

Possibility of using by-products of the steelmaking industry for removing lead from aqueous solutions^(·)

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Abstract

A study is made of the use of two steelmaking industry by-products (rolling mill scale and blast furnace sludge) as adsorbent materials for removing Pb^{2+} ions from aqueous solutions. The adsorption of Pb^{2+} on these materials has been studied by the determination of adsorption isotherms. Several variables that affect the process (contact time, initial lead ion concentration and temperature) were evaluated. The adsorption processes are analysed using the Langmuir theory. Desorption processes for the metal from loaded by-products were also studied under different experimental conditions. This paper shows that these industrial residues are effective adsorbents for lead ions in aqueous solutions within the range of working concentrations.

Keywords

Rolling mill scale. Blast furnace sludge. Lead. Adsorption. Adsorption isotherms.

Posibilidad de usar subproductos de la industria del acero para eliminar plomo de soluciones acuosas

Resumen

Se estudia el uso de dos subproductos de la industria del acero (cascarilla de laminación y lodo de horno alto) como materiales adsorbentes para eliminar iones Pb^{2+} de soluciones acuosas. La adsorción de Pb^{2+} sobre estos materiales se ha estudiado determinando las isoterms de adsorción. Se evaluaron diferentes variables que afectan al proceso (tiempo de contacto, concentración inicial de iones plomo y temperatura). Los procesos de adsorción se estudian usando la teoría de Langmuir. Los procesos de desorción de los metales también se estudiaron bajo diferentes condiciones experimentales. Este trabajo muestra que estos residuos industriales son adsorbentes efectivos de iones plomo en soluciones acuosas en el rango de las concentraciones de trabajo utilizadas.

Palabras clave

Cascarilla de laminación. Lodo de horno alto. Plomo. Adsorción. Isoterms de adsorción.

1. INTRODUCTION

The effluents generated by modern industries generally have a complex composition which includes metals (ions or complexes), suspended solids and other components^[1]. According to increasingly stringent environmental laws, these effluents must be decontaminated because of their hazard to humans, animals and plants. Metals are non-biodegradable and can accumulate in living tissues, thus becoming concentrated throughout the food chain. High levels of lead in the blood in the infantile population are an important risk of mental slight delay and of increase of the arterial pressure.

Also they can provoke changes in the conduct, as irritability, hyperactivity and lack of attention. There can appear also other neurological disorders, anemia, renal problems and alterations in the growth and development.

Several technologies have been proposed for the removal of metals, such as precipitation, ion exchange, solvent extraction, adsorption, cementation on iron, membrane processing and electrolytic methods^[2-8]. The use of different industry by-products as adsorbent materials for the removal of metals from aqueous effluents has recently begun to be developed, with the aim of seeking alternative ways of recycling certain by-products and at the

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same time finding cheaper replacements for expensive conventional sorbent materials in different situations^[2, 9-12]. In previous studies we have investigated the possibility of using a steelmaking industry by-product -rolling mill scale- in the removal of copper ions from aqueous solutions^[4].

In the present work we have investigated the capacity of rolling mill scale and blast furnace sludge to remove Pb^{2+} ions, which may be present in liquid effluents.

Rolling mill scale is a steelmaking by-product from hot rolling processes which contains variable amounts of oil and grease. Spain generates about 44,000 t of mill scale every year^[13]. The oil component in rolling mill scale makes its recycling difficult, and its direct reuse in sintering may lead to environmental pollution problems. Mill scale with a high oil content is recycled after extracting the oil in a pretreatment stage or is dumped. Coarse scale with a particle size of 0.5-5 mm and an oil content of less than 1 % can be returned to the sinter strand without any pretreatment^[13].

Blast furnace sludge is another by-product of the steelmaking industry. Gases generated during the manufacturing of pig iron are cleaned prior to their emission into the atmosphere using any of several systems. When a wet process is used the effluent consists of a sludge, which is led to a Dorr thickener to increase its concentration. This study considers the concentrated sludge obtained from such a thickener. About 31,000 t of blast furnace sludge is produced in Spain every year^[14].

