Arabian Journal of Chemistry (2013) **xxx**, xxx–xxx

King Saud University

Arabian Journal of Chemistry

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REVIEW

A review of treating oily wastewater

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Received 17 June 2013; accepted 18 July 2013

KEYWORDS

Oily wastewater;
Environmental protection;
Processing method;
Prospect

Abstract Petroleum refining unavoidably generates large volumes of oily wastewater. The environmentally acceptable disposal of oily wastewater is a current challenge to the petroleum industry. Nowadays, more attention has been focused on the treatment techniques of oily wastewater. Therefore, oily wastewater treatment has become an urgent problem, and it must be explored and resolved by every oilfield and petroleum company. The development status of treatment methods was summarized from six aspects, which contains flotation, coagulation, biological treatment, membrane separation technology, combined technology and advanced oxidation process. Finally, the development and prospect of treating oily wastewater was predicted.

Contents

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Peer review under responsibility of King Saud University.

ELSEVIER Production and hosting by Elsevier

http://dx.doi.org/10.1016/j.arabjc.2013.07.020

Please cite this article in press as: Yu, L. et al., A review of treating oily wastewater. Arabian Journal of Chemistry (2013), http://dx.doi.org/10.1016/j.arabjc.2013.07.020

1. Introduction

With industrial development, there is increase in the amount of oil used, but various technical and management developments lag behind other reasons that are not perfect and make a lot of oil into the water, forming pollution. Treating oily wastewater sources is very broad, as the oil in the oil industry, oil refining, oil storage, transportation and petrochemical industries in the production process generate lot of oily wastewater (Ahmed et al., 2007; Machín-Ramírez et al., 2008; Chen and He, 2003). Oily wastewater pollution is mainly manifested in the following aspects:

(1) affecting drinking water and groundwater resources, endangering aquatic resources; (2) endangering human health; (3) atmospheric pollution; (4) affecting crop production; (5) destructing the natural landscape, and even probably because of coalescence of the oil burner safety issues that arise (Poulopoulos et al., 2005; Hou et al., 2003). Given oily wastewater pollution background China provides the maximum allowable emission of oily wastewater concentration of 10 mg/L. Therefore, oily wastewater treatment is urgently needed in today's field of environmental engineering problems.

Domestic and foreign research institutions have tirelessly studied in-depth and discussed oily wastewater treatment methods, and the goal is both the removal of a large amount of oil, taking into account the removal of dissolved organic matter, suspended solids, soaps, pH, sulfide, ammonia, etc. (Bjarne, 2003; Hayat et al., 2002). A detailed analysis and commentary for the main methods of oily wastewater treatment will be discussed in this paper.

2. Conventional treatment methods of oily wastewater

2.1. Flotation

Flotation is pouring into the water in the form of fine bubbles, the tiny air bubbles in the adhesion of oil particles suspended in the water, because the floating density of oil is less than that of water, the formation of a scum layer is separated from the water (Moosai and Dawe, 2003). Since flotation device processing capacity, produces less sludge and separation efficiency advantages, the oily wastewater treatment has great potential (Rubio et al., 2002). Currently the most commonly used method is flotation dissolved air flotation, flotation and jet impeller flotation methods. Dissolved air flotation and flotation impeller stay there a long time, device manufacturing and repairing problems, along with high energy consumption are disadvantages. In contrast, the jet flotation method can not only save a lot of energy, but also have small air bubbles, fixtures, easy installation, operation and safety features, which have good research and application prospects. To improve flotation, flotation agents should be added, flotation agents on the one hand with breaking and sparkling role, on the other hand there are bridging adsorption, and colloidal particles can gather together while bubbles float (Tang and Liu, 2006). In addition, the original on the basis of the flotation device can be further improved to improve the oil removal efficiency, as will the flotation cell structure reduce by a square rounded corner to an overflow weir or eliminate dross and so on.

