Coffee grounds as an adsorbent for copper and lead removal form aqueous solutions

Jurgita Seniūnaitė, Rasa Vaiškūnaitė, Violeta Bolutienė

Vilnius Gediminas Technical University, Faculty of Environmental Engineering, Department of Environmental Protection, Saulėtekio al. 11, 10223 Vilnius, Lithuania

Abstract

Water contamination is an actual problem around the world. The main source of contaminated water is the industry. Industrial wastewater is contaminated with hazardous substances such as heavy metals (Cu, Pb, Zn, Cd, Cr and etc.) and petroleum products. Wastewater technology is various, one of them – the biological sorption. In this study, removal of copper (Cu) and lead (Pb) from contaminated aqueous solutions has been investigated by using coffee grounds as a natural adsorbent. The research is a bench scale experiment type and analysis have performed by using different fractions (>200 µm and <200 µm particle size) of adsorbent in solutions with four (0.5, 1.0, 1.5 and 3.0 mg/L) different concentrations of both metal. Studies showed that coffee grounds are great adsorbent for heavy metal removal from aqueous solutions. Using the >200 µm fraction of coffee grounds for copper removal the treatment efficiency is 85.9% when the metal concentration is 0.5 mg/L, while the lead is 87.2%. Increasing metal concentration in the solution of the adsorbent treatment efficiency decreases to 71.76% for Cu and 86.76 % for Pb. When the smaller fractions (>200 µm) are used in coffee grounds treatment efficiency increases by 6–1 1% for copper, and 8–9% for lead.

Keywords: adsorbtion; coffe grounds; copper; lead; aqueous solution.

Nomenclature

R	removal percentage of metal concentration, %
C_0	metal concentration before adsorption, mg/L
C_e	metal concentration after adsorption, mg/L

1. Introduction

1.1. Heavy metal sources

Heavy metal contamination of water is a serious threat to the globe ecosystem. Many industries such as metal plating, mining operation, battery manufacturing processes, the production of paints and pigments, ceramic and glass industries, release wastewaters contaminated with heavy metals into the environment [1, 2, 3]. Industrial wastewater includes Cu, Pb, Zn, Ni, Cd and Cr [4]. Toxic metals are most affected by natural ecosystems. Metal ions to accumulate in human and other animal bodies occur through trial direct intake or food chains.

Copper. Copper is a transition metal which belongs to period 4 and group IB of the periodic table with atomic number 29, atomic weight 63.5, density 8.96 g/cm^3, melting point 1083 °C and boiling point 2 595 °C [5].

Copper ions can be found in many wastewater sources, including printed circuit board manufacturing, electronics plating, plating, wire drawing, copper polishing, paint manufacturing, wood preservative using and printing operations. Typical concentrations vary from several thousand mg/1 from plating bath waste to less than 1 ppm from copper cleaning operations [6].

Copper is an essential trace element necessary for plant and animal growth. Copper ion in small amounts is used in agriculture and is an essential element for health of plants, animals and humans. In humans, it helps in the production of

blood haemoglobin. High concentration of copper creates a kind of disease, which is similar to flu. It has been proved that drinking water, including 30 grams of copper ion is fatal and the concentration of 1.3 mg/l of this ion could be a reason for the relatively common diarrhea, abdominal cramps and nausea [5, 6].

Lead. Lead is a metal that belongs to the group IV elements and period 6 of the periodic table. Pb atomic number is 82, atomic mass 207.2, density 11.4 g/cm^3, melting point 327.4 °C and boiling point 1 725 °C. It is a naturally occurring; bluish-gray metal usually found as a mineral contaminated with other elements (such as sulphur or oxygen) [5].

Lead intensive use in industries such as storage-battery manufacture, printing, pigment manufacturing, petrochemicals, fuel combustion and photographic materials. The current annual worldwide production of Pb (II) is approximately 5.4 million tons and continues to manufacturing of batteries (automobile batteries, in particular), while the remainder is used in the production of pigments, glazes, solder, plastics, cable sheathing, ammunition, weights, gasoline additive, and a variety of other products [7].

