Lead Removal from Water by Adsorption on Spent Coffee Grounds

Roberto Lavecchia, Franco Medici*, María Silvina Patterer, Antonio Zuorro

Dipartimento di Ingegneria Chimica, Materiali e Ambiente, "Sapienza" Università di Roma, Via Eudossiana 18, 00184 Roma (Italy)
franco.medici@uniroma1.it

Industrial water and drinking water contamination by lead is recognized as a public health problem in several countries of the world, including Italy. Lead is on the second position on the Agency for Toxic Substances and Disease Registry (ATSDR) list for dangerous elements. The Environmental Protection Agency (EPA) has also recognized lead as a probable human carcinogen.

In this study the potential of spent coffee grounds (SCG) for the removal of lead from contaminated water was investigated. Batch experiments were performed at 25 °C on untreated SCG. The results obtained showed that the adsorption equilibrium of lead on SCG is well described by the Langmuir equation, with a maximum adsorption capacity of 2.46 mg g^{-1}. Overall, this study strongly supports the use of SCG for the removal of lead, and probably of other metal species, from industrial and drinking waters.

1. Introduction

Water pollution by heavy metals is globally recognized as an increasing environmental problem since the starting of the industrial revolution in 18th century (Dávila-Guzmán et al., 2011). Heavy metals are elements having atomic weight between 63.5 and 200.6, and a specific gravity greater than 5.0 (Fu and Wang, 2010). Their release into the environment represents a real concern for humankind and environmental toxicology. Since heavy metals are not biodegradable and have a long biological half-life, they accumulate within the organism, where they may cause poisoning, illnesses and neurological disorders.

Lead is the second element in the ranking of interest priority owing to its potential for causing brain damage to the central nervous system (Duarte Zaragoza et al., 2010). Furthermore, lead damages kidney, liver, reproductive system, basic cellular processes and brain functions. In fact, the World Health Organization (WHO) recommends the limit dose of 10 µg L^{-1} not to be exceeded.

Thus, strict environmental protection legislation and public environmental concerns lead the search for novel techniques to remove heavy metals from water as lead enters the body mainly by ingestion (ATSDR, 2007).

Heavy metals are removed from wastewater by conventional techniques such as membrane filtration, chemical precipitation, adsorption, electro-coagulation, chelation, inverse osmosis and ion exchange (Dhir, 2014). Adsorption process is preferred due to its efficiency of removal from dilute solutions (Azouaou et al., 2010).

Although the use of commercially available activated carbon and zeolites of different grades is still very popular, these processes are very expensive. Thus, there is a growing demand for more efficient, economic and easily available adsorbents for the removal of lead, particularly if the substrates are waste (Zuorro and Lavecchia, 2010, 2011, 2012, 2013).

In recent years, natural materials like bauxite, lignite, wood, coal, and agricultural waste materials such as rice and wheat waste, tea and coffee waste, and fruit peels have been tested aiming at reducing costs of production (Dhir, 2014).

The present study was carried out to compare the potential of adsorption of lead onto natural materials and agricultural residues. Another aim of this work was to investigate the adsorption equilibrium of lead on to the more efficient adsorbent in order to estimate the parameters that describe the phenomenon.

2. Experimental

2.1 Materials
Lead nitrate (CAS No. 10099-74-8) with purity >99% was purchased from Carlo Erba s.p.a. (Milan, Italy). Synthetic lead solutions were prepared by adding an appropriate amount of lead nitrate to distilled water.
Bauxite was obtained from sedimentary deposits quarried in Texas (USA), bentonite was extracted from Tivoli (Roma, Italy). Two volcanic lithotypes were also used as adsorbents: a liparite from the Lipari Volcano (Messina, Italy) and a pozzolana from the Alban Hills Volcano (Lunghezza, Italy).
Spent coffee grounds (SCG) were obtained from industrial plant located in Ciampino (Roma, Italy), coffee silverskin was from roasting plants in Trieste (Trieste, Italy) and Pomezia (Roma, Italy) and green coffee was from a production plant in Peru. Finally, olive pomace was from Villa Latina (Frosinone, Italy).