2. MATERIALS AND METHODS

The mill scale used in this work was supplied from a hot rolling mill in an electric steelshop in northern Spain. It was dried at 80 °C for 24 h, revealing an initial moisture content of 5 %. For its chemical analysis the mill scale was crushed to obtain a grain size of < 40 μ m. The chemical composition of the ground sample was determined by wavelength dispersion X-ray fluorescence analysis (WDXRF) using a Philips PW-1404 spectrometer. The analysis of metallic iron was performed by titrating with a 0.1 N $K_2Cr_2O_7$ solution with barium diphenylamine-sulfonate as indicator. For this determination the sample was first treated with a bromine-methanol solution, filtering of the residual oxides with a 20 mm crucible, with the Fe^0 soluble in bromine-methanol passing into the filtrate^[15].

The original sludge, provided by a Spanish company, was a 57 % w/w suspension of solids in

water. The suspension was vacuum-filtered and the resulting solid was dried at 80 °C for 24 h before being crushed to yield a powder of a particle size of less than 40 μ m. The chemical composition of the sample was determined by wavelength dispersion X-ray fluorescence analysis (WDXRF) using a Philips PW-1404 spectrometer. Carbon and sulfur analyses in both cases were carried out by combustion in a Leco CS-244 oven and infrared detection.

The crystalline mineralogical composition of these by-products was determined by X-ray diffraction (XRD) using a Siemens D-5000 diffractometer ($Cu K_{\alpha}$ radiation).

The N_2 adsorption isotherm was determined at 77 K for samples previously degasified at 60 °C and 10^{-5} torr for 120 min, using a Coulter SA-3100 unit. The isotherm data was used to determine the BET specific area values of the materials studied. For the removal of lead experiments the mill scale previously dried at 80 °C for 24 h was passed through a screen, using only the < 0.5 mm fraction in the tests^[12]. Pb^{2+} solutions were prepared by dissolving $Pb(NO_3)_2$ (chemical of reagent grade) in 0.01 M $NaNO_3$, in order to maintain a constant ionic strength of the dissolution. 100 ml of the metal solution was added to 10 g of mill scale in Erlenmeyer flasks. Adsorption tests with the mill scale were performed using aqueous metallic solutions with concentrations varying between 0.015 and 3.0 g/l. On the other hand, 100 ml of the metal solution was added to 5 g of sludge. Removal tests with the sludge were performed using aqueous solutions with concentrations varying between 0.015 and 10 g/l. The samples were kept in constant suspension by means of a thermostatically-controlled Lauda MS-20 unit at different temperatures (between 20 and 80 °C) for an equilibrium time of 5 h. Tests were previously performed at different reaction times in order to determine the equilibrium time. The equilibrium pH was $pH_{eq} = 5.0 \pm 0.1$. The pH was controlled using a Crison 517 pH-meter. The resulting suspensions were filtered and the solutions analysed by atomic absorption spectrophotometry (AAS) with a Varian SpectrAA-220FS spectrophotometer. Reproducibility of the results was ± 2 %. All experimental work used deionized water. The adsorption tests were realized before with samples of the adsorbent materials and deionized water. The lead concentration in solution was determined being zero so much with mill scale as with sludge. The amount of metallic ion adsorbed on the mill scale and the sludge was determined by establishing the difference between the initial concentration and the equilibrium concentration.

3. RESULTS AND DISCUSSION

3.1. Characterisation of materials

Rolling mill scale has a laminar morphology and low specific surface area ($S_{\text{BET}} = 0.43 \text{ m}^2/\text{g}$). It is composed mainly of a mixture of iron oxides: wustite (FeO), hematite ($\alpha\text{-Fe}_2\text{O}_3$) and magnetite (Fe_3O_4), and metallic iron. Its iron content is $\text{Fe}_{\text{total}} = 68.20 \%$ ($\text{Fe}^0 = 7.20 \%$ ($< 0.5 \text{ mm}$ fraction)). The chemical composition of the mill scale is shown in table I. Approximately 2 % of mill scale is composed of oils and greases from the lubrication of the rolling machines.

Blast furnace sludge is a complex heterogeneous material with a specific surface area of $27.43 \text{ m}^2/\text{g}$. Its morphology shows heterogeneity in the shape and size of the different particles. The sludge is composed mainly of hematite ($\alpha\text{-Fe}_2\text{O}_3$) and coke with minor quantities of wustite (FeO), magnetite (Fe_3O_4), maghemite ($\gamma\text{-Fe}_2\text{O}_3$), calcium ferrite ($\text{CaO}\cdot\text{Fe}_2\text{O}_3$), quartz (SiO_2) and calcium and aluminium silicates. Its iron content is $\text{Fe}_{\text{total}} = 33.00 \%$. The chemical composition of the sludge is shown in table II.

