

Kinetics and Thermodynamics of Some Heavy Metals Removal from Industrial Effluents Through Electro-Flotation Process

K. A. Selim¹, F. I. El Hosiny², M. A. Abdel Khalek¹, I. Osama¹

¹Central Metallurgical Research & Development Institute (CMRDI), Cairo, Egypt

²Faculty of Science, Ain Shams University, Cairo, Egypt

Email address:

k2selem@yahoo.com (K. A. Selim), fouadelhosiny@gmail.com (F. I. El. Hosiny), kalekma@yahoo.com (M. A. A. Khalek), gigi_abdelatif@yahoo.com (I. Osama)

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Abstract: The electrokinetic of chromium, copper, silver and gold ions removal from synthetic and wastewater via electro-flotation was investigated. Kinetics and thermodynamic parameters of the electro-flotation process were determined. The effect of initial pH and metal ion concentration, treatment time and temperature showed that the maximum removal was achieved at pH 6. The order of the metal ions removal is $\text{Cr}^{3+} > \text{Cu}^{2+} > \text{Ag}^+ > \text{Au}^+$. The removal process follows pseudo first-order kinetics and the adsorption is a heterogeneous system characterized by *physical adsorption* which is exothermic. Negative values of entropy change ΔS° and Gibbs free energy change ΔG° indicate that this adsorption process is spontaneous and less favorable at high temperatures. The treatment of electroplating wastewater showed that the removal efficiency was ranging between 96 - 99%. The electrical energy consumption was 0.033 Kwh/L.

Keywords: Electro-Flotation, Wastewater, Heavy Metals, Kinetics, Thermodynamics

1. Introduction

The most important object of the environment is water (as an element of life on the Earth) used practically in all the spheres of human activities, however its usage and return into sources almost always leads to pollution of reservoirs. Progressing pollution of raw water sources leads to the situation that by the end of 21st century many countries, being previously rich in water resources, will suffer considerable difficulties in reserves of pure water [1]. Industrial effluents from many industries contain high amounts of heavy metal ions, such as chromium, cadmium, copper, zinc, nickel, gold and silver which are non-biodegradable and they are known to be toxic and carcinogenic. Different separation techniques could be used as precipitation, ion exchange, adsorption, electro-dialysis and filtration [2-7]. Such techniques are generally multistep, time consuming and require extensive equipment, chemicals and handling [8-11].

Thus, one can see that electro-flotation is among five most perspective electrochemical methods of water

purification, it possesses a whole complex of positive characteristics. Thus, when electro-flotation is used, there is no need in building of a complicated reagent complex, it can be easily controlled by factors traditional in chemical processes (temperature, pressure, catalysts etc.), but also due to electrochemical factors (current force, electrode potential etc.), which can be easily regulated; thus, creating conditions for realization of desirable reactions and suppression of collateral processes [12, 13].

Electro-flotation (EF) is carried out according to relatively simple technological schemes in compact apparatus, which are simple in exploitation, can be easily controlled and automatized. As a result of their application, the total mineralization of the system does not increase within the framework of ecological limitations. The electro-flotation technique depends on the generation of hydrogen and oxygen gases during electrolysis of water. The gas bubbles formed on the electrode surface contact with the particulate matter; then the attached combination rise up to the surface where they may be removed by skimming [14, 15].

This paper investigated the kinetics and thermodynamics

of electro-flotation of some heavy metals, such as chromium, copper, silver and gold from synthetic aqueous solutions and wastewater obtained from local electroplating workshop.

2. Materials and Methods

2.1. Chemicals

KCl, CrCl_3 , $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, AgNO_3 and AuCl of analytical grade; not less than 99.9% purity (Sigma-Aldrich and Merck) were used for synthetic solutions preparation. The pH was adjusted by 0.01 M solutions of HCl and NaOH as required. The wastewater was supplied by electroplating workshop located in Sagha area, Cairo, Egypt.

2.2. Procedure

A laboratory model DC power supply apparatus (Farnell Instruments LTD) was used to maintain a constant DC current. Voltage and current were measured by a multimeter (PHYWE). The pH and the temperature were measured using a Hanna (HI8314) pH meter connected to a combined electrode and comprising a temperature sensor (HI1217D).

