UTILISATION OF CEMENT KILN DUST FOR THE REMOVAL OF LEAD AND ZINC IONS FROM AQUEOUS SOLUTIONS

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Abstract
Cement kiln dust (CKD) is the fine-grained alkaline by-product of combustion of raw materials in cement production. In this study, batch experiments were conducted to investigate the removal of metal ions from aqueous solutions using CKD. Metal adsorption was influenced by the initial concentration as the amount adsorbed increased from 2.45 mg/g (at 5mg/L) to 78.57mg/g (at 250 mg/L) for Pb^{2+} and 2.35mg/g (at 5mg/L) to 225 mg/g (at 500mg/L) for Zn^{2+}. Maximum percent removal efficiencies of 95% (after 90 minutes) and 91% (after 60 minutes) were observed for Pb^{2} and Zn^{2+} respectively. The Langmuir isotherm best described the adsorption process with maximum monolayer adsorption capacities of 52.63mg/g and 83.31mg/g for Pb^{2} and Zn^{2+} respectively. This study demonstrated the potential of CKD for metal removal from contaminated aqueous systems.

Keywords: *Cement kiln dust, Adsorption, Heavy metals, Isotherms*

Introduction

Heavy metals discharged in untreated wastewater into the environment are persistent, non-degradable, toxic and detrimental to human health and the environment (Shareef, 2009; Fu and Wang, 2011). Prolonged exposure to these metals can cause serious disturbances such as headache, nausea, vomiting, and diarrhea, damage to some organs or even death. Some heavy metals are classified as suspected carcinogens (Karabulut et al. 2000; Chen, 2005; Paulino et al., 2006).

Several technologies are used in the removal of metals from wastewater. These methods include chemical precipitation, chemical oxidation, ion-exchange, adsorption and coagulation-flocculation. However some of these methods are expensive, with large volumes of sludge generated and requiring disposal. Adsorption has been established as an effective, relatively economical method of metal removal particularly when low-cost adsorbents such as agricultural and industrial by-products are used (Bayat, 2002; Ochie et al., 2008; Ahmad et al., 2010; Barakat, 2011; Fu and Wang, 2011; Bilal et al., 2013).

Cement kiln dust (CKD) is the fine-grained alkaline by-product of combustion of raw materials in cement production. It is carried in the exhaust gases to be captured by the dust collection system during the cement manufacturing process (Peethamparan et al., 2008; Mackie et al., 2010; El Zayat et al., 2014). This material is often not reused in the cement production process due to high concentrations of alkalis and thus requires disposal (Kunal and Siddique, 2016). Applications of CKD in soil stabilization, wastewater treatment and soil fertilization have been investigated by researchers (Sreekrishnavilasam et al., 2007; Kunal et al., 2012; Salem et al., 2012; El-Refaey, 2017). Pigaga et al. (2005) investigated the removal of some heavy metals from aqueous solutions with CKD. The results showed that the adsorbent had the capacity to remove Cu, Ni, Pb, Cd and Co from aqueous solutions and neutralize acidic wastewaters. However there is the need to carry out adsorption isotherm studies to understand the mechanism of metal uptake by the adsorbent.

In this study, the utilization of cement kiln dust as a low-cost industrial adsorbent for the removal of heavy metals (lead and zinc) from aqueous solutions was investigated. The effects of initial metal concentration and contact time on the adsorption process were studied.

Materials and Methods

Cement Kiln Dust (CKD)

Cement kiln dust (CKD) was obtained from the cement production plant of BUA Cement Factory, Okpella, Edo State, Nigeria. The material was stored in a tightly sealed polyethylene container prior to use as-received. The chemical and physical properties of the absorbent (CKD) obtained from the factory are shown in Tables 1 and 2.

