

Adsorption Efficiency of Coffee Husk for Removal of Lead (II) from Industrial Effluents: Equilibrium and Kinetic Study

Shifare Berhe¹, Dejene Ayele², Abi Tadesse³, Abrha Mulu⁴

¹Chemistry Department, College of Natural Science, Jigjiga University

²Department of Chemistry, College of Natural Science, Jimma University

³Department Chemistry, College of Natural Science, Haramaya University

⁴Department Chemistry, College of Natural Science, Aksum University

Abstract- This study was carried out to investigate the efficiency of Ethiopian coffee husk (husk of coffee Arabica) to adsorb Pb(II) from industrial effluents using batch experiment. During the batch experiment effects of some parameters such as pH, dose of coffee husk, contact time, initial concentration(Pb(II)), and agitation speed were evaluated and the results indicate that optimum condition for Pb (II) adsorption were pH, 5; contact time, 90 minutes; dose of coffee husk, 2 g; initial concentration, 50 mg/L and agitation speed, 200 rpm. The coffee husk yielded a maximum adsorption efficiency of 95.14%. The residual metallic ion concentrations were determined using Atomic Absorption Spectrometer (AAS). Surface properties of the adsorbent were studied using Fourier Transform Infra-red (FTIR) spectrometer. The linear form of Langmuire and Freudlich models were applied to represent adsorption data. The calculated equilibrium data of Pb(II) were well fitted to both Langmuir and Freudlich isotherm models with maximum adsorption capacity (q_{max}) of 50 mg/g. Two kinetic models were used to determine the adsorption mechanism and the kinetic data were correlated ($R^2 = 0.99$) well with the pseudo second order kinetic model for the adsorption study of Pb(II) which implies that adsorption follows second order kinetics. To evaluate the practical applicability of the coffee husk, adsorption study was also carried out using real samples collected from waste water generated auto-garage and battery charging workshop.

Index Terms- coffee husk, adsorption capacity, removal efficiency, adsorption isotherm.

I. INTRODUCTION

The release of huge amounts of industrial effluents containing heavy metal ions such as Pb(II), Cd(II), Cu(II) etc are becoming a serious environmental problem due to its toxicity to aquatic and terrestrial life including human beings. Heavy metals present in these effluents are more stable and persistent environmental contaminants; since they cannot be degraded or destroyed. Thus they tend to accumulate in ground water, the soil, seawater and sediments, which cause deleterious effects on the health of many biological species and on the environment. Lead, is one of the typical heavy metals even at very low concentration, may bring substantial threat to human health through the food chains. it is released into the environment in

different ways, including lead acid batteries, pulp and paper, petrochemicals, refineries, printing, pigments, photographic materials, explosive manufacturing, ceramic, glass, paint, oil, metal, phosphate fertilizer, electronic goods, wood production and also combustion of fossil fuel, forest fires, mining activity, automobile emissions, sewage wastewater and sea spray (Conrad and Hansen, 2007).

The presence of high levels of lead in the environment may cause long-term health risks to humans and ecosystems. It is a poisonous metal that can damage nervous connections (especially in young children) and cause blood and brain disorders. When present above 0.05 mg / L in drinking water, Pb(II) is a potent neurotoxic metal(Sag *et al.*, 1995). Acute lead poisoning in humans affects the central nervous system, the gastrointestinal system, the liver, and the kidneys, and it can directly or indirectly cause serious health issues, such as anemia, hepatitis, nephritic syndrome, and encephalopathy. It is therefore mandatory that their levels in drinking water, waste water and water used for agricultural and recreational purposes must be reduced to within the allowable concentrations recommended by national and international health authorities such as the World Health Organization. Lead removal from the wastewater prior to discharge into environment is, therefore, necessary (Groffman *et al.*, 1992).

Therefore, the removal of Pb(II) from wastewater has received much attention in recent years. As the result, the development of reliable and economical feasible methods for the removal of lead from waste water is particularly significant from aquatic environment. Some of heavy metal polluted effluent treatment technologies are chemical precipitation (Sampaio *et al.*, 2009), reverse osmosis (Cadotte *et al.*, 1981), ion exchange (Alyuz, 2009), solvent extraction, flocculation, membrane separation, electrolysis (Bessbousse *et al.*, 2008), photochemical reactions (Fox and Dulay, 1993), activated sludge (Bromley-Challenor *et al.*, 200), magnetic separation (Karapinar, 2003). However, these technologies are becoming uneconomical and unfavorable (some of them produce large toxic sludge like precipitation) to remove heavy metals from industrial wastewaters (Ahalya *et al.*, 2005).

Searching for a low cost and easily available adsorbent has led to the selection of materials from agricultural and biological origin, along with industrial by-products, as adsorbents. Biological treatment using either living or dead microorganisms or plants, offers unique capabilities to concentrate and reduce the

levels of heavy metals to environmentally acceptable limits in economically and environmentally friendly manner (Volesky, 2001).

The adsorption of metals on different microbial and agricultural wastes like treated and untreated rice husk, Parthenium carbon, walnut hull, wood-rotting mushrooms, mango seed husks, barley straws, bituminous coal, sphagnum peat moss, coconut husks and palm pressed fibers, sawdust, sugarcane bagasse, sugar beet pulp and maize cob etc in different countries have been reported (kumer, 2006).

