Treatment of industrial wastewater from paint industry by electron beam irradiation

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ABSTRACT

" The goal of this study is to use the ionizing radiation to destroy the pollutants in effluent from the segment of polymeric coatings for automotive and repainting, allowing the use of part of effluent as reuse water. Samples were irradiated at Electron Beam Accelerator applying absorbed doses of 10, 30, 50, 80 and 100 kGy. The results, in this preliminary stage, showed a reduction of organic compounds and suspended solids. "

Keywords: industrial effluent, Ionizing radiation, automotive paint

1.INTRODUCTION

Every day the world is more colorful and charming, due to the colors conferred to objects like cars, appliances, transportation equipment collective (bus, plane, ships and trains), equipment maintenance, graphic arts, among other residences, for systems coatings. In most cases this effect is achieved through the use of organic coatings (paint, adhesive polymer layer, and booting) or inorganic (electrodeposited metals and inorganic enameling).

Generally more than 80% of the forms coatings are used in the form of paint, this fact can be observed by the use of paints (solvent-based, solvent-free, and water-based powder). The choice to paint coating is due to practicality, the wide range of available colors and easy application.

The paint industry, only in the western world, represent around 22 billion dollars and according to ABRAFATI (2011) the industry's growth in 2011 will be around 6.7%, which is lower than 2010 that was 10.3%. [1]

Paint can be conceptualized as a film or a layer of polymer, to protect, to signal and to illuminate or even to embellish the substrate on which it is applied. Basically, this polymeric compound is formed by elements such as: resin, pigments, fillers, solvents and additives [1,11,16,19].

The main component of paint is resin (binder), which is responsible for the formation of the film, beauty and the protection of the substrate.

The pigments are usually formed by inorganic and organic substances which function is to provide color, opacity, and protection. The pigments of organic origin present more vivid colors, than that of inorganic origin. Solvents are substances used for applying and spreading the paint, for dissolving the resin and for controlling the drying paint among other functions. [11,19]

Finally, agents are additives used in small quantities, to correct a problem or even to give some property. Examples of additives are the antioxidant agents, antibubbles, spreading, thickeners, thyrotrophic, among others [11,16,19].

The main kind of paint are: curable paint by oxidation (synthetic enamels and alkyd), air drying (acrylic, vinyl and nitrocellulose), healing of two components (epoxy and polyurethane) heat curing (stove enamel and polyester, silicone) and uv curing (acrylates, polyester and epoxy)

Despite its advantages the paint manufacturing process promotes the generation of wastes and effluents those are pollutants due materials used in its production process.

The waste and wastewater generated in the production of paint, are sent to an Effluent Treatment Station, so they do not cause the contamination of rivers and springs water, pose a threat to humans and to society.

The physical treatment involve steps such as filtration, sedimentation, decantation, flotation, and osmosis separation, since the use processes such as chemical steps: adjustment of the pH, addition of substances to oxidize, reduce, and neutralizer to coagulate finally in step with regard to biological action of microorganisms such as bacterial and activated sludge to minimize the degree of hazard of the waste and effluent,

It is important to point out the characterization and the legal requirements before opting for the technology of industrial effluent treatment, and to remember that the process should seek to address environmental sustainability.[19]

The water is now a scarce natural resource, so use it wisely and get your recycling and an issue of environmental sustainability.The reuse of the treated effluent is one of the possibilities that should be considered in order to minimize the environmental impacts and to reduce the use of natural resources. [15]

Among the various processes for treating industrial effluents, the processes that involving chemical reactions become more effective in treatment of hazardous waste, however, some of them can cause environmental impacts. These treatments include neutralization, the reduction of color and turbidity. Other reagents that are added at this stage are the flocculants (aluminum, ferric chloride, polymers) that induce sedimentation of the pollutants. However, for various industrial processes (especially organic) these methods are insufficient for complete removal of impurities, especially with regard to Biochemical Oxygen Demand (BOD), Chemical Oxygen Demand (COD), and color. [2,3,5,6,7,12,13,17]

New technologies for the treatment of aqueous effluents in Brazil are gradually becoming available and more competitive. Although the tendency is be part of the market alongside traditional methods. These techniques include, for example, the modern separation techniques, ion exchange, electrolysis, ultrafiltration, reverse osmosis, and Advanced Oxidation Processes (AOP). [9,10,14,15]

Chemical oxidation processes are promising to restore the environment. These processes aim the degradation of toxic organic compounds, and formation of simpler molecules. The most efficient path for the oxidation is the attack by hydroxyl radical (OH).

