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

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by

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Submitted

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

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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 byFe_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, अर्थात। 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 पुन: 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।

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cm	Centimeter
cm/s	Centimeter per second
COD	Chemical Oxygen Demand
diam.	Diameter
EDS	Energy-dispersive X-Ray Spectroscopy
Fe_3O_4	Magnetite nanoparticles
$FeCl_2.2H_2O$	Ferrous Chloride Dihydrate
$FeCl_2$	Ferrous Chloride
$FeCl_3.6H_2O$	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_3O_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