Removal Kinetic of Fine lead Particles from Wastewater of Battery Manufacturing Plants

Ahmed Hasan Abdul-Jabbar

University of Anbar -Collage of Science.

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ABSTRACT

Removal of heavy metals from water and wastewater has received a great deal of attention. Froth flotation technique is one of the most technologies being used for treatment of polluted water, where it considered low cost process than others. This study records lab scale experiments to test efficiency of multistage froth flotation column in removing a heavy metal, (Pb fine particles less than 45 µm) from wastewater of battery industry. Solutions concentration of Pb (100ppm) was prepared and passed through flotation column. The removal efficiency was quite high for Pb ranging from 62.4-96.3% and maximum removal occurred at frother concentration (20 ppm) and superfacial gas velocity (4 cm/sec), where caprylic acid and hexanol are used as frother in this study. Attempts made to analyze the kinetic behavior of the process indicate that it follows the first-order classical rate equation for the kinetic of froth flotation process. In the proposed equation, values of the constants correlation coefficient (R) and kinetic flotation constant (k), evaluated from the experimental results then (k) related to the frother dosages and superfacial gas velocity.

Introduction

Removal of heavy metals from industrial wastewater is of primary importance because they are not only causing contamination of water bodies but are also toxic to many life forms. Industrial processes generate wastewater containing heavy metal contaminants. Since most of heavy metals are non-degradable into non-toxic end products, their concentrations must be reduced to acceptable levels before discharging them into environment. Otherwise these could pose threats to public health and/or affect the aesthetic quality of potable water. According to World Health Organization (WHO) the metals of most immediate concern are chromium, zinc, iron, mercury and lead[1].Battery industry processing sector is highly polluting sector utilizes variety of chemicals. Battery industry wastewater is highly polluted in terms of COD, TSS, Pb, Cr and Zn.

The value of these parameters is very high as compared to the values in National Environment Quality Standards (NEQS)[2].In advanced countries, removal of heavy metals in wastewater in normally achieved by advance technologies such as ion exchange, chemical precipitation, ultra filtration, or electrochemical deposition do not seem to be economically feasible for such industries because of their relatively high costs.

Therefore, there is a need to look into alternatives to investigate a low-cost method, which is effective and economic, and can be used by such industries. To overcome this difficulty there is strong need to develop economical froth flotation process, which can be used in developing countries. Previous removal methods were for heavy metals (Pb,Ag, Au, Co & Ni) with economical materials [3].

Flotation is a term commonly used for several different processes involving physical as well as chemical interactions between the solid surfaces of a substance and dissolved metal pieces. Thus, Flotation in general can be influenced by changes in hydro chemical parameters such as pH and gas and liquid flow rates [4].

The aim of this study was to find out the effectiveness for removal of Pb solid particles in battery industry wastewater. This material has very fine sizes less than 45 µm and is uniform in its physical and chemical properties and easily available.

* Corresponding author at: University of Anbar -Collage of Science, Iraq.E-mail address:

Materials and methods

To perform the experiment, working solution of (100ppm) Pb was prepared by dissolving the respective metal[5]. Experiment was conducted in lab scale multi-stage froth flotation column where installed in Chemical engineering department in the University of Technology . A 10-cm outside diameter Perspex column with 5mm wall thickness was divided into three sections. Each sections is of 70 cm length. The height of column body is 2.25 m, and the effective column volume is about 17.7 liter, which is shown schematically in Figure (1). A 50 cm long draft plastic tube of 6 cm outside diameter and 3mm wall thickness is installed concentrically in each section. These draft tubes are serving as stages. Between two adjacent draft-tubes, there is a cone baffle. 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, which facilitates a net downward flow of liquid while prevents gas by-pass to the outside of draft tube in the upper stage. A pair of flanges, which are machined from 5 cm thick Plastic flat sheets, connects two adjacent sections. Before starting the experiments the effluent concentration was measured from the bottom stage of column each 4 minutes until reaching the steady state condition when the effluent concentration stop dropping with time where this time was 20 minutes.

