Chapter 3 Catalytic thermolysis treatment of petroleum refinery wastewater collected from effluent treatment plant

Abstract

Catalytic thermolysis of petroleum refinery wastewater was investigated as a pretreatment process. The effects of various parameters like temperature, pH, dose of catalyst, and time were investigated for COD, turbidity, and element reduction. $CuSO_4$, $FeSO_4$, $FeCl_3$, and 1:1 ratio (V: V) mixture of $CuSO_4$ and $FeCl_3$ were used as a catalyst. The maximum reduction of COD and turbidity were 90% and 98% by mixture (1:1) of $CuSO_4$ and $FeCl_3$ at 70˚C, 7 pH, 1.0 kg/m^3 dose in 90 minutes reaction time. The removal of an element like Cr, Mn, Ni, and Pb was analyzed by ICP-OES. The sludge precipitated after catalytic thermolysis was characterized using SEM-EDX, FTIR, and TGA/DTA analyses. Sludge from $CuSO_4$ and mixture of $CuSO_4$ and $FeCl_3$ treatment has a compact structure with irregular granule which favors adsorption.

3.1 Introduction

The petroleum industry consists of major operations such as exploration, refining, storage, and distribution where water is used for cooling and cleaning purposes [8, 10, 109]. The refineries and petrochemical industries consume maximum water and are the major source of wastewater generation [2]. The wastewater from petroleum refinery contains oil and grease, organic matter, soluble metal salts, and other chemicals like ammonia, sulfides, deuterium, and various toxic substance including metals [9, 10, 110].

Regarding the thermochemical treatment process classification and thermolysis process as discussed in chapter 1. The thermochemical treatment (catalytic or non-catalytic) can be an effective process for wastewater purification [42, 43]. Verma et al. [111] observed a COD reduction of 77.22% by using $FeCl_3$ as a catalyst in the thermolysis of terephthalic acid (TPA) bearing wastewater from a petrochemical plant. They also reported that the use of $CuSO_4.5H_2O$ resulted in larger floc size at a higher temperature, however, iron salts showed the opposite trend. Various likewise literature are prevailing available are reported with their optimum condition of thermolysis such as pH, dosage of catalyst, time of reaction, and temperature as discussed in chapter 2. Apart from these studies, as per the author's knowledge treatment of petroleum wastewater has not been carried out by using thermolysis.

Therefore, in the present chapter, wastewater from the effluent treatment plant (ETP) of petroleum industry was treated using a catalytic thermolysis process using $FeCl_3$, $FeSO_4$, $CuSO_4$, and a mixture of $FeCl_3$ and $CuSO_4$ (ratio 1:1 in terms of volume) as a catalyst. The effect of temperature, pH, dosage, and time at constant RPM was investigated. The optimum values of these parameters were obtained for maximum reduction in COD and turbidity. Further, a reduction in metal content was investigated by using ICP-OES analysis. The characteristics of

sludge generated during catalytic thermolysis process were also investigated by using TGA/DTA, FTIR, and SEM-EDX analyses.

3.2 Materials and Methods

3.2.1 Collection of wastewater sample

Petroleum refinery wastewater (PRE) was collected from the flow equalization tank of the ETP of a petroleum refinery in the month of august situated in Northern India. The ETP wastewater consists of water mainly drained from the cooling process and cleaning process. The collected wastewater was mixed with concentrated H_2SO_4 (2 ml/L) and stored in a refrigerator at 4°C to prevent the photo-catalyzed change in the composition of the effluent. The stored wastewater sample was used as such in further experiments without any dilution.

3.2.2 Chemicals

All the chemicals used during the experiments were of analytical reagent (AR) grade. The cupric sulfate, ferrous sulfate, ferric chloride anhydrous, sodium hydroxide (NaOH), sulphuric acid (H_2SO_4), and hydrochloride acid (HCl) were procured from Fisher Scientific, Mumbai.

3.2.3 Analysis of wastewater

The COD was determined by the standard method of dichromate closed reflux in which the sample is oxidized by a standard amount of potassium dichromate oxidizing mixture [112] using a water testing unit (RD125, Lovibond, India). After completion of oxidation, the excess amount of reagent is measured photometrically by the Photometer-system (MD100, Lovibond, India). First, the samples were centrifuged (Centrifuge model R-4C, Remi Instruments, India) to obtain the precipitate and clear supernatant of the treated wastewater, and then it was used for the measurement of COD. The turbidity measurement was carried out using a turbidity meter (ITS-1000, ISO-TECH, India). The turbidity of the sample was measured after filtration through filter

paper (Whatman filter paper grade-1). The metal present in wastewater was analyzed by an ICP-OES analyzer (iCAP 7400 ThermoFisher Scientific, India).

3.2.4 Experimental setup and procedure

The rotamantle with the magnetic stirrer and the temperature controller (BL-221 D Biolab, India) was used for the thermolysis process. A 0.5 L three-necked borosilicate glass flask placed in the rotamantle was used to perform the thermolysis experiments in the temperature range of 50 to 90˚C. In the middle neck of the flask, a vertical glass condenser was fitted to prevent the loss of vapors produced. In one of the side necks, a thermometer was installed to record temperature and on the other neck, a thermocouple controller sensor was installed. The speed of agitator was adjusted by the rotamantle. The pH was adjusted from 3 to 11 using 1N NaOH for the alkaline region and 1N HCl for the acidic region. The volume of wastewater used for the treatment in each case was 250 ml. The thermolysis experiments were carried out at an interval of 10˚C using $FeCl_3$, $FeSO_4$, $CuSO_4$, and $CuSO_4$+ $FeCl_3$ in the volume by volume ratio of 1:1 as a catalyst. The temperature was varied in the range of 50 to 90˚C (at 10˚C interval); dose of all the four catalysts was varied in the range of 0.2- 1.00 kg/m^3 at fixed 120 RPM. The retention time was varied from 20 to 120 minutes. At the end of each experiment, the content in the reaction flask was centrifuged; the supernatant was used for the COD determination and sludge formed was used for further characterization. All the experiments were performed in triplicate and the average values are reported.

3.2.5 Analysis of sludge generated after thermolysis

The SEM coupled with EDX analyzer (QUANTA 450 FEI EDAX, USA) was used to analyze the surface morphology and to detect the elements present in sludge generated after thermolysis. FTIR analyzer (Nicolet 5700 FTIR, USA) was employed to analyze the functional

group present in the sludge. The mass loss behavior of sludge was investigated by the thermogravimetric analyzer (NETZSCCH STA 449F3, CIS-50 ANKERSMID, USA). Approximately 10 mg of the sample was heated in an alumina crucible in a dynamic atmosphere from the ambient temperature to 1100 ˚C at the heating rate of 10 $Kmin^{-1}$ using calcined Al_2O_3 as the reference material.

3.3 Results and discussion

3.3.1 Characterization of raw PRE

The raw PRE sample was characterized for its COD, BOD, TDS, turbidity, pH, color, and metal content as shown in Table 3.1.

Table 3. 1 Commonly measured parameters of Raw PRE

Parameter	Raw PRE	Parameter	Raw PRE
pH	8.7	Ni	0.448
Oil &Grease (mg/l)	0.005	Cu	2.472
COD (mg/l)	5160	V	0.028
BOD	2180	Pb	0.178
TDS	23000	Fe	15.54
Turbidity	30.49	Mg	83.32
color	450	Ca	239
Cr(total)	3.02	K	59.6
Mn	4.584	As	0
Zn	0		

All parameters in mg/l except pH in a standard unit, Turbidity in N.T.U., color in P.C.U, and temperature increases in ℃.