Coffee husk used as an adsorbent in this study is one of the agricultural by products or wastes obtained from coffee processing units. Coffee husk is an abundant and a low-cost adsorbent material on a large scale in many African countries especially in Ethiopia. Ethiopia is home land of coffee & the prominent producer of coffee in Africa, and has many Coffee processing units. The huge amount of coffee production and the increasing number of coffee husk residue from processing units in the country indicates the likely increase in quantities of coffee husk residue from processing units. In this study, coffee husk which was an agricultural waste were used as an adsorbent to remove Pb (II) from aqueous solutions and industrial effluent (effluents from battery charging workshop) under different experimental condition (contact time, pH, amount of adsorbent and initial concentration). The adsorption isotherm and kinetic studies were carried out to explain nature and rate of adsorption process respectively.

II. MATERIALS AND METHODS

2.1. Preparation of Adsorbent

Coffee husk collected from coffee Hirna coffee processing unit was used in this study as adsorbent. Then the collected coffee husk sample was powdered by using electrical mill and allowed to pass through different mm sieves (8, 6, 4, 2, 1 mm) and the powdered coffee husk was washed with distilled water to remove dirt and boiled to remove color. Finally, it was dried at 105 °C for 5 h in a convection oven and treated with 2% formaldehyde solution in order to reduce biodegradation of organic compounds and avoid mould formation during batch sorption (Chen, 2005).

2.2. Adsorbate Solutions

Stock standard solutions of Pb(II) having concentrations of 1000 mg/L were prepared from analytical reagent grade lead nitrate (Pb(NO₃)₂) dissolving 1.6g (Pb(NO₃)₂) in deionized water. Finally, 5.00 ml of concentrated nitric acid solution was added to stock solution and these solutions were used to prepare working solutions of various concentrations by appropriate dilution.

2.3. Batch Adsorption Experiment

Batch adsorption studies were carried out using 250 ml Erlenmeyer flask. The effects of different parameters such as adsorbate (Pb(II)) concentration, adsorbent(coffee husk) dose, agitation time and pH were studied. Standard solutions of the Pb(II) were mixed with the coffee husk and agitated at different agitation rate on a mechanical shaker.

This was carried out by varying Pb(II) concentrations, pH and mass of coffee husk used for adsorption. Finally, the resulting suspension of the metal ion was filtered using a Whatman No. 42(125mm) filter paper and the filtrates were analyzed by AAS (GBC 932 plus). All experiments were performed in triplicate, and mean values were considered in data analysis. The percentage of Pb(II) removal (%adsorption) and q_e (mg/g) amount of Pb(II) adsorbed per unit mass of the coffee husk were determined using the following equations or relationships.

$$\text{Adsorption (\%)} = ((C_0 - C_e)/C_0) \times 100 \quad (1)$$

Where C₀ = initial concentration Pb(II) (mg/L) and C_f = final concentration (mg/L) of Pb(II)

$$q_e = (C_0 - C_e) V/M \quad (2)$$

Where q_e = adsorption capacity at equilibrium (mg/g), C₀ = initial concentration of Pb(II) (mg/L), C_e = equilibrium concentration of Pb(II) (mg/L), M = mass of coffee husk (g), V = volume of the solution

2.4 Desorption Studies

In order to regenerate or elute Pb(II) from the coffee husk, desorption experiment was carried out using the desorbing media – distilled water at pH ranges 1 to 7 using dilute solutions of 0.1 M NaOH and 0.1 M HCl. Then they were agitated for the equilibrium time of adsorbate. The desorbed adsorbate in the solution was separated and analyzed for the residual Pb(II). The recovery percentage was obtained according to Arica *et al.*(2003) using the following equation.

$$\text{Desorption efficiency (\%)} = (\text{Desorbed} / \text{Adsorbed}) \times 100 \quad (3)$$

Desorbed = concentration of metal ion in desorbing solution after desorption process.

Adsorbed = (C₀ - C_e) where C₀ and C_e are initial and equilibrium concentration of the heavy metal ion respectively.

2.5. Infrared Spectroscopic Analysis

The Fourier Transform Infrared Spectrometer (FTIR Presige 21, Gemen) was used to identify the functional groups present in the coffee husk involved in Pb(II) adsorption process. For this purpose 2 mg of ground coffee husk was placed on KBr disk and dissolved with 10 drops of paraffin. Then the KBr disk with the sample was immediately put into sample holder. Then FTIR spectra were recorded.

III. RESULTS AND DISCUSSION

3.1. Effect of Adsorbent Dose

The effect of the adsorbent dose was studied at room temperature by varying the adsorbent amounts from 0.5 to 12 g. For all these runs, initial concentration of Pb (II), pH, agitation speed and contact time was kept constant. Figure-1 shows that adsorption efficiency of different doses of coffee husk as adsorbent. The result revealed that adsorption efficiency for removal of Pb(II) increased with adsorbent dose in the range from 0.5- 2 g and showed little variation with further increment.

This is due to limited availability of adsorbate species for a relatively larger number of surface sites on the adsorbent at higher dosage of adsorbent. It is reasonable that with higher dosage of adsorbent, there would be greater number of exchangeable sites for metal ions (Selvaraj *et al.*, 1997, Babel and Kurniawan, 2004). Therefore, the maximum removal efficiency of Pb (II) was obtained at an coffee husk dose of 2 g. In all subsequent studies, the amount of coffee husk was taken as 2 g of coffee husk. In the case of adsorption capacity the reverse trend was observed as the dose of the adsorbent increased i.e., the adsorption capacity decreased as the dose of the sorbent was increased. Since adsorption capacity is expressed as the mass of metal ion adsorbed per unit mass of the adsorbent, its value decreases when the mass of the metal ion adsorbed gets smaller for the same increase in the mass of the adsorbent. This is then the reason for the observed decrease in adsorption capacity with an increase in adsorbent dose.