Lead is a highly toxic metal and has the ability to accumulate in living organisms. Assimilation in the human body of relatively small amounts of Pb over a long period of time can lead to malfunctioning of certain organs and chronic toxicity. It can damage practically all tissues, particularly the kidneys and the immune system. Intense exposure to high Pb levels (from 100 to 200 g/day) causes encephalopathy with the following symptoms: vertigo, insomnia, migraine, irritability, and even convulsions, seizures, and coma [5, 7].

Copper as lead can damage the health of all living organisms; therefore heavy metals should be prevented from reaching the natural environment [8].

1.2. Adsorption

Various technologies exist for the removal of such metals, such as filtration, evaporation, precipitation, electro precipitation, chemical precipitation, electro coagulation, cementing and separation by membrane, the solvent extraction and the exchange of ions on resins [3, 9, 10]. But these methods are enough expensive. Therefore, recently have been sought a cheaper metal removal from aqueous solution's technology. One of these technologies is adsorption.

Adsorption is a fundamental process in the physiochemical treatment of contaminated solutions. Adsorption is a separation process in which certain components of the fluid phase are transferred to the surface of the solid adsorbents. When a solid surface is exposed to a fluid phase, the molecules from the bulk of the fluid phase have a tendency to accumulate or concentrate at the surface of a solid. Separation occurs because differences in molecular weight, shape, or polarity cause some molecules to be held more strongly on the surface than others or because the pores are too small to admit the larger molecules. The adsorption operation can be batch; semi-batch and continuous batch operations are generally conducted when small amounts are to be treated [11, 12]. The equilibrium distribution depends on the contact time in batch operation.

Types of adsorption. At molecular level, adsorption is due to attractive interactions between a surface and the species being adsorbed.

− Physical adsorption: It is a result of intermolecular forces of attraction between molecules of the adsorbent and the adsorbate. In this case, the molecular attractive forces that retain the adsorbent on the surface are purely physical are called Vander Walls forces. This is a readily reversible phenomenon. The energy of interaction between the adsorbate and adsorbent has the same order of magnitudes as, but is usually greater than the energy of condensation of the adsorptive. Therefore, no activation energy is needed.

− Chemical adsorption: It is a result of chemical interaction between the solid and the adsorbed substance. It is also called activated adsorption. It may be exothermic or endothermic processes ranging from very small to very large magnitudes. The elementary step in chemisoption often involves large activation energy [11, 12].

1.3. Variety of adsorbents

There are various types of adsorbent for heavy metal removal from aqueous solutions. Most popular are activated carbon, chitosan, zeolites and silica gel.

Activated carbon. Activated carbon is a highly porous, amorphous solid consisting of micro crystallites with a graphite lattice, usually prepared in small pellets or a powder. Activated carbon have high abrasion resistance, high thermal stability and small pore diameters, which results in higher exposed surface area and hence high surface capacity for adsorption [12].

Chitosan. Chitosan and its derivatives are examples of value-added materials. They are produced from chitin, which is a natural carbohydrate polymer found in the skeleton of crustaceans, such as crab, shrimp. Chitosan is a polymer obtained from deacetylation of chitin [13].

Zeolites. Zeolites are micro porous crystalline solids with well defined structures. Naturally-occurring zeolites are hydrated aluminosilicate materials with high cation exchange capacity [14]. Adsorption in zeolites is actually a selective and reversible filling of crystal cages, so surface area is not a pertinent factor [12].

Silica gel. This is a chemically inert, nontoxic, polar and dimensionally stable (<400 °C or 750 °F) amorphous form of SiO$_2$. It is prepared by the reaction between sodium silicate and acetic acid, which is followed by a series of after-treatment processes such as aging, pickling, etc. These after treatment methods result in various pore size distributions [12].

Also metal removal can be used peat moss, clay, activated alumina, activated charcoal, polymeric adsorbents, calcite and hydroxyapatite, modified cement and others.