Electro-flotation was conducted in a cylindrical glass cell of 400 ml in which aliquot solutions of 300 ml were placed and slowly stirred with a magnetic bar at 120 rpm. A pair of commercially obtained aluminum plates of size $6\text{cm} \times 5\text{cm} \times 0.5\text{cm}$ immersed to a 6 cm depth with an effective area of 30cm^2 each was used as electrodes in the experiments. The inter-electrode distance was 4cm. The added NaCl (0.2%) serves for preventing passivation on the aluminum electrode surface and decreasing the excessive ohmic drop in the solution. The residual heavy metals concentrations were determined by Atomic Absorption Spectroscopy (Perkin Elmer, Model AAnalyst 200). The removal percent of metal ions and amount of metal ions adsorbed on $\text{Al}(\text{OH})_3$ (q_e) was calculated by Eqs. (1) and (2), respectively [16]:

$$\text{Removal}(\%) = \frac{C_0 - C_t}{C_0} \times 100 \quad (1)$$

Where, C_0 and C_t are the concentrations of metal ions (mg/L) at times, zero and t, respectively.

$$q_e = \frac{(C_0 - C_t)V}{M} \quad (2)$$

Where q_e is the sorption capacity of $\text{Al}(\text{OH})_3$ in (mg/g), V is the volume of the aqueous solution in L and M is the mass of $\text{Al}(\text{OH})_3$ in (g).

3. Results and Discussion

3.1. Effect of pH

The pH is an important factor for removal efficiency of metal ions so the initial pH was investigated for its effect on the removal percent. Figure 1 shows that the removal efficiency for all studied metal ions is very low in the pH range 2-3. It increases considerably at pH 4, remains high and almost constant in the pH range 5-6. The maximum values were 80.5,

74.9, 64.1 and 52.2% for Cr^{3+} , Cu^{2+} , Ag^+ and Au^+ , respectively at the pH 6. The lower removal efficiency at strong acidic medium is due to the higher solubility of $\text{Al}(\text{OH})_3$ which is not useful for water treatment [17, 18]. The removal mechanism of metal ions is based on their adsorption on the $\text{Al}(\text{OH})_3$ flocs. The electroless deposition occurs mainly at the anode where, due to electro-dissolution, the aluminum surface is more active than that of the cathode [15]. The experimental results indicated that the order of removal efficiency for metal ions was as follows: $\text{Cr}^{3+} > \text{Cu}^{2+} > \text{Ag}^+ > \text{Au}^+$. These results may be due to that the ionic charge and ionic radius. The higher removal efficiency was achieved with higher ionic charge and smaller ionic radius, Table 1 [19].

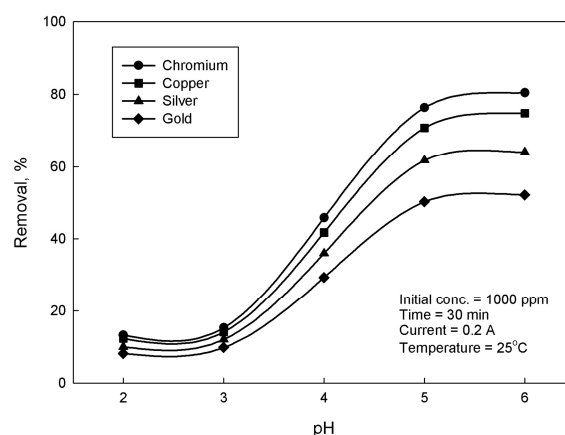


Figure 1. Effect of Initial pH on Removal Efficiency of Heavy Metal Ions.

Table 1. Atomic Weight, Ionic Charge and Ionic Radii for Heavy Metal.

Element	Symbol	Atomic Wt.	Ionic charge	Atomic radius (\AA)	Ionic radius (\AA)
Chromium	Cr^{3+}	51.996	3+	1.850	0.615
Copper	Cu^{2+}	63.546	2+	1.570	0.730
Silver	Ag^+	107.868	1+	1.750	1.150
Gold	Au^+	196.966	1+	1.790	1.370

3.2. Effect of Treatment Time

The effect of the time required for their quantitative removal were carried out with five different aliquot solutions containing 200, 500, 1000, 1500, 2000 and 2500 mg/L of each metal ion. Figure 2 shows the variations of the initial concentrations of chromium, copper, silver and gold with time. From sub-figures it is clear that there is no direct correlation exists between metal ion concentration and removal efficiency. Certainly, for higher concentrations longer time for removal is needed, but high initial concentrations were reduced significantly in relatively less time than lower concentrations. The electro-flotation process was more effective at the beginning when the concentration was higher than that at the end of the operation when the concentration was low. The rate of electrochemical reactions taking place on the electrode surface increased with time. The coagulant concentration produced by electrolysis [aluminum hydroxide, $\text{Al}(\text{OH})_3$] is typically directly proportional to the amount of electricity. It has some influence on the chemical dissolution of aluminum cathode, as it affects the rate of hydroxyl ion production at the cathode.

