Eng. & Tech. Journal, Vol.28, No.20, 201

Removal of Copper Ions From Wastewater By Multi Stage Flotation

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Received on: 11/1/2010
Accepted on:7/10/2010

Abstract

Removal of heavy metals from wastewater is of primary importance because they are not only causing contamination of water bodies but are also toxic to many life forms. One potential application of ion flotation is to treat large volumes of dilute aqueous waste solutions contaminated by heavy metals ions. Cupric ions have been removed from dilute aqueous solutions, in acidic conditions, using **M**ULTI-**ST**AGE **L**OOP **FLOT**ATION **(MSTLFLO)** column. The column consists of three stages of 70 cm long and 10 cm outside diameter. The total height of the column is 2.25 m. Three draft tubes are used inside the column each of 50 cm long. The results indicated that **MSTLFLO** is an effective process for the removal of Cu^{+2} ions from aqueous solutions. As high as 94% of the cupric ions were removed at air superficial velocity of 2.3 cm/s (equivalent to air rate of 50 l/min.) and 20ppm frother concentration in the presence of sodium dodecyl sulfate (SDS) as a collector. An empirical correlation representing the relationship between the overall removal efficiency, the superficial air velocity and the concentration of the frother was proposed.

ازالة ايونات النحاس من المياه العادمة بواسطة منظومة تطويب متعددة المراحل

الخلاصة

ازالة المعادن الثقيلة من المياه العادمة له اهمية قصوى لانها لاتسبب فقط تلويث موارد المياه بل لأنها مواد سامة لأشكال الحياة المختلفة. أحد الأستخدامات المهمة لتكنولوجيا تطويف الأيونات هو معالجة الكميات الكبيرة من المياه العادمة الملوثة بأيونات المعادن الثقيلة. في هذا البحث تم دراسة ازالة ايونات النحاس من محاليل مائية مخففة وفي وسط حامضي باستخدام منظومة تطويف متعددة المراحل . يتكون العمود من ثلاثة مراحل (اسطوانات) بطول 70 سم وبقطر خارجي 10 سم , أما الأرتفاع الكلي للعمود فيبلغ 2.25 م. استخدمت كذلك ثلاثة اسطوانات داخلية ثبتت داخل البرج بطول 50 سم . النتائج أظهرت ان منظومة التطويف متعددة المراحل هي منظومة فعالة لأزالة أيونات النحاس من المحاليل المائية المخففة. مايقارب ال 94% من أيونات النحاس تم ازالتها باستخدام معدل تدفق للهواء بحدود 50 لتر/دقيقة, تركيز الموغف (Frother) 20 جزء/مليون وبوجود مادة sodium dodecylsulfate كمجمع (Collector). تم استنتاج معادلة تجريبية تمثل العلاقة بين نسبة الأزالة الكلية, سرعة الهواء وتركيز الموغف.

1. Introduction

Industrial water is one of the major sources of aquatic pollution. Aquatic pollutants include organic compounds, pathogens, and heavy metals. Among these pollutants,

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https://doi.org/10.30684/etj.28.20.15
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heavy metals have gained relatively more significance in view of their persistence and toxicity. According to World Health Organization (WHO) the metals of most immediate concern due to their high toxic nature even at very low concentrations are chromium, copper, zinc, iron, mercury and lead (WHO,1998). These toxic metals can cause accumulative poisoning, cancer, and brain damage when they are found above the tolerance levels (ATSDR,1999).

Copper has received considerable attention owing to its uses in metallurgy, chemical industries and is necessary for other many biological important functions (Freematle, 1989; Khalifa et al.,2001). When levels of Cu exceed certain values, however, defense mechanisms to protect against excess Cu are overcome and toxicity results.

The concentration of heavy metals in the industrial wastewater from these industries should be decreased to the permissible limits; therefore the ground water will not be affected. Chemical precipitation, coagulation, solvent extraction, membrane separation, ion exchange, adsorption and flotation are commonly applied in the treatment of industrial effluents. Of these, flotation has shown to have great potential of modern equipment available owing to its: simplicity; flexibility and effectiveness of operation; low space requirements; the production of small, concentrated volumes of sludge; and the fact that it may be applied to treat large volumes of dilute aqueous waste solutions contaminated by heavy metal ions {(Parekh and Miller,1999); (Voronin and Dibrov,1999); (Zabel,1999); (Matis and Zouboulis,2001); (Rubio,2002); (BlÖcher et al.,2003); (Stoica and Oproiu,2004); (Ghazy et al.,2004;2008); (Turtureanu and Georgescu,2008)}.

