

Equilibrium analysis for heavy metal cation removal using cement kiln dust

Mohamed El Zayat, Sherien Elagroudy and Salah El Haggag

ABSTRACT

Ion exchange, reverse osmosis, and chemical precipitation have been investigated extensively for heavy metal uptake. However, they are deemed too expensive to meet stringent effluent characteristics. In this study, cement kiln dust (CKD) was examined for the removal of target heavy metals. Adsorption studies in completely mixed batch reactors were used to generate equilibrium pH adsorption edges. Studies showed the ability of CKD to remove the target heavy metals in a pH range below that of precipitation after an equilibrium reaction time of 24 h. A surface titration experiment indicated negative surface charge of the CKD at pH below 10, meaning that electrostatic attraction of the divalent metals can occur below the pH required for precipitation. However, surface complexation was also important due to the substantive metal removal. Accordingly, a surface complexation model approach that utilizes an electrostatic term in the double-layer description was used to estimate equilibrium constants for the protolysis interactions of the CKD surface as well as equilibria between background ions and the sorbent surface. It was concluded that the removal strength of adsorption is in the order: Pb > Cu > Cd. The experiments were also supported by Fourier transform infrared spectroscopy (FTIR).

Key words | adsorption equilibrium, cement kiln dust, FTIR, heavy metals, triple-layer surface complexation modeling

Mohamed El Zayat (corresponding author)
(ASCE/EWRI), Environmental Engineering PhD Program,
American University in Cairo,
P.O. Box 74,
New Cairo 11835,
Egypt
E-mail: m_elzyat@aucegypt.edu

Sherien Elagroudy
Egypt Solid Waste Management Center of Excellence,
Ain Shams University,
1 El-Sarayut St., Abassia,
Cairo 11517,
Egypt

Salah El Haggag
Department of Mechanical Engineering,
American University in Cairo,
P.O. Box 74,
New Cairo 11835,
Egypt

INTRODUCTION

Inorganic constituents, such as heavy metals, are carcinogenic due to the fact that they can bio-accumulate in our bodies, resulting in an increase in the concentration of toxic chemicals in the biological organism (Lenntech 2013). Heavy metals, such as lead, copper, and cadmium, have been also named as toxic metals due to their severe effect on human beings (Mahajan & Sud 2013). They can find their way to soil and then into freshwater bodies and groundwater as a leachate from industrial effluents (Lef 2013). The most commonly used techniques for heavy metal recovery are reduction, precipitation, ion exchange, and adsorption (Dabrowski 2001; Fenglian & Wang 2011). However, most of these methods incurred high capital and operational costs (Barakat 2011). Motivated by cost considerations, the efficiency of cement kiln dust (CKD) on heavy metal recovery is investigated in this study. CKD is an industrial waste which is considered a problematic issue (USEPA 1993). CKD has high content of calcium oxide (CaO) that results in it being used as a

replacement for lime in treating acidic wastewater (Mackie *et al.* 2010). It has been also used as a chemical coagulant for wastewater treatment, resulting in reduction in the concentration of total suspended solids (TSS), biochemical oxygen demand (BOD), chemical oxygen demand (COD), and P-total of wastewater effluent (Abo-El Hassan 2008; El Zayat *et al.* 2012). Taha 2003 investigated the effect of CKD on the mobility of heavy metals present in municipal wastewater and sludge. She found that CKD is capable of reducing disease-causing organisms, in wastewater, and is more effective for sewage sludge. Moreover, many researches were conducted to investigate the influence of the physicochemical properties of CKD for soil and sludge stabilization (Khaled 2000; Peethamparan *et al.* 2008). It was found that the CKD has a high propensity to stabilize both soil and sludge and kill pathogens because of the CKD alkalinity. The capacity of CKD, as heavy metals scavenger, for chromium uptake from aqueous solutions has also shown good

results (El Awady & Sami 1997). However, CKD has not been tested extensively for the removal of some other heavy metals from industrial wastewater, such as lead, copper, and cadmium. Moreover, a huge lack of titration experiments for CKD in the literature was observed besides computational modeling of the adsorption capacity of the CKD.

Surface complexation models were used to interpret metal ion adsorption equilibria. In this study, the triple-layer surface complexation model (TL-SCM) was used for the determination of sorbent surface equilibrium constants from potentiometric titration data. These values were then used to estimate adsorption equilibrium constants from pH adsorption edge data for the three target heavy metals used in the batch experiments in the bench scale, namely lead, copper, and cadmium. The ultimate objective of these studies is to use the model as a scale-up tool for design of either pilot- or full-scale units.

