Investigation of catalytic and fuel additive applications of copper/copper(I) oxide/copper(II) oxide (Cu/CuO/Cu2O) microspheres synthesized by hydrothermal method using sucrose as template

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Abstract
Role of sucrose in sequential reduction of copper (II) ions is investigated. Copper/copper(I) oxide/copper(II) oxide (Cu/CuO/Cu2O) microspheres are synthesized via hydrothermal method using sucrose as template. Size of microparticles lies in 9–16 μm range. Formation mechanism of spherical architecture is also proposed. Synthesized spheres are used in two major applications: (i) catalyst for degradation of methyl red (MR) and methyl blue (MB) (ii) fuel additive in commercial diesel. The rate constant of degradation of both dyes (MB and MR) is not found equal under similar conditions. Results indicated that increased concentrations of microparticles in diesel significantly affect properties.

1. Introduction

Chemical and physical properties of nano/micro particles greatly depend on their shapes and sizes. These extraordinary properties of nanoparticles make their successful use in fields of electronics [1], catalysis [2, 3], drug delivery [4] and nanofluids [1]. Nano/micro particles possess different shapes like rods [5], ribbons [5], belts [7], platelets [8, 9] and spheres [4]. Study of copper oxide nanoparticles is particularly interesting because it shows interesting chemical and physical characteristics [10–13]. Copper is a p-type semiconductor and 3-d transition metal. It can undergo various types of reactions because of multiple oxidation states (Cu(0), Cu(I) and Cu(II)) [14]. There are various methods by which copper oxide nanoparticles can be synthesized. Some of them are co-precipitation [15], sol–gel [16], thermal decomposition [17], ionic liquid-assisted [18], hydrothermal [19–22] and reverse micelle methods [23]. Crystallinity, size, morphology and composition of nano/micro particles can be easily controlled in hydrothermal method [24]. Copper oxide nano/micro particles of morphologies like rods [25], spheres [26] and dandelion [27] are successfully prepared by this method. Stabilizers strongly affect the morphology and size of particles [28]. Sucrose [29] and glucose [30] are mild reducing agents and stabilizers. These stabilizers help to synthesize spherical morphology with desired composition. This property of sucrose has been used in this work for synthesis of spherical copper/copper(I) oxide/copper(II) oxide (Cu/CuO/Cu2O) microparticles. Spherical morphologies are preferred for fuel additive and catalytic applications because surface area to volume ratio of these morphologies is high as compared to other morphologies.

Organic dyes create environmental problems therefore the removal of these dyes from water is a hot topic [31]. Number of methods has been adopted for the purification of water such as electrochemical, ozonation, adsorption and catalytic degradation. Naked, composites and wrapped modifications of metal based nanoparticles have been used as catalyst for degradation of pollutants. Researchers have been diverted towards green nanocatalysis means such nanocatalyst is used whose synthesis and application helps to reduce pollution.
Zhang et al have been contributed a lot of work in this field. Zhang et al have been extensively studied catalytic degradation using titanium dioxide-kaolin composite [32, 33], iron oxide nanoparticles [34], calcium tungstate/bismuth tungstate composite [35], core-shell bismuth tungstate/carbon nitride [36], hollow porous spherical bismuth aluminate [37], wrapped bismuth oxide carbonate-graphene [38] as catalysts. Green synthesis approach has been used for synthesis of these catalysts. It shows various assemblies of nanoparticles have been used as catalysts but mixed alloy of metal oxides have not been used earlier. Mixed copper oxide has tendency for fast electron transfer due to combination of stable and unstable metal ion oxidation states. Synthesized Cu/CuO/Cu2O microparticles are a good candidate as it possesses zero, mono and divalent metal states, so it has ability to facilitate the electron-hole transfer. Therefore spherical Cu/CuO/Cu2O microparticles are synthesized using sucrose in this work for catalytic applications. Sucrose is not very harmful in comparison to other stabilizers like sodium dodecyl sulfate, sodium dodecyl sulfonate and cetyl trimonium bromide. Different metals and metal oxides have been used as fuel additive [39–43]. Additives are used to increase the calorific value of fuel and reduce fuel pollution effects. Metals are more efficient additive as compared to metal oxide due to fast electron transfer properties and metal oxides are preferred due to high affinity for oxygen adsorption [44–46]. Fuel is oxidized in the presence of oxygen and produce energy for running engines. Therefore it is preferred to synthesize such additives which contain properties of metal and metal oxide both. Cu/CuO/Cu2O microparticles possess properties of metal and metal oxide. Therefore it is synthesize in this work to study role as fuel additive.

