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Case study

Environmental assessment of lubricants before and after wire drawing process

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Abstract

Iron wire drawing processes involve the use of solid lubricants made of powdered raw materials, which lead to industrial wastes after being used. These wastes, based on stearates, have a negative effect on the environment. This study deals with the environmental assessment of some lubricants before and after the wire drawing process in a Spanish factory. The parameters evaluated for this study have been total organic carbon (TOC), mobility of zinc and lead, and ecotoxicity (EC_{50}). Results show that wastes have more ecotoxicity than the original lubricants due to the content of metals that lubricants pick up from the wire, as pickling, patenting and galvanising take part in the manufacture. The capture of metallic particles leads to a reduction of TOC and an increase in ecotoxicity. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Wire drawing; Solid lubricants; Wastes; Ecotoxicity

1. Introduction

Wire drawing processes are well established [1]. The efficiency of a drawing technique mainly depends on the lubricating methods. The lubricants selection is done taking into account quality criteria, wire mill activity and operational efficiency, which includes the costs of operation. Moreover, these costs of operation could be higher if environmental criteria were not taken into account to choose the appropriate lubricant. The chemical pretreatment of working material, pickling and phosphating, pollute rinsing waters with chloride and phosphoric acid, metal ions, phosphate, chlorate, nitrate and nitrite; consequently, waste water treatment is necessary. Research and development activities are focused now on the

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substitution of powder lubricants for pellets; the substitution of pretreatment steps of wire, introducing new coating salts; the evaluation of the new processes of pickling; and the development of new lubricants acting as coating lubricants as well [2–4]. All of these alternatives are good examples of combining technical developments and economical aspects with environmental protection. Lubricant and waste reduction are obtained. Specific steps in wire drawing are galvanising and patenting processes that involve zinc and lead coating, respectively.

This work deals with the environmental assessment of several lubricants in a wire drawing process. The activity is carried out in a company in Cantabria (northern Spain). The common lubricants used in the activity were taken before and after their application in the wiring process; in order to evaluate their hazardous behaviour, a characterisation of lubricants and wastes was performed. Following regulatory criteria of previous works [5,6] the control parameters have been established taking into account the Spanish regulations on hazardous wastes, the technical specifications of the lubricants and the process itself. For this process, the variables: total organic carbon (TOC), mobility of zinc and lead, and ecotoxicity (EC_{50}) were evaluated. A comparison between the results obtained for the lubricants and for the wastes after the use of lubricants was accomplished. Other relevant wastes from the wiring process were also evaluated in order to have more information about the influence of heavy metals and TOC on the ecotoxicity. Some wastes are mixtures of calcium stearate, some of potassium stearate, and others are heterogeneous mixtures of dust taken from the floor of the factory. All of them contribute significantly to the total volume of wastes.

2. Materials and methods

2.1. Sample collection

Five different lubricants and their corresponding wastes were collected in order to establish their environmental characterisation. In addition, other six wastes were taken to have a wider information on environmental parameters of the wastes from wire drawing process. Specific steps of the process as well as contribution to the total amount of each waste were considered to do the experimental design.

2.2. Lubricants and wastes

The lubricants taken for this study belong to different trade marks which are commonly used in the wiring process. They consist of sodium stearates (L1, L2), molybdenum disulphide (L3) and calcium stearates (L4, L5). Before the wire drawing process, other additional processes are involved to achieve the technical specifications of each product modifying the characteristics of the industrial waste. There is a pretreatment of acid pickling and precoating, and depending on the requirements of the wires, some operations of patenting and galvanising may be required. After these operations, during the wire drawing process, the wastes W1, W2, W3, W4 and W5, directly associated to the above mentioned lubricants, were obtained. Other wastes have the same calcium stearate base (W6, W7) and potassium

