Equilibrium Sorption Isotherms for Removal of Heavy Metals Using Cement Kiln Dust

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Abstract

The removal of lead, copper, and cadmium from aqueous solution using cement kiln dust (CKD) has been investigated under batch equilibrium technique setup. The adsorption behavior of the target metals is examined as a function of pH, contact time, sorbent dose and initial metal concentration. The metal hydroxide precipitation is studied to determine the separation behavior. The lead hydroxide precipitation is dominant at pH > 6.0 while copper and cadmium precipitation reached 90% at pH > 8.0. A surface titration experiment reveals negative surface charge of the CKD at pH < 10 that means electrostatic attraction is the dominant phenomenon for divalent metals. Langmuir and Freundlich isotherms were performed to show the adsorption capacity of CKD. They show an adsorption order of Pb≥ Cu> Cd which is compatible respectively with their electronegativity; 1.854, 1.85, and 1.52. The sorption capacity of CKD at the optimum conditions is 14.85, 14.65, and 14.1 mg/g for lead, copper, and cadmium, respectively.

Keywords: Sorption Isotherms; Heavy Metals; Surface Titration; Cement Kiln Dust (CKD); Batch Equilibrium

1. Introduction

Heavy metals are considered the main constituent of toxic substances in wastewater. Heavy metals are about 40 elements with a density greater than 5 gm /cm3 (e.g. Pb, Cd, Cu...). Heavy metals are dangerous and carcinogenic as they can bio-accumulate in living being causing increase of chemical concentration in the biological organism compared to the chemical's concentration in the environment [1]. Lead, cadmium, and copper are the most common toxic heavy metals [2]. The main sources of these heavy metals in wastewater are streams from electric battery manufacturing, lead smelting, glass industry, electroplating, and oil/gas exploration and drilling [3]. Current remediation of wet-waste or muddy sludge using anaerobic digestion or thermochemical target the production of landfill gas or syngas [4,5], yet the residual which is essentially is rich with metals continue to pose disposable environmental threat. They can also leach directly into the water supply from water service lines and interior household pipes and fixtures [6]. Heavy metals uptake can be carried out using phytoremidiation, chemical precipitation, ion exchange, and adsorption [7]. Most of these technologies are not eco-friendly due to their demand on energy as well as their low efficiency [8, 9]. However, among these technologies, adsorption is considered the most reliable option [10]. Adsorption is a process where molecules accumulate at a surface or interface of another media. Adsorption can be based on a chemical binding which is called chemisorption, or surface-based physical forces attraction, such as Van Der Waals force, and is referred as physiosorption [11]. Adsorption depends on the agitation time, initial metal concentration, and adsorbent dose, as well as the solvent pH [12, 13]. Adsorption kinetics need to be understood in order to help in predicting the operating time of an adsorption process [14]. A variety of effective adsorbent materials have been introduced, such as activated carbon [12, 15], rice bran [16], coal fly ash [13], anaerobic granular biomass [17], and iron oxide [18]. Recently, efforts have been exerted to utilize specific waste streams, such as waste iron oxide and saw dust, as sorbent materials in order to minimize the processing costs and to mitigate any anticipated environmental and health impacts. Phuengprasop in 2011 treated modified sewage sludge with iron oxide for metal ions removal [19]. Waste iron oxide was also used in modifying waste silica to produce an effective adsorbent for metal removal from wastewater [20]. Moreover, Liu in 2014

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studied the kinetic and thermodynamic of waste iron oxide alone on metal ion removal. Saw dust has also been utilized to remove heavy metals from aqueous solutions [21]. The saw dust shows high affinity to adsorb metal ions from wastewater [22, 23]. Wastewater purification and treatment is an energy intensive process [24]. Accordingly, investigating innovative and affordable treatment techniques is vital. CKD is the byproduct of the Portland cement production and it's characterized with high calcium oxide (CaO) contents. It can be used as a replacement for lime in treating acidic wastewater [25]. Ali in 2011 investigated the effect of CKD on the removal of some rare earth elements, such as yttrium (Y^{3+}) and lutetium (Lu^{3+}) [26]. He found that CKD is highly capable to adsorb these element ions. The capacity of CKD, as heavy metals scavenger, for chromium uptake has also shown good results [27]. However, CKD has not been tested extensively for the removal of some other heavy metals, such as lead, copper, and cadmium. This work aims at to investigate the influence of various experimental parameters (pH, contact time, sorbent dose, and initial metal concentration) on the adsorption of lead, copper, and cadmium on CKD as a potential and low cost adsorbent. Moreover, the experimental results were evaluated using both Langmuir and Freundlich isotherm models to obtain the needed parameters.