3.3.2 Effect of temperature on COD and turbidity of PRE

The effect of temperature was analyzed by performing the experiments at fixed conditions (7 pH, 0.4 kg/m^3 catalyst dose, 120 minutes, 120 RPM). The COD reduction at ambient

temperature 30°C was 12, 10.5, 17, and 20% for $CuSO_4$, $FeSO_4$, $FeCl_3$, and $CuSO_4+FeCl_3$, respectively. Experiments were performed from 50 to 90°C, to examine the result of temperature. The COD removal increased up to an optimum temperature and then decreased with further increase in temperature. The optimum temperature for maximum reduction in COD varied for every catalyst. With the temperature increases, there are increases in the adsorption phenomena mainly due to an increase in the number of adsorption sites of the absorbent which is caused by breaking off some internal bonds near the active surface of the catalyst [113]. The effect of temperature on the COD reduction is shown in Fig. 3.1(a). The optimum temperature for raw PRE, $CuSO_4$, $FeSO_4$, $FeCl_3$, and $CuSO_4+FeCl_3$ were found to be 90, 80, 70, 60, and 70°C, respectively, with 12, 57, 63, 60, and 64% reduction in COD, respectively. Temperature affects the electrical double layer around the charged particles and species, both on the particle surface and in solution. With the increase in temperature, there might be a significant increase in the surface charge density and a decrease in the electrical double layer [114-116]. This may lead to the destabilization of agglomerated colloids. The $CuSO_4+FeCl_3$ contains both Fe (III) and Cu (II) ions as catalysts; leading to the enhancement in the rate of charge neutralization and hence flocculation. As a result, the agglomeration of ions increases. This directly affects the rate of removal of particles from the wastewater and an increase in the COD reduction [116]. The particle surface potential decides the repulsive force between the particles [117]. When the temperature during thermolysis is increased beyond the optimum temperature, the particle surface force starts increasing. The COD reduction decreased due to an increase in the surface force of the particles which led to an increase in repulsive potential between the particles [117]. The maximum COD removal is the result of an increase in the charge neutralization ability of the catalyst and sweep flocculation, where maximum charges are neutralized [48].
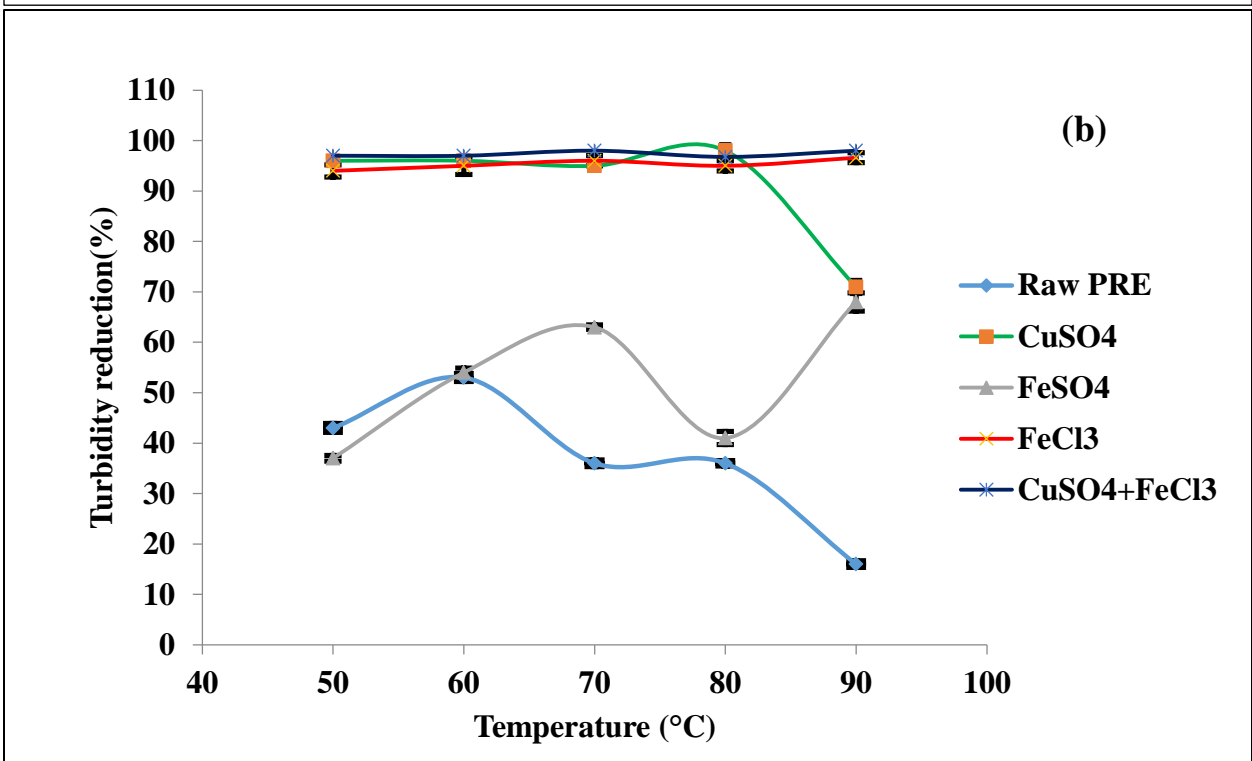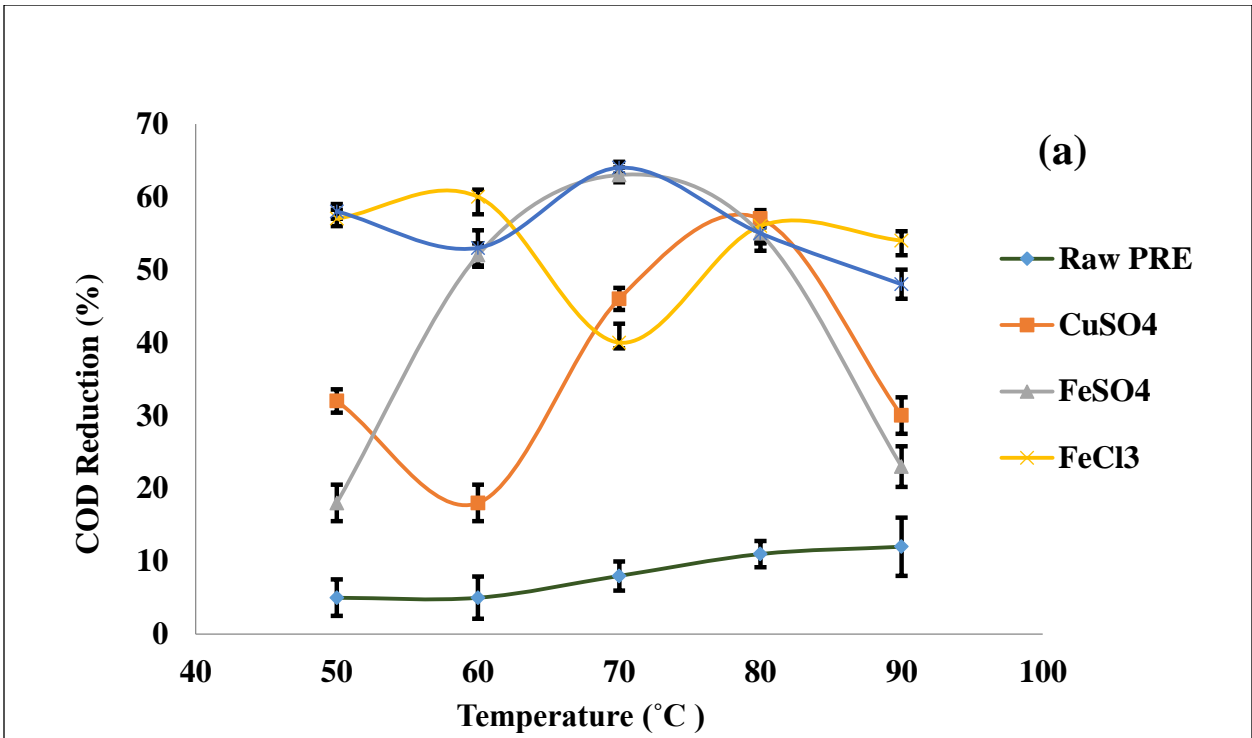
Figure 3. 1 (a) COD reduction (%), (b) Turbidity reduction (%) v/s temperature change of PRE at the fixed condition of 7 pH, 0.4 kg/m^3 catalyst dose, 120 min time, and 120 RPM.

Fig. 3.1(b) shows the variation of turbidity reduction (in '%') with temperature for raw and treated PRE. It is seen that raw PRE has the least reduction in turbidity and the average level of turbidity reduction is decreasing with the increasing temperature. The reduction in turbidity for raw PRE, $CuSO_4$, $FeSO_4$, $FeCl_3$, and $CuSO_4+FeCl_3$ catalyst at a condition of maximum COD reduction, and at optimum temperature was noted to be 53, 98, 63, 95, and 98%, respectively. The catalyst $CuSO_4$, $FeCl_3$, and $CuSO_4+FeCl_3$ showed a constant reduction in turbidity (nearly 98%) till 80˚C. On further increase in temperature, the pattern of $FeCl_3$ and $CuSO_4+FeCl_3$ remained the same but in the case of $CuSO_4$, a sudden COD reduction to 71% is observed. $CuSO_4$ in highly basic medium (greater than 10 pH) form the $Cu(OH)_2$ stable black color flocs which settled down very fast. Thus, negative charge particles of PRE do not agglomerate with Cu ions, which attribute to a decrease in turbidity reduction. In a highly basic medium, $CuSO_4$ exists as $Cu(OH)_3^-$, $Cu(OH)_4^{-2}$ and $Cu(OH)_2$ by the speciation diagram of Cu [118]. Consequently, the adsorption phenomenon dominates. However, charged neutralization does not occur in the basic medium for $CuSO_4$ catalyst. The $FeSO_4$ shows an entirely different trend. Initially, a 63% reduction was observed until the optimum temperature of 70˚C. On further increase in temperature, the reduction in turbidity decreased to 43% at 80˚C. Once again, on further increase in temperature, a 68% reduction in turbidity was noted at 90˚C. With the increase in temperature, the suspended particles present in PRE form colloidal solutions, which affect the turbidity of the PRE directly.

