ENVIRONMENTAL ENGINEERING

Estudio cinético de la adsorción de iones metálicos de aguas residuales en sub-productos de la industria del carbón

INGENIERÍA AMBIENTAL

Kinetic study of metal ion adsorption from wastewater onto coal industry by-products

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Resumen

Se llevó a cabo un estudio comparativo sobre el uso de cenizas volantes y clinker natural como adsorbentes de metales pesados de agua contaminada a partir de experimentos de adsorción a temperatura ambiente. Las concentraciones de metales pesados en los filtrados se determinaron por espectrometría de emisión atómica por plasma inductivamente acoplado. En los estudios de adsorción en batch, la retención aumento con el aumento del tiempo de contacto, la cantidad de adsorbente y el pH de la solución. La adsorción de los metales a partir de la solución contaminada artificialmente fue Cr>Cu>Pb>Ni>Zn, mientras que a partir de drenaje ácido de mina fue Pb>Zn>As>Fe>Cr>Cu>Ni. Las constantes de primer orden de Lagergren se calcularon para concentraciones iniciales de iones metálicos específicas, dando un excelente ajuste como lo indica el coeficiente de correlación (R^2), con valores próximos o iguales a 1 para el tratamiento de la solución contaminada artificialmente y de 0.25 a 0.99 para el tratamiento del drenaje ácido de mina. Los datos de este estudio revelan que los cationes metálicos en solución acuosa pueden ser adsorbidos exitosamente en cantidades significativas por los adsorbentes usados.

Palabras Claves: Cenizas volantes, Clinker natural, Agua contaminada, Metales pesados, Adsorción.

Abstract

A comparative study on the use of fly ash (FA) and natural clinker (NC) as heavy metal adsorbents from polluted water was carried out using adsorption experiments at room temperature. The concentrations of heavy metals in the filtrates were determined by inductively coupled plasma-atomic emission (ICP-AE) spectrometry. In batch mode adsorption studies, removal increased with an increase of contact time, adsorbent amount and solution pH. Adsorption of metals from artifitially poluted sulution (APS) was Cr>Cu>Pb>Ni>Zn, whereas from acid mine drainage (AMD) was Pb>Zn>As>Fe>Cr>Cu>Ni. The Lagergren's first-order rate constants were calculated for specific initial concentrations of metal ions, giving an excellent fit as indicated by the correlation coefficient (R^2), with values close or equal to 1 for treated APS and from 0.25 to 0.99 for treated AMD. Data from this study reveal that metal cations from aqueous solution can be adsorbed successfully in significant amounts by the used adsorbents.

Keywords: Fly ash; Natural clinker; Polluted water; Heavy metals; Adsorption

1. Introduction

The major sources of wastewater can be classified as municipal, industrial, and agricultural. Different types of polluted aqueous effluents may be produced as a result of mining, containing relatively high levels of heavy metals. AMD is a serious environmental problem associated to the mining industry that result from the oxidation of complex sulphides by atmospheric oxygen and bacteria thus originating the formation of sulphuric acid and the dissolution of iron and heavy metals. Although AMD is naturally occurring, mining activities may greatly accelerate its production because open pit and underground mine walls, overburden and mine waste piles exposes fresh iron and sulphide surfaces to oxygen. Predictions of the future loading of dissolved metals from inactive mine sites suggest that sulfide oxidation and the release of dissolved metals will continue for decades to centuries (Dubrovsky et ál., 1985). Estimated costs for stabilization of these sites are in the billions of dollars (Feasby et ál., 1991). AMD is characterized by a low pH-value and high levels of sulfate and metals (Mohan and Chander, 2000), resulting from the weathering of sulfide minerals, such as pyrite (FeS_2) to release dissolved Fe^{2+}, SO_4^{2-} and H^+, followed by the further oxidation of Fe^{2+} to Fe^{3+} and the precipitation of iron as a hydroxide or similar substances, producing more H^+. AMD typically contains high concentration of dissolved iron which may exists either in the reduced form (Fe^{2+}) or in the oxidized form (Fe^{3+}), and its acidity is comprised of hydrogen ion acidity and mineral acidity (iron, aluminum, manganese and other metal ions depending on the specific geologic setting and metal sulfide). In the United Kingdom, discharges of AMD from abandoned mines contain a variety of heavy metals that adversely affect different hydrographic basins and are exempt from regulatory control.