Table I. Chemical composition of the rolling mill scale

Table I. Composición química de la cascarilla de laminación

Element	Weight (%)
Fe	68.20
Mn	0.48
Cu	0.47
Si	0.25
Ca	0.13
Ni	0.11
Cr	0.07
Mg	0.05
Hf	0.04
Ho	0.04
Zn	0.03
Co	0.03
As	0.03
Ir	0.03
Sn	0.03
P	0.02
Ga	0.02
Pt	0.02
S _{total}	0.04
C _{total}	0.21

Table II. Chemical composition of the blast furnace sludge

Table II. Composición química del lodo de horno alto

Element	Weight (%)
Fe	33.00
Si	3.65
Al	1.70
Ca	2.30
Mg	0.70
K	0.18
Na	0.06
Zn	1.20
Pb	0.75
S _{total}	1.15
C _{total}	34.05

3.2. Adsorption experiments

3.2.1. Influence of temperature

Figure 1 shows the relationship between the different quantities of Pb^{2+} ions removed (or adsorbed) per unit of mass of adsorbent material (mill scale or sludge) and the equilibrium concentration of the metal ion at different temperatures for a reaction time of 5 h. The amount of Pb^{2+} removed per unit of mass of mill scale remains practically constant with temperature (Fig. 1 a)). In figure 1 b) is observed that all the sorption isotherms exhibit a similar shape. The adsorption capacity of sludge increases with temperature.

3.2.2. Adsorption isotherms

Analysis of the relationship between adsorbent materials adsorption capacity and metal cation concentration at equilibrium was performed using the equations of Langmuir:

$$C/X = 1/X_m b + C/X_m \quad (1)$$

where, X is the amount of metal ion adsorbed per unit of mass of mill scale or sludge, X_m and a indicate the adsorption capacity of the adsorbent material, b and n are constants referring to adsorption intensity and C is the cation concentration at equilibrium.

The Langmuir isotherm is based on the assumptions that every adsorption site is equivalent

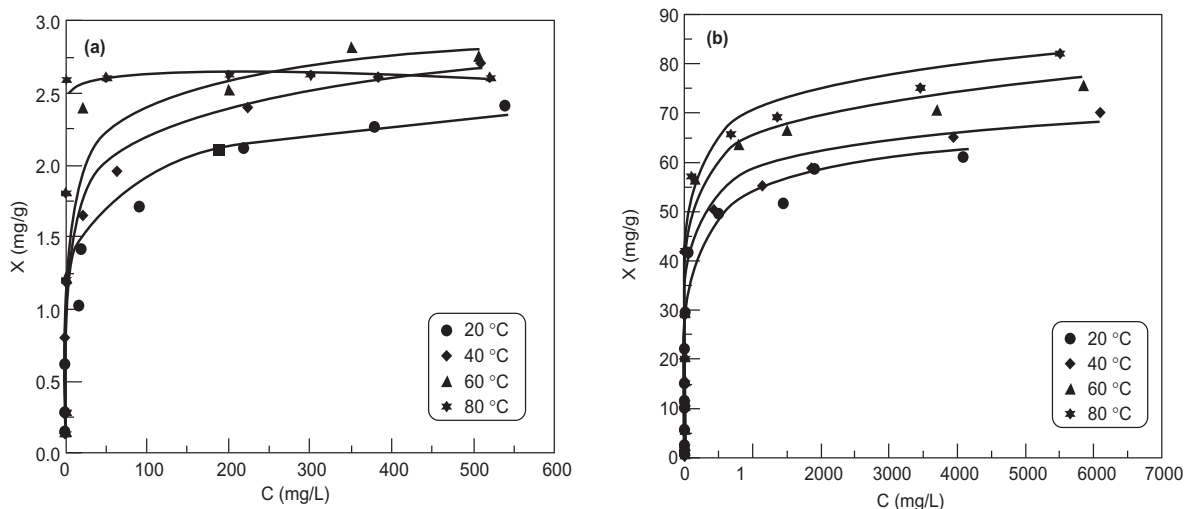


Figure 1. Mass of Pb^{2+} ions adsorbed per unit of mass of adsorbent material as a function of the cation equilibrium concentration in solution. X = Amount of metal ion adsorbed per unit of mass of mill scale or sludge, C = Cation concentration at equilibrium. Equilibrium time = 5 h, (a) Mill scale, (b) Sludge.

