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Short Communication

Eco-Friendly, Non-Toxic Cutting Fluid for Sustainable Manufacturing and Machining Processes

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Mineral oils, chemically synthesized emulsifiers, and additives are the basic ingredients of commercially available metal working fluids. Its application in metal cutting have earned widespread acceptance all over the world. However, their harmful effects on the environment and life threatening health hazards to workers are of great concern and calls for a better alternative. In this present study a green metalworking fluid / green cutting fluid (GCF) was formulated and the performance was evaluated comparing with the commercial metal working fluid (COM) used in industries for machining processes. The obtained eco-friendly formulation has material properties equivalent to the commercial formulation without any environmental hazard. GCF is comparable to COM in corrosion prevention, inhibition of microbial growth and other machining processes. It was reported that vegetable oil based green cutting fluids have more of Gram-negative bacterial growth where as mineral oil based ones have more of Gram-positive bacteria. These bacteria cause environmental hazards and antimicrobials can be included for better antimicrobial properties. GCF supersedes COM by being non-toxic at LC50 >1000 mg/L and COM being toxic at LC50 < 100 mg/L according to OECD 203 tests methods. GCF, produced only from renewable sources is non-toxic and biodegradable and helps contribute towards green and sustainable manufacturing processes without any environmental pollution or hazards.

Keywords: metalworking fluids, corrosion, non-toxic, renewable sources, drilling, turning, surface roughness

1. Introduction

Metal cutting fluids or coolants are used in manufacturing industries to keep the work zone at a stable temperature, to lubricate chip-tool interface and to flush away chips [1,2]. Several types of cutting fluids are available commercially, which include neat cutting oil, water-soluble cutting fluids, synthetic and semi synthetic cutting fluids. Conventional cutting fluids have mineral oil as base along with different additives for performance enhancement. Mineral oil has a poor biodegradability thus becoming a source of environmental pollution in long term. A major issue lies in their inappropriate disposal, which results in surface water and ground water contamination, air pollution, soil contamination and consequently, agricultural products and food contamination [3,4]. Even when cutting fluid disposal is managed properly, the cutting fluid associated with chip removal can create problem [5]. Mineral oil based formulations can cause ground water pollution up to 100 years and it can reduce the growth of plants and life span of aquatic life [6].

Mineral oil is derived from one of the finite resources of planet earth; the fossil fuels. It is therefore necessary to adopt sustainable technologies of product designing. A sustainable product should be able to completely replenish or recycle its raw materials utilized for product designing, after completion of its life cycle. A cutting fluid has many additives to enhance its performance along with mineral oil and emulsifiers. These additives are highly toxic to ecosystem, non-renewable and non biodegradable in nature [7].

Many biocides used in complex mixtures of cutting oil make it an irritant and is the reason for several occupational diseases like dermatitis, oil acne, respiratory-tract infections and many other allergic

reactions [8]. The alkalinity of cutting fluids promotes the selective growth of many pathogenic microorganisms. Many incompletely oxidized products of anaerobic microorganisms create foul smell after a period of stagnation. Microbiology of cutting fluid is very complex with different microbes dominating with different biochemical activity at different stages. The microbial toxins and enzymes thus generated, particularly in the water soluble cutting fluids, and frequently used chemical biocides to kill microbes, are carcinogenic and can lead to cancer [9].

Scientists and tribologists developed various alternatives to overcome the limitations of mineral oil based cutting fluids. Synthetic lubricants, animal tallow and solid lubricants are the alternatives presently in use. Vegetable oil is the other highly attractive substitute for mineral oil due to its renewable, environment friendly, relatively non-toxic and readily biodegradable properties [10]. Vegetable oils are the esters of glycerol and fatty acids. Advantages of vegetable oils include good solvency, high lubricity, low volatility, and high load carrying capacity, low emission of hydrocarbons, higher fire resistance and good thermal properties [11,12]. The present developments include the cutting fluid developed from vegetable oils like soybean oil, castor oil, palm oil, rapeseed oil and canola oil. These vegetable oils have larger number of unsaturation in their chemical structure that makes it more prone to oxidative degradation [13,14]. The oxidative degradation of the base oil in cutting fluid hinders its cutting properties leading to severe metal corrosion. In this study, we have used coconut oil as a base for GCF. Coconut oil contains more than 90% saturated fatty acids and is more resistant to oxidative degradation [15]. Coconut oil as neat cutting fluid has better cutting force in comparison with other vegetable oils, which include groundnut oil, palm kernel oil etc. Coconut oil emulsion with acacia powder has better properties for grinding fluid [16]. In this study, we have developed a complete green coconut oil based cutting oil emulsion, where both emulsifier and additive are relatively non-toxic to aquatic system, renewable and sustainable in nature. Gram-positive and Gram-negative bacterial growth is comparable with the commercial sample and the antimicrobial properties can be improved by adding additional antimicrobials.

2. Materials and methods

2.1. Formulation of green cutting fluid (GCF)

A new green cutting fluid from renewable components was developed with non-toxic, biodegradable, ecofriendly base materials. Coconut oil used as base oil was obtained from oil mill as raw coconut oil without any chemical refining. The food grade emulsifiers EF-1 (Polysorbate 85), EF-2 (Polysorbate 80) and EF-3 (Triethanolamine) were obtained from emulsifier market with 99.98% of purity. Green additives (essential oils) A-1 and A-2 were obtained from Falex International Export and Import, Bangalore, with 99.98% of purity. A-1 and A-2 are the essential oils extracted from the leaves of *Azadirachta indica* and *Cymbopogon citratus* respectively. Green additive A-3 was extracted from leaf and stem of *Centella asiatica* in coconut oil and A-4 was filtered syrup made from jaggery obtained commercially. GCF was prepared using the following components;

(a) Coconut oil base (50 mass%)
(b) Emulsifiers (40 mass%) - [EF-1 (77 mass%); EF-2 (20 mass%); EF-3 (3 mass%)]
(c) Additives - A-1 (1 mass%), A-2 (3 mass%), A-3 (3 mass%), A-4 (3 mass%)

The cutting oil was mixed with deionized water in 1 : 20 ratio for further testing and characterization.