The most widely used technique of treatment of AMD for the removal of heavy metals consists in the neutralization with limestone ($CaCO_3$) or similar materials, resulting in the precipitation of Fe and Mn and other metal hydroxides and also gypsum ($CaSO_4$). Treatment of AMD with limestone can increase the pH to 6.0-7.5 (Pearson and McDonnell, 1975), allowing the metals to be removed from solution. A number of methods for the removal of heavy metals from AMD have been investigated (Webster et ál., 1998; Feng et ál., 2000; Chartrand and Bunce, 2003; Santos et ál., 2004; Gibert et ál., 2005; Wei et ál., 2005; Kalin et ál., 2006), although adsorption has been the preferred method for heavy metal removal, because it is considered to be a particularly effective technique. However, in general these methods are unsustainable in developing countries due to high capital and operating costs. Chemicals can effectively remove certain toxic substances from polluted media but it is presumed to be costly. Therefore, future work should consider experimental investigation of water treatment technology without chemicals, when AMD is treated with natural adsorbents. Numerous types of adsorbents such as organic and inorganic materials have been tested for their ability to remove heavy metals. Water researchers are seeking cheaper raw materials low-cost sorbents such as zeolites and clay minerals with application in sorption of heavy metals from polluted effluents. Such adsorbents would be a viable replacement or supplement to chemicals, although they should be readily available, economically feasible, and should be regenerated with ease.

Globally, coal industry worldwide produces millions of metric tons per year of coal combustion wastes, which include fly ash, bottom ash, boiler slag, flue gas desulfurization sludge and low-volume wastes, including runoff from coal reserve piles and liquid wastes that are formed during cleaning and routine operations. In general, these wastes are used beneficially in small portions as solid wastes in landfilled, although their disposal poses major challenges and serious environmental problems.

On the other hand, spontaneous combustion of coal seams is a natural phenomenon that has occurred in carboniferous basins. Coal geologists refer as natural clinker to thermally altered sedimentary rocks associated with naturally burned coal seams during the recent geologic past (since early Pliocene time), which are common geologic features that have been reported

throughout the world (De Boer et ál., 2001), covering extensive areas of carboniferous basins, where down cutting of streams exposed coal seams and enhanced the possibility of spontaneous combustion, a natural phenomenon that can occur at any site where deformation, uplift and dissection have exposed coal to the air (Zhang et ál., 2004). However, the degree of thermal alteration produced by burning coal beds is variable, and a single outcrop may contain altered rocks ranging from slightly baked to entirely fused (Cosca et ál., 1989). The use of zeolites in environmental remediation is restricted due to procurement problem and prohibitive cost, which can be sorted by using low-cost raw materials like FA and NC. The purpose of this study was to evaluate the use of these coal by-products in the purification of polluted effluents, comparing the results obtained with model solutions with those obtained with AMD to establish differences in the removal efficiency.

2. Experimental methods and materials

2.1 Starting materials

FA was supplied by the Rugeley Power Station, West Midlands (England), being generated by pulverized coal combustion and classified as Class F FA, which is produced from burning anthracite and bituminous coals. NC was collected in an open pit of the Cerrejón coal mining site, situated in the Guajira department (Colombia). The raw materials were prepared by grinding with a SpectroMill Ball Pestle Impact grinder and sieved on 200 mesh and then ground and particles of < 150 μm selected for sorption experiments. Nitrate salts like $Cu(NO_3)_2.3H_2O$ (99.0% purity, Sigma-Aldrich), $Pb(NO_3)_2$ (analytical grade, Aldrich Chemical Co.), $Zn(NO_3)_2.6H_2O$ (98.0% purity, Sigma-Aldrich), $Cr(NO_3)_3.9H_2O$ (97.0% purity, Fluka) and $Ni(NO_3)_2.6H_2O$ (analytical grade, Aldrich Chemical Co.) of the required metals were used to formulate the APS. The correct weight of the nitrate salts and other compounds, such as CH_3COOH (99.5% purity, Aldrich Chemical Co.), $C_6H_{12}O_6$ (analytical grade, Sigma-Aldrich), $CaCl_2$ (95.0% purity, Merck), KCl (99.9% purity, Aldrich Chemical Co.), NH_4Cl (analytical grade, Aldrich Chemical Co.), KH_2PO_4 (99.9% purity,

Aldrich Chemical Co.), $MgSO_4$ (99.0% purity, Fisher), were then weighed out and dissolved in distilled water to formulate the artificially polluted stock solutions (1000 mg/l) containing the selected metals. AMD used in this study was collected from a deep transient pond from rainfall between spoil heaps by the entry road of the Parys Mountain copper-lead-zinc deposit of Anglesey (North Wales), which is strongly acidic (pH < 2) and metal-rich due to the oxidation of sulphide minerals, and its orange-brown colour is due to the very high concentrations of ferric iron in solution.

2.2 Adsorption experiments and water analyses

Batch sorption tests were carried out at room temperature using FA and NC as sorbents. Dosages of 0.25 or 0.5 g of sorbent were mixed with 20 ml of APS or AMD in PVC plastic containers by continuous mechanical shaking at a speed of 150 rpm and different contact time intervals (5, 19, 30, 45, 60, 120, 180, 240 and 300 minutes for APS, and 5, 19, 30, 45, 60, 120, 180, 240 and 1440 minutes for AMD) to explore their ability to remove heavy metals. The mixtures were removed from the shaker and filtered. The leachates stored in a refrigerator for chemical analyses. All measurements were done according to the Standard Methods for the Examination of Water and Wastewater. Analysis of the APS and the leachates obtained after batch experiments were initially performed using pH (pH 211 Auto-calibration bench pH/mV meter - Hanna instruments) and electrical conductivity (Conductivity meter - version Cond 315i - WTW). The metal concentrations were determined using a Thermo Jarrell-Ash ICAP-9000 ICP-AE Spectrometer.