Experament setup

A typical three-stage flotation column, as applied to synthetic wastewater treatment, is shown in the Figure (1). Air is introduced into the bottom stage of column, after passing through a regulator, a flow meter and a porous sparger with a mean pore size of 700 μm. A stable simulated wastewater, which was prepared by mixer fixed inside feed tank, is pumped to the top of column via a liquid distributor. Treated clean water leaves the column from the bottom discharge pipe, while foam and o pollutant(Pb fine particles) go out from the top of the column into a foam discharge tank. Three draft tubes are installed concentrically in the column as stages. Each stage can be viewed as a subset of a bubble column similar to that in an air-lift reactor.

The following steps were done in the experimental work:

STEP ONE:

1. The mixer is switched on for 60 min to get homogeneous solution of mixed pollutant.
2. Solution of wastewater is fed from the top of the flotation column by water distributor at liquid velocity(1.34 cm/sec), about (380 l/hr).
3. Air is fed from the bottom of column through the porous sparger at various superfacial gas velocity (1,2,3,4 cm/sec), equals (283,565,848,1130 l/hr), and the dose of frother (Caprylic acid and Hexanol) (5,10,15,20 ppm)[6], is mixed with wastewater feed.
4. The circulation is kept for 20 min. to get good separation and highest values of removal efficiency.
5. Sample is taken from the bottom, middle , and top stage of the flotation column, where operation conditions with respect of superfacial gas velocity, and frother concentration change at each run.
6. Effluents concentrations are calculated for Pb where solid particles concentration is calculated by gravimetric method.
7. The removal efficiencies are calculated for each stage of pollutant (Pb solid particles) as in the following equation:

$$R.E\% = \frac{C_\circ - C_\infty}{C_\circ} \times 100 \quad \text{..... (1)}$$

STEP TWO:

Majority of the researchers have proposed flotation kinetics to follow a first-order reaction. A classical first-order rate equation, which is being commonly used, is represented as follows[7,8]:

$$-\frac{dC}{dt} = kC^n \quad \text{.................... (2)}$$

In this model a first-order separation was assumed. By integrating equation (2), it can be written as:

$$C - C_\circ = \exp(-kt) \quad \text{.......... (3)}$$

Or in the form :

$$\ln\frac{C}{C_\circ} = -kt \quad \text{...................... (4)}$$

Classical method to find value of flotation constant (k) is plotting ($\ln C/C_\circ$) versus time (t), but in this research it could be used another technique to find value of *k* to avoid tedious calculation for many runs of experiments that includes plots of each case. STATISTICA Program (V 6.0) was applied. The procedure “Non-linear estimation”, which allows to analyze the relationship between dependent variable, i.e. C, and independent variable, i.e. and *K*, was used. The program also allows to find the determination coefficient (*R*),where initial concentration of (Pb) is

(100ppm),where the effluent concentration from bottom stage measured at each (4 min) until reaches (20 min) that represent final time at which effluent concentration stops dropping. The following empirical correlation was applied for all cases at different operating condition depending on equation (4):

$C=100\times\exp(-kt)$ ……………… (5)

Results And Discussion

Separation Results

Water/particle slurry is fed into the top stage at a concentration equivalent to 100 ppm in bulk stream. Four concentrations (5.10,15,20 ppm) of caprylic acid and hexanol as a frother are applied. Treated water samples are taken at the bottom, middle and top stage of the column when steady state operating condition is achieved. Figure (2) shows effect of gas velocity on removal efficiency for different stage at Cf =5ppm.it could be observed from figure that removeal efficiency of solid particles of Pb increase with increasing superfacial gas velocity, where maximum removal efficiency obtained at (4 cm/sec) in the bottom stage (76.3%).This is because increasing gas holdup and number of bubbles that attached more amount of very fine particles.

