Recovery of Manganese Ore using pine oil as frother in Froth Flotation

K. Ganapati[1], Dr. Ch. Asha Immanuel Raju[2], Prof. P. J. Rao[3] and Dr. P. Bhavya Manjeera[4]

Abstract

Over the course of the decade, there was a rapid rise in industry demand for manganese ore. The fundamental focal point of the review is to recuperation Mn from its mineral. For the purpose of separating Mn from ore and concentrating it, this process employs direct flotation. Pyrolusite and Psilomelane as Mn-bearing mineral phases and quartz as the gangue mineral were identified in the X-ray diffraction studies. Different variables, such as pH, oleic acid, and dosages of pine oil (the "Frother"), were used in the experiments. The best conditions for testing Mn yield were found to be pH 8.0, a dosage of 0.6 lit/ton of pine oil, and 1.2 lit/ton of oleic acid. From this Manganese ore, a concentrate of 44.69% Mn could be obtained at a weight of 76.46 percent. The Frother dose meaningfully affects Mn recuperation where as Gatherer measurements affect Mn recuperation. Manganese ore flotation shows that at optimal variables, a fine particle size of 175 m is used to achieve a recovery of 86.52%.

Keywords: *Pyrolusite, Psilomelane, Froth floatation, Oleic Acid, Pine oil, X-Ray Diffraction*

[1] Research Scholar, Chemical Engineering Department, Andhra University, Visakhapatnam, AP, INDIA

[2] Associate Prof, Chemical Engineering Department, Andhra University, Visakhapatnam, AP, INDIA

[3] Retired Prof, Chemical Engineering Department, Andhra University, Visakhapatnam, AP, INDIA

[4] Research Scholar, Chemical Engineering Department, Andhra University, Visakhapatnam, AP, INDIA

Corresponding Author: K. Ganapati, Research Scholar, Chemical Engineering Department, Andhra University, Visakhapatnam, AP, INDIA, +91-9491964114, gani.chem809@gmail.com

17

Eur. Chem. Bull. 2023, 12(5), 17-29

1. Introduction

Manganese Plays A Strategic Role In A Number Of Metallurgical Fields Worldwide, Including The Production Of Steel And Alloys. According To Top (2019), About 90% Of The World's Mn Is Used In The Desulfurization And Strengthening Of Steel And Cast Iron, While The Remaining 10% Is Used In A Variety Of Non-Metallurgical Applications Like Batteries, Chemicals, Electrochemical, Foods, And Pharmaceuticals. Ferromanganese Alloys Are Typically Made Through Direct Smelting With High-Grade Manganese Ores. High-Grade Manganese Ore, On The Other Hand, Is Seriously Depleting As A Result Of The Rapidly Expanding Demand. Chinese Modern Arrangements Of Manganese Metals Are Sorted By Mn/Fe Mass Proportion. The Manganese Minerals With A Mn/Fe Mass Proportion > 5 Are Business Grade Mn-Metals While Minerals With Low Mn/Fe Mass Proportion (< 3) Are Considered As Ferruginous Manganese Minerals. All Over The World, These Resources Made From Ferrous Ore Are Abundant [1].

The Requirement For High-Grade Ore Deposits That Can Be Exploited Relatively Cheaply To Provide Manganese At Reasonable Prices Is The Primary Issue Facing The Global Manganese Industry At The Moment. However, As The Grade Of Manganese Ores Has Generally Decreased, The Industry Has Decided To Reduce The Grade Of Ferromanganese Produced While Simultaneously Requiring Steels With Higher And More Stringent Specifications. As A Result, There Is A Pressing Need To Develop Methods For Exploiting And, More Specifically, Beneficiating Low-Grade Deposits In Order To Meet The Stringent Requirements For Product Quantity And Quality [2].

Frothers Are Surfactants, Normally Natural Heteropolar Mixtures Like Alcohols Or Polyglycol Ethers. Due To The Heteropolar Nature, The Frother Adsorbs At The Air/Water Interface And Accordingly, Brings Down The Water Surface Strain. This Makes The Bubbles Smaller And, More Importantly, Keeps The Froth Stable When It Reaches The Top Of The Slurry. On The Off Chance That The Air Pockets Burst When They Arrive At The Air/Water Surface Any Minerals They Convey Will Drop Once Again Into The Slurry Shaping A Rubbish At The Surface. The Frother's Primary Function Is To Stabilize The Froth That Forms At The Interface So That The Concentrate Can Be Extracted From The Flotation Cell. For The Mineral Particles To Be Re-Pulped For Further Processing, The Froth Must Break When Removed From The Cell [3].

Froth Flotation Is Essentially A Surface Selectivity-Based Separation Method For Separating Hydrophilic From Hydrophobic Materials. This Method Makes Use Of A Lot Of Surfactant Reagents, Which Selectively Alter The Hydrophobicity Of Mineral Surfaces To Achieve A Wide Range Of Separations. It Is The Most Widely Used And Cheapest Metallurgical Method For Separating Minerals With Chemical Similarities And Concentrating Ores For Cost-Effective Smelting. This Interaction Has Been Portrayed As The Indispensable Activity Utilized For Recuperation And Redesigning Of Sulfide Minerals. Initially, Some Naturally Occurring Chemicals Like Fatty Acids And Oils Were Used As Flotation Reagents. Later, Additional Collector Reagents, Surfactants, And Synthetic Compounds Were Used To

Separate A Wide Range Of Materials [4].