3.3.3 Effect of pH on COD and turbidity of PRE at optimum temperature

The effect of pH on COD reduction in raw PRE and various catalysts at 0.4 kg/m^3 dose, 120 min, and at 120 RPM at their respective optimum temperatures are depicted in Fig. 3.2(a). The optimum pH for raw PRE was 9 with 25% COD reduction. In the case of raw PRE, there is a slow increase in the reduction of COD levels that could be attributed to the loss of volatile

components and breakdown of emulsion. The maximum reduction in COD for raw PRE, $FeCl_3$, $FeSO_4$, $CuSO_4$, and $CuSO_4+FeCl_3$ at their optimum temperatures was found to be 20, 73, 68, 66, and 64%, respectively, at corresponding optimum pH of 9, 9, 9, 5, and 7, respectively. The increase in precipitation was observed in the wastewater when the original pH was adjusted to 3 and 11. In Fig. 3.2(a), COD reduction at 3 pH for raw PRE, $CuSO_4$, $FeSO_4$, $FeCl_3$, and $CuSO_4+FeCl_3$ were 9, 20, 17, 28, and 23%, respectively, while, at 11 pH, respective COD reduction of 10, 26, 28, 16, 20% was observed at their optimum temperature. Similar results were observed for COD reduction at pH 3 and 11.

The maximum reduction in COD could be pragmatic by thermolysis at the condition where the maximum rate of charge neutralization, adsorption, and sweep flocculation will occur collectively. When the metal salts are dissolved in water, the metal ion hydrolyzed and hydrated to form mono and polymeric species like MOH^{+2}, $M(OH)_2^+$, $M_2(OH)_2^{4+}$, $M(OH)_4^{5+}$, $M(OH)_3^0$ and $M(OH)_4^-$ (M stands for metal present in metal salt i.e. Cu and Fe). When these cations are hydrolyzed, the chloride and sulfates ions formed are very soluble and non-reactive in solution. The positively charged species follow the charge neutralization process, and the neutral and negatively charged species follow the adsorption process and sweep flocculation. The wastewater contains various contaminants with negatively charged functional groups. Their molecular weight, size, and hydrophobicity affect the optimum pH for COD reduction. The $CuSO_4$, $FeSO_4$, $FeCl_3$, and $CuSO_4+FeCl_3$ catalysts rapidly dissolve in water to form cations and anions. When the metal salts are dissolved in water, the metal ion is instantaneously hydrolyzed and hydrated to form mono and polymeric species like MOH^{+2}, $M(OH)_2^+$, $M_2(OH)_2^{4+}$, $M(OH)_4^{5+}$, $M(OH)_3^0$ and $M(OH)_4^-$ (M stands for metal present in metal salt i.e. Cu and Fe). The anions of sulfate and chlorides are nonreactive and very soluble. However, some insoluble species are also formed
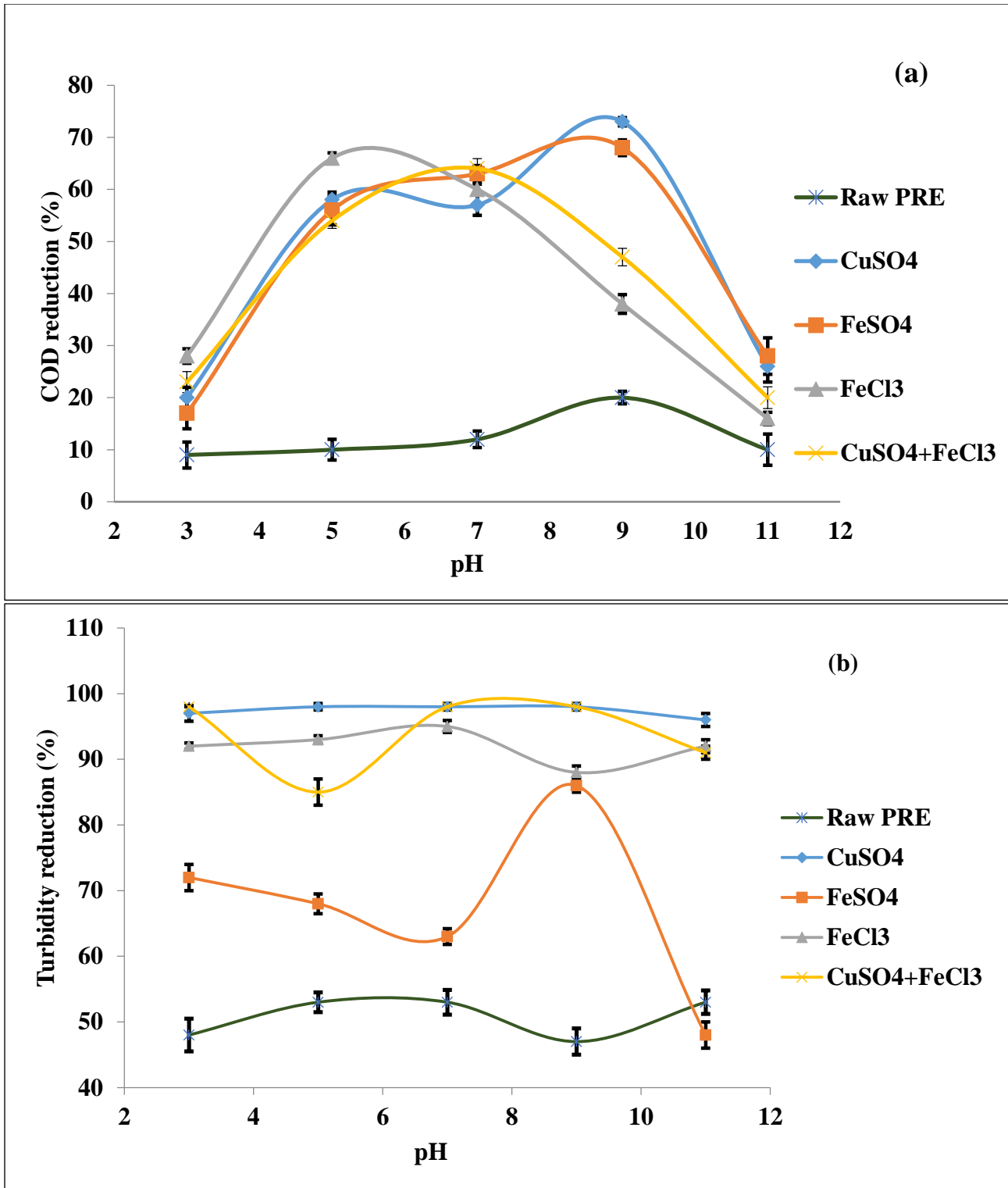
Figure 3. 2 (a) COD reduction (%), (b) Turbidity reduction (%) v/s pH of raw PRE, CuSO$_4$, FeSO$_4$, FeCl$_3$ and CuSO$_4$+FeCl$_3$ at optimum temperature of 80, 70, 60, 70˚C and fixed time (120 min) and 120 RPM.

which are precipitated in the solution. The Cu and Fe containing catalysts at their optimum pH as shown in form the $Cu(OH)_2$ and $Fe(OH)_3$ complexes. Generally, the metal hydroxides have an amorphous structure and very low solubility. The surface area for adsorption increases with an increase in flocs formation and metal hydroxide formation, and also, due to the electrostatic action of acid anions. The formation of bigger flocs takes place by the adsorption of ions and species through van der Waal forces followed by collision and agglomeration. As a result, all the inorganic and organic species are adsorbed and precipitated out [119]. In the case of $FeSO_4$, Fe(II) is oxidized to Fe(III). In the basic medium, Fe(II) in water forms $Fe(OH)^+$ and $Fe(OH)_2$, while, in highly basic medium (pH greater than 10.5), Fe(II) forms $Fe(OH)_4^-$ and the $Fe(OH)_5^{-2}$ ions by the speciation diagram of Fe which are not able to remove the anions present in the wastewater [119, 120]. Thus, COD removal efficiency of Fe containing catalyst decreases at high pH. A significant COD reduction was noted between pH 5 to 9. For metal sulphate the best result was observed in a basic medium, while, metal chloride shows satisfactory results in a slightly acidic medium.

