

RECOVERY OF OIL FROM EMULSION EFFLUENTS OF STEEL - ROLLING MILLS USING MAGNETITE NANOPARTICLES

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**DEPARTMENT OF CHEMICAL ENGINEERING
INDIAN INSTITUTE OF TECHNOLOGY DELHI
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EFFLUENTS OF STEEL - ROLLING MILLS USING
MAGNETITE NANOPARTICLES**

by

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DEPARTMENT OF CHEMICAL ENGINEERING

Submitted

In fulfilment of the requirements of the degree of Doctor of Philosophy

to the



**INDIAN INSTITUTE OF TECHNOLOGY DELHI
OCTOBER 2019**

DEDICATED TO
MY PARENTS AND THE ALMIGHTY

CERTIFICATE

This is certify that the Ph.D. thesis entitled “**RECOVERY OF OIL FROM EMULSION EFLUENTS OF STEEL-ROLLING MILLS USING MAGNETITE**

NANOPARTICLES” submitted by **Ms. PARSANTA**, a RESEARCH SCHOLAR to the Department of Chemical Engineering, Indian Institute of Technology (IITD), New Delhi, for award of the degree of **DOCTOR OF PHILOSOPHY** is a record of the bonafide research work carried out by her. **Ms. PARSANTA** has worked under my supervision for the submission of this thesis, which to my knowledge has reached the requisite standard.

This thesis or part of it has not been presented or submitted to any other University or Institute for any degree or diploma.

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ABSTRACT

Oil-in-water emulsions are used in large amounts in hot-rolling mills of steel industries for cooling and lubrication of contacting metal surfaces. These emulsions are comparatively stable kinetically and have high specific heats and enable high heat transfer coefficients, and therefore can be used under high temperature and pressure conditions. These emulsions are, however, hazardous to the environment, and hence cannot be disposed off as such. The Ministry of Environment and Forests has set the permissible limit of 10 mg/l of oil for disposal. These emulsions are notoriously difficult to break. The other conventional processes such as acidification, centrifugation, coagulation, ultrafiltration, UV radiation, ozone treatment, thermal irradiation, and electrolytic method are either energy intensive, time-consuming, costly, or non-eco-friendly. The present work is focused on the treatment of such tough emulsions, by magnetite (Fe_3O_4) nanoparticles (MNPs), in which oil and water are effectively separated. The Fe_3O_4 nanoparticles are superparamagnetic in nature. These can be synthesized by several methods such as co-precipitation, sol-gel, and thermal decomposition. Among these, co-precipitation method is the best method if Fe_3O_4 nanoparticles are required in bulk amounts. The present work is based on co-precipitation for the synthesis of magnetite nanoparticles at room temperature. These nanoparticles were used for the demulsification of emulsion effluents of steel-rolling mills, and were characterized by XRD, SEM, and TEM techniques. A system was also developed for (i) a continuous production of MNPs, (ii) a continuous treatment of emulsion effluents, and (iii) continuous separation of oil loaded MNPs and treated emulsion. Effect of linear velocity of the belt on phase separation (of oil loaded MNPs and treated emulsion) was studied, while keeping the flowrates of (i) emulsion, and (ii) aqueous slurry of MNPs

constant. The separation increased with an increase in the linear velocity of the conveyor belt. Effect of different parameters, viz. concentration of oil in emulsion, flow rate of emulsion and flow rate of aqueous slurry of MNPs were studied. These nanoparticles could easily be retrieved by simple application of an external magnetic field. The recovered nanoparticles could be reused several times. In conclusion, it can be stated that demulsification by Fe_3O_4 nanoparticles is quick, eco-friendly and cost-effective.

