Sustainable treatment of emulsion effluents from steel-rolling mills using magnetite (Fe$_3$O$_4$) nanoparticles

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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 exhibit high specific heats and heat transfer coefficients, and therefore can be used under high temperature and pressure conditions in the hot-rolling mills of steel industries. These emulsions used in the steel industries are however hazardous to the environment, and cannot be disposed off as such. The Ministry of Environment and Forests (MOEF, government of India) has set the permissible limit of 10 mg/l of oil for disposal. These emulsions are notoriously difficult to break. The present work is focused on the treatment of such tough emulsions, by Fe$_3$O$_4$ nanoparticles, in which oil and water are effectively separated. The other conventional processes such as acidification, centrifugation, coagulation, ultrafiltration, UV irradiation, ozone treatment, thermal irradiation, and electrolytic method are either energy intensive, time-consuming, costly, or non-eco-friendly. The Fe$_3$O$_4$ nanoparticles were synthesized by a co-precipitation method and characterized by XRD, SEM, and TEM. An experimental setup was built in-house for the treatment of emulsion effluents on a conveyor belt. Experiments were conducted using 1 % (v/v) o/w emulsion and different weight percentages of nanoparticles in an aqueous slurry. The mass balances of oil, water, and nanoparticles were checked and showed good recoveries. This process is economical, eco-friendly, less energy-intensive, and less time-consuming when compared to the other established procedures.

KEYWORDS: emulsion effluents, steel-rolling mills, hot-rolling mills, magnetic nanoparticles, Fe$_3$O$_4$ nanoparticles, co-precipitation.

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INTRODUCTION

In all the metal-working industries, long-lasting oil-in-water (o/w) emulsions are used in large amounts for cooling and lubrication of contacting metal surfaces. The main advantages of using o/w emulsions are in terms of their properties such as kinetic stability and high specific heats and high heat transfer coefficients provided by them and therefore can be used under high temperature and high-pressure conditions in the hot-rolling mills of steel industries (Mang, 2017). Such emulsions are, however, hazardous to the environment if disposed off as such. These are carcinogenic, toxic, and mutagenic. Hence, prior to their disposal, an adequate treatment of such oily wastewaters is essential. The conventional techniques such as acidification (Kovacs et al., 1968), deemulsification with chemicals (Rajak et al., 2016), air flotation (Rajak et al., 2015), membrane separation (An et al., 2018), ultrafiltration (He and Jiang, 2008; Nayak et al., 2017), gravity separation (Berman and Tamir, 2003), electro coagulation (Mandal et al., 2003; Cerqueira et al., 2011), and use of activated charcoal (Rajak et al., 2018) are already available. These are either energy intensive, non-eco-friendly, costly, or time-consuming, or all of these. The present work is based on de-emulsification of persistent oil-in-water emulsions, using nanoparticles. This process is energy efficient, eco-friendly, cost-effective, and quick.

EXPERIMENTAL WORK

Characterization of oil-water emulsion

1. Stability of emulsion: The emulsion was fairly stable. There was no apparent change in the appearance of the emulsion till six months. It remained whitish. When this emulsion was stirred at 2200 RPM in an open vessel, a thin film of foam appeared. When the agitation was stopped the foam disappeared very quickly (within a few seconds) at the surface.

2. Size of oil droplets: The emulsion consists of very fine oil droplets in water. An oil-soluble dye (Sudan Red dye) was added to a sample of the emulsion. The emulsion became pinkish. One drop of this emulsion (containing dye in it) was put on a glass slide. This was then observed under a microscope. The oil droplets become visible because of the dye. It can be seen that the oil droplets are in a very narrow size range 1-2 μm (figure 1). The space in between the oil droplets indicates water.

![Figure 1. Optical microscopic image of emulsion with Sudan Red in it at 100X magnification.](image)

Materials and Methodology for the Synthesis of Magnetically Responsive Nanoparticles

The involved materials include ferric chloride (FeCl3), acetone ((CH3)2 CO) (99%) and ammonia solution (NH3OH) (25%) were purchased from Fisher Scientific, and ferrous chloride (FeCl2.2H2O) was purchased from CDH. All the chemicals used were of LR grade and used as received without further purification. Water from an RO (Reverse osmosis) unit was used as a solvent for the whole process (Berger et al., 1999).
Magnetite nanoparticles were synthesized by the co-precipitation method. The basic chemical reactions involved are as follows.

\[ 2\text{FeCl}_3 + 6\text{H}_2\text{O} = 2\text{Fe(OH)}_3 + 6\text{HCl} \]
\[ \text{FeCl}_2 + 2\text{H}_2\text{O} = \text{Fe(OH)}_2 + 2\text{HCl} \]
\[ 2\text{FeCl}_3 + \text{FeCl}_2 + 8\text{NH}_3 + 4\text{H}_2\text{O} = \text{FeO(Fe}_2\text{O}_3) + 8\text{NH}_4\text{Cl} \]

2M FeCl₃ and 2M FeCl₂ anhydrous salts solutions were prepared using RO water. Ammonium hydroxide solution was added dropwise to the mixture of salt solutions until the colour of the solution turned black. This black colour indicated the formation of Fe₃O₄ nanoparticles.

**Characterization of Fe₃O₄ nanoparticles**

XRD analysis reveals that the characteristic peaks can be perfectly indexed to fcc magnetite. No peaks for impurities were detected.

For TEM analysis the samples were prepared in acetone suspension. Two drops of the suspension were put on carbon-coated copper grid. It was dried at room temperature. This copper grid was observed under a microscope (JEM-1400, 120 KV). The evaluation of the average shape and size of MNPs was performed by computer based software (TEMCON). It could be observed that most of the particles are in the size range of 5-10 nm. This is in the agreement with the observations reported in literature (Mahdavi et al., 2013).

