Comparative performance of cement kiln dust and activated carbon in removal of cadmium from aqueous solutions
Ahmed A. El-Refaey

ABSTRACT
This study compared the performance of cement kiln dust (CKD) as industrial byproduct and commercially activated carbon (AC) as adsorbent derived from agricultural waste for the removal of cadmium (Cd\(^{2+}\)) from aqueous solutions. CKD and AC were characterized by Fourier transform infrared (FTIR) and scanning electron microscopy (SEM) and surface areas demonstrate the differences of physicochemical properties. Batch equilibrium experiments were conducted for various intervals extended to 96 h at 20, 25 and 30 °C to investigate the efficiency of the sorbents in the removal of Cd\(^{2+}\). CKD expressed high affinity for removal of Cd\(^{2+}\) and was not affected by temperature, while AC was significantly affected, which reflects dissimilarity in the retention mechanisms defendant in CKD and those pursued by AC. The results were explained by changes of FTIR and SEM images before and after sorption experiments. The suggestion is that electrostatic ion exchange and complex reactions are the main mechanisms for Cd\(^{2+}\) removal. The kinetic data were evaluated by fractional power, Elovich, pseudo-first order and pseudo-second-order kinetic models. The pseudo-second-order kinetic model was found to correlate with the experimental data well. These results revealed that CKD can be used as a cost-effective and efficient sorbent for Cd\(^{2+}\) removal in comparison with AC.

Key words | activated carbon, adsorption kinetics, cadmium, cement kiln dust

INTRODUCTION
Water environmental pollution due to toxic heavy metals is a serious environmental and public health issue. The removal of heavy metals has become important to maintain water quality standards that are suitable for environmental and human health. Cadmium has been classified by the World Health Organization (WHO) as a probable human carcinogen (WHO 2010). Cadmium exposes human health to severe risks such as kidney damage, renal disorder, itai-itai disease (excruciating pain in the bone), hepatic damage, cancer, hypertension, and high levels of exposure will result in death (Kurniawan et al. 2006; Fenglian & Wang 2011). Cadmium can be released into the environment in a number of ways, including natural activities, such as volcanic activity, weathering and erosion, and river transport, and human activities such as tobacco smoking, mining, smelting and refining of non-ferrous metals, fossil fuel combustion, incineration of municipal waste (especially cadmium-containing batteries and plastics), manufacture of phosphate fertilizers, and recycling of cadmium-plated steel scrap and electric and electronic waste (WHO 2010).

In general, the technical applicability, plant simplicity and cost-effectiveness are the key factors in selecting the most suitable treatment for inorganic effluent (Barakat 2010). The removal of heavy metal is achieved through various techniques such as chemical precipitation, chemical oxidation and reduction, filtration, electrochemical treatment, evaporative recovery, solvent extraction, ion-exchange, reverse osmosis or adsorption (Ochie et al. 2008). Among these processes, the adsorption with the selection of a suitable adsorbent can be an effective technique for the removal of heavy metals from aqueous solution (Suzuki et al. 2005). Using a low-cost adsorbent is the main issue for the removal of these toxic metals. Large scale, economic sorbents can be defined as materials which are abundant in
nature or can be found as a byproduct or waste from industry. Recently, research efforts have been directed towards the use of industrial waste as an adsorbent material in an attempt to minimize processing costs and with the protection of the environment and public health. Cement kiln dust (CKD) is often used as the generic term for dust created in the kiln and collected from the cement manufacturing process. CKD is a fine-grained, alkaline material that is generated as a byproduct of the cement manufacturing process. CKD has been used as a chemical addition for soil and waste stabilization, building block manufacturing, etc. (Rahman et al. 2011). Also, it was indicated that CKD can effectively remove copper, nickel and zinc ions from solutions by adsorption as a potentially important sorbent due to the high specific surface area, high amount of alkaline oxides and excellent thermal resistance (Zaki et al. 2007; Rahman et al. 2011). On the other hand, activated carbon (AC) is considered one of the common commercial adsorbents for the removal of heavy metals from water and wastewater, but it is classified as one of the lowest priced materials (Kurniawan et al. 2006; Saleh et al. 2016). AC remains one of the most important microporous adsorbent. This adsorbent has very complex surface characteristics, with high porosity, high physico-chemical stability, high adsorptive capacity, high mechanical strength, high degree of surface reactivity and a variety of surface groups. The surface characteristics of AC depend on the raw material used and the method of activation (Yahya et al. 2015).

