

Coffee grounds as low-cost adsorbent for the removal of copper (II) and lead (II) from aqueous solutions

J. Seniūnaitė, R. Vaiškūnaitė*, D. Paliulis

Department of Environmental Protection and Water Engineering, Vilnius Gediminas Technical University, Saulėtekio al. 11, Vilnius, Lithuania, LT-10223

Received March 4, 2017; Revised November 10, 2017

This work aims to study the removal of Cu (II) and Pb (II) from aqueous solutions with commercial coffee wastes (coffee grounds). Materials with no further treatment such as coffee residues from café may act as adsorbents for the removal of Cu (II) and Pb (II). Coffee ground fraction <200 μm was used in the experimental research. The effect of pH (2.0, 3.0, 4.0 and 5.0), contact time (15, 30, 60, 90, 120, 150, 180, 300, 480 and 720 min) and initial concentration of Cu(II) and Pb(II) (10 mg/L, 20 mg/L, 30 mg/L, 40 mg/L, 50 mg/L) on the adsorption was studied. The optimum values of the process variables were: contact time, 120-720 minutes; pH, 5.0; initial Cu(II) and Pb(II) concentration 20 mg/L. Equilibrium data fitted well to Langmuir and Freundlich models for Pb (II) and Cu (II) with high R^2 values. Studies have shown that coffee grounds are a suitable adsorbent for heavy metals removal from water.

Keywords: coffee grounds, adsorption, copper, lead, heavy metals, Freundlich isotherm, Langmuir isotherm

INTRODUCTION

Water pollution due to the disposal of heavy metals continues to be a great worldwide problem. Heavy metals pollution occurs in industrial wastewater that is emitted by metal plating facilities, mining operations, battery-manufacturing processes, production of paints and pigments, and ceramic and glass industries [1]. This wastewater commonly includes ions of copper, lead, etc. [2]. Heavy metals are “eternal pollutants” – they tend to accumulate and migrate from one place to another and are never destroyed. Not only impact of individual heavy metals is dangerous, but also their combined synergistic effect.

Copper (Cu) ions can be found in many wastewater sources including printed circuit board manufacturing, electronics plating, plating, wire drawing, copper polishing, paint manufacturing, use of wood preservatives and printing operations. Typical concentrations vary from several thousand mg/l from plating bath waste to less than 1 mg/L from copper cleaning operations [3]. It has been proved that high concentration of copper ion could be a reason for the relatively common diarrhoea, abdominal cramps and nausea [3,4]. High excess of Cu can cause autoimmune reactions that damage the central nervous system, liver, kidneys, cause gastritis, peptic ulcer disease, lung disease or liver cirrhosis [5].

Lead (Pb) has environmental importance due to its well known toxicity and intensive use in industries such as storage-battery manufacture,

printing, pigment manufacturing, petrochemicals, fuel combustion and photographic materials [6]. Assimilation in the human body of relatively small amounts of Pb (II) over a long period of time can lead to malfunctioning of certain organs and chronic toxicity. Children exposed to lead are at risk for impaired development, lower IQ, shortened attention span, hyperactivity, and mental deterioration, children under the age of six being at a more substantial risk. Adults usually experience decreased reaction time, loss of memory, nausea, insomnia, anorexia, and weakness of the joints when exposed to lead. Lead can cause serious injury to the brain, nervous system, red blood cells, and kidneys [4–6]. Copper and lead have a negative impact on ecosystems and living organisms, therefore, the removal of these heavy metal ions from wastewater is important from the perspectives of human health. Several techniques for heavy metals removal have been developed, including filtration, precipitation (electrochemical), electrocoagulation, membrane filtration [1]. Although the above-mentioned methods are widely used, they require high exploitation costs or application of complex technical solutions, so a cheaper and adaptable technology for removal of heavy metals from water is needed. Because of its low cost, simplicity of design, and ease of operation, the adsorption technique has been the most extensively used one of these techniques. Adsorption is a recognized method for the removal of heavy metals from wastewater having low concentration of heavy metal. The adsorption process offers flexibility in design and operation and in many cases produces high-quality treated

* To whom all correspondence should be sent.

E-mail: rasa.vaiskunaite@vgtu.lt

effluent. Moreover, this adsorption is reversible and adsorbents can be regenerated by suitable desorption techniques [7].

Activated carbon is widely used in the world for heavy metal adsorption. Due to the lengthy and costly preparation of adsorbents, its price is high, which limits its use for water treatment. Recently, the use of organic waste (tea sludge, sawdust, rice husks, etc.) is gaining popularity for heavy metals biosorption. The most important advantage of these sorbents is the low cost. However, there is a lack of literature dealing with the possible application of coffee residues as adsorbents (i.e. for metals). In general, "coffee residues" are generally called the solid wastes discarded from the extraction process of instant coffee manufacturing, and the final residues originated from cafeterias. In the last years, the instant coffee industry has experienced a constant growth, as instant coffee has become one of the most popular kinds of coffee drinks by millions of people around the world. As a consequence, large amounts of coffee grounds, which are the solid residues obtained during the processing of coffee powder with hot water or steam to prepare instant coffee, have been generated worldwide (in the order of 6 mln tones/year) [8]. The annual amount of coffee consumed by a Lithuanian inhabitant is about 5.5 kg according to data of Lithuanian Consumer Institute (2012), therefore a big amount of coffee grounds are generated in Lithuania as waste every year. Coffee waste as adsorbent was tested for adsorption of various metals – lead, cadmium, nickel, indium, strontium, etc. [9-17]. Coffee grounds are also used for adsorption of dyes [18-20]. Also coffee pulp was tested as adsorbent for adsorption of organic compounds [21].