The Advanced Oxidation Process (AOP) using electron accelerators have been adopted by several countries for the removal of organic compounds and biological degradation in domestic sewage. The electron beam irradiation has shown to be efficient in the degradation of organic compounds such as benzene, toluene, xylene and phenol, and also chlorinated compounds (ethylene dichloride, chloroform) and oxygenates such as methylisobutylketone. [8,9,10,14,]

Irradiation leads to the breakdown of compounds into simpler molecules and radicals and the latter can recombine to form other molecules. Several by-products of reactions have been identified in irradiated solutions. Getoff study of degradation of chloroform, found mainly aldehyde as a stage of degradation.[9,10]

The object of this study is the industrial effluent from the process of resins, water based paint and electrophoresis paint. This effluent is composed of waste generated during the cleaning of water-based paint, paint's tanks and washing paint pots electrophoresis; washwater tanks manufacture and storage of resin materials, water washes of the resin reactors and washwater of filling machines for water-based paints.

The results of the analyzes of samples of raw wastewater, treated by chemical physical system versus through the treatment process by EB, allows the assumption that the ultimate goal is very promising.

Among the main advantages of the process of irradiation treatment can include: a) Compliance with legal requirements Article 19A of the parameter; b) the processing time is less than the processes used by conventional; c) Reduction of organic compounds more complex to less complex; d) Reduction of the index of COD; e) Is an innovative process; f) is a contribution to environmental sustainability; g) There is a possibility to reuse the water for washing floors; h) There is the possibility of developing a mobile system for the treatment of small quantities in effluent; The process may represent a new business opportunity.

The disadvantages of using the irradiation process can include: a) little-known technology; b) Cost possibly more expensive than traditional processes; c) Paradigm fear, when dealing with processes that are used for irradiation.

2.EXPERIMENTAL

2.1.The object of study

It was regarded as an object of study the industrial effluent liquid from a paint industry for automobiles, industry, and general repair. This effluent originates of washing equipment (pots, buckets, drums, dispersers hoods, shovels, trowels, buckets, drums and other instruments), with of residues of organic pigments, inorganic pigments, solvents, resins and paints.

2.2.Location of sample collection

Crude samples were collected in the receiving tank effluent, except the samples 1 to 4 that were also collected after physical chemical treatment.

2.3.Sampling and the reference used

To evaluate and compare the parameters was measured using the statutory requirement Decree 8468/1976, Article 19A, which determines the concentration patterns of each chemical element in an industrial effluent, before being discarded to a river for preventing pollution.[19]

In the first four output measurements (samples 1 to 4), it was found the effluent to the level of service requirement Article 19A, when treated by chemical physical process (the current process used by the company paint) and the other measurement (samples 5 to 11) showed the behavior of the effluent after being treated by Electron Beam (EB), the service requirement of Article 19A.

The sampling was performed in accordance with technical standard (ABNT NBR 5764, 1986). All samples were collected at the entrance of the Industrial Wastewater Treatment Plant (Fig.1). The frequency of collection is monthly, in order to determine the variations of the same due to seasonality of the production process of paints and waste generation and waste paint. For the present study it was considered the samples collected from April 2011 to February 2012 consecutive months, and are called 1 to 11.

Figure 1. Aspect of crude sample of effluent collected in the entrance of the Industrial Wastewater Treatment Plant

The electron beam irradiation was carried out using the Radiation Dynamics Inc. USA Electron Beam Accelerator, with 1.5 MeV and 37 kW, in batch systems. The irradiation parameters used was 4.0 mm sample width, 112 cm (94.1%) scan and 6.72 m/min speed conveyor stream. The Applied absorbed doses were 10, 30, 50 kGy for samples of 1 to 4 initially and on a second step, 50, 80 and 100 kGy for samples 5 to 11. In Figure 2 the samples prepared for electron beam irradiation are showed.[19]

Figure 2. Samples prepared for electron beam irradiation

3. RESULTS AND DISCUSSION

In Table 1 are presented the physical-chemical characterization of the samples and chemical analysis compared to Specification in the Article 19A, before irradiation. All the parameters of both samples have lower values than the specified.