Therefore, the aim of this research is to investigate and evaluate the removal performance of cadmium (Cd²⁺) by cement kiln and an industrial byproduct and commercial AC as low-cost adsorbents derived from agricultural waste. In order to achieve these aims, adsorption experiments were carried out at different time intervals extended to 96 h at different temperatures: 20, 25 and 30 °C. Various kinetic evaluations have been used to describe the adsorption process and understand the adsorption mechanism. Fractional power, Elovich, pseudo-first-order and pseudo-second-order models were applied.

MATERIALS AND METHODS

Characterization of CKD and AC

CKD was obtained from El-Amerya cement plant, Alexandria, Egypt. The main components are calcium carbonate of 47.6%; oxides of aluminum of 4.2%; iron of 2.8% and magnesium of 2.3%; free lime of 4.8% and some alkali salts such as sodium and potassium (Mahmoued 2010). For comparison, samples of commercial AC were also grinded by porcelain mortar and sieved using a 0.5 mm-polypropylene sieve, then stored in plastic jars. Total carbon, nitrogen and hydrogen content in AC were 71.33%, 0.3%, and 2.51%, respectively, and were determined by CHNS analyzer (Elementar, Vario EL, Germany). The pH of CKD and AC was measured in distilled water (1:2.5 H₂O). CKD was alkaline (pH = 10.20) and relatively high in total carbonate concentrations (47.60%). CKD was recorded compared to AC in Table 1.

The specific surface area of CKD and AC were determined from N₂ isotherms at 77 K using a gas sorption analyzer (Beckman Coulter SA(TM) 3100 Surface Area and Pore Size Analyzer). The samples were degassed for 6 h under vacuum at 473 K prior to conducting adsorption measurements. The N₂ adsorbed per gram of sample was plotted versus the relative vapor pressure (P/Po) of N₂ ranging from 0.02 to 0.2, and the data were fitted to the Brunauer–Emmett–Teller (BET) equation to calculate surface area. Total pore volume was estimated from N₂ adsorption at P/Po = 0.5. The Barrett–Joyner–Halenda (BJH) method was used to determine the pore size distribution from the N₂ desorption isotherms (Nader 2015).

Functional groups compositional analysis of CKD and AC was carried out using Fourier transform infrared spectrometry (FTIR) before and after adsorption experiments. FTIR spectra of the adsorbent were recorded in the range 400–4,000 cm⁻¹ using infrared spectrophotometer; model FT/IR-5300, JASCO Corporation, Japan. A small amount of CKD and AC sample was mounted on a potassium bromide (KBr) disc which had been previously scanned as a background.

The surface physical morphologies of CKD and AC were examined by conducting a scanning electron microscopy (SEM) experiments. SEM analysis of samples was performed by using a Philips SEM-505 scanning electron microscope. The SEM instrument was operated at 300 kV/SE and 50 °C inclination. Before analysis, all samples were gold-coated in a sputter-coating unit (Edwards Vacuum Components Ltd, Sussex, UK) for electrical conduction. The micrographs were recorded at various magnification scales using

<table>
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<th>Table 1</th>
<th>Characteristics of CKD and AC</th>
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<tr>
<td>pH</td>
<td>Total CaCO₂%</td>
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<tr>
<td>CKD</td>
<td>10.20</td>
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<td>AC</td>
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photographic techniques to characterize the morphology of CKD and AC, which were dried overnight at approximately 105°C under vacuum before SEM analysis. SEM images were obtained for CKD and AC samples before and after adsorption experiments.