2.2 Methods
The adsorbent materials were preliminary ground and sieved by ASTM No. 35 sieve (nominal mesh opening ≤ 500 μm). The resulting materials were washed with distilled water and dried at 110 °C in an electric over for three hours. Then they were cooled in air to room temperature and stored in closed containers.
To assess the ability of each adsorbent to remove lead from water, preliminary batch tests were conducted. One g of any ground adsorbent was contacted with 100 mL of 10 mg L^{-1} lead solution for 3 h under agitation of 300 rpm. After this time, the samples were filtered on paper and the residual lead concentration was measured. A similar procedure was used for equilibrium experiments.
In these experiments the liquid-to-solid ratio was set at 100 mL g^{-1} and the initial lead concentration was varied between 5 and 300 mg L^{-1}.
Batch experiments were performed at room temperature (25 ± 2 °C). The concentration of lead in the aqueous solution was determined by an X-ray fluorescence spectrometer (TRACeR IV, Bruker AXS, Germany). Standard lead solutions at concentrations ranging from 3 to 300 mg L^{-1} were used to construct the calibration curve (ASTM, 2008; Kaiser and Wright, 2011).

3. Results and discussion

3.1 Preliminary batch tests
Batch screening tests gave the results presented in Table 1. As can be seen bauxite, coffee silverskin and SCG were the best adsorbents, with percent lead removal efficiencies of 97%, 93% and 85%, respectively.
Despite their high adsorption capacity, bauxite and coffee silverskin were excluded from the subsequent experiments because of some disadvantages. In particular, bauxite is a raw material for aluminum production which makes it a valuable material. It also needs a preliminary grinding treatment before its use as an adsorbent. Coffee silverskin has a low density which makes it difficult to deal with and also to be recovered after adsorption. On the other hand, SCG are an agricultural waste with no commercial value. They are abundantly available in Italy and therefore represent an economic adsorbent material. Because of these reasons and their significantly high lead removal capacity, SCG were selected for subsequent experiments.

Table 1: Results of preliminary screening tests. C_f [mg L^{-1}] is the final concentration of lead in solution, Ads % is the percent lead removal.

Material	C_f, mg L^{-1}	Ads %
SCG	1.50	85.0
Green coffee	2.10	79.0
Coffee silverskin (var. *arabica*, Illy)	0.80	92.0
Coffee silverskin (var. *robusta*, Illy)	0.80	92.0
Coffee silverskin (var. *arabica*, Trombetta)	0.70	93.0
Coffee silverskin (var. *robusta*, Trombetta)	0.70	93.0
Bauxite	0.30	97.0
Olive pumice	2.20	78.0
Bentonite	2.90	71.0
Liparite	1.70	83.0
Pozzolana	1.60	84.0

3.2 SCG characterization
The chemical and mineral composition of SCS was derived from the literature (Ballesteros et al., 2014; Pujola et al., 2013). The most significant data are summarized in Table 2 and Table 3.

XRF spectroscopy analysis of SCG was carried out to obtain qualitative information about the composition of this material. As apparent from Figure 1, potassium, calcium, sulfur and phosphorus were the elements present in higher amounts.

Table 2: Chemical composition of SCG.

Component	Amount (g/100 g dry material)
Cellulose (Glucose)	12.40 ± 0.80
Emicellulose	39.10 ± 1.94
Arabinose	3.60 ± 0.52
Mannose	19.70 ± 0.85
Galattose	16.43 ± 1.66
Xylose	n.d.
Lignin	23.90 ± 1.70
Insoluble	17.59 ± 1.56
Soluble	6.31 ± 0.37
Fat	2.29 ± 0.30
Ashes	1.30 ± 0.10
Protein	17.44 ± 0.10
Nitrogen	2.79 ± 0.10
C/N ratio	16.91 ± 0.10
Total dietary fiber	60.46 ± 2.19
Insoluble	50.78 ± 1.58
Soluble	9.68 ± 2.70

Table 3: Mineral composition of SCG.