Figura 1. Masa de iones Pb^{2+} adsorbidos por unidad de masa de material adsorbente en función de la concentración del catión en solución en el equilibrio. X = Cantidad de ión metálico adsorbido por unidad de masa de cascarilla o lodo, C = Concentración del catión en el equilibrio. Tiempo de equilibrio = 5 h, (a) Cascarilla, (b) Lodo.

and that ability of a particle to bind there is independent of whether or not adjacent sites are occupied^[16].

Figure 2 shows Langmuir isotherms for the adsorption of Pb^{2+} in aqueous solution on mill scale and/or sludge at different temperatures. The metal

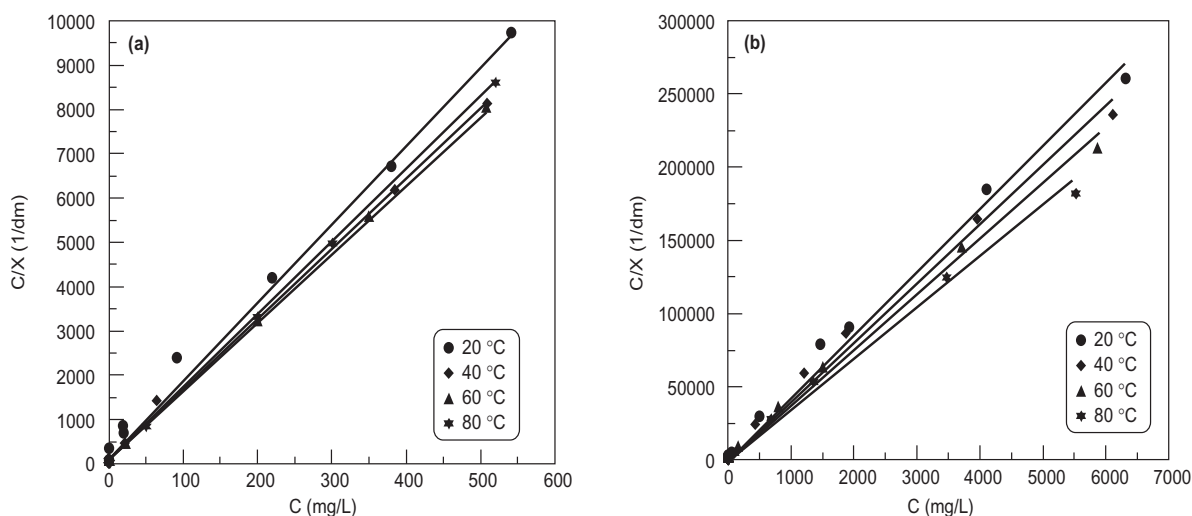


Figure 2. Langmuir isotherms. X = Amount of metal ion adsorbed per unit of mass of mill scale or sludge, C = Cation concentration at equilibrium. Equilibrium time = 5 h, mill scale concentration = 100 g/l and sludge concentration = 50 g/l, (a) Mill scale, (b) Sludge.

Figura 2. Isotermas de Langmuir. X = Cantidad de ión metálico adsorbido por unidad de masa de cascarilla o lodo, C = Concentración del catión en el equilibrio. Tiempo de equilibrio = 5 h, concentración de cascarilla = 100 g/l y concentración de lodo = 50 g/l, (a) Cascarilla, (b) Lodo.

solution concentration was varied and the reaction time was fixed at 5 h. The Langmuir values X_m and b were calculated respectively as the slope and the C/X -intercept of each isotherm line at different temperatures and are shown in table III. The experimental results fit the Langmuir model well for both studied materials ($R^2 \geq 0.994$ – mill scale and $R^2 \geq 0.990$ - sludge).

In table III is observed also that the adsorption of Pb^{2+} on mill scale is practically independent of temperature and the adsorption capacity of this adsorbent material is very low ($X_m = 2.74$ mg/g – $T = 60$ °C) (Fig. 3 a)); but the adsorption of metal on sludge is dependent of temperature (Fig. 3 b)). The adsorption

capacity of sludge rises with the increase of temperature.