3. Results and discussion

3.1 Water treatment experiments

3.1.1 Batch experiments using APS

Raw materials (FA and NC) were investigated in terms of their potential as adsorbents during the treatment of model solutions artificially polluted with selected metals. The values of pH, EC and concentration of metal ions in the APS and those of

the leachates obtained after treatment are summarized in Table 1. The kinetics of the neutralization reaction was investigated by monitoring the pH and electrical conductivity (EC).

Figure 1 illustrates the variation of solution pH and EC throughout the time during the batch reactions of FA and NC with the APS. As shown in Figure 1a, an almost constant pH trend was observed using NC (4.53-4.99), with no breakthrough to alkaline pH. However, FA caused pH increasing rapidly from 3.82 to 10.76 within the first 5 minutes. This cannot be explained as the result of the free CaO present in FA, taking into account that FA is a class F $[(SiO_2+Al_2O_3+Fe_2O_3) \geq 70\%]$ with a very low content of CaO. Therefore, during the equilibration of FA with the aqueous media, the neutralization of the APS's pH can be attributed to the fact that the FA surface is spanned by charged OH-silanol groups and hydrolysis of these surface-SiOH sites (Hendricks, 2005). The reaction rate decreases as equilibrium is approached, with an apparent equilibrium pH of 11.80 being reached within 1 hour. The lack of buffering capacity for the APS can be attributed to the very low concentration of Fe^{3+}/Fe^{2+}, Al^{3+}, Mn (Uhlmann et al., 2004). The pH had a very important role in the adsorption/removal of the contaminants probably due to the charge developed on the surfaces of the adsorbent as the pH increase. The EC (Figure 1b) also shows an abrupt increase from 3.76 to 7.94 mS/cm within the first 5 minutes, which becomes stable after 1 hour of contact time, when FA was used as sorbent. However, NC shows a very constant behaviour.

Table 1. pH, EC and metal ion concentration data in the raw and treated APS.

Contact time (min)	pH	E C (mS/cm)	T (°C)	Heavy metal concentration (ppm)				
				Cu	Pb	Zn	Cr	Ni
APS	3.82	3.76	15.5	8.12	6.35	3.56	8.32	6.27
Batch reaction of FA								
5	10.76	7.94	16.60	0.05	0.30	0.02	0.04	0.31
10	11.2	9.44	16.80	0.00	0.00	0.00	0.10	0.00
30	11.3	10.27	16.60	0.00	0.00	0.00	0.08	0.00
45	11.67	13.45	16.90	0.00	0.00	0.00	0.06	0.00
60	11.8	13.31	17.20	0.00	0.00	0.00	0.08	0.00
120	11.67	15.08	17.40	0.00	0.00	0.00	0.10	0.00
180	11.77	14.53	18.00	0.00	0.00	0.00	0.09	0.00
240	11.71	14.18	18.50	0.00	0.00	0.00	0.08	0.00
300	11.9	15.26	19.10	0.00	0.00	0.00	0.10	0.00
Batch reaction of NC								
5	4.53	4.32	16.4	1.76	1.85	2.32	0.01	1.81
10	4.99	4.63	16.3	1.29	1.63	2.17	0.01	1.57
30	4.93	4.14	16.9	1.69	1.70	2.07	0.02	1.68
45	4.85	4.26	16.9	1.42	1.87	2.27	0.02	1.82
60	4.75	4.3	17.2	1.33	1.70	2.14	0.01	1.60
120	4.68	4.16	18.1	1.35	1.49	1.86	0.03	1.45
180	4.82	4.25	18.4	1.40	1.61	1.87	0.03	1.54
240	4.92	4.15	18.8	1.20	1.53	1.85	0.04	1.46
300	4.84	4.08	16.6	1.24	1.51	1.83	0.04	1.43

