

ASSESSMENT REMOVAL OF HEAVY METALS IONS FROM WASTEWATER BY CEMENT KILN DUST (CKD)

Taha A. Waly¹, A. M. Dakroury², G. E. Sayed³ and S. A. El-Salam¹

¹ Egyptian Fuel Manufacturing Pilot Plant (FMPP),
Atomic Energy Authority, Egypt
Tel: +20127101767, Fax: +2024691756

² Hot Lab Center and Waste Management, Atomic Energy Authority, Egypt

³ Department of Chemistry, Faculty of Science, Benha University, Egypt

ABSTRACT

The effective removal of HM ions from aqueous wastes is among the most important issues for many industrialized countries. The present work has been carried out to study the adsorption of Cd (II), Al (III), Co (II) and Zn (II), by adsorption technique using CKD which, is both a waste and a pollutant. The sorption process was examined in terms of its equilibria and kinetics. Batch adsorption experiments were conducted to evaluate the removal of Cd (II), Al (III), Co (II) and Zn (II), onto CKD waste over a wide range of operation conditions of sorbat concentration, pH, contact time, sorbent dose. The batch experiments showed that the most effective pH range was found to be 5.5 to 8. Time-dependent experiments for the removal efficiency of HM ions showed that Al (III) required a shortest contact time, for Zn (II) and Cd (II), binding to the CKD was rapid and occurred within 20 to 40 min and completed for Co (II) within 4 hrs. High sorption capacities were observed for the four HM ions. The binding capacity experiments revealed the following amounts of HM ions bound per gram of CKD: 165.994 mg/g, 75.389 mg/g, 64.296 mg/g and 108.875 mg/g for Zn (II), Al (III), Co (II) and Cd (II), respectively. The equilibrium data for HM ions fitted both Langmuir and Freundlich models and based on Langmuir constant. The adsorption isotherm studies clearly indicated that the adsorptive behavior of HM ions on CKD satisfies not only the Langmuir assumptions but also the Freundlich assumptions, i.e. multilayer formation on the surface of the adsorbent with an exponential distribution of site energy.

Keywords: Sorbat, Sorbent, Adsorption, Freundlich, Langmuir and Neutralization.

Abbreviations: CKD: cement kiln dust, HM: heavy metal.

INTRODUCTION

Industrial and mining waste waters are the major source of pollution by heavy metals. Furthermore, in developing countries, many industries are operated at small or medium scale, or even as a family business within the residential premises of the

owner. These smaller entities can generate a considerable pollution load, which, in many cases, is discharged directly into the environment without any facilities for waste-water treatment. This is because the capital investment, turnover and profit for these industries are also small. Heavy metals can pose health hazards if their concentrations exceed allowable limits. Even when the concentrations of metals do not exceed these limits, there is still a potential for long-term contamination, since heavy metals are known to be accumulated within biological systems. In recent years, increasing awareness of the environmental impact of heavy metals has prompted a demand for the purification of industrial waste water prior to discharge into natural waters. This has led to the introduction of more strict legislation to control water pollution. In this study several metal ions have been investigated such as **Zinc** that is present in waste water stream from steel works, rayon fiber manufacture, production and recalculation of cooling water system employing cathodic treatment also in electroplating process [1]. **Cadmium** causes intoxication of liver, kidneys, brain, lungs, heart and testicles. It is a carcinogen. **Cobalt** is a microelement involved in such essential processes as nitrogen fixation. The lack of cobalt can lead to abnormal angiogenesis and dangerous diseases in cattle; it is a vital component of cobalamin. On the other hand, despite of the fact that it is an essential microelement, at higher concentrations cobalt can have dangerous effects on living organisms. Cobalt compounds are classified as class II, which means they are not extremely toxic. However, one of the main potential effects of cobalt compounds is decrease of natural ability of rehabilitation of water reservoirs. In plants, cobalt becomes toxic at a concentration of 0.1 – 0.3 mg / l. people exposed to cobalt compounds were reported to suffer from defective metabolism of proteins and carbohydrate, anemia, Basedow disease, carcinogenic and mutagenic effects [2]. Treatment processes for metals contaminated waste streams include chemical precipitation, membrane filtration, ion exchange, adsorption, and electro deposition. Cost effective alternative technologies or sorbents for treatment of metals contaminated waste streams are needed. However, most of the methods suffer from some drawbacks as high capital and/or operational cost or the disposal of the residual metals sludge [3]. Adsorption processes for heavy metals contaminated wastewater have been proved to be successful by many researchers [4-6]. In this regard the use of abundant low cost and effective adsorbent materials is of interest. Activated carbon has been recognized as a highly effective adsorbent for the treatment of heavy metals in waste water [7]. However, it is relatively expensive to produce. Therefore, there is increasing research interest using alternative low-cost adsorbents. Many such materials have been investigated, including microbial biomass, peat, compost, leaf mould, palm press fibre, coal straw, wool fibre and rice milling by-products [8,9] not all of these are effective. Therefore, it is still important to identify suitable low cost adsorbents for heavy metal removal. In this study we have investigated the interaction of CKD with Cd (II), Al (III), Co (II) and Zn (II). The cement industry in Egypt applies dry processes in cement manufacture and releases a large amount of by-pass cement kiln dust (CKD), is both a waste and a pollutant. Therefore, it was desired to make use of this waste and to save the environment.