2.2. Hydrophilic-lipophilic balance (HLB)

HLB is the ratio of water-soluble and lipid soluble portion of a molecule. Present study prepared emulsifiers by mixing two different emulsifiers with HLB value of 4 and 16 in different proportion to obtain reference scale for HLB with ranges of 4, 6, 8, 10, 12, 14 and 16. HLB values of test samples like coconut oil and different green additives were determined. HLB is measured mixing 2 g of test sample with 2 g of reference scale emulsifiers and adding 10 ml of distilled water and stirring for 15 min. Sample with emulsifier of particular HLB value and no separation or least separation of oil and water is considered as the HLB value required by test sample to obtain a stable emulsion [17].

2.3. Stability of emulsion

Different ratios of emulsifiers and coconut oil (Table 1) were mixed to develop a stable emulsion of GCF. Stability of emulsion was checked by measuring particle size and zeta potential. Particle size and zeta potential was measured in 90 Plus Particle size analyzer (Brookhaven Instruments Corporation). Oven test was performed to check for storage stability as per the guidelines of ASTM D3707 method [18]. A 100 ml test sample was kept at 85°C in 100 ml measuring cylinder for 48 hours. Sample was measured for amount of free water, oil and emulsion after incubation.

2.4. Corrosion tests

Corrosion tests of cutting fluid samples were carried out as per the guidelines of ASTM D4627 method [19].

Table 1 Proposed ratios of emulsifier: coconut oil for stable emulsion

Ratio used (Emulsifier: Coconut oil)	Visual Stability for Fifteen Days
1.0 : 1.25	Stable
1.0 : 1.5	Stable
1.5 : 2.5	Not stable
1.8 : 2.5	Not stable
2.2 : 2.5	Not stable

12 g of cast iron chips were weighed and placed on the filter paper in a Petri dish. 25 ml of cutting fluid sample was added to Petri dish and after 4 h incubation; the cutting fluid is drained out. Dish was covered and allowed to stand for 72 hours. Anticorrosion properties of cutting fluids were correlated to the amount of rusting stain on the filter paper. The weight loss of the cast iron chips at 24, 48 and 72 hours was measured on cleaning the chips exposed to cutting fluid by ultrasonication using acetone for 20 minutes. On drying, the weight of the cast iron chips was measured and calculated for the weight loss on corrosion.

3. Performance analysis of cutting fluid in machining-turning and drilling

To assess the machining performance of cutting fluids turning and drilling experiments were carried out on mild steel. Coolants based on vegetable oils shown ability to deliver machining performance in most applications was significantly superior to that of mineral based cutting fluids [20]. Turning experiments were performed in a lathe equipped with a 3-axis dynamometer to measure tangential force, feed force and radial force. Commercial grade AISI 1018 mild steel cylindrical rod of diameter 25 mm was used as work piece. Carbide cutting tool insert with rake angle of 15° was used for turning operation; it is fixed to the dynamometer insert holder. 5% of cutting fluid emulsion was prepared with deionized water for all experiments. Cutting fluid emulsion was supplied to the point of cutting by a pump through a single nozzle with the flow rate of 3.0 L/min. Different parameters used to evaluate the cutting fluid performances are given in Table 2.

Drilling experiments were also carried out using AISI 1018- mild steel. HMT FN2 universal milling machine was used for this purpose. Holes were drilled keeping the work piece in submerged condition. Magnum instruments drill dynamometer was used for measuring the force and torque. Drilling operation was carried out using a 10 mm diameter HSS drill bit for drilling holes of 30 mm depth for the various combinations of controllable parameters mentioned in Table 3, with each experiment being repeated four times.

Table 2 Turning parameters to evaluate machining performance of cutting fluids

Levels	Speed (RPM)	Depth of cut [mm]
−1 [Low]	421	0.25
0 [Med]	646	0.5
1 [High]	1000	0.75

Table 3 Drilling parameters to evaluate machining performance of cutting fluids

Levels	Speed (RPM)	Feed (mm/min)
−1 [Low]	355	16
0 [Med]	710	25
1 [High]	1120	40

4. Microbial inhibition tests

The microbial inhibition test was carried out using microorganism, which can grow profusely in the cutting fluids; *Salmonella* Typhimurium 14028, *Pseudomonas aeruginosa* (PA01) and *Staphylococcus aureus* (ATCC 25923). The 1×10^5 CFU from an overnight culture was inoculated into the cutting fluid samples and incubated for 4 weeks. Every week samples were serially diluted and plated on LB agar and incubated at 37°C for 12 h. Colonies were counted and total CFU/ml was calculated and plotted.

4.1. Total aerobic microbial count (TAMC)

The TAMC of cutting fluid samples was determined by serial dilution and plating, where the samples collected regularly from storage tanks was used. 100 µL of each sample was serially diluted and plated on Soybean-Casein Digest Agar (SCDA) medium and incubated at 37°C for 12 h and colonies were enumerated. This experiment was carried out for 4 weeks of sample storage.

5. Cytotoxicity tests by MTT assay

The *in vitro* cytotoxicity of cutting fluid samples was assessed by MTT assay. HaCaT cell lines (immortal human keratinocyte line) were maintained in Dulbecco's Modified Eagle's Medium (DMEM, Sigma) supplemented with 10% fetal bovine serum and incubated in 5% CO_2 at 37°C. 5×10^4 cells were seeded into a 96 well plate and incubated for 8 h. The cells were incubated with 50 µg/ml of GCF and COM for different time duration. A volume of 20 µl MTT dye (5 mg/ml) was added into each well and incubated for 4 h at 37°C. The MTT is reduced to insoluble formazan crystals, depending on the viability of cells. The medium is replaced with equal volume of dimethyl sulfoxide (DMSO) and allowed to stand for 30 mins to dissolve the formazan into a purple coloured solution. The absorbance at 550 nm was measured in a SPECTRAmax PLUS 384 spectrophotometer. Cell viability was calculated as a percentage of control cells (untreated cells) at different time points.