2. Ion Flotation

Ion flotation involves the removal of surface inactive ions (colligend) from aqueous solutions by adding surfactants which act as collectors. The subsequent passage of gas bubbles through the solution transfers the surface-active ions to the top (Doyle,2003; Lazaridis,2004). Compared to other separation methods, ion flotation has advantages in its ease of operation and low costs. It shows particular promise for treating large volumes of dilute aqueous solutions (Doyle and Lui, 2003).

Although there are many different types of flotation devices, agitated cell and bubble column are the two most widely used configurations. Mechanic flotation cells work well in mineral processing systems. However, large space requirement and high power consumption are their main drawbacks. The invention of flotation column in the early 1960s is considered to be the beginning of a new trend in flotation separation (Finch and Dobby, 1990). Recently, several different designs based on the idea of conventional flotation column were reported in the literatures. A packed column was used by Yang (1986) for separating floatable particles from a mixture of floatable or non-floatable particles. Miller (1988) used cyclonic column which is a kind of flotation column with a tangential inlet on the top and an annular outlet at its bottom. A high throughput design flotation column consisting of two concentric columns for the beneficiation of mineral ores was used by Jameson (1990). For fine coal beneficiation, Yoon (1992) used a micro-bubble flotation column with two types of bubble spargers to generate small bubbles. Lai's (2000) cyclonic flotation column provided an effective way for the deep cleaning of pyrite in coal. Because of the centrifugal force a higher pyretic sulfur rejection than that of a conventional cell was obtained.

Multi-**St**age **L**oop-**FLO**w ***(MSTLFLO)*** flotation column can be viewed as an integration of multistage flotation process and bubble column with draft tubes. It introduces proper hydrodynamic behaviors in the column. A loop flow, caused by pressure difference between inside and outside regions of draft tubes, can keep most of small air bubbles within the contact region in each stage. Therefore, MSTLFLO process has several important advantages, as compared with conventional flotation processes, which include: reduction in back mixing, increase in interfacial area, improvement of mixing and contact between bubbles and particles, less surfactant requirement, and higher separation efficiency (Gu, 1998). It has been applied for fine coal beneficiation (He and Chiang, 1995); for the removal of metal oxide precipitates from nuclear power plant DECON water (Shi and Chiang, 1998); and oily water treatment {(Gu and Chiang,1999); (Shi and Chiang, 2000;2001)}. Other potential applications include de-inking of recycled paper pulp and removal of emulsified oil/grease droplets from produced water (Beneventi and Benesse, 2009).

A deep insight for the high potential application, hydrodynamic properties and kinetic modeling of MSTLFLO process for simultaneous removal of mixed pollutants {emulsified mineral oil, suspended particles (powdered activated carbon or glass beads), and dissolved phenol (as a representative chemical)} from industrial wastewater has been recently demonstrated by Shi (2005) using 4" and 12" flotation columns. A similar study has been conducted by Abduljabbar (2008) who investigated the potential and the hydrodynamic performance of a 10cm MSTLFLO flotation column equipped with three draft tubes for the removal of mixed contaminants from simulated wastewater. Empirical expressions for the kinetic parameters, gas holdup and bubble rise velocity in terms of the operating variables were proposed.

As indicated earlier, a MSTLFLO flotation column has been successfully applied to solid separations (as in metal oxide removal and fine coal beneficiation); oily water treatment and mixed contaminants removal from wastewater. Thus the possibility of applying MSTLFLO flotation column to deal with the removal of copper(II) from simulated wastewater was explored in the present study.

3. Experimental Work

3-1 Materials

Collector: Reagent grade sodium dodecylsulfate (SDS,$C_{12}H_{25}SO_4Na$).

Frother: Pure ethanol.

Colligned: Reagent grade $CuCl_2.2H_2O$.

Standard 1 M HNO_3 solution: pH adjustment.

Aqueous solutions of Cu^{+2} ions were prepared by dissolving $CuCl_2$ in deionized water. The initial Cu^{+2} ion concentration of the solution was kept at 100ppm.