EXPERIMENTS

1. Adsorbent CKD

CKD generated in large quantities for example in tourah portoland cement factory, the production of CKD is around 5.35 of the total production of the dry kilns, which is about 9000 ton/day. So the amount of CKD is about 477 ton/day. In this company 205 of the total CKD produced may be recycled to the wet process but the residual amount is discharged in the desert after granulation by using water. The amount of water needed to granulate this amount of CKD, was about 304 m³/day, this calculation based only on CaO only. These big amounts of CKD produced and the amount of water needed cost the company a lot of unprofitable money and effort. As received CKD was kept all the time on a dessicator to a void the conversion of CaO to CaCO₃.CKD has average particle size 3μ during the adsorption process .the pH of 4g/l suspended CKD in deionized water was 10. X-ray florescence, Micromeritics GEMINI 2360 surface area analyzer, Micromeritics SEDI-GRAPH 5100 particle size analyzer and Micromeritics ACCUPYC 1330 density analyzer are devices were used for the physical and chemical analysis of CKD.

2. Chemicals

Analytical grade reagents were used for heavy metal solution, ACS reagent grad concentrated hydrochloric acid, NaOH and buffer solutions (E.Merck) were used to adjust pH values of samples. In all experimental work, demineralised water was used.

3. Adsorbate solution

Synthetic stock solution of heavy metals was prepared by dissolving required quantity of Analar grade salts in the demineralised water. The salts used are Cadmium chloride, Zinc nitrate, Cobalt chloride, Aluminum nitrate, for Cd (II), Zn (II), Co (II), Al (III), respectively, for the preparation of stock solution. The stock solution was further diluted with distilled demineralised water to desired concentration for obtaining the test solutions.

4. Batch mode adsorption studies

The adsorption of heavy metals on cement kiln dust was studied by batch technique. The general method used for this study is described as below:

A known weight of adsorbent (e.g. 0.5–1.5 g) was equilibrated with 50 ml of the heavy metals CdCl₂, CoCl, Zn (No₃)₂ and Al (No₃)₃ with a known starting concentration in a plastic bottles at a fixed temperature (24+1)°C in a thermostatic mechanical shaker (WIDSONS Scientific) for a known period (5 min–24 h) of time. After equilibration, the suspension of the adsorbent was separated from solution by filtration using Whatman filter paper No. 1. The concentration of heavy metal ions remaining in solution was measured by Inductive Coupled Plasma –Atomic Emission

Spectroscopy (ICP-AES). The effect of several parameters, such as pH, concentrations, contact time and adsorbent dose on the adsorption was studied. The pH of the adsorptive solutions was adjusted using hydrochloric acid, sodium hydroxide and buffer solutions when required. Adsorption of metal ions on the walls of glass flasks determined by running the blank experiments was found negligible. The results of these studies were used to obtain the optimum conditions for maximum heavy metals removal from aqueous solution.

5. Removal and adsorption of heavy metals

The percent heavy metal removal was calculated using the following equation:

$$\%R = \frac{C_o - C}{C_o} * 100 \quad (1)$$

Where: C_o Initial heavy metal ion concentration of test solution, mg/l.

C : Final equilibrium concentration of test solution, mg/l.

The adsorbed phase concentration was calculated using the following equation

$$q = (C_o - C) * \frac{v}{m} \quad (2)$$

Where:

q : Amount of heavy metal ions adsorbed per unite mass of adsorbent, mg/g

v : is the volume of the solution in, L

m : is the weight of dry CKD in, gm

QC aspect: To insure the accuracy, reliability, and reproducibility of the collected data, all the batch experiments were carried out in duplicate and the mean values of two data sets are presented. When the relative error exceeded the relative stander deviation by more than 1.0%, the data were disagreed and a third experiment was conducted until the relative error fell within an acceptable range.

RESULTS AND DISCUSSION

CKD was utilized to remove heavy metals such as: Zn (II), Co (II), Cd (II), and AL (III) from wastewater. Therefore, the parameters affecting heavy metals removal from synthetic solution such as; the effect of residence time, the effect of pH, the effect of variation sorbent amount added the effect of variation initial sorbate concentration (Zn, Co, Cd, and AL ions) and finally studying the effect of temperature on the adsorption of these heavy metal ions. Inductive Coupled Plasma –Atomic Emission Spectroscopy (ICP-AES): It is used to analysis of trace elements in a wide range of samples and samples types.

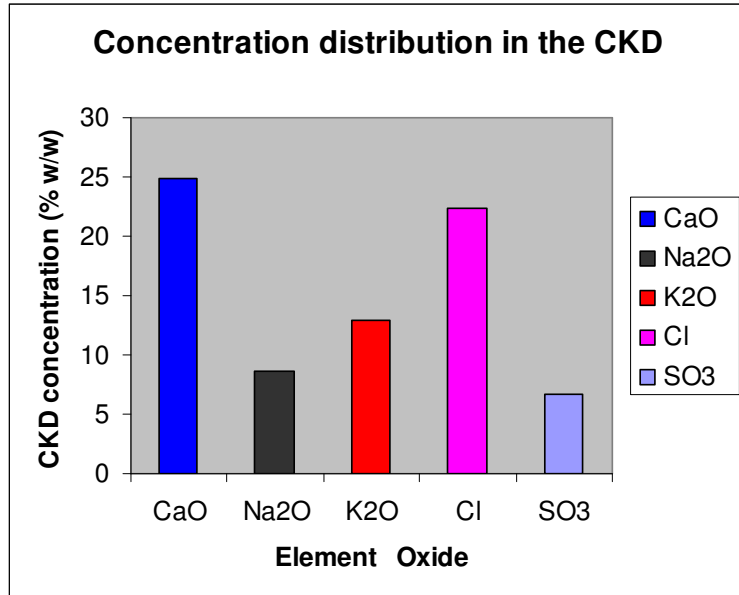
1. Analysis of CKD

The sample of CKD obtained from companies was analyzed by X-ray fluorescence (XRF), the percent composition of the CKD are shown in Table (1) the main