The present study involves synthesis of Cu/CuO/Cu2O microspheres via hydrothermal method and study of its applications as catalyst and additive. Simultaneous synthesis of all three phases of copper is a new approach. It acts as better catalyst because of Cu(I) which is highly unstable and act as strong reducing agent in the presence of hydrogen peroxide (H2O2). Product is used as catalyst for degradation of MR and MB dyes. The difference in apparent rate constant (kapp) of degradation of these dyes helps to understand the role of functional group and structure of dye in its degradation. Effect of additive dose on fuel parameters is studied and helps to devise new methods towards efficient combustion of existing fuels. Phases of product composition are characterized by XRD and morphology is analyzed by SEM.

2. Materials and methods

2.1. Materials
Copper sulphate (CuSO4·5H2O), sucrose (C12H22O11), methyl red (MR) and methyl blue (MB) were used as such without any further purification. Distilled water was used for solution preparation. All chemicals of analytical grade (99.9% purity) were used and purchased from Sigma-Aldrich USA.

2.2. Synthesis of microparticles
1 g CuSO4·5H2O was dissolved in 20 ml water and 5 g sucrose was dissolved in 30 ml water separately. Later both solutions were mixed and stirred at room temperature for 30 min using magnetic stirrer. Then reaction mixture was put into Teflon vessel. Teflon vessel was placed in a stainless steel hydrothermal autoclave reactor and heated for 24 h at 180 °C in a thermostatic oven. After 24 h, reactor was cooled to room temperature and reaction mixture was centrifuged at 4000 rpm. Product was collected at bottom of centrifugation tubes and supernatant was wasted. Obtained product was washed several times with ethanol and water. After washing, product was dried at 60 °C for 8 h in a thermostatic oven. Final product was ground to fine powder and calcined for 4 h at 550 °C in a muffle furnace. This product was labeled as product A. Product B was also prepared by same scheme with 12 g sucrose (figure 1).

2.3. Catalytic and fuel additive applications of Cu/CuO/Cu2O microparticles
Catalytic activity of synthesized product B was analyzed by studying degradation of MR and MB dye in the presence excess of H2O2. Kinetics of catalytic degradation of MR and MB dyes were studied by monitoring absorbance at 520 nm and 660 nm at various time intervals respectively. 4 ml of 3.87 ppm MR dye solution and 0.001 g catalyst were stirred for 15 min at room temperature. Then 0.7 ml of 1.21 M H2O2 was added under constant stirring and absorbance of reaction mixture was monitored at 520 nm at different time intervals. The absorbance was measured till no change in its value is observed with time. Same procedure was repeated with 0.002, 0.003, 0.004 and 0.005 g catalyst to investigate the effect of catalyst dosage. 4 ml of 5 ppm MB solution and 0.001 g catalyst were stirred for 15 min at room temperature then 0.7 ml of 1.21 M H2O2 was added into it. Absorbance was measured at 660 nm till its value remains constant with time. H2O2 is in excess, so the kinetics of catalysis was studied with the help of following pseudo-first order equation (1).
\[
\ln \left( \frac{A_t}{A_0} \right) = -k_{\text{app}} \times t
\]  

(1)

Where \( A_0 \) and \( A_t \) are absorbance of dye at time 0 and \( t \) respectively. \( k_{\text{app}} \) is apparent rate constant of catalytic degradation. Slope \( (k_{\text{app}}) \) of this plot is determined by using ORIGIN Software.