6. Aquatic toxicity

6.1. Acute fish toxicity

Aquatic toxicity of each ingredient and final composition of cutting fluid samples were measured by following OECD 203 test method for acute fish toxicity test [21]. A pool of fish having less than 5% of mortality rate prior to testing was used in experiments. Seven fishes were exposed to test substances for 96 hours.

Concentration of test substance increased at the geometric series of 2.2. Dissolved oxygen and pH of each sample was determined every 24 h. Mortality was recorded at 24, 48, 72 and 96 h. Lethal concentration 50 (LC50) of the samples was estimated by calculating the concentration at which fifty percent of fishes are being killed.

6.2. Fish embryo toxicity test (FET)

6.2.1 Maintenance and egg production

Zebra fish aged from 6 to 24 months were used for egg production and the spawners are free from externally visible diseases and pharmaceutical treatments. The day before the test, males and females in a ratio of 2 : 1 were placed in breeding chambers before the onset of darkness. Mating, spawning and fertilization take place within 30 minutes after the onset of light in the morning. The eggs were collected and transferred to temperature controlled incubators 26 ±1°C, and only the fertilized eggs were used for testing [22].

6.2.2. FET

The Lethal concentration (LC50) of both GCF and COM was determined performing FET. The 24 hours post fertilization (hpf) embryos were used for FET test according to OECD [23]. In two replicates for each test concentration, 10 embryos were transferred per well into a 24-well plate with test concentration of 1 µg/L, 10 µg/L, and 100 µg/L and incubated at 26 ±1°C. The embryos were inspected at 24, 48, 72 and 96 h of exposure equivalent to 48, 72, 96 and 120 hpf respectively.

7. Results

7.1. Formulation and characteristics of green cutting fluid (GCF)

GCF is composed of ingredients from natural renewable sources. The ratios of the components in GCF were optimized to get stable cutting fluid properties comparable with the commercial cutting fluid. The standardized composition of GCF includes emulsifiers (40% w/w) along with green additives A-1 (1 mass%), A-2 (3 mass%), A-3 (3 mass%) and A-4 (3 mass%) to the coconut oil base (50 mass%). GCF and COM were tested for different physical parameters viz. pH, viscosity, stability, colour and corrosion grade and the results show that GCF has properties comparable to commercial cutting fluid as shown in Table 4. The pH of 7.5 and corrosion grade of 3 makes GCF a more suitable cutting fluid for industrial purposes.

7.2. Hydrophilic-Lipophilic balance (HLB)

HLB value determines the polarity of the emulsifier required to develop a stable emulsion of GCF which was determined to be around 12. There was no oil-water separation in the GCF emulsion prepared with the emulsifiers having ~12 HLB value. The HLB value for each ingredient is given in Table 5. Stable emulsion of coconut oil with green additives was developed with the emulsifier having ~12 HLB value which is stable.

Table 4 Characteristics of cutting fluids

S NO	Property	Value	
		GCF	COM
1	pH value	7.5	8.6
2	Viscosity	9.18×10^{-4} Pa·s	9.30×10^{-4} Pa·s
3	Stability	Stable	Stable
4	Colour	Whitish	Milky white
5	Corrosion Grade	3	4

Table 5 Toxicity level and HLB value of coconut oil, emulsifiers and green additives

Sample name	Toxicity level (LC50) mg/L	HLB Value
Coconut oil	> 2342.56	12.0
EF-1	> 1064.8	11.0
EF-2	> 1064.8	15.0
EF-3	> 1064.8	12
EF-1 + EF-2 + EF-3	> 1064.8	12
A-1	≥ 1064.8	8
A-2	≥ 1064.8	16
A-3	≥ 1064.8	12
A-4	≥ 1064.8	-
GCF: Coconut oil + EF-1 + EF-2 + EF-3 + A-1 + A-2 + A-3 + A-4	≥ 1064.8	12
Commercial cutting fluid (COM)	≤ 100	-

7.3. Emulsion stability of green cutting fluid

Emulsion stability of green cutting fluid was measured by particle size, zeta potential and oven test measurements. Emulsifier to Coconut oil ratio of 1.0 : 1.25 was found to be much stable than any other ratio formulated (Table 1). The average particle size of GCF found to be 73.1 nm in comparison to 252.90 nm of COM and zeta potential of GCF was found to be −22.43 mV better than −49.76 mV zeta potential of COM (Table 6). Storage stability of emulsions was determined through visual appearance where GCF showed least separation or creamy layer, while COM formed a creamy layer with oily phase after 45 days (Table 6). Oven test as per ASTM D3707-89 (Table 7) was used to assess the thermal stability by measuring the separation of emulsion sample into oil and water after heating at 85°C for 48 h in a thermostatically controlled oven. Oil separation was observed for COM, whereas GCF showed least separation of emulsion. Based on all the parameters measured, the stability of GCF proved to be better than COM.

7.4. Anticorrosion properties

The ASTM D4627 and weight loss method was used to determine the corrosion rate of cutting fluid samples. As per ASTM D4627 the rate of corrosion is graded from 1 to 10, where 1 is non-corrosive, 5 being medium and 10 is highly corrosive. GCF showed less corrosion with grade of 3 in comparison to COM showing corrosion with grade of 4. The weight loss in the iron chips was measured for GCF was found to be 147 mg comparable to COM inducing 154 mg weight loss after 72 h incubation period (Fig. 1). The result clearly demonstrates that the corrosion rate of GCF is comparable to COM.

7.5. Machining performance of cutting fluids on mild steel

The machining properties of formulated cutting fluid were determined by measuring the forces generated during turning and drilling experiments. Experimental results for turning at a set parameter of 421 rpm and 1000 rpm for different depth of cuts, has shown that GCF performed better than COM. In all the given condition, dry turning gave higher cutting force values (tangential & feed).Vegetable based lubricants are effective due to its strong interactions with the lubricated surface.The influence of tribo film formed by cutting fluid between tool and work in each experiment could have brought the difference in results. The results (Fig. 2(a,b)) clearly indicate that GCF, on turning had better machining properties in comparison to COM.