It is seen that the reduction in turbidity for raw PRE has remained constant at around 50±3 % over the entire pH range. In the case of $CuSO_4$, $FeCl_3$, and $CuSO_4+FeCl_3$ the percentage reduction has varied between 88 to 98 %. Slight decreases in a reduction in the case of $CuSO_4$ and $FeCl_3$ can be attributed to the formation of hydroxides at basic pH value.

The effect pH on reduction in turbidity for various metal salts used is shown in Fig. 3.2(b). It is seen that the turbidity reduction for raw PRE has remained constant at around 50±3 % over the entire pH range. The maximum turbidity removal of 98% was obtained in case of $CuSO_4$ at its optimum pH (9) and temperature (80°C). In the case of $CuSO_4$, $FeCl_3$, and $CuSO_4+FeCl_3$ the percentage reduction has varied between 88 to 98%. A similar reduction in turbidity is observed in the case of pH variation from 3 to 11. However, a different trend was perceived in the case of

other metal salts. The raw PRE and $FeCl_3$ show a similar pattern with maximum removal of 53 and 95%, respectively, at their optimum temperature. In the case of $FeSO_4$ and $CuSO_4+FeCl_3$, maximum turbidity reduction was observed at the same pH of 9, while the minimum reduction was obtained at pH 11 and 5, respectively.

3.3.4 Effect of catalyst dose on reduction in COD and turbidity

The effect of dose of catalyst on the extent of reduction in COD and turbidity was analyzed at optimum temperature and pH and results are shown in Fig. 3.3(a-b). The pH of PRE decreases with the increase in dose of the catalyst due to the acidic nature of their solution. This variation in the acidic nature of the solution plays an important role in the COD reduction during dose variation. The dose of the various catalyst was varied from 0.2-1.0 kg/m^3. The optimum dose for $FeCl_3$ was found to be 0.2 kg/m^3 with a maximum COD reduction of 82% while, for $CuSO_4$, $FeSO_4$ and $CuSO_4+FeCl_3$, the optimum COD reduction was 79% at 0.6 kg/m^3, 78% at 0.6 kg/m^3, and 76 % at 1.0 kg/m^3, respectively, at their optimum temperature and pH. The COD reduction for $CuSO_4$ and $FeCl_3$ decreased with an increase in dose after optimum value. COD reduction for $FeSO_4$ was reduced to 52 % when the dose increased beyond optimum value till 0.8 kg/m^3. After that COD reduction increased by up to 60%. With the increase in catalyst dose, the adsorption surface area increases due to an increase in the hydroxide precipitates of the metal ions, and subsequent formation of flocs between precipitation of metal hydroxide ions and acid anions complex by electrostatic interaction. The inorganic and organic substances get absorbed on the metal hydroxide flocs, as a result, enhanced the removal of colloids. The surface charge of the particles gets reversed with the addition of dose beyond the optimum value due to the continuous adsorption of mono and polynuclear hydrolyzed species of ferric chloride. When the colloidal particles become positive charge, they cannot be removed by perikinetic flocculation [48].
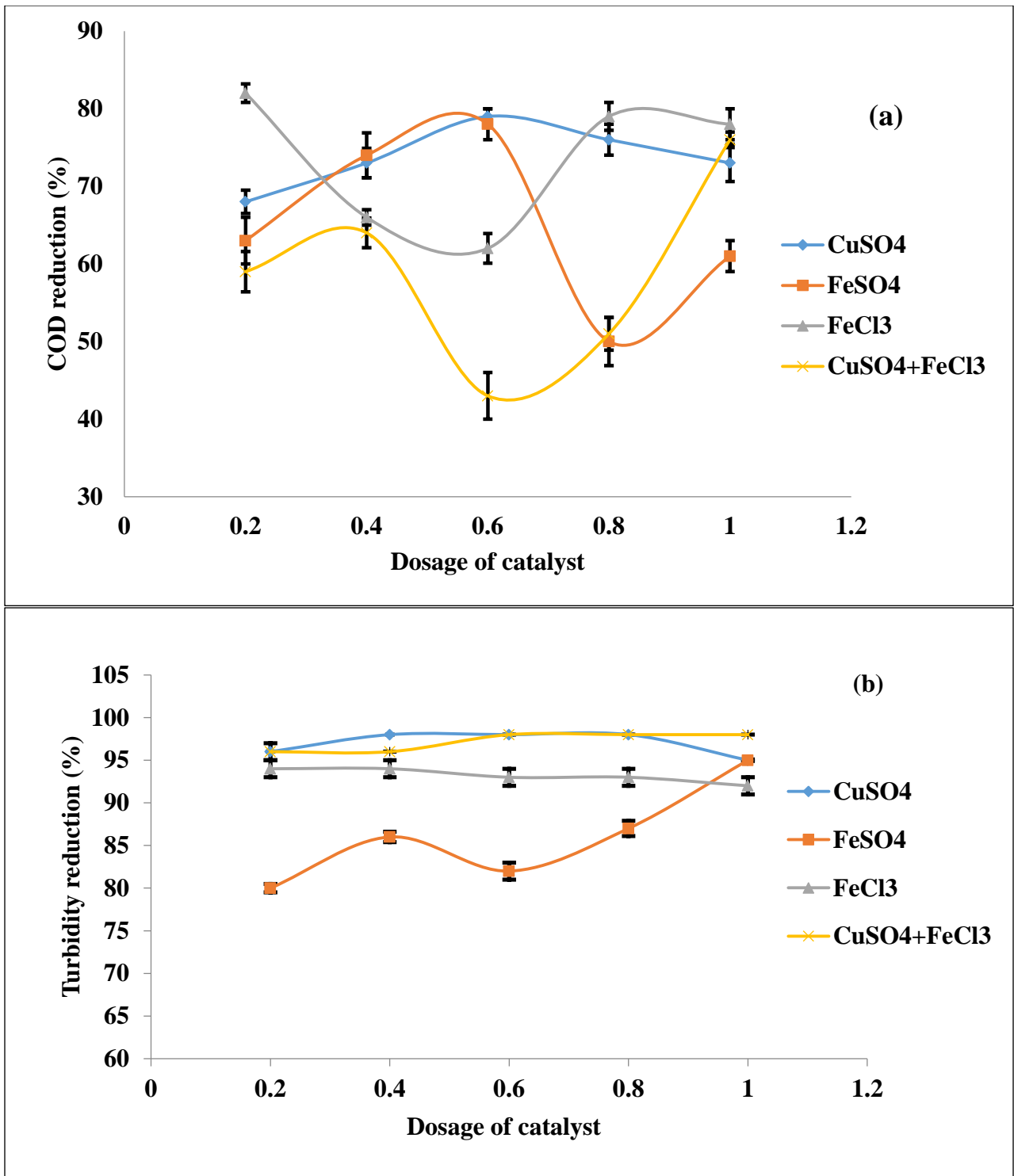
Figure 3. 3 (a) COD reduction (%), (b) Turbidity reduction (%) v/s dose (kg/m^3) for CuSO$_4$, FeSO$_4$, FeCl$_3$ and CuSO$_4$+FeCl$_3$ at optimum temperature of 80, 70, 60, 70°C and pH 9, 9, 5, 7, time (120 min), and 120 RPM.
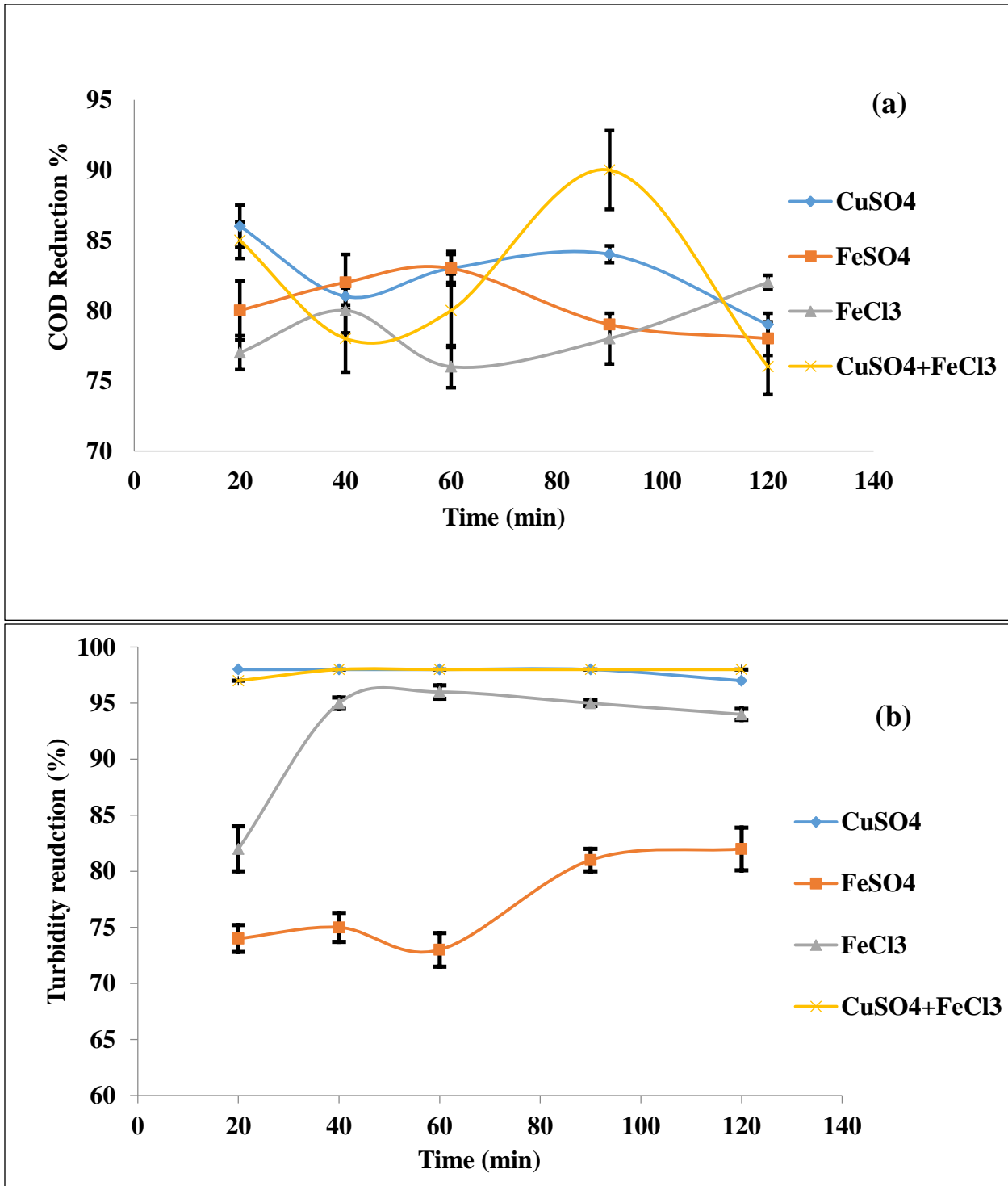
Figure 3. 4 (a) COD reduction (%), (b) Turbidity reduction (%) v/s time (min) for $CuSO_4$, $FeSO_4$, $FeCl_3$ and $CuSO_4+FeCl_3$ at optimum temperature of 80, 70, 60, 70˚C; pH 9, 9, 5, 7; dose 0.6, 0.6, 0.2, 1.0 kg/m^3, respectively, and at 120 RPM.