APS, artificially polluted solution; FA, fly ash; NC, natural clinker
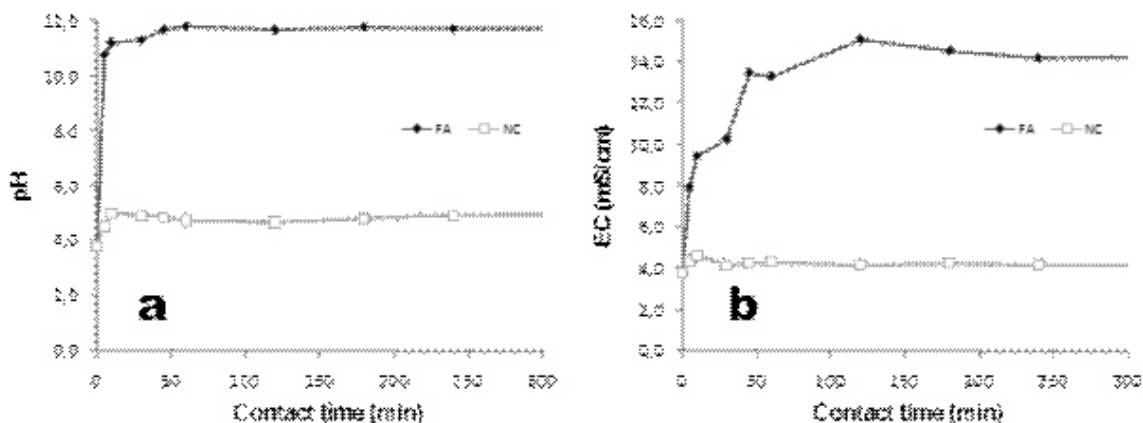
Figure 1 . pH (a) and EC (b) variation as a function of time in APS treated with coal by-products. Starting reaction conditions: pH = 3.82, EC = 3.76 mS/cm, sorbent dosage = 0.5 g, and volume of APS = 20 ml.

The kinetics of the metal ions adsorption was also studied over 24 hours. Metal removal trends as a function of contact time after batch reaction are illustrated in Figure 2. Results indicate that FA produced a steep decrease in Cu, Pb, Zn and Ni concentration within the first 5 minutes, reaching very low residual concentrations. However, after 10 minutes plateau values were reached for the rest of the time intervals, indicating a complete removal. Cr shows an abrupt increase in concentration from 5 to 10 minutes due to the dominant occurrence of $Cr(OH)_4^-$ at pH>10, which increases the solubility of Cr^{3+}. It decreases from 10 to 45 minutes and increase again from 45 to 120 minutes. Cr tends to stabilize at values between 0.08 and 0.11 ppm. With the exception of Cr, the heavy metal exchange character is irreversible. In general, NC produced inconsistency in the variation of heavy metal concentration, which is shown by the fluctuations observed during the batch experiments, although a lower sorption of Zn, Pb, Ni and Cu was observed which can be attributed to the higher selectivity to Cr by NC. The poor ion-uptake capacity of NC can be explained by the competition between hydronium ions and metal ions for exchange sites (Hendricks, 2005).

The removal efficiency of metal ions by FA and NC produced the following ranges: Cu from 93 (NC) to 100% (FA); Pb from 96 (NC) to 100% (FA); Zn from 50 (NC) to 100% (FA); Ni from 78 (NC) to 100% (FA); Cr 100% (FA and NC). All metal ions were rapidly removed by FA within 30 minutes with 99-100% of the metal removal achieved in the first 5 minutes. However, NC produced lower metal removal (40-84%), except for Cr (100%). Therefore, the competition for sorbent adsorption sites in the presence of Cr produced a decrease in the uptake of the other metal ions. No significant adsorption was observed after 60 minutes of reaction.