2. Methodology

2.1. Cement Kiln Dust (CKD)

The used CKD is kept in desiccators all the times to maintain the moisture and chemical contents. The physical and chemical properties of the collected samples are shown in Table 1. The surface properties such as particle size and specific gravity are measured using Le Chatelier flask (ASTM C188-95). The surface area is calculated based on the mercury displacement method (ASTM C 204). An INCA Oxford Energy Dispersive Microscopy (EDM) is conducted to detect the type of the attached crystals for each material that appeared in the Scanning Electron Microscope (SEM) as seen in Figure 1 and 2. The EDM shows the elemental and chemical formations of the CKD.

Table 1: Physical and Chemical Properties of CKD

Physical Parameters	Value	Unit
Particle Size	~ 74	Microns
Bulk Density	0.7	Gm/cm3
Specific Gravity	2.5	Dimensionless
Surface Area	4,000	Cm2/gm
Chemical Elements	Weight%	Atomic%
Na K	9.91	15.38
Al K	1.02	1.35
Si K	3.92	4.98
S K	2.63	2.92
Cl K	18.74	18.86
K K	6.88	6.28
Ca K	55.30	49.21
Fe K	1.60	1.02
Totals	100.00	

(a) 200 X   (b) 500 X

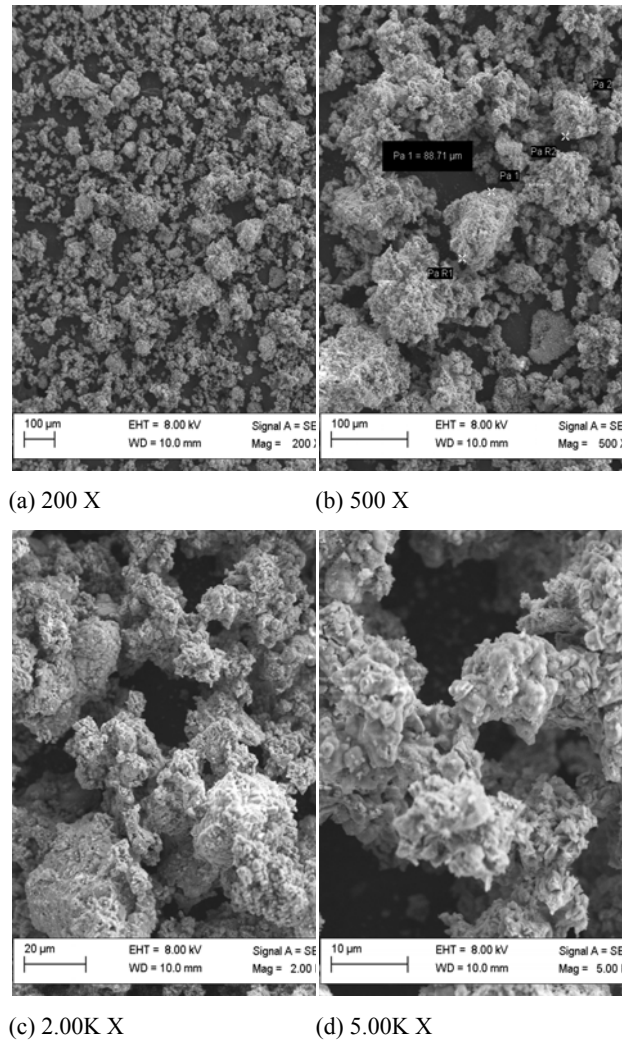(c) 2.00K X   (d) 5.00K X

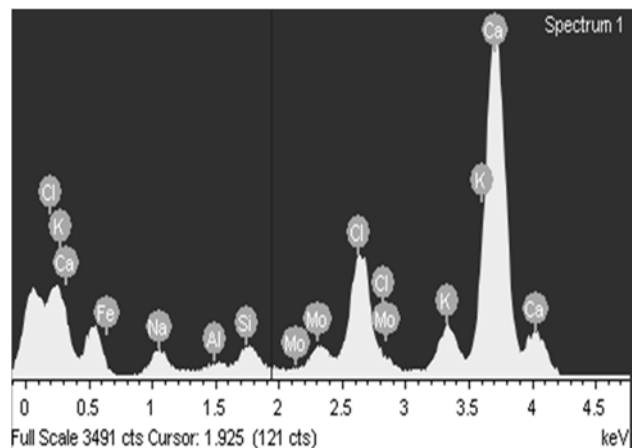**Figure 1: SEM Captures for CKD with different Magnifications**

Figure 2: EDX Analysis of CKD

2.2. Surface Titration Study

Sorbent samples are titrated potentiometrically to observe the acid-base nature of the CKD surface. The experiment is conducted for different ionic backgrounds of 0.1M, 0.01M, and 0.001M using NaNo3 to standardize the solution. 0.1 g of dry CKD is suspended in a Teflon reaction vessel containing 50 ml of DDW at room temperature to yield a solid concentration of 2

gm/L. The suspension is continuously stirred and purged by ultra-pure nitrogen gas prior to titration in order to remove CO_2 that would interfere with an acid-base titration. Standard 0.1M HNO_3 and 0.1 M NaOH are accurately added to adjust the pH. Total volume of acid or base added is < 5% of the sample volume to minimize the dilution effects. The pH is measured every 0.1 ml increment of either acid or base.