Four different fuel dispersions 40, 60, 80 and 100 ppm were made by adding 0.004, 0.006, 0.008 and 0.010 g of synthesized product B in 100 ml of commercial diesel. Every dispersion was sonicated for 5 min before study of parameters.

### 2.4. Characterization

XRD pattern was recorded using Joel JDX-3532 diffractometer with Cu-K\( \alpha \) radiation at 2\( \theta \) ranging from 10–80\( ^\circ \). SEM Quanta 250, FEG (USA) was used to scan the images of synthesized product. Synthesized microparticles were used as additive to check the efficiency of commercial diesel. Catalytic degradation of MR and MB were monitored using 2JI-0004 UV-Visible spectrophotometer.

### 3. Results and discussion

#### 3.1. Effect of sucrose amount on the morphology of products

The morphology of the obtained product A is investigated by SEM. The SEM images of product A synthesized by hydrothermal method can be seen in figure 2. The images recorded at 2400 X and 3000 X magnifications. Overall view of the product is shown in figure 2(a) scanned at 2400 X magnification. It shows in this image that the product is consist of small particles. The shape of the particles appears irregular and geometry of the particles is also not specific. Size of the particles lies in range of 4–10 \( \mu \)m. Particles shown in this figure possess many sides. All the particles do not possess uniform morphology. Magnified image of product at 5000 X magnification is given as figure 2(b). It shows the polydispersity of the product clearly. It seems that particles do not have enough template sucrose surface to grow and agglomeration occurs. Sucrose was used in the small amount in synthesis of Product A and its particles do not surrounded by enough sucrose which can hinder agglomeration. Therefore, the product is also synthesized by changing the experimental condition.

Size and morphology of the synthesized product B are investigated with the help of SEM images. Figure 3(a) is scanned at 1000X magnification. The spherical shaped particles can be seen in the figure. As images are scanned further at higher magnifications it can be seen that all the particles do not possess the uniform morphology. Figure 3(b) has been recorded at 2000X. Figure 3(c) shows the magnified image of Cu/CuO/Cu_{2}O.
Figure 2. SEM images of product A particles synthesized by hydrothermal method in the presence of 5 g sucrose. (a) SEM image scanned at 2400 X and (b) 5000 X magnifications.

Figure 3. SEM images of Cu/CuO/Cu2O microparticles (Product B) synthesized by hydrothermal method. (a) SEM image of product at 1000X, (b) magnified view of surface of particles at 4000X, (c) SEM image of product at 2000X, and (d) View of hole at surface of spherical particles.
microparticles. The size of synthesized particles lies between 9–15 μm. It is observed few particles are joined with each other at one end. Spherical shaped particles possess a depression at one side of particle which is possibly because of carbon dioxide gas is trapped inside the spheres which left during the calcination and leave behind a hole on the surface. This shows that particles are hollow from inside. Figure 3 also shows that walls of particles are multiple layered and walls are formed from layer by layer assembly. Nuclei arranged and formed a layer. These layers are arranged around one another and formed a spherical microparticle. Role of sucrose is important here. It is self-destructive template. It is acted as template and provides surface for growth of Cu/CuO/Cu2O microparticles. The synthesis of hollow spheres of CuO particles has been reported before by Titirici et al. [21].

