactuca sativa L.), Journal of Environmental Biology 31 (2010) 273-276.

[3] M. González-Muñoza, M. Rodrígueza, S. Luquea, J. Álvarez, Recovery of heavy metals from metal industry waste waters by chemical precipitation and nanofiltration, Desalination 200 (2006) 742-744.

[4] A.G. Chmielewski, T.S. Urbtiski, W. Migdal, Separation technologies for metals recovery from industrial wastes, Hydrometallurgy 45 (1997) 333-344.

[5] K. Bosecker, Microbial leaching in environmental cleanup programmes, Hydrometallurgy 59 (2001) 245-248.

[6] W. Verstraete, Environmental Biotechnology for Sustainability, Journal of Biotechnology 94 (2002) 93-100.

[7] S. Syed, A green technology for recovery of gold from non-metallic secondary sources, Hydrometallurgy 82 (2006) 48-53.

[8] T. Havlik, D. Orac, M. Petranikova, A. Miskufova, F. Kukurugya, Z. Takacova, Leaching of copper and tin from used printed circuit boards after thermal treatment, Journal of Hazardous Materials 183 (2010) 866-873.

[9] M. Hoque, O. Philip, Biotechnological recovery of heavy metals from secondary sources - An overview, Materials Science and Engineering C 31 (2011) 57-66.

[10] J. González, J. Rivarola, M. Ruiz, Kinetics of chlorination of tantalum pentoxide in mixture with sucrose carbon by chlorine gas, Metallurgical and Materials Transactions B 35 (2004) 439-448.

[11] M.W. Ojeda, E. Perino, M. Ruiz, Gold extraction by chlorination using a pyrometallurgical process, Minerals Engineering 22 (2009) 409-411.

[12] T. Kinoshita, S. Akita, N. Kobayashi, S. Nii, F. Kawaizumi, K. Takahashi, Metal recovery from non-mounted printed wiring boards via hydrometallurgical processing, Hydrometallurgy 69 (2003) 73-79.

[13] F. Veglio, R. Quaresima, P. Fornari, S. Ubaldini, Recovery of valuable metals from electronic and galvanic industrial wastes by leaching and electrowinning, Waste Management 23 (2003) 245-252.

[14] J.E. Silva, A.P. Paiva, D. Soares, A. Labrincha, F. Castro, Solvent extraction to the recovery of heavy metals from galvanic sludge, Journal of Hazardous Materials 120 (2005) 113-118.

[15] O. Ruiz, C. Clemente, M. Alonso, F. Alguacil, Recycling of an electric arc furnace flue dust to obtain high grade ZnO, Journal of Hazardous Materials, 141 (2007) 33-36.

[16] S.E. Kentish, G.W. Stevens, Innovations in separation technology for the recycling and re-use of liquid waste streams, Chemical Engineering Journal 84 (2001) 149-159.

[17] K. Xu, T. Deng, J. Liu, W. Peng, Study on the recovery of gallium from phosphorus flue dust by leaching with spent sulfuric acid solution and precipitation, Hydrometallurgy 86 (2007) 172-177.