Wang (2007) applied a settling tank simulation and carried out sedimentation tank, combined with the flotation process in a small pilot study, when the influent concentration of oil was 3000–14000 mg/L, the effluent quality of the oil average concentration was of 300 mg/L or less, and the minimum has reached 97 mg/L, the flotation process improving the degreasing effect. Zhu and Zheng (2002) used peeling flotation to make refinery wastewater treatment, oil removal rate was 81.4%, and suspended solid removal rate was 69.2%. Flotation oily wastewater treatment, is a mature technology, oil and water separation effect is good and stable, but the drawback is that scum is intractable. Li et al. (2007) applied dissolved air flotation and column flotation together to the tower separation system oily wastewater treatment, to obtain high oil–water separation efficiency. Hamia et al., 2007 investigated the dissolved air flotation unit to add activated carbon treatment performance. The results revealed that when the carbon content was of 50–150 mg/L when, COD removal rate was from 16–64% to 72–92.5% rise, the BOD removal rate was from 27–70% to 76–94%, the processing of BOD and COD values were later reduced to 45%–95 mg/L and 110%–200 mg/L respectively. (Al-Shamrani et al., 2002) conducted a dissolved air flotation separation of oil and water experiments and found that by a pretreatment of aluminum sulfate for flocculation, when the water quality of the oil concentration was of 100 mg/L, the oil base can be removed by flotation. Painmanakul et al. (2010) studied the treatment of oily wastewater containing anionic surfactant at Critical Micelle Concentration (CMC) by the Modified Induced Air Flotation (MIAF) process. The study has shown that the removal efficiency, considered in terms of COD, was related to the alum dosage, pH value and gas flow rate. Moreover, the interfacial area (a) obtained experimentally from the bubble hydrodynamic parameters (bubble size, bubble rising velocity, bubble formation frequency) and the velocity gradient (G) has been

Table 1 Oily wastewater treatment by flotation.

Flotation type	Treatment effect	References
Flotation	Oil removal is more than 90%	Wang (2007)
Peeling flotation	Oil removal is 81.4%	Zhu and Zheng (2002)
Dissolved air flotation	COD removal rate is 92.5%	Hamia et al. (2007)
Dissolved air flotation	Oil removal is more than 90%	Al-Shamrani et al. (2002)

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Table 2 Oily wastewater treatment by coagulation.

Coagulant type	Treatment effect	References
CAX	Oil removal is more than 98%	Lin and Wen (2003)
Aggregation zinc silicate and anionic polyacrylamide	Oil removal is 99%	Zhu and Zheng (2002)
Poly-aluminum zinc silicate chloride	COD removal is 71.8%	Cong et al. (2011)

proven to be the important parameter for controlling the flotation process efficiency and operation costs. The simple proposed correlation, based on the *a*/*G* ratio, provides a relatively a good coincidence between the experimental and predicted values of treatment efficiencies in this study. Table 1 depicts oily wastewater treatment by flotation.

2.2. Coagulation

Concrete technology because of its adaptability, can remove emulsified oil and dissolved oil and some difficult biodegradable organic polymer is characterized by the complex and is widely used in recent years in oily wastewater treatment(Ahmad et al., 2006). However, due to the complexity of oily wastewater composition, the object selected for particular treatment coagulants cannot make predictions in theory; there must be a lot of experiments to screen.

(Lin and Wen, 2003) for the treatment of oily wastewater oil industry has developed a composite coagulant CAX, when the original oil in water concentration was 207 mg/L, COD concentration was 600 mg/L, after coagulation treatment, oil and COD removal efficiency reached 98% and 80% respectively. Zeng et al. (2007) using aggregation zinc silicate (PISS) and anionic polyacrylamide (A-PAM) composite flocculant oily wastewater treatment, improved oil removal efficiency up to 99%, suspended solids concentration was less than 5 mg/L, and met back water requirements. However, this method has higher costs, could easily lead to secondary pollution of water bodies, the subsequent processing difficulties and other issues, the development of new cost-effective composite flocculant is a trend. Cong et al. (2011) applied poly-aluminum zinc silicate chloride to treat oily wastewater. The best flocculation condition is determined as the optimal dosage is 35 mL, the most suitable range of pH is 7–8, and the best mole ratio of zinc, aluminum and silicon is 1:1:2. At this time the removal rate of turbidity is 98.9%, the removal rate of chromaticity is 91.3%, and the removal rate of COD is 71.8%. The check experiment of PASC is done, and the results indicate that the properties of PAZSC are superior to those of PASC. Table 2 depicts oily wastewater treatment by coagulation.

