ADSORPTION OF COPPER AND LEAD USING COFFEE GROUND

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Abstract- The contaminated waters have become a serious threat to the environment. The main sources of contaminated water are from industries which releases hazardous heavy metal (Cu, Pb, Zn, Cd, Cr and etc.) In this study, removal of copper and lead has been investigated by using coffee ground as adsorbent. Coffee ground was used as adsorbent to avoid environmental pollution and profitable uses waste. The effects of relevant parameters including adsorbent dose, initial concentration and contact time adsorption were examined. This experiment was conducted at room temperature and no pH adjustment was made prior to the analysis. Batch adsorption revealed that the amount of copper and lead ion adsorbed increases as the adsorbent dose increase. The equilibrium was achieved at 120 min for copper and lead ions. Based on linear regression, the best fit for copper and lead ions was pseudo second order. The data indicated that the adsorption of copper and lead ions by coffee grounds was best described by Langmuir isotherm model. Result showed both physisorption and chemisorption mechanisms controlled the adsorption rate and capacity respectively.

Keywords—Adsorption, Coffee Ground, Heavy metal, Cu(II), Pb(II).

I. INTRODUCTION

Water is important since it is very useful in our daily life. Water are used for drinking, bathing and other purpose. Water pollution by industrial has become an earnest threat to the environment. Heavy metals such as lead, nickel, cadmium, mercury and chromium metals are very harmful to human health and environment because of the high toxicity of heavy metals. Constant vulnerable to the heavy metals may cause side effect to our body [1]. Heavy metals are stable and persistent since they cannot be destroyed or eradicated by itself. Thus, it would gather in ground water, soil, seawater and sediments. The accumulation of heavy metal would cause effects on the health of many biological species and on the environment [2].

Lead is considered among more toxic compared than other metals (e.g iron, copper and zinc) due to its cumulative nature and detrimental effect on human health. The excessive intake of lead would affect the nervous system, blood circulation reproductive system and kidney failure [3]. Usually the amount of lead in plant are from concentration of soil. As potations incline to be acidic, the utilization of any lead-containing products in their manufacture, distribution or storage will raise lead levels.

In many countries, lead is present in drinking water. For example, in Japan, lead is widely utilized in piping because lead is plausible and facile to engender [4]. This has caused the dissolved of lead in tap water and has been used for drinking. According to the World Health Organization (WHO), the safe consumption of drinking water must less than 0.01 mg/l [5, 6].

Similar to lead, copper is not biodegradable and tend to accumulate in body organs and threat the health of living organisms [7]. Copper is used in agriculture and it is essential element for health, plants and humans. In human, its help in production of blood hemoglobin. However, higher concentration of copper creates a kind of diseases [8].

The presence of a very small amount of copper (II) in drinking water causes damages liver and eye damage at high uptakes for the growth of all biological creatures [9, 10]. It has been proven that drinking water, including 30 grams of copper ions is fatal and the concentration of 1.3 mg/L of this ion could be a reason for relatively common diarrhea, abdominal cramps and nausea[11].

There are several common technologies for the removal of heavy metal from wastewater such as ion exchange, filtration, cementing and separation by membrane and electro coagulation chemical precipitation. However, the method are complex, energy-intensive and expensive[12]. Among the various method, adsorption is considered most suitable because it can remove both organic and inorganic pollutants [13].

Various type of adsorbent was tested for their adsorption capacity to remove heavy metal from wastewater such as activated alumina, zeolites, and activated carbon. In the industrial context, the application of agricultural waste such as spent tea, red mud, chitosan, sawdust and rice husk have been identified as substitution in removal of lead. Among these, coffee ground is the popular beverage all over the countries. In Malaysia, the coffee is exported is 80,484 in 2013[14]. As the consequence, large amount of coffee ground which are residue obtained during the processing of coffee powder that have been generate. [15, 16]. Coffee ground can withal be reused as compost and animal victual. Converting the waste into useful resource could decrease the waste. However, most of the coffee grounds were discard or flare as waste. This would result the production of carbon dioxide in atmosphere [17]. Coffee ground is having fine particle size, high humidity, organic load and acidity. However, it has low surface area compared with activated carbon. Coffee ground has a wide range of great organic component that encourage their adsorption efficiency [18].