For samples 1 to 4 were analyzed with the input and output (given the current treatment system studied paints industry, which is a physicochemical process). The remaining samples were analyzed and the entry of effluent treatment with EB for comparison of methods of treatment

TABLE 1. Chemical Analysis of samples compared to Specification – Dec 8468/1976 Article 19A

Parameter	Specification Article 19 A Dec 8468/76	Unit	1	1 outlet	2	2 outlet	3	3 outlet	4	4 outlet	5	5 Trat 50 kGy	6	6 Trat 50 kGy	7	7 Trat 50 kGy	8	8 Trat 50 kGy	9	9 Trat 50 ky	10	10 Trat 50 kGy	11	11 Trat 50 kGy
Total Arsenic	1500	μgAs/L	<10.0	<10.0	<10.0	<10.0	<10.0	<10.0	<10.0	<10.0	<10.0	<10.0	<10.0	<10.0	<10.0	<10.0	<10.0	<10.0	<10.0	<10.0	<10.0	<10.0	<10.0	<10.0
Total Cadmium	1.5	mgCd/L	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Total Lead	1.5	mgPb/L	<0.50	<0.50	<0.50	<0.50	<0.50	<0.50	<0.50	<0.50	<0.50	<0.50	<0.50	<0.50	<0.50	<0.50	<0.50	<0.50	<0.50	<0.50	<0.50	<0.50	<0.50	<0.50
Total Cyanide	0.2	mgCN/L	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	0.06
Total Cooper	1.5	mgCu/L	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.15	<0.10	0.13	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	0.97	<0.10	<0.10	0.18	0.11
Hexavalent Chrome	1.5	$mgCr_6/L$	0.65	0.14	<0.01	<0.01	0.16	0.02	<0.01	<0.01	*	*	<0.01	<0.01	<0.01	<0.01	0.37	<0.01	0.05	<0.01	<0.01	<0.01	1.17	<0.01
Total Chrome	5.0	mgCr/L	0.91	0.51	0.07	0.19	0.43	<0.05	0.40	0.06	0.24	0.12	0.14	<0.05	0.15	0.14	0.53	0.55	1.40	6.75	0.12	0.19	2.54	1.76
Total Tin	4000	μgSn/L	1258	<25.00	<25.00	<25.00	189	209	1505	54.14	1356	1094	2746	71.69	2808	<0.25	4942	19710	1267	1252	263	479	17300	1297
Total Phenol	5.0	mg/L	<0.10	<0.10	<0.10	437	<0.10	<0.10	<0.27	0.25	<0.10	0.38	<0.10	0.17	<0.10	0.28	0.61	0.51	0.77	0.76	1.22	0.90	0.22	0.86
Soluble Iron	15.0	mgFe/L	<0.30	<0.30	<0.30	0.55	<0.30	<0.30	<0.30	<0.30	10.96	12.79	1.03	<0.30	88.75	1.94	6.97	<0.30	<0.30	<0.30	1.43	0.40	<0.30	<0.30
Fluoride	10.0	mgF/L	1.39	1.36	0.86	1.07	1.82	1.13	0.93	1.40	2.95	2.72	0.90	1.37	1.15	1.46	0.85	<0.50	1.33	1.34	1.58	0.71	1.78	1.51
Total Mercury	1500	μgHg/L	<0.50	<0.50	<0.50	<0.50	<0.50	<0.50	<0.50	<0.50	<0.50	<0.50	<0.50	<0.50	<0.50	<0.50	<0.50	<0.50	<0.50	<0.50	<0.50	<0.50	<0.50	<0.50
Total Nickel	2.0	mgNi/L	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	0.11	0.09	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	0.12	<0.05	<0.05	<0.05	<0.05
Oil and Total grease	150	mg/L	11.9	<0.10	11.5	45.4	35.9	<0.10	84.1	<0.10	108	95.6	18.4	18.7	22.3	90.6	123	97.6	40.7	148	18.5	32.9	64.1	283
pH/temperature	6.0 -10	pH/ºC	9.47 / 19	7.94 / 19	6.91 / 21	7.61/ 21	9.10 / 21	6.94/ 21	7.42 / 21	7.11/ 21	9.23/ 20	8.15 / 19	6.18/ 19	5.95/ 19	6.43/ 20	7.73/ 20	9.01/ 20	7.44/ 20	7.44/ 20	5.95/ 20	6.64/ 20	5.58/ 19	10.00/ 21	8.59/ 21
Total Silver	1.5	mgAg/L	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
Total Selenium	1500	μgSe/L	<10.00	<10.00	<10.00	<10.00	<10.00	<10.00	<10.00	<10.00	<10.00	<10.00	<10.00	<10.00	<10.00	<10.00	<10.00	<10.00	<10.00	<10.00	<10.00	<10.00	<10.00	<10.00
Sedimentable Solids	20	mg/L	0.1	0.1	0.1	11.0	0.3	<0.10	13.0	0.2	**	3.0	5.5	2.5	0.9	4.0	4.5	15	250	350	<0.1	1.7	3.3	50
Total Sulfate	1000	$mgSO_4/$	88.95	89.34	94.86	88.37	115	83.58	64.20	57.69	150	148	168	168	190	220	54.57	37.63	118	120	139	141	77.03	73.13
Total Sulfide	1.0	mgS/L	<0.10	<0.10	<0.10	0.26	<0.10	<0.10	<0.10	<0.10	*	*	<0.10	<0.10	0.33	0.15	<0.10	<0.10	<0.10	0.28	<0.10	<0.10	<0.10	0.31
Total Zinc	5.0	mgZn/L	0.20	0.18	0.22	0.58	0.55	0.17	1.07	0.56	2.69	2.07	1.44	1.19	36.74	1.57	1.47	2.55	1.56	9.40	0.55	0.67	1.77	4.77
COD		mgO2/L									31554	22330	34000	32500	30303	29412	29703	26263	21000	25000	27228	25743	39604	36275
COD 80 kGy		mgO2/L										23301		35000		28961		24242		36000		25743		36765
COD 100 kGy		mgO2/L										22616		32500		29412		26263		25000		25248		34804