In this study, we investigated the application of the coffee grounds and measured the amount of copper (II) and lead ions (II) adsorbed onto the coffee grounds from synthetic wastewater. Moreover, impact of pH and contact time with adsorbent on the adsorption efficiency was evaluated.

METHODOLOGY

Preparation of adsorbents. The low-cost commercial medium-roasted ground coffee (Arabica variety) was used as an adsorbent. Coffee grounds were untreated coffee residues collected from coffee machines of local cafeterias. Sieve analysis was used to divide the coffee residues into two size fractions (<200 μm and >200 μm) with a vibratory sieve shaker Retsch AS 200 [22]. According to our research results, the fraction of

coffee grounds < 200 μm was selected for further experimental research. These residues were untreated, only washed with deionized water (Demiwa 3 roi system) until a pH close to 6.0 was achieved. Finally the grounds were oven-dried (SNOL 3.5) at 100–105 °C for 24 h, cooled to room temperature and were suspended in a plastic container in order to protect against adverse environmental impact [23].

Elemental analysis of adsorbent. The thermal field emission scanning electron microscope JEOL JSM-7600F with energy dispersive X-ray spectroscopy detector was used for elemental analysis of <200 μm coffee ground.

Determination of dry bulk density. Determination of dry bulk density of coffee ground sized smaller than 200 μm was carried out applying standard ISO 567:1995.

Adsorbate. Lead and copper atomic spectroscopy standard solutions of 1000 mg/L \pm 2 mg/L (2% HNO₃) (ROTI®STAR) were used as the source of Cu (II) and Pb (II) in the synthetic wastewater. The aqueous solutions containing Cu²⁺ and Pb²⁺ cations of concentration 10 mg/L, 20 mg/L, 30 mg/L, 40 mg/L, 50 mg/L were prepared by diluting the standard metal solutions (Cu(II) and Pb(II)) in a measuring flask to the 100 mL mark with deionized water. All chemical reagents were of analytical grade and were used in the experiments as received without further purification. Deionized water used in experiments meets the requirements of standard LST EN ISO 3696:1996 (Water for analytical laboratory use – specification and test methods). All volumetric flasks used in the experiments were of an accuracy class.

Effect of sorption time on the removal of heavy metals. The sorption time is assessed by analyzing the static heavy metals sorption from the aqueous solution. The aim of these experiments was to determine the time when the equilibrium of adsorption is achieved. Durations of 15, 30, 60, 90, 120, 150, 180, 300, 480 and 720 min were selected for adsorption research. The experiments of static heavy metals adsorption from aqueous solution were performed by mixing an adsorbent sample with the heavy metal solution in a 1:100 ratio of adsorbent and solution mass (i.e., 1 g of adsorbent and 100 ml of aqueous solution) using capped bottles (200 ml). The suspensions were shaken at 21 \pm 1 °C at 20 rpm for the mentioned contact time applying Rotoshake RS12. The samples were filtered (using glass filter with 0.45 μm pores) and the heavy metal concentrations in the filtrate were measured applying AAS method [1].

Batch mode adsorption studies (Effect of pH on the removal of heavy metals). The maximum allowable concentration (MAC) of lead and copper in wastewater to be discharged to wastewater collection system is 0.5 and 2.0 mg/L, respectively (Regulation on wastewater management, *Official Gazette*, No. 110-4522, 2007). The influence of different pH values was studied in the range of 2.0, 3.0, 4.0 and 5.0 (10 mg/L Cu (II) and Pb (II) solution). The effect of pH was followed by mixing 1 g of adsorbent with 100 mL of metal single-component solution. The pH value, ranging between 2.0 and 5.0, was kept constant throughout the adsorption process by micro-additions of HNO₃ (0.1 M) or NaOH (0.1 M). pH was measured with Mettler Toledo seven Multi pH meter. The suspension was shaken at 20 rpm at constant temperature (21±1 °C) for selected contact time (from 15 to 720 min) with Rotoshake RS12. Calibration curves were prepared before each sample measurement.

Effect of concentration. The concentration of Cu(II) and Pb(II) was assessed by analyzing the static heavy metals sorption from the aqueous solution. The aim of these experiments was to determine the concentration of metal when the equilibrium of adsorption is achieved. Concentrations of 10, 20, 30, 40 and 50 mg·L⁻¹ were selected for Freundlich and Langmuir adsorption isotherm creation.

Freundlich isotherm is widely applied in heterogeneous systems [24]. The slope ranging between 0 and 1 is a measure of the adsorption intensity or surface heterogeneity, becoming more heterogeneous as its value gets closer to zero.