3.2. XRD analysis

XRD pattern of synthesized product B is given as figure 4. Strong diffraction peaks present at 2-theta values 35.44°, 35.53° and 38.45° are associated with planes (111), (111) and (202) respectively represent the presence of CuO phase (PDF No 901–5823) Diffraction peaks present at 2-theta values 36.42°, 42.30° and 61.37° having miller indices (111), (020) and (202) respectively are characteristics to Cu2O (PDF No 96–900–5770) Diffraction peaks present at 2-theta values 43.04° and 50.12° are characteristic to Cu (PDF No. 96–151–2505) figure 4 shows that synthesized product is consists of three phases, i.e., Cu, CuO and Cu2O. Diffraction peaks corresponding to these phases are individually labelled in figure 4. All the peaks are very sharp which proves the highly crystalline structure of Cu/CuO/Cu2O microparticles. No extra peak is observed in XRD pattern indicates that product is highly pure. The summary of crystal system, lattice parameters, atomic co-ordinates, space group, volume, density bond lengths, bond angles and d-spacing of Cu, CuO and Cu2O phases are given in table 1. Face centered cubic structure of Cu unit cell is shown in figures 5(a), (b) shows. One Cu atom is present at center of each face of cube and shared between two unit cells. Total fourteen Cu atoms are present per unit cell.

![Figure 4. XRD pattern of Cu/CuO/Cu2O microparticles (Product B).](image-url)

### Table 1. Details of different lattice parameters of Cu, CuO and Cu2O obtained from XRD data analysis.

| Parameters | Details | Details | Details |
|------------|---------|---------|---------|
| Phase      | Cu      | Copper oxide (CuO) | Cuprite (Cu2O) |
| Space group| Fm-3m (225) | C12/c1 (15) | Pn-3 (201) |
| Lattice    | Cubic   | Monoclinic | Cubic   |

| Lattice parameter | Details | Details | Details |
|-------------------|---------|---------|---------|
| a, b and c (Å)    | 3.6369, 3.6369 and 3.6369 | 4.6776, 3.4593 and 5.1264 | 4.2696, 4.2696 and 4.2696 |
| α, β and γ (degree)| 90.000, 90.000 and 90.000 | 90.000, 98.965 and 90.000 | 90.000, 90.000 and 90.000 |
| Density (g cm⁻³)  | 8.772  | 6.448  | 6.105  |
| No. of atoms per unit cell | 14 | 22 | 13 |

| Atom coordinates | Details | Details | Details |
|------------------|---------|---------|---------|
| x, y and z coordinates of Cu | 0.000, 0.000 and 0.000 | 0.250, 0.250 and 0.000 | 0.250, 0.250 and 0.250 |
| x, y and z coordinates of O | — | 0.000, 0.452 and 0.250 | 0.000, 0.000 and 0.000 |
Figures 6(a), (b) shows the structure of CuO possessing monoclinic lattice associated with C2/c space group. Figure 6(a) shows that each Cu atom is bonded with four oxygen atoms and formed square planar polyhedron. Two central square planar polyhedra are present within the unit cell while the four are present on the outer sides and shared with neighboring unit cells. Figure 6(c) shows that four CuO unit cells arranged side by side. Cubic unit cell of Cu₂O can be seen in figures 7(a)–(c) figure 7(a) shows the body center unit cell where one oxygen atom is present in the center four on the corners of cube. Four Cu atoms are bonded with central oxygen atom. Figure 7(b) shows the orientation of Cu and oxygen atoms by lattice planes. Each plane is comprised of three Cu atoms. Figure 7(c) shows the four unit cells and clearly shows the body centered structure of Cu₂O unit cell. XRD analysis gives information about the presence of Cu, CuO and Cu₂O phases which is not possible to know from SEM images. SEM only gives morphology and surface analyses of product.
3.3. FTIR analysis

FTIR spectra of Cu/CuO/Cu2O microparticles (Product B) is shown in figure 8. Many peaks around 400–800 cm⁻¹ are due to vibrations of Cu-O and Cu-Cu bonds. Broad absorption band between 3400 and 3000 cm⁻¹ can be ascribed to hydroxyl groups (due to moisture).