2. Reagents

Reagents used in this experiment are pine oil as frother and Oleic Acid as a collector [5].

3. Materials and Methods

3.1 Description of the equipment

The experimental setup that was used in this study, as depicted in Fig. 4.0 is a 0.5-liter Sub Aerated (Mechanical - Cum - Air Vertical) flotation cell. It mostly consists of an impeller and a tank with a square cross section. The pulp's conditioning and dispersion are affected by the impeller's violent agitation. A spindle connected to a 110w variable speed motor powers the impeller that is attached to the end of the steel shaft. Strobo-Scope is used to measure the speed. The mineralized forth passes over the weir in the flotation cell, and skimming is used to remove the froth-mineral association.

The pH of the mash is kept up with at 8, with the expansion of NaOH or corrosive (HCl), which can be estimated by pH meter [6]. A spindle-integrated air pump is used to aerate vertically. Up to the range of saturated froth observed in the cell, air is supplied.

The specification of the motor is given below,

Power : 100W

Voltage : 230 V, 50Hz, Single phase

R.P.M : 950 rpm

Current : 0.2 Amp

The specification of the motor is given below:

Model concord : 1900

Air output : 1.2 liter/minute

Frequency : 50 Hz

Power : 3 watts

Voltage : 240 V

Fig.1 Denver Sub Aeration Flotation Cell

3.2 Experimental procedure for froth flotation

There are three steps to the experimental process.

1. Preparation of feed and Feed Analysi

2. Manganese ore flotation under specific conditions

3. Examining the product

3.2.1(a) Feed preparation:

The manganese ore lumps are first disintegrated in a disintegrator, then ground to the required size in a roll crusher, and finally fed through a ball mill up to -200μ m. Using a Ro-tap sieve shaker, we can separate different size fractions from the feed, ranging from 0.5 mm to 0.1 mm, and -200μ m mesh size fractions are taken [6].

3.2.1(b) Analysis of Feed:

Analysis was carried out on –200 μ feed size.

3.2.2(a) Determination of Mn, Iron and silica:

0.1 gm of sample was taken. This sample along with the reagents conc. HNO_3 (5 ml) and conc. HCl (5 ml) was digested in microwave accelerated reaction system. In the microwave heating the power level of 400 W, ramp time of 15 min, pressure of 800 psi, temperature of 200 ^{0}C and hold time of 15 min was maintained [7-9]. These digested samples were run in inductively coupled plasma atomic emission spectroscopy. Using this ICPAES, the percentages of Mn, iron and silica in manganese ore are found.

3.2.2(b) Flotation of Manganese ore under specified conditions:

A 0.5-liter laboratory Sub Aerated

19

(Mechanical-cum-air vertical type) flotation cell was used in all of the flotation studies. For the purposes of these tests, pine oil and oleic acid were utilized as collector and frother respectively. By adjusting with NaOH and acid (HCl), approximately 100 gm of the sample was conditioned with the required amount of collector at a pulp density of 20% for approximately five minutes at pH 8. The slurry was weaken and drifted with frother for five minutes. Metal concentration was measured and analyzed in the collected, dried, and weighed tailings and froth. Initially, experiments were conducted to determine the most effective collector dosage, and then the effect of frother dosage at constant collector dosage was evaluated. The ideal speed of the impeller is 950 rpm[10]. The pH of the mash is estimated by utilizing the pH meter at consistent temperature for all trials. While doing the whole tests the consistent wind current pace of 2.4 liter/minute was provided by utilizing two pneumatic machines of each having a limit of 1.2 liter/minute into conditioned manganese pulp in the floatation cell

3.2.3 Analysis of the Floated products:

The amounts of manganese, iron and silica in float product and tailings are determined by using ICPAES Analysis [11].

Table-01 displays the range of variables examined in this study. Unless otherwise specified, Oleic Acid (1.2 lit/ton) is the collector and pine oil (0.6 lit/ton) is the frother in all experiments.

Table-01 Range of Variables

Variable	Min	Max
Collector Dosage	0.3 lit/ton	1.5 lit/ton
Frother Dosage	0.2 lit/ton	1.0 lit/ton
Flotation time	min	20 min
pH	6.5	10

4. Results and Discussions

Experiments were conducted using 100 gm of Manganese ore of –200 mesh is used as a feed, pine oil as frother and Oleic Acid as a collector [12].

