

Utilization of Cement Kiln Dust in Adsorption Technology

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Abstract—This paper involves a study of the heavy metal pollution of the soils around one of cement plants in Libya called Suk-Alkameas and surrounding urban areas caused by cement kiln dust (CKD) emitted. Samples of soil was collected from sites at four directions around the cement factory at distances 250m, 1000m, and 3000m from the factory and at (0-10)cm deep in the soil. These samples are analyzed for Fe (iii), Zn(ii), and Pb (ii) as major pollutants. These values are compared with soils at 25 Km distances from the factory as a reference or control samples. The results show that the concentration of Fe ions in the surface soil was within the acceptable range of 1000ppm. However, for Zn and Pb ions the concentrations at the east and north sides of the factory were found six fold higher than the benchmark level. This high value was attributed to the wind which blows usually from south to north and from west to east. This work includes an investigation of the adsorption isotherms and adsorption efficiency of CKD as adsorbent of heavy metal ions (Fe (iii), Zn(ii), and Pb(ii)) from the polluted soils of Suk-Alkameas city. The investigation was conducted in batch and fixed bed column flow technique. The adsorption efficiency of the studied heavy metals ions removals onto CKD depends on the pH of the solution. The optimum pH values are found to be in the ranges of 8-10 and decreases at lower pH values. The removal efficiency of these heavy metals ions ranged from 93% for Pb, 94% for Zn, and 98% for Fe ions for 10 g.l⁻¹ adsorbent concentration. The maximum removal efficiency of these ions was achieved at 50-60 minutes contact times at which equilibrium is reached. Fixed bed column experimental measurements are also made to evaluate CKD as an adsorbent for the heavy metals. Results obtained are with good agreement with Langmuir and Drachsal assumption of multilayer formation on the adsorbent surface.

Keywords—Adsorption, Cement Kiln dust (CKD & CAC), Isotherms, Zn and Pb ions.

I. INTRODUCTION

THE heavy metal pollution of urban soils has been investigated in many cities in the world. The effects are very dangerous with regards to crops grown in the cities and around it. Data as well as maps showing different levels and patterns of pollution have been published [1]. There has been emphasis in the last few years on such environmental pollution problems as water pollution, solid waste disposal, air pollution and solid pollution by heavy metals. In industrial cities, metallurgical industry seems to contribute substantially to the heavy metals problems of the soil. Heavy metals and other toxic pollutants are very harmful due to their toxic nature, and their resistance to degradation. In Egypt alone the dust emitted from cement factories is estimated to be about two million tons [2]. This finely dust is emitted from cement kilns and

must be disposed off as waste disposal sites. Extensive researches are conducted worldwide to reuse and utilize CKD as adsorbents, fertilizers, constructing materials, and improving sand soil properties. The main achievements will be to minimize the undesirable environmental impacts as well as economical improvements of related projects. Waste water treatments have received great attention recently to remove heavy metals. The most important technologies include chemical precipitation, filtration, ion exchange, reverse osmosis and membrane technology. However, all these technologies have advantages, range of uses, and application limitations. In the last few years adsorption has shown to be a promising alternative method for removing metal ions from liquid wastes [3]. The removals of heavy metal ions from industrial wastes using different adsorbents are of great applications. In this work CKD is used as adsorbents of heavy metal ions including Fe, Pb, and Zn. Table I includes existing and emerging technologies for metal separation.

TABLE I
EXISTING AND EMERGING TECHNOLOGIES FOR METAL SEPARATIONS

Conventional treatment technologies	Precipitation, oxidation, reduction, concentration
Established recovery technology	Evaporative recovery, Ion exchange, Membrane separation
Emerging recovery technologies	Differential precipitation, Selective adsorption

II. MATERIAL AND METHOD

A. Adsorption Experiment Study

Cement kiln dust (CKD) used in this study was collected from bi-path of Suk Alkameis Portland cement factory in Libya. A map and sampling station around the cement factory is constructed and the samples are collected equally from all four directions [4]. Extraction and analyses are performed for the selected samples using soil samples with Hydrogen peroxide. Details are provided [4]. The dissolving process is carried out with HNO₃ and followed by filtration. Atomic absorption spectrometry is used to determine heavy metals contents. Atomic absorption spectrophotometer was set according to the heavy metal constituent. The values of measurements of the adjusted set values are listed in Table II.