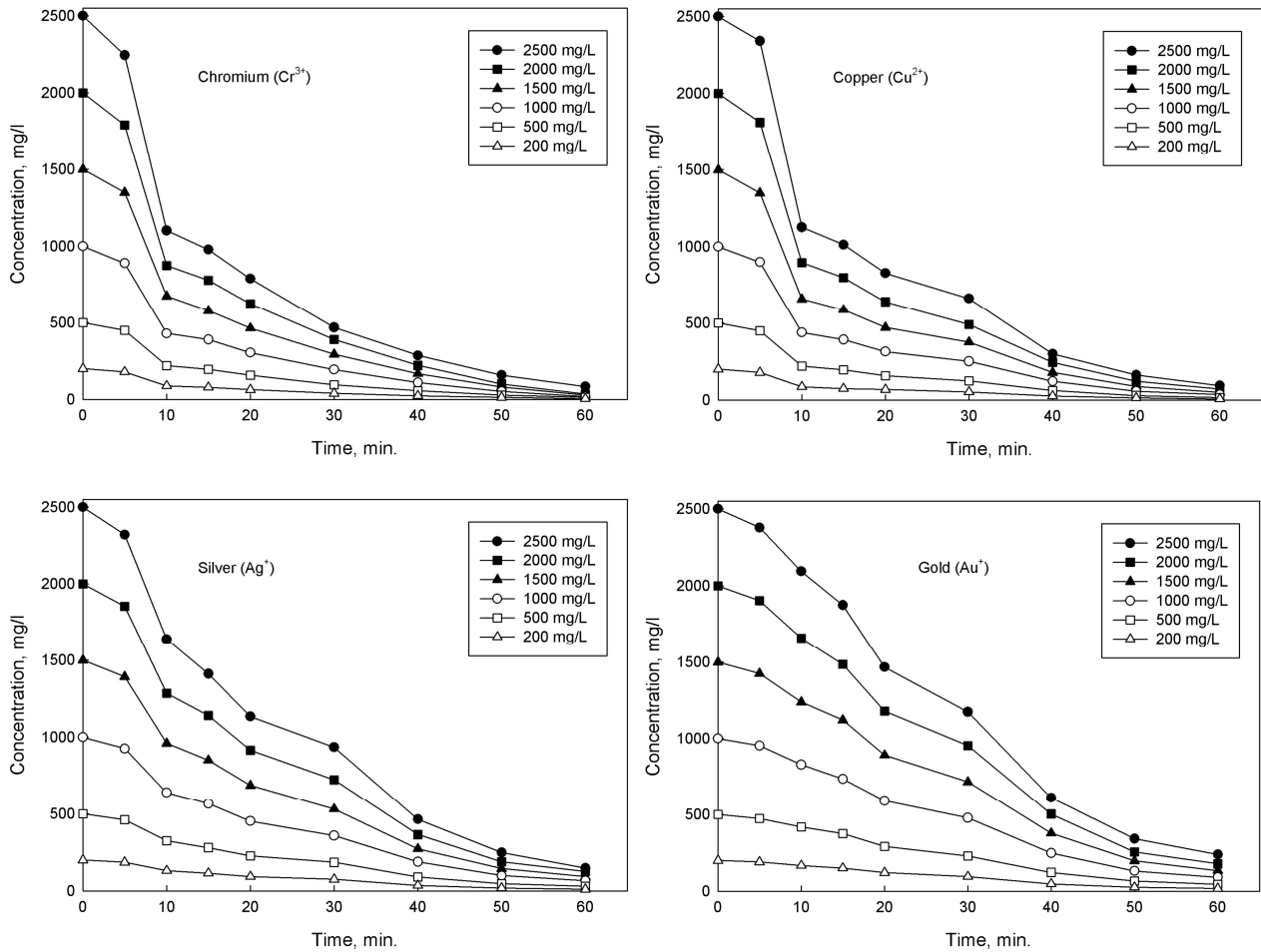


Figure 2. Equilibrium Concentration of Metal Ions as a Function of Treatment Time.