3.4. Formation mechanism

Formation mechanism of Cu/CuO/Cu2O microparticles is given as figure 9. Copper sulfate solution is heated at 180 °C with sucrose solution in autoclave for 24 h. At this stage carbon cores are present because of the fair amount of sucrose was used as reductant and acted as template for the synthesis of Cu/CuO/Cu2O microparticles. Carbon dioxide gas is also present in the spheres which left when product is further heated. These carbon molecules are removed by further heating at 550 °C for 4 h to obtain Cu/CuO/Cu2O microparticles.

3.5. Cu/CuO/Cu2O microparticles as catalyst for degradation of MR and MB

Synthesized product was used as catalyst for the degradation of MB and MR dyes. The structures of dyes are given as figure 10. It is well known that the dye undergo self-decomposition but its rate of degradation is very slow. Control experiments with dye (absence of catalyst) have been performed and no significant change in absorbance at λmax of dye is observed. Dark experiments have been also performed at 0.001 g dose of catalyst.
But significant adsorption–desorption was not observed. This shows that dye removal by adsorption–desorption needs large quantity of adsorbent. Therefore further study has been carried out by using synthesized microparticles as catalyst. The catalytic activity of the dye was measured in the presence of excess of $\text{H}_2\text{O}_2$ so that the degradation obeys pseudo first order kinetics. Figure 11 shows the plot of $\ln\left(\frac{A_t}{A_0}\right)$ versus time for MR and MB dyes at different concentrations of catalyst in the presence of $\text{H}_2\text{O}_2$. Figure 11(a) shows the plot of $\ln\left(\frac{A_t}{A_0}\right)$ of MR degradation at various catalyst dosages. Value of $\ln\left(\frac{A_t}{A_0}\right)$ decreases with the passage of time which indicates that concentration of dye is decreasing in sample. It means the catalyst is degrading the dye into less harmful products [47, 48]. The color of sample solution is discharged which shows that products do not absorb in Visible range. Values of $k_{\text{app}}$ was calculated from the slope of plot of $\ln\left(\frac{A_t}{A_0}\right)$ as a function of time. The comparison of all plots of figure 10(a) shows that concentration of catalyst affects the degradation process. The slope of all plots are found to be different from each other. In case of MB, figure 11(b) shows the plot of $\ln\left(\frac{A_t}{A_0}\right)$ versus time for various catalyst dosages. Value of $\ln\left(\frac{A_t}{A_0}\right)$ also is decreased with time for MB which showed that catalyst is degraded the dye in reaction mixture.

3.5.1. Effect of catalyst dosage on $k_{\text{app}}$

Figure 12 shows the comparison of $k_{\text{app}}$ for degradation of MR and MB at different concentrations of catalyst. Value for $k_{\text{app}}$ of MR are found to be 0.0031, 0.0109, 0.0362, 0.004 and 0.0049 min$^{-1}$ for 0.24, 0.48, 0.73, 0.97 and 1.21 mg ml$^{-1}$ concentrations of catalyst respectively. This clearly indicates that concentration of catalyst affects $k_{\text{app}}$ for degradation for Mr $k_{\text{app}}$ for MB dye was also studied using the different concentrations of catalyst Cu/CuO/Cu$_2$O microparticles. Figure 12 shows plot of $k_{\text{app}}$ for degradation of MB are 0.0055, 0.0074, 0.0337, 0.0223 and 0.0049 min$^{-1}$ for 0.24, 0.48, 0.73, 0.97 and 1.21 mg ml$^{-1}$ concentrations of catalyst respectively. The plot shows that concentration of catalyst significantly effect the $k_{\text{app}}$ of both dyes. The value of $k_{\text{app}}$ is increased by more than double on doubling the catalyst dose from 0.24 to 0.48 mg ml$^{-1}$. Figure 12 shows that $k_{\text{app}}$ value is linearly increased with increase in catalyst dosage because surface area of catalyst for degradation of dye is increased with increase in catalyst dosage. It is also observed that $k_{\text{app}}$ value is increased with increase in catalyst
dosage upto 0.73 mg ml$^{-1}$. The value of $k_{\text{app}}$ is decreased with increase in catalyst dosage greater than 0.73 mg ml$^{-1}$. Maximum value of $k_{\text{app}}$ of degradation of MB and MR are observed at 0.73 mg ml$^{-1}$ of catalyst dosage. The trend of $k_{\text{app}}$ indicates that reaction mixture has saturated with catalyst at 0.73 mg ml$^{-1}$ dosage, so more dye molecules cannot adsorb on the surface of catalyst even its high dosage. Excess amount of catalyst hinders the diffusion of dye molecules, that’s why $k_{\text{app}}$ value is decreased at high catalyst dosage.