सार

तेल-इन-वाटर इमल्शन का उपयोग स्टील उद्योगों के गर्म-रोलिंग मिलों में बड़ी मात्रा में किया जाता है जो धातु की सतहों से संपर्क करने के लिए ठंडा और चिकनाई प्रदान करता है। ये इमल्शन तुलनात्मक रूप से स्थिर रूप से स्थिर होते हैं और इनमें उच्च विशिष्ट हीट होते हैं और उच्च हीट ट्रांसफर गुणांक को सक्षम करते हैं और इसलिए इसका उपयोग उच्च तापमान और दबाव की स्थिति में किया जा सकता है। हालाँकि ये इमल्शन पर्यावरण के लिए खतरनाक हैं और इसलिए इनका निपटान नहीं किया जा सकता है। पर्यावरण और वन मंत्रालय ने निपटान के लिए 10 मिलीग्राम / लीटर तेल की अनुमेय सीमा निर्धारित की है। इन पायस को तोड़ने के लिए कुख्यात हैं। अम्लीकरण, अपकेंद्रण, जमावट, अल्ट्राफिल्ट्रेशन, यूवी विकिरण, ओजोन उपचार, थर्मल विकिरण और इलेक्ट्रोलाइटिक विधि जैसी अन्य पारंपरिक प्रक्रियाएं या तो ऊर्जा गहन समय लेने वाली, महंगी या गैर-पर्यावरण-अनुकूल हैं। वर्तमान कार्य इस तरह के कठिन पायस के उपचार पर केंद्रित है मैग्नेटाइट (Fe_3O_4) नैनोकणों (MNP) द्वारा जिसमें तेल और पानी को प्रभावी रूप से अलग किया जाता है। Fe_3O_4 नैनोपार्टिकल्स प्रकृति में सुपरपैरामैग्नेटिक हैं। इन्हें सह-वर्षा सोल-जेल और थर्मल अपघटन जैसे कई तरीकों से संश्लेषित किया जा सकता है। इनमें से सह-वर्षा विधि सबसे अच्छी विधि है यदि Fe_3O_4 नैनोकणों को थोक मात्रा में आवश्यक है। वर्तमान कार्य कमरे के तापमान पर मैग्नेटाइट नैनोकणों के संश्लेषण के लिए सह-वर्षा पर आधारित है। इन नैनोकणों का उपयोग स्टील-रोलिंग मिलों के पायस अपशिष्टों के विघटन के लिए किया गया था और इन्हें ^{XRD, SEM} और ^{TEM} तकनीकों की विशेषता थी। (i) एमएनपी के निरंतर उत्पादन के लिए एक प्रणाली भी विकसित की गई थी, (ii) इमल्शन प्रवाह और

(iii) तेल से लदे MNP का निरंतर पृथक्करण और उपचारित इमल्शन। चरण पृथक्करण पर बेल्ट के रैखिक वेग का प्रभाव (तेल से लोड किए गए एमएनपी और उपचारित इमल्शन का) का अध्ययन किया गया जबकि (i) इमल्शन और (ii) एमएनपी के जलीय घोल को रखा गया।

स्थिर। कन्वेयर बेल्ट के रैखिक वेग में वृद्धि के साथ अलगाव बढ़ गया। विभिन्न मापदंडों का प्रभाव अर्थात् इमल्शन में तेल की एकाग्रता, इमल्शन की प्रवाह दर और MNP के जलीय घोल की प्रवाह दर का अध्ययन किया गया। इन नैनोकणों को बाहरी चुंबकीय क्षेत्र के सरल अनुप्रयोग द्वारा आसानी से प्राप्त किया जा सकता है। बरामद नैनोकणों का कई बार पुनः उपयोग किया जा सकता है। निष्कर्ष में यह कहा जा सकता है कि Fe_3O_4 नैनोपार्टिकल्स द्वारा डिस्मिलिफिकेशन त्वरित पर्यावरण के अनुकूल और लागत प्रभावी है।