In this study, an attempt is made to study potential of contact time, initial concentration and adsorbent dose for removal lead from aqueous solution. Moreover, the adsorption isotherm and adsorption kinetic are analyse for their application at variable operating conditions.

II. METHODOLOGY

A. Preparation of adsorbent and synthetic wastewater

The adsorbent used in this study was coffee ground which was collected from Starbuck, Bukit Raja, Klang. The accumulated coffee ground was washed several times to remove dirt and colour. The resulted coffee grounds were washed boiled with distilled water and it was dried at 100ºC in an oven for 5 h. Coffee grounds was cooled in room temperature and stored in airtight container until needed to be used.

A synthetic contaminated wastewater was prepared by dissolving 1 g of Pb(II) and Cu(II) ions in distilled water at room temperature.

Lead nitrate (99%, Merck) and copper nitrate (99%, Merck) of predetermined concentrations used was prepared by diluting the stock solution.

B. Batch adsorption

The effect of adsorbent dose was conducted by adding 0.2 g, 0.4 g, 0.6 g, 0.8 g and 1.0 g of coffee ground in Erlenmeyer flask of 200 mL containing 150 mg/L Cu (II) ion. The mixture of coffee ground and Cu(II) ion was placed in incubator shaker at 140 rpm for 24 h.

The effect of initial ion concentration of Cu(II) ions was studied by mixing 1 g of coffee ground with 200 mL of Cu(II) ion solution of different initial concentration 50, 100, 150, 200 and 250 mg/L. The suspension was shaken at 140 rpm for 24 h in an incubator shaker. The data obtained were fitted with Langmuir and Freundlich models.

The effect of contact time was studied by mixing 1 g of coffee ground with 200 mL of Cu(II) solution with initial concentration of 50 mg/L. The suspension was put in a shaker for 24 h on an orbital shaker with agitation rate was fixed at 140 rpm. Sample was collected at interval times 30 min, 1 hr, 1hr 30 min, 2 hr, 2 hr 30min and 3 hr. The kinetic data were fitted with pseudo-first order and pseudo-second-order models.

The method above was repeated using activated carbon (99%, Sigma) and Pb(II) ions. After the adsorption experiment, the sample were filtered using filter syringe. 1 mL of HNO_3 with 1% concentration was added to the sample. The percentage removal of Pb(II) and Cu(II) ions was calculated using equation (1)

$$\text{Percentage of Adsorption} = \frac{C_O - C_{eq}}{C_o} \times 100\% \qquad (1)$$

Where C_o is the initial concentration of Pb(II) and Cu(II) ion in mg/L and $C_{eq}$is the final concentration of Pb(II) an Cu(II) in mg/L.

C. Adsorbent characterization

The coffee ground was analyzed using Fourier Transform Infrared (FTIR) spectrophotometric to identify the characteristic functional group distribution in the adsorbent coffee ground. The identification of functional group is important to explain the removal capacity of coffee ground. The pellets used in the analysis are prepared by using spectrometric grade in hydraulic press.

D. Analysis

Both sample of Pb(II) and Cu(II) were analyzed by using Atomic Adsorption Spectrophotometer (Hitachi, Z2000). The samples were diluted 10 times with distilled water before measures in Atomic Adsorption Spectrophotometer due to the sensitivity of the instrument.

E. Adsorption kinetic

There two type of adsorption kinetic models which were pseudo-first order model and pseudo second order models [19]. In order to determine the suitable kinetic model, the equation was used to plot the graph. The kinetic model was chosen as the graph was best fitted.

The pseudo first order model and pseudo second order models can be expressed as in Equation (2) and Equation (3), respectively.

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.203} t \qquad (2)$$

Where q_e and q_t were the amount of Cu(II)and Pb(II) adsorbed equilibrium and at any time (t) respectively, and k_1 (min^{-1}) was the rate constant of pseudo first order model. The value of q_e and k_1 was obtained from the slope and intercept from linear plot of ln(q_e-q_t) Vs time.