From figures (2 to 5) it could be observed that values of removal efficiencies increase with increasing dose of frother (caprylic acid), where maximum value obtained at (20 ppm) and (4cm/sec) at the bottom stage (96.3%).From figures(6 to 9) it could be observed that removal efficiency increases with increasing both frother concentration and gas velocity in presence of hexanol, but it was less than in case of using caprylic acid , where only (94.3%) removal efficiency obtained , while (96.3%) for caprylic acid in same operating condition (Cf=20ppm and Vg=4cm/sec).This because caprylic acid has longer branched chain than hexanol, where longer branched chains has a greet solubility with wastewater than short one therefore, caprylic acid has a good ability to promote separation than hexanol.This behavior as same as the behavior obtained by (Abduljabbar ,Shiao, Hanapi and Wan)[9,10,11,13] . Generally, addition of frother up to a certain concentration has produced impact on reducing bubble size , because the interfacial surface tension is reduced. Reduced bubble size means reduced bubble rise velocity and consequently the chances of attachment between bubbles and particles will increase.

Generally, a phenomenon of increasing the removal efficiency of Pb particles it could be observed as we get far away from the top of the column, this occur because many reasons , the attachment between small particle and bubbles increases from the bottom stage through in middle stage to top stage, because of obvious changes in surface tension , and aggregation of particles in the collection and frothing zone. That means the amount of fine solid particles decreasing as we get far from the top of the column where frother and air bubbles try as possible as carrying a large number of fine particles to the surface (i.e top stage) and hence concentration of particles decreases and removal efficiency becomes lager in the bottom stage than middle and top stage.

Kinetic of Flotation Results

Kinetic flotation constants for each run are determined using non linear regression by STATISTICA as described before. The determination coefficient, *R*, which quantifies the accuracy of regression model, is also calculated for each case. In general, a correlation is regarded as accurate when *R* is greater than 0.90. The values of *R* are all greater than 98%, indicating the robustness of the rate expression for fine particle removal. Figure (10) shown an example of (k) estimation using STATISTIC software at Vg= 1cm/sec. and Cf=5 ppm

From Table(1) ,it can be seen that kinetic constants increase with Vg and frother concentration, where increasing flotation time leads to increase the chance of attachment between particles and bubbles. When Vg increases from 1.0 cm/s to 4.0 cm/s at 20 ppm frother (caprylic acid) concentration in Pb separations, the values of kinetic constant increases from (0.154089 to 0.222382 1/min), which means that the rates of solid separation are almost increased. This result indicates that at high Vg, not only a better mixing environment is provided but also a faster separation process is achieved.

Empirical Correlations Obtained

From the experimental data, using the non-linear regression estimation, removal constant of pollutant (Pb) is correlated with superfacial gas velocity and frother concentration for both caprylic acid and hexanol. correlation coefficient for equation was estimated and observed-predicted graphs also plotted as shown in Figures (11),(12),(13) and(14). As expected kinetic flotation constant has proportion with each superfacial gas velocity and frother concentration.The following correlation was obtained using the following mathematical formula:

$k=a*(V_g^b)*(C_f^d)$ … (6)

Where a.b.d empirical constants

$k=0.015508*(V_g^{0.122308})*(C_f^{0.69661})$, R= 0.9797 …. (7)

$K1=0.021707*(Vg^{0.936056})*(Cf^{0.190508})$, R= 0.99803 (9)

The flotation column is shown to be an efficient one-step separation process for simultaneous removal of the heavy metals fine particles less than 45 µm. Based on the results of experimental measurements, the following conclusions are drawn :

1. Multistage froth flotation process shows high efficiency in removing fine solids particles (fine lead particles) smaller than 45 µm. Under optimum operating conditions, as much as 96.3%, could be removed.
2. A generalized correlation for kinetic constants has been established in terms of hydrodynamic parameters (frother concentration and superfacial gas velocity).
3. Flotation process could be obeyed to classical first order rate of separation .
4. Frother concentration has an important effect on removal efficiency, where (Caprylic acid) gave higher removal efficiency than (hexanol) at the same concentration 20 ppm .