Freundlich isotherm is expressed as:

$$q_e = K_F C_e^{1/n}, \quad (1)$$

or in linear form:

$$\log q_e = \log K_F + \frac{\log C_e}{n}, \quad (2)$$

where q_e - amount of adsorbate in the adsorbent at equilibrium (mg/g); K_F - Freundlich isotherm constant (mg/g); C_e - equilibrium concentration (mg/L); n - adsorption intensity.

Langmuir isotherm

Langmuir adsorption isotherm, originally developed to describe gas–solid phase adsorption onto activated carbon, has traditionally been used to quantify and compare the performance of different bio-sorbents. In its formulation, this empirical model assumes monolayer adsorption (the adsorbed layer is one molecule in thickness); adsorption can only occur at a finite (fixed) number of definite localized sites, which are identical and equivalent,

with no lateral interaction and steric hindrance between the adsorbed molecules, even on adjacent sites.

Langmuir isotherm is expressed as:

$$q_e = \frac{Q_0 b C_e}{1 + b C_e}, \quad (3)$$

or in linear form:

$$\frac{1}{q_e} = \frac{1}{Q_0} + \frac{1}{b Q_0 C_e}, \quad (4)$$

where q_e - amount of adsorbate in the adsorbent at equilibrium (mg/g); Q_0 - maximum monolayer coverage capacity (mg/g); b - Langmuir isotherm constant (L/mg); C_e - equilibrium concentration (mg/L).

Percent adsorption decreased while metal uptake per unit weight of adsorbent increased as the initial Cu(II) and Pb(II) concentration increased from 10 to 50 mg·L⁻¹ and after that percentage adsorption became constant.

Analytical method. Lead and copper concentrations were determined using atomic absorption spectrophotometer (AAS model Buck Scientific 210 VGP) operated with an air-acetylene flame, a slit of 0.7 mm at 283.2 and 324.7 nm wavelength, accordingly.

Evaluation of adsorption capacity. The adsorption capacity (Q) of the adsorbent was calculated by the following equation [2, 18]:

$$Q = \frac{(C_i - C_f) \cdot V}{m}, \text{ mg/g}; \quad (5)$$

where C_i – the concentration of metal ion before adsorption, mg/L; C_f – the concentration of metal ion after adsorption at the equilibrium state, mg/L; V – the volume of solution l; m – the sorbent mass, g.

Statistical analysis. Each analysis was prepared and analysed in triplicate. The average of the results and the standard deviation values were calculated.

RESULTS AND DISCUSSION

Determination of chemical composition of coffee ground. Elemental analysis provided the complete elemental composition of adsorbent as shown in Table 1.

Table 1. Composition of coffee grounds

Chemical element	Composition (weight %)
Carbon	68.80
Nitrogen	5.46
Oxygen	25.42
Silicon	0.09
Other elements	0.23
Total	100.00

It can be assumed that the carbon content in coffee grounds is affected by the coffee roasting. Average-roasted coffee grounds were used in the experimental studies. The effective parameter on molecules adsorption is the particle size of the adsorbent. Pollution uptake in adsorption process is a function of specific surface or external surface of adsorbent. According to our experimental results, it could be concluded that coffee grounds size has no significant impact on the adsorption of copper and lead, therefore only the smaller fraction (<200 μm) was selected for research. Similar results were observed in case of cadmium adsorption on coffee grounds. A series of experiments were performed in the range of particle size [225–800 μm] as a function of contact time [9]. It was observed that the rate of cadmium adsorption was not remarkably affected by the change in the particle size (change in surface area) of the coffee grounds. This statement can indicate that the adsorption takes place at the surface of the adsorbent and the functional groups are probably responsible for the adsorption of metal ions on the coffee grounds. It was found that bulk density of coffee grounds was 0.53 g/cm³.

Effect of contact time. In order to define the kinetics of copper and lead adsorption, the parameters of the adsorption process were studied for contact time ranging between 15 and 720 min at room temperature (21±1°C) by monitoring the percent removal of copper and lead by the

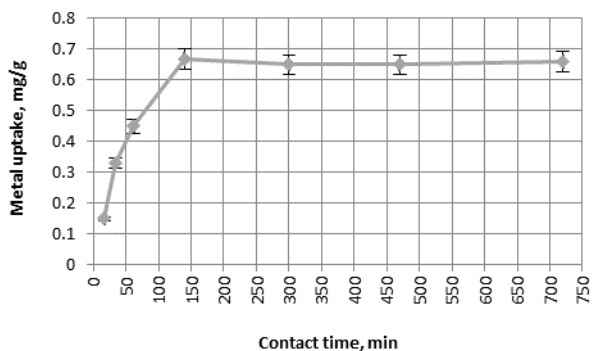


Fig. 1. Effect of contact time on the adsorption of Cu (II) onto coffee grounds (pH = 5.0, 10 mg/L ion concentration, adsorbent: solution ratio 1:100 w:v, T = 21±1 °C, 15–720 min contact)

The plots could be split in three distinct regions: (i) 0–30 min, indicating the instantaneous adsorption of ions, suggesting rapid external diffusion and surface adsorption; (ii) 30–120 min, showing a gradual equilibrium; (iii) 120–720 min, indicating the equilibrium state.