MATERIALS AND METHODS

Cement kiln dust

CKD samples were obtained from a local cement manufacturing plant in Upper Egypt. CKD usually has a diameter below 10 μm , which is within the range of respiration for humans (Peethamparan 2006). However, it might vary between 10 and 50 μm based on the storage process. The used CKD has a particle size of approximately 74 μm and surface area of approximately 4,000 cm^2/g . Due to the fineness of the CKD particles used, a larger surface area is available for the reaction of CaO with water to produce $\text{Ca}(\text{OH})_2$. This indicates that the oxide particles present in CKD may demonstrate great reactivity. Increased surface area also allows more space for metal adsorption, since CKD has been proved to act as both a neutralizing agent and a sorbent (Mackie *et al.* 2010). Ca content in CKD was found to be 55.30% by weight using energy dispersive microscopy analyses. This result matches those of Mackie *et al.* (2010) who proved that CKD can contain up to 61.3% by weight of total CaO. High Ca concentration has a positive effect on wastewater treatment (Abo-El Hassan 2008; Ayoub *et al.* 2011).

Surface titration

Sorbent samples were titrated potentiometrically in order to estimate surface charge characteristics. In this study, 0.1 g of dry CKD sample was suspended in a Teflon reaction vessel containing 50 ml of deionized distilled water at room

temperature to yield a solid concentration of 2 g/l. The suspension was 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 0.1 M HNO_3 and 0.1 M NaOH were added precisely to adjust the pH. The pH was measured by a pre-calibrated Schott pH meter. NaNO_3 was used as an ionic background in order to standardize the solution. Total volume of acid or base added was less than 5% (5 ml) of the sample volume to minimize the dilution effects. The pH was measured every 0.1 ml addition of either acid or base. The experiment was done for ionic backgrounds of 0.1, 0.01, and 0.001 M in order to examine the impact of background total dissolved solids concentration on CKD surface charge.

Batch equilibrium experiments

To assess adsorbent capacity and the equilibrium relationship between adsorbent and adsorbate, a whole sorption isotherm was derived. The sorption isotherm is the ratio between the quantity of heavy metals adsorbed and that remaining in solution at fixed temperature at equilibrium. The purpose of this set of experiments was to determine: (1) precipitation pH ranges of the synthetic solutions of lead, copper, and cadmium; (2) most suitable pH for metal adsorption by CKD; (3) optimum CKD dose and contact time on metal uptake; and (4) absorption capacity of CKD at different heavy metal concentrations. The effect of initial pH, contact time, initial CKD dose, and metal concentration on CKD adsorption equilibrium was examined. All synthetic heavy metal solutions used in the batch equilibrium experiments had the same initial concentration of 30 ppm except for the identification of the optimum metal concentration experiments, where metal concentration ranged from 10 to 200 ppm. The target equilibrium pH range was 3–11, and a reaction time of 24 h was examined. CKD dose varied from 0.15 to 2.0 g/l. A 0.01 M NaNO_3 was used as the ionic background in order to standardize the solutions. Metal concentrations were determined using an atomic absorption spectrophotometer (GBC model SensaAA dual flame atomization system). The batch experiments were conducted using plastic bottles manufactured by Nalgene (USA) over an orbital shaker to ensure proper mixing and agitation.

Fourier transform infrared

Fourier transform infrared (FTIR) analysis is a powerful tool for studying the mechanism of adsorption (Volesky 2003). It

is an analytical technique used to identify organic and inorganic materials by measuring the absorption of various infrared light wavelengths by material interest. CKD samples before and after metal removal were analyzed using an FTIR spectrometer (model Bruker vector 22). The translucent disks of the CKD were obtained by milling 5 mg of each sample with 400 mg potassium bromide to form a fine powder. Then, the powder was compressed into a thin pellet and analyzed in the mid-IR region (4,000–400 cm^{-1}).

Sorption equilibrium

Chemical equilibrium constants from experimental data were determined using the FITEQL computer program. FITEQL 3.1 is a non-linear least-squares optimization program (Herbelin *et al.* 1999) that is available from John C. Westall of the Oregon State University. First, a TL-SCM was used for the determination of sorbent surface equilibrium constants from potentiometric titration data. These values were then used to estimate adsorption equilibrium constants from pH adsorption edge data for the three target heavy metals: lead, copper, and cadmium.

RESULTS AND DISCUSSION

Adsorption equilibrium and constant

The simulation of the adsorption mechanism is important to verify the performance of CKD and to facilitate the design of adsorption units. The triple-layer model (TLM) can consider inner layer (*o*-plane) and outer layer (β -plane) surface complexes with adsorbable and electrolyte species in addition to diffuse layer interactions as in conventional double-layer theory (Hizal & Apak 2006). Mathematical depiction of the TLM includes mass balances, charge balances, and surface equilibrium equations as follows.