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} - \frac{t}{q_e} \qquad (3)$$

where q_e (mg g^{-1}) was the maximum adsorption capacity and q_t (mg g^{-1}) was the amount of adsorption at time t (min) and k_2 (g mg^{-1} min^{-1}) is the rate constant of pseudo second order equation, can be estimate from the slope t/q_t Vs. time.

F. Adsorption isotherm

Adsorption isotherm is an equilibrium relationship which are important for optimize the adsorption mechanism pathways, expression of surface properties and capacities of adsorbent. The adsorption isotherm allows to determine the maximum adsorption capacity of the adsorbent as a function of mathematical linear regression [18]. The higher R^2 were considered as best fit. There are two type of adsorption isotherm which were Langmuir isotherm and Freundlich isotherm. The Langmuir isotherm and Freundlich isotherm can be expressed as in Equation (4) and Equation (5) respectively.

$$\frac{C_e}{q_e} = \frac{1}{K_L Q_m} + \frac{C_e}{Q_m} \qquad (4)$$

$$\log q_e = \log k_f + \frac{1}{n} \log C_e \qquad (5)$$

where Q_e (mg/g) is the equilibrium metal concentration, Q_{max} (mg/g) is the maximum amount of adsorption, K_L (L/mg) was the Langmuir adsorption constant, K_f ($mg^{1-1/n}L^{1/n}$/g) is the Freundlich constant and n is the constant depicting the adsorption intensity.

III. RESULTS AND DISCUSSION

A. Adsorbent characterization

The spectra of coffee ground are shown in Figure 1. The FTIR spectroscopic indicated broad band observed at 3304 cm^{-1} was assigned to the stretching of O-H group due to inter and intra-molecular hydrogen bonding of polymeric compound. The O-H stretching vibration occur within a broad range of frequencies indicating the presence of free hydroxyl group and bonded O-H bands of carboxylic acids. The band at 2922 cm^{-1}indicated the symmetric or asymmetric C-H stretching vibration of aliphatic acids. The absorption peaks at 1740 $cm^{-1}$was assigned to the resulting carboxyl linkage derived from xanthine derivatives such as caffeine [20]. This significant band in the spectrum indicated the possible involvement of functional groups and the surface of coffee ground during the adsorption process.

Beside FTIR, thermo-gravimetric analyser (TGA,Mettler Toledo) was used to analysis amount and rate (velocity) of change in the mass of a sample as a function of temperature controlled atmosphere. TGA experiments were performed using 20-25 mg. Samples with the heating range of 25-950^{0}C at heating rates of 20^{0}C under a nitrogen flow of 100 cm^3/min. The conversion curves indicate that mass loss of coffee ground occurred at temperatures ranging from 250 to 900 °C show in Fig 2.