The gas bubbles generated in the flotation column was relatively small and spherical in the presence of frother, and it helps to carry the fine particles to the upward to lip of flotation column.

Table (1) Results of Kinetic Constant of Flotation and Removal Efficiency of Pb Fine Particles Using Caprylic Acid and Hexanol

BottomStage					
Vg (cm/sec)	**Cf (ppm)**	**R.E%**	**R.E1%**	**K1(1/min)**	**K(1/min)**
1	5	62.4	53.7	0.036036	0.048655
2	5	66.3	63.4	0.053501	0.051336
3	5	72.1	68.6	0.076184	0.058752
4	5	76.3	73.5	0.113815	0.063982
1	10	75.1	71.2	0.036647	0.070739
2	10	76.5	73.5	0.051628	0.072681
3	10	80.1	77.4	0.090775	0.081284
4	10	83.2	80.3	0.126166	0.090444
1	15	89.7	85.7	0.04716	0.107441
2	15	91.0	88.3	0.067105	0.119209
3	15	93.1	91.2	0.102613	0.130330
4	15	94.2	93.1	0.137917	0.146530
1	20	90.3	88.4	0.0481	0.154089
2	20	91.5	89.6	0.069012	0.168952
3	20	94.1	92.5	0.100225	0.191467
4	20	96.3	94.3	0.142807	0.222382

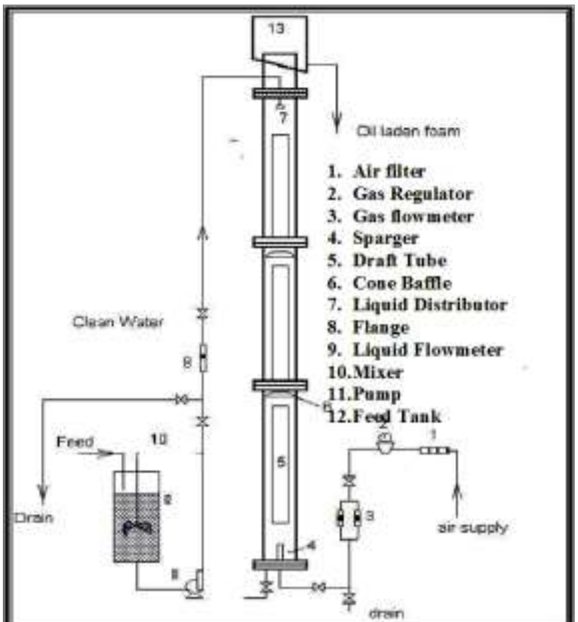

Figure (1) A Multi-Stage Loop-Flow Column

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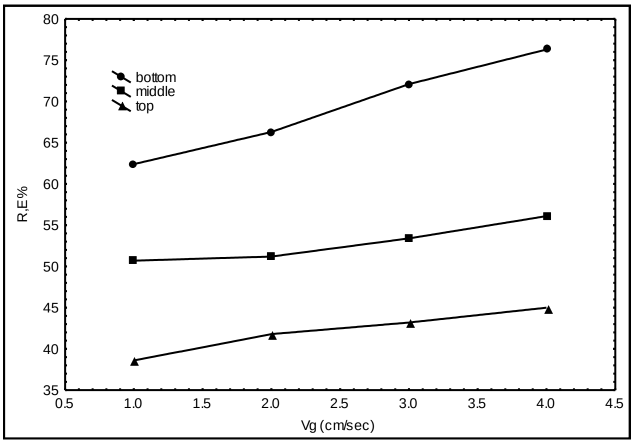

Figure (2) Effect of Gas Velocity on Removal Efficiency for Different Stage at Cf =5ppm of Caprylic acid