According to Kyzas data [27] Cu (II) adsorption equilibrium onto coffee waste was achieved after

adsorbent. Figure 1 depicts the effect of contact time on the adsorption of Cu (II) onto coffee grounds.

Results presented in Fig. 1 show that the removal rate of Cu (II) ions was rapid in the first few minutes. The sorption equilibrium was achieved in 120 min. Figure 2 depicts the effect of contact time on the adsorption of Pb (II) onto coffee grounds.

Equilibrium experiments were conducted to study the effects of contact time and initial pH on the adsorption of copper and lead. Using the >200 μm fraction of coffee grounds for copper removal the treatment efficiency was 85.9% when the metal concentration was 0.5 mg/L, while the removal efficiency of lead was 87.2% [25]. According to Agwaramgbo *et al.* [28] 88.0% Pb removal efficiency was achieved by applying coffee grounds (initial lead concentration was 1300 mg/L). The maximum Pb removal efficiency according to our experimental data was about 84.5%. According to Gupta *et al.* [30] maximum adsorption capacity for Pb (II) onto coffee modified with ZnCl₂ solution was 63 mg/g. According to Rafiq *et al.* [33] coffee husk adsorption capacity for Cu (II) was 7.5 mg/g. Kyzas found maximum adsorption capacity of 70 mg/g for Cu (II) [31]. The maximum adsorption capacities were 0.845 mg/g for lead (II) and 0.657 mg/g for copper (II), which was considered high for untreated material.

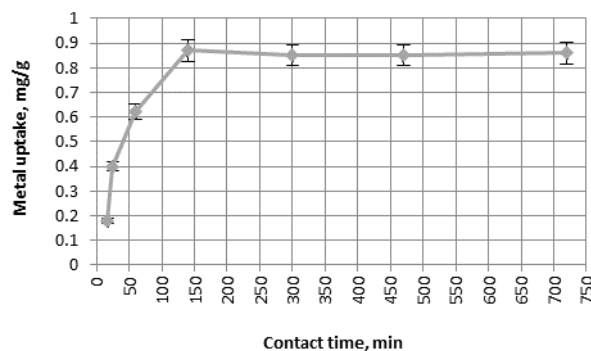


Fig 2. Effect of contact time on adsorption of Pb (II) onto coffee grounds (pH = 5.0, 10 mg/L ion concentration, adsorbent solution ratio 1:100 w:v, T = 21±1 °C, 15–720 min contact)

120 min, but according to Dutta *et al.* (2015) equilibrium conditions of cadmium adsorption onto coffee grounds were achieved in less than 30 min [18,25]. The adsorption equilibrium time depends on metal concentration and adsorbent dose. It can be seen that the adsorbed amount of Pb (II) and Cu (II) ions increases with contact time up to 120 min, after that maximum removal is attained. Due to the not so quick adsorption rate (120 min), it can be

inferred that physi-sorption is predominant in this adsorption process. 120 min was selected as the optimum contact time for all further experiments.

The effect of solution pH. Aqueous phase pH governs the speciation of metals and also the dissociation of active functional sites on the sorbent. It has been identified as the most important variable affecting metal adsorption onto adsorbent, this partly because hydrogen ions themselves are strongly competing with adsorbate. To characterize the effect of pH on Cu (II) and Pb (II) adsorption using coffee grounds, a set of equilibrium adsorption experiments were conducted by modifying the pH from 2.0 to 5.0. The pH of the aqueous medium not only affects the solubility of the metal ions but also the ionic form in which they will be present in the solution and the type and ionic state of the functional groups at the biosorbent surface. The choice of pH range (2.0–5.0) in the present study was based on the fact that

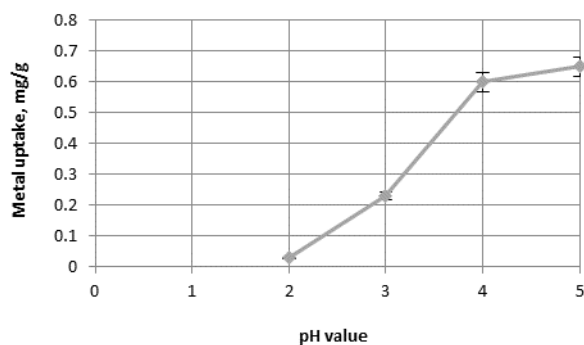
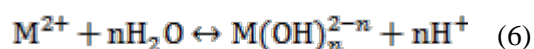


Fig. 3. Effect of pH on adsorption of Cu (II) onto coffee ground from single metal solution (10 mg/L ion concentration, adsorbent solution ratio 1:100 w:v, T = 21±1 °C, 720 min contact)

The pH of solution was identified as the most important variable governing metal adsorption on the adsorbent. The amount of Pb (II) ions adsorbed by coffee grounds increased with the increase in pH from 2.0 to 5.0. The heavy metal-removal capacity increased very sharply with an increase in pH from 3.0 to 5.0. The low metal adsorption at pH 3.0 was attributed to the competition that metal ions face from hydrogen ions for the available adsorption sites. The results showed that pH is an important parameter affecting the adsorption of heavy metals. No adsorption of metal ions was observed for pH less than 2.0 according to our research data.