[18] M.K. Jha, V. Kumar, R.J. Singh, Review of hydrometallurgical recovery of zinc from industrial wastes, Resources Conservation and Recycling 33 (2001) 1-22.
[19] D. Mishra, D.J. Kim, D.E. Ralph, J.G. Ahn, Y.H. Rhee, Bioleaching of vanadium rich spent refinery catalysts using sulfur oxidizing lithotrophs, Hydrometallurgy 88 (2007) 202-209.
[20] H.B. Zhou, W.M. Zeng, Z.F. Yang, Y.J. Xie, G.Z. Qiu, Bioleaching of chalcopyrite concentrate by a moderately thermophilic culture in a stirred tank reactor, Bioresource Technology 100 (2009) 515-520.
[21] C.L. Brierley, How will biomining be applied in future, Transactions of Nonferrous Metal Society of China 18 (2008) 1302-1310.
[22] J. Cui, L. Zhang, Metallurgical recovery of metals from electronic waste: A review, Journal of Hazardous Materials 158 (2008) 228-256.
[23] C. Cerruti, G. Curutchet, E. Donati, Bio-dissolution of spent nickel-cadmium batteries using *Thiobacillus ferrooxidans*, Journal of Biotechnology 62 (1998) 209-219.
[24] H. Brandl, R. Bosshard, M. Wegmann, Computer-munching microbes: metal leaching from electronic scrap by bacteria and fungi, Hydrometallurgy 59 (2001) 319-326.
[25] A.T. Lombardi, O. Garcia, Biological leaching of Mn, Al, Zn, Cu and Ti in an anaerobic sewage sludge effectuated by *Thiobacillus ferrooxidans* and its effect on metal partitioning, Water Research 36 (2002) 3193-3202.
[26] H.Y. Wu, Y.P. Ting, Metal extraction from municipal solid waste (MSW) incinerator fly ash-chemical leaching and fungal bioleaching, Enzyme and Microbial Technology 38 (2006) 839-847.
[27] F. Carranza, R. Romero, A. Mazuelos, N. Iglesias, O. Forcat, Biorecovery of copper from converter slags: slags characterization and exploratory ferric leaching tests, Hydrometallurgy 97 (2009) 39-45.
[28] B.P. Xin, D. Zhang, X. Zhang, Y.T. Xia, F. Wu, S. Chen, L. Li, Bioleaching mechanism of Co and Li from spent lithium-ion battery by the mixed culture of acidophilic sulfur-oxidizing and iron-oxidizing bacteria, Bioresource Technology 100 (2009) 6163-6169.
[29] G. Zheng, L. Zhou, S. Wang, An acid-tolerant heterotrophic microorganism role in improving tannery sludge bioleaching conducted in successive multibatch reaction systems, Environmental Science and Technology 43 (2009) 4151-4156.
[30] B. Bayat, B. Sari, Comparative evaluation of microbial and chemical leaching processes for heavy metal removal from dewatered metal plating sludge, Journal of Hazardous Materials 174 (2010) 763-769.
[31] S.D. Kim, J.E. Bae, H.S. Park, D.K. Cha, Bioleaching of cadmium and nickel from synthetic sediments by *Acidithiobacillus ferrooxidans*, Environmental Geochemistry and Health 27 (2005) 229-235.
[32] S. Tiwari, B. Kumari, S.N. Singh, Evaluation of metal mobility/immobility in fly ash induced by bacterial strains isolated from the rhizospheric zone of Typha latifolia growing on fly ash dumps, Bioresource Technology 99 (2008) 1305-1310.
[33] C. Wiles, Municipal solid waste combustion ash: state-of-the-knowledge, Journal of Hazardous Materials 47 (1996) 325-344.