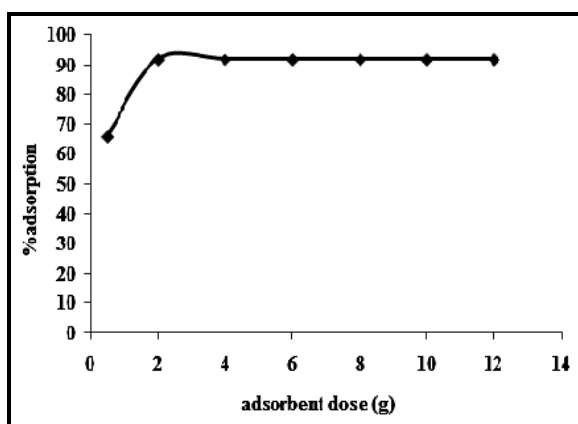


Fig.1. Pb (II) removal efficiency (%): (Co =50 mg/L, contact time = 90 min, solution pH = 4, agitation speed = 150 rpm)

3.2 Effect of Agitation Speed

Results of agitation speed effect on adsorption of Pb(II) which is illustrated in Figure 2 shows that adsorption efficiency of a coffee husk increased from 75.22% to 90.46% when the agitation rate increased from 50 to 200 rpm. According to the research carried out by Nomanbhay and Palanismay (2005), the increase in agitation rate improves the diffusion of metal ions towards the adsorbent surface and the same thing was observed in this study. Therefore, decreased value of the Pb(II) adsorbed by coffee husk after 200 rpm is the result of too vigorous agitation rate which causes more metal ions to be desorbed from the adsorption sites.

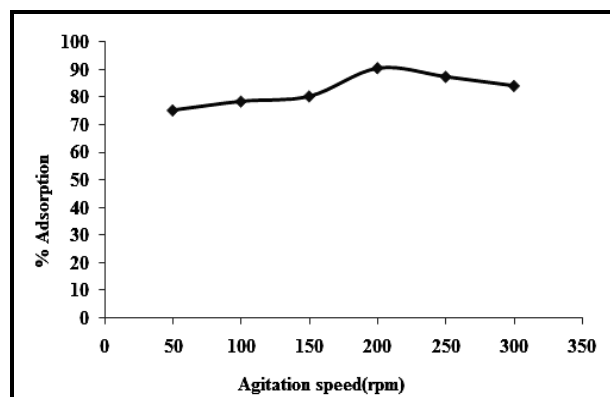


Fig.2 Effect of agitation speed on Pb (II) removal efficiency (pH = 5, dose = 2 g, time = 90 min, Co = 50 mg/L)

3.3. Effect of Contact Time

The effect of contact time on Pb (II) adsorption efficiency of coffee husk as adsorbent illustrated in figure 3 and the result shows that the adsorption process took place in two stages. The first stage was rapid, where about 97.1%, of adsorption was completed and second stage represented a slow progress of adsorption. The rapid initial adsorption may be attributed to the accumulation of metals on to the surface of adsorbent, due to the large number of free binding sites. With the progressive occupation of these sites, the process in the second stage became slower. This is in accordance with the observations of other similar studies (Sangi *et al.*, 2008; Qaiser *et al.*, 2009). The removal efficiency turned sharply at contact time of 90 minute and this optimum time was selected as contact times for all experiments.

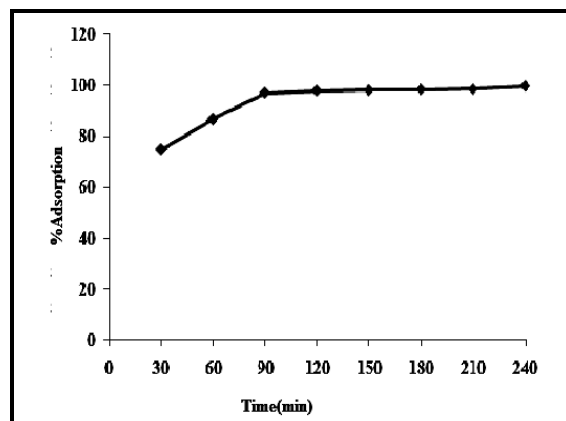


Fig. 3 Pb(II) removal efficiency (%) at various contact time (Co = 50 mg/L, dose = 2g, solution pH = 4, agitation speed = 200 rpm)

3.4. Effect of pH

The effect of pH on the extent of adsorption of the Pb (II) on to the coffee husk was studied by varying the pH in the range 2 to 9 with metal concentration 50 mg/L and at an agitation speed of 200 rpm. The contact time was set at 90 min. The obtained results are illustrated in Figure-4.

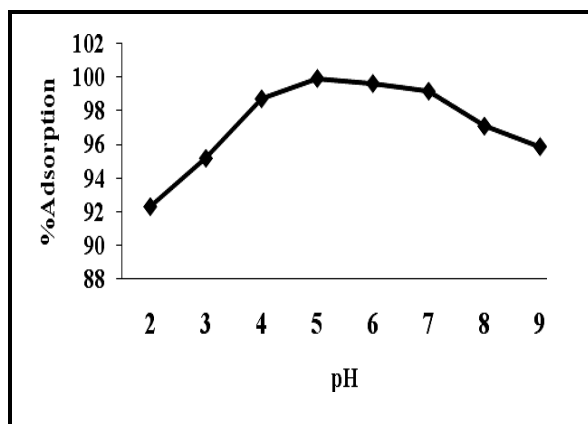


Fig.4. Effect of pH on Pb(II) removal efficiency (%) ($C_o = 50$ mg/L, dose = 2 g, time = 90 min, agitation speed = 200 rpm)