The force and torque values obtained by drilling experiments using GCF and COM were almost similar. At 355, 710 and 1120 rpm with feed rates 4 mm/min, 10 mm/min and 25 mm/min respectively, lesser cutting force was measured with GCF compared to COM. COM showed same trends at the conditions of 4 mm/min at 355

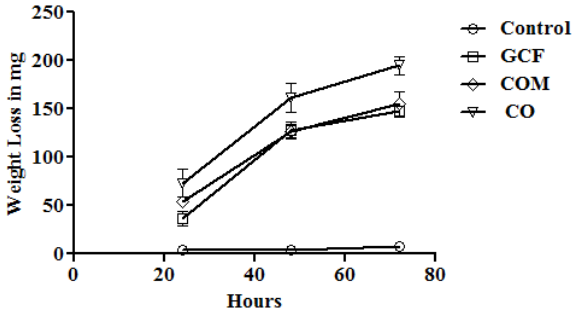

Fig. 1 Rate of Corrosion by weight loss method. The weight loss method as per ASTM D4627 was performed to assess the corrosion rate of GCF and COM for 72 h using iron chips. Data shown as Mean ± SD of triplicate values for individual experiments. Control - Dry Fe chips; GCF - Green cutting fluid; COM- Commercial Mineral oil based cutting fluid; CO- Coconut oil emulsion without additives

Table 6 Comparison of particle size, zeta potential, visual appearance of emulsion stability

Sample name	Particle size (nm)	Zeta potential (mV)	Emulsion Stability in visual appearance		
			15th Day	30th Day	45th Day
Coconut oil emulsion	100.06	−26.05	Not separated	Thin creamy layer	Thin creamy layer
GCF	73.1	−22.43	Not separated	Very thin creamy layer	Thin creamy layer
COM	252.90	−49.76	Not separated	Thin creamy layer	Thick creamy layer and thin emulsion

Table 7 Assessment of storage stability by oven test

Sample name	Amount of oil (ml)	Amount of water (ml)	Amount of emulsion (ml)
Green cutting fluid (GCF)	1	88	11
Commercial cutting fluid (COM)	1	91	8

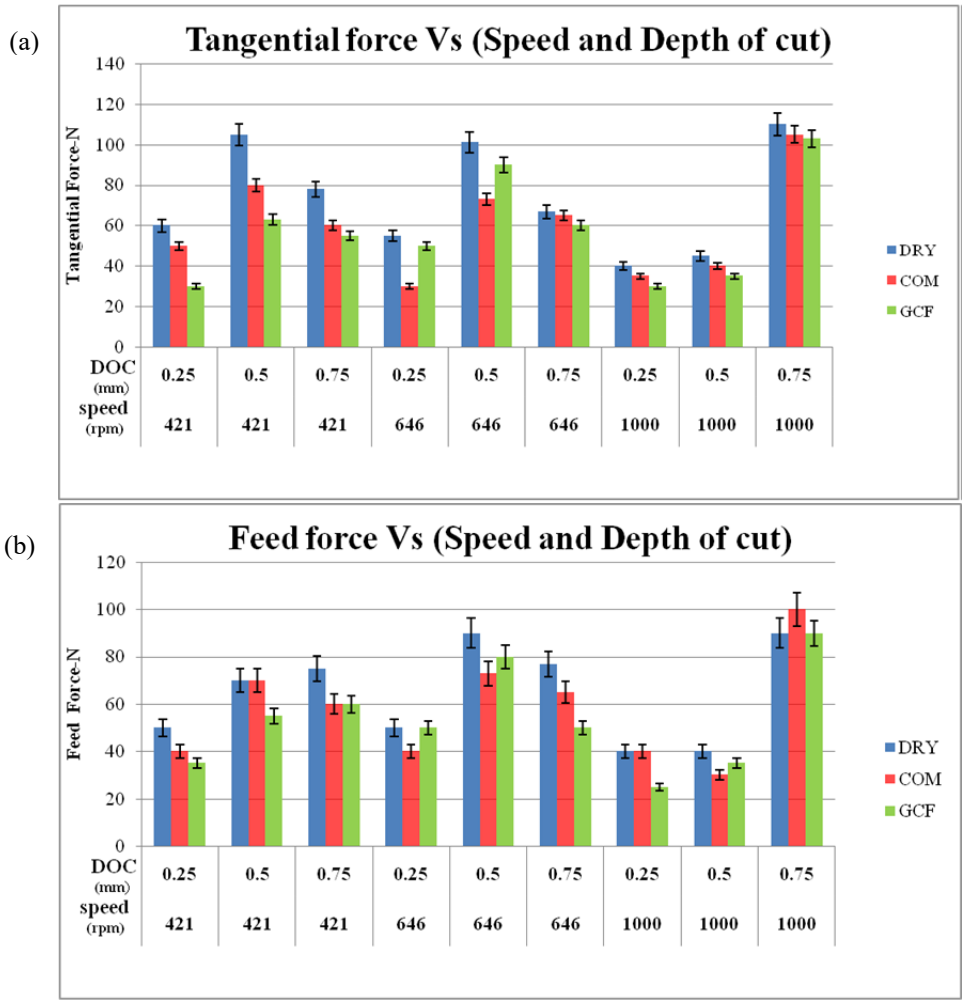

Fig. 2 Performance analysis of cutting fluids on Mild steel by turning experiments. (a) Tangential force measurement and (b) Feed force measurement for various speed and Depth of Cut. COM-Commercial Mineral oil based cutting fluid; GCF-Green cutting fluid; DRY- experiment without lubrication

rpm and all feed rates at 1120 rpm. Furthermore GCF showed higher cutting force than COM at the conditions of 10 mm/min at 355 rpm, 25 mm/min at 710 rpm and 4 mm/min at 1120 rpm. In few combinations of speed and feed rates lesser cutting force values and higher torque values were recorded with GCF compared to COM, during a cutting operation, the chip flows on the rake face and the chip may interfere in fluid reaching the zone of cutting which in turn may affect the force and torque required in shearing the material.The form and thickness of chips directly or indirectly indicate the nature of chip-tool interaction influenced by the machining environment [20]. Force and torque values were decreasing with the application of cutting fluid, as it will be acting as a lubricant at the interface between tool and work piece, in turn reducing friction by penetrating into the tool work interface. With increase in the spindle speed the thrust force value decreased and an increase in feed rate increased the thrust force which is plotted in graph (Fig. 3(a,b)). Increasing the feed rate increased the surface roughness value as material removal is high. And an increase in the spindle speed decreased the surface roughness value.The performance of green cutting fluid was stable and efficient with variation to the cutting speed and feed rates, which gives a thrust for further study, analysis and improvement. The results observed in turning and drilling experiments indicates that GCF is comparable to COM in machining processes and could be a viable replacement as it is even environmentally benign.