Adsorption of heavy metals on conventional adsorbents such as activated carbon had been used widely in many applications as an effective adsorbent, and the activated carbon produced by carbonizing organic materials is the most widely used adsorbent [15]. However, need a lot funds for the preparation of adsorbents, so its price is high and it is limits its use in contaminated solution treatment applications. There is a lot of research to find cheaper materials to be used as adsorbents for heavy metal removal. The literature showed that the industrial waste (such as tea wastes, sawdust, rice husk and etc.) can be used for removal of heavy metals. In Tables 1 and 2 show various adsorbents treatment efficiencies for copper and lead [8, 14–21].

Table 1. Various adsorbent for Cu removal from contaminated solutions

Adsorbent	Treatment efficiency (%)	Reference
Sawdust	98.1–93.6	[8]
Activated charcoal	45–50	[16]
Baobab fruit shells	38	[17]
Papaya wood	97.8	[18]
Wheat shell	99	[19]
Waste fruit residues	96	[20]
Cocoa shells	95	[21]

Table 2. Various adsorbent for Pb removal from contaminated solutions

Adsorbent	Treatment efficiency (%)	Reference
Sawdust	98.6–95.4	[8]
Indigenous clay	80.3–51.3	[14]
Baobab fruit shells	41	[17]
Waste fruit residues	96	[20]
Cocoa shells	70	[21]

In this study coffee ground as heavy metal adsorbent has been used. Coffee ground treatment efficiency in removing metals from aqueous solutions has been determined. Heavy metals studied were copper and lead.

2. Material and Methods

2.1. Preparation of adsorbents

In this study, coffee grounds have been used for adsorption experiments. Coffee grounds were been washed and rinsed with distilled water. After drying in 100°C, a part of the coffee grounds were ground and sieved (sieve mesh size 200 μm) [22]. Both fractions of coffee grounds were put in sealed polyethylene for preservation so that it not reacts with neighboring environment [23]. The experiments were performed using 2 different fractions: a particle size >200 μm and <200 μm, because literature indicates that treatment efficiency depends by various parameters such as pH, temperature and others. One of them is the adsorbent particle size.

2.2. Preparation of heavy metal solutions

Cu and Pb with 4 different concentrations of 0.5 mg/L, 1.0 mg/L, 1.5 mg/L and 3.0 mg/L were prepared using standard metal solutions (conc. 1000 mg/L).

2.3. Procedure

12 flasks are taken each containing 0.5 g (a particle size >200 μm) of coffee grounds used as an adsorbent, 100 ml solution with known concentration of Cu were added, thereupon we had 3 similar concentration of each experiment. All these flasks were places into a shaker with 120–130 rpm. After 1-hour contact time, the contents of flasks were filtered through "VWR Qualitative filter paper 413" filter paper so that turbidity does not interference in this result. Copper concentration of the filtered solution after contact time was determined by atomic adsorption spectroscopy. The same procedure has been done

for another coffee grounds particle size (< 200 μm) and Cu solutions, and both coffee ground's fractions with lead solutions [22, 23].

2.4. Data analysis

The removal percentages *(R, %)* were calculated according to equation (1):

$$R\left(\%\right)=\frac{C_0-C_e}{C_0}\times100 \,,$$ (1)

where C_0 – metal concentration before adsorption, mg/L; C_e – metal concentration after adsorption, mg/L [24].

3. Results and Discussion

3.1. Effects of adsorbent particle size

Tables 3 and 4 show the residual heavy metal (Cu and Pb) concentrations in solution after 1-hour contact time using different adsorbent fractions.

Table 3. Concentration of residual copper after adsorption by coffee grounds

Coffee ground fraction	Concentration of Cu (mg/L)			
	0.5	1.0	1.5	3.0
Particle size <200 μm	0.0703	0.1437	0.3167	0.8473
Particle size >200 μm	0.0140	0.0737	0.1577	0.6657

Table 4. Concentration of residual lead after adsorption by coffee grounds

Coffee ground fraction	Concentration of Pb (mg/L)			
	0.5	1.0	1.5	3.0
Particle size <200 μm	0.0189	0.0385	0.0585	0.1331
Particle size >200 μm	0.0610	0.1284	0.1976	0.3966

Tables 3 and 4 present the removal percentages from the initial concentration for various initial concentrations of the metals, with different fractions of adsorbent (coffee grounds). The adsorption rate is dependent on the adsorbent particle size as well as the initial concentration of metal in the synthetic solutions. The percentage of heavy metal removal increased with the decreased coffee grounds adsorbent particle size. Copper removal from aqueous solution efficiency increased 6–1% when it was used in smaller fractions (<200 μm) coffee grounds. Lead treatment efficiency increased by 8–9%. The results show that lower residual concentrations obtained when the coffee grounds have a smaller particle size (<200 μm).