Mass balances for the electrolyte species, assuming NaNO_3 background as in experimental runs, are:

$$C_{T,\text{NO}_3^-} = [\text{NO}_3^-] + [>\text{SOH}_2^+ - \text{NO}_3^-] \quad (1)$$

$$C_{T,\text{Na}^+} = [\text{Na}^+] + [>\text{SO}^- - \text{Na}^+] \quad (2)$$

The surface site balance, considering an inner layer, the surface complex for an adsorbed divalent metal species,

Me^{2+} , is:

$$C_{T,\text{SO}^-} = [>\text{SOH}_2^+] + [>\text{SOH}] + [>\text{SO}^-] + [>\text{SO}^- - \text{Na}^+] + [>\text{SOH}_2^+ - \text{NO}_3^-] + [>\text{SOMe}^+] \quad (3)$$

Total soluble Me(II) mass balance for the equilibrium condition is:

$$C_{T,\text{Me(II)(sol)}} = [\text{Me}^{2+}] + [\text{MeOH}^+] + [\text{Me}(\text{OH})_2^0] + [\text{Me}(\text{OH})_3^-] + \dots \quad (4)$$

The inner layer charge balance equates total adsorbed concentrations in the inner layer with the total charges in the *o*-plane. For the inner-layer adsorbed complex:

$$[>\text{SOH}_2^+] + [>\text{SOH}_2^+ - \text{NO}_3^-] + [>\text{SOMe}^+] - [>\text{SO}^-] - [>\text{SO}^- - \text{Na}^+] = \frac{S_C S_A}{F} C_1 (\psi_O - \psi_\beta) \quad (5)$$

where S_C is the concentration of solid (g/l), S_A is the surface area of the adsorbent, F is a Faraday constant (coulombs/mole), C_1 is the inner-layer capacitance (F/m^2), and ψ_i is the average electrostatic potential (volt) at the *o*- and β -planes, respectively (Sreejalekshmi *et al.* 2009).

The analogous outer-layer charge balance is:

$$[>\text{SO}^- - \text{Na}^+] - [>\text{SOH}_2^+ - \text{NO}_3^-] = \frac{S_C S_A}{F} [C_1 (\psi_\beta - \psi_O) + C_2 (\psi_\beta - \psi_d)] \quad (6)$$

where C_2 is the outer-layer capacitance (F/m^2), and ψ_d is the average electrostatic potential (volt) in the diffuse layer.

The charge balance for the diffuse layer is:

$$C_2 (\psi_d - \psi_\beta) = 0.1174 \sqrt{I} \sinh\left(\frac{F\psi_d}{2RT}\right) \quad (7)$$

where R is the universal gas constant ($\text{cal}/(^{\circ}\text{K} \cdot \text{mole})$), T is the absolute temperature ($^{\circ}\text{K}$), and I is the ionic strength (mol/l).

The metal-hydrolysis mass law expression is:

$$K_{n,\text{hydrolysis}} = \frac{[\text{Me}(\text{OH})_n^{2-n}][\text{H}^+]}{[\text{Me}^{2+}]} \quad (8)$$

Metal ion adsorption from aqueous solution is assumed to occur at functional group sites on the surface of CKD. The predominant adsorption sites for this case are assumed

to be $>\text{SOH}_2^+$, $>\text{SOH}$, and $>\text{SO}^-$. The following protolysis reactions describe the acid-base chemistry of the surface:



where the surface species $>\text{SOH}_2^+$, $>\text{SOH}$, and $>\text{SO}^-$ can acquire protons in solution.

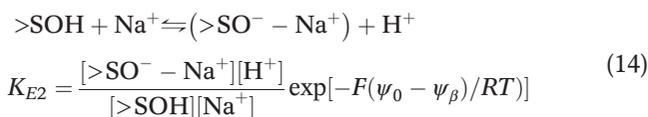
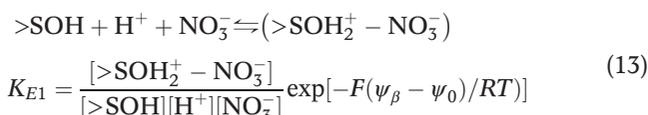
TL-SCM expressions for the equilibrium constants are:

$$K_{S1} = \frac{[>\text{SOH}_2^+]}{[>\text{SOH}][\text{H}^+]} \exp(F\psi_0/RT) \quad (11)$$

$$K_{S2} = \frac{[>\text{SO}^-][\text{H}^+]}{[>\text{SOH}]} \exp(-F\psi_0/RT) \quad (12)$$

where K_{S1} and K_{S2} are the equilibrium constants for the respective surface protolysis reactions, and F , R , T , and ψ_0 are as defined previously (Sreejalekshmi et al. 2009).