7.6. Microbial test

It was reported that vegetable oil-based cutting fluids were associated with Gram-negative bacteria whereas; mineral oil-based cutting fluids were associated with Gram-positive bacteria [24]. Microbial plating technique was used to determine the microbial inhibition potential of the cutting fluid over a period of 4 weeks. The pathogenic organisms *Salmonella* Typhimurium, *Pseudomonas aeruginosa* and *Staphylococcus aureus* were used as test organisms. The progression of colony

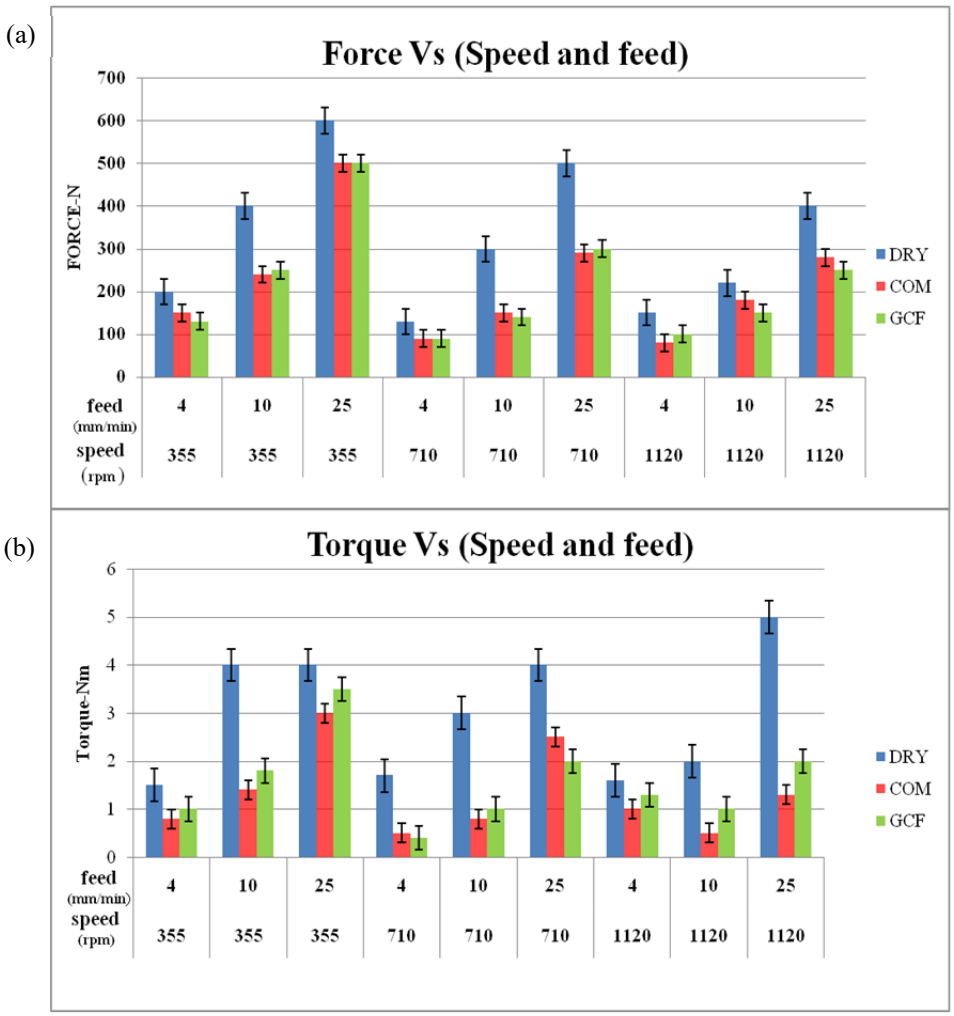

Fig. 3 Performance analysis of cutting fluids on Mild steel by drilling experiments. (a) Force variation with speed and feed rates and (b) Torque variation for different speed and feed rates. COM-Commercial Mineral oil based cutting fluid; GCF -Green cutting fluid; DRY- experiment without lubrication

counts for *S.* Typhimurium after 4 weeks were found to be 4×10^7 CFU/ml in GCF in comparison with 8×10^6 CFU/ml in COM (Fig. 4(a)). The colony counts for *P. aeruginosa* increased to reach 3×10^7 CFU/ml for GCF whereas 2.5×10^7 CFU/ml was observed in COM (Fig. 4(b)). The colony counts for *S. aureus* increased exponentially in GCF to reach 3.2×10^8 CFU/ml compared to slow progression to 2.9×10^8 CFU/ml in COM (Fig. 4(c)). Total microbial growth in the used cutting fluids was measured at different duration for 4 weeks (Fig. 4(d)). It was observed that COM and GCF showed similar total aerobic microbial count at 28 days. The bacterial growth in the cutting fluid causes health hazards and GCF showed similar microbial growth compared to COM.