The surface charge of CKD is calculated using Equation (1) [28, 29]:

$$\sigma = \frac{F}{AS}[C_A - C_B - (H^+) + (OH^-)] \qquad (1)$$

Where F is Faraday constant (96485.339 Coulomb/mole), S is the sorbent concentration (2 g/l) according to this study, and A is the surface area of sorbent which is 0.4 m2/g. H^+ is 10 (pH value) and OH^- is 10 (14-pH value). C_A and C_B are the added acid or base in moles/L; respectively. σ is the surface charge density.

2.3. Batch Equilibrium Isotherm Studies

The sorption isotherm is the ratio between the quantity adsorbed and the remaining in solution at fixed temperature at equilibrium. The optimum environmental factors such as initial pH, contact time, initial CKD dose, and initial metal concentration are studied in this set of experiments. These factors are known with their significant effect on the adsorption equilibrium. The purpose of this set of experiments is to determine the equilibrium-pH adsorption edge and the adsorption capacity of CKD. The precipitation phenomenon for a particular solution-phase condition is identified by performing a run with no sorbents. The batch experiments are carried out in well-sealed 125 ml high density polyethylene (HDPE). When these agitated, they can be assumed to function as completely mixed batch reactors. Different CKD dosages are tested (0.15 to 2.0 g/l) with 50 ml of synthetic aqueous solutions containing the target metal of interest at pre-established conditions of ionic strength (0.01M) and initial metal concentration of 10 to 200 mg/l. The pH of individual samples is varied between 3.0 and 11.0. During a 24 hours reaction period on an orbital shaker by centrifuging at 175 rpm, samples from each reactor at different reaction times are collected and filtered through a prewashed micro membrane filter (0.7μm) to separate the solid after measuring the equilibrium pH. The filtered solution is then adjusted to pH< 2.0 using 1:1 HNO_3, and then analyzed by atomic adsorption spectrometer (model sense AA). The percent removal (%R) and adsorbed phase concentration (q) are then computed by Equation (2) and Equation (3) respectively:

$$\%R = \left(1 - \frac{c}{c_0}\right)100 \qquad (2)$$

$$q = (C_o - C)V/W \qquad (3)$$

Where C_o and C are the initial and final heavy metal concentration (mg/l), respectively. q is the adsorbed quantity of heavy metal per gram of sorbent (CKD) (mg/g). V is the volume of the solution (L). W is the weight of dry sorbent (CKD) (gm).

2.4. Sorption Isotherm Models

Langmuir Isotherm

The Langmiur isotherm is applied for the sorption equilibrium on CKD according to Equation (4):

$$\frac{1}{q_e} = \frac{1}{b} + \frac{1}{abC_e} \qquad (4)$$

Where q_e is the mass of heavy metal adsorbed per gram of adsorbent. C_e is the equilibrium heavy metal concentration in liquid phase, mg of heavy metal/liter, a is Langmuir constant, liter/mg of heavy metal, and b is monolayer coverage, mg of heavy metal/gm of adsorbent.

Freundlich Isotherm

The Freundlich isotherm is often used for heterogeneous surfaces according to Equation (5):

$$Logq_e = LogK_f + \frac{1}{n}LogC_e \qquad (5)$$

Where q_e is the mass of heavy metal adsorbed per gram of adsorbent. C_e is the equilibrium heavy metal concentration in liquid phase, mg of heavy metal/liter. K_f and n are constants incorporating all factors affecting the adsorption process such as adsorption capacity and intensity of adsorption.

3. Results and Discussion

3.1. Surface Titration

The surface titration results show that the CKD is an alkaline material because the DDW pH increased by about 4 pH points regardless the ionic background. It is obvious that CKD has a consistent behavior during titrating it with NaOH. On the other hand, the CKD behavior does not show regular reaction when titrated with HNO_3. This means that CKD has a significant resistance to pH change with acid addition. This might be due to the affinity of CKD to adsorb H+ ions by its naturally alkaline surface when HNO_3 is added.

Figure 3 shows the acid-base titration curve of CKD aqueous solution. It is characterized by a weak acid system at different ionic backgrounds. The three curves intersect at ≈ pH 10.0. This means that the system will thermodynamically tend to drive toward this point. It also indicates that the surface charge of the sorbent is neutral at pH 10, which is referred to zero point of charge (pH$_{zpc}$). The pH$_{zpc}$ is used to characterize the materials engineering, wastewater management, etc. [30].

