An Overview of Physibillity of Silver Particle in Photographic Waste

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Abstract— A novel, simple, fast, cheap and pollution-free method was developed for recovering the silver from waste X-ray photographic films. The waste X-ray/ photographic films contain 1.5 - 2 % (w/w) black metallic silver which is recovered and reused. Around 18-20% of the world's silver needs are supplied by recycling photographic waste. The method has a number of advantages because it obviates the need for heating, sedimentation, filtration and melting steps. Moreover, all experiments were carried out in the same flask, unlike other techniques. At the end of the treatment, gelatine layer was completely removed leaving the polyester film clean and silver was recovered in the hydolysate, both of which can be reused. Various parameters such as pH, temperature, time, efficiency etc on silver removal from the film were studied. In photographic industry, silver is recovered from development and fixing solution, spent rinse water and scrap film. To overcome the problem our method has a great potential and has been reported as an advanced technique for recovery of silver.

Key words: Silver recovery, waste photographic film, fixer solution, sodium hydroxide (NaOH)

I. INTRODUCTION

Solid waste (SW), commonly known as trash or garbage in the U.S. and as refuse or rubbish in the UK, is a waste type consisting of everyday items that are discarded by the public. "Garbage" can also refer specifically to food waste, as in a garbage; the two are sometimes collected separately. In 1947 cities and towns in India generated an estimated 6 million tonnes of solid waste; in 1997 it was about 48 million tonnes. More than 25% of the municipal solid waste is not collected at all; 70% of the Indian cities lack adequate capacity to transport it and there are no sanitary landfills to dispose of the waste. Over the last few years, the consumer market has grown rapidly leading to products being packed in cans, Aluminium foils, plastics, and other such non-biodegradable items that cause incalculable harm to the environment.

Increasing industrialization and urbanization worldwide had caused serious pollution all around the world, especially in the aquatic environment. Wastewaters produced by humans are frequently laden with toxic heavy metals such as copper, silver, mercury, etc. The soluble form of these heavy metals is very dangerous because it is easily transported and more readily available to plants and animals. For humans, poisoning by these metals can result in severe dysfunction of kidney, reproduction system, liver, brain and central nervous systems Hence, to remove the toxic heavy metals from wastewaters has become increasingly focused. Furthermore, recovery of the precious metals like silver, gold and platinum will not only solve the environmental problems but also have profitable potential.

A. Photographic Waste:

Although reductions in volumes of printing waste have forced most of our competitors to increase their charges for collection and recycling of Digital Printing Waste, our rates have been largely unaffected. Due to the variety of collection vehicles at our disposal, meaning we can send smaller vehicles for collections, saving fuel and minimizing our carbon footprint.

Fig. 1: Photographic waste generated from printing press

Photographic waste is the waste generated by the photographic processing machine in paper and printing industries. X-ray film also is one of the photographic wastes generated by hospital and biochemical lab. Photographic waste contains silver that is the main material use to transfer image. It contains soluble silver thiosulphate complex and smaller amount of silver sulphite. The light-sensitive properties of silver compounds are the key to most photographic processes, and the basis of most of the waste produced. Like the compounds of many other heavy metals, they are highly toxic, and classified as special wastes.

Photographic fixer is a mix of chemicals used in the final step in the photographic processing of film or paper. The fixer stabilizes the image, removing the unexposed halide remaining on the photographic film or photographic paper, leaving behind the reduced metallic silver that forms the image. By fixation, the film or paper is insensitive to further action by light. Without fixing, the remaining silver halide would darken and cause fogging of the image. Fixation is commonly achieved by treating the film or paper with a solution of thiosulphate salt. Popular salts are sodium thiosulphate commonly called hypo and ammonium thiosulphate commonly used in modern rapid fixer formulae.[17]

B. Composition of Photographic Film:

The major recording medium used in radiology is X-ray film - although the situation is changing with the introduction of new technologies in recent years. The film can be exposed by the direct action of X-rays, but more commonly the X-ray energy is converted into light by intensifying screens and this light is used to expose the film, as described above. The basic structure of the film is outlined in Figure below[2]

