

Full Length Research Paper

Adsorptive Removal of Pb(II) and Cr(VI) from Wastewater using Acid Untreated Coffee Husk

Haftu G. Alemayehu, Abiyu K. Burkute and Asnake G. Ede*

Arba Minch University, College of Natural Sciences, Chemistry Department, P.O.Box 21

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This study reports the biosorption of Pb (II) and Cr(VI) on surface of cleaned, sundried and powdered but acid untreated normal coffee husk. The functional groups identified at the surface of the coffee husk were OH⁻, -COOH, and -NH. A contact time of 6 hours assured attainment of equilibrium for both metal ions. The maximum adsorption capacity of Pb (II) and Cr (VI) was 50.54 ± 0.63 and 49.21 ± 0.74 mg g⁻¹, respectively. As the dose increased, removal efficiency increased with statistical significance ($p < 0.05$). The optimum pH for Pb(II) and Cr(VI) removal was 5.5 ± 0.01 and 2.2 ± 0.01 , respectively. The optimum temperature for removal of Pb(II) and Cr (VI) was $27.5 \pm 0.02^{\circ}\text{C}$ and $37.5 \pm 0.2^{\circ}\text{C}$, respectively. The experimental sorption equilibrium followed both Langmuir ($R^2=0.944$) and Freundlich ($R^2=0.930$) relatively more of Langmuir. The experimental data fitted pseudo first ($R^2=0.930$) and second ($R^2=0.955$) order kinetic models, being relatively better described by the pseudo-second-order. The reaction was spontaneous as ΔG° (-5.63 kJ/mol). This showed coffee husks are suitable candidates for use as biosorbents in the removal of heavy metals from aqueous solutions.

Keywords: Biosorption, adsorption isotherms, coffee husks, kinetics model, spontaneous, optimum

*Corresponding Author E-mail: astuasnegude@gmail.com, haftom.gebrekiros@amu.edu.et

INTRODUCTION

Industrial activities and mining operations have exposed man to the toxic effects of metals. Heavy metals are present in the soil, natural water, and air, in various forms. Moreover, may become contaminants in food and drinking water (Bhattacharyya *et al.*, 2006). Some of them are constituents of pesticides, paints, and fertilizer application. Heavy metals are persistent contaminants that accumulate in the environment. The discharge of heavy metals into aquatic ecosystems has become a matter of concern over the last few decades. The pollutants of serious concern include lead, chromium, and

mercury, due to their carcinogenic, teratogenic and mutagenic nature.

Severe lead poisoning can cause encephalopathy, with permanent damage, while moderate lead poisoning result in neurobehavioral and intelligent deficit (Chen *et al.*, 2007; Nadeem *et al.*, 2006). Lead poisoning in humans causes severe damage to kidney, nervous system, reproductive system, liver and brain. Chromium (VI) is carcinogenic to both humans and animals. The hexavalent form is 500 times more toxic than the trivalent (Mungasavalli *et al.*, 2007). According to the United States

Environmental Protection Agency (USEPA) the maximum permissible limits in wastewater and potable water are 0.1 mg l⁻¹ and 0.015 mg l⁻¹ for lead(II) and 1.0 mg l⁻¹ and 0.05 mg l⁻¹ for chromium(VI), respectively. The conventional methods for treatment of Pb (II) and Cr (VI) wastes include: precipitation, adsorption with activated carbon, ion exchange, membrane processes, oxidation and reduction (Wang *et al.*, 2003). These methods are expensive and often generate chemical sludge, whose disposal is problematic.

Biosorption has distinct advantages over the conventional methods which include: reusability of biomaterial, low operating cost, and selectivity for specific metal, short operation time and no chemical sludge. In the recent years many biosorbents materials of agricultural based have been utilized for heavy metal biosorption. These include: coconut husk and shell, sea weeds (Amuda *et al.*, 2007), maize leaf, coffee beans (Kaikake *et al.*, 2007). *The present research described the utilization of cleaned, sundried and powdered but not acid treated coffee husk for the biosorption of Pb (II) and Cr (VI) from wastewater. Influence of operating conditions like temperature, pH, biosorbent dose and initial metal concentrations on biosorption process was investigated. The equilibrium, kinetics and thermodynamics of biosorption process were also studied.*

