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Removal of Heavy Metals by Cement Kiln Dust

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Heavy metals and other toxic pollutants are considered extremely pernicious because they are toxic, nondegradable, and environmentally persistent (Weng C.H., 1994). Electroplating, metal finishing and or leather tanning are producing wastewater streams contaminated with heavy metals such as chromium, zinc, cadmium, lead, nickel, and mercury. In Egypt, the dust emitted is estimated to be about two million tons (*Authorities of Cement Companies*), and is accumulating annually at domestic cement plants. This finely divided dust is emitted from cement kilns, and must be disposed of at waste disposal sites. The cost for storage, transportation, and disposal are high. To minimize the undesirable environmental impacts and to conserve materials, many researches have been conducted for recycling or reusing the CKD as raw materials, fertilizer, constructing material and improving the sand soil properties (Thorbjorn, 1969). Recently, the use of CKD as adsorbent in wastewater treatment has a great attention as no cost material and clay structure (El-Awady, 1996). For many years, most metal- rich wastewaters were treated by conventional alkaline neutralization precipitation (ANP) process, as well as Coagulation, pH adjustment, reduction, polymer coagulant, electrokinetic process (Kaichum, 1994; Masaki, 1994; Mcintosph et al, 1995; Weng et al, 1994; Yuasa et al 1994, Zhang, 1994). The aim of this study is to evaluate the capability of CKD, as heavy metals scavenger, for removing some heavy metals such as chromium, iron, cobalt, and copper from aqueous solutions. Moreover, the treatment of tannery industrial wastewater was taken as a case study.

MATERIALS AND METHODS

Cement kiln dust (CKD) used in this study was collected from the bipath of Portland Cement Factory, Cairo, Egypt. The CKD was dehydrated at 105 °C for 24 hr's before using. Energy dispersive X- ray analysis (EDAX, Philips EDAX 9100) was used to characterize the chemical composition of CKD, Table (1). Scanning electron microscope analyses showed the dust was composed of spherical particles with a core of calcium

Table 1. Major chemical constituents of CKD

Components	Al_2O_3	SiO_2	CaO	Fe_2O_3	K_2O	MgO	Na_2O	TiO_2
Average (%).	7.1	21.8	43.9	4.71	6.1	2.5	6.25	1.0

carbonate and clay and an alkali coating (Wilson et al, 1986). Batch adsorption experiments were carried out by preparing series of 100 ml solutions of standard metal ion solutions from commercial chromic sulfate ($Cr_2(SO_4)3$), ferric chloride ($FeCl_3$) , copper sulfate ($CuSO_4$) , and cobalt sulphate ($CoSO_4$) as follows : Cr^{+3}, 100 mg /L ;

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Fe^{+3}, 400 mg /L; Cu $^{+2}$ 1,000 mg /L and Co^{+2}, 100 mg / L , respectively. The concentrations of the residual ions in the filtrates were determined colorimetrically using Perkin Elmer Lambda 3A UV / VIS Spectrophotometry, at the maximum wavelengths 610, 340, 650, and 510 nm for (Cr, Fe, Cu and Co), respectively. Composite samples of chromium tank as well as final effluent were collected from Cairotan wastewater stream as a case study. Superfloc Flocculant from American Cyanamide Company, N. J., U. S. A., was used. All physico - chemical analyses were determined according to the American Standard Methods (APHA, 1992). ICP (Inductively Coupled Plasma, Perkin - Elmer Emission Spectrometer Plasma 400) was used for the determination of metal ion concentrations in the tannery industrial wastewater and treated samples. In order to obtain the optimum operating conditions : The required amount of adsorbent, CKD, was weighed and added to a 125 ml stoppered conical flask containing 100 ml of the prepared metal solutions. The flask was shaken for the desired time at room temperature (23 + 1) °C, after which it was filtered through Whatman filter paper No. 1. Rapid solid liquid separation was achieved on addition of a trace amount of Superfloc Flocculant. Optimum pH, equilibrium time, shaking rate, CKD dose were investigated. Equilibrium contact time between 0.0 and 2.0 hours , optimum pH values from 2.0 to 9.0, optimum shaking rates ranging from 0.0 to 200 rpm, and cement dust doses from 0.0 to 40.0 gm /L were determined, by shaking 1.0 gram of dried cement samples with 100 ml of each metal solution. Filtrations were carried out, and the residual metal cations were determined and the percent metal removal was plotted against pH, contact time, rpm, and cement dose, respectively.