7.7. Cytotoxicity test

HaCaT cell lines were used as a model system to study the toxicity of cutting fluids in human keratinocyte cell lines. The cutting fluid samples (GCF, COM) on incubation with 5×10^4 cells in a 96-well plate at different time points starting from 2 h to 24 h was assessed for their cytotoxicity by MTT assay. The COM sample caused a significant cell death at 50 µg/ml concentration but GCF sample (50 µg/ml) did not affect the viability of the cell lines. The results (Fig. 5(a)) clearly indicates that COM is toxic compared to GCF which does not have any toxic effect at a concentration of 50 µg/ml. Even in 2 h, COM showed significant reduction in cell viability and no significant reduction in cell viability on incubation with GCF was observed up to 24 h. These results clearly indicate the toxicity of commercial cutting fluids in human keratinocyte cell lines.

7.8. Aquatic toxicity

7.8.1 Acute fish toxicity tests

Aquatic toxicity with zebra fishes was performed to determine the toxicity as per OECD 203 method [21]. Test sample with LC50 > 1000 mg/L of water is

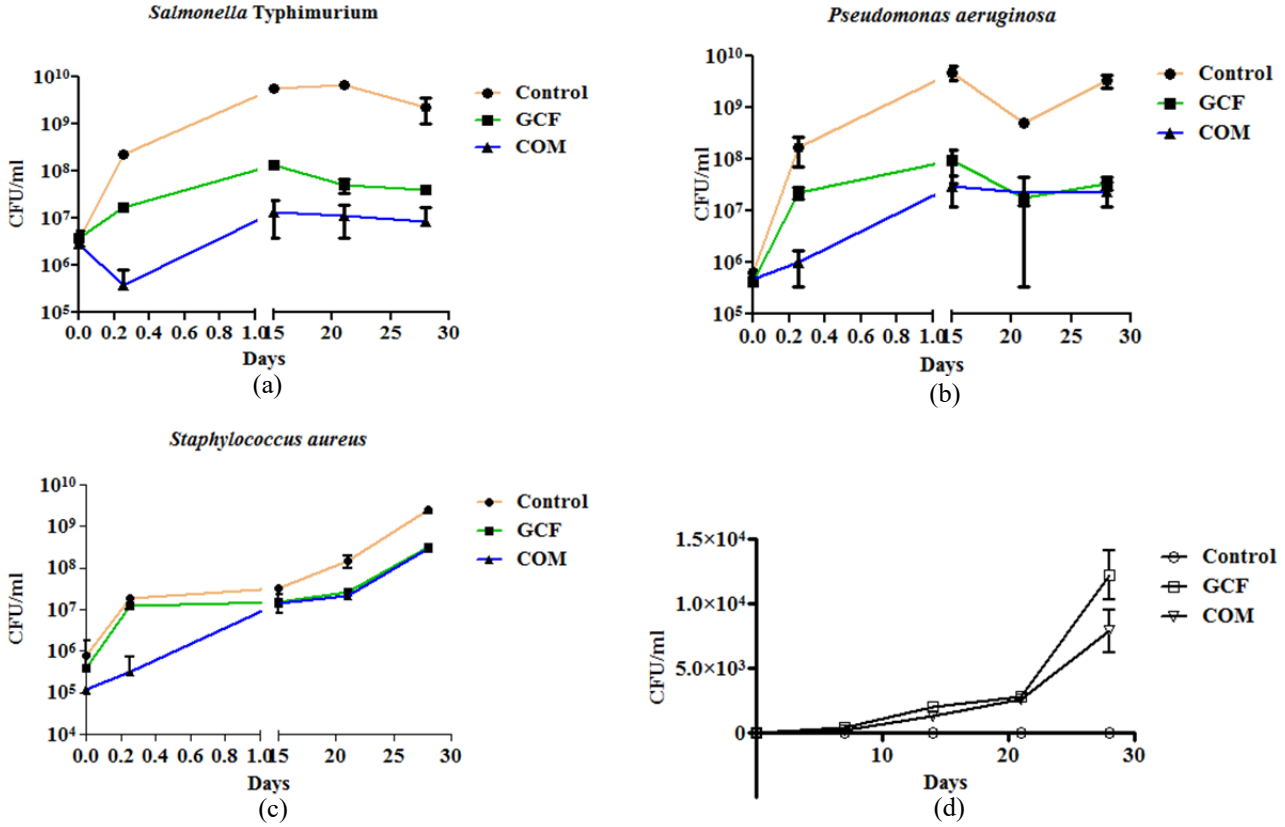

Fig. 4 Effect of cutting fluids on microbial growth. Effect of GCF and COM in (a) *Salmonella* Typhimurium and (b) *Pseudomonas aeruginosa* (c) *Staphylococcus aureus* was determined by serial dilution and plating. 1 × 10^5 CFU was inoculated in GCF or COM and incubated at 37°C and at different time points the culture was plated to check the microbial growth up to 4 weeks. Data shown as Mean ± SD. Experiment was performed three times and representative data is shown. Control- coconut oil emulsion without additives; GCF- Green cutting oil; COM- Commercial Mineral oil based cutting fluid. (d) Total Microbial Count (TMC) in cutting fluid samples. TMC in GCF and COM was determined by plating technique for 4weeks. SCDA plates incubated at 37°C for 48 h and the colonies were enumerated. Data shown as Mean ± SD of triplicate values of independent experiment. Control- Sterile water; GCF -Green cutting fluid; COM- Commercial Mineral oil based cutting fluid

considered as relatively non-toxic to the aquatic system [21]. The toxicity of coconut oil, emulsifiers (EF), different green additives, GCF and COM were tested for the acute fish toxicity (Table 5). LC50 value for Coconut oil was estimated as > 2342.56 mg/L and EF and green additives were estimated as > 1064 mg/L. The GCF with green additives has a LC50 value ≥ 1064 mg/L. Commercial cutting fluid (COM) has a LC50 value of 100 mg/L and the toxicity is 10 times higher than GCF. Survival assay of zebra fish showed that all the fish died within 24 h when 100 mg/L commercial cutting fluid (COM) was used whereas no toxicity was observed when 1064 mg/L GCF was used (Fig. 5(b)). This result clearly indicates that, even 10 times higher concentration of GCF has no observed aquatic toxicity.