3.3. Kinetic Modeling

In order to investigate the mechanism of removal process, particularly potential rate-controlling step, the pseudo-first-order and the pseudo-second-order kinetic models were used to test the dynamic experimental data. The integrated rate law solutions for first and second order expressions are different functions but all can be written in the form of a straight line. This means that the plot of the concentration as a function of time for each expression below should yield a straight line for the correct order.

$$\text{Pseudo-first-order model } \ln [C] = \ln [C_0] - kt \quad (3)$$

$$\text{Pseudo-second-order model } 1/[C] = 1/[C_0] + kt \quad (4)$$

Figure 3 shows that the plot of $\ln[C]$ versus t gives a straight line as per pseudo-first-order adsorption kinetics which allows computation of the rate constant K_1 with high linear regression coefficient ($R^2 \geq 0.97$ for all metal ions, Table 2, suggest that the metal ion removal process follows pseudo first-order kinetics. Figure 4 shows that the plot of $1/[C]$ versus time t gives a straight line as per pseudo-second-order adsorption kinetics which allows computation of the rate constant K_2 with very poor linear regression coefficient (R^2) of 0.68–0.84, Table 3, which suggests that the metal ion

removal process doesn't follow pseudo second-order kinetics.

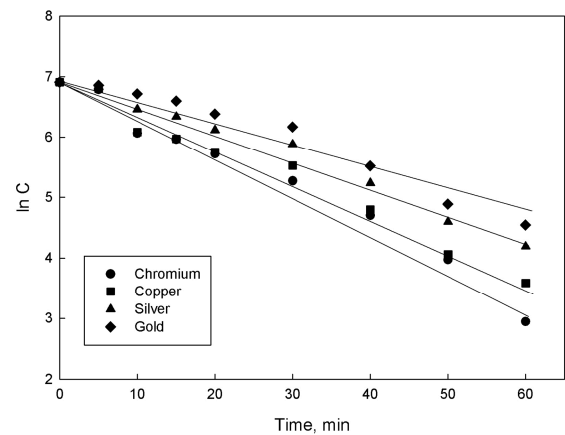


Figure 3. Plotting of Pseudo-First Order Model.

Table 2. Pseudo-First Order Model Constants.

Item	Cr ³⁺	Cu ²⁺	Ag ⁺	Au ⁺
R ²	0.9794	0.9803	0.9857	0.9693
Intercept = $\ln [C_0]$	6.9562	6.8923	7.0182	7.1262
Slope = $-K_1$	-0.0620	-0.0546	-0.0461	-0.0415
K ₁	0.0620	0.0546	0.0461	0.0415