ingredient or the major component of CKD are calcium oxide, besides sodium oxide, potassium oxide, sulfur-tri-oxide, silicate and chloride. The alkalinity nature of the dust makes it a good neutralizing agent for acidic wastewater stream.

Table (1): X-ray Fluorescence analysis of CKD

Ingredients	% Average Percent
SiO ₂	3.14
TiO ₂	0.05
Al ₂ O ₃	0.38
Fe ₂ O ₃	0.61
MnO	0.01
MgO	0.22
CaO	24.85
Na ₂ O	8.61
K ₂ O	12.95
P ₂ O ₅	0.04
Cl	22.35
SO ₃	6.71
L.O.I	19.45



2. Effect of initial concentration of heavy metal ions

The effect of initial concentration on the percentage removal of heavy metals by CKD is shown in (Fig. 1) It can be seen from the figure that the percentage removal decreases with the increase in initial heavy metal concentration. For Zn (II) is seen the percentage removal is almost complete (nearly 90-100%) throughout the initial metal ions concentration range (384.55-1825.8) mg/L for 10 g/L adsorbent dose, at pH 5.89 and equilibrium contact time. For Cd (II) and Al (III) at same adsorbent dose and equilibriums contact time, there are gradually drop in percentage removal at higher initial concentration, whereas for Co (II) the percentage removal is highly effective >80% below 600 mg/l initial concentration after which percentage removal decreases sharply to below 70%. At higher initial concentrations, Cd (II) shows greater percentage removal than Al (III). At lower initial metal ion concentrations, sufficient adsorption sites are available for adsorption of the heavy metals ions. Therefore, the fractional adsorption is independent of initial metal ion concentration. However, at higher concentrations the numbers of heavy metal ions are relatively higher compared to availability of adsorption sites. Hence, the percent removal of heavy metals depends on the initial metal ions concentration and decreases with increase in initial metal ions concentration. The difference in percentage removal of different heavy metal ions at the same initial metal ions concentration, adsorbent dose and contact time may be attributed to the difference in their chemical affinity and ion exchange capacity with respect to the chemical functional group on the surface of the adsorbent.

The percentages of removal of Zn (II), Al (III), Co (II) and Cd (II) solutions, in which concentrations were 100–2000 mg/L, were evaluated by using CKD showed high removal efficiency for all metals. These results are shown in Fig. 1. In these adsorbents, high removal efficiency (95%) was obtained over the Zn (II), Cd (II) and Al (III) concentration range 100–800 mg/L. However, the removal percentage gradually decreased with increasing the concentration (>800 mg/L).

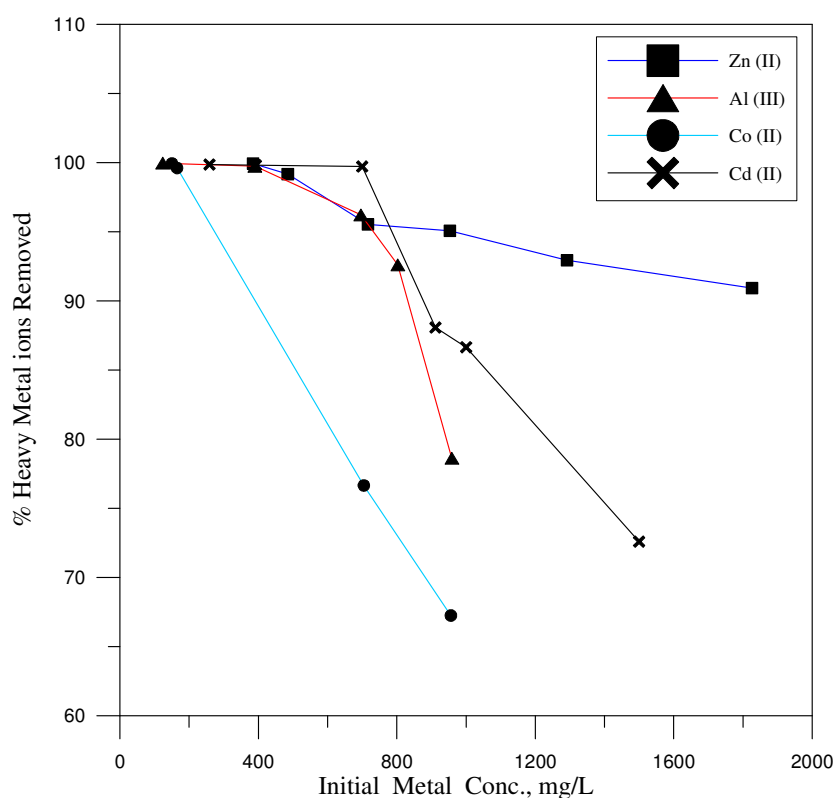


Figure 1. Effect of initial concentration on the percent removal of heavy metal ions by using CKD.