Observation:

1) The results of Hexavalent Chrome and sulfide are not metrologically reliable due there is substances (*)
2) The results of Sedimentable solids were not performed because the existing was very small (**)
3) The effluent samples 1,2,3 and 4 were analyzed in the input and output samples were analyzed to compare the current process by the company ink (for physical chemical process). For these samples were analyzed only treated effluent parameters sedimentable solids, greases oils and fats.
4) For samples 5-11 (August 2011 and February 2012) were made for analysis of Article 19A irradiated with 50 kGy for the purpose of comparison the treatment process (Physical Chemical Electron Bean).
5) The samples are underlined in black for the effluent, collected in the tank inlet Effluent Treatment Plant of Industrial paint company studied. Samples underlined in red (from 1 to 4) are related to the process effluent treated physicochemical adopted by the firm of paints, However, the samples (5 to 11) were treated by irradiation process.

Three physical chemical analyzes of each sampling were performed, one of the effluent, the second one of the effluent treated by different physical-chemical process, and the third one of the treated effluent through the process of electron beam irradiation (EB) at dosages of 10, 30 and 50 kGy. These data are presented in TABLE 1.

It is observed that the results found by both physical chemical treatment (process currently used by the paint industry studied), and the irradiation treatment, were effective because the results remained the effluent within the requirements specified by Article 19A.

The samples presented different aspects, depending on the received dose became clearer after irradiation as showed in Figure 3,

Figure 3 Irradiated samples

In this new stage it was performed monitoring of the parameter Chemical Oxygen Demand (COD). The results of the measured parameters for the crude sample entry (processing station) and to the samples treated with doses 50, 80 and 100 kGy are presented in Table 2. That COD after treatment with irradiation showed promising results, since the results of all applied doses showed a reduction, except for the sample 9 that presented an increase and need to be investigated.

