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Extraction of copper ions from aqueous solution by naphthenic acids in a reciprocating batch reactor

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The present work is to study the main factors affecting the rate of extraction of copper ions from aqueous copper sulphate solution by a solution of naphthenic acids in kerosene using an oscillating perforated disc in a batch reactor, as a mean for enhancing the rate of mass transfer. The variables studied were, amplitude and frequency of oscillation (vibration intensity = $4A_mf$), initial concentration of copper ions, volume phase ratio (aqueous/organic), disc diameter, hole diameter, hole number per unit area and solution temperature. The activation energy of the reaction was found to be 1600 cal/mol which indicates that the reaction is diffusion-controlled . An overall correlation for the extraction of copper in terms of mass transfer coefficient was obtained in the form: $Sh = 6.05\ Re^{0.8}\ Sc^{0.33}\ (d/d_h)^{-0.4}$ with an average deviation of 15.5%. The maximum percent recovery of copper was found to be 58%. The technical importance of the present work in the area of copper purification and extraction from low grade copper ores and waste streams resulting from metal finishing industry is pointed out.

تتناول هذه الدراسه العوامل التي تؤثر علي حركية تفاعل استخلاص ايونات النحاس من محلوله المائي بواسطة الاحماض النفثينيه ؛ وذلك باستخدام قرص ثوثقوب يتحرك حركة ترددية كوسيله لزيادة معدل استخلاص ايونات النحاس. والمتغيرات التي تمت دراسة تأثيرها على معدل إنتقال الماده من الوسط المائي (كبريتات النحاس) الي الوسط العضوي (حامض النافثينيك) هي :شدة الإهتزاز ؛ تركيز ايون النحاس ؛ سعة الإهتزاز؛ النسبه ما بين الطور المائي و الطور العضوى ؛درجة الحراره ؛ قطر قرص التقليب ؛ قطر الثقوب ؛ عدد الثقوب في قرص التقليب و قد وجد أن قيمة طاقة التنشيط لعملية الإستخلاص هي ١٦٠٠ سعرحرارى/جرام جزيئى ؛ وهذا يدل أن عملية الأنتشار هي العامل المتحكم فى عملية الإستخلاص و ليس التفاعل الكيميائي بين أيونات النحاس و الاحماض النفثينيه. و قد وجد ان اعلى نسبة استخلاص تم الحصول عليها هىفى حدود ٥٨% و من ناحية اخرى فقد عولجت النتائج العمليه التي تم الحصول عليها رياضيا ووضعت في صورة أربع مجموعات عديمة الأبعاد ؛ ووضعت معادله عامة لعملية إنتقال الماده الكلي علي الصوره الأتيه:
$Sh = 6.05\ Re^{0.81}\ Sc^{0.33}\ (d/dh)^{-0.4}$ وهذه المعادله تربط النتائج في حدود ١٥,٥%. وهذه المعادلة يمكن استخدامها فى تصميم وتشغيل المفاعل المقترح فى الصناعة و لقد تم تفسير النتائج التي تم التوصل اليها تم التوصل اليها في ضؤ نظرية انتقال الماده.ايضا تم توضيح الأهميه التطبيقيه لهذا البحث التى تقع في مجال تنقية النحاس أثناء عملية استخلاصه من خامات النحاس ذات الرتبه المنخفضه وكذلك في عمليات إستخلاص النحاس من مخلفات مصانع تشطيب المعادن.

Keywords Extraction of copper, Naphthenic acids, Reciprocating contactor, Wastewater treatment, Mass transfer

1. Introduction

An extremely important development lies in the application of the technique of liquid extraction to metallurgical processes, of these is the extraction of copper from acid leach liquors and subsequent deposition of copper by electro- winning [1]. In many of these processes, some form of chemical complex is formed between the solute and the solvent so the kinetics of the process become important. The extraction operation may be either physical or chemical operation. The chemical operations have been classified by Hanson [2] as follows:

(a) those involving cation exchange, for example, the extraction of metals by carboxylic acids.
(b) those involving anion exchange, such as the extraction of anions involving a metal with amines.
(c) those involving the formation of an additive compound, for example, extraction with neutral organo-phosphorus compounds.

The extraction of metals using carboxylic acids as extracting agents can be most simply described by the following equilibrium [3].