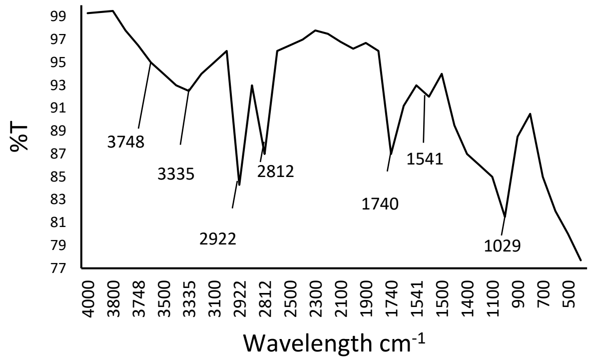

Fig. 1: Fourier transform infrared spectroscopy of the coffee ground

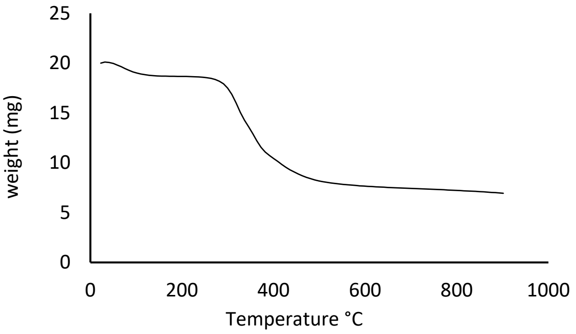

Fig 2: TGA curves obtained from coffee ground

B. *The effect of adsorbent dose*

The effect of adsorbent dose on the Cu(II) and Pb(II) adsorption capacity of activated carbon and coffee ground is illustrated in Fig 3 and fig 4, respectively. The Cu(II) uptake due to adsorption increase with the increasing dosage of adsorbent (activated carbon and coffee ground). As reported by Agwaramgbo, et al. [21] the adsorption percentage adsorption copper and zinc obviously increased due to the increase in the adsorbent quantity and the number of adsorbent sites[21]. The saturation in the adsorption profile is attributable to the high solid concentration which blocks the available site, resulting in a lower total number of available sites for adsorption [22]. Furthermore, the trend shown in Fig. 3 suggests higher percentage of Cu(II) uptake with activated carbon compared with coffee ground. The Pb(II) uptake with activated carbon are higher than coffee ground. The coffee ground gave better performance in term of adsorption uptake for lead compare to copper. The ability of the adsorbent to bind metals depends on functional group and affinity of these groups to bind to specific metal.

C. *The effect initial concentration*

Fig. 5 and Fig. 6 shows the effect of the initial Cu(II) and Pb(II) concentration on the adsorption percentage respectively. According to Fig. 5, the adsorption percentages decreased with an increase in the initial concentration of Cu(II) with activated carbon especially when the initial concentration was increased to 200 mg/L for activated carbon. A further increase in the initial concentration to 250 mg/L did not increases the adsorption capacity, suggesting that a plateau had been reached. For the coffee ground, the adsorption increases with an increase in the initial concentration at 100 mg/L. A further increase in the initial concentration at 250 mg/L shows the increasing of the adsorption capacity. Fig 6 shows the percentage removal of Pb(II) with increasing of the initial Pb(II) concentration for activated carbon and coffee ground. Resulted in the decreasing in the percentage removal for coffee ground from 91% to 66 % with initial concentration of 200 mg/L to 250 mg/L respectively. The further increases on the initial concentration is expected to decrease the percentage removal. This is trend happened due to saturation of adsorption site.

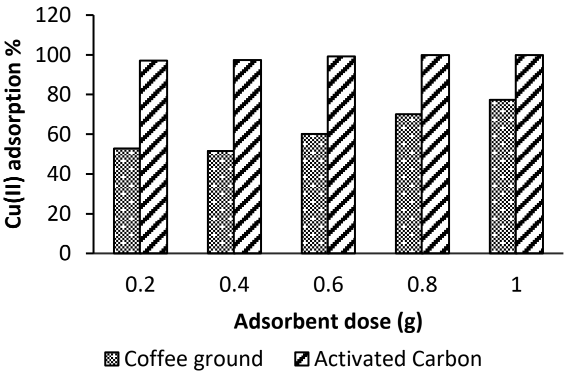

Fig 3: Effect of adsorbent dose for the adsorption of Cu(II) on activated carbon and coffee ground

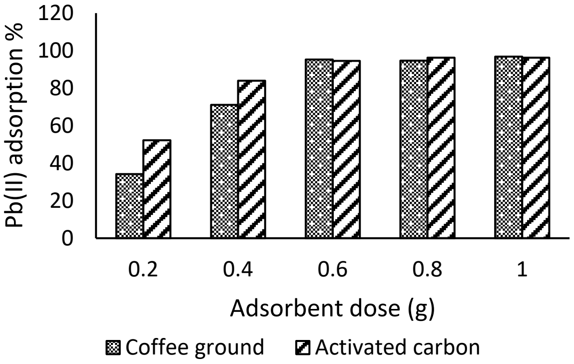

Fig 4: Effect of adsorbent dose of Pb(II) on activated carbon and coffee ground

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D. *The effect on contact time*