MATERIALS AND METHODS

Adsorbent Collection, Preparation and Characterization

The coffee husk was collected from coffee processing unit, Hawassa, Ethiopia and was powdered and sieved to get uniform size 50 mesh particle sizes. Then, it was washed with distilled water to remove dirt and boiled to remove color, and dried at 105°C for 5 hrs in a convection oven. Next, it was treated with 2% formaldehyde solution in order to reduce organic leaching and avoid mould formation during batch sorption. Fourier Transform Infrared Spectroscopy (FTIR), SHIMADZUFTIR8400S (Kyoto Japan), was used to determine the functional groups responsible for the adsorption of metals. The pH of point of zero charge (pH_{PZC}) determination was estimated according to the titration procedures described in (Valdés *et al.*, 2002):

Preparation of Adsorbate Solution

A stock solution of 1000 mg/L of Cr (VI) was obtained by dissolving 3.734 g of potassium dichromate in of distilled water. Similarly, 1000 mg/L concentrations was prepared by dissolving; 1.6 g lead nitrate in distilled water. The stock solutions were further diluted to obtain, solutions of various known concentrations of lead and chromium in

the concentration range they exist in natural wastewaters.

Metals Analysis by FAAS

Water samples were analyzed for metals using Flame Atomic Absorption Spectroscopy (FAAS). Operational parameters such as wavelength, energy, lamp and burner alignment and slit width for Pb and Cr were adjusted according to the working standards. Standards used in establishing the analytical curve for trace metal determinations were prepared from standard 1000 mg/L stock solutions.

Sorption isotherms

Both Langmuir and Freundlich models were tested for equilibrium description. Langmuir equation, based on a theoretical model, assumes monolayer adsorption over an energetically homogeneous adsorbent surface. It does not take into consideration interactions between adsorbed molecules. It can be represented by the equation:

$$q_e = q_{max} K_L C_e / (1 + K_L C_e)$$

Where q_e corresponds to the amount adsorbed per gram of adsorbent at equilibrium (mg/g), C_e is the solute concentration (mg/L) in the aqueous solution at equilibrium, and q_{max} and K_L are constants related to the maximum adsorption capacity (mg/g) and the adsorption energy (L/mg), respectively. Freundlich's equation is an empirical model based on heterogeneous adsorption over independent sites and is given by:

$$Q_c = K_F C_e^{1/n}$$

Where, K_F is related to binding energy and adsorption capacity and n is related to the intensity of adsorption-incorporating all the factors affecting adsorption capacity and intensity.

Sorption kinetics

The controlling mechanism of the metal biosorption process was investigated by fitting first and second-order kinetic models to the experimental data. The linearized first-order kinetic model is given as:

$$\log(q_e - q_t) = \log q_e - 0.4342 k_1 t$$

Where q_e and q_t are the amounts of metal ions adsorbed per unit mass of biosorbent (mg/g) at equilibrium and at time t , respectively, and k_1 is the rate constant for first-order adsorption (min⁻¹). The linearized second-order kinetic model is given as:

$$t/a_t = 1/k_2 q_e^2 + t/q_e$$

Where, k_2 is the rate constant for the second-order adsorption kinetics (g mg⁻¹ min⁻¹). The straight-line plots of $\log(q_e - q_t)$ against t and of t/q_t against t were used to determine the rate constants.

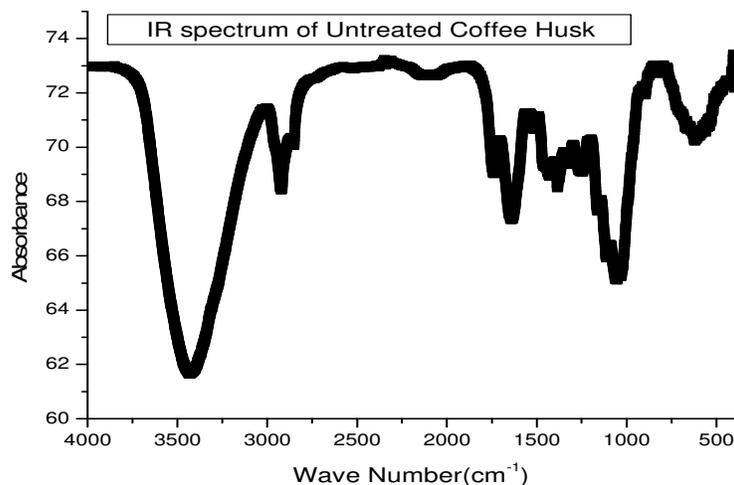


Figure 1. IR spectrum of acid untreated powdered coffee husk

Biosorption equilibrium

The essential characteristics of Langmuir isotherm can be expressed in terms of a dimensionless separation factor, which describes the type of isotherm and is defined by the equation:

$$r = 1 / (1 + K_L C_{eq})$$

Where, K_L is a Langmuir constant, which indicates the nature of adsorption and indicates the shape of the isotherm accordingly. C_{eq} is the equilibrium concentration of Chromium ion. If,

$r > 1$,Unfavorable, $r=1$ Linear, $0 < r < 1$ favorable, $r=0$ irreversible

Standard Gibb's free energy test

The thermodynamic parameters such as Gibbs free energy (ΔG°), enthalpy change (ΔH°), and entropy change (ΔS°) were calculated. ΔG° test was employed whether the coffee husks-Chromium binding is spontaneous or non-spontaneous. ΔH° was evaluated where the reaction is endothermic or exothermic and helps to study the effects of temperature on adsorption.

RESULTS AND DISCUSSION

Characterization of the biosorbent

The functional groups at the surface of the coffee husk as characterized by SHIMADZUFTIR8400S(Kyoto Japan) were free OH^- (phenolic or alcohol) between 3547.60-3450.57, OH^- stretch between 2957.97-2850.91, $-\text{COOH}$ between 1700-1650, $-\text{NH}$ (primary ammine) between 1411.95,(Figure 1). This study is in agreement with (Oliveira et al.,2007).

Effects of pH

The experimental titration provided an average pH of zero point charge (pH_{PZC}) values in the range of 1.5-1.9 and therefore pH values was maintained above 1.9 to ensure a predominant negatively charged surface on coffee husk for removal of cation. Lead introduces a limiting pH value of 4.5, above which its precipitation begins in the form of insoluble hydroxide. The hydrolysis of Cr (VI) will predominantly produce anionic species at very low $\text{pH} < 1$ values thus, requiring a predominant positively charged surface for its efficient removal. The effect of pH (in the range 2-5) on uptake of metal is statistically significant ($p < 0.05$) (Figure 2). The results presented show excellent removal capacities for both Pb(II) and Cr(VI) by using cleaned and powdered acid untreated coffee husk (UCH) ($P < 0.05$). The optimum pH for Pb(II) and Cr(VI) removal was 5.50 ± 0.01 and 2.2 ± 0.01 , respectively. This is nearly in line with (Oliver et al.,2007) .At higher values of pH chromium ions precipitate as $\text{Cr}(\text{OH})_3$.The dependence of metal uptake on pH is related to both the surface functional groups present on the biomass and the metal chemistry in solution. At low pH, the surface ligands are closely associated with the hydronium ions (H_3O^+) and restricted the approach of metal cations as a result of the repulsive force. Furthermore, the pH dependency on the metal ions uptake by biomasses can also be justified by the association–dissociation of certain functional groups, such as the carboxyl and hydroxyl groups present on the biomass. In fact, it is known that low pHs, most of the carboxylic groups are not dissociated and cannot bind the metal ions in solution, although they take part in complexation reactions (Chubar et al., 2004).

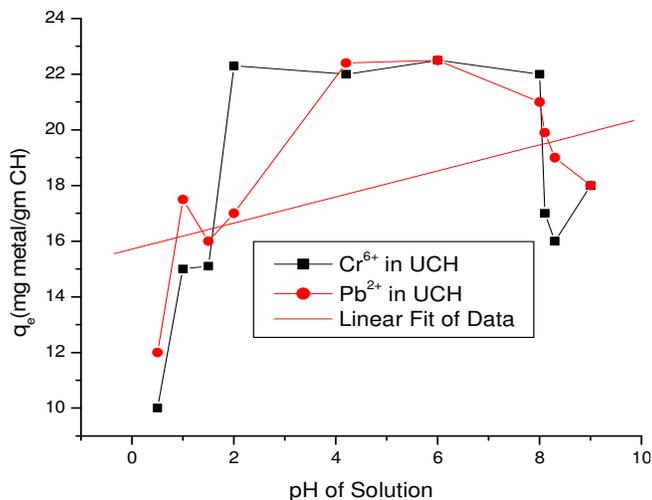


Figure 2. Effects of pH of solution on adsorption of Cr⁶⁺ and Pb²⁺ on to acid untreated coffee husk at 25°C ;solution volume =0.01L;contact time =4 hrs, metals concentration =25ppm,adsorbent dose=0.05gm