Figure 4 shows that CKD surface is positively charged at pH more than ≈ 10.0 (alkaline conditions) and negatively charged under pH= 10.0. CKD has weak negative charges from pH<10.0 to pH> 3.0 and strong negative charge at the acidic conditions. The surface charge varies from 63.7 C/m2 to -130 C/m2. The CKD negative charge has a significant impact on adsorbing heavy metals by electrostatic attraction where heavy metals have positive charge (M+2). However, the identification of the preferable pH for adsorption can be a complicated issue. Accordingly, one of the main roles of batch experiments is to identify the optimum pH value for metals uptake.
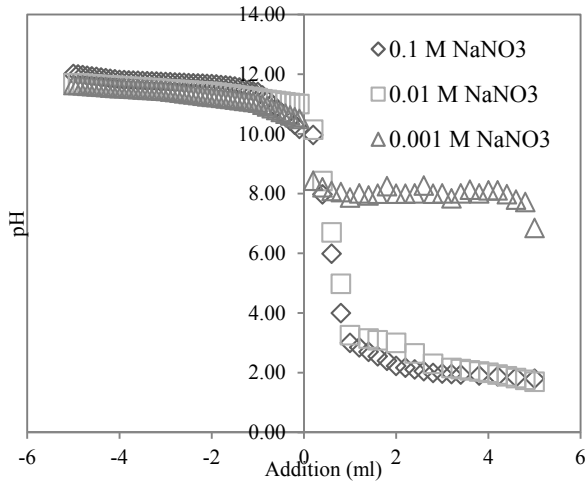
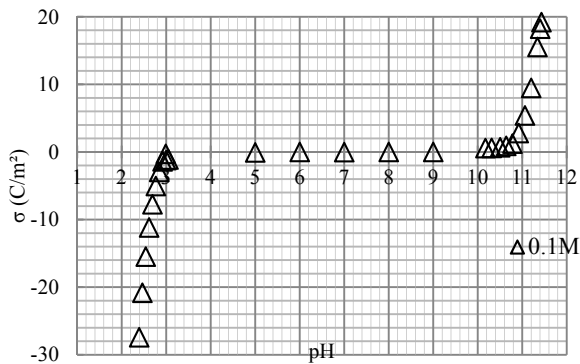**Figure 3: Surface Titration Data of CKD at Three Different Ionic Strengths**

Figure 4: Sorbent Surface Charge at different pH values at Ionic Background of 0.1 M

3.2. Batch Equilibrium Studies

The parameters which affect the adsorption of the targeted metal cations (Pb (II), Cu (II), and Cd (II)) are investigated and determined. These parameters are pH, shaking time, sorbent (CKD) dose, and initial metal concentration. Studying the sorption behavior provides data for isotherm models to describe the equilibrium. The metal hydroxide precipitation is identified first without adding CKD.

3.2.1. Metal Hydroxide Precipitation

Precipitation experiments show that the metal hydroxide precipitation from the synthetic solutions limits the suitable operation pH for adsorption. This is because the insoluble metals at higher pH values make the actual adsorption mechanism hard to study. The experiment is carried out at different pH values (3–11) to investigate the metal hydroxide precipitation pH range of 30 mg/l for each target metal individually without using of CKD.

Figure 5 shows the removal of M^{+2} (Pb, Cu, and Cd) as hydroxides from the solution as a function of pH. Figure 5 concludes that drastic change in lead precipitation started at pH value of 6.0 to reach 87 %. From this pH and beyond, the precipitation is the dominant mechanism of lead removal. This observation has been also confirmed by other authors [31, 32]. While for both copper and cadmium, the precipitation started at pH 8.0 to reach approximately 90%. PH values higher than 8.0 reduces the solubility of different heavy metals [33, 34].

Therefore, the metal aqueous solution pH should be controlled to avoid amphoteric metal ions dissociation [35].
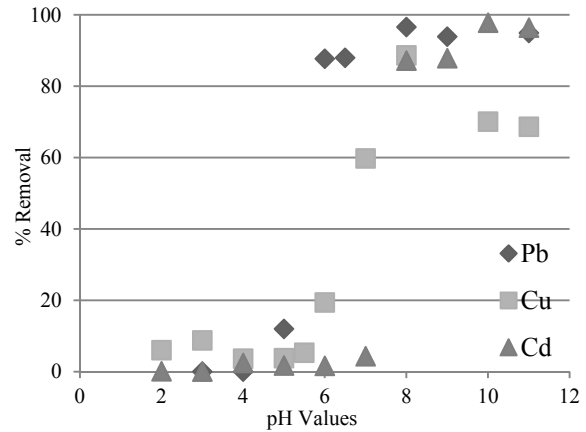