Fig 7 shows a rapid initial uptake rate of Cu(II) at the beginning until 60 min and thereafter, the adsorption rate became practically constant for coffee ground. The increased for activated carbon at the 60 min and decreased until 120 min of treatment time. After 120 min, the adsorption for activated carbon increase until 180 min. However, Fig. 8 shows a little increased in adsorption of coffee ground until 180 min. For activated carbon, the adsorption decreased at 120 min adsorption time but continues increased until 180 min. The variation in the extent of adsorption because of all sites on the surface of adsorbent were vacant and the solute concentration gradient was relatively high. Generally, when adsorption involves a surface reaction process, the initial adsorption is rapid.

E. *Adsorption kinetic*

In order to design and model the adsorption process. It is importance to model the kinetic data as it provides valuable insight about the mechanism involved in controlling the adsorption. The kinetic of metal adsorption was modeled using pseudo first order and pseudo-second order models (Fig 9 and 10). Based on the R^2 value, pseudo-second order model is the best fitting for both Cu(II) and Pb(II). According the correlation (R^2) exported for Cu(II) on, the best finding was pseudo-second order equation ($R^2 = 0.999$ and 0.999 for both activated carbon and coffee ground respectively) while the for the Pb(II) (R^2= 0.996 and 0.999 for activated carbon and coffee ground respectively). The both model parameters are listed in Table 1. Therefore, the adsorption could be explained to have chemisorption as a rate-controlling mechanism, was better able to describe the adsorption mechanism of Cu(II) and Pb(II) onto both adsorbents (activated carbon and coffee ground. It can be concluded that chemisorption controls the mechanism Similar observation have been reported in the literature Dhir and Kumar [23]. It can therefore be inferred that both physisorption and chemisorption control the adsorption rate and capacity respectively[24].

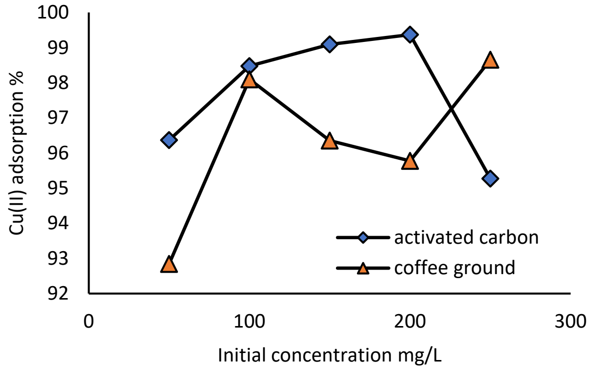

Fig 5: Effect of initial concentration of Cu(II) on activated carbon and coffee ground

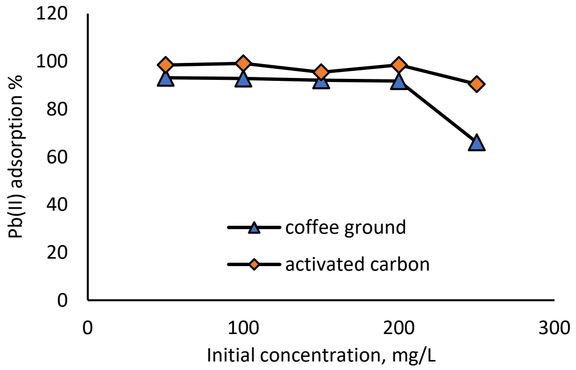

Fig 6: Effect of initial concentration of Pb(II) on activated carbon and coffee ground

F. Adsorption Equilibrium

The adsorption equilibrium was studied using Langmuir and Freundlich isotherm equations. The various constants deduced from the model are listed in Table 2. By comparing the correlation coefficient of the Langmuir and Freundlich adsorption in Table 2, it can be easily inferred that the Langmuir model is more suitable than Freundlich model. For the Langmuir in Cu(II) the value $R^2 = 0.559$ and 0.390 for activated carbon and coffee ground respectively. Moreover, for the Langmuir in Pb(II) the value $R^2 = 0.743$ and 0.999 for activated carbon and coffee ground respectively. According to the Langmuir model, the maximum adsorption capacity of coffee ground in lead is 16.42 mg/g which is almost the same as reported in previous studies 16.23 mg/g [24].

