Chapter 2 Literature Review and Objectives

Abstract

In this chapter, the literature review related to the treatment of petroleum refinery effluent (PRE) by catalytic thermolysis, coagulation, and flocculation process and the physicochemical characterization of the hazardous oily petroleum sludge has been discussed. Chapter 2 has been divided into three parts: (1) literature review on catalytic thermolysis, (2) literature review on coagulation and flocculation for wastewater treatment, (3) literature review on physicochemical characterization of petroleum sludge. Based on the literature review the research gaps have been specified and the research aim of the present thesis has been decided.

2.1. Literature review

2.1.1 Treatment of petroleum refinery effluent using thermolysis

The catalytic thermal treatment of industrial wastewater from agro-industry, distillery, dye, petroleum, pulp and paper, sugar, textile industry, etc. has been reported by several authors. A summary of the available information is given in Table 2.1. Sufficient reduction in COD, color, etc. of the treated effluent has been reported.

Kumar et al. [64] reported 71.6% COD and 87.2% color reduction by catalytic thermolysis for textile industry effluent at optimum conditions of 4 pH, 4 kg/m^3 coagulant dosage, 4 h reaction time (R_t), and 95˚C operating temperature by using $CuSO_4.5H_2O$ catalyst. Prajapati et al. [65] investigated catalytic thermolysis of alcohol distillery effluent using $CuSO_4$, CuO, and $FeSO_4$ as catalysts and observed optimum 80.4% COD and 72% color removal by CuO at pH 5, 4g/dm^3, and 95˚C in 6 h. Garg et al. [66] studied catalytic thermal treatment of pulp and paper mill effluent using $CuSO_4$, 60% CuO/40% CeO_2, activated carbon, 5% CuO/95% activated carbon as catalysts. They reported 63.3% COD reduction at 5 kg/m^3 and 92.5% color at 2 kg/m^3, respectively by using $CuSO_4$ at pH 5 and 20-95˚C in 1 h. Also, the change in temperature does not show a significant change in the range of 20-95˚C. Chaudhari et al. [67] used CuO, MnO_2-CeO_2, and ZnO as catalysts for treating distillery effluent at 140^{o}C by catalytic thermolysis and observed a maximum 60% reduction in COD in 6 h by using CuO at pH 2 with 3 kg/m^3 catalyst loading. Su et al. [68] reported the catalytic thermolysis treatment of cibacron blue in aqueous solution by using $CuSO_4$ and observed the maximum 66.14% color removal at pH 2, 2 kg/m^3, and 95˚C. Sahu et al. [69] performed experiments on catalytic thermolysis of sugar industry using CuO, ZnO, FeO, and MnO as catalysts for R_t 9 h and observed 84.2% COD and 89.6%

Table 2. 1 Summary of experimental results on the treatment of different industrial effluents using catalytic thermolysis.

Type of Industry/ source of wastewater	**Catalyst selected**	**Optimum catalyst and conditions**	**Reaction time (R_t)**	**Optimum removal**	**References**
Textile industry	$CuSO_4.5H_2O$, CuO, ZnO, Al_2SO_4, and $FeSO_4.7\ H_2O$	$CuSO_4.5H_2O$ at pH 4, 4 kg/m^3, and 95˚C	4 h	71.6% COD and 87.2% color	[64]
Distillery plant	$CuSO_4$, CuO, and $FeSO_4$	CuO at pH 5, 4g/dm^3, and 95˚C	6 h	80.4% COD and 72% color	[65]
Pulp and paper	$CuSO_4$, 60% CuO/40% CeO_2, activated carbon, and 5% CuO/95% activated carbon	$CuSO_4$ at pH 5, 20-95˚C (variation in temperature does not impact on COD removal)	1 h	63.3% COD (at 5 kg/m^3 and 92.5 % color (at 2 kg/m^3)	[66]
Distillery industry	CuO, MnO_2-CeO_2, and ZnO	CuO at 2 pH, 3 kg/m^3, and 140˚C	6 h	60% COD	[67]
Cibacron Blue (RCB) in aqueous solution	$CuSO_4$	$CuSO_4$ at pH 2, 5 g/L, and 95˚C	3 h	66.14% color	[68]
Sugar industry	CuO, ZnO, FeO, and MnO	CuO at pH 5, 5 kg/m^3, and 85˚C	9 h	84.2% COD and 89.6% color	[69]