4.1. Effect of Flotation time

The experiments utilized oleic acid as a collector, pine oil as the frother, and 100 grams of manganese ore with a mesh of –200. Fig.1 depicts the proportion of recovered metal in relation to flotation time. Fig.2 portrays the float's foam weight over the long haul. In addition, as depicted in Fig. 3, the metal focuses in the concentrate increase over time up to nine minutes and remain constant thereafter. Showing 9 minutes is the best season of floatation. Consequently, the flotation time used in all of this study's experiments is nine minutes[13-15].
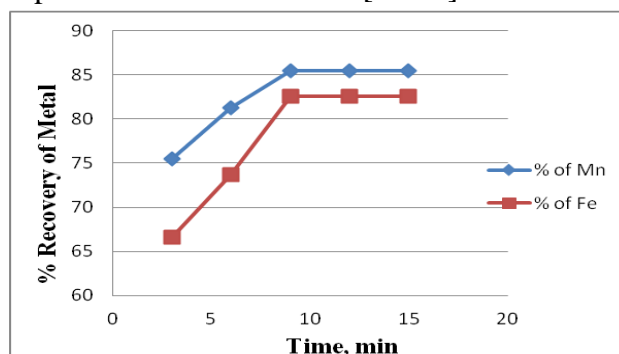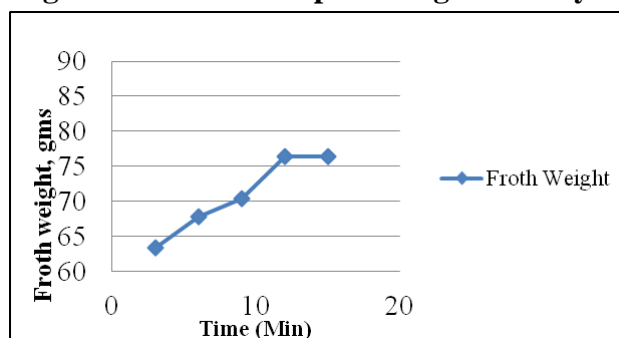

Fig. 1 Role of time on percentage recovery
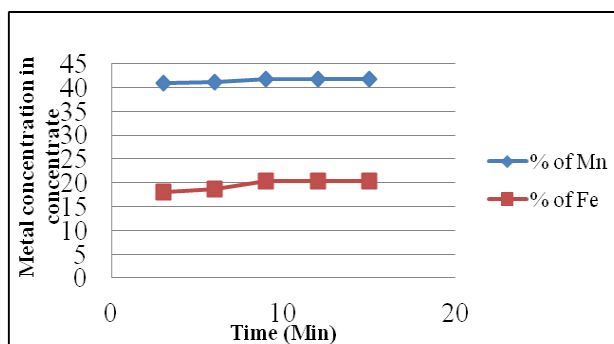

Fig. 2 Role of time on froth weight

Fig. 3 Role of time on metal concentration in concentrate

4.2 Effect of pH on percentage recovery

Fig.4 depicts the relationship between pH and metal recovery, indicating that the pH had an effect on metal recovery within the scope of this investigation. However, the metal recovers more quickly up to pH 8. An additional increase in pH reduces metal recovery, indicating that the optimal pH for metal recovery is 8. This suggests that a pH of 8 can improve metal recovery [16]. According to Fig. 5, the forth weight rises with pH up to a range of 8, and as pH rises further, the froth weight decreases. Further, the metal focus in the concentrate somewhat increments with pH up to 8 as displayed in Fig.6. As the pH rises, the concentration of metals falls. Consequently, pH 8 is used in all of this study's experiments. Oleic Acid is used as a collector (1.2 lit/ton) and pine oil is used as a frother (0.6 lit/ton) in all of these tests [17-18].
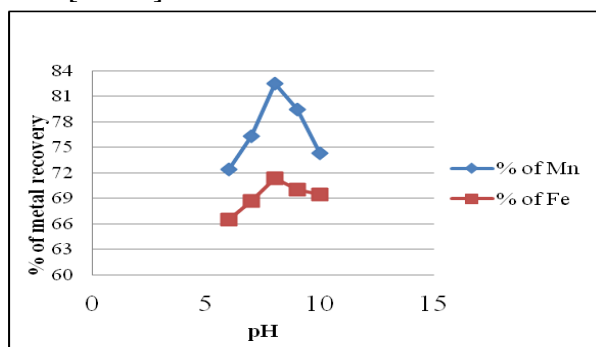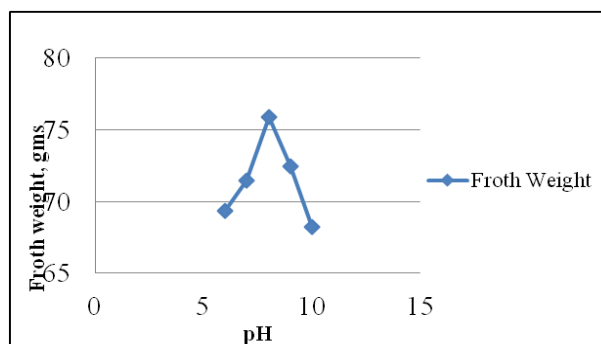