Table 1: Kinetic constants for the adsorption of Cu (II) and Pb (II) with activated carbon and coffee ground

	Pseudo-first order		Pseudo-second order	
Adsorbate-adsorbent	k(min^{-1})	R^2	K_2(g/mg/min)	R^2
Cu(II)-Activated carbon	1.6E^{-6}	0.00002	0.7633	0.999
Cu(II)-Coffee ground	0.0009	0.524	0.8362	0.999
Pb(II)-Activated carbon	1.4465	0.132	0.6281	0.996
Pb(II)-Coffee ground	0.0002	0.756	0.7283	0.999

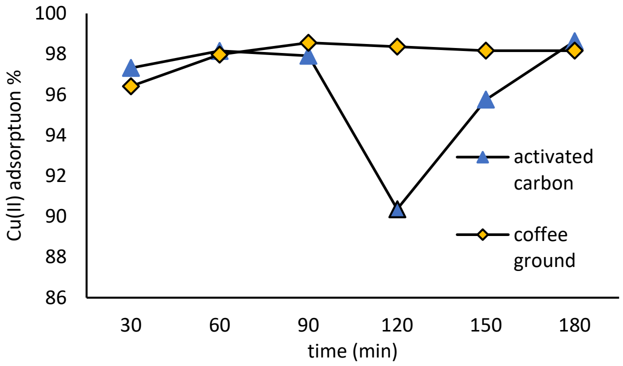

Fig 7: Effect of contact time of Cu(II) on activated carbon and coffee ground

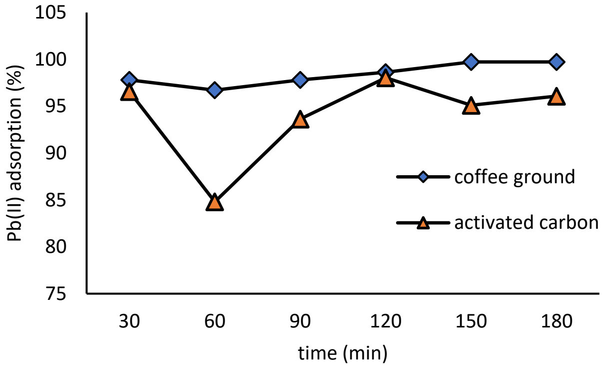

Fig 8: Effect of contact time of Pb(II) on activated carbon and coffee ground

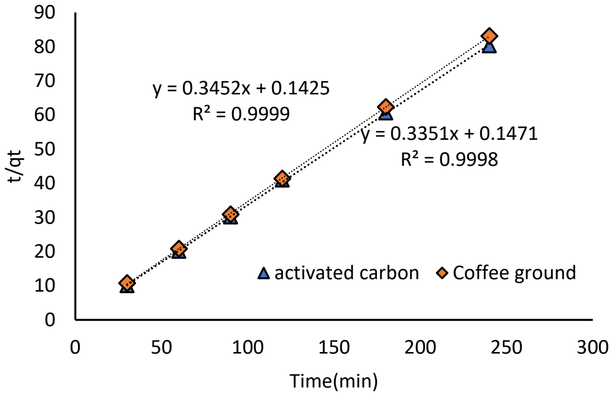

Fig 9: Pseudo-second order kinetic for adsorption of Cu(II) with activated carbon and coffee ground

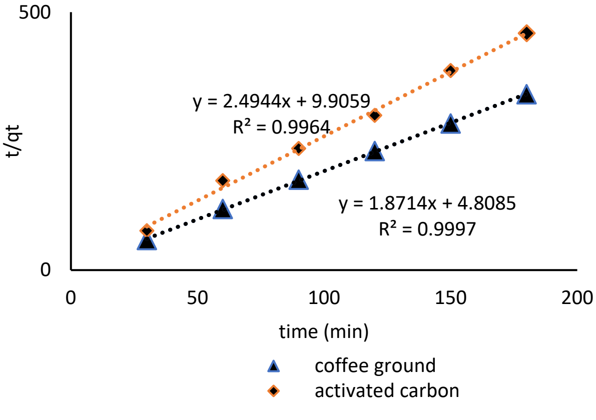

Fig 10: Pseudo-second order kinetic for adsorption of Pb(II) with activated carbon and coffee ground