2.3. Biological treatment

Biological treatment is the use of microbial metabolism, so that the water was dissolved, colloidal organic pollutants into harmless substances are stable (Kriipsalu et al., 2007; Sirianuntapiboon and Ungkaprasatcha, 2007). Currently handles more mature technology and is used frequently in activated sludge and biological filter methods. Activated sludge in the aeration tanks uses the current state vector as purifying microorganisms, by adsorption, and concentrated on the surface of the activated sludge microorganisms to decompose organic matter. The biofilter biological filter method is inside, so that the micro-organisms are attached to the filter, waste water from the top go down through the filter surface during adsorption of organic pollutants and decomposition by microorganisms will be destroyed. Biotechnology is the key to biological species and biological treatment processes, according to the particularity of oily wastewater developed in efficient biological species and the treatment process is a hot research field (Li et al., 2006). Fungi can effectively reduce the chemical oxygen demand of water, polyvinyl alcohol with a bacterial cell can be used to secure the loop processing of waste and obtain a high COD removal. Studies show (Li et al., 2005), that in the system the addition of nitrogen (such as ammonium sulfate) can increase the COD removal. The biological methods combined with other methods will achieve better treatment effect. Scholz and Fuchs (2000) studied the membrane bioreactor, the bioreactor coupled with an ultrafiltration membrane unit, the oil removal rate reached 99.99%, COD and TOC removal rates were 97%, 98% respectively. Liu et al. (2013) treated heavy oil wastewater with large amounts of dissolved recalcitrant organic compounds and low nutrient of nitrogen and phosphorus by an upflow anaerobic sludge blanket (UASB) coupled with immobilized biological aerated filters (IBAFs). By operating the system for 252 days (including the start-up of 128 days), the chemical oxygen demand (COD), ammonia nitrogen (NH_3–N) and suspended solid (SS) in the wastewater were removed by 74%, 94% and 98%, respectively. GC–MS analysis indicated that most of alkanes were degraded by the UASB process, while the I-BAF played important roles both in degrading organic compounds and in removing the NH_3–N and SS. The bacterial community structural analysis based on the PCR-DGGE technology reveals that the predominant bacteria in the UASB reactor belong to the Bacillales and Rhodobacterales, and that in the I-BAF was identified as uncultured soil bacterium. Our results suggest that the combined biotreatment system has immense potential in large-scale treatment of heavy oil wastewater. Zhao et al. (2006) investigated the use of B350 M and B350 group microorganisms immobilized on carriers in a pair of Biological Aerated Filter (BAF) reactors to pre-treat oil field wastewater before desalination. The results indicated that operating the biodegradation system is kept for 142 days with a hydraulic retention time (HRT) of 4 h and a volumetric load 1.07 kg COD $(m^3\,d)^{-1}$ at last, the reactor immobilized with B350 M achieved mean degradation efficiencies of 78% for total organic carbon (TOC) and 94% for oil, whereas that with B350 only reached 64% for TOC and 86% for oil. The influent wastewater contains organic substances from $C_{13}H_{28}$ to $C_{32}H_{66}$, and a total of 16 polycyclic aromatic hydrocarbons (PAHs). The degradation efficiencies of PAHs in the BAF immobilized with B350 M and B350 microorganisms are 90% and 84%, respectively.

Wu et al. (2009) examined the ability of Yarrowia lipolytica W29 immobilized by calcium alginate to degrade oil and chemical oxygen demand (COD). The results showed that immobilized cells had high thermostability compared to that of free

Table 3 Oily wastewater treatment by biological treatment.