3.2. Effects of initial concentration

Metal adsorption is influenced by the initial concentration of metal ions in aqueous solutions. In the present study, the initial metal concentration is varied from 0.5 to 3.0 mg/L for each of the adsorbent fractions. Figures 2 and 3 show the effect of initial concentration on the removal percentage of metal ions.

The removal efficiency of Cu decreases from 85.2 (for 0.5 mg/L) to 71.8% (for 3.0 mg/L), coffee grounds particle size is >200μm and contact time is 1 hour, when used for smaller adsorbent fraction of copper removal efficiency decreased from 97.2 (metal conc. 0.5 mg/L) to 77.8% (metal concentration = 3.0 mg/L).

Lead removal efficiency with >200 μm particle size of coffee grounds, at 0.5–3.0 mg/L of metal concentrations remained almost unchanged, and were 86–87%. With lower adsorbent fraction (<200 μm) lead removal efficiency is 95–96%.

The results show that the coffee grounds cleaning efficiency is also dependent on the metal the removed. By comparing the copper and lead in treatment efficiency using coffee grounds with adsorbents whish are presented in figures 1 and 2 we can conclude that the coffee grounds are an effective and suitable adsorbent to remove heavy metals from aqueous solution.
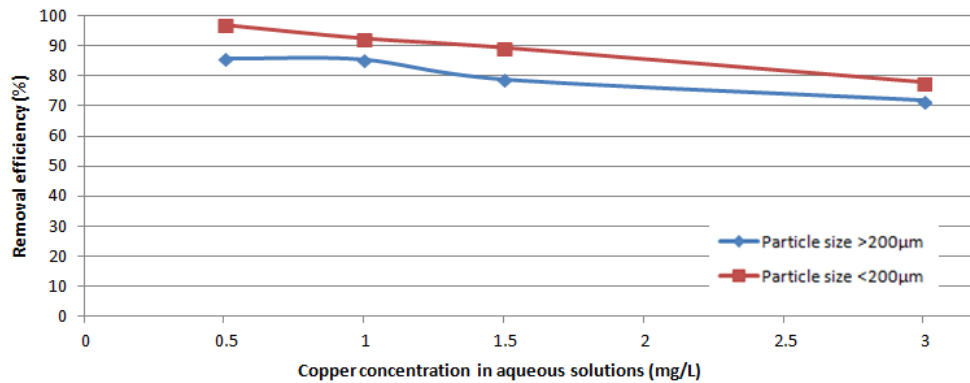
Fig. 1. Adsorption percent of cooper by two fractions of coffee grounds

Figure 1 shows that the copper adsorption efficiency is of 86% (particle size >200 μm) and 97% (particle size <200 μm) using coffee grounds, while Cu concentration is 0.5 mg /L. When Cu concentration amounted 3.0 mg/L; adsorption efficiency decreased from 72 to 78%.
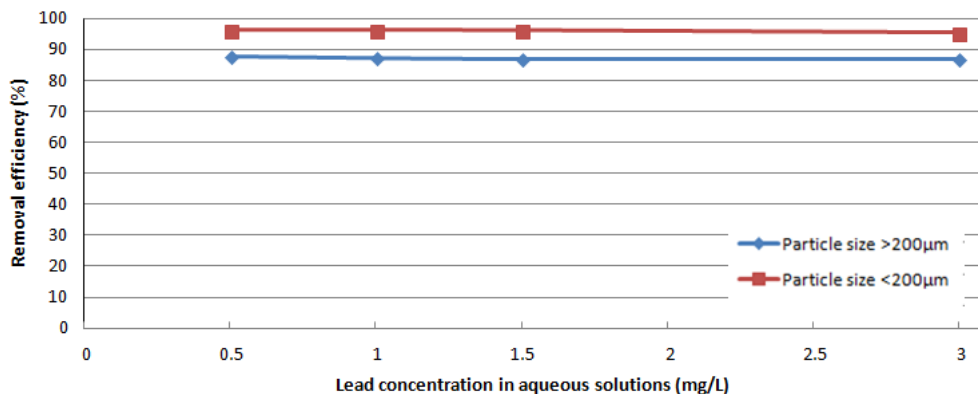