$$Me^{n+} + nRCOOH = (RCOO)_n\ Me + nH^+ \quad (1)$$

Aqueous organic organic aqueous,

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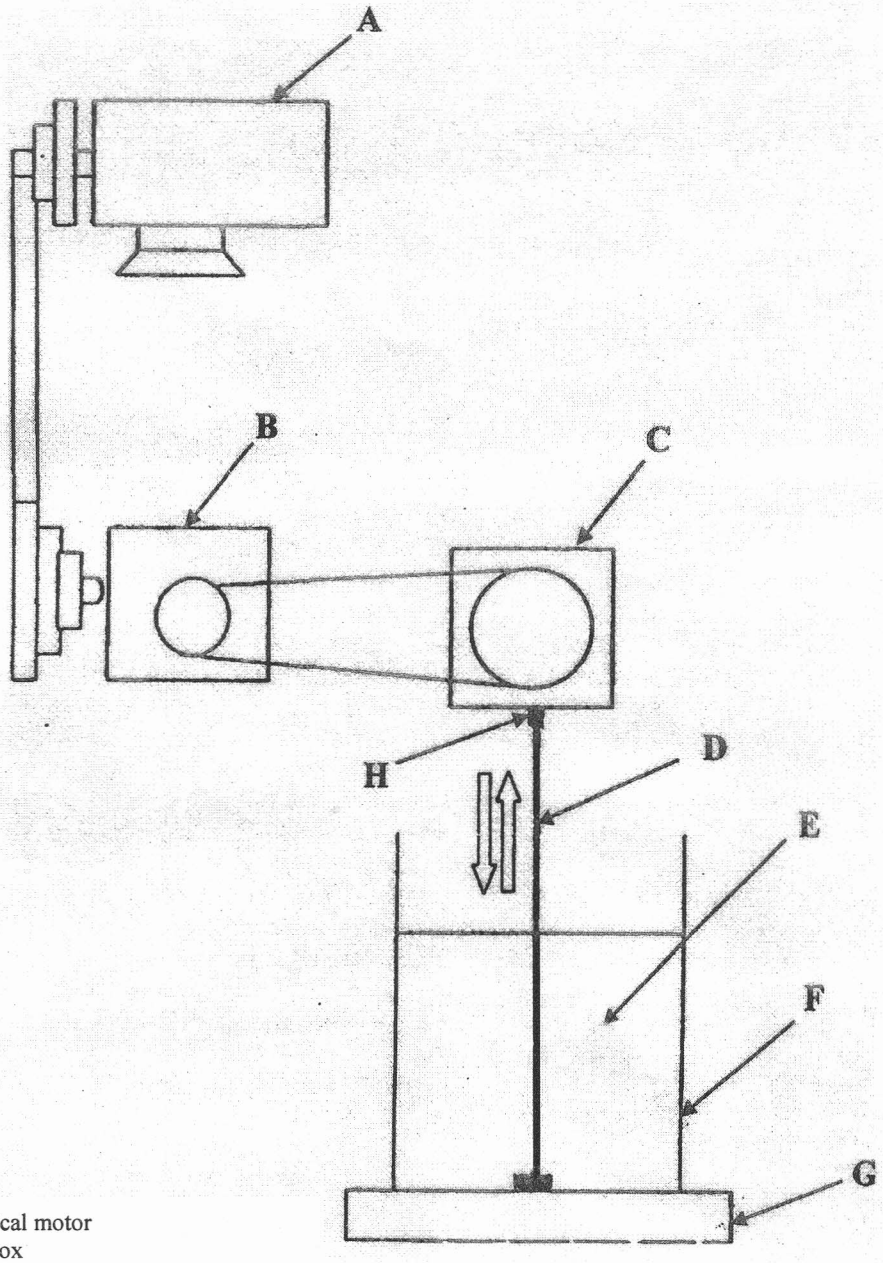
where "*Me*" stands for n-valent metal. This equation shows that carboxylic acids behave as cation exchangers and are suitable for extracting metals from aqueous solutions. The above equation is actually an oversimplification, but it serves to indicate the pH dependence of the process. It was found that the extraction of metals depends largely on the pH of the solution and that it was necessary to raise the pH almost to the point at which metals hydroxides were precipitated before appreciable amounts of the metals could be extracted such as the work shown by Fletcher and Wilson [4], who used naphthenic acid as a cation exchanger for extracting different metal ions such as Cu^{++}, Ni^{++}, Zn^{++}, Fe^{+++}, etc. from aqueous solutions. It was found that selective extraction of the heavy metal ion is possible by adjusting the pH of the solution, also the acid has the advantage of being readily available and can be regenerated, and its great stability makes it suitable for use in continuous extraction processes.

Oprea et al. [3] studied the extraction of Cu ions from aqueous $CuCl_2$ solutions with a solution of 37.5% naphthenic acid in kerosene, in the presence of a sufficient amount of NaOH to raise the pH of the exhausted aqueous solution from 3 to 6.5. The extracted Cu ions were recovered from the extract by addition of HCl. Vernon et al. [5]. investigated the characteristics of the flotation-extraction processes for non-ferrous metal recovery by using an aqueous Cu–containing solution and naphthenic acid as a model system.

Chirkst et al. [6] extracted Cu^{++} ions from dilute aqueous solutions with naphthenic acids in decane. The dependence of the distribution ratio on the pH of the equilibrium aqueous phase was determined, and the extraction equilibrium constant and Gibbs energy were calculated.

Grishchenko et al. [7] found that in the extraction of copper and cobalt by kerosene is formed, as well as a small quantity of basic salt, while in extraction with an excess of extraction agent, only a neutral salt is formed. In the extraction of nickel by naphthenic acid a mixture of basic and neutral salts is formed. Only at a fourfold excess of extraction agent is a neutral salt of nickel naphthenate formed. Velea et al. [8] found that the extraction with naphthenic acids can be used as a method of treating sulfate solutions with pH less than 7 or ammonia solutions with pH greater than 7 containing Ni, Co and Cu ions. The extraction efficiency of Ni, Co and Cu ions by naphthenic acids in ammonia solution is as follows: Ni > Cu> Co. The effect of nitrogen sparging on the rate of mass transfer in the extraction of copper from aqueous solution by a kerosene solution of naphthenic acids was studied by Fadali [9], where many variables were investigated such as, nitrogen flow rate, copper ion concentration, and extraction temperature. It was found that the mass transfer coefficient of copper extraction was related to the gas flow rate (V) by the equation: K=constant (V). The effect of temperature on the mass transfer coefficient was found to obey Arrhenius equation with an activation energy of 2875 calories/mole which confirmed the fact that the reaction is diffusion-controlled.

Vibration or reciprocation has been found by many authors to be a very effective tool for enhancing the rate of mass transfer to a great extent, enhancement ratio ranging from2.5 to 10 times compared to the value without pulsation was reported [10-12].In line with this direction the aim of the present work is to study the factors affecting the extraction of copper ion from a synthetic solution of copper sulphate using naphthenic acids (carboxylic acid) as extracting agent in a batch reactor provided with a reciprocating perforated disc as a tool for enhancing the rate of mass transfer. Variables studied were frequency and amplitude of pulsation (pulsation or vibration intensity), copper ion solution concentration



A. Electrical motor
B. Gear box
C. Mechanical vibrator
D. Teflon isolated stem
E. Perforated plexiglass disc
F. Test column
G. Wooden base
H. Teflon sleeve

Fig. 1. Experimental apparatus.