[34] S. Iretskaya, A. Nzihou, C. Zahraoui, P. Sharro, Metal leaching from MSW fly ash before and after chemical and thermal treatments, Environmental Progress 18 (2004) 144-148.
[35] P. Bosshard, R. Bachofen, H. Brandl, Metal leaching of fly ash from municipal waste incineration by *Aspergillus niger*, Environmetal Science and Technology 30 (1996) 3066-3070.
[36] M. Tateda, M. Ike, M. Fujita, Comparative evaluation of processes for heavy metal removal from municipal solid waste incineration fly ash, Journal of Environmental Science 10 (1998) 458-465.
[37] H.A. Sloot, D.S. Kosson, O. Hjelmas, Characteristics treatment and utilization of residues from municipal solid waste incineration, Waste Management 21 (2001) 753-765.
[38] F. Ariese, K. Swart, R. Morabito, C. Brunori, S. Balzamo, J. Slobodnik, E. Korenková, P. Janoš, M. Wildnerova, J. Hlavay, K. Polyák, P. Fodor, H. Muntau, Leaching studies of inorganic and organic compounds from fly ash, International Journal of Environmental Analytical Chemistry 82 (2001) 751-770.
[39] K. Fedje, C. Ekbergb, G. Skarnemarkc, B. Steenari, Removal of hazardous metals from MSW fly ash-An evaluation of ash leaching methods, Journal of Hazardous Materials 173 (2010) 310-317.
[40] T. Ishigaki, A. Nakanishi, M. Tateda, M. Ike, M. Fujita, Bioleaching of metal from municipal waste incineration fly ash using a mixed culture of sulfur-oxidizing and iron-oxidizing bacteria, Chemosphere 60 (2005) 1087-1094.
[41] C. Brombacher, R. Bachofen, H. Brandl, Development of a laboratory-scale leaching plant for metal extraction from fly ash by *Thiobacillus* strains, Applied and Environmental Microbiology 64 (1998) 1237-1241.
[42] T. Xu, Y. Ting, Fungal bioleaching of incineration fly ash: Metal extraction and modeling growth kinetics, Enzyme and Microbial Technology 44 (2009) 323-328.
[43] W. Krebs, R. Bachofen, H. Brandl, Growth stimulation of sulfur oxidizing bacteria for optimization of metal leaching efficiency of fly ash from municipal solid waste incineration, Hydrometallurgy 59 (2001) 283-290.
[44] A.M. Bernardes, D.C.R. Espinosa, J.A.S. Tenório, Recycling of batteries: a review of current processes and technologies, Journal of Power Sources 130 (2004) 291-298.
[45] T. Anulf, SAB-NIFE recycling concept for nickel-cadmium batteries-an industrialized and environmentally safe process, Proceedings of the 6th International Cadmium Conference, Cadmium Association, 1990, 161-163.
[46] M.E. Schweers, J.C. Onuska, R.K. Hanewald, A pyrometallurgical process for recycling cadmium containing batteries, Proceedings of the HMC-South'92, New Orleans, 1992, 333-335.
[47] A. Cox, D.J. Fray, Recycling of cadmium from domestic sealed Ni-Cd battery waste by use of chlorination, Mineral Processing Extraction Metallurgy 108 (1999) 153-158.
[48] D. Espinosa, J. Tenorio, Fundamental aspects of recycling of nickel-cadmium batteries through vacuum distillation, Journal of Power Sources 135 (2004) 320-326.
[49] L. Zhan, Z. Xu, Application of vacuum metallurgy to separate pure metal from mixed metallic particles of crushed waste printed circuit board scraps, Environmental Science and Technology 42 (2008) 7676-7681.