Fig. 4 Effect of pH on percentage recovery

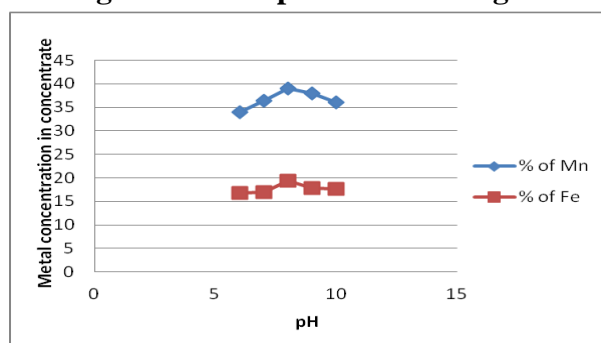**Fig. 5 Effect of pH on froth weight**

Fig.6 Effect Of pH On Metal Concentration In Concentrate

4.3 Role Of Collector Dosage On Percentage Recovery

To determine the optimal collector dosage, tests were carried out with various quantities of collectors. Fig.7 demonstrates that the percentage of recovered metal varies with collector dosage. 1. With an increase in collector dosage, metal recovery increases for all metals up to a dosage of 1.2. As can be seen in Fig.8, as the collector dosage rises, so does the froth weight. 2, but the collector dosage of 1.2 decreases the froth weight. As per Fig.9, the convergence of metals in the concentrate ascends until the measurement of 1.2 and afterward diminishes. These results indicate that, within the study's range, the collector dosage of 1.2 lit/ton is the most effective for upgrading metal [19].
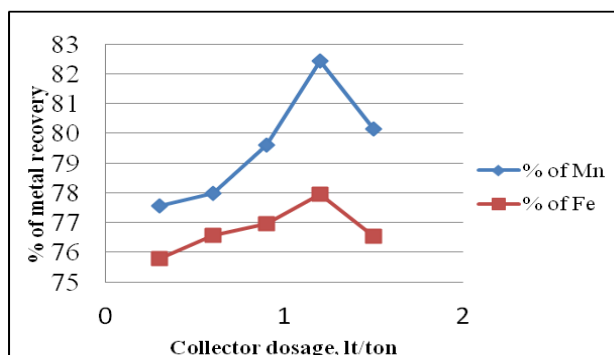
21

Eur. Chem. Bull. 2023, 12(5), 17-29

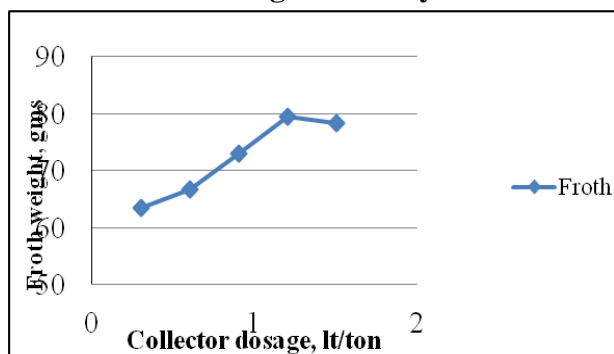**Fig.7 Role Of Collector Dosage On Percentage Recovery**

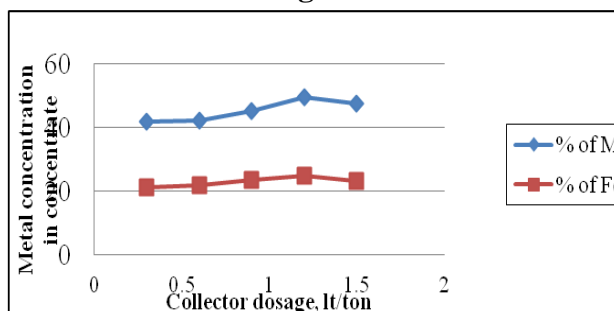**Fig. 8 Role Of Collector Dosage On Froth Weight**

Fig.9 Role Of Collector Dosage On Metal Concentration In Concentrate

4.4 Effect of Frother dosage on percentage recovery

The variation in metal recovery is depicted in Fig. 10,11,12 using pine oil as a frother and oleic acid (1.2 lit/ton) as a collector. At a pH of 8, the frother dosage has little effect on metal recovery; however, metal recovery can reach 0.6 lit/ton as the frother dosage rises. Metal recovery suffers as a result of further expansion in frother measurement. Consequently, these findings suggested that the optimal dosage of pine oil frother for metal recovery is 0.6 lit/ton [20].
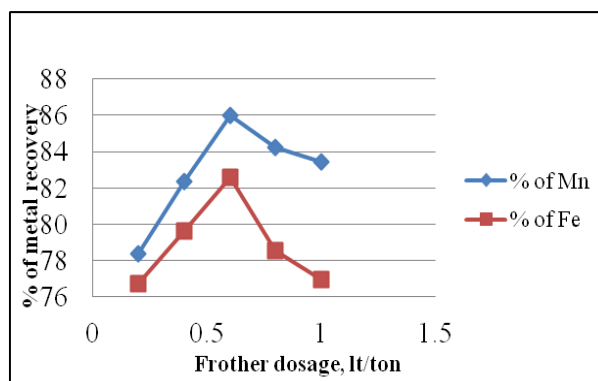

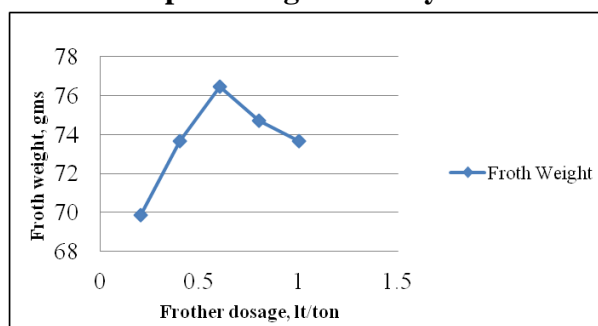**Fig. 10 Effect of frother dosage on percentage recovery**