The results in Figure 4 depicted clearly that lead adsorption increases with an increase in pH in the range between pH 2 and 5, whereas it decreases with further increase above pH 5. Maximum adsorption of Pb^{+2} was attained at pH 5 in which 99.9% of the lead in the solution were removed. At low pH (below 3), there was excessive protonation of the active sites at coffee husk surface which prohibited the formation of links between Pb (II) ions and the active sites. At moderate pH values (3 to 5), linked H^+ was released from the active sites and this resulted in an increase in the amount of metal ions adsorbed. At higher pH values (above 5), the precipitation was dominant or both ion exchange and aqueous metal hydroxide formation could become significant processes. Similar results were obtained by Senthilkumar (2009) studying the adsorption efficiency bael tree leaf powder for removal of Pb(II) from aqueous solution.

3.5. Effect of Initial Concentration

Results of the study on the influence of initial Pb (II) concentration on the removal efficiency of the coffee husk are depicted in Figure 5 and the obtained result indicated that the adsorption efficiency coffee husk increase initially and then decrease from 95.1% at 50 mg/L to 72.5% at 120 mg/L Pb (II).

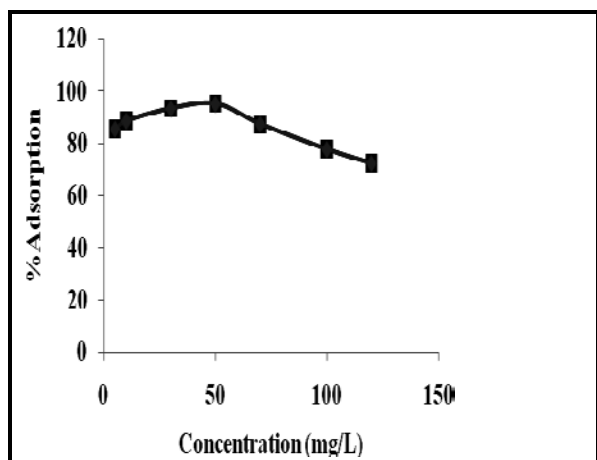


Fig.5 Effect of initial concentration on Pb (II) removal efficiency (%) (pH = 5, dose = 2 g, time = 90 min, agitation speed = 200 rpm)

At lower concentrations, the number of moles of lead ion is small relative to the available adsorption sites on the adsorbent. Subsequently, adsorption becomes independent of initial concentration and as a result adsorption was found to increase. However, at higher concentrations, most of the adsorption sites will be occupied by lead ions and the available sites of adsorption become fewer, hence the percentage removal of lead ions which depends up on the initial concentration decreases.

3.6. Adsorption Equilibrium

Adsorption isotherm is needed to explain the adsorption process and to determine the adsorption efficiency of an adsorbent. Out of the different adsorption isotherm models, Langmuir’s and Freundlich’s models have been preferred by most of the studies concerning about adsorption. The present experiment also used Langmuir’s and Freundlich’s equations to explain the adsorption mechanism of the adsorbent considered.

3.6.1 Adsorption isotherms

The study was carried out by using 0.5 g, 2 g, 4 g, 6 g, 8 g, 10 g and 12 g dose of coffee husk. Figure 6 shows the relationship between the quantity of Pb (II) adsorbed per gram of adsorbent and the equilibrium liquid phase concentration at room temperature. Adsorption equilibrium isotherm models were used describe the adsorption process and the results obtained were analyzed using different isothermal equations. The graph obtained by Langmuir equation shows that the relation between $1/C_e$ in the x axis and $1/q_e$ in the y axis. On the other hand, the graph of Freundlich’s equation shows the relationship between $\log C_e$ in the X axis and $\log q_e$ in the y axis.

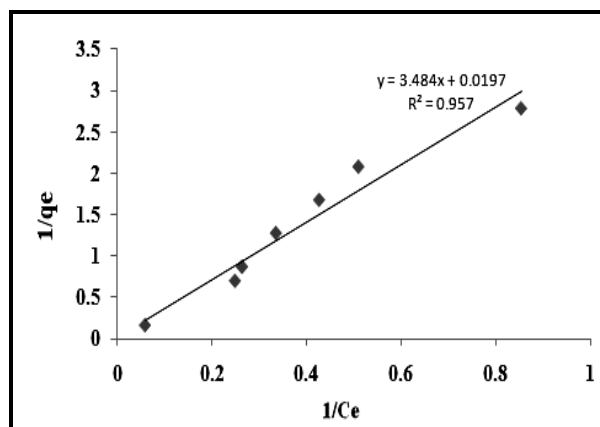


Fig.6 Langmuir adsorption isotherm of Pb (II)

According to figure.6:

Intercept Y ($1/q_m$) = 0.0197, $q_m = 50.8$
 Slope ($1/bq_m$) = 3.484, $bq_m = 0.2870$,
 Langmuir’s equation, $q_e = \frac{0.2870C_e}{(1+0.00574C_e)}$

Using Langmuir’s equation, the maximum adsorption capacity by coffee husk was obtained as 50.8 mg/g. That is one gram of the coffee husk can absorb 50.8 mg lead. The value of R_L obtained is $1/1.287 = 0.78$. The shape of isotherm by Langmuir’s equation was therefore, favorable isotherm. This

means that at equilibrium high concentration of lead was adsorbed on coffee husk surface compared to its amount remained in aqueous solution.