Table 1: Chemical Properties of Cement Kiln Dust (CKD)

Chemical Constituents	Composition (wt %)
CaO	43.40
Fe_2O_3	2.75
Al_2O_3	3.68
SiO_2	14.21
MgO	1.15
Na_2O	3.00
K_2O	2.20
Cl	0.07
SO_3	1.88
Others	1.80
Loss Of Ignition (LOI)	25.86

Table 2: Physical properties of cement kiln dust

Properties	Units	Values
Hydration Modulus		2.59
Pore Volume	mm^3/g	39.45
Moisture content	%	6.4
Bulk Density	g/cm^3	0.63
Dry density	g/cm^3	2.4

Heavy metal Solutions

Synthetic stock solutions of heavy metals were prepared using nitrate salts (Pb $(NO_3)_2.7H_2O$ and Zn $(NO_3)_2.6H_2O$) and deionized water. Hydrochloric acid (HCL) and sodium hydroxide (NaOH) were used for pH adjustment.

Adsorption Experiments

Batch adsorption experiments were conducted by shaking 0.1g of CKD in 50ml of metal solution at 125 rpm and pH 5.5. All experiments were conducted at room temperature. The effects of initial metal concentration (5-250 mg/L Pb^{2+} and 5-500mg/L Zn^{2+} at contact time of 180 minutes for) and contact time (5-180 minutes at initial concentration of 40mg/L) were studied. At the end of each experiment, solutions were filtered using 0.45µm filter paper and analyzed using an atomic absorption spectrometer (AAS). The percent metal removal efficiency was calculated using the equation:

$$\% \, Removal \, Efficiency = \frac{C_o - C_e}{C_o} \quad (1)$$

Where, C_o and C_e are the initial and final metal ion concentrations respectively (mg/L)
The Adsorption Capacity (q_e) of the adsorbent was calculated using the equation:

$$q_e = \frac{(C_o - C_e)v}{m} \quad (2)$$

Where, q_e is the adsorption capacity of CKD (mg/g),C_o and C_e are the initial and final metal ion concentrations respectively (mg/L), m is the mass of CKD and v is the volume of aqueous solution (L).

Adsorption Isotherms

The metal removal performance of CKD was further evaluated using the linearized forms of the Langmuir and Freundlich isotherms. The linearized Langmuir isotherm used is given as (Foo and Hameed, 2010):

$$\frac{1}{q_e} = \frac{1}{Q_o} + \frac{1}{bQ_o C_e} \quad (3)$$

Where q_e is the mass of heavy metal adsorbed per gram of adsorbent at equilibrium(mg/g), *Ce* is the equilibrium heavy metal concentration in liquid phase (mg/L), *b* is the Langmuir isotherm constant (L/mg) and Q_o is maximum monolayer coverage capacity(mg/g).
The linearized form of the Freundlich isotherm is (Foo and Hameed, 2010):

$$\mathrm{Log}q_e = \mathrm{Log}k_f + \frac{1}{n}\mathrm{Log}c_e \quad (4)$$

Where *qe* is the mass of heavy metal adsorbed per gram of adsorbent (mg/g), *Ce* is the equilibrium heavy metal concentration in liquid phase (mg/L), *Kf* and *n* are constants incorporating all factors affecting the adsorption process such as adsorption capacity and intensity of adsorption.

Results and Discussion

Effect of Initial Concentration of Metal Ions

The effect of initial metal concentration on the adsorption of metals by CKD was investigated. It was observed that as the initial concentration of the adsorbate increased, there was a corresponding increase in the adsorption capacity and decrease in the percent uptake of metal ions as shown in Figures 1 and 2.