The results of turbidity reduction with catalyst dose are shown in Fig. 3.3(b) about 98% of reduction has been obtained for $CuSO_4$ and at all concentrations of catalysts. For $FeCl_3$, the reduction in turbidity slowly decreased with an increase in dose and varied in the range of $93 \pm 1\%$. $FeCl_3$ in water forms stable $Fe(OH)_3$ complex and releases H^+ ions. With an increase in the dose of catalyst, the concentration of stable Fe complex increased hence, result in a lower reduction in turbidity. However, $FeSO_4$ behaves differently. For $FeSO_4$, reduction in turbidity is lowest at the optimum dose of 0.2 kg/m^3 and after that turbidity increased with the increase of dose except for the dose 0.6 kg/m^3 at which maximum COD reduction is observed. That could be attributed due to the formation of stable $Fe(OH)_2$ and SO_4^{-2} complex in large amounts and it settled without neutralizing the negative particles present in raw PRE.

3.3.5 Effect of treatment time on COD and turbidity reduction at optimum condition

The effect of time on COD and turbidity reduction is shown in Fig. 3.4(a-b). The maximum COD reduction (90%) was observed in case of $CuSO_4+FeCl_3$ at 90 min at optimum temperature, pH, and dose. The optimum time for $CuSO_4$, $FeSO_4$, and $FeCl_3$ was found to be 20, 60, and 120 min respectively, with corresponding COD reduction of 86, 83, and 82%, respectively. The reduction in turbidity for both $CuSO_4+FeCl_3$ and $CuSO_4$ was found to be 98% (Fig. 3.4b). The maximum reduction in COD for $FeSO_4$ and $FeCl_3$ was observed to be 85 % at 60 min and 83 % at 120 min. However, the reduction in turbidity for $FeSO_4$ and $FeCl_3$ was observed to be 82% at 120 min, and 96% at 60 min, respectively.

3.3.6 ICP-OES analysis

The elements present in raw PRE and treated wastewater were analyzed by the ICP-OES. The results are presented in Table 3.2. The maximum reduction of Cr, Mn, Ni, Pb present in raw PRE was observed in the case of $CuSO_4+FeCl_3$ as a catalyst. Due to the presence of Cu and Fe in the

catalyst, the percentage of Fe and Cu has increased accordingly in samples. The metals like Mg, Ca and K are removed from the PRE in case of all catalysts used.

Table 3. 2 The ICP-OES result of PRE and treated PRE after catalytic thermolysis by catalyst $CuSO_4$, $FeSO_4$, $FeCl_3$, and $CuSO_4+FeCl_3$, respectively.

Element	Raw PRE (mg/L)	$CuSO_4$ (mg/L)	$FeSO_4$ (mg/L)	$FeCl_3$ (mg/L)	$CuSO_4+FeCl_3$ (mg/L)
Cr	3.02	2.16	2.61	1.8	1.62
Mn	4.584	1.25	1.68	1.88	0.99
Zn	ND	ND	ND	ND	ND
Ni	0.448	0.129	0.158	0.166	0.072
Cu	2.472	150.214	1.65	1.08	114.516
V	0.028	0.001	0.002	0.001	0.001
Pb	0.178	0.167	0.154	0.149	0.144
Fe	15.54	5.418	270.012	294.012	6.21
Na	ADL	ADL	ADL	ADL	ADL
Mg	83.32	0	0	0	0
Ca	239	0	0	0	0
K	59.6	0.001	0	0	0

ND: not detected, ADL: above the detection limit of the instrument

3.3.7 Characterization of Sludge

3.3.7.1. FTIR analysis of Sludge

In thermolysis, the thermal decomposition of high molecular weight compounds takes place into small molecular weight compounds. FTIR analysis was studied to analyze the functional groups associated with sludge formed during thermolysis using different catalysts (Fig. 3.5). FTIR spectra exhibit similar peak locations for all the catalysts used in thermolysis, however, relative transmittance intensity changes for every catalyst. The broad range of FTIR spectra between 3200-3500 cm^{-1} appears due to the hydroxyl group present in the wastewater

[121]. The presence of the C-H bends and the N-H bend appear in the waveband of 1450-1470 cm^{-1} and 1510- 1560 cm^{-1}, respectively. The broad and medium peaks of alkyl halide groups appear in the range of 500 to 800 cm^{-1}. The presence of aromatic compound C=C stretch ring is found in the range of 1450-1600 cm^{-1} with two to four bends. The aromatic compound vibrations are very strong due to the out of plane bending [122, 123]. The band in the regions of 1650-1690 cm^{-1} confirms the presence of the C=O group of amides [122]. The sharp peaks in between 2500-