Value of $k_{\text{app}}$ of degradation of MR is found to be smaller than that of MB at 0.24, 0.48 and 0.73 mg ml$^{-1}$ catalyst dosages. The value of $k_{\text{app}}$ of degradation of MR is found to be greater than that of MB at 0.97 and 1.21 mg ml$^{-1}$ catalyst dosages. Apparently, the degradation of MB looks difficult as compared to that of MR from comparison of their molecular structures (figure 10). MR contains azo group which is observed as easily oxidizable group but here degradation of MR is slow as compared to that of MB. Azo group develops strong coordinate covalent bond with active sites of Cu/CuO/Cu$_2$O microparticles, while such electron donating group is not present in structure of MB. Due to bonding the degradation of MR and desorption of its products from catalyst surface becomes difficult, hence value of $k_{\text{app}}$ decreases. Most commonly used catalysts are TiO$_2$ and ZnO [49, 50]. Degradation of MR using TiO$_2$ was reported and observed that the degradation rate constant was increased as concentration of catalyst was increased [50]. Cu/CuO/Cu$_2$O microparticles are first time used for the degradation of MR and MB dyes. The SiO$_2$ nanoparticles were employed for the photocatalytic degradation of MR. It was observed that the rate of degradation was increased in the presence of SiO$_2$ nanoparticles but it was further enhanced when the SiO$_2$ nanoparticles were doped with silver and gold. This proves that metals are good catalyst. Prepared Cu/CuO/Cu$_2$O microparticles possess mixed oxidation states because of presence of Cu, CuO and Cu$_2$O. Band gap of Cu, CuO and Cu$_2$O is found to be 0, 1.0 and 1.1 eV respectively [51]. Conduction band of Cu$_2$O is above all in potential diagram and valence band of CuO is present below all in potential diagram. Cu$_2$O is highly unstable and Cu(I) acts as reducing agent. Whereas CuO has Cu(II) which is stable as compared to Cu(I). Multiple electron bands are present in microparticles due to presence of Cu(0), Cu(I) and Cu(II) Cu(0) has ability to donate electrons to Cu(I) and Cu(II). Hence holes are easily created due to electron transfer. These holes are occupied by electrons donated by negatively charged hydroxyl radicals produced by H$_2$O$_2$ dissociation. Electrons of conduction band and oxygen molecules react and produced negatively charged oxygen radicals (O$_2^-\cdot$). These radicals react with H$_2$O$_2$ and produce hydroxyl radicals (OH). Holes of valence band converts water and hydroxide ions into OH. O$_2^-\cdot$ and OH are reactive species. These species react with azo bonds of dye and catalyze their decomposition into carbon dioxide, water and ammonia [3]. Thus a chain of electron is started. Therefore synthesized Cu/CuO/Cu$_2$O microparticles acts as good catalyst for degradation of MR and MB.