The hydrolysis reactions of divalent metal cations can be represented by the general reaction:



However, based on the equilibrium constants, only the first hydrolysis reaction (n=1) is considered significant for lead ions [23]:

approximately at pH 5.5 precipitation of Cu and Pb starts in aqueous solution [18, 26]. According to our research data at lower pH levels (<2.0) desorption of adsorbed metals from coffee grounds starts. Fig. 3 shows the effect of pH on the removal of Cu (II) ions onto coffee grounds from aqueous solutions.

The amount of copper ions sorbed by coffee grounds increases with the increase in pH from 2.0 to 5.0. Copper is mainly present in the form of Cu (II), with smaller amounts of CuOH between pH 2.0 and 5.0 [33]. At pH = 2.0 the removal of Cu (II) percentage was 3.5%. After pH 3.0 the uptake of Cu (II) increases sharply up to pH = 5 – metal uptake increases from 0.223 to 0.657 mg/g. No pH values over 5.0 were studied since precipitation of Cu (II) ions starts. Fig. 4 shows the effect of pH on the removal of Pb (II) ions onto coffee grounds from aqueous solutions.

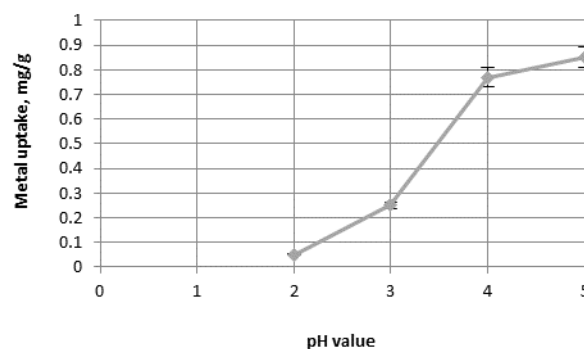
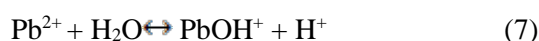


Fig. 4. Effect of pH on adsorption of Pb (II) onto coffee ground from single metal solution (10 mg/L ion concentration, adsorbent solution ratio 1:100 w:v, T = 21±1 °C, 720 min contact)



At pH = 2.0 the percentage removal of Pb (II) was 4.4%. After pH 3.0 the uptake of Pb (II) increased sharply up to pH = 5.0 – Pb uptake increased from 0.255 to 0.845 mg/g. No pH values over 5.0 were studied since precipitation of Pb (II) ions starts. In all cases, the adsorption of Pb (II) ions onto coffee grounds presented higher metal removal percentages than Cu (II). The optimum pH selected was pH = 5.0 both for Cu (II) and Pb (II). According to Dávila Guzmán *et al.* [11] optimum pH for Cu²⁺ adsorption is 4.5–5.0. Maximum adsorption capacity of adsorbent depends on the initial concentration of metal; due to the low initial concentration, the achieved maximum adsorption capacity was lower than that determined by other researches [11].

Coffee is composed of cellulose and alkaloids such as trigonelline, quinolinic acid, tannic acid,

nicotinic acid, and caffeine [18]. Adsorption mechanism of coffee grounds could be easily explained. In the case of cations (as copper or lead), the possible hypotheses are clear enough. The coffee materials primarily contain weak acidic and basic functional groups. It follows from the theory of acid-base equilibria that at $2.0 < \text{pH} < 7.0$ the binding of heavy metal cations is determined primarily by the state of dissociation of the weak acidic groups. Carboxyl groups ($-\text{COOH}$) are the important (but not the only) groups for metal uptake by these materials. At $\text{pH} = 7$, there are lower numbers of competing hydrogen ions and higher numbers of ligands are exposed with negative charges, resulting in higher copper or lead adsorption. The minimal adsorption at low pH may be due to the higher concentration and high mobility of H^+ , which are preferentially adsorbed rather than metal ions. Increasing the pH of the solution, the lower number of H^+ (with higher negative surface charge) results in higher copper or lead adsorption [27-30]. Nevertheless, at higher pH values determination of metal sorbed is overvalued because of metal precipitation [36].

This pH value depends on metal concentration in solution. It can be seen that the adsorption percentages are very low in strong acidic medium for the untreated coffee ground. Metal ions are not adsorbed at low pH, opening up the possibility for these adsorbents to be used repeatedly for adsorption of metal ions with stripping in acid solution.

The pH selected as optimum for adsorption experiments was $\text{pH} = 5$, where the adsorbents presented the maximum removal just before the pH-zone of 5.5 where precipitation and hydrolysis phenomena dominate. Desorption of heavy metals could be carried out at low pH values. According to Kyzas [18] the optimum pH found for desorption was $\text{pH} = 2.0$ for Cu (II) [31-35].