Solutions for ion flotation were prepared by adding stoichiometric amounts of collector and colligend and different concentrations of the frother (ethanol), these were 5, 19, 15 and 20 ppm. The final pH of the solution was adjusted using 0.1 M HNO_3. The initial concentrations of collector and colligend are carefully selected to ensure that no precipitation occurred in the bulk solution.

3-2 Experimental Set-up

A three-stage flotation column made of Plexiglas, with a total height of 2.25 m and 10 cm outside diameter was constructed to fulfill the requirements of the present study. A Schematic diagram of the experimental set-up is shown in Figure (1). The working column is divided into three sections, each of 70 cm long. The effective column volume is 17.7 liters. A 50 cm long draft plastic tube of 6 cm outside diameter and 3 mm wall thickness is installed concentrically in each section. Figure (2) shows the geometry of the MSTLFLO flotation column. The draft tubes are serving as stages. Each draft tube divides the column into two distinct regions: central region (riser) and annular region (downcomer), respectively. There is a difference in gas holdups between inside and outside of tube. This in turn induces a pressure drop and therefore a liquid circulation (or loopflow) from the outside (annular region) to the inside (central region) of each draft tube. Between two adjacent draft-tubes, there is a cone baffle. The distance between the bottom edge of draft tube and the topside of cone baffle is 5 cm. Clearance between the inside wall of column and the lower edge of cone baffle is 0.3 cm. Cone baffle plays an important role on flow pattern and mixing conditions in MSTLFLO process. The function of cone baffle is to prevent inter-stage mixing. It allows a net liquid flow downward through the small clearance (~0.3 cm gap) between the lower edge of cone and the inner wall of column, while gas by-pass can be prevented. Each cone baffle directs rising bubbly stream from lower stage into the riser region of upper stage and minimize backmixing between two adjacent stages. A pair of flanges, which are machined from 5 cm thick Plastic flat sheets, connects two adjacent sections. Air is introduced into the bottom stage of the column, after passing through a regulator, a flow meter and a porous sparger with a mean pore size of 700 µm. Treated clean water leaves the column from the bottom discharge pipe, while pollutants go out from the top of the column into a foam discharge tank. Before starting the experiments the effluent concentration was measured from the bottom stage of the column each 4 minutes until reaching steady state condition (when the effluent concentration stops dropping with time).

3-3 Experimental procedure

1. Aqueous solution of Cu^{+2} ions (concentration equivalent to 100 ppm in bulk stream) was fed into the top stage of the flotation column through water distributor at a rate of 380 l/hr (1.34cm/s). Four different concentrations (5, 10, 15, and 20 ppm) of ethanol as frother were used.
2. Air was fed from the bottom of column through the porous sparger at various flow rates of 20, 30, 40, and 50 l/min.
3. The circulation was kept for 20 minutes to reach steady state condition.
4. Samples are taken from the top, middle and bottom stages of the flotation column.
5. The cupric ion concentration was analyzed by a flame atomic absorption spectrophotometer.

6. The removal efficiency was calculated as:

$$RE\% = \frac{C_0 - C}{C_0} \times 100 \quad \ldots.\ (1)$$

Where C_0 is the initial Cu^{+2} ions concentration in the feed wastewater and C is the residual Cu^{+2} ions concentration in the effluent treated wastewater.

4. Results and Discussion

In a process driven by the presence of a swarm of bubbles, like flotation, it is obvious that the interfacial area of the bubbles present in the gas-liquid dispersion is important for its effectiveness. This is related to the amount of gas being held up in the dispersion phase which is regulated by its volumetric flow rate. Figures (3 to 6) show the effect of superficial gas velocity on the residual cupric ion concentration in the top, middle and bottom stages at different frother (ethanol) concentrations (5,10,15,and 20ppm). Figure (7) illustrates that as V_g increased Cu^{+2} ions overall recovery went through a maximum at $V_g \approx 2.3$cm/s and then steadily decreased at higher superficial gas velocities. For 12-in MSTLFLO flotation column, Shi (2008) found that when V_g was greater than 3.0 cm/s, gas holdup reaches beyond 50%. At such a high gas holdup, unstable loop flow occurs because of insufficient quantity of liquid phase and it results in a decrease in separation efficiency. Generally the gas holdups in 12-in column are lower than that in the 4-in column at comparable frother concentrations. So in a column of 4-in, it is expected that beyond $V_g \approx 2.3$cm/s unstable operating conditions exist resulting in a decrease in the removal efficiency. Also these figures indicate that the rate of removal is higher in the top section, this is mainly due to the higher gas holdup in the top section (Shi ,2005).