### 3.6. Cu/CuO/Cu$_2$O microparticles as fuel additive

Cu/CuO/Cu$_2$O microparticles synthesized via hydrothermal method is used as an additive for commercial diesel to check whether its efficiency is enhanced by the additive or not. Different parameters of fuel such as fire point, flash point, cloud point, pour point, kinematic viscosity and specific gravity were studied for this purpose. Samples were prepared for these parameters to be analyzed by 40, 60, 80 and 100 ppm dosage of Cu/CuO/Cu$_2$O microparticles. Obtained readings in the presence of additive are compared with that of control sample which does not contain any additive.
Table 2. Effect of different concentrations of Cu/CuO/Cu2O microparticles additive on the different parameters of diesel.

| Parameters       | Concentration of additive |
|------------------|---------------------------|
| **Flash point**  |                           |
| 0 ppm            | 69 °C                     |
| 40 ppm           | 57 °C                     |
| 60 ppm           | 56 °C                     |
| 80 ppm           | 55 °C                     |
| 100 ppm          | 53 °C                     |
| **Fire point**   |                           |
| 0 ppm            | 71 °C                     |
| 40 ppm           | 65 °C                     |
| 60 ppm           | 62 °C                     |
| 80 ppm           | 60 °C                     |
| 100 ppm          | 56 °C                     |
| **Kinematic viscosity** |                   |
| 0 ppm            | $3.48 \times 10^{-4}$ m$^2$s$^{-1}$ |
| 40 ppm           | $3.56 \times 10^{-4}$ m$^2$s$^{-1}$ |
| 60 ppm           | $3.70 \times 10^{-4}$ m$^2$s$^{-1}$ |
| 80 ppm           | $4.10 \times 10^{-4}$ m$^2$s$^{-1}$ |
| 100 ppm          | $4.40 \times 10^{-4}$ m$^2$s$^{-1}$ |
| **Specific gravity** |                        |
| 0 ppm            | 0.857 g cm$^{-3}$         |
| 40 ppm           | 0.838 g cm$^{-3}$         |
| 60 ppm           | 0.839 g cm$^{-3}$         |
| 80 ppm           | 0.845 g cm$^{-3}$         |
| 100 ppm          | 0.843 g cm$^{-3}$         |
| **Cloud point**  |                           |
| 0 ppm            | 6 °C                      |
| 40 ppm           | 2 °C                      |
| 60 ppm           | 0 °C                      |
| 80 ppm           | −1 °C                     |
| 100 ppm          | −3 °C                     |
| **Pour point**   |                           |
| 0 ppm            | −5 °C                     |
| 40 ppm           | −7 °C                     |
| 60 ppm           | −9 °C                     |
| 80 ppm           | −10 °C                    |
| 100 ppm          | −10 °C                    |
| **Calorific value** |                      |
| 0 ppm            | 32000 Jg$^{-1}$           |
| 40 ppm           | 32489 Jg$^{-1}$           |
| 60 ppm           | 30485 Jg$^{-1}$           |
| 80 ppm           | 34232 Jg$^{-1}$           |
| 100 ppm          | 31910 Jg$^{-1}$           |

Table 2 exhibits that by increasing the additive dosage fire and flash points are decreased. The value of fire point and flash point of pure diesel are 71 °C and 69 °C respectively. It was observed that values of fire and flash points of control sample are higher than that of samples containing additive. For the sample of 40 ppm the value of fire and flash points are decreased to 65 °C and 55 °C respectively. Flash and fire points of 100 ppm sample are 56 °C and 53 °C respectively. These results suggest that the values of fire and flash point are greatly affected by the concentration of additive and as the concentration of the additives is increased the combustion parameters, flash and fire point are significantly decreased. Cu/CuO/Cu2O microparticles as additive in diesel are increased the volatility of diesel and lowered the flash and fire points. Decreased values of flash and fire points means that the modified diesel requires low temperature for burning but on the other hand requires safe handling. Khalid et al have also measured the fire and flash points for diesel by adding tin oxide nanocubes as additive [32]. It was reported that tin oxide is lowered the flash and fire points of diesel to 50 °C and 58 °C respectively whereas synthesized Cu/CuO/Cu2O product as additive further decreased the fire point of diesel.