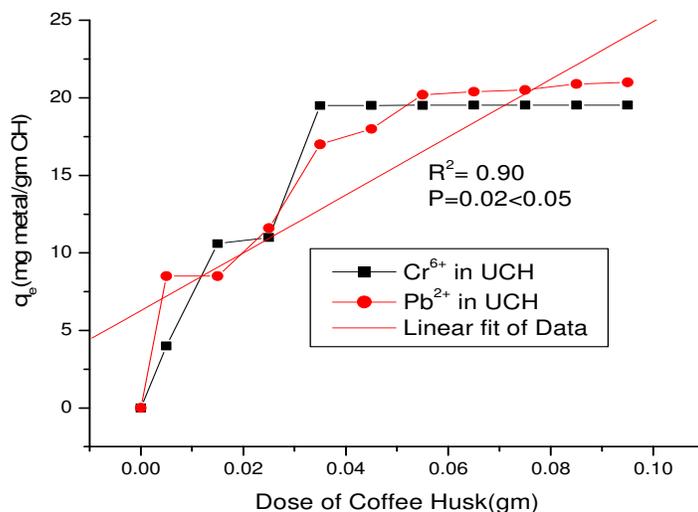


Figure 3. Effects of adsorbent mass adsorption of Cr⁶⁺ and Pb²⁺ on to acid untreated coffee husk at 25°C ;pH =2;solution volume =0.01L;contact time =4hrs,initial metals concentration=25ppm

Effects of adsorbent mass

The removal efficiency increased as adsorbent mass increased ($R^2=0.90$) from 0.005 to 0.05gm and is statistically significant ($p=0.02<0.05$) (Figure 3). This is due to increases the number of binding sites for the ions also increases. After some point, sorption capacity was constant with biomass concentration due to a screen effect between cells; this produced a block of the cell active sites by an increase of biomass in the system. This is in agreement with (Mohan et al.,2005).

Effects of Contact Time

Pb²⁺ ions had the highest percent removal of 93% at the end of 5 hrs followed by Cr⁶⁺ ions of 91%.This is positively and linearly correlated ($R^2=0.910$) and statistically significant ($P=0.01<0.05$) (Figure 4).This is because the rate of adsorption increased as time goes as reaction rate increases with time. This result is important, as equilibrium time is one of the important parameters for an economical wastewater treatment system. This finding is in line with (Chojnacka, 2006) but slightly contradicting with the findings of (Oliveira et al., 2007).

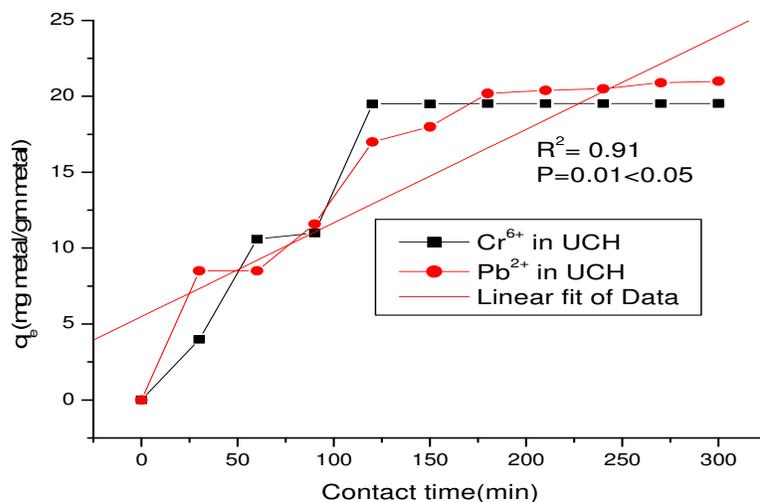


Figure 4. Effects of contact time on adsorption of Cr⁶⁺ and Pb²⁺ on acid untreated coffee husk at 25°C ;pH =2;solution volume =0.01L;contact time =4 hrs, initial metals concentration=25ppm,adsorbent dose=0.05gm