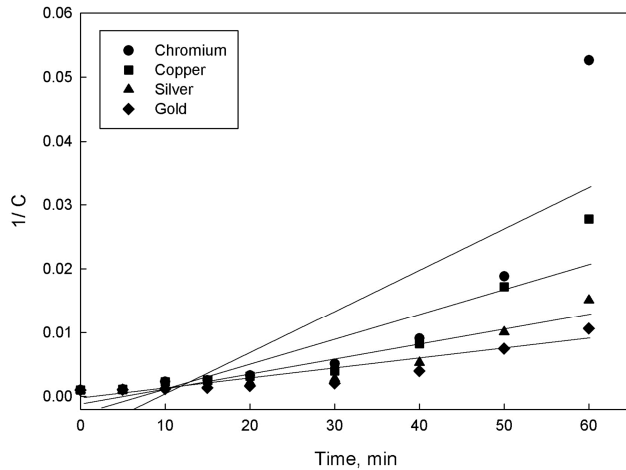


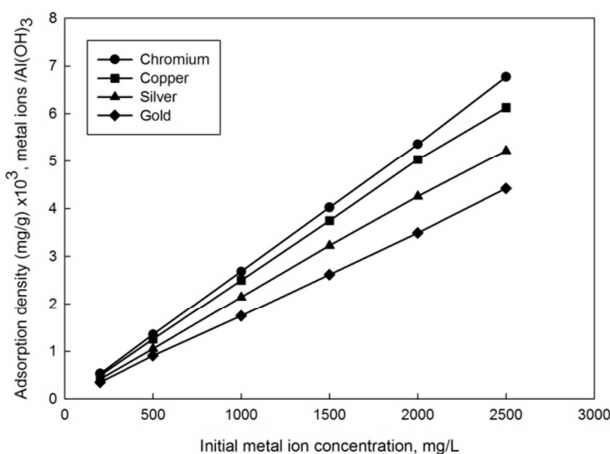
Figure 4. Plotting of Pseudo-Second Order Model.

Table 3. Pseudo-Second Order Model Constants.

Item	Cr ³⁺	Cu ²⁺	Ag ⁺	Au ⁺
R ²	0.6803	0.8237	0.8476	0.8475
Intercept = 1/C ₀	-0.0062	-0.0027	-0.0010	-0.0005
Slope = K ₂	0.0007	0.0004	0.0002	0.0002
K ₂	0.0007	0.0004	0.0002	0.0002

3.4. Effect of Initial Metal Ion Concentration

The effect of different concentrations of Cr³⁺, Cu²⁺, Ag⁺ and Au⁺ on the adsorption has been determined. The amount of metal ions adsorbed is a function of the initial concentration of the adsorbate (metal ions), making it an important factor in effective adsorption. The effect of initial metal ion concentration on the adsorption onto Al (OH)₃ is shown in Figure 5. It was clear that the adsorption capacities of adsorbent increased with increasing the initial metal ion concentrations, as the increasing concentration gradient overcomes the resistance to mass transfer of metal ions between the aqueous phase and the adsorbent [20].

Figure 5. Effect of Initial Metal Ion Concentrations on Their Adsorption Density by Al (OH)₃.

3.5. Isotherm Analysis

The most appropriate method in designing the adsorption systems is to have an idea about the adsorption isotherm.

Two equilibrium isotherm equations are used to find out the relation between the equilibrium concentrations of the adsorbate in the liquid phase and in the solid phase. These isotherms are as follows.

Freundlich isotherm

The Freundlich adsorption isotherm, which assumes that adsorption takes place on heterogeneous surfaces, can be expressed [21] as

$$\ln q_e = \ln k_f + \frac{1}{n} (\ln C_e) \quad (5)$$

Where q_e is the amount of the metal ion adsorbed at the equilibrium time, C_e is the equilibrium concentration of the metal ion in solution. K_f and n are isotherm constants which indicate the capacity and the intensity of the adsorption, respectively [21]. The isotherm constants can be calculated from the intercept and slope of the plot between $\ln q_e$ and $\ln C_e$. Figure 6 shows fitting the results on Freundlich isotherm. Freundlich constants i.e. adsorption capacity, K_f and rate of adsorption, n , are calculated from this plot. The value of ' n ' < 1 which indicates the favorable nature of adsorption, Table 4 [22]. Thus, it describes a heterogeneous system characterized by physical adsorption.

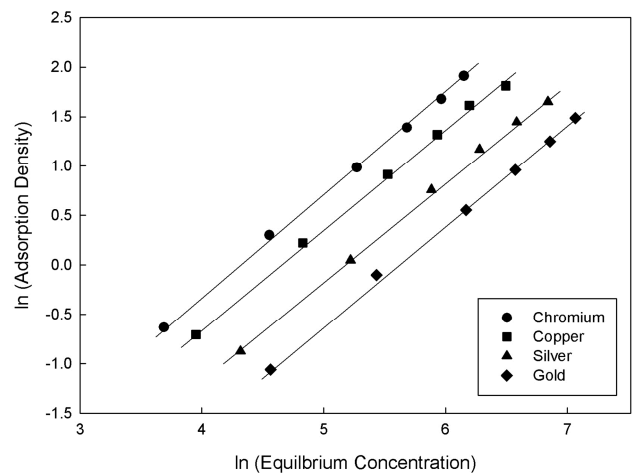


Figure 6. Fitting of Results on Freundlich Isotherm.

Table 4. Freundlich Isotherm Constants.