Interactions of electrolyte ions with the surface species are according to the following reactions in correspondence to the equilibrium expressions:



where ψ_β is the average potential (volt) of the outer, or β , plane. Model calculations also required the surface area of the sorbent (m^2/g), surface site density (sites/nm^2) and linear charge potential (F/m^2). Figure 1 shows the potentiometric data plot at two ionic strengths compared to the TL-SCM simulations. The pH of zero charge is ~ 10.0 . The $\log K_i$ values are:

$$\log K_{S1} = 1.6, \quad \log K_{S2} = -2.8, \quad \log K_{E1} = 3.50, \\ \log K_{E2} = -5.30$$

For heavy metal adsorption, the hydrolysis and precipitation of Me(II) hydroxides should be included in the analysis. It was obvious that significant lead precipitation occurs at pH as low as 6–7, while precipitation of copper is from pH 7 to 8, and cadmium is at pH ~ 8 . Therefore, the adsorption mechanism will take place at pH values less than the precipitation values. For all three target metals, the predominant aqueous specie is Me^{2+} at these lower pH values. Therefore, the most likely adsorption reactions used in the TLM-SCM of adsorption equilibria were inner- and outer-layer complexes of Me^{2+} as follows:

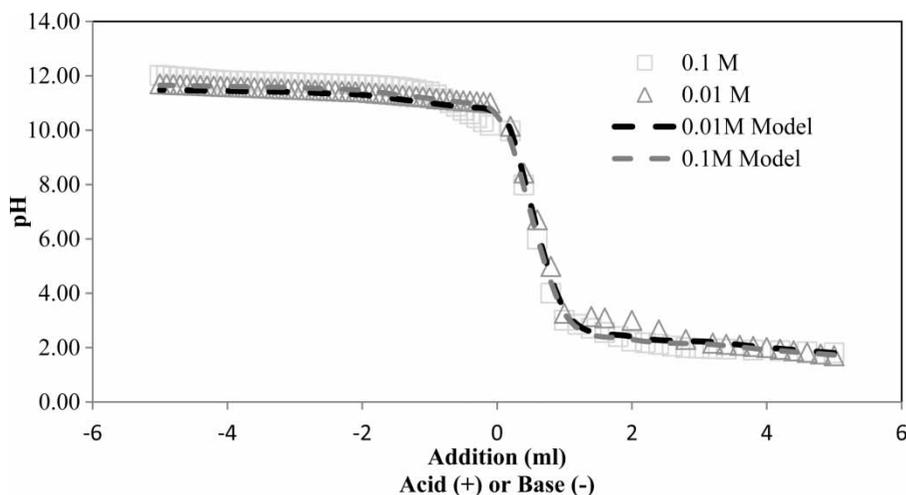
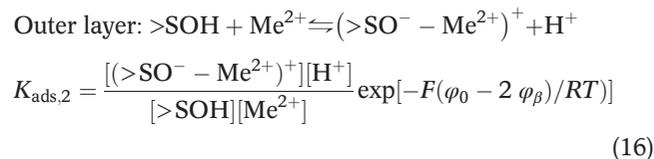
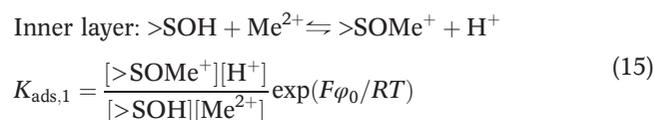


Figure 1 | Potentiometric titration data and TL-SCM simulation for CKD using FITEQL 3.1.

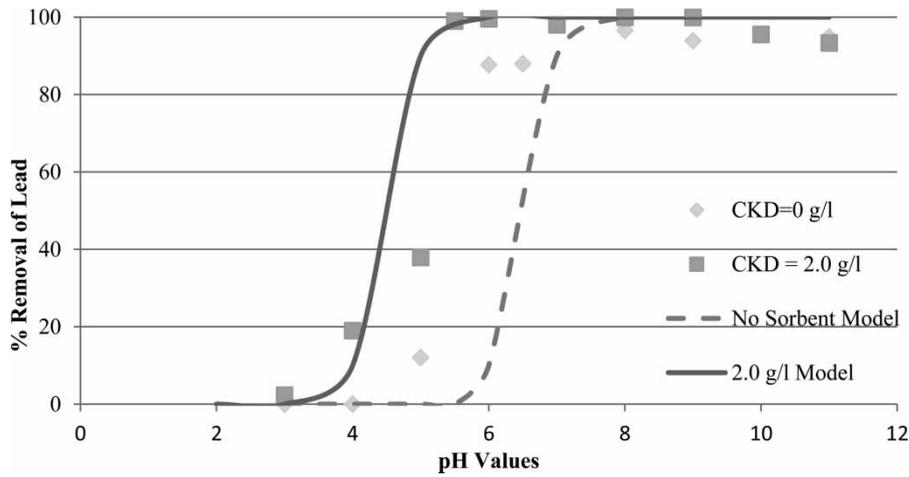


Figure 2 | Pb(II) adsorption edges with TL-SCM.