Synthetic dye	$CuSO_4 \cdot 5H_2O$, CuO, $MgSO_4 \cdot 7H_2O$, $FeCl_3$, $CaCl_2$, and $FeSO_4 \cdot 7H_2O$	$CuSO_4 \cdot 5H_2O$ at pH 11, 4 g/L, and 60 ± 2°C	1.5 h	95% COD and 68 % color	[70]
Agro-industry effluent	CA, PACl, PAS, ACH, and without catalyst	CA at pH 4.5, 5 kg/m^3, and 85˚C	9 h	72% COD and 74% color	[71]
Petroleum refinery	$CuSO_4$, $FeCl_3$, and $FeSO_4$	$FeCl_3$ at pH 7, 3 kg/m^3, and 50˚C	20 min	77.2% COD	[72]

color removal by CuO at pH 5, 5 kg/m^3, and 85˚C**.** Kumar et al. [70] treated synthetic dye effluent using $CuSO_4\cdot5H_2O$, CuO, $MgSO_4\cdot7H_2O$, $FeCl_3$, $CaCl_2$, and $FeSO_4\cdot7H_2O$ as a catalyst by catalytic thermolysis and reported optimum 95% COD and 68% color reduction by using $CuSO_4\cdot5H_2O$ at pH 11, 4 g/L, 60± 2°C and R_t 1.5 h. Sahu et al. [71] investigated catalytic and non-catalytic thermolysis of agro-industry effluent by using commercial alum (CA), polyaluminum chloride (PACl), polyaluminum sulphate (PAS), aluminium chlorohydrate (ACH) as catalysts. They observed a maximum 72% COD and 74% color reduction at pH 4.5, 5 kg/m^3, R_t 9 h, and 85˚C. Verma et al. [72] reported results for the petroleum refinery effluent treatment using $CuSO_4$, $FeCl_3$, and $FeSO_4$ as catalysts by catalytic thermolysis and observed maximum 77.2% COD reduction using $FeCl_3$ at pH 7, 3 kg/m^3, R_t 20 min and 50˚C

It is seen that the catalysts used for various industrial effluents are mainly the inorganic salts of metals like Cu, Fe, Al, and Zn. The main parameters chosen for the analysis of wastewater quality are COD and color. The temperatures under optimum conditions for all kinds of industrial wastewater are below the boiling point of water and pressure is the normal atmospheric pressure. The dosage of coagulants selected is also in the lower range for the optimum reduction in selected dependent parameters. The R_t for catalytic thermolysis is in-between 20 min to 9 hr. The maximum COD reduction observed is 95% by using $CuSO_4$ catalyst at R_t 1.5 h in alkaline medium [70] and the maximum color reduction of 92.5% is observed with CuSO4 at R_t 1 h [66].

2.1.2. Treatment of PRE through coagulation and flocculation

Coagulation and flocculation have been effectively used for treating wastewaters from the beverage industry, brewery units, chitin processing units, domestic wastewater, dyeing units, landfill leachates, heavy oil processing units, palm oil mills, palm oil mill biogas plants, petroleum refinery units, polymer units, pulp and paper mills, recycled paper making units, sauce manufacturing units, and textile units. A summary of the available published results is given in Table 2.2.