The effectiveness of flotation mostly depends on the interfacial properties of components in the mixtures to be separated. These interfacial properties can be modified by adding different surface active reagents (surfactants). An ionic surface-active reagent {collector, sodium dodecylsulfate (SDS,$C_{12}H_{25}SO_4Na$)}, which can preferentially concentrate at the solution/vapor interface, was added to the solution. The collector (SDS), have the opposite charge to the ions to be removed (Cu^{+2}) from the solution (the colligend). The colligend is then electrostatically adsorbed at the interface. As gas bubbles rise through the solution, the co-adsorbed colligend ions are removed from the mother solution along with the collector, and report to a foam phase that can be physically removed. Ethanol (frother) is a heteropolar surface-active compound containing a polar group (OH) and a hydrocarbon radical, capable of adsorbing in the water–air interface. The frother molecules are arranged at the air–water interface such that the hydrophilic or polar groups are oriented into the water phase and the hydrophobic or nonpolar hydrocarbon chain in the air phase. In fact, the frother creates conditions for froth formation. The flotation froth is a three-phase system. The frother concentrates at the interface of water and air bubbles, forming an envelope around the bubbles, which prevents them from colliding or touching. Frothers also lower the surface tension of the water. The forces created around the air bubble in the presence of a frother prevent the bubbles from collapsing

(Srdjan,2007). Figure (7) shows that increasing frother concentration increases the cupric ions overall removal efficiency. Increasing frother dosage provides larger gas holdup and therefore increase collisions frequency between bubbles and the adsorbed surfactant (SDS) and counterions (Cu^{+2}) at an air/aqueous solution interface. Increasing the frother dosage affect the removal efficiency to different extents. Figure (7) shows that increasing frother concentration from 5ppm to 10ppm (for $V_g \approx 2.3$cm/s) increases the removal efficiency by ≈10%, while increasing the frother concentration from 10ppm to 20ppm only increases the removal efficiency by 2.5% .

As indicated earlier, the removal efficiency is a function of superficial gas velocity V_g and frother concentration C_f. Consequently, an empirical expression for the overall removel efficiency in terms of V_g and C_f is suggested as follows:

$$RE\% = aC_f^{\,b}V_g^{\,c} \qquad \ldots..\ (2)$$

Where, a, b and care constants; V_g is superficial gas velocity and C_f is frother concentration. STATISTIC software (StatSoft, 2000) was applied to evaluate the empirical constants of equation (2). An implicit nonlinear numerical method (Quasi-Newton) is applied as regression method. Initial values and step sizes are automatically allocated by the software. In this regression, second order (partial) derivatives of the loss function are used to determine iteration steps. Determination constant coefficient, R, is used to quantify the accuracy of regression. Figure (8) is 3D surface plot for the effect of superficial gas velocity and the frother concentration on the overall removal efficiency. The equation representing the system is given as:

$$RE\% = 67.7C_f^{\,0.106}V_g^{\,0.0286} \qquad \ldots..\ (3)$$

The determination coefficient, R = 0.9215. The relation ship between predicted and observed overall removal efficiency is shown in figure (9).

5. Conclusions

The recovery of cupric ions from aqueous solutions by multi-stage loop flotation has been investigated. The following conclusions are drawn:

1. The MSTLFLO approved to be an effective process for the removal of heavy metal ions (Cu^{+2}) from aqueous solutions.
2. An optimum gas flow rate, corresponding to a superficial gas (air) velocity of 2.3cm/s. yields maximum cupric ions removal efficiency. Higher and lower flow rates result in poorer performances.
3. The frother concentration seems to affect the removal efficiency with different extents.
4. The maximum removal efficiency obtained was 94% at 20ppm frother concentration and air superficial velocity of 2.3cm/s.
5. An empirical correlation was proposed to simulate the performance of the MSTLFLO column and succeeded to explain the performance with 95% confidence level.