The minimum temperature at which petroleum diesel shows cloudy appearance is known as cloud point. This is because of presence of paraffin in petrochemicals which makes the diesel inefficient at low temperatures. Cloud point is observed for petroleum diesel at different concentration of additive. The cloud point for pure diesel is observed ~6 °C which is gradually decreased as the concentration of additive dosage is increased. At 40 ppm concentration the cloud point is dropped to 2 °C and at 60 ppm concentration it is decreased to 1 °C, −1 °C and −2 °C cloud point is observed at 80 ppm and 100 ppm concentration of additive respectively. The temperature at which petroleum diesel loses its flowing property and seems semi-solid, is its pour point. Pour point of samples having 40, 60, 80 and 100 ppm additive were measured and are given in table 2.

It is observed that the cloud and pour points are decreased with increase in concentration of Cu/CuO/Cu2O microparticles additive. Khalid et al have reported that cloud point of diesel containing 40 ppm tin oxide nanocubes is 2 °C [32]. The cloud point is decreased to −3 °C as the concentration of Cu/CuO/Cu2O microparticles additive is increased to 100 ppm. Pour point does not significantly affected by the concentration of tin oxide microcubes whereas concentration of Cu/CuO/Cu2O microparticles as additive lowers the pour point from −5 to −10 °C.

Table 2 shows that kinematic viscosity of samples containing additive are gradually increased with increasing additive dose. The value of kinematic viscosity is increased from $3.48 \times 10^{-4}$ m$^2$s$^{-1}$ to $4.40 \times 10^{-4}$ m$^2$s$^{-1}$ for 0 to 100 ppm concentration of additive. High concentration of additive is increased the viscosity of diesel by adsorbing diesel molecules, hence increased the resistance between layers. Calorific value of pure diesel is observed to be 32000 J g$^{-1}$. For 40 ppm and 60 ppm samples the calorific values are 32500 J g$^{-1}$ and 30400 J g$^{-1}$ respectively. The calorific value of 80 ppm concentration is also increased further and found to be 34412 J g$^{-1}$. The calorific value is observed to be decrease with increase in additive concentration greater than 80 ppm. Cu/CuO/Cu2O microparticles as additive provide high surface area which help in catalyzed combustion of diesel and more energy is obtained.

4. Conclusion

SEM images are proved that sucrose is a suitable template for synthesis of spherical microparticles. The reduction of metal ions is dependent upon the concentration of template, hence mixed oxide Cu/CuO/Cu2O microparticles is fabricated at moderate concentration of sucrose. Presence of three phases Cu, CuO and Cu2O are confirmed by XRD analysis. SEM images revealed that diameter of particles lie in 9–16 μm range. The surface of particles is smooth with a small opening at one side of sphere. The degradation of MR and MB were analyzed using Cu/CuO/Cu2O microparticles as catalyst. $k_{app}$ of catalytic degradation of MB is found to be greater than that of MR which is might be due to the azo group present in structure of MR. Initially $k_{app}$ of degradation is observed to increase with increase in catalyst dose but $k_{app}$ value is also observed to decrease at very high...
concentration of catalyst. Highest $k_{\text{app}}$ value is observed at 0.73 mg mL$^{-1}$ catalyst dose. Synthesized product is also used as additive for fuel and various parameters of fuel are studied at 40, 60, 80 and 100 ppm concentration of Cu/CuO/Cu$_2$O microparticles. Efficiency of diesel is clearly increased due to Cu/CuO/Cu$_2$O microparticles because calorific value is significantly increased, and fire point is decreased. Results of both of these applications suggest Cu/CuO/Cu$_2$O microparticles an interesting choice for catalysis and additive. Because it contains Cu(II), Cu(I) and Cu(0) oxidation states which facilitates the electron transfer and the presence of all of these oxidation states can be controlled easily by the amount of template sucrose.

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