Biological treatment type	Treatment effect	References
Membrane bioreactor	COD removal is 97%	Scholz and Fuchs (2000)
Upflow anaerobic sludge blanket	COD removal is 74%	Liu et al. (2013)
Biological aerated filter reactor	Oil removal is 94%	Zhao et al. (2006)
Yarrowia lipolytica W29 immobilized by calcium alginate	COD removal is 82%	Wu et al. (2009)

cells, and substrate concentration significantly affected the degrading ability of immobilized cells. Storage stability and reusability tests revealed that the oil degradation ability of immobilized cells was stable after storing at 4 °C for 30 d and reuse for 12 times, respectively, the COD degradation rate of immobilized cells was also maintained at 82% at the sixth cycle. These results suggested that immobilized Y. lipolytica might be applicable to a wastewater treatment system for the removal of oil and COD. Table 3 depicts oily wastewater treatment by biological treatment.

2.4. Membrane separation technology

Membrane separation technology is the use of a special porous material manufactured for the interception role in the physical removal of a certain way of the trapped particle size of contaminants (Lin et al., 2006). The difference in pressure driven membrane separation process is generally divided into microfiltration, ultrafiltration and reverse osmosis of three kinds. The membrane separation technology is characterized by: waste oil according to the particle size membrane MWCO reasonable certainty, and the process in general has no phase change, a direct realization of oil–water separator; without pharmaceutical dosing, so less pollution; reprocessing costs low, the separation process has less energy consumption; separation of water has low oil content, but good effect. It still requires the use of different materials and methods of preparing the novel and economical performance of film to improve existing treatment processes, thereby overcoming some of the technology (such as thermal stability, resistant to corrosion, film is likely to be contaminated, the process having small volume) shortcomings. In addition, a single membrane separation technology is not a good solution to the problem of oily wastewater treatment. It needs to be different or be a membrane separation technology combined with traditional methods of membrane separation technology combined treatment of wastewater, such as ultrafiltration and reverse osmosis joint, salt joint analysis method and reverse osmosis, ultrafiltration and microfiltration joint and other methods.

Yu et al. (2006) applied a tubular UF module equipped with polyvinylidene fluoride membranes modified by inorganic nano-sized alumina particles to purify oily wastewater from an oil field and analyzed the membrane water permeations of the UF process The results indicate that after UF treatment, oil content was below 1 mg/L, suspended solids content was below 1 mg/L, and solid particle median diameters were less than 2 μm. The quality of the permeation water met the requirement by oilfield injection or drainage. Fouled membranes and washed membranes were analyzed by scanning electron microscopy, and fouled membranes were backwashed with different solutions. Results show that the addition of nano-sized alumina particles improved membrane antifouling performance, and the flux recovery ratio of modified membranes reached 100% washing with 1 wt.% of OP-10 surfactant solution (pH 10). Song et al. (2006) used extruded tubular carbon matrix obtained from carbonization microfiltration carbon, low cost, suitable for the treatment of oily wastewater. The optimum conditions (pore size of 1.0 μm; operating through pressure of 0.10 MPa; flow rate of 0.1 m/s) under the treatment of oily wastewater, were oil removal efficiency up to 97%, the oil content of less than 10 mg/L, reaching national wastewater discharge standards. Zhang et al. (2009) applied polysulfone to treat oily wastewater. The results reveal that oil retention is 99.16% and oil concentration in the permeation is 0.67 mg/L, which meet the requirement for discharge (< 10 mg/L). It can be concluded that the composite membranes developed in the study are reasonably resistant to fouling and hence the developed PSF membranes are considered feasible in treating oily wastewater. Fig. 1 is schematic diagram of the experimental equipment.