Fig.11 Effect of frother dosage on froth weight
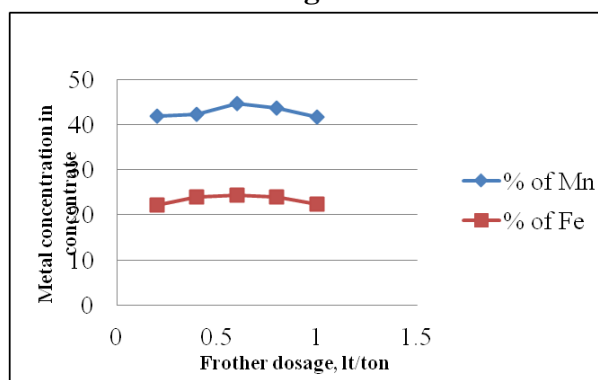
Fig.12 Effect of frother dosage on metal concentration in concentrate

4.5 Response surface methodology

The RSM comprises of a gathering of observational strategies dedicated to the assessment of relationship existing between a bunch of controlled exploratory factors and estimated reactions as indicated by at least one chose standards. Time, pH, the amount of collector, and the amount of frother were examined to see how they affected optimization studies. The analysis of variance

22

(ANOVA) was used to evaluate the statistical significance model. The model's fit was checked by finding the coefficient (R^2) [21].

4.6 Optimization using Central Composite Design

Critical values; Variable: % Recovery (float-manganese)

Solution: maximum

Predicted value at solution: 90.094

+84.261X_3 + 102.438X_4 – 99.2-0.422X_1^2 – 3.593X_2^2 – 37.838X_3^2 – 82.635X_4^2 +0.073 X_1X_2 +0.156 X_1X_3 +0.817X_2X_3

$$+84.261X_3 + 102.438X_4 - 99.2 - 0.422X_1^2 - 3.593X_2^2 - 37.838X_3^2 - 82.635X_4^2 + 0.073\,X_1X_2 + 0.156\,X_1X_3 + 0.817X_2X_3$$

Table 2

Variable	Name	Range and Levels			
		-2	-1	0	1
X_1	Time (Min)	3	6	9	12
X_2	pH	6	7	8	9
X_3	Amount of Collector (gms)	0.6	0.9	1.2	1.5
X_4	Amount of Frother (gms)	0.2	0.4	0.6	0.8

The following equation represents multiple regression analysis of the experimental data for the Manganese Ore:

$Y = -249.766 + 6.911X_1 + 56.07X_2$

Table-3

S.No	Time	pH	Amount of Collector	Amount of Frother	Experimental % recovery	Predicted
1	6	7	0.9	0.4	74.96	74.99
2	6	7	0.9	0.8	76.32	76.30
3	6	7	1.5	0.4	75.06	75.05
4	6	7	1.5	0.8	76.36	76.36
5	6	9	0.9	0.4	74.54	74.52
6	6	9	0.9	0.8	75.84	75.83
7	6	9	1.5	0.4	75.56	75.56
8	6	9	1.5	0.8	76.86	76.87
9	12	7	0.9	0.4	74.78	74.77
10	12	7	0.9	0.8	76.08	76.08
11	12	7	1.5	0.4	75.38	75.39
12	12	7	1.5	0.8	76.68	76.70
13	12	9	0.9	0.4	75.18	75.18
14	12	9	0.9	0.8	76.48	76.49
15	12	9	1.5	0.4	76.76	76.78
16	12	9	1.5	0.8	78.12	78.09
17	3	8	1.2	0.6	74.32	74.33
18	15	8	1.2	0.6	75.36	75.34

19	9	6	1.2	0.6	75.22	75.21
20	9	10	1.2	0.6	76.12	76.13
21	9	8	0.6	0.6	75.58	75.59
22	9	8	1.8	0.6	77.26	77.25
23	9	8	1.2	0.2	75.52	75.51
24	9	8	1.2	1	78.12	78.13
25	9	8	1.2	0.6	90.04	90.04
26	9	8	1.2	0.6	90.04	90.04
27	9	8	1.2	0.6	90.04	90.04
28	9	8	1.2	0.6	90.04	90.04
29	9	8	1.2	0.6	90.04	90.04
30	9	8	1.2	0.6	90.04	90.04

Table-4

	Regression	Std.Err.	t(15)	p	-95.%	+95.%
Mean/Interc.	-249.766	0.351956	-709.65	0.000000	-250.516	-249.016
(1)time, mins(L)	6.911	0.016582	416.80	0.000000	6.876	6.947
time, mins(Q)	-0.422	0.000401	-1052.27	0.000000	-0.423	-0.421
(2)pH(L)	56.077	0.064144	874.23	0.000000	55.940	56.213
pH(Q)	-3.593	0.003612	-994.81	0.000000	-3.601	-3.585
(3)Amount of collector, gms(L)	84.261	0.172670	487.99	0.000000	83.893	84.629
Amount of collector, gms(Q)	-37.838	0.040129	-942.90	0.000000	-37.923	-37.752
(4)Amount of frother, gms(L)	102.438	0.248728	411.85	0.000000	101.907	102.968
Amount of frother, gms(Q)	-82.635	0.090291	-915.21	0.000000	-82.828	-82.443
1L by 2L	0.073	0.001576	46.52	0.000000	0.070	0.077
1L by 3L	0.156	0.005254	29.61	0.000000	0.144	0.167
1L by 4L	-0.000	0.007881	-0.00	1.000000	-0.017	0.017