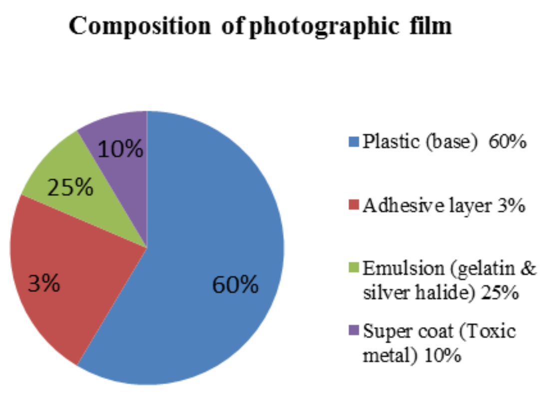

Fig. 2: Composition of Photographic Film

Various Treatments methods to recover silver from photographic film and fixer solution

The silver to be recovered may be present in different forms as insoluble silver halide, a soluble silver thiosulphate complex, a silver ion, or elemental silver, depending upon the type of process and the stage at which it is recovered (Messerschmidt, 1988). A number of techniques are available to remove silver from silver rich photographic processing solution. Of these, three are used in virtually all practical methods of silver recovery. (KODAK, 1999)

The methods are

- Electrolysis
- Metallic replacement
- Chemical precipitation
- Adsorption

II. LITERATURE REVIEW

A.D. Bas, E.Y. Yazici et al (2012), examined that recovery of silver from X-ray film processing effluents by precipitation was studied. Hydrogen peroxide was used as the precipitating agent. The results have shown that precipitation process is highly exothermic in nature with the evolution of copious amount of heat apparently owing to the concomitant oxidation of thiosulphate. The precipitation of silver by hydrogen peroxide is a fast reaction, which is almost complete within minutes.[1]

Ashish Modi, Kishan Shukla, et al (2012), suggested that the waste photographic films/X-ray contains 1.5 - 2 % (w/w) black metallic silver which is recovered and reused. Around 18-20% of the world's silver needs are supplied by recycling photographic waste. It is the better method then other method technically, chemically, & economically. The recovery of silver (I) from aqueous medium was studied using a thiourea-modified chitosan resin. The results suggested that the adsorption process was dependent on contact time, initial metal ion concentration, solution pH and temperature.[2]

Orubite – Okorosaye, K and Jack et al (2012), examined the concentration of silver in some photographic wastes (photographic solution, stabilizer solution and photographic films) in this study. Plantain ash solution (PAS) of different concentrations was used as solution for stripping the films and as extracting for the photographic solutions. Products obtained were analyzed for silver content. The concentration of silver was measured using UV-visible spectrophotometer at a wavelength of 380nm, path length 1cm using silver nitrate for calibration. Results obtained revealed that plantain ash solution extracted silver from the various wastes in all the concentrations of PAS used. However the silver content was observed to be highest in the photographic film and fixer solution and lowest for stabilizer solution in the particular instance.[12]

Rivera, F. Patino, M. Cruells et al (2004), suggested that the recovery of silver contain electrolytic effluent is attractive due its high economic value. These effluents consider toxic waste and it is not possible to dump them directly without detoxication process. One of the most possible way is precipitation with sodium ditonite, sodium borohidried or hydrazine monohydrate. In this work, the most significant aspect related to use of these reagent is presented. Results of silver precipitation with sodium ditonite from effluent containing thiosulfate without previous elimination of other species are also presented. Silver concentration in final effluent is <1 ppm.[5]

Nuri NAKIBOGLU, Duygu TOSCALI et al (2003), suggested a novel, simple, fast, cheap and pollution-free method was developed for recovering the silver from waste X-ray photographic films with NaOH stripping. The method has a number of advantages because it obviates the need for burning, oxidizing, electrolysis or purifying steps. Silver recovery conditions were optimized and silver a purity level of 99% was recovered.[10]