The immobilization of heavy metals from aqueous media is a complex process, which consists of ion exchange and adsorption and is likely to be accompanied by precipitation of metal hydroxide complexes on active sites of the particle surface (Peric et al., 2004). The addition of an alkaline material such as FA to the APS increased the pH>9 and most of metal ions could be hydrolyzed and precipitated as suggested by Evangelou and Zhang (1995). The efficiency of the tested FA with respect to metal retention and/or metal concentration control during its application for the treatment of metal-bearing aqueous media is governed by parameters like contact time, pH, temperature and FA origin (Hequet et al., 2000). On the other hand, mechanisms of interactions, such as precipitation and adsorption, between a specific metal and this coal-by product are strongly influenced by pH.
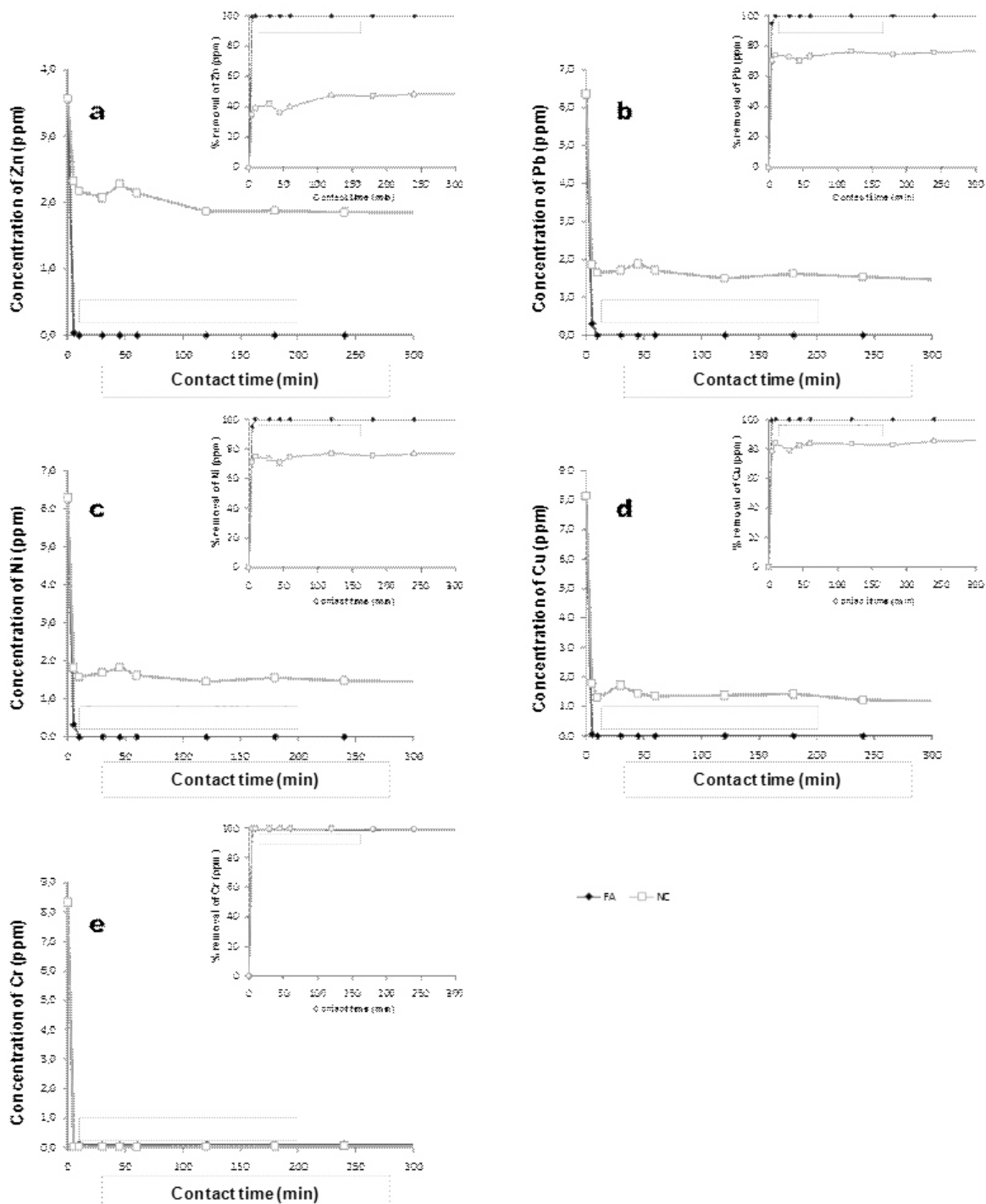
Figure 2. Heavy metal concentration variation as a function of time during the adsorption batch experiments with the following starting reaction conditions: pH = 3.82, EC = 3.76 mS/cm, sorbent dosage = 0.5 g, and volume of APS = 20 ml.

Table 2. pH, EC and concentration data of metal ions in the raw and treated AMD.

Contact time (min)	pH	E C (mS/cm)	T (°C)	Heavy metal concentration (ppm)						
				Cu	Pb	Zn	Cr	Ni	As	Fe
AMD	1.96	3.77	16.00	31.90	2.10	73.83	0.05	0.02	4.81	1355.33
Batch reaction										
5	2.54	6.47	20.60	56.64	1.35	52.12	0.36	0.12	3.03	913.57
10	2.56	6.93	20.60	53.73	1.23	50.52	0.31	0.08	2.92	901.30
30	2.51	5.85	20.90	53.65	1.30	51.35	0.39	0.12	3.01	904.80
45	2.13	5.73	20.80	66.58	1.96	62.85	0.70	0.51	3.59	1068.04
60	2.46	5.48	21.50	55.73	1.60	52.41	0.58	0.42	3.01	906.62
120	2.38	5.01	21.20	55.28	1.41	51.86	0.46	0.24	3.00	914.04
180	2.38	5.00	21.70	56.62	1.58	53.49	0.55	0.38	3.03	941.46
240	2.34	5.13	22.70	55.17	1.46	53.23	0.54	0.32	3.13	916.34
1440	2.66	5.04	20.90	79.07	1.96	72.35	0.79	0.52	4.13	1156.62
Batch reaction										
5	2.42	8.80	20.60	48.55	1.14	48.26	0.05	0.03	2.25	853.62
10	3.04	8.91	20.50	49.74	1.17	49.41	0.05	0.03	2.31	891.74
30	2.64	8.87	20.70	48.64	1.15	49.11	0.05	0.04	2.30	864.14
45	2.00	8.93	21.00	49.49	1.23	49.29	0.04	0.07	2.33	882.10
60	1.92	8.82	21.20	49.37	1.68	49.26	0.23	0.51	2.29	877.85
120	1.92	8.76	21.40	48.76	1.22	49.53	0.042	0.05	2.31	883.55
180	1.92	8.93	21.50	50.30	1.26	50.72	0.06	0.09	2.38	909.89
240	1.86	8.95	22.40	53.79	1.29	52.88	0.03	0.15	2.62	890.04
1440	1.86	10.38	20.50	76.41	2.40	71.04	0.39	0.85	3.61	1168.67