3.2.3. Thermodynamic values

The values for the apparent equilibrium constant (K_c) of the adsorption process of lead in aqueous solution on by-products of the steelmaking industry were calculated with respect to temperature^[17] at different initial concentration values and constant mill scale or sludge concentration (100 g/l – mill scale and 50 g/l – sludge) and residence time (5 h):

Table III. Langmuir parameters as a function of temperature. Rolling mill scale concentration = 100 g/l, blast furnace sludge concentration = 50 g/l

Tabla III. Parámetros de Langmuir en función de la temperatura. Concentración de la cascarilla de laminación = 100 g/l, concentración del lodo de horno alto = 50 g/l

Ion	Rolling mill scale			R^2	Blast furnace sludge		
	T (°C)	X_m (mg/g)	b (l/mg)		X_m (mg/g)	b (l/mg)	R^2
Pb^{2+}	20	2.45	0.062	0.994	64.17	0.017	0.990
Pb^{2+}	40	2.72	0.145	0.998	68.23	0.018	0.991
Pb^{2+}	60	2.74	0.751	1	73.65	0.030	0.990
Pb^{2+}	80	2.60	2.005	1	79.87	0.033	0.990

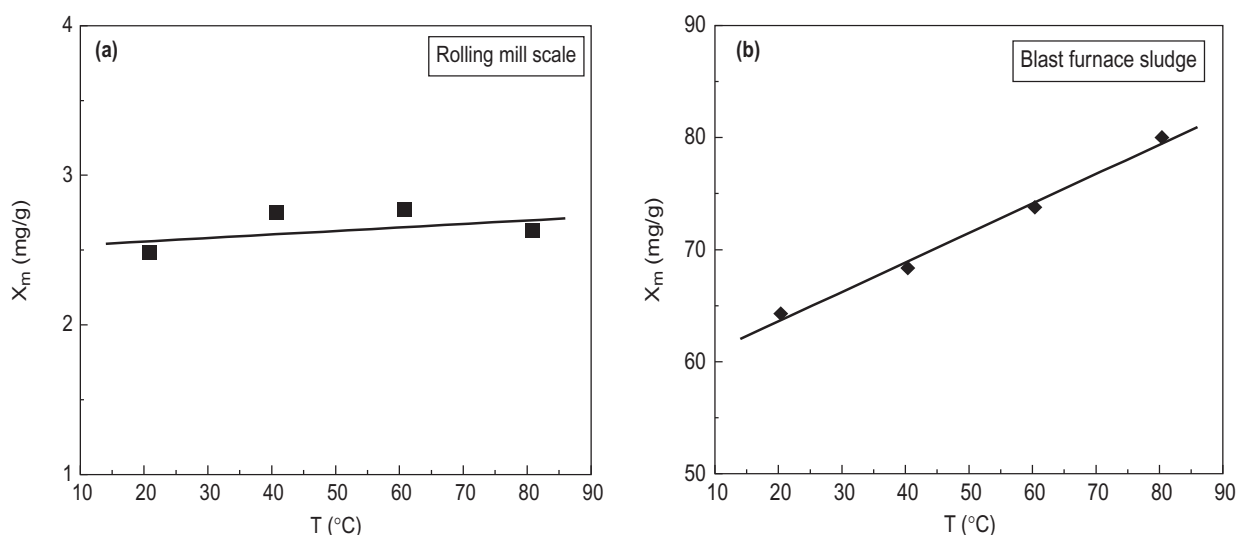


Figure 3. Variation of X_m with temperature. X_m indicate the adsorption capacity of the adsorbent material. Equilibrium time = 5 h, mill scale concentration = 100 g/l and sludge concentration = 50 g/l, (a) Mill scale, (b) Sludge.

Figura 3. Variación de X_m con la temperatura. X_m indica la capacidad de adsorción del material adsorbente. Tiempo de equilibrio = 5 h, concentración de cascarilla = 100 g/l y concentración de lodo = 50 g/l, (a) Cascarilla, (b) Lodo.

$$K_c = \% \text{ adsorción} / 100 - \% \text{ adsorción} \quad (2)$$

Table IV also shows the thermodynamic values ΔG° , ΔH° and ΔS° for the adsorption processes of lead. In the case of the mill scale, the K_c values are practically independent of temperature. K_c values increased with temperature in the case of the Pb adsorption process on sludge. These values were calculated from the K_c values using equation 3 and equation 4:

$$\Delta G^\circ = -RT \ln K_c \quad (3)$$

$$\ln K_c = \Delta H^\circ / RT + \Delta S^\circ / R \quad (4)$$

The ΔG° values (negative ΔG° values, consistent with spontaneous reactions) of Pb decreased with temperature in the case of adsorption process on sludge. ΔH° values were positive, consequently the adsorption of Pb^{2+} on sludge and mill scale may be considered an endothermic process. This result is in agreement with the variation of X_m with temperature shown in table III. Values for ΔS° were positive and didn't show significant variation with temperature.