TABLE OF CONTENTS

SECTIONS	PAGE NO.
CERTIFICATE	i
ACKNOWLEDGEMENTS	ii
ABSTRACT	iv
CONTENTS	vi
LIST OF FIGURES	ix
LIST OF TABLES	xiii
LIST OF ABBREVIATIONS	xiv
CHAPTER 1. INTRODUCTION	1-4
1.1 Introduction	1
1.2 Magnetic nanoparticles	2
1.3 Aim and scope	3
1.4 Objectives of research work	4
1.5 Organization of thesis	4
CHAPTER 2. LITERATURE SURVEY	5-21
2.1 Introduction	5
2.2 Emulsion	5
2.2.1 Stability of emulsion	7
2.2.2 Instability of emulsion	8
2.3 Conventional techniques	9
2.4 Demulsification by magnetite nanoparticles (MNPs)	19

2.5 Materials and methodology for the synthesis of magnetically responsive nanoparticles	20
2.6 Concluding remarks	21
CHAPTER 3. SYNTHESIS OF MAGNETITE NANOPARTICLES AND PRELIMINARY STUDIES	22-39
3.1 Emulsion effluent	22
3.1.1 Composition and characterization of industrial effluent	23
3.1.1.1 Development of procedure for the analysis	23
3.1.1.2 UV-Vis spectrophotometric method	23
3.1.2 Simulation of industrial effluent: Synthetic emulsion	25
3.2 Magnetite nanoparticles	28
3.2.1 Synthesis of magnetite nanoparticles (MNPs): batch process	28
3.2.2 Characterization of MNPs	29
3.3 Preliminary and Exploratory studies for de-emulsification	31
3.3.1 Demulsification: Determination of the ratio of MNPs to the emulsion	31
3.3.2 Treatment studies with 100 g of MNPs	32
3.3.3 Studies with mechanical stirring	32
3.3.4 Quality of treated effluent	33
3.3.5 Treatment of synthetic emulsion with slurry of MNPs (freshly prepared)	33
3.3.6 Treatment with iron dust	34
3.4 Re-use	35-36
3.4.1 Re-use of recovered water	34
3.4.2 Re-use of MNPs	35
3.5 Concluding remarks	39
CHAPTER 4. DEVELOPMENT OF A CONTINUOUS PROCESS	40-67

4.1 Conveyor belt setup assembled in house	41
4.2 Continuous phase separation (solid phase and liquid phase): Experimental studies	42
4.2.1 Preliminary studies: Effect of increase in linear velocity of belt	43
4.2.1.1 Experiments with water	43
4.2.1.2 Experiments with slurry of MNPs in water	43
4.2.2 De-emulsification along with phase separation studies : Experiments with mixture of emulsion and slurry of MNPs	44
4.2.3 Development of experimental procedure	46
4.2.4 Continuous feed of MNPs and continuous feed of emulsion in the mixer (II) i.e. continuous demulsification	49
4.2.5 Continuous production of MNPs and their application	51
4.3 Complete assembly of the continuous setup	53
4.3.1 Procedure for continuous experiments	54
4.3.2 Effect of different parameters	57
4.3.2.1 Effect of concentration of oil in the emulsion	57
4.3.2.2 Effect of emulsion flow rate	62
4.3.2.3 Effect of MNP's water slurry flow rate	63
4.3.2.4 Effect of linear velocity of the conveyor belt	64
4.3.3 Best conditions for the treatment of 1% (v/v) emulsion	66
4.4 Limitations of the study	67
4.5 Concluding remarks	67
CHAPTER 5. CONCLUSIONS AND RECOMMENDATIONS	68-70
REFERENCES	71
APPENDIX A	77
APPENDIX B	90
APPENDIX C	94
APPENDIX D	98
CV	99