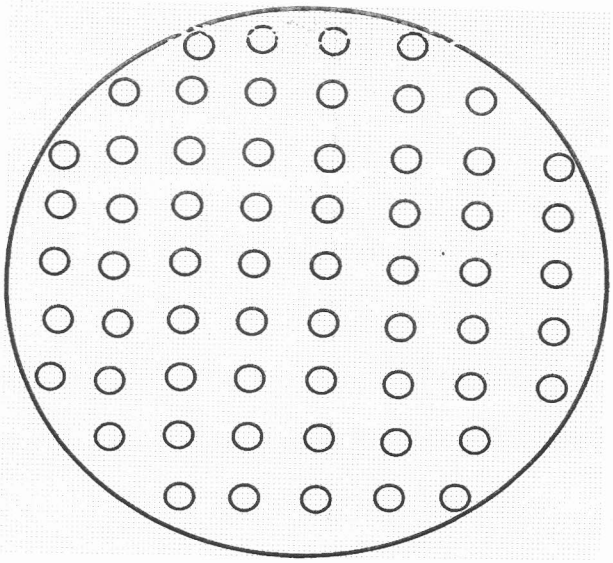


Fig. 2. Perforated Plexiglass disc

2.5. Analysis

The samples were analyzed by iodometry [13], where potassium iodide was added to the sample and the librated iodine was titrated with standard 0.1 M sodium thiosulphate solution.

3. Results and discussions

For the simple batch reactor used in the present work, the kinetics of the extraction can be represented by the following eq. (14, 15)

$$V_s \ln (C_o\text{-}Ce)/(C\text{-}Ce) = KAt\,, \qquad (2)$$

where K is the mass transfer coefficient, C_o, C_e and C: are the initial, equilibrium and concentration of Cu^{+2} at any time t, V_s is the solution volume, and A is the active interfacial area between the aqueous and the organic phases. In view of the difficulty of determining the interfacial area, so the volumetric mass transfer coefficient K' ($K'=KA$) was used instead of K accordingly eq. (2) becomes.

$$V_s \ln (C_o\text{-}Ce)/(C\text{-}Ce) = K't\,. \qquad (3)$$

The volumetric mass transfer coefficient was obtained under different conditions by plotting $\ln (C_o\text{-}Ce)/(C\text{-}Ce)$ Vs t as shown in fig. 3, the slope of the resulting straight line is K'/V_s from which K' can be calculated.

3.1. Effect of amplitude, frequency and vibration intensity on the rate of mass transfer

Figs. 4, 5 show that the volumetric mass transfer coefficient increases with increasing the amplitude, frequency and vibration intensity respectively.The increase in the rate of mass transfer with increasing amplitude, frequency and vibration intensity (V_i=4A_mf), may be ascribed to the fact that increasing the amplitude and frequency of oscillation increase the degree of mixing between the two immiscible phases. The increase in the degree of mixing and the subsequent enhancement in the rate of mass transfer may be explained as follows:

(i) disc reciprocation induces oscillatory flow in the form of large recirculating eddies [16] between the two phases which reduces the thickness of the diffusion layer at the interface between the organic phase and the aqueous phase with consequent increase in the rate of mass transfer between the two phases..

(ii) disc reciprocation induces a jetting effect through the holes of the disc with a consequent generation of small scale high frequency eddies [17] which enhances the rate of mass transfer via: (a) decreasing the diffusion layer thickness at the interface between the organic and aqueous phases.

(b) increasing internal circulation inside the droplets by virtue of the high shear stress exerted by the eddies on the droplets [18].

(c) increasing the surface renewal effects through repeated droplets breakdown and coalescence [18].

(iii) Also higher rates of mass transfer can evidently stem from the random variation of interfacial tension at the interface which result from local concentration variations as mass transfer occurs, and so depend partially on the rate of change of interfacial tension, with solute concentration. The instability which develops causes ripples and roll cells which create circulation between the surface and the bulk liquid. This surface tension driven flow is known as the Marangoni effect [19].

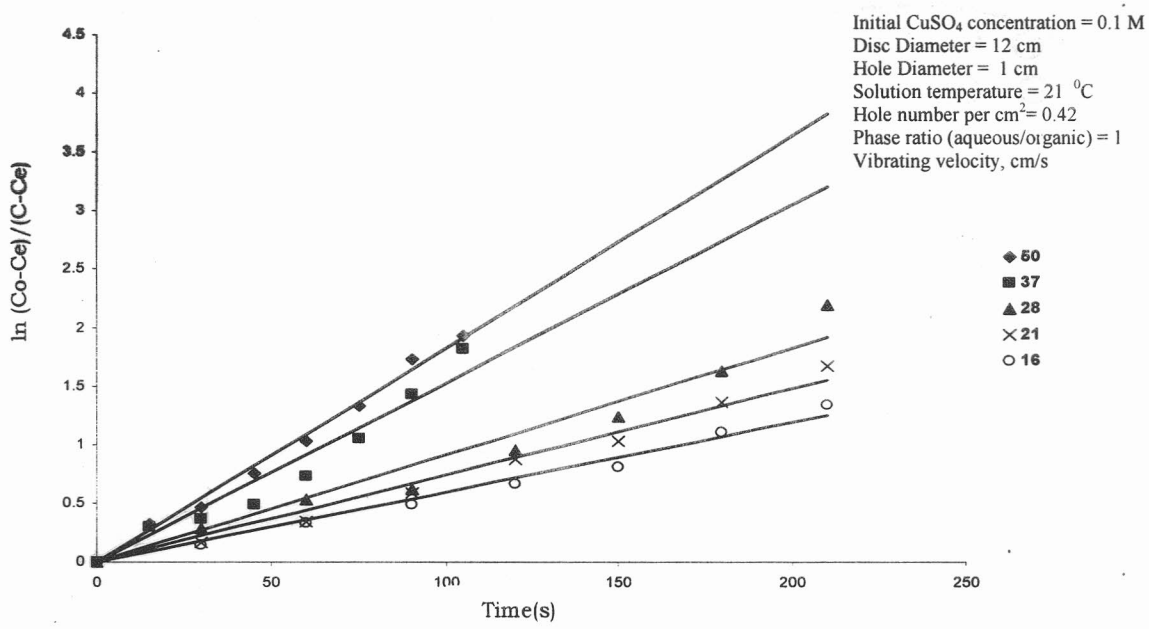


Fig. 3. Plot of ln (C_o-C_e) / $(C-C_e)$ Vs time at different vibrating velocities.