[50] K. Huang, J. Li, Z. Xu, A novel process for recovering valuable metals from waste nickel-cadmium batteries, Environmental Science and Technology 43 (2009) 8974-8978.
[51] D. Espinosa, A. Bernardes, J. Tenório, An overview on the current processes for the recycling of batteries, Journal of Power Sources 135 (2004) 311-319.
[52] N. Onderzoek-TNO, D. Holland, J. Erkel, Recovery of Cd and Ni from batteries, US Patent 5407463, April 18, 1992.
[53] B. Galán, F. San, A. Irabien, I. Ortiz, Viability of the separation of Cd from highly concentrated Ni-Cd mixtures by non-dispersive solvent extraction, Chemical Engineering Journal 70 (1998) 237-243.
[54] C.A. Nogueira, F. Delmas, Leaching behaviour of electrode materials of spent nickel–cadmium batteries in sulphuric acid media, Hydrometallurgy 52 (1999) 267-287.
[55] B.R. Reddy, D.N. Priya, K.H. Park, Separation and recovery of cadmium(II), cobalt(II) and nickel(II) from sulphate leach liquors of spent Ni-Cd batteries using phosphorus based extractants, Separation and Purification Technology 50 (2006) 161-166.
[56] C. Yang, Recovery of heavy metals from spent Ni-Cd batteries by a potentiostatic electrodeposition technique, Journal of Power Sources 115 (2003) 352-359.
[57] M.N. Stefanuț, A. Cata, P. Sfîrloaga, Electrochemical recovery of nickel and cadmium from spent Ni-Cd batteries, Chemical Bulletin of Politehnica University 53 (2008) 1-2.
[58] N. Zhu, L. Zhang, C. Li, C. Cai, Recycling of spent nickel-cadmium batteries based on bioleaching process, Waste Management 23 (2003) 703-708.
[59] L. Zhao, N. Zhu, X. Wang, Comparison of bio-dissolution of spent Ni-Cd batteries by sewage sludge using ferrous ions and elemental sulfur as substrate, Chemosphere 70 (2008a) 974-981.
[60] L. Zhao, D. Yang, N. Zhu, Bioleaching of spent Ni-Cd batteries by continuous flow system: Effect of hydraulic retention time and process load, Journal of Hazardous Materials 160 (2008b) 648-654.
[61] O. Velgosova, J. Kadukova, A. Mrazikova, A. Blaskova, M. Petoczova, H. Harvathova, M. Stofko, Influence of selected parameters on nickel bioleaching from spent nickel-cadmium batteries, Mineralia Slovaca 42 (2010) 365-368.
[62] J.D. Lawrence, Graham's electroplating engineering handbook, fourth ed. Chapman & Hall, New York, 1996.
[63] J. Magalhaesa, J. Silva, F. Castro, J. Labrincha, Physical and chemical characterisation of metal finishing industrial wastes, Journal of Environmental Management 75 (2005) 157-166.
[64] M.A. Jordan, S. Mcginness, C.V. Phillips, Acidophilic bacteria-their potential mining environmental applications, Minerals Engineering 9 (1996) 169-181.
[65] A. Boularbah, J.L. Morel, G. Bitton, M. Mench, A Direct solid phase assay for heavy metal toxicity. II. Assessment of heavy metal Immobilization in soils and bioavailability to plants, Journal of Soil Contamination 5 (1996) 395-404.
[66] Y.T. Wang, H. Shen, Bacterial reduction of hexavalent chromium, Journal of Industrial Microbiology 14 (1995) 159-163.