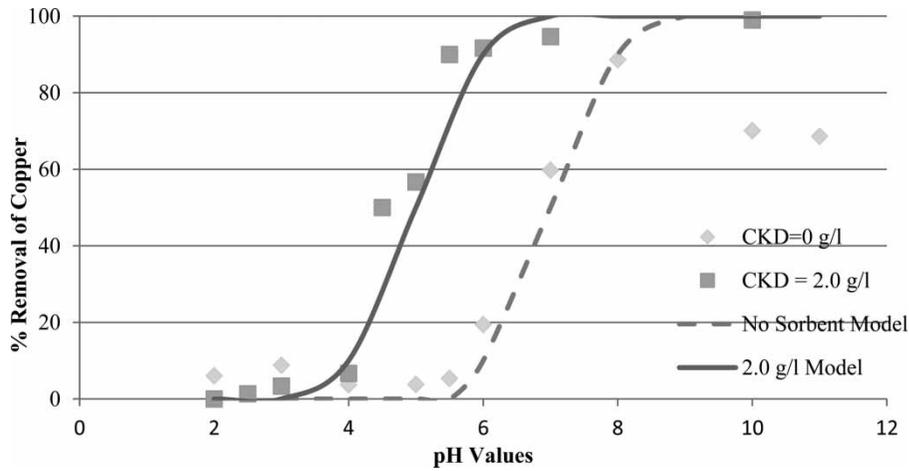


Figure 3 | Cu(II) adsorption edges with TL-SCM.

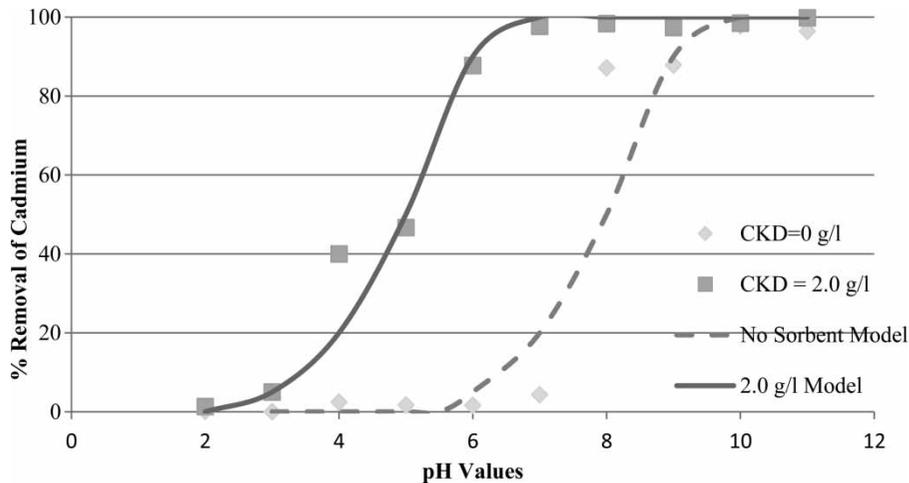


Figure 4 | Cd(II) adsorption edges with TL-SCM.