Amuda et al. [73] used $FeCl_3.6H_2O$ as a coagulant and anionic polyacrylamide (A-PAM) as a flocculant for treating the beverage industry effluent by coagulation and flocculation. They observed 73% COD, 95% total phosphorus (TP), and 97% total suspended solids (TSS) removal at the optimum condition of pH 9 and dosage 300 mg/L when coagulant was used alone and use of coagulant along with flocculent resulted in maximum 91% COD, 99% TP, and 97% TSS removal at pH 9 using $FeCl_3{\cdot}6H_2O$ dose of 300 mg/L and A-PAM dose of 25 to 100 mg/L. Sher et al. [74] investigated the polymer industry effluent by using aluminium sulfate $Al_2(SO_4)_3$ as coagulant and A-PAM as flocculent and observed 98% removal of COD, 91% of suspended solids (SS), and 99% of turbidity at the optimum pH of 6 and 9 for coagulation and flocculation process, respectively, and the dosages of coagulant and flocculent were 7.5 mL/L. Aziz et al. [75] observed 94% color reduction for landfill leachate effluent by using $FeCl_3$ as coagulant at pH 4, and dosage 800 mg/L among Al_2SO_4, $Fe_2(SO_4)_3$, $FeCl_3$, and $FeSO_4$ as coagulants selected for coagulation and flocculation. Simate et al. [76] performed the coagulation and flocculation for brewery wastewater by using carbon nanotubes (CNT), pristine, and $FeCl_3$ as coagulants and found that the $FeCl_3$ as a superior coagulant. They also reported turbidity and COD reduction with the change of zeta potential change through the experimental conditions chosen. Johnson et al. [77] performed the coagulation and flocculation on chemical enhanced primary treatment plant effluent by using $FeCl_3$ and observed a maximum 80% TSS reduction, and the removal of the metals like chromium (Cr), lead (Pb), copper(Cu), zinc (Zn), and nickel (Ni) at 40 mg/L dosage. Golob et al. [78] reported the 100% color reduction along with a reduction in total organic carbon (TOC), COD, adsorbable organic halides (AOX), biochemical oxygen demand (BOD), and surfactant at pH nearly equal to neutral by using coagulants namely $Al_2(SO_4)_3.18H_2O$, $FeSO_4.7H_2O$, $FeCl_3.6H_2O$, and flocculent commercial cationic (Colfloc RDeCiba) for dye-bath effluents by using coagulation and flocculation treatment. Hargreaves et al. [79] performed the coagulation and flocculation by using coagulant $FeCl_3$ with flocculent floculan and observed the removal of metals like Cu, Zn, and Pb. Ahmad et al. [80] observed maximum water recovery by 78% for palm oil mill effluent which was treated by coagulant envifloc-40L with flocculent profloc 4190 at pH 6, dosage 1500 mg/L of coagulant and dosage 300 mg/L of flocculent. Zahrim et al. [81] observed 90% color reduction by using coagulant $FeCl_3$ at pH 10, and dosage 8000 mg/L for treatment of palm oil mill biogas plant effluent by coagulation and flocculation treatment among $FeCl_3$, magnesium hydroxide, aluminium chlorohydrate, and polydiallyldimethylammonium chloride (polyDADMAC) used as a coagulant. Martin et al. [82] performed coagulation and flocculation for treatment of sauce manufacturing effluent by using coagulant Al-poly Cl 18 wt% and flocculent A-PAM and they observed 82% COD, 72% turbidity, and 13% TOC reduction in an alkaline medium where the coagulant and flocculant dosage were 0.4 mL/L and 7 mL/L, respectively. Dotto et al. [83] performed the treatment of chitin effluent by using $Al_2(SO_4)_3$ and chitin as a coagulant and reported that the $Al_2(SO_4)_3$ at pH 6 or 8.5 and dosage 300 mg/L reduced 20% TS, 89% SS, and 85% turbidity of effluent. Wang et al. [84] performed the coagulation and flocculation experimentally for treatment of pulp mill wastewater by using $AlCl_3$ as a coagulant and *g*-PAM-*g*-PDMC [polyacrylamide and poly (2-methacryloyloxyethyl) trimethyl ammonium chloride] as flocculent and observed the water recovery, supernatant turbidity, and lignin removal was optimum at pH 8.35, and dosage of coagulant 871 mg/L and flocculent 22.3 mg/L.

Table 2. 2 Treatment summary of industrial wastewaters using coagulation and flocculation. [Coagulant: Cog; Flocculant: Floc; RM: rapid mixing; SM: slow mixing; ST: settling time]