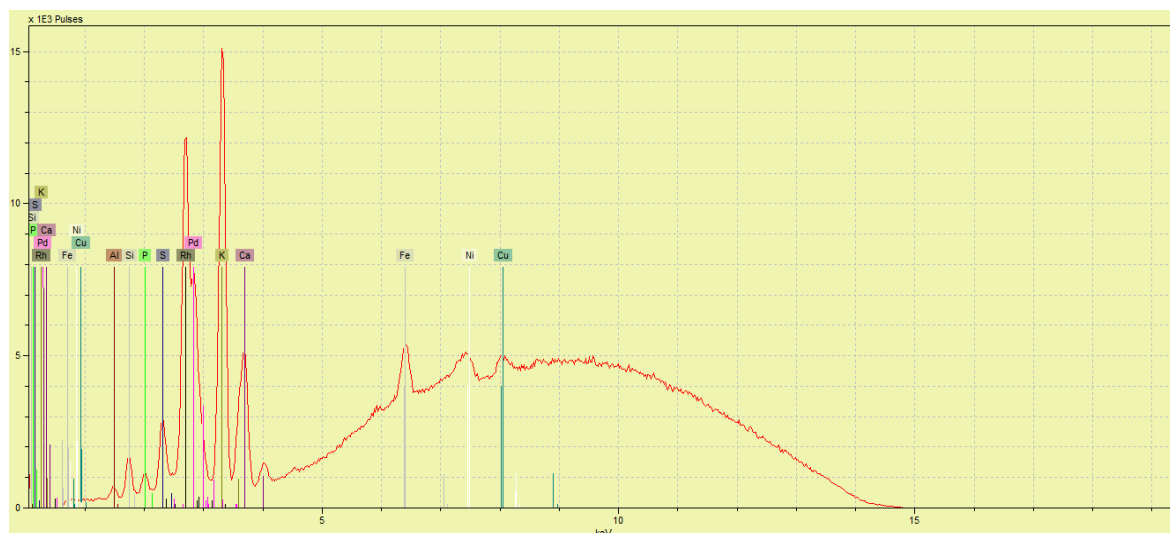| Mineral element	Amount (mg/kg dry material)
Potassium	11,700 ± 0.01
Calcium	1,200 ± 0.01
Magnesium	1,900 ± 0.01
Sulfur	1,600 ± 0.01
Phosphorus	1,800 ± 0.01
Iron	52.00 ± 0.50
Aluminum	22.30 ± 3.50
Strontium	5.90 ± 0.01
Barium	3.46 ± 0.05
Copper	18.66 ± 0.94
Sodium	33.70 ± 8.75
Manganese	28.80 ± 0.70
Boron	8.40 ± 1.10
Zinc	8.40 ± 0.20
Cobalt	15.28 ± 0.05
Nickel	1.23 ± 059
Lead	<1.60

Figure 1: XRF spectroscopy analysis of SCG

3.3 Equilibrium studies

The time needed to reach equilibrium was of the order of 3 h and independent of the initial lead concentration (Figure 2). The equilibrium concentration in the liquid phase (c_e) were determined after this time and the concentration in the adsorbed phase (q_e) was calculated from a mass balance of lead as:

$$q_e = \frac{V_L}{m}\left(c_0 - c_e\right) \tag{1}$$

where V_L is the volume of the aqueous solution, m is the mass of adsorbent, c_o e c_e are the initial and the equilibrium lead concentrations. Different models were used to analyse the equilibrium data (Djati Utomo and

Hunter, 2009): the Langmuir equation (Eq. 2), the Freundlich equation (Eq. 3) and the Dubinin-Radushkevich (D-R) equation (Eq. 4). They were used in the following forms:

$$q_e = \frac{q_{max}bc_e}{1+bc_e} \qquad (2)$$

$$q_e = K_F c_e^{1/n} \qquad (3)$$

$$q_e = q_{max} \exp\left(-B\left(RT\ln\left(1+\frac{1}{c_e}\right)\right)^2\right) \qquad (4)$$

In Eq. (2) q_{max} is the maximum adsorption capacity (mg g^{-1}), corresponding to a complete monolayer on the adsorbent, and b is the Langmuir constant (L mg^{-1}), which can be related to the affinity of the adsorbing species for the adsorption sites on the solid.

In Eq. (3) K_F is the Freundlich adsorption capacity (mg g^{-1}) and n is a dimensionless constant that represents the adsorption intensity. It is generally stated that values of n in the range 2–10, 1–2 and <1 indicate, respectively, good, moderate and poor adsorption characteristics (Lavecchia et al., 2012).

In Eq. (4) B (mol^2 kJ^{-2}) is a constant related to the adsorption energy, R (8.314 J mol^1 K^{-1}) is the gas constant, and T (K) is the absolute temperature. The constant B gives the mean free energy E (kJ mol^{-1}) of adsorption per molecule of the sorbate when it is transferred to the surface of the solid from infinity in the solution. It can be computed from the following relationship:

$$E = \frac{1}{(2B)^{0.5}} \qquad (5)$$

This parameter gives information about the adsorption nature. Values of $E < 8$ kJ mol^{-1} indicates physical adsorption meanwhile a magnitude of E between 8 and 16 kJ mol^{-1} evidences a chemisorption process (Azouaou et al., 2010).