LIST OF FIGURES

S. No.	Figure No.	Title	Page No.
1	2.1	Schematic diagram of the mechanism of de-emulsification.	19
2	2.2	Structure of magnetite (Fe_3O_4) nanoparticles.	20
3	3.1	UV peak at 223 nm of emulsion effluent.	24
4	3.2	Calibration curve of emulsion dilution with water at 223 nm wavelength.	25
5	3.3	Comparison of steel-rolling mills emulsion effluent and 1 % (v/v) synthetic emulsion.	26
6	3.4	Optical microscopic image of emulsion with Sudan red dye IV at 100X magnification.	28
7	3.5	XRD analysis of Fe_3O_4 nanoparticles.	29
8	3.6	SEM image of Fe_3O_4 nanoparticles.	30
9	3.7	TEM image of Fe_3O_4 nanoparticles.	30
10	3.8	Calibration curve for turbidity (NTU) measurement.	33
11	3.9	Re-use of MNPs on the demulsification of 10 % (v/v) emulsion.	38
12	4.1	Schematic representation of the batch setup (built-in-house) for treatment of emulsion effluent using Fe_3O_4 nanoparticles (original setup in Appendix A).	42
13	4.2	Continuous feed of MNPs slurry and emulsion.	51
14	4.3	Aspirator bottle.	52
15	4.4	Mixer tank.	52
16	4.5	Continuous production of MNPs.	52
17	4.6	Complete assembly of the continuous process setup.	53
18	4.7	Turbidity of 1% (v/v) emulsion on continuous setup at oil collector end.	58
19	4.8	Turbidity of 1% (v/v) emulsion on continuous setup at water collector end.	58

20	4.9	Concentration of oil % (v/v) in treated emulsion at oil collector end.	59
21	4.10	Turbidity measurement of treated emulsion at oil collector end: consolidated data.	60
22	4.11	Concentration of oil % (v/v) in treated emulsion at oil collector end: consolidated data.	60
23	4.12	Turbidity of treated emulsion on continuous setup at oil collector end.	62
24	4.13	Turbidity of treated emulsion on continuous setup at oil collector end: effect of emulsion flow rate: consolidated data.	63
25	4.14	Turbidity of treated emulsion on continuous setup at oil collector end.	63
26	4.15	Turbidity of treated emulsion on continuous setup at oil collector end: effect of slurry flow rate: consolidated data.	64
27	4.16	Turbidity of treated emulsion on continuous setup at oil collector end.	65
28	4.17	Turbidity of treated emulsion on continuous setup at oil collector end: effect of linear velocity of conveyor belt: consolidated data.	65
29	4.18	Effect of emulsion flow rate on demulsification process.	66
30	A.1	Emulsion effluent of steel-rolling mills after filtration through wire mesh, becomes whitish in appearance. Its floating oil separated from emulsion through separating funnel.	77
31	A.2	Emulsion effluent after filtration through separating funnel. It was used in further experiments.	77
32	A.3	Synthesis of MNPs setup.	78
33	A.4	Black color MNPs dry powder.	78
34	A.5	Steps of demulsification of emulsion: a. emulsion, b. MNPs, c. after mixing of emulsion and MNPs placed on permanent magnet, d. recovered water, e. recovered MNPs, f. washing of MNPs with acetone, g. oil acetone extract, and h. recovered oil.	79
35	A.6	Treatment of emulsion with iron dust.	79
36	A.7	Thick paste formation.	79
37	A.8 a	Pulley attached with motor.	80

38	A.8 b	Pulley for attachment on setup.	80
39	A.8 c	Conveyor belt.	80
40	A.8 d	Conveyor belt arrangement on basic setup.	80
41	A.9.a	Mixer I	81
42	A.9.b	Mixer II	81
43	A.9.c	Mixer III	81
44	A.9.d	Mixer IV	81
45	A.10.a	Water collector made from aluminum sheet.	82
46	A.10.b	Rusting in aluminum sheet.	82
47	A.10.c	Water collector made from perspex sheet (finally used).	82
48	A.11	Continuous system with steel mixer and belt conveyor modified with side wall, water collector of aluminum sheet.	83
49	A.12.a	Conveyor belt and magnet dimensions.	84
50	A.12.b	Conveyor belt with side wall and three magnets linearly arranged below it.	84
51	A.12.c	Belt modified (circumference increases) six magnets place below it.	85
52	A.12.d	Belt conveyor with six linearly arranged magnets.	85
53	A.13.	Modified system I by using magnetic stirring for mixing of MNPs slurry, digital mixer controller and perspex sheet water collector.	86
54	A.14	Modified system II using mixer type II and pillar like arrangement of magnets below it.	87
55	A.15	Peristaltic pump.	88
56	A.16	Variable frequency drive.	88
57	A.17	Complete assembly of setup for continuous production of MNPs, continuous demulsification and continuous phase separation.	89
58	B.1	UV peak of dye in emulsion effluent at different concentrations.	90