Type of Industry/ source of wastewater	**Coagulant/ Flocculent**	**Optimum conditions**	**Treatment time**	**Optimum removal**	**References**
Beverage industry	Cog:$FeCl_3 \cdot 6H_2O$ Floc: A-PAM	$FeCl_3 \cdot 6H_2O$ at pH 9, and 300 mg/L	RM: 2 min at 200 RPM SM: 30 min at 60 RPM ST: 60 min	73% COD, 95% TP and 97% TSS	[73]
		$FeCl_3 \cdot 6H_2O$ at 300 mg/L and 25-100 mg/L PA at pH 9	RM: 2min at 200 RPM SM: 30 min at 60 RPM ST: 60 min	91% COD, 99% TP and 97% TSS	
Textile industry	Chitosan	Chitosan at pH 4, and 30 mg/L	RM: 1 min at 250 RPM SM: 20 min at 30 RPM ST: 30 min	72.5% COD, and 94% Turbidity	[85]
Industrial polymer effluent	Cog: $Al_2(SO_4)_3$ Floc: A-PAM	$Al_2(SO_4)_3$ at 6 pH, PA at 8 pH, and 7.5 mL/L	RM: 5 min at 200 RPM SM: 5 min at 40 RPM ST: 30 min	98% COD, 91% SS, and 99% Turbidity	[74]
Landfill leachate	Al_2SO_4, $Fe_2(SO_4)_3$, $FeCl_3$, and $FeSO_4$,	$FeCl_3$ at pH 4, and 800 mg/L	RM: 1 min at 350 RPM SM: 19 min at 50 RPM ST: 60 min	94% Color	[75]
Brewery	Carbon nanotubes	$FeCl_3$	RM: 3 min at 150 RPM	No synergistic	[76]

wastewater	(CNT), pristine, and $FeCl_3$		SM: 20 min at 60 RPM ST: 30 min	effect between CNTs and $FeCl_3$, the two should not be used as coagulants together	
Chemically enhanced primary treatment	$FeCl_3$	$FeCl_3$ at 40 mg/L	RM: 1 min at 160 RPM SM: 25 min at 20 RPM ST: 85 min	80 % TSS, 200% Cr, 475% Pb, and Cu, Zn, and Ni removal	[77]
Dye bath effluents	Cog: $Al_2(SO_4)_3.18H_2O$, $FeSO_4.7H_2O$, $FeCl_3.6H_2O$, and Floc: Commercial cationic	pH values near neutral	RM: 2 min at 100 RPM SM: 20 min at 20 RPM ST: 30-150 min	100% Color removal and also TOC, COD, AOX, BOD, and anionic surfactants reduced	[78]
Municipal wastewater	Cog: $FeCl_3$ and Floc: floculan	-	RM: 2 min at 100 RPM SM: 30 min at 30 RPM ST: 30 min	Remove Cu, Zn, Pb, and Cu and Zn conjugate with colloidal organic carbon	[79]
Palm oil mill effluent	Cog: Envifloc-40L,	At pH 6 for Envifloc-40L 1500	RM: 30 sec at 200 RPM SM: 20 min at 30 RPM	78% Water recovery	[80]

	Floc: Profloc 4190	mg/L, and Profloc 300 mg/L	ST: 30 min		
Palm oil mill biogas plant wastewater	$FeCl_3$, magnesium hydroxide, aluminium chlorohydrate, and polyDADMAC	$FeCl_3$ at pH 10, and 8000 mg/L	Not available	90% Color	[81]
Sauce manufacturing wastewater	Cog: Al-poly Cl 18 wt%, Floc: A-PAM	At alkaline pH, 0.4 mL/L of Al-poly Cl 18 wt%, 7.0 mL/L of A-PAM	RM: 2 min at 160-180 RPM SM: 1 min at 40-50 RPM ST: 20 min	82% COD, 72% Turbidity and 13% TOC	[82]
Chitin effluent	Chitin and $Al_2(SO_4)_3$	$Al_2(SO_4)_3$ at pH 6.0 or 8.5, and 300 mg L^{-1}	RM: 1 min at 120 RPM SM: 10 min at 20 RPM ST: 5 min	20% TS, 89% SS, and 85% Turbidity	[83]
Pulp mill wastewater	Cog: $AlCl_3$ and Floc: Natural polymer, starch-*g*-PAM-*g*-PDMC	At pH 8.35 Cog: 871 mg/L, and Floc: 22.3 mg/L	RM: 2 min at 200 RPM SM: 10 min at 40 RPM ST: 5 min	Supernatant turbidity, lignin removal, and water recovery efficiency enhanced	[84]