The parameters appearing in the above equations were obtained by fitting the experimental data to the linearized form of each equation, as shown in Figures 3–5. We obtained: $q_{max} = 2.46$ mg g^{-1} and $b = 0.15$ L mg^{-1} for the Langmuir equation, $K_F = 0.51$ mg g^{-1} and $n = 3.12$ for the Freundlich equation and $q_{max} = 1.81$ mg g^{-1}, $B = 0.76$ mol^2 kJ^{-2} and $E = 0.81$ kJ mol^{-1} for the D-R equation. Examination of the correlation coefficients (R^2) reveals that the Langmuir equation provided the best fit to the data. This can be better appreciated from Figure 5, where the adsorption isotherms resulting from the three models are plotted together with the experimental data.
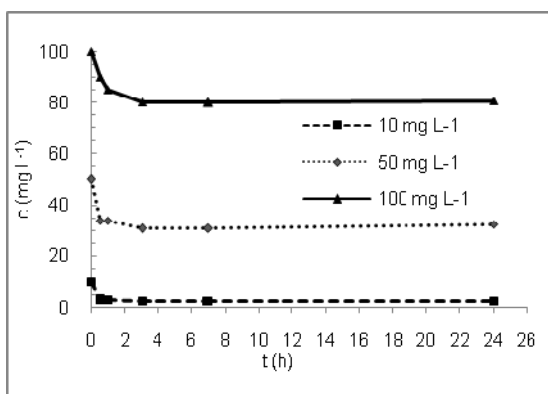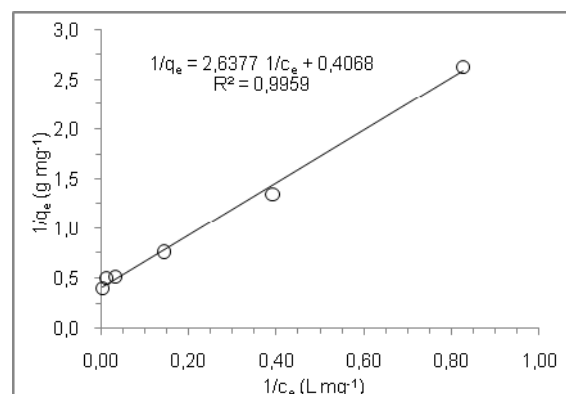

Figure 2: Lead concentration decay curves

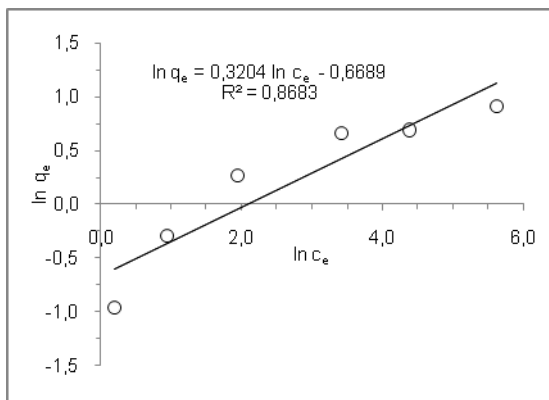
Figure 3: Langmuir plot for lead adsorption on SCG

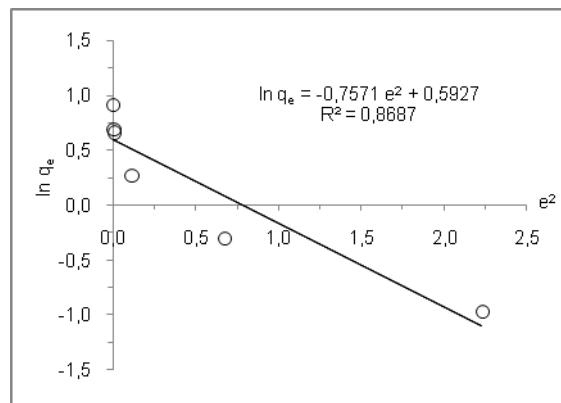*Figure 4: Freundlich plot for lead adsorption on SCG*

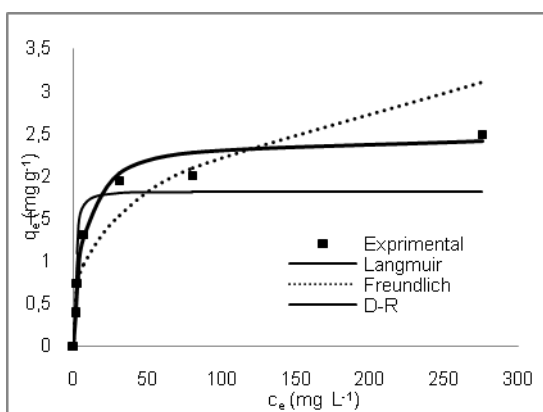*Figure 5: D-R plot for lead adsorption on SCG*

Figure 6: Comparison of adsorption model responses for lead adsorption on SCG

Based on these results, it can therefore be inferred that lead adsorption on SCG is well described by the Langmuir model. This result is in agreement with those of Dávila-Guzmán et al. (2011), who investigated the biosorption of lead on SCG, and of Azouaou et al. (2010), who studied the adsorption of cadmium on the same material.