SEM analysis revealed that the nanoparticles were agglomerated due to lack of use of any capping agent during synthesis (Shen et al., 2009).

**Experimental set-up**

It consists of a mixer equipped with a mechanical stirrer, and a peristaltic pump which provides a constant flow rate. A conveyor belt is placed with an inclined portion under the mixer rotating on three pullies (figure 2). The lower pulley (3) is attached to a variable frequency drive (VFD) which gives a constant linear velocity to the belt. A set of permanent magnets is placed below the conveyor belt at the site where the mixture from the mixer falls on the conveyor belt. A scraper is used at the upper end of the belt to scrape off the carried-over material. A collector (for oil and nanoparticles) was placed below the scraper to collect all the material scraped off the conveyor belt. Another collector was placed below the lower pulley to collect the treated water.

**De-emulsification using magnetic nanoparticles /breaking of the emulsion:** When a batch of emulsion and MNPs slurry is mixed together for 10 minutes, the oil droplets in the emulsion get loaded with the magnetic nanoparticles and get partially coalesced. This mixture then falls on to the rotating conveyor belt, through the peristaltic pump, where the separation of phases occurs under the influence of the magnetic field applied with the help of permanent magnets.

**Separation of phases:** As the mixture falls continuously on to the conveyor belt (permanent magnet site), the partially coalesced oil droplets loaded with nanoparticles get stuck on to it due to the applied magnetic field and get carried along to the upper end (pulley (2)) of the conveyor belt. The carried-over material is scraped off the belt by the scraper, and gets collected in to the oil collector. The treated waste water gets collected in the water collector. The volume of collected treated water was measured. The recovered amounts of oil, water, and nanoparticles were also measured.
RESULTS AND DISCUSSION

Figure 3 shows the XRD pattern of pure magnetite (Fe$_3$O$_4$) nanoparticles synthesized by the chemical co-precipitation method (Zhou et al., 2015). TEM analysis (Figure 4) confirms the synthesis of magnetite (Fe$_3$O$_4$) nanoparticles of approximately 10nm size.

Figure 2. Schematic diagram of the setup

An incomplete de-emulsification was observed when a slurry of 5.6 % (w/v) was used, due to an insufficient amount of nanoparticles. A complete de-emulsification was observed with 6.7 % (w/v) slurry to a thin paste of oil-loaded nanoparticles and a little amount of water. Supernatant water (i.e. the treated emulsion) was completely transparent. For example, 2500 ml of emulsion containing 1 % (v/v) oil in it was treated with 1500 ml of suspension containing 100.7 g of MNPs. The oil content in the supernatant water was determined with the help of a turbidity meter. The turbidity meter was calibrated beforehand. The quality of treated effluent corresponded to less than 10 mg oil /litre of treated effluent. This

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**Figure 3.** XRD peaks of magnetite nanoparticles.

**Figure 4.** TEM image of magnetite nanoparticles.
corresponded to the removal of more than 99 % oil from the original emulsion.

But with 16.2 % (w/v) slurry, a thick paste of oil loaded nanoparticles was observed a complete de-emulsification. We got 32% (v/v) of oil, 97 % (v/v) of water, and 97.57% (w/v) of nanoparticles using 16.2 % (w/v) of slurry, while only 30.4 % (v/v) of oil, 77.5 % (v/v) of water, and 80.85 % (w/v) of nanoparticles were recovered using 6.7% (w/v) of MNPs slurry concentration.

**Proposed mechanism:** The MNPs are particles in the nanosize range (5-10 nm). Due to the very small size, the particles have a high surface energy. Because of this high surface energy, the stabilizer of the emulsion (soap solution or surface active agent) dissociates itself from the oil and adsorbs onto the particles. This results in the separation of very fine droplets of oil. The MNPs are oleophilic (oil has a very strong affinity for nanoparticles). The oil droplets therefore get adsorbed on the MNPs.

The oil-loaded MNPs and the MNPs loaded oil droplets settle very quickly in presence of the magnetic field.

![Figure 5.a. Thick paste of oil-loaded nanoparticles at oil collector end, b. Recovered oil.](image)

**CONCLUSIONS:**

1. MNPs (Fe₃O₄) were synthesized in the laboratory by co-precipitation method. The particles were in the size range 5-10 nm.

2. A belt conveyor system was developed for treating oil-in-water emulsion.

3. The MNPs can effectively treat the emulsion effluents of steel rolling mills (a) About 100 g of MNPs contained in 1500 ml slurry (6.7 %, w/v) can de-emulsify 2500 ml of oil in water emulsion (1 %, v/v) in a stirred vessel. The treated emulsion was completely transparent. More than 99 % of oil could be removed.

   (b) The quality of recovered water (treated effluent) met the permissible limit (< 10 mg of oil /l of water) for disposal.

4. (a) However complete phase separation (separation of oil and treated water) could not be achieved with the above conditions on the present belt conveyor system.

   (b) Complete phase separation could be achieved when 242 g of MNPs contained in 1500 ml slurry (16.2 %, w/v) were used for treatment of 2500 ml of oil-in-water emulsion (1 % v/v).

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**Conflict of interest statement**

The author declares no competing or conflict of interests. The funders had no role in study design, writing of the manuscript and decision to publish.

**Authors’ contributions**

Parsanta modified the basic set-up and conducted the experimental work. Professor Ashok N. Bhaskarwar suggested the basic idea and kept the problem alive over the past two decades.

**REFERENCES**