Paper recycling wastewater	Cog: Alum and PACl Floc: C-PAM	At pH 6.85, alum 41 mg/L and C-PAM 7.52 mg/L	RM: 2 min at 150 RPM SM: 20 min at 40 RPM ST: 30 min	91.30% COD and 95.82% Turbidity	[86]
Saline wastewater	$Al_2(SO_4)_3$ and $FeCl_3$	$Al_2(SO_4)_3$ at pH 7, and 70 mg/L	RM: 1 min at 200 RPM SM: 20 min at 30 RPM ST: 180 min	65% TPH, and 80% Turbidity	[87]
Petroleum industry	Al_2SO_4, PACl, $FeCl_3$, $FeSO_4$,and without coagulant	$FeCl_3$ at pH 5.6, and 3000 mg/L	RM: 1 min at 120 RPM SM: 30 min at 40 RPM ST: 90 min	75.5% COD	[88]
Petroleum refinery effluent	Cog: PAX-18 (17% Al_2O_3), $Al_2(SO_4)_3$ and $Fe_2(SO_4)_3$, Floc: NALCO 71408	28.6 mg/L PAX-18 and 4.5 mg/L NALCO 71408	RM: 3 min at 150 RPM SM: 20 min at 20 RPM ST:15 min	80% COD, TOC and Turbidity	[89]
Heavy oily wastewater	Poly-zinc silicate (PZSS), PAC, PFS, A-PAM	At pH 6.5–9.5, PZSS 100 mg/L, and A-PAM 1.0 mg/L	RM: 5 min at 120 RPM SM: 3-5 min at 30-50 RPM ST: 40 min	99% Oil removed	[90]

Birjandi et al. [91] treated the paper recycling effluent through coagulation and flocculation by using alum as a coagulant and cationic polyacrylamide (C-PAM) as flocculant. They observed 91.3% COD and 95.82% turbidity removal at pH 6.85 and dosage of alum as 41 mg/L and C-PAM as 7.52 mg/L. Di Bella et al. [87] reported the saline wastewater treatment by coagulation and flocculation using $Al_2(SO_4)_3$ and $FeCl_3$ as a coagulant. They observed a maximum 65% of Total Petroleum Hydrocarbons (TPH) and 80% turbidity removal by using $Al_2(SO_4)_3$ coagulant at pH 7 and dosage 70 mg/L. Ariffin et al. [85] experimentally observed the effect of natural coagulant chitosan on the textile industry effluent by using coagulation and flocculation treatment and they observed 72.5% COD and 94% turbidity reduction at pH 4 and dosage 30 mg/L. Verma et al. [88] performed the coagulation and flocculation treatment for the petroleum industry effluent by using coagulants such as Al_2SO_4, PACl, $FeCl_3$, $FeSO_4$, and also without coagulant. They reported the optimum 75.5% COD reduction at pH 5.6 and dosage 3000 mg/L by using $FeCl_3$ as a coagulant. Santo et al. [89] reported the treatment of PRE by using coagulants such as PAX-18 (17% Al_2O_3), $Al_2(SO_4)_3$ and $Fe_2(SO_4)_3$and NALCO 71408 as a flocculant and observed the maximum 80% reduction in COD, TOC and turbidity of effluent at optimum conditions of 28.6 mg/L PAX-18 as a coagulant and 4.5 mg/L NALCO 71408 as flocculant. Zeng et al. [90] performed the oil removal experimentally from heavy oily wastewater through CF treatment by using Poly-zinc silicate (PZSS), poly-aluminium chloride (PAC), and polyferric sulfate (PFS) as coagulant and A-PAM as flocculant. They observed the 99% oil removal in-between pH 6.5-9.5, PZSS 100 mg/L, and P-Pam 1.0 mg/L as optimum dosages. The maximum COD is reduced by the Al based coagulant for industrial polymer effluent along with 91% SS and 94% turbidity reduction. A 100% color removal for dye bath effluent is observed by coagulation and flocculation treatment. A hazardous and harmful metal above acceptable limits like Cr, Pb, Ni, and Cu which are present in the wastewater frequently can be removed by the coagulation and flocculation treatment. The organic-based coagulant like chitin and chitosan have fewer removal characteristics as compared to inorganic metal salt used as a coagulant [85]. For coagulation and flocculation like catalytic thermolysis, the Cu, Fe, and Al based coagulants are mainly chosen for the effluent treatment which reduced the parameters like COD, TSS, SS, color, turbidity, TOC, AOX, TP and varies the pH of the effluent. The flocculants like cationic polyacrylamide (C-PAM), NALCO, and starch-based are used along with coagulants in the coagulation and flocculation process are mentioned in the Table 2.2. The optimum range of effluent pH is in-between 4-9; coagulant dosage varies 40-3000 mg/L and flocculants dosage varies in-between 4.5-300 mg/L by summarising the prevailing literature. The treatment time for coagulation and flocculation is divided into three parts such as rapid mixing (RM), slow mixing (SM), and settling time of the floc (ST). The range of RM, SM, and ST are 1-5 min, 3-30 min, and 30-10 min, respectively in the prevailing literature as discussed in Table 2.2. The revolution per minute (RPM) of the paddle used for coagulation and flocculation mixing is in the range of 100- 350 RPM for RM; 20- 60 RPM for SM as reported in the Table 2.2.