Item	Cr ³⁺	Cu ²⁺	Ag ⁺	Au ⁺
R ²	0.9993	0.9985	0.9989	0.9988
Slope (1/n)	1.0494	1.0702	1.0284	1.0198
n	0.9529	0.9344	0.9723	0.9805
Intercept (ln k _f)	-4.3714	-4.6452	-5.2454	-5.5909
K _F	12.6×10 ⁻³	9.6×10 ⁻³	5.2×10 ⁻³	3.7×10 ⁻³

Langmuir isotherm

According to Langmuir model, adsorption occurs uniformly on the active sites of the adsorbent and once an adsorbate occupies a site, no further adsorption can take place at this site [23]. The linearized form of Langmuir can be written as [21].

$$\frac{C_e}{q_e} = \frac{C_e}{q_{max}} + \frac{1}{b \cdot q_{max}} \quad (6)$$

Where C_e is the concentration of metal ions in solution at equilibrium (mg/L), q_e is the amount of metal ions at equilibrium in unit mass of adsorbent, q_{\max} and b are the Langmuir coefficient related to adsorption capacity and adsorption energy respectively. These were determined from the slope and intercept of the plot of C_e/q_e against C_e as shown in Figure 7. The Langmuir model doesn't fit the data for metal ions. Thus, it doesn't represent a monolayer sorption process as *chemical adsorption*. The maximum adsorption capacity of q_{\max} , and constant are related to the binding energy of the sorption system, b is calculated in Table 5.

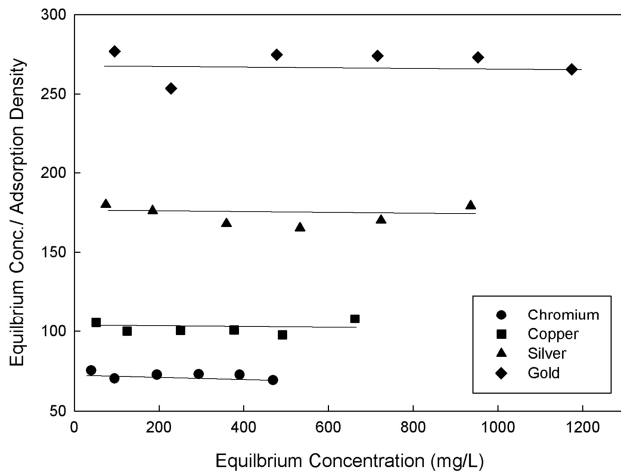


Figure 7. Fitting of Results on Langmuir Isotherm.

Table 5. Langmuir Isotherm Constants.

Item	Cr ³⁺	Cu ²⁺	Ag ⁺	Au ⁺
R ²	0.2688	0.0341	0.0197	0.0036
Slope (1/q _{max})	0.0068	0.0031	0.0026	0.0013
Intercept (1/b.q _{max})	73.97	101.04	174.41	268.87
q _{max} (Calculated)	147.05	322.5	384.6	769.2
q _{max} (Experimental)	6.77	6.126	5.217	4.420
b	9.19×10 ⁻⁵	3.07×10 ⁻⁵	1.49×10 ⁻⁵	4.84×10 ⁻⁶

A further analysis of the Langmuir equation can be made on the basis of a dimensionless equilibrium parameter, R_L , also known as the separation factor, Table 6, given by [22]

$$R_L = \frac{1}{(1+bC_0)} \quad (7)$$

Where b is the Langmuir constant and C_0 is the initial metal ion concentration. The value of R_L is indicator of the shape of adsorption isotherm to be favorable or unfavorable. The value of R_L between 0 and 1 indicates favorable adsorption, while $R_L=1$ suggests unfavorable adsorption and the adsorption process is linear adsorption, while $R_L=0$ represents irreversible adsorption. Table 6 shows that the $R_L \geq 1$ which indicate unfavorable chemical

adsorption [31].

Table 6. The Dimensionless Equilibrium Parameter, R_L .

b →	9.19×10 ⁻⁵	3.07×10 ⁻⁵	1.49×10 ⁻⁵	4.84×10 ⁻⁶
C ₀ ↓	R _L			
Ppm	Cr ³⁺	Cu ²⁺	Ag ⁺	Au ⁺
200	1.0187	1.0062	1.003	1.001
500	1.0482	1.0156	1.0075	1.0024
1000	1.1012	1.0317	1.0151	1.0049
1500	1.1599	1.0483	1.0229	1.0073
2000	1.2252	1.0654	1.0307	1.0098
2500	1.2983	1.0831	1.0387	1.0122

3.6. Thermodynamic Study

The dependence of the removal efficiency of the temperature has been investigated at 25, 40, 50, and 60°C and is shown in Figure 8. It shows that with increasing the temperature the removal efficiency decreased. This behavior indicates that this process is an exothermic process [24].