3.3. Desorption experiments

The resultant products of the adsorption process are products loaded with heavy metals and these residues cannot be incorporated into the sinter feed for recycling due to the fact that these might accumulate

Table IV. Thermodynamic values of the adsorption processes

Tabla IV. Valores termodinámicos de los procesos de adsorción

Ion	C_0 (mg/l)	T (°C)	$\ln K_c$	ΔG° (kJ/mol)	ΔH° (kJ/mol)	ΔS° (kJ/K mol)
Rolling mill scale						
Pb^{2+}	780	20	-0.8	—	—	—
Pb^{2+}	780	40	-0.6	—	—	—
Pb^{2+}	780	80	-0.7	—	—	—
Blast furnace sludge						
Pb^{2+}	2950	20	1.59	-3.88	28.26	0.11
Pb^{2+}	2950	40	1.74	-4.53	28.26	0.11
Pb^{2+}	2950	80	3.41	-10.01	28.26	0.11

on the wall of the blast furnace and damage the refractories.

Previous experiments^[15] have shown that desorption of Pb^{2+} from these loaded steelmaking industry by-products, cannot be achieved using water and can be achieved with HCl 1 M, but chemical attack by diluted mineral acids (HCl 1 M) also promoted the dissolution of the by-product.

Thus the stability of the loaded mill scale was studied for various times to assess the possibility of dumping the material in a landfill. In the experiment performed for a short time "leaching analysis"^[17] mill scale loaded with Pb^{2+} (0.07 mg/g) was used and 200 ml of distilled water was added to 12.5 g of the loaded mill scale in an Erlenmeyer flask. The samples were kept in constant suspension at $pH = 5.00 \pm 0.01$ (adjuste with acetic acid 0.5 mol/l) for 24 h. The results of the leaching analysis shows that the concentration of Pb ($[Pb]_{\text{leached}} = 0.3 \text{ mg/g}$, $Pb_{\text{leached}} = 9.7 \%$) is less than the EPA limit^[18] ($[Pb]_{\text{leached}} = 5.0 \text{ mg/g}$).

"Long times^[15] stability experiment" was carried out over 135 days at 20 °C. Mill scales loaded with Pb^{2+} (1.00 mg/g) were used with 120 ml of distilled water added to 0.5 g of loaded mill scale in Erlenmeyer flasks. The test was carried out at $pH = 5.00 \pm 0.01$ and $pH = 3.00 \pm 0.01$ (adjusted with sulfuric acid 50 % v/v). The results show ($[Pb]_{pH=5.00} = 0$ and $[Pb]_{pH=3.00} = 0.6 \text{ mg/l}$) that at pH 5.00 $[Pb^{2+}]$ under the experimental conditions studied is smaller than the limit defined by the Spanish Law 29/1985^[19] (legal limit = (0.5 - 0.2) mg/l). At pH = 3.0 both $[Pb^{2+}]$ is above their limits under the experimental conditions studied.

Previous studies^[9] with loaded blast furnace sludge had proposed an alternative process to dumping because of its easily leached metal content. This process converts the loaded sludge into pellets using a disc pelletizer with a mixture of calcium carbonate, coke and bentonite^[10]. The pellets obtained are then mixed with SiO_2 and heated to about 1,000 °C in a controlled atmosphere in an electric furnace to release molten iron and the loaded metal together with a slag. The iron, with a purity of approximately 95-96 wt %, may be recycled in the steelmaking process^[9]. This method avoids the dumping of a sludge which, because of its easily leached metal content, is a toxic and hazardous waste.

4. CONCLUSIONS

The present investigation evaluates the use of two steelmaking industry by-products (rolling mill scale and blast furnace sludge) as adsorbents for the elimination of lead ions from aqueous solutions.

The removal of lead occurs through an adsorption process of lead ions on the surface of steelmaking industry material. The experimental results were well fitted, in each case, with the Langmuir isotherms.