7.8.2 Fish Embryo toxicity (FET)

FET was used to assess the toxicity of cutting fluids on the embryos at an age of 24 hpf and incubated up to 120 hpf for different concentration of GCF and COM. The LC50 value for GCF after 120 hpf was estimated to be 100 µg/L compared to the LC50 of COM to be < 1 µg/L. The LC50 value for COM was 100 times greater than LC50 value of GCF. This result (Fig. 5(c)) clearly indicates that COM is highly toxic to the fish embryos where as GCF is relatively non-toxic.

7.9. Total aerobic microbial count

Microbial contamination of cutting fluid samples was assessed by plate counting on SCDA medium. The gradual progression of the microbial growth in the cutting fluid samples was observed for 4 weeks after emulsion preparation and both GCF and COM samples showed comparable microbial mass. In the 4th week the bacterial mass increased to 1.2 × 10^4 CFU/ml in GCF sample and 7.9 × 10^3 CFU/ml in COM sample (Fig. 4(d)).

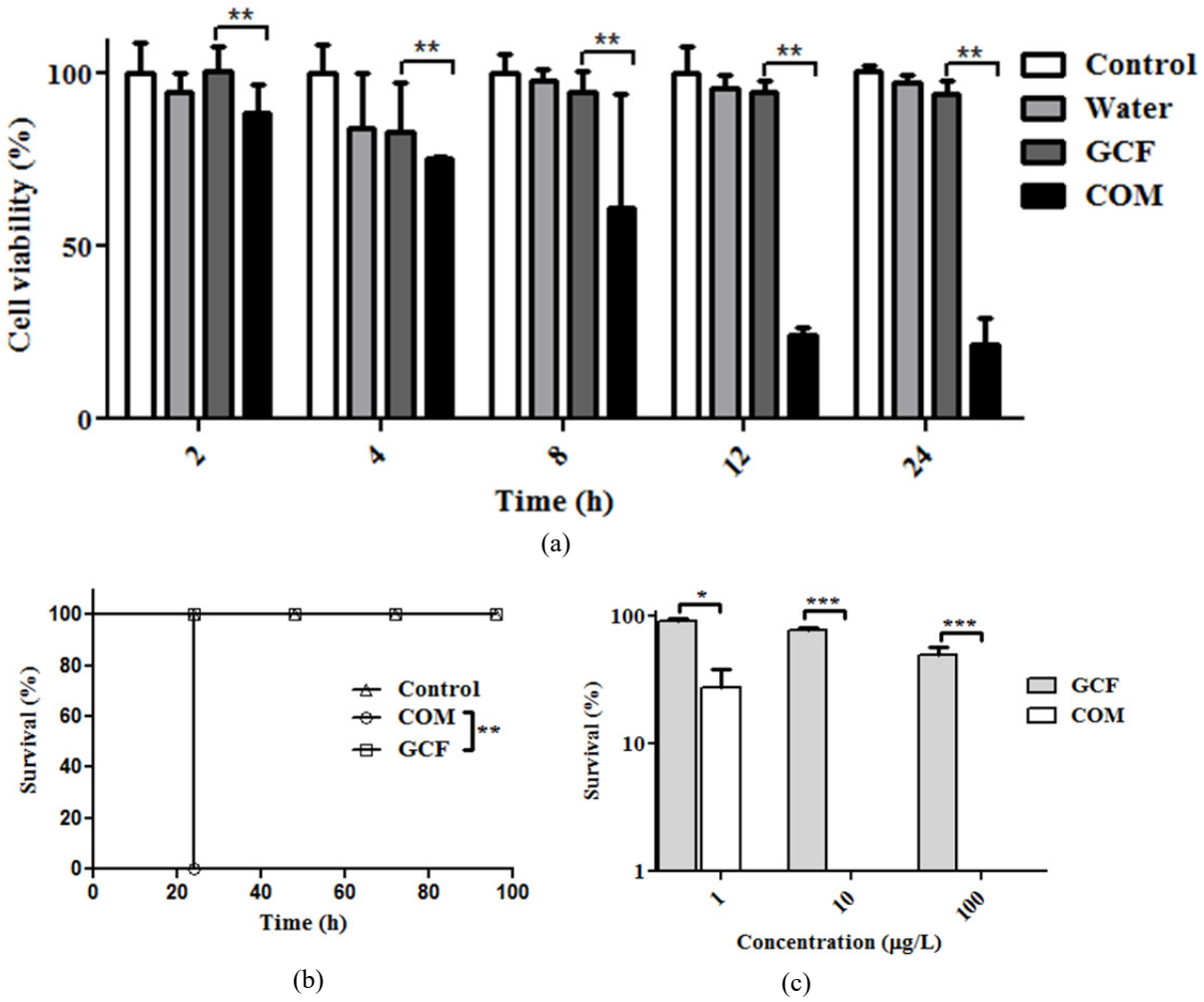

Fig. 5 Toxicity assessment of GCF and COM. (a) Viability of HaCaT cell lines treated with cutting fluid samples by MTT assay. MTT assay was performed to assess the cytotoxicity of GCF & COM in HaCaT cell lines. 1×10^4 cells were seeded in a 96-well plate with 20 µl of 50 µg/ml concentration of GCF & COM. OD at 550 nm was taken at different time points. One-Way ANOVA was performed. Analysis are indicated by bracket and asterisks as follows: *, $P < 0.01$; **, $P < 0.001$; ***, $P < 0.0001$. Control- Growth medium; GCF -Green cutting fluid; COM-Commercial Mineral oil based cutting fluid. (b) Survival assay of Zebra fish as per OECD 203 using cutting fluids. Toxicity of GCF and COM was determined by survival assay. Seven zebra fishes were exposed to 1064 mg/L of GCF and 100 mg/L of COM for 96 h. Statistical significance by the log rank test are indicated by bracket and asterisks as follows: **, $P < 0.0025$. OECD- Organization for Economic Co-operation and Development; LC50- Lethal concentration to kill 50% of the population. (c) Fish Embryo Toxicity Test. FET was performed to assess the LC50 value for GCF and COM. The 24 hpf embryos are exposed to 1.0 µg/L; 10 µg/L and 100 µg/L concentrations of GCF and COM up to 120 hpf. The embryo test is classified valid, only when the mortality of control is ≤ 10%. Values that are statistically significant by Student's t-test are indicated by bracket and asterisks as follows: *, $P < 0.01$; **, $P < 0.001$; ***, $P < 0.0001$. LC50- Lethal concentration to kill 50% of the population; hpf - hours post fertilization