**Adsorption experiments**

Separate suspensions (4 g adsorbent/0.8 L in 0.01 M KCl) were prepared in batch reactors for CKD and AC treatment. Suspensions were equilibrated for 24 h by shaking end-over-end at 300 rpm. After pH measurement, Cd^{2+} was added to each reactor as CdCl₂·H₂O for the final concentration of 1.5 mM in each reactor (at t = 0). The adsorption isotherm was conducted at temperature 20, 25 and 30°C and contact time extended to 96 h. Suspensions were filtered (0.45 μm) immediately following the pH measurement. Cadmium ion concentrations were determined in filtrate using Atomic Absorption Spectrophotometer Varian Spectra (model 220). All Cd^{2+} concentrations and pH measurements were carried out in duplicate.

The adsorption amount (q_t) and the adsorption percentage (S%) is calculated according to:

\[
q_t = \frac{(C_o - C_t)V}{m}
\]

\[
S\% = \frac{(C_o - C_t)}{C_o} \times 100
\]

where q_t is the adsorption amount of metal ion at time t (mg g⁻¹), S% is the adsorption percentage (%), m is the weight of CKD sample (g), V is the volume of solution (L), and C_o and C_t are the initial and equilibrium concentrations of Cd^{2+} ions in solution, respectively.

**Adsorption kinetic studies**

In order to estimate the removal kinetics of Cd^{2+} from aqueous solutions by CKD and AC, fractional power, Elovich, pseudo-first-order and pseudo-second-order models were applied. The fractional power model is a modified form of the Freundlich equation and may be expressed by Equation (3) (Ho & McKay 2002) or its linear form as given in Equation (4):

\[
q_t = at^b
\]

\[
\ln q_t = \ln a + b \ln t
\]

where q_t is the amount of Cd^{2+} sorbed by CKD and AC at a time t, while a and b are constants with b < 1; ab is specific sorption rate at unit time.

One of the most useful models for describing adsorption is the Elovich equation and can be described by a semi-empirical equation (Inyang et al. 2016), which is given by:

\[
\frac{dq_t}{dt} = \alpha \exp (-\beta q_t)
\]

or in integrated form:

\[
q_t = \frac{1}{\beta} \ln (a\beta) + \frac{1}{\beta} \ln t
\]

where \(a\) is the initial adsorption rate (mg g⁻¹ min⁻¹), and the parameter \(b\) is related to the extent of surface coverage and activation energy for chemisorption (g mg⁻¹). Thus, the constants can be obtained from the slope and intercept of the linear plot of q_t versus ln t.

The adsorption kinetic data were described by the pseudo-first-order model (Lagergren 1898) and is given by:

\[
\log (q_e - q_t) = \log q_e - k_1t/2.303
\]

where \(k_1\) is the pseudo-first-order rate constant (min⁻¹) and \(q_e\) (mg g⁻¹) is the adsorption capacity at equilibrium and \(q_t\) (mg g⁻¹) is the amount of metal adsorbed at any time t. On the other hand, pseudo-second-order model (Ho 2006) is expressed as:

\[
\frac{t}{q_t} = \frac{1}{k_2q_e^2} + \frac{t}{q_e}
\]

where \(k_2\) (g mg⁻¹ min⁻¹) is the pseudo-second-order rate constant. The values of \(q_e\), \(k_1\) and \(k_2\) were calculated from the slopes and intercepts of the adsorption.