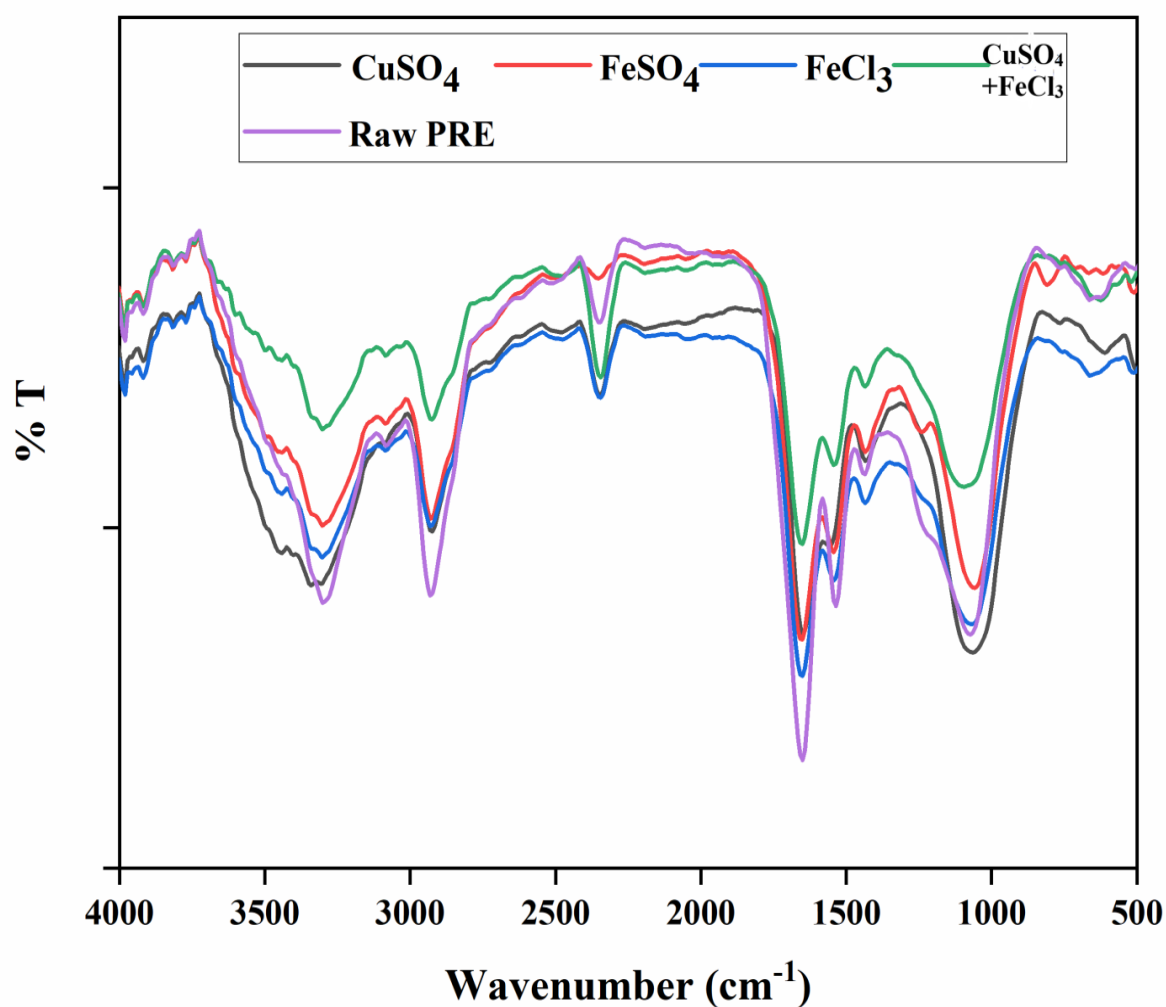Figure 3. 5 FTIR spectra of sludge precipitated from PRE and treated wastewater with different catalysts.

3500 cm^{-1} correspond to carboxylic acid groups present in sludge. The very profound presence of alkane is found in the range of 2850-3000 cm^{-1} and alcohol in the range of 3300-3400 cm^{-1} in the sludge of treated PRE. This clearly shows the presence of the free O-H and hydrogen-bonded (O-H) group [122]. There is a difference in peaks observed in dried sludge of PRE wastewater and the treated dried sludge after the thermolysis with few shifting of peak positions in FTIR as in Fig 3.5. The FTIR results showed that in case of sludge from raw PRE, the transmission intensity of hydroxyl groups was higher, while, in the case of sludge from catalytic thermolysis lower intensity was observed. This attributed to the neutralization of negative complex present in PRE by catalysts. This behavior confirms that the species of PRE wastewater gets adsorbed to catalyst through some inherent complex chemical phenomenon, which results in the removal of COD by the inorganic catalyst.

3.3.7.2 SEM and EDX analysis of sludge

The surface morphology and relative abundance of elements present on the surface of sludge were investigated by SEM-EDX analysis [61, 124]. SEM images of sludge from different catalyst are shown in Fig 3.6 (a-d), while, EXD results are mentioned in Table 3.3. SEM images confirmed that sludge precipitated after treatment with CuSO$_4$ and CuSO$_4$+FeCl$_3$ have a compact structure with irregular granule units (Fig. 3.6 (a) and (d)), while, sludge obtained after treatment of PRE with FeSO$_4$ has a wrinkled structure with three-dimensional, porous granules (Fig. 3.6 (b)). In the case of FeCl$_3$ treatment, sludge has a hard and durable structure (Fig. 3.6 (c)). The previous studies have confirmed that the compact and irregular structure is more favorable for the adsorption and connecting colloidal particles and enhancing the sedimentation of the flocs [29, 125, 126]. The wrinkled and porous structure present in FeSO$_4$ indicates that it favors the sweep flocculation for the colloidal particles in the wastewater mixture.
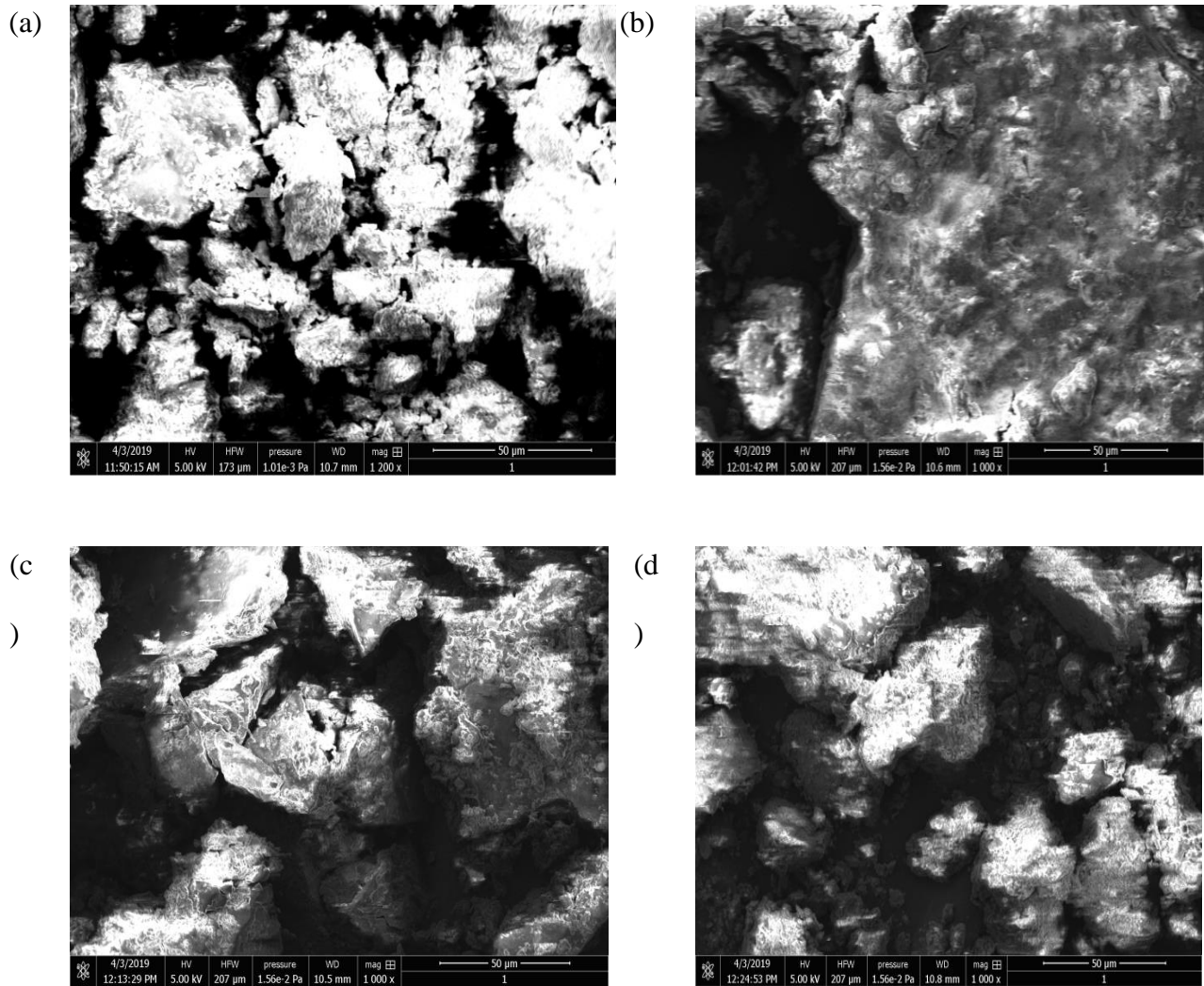
(a)

(b)

(c
)

(d
)

Figure 3. 6 SEM image of sludge formed after catalytic thermolysis (a) $CuSO_4$ (b) $FeSO_4$ (c) $FeCl_3$ (d) $CuSO_4+FeCl_3$.