TABLE 2 Determination of COD after electron beam irradiation

	Determination of COD (mgO2/L)			
Sampling	**100 kGy**	**80 kGy**	**50 kGy**	**Untreated**
5	22816	23301	22330	31554
6	32500	35000	32500	34000
7	29412	26961	29412	30303
8	26263	24242	26263	29703
9	25000	36000	25000	21000
10	25248	25437	25743	27228
11	34804	36765	36725	39604

The samples treated by irradiation significant reductions in COD content. Variations of these reductions are clearly observed in a Table 2.

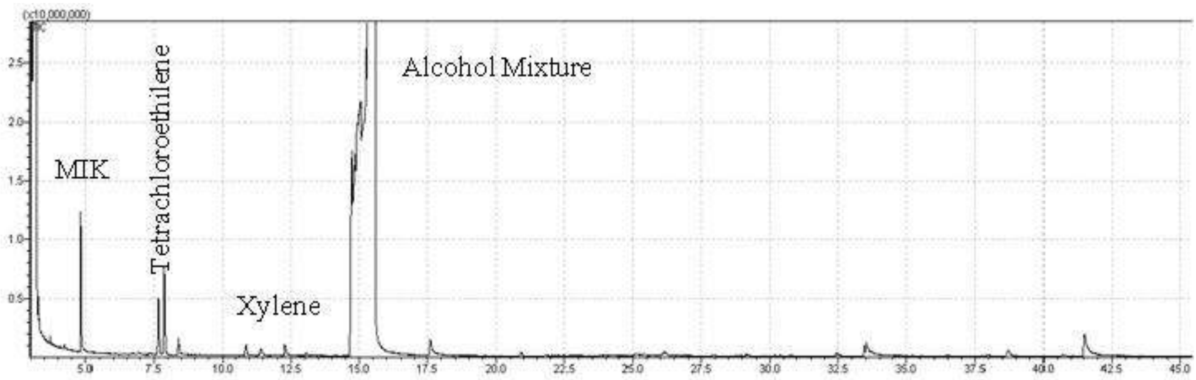
The results were very good since the waste is composed of complex organic products, derived pigments, resins and solvents used in the manufacturing process of the paint.

In the study of AOP (Advanced Oxidation Process) with ionizing radiation it is important to point out that not only the removal of pollutants is important, but should be considered the formation of by products after irradiation. To determine the products that can be formed, it is necessary to study the destruction mechanism of the compound.

In Figure 4 is showed the obtained chromatogram of untreated sample. The mains compounds identified by mass spectrometry was MIK (Methyl Isobutyl Ketone), tetrachloroethilene, xylene and a mixture of alcohol that was not totally identified yet. These compounds will be analyzed in irradiated samples and its removal will be calculated.

It is expected that MIK, tetrachloride and xylene will be removed with efficiency components to be toxic to the aquatic environment. But these expectations need to be better investigated.

With regard to larger molecules possibly originating from residues of resin, pigment, and solvent mixtures, it is expected that the technology permits the breaking of these molecules, leading to compounds simple and less pollutants.



The Table 5 show this results. In this table it observe significant reductions in the areas thus indicating that the process is producing satisfactory results.

Figure 4 Chromatogram of sample 1 with the identification of the main compounds

CONCLUSION

Analyzing the initial results of this research it is possible to conclude that they represent a promising new technology for the treatment of industrial wastewater with pollutant loads formed by organic complexes.

Further research should be developed to optimize the processes of oxidation and breakdown of complex molecules, as well as to determine a standard for the waste water that can be reused in the process of washing of floors and other areas, thus contributing to the economy natural resources and for environmental sustainability.

Finally this study is relevant because it is an alternative treatment that can minimizes the environmental impacts of these industrials effluent.

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REFERENCES

1.ABRAFATI: ***Associação Brasileira dos Fabricantes de Tintas,*** http://www.abrafati2009.com.br/index.php (2011).

2.ALMEIDA, E. et al. Tratamento de efluentes industriais por processos oxidativos na presença de ozônio. *Química Nova*, São Paulo, **v. 27, n. 5,** Oct. pp.(818-824) 2004.

3.AMERICAN PUBLIC HEALTH ASSOCIATION.*Stand**ard Methods for the Examination of Water and Wastewater***. 17 ed. Washington, DC. APWA, AWWA, WPCF, 1997.