TABLE II
OPERATING CONDITIONS

	Fe	Pb	Zn
Wave Length mm	217	217	217
Slit width	0.2	0.4	0.4
Fuel flow L.m ⁻¹	1.0	5.0	5.0
Burner height mm	1.0	10	10

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B. Adsorbent

Experiments were conducted using cement by-pass kiln dust as adsorbent for the removal of heavy metals from soil in the neighbor of Suk Alkhamis cement factory. CKD was dehydrated at 105°C for 24 hours. X-ray fluorescent analysis was used to characterize the chemical composition of CKD as shown in Table III.

TABLE III
THE CHEMICAL COMPOSITION OF CKD (X-RAY FLUORESCENCE ANALYSIS OF CKD)

Component	Average %
CaO	62.90
SiO ₂	15.56
Al ₂ O ₃	2.570
MgO	1.430
K ₂ O	1.320
SO ₃	0.620
Cl	0.540
TiO ₂	0.240

III. RESULT AND DISCUSSION

A. Fixed Bed Studies

Fixed bed column adsorption studies were conducted on a solution of the three heavy metal ions Fe, Zn, and Pb. Using CKD as adsorbent with different flow rates (5, 10 and 15 ml.min⁻¹). The results are plotted in Figs. 1 (a), (b). The figures show the influence of feed flow rate on breakthrough curves for the heavy metal ions investigated. The results of column flow studies are important to develop a model which represents accurately the results which could be used for design purposes. Several models are listed in the literature. Generally the actual amount of Fe (iii) adsorbed per unit mass of adsorbent increased with an increase in the time before equilibrium reached.

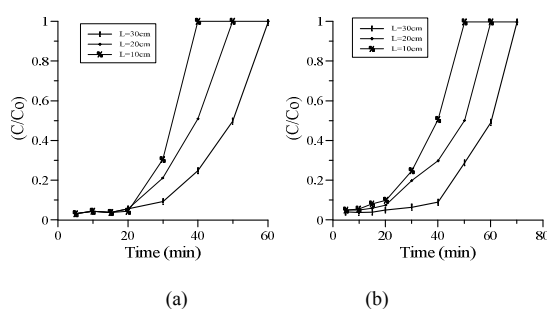


Fig. 1 Breakthrough curves for the removal of Fe (iii) on CKD for different bed heights (a) Fe (iii) on for different bed height $Q_v = 10$ ml/min., $C_o = 86.6$ mg/l, (b) Fe (iii) on CKD for different bed height $Q_v = 5$ ml/min., $C_o = 86.6$ mg/l

B. Equilibrium Adsorption Isotherm

In order to estimate the maximum capacities of CKD and CAC, it is necessary to know the quantity of adsorbed Zn, Pb as a function of adsorbate concentration in the solution. Three models have been investigated; Langmuir, Drachsal and Freundlich.

1. The Langmuir Isotherm

The adsorption isotherms were analyzed using the Langmuir equation which has found successful application in many processes. The Langmuir isotherm equation is represented as:

$$\frac{q}{q_m} = \frac{K_L C}{1 + K_L C} \quad (1)$$

where q (mg.g⁻¹) is the amount adsorbed per unit mass of adsorbent corresponding to complete coverage of sites, q (mg.g⁻¹) is the equilibrium concentration of adsorbate in solution, q_m (mg.g⁻¹) the adsorption capacity of the adsorbent and the Langmuir constant K_L (L.mg⁻¹).

2. The Freundlich Isotherm

The Freundlich isotherm is derived to model of the multilayer adsorption and for the adsorption on heterogeneous surfaces, and is most frequently used to describe the adsorption of organic components in solution.

$$\frac{q}{q_m} = k_f C^n \quad (2)$$

where, q (mg.g⁻¹) is the equilibrium concentration of adsorbate in solution, q_m (mg.g⁻¹) the adsorption capacity of the adsorbent, k_f adsorption equilibrium constant (L³ mg⁻¹)ⁿ and n is the constant related to adsorption intensity.

3. The Drachsal Isotherm

This adsorption isotherm is derived from Langmuir and Freundlich, with the following assumptions: enthalpy of adsorption independent of coverage; no interaction between neighboring molecules; initial surface adsorption followed by a strong solute-solute interaction [4]-[6]. It implies an exponential repartition of the energy of adsorption.

$$\frac{q}{q_m} = \frac{(bC)^n}{1 + (bC)^n} \quad (3)$$

where, q (mg.g⁻¹) is the equilibrium concentration of adsorbate in solution, q_m (mg.g⁻¹) the adsorption capacity of the adsorbent, b adsorption equilibrium constant (L³ mg⁻¹) and n is the constant related to adsorption intensity.