24

Eur. Chem. Bull. 2023, 12(5), 17-29

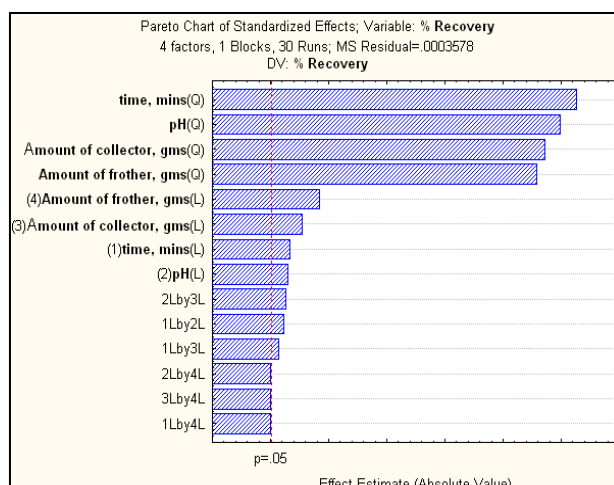| 2L by 3L | 0.817 | 0.015763 | 51.81 | 0.000000 | 0.783 | 0.850 |
| 2L by 4L | -0.000 | 0.023644 | -0.00 | 1.000000 | -0.050 | 0.050 |
| 3L by 4L | 0.000 | 0.078813 | 0.00 | 1.000000 | -0.168 | 0.168 |

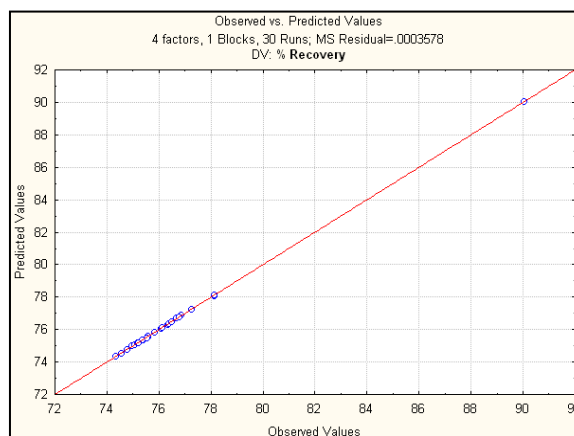**Fig. 13 Pareto Chart of Standardized Effects**

Fig.14 Observed vs Predicted Values

The anticipated ideal arrangement of conditions for percentage recovery is

Time = 9.105

pH = 8.035

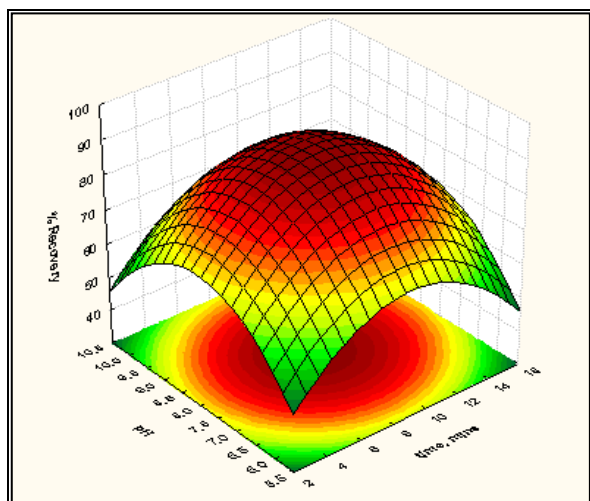Amount of Collector = 1.218

Amount of Frother = 0.619

25

Eur. Chem. Bull. 2023, 12(5), 17-29

Recovery With time and amount of frother

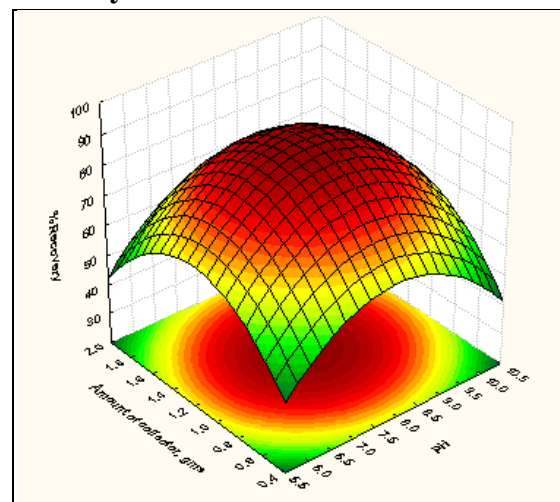**Fig.15 Variation Of Percentage of Recovery With Time and pH**