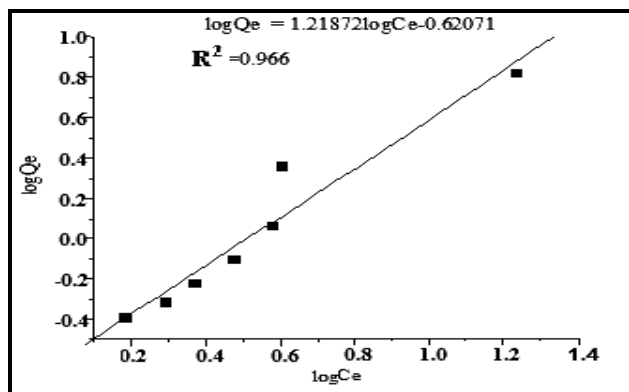


Fig.7. Freundlich adsorption isotherm for Pb(II)

For linearization of the data, the Freundlich equation is written in logarithmic form.

$$\text{Log } x/m = \text{logK} + 1/n \text{ log } C_e$$

According to Fig 7,

$$\begin{aligned} \text{Slope } 1/n &= 1.2187 \\ \text{Intercept Y (logk)} \text{ logK}_f &= -0.6207 \\ \text{Constant } K_f &= 0.2395 \end{aligned}$$

$$\text{Freundlich's equation } q_e = K_f C_e^{1/n} = 0.2395 C_e^{1.2187}$$

The values of 1/n and n obtained from Freundlich's equation were 1.22 and 0.82 respectively. It means that the surface of coffee husk becomes less heterogeneous which leads to less adsorption intensity. The lead adsorption on coffee husk also fitted to both models since the correlation coefficients (R^2) are 0.957 and 0.966.

Table 1 Langmuir and Freundlich constants for the adsorption of Pb (II)

Langmuir		Freundlich				
q_{max}	b	R^2	R_L	K_f	1/n	R^2
50.8	0.006	0.957	0.777	0.240	1.22	0.966

q_{max} = maximum adsorption capacity (mg/g), b = constant related to binding energy, R^2 = correlation coefficient, R_L = separation factor, K_f = Freundlich adsorption capacity, n = Freundlich constant related to intensity of adsorption.

3.6.2. Comparison of adsorption capacity of coffee husk with other adsorbents

Table 2 Comparison of adsorption capacity of coffee husk for Pb (II) with other adsorbents

Adsorbent	q_{max} (mg/ g)	References
Palm kernel fibre	40.2	Ho <i>et al.</i> , 2005

Tree tern	40.0	Ho <i>et al.</i> , 2004
Na-montmorillonite	9.6	Abollino,2003
Sawdust	21.05	Li <i>et al.</i> , 2007
Modified peanut husk	29.14	Li <i>et al.</i> , 2007
Fly ash	17.2	Alinoor., 2007
Coffee husk	50.8	Present study

The comparison of adsorbent capacity of coffee husk with other materials reported in literature is given in Table 2. Accordingly; the adsorption capacity of coffee husk obtained is higher than adsorbents from various industrial and low cost adsorbent.

3.7. Adsorption Kinetics

Adsorption kinetics, which describes the solute adsorption rate, is an important characteristic in evaluating the efficiency of adsorption. The adsorption data (at pH 4) for initial Pb (II) concentration of 50 mg/L is shown from Figure 8. The 2 g of coffee husk were taken for this study. The plot shows that the adsorption of Pb (II) with different contact time consists of two phases; an initial rapid phase where adsorption was fast and a second slower phase where adsorption equilibrium uptake was achieved. In adsorption process identification of the slowest step or rate determining step is very crucial. Previously several researchers used different kinetic models, such as Lagergren's pseudo first order, pseudo second order, Elovich kinetic equation, and parabolic diffusion model, in order to predict the mechanism involved in the adsorption process. Currently, the Lagergren pseudo first order and pseudo second order models have been widely used for adsorption systems due to their good representation of the experimental data for most of the adsorbent-adsorbate systems (Inbaraj *et al.*, 2002; Mall and Upadhyay, 1998). Therefore, the two kinetic models were applied. The pseudo- first order model can be represented in the following form

$$dq_t / dt = k_1 (q_e - q_t) \tag{4}$$

Where k_1 is the rate constant, q_e and q_t are the amounts of the metals adsorbed (mg/g) at equilibrium and at any time t, respectively. This equation can be integrated to yield a linearized form at initial conditions where $q_t = 0$, $t = 0$ and at any time t, where $q_t = t$ and $t = t$.

$$\log (q_e - q_t) = \log q_e - k_1 t / 2.303 \tag{5}$$

In this equation, the rate of adsorption is assumed to be proportional to the difference between the adsorption capacity at equilibrium (q_e) and the adsorption capacity at time t (q_t). The pseudo- first order kinetics is applicable if the plot of $\log (q_e - q_t)$ against t shows linear relationship. A straight line plot of $\log (q_e - q_t)$ versus t was used to determine the rate constant, k_1 and correlation coefficient, R^2 (0.915) as shown in Figures 8. The values of k_1 (L/min^{-1}) and q_e (cal) in mg/g of Pb (II) predicted from those plot are 2.12×10^{-2} and, 1.10. The result shows that the pseudo-first order rate equation did not adequately describe the adsorption result of Pb(II). The pseudo second order rate equation is expressed as shown in equation 6 (HO and McKay, 1999):

$$dq_t / dt = k_2 (q_e - q_t)^2 \tag{6}$$

Where, k_2 is equilibrium rate constant of second order kinetics model ($\text{g mg}^{-1} \text{min}^{-1}$). After integrating equation (6) for a condition $q_t = 0$ at $t = 0$ and $q_t = q_t$ at $t = t$, it can be obtained:

$$t/q_t = 1/k_2 q_e^2 + t/q_e \quad (7)$$

Equation (7) can be rearranged to obtain a linear form:

$$t/q_t = 1/h + t/q_e \quad (8)$$

Where initial adsorption rate ($\text{mg g}^{-1} \text{min}^{-1}$), $h = k_2 q_e^2$