3. Effect of adsorbent dose

The results for adsorptive removal of heavy metals with respect to adsorbent dose are shown in (Fig. 2) over the range 10–30 g/L, at pH 5.89 and 6.17 for Al (III) and Cd (II), respectively and 8 for Zn (II) and Co (II), the percentage removal of heavy metals is seen to increase with adsorbent dose. From (Fig. 2), the percentage removal of Al (II) ions show 100% removal throughout the range of concentrations studied (within initial concentration 803.10 mg/L). It is observed that there is a sharp increase in percentage removal with adsorbent dose for Zn (II) and Cd (II) ions but in case of Co (II) ions, there is gradual increase in percentage removal with increasing dose. It is apparent that the percent removal of heavy metals increases rapidly with increase in the dose of the adsorbents due to the greater availability of the exchangeable sites or surface area. Moreover, the percentage of metal ion adsorption on adsorbent is determined by the adsorption capacity of the adsorbent for various metal ions.

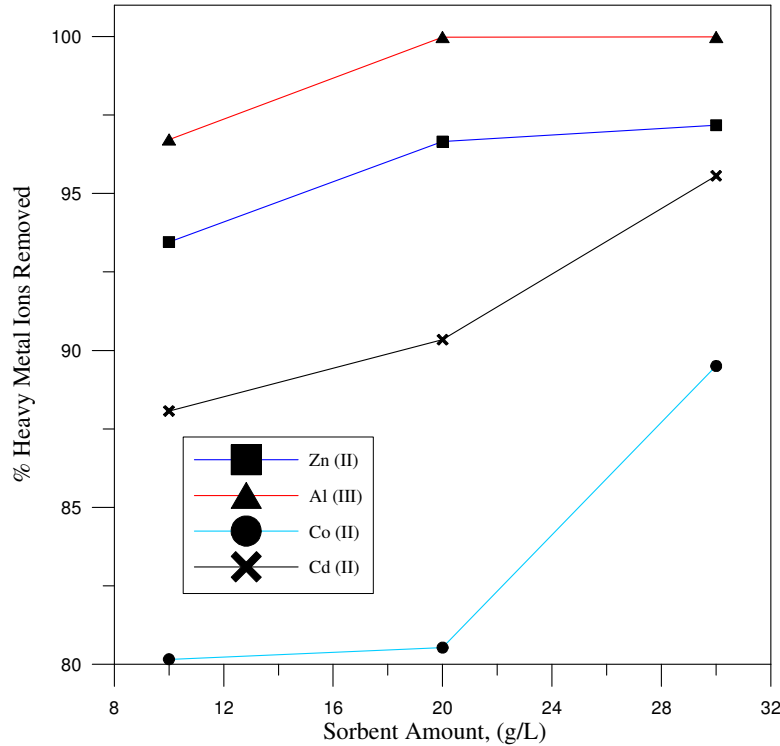


Figure 2. Effect of variation sorbent dose on heavy metal ions removal by using CKD, at 130 rpm and temp 30°C.

4. Batch contact time studies

Figure 3 indicates that removal efficiency increased with an increase in contact time before equilibrium is reached. Other parameters such as dose of adsorbent, pH of solution and agitation speed was kept optimum, while temperature was kept at 30°C. It is observed that for Al (III) ions, the percentage removal is nearly 100% even throughout the all contact times. Hence the Al (III) require a shortest contact time. In case of Zn (II) and Cd (II), ions rise sharply in percentage removal with increasing contact time. It can be seen that Zn and Cd removal efficiency by using CKD increased from 80% to 95% when contact was increased from 20 to 40 min. On other hand, percentage removal of Co (II) increases gradually with contact time, reaching nearly 100% removals only at around 4 h. It is evident from the results that the contact time required to attain equilibrium is dependent on the initial concentration of heavy metals. For the same concentration, the percentage removal of heavy metal increases with increase of contact time till equilibrium is attained. The optimal contact time to attain equilibrium with CKD was experimentally found to be about 40 min for Zn (II), 5 min. for Al (III), 1 h for Cd (II) and 4 h for Co (II). This result is important, as equilibrium time is one of the important parameters for an economical wastewater treatment system.

It has been observed that [12] the mechanism of metal removal from the aqueous metal involved four steps: (i) migration of metal ions from the bulk solution to the

surface of the adsorbent; (ii) diffusion through boundary layer to CKD surface; (iii) adsorption at a binding site and (iv) intra particle diffusion into the interior of the CKD. The boundary layer resistance will be affected by the rate of sorption and increasing the agitation time will reduce this resistance and increase the mobility of the ions. However, because the process is time dependent, after about 40 min, 5 min, 1 hr and 4 hr for Zn (II), Al (III), Cd (II) and Co (II), respectively of agitation, adsorption remains slightly or relatively constant. This observation is in agreement with the proposed mechanism obtained from the sorption characteristic study.