Table 1 | Equilibrium constants for TL-SCM of adsorption edges

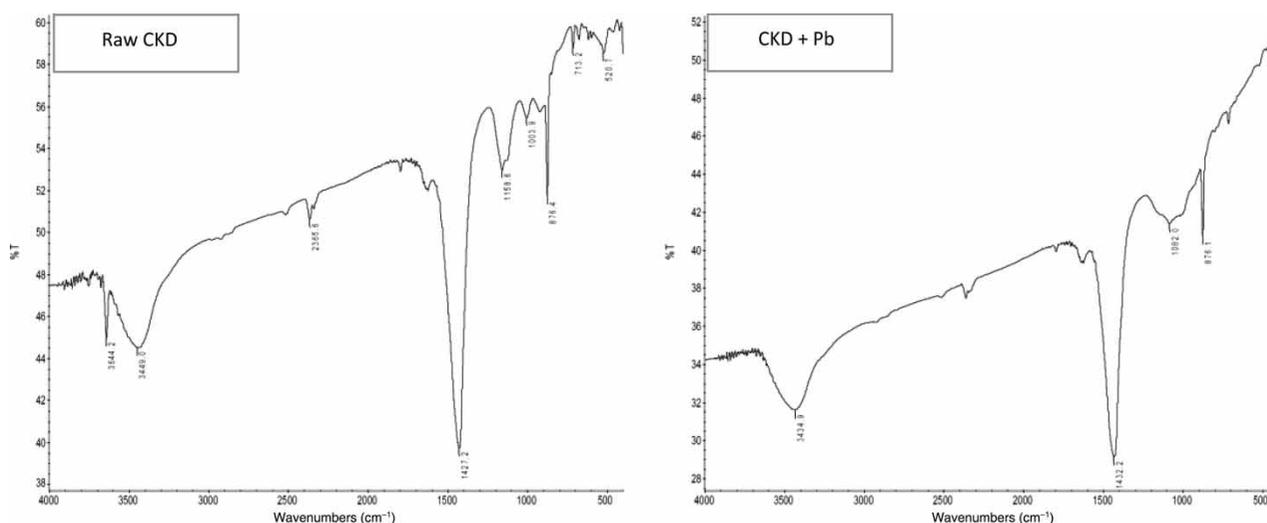
Reaction	Log K
Lead	
Hydrolysis: $\text{Pb}^{2+} + \text{H}_2\text{O} \rightleftharpoons \text{PbOH}^+ + \text{H}^+$	-7.71
$\text{Pb}^{2+} + 2\text{H}_2\text{O} \rightleftharpoons \text{Pb}(\text{OH})_2 + 2\text{H}^+$	-17.12
$\text{Pb}^{2+} + 3\text{H}_2\text{O} \rightleftharpoons \text{Pb}(\text{OH})_3^- + 3\text{H}^+$	-28.06
Solubility: $\text{Pb}^{2+} + 2\text{H}_2\text{O} \rightleftharpoons \text{Pb}(\text{OH})_{2(\text{s})} + 2\text{H}^+$	-12.80
Layer SC: $>\text{OH} + \text{Pb}^{2+} \rightleftharpoons >\text{OPb}^+ + \text{H}^+$	-1.80
Copper	
Hydrolysis: $\text{Cu}^{2+} + \text{H}_2\text{O} \rightleftharpoons \text{CuOH}^+ + \text{H}^+$	-5.80
$\text{Cu}^{2+} + 2\text{H}_2\text{O} \rightleftharpoons \text{Cu}(\text{OH})_2 + 2\text{H}^+$	-14.80
$\text{Cu}^{2+} + 3\text{H}_2\text{O} \rightleftharpoons \text{Cu}(\text{OH})_3^- + 3\text{H}^+$	-26.20
Solubility: $\text{Cu}^{2+} + 2\text{H}_2\text{O} \rightleftharpoons \text{Cu}(\text{OH})_{2(\text{s})} + 2\text{H}^+$	-12.70
Layer SC: $>\text{SOH} + \text{Cu}^{2+} \rightleftharpoons (>\text{SO}^- - \text{Cu}^{2+})^+ + \text{H}^+$	-1.88
Cadmium	
Hydrolysis: $\text{Cd}^{2+} + \text{H}_2\text{O} \rightleftharpoons \text{CdOH}^+ + \text{H}^+$	-10.03
$\text{Cd}^{2+} + 2\text{H}_2\text{O} \rightleftharpoons \text{Cd}(\text{OH})_2 + 2\text{H}^+$	-20.35
$\text{Cd}^{2+} + 3\text{H}_2\text{O} \rightleftharpoons \text{Cd}(\text{OH})_3^- + 3\text{H}^+$	-33.30
Solubility: $\text{Cd}^{2+} + 2\text{H}_2\text{O} \rightleftharpoons \text{Cd}(\text{OH})_{2(\text{s})} + 2\text{H}^+$	-18.60
Layer SC: $>\text{SOH} + \text{Cd}^{2+} \rightleftharpoons (>\text{SO}^- - \text{Cd}^{2+})^+ + \text{H}^+$	-3.20

Results of batch equilibrium pH adsorption edge experiments at CKD of 0 and 2.0 g/l are presented in Figures 2–4 for Pb, Cu, and Cd, respectively. Metal hydroxide precipitation calculated using the FITEQL model at CKD of 0 and 2.0 g/l are also presented in Figures 2–4. It was observed that the lead hydroxide precipitation is the dominant phenomenon at pH values

greater than 6.0, while for both cadmium and copper, the precipitation started at pH 8.0. It can be concluded that substantial adsorption occurred at pH values less than those of precipitation. Adsorption equilibrium constants as well as those for metal hydrolysis and metal-hydroxide precipitation are listed in Table 1. The adsorption obviously took place by electrostatic attraction of Me^{2+} cations to the CKD surface for $\text{pH} < \text{pH}_{\text{zpc}}$ (10.0) where the sorbent surface charge is negative. However, for all three target metals, notable removal of metal at approximately pH 5.5 was observed, indicating that surface complexation reactions are also important. It is likely that heavy metal uptake at higher pH values is a combination of adsorption, precipitation, and complex surface interaction processes that might occur simultaneously. In terms of adsorption capacity in $\mu\text{M/g}$ at pH values between 5 and 6, the uptake capacity followed the trend of $\text{Pb} > \text{Cu} > \text{Cd}$, which is consistent with the electro-negativity of these metals (1.854, 1.85, and 1.52, respectively).

Fourier transform infrared

The FTIR experiment was conducted in order to determine the chemical bonds between the target heavy metals and the sorbent (CKD) by obtaining an infrared absorption spectrum before and after the metal adsorption. The chemical bonds in a molecule can be determined by interpreting the infrared absorption spectrum. As shown in Figures 5–7, the FTIR analysis indicated that there is a difference in the band intensity and frequency of the main functional groups on the