RESULTS AND DISCUSSION

Table 1 shows that the major components of CKD are alumina, calcium oxide, ferric oxide, silica, and titanium oxide. Each of these components can be an ideal adsorbent. Moreover, the alkaline nature of the dust makes it a good neutralizing agent. In order to maximize metal adsorption by this wastedust, it is recommended to use it for treating acidic wastewater streams. Results obtained in Fig 1 shows the effect of pH values on the percent removal of (Cr^{+3}, Fe^{+3}, Cu^{+2}, and Co^{+2}) ions from aqueous solutions. It is clear that the removal of the metal ions is gradually increased with increasing the pH until equilibrium range from 2.5 to 4.5 , while the percent removal slightly decreases with increasing the pH values; this may be due to metal cations hydrolysis (Baes, 1976). The chemical analysis of CKD shows that sodium and potassium oxides have dominant effect on the increase of the pH of the aqueous CKD soaked solution. The mechanism of heavy metals removal from acidic wastewater may be explained as follows :

(1) Heavy metals hydrolysis : $X_2O + H_2O \Rightarrow 2\ X(OH)$

$$MSO_4 + X(OH) \Rightarrow M(OH)_n \downarrow + X\,SO_4$$

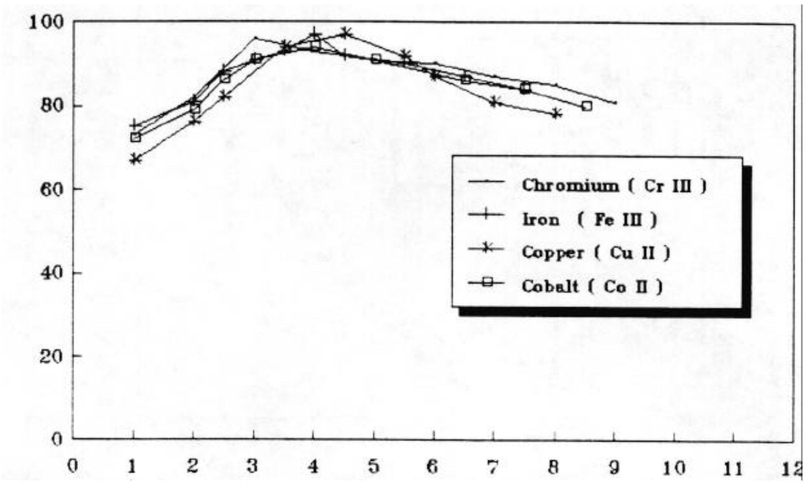
Where X : K, Na , M : Cr, Fe, Cu, Co. and n : 2, 3 .

(2) Adsorption of Heavy metals on the CKD fine particles :

$$M(OH)_n + CKD \Rightarrow CKD - \{ - M(OH)_n \}$$

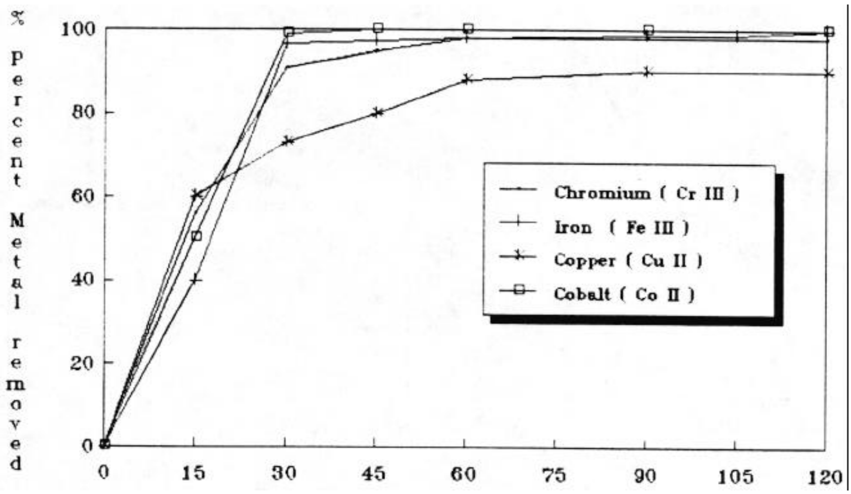
Where the major component of the remained CKD is a clay material in nature with good adsorption properties.