AMD, acid mine drainage; FA, fly ash; NC, natural clinker

3.1.2 Batch experiments using AMD

In the following section we discuss the results of adsorption experiments performed with FA and NC to treat AMD. Table 2 summarizes the values of the pH, EC and concentration of metal ions in the untreated AMD and those of the leachates obtained after treatment. Here, we consider very important to examined the As and Fe removal, taking into account that As is known to be a hazardous contaminant in drinking water that causes different diseases, and Fe that generally not produce polluted effluents in terms of metal toxicity, but can be highly ferruginous and visibly unsightly as Fe oxyhydroxide precipitates are deposited as coating effectively smothers the environment and prevents life from flourishing (McGinness, 1999). Figure 3 shows the pH and EC trends for the neutralization reactions between the AMD and the raw materials. A pH increase from 1.96 to 2.54 (FA) and 2.42 (NC) was observed within 5 minutes. The reaction rates decrease as equilibrium is approached. The pH was stabilized within 1 hour when the raw materials were reacted with AMD. The final pH ranges from 1.86 to 2.66. In this case, there was also not observed breakthrough to alkaline pH, which indicates that contact time did not affect the alkalinity using a dosage of 0.25 g. However, Ríos et al. (2008) have determined that using a higher sorbent dose a strong change in pH was observed. EC ranges from 5.00-6.93 (FA) to 8.76-10.38 (NC) mS/cm were obtained. We have carried out additional experiments increasing the sorbent dose (1 g), resulting an increase of pH in the batch experiments after 24 hours of contact time, with pH values between 4.20 and 9.43, except when NC was used (pH $\geq$ 1.85).
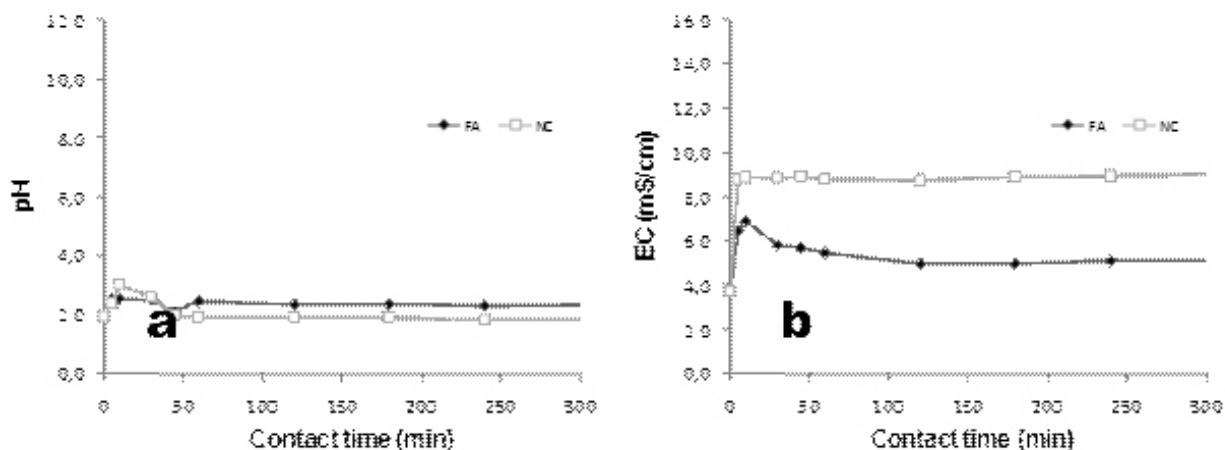
Figure 3. pH (a) and EC (b) variation as a function of time in AMD treated with coal by-products. Starting reaction conditions: pH = 1.96, EC = 3.77 mS/cm, sorbent dosage = 0.25 g, and volume of AMD = 20 ml.

Metal removal trends as a function of contact time after batch reaction (results not shown) reveal that when FA or NC were added to the AMD a sudden drop in Pb, Zn, Fe and As and a sudden increase in Cu, with a small increase in Ni was observed after 5 minutes. An abrupt increase in Cu, Pb, Zn, Ni, Fe and As was observed after 45 minutes and then decrease to stabilize, when FA was used. A similar behaviour was observed using NC as sorbent, although just for Pb and Ni and after 1 hour. The addition of FA and NC produced an abrupt decrease in those elements after 45 minutes, except Cr (for FA), Ni and Cu, which show a strong reversal character. In general, Cr shows a constant behaviour and very low concentrations, except when FA was used as a consequence of the dominant occurrence of chromium species in acidic conditions, which increases the solubility of Cr^{3+} in FA). The % of removal efficiency show that the use of raw materials produced the following ranges Pb from 42-46 to 94-96%; Zn from 32-33 to 40-42%; As from 39-53 to 99-100%; Fe from 33-37 to 100%. Cu, Cr and Ni produced negative % values, which indicate the poor removal efficiency.