Table 1
Solid lubricants and wastes

Solid lubricants		Wastes
Main component		**Processes**
Sodium stearate		
L1	W1	Pickling–phosphating–borax–dry wiredrawing
L2	W2	Pickling-phosphating–borax–dry wiredrawing
Molybdenum disulphur		
L3	W3	Pickling–phosphating–borax–dry wiredrawing
Calcium stearate		
L4	W4	Pickling–borax–dry wiredrawing
L5	W5	Patenting–pickling–galvanising–dry wiredrawing
NA	W6	Patenting–pickling–galvanising–dry wiredrawing
NA	W7	Patenting–pickling–galvanising–dry wiredrawing
Potassium stearate		
NA	W8	Pickling–dry wiredrawing–wet wiredrawing
Mixing of lubricants of different components		
NA	W9	Floor dust from area 1
NA	W10	Floor dust from area 2
NA	W11	Floor dust from area 3

NA: not available.

stearate base (W8). Finally, there are wastes based on a mixture of dust deposited on the floor (W9, W10, W11). Table 1 shows a description of the lubricants and the processes originating the wastes.

2.3. Experimental procedure

Once the samples were collected, they were homogenised in the laboratory and submitted to the TCLP extraction procedure. The samples were prepared in triplicate and turned over for 18 h. The pH after the 18 h extraction procedure was recorded and the leachate was filtered through a 0.65 μm cellulose nitrate filter [7]. The ecotoxicity, according to the Spanish regulation, was evaluated in the filtered leachates. The concentration of metals: zinc and lead, was also analysed in this solution. Taking into account the composition of lubricants, the TOC was determined directly in all samples.

Zinc and lead were analysed by atomic absorption spectrometry in a Perkin-Elmer 1100B spectrophotometer. The ecotoxicity bioassay has been applied to TCLP leachates according to the Microtox® test, which is based in the inhibition of the luminescence of the marine bacterium "photobacterium phosphoreum". The lyophilised bacterial reagent was supplied by Microbics. The Microtox® bioassay was conducted at a constant time and temperature (15 min, 15°C). Bioassays were performed according to the standard procedure in a Microtox® model 500 [8]. Results were expressed as 15 min EC_{50} values calculated with the Microtox reduction software supplied by Microbics Corp., where EC_{50} ($mg\,l^{-1}$) is expressed as the effective concentration of toxicant (leachate) that causes 50%

decrease in light output. Results were compared to the values set by the Spanish regulations ($EC_{50} \leq 3000\,mg\,l^{-1}$) to identify if a waste was hazardous from a ecotoxicity point of view (H14, ecotoxicity characteristic) [9–12].

2.4. Total organic carbon

This parameter allows the determination of organic matter present in the samples. This constitutes one important parameter for the classification of a solid waste. To evaluate this parameter an EUROGLAS TOC 1200 instrument, following the ISO standard guidelines [13,14], has been used.

3. Results

Table 2 shows the TOC, expressed in mass percentage, for lubricants and wastes, respectively. In general, it can be observed a high amount of TOC in the samples, particularly high are the values obtained for L1 and L2, lubricants based on sodium stearate. The TOC for wastes ranges between 25 and 84%, except for W4, W9, W10 and W11 wastes, in which values fall down to 15–20%. The TOC decrease is related to the amount of metallic particles mixed with the lubricants during the process. It has to be noticed the high value of TOC for W8 waste, given in $mg\,l^{-1}$, due to its liquid form.

3.1. Zinc and lead mobility

Mobilisation of zinc and lead for lubricants and wastes in TCLP leachates leads to the results shown in Table 3. The requirements adopted by US EPA were taken due to the