The effects of contact time on the percent removal of heavy metals under investigation are shown in Figure 2. It is clear that : (a) prolonging the contact time up to a certain limit (which is 30 minutes in cases of cobalt and chromium and 60 minutes in the case of copper) is accompanied by a noticeable increase in the removal percent, and beyond this



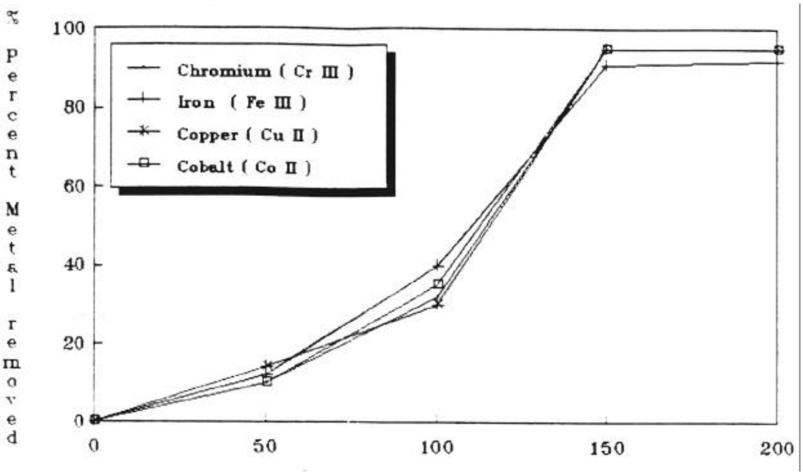
pH - value

Figure 1. Effect of pH - values on heavy metals removal by using CKD,at 30 min., 150 rpm and 10 g CKD / L.



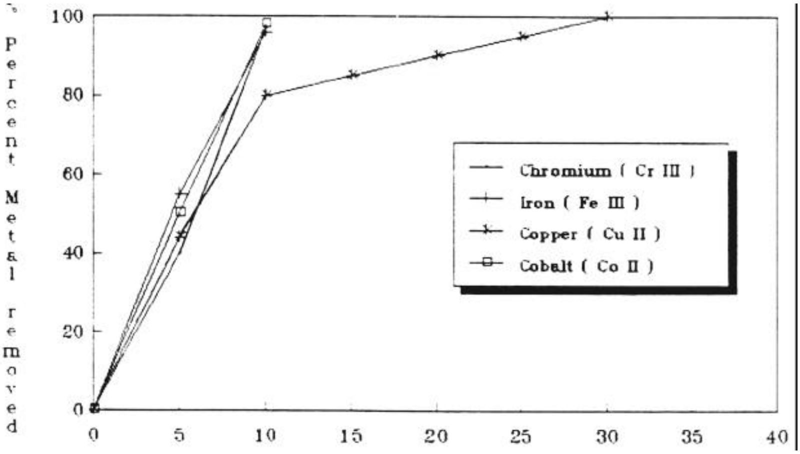
Contact Time (min.)

Figure 2. Effect of contact time on heavy metals removal using CKD, at pH (2.5-4.5), 10 g CKD / L, and 150 rpm.



RPM (Excursions per minute,

Figure 3. Effect of RPM on heavy metals on using CKD, at pH(2.5-4.5). 30 min., and 10 g CKD / L.



CKD dose (g / l)

Figure 4. Effect of CKD dose on heavy metals removal using CKD,at pH(2.5-4.5), 30 min., and 150 rpm.

limit the latter slows down and levels off which could be due to the shortage of metal ions, and (b) the removal percent in case of iron increases gradually with time, until attaining complete removal at 120 minutes. The relationship between the efficiency of metal removal and the number of excursions is illustrated in Figure 3. Different rpm's are applied ranging between 50 and 200 rpm. The results obtained show that the optimum shaking rate which gives the maximum percentage removal is attained at 150 rpm regardless of the heavy metal used. The effect of cement dust doses on the removal capacity of metal ions under the optimum operating conditions were investigated.