The elemental composition of the sludge produced in the thermolysis process by the different catalyst is presented in Table 3.3. Among the 16 elements detected by EDX, carbon, oxygen, and lead were found in a higher percentage for all sludge than the other elements. The detection of carbon on the surface of sludge is attributed to the COD reduction capacity of sludge [88]. Maximum carbon was found in the case of $CuSO_4+FeCl_3$ at its optimum condition of

temperature; pH, dosage, and time at fix 120 RPM. This result is well supported by the efficiency of $CuSO_4+FeCl_3$ for COD reduction which was discussed in section 3.

Table 3. 3 The EDAX result of the sludge formed by the catalytic thermolysis of the raw PRE, $CuSO_4$, $FeSO_4$, $FeCl_3$, and $CuSO_4+FeCl_3$.

| S.NO.	Element	Raw PRE (%)	$CuSO_4$ (%)	$FeSO_4$ (%)	$FeCl_3$ (%)	$CuSO_4+FeCl_3$ (%)
1.	Carbon	42	24	22	32	38
2.	Oxygen	19.5	24.5	23	21	21
3.	Sodium	1.5	5	2.5	4.5	5.5
4.	Magnesium	2	5.5	3.5	1	2
5.	Aluminium	5	6.5	8	6.5	5
6.	Lead	18.5	11.5	16	14	11
7.	Silver	1	2	2	2	1.5
8.	Potassium	2.5	2	2.5	1.5	1.5
9.	Calcium	2.0	5.5	6	2	2.5
10.	Chromium	1	1	1	1.5	1
11.	Manganese	1	1	1	1	1
12.	Iron	2	2	10	10.5	4.5
13.	Nickel	.5	1	1	0.5	1
14.	Copper	0.5	7.5	1	1	4
15.	Zinc	0.5	0.5	0.5	0.5	0.5
16.	Mercury	.5	0.5	0	.5	0

3.3.7.3 TGA, DTG, and DTA analysis of the sludge

Fig. 3.7 (a-c) depicts the thermal degradation behavior of the precipitated sludge obtained after the catalytic thermolysis of refinery wastewater using four different catalysts in terms of thermo-gravimetric analysis (TGA), differential thermogravimetric analysis (DTG), and derivative thermal analysis (DTA) results versus temperature plots. These data were obtained at a

heating rate of 10 °C/min in the presence of an inert atmosphere (nitrogen gas flow rate = 200 ml/min) over a temperature range of 35 to 1100 °C. Fig. 3.7(a) depicts the thermal degradation finger-prints for sludge obtained after thermolysis with $CuSO_4$, $FeSO_4$, $FeCl_3$, and $CuSO_4+FeCl_3$ catalyst. It is seen that within the temperature range of ambient to about 1100 °C all the four sludge samples exhibit similar variation in weight loss with temperature. In each case of catalyst, there are three distinct zones. In Zone I, there is a slow decrease in the mass of all four sludge samples, but some low peaks indicating the occurrence of exothermic and endothermic changes due to loss of moisture and formation and vaporization of some low boiling components are discernible between ambient to 200 °C. In Zone II (around 200 to 450 °C) there is a fast and steady decrease in the mass of sludge samples with big exothermic peak (Fig 3.7 (c)). This can be attributed to the decomposition of a major portion of sludge constituents that are primarily organic. In Zone III (450 to 1050 °C), the rate of decrease in mass of the residual sludge sample once again becomes slow up to 1100 °C, beyond which once again a faster decline in mass is observed. This region is characterized by the conversion of high boiling point organics to char and inorganic compounds (including coagulants used) to their respective oxides [127-129].

In Fig. 3.7 (b), it is interesting to see that the peaks for sludge samples obtained with $FeSO_4$, $FeCl_3$, and $CuSO_4+FeCl_3$ as a catalyst are nearly similar in shape and height. However, the peak obtained for the sludge obtained with $CuSO_4$ is much shorter in comparison and also shows two sub-peaks in zone II indicating the difference in degradation mechanism [130]. This change in the shape of the peak for $CuSO_4$ sludge can be attributed to the formation of only CuO as the final product of degradation. Meanwhile, in zone II only a single peak is observed in the case of sludge samples obtained when $FeSO_4$, $FeCl_3$, and $CuSO_4+FeCl_3$ were used as a catalyst. Fig. 3.7 (c) shows the DTA plot of sludge. The negative slope of peaks denotes the endothermic reaction
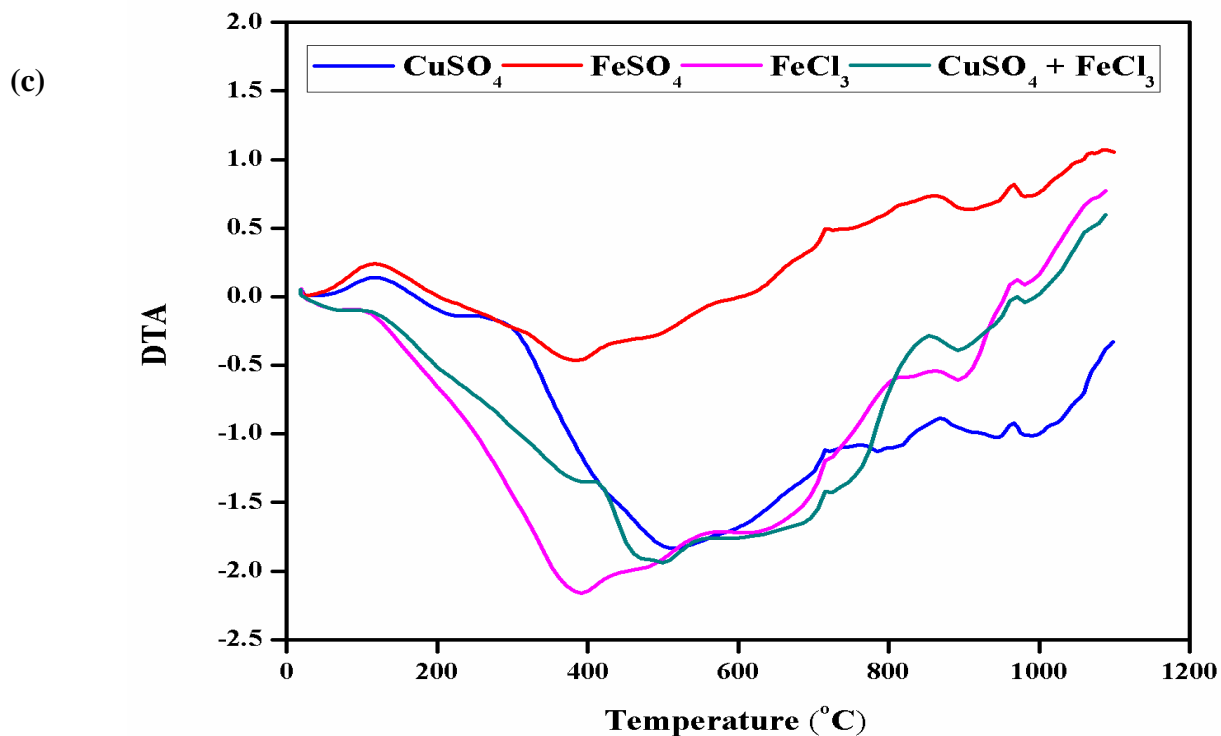
56

(a)

(b)