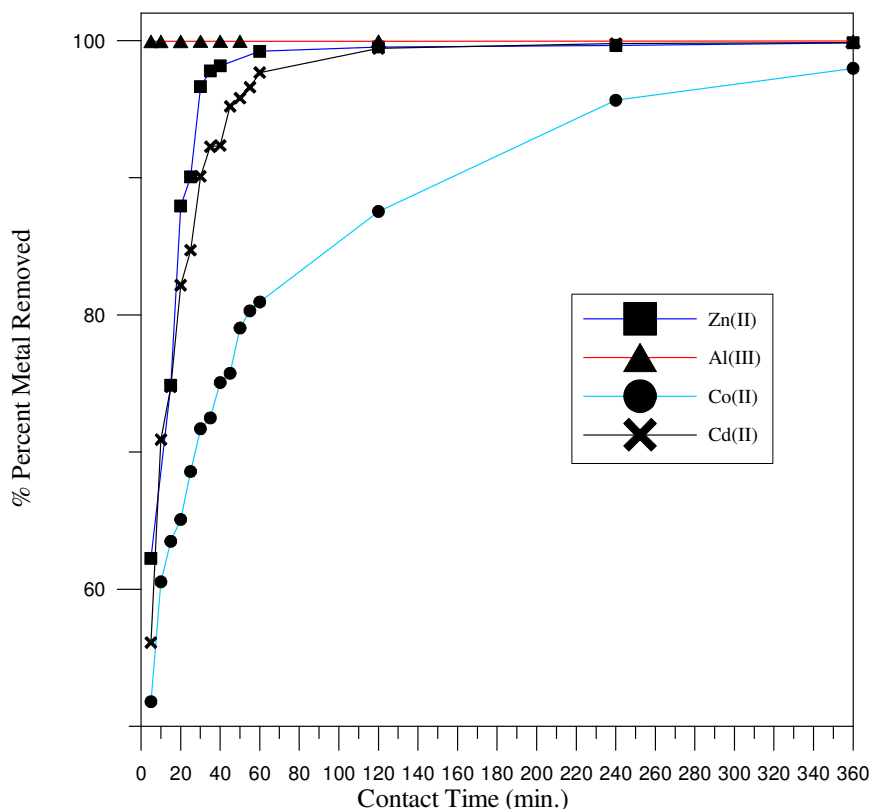


Figure 3. Effect of contact time on the percent heavy metal ions removal by using CKD.

5. Effect of pH

PH is one of the most important parameters controlling uptake of heavy metals from wastewater and aqueous solutions. Figure 4 shows the percent removal of the four heavy metals as a function of pH at heavy metal concentrations of 384.55, 123.60, 150.40, 258.51 mg/l for Zn (II), Al (III), Co (II), Cd (II), respectively and a CKD concentration of 10 g/L. In general, the amount of heavy metal removed increased as pH increased, and sharply reached over 90% removal at a specific pH value. As shown in diagram given by Heechan et al. [11], the precipitation of the heavy metal ions was less than 20% at pH's below 8, indicating that the removal of the metals was mainly accomplished by adsorption. As pH increased from 5.5 to 8, it can be expected

that the CKD surface becomes more negatively charged. Thus, more favorable electrostatic attraction forces enhanced cationic metal ion adsorption as pH increased. However, the dependence of heavy metal adsorption on pH was different for each metal. The removal of zinc was about 80% at pH 6.5 and it increased to 99% at pH 8. For Aluminum, 85% was removed at pH 5 and it increased to 99% at pH 6. For cadmium, 90% was removed at pH 5.5 and it increased to 99% at pH 6.2. For Cobalt, removal increased proportionally with increasing pH from 50% at pH 6–90% at pH 8. The percentage adsorption increases with pH to attain a maximum at pH 6-8 and thereafter it decreases with further increase in pH. The maximum removal of Zn (II) and Co (II) at pH 8 were found to be nearly 99 and 90%, respectively, whereas, for Al (III) 99% removal at pH 6 and for Cd (II) 99% removal at pH 6.2. In all cases, over 99% of all the four metals were removed except cobalt reached 90% at pH 8. It is often suggested that the tendency of metal cations to adsorb to oxide surfaces is highly correlated with their tendency to undergo hydrolysis reactions in solution [12]. Metal cations in aqueous solutions hydrolyze according to the generalized expression for divalent metals.

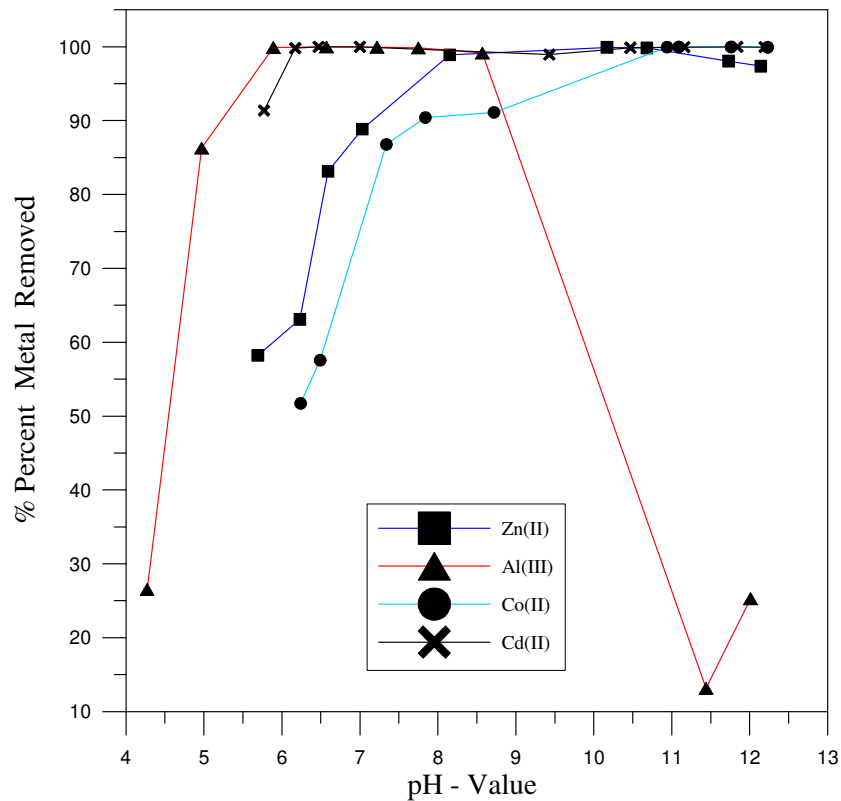


Figure 4. Effect of different pH - values on heavy metal ions removal by using CKD