S. Shankar, S. V. More et al (2010), examined that the waste X-ray/ photographic films contain 1.5 - 2 % (w/w) black metallic silver which is recovered and reused. Around 18-20% of the world's silver needs are supplied by recycling photographic waste. Since silver is linked to gelatin in the emulsion layer, it is possible to break the same and release the silver using photolytic enzymes. Alkaline protease from Conidiobolus coronatus was investigated for enzymatic hydrolysis of gelatin from waste X-ray films. At the end of the treatment, gelatin layer was completely removed leaving the polyester film clean and silver was recovered in the hydrolysis, both of which can be reused.[14]

Han Zhouxiang, Wei Jianying et al (2008), discusses a method to recover silver from waste X-ray films with the spent fixing bath. At first, the silver in the waste fixing bath was reduced by KBH_4 at pH 8 ~ 9. Then the silver-free fixing bath was oxidized by air and some main components were replenished. As a leaching solution, the silver-free spent fixing bath was used to recover silver on the waste X-ray films. The total silver recovery from the spent fixing bath and waste X-ray films was 98.0% and 95.8%, respectively.[17]

Junhua Li , Daizhi Kuang et al (2012), determine a new kind of nanocomposite based on silver nanoparticle (AgNPs)/graphene oxide (GO) was conveniently achieved through a green and low-cost synthesis approach using glucose as a reducing and stabilizing agent, and the synthetic procedure can be easily used for the construction of a disposable electrochemical sensor on glassy carbon electrode (GCE). The nanocomposite was detailed characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM), energy dispersive X-ray spectroscopy (EDX), Fourier transform infrared spectroscopy (FTIR) and electrochemical impedance spectroscopy (EIS). The experimental results demonstrated that the nanocomposite possessed the specific features of both silver nanoparticle and graphene, and the intrinsic high specific area and the fast electron transfer rate ascribed to the nano hybrid structure could improve its electro catalytic performance greatly. The resulting sensor displays excellent repeatability and long-term stability; finally it was successfully applied to detect tryptophan in real samples with good recoveries, ranging from 99.0% to 103.0%.[18]

S. Anju, Srinivasa Rao Kondari et al (2009), examined the consumption of X-ray, MRI and CT scan films are increasing rapidly. Silver is the major cast component which is present as thin coating on these films. Waste prints, negatives and used films are disposed often in municipal waste streams, ending up in landfills or incinerators. By employing microbial enzyme like protease, silver is efficiently extracted from films into solution from where it can be recovered by chemical precipitation or by electrolysis.[14]

E.Y. Yazici, A.D. Bas, and H. Deveci (2008), examined the recovery of silver from waste X-ray films (0.7% Ag) by ammoniacal copper thiosulphate leaching was studied. The experiments were designed using Taguchi L_9 (3^3) experimental design. The effects of concentration of thiosulphate, (0.005-0.5 M $S_2O_3^{2-}$), copper (0.005-0.5 M Cu^{2+}), and ammonia (0.005-1 M NH_3) on the extent of silver recovery from X-ray films were investigated at three levels. The experimental data were analyzed using statistical software.[4]

Marinkovic, Korac, Kamberovic et al (2006), suggested a hydrometallurgical method of recycling of silver from exposed X-ray films. Base outline of this process is hydrometallurgical separation of inorganic component of films from polymer substratum by leaching with oxalic acid solution. Experiments included investigations concerning optimal parameters of leaching process for treatment of exposed X-ray films, such as temperature, time, acid concentration and solid/liquid ratio. An advantage of this method is production of silver in metallic form directly from leaching process with no side-products and possibility of recycling of leaching agents. Presented results of silver leaching from exposed X-ray films show technological justification of oxalic acid usage as leaching agents.[8]