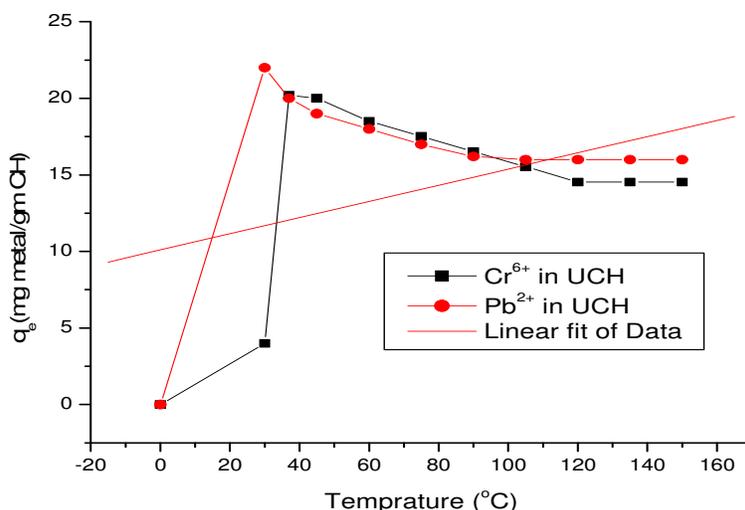


Figure 5. Effects of temperature on adsorption of Cr⁶⁺ and Pb²⁺ on acid untreated coffee husk at 25°C; pH =2; solution volume =0.01L; contact time =4 hrs, initial metals concentration=25ppm, adsorbent dose=0.05gm.

Biosorption Equilibrium

Normally temperature stimulates the molecules functional groups and surface morphology of the adsorbent and metals during adsorptions processes (Figure 5). From the data the thermodynamic parameters such as Gibbs free energy (ΔG°), enthalpy change (ΔH°), and entropy change (ΔS°) were calculated using

$$\Delta H^\circ = \Delta G^\circ + T\Delta S^\circ$$

The magnitude of ΔG° (KJ/mol) at equilibrium was calculated using

$$\Delta G^\circ = -RT \ln K_a$$

Where, R is universal gas constant, 0.008314 kJ/mol.K; T is absolute temperature (K) and K_a the sorption equilibrium constant from Langmuir. The value of ΔG° at temperature of 25°C was -5.63 kJ/mol using Langmuir isotherm (Figure 6). The positive value of ΔH° (0.06kJ/mol) indicated that the adsorption reaction was endothermic and has strong affinity of coffee husk towards ions. In addition, the negative value of ΔS° (-20 kJ/mol.K) also suggested that the adsorption was enthalpy driven and spontaneous in nature. This is in agreement with (Memon *et al.*,2008):

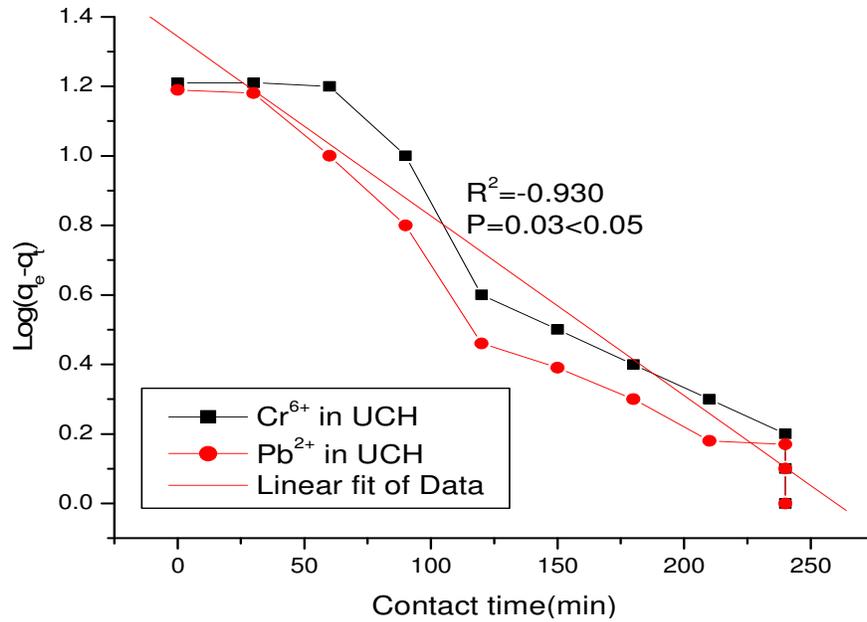


Figure 6. Pseudo first-order sorption kinetics of Pb²⁺ and Cr⁶⁺ onto UCA and ACH. Temperature: 27 °C; biomass concentration: 0.05 g/l; pH=4.