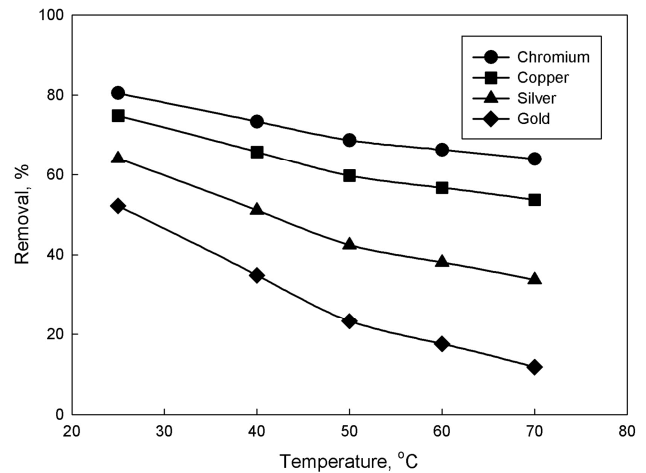


Figure 8. Effect of Temperature on the Removal Efficiency of Metal Ions.

The thermodynamic parameters; Gibbs free energy change (ΔG°), enthalpy change (ΔH°), and entropy change (ΔS°); for the sorption of metal ions by Al (OH)₃ at various temperatures were calculated to evaluate the thermodynamic feasibility and the spontaneous nature of the process. The change in enthalpy (ΔH°) and entropy (ΔS°) were calculated using the van't Hoff [25]:

$$\ln K_c = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (8)$$

Where $k_c = F_e / (1 - F_e)$, and $F_e = (C_0 - C_e) / C_0$, T is the temperature in degree K, and R is the gas constant [8.314 J/mol K]. The values of ΔH° and ΔS° have been computed from the slope and the intercept of the plot of $\ln k_c$ vs. $1/T$ (Figure 9) which gives a straight line with an acceptable coefficient of determination ($R^2 \geq 0.97$). From the plot of $1/T$ against $\ln k_c$, Slope = $-\Delta H^\circ / R$ and Intercept = $\Delta S^\circ / R$.

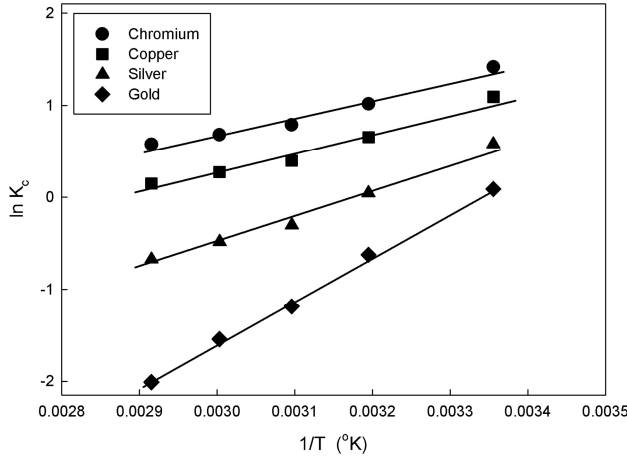


Figure 9. Effect of Temperature on the Removal Kinetic of Metal Ions.

Table 7. Thermodynamic Parameters; Enthalpy Change, ΔH° , and Entropy Change, ΔS° .

Item	Chromium	Copper	Silver	Gold
R ²	0.9693	0.9738	0.9850	0.9978
Slope	1924.9	2163.8	2870.4	4763.4
Intercept	-5.09	-6.22	-9.10	-15.88
ΔH° KJ/mol	-16.0	-17.9	-23.9	-39.6
ΔS°	-42.4	-51.7	-75.7	-132.0

The values of ΔH° are -16.0, -17.9, -23.9 and -39.6 kJ/mol for Chromium, Copper, Silver and Gold ions, respectively. They suggest that the reactions are exothermic and their values are lower than 40 kJ/mol which indicates a physical controlled process [26]. The negative value of ΔS° shows that decreasing randomness at the solid/liquid interface during the adsorption, indicated that the adsorption was not favorable at higher temperatures. The values of the standard Gibbs free energy change, Table 8, (ΔG°) were estimated using the following equation.

$$\Delta G^\circ = -RT \ln K_c \quad (9)$$

Table 8. Gibbs Free Energy Change (ΔG°).