Table 2
Content of TOC of lubricants and wastes

Lubricants				Wastes		
Sample		Moisture (%)	TOC (%)	Sample	Moisture (%)	TOC (%)
Sodium stearate	L1	3.95	79.92 ± 2.76	W1	3.09	41.44 ± 3.42
	L2	2.48	70.83 ± 4.21	W2	4.12	52.70 ± 7.22
Molybdenum disulphur	L3	0.57	19.64 ± 0.38	W3	1.84	33.57 ± 5.86
Calcium stearate	L4	0.00	30.30 ± 4.94	W4	2.97	18.31 ± 3.28
	L5	0.34	37.25 ± 1.59	W5	1.12	24.84 ± 5.10
	–	–	–	W6	1.44	47.09 ± 9.40
	–	–	–	W7	1.97	84.01 ± 7.54
Potassium stearate	–	–	–	W8	Liquid	6996 ± 707[a]
Mixing of lubricants				W9	3.28	14.72 ± 0.61
				W10	3.63	15.66 ± 0.16
				W11	4.19	20.96 ± 0.15

[a] Concentration of TOC expressed in $mg\,l^{-1}$.

Table 3
Mobility of zinc and lead from lubricants and wastes (TCLP leachate)

Lubricants					Wastes			
Sample		pH_{TCLP}	Lead ($mg\,l^{-1}$)	Zinc ($mg\,l^{-1}$)	Sample	pH_{TCLP}	Lead ($mg\,l^{-1}$)	Zinc ($mg\,l^{-1}$)
Sodium stearate	L1	6.51 ± 0.29	0.05 ± 0.01	0.06 ± 0.04	W1	8.80 ± 0.08	0.23 ± 0.02	1.15 ± 0.50
	L2	8.92 ± 0.02	0.08 ± 0.00	0.02 ± 0.00	W2	8.77 ± 0.00	0.07 ± 0.00	0.03 ± 0.01
Molybdenum disulphur	L3	12.30 ± 0.05	0.64 ± 0.03	0.06 ± 0.02	W3	12.67 ± 0.04	0.66 ± 0.05	3.36 ± 2.24
Calcium stearate	L4	12.34 ± 0.02	0.68 ± 0.02	0.05 ± 0.00	W4	12.37 ± 0.02	0.98 ± 0.03	0.06 ± 0.00
	L5	12.28 ± 0.06	0.53 ± 0.02	0.06 ± 0.00	W5	12.15 ± 0.05	0.67 ± 0.05	4.84 ± 0.19
	–	–	–	–	W6	12.35 ± 0.04	1.29 ± 0.33	5.25 ± 0.73
	–	–	–	–	W7	9.51 ± 0.10	0.26 ± 0.03	0.14 ± 0.04
Potassium stearate	–	–	–	–	W8	12.64 ± 0.00	0.47 ± 0.05	0.65 ± 0.01
Mixing of lubricants					W9	5.98 ± 0.11	10.77 ± 0.79	1821.25 ± 70.40
					W10	6.29 ± 0.17	9.23 ± 1.51	1749.17 ± 348.94
					W11	6.23 ± 0.03	1.38 ± 0.07	185.09 ± 4.62

lack of a quantitative concentration of these metals in the Spanish and European Union regulations. Taking into account US EPA references for toxicity, the regulated value for lead is $Pb = 5\,mg\,l^{-1}$ which is the limit for characterisation of hazardous wastes [7]. A reference value for zinc can be taken from the best technologies limits as $Zn = 4.3\,mg\,l^{-1}$ [15].

As it can be seen in Table 3, lubricants do not mobilise any significant concentration of lead and zinc. However, wastes mobilise higher concentrations than the considered limit. W9 and W10 wastes mobilise both metals above the mentioned limits. Besides, W5 and W11 wastes also leachate out a higher concentration of zinc.

3.2. *Ecotoxicity*

Results of ecotoxicity of lubricants and wastes are shown in Table 4. For the evaluation of the hazardous behaviour of wastes (H14), the Spanish regulations on ecotoxicity have been considered. Raw lubricants gave values above this limit, $EC_{50} = 3000\,mg\,l^{-1}$. Therefore, they are not considered to have an ecotoxicological effect on the environment.