Fig. 2. Adsorption percent of lead by two fractions of coffee grounds

Experiments showed that the coffee grounds from aqueous solution eliminate 87% (particle size >200 μm) and 96% (particle size <200 μm) lead, when metal concentration is 0.5 mg/L. With increasing in Pb concentration the adsorption efficiency almost unchanged (Fig. 2). Experimental results have indicated that coffee grounds can be excellent natural adsorbent for heavy metal removal from aqueous solutions, like wastewater of landfill leachate.

4. Conclusion

1. Studies showed that using smaller fraction's coffee ground treatment efficiency increases by 6–11%. Therefore, in order to obtain an even higher cleaning efficiency, coffee grounds should be additional crushed.
3. The copper adsorption efficiency of 86% (particle size >200 μm) and 97% (particle size <200 μm) using coffee grounds, when Cu concentration is 0.5 mg /L. When Cu concentration reached 3.0 mg/L adsorption efficiency decreased from 72 to78%.
4. Experiments show that the coffee grounds from aqueous solution eliminate 87% (particle size >200 μm) and 96% (particle size <200 μm) lead, when metal concentration is 0.5 mg/L. With increasing concentration of Pb adsorption efficiency almost unchanged.
5. Experiment and result analysis indicated that coffee grounds can be excellent natural adsorbent for heavy metal removal from aqueous solutions, like wastewater of landfill leachate.

References

[1] Bailey, S. E.; Olin, T. J.; Brick, R. M.; Adrian, D. D. 1999. A review of potentially low-cost sorbents for heavy metals, *Water Research* 33: 2469–2479. http://dx.doi.org/10.1016/S0043-1354(98)00475-8

[2] Ajmal, M.; Rao, R. A. K.; Anwar, J. A.; Ahmad, R. 2003. Adsorption studies on rice husk: removal and recovery of Cd(II) from wastewater, *Bioresource Technology* 86: 147–149. http://dx.doi.org/10.1016/S0960-8524(02)00159-1

[3] Salam, O. E. A.; Reiad, A. N.; ElShafei, M. M. 2011. A study of removal characteristics of heavy metals from wastewater by low-cost adsorbents, *Journal od Advanced Research* 2: 297–303.

[4] Argun, M. E.; Dursun, S. 2008. A new apoproach to modification of natural adsorbent for heavy metal adsorption, *Bioresource Technology* 99(7): 2516–2527. http://dx.doi.org/10.1016/j.biortech.2007.04.037

[5] Wuana, R. A.; Okieimen, F. E. 2011. *Heavy Metals in Contaminated Soils: A Review of Sources, Chemistry, Risks and Best Available Strategies for Remediation*, ISRN Technology 2011: 20.

[6] Salmani, M. H.; Ehrampoush, M. H.; Sheikhalishadi, S.; Dehvari, M. 2012. Removing Copper from Cintaminated Water Using Activated Carbon Sorbent by Continouus Flow, *Journal of Health Researches* 1(1): 11–18.

[7] Zahra, N. 2012. Lead Removal from Water by Low Cost Adsorbents: A Review, *Pakistan Journal of Analytical & Environmental Chemistry* 13(1): 1–8.