6. Explanation of mechanism of adsorption

The maximum adsorption at pH 8 may be attributed to the partial hydrolysis of M^+ , resulting in the formation of MOH^+ and $M(OH)_2$. $M(OH)_2$ would be adsorbed to a greater extent on the non-polar adsorbent surface compared to MOH^+ . With increase of pH from 4 to 8, the metal exists as $M(OH)_2$ in the medium and surface protonation of adsorbent is minimum, leading to the enhancement of metal adsorption. At higher pH, that is, above optimum pH of 8, increase in OH^- ions cause a decrease in adsorption of metal ions at adsorbent–adsorbate interface [13]. Lower solubilities of hydrolysed metal ions species may be another reason for the maximum adsorption at pH 8. Since, in lower pH range, metal is present predominantly as metal ions in the adsorptive solution, there is a competition between H^+ and M^+ ions for adsorption at the ion-exchangeable sites, leading to a low removal of metal. The extensive repulsion of metal ions due to protonation of the adsorbent surface at lower pH may be another reason for decrease in adsorption of metal in lower pH range.

7. Adsorption isotherms

The adsorption studies were conducted at fixed initial concentration of heavy metals by varying adsorbent dosage. The equilibrium data obtained were analyzed in the light of Langmuir and Freundlich isotherms.

Freundlich equation is given by [14]:

$$q_e = K_f C_e^{\frac{1}{n}} \quad (4)$$

Taking the logarithmic form of the equation

$$\text{Log}(q_e) = \text{Log}(K_f) + \frac{1}{n} \text{Log}(C_e) \quad (5)$$

Langmuir equation is given by [15]:

$$q_e = \frac{a b C_e}{1 + b C_e} \quad (6)$$

The linearized expression of this equation is

$$\frac{1}{q_e} = \frac{1}{a} + \frac{1}{a b C_e} \quad (7)$$

This equation is called the “**Double-Reciprocal Langmuir Equation**” and more suitable for situations in which the distribution of equilibrium concentrations tends to be skewed towards the lower end of the range of the equilibrium concentrations. where q_e is the amount of heavy metal ions adsorbed per unit mass of adsorbent in mg/g, C_e the equilibrium concentration of heavy metal ions in mg/l, K_f and n are Freundlich constants, ‘ a ’ is a Langmuir constant which is a measure of adsorption capacity expressed in mg/g, ‘ b ’ is also Langmuir constant which is a measure of energy of adsorption expressed in l/mg. The parameters ‘ a ’ and ‘ b ’ have been calculated from the slope and the intercept of the plots.

Figure 7 gives the Freundlich adsorption isotherm plot of $\log q_e$ versus $\log C_e$. The values of K_f and $1/n$ obtained from intercept and slope of the plot are given in Table 4. The Langmuir adsorption isotherm plot for $1/q_e$ versus $1/C_e$ is shown in Fig. 8 and the plots show two distinct regions, one for low $1/C_e$ values up to about 25 l/mg and another for higher $1/C_e$ values.

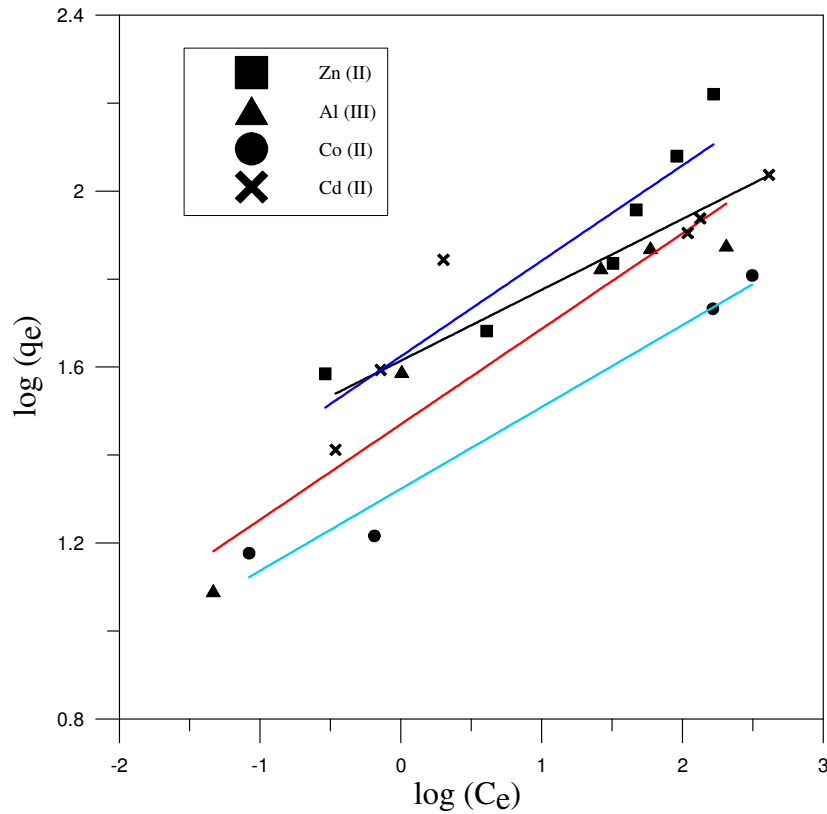


Figure 7. Freundlich adsorption isotherm of heavy metal ions by using CKD at 30°C.