[67] Y. Suzuki, Biological activated carbon treatment of effluent water from wastewater treatment process of plating industries, Separation Technology 2 (1996) 147-153.
[68] S. Yan, T. Zhang, M. Li, Y. Nan, L. Cao, Bio-leaching of heavy metals from electroplating sludge by *Thiobacillus*, Ecology and Environment 17 (2008) 1787-1791.
[69] S. Ilyas, M. Anwar, S. Niazi, M. Ghauri, Bioleaching of metals from electronic scrap by moderately thermophilic acidophilic bacteria, Hydrometallurgy 88 (2007) 180-188.
[70] M. Bertram, T.E. Graedel, H. Rechberger, S. Spatari, The contemporary European copper cycle: waste management subsystem, Ecology and Economics 42 (2002) 43-57.
[71] H. Veldbuizen, B. Sippel, Mining discarded electronics, Industry and Environment 17 (1994) 7-14.
[72] M.A. Barakat, Recovery of lead, tin and indium from alloy wire scrap, Hydrometallurgy 49 (1998) 63-73.
[73] M.S. Lee, J.G. Ahn, J.W. Ahn, Recovery of copper, tin and lead from the spent nitric etching solutions of printed circuit board and regeneration of the etching solution, Hydrometallurgy 70 (2003) 23-29.
[74] H.M. Veit, T.R. Diehl, A.P. Salami, J.S. Rodrigues, A.M. Bernardes, J.A.S. Tenório, Utilization of magnetic and electrostatic separation in the recycling of printed circuit boards scrap, Waste Management 25 (2005) 67-74.
[75] M. Choi, K. Cho, D.S. Kim, D.J. Kim, Microbial recovery of copper from printed circuit boards of waste computer by *Acidithiobacillus ferrooxidans*, Journal of Environmental Science and Health Part A -Toxic/Hazardous Substances and Environmental Engineering 39 (2004) 2973-2982.
[76] H. Deveci, A. Akcil, I. Alp, Bioleaching of complex zinc sulphides using mesophilic and thermophilic bacteria: comparative importance of pH and iron, Hydrometallurgy 73 (2004) 293-303.
[77] J. Wang, J. Bai, J. Xu, B. Liang, Bioleaching of metals from printed wire boards by *Acidithiobacillus ferrooxidans* and *Acidithiobacillus thiooxidans* and their mixture, Journal of Hazardous Materials 172 (2009) 1100-1105.
[78] G. Liang, Y. Mo, Q. Zhou, Novel strategies of bioleaching metals from printed circuit boards (PCBs) in mixed cultivation of two acidophiles, Enzyme and Microbial Technology 47 (2010) 322-326.
[79] M.S. Hahn, S. Willscher, G. Straube, Copper leaching from industrial wastes by heterotrophic microorganisms, in: A.E. Torma, J.E. Wey, V.L. Lakshamanan, Eds.., Biohydrometallurgical Technologies, The Minerals, Metals & Material Society, Warrendale, 1993, 99-108.
[80] D. Mishra, D. Kim, D. Ralph, J. Ahn, Y. Rhee, Bioleaching of spent hydro-processing catalyst using acidophilic bacteria and its kinetics aspect, Journal of Hazardous Materials 152 (2008) 1082-1091.
[81] J.S. Yoo, Metal recovery and rejuvenation of metal–loaded spent catalysts, Catalysis Today 44 (1998) 27-46.
[82] R.G. Busnardo, N.G. Busnardo, G.N. Salvato, J.C. Afonso, Processing of spent NiMo and $CoMo/Al_2O_3$ catalysts via fusion with $KHSO_4$, Journal of Hazardous Materials 139 (2007) 391-398.
[83] I. Gaballah, M. Diona, Valuable metals recovery from spent catalyst by selective chlorination, Resources Conservation and Recycling 10 (1994) 87-96.