Ulisses Condomitti, Alceu T. Silveira et al (2013), explained the electrochemical recovery of silver by employing recyclable super paramagnetic carbon materials (CM_{ag}) is reported. The proposed strategy explores the adsorption properties and the large surface area of carbon, in conjunction with the super paramagnetic properties of magnetite nanoparticle, in order to collect Ag^+ ions from the solution and to promote their rapid confinement at the working electrode surface, using an external magnet.The recovery process was successfully demonstrated in this work, by processing discarded X-ray photographic films.[19]

III. METHODOLOGY

There are a few ways of recovering the silver from x-rays, back in the days 30 years ago when we started, we used to burn the x-ray films to ash and then melt that ash in order to get the silver, of course we had to treat the gases and the pollution that this process creates, we had to actually run the smoke trough a few sets of water bins until we neutralize the smoke completely. We than had to re-melt the silver bars we got over and over until we clean the silver and bring it to 99.9% purity, this process was very expensive and almost not cost effective especially with the low value of silver. This kind of x-ray silver recovery process was good for the old days and it is now considered an obsolete method, now days as the awareness of global warming is higher; the method is replaced by an earth friendly type of silver recuperation process.[23]

Scrap X-ray film contains silver, a hazardous waste, and must be collected from Government Hospital. Spent film must be either collected in the “Scrap Film Collection Containers” located near the film developing units or to sale silver recovery units. Do not place any other items except for film into the containers. Please remove the film from any protective covers prior to putting it in the film collection containers. Scrap X-ray film may not be thrown into the regular trash or regulated medical waste.

Fig. 3: Scrap film collection (As per CDM waste management 2007)

Commodity Resource & Environmental (CRE) supplies “Silver Recovery Equipment” to satisfy the on-site “Silver Recovery” needs of every photographic imaging facility (Medical X-Ray, Graphic Arts, or Photo Lab) large or small.

In India various model of AERO product are available to recovery from photographic waste. It is too expensive because the machine rate is very high.


Fig. 4: “AERO” Silver Recovery Unit(Model:-RU8)(India)

However, many municipalities have severe limits for the allowable discharge of silver effluents even in minute amounts. In California and the Western United States, CRE offers hauling of photo chemicals. Some of our customers recover the silver on-site and then have us haul the low value effluents. Others simply have us haul their photo effluents with no pre-treatment.[24]

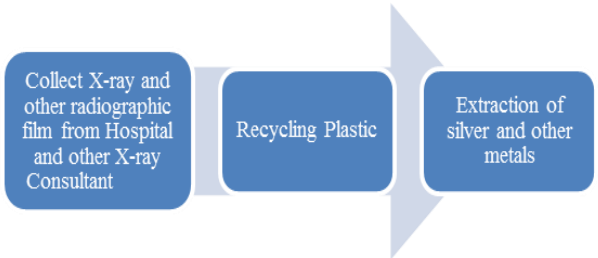

Fig. 5: Methedology for Recycle Photographic film

A. *Stage 1:*

Increase in advanced treatment facilities and rapid industrialization there are increase in amount of photo graphic facilities. Now a day every large hospital contains X-ray facilities which produce scrap film in city. In large city, there are also contain X-ray consultants to use X-ray machine to produces scrap film. So in first step to collect all these type of scarp film from Hospitals, Consultants and other customer who contain X-ray film free of cost. These institutes can sale their scrap film to other recovery unit.

B. *Stage 2:*

In this stage the process is the recycling of photographic waste material. This broadly involves segregation photographic waste and the dismantling of equipments in order to obtain recyclable material. Photographic waste is subjected to processes such as crushing, shredding, and grinding in order to segregate recyclable material from the photographic waste.

C. *Stage 3:*

The final step in the process is extraction of precious materials and safe disposal of hazardous waste. After subjecting the photographic waste to crushing, shredding, etc. material that contain precious metals is usually sent to refineries such as Umicore in Belgium, Boliden in Sweden, etc. where it is subjected to refinement and precious materials(Silver) are extracted. In India mostly incineration method is use to extract metal from scarp film

IV. CONCLUSION

From the study of literature, 80-90% silver particle in black powder foam are remove from waste X-ray photographic film.

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