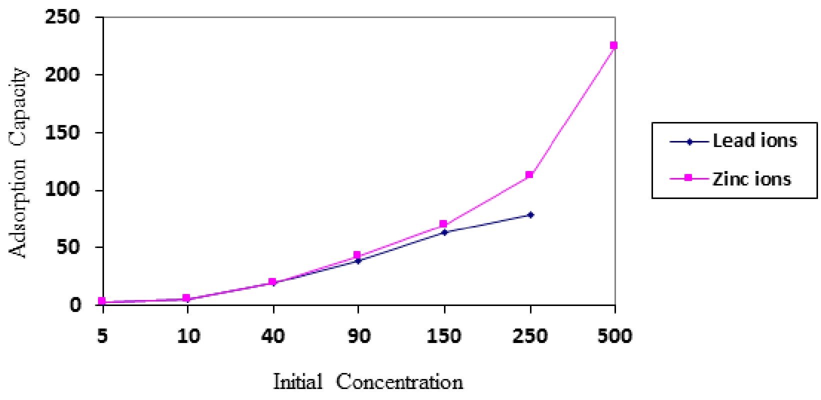

Figure 1: Effect of initial metal Concentration the adsorption capacity of CKD

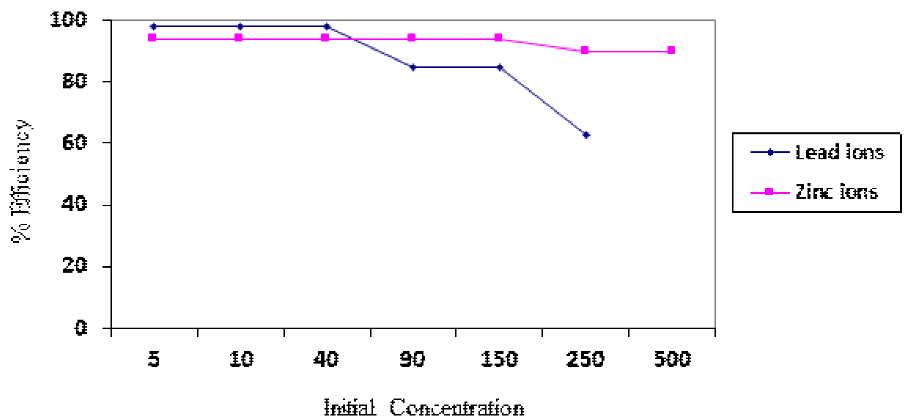

Figure 2: Effect of initial metal concentration on the % removal efficiency of CKD

The adsorption capacity of CKD increased from 2.45mg/g (at initial concentration=5mg/L) to 78.57mg/g (at initial concentration=250mg/L) for Pb^{2+} and 2.35mg/g (at initial concentration=5mg/L) to 225 mg/g (at initial concentration=500mg/L) for Zn^{2+}. Conversely, the percent metal uptake decreased from 98% to 63% and 94% to 90% for Pb^{2+} and Zn^{2+} respectively. The increased initial concentration provided the driving force required to overcome the mass transfer resistance to Pb and Zn diffusion from the liquid to the solid phase in their respective solutions and increased interaction between the metal ions and the adsorbent (Coruh et al., 2010). However the percent metal uptake decreased with increased concentration due to the saturation of available sites and the increased involvement of less energetic exchange sites (Gunay et al., 2007). These findings are consistent with metal removal studies using different adsorbents (Barakat, 2011; Fu and Wang, 2011; El Zayat et al., 2014).

Effect of Contact Time

The effect of contact time on the metal removal efficiency of the system was studied as shown in Figure 3. It was observed that the metal removal efficiency of CKD increased with time from 90% (at 5minutes) to 95% (at 180 minutes) for Pb^{2+} and 65% (at 5 minutes) to 91% (at 180 minutes) for Zn^{2+}.

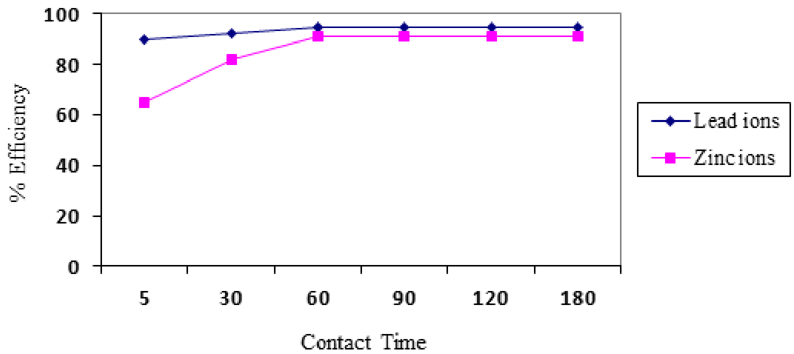

Figure 3: Effect of contact time on the % removal efficiency of CKD

The results as illustrated indicate that as the active sorption sites on CKD were saturated, there was a tendency towards equilibrium at 90 minutes for Pb^{2+} and 60 minutes for Zn^{2+}, thus showing the influence of contact time on the adsorption process.