The pseudo-second order rate constant (k_2), h and the equilibrium adsorption capacity (q_e) can be determined experimentally from the slope and intercept of the plot t/q_t versus t . The plot t/q_t versus t should give a straight line if pseudo-second order kinetics is applicable. The plot of the linearized form of the pseudo second order reaction of Pb (II) on adsorbent surface is shown in Figures 9. The plot of t/q_t versus t for pseudo second order rate equation yields a good straight line ($R^2 > 0.99$) as compared to the plot of pseudo first order. The pseudo second order rate constant and initial adsorption rate for Pb (II) was obtained as $3.25 \times 10^{-2} \text{ g mg}^{-1} \text{min}^{-1}$ and $0.44 \text{ mg g}^{-1} \text{min}^{-1}$. The theoretical values of q_e (2.49 mg g^{-1}) predicted from pseudo-second order plot also agrees well with the experimental one (2.43 mg g^{-1}) (Table 3). This suggests that the adsorption of Pb (II) by coffee husk follows pseudo-second order model, which relies on the assumption that chemisorptions is rate limiting step.

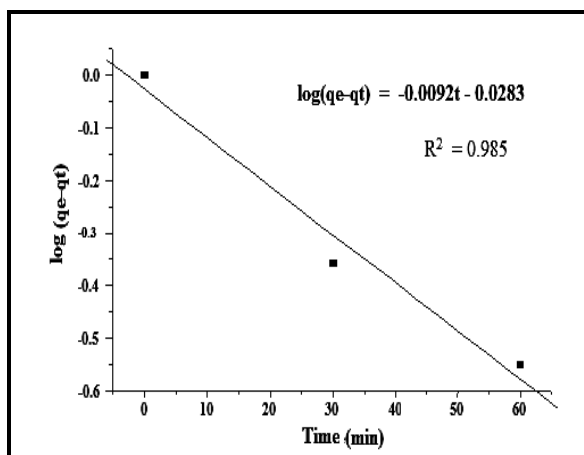


Fig. 8 Pseudo first order plot for Pb (II) at fixed solution pH and adsorbent dosage

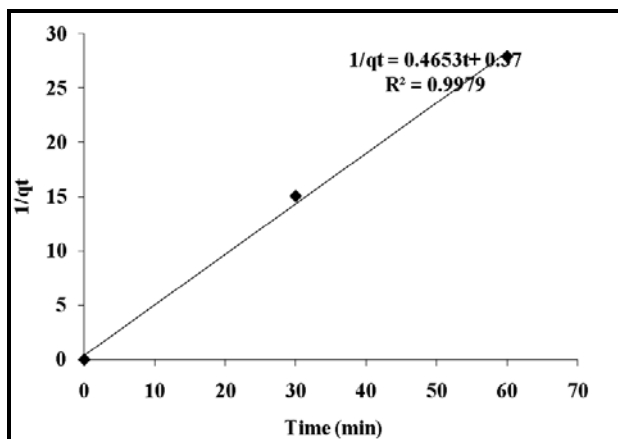


Fig. 9 Pseudo second order plot for Pb (II) adsorption at fixed solution pH and adsorbent dosage

Table 3 Adsorption kinetic rate constants for Pb(II)

Pseudo-First order		Pseudo-Second order					
Parameters							
q_e (exp)	q_e (cal)	K_1	R^2	q_e (cal)	k_2	h	R^2
2.43	1.10	2.12×10^{-2}	0.985	2.49	4.35×10^{-1}	2.70	0.998

q_e (exp) = experimental equilibrium adsorption capacity(mg/g), q_e (cal) = calculated equilibrium adsorption capacity(mg/g), K_1 = pseudo first order rate constant(L/min^{-1}), R^2 = correlation coefficient k_2 = pseudo second order rate constant($\text{g mg}^{-1} \text{min}^{-1}$), h = initial adsorption rate mg/g min).

3.8 Desorption studies

Desorption of Pb (II) from lead loaded adsorbents increased with decrease in the initial pH. At pH 1, 75.98% of Pb (II) was desorbed from coffee husk. Lead (II) was removed maximally at an initial pH of 1.0. At acidic conditions, H^+ ions protonate the adsorbent surface by replacing the adsorbed metal ions on the adsorbent surface leading to desorption of the positively charged metal ion species. As the pH increases, desorption of Pb (II) from lead loaded adsorbents gradually decreases. This is due to the less availability of H^+ that can displace the lead ion. The above figure shows the effect of pH on desorption of Pb(II) from coffee husk. For this desorption process a distilled water (pH 1-7) was used.