Nomenclature:

C	Residual Cu^{+2} ions concentration, ppm
C_f	Frother Concentration, ppm
C_0	Initial Cu^{+2} ions concentration, ppm
MSTLFLO	Multi-Stage Loop Flotation
R	Correlation

	coefficient
RE%	Overall removal efficiency
V_g	Superficial gas velocity, cm/s

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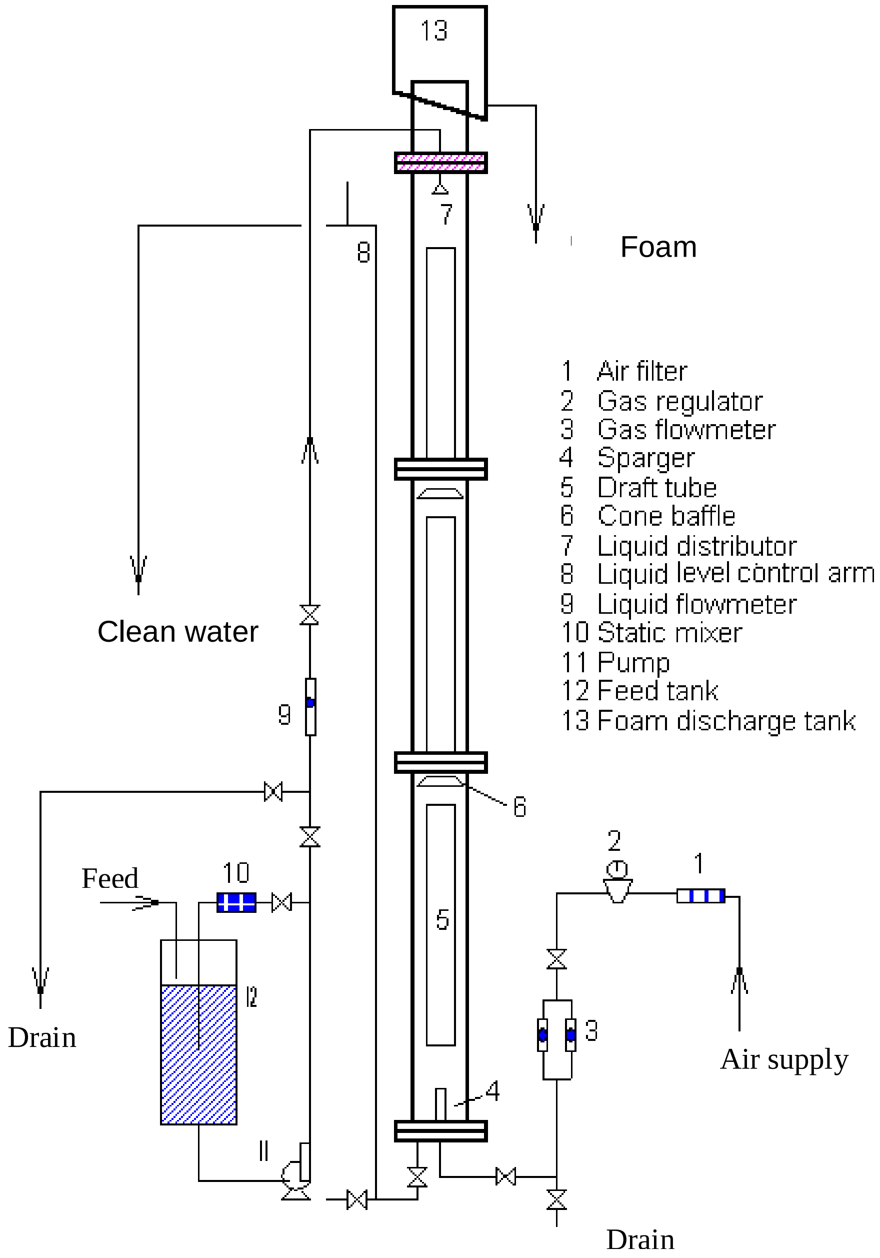