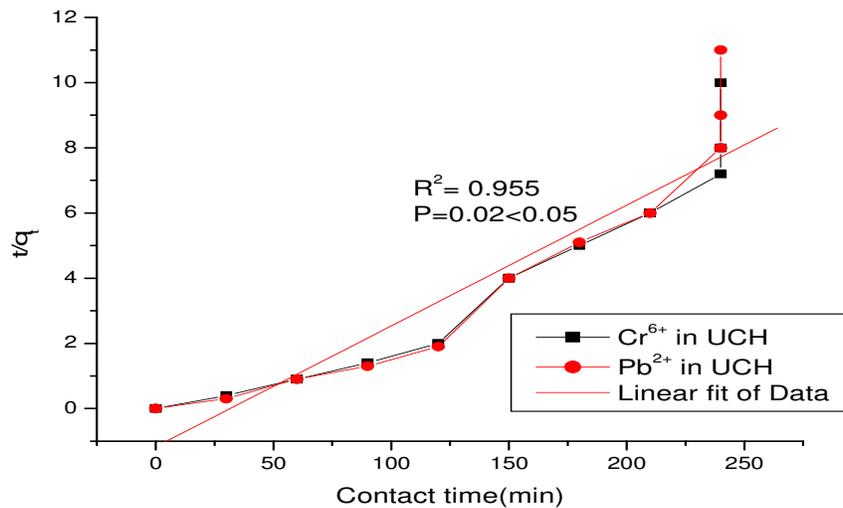


Figure 7. Pseudo second-order sorption kinetics of Pb²⁺ and Cr⁶⁺ onto UCA and ACH. Temperature: 27 °C; biomass concentration: 0.05 g/l; pH=4.

Biosorption kinetics

A straight line of $\log(q_{eq}-q_t)$ versus t suggested the applicability of this pseudo first order as it is linearly and negatively correlated with time and statistically significant ($R^2=-0.930;p<0.05$) (Figure 6). This is in agreement with (Lagergren, 1898; McKay *et al.*,1999). Similarly, the plot of t/q against t provided linear relationship ($R^2= 0.944$) and from which q_e and k was determined. It is in line with the findings of (Ho and McKay, 1999). It confirmed that

the adsorption followed pseudo-second order reaction (Figure 7).

Adsorption Isotherms

The equilibrium sorption data for all metal ions produced convex upward curves, which are indicative of strong sorption (Table 1, Figure 8 and Figure 9). The experimental data fitted to both Langmuir ($R^2=0.944$) and

Table 1. Langmuir and Freundlich constants for sorption of metals by Activated Coffee Husk

Langmuir	$b=0.03$	$q_{max}=5.9\text{mg/g}$	$R^2=0.944$	Cr^{6+}
Freundlic	$K_F=9.902$	$n=1.256$	$R^2=0.930$	Cr^{6+}
Langmuir	$b=0.02$	$q_{max}=7.2\text{mg/g}$	$R^2=0.970$	Pb^{2+}
Freundlic	$K_F=9.900$	$n=2.5$	$R^2=0.940$	Pb^{2+}