2.1.3 Physico-chemical characterization of petroleum sludge

The physicochemical characterization of sludge generated in industrial plants reported in the prevailing literature and the results of analysis based on physicochemical characterization are reported in Table 2.3. Ahmed et al. [92] examined the physicochemical characterization of compost of the tannery industry sludge to learned about the stability and maturity of the final product attained by a sequence of the extraction process. They reported 70-80% of a heavy metal fraction is associated with the residual fraction of sludge. Patel et al. [93] investigated the physicochemical characterization which includes metals concentration and calorific value of

Table 2. 3 Summary of physicochemical characterizations of various types industrial sludge.

Type of Industry/ source of wastewater	**Process used**	**Physico-chemical characterization**	**Analysis result**	**Reference**
Tannery sludge	extraction process	Metals	Heavy metals were associated with the residual fraction (70– 80%).	[92]
Printing and textile wastewater	-	Metals, and calorific value	Finding a suitable management option requires an extensive characterization.	[93]
Activated sludge	-	Floc size, density, specific surface, carbohydrate content, dehydrogenase activity, and settleability	A strong correlation between floc size, density, and size was obtained.	[94]
Sewage sludge	Sludge predation by the aquatic worm	Sedimentation, filtration, and dewatering	Worm predation improved settling characteristics of the sludge. Worm predation negatively impacts sludge filterability.	[95]
Dried activated sludge	Biosorption of copper ions from aqueous solution	Metal removal, and FTIR	The particle size and initial metal concentration were effects the biosorption capacity of dried activated sludge.	[96]
Sewage sludge		Sludge density, particle size distribution, water holding	Sludge application to soil may change the physicochemical properties of soil.	[97]

		capacity, void volume, pH, EC, total organic carbon, and hydrophobicity		
Textile, Petroleum, Municipal and Winery industrial activated sludge	physicochemical characterization based on extracellular polymer substance (EPS)	Surface charge, bound water, and contact angle	EPS compositions depend on the wastewater type rather than the operating conditions.	[98]
Municipal solid waste	Composting	Elemental composition	Elements can vary the potential mobility and bioavailability of sludge in the environment.	[99]
Anaerobic granular sludge	-	pH, size, surface roughness, and the TSS	The physicochemical characterization of sludge confirmed the limit viscosity as an overall parameter.	[100]
Sewage sludge	Composting under semi-permeable film at full scale	Enzymatic activity	The enzymatic activities were more intense under the semi-permeable covered.	[101]
Sewage sludge	Effect of chemical pre-treatment on microplastic	pH	Pre-treatment indicated that polyamide (PA) and PET are not resistant to acid and alkali treatment.	[102]

Biological wastewater treatment system.		Settleability, permeability, morphology, mechanical stability, rheology, porosity, surface adsorbability, surface hydrophobicity and thermodynamics, and EPS	Microbial granulation is one of the best techniques in biological wastewater treatment.	[103]
Sewage sludge.	Ozonation	Properties and dewaterability	Settleability of sludge was improved after the ozonation processes.	[104]
Granular activated sludge	Sludge Cultivation with synthetic sucrose-rich wastewater	Specific gravity, and surface hydrophobicity	Settleability and strong structure of sludge.	[105]
Sewage sludge	-	Sludge composition, structure with dewatering properties	A fraction of EPS in sludge was important for sludge structure, and the floc stabilizing of EPS was not consistent.	[106]
Oily sludge	Solvent extraction by using light naphtha, heavy naphtha, kerosene, gasoline, and methyl	Oil extraction, solid separation, and water separation	95% crude oil extraction efficiency, 24% solid separation, and 94% water separation by methyl ethyl ketone	[107]