Table 2: Langmuir and Freundlich isotherm Model of Cu(II) and Pb(II) with activated carbon and coffee ground

	Langmuir			Freundlich		
Adsorbate-adsorbent	Q_m	k_L	R^2	K_f	n	R^2
Cu(II)-Activated carbon	1.859	0.229	0.559	0.854	166.7	0.00009
Cu(II)-Coffee ground	8.591	0.179	0.293	1.139	2.636	0.390
Pb(II)-Activated carbon	6.794	0.0278	0.743	0.236	1.118	0.598
Pb(II)-Coffee ground	16.42	0.0367	0.999	0.882	15.625	0.799

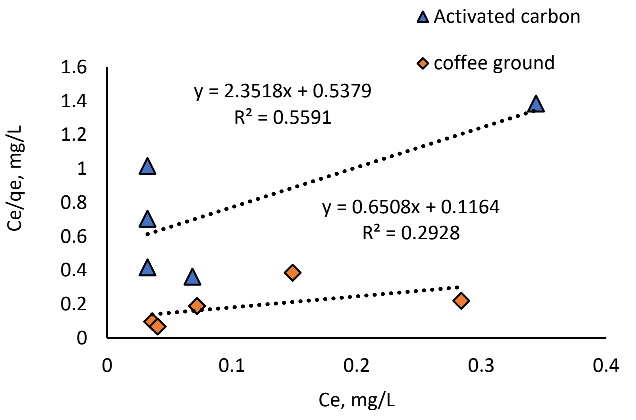

Fig 11: Langmuir model for adsorption of Cu(II), indicating correlation coefficient for activated carbon and coffee ground

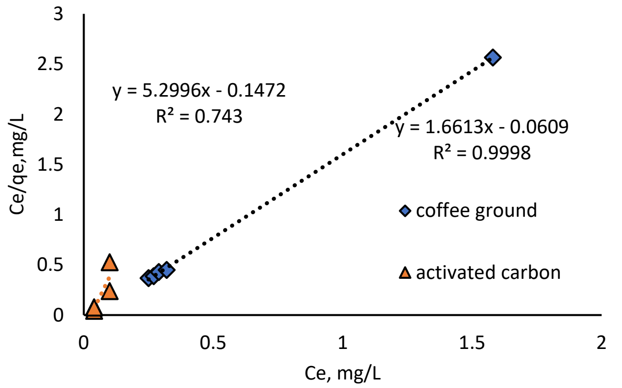

Fig 12: Langmuir model for adsorption of Pb(II), indicating correlation coefficient for activated carbon and coffee ground

IV. CONCLUSION

In this study, coffee ground was used as adsorbent for removal of Cu(II) and Pb(II) from aqueous solution. Moreover, activated carbon was used to compare percentage of adsorption with coffee ground. The adsorption capacity of an adsorbent is dependent on a variety of factor such as adsorbent dose, initial concentration and contact time. Although, copper and lead have same charged, the nature and mode of their interaction with adsorbent greatly differed as the data suggested. The percentage removal for Cu(II) and Pb(II) increases as the activated carbon and coffee ground was increases. The adsorption rate was rapid over an initial period and decreased at 120 min for Cu(II) with activated carbon and for Pb(II) the adsorption rate decreased at 60 min but continues increased until 180 min. However, for the coffee ground with Cu(II) and Pb(II) constantly stable until 180 min. The kinetic data were best described pseudo-second order model. The Cu(II) and Pb(II) was modeled using adsorption isotherm models. The adsorption equilibrium data showed best fit with Langmuir isotherm model for both adsorbent.

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