Temp, °C	ΔG°			
	Chromium	Copper	Silver	Gold
25	-3512	-2708	-1436	-218
40	-2646	-1704	-114	1622
50	-2115	-1061	818	3190
60	-1883	-749	1342	4275
70	-1644	-422	1920	5730

For chromium and copper ions, the values of ΔG° at all tested temperatures are negative which indicate that this adsorption process is spontaneous in nature whereby no energy input from outside of the system is required. The increase in the ΔG° with increasing temperature indicates that the process becomes less favorable at high temperatures [27]. For silver and gold ions, the values of ΔG° are negatively up to 40°C and 25°C, respectively which indicate that this process is spontaneous in nature whereby no energy input from outside of the system is required. On the other hand, at high temperatures the ΔG° are positive values which indicate that this process is not spontaneous and energy input

from outside of the system is required.

3.7. Application

Treatment of the wastewater which supplied by an electroplating workshop using electro-flotation technique showed that the removal efficiency was ranging between 96 - 99% for all constituents. Table 9 shows the evaluation of treated wastewater at an operating voltage of 30 V and at an electric current of 2 Ampere for 10 min. The cost in wastewater treatment with electro-flotation is the expenditure on mass loss of electrodes and the electrical energy consumption. The energy consumption E was calculated from equation (7):

$$E = \frac{U.I.t}{V \times 1000} \quad (10)$$

Where U = applied voltage (V), I = current intensity (A), t = time (hr) and V = volume of treated wastewater (L). The energy consumption amounts to 0.033 Kwh/L of treated wastewater.

Table 9. Evaluation of Electro-flotation Treatment of Wastewater.

item	Before treatment	After treatment	Removal%
pH	5.4	7.03	--
TS	928 mg/l	36.5	96
Oil & grease	32 mg/l	1.28	96
Chromium	142 mg/l	1.42	99
Copper	213 mg/l	2.39	99
Gold	82 mg/l	0.68	99
Silver	108 mg/l	1.01	99
Cadmium	27 mg/l	0.16	99
Nickel	12 mg/l	0.04	99

4. Conclusions

Electro-flotation of some heavy metal ions showed that, the removal efficiency is very low in the pH range 2-3. The maximum values were 80.5, 74.9, 64.1 and 52.2% for Cr^{3+} , Cu^{2+} , Ag^+ and Au^+ , respectively at pH 6. The order of metal ions removal was $\text{Cr}^{3+} > \text{Cu}^{2+} > \text{Ag}^+ > \text{Au}^+$, which may be due to the ionic charge and the ionic radius. There is no direct correlation existing between the metal ion concentration and the removal efficiency. Certainly, for higher concentrations longer time for removal is needed. The metal ion removal process follows pseudo first-order kinetics. Freundlich isotherm model indicates that the adsorption is a heterogeneous system which is characterized by physical adsorption. The dimensionless equilibrium parameter R_L values were ≥ 1 which indicates unfavorable chemical adsorption.

The values of ΔH° were -16.0, -17.9, -23.9 and -39.6 kJ/mol for Chromium, Copper, Silver and Gold ions, respectively. They suggest that the reactions are exothermic and their values, < 40 kJ/mol, indicating a physically controlled process. The negative value of ΔS° shows a decrease in randomness at the solid/liquid interface during the adsorption, which indicated the adsorption was not favorable at higher temperatures. The standard Gibbs free energy changes (ΔG°) for chromium and copper ions are negative, which indicate that this adsorption process is

spontaneous. The increase in the ΔG° with increasing temperature indicates that the process becomes less favorable at high temperature. The positive ΔG° at high temperature for silver and gold indicates that this process is not spontaneous and that an energy input from outside of the system is required. Treatment of the electroplating wastewater showed that the removal efficiency was ranging between 96 - 99% for all constituents. The energy consumption for wastewater treatment was 0.033 Kwh/L.

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