Fig.18 Variation Of Percentage of Recovery With amount of collector and pH
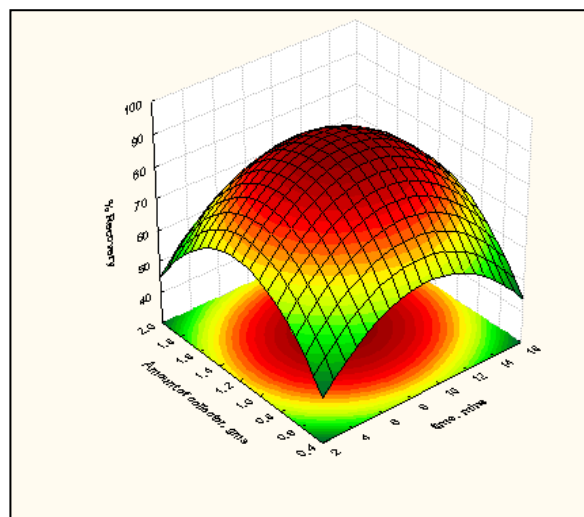

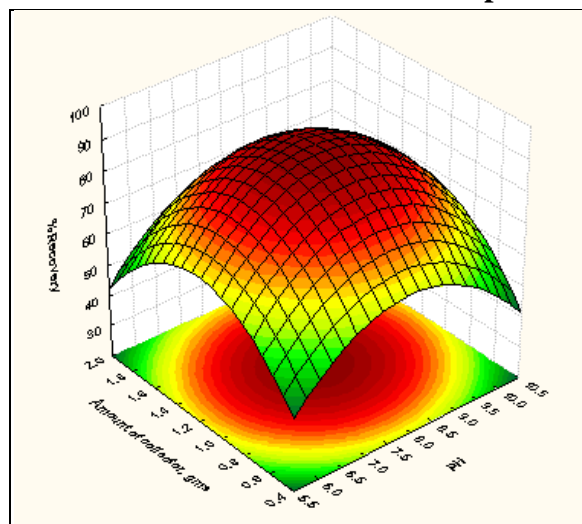**Fig.16 Variation Of Percentage of Recovery With time and amount of collector**

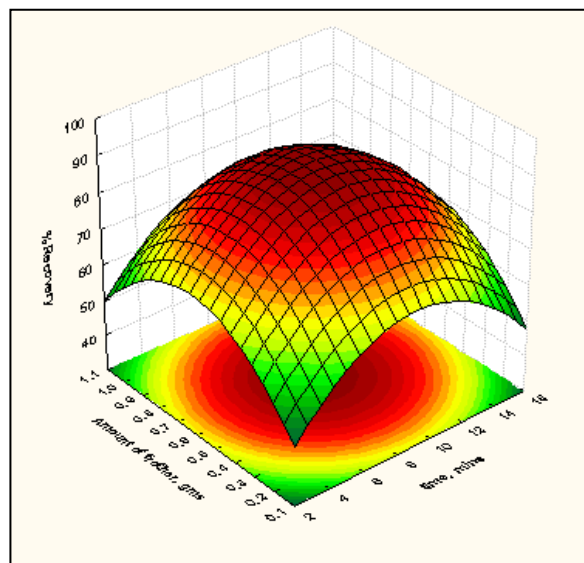**Fig.19 Variation Of Percentage of Recovery With amount of frother and pH**
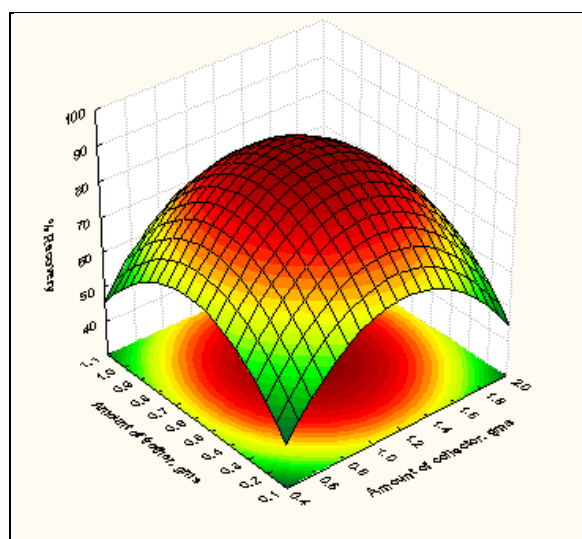

Fig.17 Variation Of Percentage of

Fig.20 Variation Of Percentage of

26

Recovery With amount of collector and amount of collector

Variable	CCD	Experimental value
Time (Min)	9.105	9
pH	8.035	8
Amount of Collector (gms)	1.218	1.2
Amount of Frother (gms)	0.619	0.6
% Recovery	90.09	86.01

The area in the highest peak in red zone represents the optimum values of the parameters [22].

Table-5 Comparison between optimum values from CCD and experimentation

5. Conclusions

The Best Flotation Time Can Be Estimated To Be 540 Seconds, Or 09 Minutes. For Better Upgradation, The Best Amount Of Collector (Oleic Acid) Is Found To Be 1.2 Lit/Ton. For Better Upgradation, The Best Amount Of Frother (Pine Oil) Is Found To Be 0.6 Lit/Ton. Using 1.2 Lit/Ton Diesel Oil As A Collector And 0.6 Lit/Ton Pine Oil As A Frother, Manganese Ore Can Be Recovered At A Recovery Rate Of 86.01%. In Order To Improve The Efficiency Of The Flotation, The Ph Is Kept At 8.