The essential characteristics of Langmuir isotherm can be described by a separation factor or equilibrium constant R_L , which is defined as,

$$R_L = \frac{1}{1 + bC_i} \tag{8}$$

Where C_i is the initial concentration of heavy metal ions (mg/l) and b is Langmuir constant which indicates the nature of adsorption. The separation factor R_L indicates the isotherm shape and whether the adsorption is favourable or not, as per the criteria given below.

R_L - values	Adsorption / Type of isotherm
$R_L > 1$	Unfavorable
$R_L = 1$	Linear
$0 < R_L < 1$	Favorable
$R_L = 0$	Irreversible

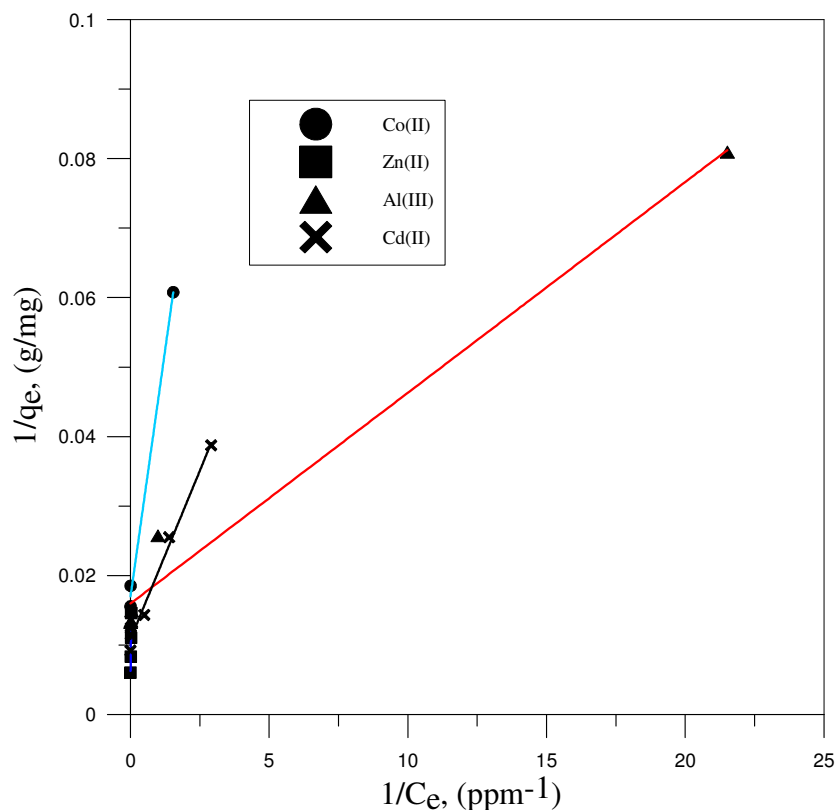


Figure 8. Langmuir adsorption isotherm of heavy metal ions by using CKD at 30°C.

The values of Langmuir constants ' a ', ' b ' and R_L are presented in Table 3. Since R_L values lie between 0 and 1 for all four adsorbants studied, it is seen that the adsorption of heavy metal ions is favourable [18]. Adsorption capacity as indicated by value of ' a ' is seen to be maximum for CKD, i.e. Zn(II) (233.18 mg/g), Cd(II) (92.35 mg/g), Al(III) (62.64 mg/g), and Co(II) (58.77 mg/g) with a much lower capacities. The energies of adsorption, as indicated by ' b ' are seen to be highest for Al (III) (5.26 L/mg), Co (II) (4.12L/mg), Cd (II) (1.12 L/mg), and Zn (II) (0.013 L/mg) in that order. A comparison of the Freundlich adsorption isotherms for the metal ions show that n in that order Cd (II) > Co (II) > Al (II) > Zn (II). The values of n lie between 1 and 10 indicating favourable adsorption [17]. K_f seen to be Zn (II) > Cd (II) > Al (II) > Co (II). This gives a similar inference as that obtained from Langmuir isotherms.

Table 3. Values of Langmuir isotherm constants for adsorption of heavy metal ions by using CKD

Metal ions	slop	a(mg/g)	intercept	b(L/mg)	R ²	R _L
Zn(II)	0.328784528	233.1785	0.004288560825	0.013044	0.992037	0.0950
Al(III)	0.003033405	62.63779	0.01596480332	5.262996	0.982052	0.0015
Co(II)	0.004133276	58.77456	0.01701416256	4.116386	0.997344	0.0016
Cd(II)	0.009701566	92.35398	0.01082790419	1.116098	0.986492	0.0034

Table 4. Values of Freundlich isotherm constants for the adsorption of heavy metal ions by using CKD

Metal ions	slop	K_f	intercept	n	R²
Zn (II)	0.2169544939	42.1260480	1.624550719	4.609262	0.862792
Al (III)	0.2168382642	29.5201782	1.470118976	4.611732	0.925075
Co (II)	0.1859835242	21.0527929	1.32330972	5.37682	0.974276
Cd (II)	0.1610804879	41.1513419	1.614384002	6.208077	0.818879

The adsorption isotherm studies clearly indicated that the adsorptive behavior of heavy metal ions on CKD satisfies not only the Langmuir assumptions but also the Freundlich assumptions, i.e. multilayer formation on the surface of the adsorbent with an exponential distribution of site energy.