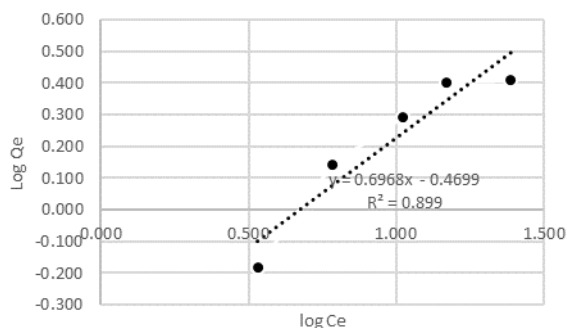


Fig. 5. Freundlich plots for Cu (II) adsorption at pH 5.0 on coffee grounds, adsorbent solution ratio 1:100 w:v, $T = 21 \pm 1$ °C, 720 min contact, Freundlich isotherm parameters: $n=1.435$, $K_F=0.339$

Figures 5-8 show the Freundlich and Langmuir adsorption isotherms of Cu(II) and Pb(II), for an initial pH 5, by coffee grounds. The physical parameters for the adsorption of Cu(II) and Pb(II) are determined from the linear Freundlich (Figures 5, 6) and Langmuir isotherms and are tabulated in figures 5, 6, 7 and 8.

Results presented in Figs. 5 and 6 show that the removal rate of Cu(II) and Pb(II) ions can be described with Freundlich isotherm.

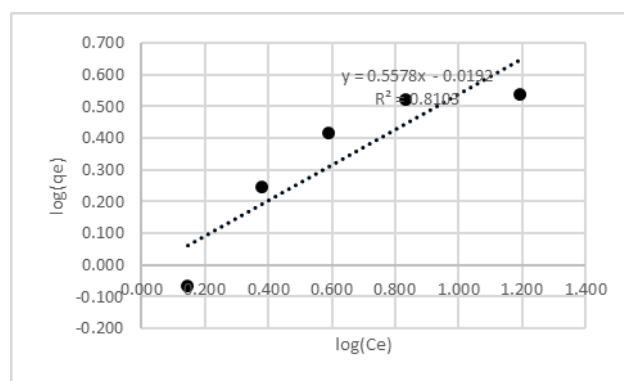


Fig. 6. Freundlich plots for Pb (II) adsorption at pH 5.0 on coffee grounds, adsorbent solution ratio 1:100 w:v, $T = 21 \pm 1$ °C, 720 min contact, Freundlich isotherm parameters: $n=1.793$, $K_F=0.957$

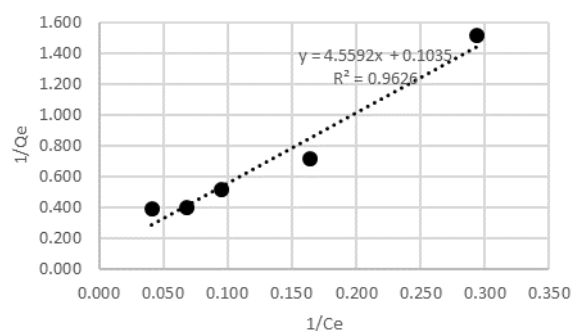


Fig. 7. Langmuir plots for Cu(II) adsorption at pH 5.0 on coffee grounds, adsorbent: solution ratio 1:100 w:v, $T = 21 \pm 1$ °C, 720 min contact, Langmuir isotherm parameters: $Q_0=9.662$, $b=0.023$.

The values of the Freundlich isotherm parameters as well as the correlation coefficient (R^2) of the Freundlich equations are given in Figs. 5 and 6.

The Freundlich constant, K_F unlike the Langmuir constant, Q_0 does not predict the saturation of the solid surface by the monolayer coverage of the adsorbate but it gives a relative measure of the adsorption capacity and estimates bond strength. The value of “ n ” discloses the adsorption pattern. The favorable adsorption is understood from the values of $1 < n < 10$ while irreversible adsorption is noticed from $n > 10$ and unfavorable adsorption from $n < 1$. Favorable

adsorption was registered, because n was in the range $1 < n < 10$ in both cases (Cu(II) and Pb(II)). Results presented in Figs. 7 and 8 show that the removal rate of Cu(II) and Pb(II) ions can be described with Langmuir isotherm. The values of the Langmuir isotherm parameters, as well as the correlation coefficient (R^2) of the Langmuir equations are given in Figs. 7 and 8.

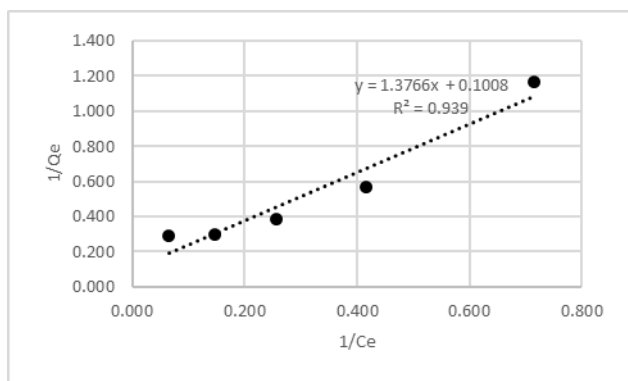


Fig. 8. Langmuir plots for Pb (II) adsorption at pH 5.0 on coffee grounds, adsorbent solution ratio 1:100 w:v, $T = 21 \pm 1$ °C, 720 min contact, Langmuir isotherm parameters: $Q_0=9.921$, $b=0.073$

The separation factor (R_L) can be used to determine whether or not the adsorption process will be favorable [37]. The parameter predicts that the type of isotherm could be irreversible ($R_L=0$), favorable ($0 < R_L < 1$) or unfavorable ($R_L > 1$). For the present study, the values of R_L obtained at different initial heavy metal (Cu(II) and Pb(II)) concentrations are presented in Table 2. These values are between zero and one indicating that the adsorption was favorable.