**RESULTS AND DISCUSSION**

**Characteristics of CKD and AC**

**Surface area and pore analysis**

Surface area and pore volume are important physical properties that play major roles in purification, as well as in stability. The BET technique is the most common method for determining the surface area of powders
and porous materials. Results indicated a mixed porosity nature (micro-/mesoporous). While the adsorbent is microporous solids with high external surface area, the BET equation has rigorous limitations. Adsorption in micropores does not go on by successive buildup of layers as disclosed by the BET model. However, the BET method has been used for microporous adsorbents owing to its simplicity and reasonable forecasts (Girgis et al. 2011). Results indicated that the amount of adsorbed N₂ at relative pressures increased continuously in CKD compared with AC, therefore, the specific surface area of CKD was higher than AC 20.98 m²/g and 3.96 m²/g, respectively (Table 1). Total pore volume for CKD (37.30 mm³ g⁻¹) was higher than AC (13.9 mm³ g⁻¹). Properties of CKD depend upon the raw materials, plant configuration, and the preprocessing type (Rahman et al. 2011). Pore size distribution of CKD is mainly dependent on the nature of the raw materials and condition of carbonization and activation (Yahya et al. 2015). Desorption BJH pore size distribution for CKD and AC were identified in Table 2. Pore size distribution in CKD was similar to AC except in two ranges: 20–80 nm and <6 nm. Whereas the pore diameter range of 20–80 nm, which mainly contributed to a fraction of macropore and mesopore, was higher in AC (38.47%) than in CKD (26.55%). Otherwise, the pore diameter range of <6 nm that related to micropores in CKD was (37.67%) higher than in AC (20.18%). The BJH pore diameters and pore volumes confirmed that micropore formation in CKD tended to be more than formed in AC (Table 2). Micropores contribute to mainly surface area, while macropores contribute as a channel to micropore surfaces (Yahya et al. 2015).

FTIR analysis

FTIR technique is an important device to recognize the features of functional groups. Most studies utilize FTIR just to determine the availability of certain surface functional groups as part of the structure of sorbents, although further probing the influence of these groups towards the metal binding process is also possible (Ochie et al. 2008). The FTIR spectra of the CKD and AC before and after the sorption of Cd ions from aqueous solutions are presented in Figure 1. The FTIR spectrum of CKD shows peak positions at 3,433.06, 1,514.23, and 1,095.49 cm⁻¹. The band at 3,433.06 is due to O–H (hydroxyl) while the bands at 1,514.23 and 1,095.49 reflect the carbonate and silicate; similar data were obtained by Al-Ghouti et al. (2011) and Saraya & Aboul-Fetouh (2012). On the other hand, the values of FTIR spectra of AC (Figure 1) showed the bands located at 3,419.56, 1,599.84, 1,438.80 and 510.14 cm⁻¹, corresponding mainly to the presence O–H (hydroxyl), asymmetric C–H and aromatic C–C O–H bend (carboxylic acids), C–N stretch (aliphatic amines), C–H aromatic and alkyl halide stretch (e.g. C–Cl) (Saleh et al. 2012). Slight shifts were observed in FTIR bands of studied sorbents after the sorption reaction with cadmium ions (Figure 1). This confirms the attachment of cadmium ions on CKD and AC.

Scanning electron microscopy

Characterization of sorbents by SEM offers topographical and elemental information of the solids with a virtually large depth of field, allowing different specimen parts to

| Table 2 | Desorption Barrett–Joyner–Halenda (BJH) pore size distribution for CKD and AC |
|---|---|---|---|
| Pore diameter range nm | CKD ml g⁻¹ | % | AC ml g⁻¹ | % |
| >80 | 0.00283 | 7.88 | 0.00124 | 8.75 |
| 20–80 | 0.00955 | 26.55 | 0.00546 | 38.47 |
| 16–20 | 0.00217 | 6.02 | 0.00101 | 7.09 |
| 12–16 | 0.00182 | 5.07 | 0.00105 | 7.40 |
| 10–12 | 0.00170 | 4.74 | 0.00077 | 5.46 |
| 8–10 | 0.00158 | 4.40 | 0.00061 | 4.30 |
| 6–8 | 0.00276 | 7.68 | 0.00119 | 8.36 |
| <6 | 0.01355 | 37.67 | 0.00286 | 20.18 |

Figure 1 FTIR spectra of the CKD and AC before and after the sorption of Cd ions from aqueous solutions.
Figure 2 | Scanning electron micrographs (SEM) of CKD and AC before and after the removal reactions of Cd ions from aqueous solutions at 25 °C.