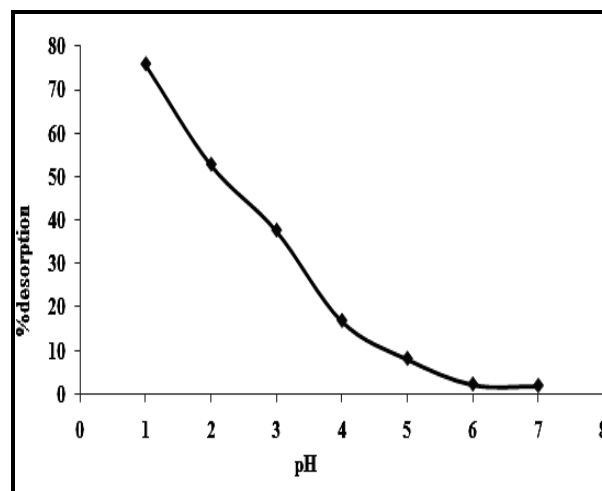


Fig. 10 Effect of pH on desorption of Pb (II)

3.9. Adsorption of Pb (II) from industrial effluents (battery charging workshop)

The feasibility and efficiency of adsorption process depends not only on the properties of the adsorbents, but also on successful application of adsorbent in industrial effluents. Therefore, perusal of data obtained from the effluent collected from auto-garage and battery charging workshop of Haramaya

University was used to conduct experiment to determine the adsorption efficiency of coffee husk. The Pb(II) removal efficiency of coffee husk from industrial effluent was obtained as 88.04% (Table 4). Moderate reduction was recorded in adsorption efficiency of the coffee husk for removal of Pb(II) from industrial effluents than from synthetic solutions. This could be due to various impurities present in industrial effluents in the form of anions i.e., SO_4^{2-} , NO_3^- and Cl^- etc that may compete for binding sites on coffee husk.

Table 4 Pb(II) removal efficiency of coffee husk from real solution

Initial Concentration (mg/L)	Concentration after adsorption	removal efficiency (%)	adsorption capacity (mg/g)
10.51±0.002	1.26±0.033	88.04	0.46

3.9 Infrared Spectroscopic Studies

Samples of the adsorbent used in the present study; namely coffee husk, were subjected to Fourier Transform Infrared Spectrometer, FTIR (Presige 21, Gemen). The FTIR Spectroscopic analysis indicated broad bands at 3441 cm^{-1} , may be representing bonded -OH groups rather than -NH groups. This is because of the peak of O-H stretching is broad with rounded tip but the peak for bonded-NH group is a broad peak with two sharp spikes (primary amines), a broad peak with one sharp spike (secondary amines) or no signal (tertiary amines). The bands observed at about $2955\text{--}2852\text{ cm}^{-1}$ may shows the presence of C-H stretching but not aldehydic C-H because the aldehydic C-H stretching vibration occurs in the region of $2830\text{--}2700\text{ cm}^{-1}$ with the appearance of two intense bands. The peaks around 1722 cm^{-1} correspond to the C=O group and at $1652\text{--}1616\text{ cm}^{-1}$ C=C. The C-O band absorption peak is also observed at 1035 cm^{-1} . These types of functional groups are important sorption sites of coffee husk to participate in Pb(II) binding from aqueous solution or industrial effluents.

IV. CONCLUSIONS

In this study, batch adsorption experiments for the removal of Pb (II) from aqueous solutions and industrial effluents have been carried out using coffee husk as a low cost, readily available adsorbent. The adsorption characteristics have been examined at different pH values, initial metal ion concentrations, contact time and adsorbent dosages. The effect of adsorbent dosage on the adsorption of Pb(II) by coffee husk showed that the percentage of Pb(II) removed increased with increase in adsorbent dosage due to increased adsorption surface area. Then 2g of coffee husk was selected as an optimum dosage through the experiment. The optimum pH for the removal of Pb(II) was 5. The amount of the Pb(II) removed at optimum pH increased with increase in initial Pb(II) concentration but the percentage adsorbed decreased with increase in initial metal concentration. Adsorption data for wide ranges of adsorbent doses were treated by Langmuir and Freundlich isotherms and then calculated equilibrium data of Pb (II) were well fitted to both Langmuir and Freundlich isotherm models. Comparison of the adsorption capacity of the coffee husk with that cited in literature reveals that coffee husk has also higher adsorption capacity. The kinetic data correlated ($R^2 = 0.99$)

well with the pseudo second order kinetic model for the sorption studies of Pb(II) which implies that adsorption follows second order kinetics.

Desorption studies of the adsorbates showed that regeneration of the Pb(II) is possible. Ion exchange might be the main mechanism by which the Pb(II) was attached to the adsorbents. Physical adsorption played a minimal role in the process.

The absorption spectra revealed that -C-O, -O-H and C=O bonds were predominant in the surface of the adsorbents and played a major role in the adsorption of Pb(II) from aqueous solution and industrial effluents. Coffee Husk as agro-industrial waste has negligible cost and has also proved to be an efficient adsorbent for the removal of Pb(II) from aqueous solution and industrial effluents. Furthermore, these adsorbed metal can be easily desorbed and the biomass be incinerated for final disposal. This adsorbent is of low cost; its utility will be economical and can be viewed as a part of a feasible waste management strategy.

ACKNOWLEDGMENT

The Authors are thankful to Haramaya University for providing financial support and other necessary facilities to accomplish this research work.