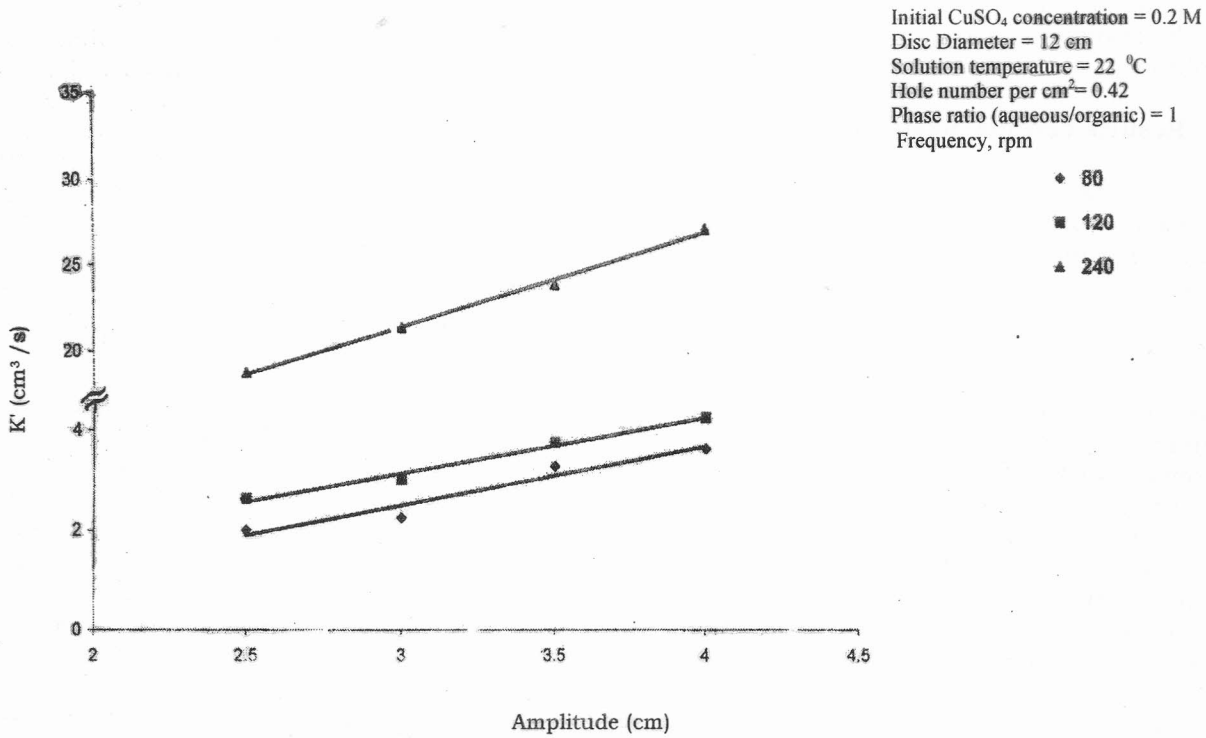


Fig. 4. Plot of volumetric mass transfer coefficient Vs amplitude at different frequencies.

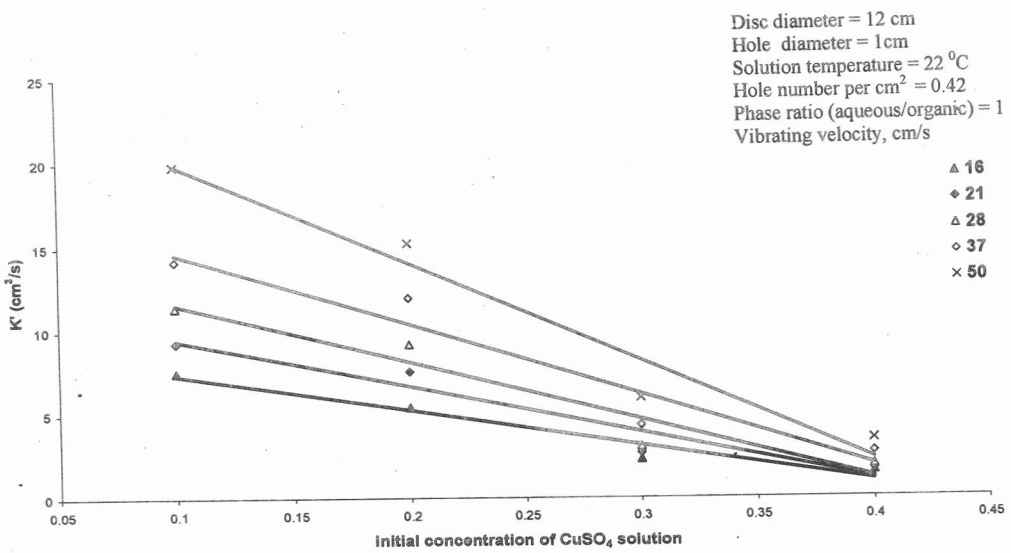


Fig. 5. Plot of volumetric mass transfer coefficient Vs initial $CuSO_4$ solution concentrations at different vibrating in velocity.

3.2. Effect of Cu^{++} concentration on the rate of mass transfer

Fig. 6 shows that for a given vibrating velocity the volumetric mass transfer coefficient decreases with increasing the copper ions concentration, this may be ascribed to the fact that as copper ions concentration increases, the solution viscosity increases and the ions diffusivity decreases, accordingly the mass transfer coefficient decreases.