(c)
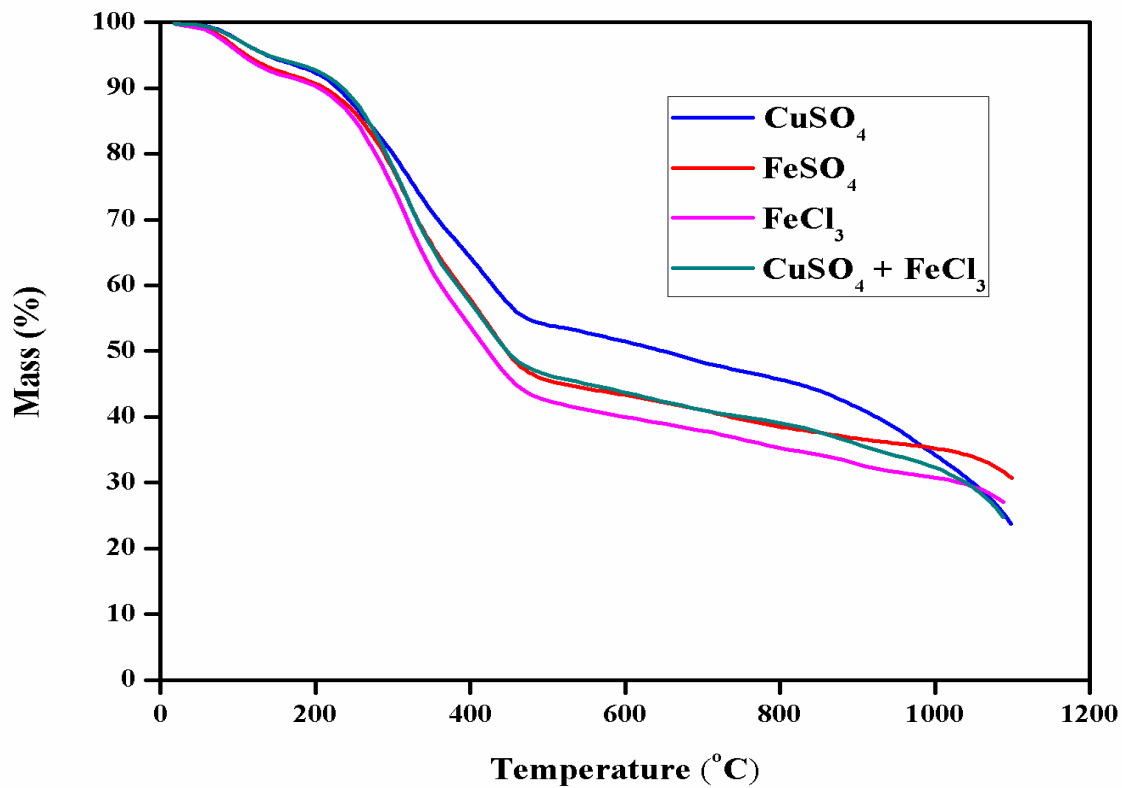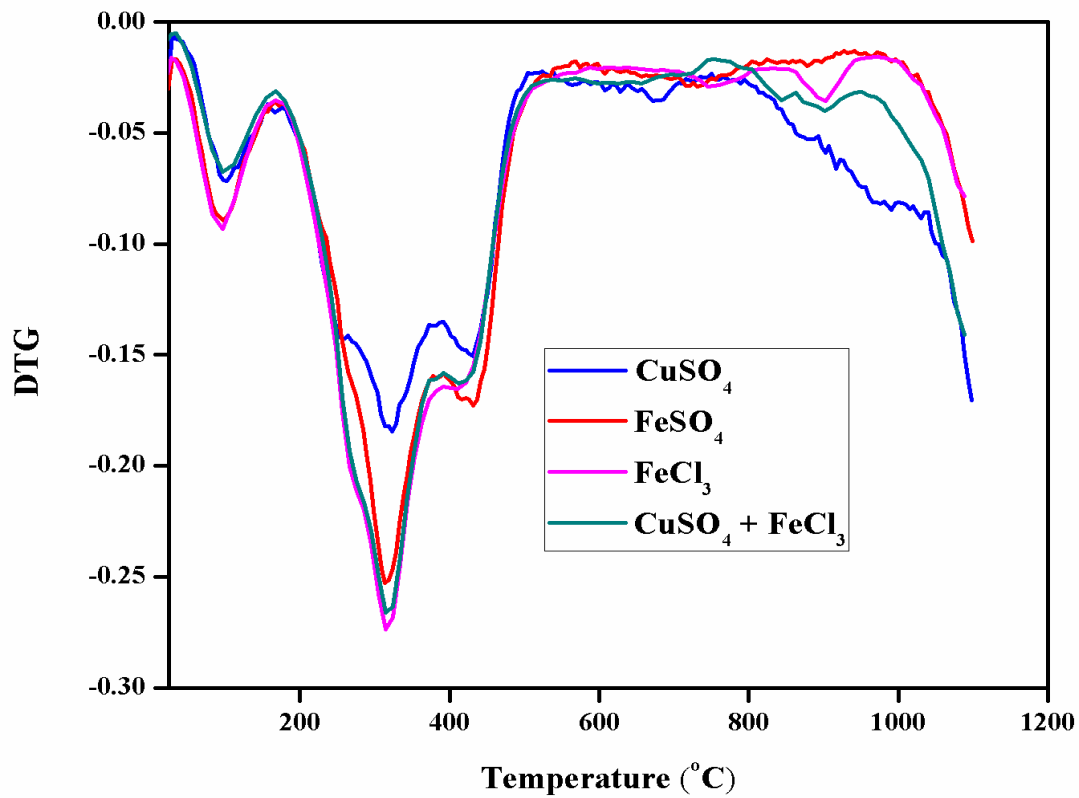
Figure 3. 7 TGA, DTG, and DTA plots of sludge obtained after catalytic thermolysis: (a) TGA, (b) DTG, and (c) DTA.

while the positive slope peak inferred exothermic reaction [131]. The exothermic reaction attributes to oxidation, adsorption, and chemisorption while, the endothermic reactions characterizes the reduction, desorption, and vaporization [132]. From ambient temperature to 200 ℃, two peaks- one indicates an endothermic process and the second indicates an exothermic is observed. After 200 ℃, the copper-based sludge showed mainly exothermic behavior till 500 ˚C, and the iron-based catalyst showed similar behavior till 400 ˚C (Fig. 3.7 (c)). The exothermic behavior till certain temperature favors the utilization of sludge as a co-fuel or it can be decomposed via wet air oxidation.

3.3.8 Comparative discussion of results

It was found that optimum condition in the case of $CuSO_4+FeCl_3$ as catalyst was obtained at pH 7, dosage 1 kg/m^3, temperature 70˚C, and 90 min with a maximum 90% COD and 98% turbidity reduction. The optimum condition for $CuSO_4$ as catalyst was obtained at pH 9, dosage 0.6 kg/m^3, temperature 80˚C, and 20 min with the 86% COD and 98% turbidity reduction. In the case of $FeSO_4$ the optimum conditions for COD reduction of 83% were at pH 9, dosage 0.6 kg/m^3, temperature 70˚C, 120 min, while 84 % COD reduction was obtained at pH 5, dosage 0.2 kg/m^3, temperature 60˚C, 60 min in case of $FeCl_3$. However, optimum conditions for maximum turbidity reduction for $FeSO_4$ (95%) and $FeCl_3$ (84%) was attained at pH 9, dosage 0.6 kg/m^3, temperature 70˚C, 60 min and pH 5, dosage 0.2 kg/m^3, temperature 60˚C, 120 min, respectively. It was found that mixed coagulants delivered better results as compared to individual coagulants.

3.4 Conclusion

In the present chapter, catalytic thermolysis of petroleum wastewater was investigated for a reduction in COD, turbidity, and removal of metal contaminants. The characterization of sludge is studied to understand its nature for possible use as a co-fuel. The $CuSO_4$, $FeSO_4$, $FeCl_3$, and 1:1 ratio (V: V) mixture of $CuSO_4$ and $FeCl_3$ ($CuSO_4+FeCl_3$) were used as catalysts. The effect of temperature, pH, dose of catalyst, and time was studied. The results showed that the catalyst 1:1 ratio mixture of $CuSO_4$ and $FeCl_3$ reduced COD by 90% and turbidity by 98% under the optimum conditions as temperature 70˚C, pH 7, dose 1 kg/m^3 and time 90 min. $CuSO_4$ catalyst gave a reduction of COD and turbidity by 86% and 98% respectively, at temperature 80˚C, pH 9, dose 0.6 kg/m^3 and time 20 min. The maximum turbidity was removed by both the copper-containing catalyst. Temperature and pH had a significant impact on the reduction of turbidity, while time and dose had minimal effect. The ICO-OES analysis showed that elements such as Cr, Mn, Ni, Pb

can be effectively removed from PRE by using (1:1) mixture of $CuSO_4$ and $FeCl_3$ as a catalyst. The FTIR results showed that in case of sludge from raw PRE, the transmission intensity of hydroxyl groups was higher, while, in case of sludge from catalytic thermolysis lower intensity was observed. The SEM analysis revealed that sludge obtained with $CuSO_4$ and $CuSO_4$+$FeCl_3$ had a compact structure with irregular granules which may be more favorable for sedimentation. While a wrinkled and porous structure present in $FeSO_4$ indicates that it favors the sweep flocculation for the colloidal particles in the wastewater. The thermogravimetric analysis confirmed that three distinctive zones of decomposition were identified. Zone I and III correspond to a slow decrease in mass loss due to the removal of moisture, low boiling point compounds, and decomposition of high boiling point compounds, respectively. While, zone II is associated with a fast and steady decrease in mass, due to the decomposition of a major part of sludge (organic). The decomposition of copper-based sludge showed highly exothermic behavior till 500˚C and iron-based catalyst showed similar behavior till 400˚C. The exothermic behavior up to these temperatures favors the utilization of sludge as a co-fuel or it can be decomposed via wet air oxidation.

Overall one can conclude that for the pre-treatment of petroleum refinery effluent, a slightly basic pH is better for the copper-based catalyst and slightly acidic pH for an iron-based catalyst. For COD and turbidity reduction, the copper-based catalyst gives a better result.