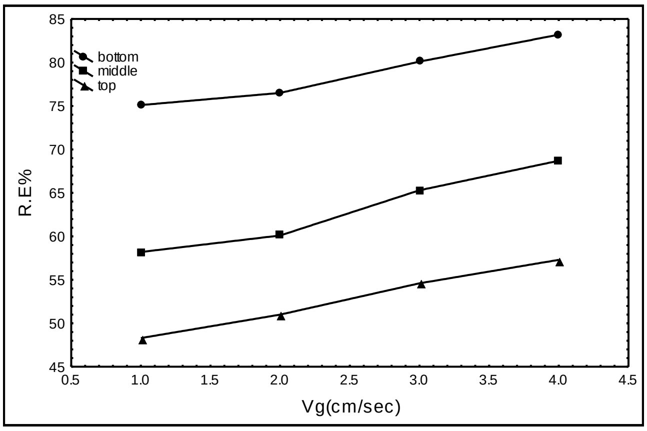

Figure (3) Effect of Gas Velocity on Removal Efficiency for Different Stage at Cf =10ppm of Caprylic acid

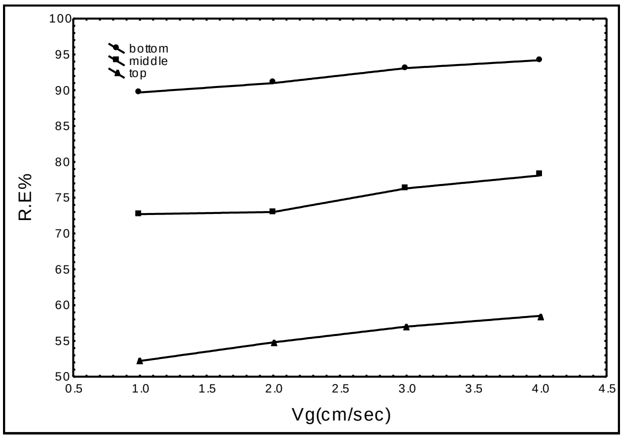

Figure (4) Effect of Gas Velocity on Removal Efficiency for Different Stage at Cf =15ppm of Caprylic acid

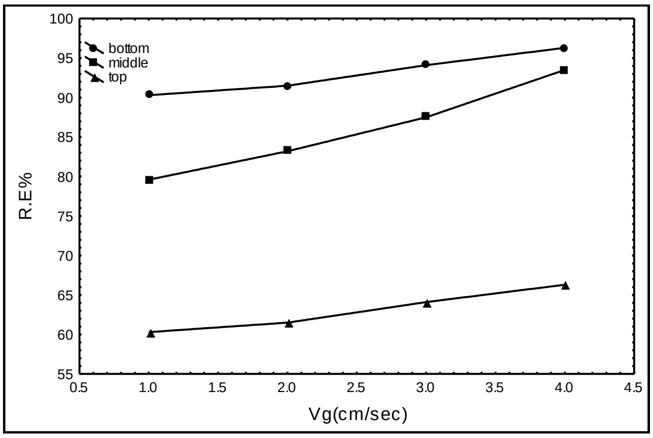

Figure (5) Effect of Gas Velocity on Removal Efficiency for Different Stage at Cf =20ppm of Caprylic acid

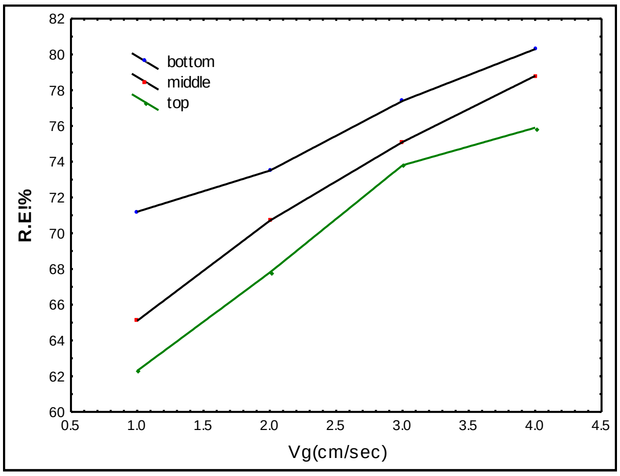

Figure (6) Effect of Gas Velocity on Removal Efficiency for Different Stage at Cf =5ppm of Hexanol