4. Result of the Equilibrium Models

Figs. 2 and 3 represent three adsorption isotherms models has been examined for Zn (ii), and Pb (ii) ions for CKD and commercial activated carbon CAC adsorbents at 22°C and a flow rate of 10 g.l⁻¹. Figs. 2, 3 present a good agreement between the predicted and experimental data for two isotherm models Langmuir and Drachsal better than the Freundlich model. It is more suitable for situations in which the distribution of equilibrium concentration tends to be skewed towards the lower end of the range of the equilibrium

concentration. The final results of the parameters models are presented in Tables IV, V.

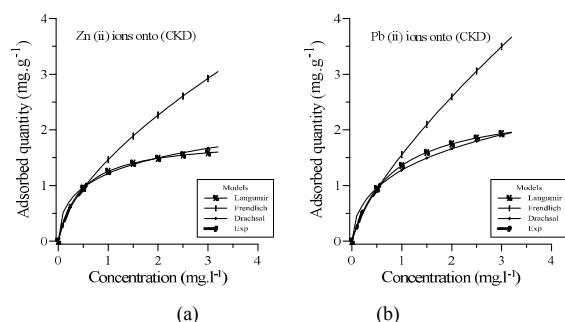


Fig. 2 Langmuir adsorption isotherm at 22°C onto (10 g.l⁻¹ CKD) (a) Zn (ii) ions (b) Pb (ii) ions

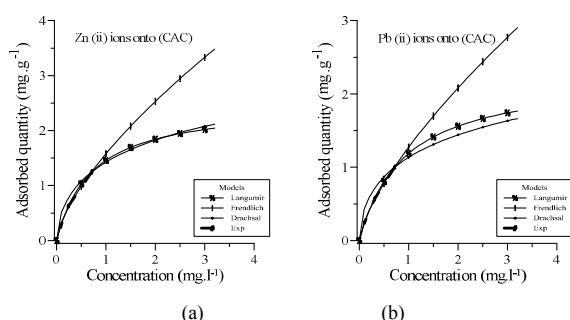


Fig. 3 Langmuir adsorption isotherm at 22°C onto (10 g.l⁻¹ CAC) (a) Zn(ii) ions (b) Pb (ii) ions

The final parameters of three models are listed in the following tables.

TABLE IV

THE LANGMUIR, DRACHSAL AND FREUNDLICH CONSTANTS FOR THE ADSORPTION OF Pb(II) AND Zn(II) BY CKD 22°C AND 10 G.L⁻¹ CKD

Model	Pb(ii)			Zn(ii)		
Langumir	q_m	b	K_L	q_m	b	K_L
	mg.g ⁻¹	l.mg ⁻¹	l.mg ⁻¹	mg.g ⁻¹	l.mg ⁻¹	l.mg ⁻¹
Drachsal	q_m	b	m	q_m	b	m
	mg.g ⁻¹	--	--	mg.g ⁻¹	--	--
	5.107	0.13	0.53	3.53	0.485	0.266
Freundlich	q_m	k_f	n	q_m	k_f	n
	mg.g ⁻¹	---	---	mg.g ⁻¹	---	---
	1.048	1.48	0.74	0.938	1.560	0.629

TABLE V

THE LANGMUIR, DRACHSAL AND FREUNDLICH CONSTANTS FOR THE ADSORPTION OF Pb (II) AND Zn (II) BY CKD 22°C AND 10G.L⁻¹ CAC

Model	Pb(ii)			Zn(ii)		
Langumir	q_m	b	K_L	q_m	b	K_L
	mg.g ⁻¹	l.mg ⁻¹	l.mg ⁻¹	mg.g ⁻¹	l.mg ⁻¹	l.mg ⁻¹
Drachsal	q_m	b	m	q_m	b	m
	mg.g ⁻¹	--	--	mg.g ⁻¹	--	--
	3.657	0.53	0.22	4.547	0.554	0.243
Freundlich	q_m	k_f	n	q_m	k_f	n
	mg.g ⁻¹	---	---	mg.g ⁻¹	---	---
	0.846	1.51	0.78	0.991	1.592	0.679

IV. CONCLUSION

The adsorption equilibrium parameters have been estimated for Zn (ii) and Pb (ii) using two types of commercially available adsorbents (CKD & CAC) at 22°C and a different flow rates. The adsorption isotherm studies indicates that the adsorptive behavior of heavy metals ions on CKD satisfies not only the Langmuir isotherm but also the Drachsal assumption, i.e. multi layer formation on the surface of the adsorbent with an exponential distribution of site energy. It was concluded that the sorption capacity of CKD which is a cheap and by product adsorbent could be used as an adsorbent for the removal of heavy metals ions from waste water and also the removal of other kinds of pollutants like nonpolar organic compounds.

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