[8] Meena, A. K.; Kadirvelu, K.; Mishra, G. K.; Rajagopal, C.; Nagar, P. N. 2008. Adsorptive removal of heavy metals from aqueous solution by treated sawdust (Acacia arabica), *Journal of Hazardous Materials* 150(3): 604–611. http://dx.doi.org/10.1016/j.jhazmat.2007.05.030

[9] Aydin, H.; Bulut, Y.; Yerlikaya, C. 2008. Removal of copper (II) from aqueous solution by adsorbtion onto low-cost adsorbents, *Journal of Environmental Management* 87: 37–45. http://dx.doi.org/10.1016/j.jenvman.2007.01.005

[10] Babel, S.; Kurniawan, T. A. 2003. Low-cost adsorbents for heavy metals uptake from contaminated water: A review, *Journal of hazardous Materials* 97: 219–243. http://dx.doi.org/10.1016/S0304-3894(02)00263-7

[11] Yadla, S. V.; Sridevil, V.; Lakshmi C. 2012. A Review in adsorbtion of heavy metals from Aqueous Solution, *Journal of Chemical, Biological and Physical Sciences* 2(3): 1585–1593.

[12] Singh, U.; Kaushal, R. K. 2013. Treatment of Waste water with Low cost Adsorbent – a Review, *VRSD international Journal of Technical & Non–technical Reasearch* 4(3): 33–42.

[13] Renge, V. C.; Khedkar, S. V.; Pande, S. V. 2012. Removal of heavy metals from wastewater using low cost adsorbents: A Review, *Scientific Reviews & Chemical Contaminations* 2(4): 580–584.

[14] Shareef, K. M. 2009. Sorbents for Contaminants Uptake from Aqueous Solutions. Part I. Heavy Metals, *World Journal of Agricultural Sciences* 5(S): 819–831.

[15] Amarasinghe, B. M. V. P. K.; Williams, R. A. Tea waste as a low cost adsorbent for removal of Cu and Pb from wastewater, *Chemical Engineering Journal* 132(1-3): 299–309. http://dx.doi.org/10.1016/j.cej.2007.01.016

[16] Dave, P. N.; Subrahmanyam, N.; Sharma, S. 2009. Kinetics and thermodynamics of copper ions removal from aqueous solution by use of activated charcoal, *Indian Journal of Chemical Technology* 16: 234–239.

[17] Chigondo, F.; Nyamunda, B. C.; Sithole, S. C.; Gwatidzo, L. 2013. Removal of lead (II) and copper (II) ions from aqueous solution by baobab (Adononsia digitata) fruit shells biomass, *IOSR Journal of Applied Chemistry* 5(1): 43–50. http://dx.doi.org/10.9790/5736-0514350

[18] Das, N.; Karthika, P.; Vimala, R.; Vinodhini, V. Use of natural products as biosorbent of heavy metals, *Natural Product Radiance* 7(2): 133–138.

[19] Basci, N.; Kocadagistan, E.; Kocadagistan, B. 2004. Biosorbtion of copper (II) from aqoeous solutions by wheat shell, *Desalination* 164(1): 135–140. http://dx.doi.org/10.1016/S0011-9164(04)00172-9

[20] Senthilkumaar, S.; Bharathi, S.; Nithhyanandhi, D., Subburam, V. 2000. Biosorption of toxic heavy metals from aqueous solutions, *Bioresource Technology* 75: 163–165. http://dx.doi.org/10.1016/S0960-8524(00)00021-3

[21] Neunier, N.; Laroulandie, J.; Blais, J. F.; Taygi R. D. 2003. Cocoa shells for heavy metal removal from acidic solutions, *Bioresource Technology* 90: 255–263. http://dx.doi.org/10.1016/S0960-8524(03)00129-9

[22] Mahvi, A. H.; Nagipour, D.; Vaezi, F.; Nazmara, S. 2005. Teawaste as An Adsorbent for Heavy Removal from Industrial Wasterwaters, *American Journal of Applied Sciences* 2(1): 372–375. http://dx.doi.org/10.3844/ajassp.2005.372.375

[23] Dalal, P. 2012. Heavy Metal removal from Tea-waste, *International Journal of Plant, Animal and Environmental Sciences* 2(4): 109–111.

[24] Mohammed, R. R. 2012. Removal of Heavy Metals from Waste Water Using Black Teawaste, *Arabian Journal for Science and Engineering* 37: 1505–1520. http://dx.doi.org/10.1007/s13369-012-0264-8