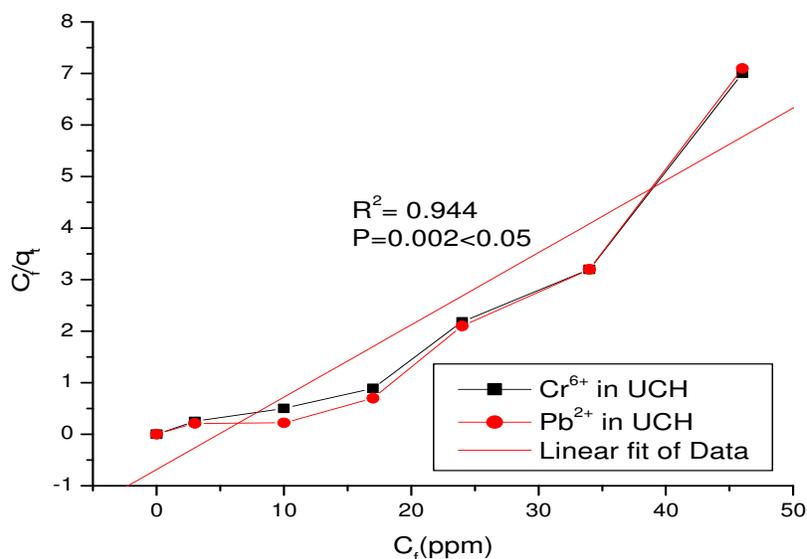


Figure 8. The linearized Langmuir adsorption isotherms of Cr^{6+} and Pb^{2+} ions by UCH Temperature: 25°C ; biomass concentration: 0.05 g/l ; $\text{pH}=4$.

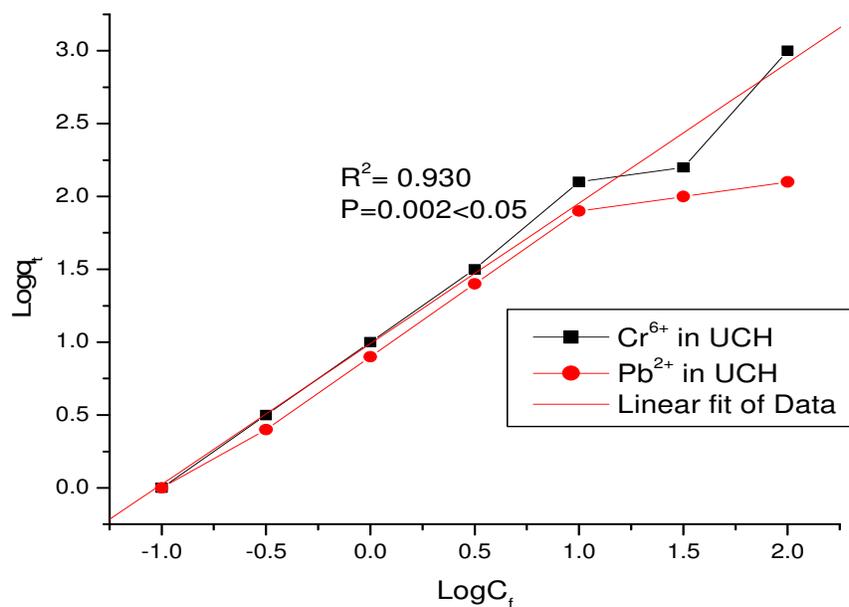


Figure 9. The linearized Freundlich adsorption isotherms of Cr^{6+} and Pb^{2+} ions by UCH. Temperature: 25°C ; biomass concentration: 0.05 g/l ; $\text{pH}=4$.

Freundlich models ($R^2=0.930$). Metal uptake capacity, represented by q_{max} in Langmuir equation was relatively higher for lead ions followed by chromium. This finding is similar with other scholar (Aksu, 2001)

$$r = 1 / (1 + K_a q_{max})$$

Where, K_a is a Langmuir constant, which indicates the nature of adsorption and indicates the shape of the isotherm accordingly q_{max} is the maximum adsorption constant. The reaction was favorable as $r=0.016$ which was between 0 and 1. The Langmuir constant, $b=0.03$ less than 1 confirmed high affinity of sorbent for sorbate.

CONCLUSION

A study of the feasibility of using dry coffee husk as acid untreated biosorbents for the removal of metal ions from aqueous solutions was successfully carried out. The biosorption efficiency was higher for both lead and chromium ions at pH 5.5 and 2.2, respectively. Biosorption kinetics was described by both a pseudo-first-order model and a pseudo-second-order model, but betterment is to pseudo-second-order model. Equilibrium was attained after 5 hours of contact time for both ions. Sorption isotherms were described by both Langmuir and Freundlich models but more is by Langmuir. As the dose increased removal efficiency increased with statistical significance. The experimental data demonstrated coffee husks to be a suitable candidate for use as biosorbents in the removal of heavy metals from aqueous solution.

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