3.2 Sorption of metal ions from aqueous solutions on the sorbents

It has been more than a hundred years since Lagergren suggested the first-order equation for describing liquidsolid adsorption systems in 1898, and it is still widely applied today. Lagergren's kinetics equation may have been the first one in describing the adsorption of liquid-solid systems based on solid capacity (Ho, 2004) and has been most widely used for the adsorption of an adsorbate from an aqueous solution. In order to distinguish kinetics equation based on adsorption capacity of solid from concentration solution, Lagergren's first-order rate equation has been called by Ho and McKay (1999) as pseudo-first order.

The sorption process considered here refers to a sorbent (FA or NC) and a polluted aqueous media (APS or AMD) containing dissolved metal ions to be sorbed. There is a strong affinity of the sorbent for the metal ions, which are attracted into the sorbent and bound there by different mechanisms. Ríos et al. (2008) consider that the main mechanism for metal uptake is precipitation of metal complexes on the surface of the sorbent and not sorption. The metal ion uptake by the sorbent is evaluated on how much metal ion can be attracted and retained in an immobilized form and can be determined by the equation (1):

$$q_e = (C_o - C_t)V/m \qquad (1)$$

C_o is the initial concentration in the untreated solution and C_t is the concentration of metal ion in solution after adsorption at a specific time (t), V is the volume of the metal-bearing solution contacted with the sorbent (L) and m is the mass of the sorbent added (g).

The removal efficiency of metal ions by the adsorbent was calculated using the expression:

% Removal Efficiency = 100(Co - Ct)/Co

The kinetics of heavy metal adsorption on FA and NC were modelled using the pseudo-first order kinetic equation suggested by Lagergren (1898), which can be written as

$$\frac{dq_t}{dt} = k_1 \left(q_e - q_t \right) \tag{2}$$

The term k_1 (min^{-1}) is the first order adsorption rate constant, q_e is the amount of metal adsorbed at equilibrium and q_t is the amount adsorbed at a specific time (t). Integrating equation (2) from $q_t \geq 0$ at $t \geq 0$, gives

$$\ln \frac{q_e - q_t}{q_e} = -k_1 t \tag{3}$$

Or

$$q_t = q_e \left(1 - e^{-k_1 t} \right) \tag{4}$$

(Non-linear form)

The first order rate equation applied throughout all the contact times. The values of q_t were non-linearly correlated with t. The plots of q_t against t for the metal ions using the raw sorbents are illustrated on Figures 4 and 5.
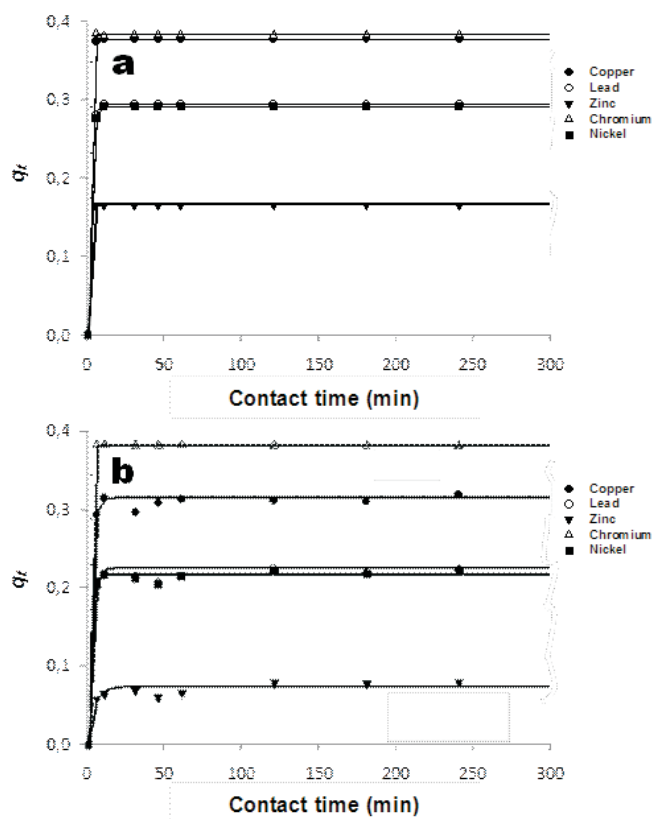