Fig. 7 shows that the percentage recovery of Cu^{++} decreases by increasing the initial concentration of $CuSO_4$ solution, the percentage recovery ranges from 22% to 58% at 0.4M and 0.1M $CuSO_4$ respectively.

3.3. Effect of volume phase ratio on the volumetric mass transfer coefficient

Fig. 8 shows that at given vibrating intensity the rate of mass transfer decreases with increasing the volume phase ratio of aqueous to organic-phase, which may be attributed to the decrease in the population of organic droplets which are available for copper extraction from the aqueous phase, in other words the total available interfacial area decreases with decreasing the volume of the organic phase.

3.4. Effect of disc diameter, hole diameter and hole number per unit area on the rate of mass transfer

From figs. 9-11 it is clear that the rate of mass transfer increases with decreasing disc diameter, increasing hole diameter and increasing the number of holes per unit area respectively. The increase in rate of extraction with increasing the hole diameter contradicts expectation which assume that the intensity of jetting effect should increase with decreasing hole diameter. The increase in the rate of mass transfer with decreasing disc diameter and increasing both hole diameter and hole number as shown in figs. 9-11 seems to be related to the effect of open area of the disc on the rate of mass transfer. It is probable that as the open area increases, large scale eddies resulting from oscillatory flow circulate freely in the agitated vessel and improve the mixing conditions in the agitated vessel. If the open area is decreased by increasing the disc diameter and decreasing hole diameter and number, the chance of eddy damping by friction with solid disc surface increases at the expense of good mixing conditions, accordingly the rate of mass transfer in the agitated vessel decreases.

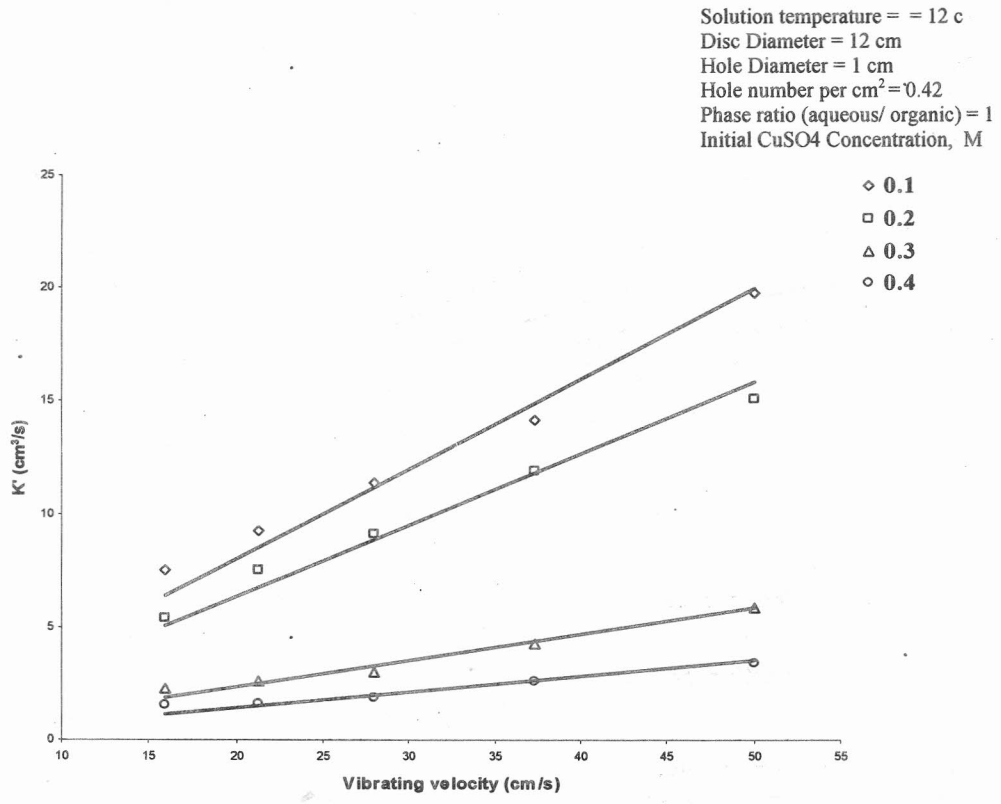


Fig. 6. Plot of volumetric mass transfer coefficient Vs vibrating velocity at different initial CuSO4 concentration.

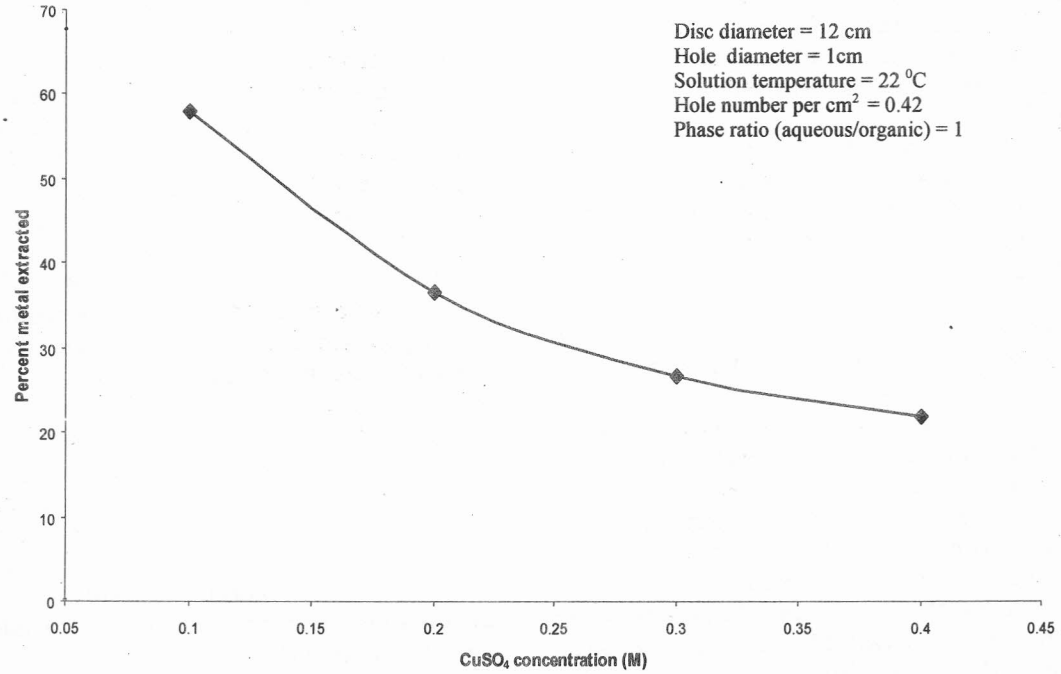


Fig. 7. Percent copper extracted at different initial CuSO4 solution concentrations.