Figure 5: Percentage Removal of Heavy Metal Using Hydroxide Precipitation

3.2.2. Effect of pH

Adsorption of metal from aqueous solution is related to the pH of the solution, as the later affects the surface charge of the metal binding sites in the sorbent and the degree of ionization [36]. The experiment is carried out to investigate the optimum pH value for metal adsorption by CKD. Batch equilibrium experiments are performed using a CKD dose of 2 gm/l in metal synthetic solutions for lead, copper, and cadmium separately. The metal solution initial concentration is chosen to be 30 mg/l and the initial pH values are adjusted to be in the range of 3 to 11. Figure 6 shows that CKD has significantly lower sorption capacity for metal uptake at pH values below 4. At pH values higher than 4, a considerable jump in the adsorption capacity of the CKD is observed to reach 38% for lead, 57% for copper, and 47% for cadmium at pH = 5.0. The metal adsorption reached its optimum capacity (>90%) at pH 5.5 ~6.0 for the three target metals. The metal uptake (Qeq) is 15 mg lead/gm of CKD (73.5 μm/gm) and 13.5 mg/gm CKD for copper and cadmium (212 μm/gm and 120 μm/gm respectively). This binding reaction between the adsorbent and the adsorbate might be due to the effect of hydroxyl (-OH) and carboxyl (-COOH) groups, since the ionization constant for a number of these groups range between 4 and 5 [37]. Above pH 6, the heavy metals tend to form insoluble micro-precipitates complexes that make a distortion in the sorption results. Therefore, the pH value of the metal solution shall not exceed pH 6 to determine actual adsorption capacities.
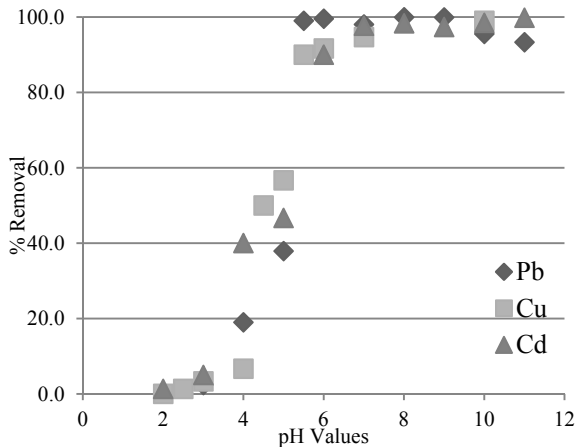
Figure 6: Effect of pH on Adsorption of 30 mg/l Heavy Metal Removal using 2g/l CKD

3.2.3. Effect of Contact Time

The required contact time taken to reach equilibrium depends on the system reaction; therefore, it is essential to determine the required contact time to reach equilibrium. Batch equilibrium experiments are performed using a CKD dose of 2.0 gm/l in a metal solution of 30 mg/l. The initial pH is adjusted at the optimum pH obtained from the first set of experiments mentioned previously (pH value of 5.5). The percentage of metal uptake is measured at time intervals from 5 minutes to 24 hours.

Figure 7 shows that the rate of metal adsorption is rapid during the first 20 minutes of the experimental runs. The lead and copper uptake amazingly reach more than 90% in the first 5 minutes while it takes 90 minutes for the cadmium to achieve 90% recovery. After then, the uptake capacity of CKD increases slowly until it reaches its breakthrough after approximately 4 hours. Accordingly, the required contact time to reach equilibrium for the target metals is 4 hours at which the uptake efficiency of CKD reaches more than 95%. The adsorption capacity of CKD at equilibrium is 14.8 mg/gm, 14.6 mg/gm, and 14.4 mg/gm for lead, copper, and cadmium respectively.
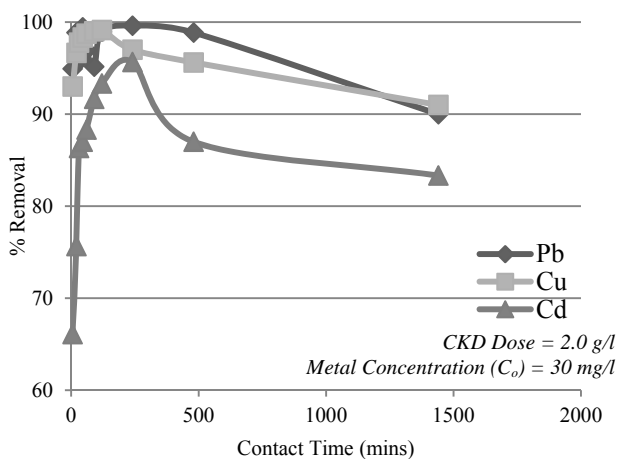

Figure 7: Effect of Contact Time on Heavy Metal Adsorption at pH 5.5 – Percentage Removal

3.2.4. Effect of Sorbent Dose

Batch equilibrium experiments are performed using different adsorption doses; 0.015%, 0.03%, 0.05%, 0.075%, 0.1%,

0.15%, and 0.2% (W/V), with an initial metal concentration of 30 mg/l at the optimum pH of 5.5 and contact time of 4 hours. Figure 8 depicts the influence of adsorption dose on the metal uptake capacity. It is obvious that the increase in adsorption dose from 0.05% to 0.2% (W/V) results in increasing the uptake of metal ions dramatically. However, this uptake values shows a reverse trend in the specific uptake (Qeq)from 43 mg Pb / gm - to 14.85gmPb / gm CKD, 27mg Cu/gm CKD to 14.55 mg Cu/gm, and 20 mg Cd/gm to 14.25mgCd/gm. This phenomenon might be attributed to the reduction in sorbent concentration (X) in the suspension at a given metal concentration (Co) which in turn increases the metal / sorbent ratio (Co/X). Hence, the metal uptake per gram sorbent (Qeq) increases. The increase in specific uptake (Qeq) with increasing in (C/X) ratio has two possible explanations: 1) the reduction in sorbent concentration decreases the electrostatic interaction between cells which increase the adsorption rate. 2) Increasing the ratio of initial metal concentration versus sorbent dose that might cause an increase in the available number of ions around the sorbent particles, and hence more easily bound to the active sites will occur as long they are not saturated [37].