Figure 4. Lagergren non linear plots (first order) at room temperature for metal ion adsorption on (a) FA and (b) NC from APS.
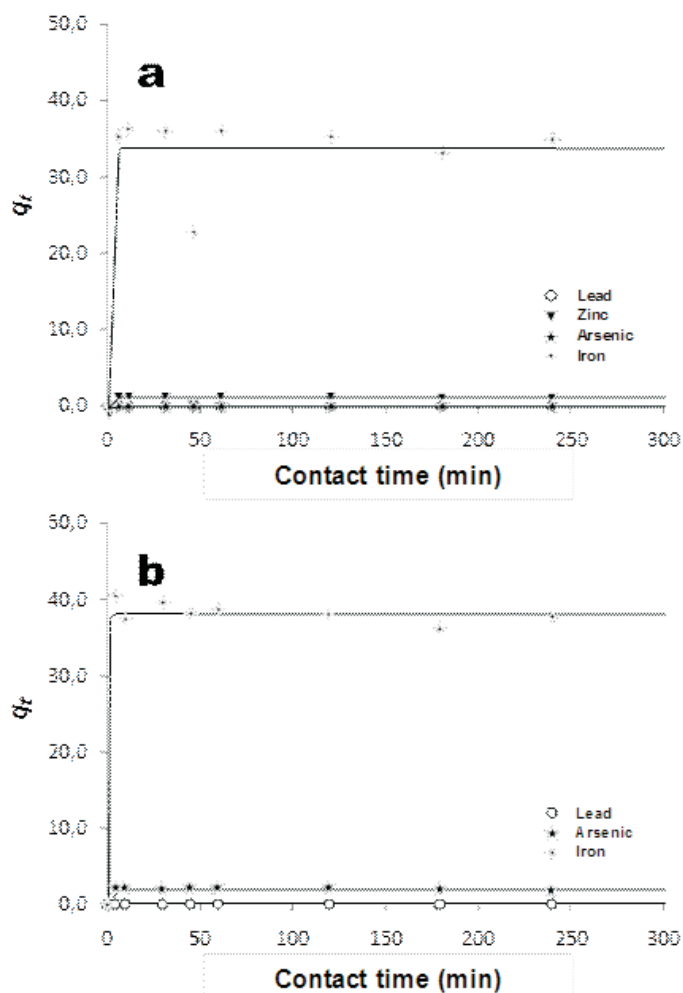
*Figure 5. Lagergren non linear plots (first order) at room temperature for
the metal ion adsorption on (a) FA and (b) NC from AMD.*

The conformity between experimental data and the model predicted values was expressed by the correlation coefficients (R^2). R^2 values for the pseudo-first order equation are shown on Tables 3 and 4, with values close or equal to 1 for treated APSs, whereas using AMDs, values ranging from 0.25 to 0.99 were obtained using the raw materials. The treatment of AMD with the raw materials produced low R^2 values, which indicates a poor correlation. In general, the correlation coefficients for these plots are excellent (in most of the cases >0.99), indicating that the model successfully describes the kinetics of the adsorption. The calculated slopes and intercepts from the plots were used to determine the rate constant k_1 and theoretical equilibrium capacity (q_e) and their values are depicted on Tables 3 and 4. The experimental q_e values were compared to q_e values determined by pseudo-first order rate kinetic model. The q_e values exhibit excellent agreement with the experimental q_e values.

4. Conclusions

A cost effective treatment procedure was proposed for the removal of heavy metals from

Table 3. Pseudo-first order kinetic parameters for the metal ion adsorption on the raw materials using APS.

Parameters	Pb	Zn	As	Fe	Cr
Fly ash					
$k_1 (min^{-1})$	1.020	0.610	0.990	11.200	0.600
q_e (experimental)	0.345	0.254	0.143	0.329	0.251
q_e (theoretical)	0.324	0.254	0.143	0.329	0.251
R^2	1.000	1.000	1.000	0.999	1.000
Natural clinker					
$k_1 (min^{-1})$	0.532	0.496	0.287	743.500	0.588
q_e (experimental)	0.301	0.245	0.071	0.332	0.198
q_e (theoretical)	0.274	0.195	0.063	0.332	0.188
R^2	0.984	0.920	0.913	1.000	0.993

Table 4. Pseudo-first order kinetic parameters for the metal ion adsorption on the raw materials using AMD.

Parameters	Pb	Zn	As	Fe	Cr
Fly ash					
$k_1 (min^{-1})$	231.510	26.650	9.644	49.122.150	---
q_e (experimental)	0.050	1.650	0.135	35.120	---
q_e (theoretical)	0.045	1.460	0.130	33.790	---
R^2	0.336	0.415	0.645	0.880	---
Natural clinker					
$k_1 (min^{-1})$	6.410	241.560	9.644	20.110	---
q_e (experimental)	0.060	1.850	0.180	37.220	---
q_e (theoretical)	0.570	1.730	0.130	37.900	---
R^2	0.249	0.505	0.647	0.990	---

APS and AMD through adsorption on FA and NC. Removal increased with increasing contact time, adsorbent amount and solution pH. The Lagergren's pseudo-first-order equation shows an excellent fit as indicated by the correlation coefficient (R^2). Data from this study reveal that metal cations from aqueous solution can be adsorbed successfully in significant amounts by the used adsorbents. The results of this investigation both contribute to the mitigation of environmental problems and turns a coal by-products, such as FA and NC, into attractive and useful products. However, further research studies on the use of these industrial wastes as starting materials in the synthesis of highly crystalline zeolitic materials under well-optimized conditions and to estimate if these materials are potentially useful for wastewater treatment or not to establish the factors affecting their application and to evaluate the social and environmental effects of their proposed utilization approach.

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6. References

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