4.ASSOCIAÇÃO BRASILEIRA DE NORMAS TÉCNICAS. ***Amostragem de produtos químicos industriais líquidos de uma só fase.*** Rio de Janeiro, ABNT, 1986. (NBR 5764).

5. ASSOCIAÇÃO BRASILEIRA DE NORMAS TÉCNICAS. ***Resíduos Sólidos – Classificação.*** Rio de Janeiro, ABNT, 2004. (NBR 10004).

6. SÃO PAULO. ***DECRETO 8468 de 8 de setembro 1976*** que aprova o regulamento da Lei 997, de 31 de maio de 1976, que dispõe sobre a Prevenção e o Controle da Poluição do Meio Ambiente**.**

7.CHERNICHARO C. A. L. ***Reatores Anaeróbios – princípios do tratamento biológico de águas residuárias.*** Departamento de Engenharia Sanitária e Ambiental da Universidade Federal de Minas Gerais, Belo Horizonte, 2000. v.5

8.ANDRADE, D.C. ***Processo de oxidação avançada por radiação ionizante na degradação do herbicida ametrina em embalagens de PEAD descartadas.*** São Paulo, 2008,**.** 72p. Dissertação de Mestrado – Instituto de Pesquisas Energéticas e Nucleares: Universidade de São Paulo.

9.DUARTE, C.L; SAMPA, M.H.O; RELA, OIKAWA, H. P.R.; SILVEIRA, C.G. Advanced oxidation process by electron-beam-irradiation induced decomposition of pollutants in industrial effluents effluents. Radiat. Phys. Chem., **63**, pp.(647-651) 2002.

10.DUARTE, C.L. ***Aplicação do processo avançado de oxidação por feixe de elétrons na degradação de compostos orgânicos presentes em efluentes industriais***. São Paulo, 1999, 153p. Tese (Doutorado) **-** Instituto de Pesquisas Energéticas e Nucleares: Universidade de São Paulo.

11.FAZENDA, J.M.R. ***Tintas e vernizes: ciência e tecnologia***. São Paulo: ABRAFATI, 2009.

12.FINGER, R.L.; KARAS, A.; Paola K. e WIECHETECK, G.K. Plano de gestão de resíduos em fábrica de tinta http://www.bvsde.paho.org/bvsaidis/uruguay30/BR10555_FINGER.pdf (2006).

13.METCALF & EDDY Inc, ***Wastewater engineering: treatment, disposal, reuse*** . 4th Ed. Singapore: McGraw-Hill, 2001.

14. RIBEIRO. M.A. ***Estudos sobre a remoção de metais tóxicos em efluentes industriais após a irradiação com feixe de elétrons***. 2002. Dissertação (Mestrado) – Instituto de Pesquisas Energéticas e Nucleares. São Paulo.

15. SILVA, M. R. A. da; OLIVEIRA, M. C. de; NOGUEIRA, R. F. P.. Estudo da aplicação do processo foto-Fenton solar na degradação de efluentes de indústria de tintas. http://www.scielo.br/pdf/eq/v29n2/22715.pdf (2004)

16. SITIVESP – Sindicato da Indústria de Tintas e Vernizes do Estado de São Paulo (Syndicate of Paint and Varnish Industry of the State of São Paulo)**.** Indicadores de consumo de tinta. http://www.sitivesp.org.br/sitivesp/index.htm (2011)

17. SPERLING, M. Von. ***Princípios do tratamento biológico de águas residuárias***, Lodos Ativados. Belo Horizonte:DESA-UFMG, 1997, v. 4.

18. EPA **-** Environmental Protection Agency. US. ***Wastes - Hazardous Waste - Definition of Solid Waste*****. Avaiable in < http://www.epa.gov/osw/hazard/dsw/index.htm > acessed in 27.02.2012**

19. NASCIMENTO, F.C. ***Mitigation of solid waste and reuse of effluent from paint and varnish automotive and industrial treated by irradiation at electron beam accelerator***. In INAC – International Nuclear Atlantic Conference,.24 to 28 October, 2011. Belo Horizonte, MG – Brasil.