Reference:

1. Manish Kumar Sinhaa , Walter Purcella , Willem A. Van Der Westhuizen, "Recovery Of Manganese From Ferruginous Manganese Ore Using Ascorbic Acid As Reducing Agent", Minerals Engineering, 197, 106406, 2020.

2. M. H. Buckenham, "Beneficiation Of Manganese Ores With Particular Reference To The Treatment Of A Low Grade Ore From Viti Levu, Fiji", New Zealand Journal Of Geology And Geophysics, 4, 136-147, 1960.

3. Gupta, A., & Yan, D. S. "Mineral Processing Design And Operation", 555–603, 2006.

4. Sangita Mondal , Animesh Acharjee, Ujjwal Mandal , Bidyut Saha, "Froth Flotation Process And Its Application", Vietnam Journal Of Chemistry , 59(4), 417-425, 2021.

5. Gao, Zhiyong, Cong Wang, Wei Sun, Yuesheng Gao, and Przemyslaw B. Kowalczuk. "Froth flotation of fluorite: A review." *Advances in colloid and interface science* 290 (2021): 102382.

6. Kupka, Nathalie, and Martin Rudolph. "Froth flotation of scheelite–A review." *International Journal of Mining Science and Technology* 28, no. 3 (2018): 373-384.

7. Castro, Sergio, and Janusz S. Laskowski. "Froth flotation in saline water." *KONA Powder and Particle Journal* 29 (2011): 4-15.

8. Ma, Mark. "Froth flotation of iron ores." *International Journal of Mining Engineering and Mineral Processing* 1, no. 2 (2012): 56-61.

9. Rao, S. Ramachandra. *Surface chemistry of froth flotation: Volume 1: Fundamentals*. Springer Science &

Eur. Chem. Bull. 2023, 12(5), 17-29

27

Business Media, 2013.

10. Assis, S. M., L. C. M. Montenegro, and A. E. C. Peres. "Utilisation of hydroxamates in minerals froth flotation." *Minerals engineering* 9, no. 1 (1996): 103-114.

11. Nunes, Aline Pereira Leite, Cláudio Lúcio Lopes Pinto, George Eduardo Sales Valadão, and Paulo Roberto de Magalhães Viana. "Floatability studies of wavellite and preliminary results on phosphorus removal from a Brazilian iron ore by froth flotation." *Minerals Engineering* 39 (2012): 206-212.

12. Segura-Salazar, Juliana, and Pablo R. Brito-Parada. "Stibnite froth flotation: A critical review." *Minerals Engineering* 163 (2021): 106713.

13. Yu, Yuexian, Liqiang Ma, Mingli Cao, and Qi Liu. "Slime coatings in froth flotation: A review." *Minerals Engineering* 114 (2017): 26-36.

14. Chen, Xumeng, and Yongjun Peng. "Managing clay minerals in froth flotation—A critical review." *Mineral Processing and Extractive Metallurgy Review* 39, no. 5 (2018): 289-307.

15. Kitchener, J. A. "The froth flotation process: past, present and future-in brief." *The scientific basis of flotation* (1984): 3-51.

16. Faramarzpour, A., MR Samadzadeh

Yazdi, B. Mohammadi, and S. Chehreh Chelgani. "Calcite in froth flotation-A review." *Journal of Materials Research and Technology* (2022).

17. Zhang, Shiyong, Zhiqiang Huang, Hongling Wang, Rukuan Liu, Chen Cheng, Zhiqun Guo, Xinyang Yu, Guichun He, and Weng Fu. "Separation of wolframite ore by froth flotation using a novel "crab" structure sebacoyl hydroxamic acid collector without Pb (NO3) 2 activation." *Powder Technology* 389 (2021): 96-103.

18. Huang, Zhiqiang, Chen Cheng, Zuwen Liu, Huiqiang Zeng, Bo Feng, Hong Zhong, Wuhui Luo et al. "Utilization of a new Gemini surfactant as the collector for the reverse froth flotation of phosphate ore in sustainable production of phosphate fertilizer." *Journal of Cleaner Production* 221 (2019): 108-112.

19. Shean, B. J., and J. J. Cilliers. "A review of froth flotation control." *International Journal of Mineral Processing* 100, no. 3-4 (2011): 57-71.

20. Marques, Gisela Ablas, and Jorge Alberto Soares Tenório. "Use of froth flotation to separate PVC/PET mixtures." *Waste Management* 20, no. 4 (2000): 265-269.

21. Barbian, N., E. Ventura-Medina, and

28

Eur. Chem. Bull. 2023, 12(5), 17-29

J. J. Cilliers. "Dynamic froth stability in froth flotation." *Minerals Engineering* 16, no. 11 (2003): 1111-1116.

22. Huang, Zhiqiang, Chen Cheng, Liqing Li, Zhizhong Guo, Guichun He, Xinyang Yu, Rukuan Liu, Haijun Han, Lanqing Deng, and Weng Fu. "Morpholine-based gemini surfactant: synthesis and its application for reverse froth flotation of carnallite ore in potassium fertilizer production." *Journal of agricultural and food chemistry* 66, no. 50 (2018): 13126-13132.

29

Eur. Chem. Bull. 2023, 12(5), 17-29