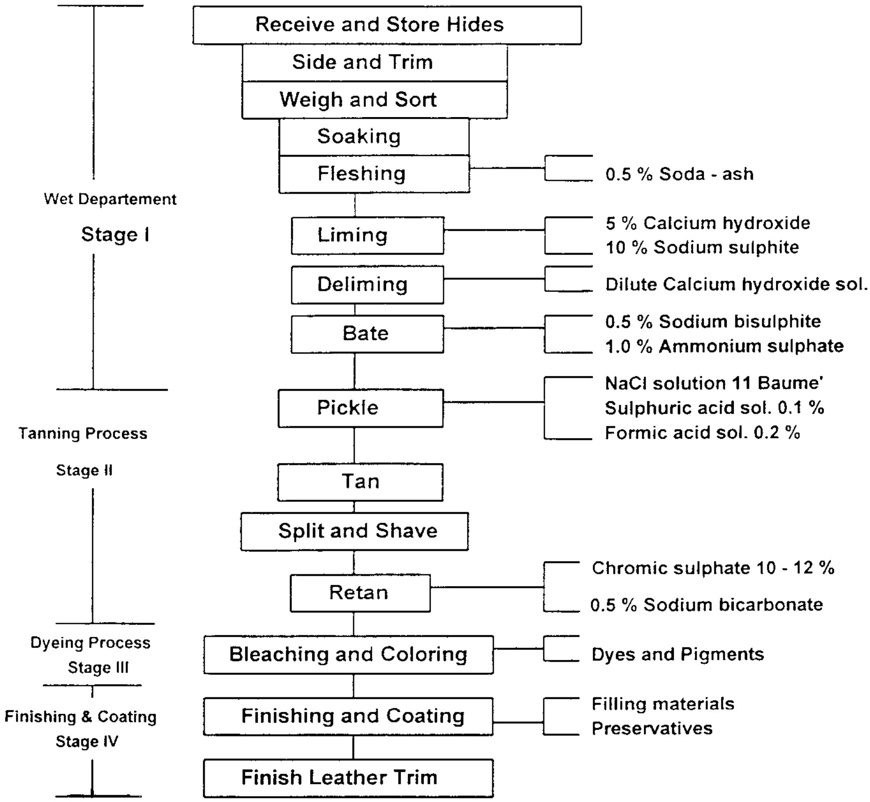
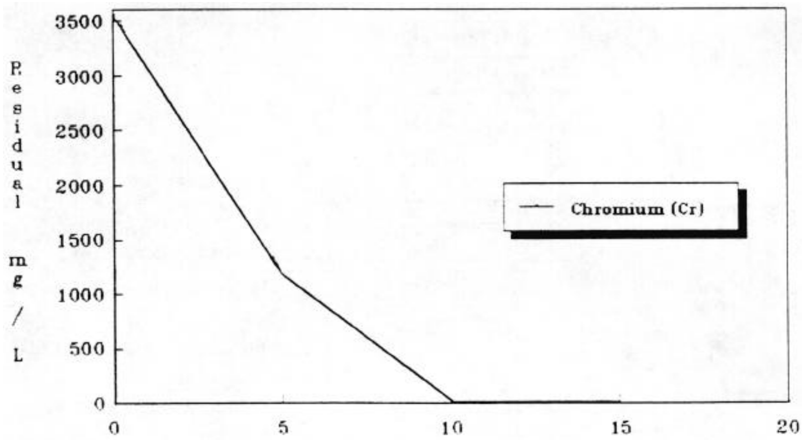


Figure 5. Schematic Diagram of Tanning Process

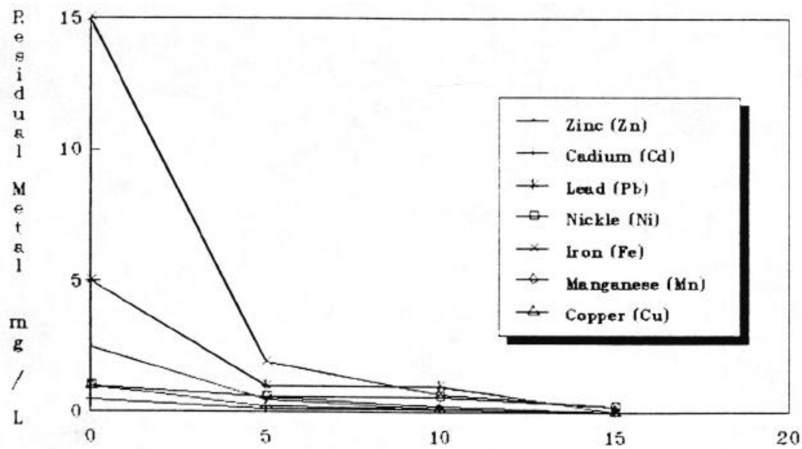
Figure 4 shows that the cement doses which give the maximum removal of chromium, iron, and cobalt ions is 10 grams CKD per liter, while it is 30 grams per liter for removal of copper ions.