59	B.2	Effect of increase in linear velocity of belt (water).	90
60	B.3	Effect of increase in linear velocity of belt (slurry).	90
61	B.4.a.	Effect of increase in linear velocity of belt (mixture of emulsion and slurry).	91
62	B.4.b.	Effect of increase in linear velocity of belt (mixture of emulsion and slurry).	91
63	B.5	Calibration curve: Flow rate (water) at different settings on peristaltic pump.	92
64	B.6	Comparative studies for the flow rate of water, slurry, mixture of emulsion and slurry, w.r.t different settings on pump (settings 2, 4, and 7).	92
65	B.7	Calibration curve: The linear velocity of conveyor belt at different frequencies on VFD.	93
66	B.8	EDS of MNPs.	93

LIST OF TABLES

S. No.	Table No.	Title	Page No.
1	2.1	Literature on filtration technique of demulsification.	9
2	2.2	Literature on coagulation techniques of demulsification.	11
3	2.3	Literature on acidification techniques of demulsification.	14
4	2.4	Literature on aeration techniques of demulsification	15
5	2.5	Literature on electrolysis techniques of demulsification.	16
6	2.6	Literature on magnetic nanoparticles techniques of demulsification.	17
7	2.7	Literature on other techniques on demulsification.	17
8	3.1	Batch demulsification studies: 5 g of MNPs used in each case.	31
9	3.2	Recovery of treated water, MNPs, and oil.	36
10	3.3	Cumulative results of re-use of MNPs on demulsification of 10 % (w/v) emulsion.	38
11	3.4	Results of complete demulsification.	38
12	4.1	Effect of linear velocity of the belt.	43
13	4.2	Recoveries at oil and water collector of the conveyor belt.	44
14	4.3	Series 1: Separation of oil loaded MNPs and treated emulsion.	46
15	4.4	Recoveries of oil, MNPs, and water.	48
16	4.5	Series 2: Experimental conditions for continuous demulsification studies.	56
17	C.1	Categories of hazardous wastes.	94
18	C.2	Different techniques used to determine the oil/water ratio.	95
19	C.3	Results for 1 % (v/v) emulsion effluents treatment.	96

LIST OF ABBREVIATIONS/ NOTATIONS

cm	Centimeter
cm/s	Centimeter per second
COD	Chemical Oxygen Demand
diam.	Diameter
EDS	Energy-dispersive X-Ray Spectroscopy
Fe ₃ O ₄	Magnetite nanoparticles
FeCl ₂ .2H ₂ O	Ferrous Chloride Dihydrate
FeCl ₂	Ferrous Chloride
FeCl ₃ .6H ₂ O	Ferric Chloride Hexahydrate
G	Gram
H	Height
JCPDS	Joint Committee on Powder Diffraction Standards
kg	Kilogram
L	Litre
mg/l	milligram per litre
min.	Minute
mins.	Minutes
ml	Milliliter
ml/min	Milliliter per minute
MNPs	Magnetite (Fe ₃ O ₄) nanoparticles
NTU	Nephelometric Turbidity Unit
o/w	Oil-in-water

RO	Reverse Osmosis
RPM	Revolution per minute
SEM	Scanning Electron Microscope
TEM	Transmission Electron Microscope
UV-Vis	UV-Vis spectrophotometry
V	Volume
v/v	volume by volume
VFD	Variable Frequency Drive
w/v	weight by volume
w/w	weight by weight
w/o	Water-in-oil
XRD	X-Ray Diffraction