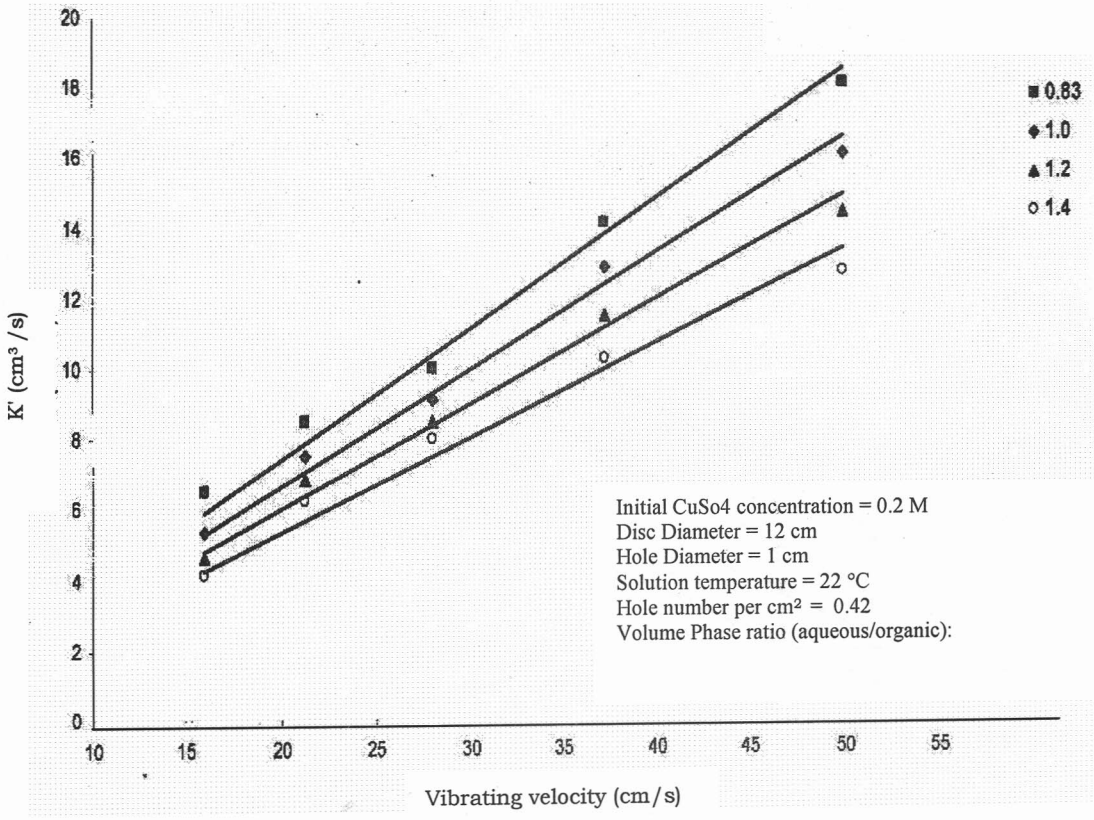


Fig. 8. plot of volumetric mass transfer coefficient Vs vibrating velocity at different disc diameters.

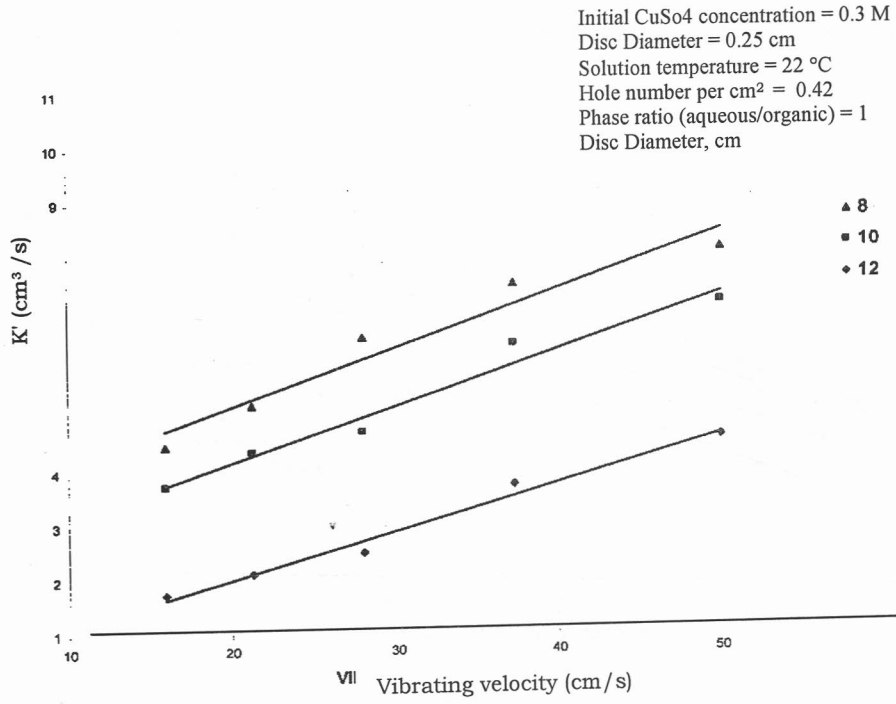


Fig. 9. Plot of volumetric mass transfer coefficient Vs vibrating velocity at different disc diameters.