3.2.5. Effect of Initial Metal Concentration

In order to identify the impact of the initial metal concentration on the adsorption mechanism, the batch equilibrium experiment runs are performed using different metal concentrations: 10, 30, 50, 70, 100,150, and 200 mg/l, with a CKD dose of 2.0 g/l. Figure 9 and Figure 10 show the influence of the initial metal concentration on the adsorption capacity of the CKD. It is obvious from both figures that the adsorption uptake efficiency together with the sorption capacity (Q_{eq}) are affected by sorbent (CKD) to sorbate (metal) ratio as concluded previously. The removal efficiency is inversely proportional to the initial metal concentration. From this experiment and the previous one:

If X >> C_o, the removal efficiency might increase and the specific uptake will decrease.

If C_o >> X, the removal efficiency will decrease while the specific uptake might increase

Where: **X** is the sorbent concentration, and **C_o** is the initial metal concentration.
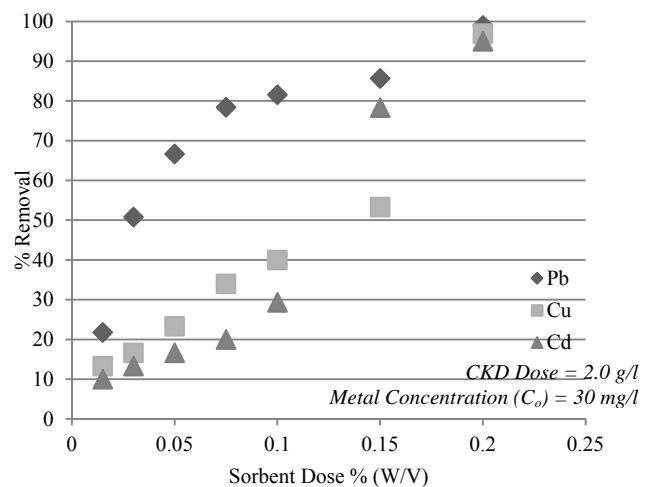

Figure 8: Effect of CKD Dose on Heavy Metal Adsorption at pH 5.5 for 4hrs Contact Time
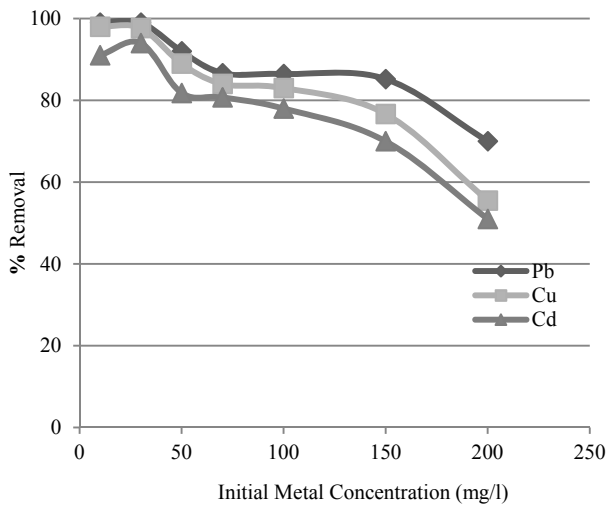
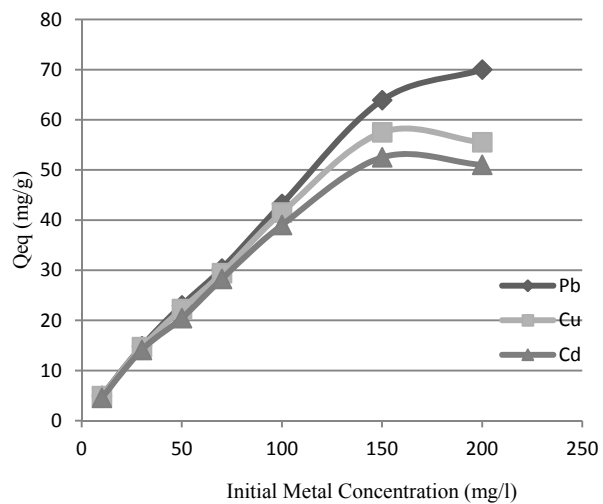**Figure 9: Initial Metal Concentration Uptake**

Figure 10: Initial Metal Concentration Specific Uptake

3.2.6. Comparing CKD to other Wastes-Adsorbents

CKD has also been compared to many other adsorbents with a focus to those generated from wastes such as waste iron oxide and sawdust. The adsorption capacity of CKD shows higher affinity for metals adsorption than these adsorbents. Zeng in 2004 examined the removal of various heavy metals using iron oxide [38]. The iron oxide used by Zeng is produced by drying tailings slurry from disposal ponds at 80°C, and it consists of 33% by weight iron oxide. He concluded that the removal efficiency for Cd and Pb are 81.07% and 99% respectively at pH 6.5, adsorbent dose of 2gm/l, and initial metal concentration of 10mg/l.