**Figure 5** | Comparison between CKD before and after Pb removal.

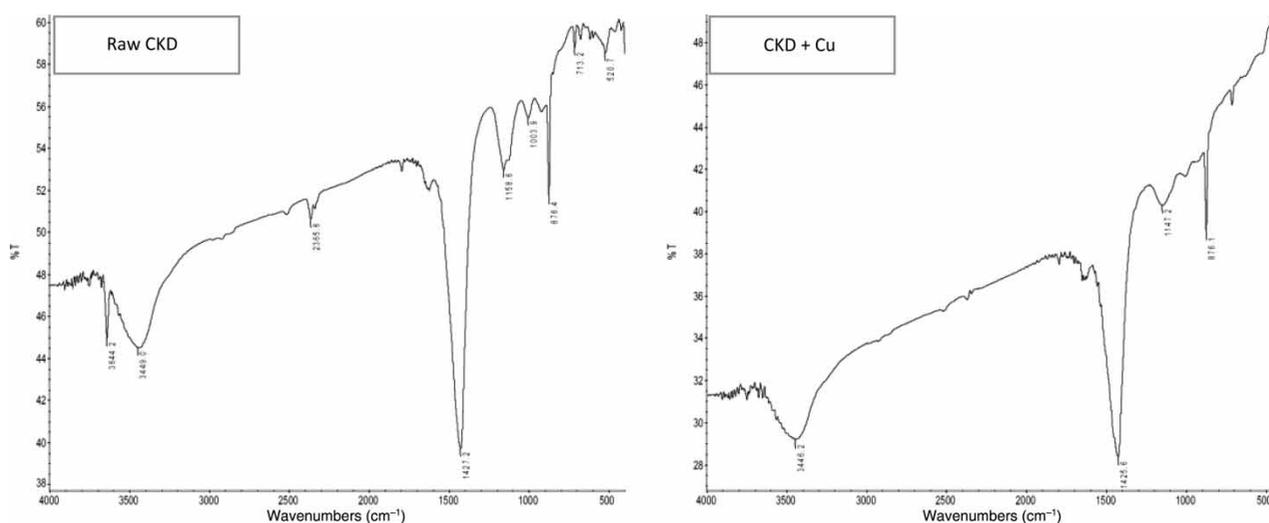


Figure 6 | Comparison between CKD before and after Cu removal.

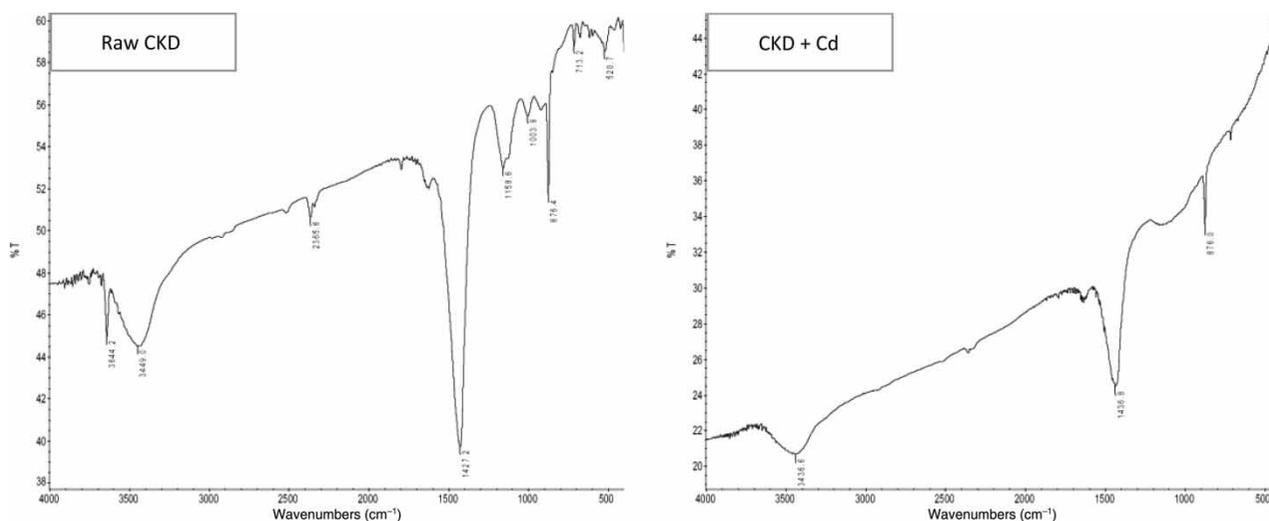


Figure 7 | Comparison between CKD before and after Cd removal.

surface of the CKD. The FTIR analysis was compared with the absorption peaks of known types of atomic bonds that are listed in the FTIR correlation tables. It is obvious that strong bonds took place with N-H (primary amines), C-H (alkyl), and C-X (aromatic) at wavelengths 3,449.0, 1,432.2, and 713 cm^{-1} . Moreover, the results of FTIR confirm that the presence of Ca-O group at wavelength range from 870 to 1,100 cm^{-1} supports the adsorption mechanism due to free CaO. This was also observed by Salem in 2012 (Salem *et al.* 2012).