As wastes concern, the W8 waste ($EC_{50} = 1057\,mg\,l^{-1}$), W9 waste ($EC_{50} = 879\,mg\,l^{-1}$) and W10 waste ($EC_{50} = 669\,mg\,l^{-1}$) show a relevant ecotoxicity. W8 deals with a liquid emulsion of potassium stearate in which a high content of copper from the wire has been dissolved. W9 and W10 correspond to dust deposited on the floor. The rest of wastes W3, W4, W5, W6 and W11 are in the moderate range of ecotoxicity.

Table 4
Ecotoxicity of lubricants and wastes

Lubricants				Wastes		
Sample		pH_{TCLP}	Ecotoxicity EC_{50} ($mg\,l^{-1}$)	Sample	pH_{TCLP}	Ecotoxicity EC_{50} ($mg\,l^{-1}$)
Sodium stearate	L1	6.51 ± 0.29	37827 ± 4638	W1	8.80 ± 0.08	105150 ± 10068
	L2	8.92 ± 0.02	36113 ± 4143	W2	8.77 ± 0.00	26362 ± 4828
Molybdenum disulphur	L3	12.30 ± 0.05	7849 ± 419	W3	12.67 ± 0.04	6525 ± 523
Calcium stearate	L4	12.34 ± 0.02	8090 ± 467	W4	12.37 ± 0.02	4902 ± 278
	L5	12.28 ± 0.06	7038 ± 308	W5	12.15 ± 0.05	7347 ± 98
	–	–	–	W6	12.35 ± 0.04	5624 ± 195
		–	–	W7	9.51 ± 0.10	121733 ± 5412
Potassium stearate	–	–	–	W8	12.64 ± 0.00	1057 ± 41
Mixing of lubricants				W9	5.98 ± 0.11	879 ± 123
				W10	6.29 ± 0.17	669 ± 129
				W11	6.23 ± 0.03	6738 ± 1101

4. Discussion

4.1. Assessment of environmental parameters between lubricants and wastes

Taking into account the relationship between lubricants and wastes, given by the groups L1/W1, L2/W2, L3/W3, L4/W4 and L5/W5, the comparison of the evaluated parameters was performed. As ecotoxicity of the samples concerns, it is noticeable that the ecotoxicity reached by the group L1/W1 was even much higher for L1 lubricant than W1 waste, but the general trend is a slight increase of ecotoxicity for wastes.

Fig. 1 deals with the effect that changes of TOC between lubricants and wastes cause on ecotoxicity (EC_{50} parameter). As long as the wire drawing process works, the lubricant picks up metallic particles from the rod as well as other lubricant dust from the environment. The capture of metallic particles decreases the TOC percentage of wastes, except for the case of molybdenum disulphide lubricant (L3) and its waste (W3), in which the TOC increases. In this case, a negative variation of TOC percentage is observed.

Lubricants in which sodium stearate is the main component (L1, L2) present larger difference of TOC respect to the corresponding wastes, but this effect does not show any relationship with ecotoxicity. For the case of molybdenum disulphide (L3), although the ecotoxicity of the corresponding waste (W3) is greater, the negative variation of TOC may means a capture of other powdered lubricant along the line. For lubricants based on calcium stearate (L4, L5), the difference of TOC is very similar, as well as the ecotoxicity values of lubricants and wastes. As it was expected, the changes of TOC do not correlate well with the ecotoxicity of samples, other factors such as composition and speciation of picked up particles may have also an influence.