REFERENCES

- Abollino, O., Aceto, M., Malandrino, M., Sarzanini, C., Mentasti, E.(2003). Adsorption of heavy metals on Na-montmorillonite: Effect of pH and organic substances. *Water Res.* 37: 1619–1627
- Ahalya, N., Ramachandra, T.V., Kanamadi, RD. (2005). Biosorption of Chromium (VI) from aqueous solutions by the husk of bengal gram (Cicer arietinum). *Electronic Journal of Biotechnology* 99: 13–15.
- Alinoor, I.J.(2007). Adsorption of heavy metal ions from aqueous solution by fly ash. *Fuel* 86: 853–857.
- Alyuz, B. (2009). Kinetics and equilibrium studies for the removal of nickel and zinc from aqueous solutions by ion exchange resins. *J. Hazard. Mater.* 167 482–488.
- Chen, J., Yang ,L.(2005). Chemical modification of Sargassum sp. for prevention of organic leaching and enhancement of uptake during metal biosorption. *Ind. Eng. Chem. Res.* 44: 9931–9942.
- Cadotte, J.E., King, R.S., Majerle, R.J., Petersen, R.J. (1981). Interfacial synthesis in the preparation of reverse osmosis membranes *J. Macromol. Sci. A: Chem.* 15, 727–755.
- Conrad, K., Hansen, H.C.B. (2007). Sorption of zinc and lead on coir. *Bioresour. Technol.*, 98(1), 89–97.
- Bessbousse, H., Rhallou, T., Verchere, J.F., Lebrun, L.(2008). Removal of heavy metal ions from aqueous solutions by filtration with a novel complexing membrane containing poly(ethyleneimine) in a poly(vinyl alcohol) matrix. *J. Membr. Sci.* 307, 249–259.
- Groffman, A., Peterson, S., Brookins, D. (1992). Removing lead from wastewater using zeolites. *Water Environ. Technol.*, 4(5), 54–59.
- Fox, M.A., Dulay, M.T. (1993). Heterogeneous photocatalysis. *Chem. Rev.* 93, 341–357.
- Freundlich, H.(1907). Ueber die Adsorption in Loesungen. *Z. physik Chem.* 57: 385-470.
- Ho, Y.S., McKay, G.(1999). Pseudo-second order model for sorption processes. *Process Biochem.* 34:451–65.
- Ho, Y.S., Ofomaja, A.E. (2005). Kinetics and thermodynamics of lead ion sorption on palm kernel fibre from aqueous solution, *Process Biochem.* 40:3455–3461.

- [14] Inbaraj, B.S., Selvarani, K., Sulochana, N. (2002). Evaluation of a carbonaceous sorbent prepared from pearl millet husk for its removal of basic dyes, *Journal of Scientific & Industrial Research*. Vol. 61, pp. 971–978.
- [15] Karapinar, N. (2003). Magnetic separation of ferrihydrite from wastewater by magnetic seeding and high-gradient magnetic separation, *Int. J. Miner. Process.* 71,45–54.
- [16] Kumar, U. (2006). Agricultural products and by-products as a low cost adsorbent for heavy metal removal from water and wastewater: A review. *Sci. Res. Essay*. 1:33-37
- [17] Lagergren, S.(1898). Zur theorie der sogenannten adsorption gelöster stoffe.
- [18] Langmuir, I. (1918).The adsorption of gases on plane surfaces of glass, mica and platinum. *J Am.Chem.Soc.* 40: 1361-1403
- [19] Li, Q., Zhai, J., Zhang, W., Wang .M ., Zhou, J.(2007). Kinetic studies of adsorption of Pb(II), Cr(III) and Cu(II) from aqueous solution by sawdust and modified peanut husk., *J. hazard. Mater.* 144 : 163-167.
- [20] Mall, I.D., Upadhyay, S.N. (1998). Studies on treatment of basic dyes bearing wastewater by adsorptive treatment using flyash, *Indian Journal of Environmental.* 40,177.
- [21] Naja, G., Mustin, C., Volesky, B., Berthelin, J.(2005). A high-resolution titrator: a new approach to studying binding sites of microbial biosorbents. *Water Res.* 39: 579–588.
- [22] Qaiser, S., Saleem, A., Umar, M.(2009). Biosorption of lead from aqueous solution by *Ficus religiosa* leaves: Batch and column study. *Journal of hazardous materials.*166, 998-1005.
- [23] Sag, Y., Ozer, D., Kutsal, T. (1995). A comparative study of the biosorption of Lead(II) ions to *Z. ramigera* and *R. arrhizas* , *Process Biochemistry* 30,169–74 .
- [24] Sampaio, R.M.M., Timmers, R.A., Xu, Y., Keesman, K.J., Lens, P.N.L. (2009). Selective precipitation of Cu from Zn in a pS controlled continuously stirred tank reactor, *J. Hazard. Mater.* 165, 256–265.
- [25] Selvaraj, K., Chandramohan, V., Pattabhi, S.(1997). Removal of Cr (VI) from solution and chromium plating industry wastewater using photo film waste sludge. *Indian Journal of Chemical Technology.* 18, 641–646
- [26] Senthil Kumar, J., Gayathri, R.(2009). Adsorption of Pb²⁺ ions from aqueous solutions onto bael tree leaf powder: isotherms, kinetics and thermodynamics study. *Journal of chemical engineering science and technology.* 4(4), 381-399.
- [27] Volesky, B. (2001). Detoxification of metal-bearing effluents: biosorption for the next century, *Hydrometallurgy* 59, 203–216.

AUTHORS

First Author – Shifare Berhe, PhD Candidate on Environmental Science, Addis Ababa University, E mail: shifare7@gmail.com

Second Author – Dejene Ayele, Professor of Environmental Analytical Chemistry, College of Natural Science, Jimma University, Email: dejeneaye@yaho.com

Third Author – Abi Tadesse, Associate Professor of Chemistry, College of Natural Science, Haramaya University, Email: abi92003@yahoo.com

Fourth Author – Abrha Mulu, PhD Candidate on Environmental Science, Addis Ababa University, Email: chem.mulu@gmail.com

Correspondence Author – Shifare Berhe, Email: shifare7@gmail.com