	ethyl ketone			
Filter oily cake sludge	Solvent extraction by n-hexane, methanol, and acetone	oil yield, pH value, antioxidant, FTIR, and GCMS analysis	66.6% oil yield, FTIR and GCMS analysis suggested that the functional groups and major components are mostly from the composition of fatty acids	[108]

sludge generated by textile and printing process wastewater in the common effluent treatment plant to find out the best management option for sludge generated. D. Andreadakis et al. [94] investigated the physicochemical characterization such as floc size, density, specific surface, carbohydrate content, dehydrogenase activity and settleability of activated sludge where the sludge settleability for non-filamentous sludges were well correlated with floc size, density, and specific surface area. Zhang et al. [95] investigate the potential effects of the worm predation process consists of inoculation of an aquatic worm into the sewage sludge by physicochemical characterization such as sedimentation, filtration, and dewatering. The results recommended the worm predation restrain the viscosity and the surface charge of sludge residual and improves the settling of characteristics of the sludge. Gulnaz et al. [96] study the bio-sorption of Cu(II) by dried activated sludge and physicochemical characterization were investigated the metal removal and difference in the function group by FTIR. They reported differences in functional groups based on Fourier Transform Infrared Spectroscopy (FTIR) data and increases in the biosorption capacity based on the metal concentration. El-Nahhal et al. [97] reported the physicochemical characterization of sewage sludge by sludge density, particle size distribution, water holding capacity, void volume, pH, electrical conductivity (EC), total organic carbon, and hydrophobicity and the results suggested that the sludge application to soil changes the physicochemical characteristics of soil. Sponza et al. [98] investigated the influence of different wastewater composition on the extracellular polymer substance (EPS) based on physicochemical characteristics such as surface charge, bound water, and contact angle. They reported based on the physicochemical characterization of textile, petroleum, municipal, and winery industrial activated sludge that the EPS compositions depend on the wastewater type rather than the operating conditions. He at al. [99] reported the municipal solid waste composting as a promising alternative for solid waste management by using physicochemical characterization such as elemental composition. The results indicated that the elements can vary the potential mobility and bioavailability of sludge in the environment. Pevere et al. [100] investigated physicochemical characterization such as pH, size, surface roughness, and the TSS content of the anaerobic granular sludge for determining the limit viscosity value. They reported the physicochemical characterization of sludge confirmed the limit viscosity as an overall parameter. Robledo-Mahon et al. [101] investigated the physicochemical characterization of sewage sludge composting under semi-permeable film at full scale to predict the enzymatic activity and results showed that the enzymatic activities were more intense under the semi-permeable covered. Li et al. [102] experimental study the effect of chemical pre-treatment on micro-plastic in sewage sludge-based on the physicochemical characterization. They reported after the pre-treatments of polyamide (PA) and polyethylene terephthalate (PET) are not resistant to acid and alkali treatment, respectively. Liu et al. [103] reported the physicochemical characterization to include settleability, permeability, morphology, mechanical stability, rheology, porosity, surface absorbability, surface hydrophobicity, and thermodynamics, and extracellular polymeric substances of microbial granules present in the sludge of the biological wastewater treatment system. The physicochemical characterization optimization reported microbial granulation as one of the best techniques for biological wastewater treatment. Zhang et al. [104] reported the ozonation of sewage sludge-based on the physicochemical characterization and also related the physicochemical characterization properties and dewaterability during the ozonation process and the results revealed that the settleability of sludge was improved after the ozonation processes. Zheng et al. [105] investigate the granular activated sludge cultivation with synthetic sucrose-rich wastewater by using physicochemical characterization such as specific gravity and surface hydrophobicity of sludge and discuss the settleability and strong structure of sludge. H. Mikkelsen et al. [106] investigate the different sewage sludge to establish the relationship between the physicochemical characterization such as sludge composition, structure with dewatering properties and the results indicated that the fraction of EPS in sludge was important for sludge structure, and the floc stabilizing of EPS was not consistent. Aldoury et Al. [107] reported the physicochemical characterization in terms of oil extraction, solid separation, and water separation of oily sludge before and after the solvent extraction treatment. They reported methyle ethyle ketone gives crude oil extraction efficiency of 95%, solid separation of 24%, and water separation of 94%. Fauzi et al. [108] investigated the solvent extraction of residual oil from filter cake sludge by using the Soxhlet method with three different solvents such as n-hexane, methanol, and acetone and also analyzed the physicochemical characterization of sludge by finding the oily yield, pH value, antioxidant, FTIR, and Gas chromatography-mass spectrometry (GC-MS). The results showed the 66.6% oil extraction by using methanol as a solvent and the FTIR and GCMS suggest the functional groups and major components are mostly the fatty acids. As a result of above discussion, to understanding the physicochemical characterization of petroleum refinery oily sludge the solvent extraction is virtuous preference for the study.