[84] M.A. Rabah, I.F. Hewaidy, F.E. Farghaly, Recovery of molybdenum and cobalt powders from spent hydrogenation catalyst, Powder Metallurgy 40 (1997) 283-288.
[85] M. Marafi, A. Stansilaus, Options and processes for spent catalyst handling and utilization, Journal of Hazardous Materials 101 (2003) 123-132.
[86] M. Marafi, A. Stansilaus, M. Absi-Halabi, Heavy oil hydrotreating catalyst rejuvenation by leaching of foulant metals with ferric nitrate-organic acid mixed reagents, Applied Catalysis B: Environmental 4 (1994) 19-27.
[87] W. Mulak, A. Szymczycha, A. Leśniewicz, W. Żyrnicki, preliminary results of metals leaching from a spent hydro-desulphurization (hds) catalyst, Physicochemical Problems of Mineral Processing 40 (2006) 69-76.
[88] L. Briand, H. Thomas, E. Donati, Vanadium(V) reduction in *Thiobacillus thiooxidans* cultures on elemental sulfur, Biotechnology Letters 18 (1996) 505-508.
[89] V. Bosio, M. Viera, E. Donati, Integrated bacterial process for the treatment of a spent catalyst, Journal of Hazardous Materials 154 (2008) 804-810.
[90] L. Zeng, C.Y. Cheng, A literature review of the recovery of molybdenum and vanadium from spent hydro-desulphurization catalysts. Part: I. Metallurgical Processes, Hydrometallurgy 98 (2009) 1-9.
[91] F. Beolchini, V. Fonti, F. Ferella, F. Vegliò, Metal recovery from spent refinery catalysts by means of biotechnological strategies, Journal of Hazardous Materials 178 (2010) 529-534.
[92] R. Gholami, S. Borghei, S. Mousavi, Bacterial leaching of a spent Mo-Co-Ni refinery catalyst using *Acidithiobacillus ferrooxidans* and *Acidithiobacillus thiooxidans*, Hydro-metallurgy 106 (2011) 26-31.
[93] K.M.M. Aung, Y.P. Ting, Bioleaching of spent fluid catalytic cracking catalysts using *Aspergillus niger*, Bio-technology 116 (2005) 159-170.
[94] F. Anjum, H. Bhatti, M. Asgher, M. Shahid, Leaching of metal ions from black shale by organic acids produced by *Aspergillus niger*, Applied Clay Science 47 (2010) 356-361.
[95] D.B. Johnson, Biohydrometallurgy and the environment: intimate and important interplay, Hydrometallurgy 83 (2006) 153-166.
[96] S. Aktas, Silver recovery from spent silver oxide button cells, Hydrometallurgy 104 (2010) 106-111.
[97] I. Buchmann, Batteries in a portable world, Second Edition, Cadex Electronics Inc., 2001, 29.
[98] A. Krebs, Recycling of household batteries and heavy metal containing wastes. Proceedings of the Global Symposium "Recycling, Waste Treatment and Clean Technology" Rewas '99, San Sebastian, Spain, vol. II, 1999, 1109-1116.
[99] E. Efimov, Izv vyssh uchebn zaved, Tsvetn Metall. 4 (1979) 47-50 (in Russian).
[100] T. Ueneish, Jpn. Patent 6036827, 1985 [CA: 104 (1986) 37514].
[101] P.R. Prax, Nat. Wiss. Chem. 34 (1985) 19–21 (Ger), [CA: 104 (1986) 147819].
[102] N. Sathaiyan, V. Nandakumar, P. Ramachandran, Hydro-metallurgical recovery of silver from waste silver oxide button cells, Journal of Power Sources 161 (2006) 1463-1468.
[103] P. Khunprasert, N. Grisdanurak, J. Thaveesri, V. Danutra, W. Puttitavorn, Radiographic film waste management in Thailand and cleaner technology for silver leaching, Journal of Cleaner Production 16 (2008) 28-36.
[104] S. Heqing, T. Wujun, A review about 2004 and Expectation for 2005 in chinese silver market, Rare Metals Letters 24 (2005) 18-23.
[105] N. Nakiboglu, D. Toscali, I. Yasa, Silver recovery from waste photographic films by an enzymatic method, Turkish Journal of Chemistry 25 (2001) 349-353.
[106] H. Zhouxiang, J. Wei, M. Zhao, J. Hu, A method to recover silver from waste X-ray films with spent fixing bath, Hydrometallurgy 92 (2008) 148-151.
[107] H. Ishikawa, K. Ishimi, M. Sugiura, A. Sowa, N. Fujiwara, Kinetics and mechanism of enzymatic hydrolysis of gelatin layers of X-ray film and release of silver particles, Journal of Fermentation Bioengineering 76 (1993) 300-305.
[108] V.I.E. Ajiwe, I.E. Anyadiegwu, Recovery of silver from industrial wastes, cassava solution effects, Separation and Purification Technology 18 (2000) 89-92.
[109] J. Marinković, M. Korać, Ž. Kamberović, I. Matić, Recycling of silver from exposed x-ray films, Acta Metallurgica Slovaca 12 (2006) 262-268.
[110] S. Shankar, S.V. More, R. Laxman, Recovery of silver from waste x-ray film by alkaline protease from *conidiobolus coronatus*, Kathmandu University Journal of Science, Engineering and Technology 6 (2010) 60-69.
[111] J. Singh, R.M. Vohra, D.K. Sahoo, Alkaline protease from a new obligate alkalophilic isolate of *Bacillus sphaericus*, Biotechnology Letter 21 (1999) 921-924.
[112] S.S. Ingale, M.V. Rele, M.C. Srinivasan, Alkaline protease production by *Basidiobolus* (N.C.L. 97.1.1): effect of 'darmform' morphogenesis and cultural conditions on enzyme production and preliminary enzyme characterization, World Journal of Microbiology and Biotechnology 18 (2002) 403-408.
[113] A. Masui, M. Yasuda, N. Fujiwara, H. Ishikawa, Enzymatic hydrolysis of gelatin layer on used lith film using thermo-stable alkaline protease for the recovery of silver and PET film, Biotechnology Progress 20 (2004) 1267-1269.