Yasemin in 2007 investigated the adsorption of lead and cadmium using sawdust produced from walnut [39]. She found that the adsorption capacity of sawdust for both metals is 3.78 and 3.32 mg/g respectively. The adsorption experiments were carried out by using 20g/l sawdust at initial metal concentration varies from 10 to 200 mg/l.

3.3. Sorption Isotherm Model

3.3.1. Langmuir Isotherm

Langmuir has traditionally been utilized to quantify the performance of different sorbents. This empirical model assumes monolayer adsorption where adsorption can only occur at a finite number of definite localized sites with no lateral interaction [40]. The isotherm measures the relation between the equilibrium concentration of the element in the solid phase (q_e, *mg/g*) and the equilibrium concentration of that element in the aqueous phase (C_e, *mg/l*). The equilibrium data resulted from the batch experiment runs are fitted with Langmuir model. The Langmuir adsorption of the targeted heavy metals (Pb, Cu, and Cd) is shown in Figure 11 to Figure 13 respectively. It also depicts the linear plot of Langmuir equation and the adsorption parameters. As shown in Table 2, the removal rate and the strength of adsorption are in the order Pb ≥ Cu> Cd. According to Langmuir, adsorption occurs uniformly on the active site of the sorbent and once a sorbate occupies a site, no further adsorption can be carried out [26]. A plot of $1/C_e$ versus $1/q_e$ would result in a straight line with a slope of $1/ab$ and intercept of $1/b$ as shown in Figure 11 to Figure 13.
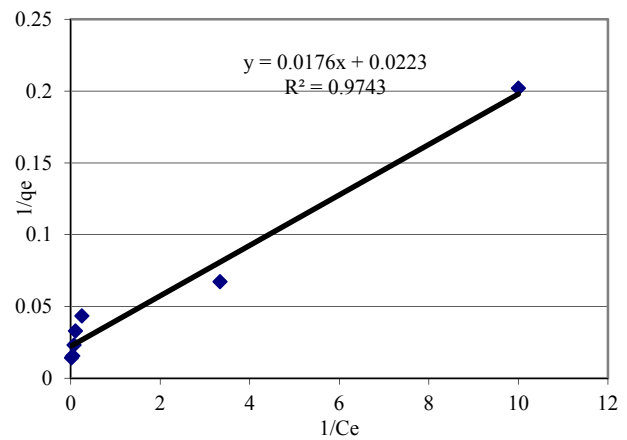

Figure 11: Langmuir Isotherm for the Adsorption of Pb (II) using CKD

Table 2: Langmuir Isotherm Parameters for Heavy Metal Adsorption by CKD

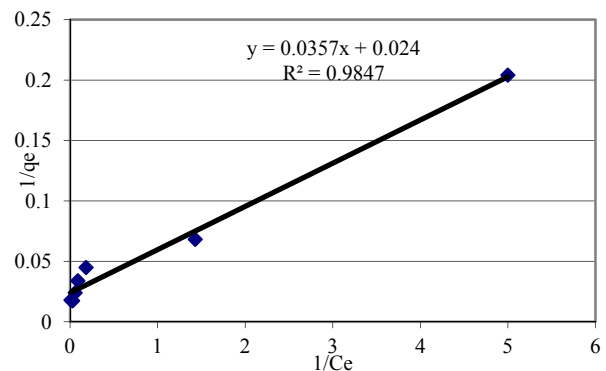| Heavy Metal	1/b	1/ab	R^2
Lead (Pb II)	0.022	0.017	0.974
Copper (Cu II)	0.024	0.035	0.984
Cadmium (Cd II)	0.016	0.167	0.934

Figure 12: Langmuir Isotherm for the Adsorption of Cu (II) using CKD
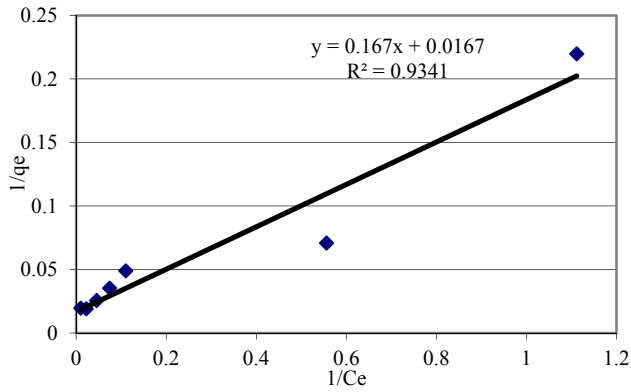
Figure 13: Langmuir Isotherm for the Adsorption of Cd (II) using CKD