In Figs. 2 and 3, it is shown the relationship between zinc and lead mobilisation in the TCLP leachate with the ecotoxicity. Lubricants do not show any significant mobility of zinc (Fig. 2). The W5 waste has reached the highest concentration of zinc, this concentration is higher than the standard limit established by US EPA ($Zn = 4.3\ mg\,l^{-1}$). However, it cannot

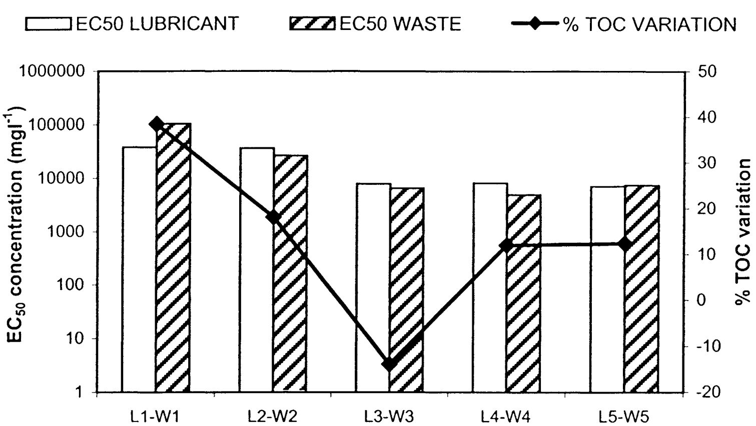

Fig. 1. Effect of variation of TOC (%) on ecotoxicity of lubricants and wastes.

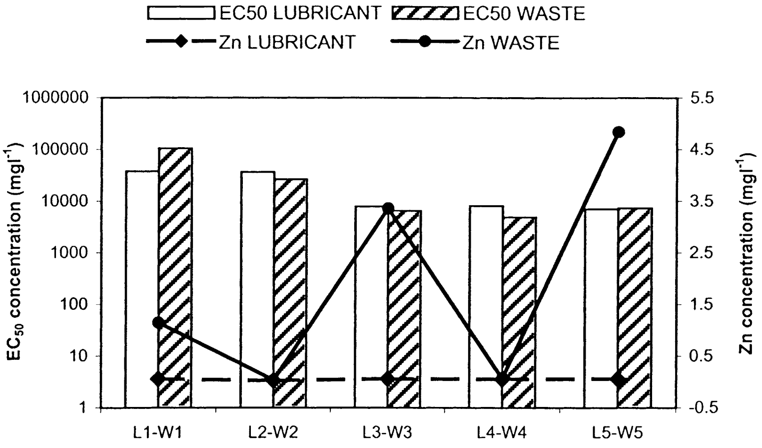

Fig. 2. Relationship between zinc mobilisation and ecotoxicity for lubricants and wastes.

be observed that the zinc mobilisation has an important effect on ecotoxicity in comparison to the rest of the wastes. The concentration of lead (Fig. 3) is low for most of the samples. Only for the W4 waste, the concentration increases to $Pb = 0.98\,mg\,l^{-1}$ in good agreement with the value of ecotoxicity ($EC_{50} = 4902\,mg\,l^{-1}$); however, this concentration is even lower than the US EPA standard to consider a waste as hazardous ($Pb = 5\,mg\,l^{-1}$).

4.2. Environmental assessment of wastes

From an environmental point of view, industrial wastes must be properly managed and environmental parameters must be considered. With this purpose, most of the wastes

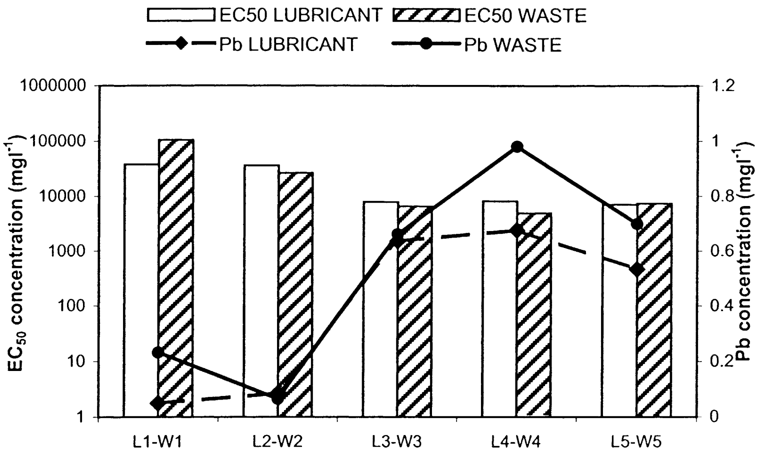

Fig. 3. Relationship between lead mobilisation and ecotoxicity for lubricants and wastes.