The Langmuir model is an indication of surface homogeneity of the adsorbent.

Table 2. R_L values and type of isotherm

Initial Cu (II) concentration, mg/L	R_L value
10	0.813
20	0.685
30	0.592
40	0.521
50	0.465
Initial Pb (II) concentration, mg/L	R_L value
10	0.578
20	0.407
30	0.313
40	0.255
50	0.215

Even though the comparison of the results obtained shows that the Langmuir equation yielded a higher R^2 value than the Freundlich equation, the closeness of both R^2 values to unity suggests that

both equations could readily be used to represent the equilibrium conditions of the system. Therefore, it is assumed that adsorption involves direct contact of metal ions onto the surface of coffee ground and thus proceeds up to monolayer coverage.

Studies have shown (Figs. 1–8) that the efficiency of the adsorption process of copper and lead ions onto coffee grounds depends not only on contact time and concentration, but also on pH of the solution. The remarkable results obtained in this study prompt us to use the coffee waste as an adsorbent for the treatment of wastewater polluted with heavy metals.

CONCLUSIONS

1. Metal uptake increases with an increase in contact time. On increasing contact time from 15 to 720 min, adsorption efficiency of Cu (II) and Pb (II) increases from 15.30 to 65.7% and from 18.40 to 84.5%, accordingly. The adsorption equilibrium of the investigated metals was achieved in 120 min, when single metal ion concentration in solution was 10 mg/L.

2. Experimental studies showed that pH of the solution has an impact on adsorption process efficiency. Copper (II) and lead (II) adsorption from aqueous solutions is most effective when the solution is weakly acidic, i.e., pH = 5.0. Maximum adsorption capacity for Cu (II) onto coffee ground was 0.657 mg/g and maximum adsorption capacity for Pb (II) onto coffee ground was 0.845 mg/g, when single metal ion concentration in solution was 10 mg/L.

3. The sorption of Pb (II) ions onto coffee grounds was by 14–30% better than the adsorption of Cu (II) ions. There are many factors having impact on the efficiency of the adsorption process such as different ion species, polarity and ionic radius.

4. This study showed that both Freundlich and Langmuir equations can be used to describe the adsorption phenomena for Pb(II) and Cu(II) onto coffee grounds.

REFERENCES

- O. E. A. Salam, A. N. Reiad, M. M. ElShafei, *J. Adv. Res.*, **2**, 297 (2011).
- M. E. Argun, S. A. Dursun, *Bioresource Technol.*, **99** (7), 2516 (2008).
- M. H. Salmani, M. H. Ehrampoush, S. Sheikhalishadi, M. Dehviri, *J. Health Res.*, **1** (1), 11 (2012).
- R. A. Wuana, F. E. Okieimen, *ISRN Ecol.*, **1**, 2011.
- A. Naudžiūnaitė, Heavy metals migration in different soil types profiles, in: Lithuanian: Sunkiųjų metalų