3.3.2. Freundlich Isotherm

The equilibrium data are also fitted with Freundlich model. A plot of *log qe* as a function of *log C_e* results in a straight line with a slope of *1/n* and intercept *log k*. The Freundlich isotherm of metals ions using CKD are shown in Figure 14 through Figure 16. The adsorption parameters calculated from these figures are summarized in Table 3. Since K_f and *1/n* are measured for the adsorption rate and strength, it is concluded that the removal strength of adsorption is in the order Pb≥ Cu> Cd which is consistent with the electronegativity of these metals (1.854, 1.85, and 1.52 respectively). The values of *1/n* < 1 correspond to a heterogeneous mode with an exponential distribution of energy of the sorption sites [26].
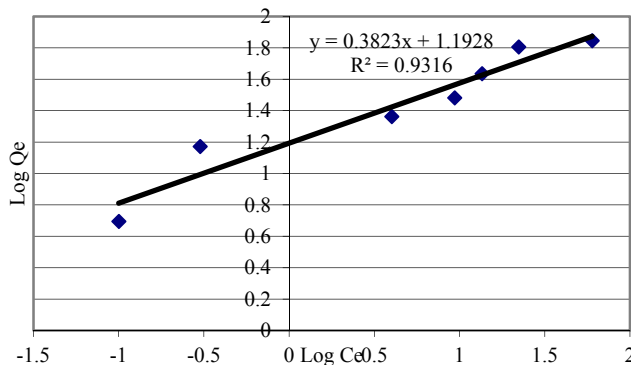

Figure 14: Freundlich Adsorption Isotherm for Pb(II) Ion Adsorption

Table 3: Freundlich Adsorption Parameters using CKD

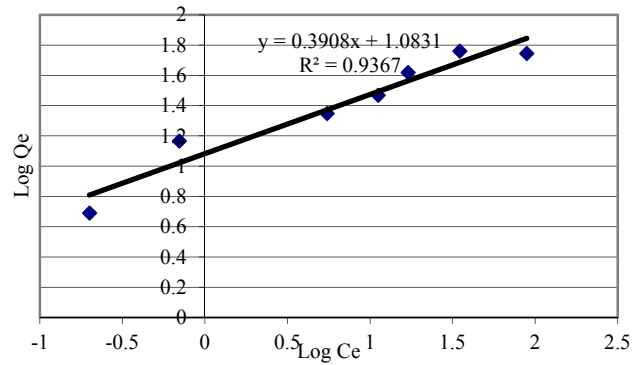| Heavy Metal	Log K_f	1/n	R^2
Lead (Pb II)	1.192	0.382	0.931
Copper (Cu II)	1.083	0.39	0.936
Cadmium (Cd II)	0.859	0.49	0.900

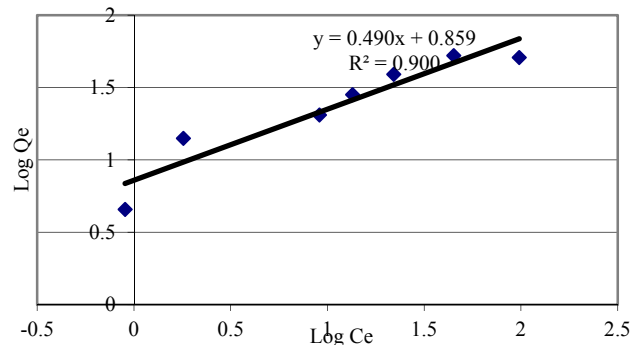**Figure 15: Freundlich Adsorption Isotherm for Cu (II) Ion Adsorption**

Figure 16: Freundlich Adsorption Isotherm for Cd (II) Ion Adsorption

4. Conclusions

- CKD has a high affinity to adsorb the target heavy metals from the aqueous solutions.

- CKD demonstrates potential to adsorb heavy metals, even at pH values less than the pHzpc. Metal removal is a result of electrostatic interactions in addition to surface complexation

- CKD shows potential to adsorb heavy metals from aqueous solutions at pH higher than 5.5.

- The removal rate and the strength of adsorption are in the order Pb≥ Cu>Cd as depicted by Langmuir and Freundlich isotherm models which are consistent with the electronegativity of these metals.

- The adsorption-pH edge indicates that there is a notable removal before pH 5.5; the removal reached its peak value at pH 5.5 ~ 6.0. Metal removal at high pH is attributed to the metal precipitation.

- CKD can be successfully used as effective, low cost and abundant sorbent for lead, copper, and cadmium and can be used as alternative to more costly materials.

- CKD shows higher affinity to adsorb heavy metals than other adsorbents specifically waste iron oxide and sawdust.

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