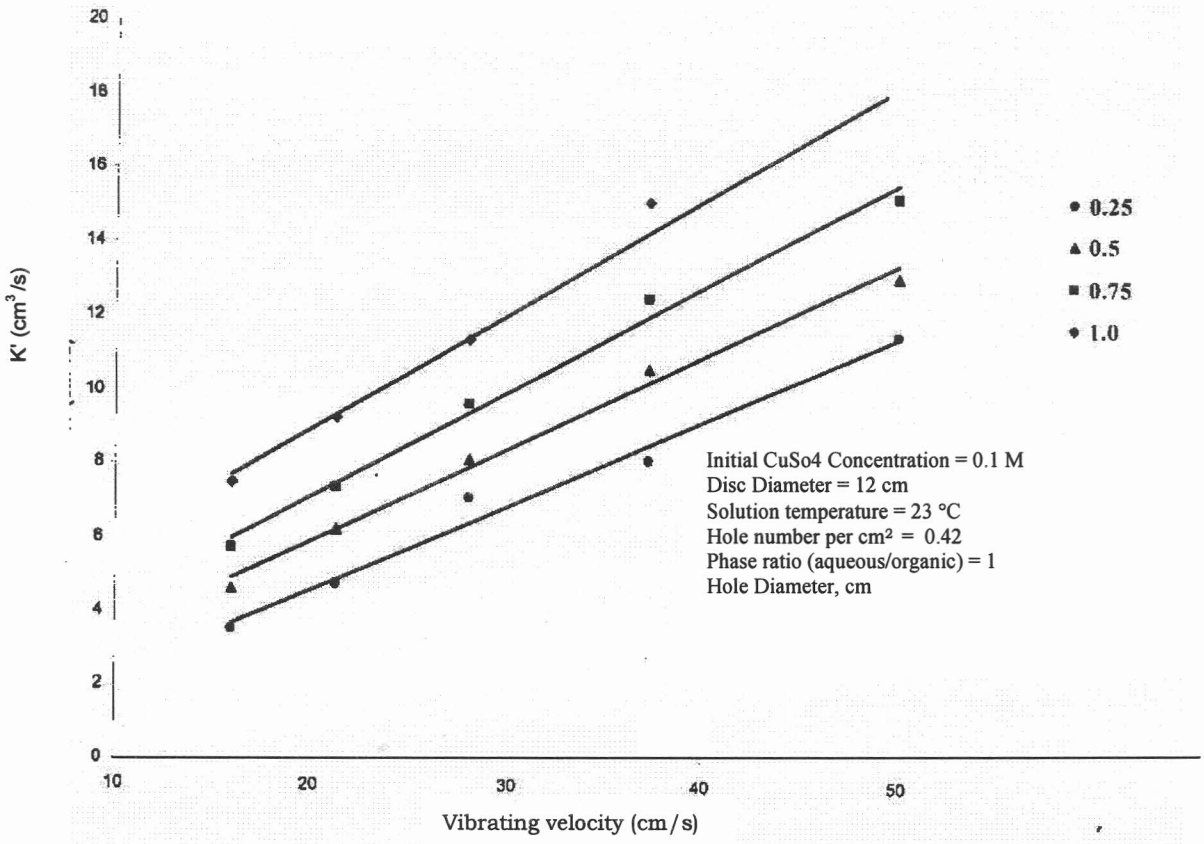


Fig.10. Plot of volumetric mass transfer coefficient Vs vibrating velocity at different hole diameters.

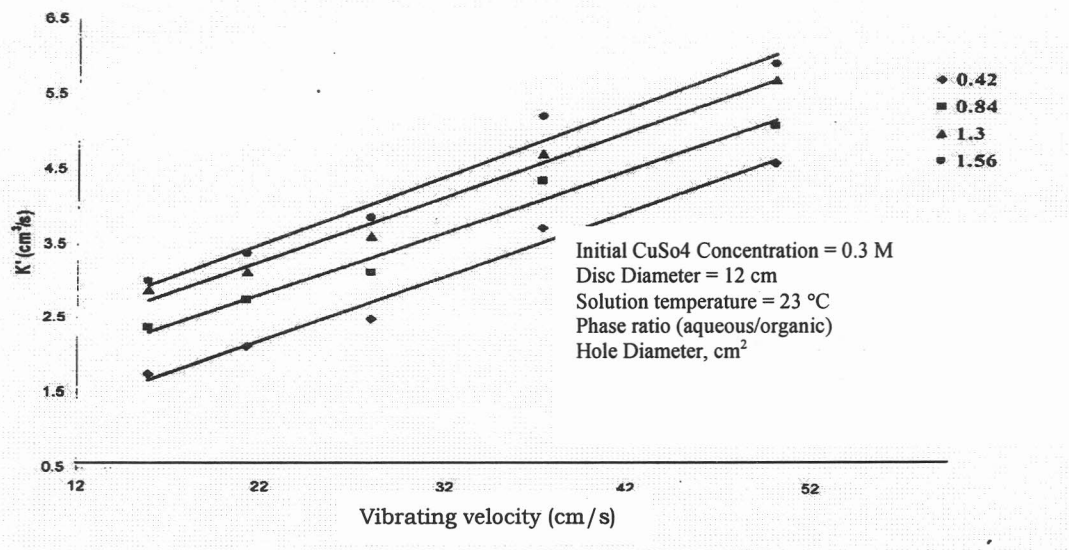


Fig.11. Plot of volumetric mass transfer coefficient Vs vibrating velocity at different hole numbers per cm².