The adsorption processes of lead ions on sludge depend on the temperature, with the amount of removed (adsorbed) ions increasing as the temperature rises. The adsorption of the Pb^{2+} on blast furnace sludge can be considered an endothermic process. In the case of adsorption process of lead ions on millscale its adsorption is not dependent on the temperature.

The data obtained shows that rolling mill scale and blast furnace sludge are effective sorbents of Pb^{2+} and perform well over a wide range of concentrations.

The results indicate that the blast furnace sludge, that has a higher specific surface has a greater affinity for the metals than the rolling mill scale, that has a lower specific surface, at all the temperatures studied.

The treated by-products cannot be recycled in the steelmaking process because of their metal content. So these loaded by-products must either be treated to desorb the metals or dumped in a controlled landfill.

The utilisation of the sludge and the mill scale as metallic ions sorbents provides a potential use for these industrial waste products.

REFERENCES

- [1] A. KABATA-PENDIAS AND H. PENDIAS, 2001. *Trace elements in soils and plants*, CRC Press Inc., Florida.
- [2] L. CURKOVIC, S. CERJAN-STEFANOVIC AND A. RASTOVĀN-MIOÉ, *Water Res.* 35(14) (2001) 3436-3440.
- [3] P.D. JOHNSON, M.A. WATSON, J. BROWN AND I.A. JEFCOAT, *Waste Manage* 2 (2002) 471-480.
- [4] F.A. LÓPEZ, M.I. MARTÍN, C. PÉREZ, A. LÓPEZ-DELGADO AND F.J. ALGUACIL *Water Res.* 37 (2003) 3883-3890.
- [5] M.I. MARTÍN, F.A. LÓPEZ, C. PÉREZ, A. LÓPEZ-DELGADO AND F.J. ALGUACIL, *J. Chem. Technol. Biot.* 80 (2005) 1223-1229.
- [6] F.A. LÓPEZ, C. PÉREZ, E. SAINZ AND M. ALONSO, *J. Chem. Technol. Biot.* 62 (1995) 200-206.
- [7] F.J. ALGUACIL, *Rev. Metal. Madrid* 39 (2003) 205-209.
- [8] F. PÉREZ-MORENO, F. PRIETO-GARCÍA, A. ROJAS-HERNÁNDEZ, Y. MARMOLEJO-SANTILLÁN, E. SALINAS-RODRÍGUEZ AND F. PATIÑO-CARDONA, *Rev. Metal. Madrid* 42 (2006) 391-395.
- [9] E. ROMERA, F. GONZÁLEZ, A. BALLESTER, M.L. BLÁZQUEZ AND J.A. MUÑOZ, *Rev. Metal. Madrid* 43 (2007) 29-41.
- [10] F.A. LÓPEZ, F. MEDINA, J. MEDINA AND M.A. PALACIOS, *Ironmaking Steelmaking* 18 (1998) 292-295.
- [11] P. ASHODAN, M. SAXENA AND S.R. ASOLEKAR, *Resour. Conserv. Recy.* 43 (2005) 239-262.
- [12] S. KUMAR, R. KUMAR AND A. BANDOPADHYAY, *Resour. Conserv. Recy.* 48 (2006) 301-314.
- [13] IISI, *The Management of Steel Plant Ferruginous By-Products*, Committee on Environmental Affairs and Committee on Technology (Eds.), 1994, Brussels.
- [14] A. LÓPEZ-DELGADO, C. PÉREZ AND F.A. LÓPEZ, *Water Res.* 32 (1998) 989-996.
- [15] M.I. MARTÍN, Tesis Doctoral, Facultad de Ciencias Químicas, Universidad Complutense de Madrid, 2004.
- [16] M. DÍAZ-PEÑA AND A. ROIG-MUNTANER, *Química Física*, vol. 2, Ed. Alhambra Universidad, Madrid, España (1988), pp. 1034-1041.
- [17] A. LÓPEZ-DELGADO, C. PÉREZ AND F.A. LÓPEZ, *Carbon* 34 (1996) 423- 426.
- [18] FEDERAL REGISTER, 1986. *Toxicity Characteristics Leaching Procedure (TCLP)*, 51(216), Friday, November 7, USA, 40643-40654.
- [19] SPANISH LAW 29/1985, 2 August 1985, Real Decreto 849/1986, 11 April 1986, BOE 103, 30 April, 1986. http://www.gestion-ambiental.com/norma/ley/REAL_DECRETO_849-1986.htm.