Cairotan Tanyard was chosen as a case study. It is located at El-Madabegh district, Old Cairo, Egypt. The annual production of the leather is half - a - million square feet. Batch process is the production system, and the company discharges annually about 1000 m^3 of industrial wastewater to the sewers *GOFI* (1996). Figure 5 shows the schematic diagram of the manufacturing process. The wastewater is created from the washing, cleaning, tanning, dyeing and finishing process. The composite wastewaters, however, are high in organic contents, suspended solids and heavy metals. The heavy metals are originated from direct chemical addition during the batch process e.g. Chromic sulphate (10-12) % solution: water soluble pigments; cellulosic materials; wax; filling materials; binding materials; and some other preservative materials, e.g. fat liquoring oils. Moreover, some auxilaries were added during the manufacturing process, e.g. nemoza. Table 2 shows the average values of the selected parameters of both industrial and combined effluents, in addition to the water quality board discharge requirements to the sewers. Effluents do not comply with the Law No. 4/ 1994 (Egyptian Standards regulating the discharge of industrial wastewaters to the sewerage network). This is due to: lower pH value of the industrial effluent, higher pH value of the final effluent, and their high organic loads.



CKD dose (g / L)

Figure 6. Effect of CKD dose on the Removal of chromium from Tannery Effluent at pH(3.6), 30 min., and 150 rpm.



CKD Dose (gm / L)

Figure 7. Effect of CKD dose on the removal of Heavy Metals from Tannery Effluent at pH (3.6), 30 min., and 150 rpm.

Also, settleable and suspended solids' concentrations do not comply with the Law. Moreover, oil and grease concentration exceeds the permissible limit. The obtained results show that the main source of heavy metals in the process were created from retanning step. Results obtained from Table 3 indicate that by increasing CKD dose from 5 g / L up to 20 g / L, enhances significantly the percentage removal of the heavy metals, thereby minimizing the residual metal ion concentration in the treated effluent (Figures 6,7). Table 4 shows that the use of CKD (20 g / L) as an adsorbent has the capability to neutralize the acidic pH-value from 3.64 to 8.2, to reduce the organic load represented as chemical oxygen demand from 3303 to 1465 mg O_2/ L (55.6 %) and the total suspended solids from 640 to 46 mg / L (92.8 %), respectively.

Table 2. Characteristics of industrial effluents and the water quality board discharge requirements to the sewers

Constituent	Unit	Chromium effl.	Final effl.	Discharge requirement
pH - value	--	3.64	12.05	6 -- 10
COD	mg O_2 / L	6480	3930	700
SS	mg / L	5100	2335	500
⇒ 10 minutes	ml / L	650	510	5
Settleable Solids ⇒ 30 minutes		500	410	10
Phosphate	mg / L	1.25	6.8	5
Oil & grease *	mg / L	92.6	358	100
Cr	mg / L	3556.2	13.2	
Zn, Cd, Pb, Ni, Fe, Mn, & Cu.	mg / L	26	1.4	10

* Oil & grease and all extractable matters by chloroform.

Table 3 Effect of CKD doses on heavy metals removals from industrial Effluents.

Metal concentration (mg/L)	Raw	Metal Removed (% R) CKD Dose (g/L) 5.0	10.0	20.0
Cr	3556	67 %	99.4 %	100 %
Zn	2.5	80 %	96 %	100 %
Cd	0.5	80 %	80 %	100 %
Pb	5.0	80 %	80 %	100 %
Ni	1.0	40 %	40 %	80 %
Fe	15.0	87.3 %	95.3%	98.7 %
Mn	1.0	40 %	80 %	100 %
Cu	1.0	80 %	90 %	100 %

Table 4 Overall removal of investigated sample, 20 g CKD/L, pH 3.6, 30 min., 150 rpm

Parameters	Unit	Chromium Tank Effl.	Treated Effl.	%R
pH - Value	----	3.6	8.2	----
COD	mg / L	3303	1465	55.6
SS	mg / L	640	46	92.8
⇒ 10 minutes		30	0.0	100
Settleable Solids	ml / L			
⇒ 30minutes		25	0.0	100
Cr	mg / L	3556.2	0.2	99.99
Zn	mg / L	2.5	0.0	100
Cd	mg / L	0.5	0.0	100
Pb	mg / L	5.0	0.0	100
Ni	mg / L	1.0	0.2	80
Fe	mg / L	15	0.2	98.7
Mn	mg / L	1.0	0.0	100
Cu	mg / L	1.0	0.0	100

On the other hand, the settleable solids' values of the treated samples reduced to zero ml / L. The adsorbent has the capability to remove most of the chromium and the heavy metals from the wastewater under investigation. Although the dose of CKD is relatively high, it has a great potential to be used as low cost raw material for tile, brick and blocks production. Our results indicate that cement kiln dust could be recommended as a material for the effective removal of metal pollutants from industrial wastewaters discharged by the tanning industries.

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