8. Discussion

Cutting fluids are widely used in industries for machining operations and over 380 million liters of cutting fluids are used every year in United States [25]. Present manufacturing processes using conventional cutting fluids are not amply ecofriendly and produce many products and byproducts, which have harmful effects on workers and environment. The mineral oil based cutting fluids with complex composition acting as irritant or allergenic are causing about 80% of occupational infections due to skin contact [26]. The petroleum based cutting fluids with hazardous effects that are toxic and less biodegradable lead to environmental problems and serious health problems like lung cancer, respiratory diseases, dermatological and

genetic disorders [24,27]. The metal particle contamination and toxic byproducts of the cutting fluids during their lifecycle affect the quality of cutting fluids after usage. Thus, disposal of cutting fluids is of great concern because it is costly and cause harmful effects on environment [28]. Therefore, designing an ecofriendly, non-toxic and sustainable product with good cutting fluid properties is of great importance.

Present study using aquatic non-toxicity as the primary criterion is to select the base oil, emulsifiers, and green additives to develop a sustainable green cutting fluid. Coconut oil with more than 90% saturated fatty acids is known to be non-toxic to aquatic system. Higher percentage of saturation in coconut oil ensures higher stability to thermal degradation and oxidative degradation of oil [29]. Being highly resistant to oxidative depletion, coconut oil produces least amount of oxides and peroxides, which could otherwise be toxic to living beings. Tribological characterization of coconut oil proved that, it can reduce wear and friction between relatively moving metal bodies [30]. Emulsifiers used were obtained commercially and they were derived products of renewable and non- toxic natural resources. Green additives, used as performance enhancer was selected based on aquatic non-toxicity. Gas chromatography analysis for green additives reveals that it contains many toxic compounds in its composition, but they were minimum in concentration, which would not cause any mortality of fishes during toxicity analysis. Previous studies consider that, a compound with LC50 higher than 1000 mg/L of water as relatively non- toxic [31]. COM contains different additives as performance enhancers, like anticorrosive agents, extreme pressure additives, anti- ageing additives, biocides and defoamers. Compounds used as additives in COM includes amines, sulfonates, petroleum sulfonates, silicone polymers tributyl phosphate, organic sulfides, zinc dithiophosphates, aromatic amines, phenol derivatives, formaldehyde releasers, organic sulfurs, phosphorous and chlorine compounds. Many of these compounds are highly toxic to aquatic system even at their minimum concentration [32].

Vegetable oils are amphoteric in nature; it contains both hydrophilic and lipophilic groups. Non-ionic emulsifiers consist of a molecule that combines both the lipophilic and hydrophilic groups. The balancing of size and strength of hydrophilic and lipophilic group by emulsifier system is called as HLB system. For coconut oil, the hydrophilic-lipophilic balance of 12 with existing emulsifiers system satisfies to develop a stable emulsion system. The ratio of emulsifier to coconut oil 1.0 : 1.25 formed a stable emulsion among other proposed ratios. The zeta potential of other ratios were less than −20 mV and showed higher particle size of range between 150 nm to 200 nm. The higher particle size of an emulsion indicates a possible coagulation of colloidal molecule and result in lower emulsion stability. Addition of green additives to the coconut oil emulsion increased the stability of emulsion. The zeta potential of GCF was much higher than coconut oil emulsion and GCF possessed least particle size. Lesser particle size indicates the least possibility of coagulation and hence higher emulsion stability. COM though had better zeta potential, but upon visual appearance test and oven tests had least emulsion stability. This result is attributed to the oil to emulsifier ratios. COM has a higher ratio of oil to emulsifier, as seen on the first day of emulsion preparation, with good visual stability and higher zeta potential. Gradually, emulsion stability on visual appearance decreased with increased particle size and lesser zeta potential. In case of GCF, with appropriate ratio of oil to emulsifier along with green additives exhibited higher emulsion stability. After fifteen days, GCF also had increased particle size and lowered zeta potential, but was better compared to COM. GCF exhibited lower corrosion rate than COM. Gas chromatography analysis of green additives showed that it contains many antibacterial and antifungal compounds (data not shown), which acted against the test organisms opted for microbial inhibition tests. Combination of A-1, A-2, A-3 and A-4 inhibited the growth of microorganisms synergistically. Machining performance on turning was determined by measuring cutting forces like tangential force and feed force. Tangential force being major component during cutting process and it defines the amount of power consumed during machining. GCF showed lesser cutting forces at lower depth of cut 646 rpm and 1000 rpm spindle speed. It is assumed that, GCF properties were as good to COM, as the force and torque values obtained were close enough. Drilling experiments also showed similar results for GCF. For few set parameters, GCF even outperformed COM. Therefore, developed GCF performed well compared to COM in both cutting fluid general properties and had comparable machining properties. GCF found to be non-toxic in comparison to the toxic COM. Conventional cutting fluids like COM is composed of the components that are harmful to the human body and environment, having a negative impact on their applications. The poor biodegradability also limits their applications in machining. The growth of microbes in the cutting fluid is the major health hazard [24] and GCF showed similar bacterial growth compared to COM. Addition of other antibacterial agents in the GCF will improve the antimicrobial effects of GCF. Therefore, GCF as performance enhancer may initiate the new era for complete green products for cutting fluid industries with better sustainability.

9. Conclusion

In this study we have developed a renewable cutting fluid as an alternative to the conventional mineral oil cutting fuid. GCF is non-toxic, biodegradable and cause no harm to environment being a sustainable product derived from renewable source. The formulated GCF is

cost effective, stable and with better machining properties. It promotes the healthy work environment and prevent workplace injuries and illness compared to the side effects of conventional mineral oil based cutting fluids.

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