Adsorption Isotherms

The experimental equilibrium data were fitted using the Langmuir and Freundlich Isotherms. The Langmuir isotherm provided a better fit for both metals based on the higher R^2 values (Pb (0.976) and Zn (0.998)) as shown in Table 3. The Langmuir isotherm plots for both metals are shown in Figures 4 and 5.

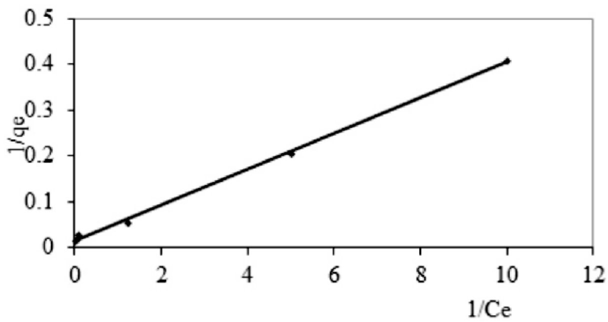

Figure 4: Langmuir isotherm for Pb^{2+} adsorption on CKD

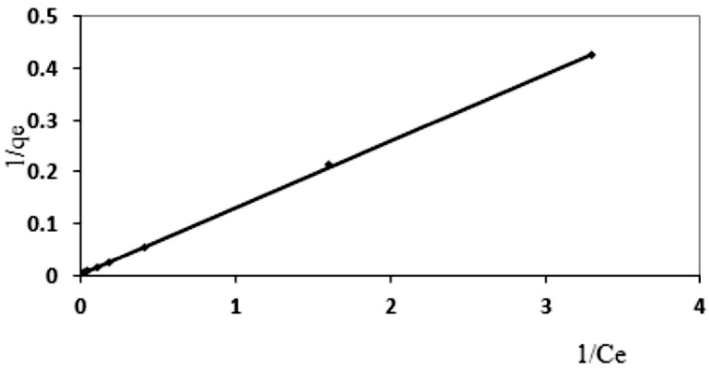

Figure 5: Langmuir isotherm for Zn^{2+} adsorption on CKD

Table 3: Adsorption isotherm constants

	Langmuir			Freundlich		
	Q_o (mg/g)	b (L/mg)	R^2	Kf	1/n	R^2
Pb	52.63	0.487	0.976	12.303	0.25	0.971
Zn	83.31	0.088	0.998	0.097	0.745	0.962

The maximum monolayer adsorption capacities from the Langmuir isotherms were 52.63mg/g and 83.31mg/g for Pb^{2+} and Zn^{2+} respectively. These results indicate homogenous monolayer adsorption of metal ions on CKD. The Langmuir isotherm is based on the assumption that adsorption is homogenous and monolayer adsorption occurs on a fixed number of definite adsorption sites with equal affinity for the adsorbate and no interaction between adjacent molecules. Hence the sites occupied by the molecules are no longer available for sorption and the isotherm reached a plateau of equilibrium saturation (Foo and Hameed, 2010).

Conclusions

In this study the utilization of cement kiln dust (CKD)-an industrial by-product of cement manufacturing, for the removal of lead and zinc ions from single component aqueous solutions was investigated. The results obtained showed that the removal performance of CKD was influenced by initial metal concentration and contact time. As the initial metal concentration increased, there was a corresponding increase in the adsorption capacity and a decrease in the percent removal efficiency within the system. The adsorption of both metals was best described by the Langmuir isotherm based on higher R^2 values (>0.976) with maximum monolayer adsorption capacities of 52.63mg/g and 83.31mg/g for Pb^{2+} and Zn^{2+} respectively, thus indicating homogenous monolayer adsorption. The findings of the study indicate that CKD could potentially be reused as a valuable adsorbent for the treatment of heavy metal contaminated aqueous systems.

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