2.2 Knowledge gap

The detailed literature review showed the following points have not been addressed for the successful treatment of petroleum refinery effluent and oily petroleum sludge:

- No work has been reported on the use of mixed $CuSO_4$+$FeCl_3$ (cupric sulphate and ferric chloride) as a coagulant/catalyst for thermolysis, and coagulation and flocculation process.

- COD and color reduction was mainly reported in the prevailing literature. Less attention has been given toward the pH change of the effluent and the parameters like TDS and turbidity for petroleum refinery effluent.

- The collective optimum of an independent variable (pH and dosage) and the dependent variable (final pH, COD, turbidity, TDS, and color) variation for the coagulation and flocculation treatment of petroleum refinery effluent was never reported.

- Less attention has been given to the detailed analysis of flocs remaining after the treatment processes such as thermolysis, and coagulation and flocculation.

- In-depth analysis of oily petroleum sludge has scarcely been reported.

- Effect of soxhlet extraction by solvents, namely, petroleum ether, hexane, toluene, and benzene on physicochemical characteristics of petroleum sludge before and after extraction has been scarcely reported for oily petroleum sludge.

- Kinetic triplet (activation energy, frequency factor, the order of reaction) of oily petroleum sludge extracted by the Soxhlet apparatus has been scarcely reported.

2.3 Research aim

- Focus on the reduction of the dependent parameters like COD, Turbidity, TDS, color, and maintain the Final pH of the real petroleum wastewater collected from the equalization tank of the effluent treatment plant of a petroleum refinery.

- The effect of temperature, pH, dosage, and time at constant RPM was investigated for 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 (V: V)) as a catalyst.

- The characteristics of sludge generated during the catalytic thermolysis process were also investigated by using Thermogravimetric analysis (TGA)/ Differential thermal analysis (DTA), FTIR, and Scanning Electron Microscopy (SEM) with Energy Dispersive X-Ray Analysis (EDX) analyses. Further, a reduction in metal content was investigated by using Inductively coupled plasma optical emission spectrometry (ICP-OES) analysis.

- The potential and the effective pre-treatment of effluent was investigated by coagulation and flocculation process using cupric sulphate, ferric chloride, and the mixture of cupric sulphate and ferric chloride in the ration of 1:1 by volume. The experiment stratagem of response surface methodology (RSM) design with a central composite design (CCD) technique was used for optimization and effectively built models for the process independent variables in terms of their effect on dependent variables. The two factors (pH, dosage) and the five responses (final pH, COD, turbidity, TDS, and color) were used for the statistical design for optimum conditions.
- The nature of flocs formed in the coagulation and flocculation process is analyzed by X-ray photoelectron spectroscopy (XPS), SEM, and EDX analysis.
- A physicochemical characteristic of petroleum sludge was investigated. The effect of Soxhlet extraction on petroleum sludge by selected non-polar solvents such as petroleum ether, hexane, toluene, and benzene have been studied.

- Sludge (before and after extraction) extracted from hexane were characterized based on proximate, ultimate, TGA/DTG/DTA, FTIR, and SEM-EDX analyses. The compounds present in liquid extracted from sludge after soxhlet extraction was analyzed through GC-MS analysis.

- The effect of Soxhlet extraction on kinetic triplets (activation energy, frequency factor, the order of reaction) using multiple regression analyses based on TGA analysis has been investigated.