CONCLUSIONS

- Cement kiln dust demonstrates potential to adsorb heavy metals, even at pH values less than the pH_{zpc} . Metal removal is a result of electrostatic interactions in addition to surface complexation.
- A TL-SCM was used to describe surface protonation of the CKD at various ionic strengths assuming $>\text{SOH}_2^+$, $>\text{SOH}$, and $>\text{SO}^-$ surface species; and the equilibrium relationship of Me(II) adsorption as a function of pH

and CKD dose. The removal rate and the strength of adsorption is in the order: Pb > Cu > Cd.

- The FTIR confirms that the active areas such as CaO present on the CKD samples play a significant role in the adsorption of heavy metals.

REFERENCES

- Abo-El Hassan, E. E. 2008 *Utilizing of Cement Kiln Dust as a Chemical Coagulant for Wastewater Treatment*. PhD Thesis, Cairo University, Cairo, Egypt.
- Ayoub, G. M., Hamzeh, A. & Semerjian, L. 2011 *Post treatment of tannery wastewater using lime/bittern coagulation and activated carbon adsorption*. *Desalination* **273** (2–3), 359–365.
- Barakat, M. A. 2011 *New trends in removing heavy metals from industrial wastewater*. *Arabian Journal of Chemistry* **4** (4), 361–377.
- Dabrowski, A. 2001 *Adsorption – from theory to practice*. *Advances in Colloid and Interface Science* **93**, 135–224.
- El Awady, M. H. & Sami, T. M. 1997 *Removal of heavy metals by cement kiln dust*. *Journal of Environmental Contamination and Toxicology* **59**, 603–610.
- El Zayat, M., Elagroudy, S. & El Hagggar, S. 2012 *Treatment of various types of wastewater using cement kiln dust*. In: *Proceeding of the 5th International Perspective on Water Resources and Environment 2012 (EWRI/ASCE)*, Marrakesh.
- Fenglian, F. & Wang, Q. 2011 *Removal of heavy metal ions from wastewater: a review*. *Journal of Environmental Management* **92**, 407–418.
- Herbelin, A. L. & Westall, J. C. 1999 *FITEQL-Version 3.1: A Program for the Determination of Chemical Equilibrium Constants from Experimental Data*. Report 94-01, Oregon State University, Corvallis, OR, USA.
- Hizal, J. & Apak, R. 2006 *Modeling of cadmium (II) adsorption on kaolinite-based clays in the absence and presence of humic acid*. *Appl. Clay Science* **32**, 232–244.
- Khaled, A. M. 2000 *Effect of Sludge Treatment Processes on Ascaris Destruction for Safe Utilization of Sewage Sludge in Egypt*. PhD Thesis, University of Newcastle Upon Tyne, UK.
- Lef 2013 <http://www.lef.org/protocols/prtcl-156.shtml> (accessed 12 December 2013).
- Lenntech 2013 <http://www.lenntech.com/heavy-metals.htm> (accessed 12 December 2013).
- Mackie, A., Boilard, S., Walsh, M. E. & Lake, C. B. 2010 *Physicochemical characterization of cement kiln dust for potential reuse in acidic wastewater treatment*. *Journal of Hazardous Materials* **173**, 283–291.
- Mahajan, G. & Sud, D. 2013 *Assessing the potential of lignocellulosic agricultural waste biomass for removal of Ni (II) metal ions from aqueous streams*. *International Journal of Scientific & Engineering Research* **4** (4), 1713–1720.
- Peethamparan, S. 2006 *Fundamental Study of Clay-Cement Kiln Dust (CKD) Interaction to Determine the Effectiveness of CKD as a Potential Clay Soil Stabilizer*. PhD Thesis, Purdue University, West Lafayette, Indiana, USA.
- Peethamparan, S., Olek, J. & Lovell, J. 2008 *Influence of chemical and physical characteristics of cement kiln dusts (CKDs) on their hydration behavior and potential suitability for soil stabilization*. *Cement and Concrete Research* **38**, 803–815.
- Salem, A., Afshin, H. & Behsaz, H. 2012 *Removal of lead by using Raschig rings manufactured with mixture of cement kiln dust, zeolite and bentonite*. *Journal of Hazardous Materials* **223–224** 13–23.
- Sreejalekshmi, K. G., Krishnan, K. A. & Anirudhan, T. S. 2009 *Adsorption of Pb(II) and Pb(II)-citric acid on sawdust activated carbon: kinetic and equilibrium isotherm studies*. *Journal of Hazardous Materials* **161**, 1506–1513.
- Taha, N. N. 2003 *Treatment of Municipal Wastewater and Sludge Using Cement Kiln Dust*. MSc Thesis, The American University in Cairo, Cairo, Egypt.
- USEPA (United States Environmental Protection Agency) 1993 *Report to Congress (1993) – Cement Kiln Dust Waste*. <http://www.epa.gov/solidwaste/nonhaz/industrial/special/ckd/cement2.htm> (accessed 15 August 2014).
- Volesky, B. 2003 *Sorption and Biosorption*. BV Sorbex, Inc., Montreal, St. Labert, Quebec, Canada.

First received 20 May 2014; accepted in revised form 8 July 2014. Available online 21 July 2014