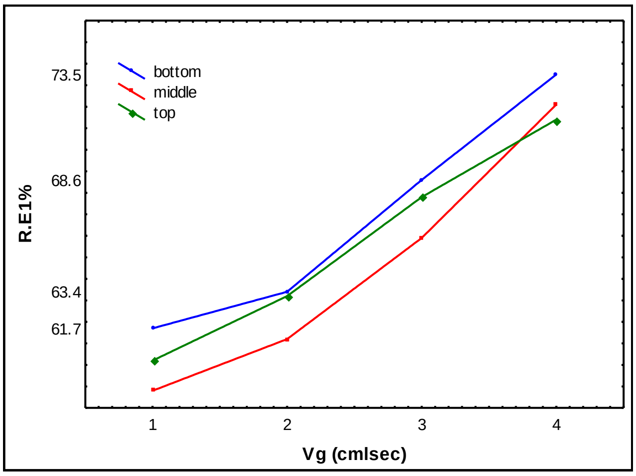

Figure (7) Effect of Gas Velocity on Removal Efficiency for Different Stage at Cf =10ppm of Hexanol

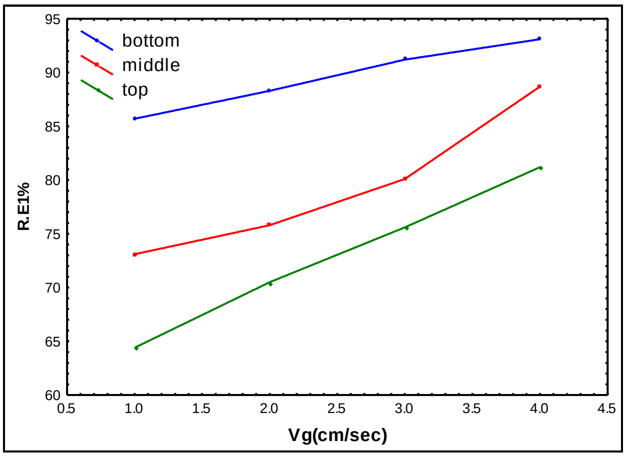

Figure (8) Effect of Gas Velocity on Removal Efficiency for Different Stage at Cf =15ppm of Hexanol

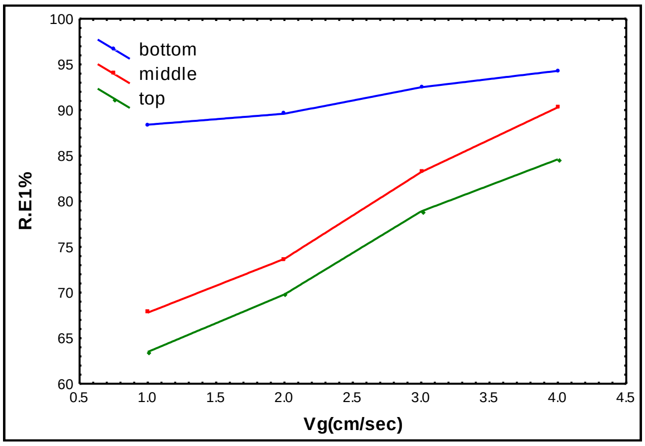

Figure (9) Effect of Gas Velocity on Removal Efficiency for Different Stage at Cf =20ppm of Hexanol