4. Conclusions

The SCG examined in this study showed promising properties as low-cost and effective adsorbent materials for the removal of lead from water. SCG are abundantly available in most countries of the world and, according to the results of the present study, can be used without being subjected to any preliminary treatment. We have also shown that the adsorption equilibrium of lead on SCG is well described by the Langmuir equation which evidences a monolayer-type adsorption. In addition, the value obtained for the parameter *E* from the D-R model demonstrates the physical nature of the phenomenon.

Future research should be directed at studying the adsorption mechanism as well as the adsorption kinetics of lead, in both batch and continuous mode, and assessing the suitability of SCG for the removal of other metal or organic contaminants from water.

References

ASTM D3559 – 08, 2008, Standard Test Methods for Lead in Water, ASTM International, West Conshohocken, PA, USA, Vol. 11.01.

ATSDR (Agency for Toxic Substances and Disease Registry), 2007, Department of Health and Human Services, Public Health Service, Toxicological profile for lead, USA.

Azouaou N., Sadaoui Z., Djaafri A., Mokaddem H., 2010, Adsorption of cadmium from aqueous solution onto untreated coffee grounds: Equilibrium, kinetics and thermodynamics, Journal of Hazardous Materials, 184, 126-134.

Ballesteros L., Teixeira J., Mussatto S., 2014, Chemical, functional, and structural properties of spent coffee grounds and coffee silverskin, Food and Bioprocess Technology, 7, 3493-3503.

Dàvila-Guzmàn N., Cerino-Cordova F., Rangel-Méndez J., Diaz-Flores P., 2011, Biosorption of lead by spent coffee ground: Kinetic and isotherm studies. AIChE Annual Meeting, Conference Proceedings, 1-9.

Dhir B., 2014, Potential of biological materials for removing heavy metals from wastewater, Environ Sci. Pollut. Res. 21, 1614-1627.

Djati Utomo H., Hunter K.A., 2009, Particle concentration effect: Adsorption of divalent metal ion on coffee grounds, Bioresource Technology, 101, 1482-1486.

Duarte Zaragoza V., Carrillo R., Gutierrez Castorena C., 2011, Lead soption-desoprtion from organic residues, Environmental Technology, 32, 4, 353-361.

Fu F., Wang Q., 2010, Removal of heavy metal ions from wastewaters: A review, Journal of Environmental Management, 92, 407-418.

Kaiser B., Wright A., 2011, Draft Bruker XRF spectroscopy user guide: Spectral interpretation and sources of interference, Kennewick (USA).

Lavecchia R., Medici F., Piga L., Rinaldi G., Zuorro A., 2012, Fluoride removal from water by adsoprtion on a high alumina content bauxite, Chemical Engineering Transactions, 26, 225-230, DOI: 10.3303/CET1226038.

Pujola, .D, Liu C., Gominho J., Olivella M.A., Fiol N., Villaescusa I., Pereira H., 2013, The chemical composition of exhausted coffee waste, Industrial Crops and Products, 50, 423-429.

Zuorro A., Lavecchia R., 2010, Adsorption of Pb(II) on spent leaves of green and black tea, American Journal of Applied Sciences, 7, 153–159.

Zuorro A., Lavecchia R., 2011, Polyphenols and energy recovery from spent coffee grounds, Chemical Engineering Transactions, 25, 285-290, DOI: 10.3303/CET1125048.

Zuorro A., Lavecchia R., 2012, Spent coffee grounds as a valuable source of phenolic compounds and bioenergy. Journal of Cleaner Production. 34, 49-56.

Zuorro A., Di Battisti A., Lavecchia R., 2013, Magnetically modified coffee silverskin for the removal of xenobiotics from wastewater, Chemical Engineering Transactions, 35, 1375-1380, DOI: 10.3303/CET1335229.

Zuorro A., Lavecchia R., 2013, Preparation and characterization on magnetically responsive biosorbents from coffee industry residues. Applied Mechanics and Materials. 394, 3-7.