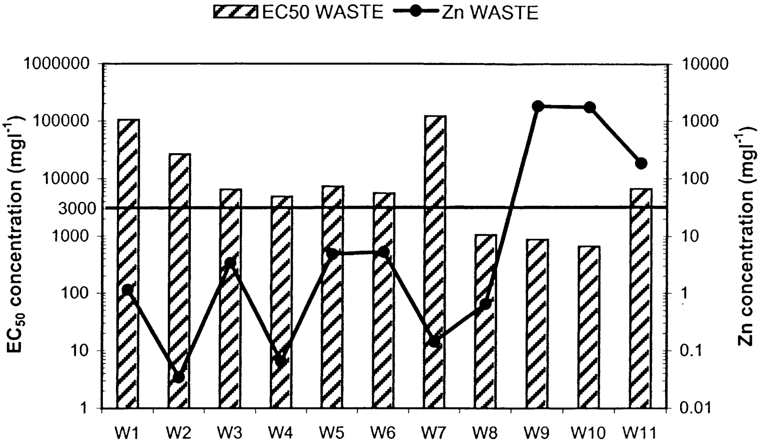

Fig. 4. Influence of zinc concentration on ecotoxicity of wastes.

originated in the factory were evaluated. The following figures show the relationship between the chemical characterisation and the ecotoxicity of the different wastes. It is also important to note the influence of the pH of TCLP leachate on the ecotoxicity.

The toxicity does not seem to be related to the percentage of TOC. In general, the hazardous behaviour of wastes increases as lower TOC present them. This effect of TOC substitution by metallic particles is clear for the wastes W8, W9 and W10 in which the ecotoxicity falls down under the Spanish limit $EC_{50} < 3000\,mg\,l^{-1}$. Wastes from molybdenum (W3) and calcium (W4, W5, W6) show an ecotoxicity near the limit ($EC_{50} = 3000\,mg\,l^{-1}$). The liquid waste of potassium (W8), shows a higher ecotoxicity. Finally, it is also noticeable the high toxicity that W9 and W10 wastes present, composed by dust deposited on the floor. These wastes (W8, W9, W10) show the lowest percentage of TOC.

Fig. 4 deals with the influence that mobilisation of zinc shows on the ecotoxicity. W9 ($Zn = 1821.25\,mg\,l^{-1}$) and W10 ($Zn = 1749.17\,mg\,l^{-1}$) wastes, based on mixtures of lubricants gave the highest concentration of zinc. It is also worthy to point out the concentration reached by W11 waste ($Zn = 185.09\,mg\,l^{-1}$). W8 waste, due to the previous coppering process, presents a high concentration of copper ($Cu = 40\,mg\,l^{-1}$), which may be responsible of the hazardous behaviour. The W5 waste ($Zn = 4.84\,mg\,l^{-1}$) and W6 waste ($Zn = 5.25\,mg\,l^{-1}$), based on calcium stearate, also have a concentration of zinc slightly above the concentration taken as reference for the leachate.

Fig. 5 deals with the influence that the mobilisation of lead may have on ecotoxicity. Most of the wastes do not mobilise any significant concentration of this metal. Only the W9 waste ($Pb = 10.77\,mg\,l^{-1}$) and W10 waste ($Pb = 9.23\,mg\,l^{-1}$) mobilise a significant concentration of lead, taking into account that the EPA standard is set at $Pb = 5\,mg\,l^{-1}$.