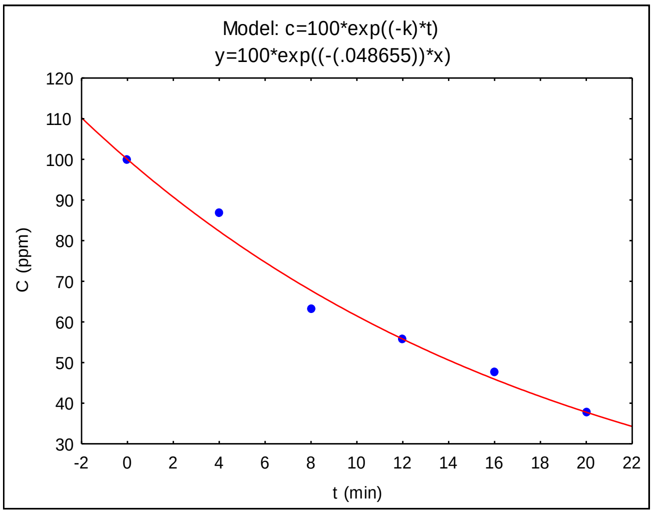

Figure (10) Example of (k) Estimation Using STATISTIC Software at Vg= 1cm/sec. and Cf=5 ppm of Caprlyic Acid

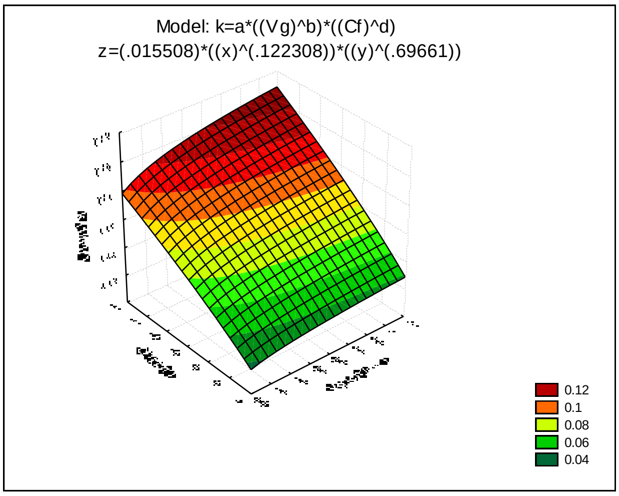

Figure (11) Relation of Kinetic Flotation Constant with Superfacial Gas Velocity and Frother concentration Using Caprylic Acid

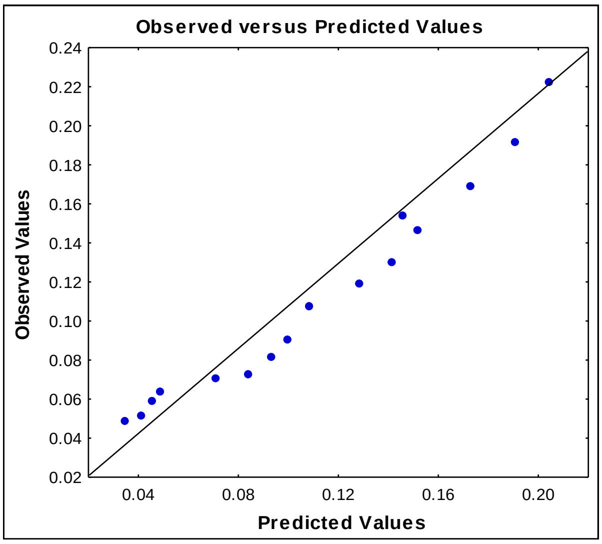

Figure (12) Relationship Between Predicted and Observed Value of Kinetic Constant Using Caprylic Acid

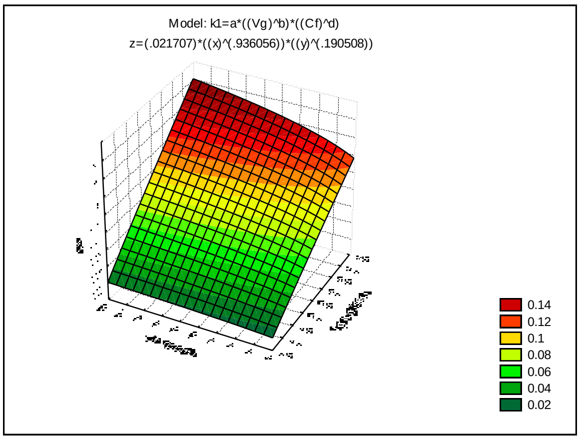

Figure (13) Relation of Kinetic Flotation Constant with Superfacial Gas Velocity and Frother concentration Using Hexanol