On the basis of regression analysis of the experimental data on the adsorptive behavior of metal ions on CKD, it may be inferred that the adsorption behavior of metal ions on CKD is in good agreement with Langmuir model. These can be attributed to three main causes (i) the formation of monolayer coverage on the surface of CKD with minimal interaction among molecules of substrate (ii) immobile and localized adsorption and (iii) all sites having equal adsorption energies. The shapes of isotherms suggest that there are high-energy adsorption sites to favor strong adsorption at low equilibrium concentrations for the CKD.

CONCLUSIONS

In this study, batch adsorption experiments were performed to evaluate the use of CKD particles as an adsorbent for heavy metal ions. It was found that Aluminum required a shortest contact time 5 min, while equilibrium was reached for Zinc and cadmium within 40-60 min and completed for Cobalt at 4 hrs.

It was found that pH of the solution has a significant impact on the percentage removal of heavy metals. Between pH 5.5 and 8, where the influence of precipitation is negligible, the percent removal was 80% - 99% for zinc, 85% - 99% for Aluminum, 90% - 99% for cadmium and 50% - 90% for cobalt. The percent removal of the heavy metal ions increased as the pH increased. Most of the metal ions had a 99% removal when the pH was 8 except cobalt had a 90% at this pH.

The adsorption isotherm studies clearly indicated that the adsorptive behavior of HM ions on CKD satisfies not only the Langmuir assumptions but also the Freundlich assumptions, i.e. multilayer formation on the surface of the adsorbent with an exponential distribution of site energy.

The results of this study have shown that CKD a cheap by- processes of cement industrial (CKD which is both a waste and a pollutant) was effective in the removal of Cd (II), Zn (II), Al (III) and Co metals in wastewater.

REFERENCES

- [1] Ismail M. A. Ibrahim. "Development of extraction systems for the recovery of certain metal ions from aqueous waste solutions", Thesis (2003) Helwan University, Egypt.
- [2] Dalia Virbalyte et al. "Interaction of heavy metal ions with cement kiln dust", *EKOLOGIJA*. 2005 Nr. 1 P, 31-36.
- [3] Mohammad Aimal, Razaqat Ali Khan Rao and Bilquees Ara Siddiqui. "Studies on the removal and recovery of Cr (VI) from electroplating waste", *Water Research*, Vol. 30, No. 3, pp. 1478-1482, 1996.
- [4] Bailey S.E., Olin T.J., Bricka R.M. and Adrian B.D. *Water Research*, 33, 2469, 1999.
- [5] Hashem A. and El-Shishtawy R.M. *Adsorption Science & Technology* 19, No. 3, 2001.
- [6] Juang R.S., Wu F.C. and Tseng R.L. *Water Research*, 33, 2403, 1999.
- [7] Reed Be and Arunachalam S. "Removal of lead and cadmium from aqueous waste stream using granular activated carbon (GAC) columns", *Environ. Prog.* 13 60-64, 1994.
- [8] Singh D. and Rawat Ns. "Adsorption of heavy metals on treated and untreated low grade bituminous coal", *Ind. J. Chem. Techno.* 4 39-41 1997
- [9] Wase Daj and Forster Cf. "Biosorbents for metal ions", Taylor and Francis, London 1997.
- [10] Gardea-Torresdey J.L., Gonzalez J.H., Tiemann K.J., Rodriguez O., Gamez G. Phytofiltration of hazardous cadmium, chromium, lead and zinc ions by biomass of *Medicago sativa* (alfalfa). *J. Hazard Mater.* 1998; 57: 29-39.
- [11] Heechan Cho, Dalyoung Oh, Kwanho Kim, A study on removal characteristics of heavy metals from aqueous solution by fly ash, *J. Hazard. Mater.* 127 (2005) 187-195.
- [12] K.K. Panday, G. Prasad, V.N. Singh, "Copper (II) removal from aqueous Solutions by fly ash", *Water Research*, 19 (1985) 869-873.
- [13] K. Periasamy, C. Namasivayam, "Removal of Ni (II) from aqueous solution and nickel industry wastewater using an agricultural waste: peanut hull", *Waste Manage.* 15 (1995), 63.
- [14] H. Freundlich, W. Heller, "Rubber die adsorption in lusungen", *J. Am. Chem. Soc.* 61 (1939) 2228.

- [15] Langmuir, The adsorption of gases on plane surface of glass, mica and platinum, *J. Am. Chem. Soc.* 40 (1918) 1361.
- [16] G. McKay, H.S. Blair, J.R. Garden, "Adsorption of dyes on chitin, equilibrium studies", *J. Appl. Poly. Sci.* 27 (1982) 3045-3057.
- [17] F. Slejko, *Adsorption Technology: A Step by Step Approach to Process Evaluation and Application*, Marcell Dekker, New York, 1985.