Figure 3 | Removal of Cd ions from aqueous solution by CKD and AC as a function of time and temperature.
stay in focus at a time. In addition to its capability to produce an actual clear image, it is useful for obtaining the topographical aspects of sorbents (Gupta & Rastogi 2008). However, the SEM technique also has limitations on its lowest detectable particle size and its inability to detect trace elements in a substance. The surface structure of CKD and AC were analyzed by SEM before and after Cd\(^{2+}\) adsorption (Figure 2). The textural and morphological structure examination of CKD and AC particles can be observed from the SEM photographs at ×10,000 magnification (Figure 2). It was observed that CKD have the finest particle sizes as well as the highest surface areas. The sharp changes between before and after adsorption observed in porous structure of CKD were more than observed in AC.

The effect of temperature on Cd\(^{2+}\) removal of Cu\(^{2+}\) by AC. Time and temperature independence of Cd\(^{2+}\) removal by CKD may reflect dissimilarity in retention mechanisms defendant in CKD and those pursued by AC.

The pH of the solution has a significant impact on the uptake of heavy metals. Significant changes in pH values were obtained with the progress of removal reactions time. It is clearly shown that removal of Cd\(^{2+}\) by CKD and AC increased with pH increases. pH changes during the adsorption reaction of Cd\(^{2+}\) with CKD increased gradually from 7.55, 7.80 and 7.80 at 20°C, 25°C and 30°C, respectively, to 8.22 after 96 h. These changes followed the same pattern as changes in Cd\(^{2+}\) removal reactions by CKD and were not influenced by changing temperature in aqueous solution. On other hand, AC removal reaction raised the pH from 7.30, 7.33 and 7.47 at 20°C, 25°C and 30°C, respectively, to 7.75 at 20 and 25°C and extended to 7.93 at 30°C after

| Table 3 | Kinetic parameters for Cd\(^{2+}\) on CKD and AC at various temperatures |
|---------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
|         | CKD      | AC          | CKD      | AC          | CKD      | AC          | CKD      | AC          | CKD      | AC          | CKD      | AC          | CKD      | AC          | CKD      | AC          | CKD      | AC          | CKD      | AC          |
| Fractional power |          |          |          |          |          |          |          |          |          |          |          |          |          |          |          |          |          |          |          |          |
| a       | 5.776    | 5.729    | 5.988    | 3.193    | 3.692    | 6.461    |          |          |          |          |          |          |          |          |          |          |          |          |          |          |          |
| b       | 0.021    | 0.023    | 0.016    | 0.073    | 0.063    | 0.004    |          |          |          |          |          |          |          |          |          |          |          |          |          |          |          |
| R\(^2\) | 0.611    | 0.687    | 0.615    | 0.958    | 0.938    | 0.886    |          |          |          |          |          |          |          |          |          |          |          |          |          |          |          |

**R**\(^2\)**

| Ellovich |          |          |          |          |          |          |          |          |          |          |          |          |          |          |          |          |          |          |          |          |          |
| α       | 1.67 × 10\(^{21}\) | 4.20 × 10\(^{21}\) | 2.91 × 10\(^{28}\) | 1.70 × 10\(^{6}\) | 2.54 × 10\(^{6}\) | 1.26 × 10\(^{11}\) |          |          |          |          |          |          |          |          |          |          |          |          |          |          |          |
| β       | 0.007    | 0.007    | 0.010    | 0.003    | 0.005    | 0.038    |          |          |          |          |          |          |          |          |          |          |          |          |          |          |          |
| R\(^2\) | 0.619    | 0.700    | 0.630    | 0.949    | 0.927    | 0.883    |          |          |          |          |          |          |          |          |          |          |          |          |          |          |          |

**Pseudo-first-order**

| q\(_e\) | 1.69 × 10\(^{-4}\) | 1.70 × 10\(^{-4}\) | 1.64 × 10\(^{-4}\) | 2.80 × 10\(^{-4}\) | 3.81 × 10\(^{-4}\) | 1.57 × 10\(^{-4}\) |          |          |          |          |          |          |          |          |          |          |          |          |          |          |          |
| K\(_1\) | 3.13 × 10\(^{-4}\) | 3.41 × 10\(^{-4}\) | 2.41 × 10\(^{-4}\) | 6.43 × 10\(^{-4}\) | 2.00 × 10\(^{-4}\) | 0.10 × 10\(^{-4}\) |          |          |          |          |          |          |          |          |          |          |          |          |          |          |          |
| R\(^2\) | 0.173    | 0.202    | 0.173    | 0.419    | 0.571    | 0.879    |          |          |          |          |          |          |          |          |          |          |          |          |          |          |          |