Finally, it can be appreciated the effect that resulting pH of TCLP leachate makes on the toxicity of wastes (Fig. 6). This factor plays an important role on the metal solubility and bacteria sensitivity. In this sense, it can be noticed a similar behaviour of ecotoxicity for W3, derived from molybdenum disulphide, and W4, W5 and W6 from calcium stearate

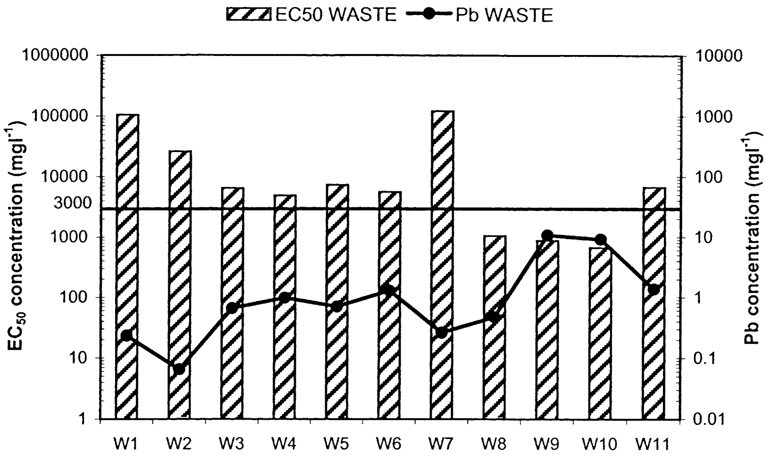

Fig. 5. Influence of lead concentration on ecotoxicity of wastes.

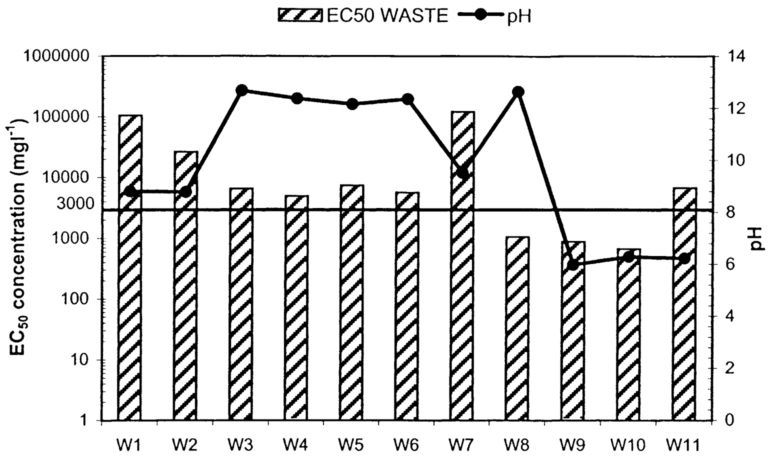

Fig. 6. Influence of pH on ecotoxicity of wastes.

lubricants. All cases have a pH value around 12, leading to ecotoxicity values in a narrow range (between $EC_{50} = 4902$ and $EC_{50} = 7347\,mg\,l^{-1}$) which bring near to the Spanish limit ($EC_{50} = 3000\,mg\,l^{-1}$).

5. Conclusions

Lubricants commonly used during the iron wire drawing processes meet the requirements on leachates ecotoxicity. However, that is not the case for their wastes as processing activities have a great influence on the final characterisation of wastes. The capture of metallic particles during the wiring process involves a reduction of TOC but an increase of heavy metals. Consequently the ecotoxicity is raised. When the processing activities involve patenting and galvanising, a high amount of lead and zinc is detected in the leachates of wastes. This is the case for wastes based on dust deposited on the floor, which present a high toxicity due to the high concentration of lead and zinc. It is also noticed, that the very alkaline pH of TCLP leachates may account for the moderate ecotoxicity that some wastes present.

Companies involved in wire drawing processes therefore need to attach more importance of the environmental management of wire drawing wastes. Better practises, which avoid the mixing of wastes are required: for example, the reduction of wastes could be obtained by replacement of powdered lubricants by pellets. Other pretreatment processes of wire should also be considered.

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