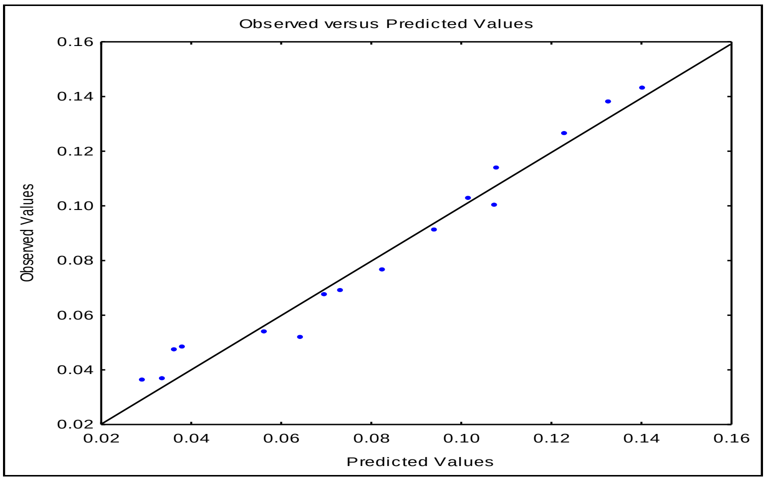

Figure (14) Relationship Between Predicted and Observed Value of Kinetic Constant Using Hexanol

NOMENCLATURE

C	Final Concentration of Wastewater	(ppm)
Cf	Frother Concentration	(ppm)
Co	Initial Concentration of Wastewater	(ppm)
K	Kinetic Flotation Constant Using Caprylic Acid	(1/min)
K1	Kinetic Flotation Constant Using Hexanol	(1/min)
R	Correlation Coefficient	(-)
R.E%	Removal Efficiency Using Caprylic Acid	(-)
R.E1%	Removal Efficiency Using Hexanol	(-)
t	Flotation Time	(min)
Vg	Superfacial Gas Velocity	(cm/sec)

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حركية ازالة حبيبات الرصاص الصغيرة من المياه القذرة لمعامل انتاج البطاريات

احمد حسن عبد الجبار

الخلاصة

ان ازالة المعادن الثقيلة من المياه والمياه القذرة تلقى اهتماما كبيرا حيث تعتبر تقنية التطويف الرغوي واحدة من اغلب التقنيات المستخدمة في معالجة المياه الملوثة وتعتبر منخفضة الكلفة اكثر من التقنيات الاخرى.في هذه الدراسة تم اختبار كفائة فصل عمود تطويف متعدد المراحل وبالحجم المختبري لازالة المعادن الثقيلة (حبيبات الرصاص باقطار اقل من 45 مايكرون) من المياه القذة لصناعة البطاريات .حضر تركيز الرصاص في تلك المياه (100 جزء بالمليون) ثم مرر ببرج التطويف حيث كانت كفاءة فصل الرصاص نوعا ما مرتفعة تراوحت ما بين (62 الى 96,3%) .بلغت اعلى كفاءة فصل عند ظروف تشغيلة عند تركيز رغوة(20 جزء بالمليون) وسرعة غاز (4 سم/ثانية) ، حيث استخدم حامض الكابريليك والهكسانول كمواد مكونة للرغوة في هذة الدراسة.تم التوصل في هذه الدراسة الى ان السلوك الحركي لعملية التطويف متعدد المراحل يخضع لقانون سرعة فصل من المرتبة الاولى حيث حسب ثابت سرعة فصل الحبيبات (K) وتم الحصول على علاقات تجريبية تربط بين ثابت الفصل وسرعة الغاز وتركيز الرغوة المستخدة وتم حساب معامل الارتباط (R) لهذه العلاقات.