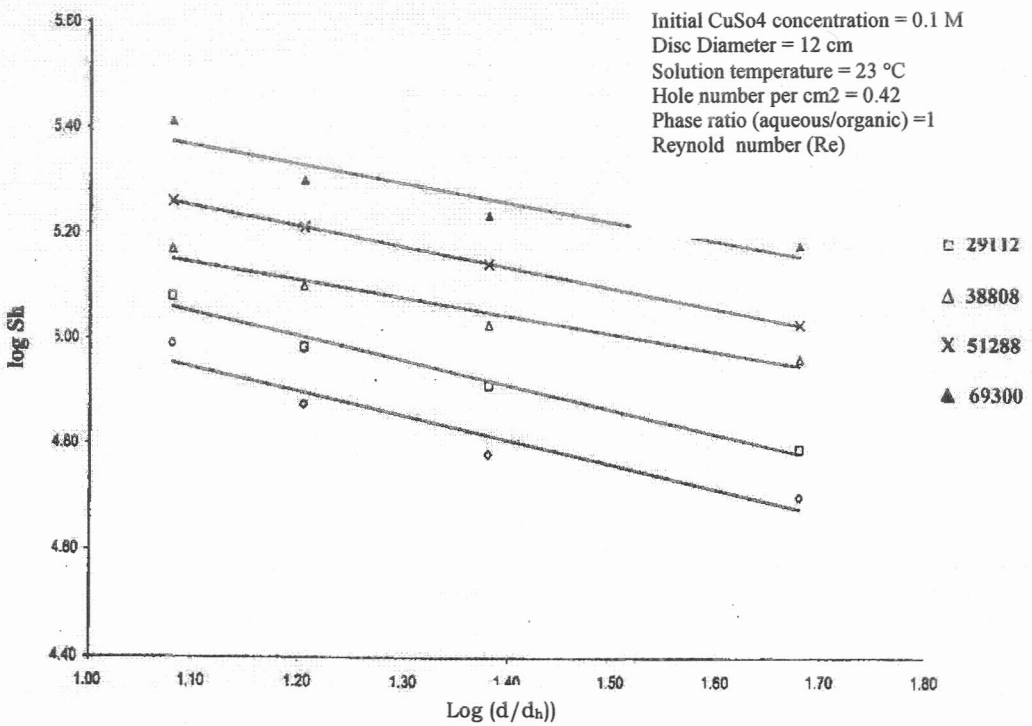


Fig.15. Plot of log Sh Vs log (d/dh) at different Sc.

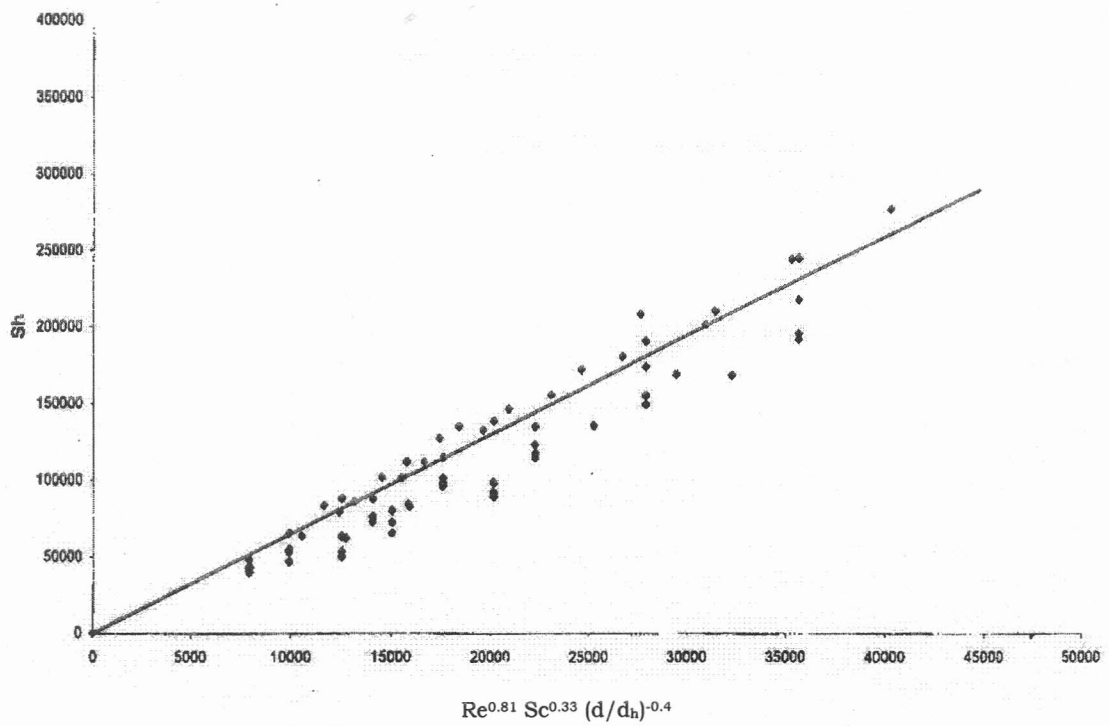


Fig.16. Overall correlation for the recovery of copper from equeous solution with naphthenic acid in kerosene using pulsating perforated disc in a batch reactor.

3.6. Overall mass transfer correlation

Dimensional analysis was used to correlate the present data aided by the aforementioned experimental results. The mass transfer coefficient can be related to other variables by the functional equation.

$$Sh = a\, Re^{a}\, Sc^{\beta}\, (d/d_h)^{\gamma}$$

Following previous mass transfer studies where the transfer area is not known [21, 22], the volumetric mass transfer coefficient rather

rate of copper extraction decreases with increasing copper ion concentration, volume phase ratio (aqueous/organic) and disc diameter. The activation energy of the extraction process was evaluated and found to be equal to 1.6 kcal/mol denoting diffusion controlled process. The data were correlated by the obtained from low grade and recovery of copper from effluents generated from processes such as and a dimensionless equation $Sh = 6.05\, Re^{0.81}\, Sc^{0.33}\, (d/d_h)^{-0.4}$.

This method can find many applications such as purification of leach liquors obtained