**Pseudo-second-order**

| q\(_e\) | 6.734    | 6.757    | 6.757    | 6.049    | 6.536    | 6.711    |          |          |          |          |          |          |          |          |          |          |          |          |          |          |          |
| K\(_2\) | 2.82 × 10\(^{-5}\) | 5.41 × 10\(^{-5}\) | 9.16 × 10\(^{-5}\) | 0.29 × 10\(^{-5}\) | 0.26 × 10\(^{-5}\) | 2.92 × 10\(^{-5}\) |          |          |          |          |          |          |          |          |          |          |          |          |          |          |          |
| R\(^2\) | 0.999    | 0.999    | 0.999    | 0.997    | 0.998    | 0.999    |          |          |          |          |          |          |          |          |          |          |          |          |          |          |          |
96 h. However, at 30 °C, AC removal reaction raised the pH with time to 7.93 compared to CKD that extended to 8.22.

According to the metal ions adsorption by surface-active materials, Cd²⁺ removal can be achieved by electrostatic interaction with negatively charged surface functional groups (cation exchange), specific metal–ligand complexation involving surface functional groups of sorbents, interactions between metals and aromatic C of sorbents and/or physical sorption controlled by surface area and porosity (Uchimiya et al. 2010; Saleh et al. 2016). The present results confirmed that more than one mechanism can be proposed to control the removal process of Cd²⁺ depending on the sorbent characteristics, supported by the sharp changes in SEM images between before and after adsorption in porous structure of CKD more than in AC (Figure 2). The high efficacy of CKD in Cd²⁺ removal process could be explained by increasing pH solutions, its high calcium carbonate and calcium oxide (CaO), surface area, oxide content, and reducing metal solubility owed to enhanced sorption and/or precipitation (Zaki et al. 2007; Hal et al. 2012; Mackie & Walsh 2012; El Zayat et al. 2014).

**Kinetic studies**

Several kinetic models, fractional power, Elovich, pseudo-first-order and pseudo-second-order have been used to determine the rate-controlling mechanism of the adsorption process. All kinetic parameters are recorded in Table 3, where a and b are constants related to specific sorption rate, α is the initial adsorption rate (mg g⁻¹ min⁻¹), β is the desorption constant (g mg⁻¹ min⁻¹), qe can be regarded as

![Figure 4](https://i.imgur.com/3F5G5.png)  
**Figure 4** | Pseudo-second-order plot for Cd²⁺ removal kinetics by CKD and AC at different temperatures.
the amounts of metals adsorbed on the adsorbent (mg g⁻¹) at equilibrium, k₁ and k₂ and min⁻¹ is the rate constant, respectively. From the kinetic parameters which have been calculated at different temperatures and times listed in Table 3, the high values of the coefficient of determination (R² > 0.99) demonstrated that the pseudo-second-order model was the more adequate to represent the adsorption kinetics of Cd²⁺ onto CKD and AC. Moreover, experimental qₑ values are very close to those calculated for the pseudo-second-order kinetic model (R² > 0.99). Therefore, the obtained results implied that the adsorption of Cd²⁺ could be best explained by the pseudo-second-order model, suggesting that the adsorption process is presumably chemisorptions (Figure 4).

CONCLUSIONS

This study investigated and compared the removal of Cd²⁺ onto CKD and AC. The results indicate the strong potential of CKD compared to AC for removing Cd²⁺ from aqueous solutions within the first 5 min of the batch reaction. The high efficacy of CKD could be explained by increasing pH solutions, its high lime content, surface area, oxide content, and reducing metal solubility owed to enhanced sorption and/or precipitation. Time and temperature independence of Cd²⁺ removal by CKD may reflect differences in retention mechanisms defendant in CKD and those pursued by AC. The pseudo-second-order kinetic model agrees very well with the dynamic behavior for the removal of Cd²⁺ by CKD and AC.

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