Figure (1) The experimental set-up

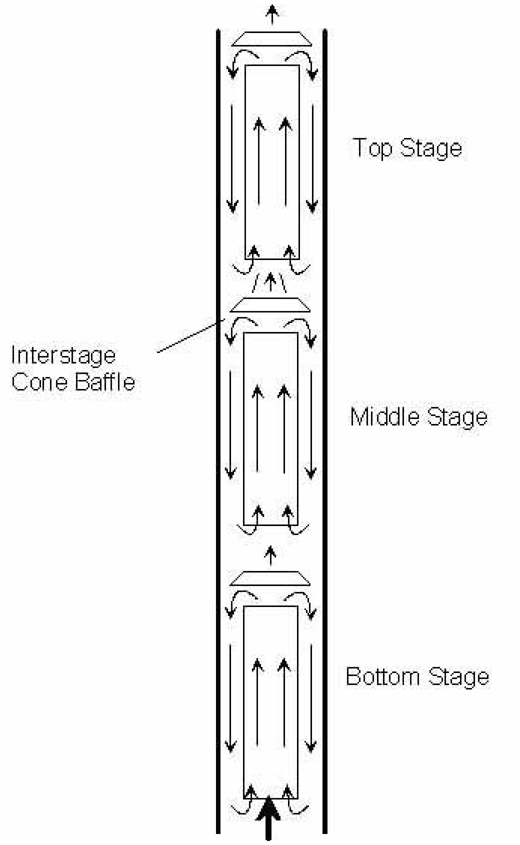

Figure (2) Geometry of MSTLFLO flotation column

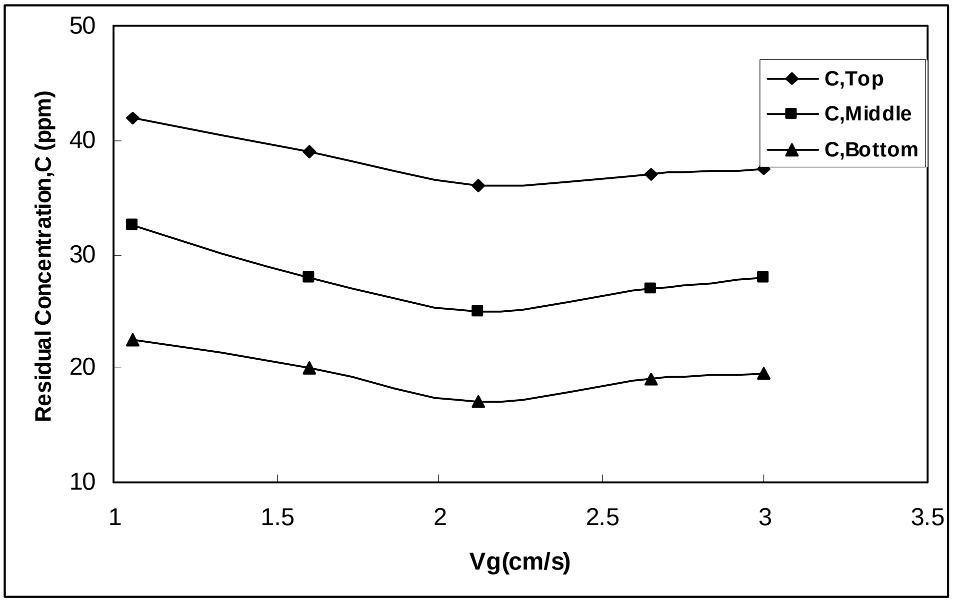

Figure (3) Effect of superficial gas velocity on the residual cupric concentration for different column stages and Cf =5ppm