- migracija skirtingų tipų dirvožemių profiliuose, Akademija, Kaunas, 2009.
6. N. Zahra, *J. Anal. Environ. Chem.*, **13** (1), 11 (2012).
 7. M. Bilal, J. A. Shah, T. Ashfaq, S. M. H. Gardazi, A. A. Tahir, A. Pervez, Q. Mahmood, *J. Hazard. Mater.*, **263**, 322 (2013).
 8. S. I. Mussatto, Ballesteros, S. Martins, J. A. Teixeira, *Sep. and Purif. Technol.*, **83**, 173 (2011).
 9. N. Azouaou, Z. Sadaoui, A. Djaafri, H. Mokaddem, *J. Hazard. Mater.*, **184** (1), 126 (2010).
 10. W. L. Chou, C. T. Wang, K. Y. Huang, Y. C. Chang, C. M. Shu, *Int. J. Phys. Sci.*, **7**, 16, 2445 (2012).
 11. N. E. Davila-Guzman, F. J. Cerino-Córdova, J. R. Rangel-Mendez, P. E. Diaz-Flores, AIChE Annual Meeting: Conference Proceedings, 2011.
 12. D. Imessaoudene, S. Hanini, A. Bouzidi, *J. Radioanal. Nucl. Chem.*, **298** (2), 893, (2013).
 13. X. Liu, D. J. Lee, *Bioresource Technol.*, **160**, 24 (2014).
 14. H. B. S. Muhammad, K. B. A. Mohammad, H. Z. Toh, *The Singapore Public Service: Integrity, Service, Excellence*, 2012.
 15. H. D. Utomo, *Nat. Resour.*, **6** (3), 152 (2015).
 16. H. Y. Yen, C. P. Lin, *Desalin. Water Treatm.*, **1**, 11154 (2015).
 17. H. Y. Yen, S. L. Huang, *Desalin. Water Treatm.*, **1**, 21328 (2015).
 18. G. Z. Kyzas, *Mater.*, **5** (10), 1826 (2012).
 19. J. Roh, H. N. Umh, C. M. Yoo, S. Rengaraj, B. Lee, Y. Kim, *Korean J. Chem. Eng.*, **29** (7), 903 (2012).
 20. K. Shen, M. A. Gondal, *J. Saudi Chem. Soc.*, **1**, 120 (2013).
 21. M. Gonçalves, M. C. Guerreiro, P. H. Ramos, L. C. A. de Oliveira, K. Sapag, *Water Sci. Technol.*, **68** (5), 1085 (2013).
 22. A. H. Mahvi, D. Nagipour, F. Vaezi, S. Nazmara, *Am. J. Appl. Sci.*, **2** (1), 372 (2005).
 23. P. Dalal, *Int. J. Plant, Anim. Environ. Sci.*, **2** (4), 109 (2012).
 24. K. Y. Foo, B. H. Hameed, *Chem. Eng. J.*, **156** (1), 2, (2010).
 25. M. S. Rajput, A. K. Sharma, S. Sharma, S. Verma, *Int. J. Chem. Sci.*, **3** (1), 9 (2015).
 26. A. Dutta, Y. Diao, R. Jain, E. R. Rene, S. Dutta, *J. Environ. Eng.*, 5001 (2015).
 27. K. B. Payne, T. M. Abdel-Fattah, *J. Environ. Sci. Health.*, **39** (9), 2275 (2004).
 28. G. Z. Kyzas, N. K. Lazaridis, A. C. Mitropoulos, *Chem. Eng. J.*, **189**, 148 (2012).
 29. L. Agwaramgbo, N. Lathan, S. Edwards, S. Nunez, *J. Environ. Protect.*, **4**, 741 (2013).
 30. N. E. Dávila-Guzmán, F. de Jesús Cerino-Córdova, E. Soto-Regalado, J. R. Rangel-Mendez, P. E. Díaz-Flores, M. T. Garza-Gonzalez, J. A. Clean, *Soil Air Water*, **41** (6), 557 (2013).
 31. V. K. Gupta, A. Nayak, S. Agarwal, *Environ. Eng. Res.*, **20** (1), 1 (2015).
 32. R. Lafi, A. ben Fradj, A. Hafiane, B. H. Hameed, *Korean J. Chem. Eng.*, **31**, 12, 2198 (2014).
 33. W. E. Oliveira, A. S. Franca, L. S. Oliveira, S. D. Rocha, *J. Hazard. Mater.*, **152** (3), 1073 (2008).
 34. S. Rafiq, M. K. Ali, M. Sakari, J. Sulaiman, S. M. Yasir, *Int. J. Environ. Bioenerg.*, **7** (2), 91 (2013).
 35. F. Barbier, G. Duc, M. Petit-Ramel, *Physicochem. Eng. Asp.*, **166** (1), 3, 153 (2000).
 36. M. Minamisawa, H. Minamisawa, S. Yoshida, N. Takai, *J. Agr Food Chem.*, **52** (18), 5606 (2004).
 37. F. Aisien, N. Amenaghawon, O. Urhobotie, *J. Eng. Sci. Tech.*, **10** (12) 1641 (2015).

УТАЙКА ОТ КАФЕ КАТО ЕВТИН АДСОРБЕНТ ЗА ОТСТРАНЯВАНЕ НА МЕД (II) И ОЛОВО (II) ОТ ВОДНИ РАЗТВОРИ

Й. Сенюнайте, Р. Вайшкунайте*, Д. Палиулис

Департамент по опазване на околната среда и хидро-инженерство,

Вилнюс Гедиминас технически университет, Саулетекио ал. 11, Вилнюс, Литва, LT-10223

Постъпила на 4 март, 2017 г.; Коригирана на 10 ноевври, 2017 г.

(Резюме)

В настоящата статия е изследвано отстраняването на Cu (II) и Pb (II) от водни разтвори с утайка от кафе от търговски обекти. Утайката е използвана като адсорбент без допълнителна обработка. В експериментите е използвана фракцията с размер на частиците <200 μm . Изследвано е влиянието на рН (2.0, 3.0, 4.0 и 5.0), контактното време (15, 30, 60, 90, 120, 150, 180, 300, 480 и 720 min) и началната концентрация на Cu(II) и Pb(II) (10 mg/L, 20 mg/L, 30 mg/L, 40 mg/L, 50 mg/L). Оптималните стойности на параметрите на процеса са: време на контакт 120-720 min; рН 5.0; начална концентрация на Cu(II) и Pb(II) 20 mg/L. Равновесните данни съответстват на моделите на Langmuir и Freundlich за Pb (II) и Cu (II) с високи R^2 стойности. Установено е, че утайката от кафе е подходящ адсорбент за отстраняване на тежки метали от води.