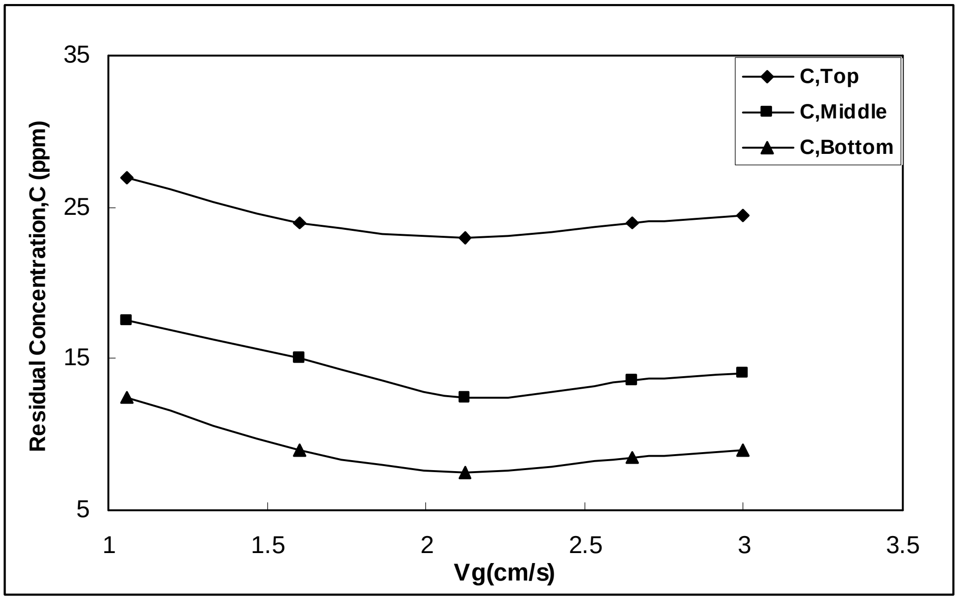

Figure (4) Effect of superficial gas velocity on the residual cupric concentration for different column stages and Cf =10ppm

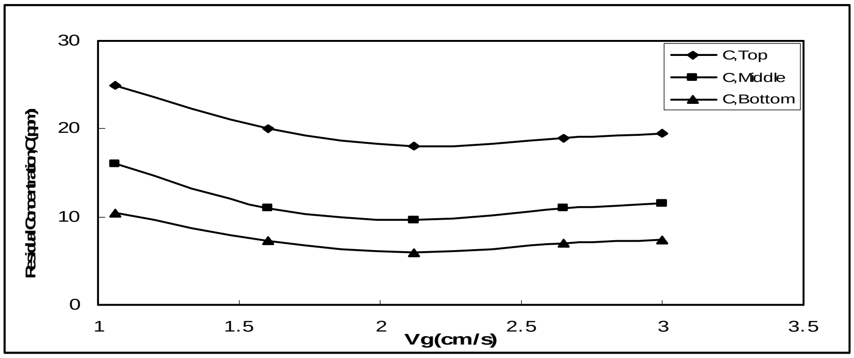

Figure (5) Effect of superficial gas velocity on the residual cupric concentration for different column stages and Cf =15ppm

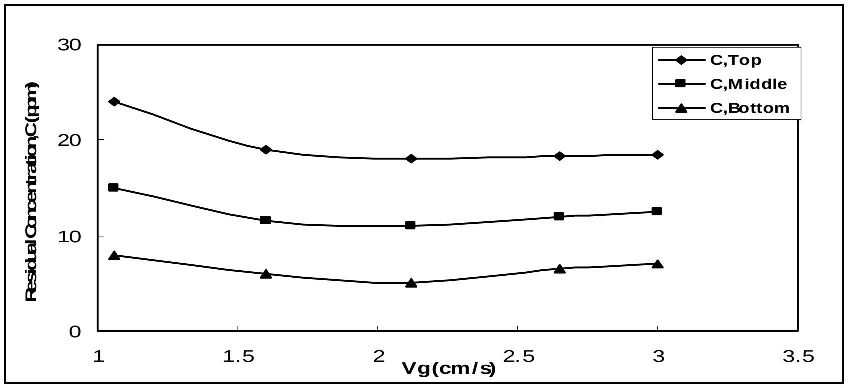

Figure (6) Effect of superficial gas velocity on the residual cupric concentration for different column stages and Cf =20ppm

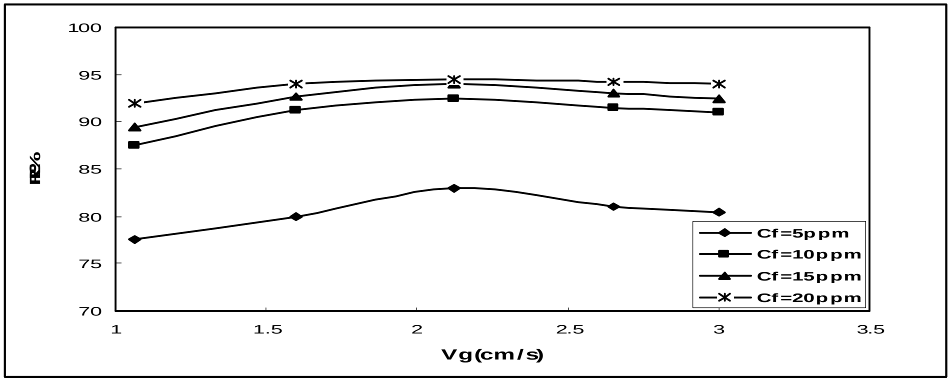

Figure (7) Effect of superficial gas velocity on the overall removal efficiency of cupric ions at different frother concentration

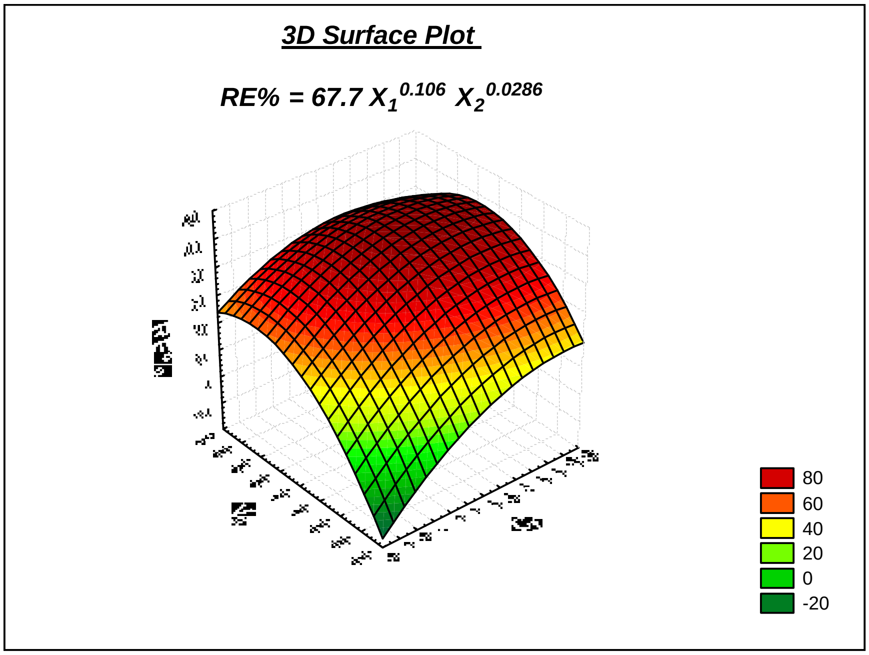

Figure (8) 3D surface plot representing the relation ship between the overall removal efficiency, frother concentration and superficial gas velocity

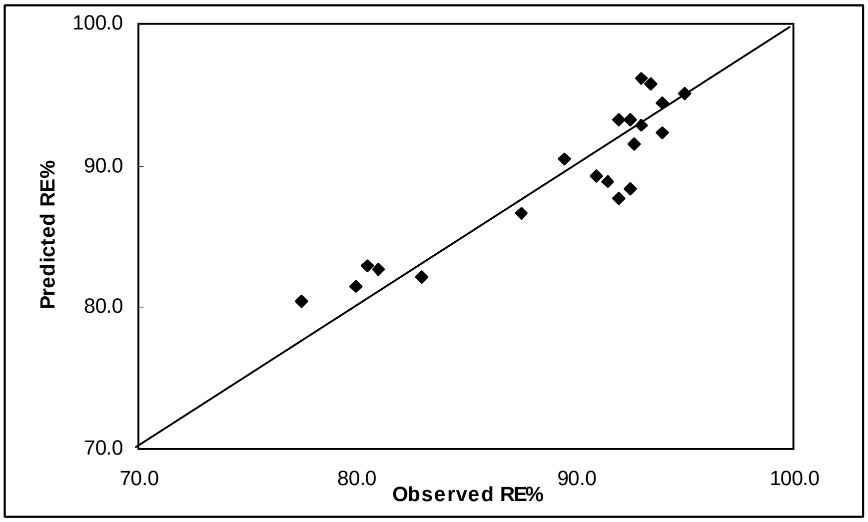

Figure (9) Predicted vs. observed cupric ions overall removal efficiency