Yang et al. (2011) developed an efficient dynamic membrane for application in oily wastewater treatment. The results showed that the deposition of MnO_2 particles onto the surface of Kaolin dynamic layer forming a Kaolin/MnO_2 bi-layer composite dynamic membrane is an effective coating technique. The optimum concentrations of the Kaolin solution and $KMnO_4$ solution should be 0.4 and 0.1 g/L, respectively. With the rise of oil concentration, the steady permeate flux decreased and the oil retention ratio increased. In the low oil concentration range from 0.1 to 1.0 g/L, the variation characteristics were more obvious. In neutral or alkaline environments, the dynamic membrane was stable with a high permeate flux and oil retention ratio of over 99%. As the temperature rose from 283 to 313 K, the steady retention ratio decreased from 99.9% to 98.2% and the steady permeate fluxes increased from 120.1 to 153.2 L m^{-2} h^{-1}.

Hua et al. (2007) studied Cross-flow microfiltration (MF) processes with oily wastewater using a ceramic membrane with

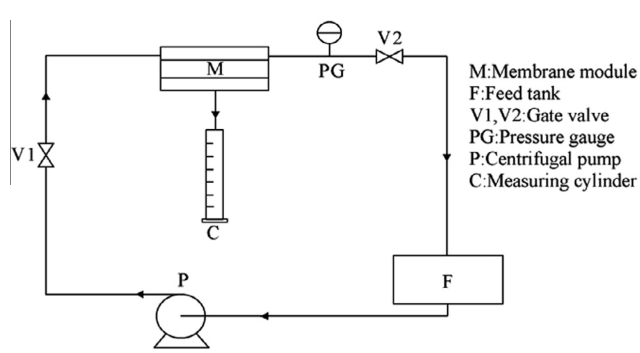

Figure 1 Schematic diagram of the experimental equipment (Zhang et al., 2009).

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50 nm pore size. The results showed that there were different degrees of effect on the permeate flux by these parameters. The TOC removal efficiencies higher than 92.4% were achieved under all experimental conditions. A non-steady model of the accumulation volume of permeation was developed. It was found that the predicted values from the model were in good agreement with the experimental results. A sensitivity analysis (SA) of the model was also conducted to identify the degree of influence of the parameters on the accumulation volume of permeation. The results showed that the accumulation volume of permeation was significantly affected by the transmembrane pressure, indicating the model was reliable. Cui et al. (2008) prepared NaA zeolite microfiltration (MF) membranes on α-Al_2O_3 tube by in situ hydrothermal synthesis method and investigated water separation and recovery from oily water. Better than 99% oil rejection was obtained and water containing less than 1 mg/L oil was produced at 85 L m^{-2} h^{-1} by NaA1 at a membrane pressure of 50 kPa. Consistent membrane performance was maintained by a regeneration regime consisting of frequent backwash with hot water and alkali solution. Um et al. (2001) studied gas injection in crossflow ultrafiltration of oily wastewater. By the nitrogen gas injection, homogeneous liquid phase oil/water emulsion was changed to heterogeneous gas–liquid phase. The injected gas causes a positive effect of promoting turbulence, but it also has a negative effect of decreasing the effective membrane area due to the partial occupation of membrane pores by bubbles. The efficiency of the gas injection was found out to be dependent on bubble fractions in the mixture: at sufficient bubble fractions the higher flux was observed. But at lower bubble fractions the flux rather decreased compared with that without gas injection.

Abadi et al. (2011) employed a tubular ceramic MF (α-Al_2O_3) system for the treatment of typical oily wastewater. This system could produce a permeate with the oil and grease content of 4 mg/L that meets the National Discharge Standard and exhibited TOC removal efficiency to be higher than 95%. Also, effects of operating parameters such as transmembrane (TMP), cross flow velocity (CFV) and temperature on permeate flux, TOC removal efficiency and fouling resistance (FR) were investigated. The recommended operating conditions are TMP of 0.125 MPa, CFV of 2.25 m/s and temperature of 32.5 °C. In this system, backwashing was used to remove oil droplets and particulates that block the membrane pores, and the results showed that backwashing could prevent permeate flux decline significantly.

Mittal et al. (2011) prepared a low-cost, hydrophilic ceramic – polymeric composite membrane from clay, kaolin and a small amount of binding materials for the treatment of oily wastewater. It was found that higher pressure and higher initial oil concentration resulted in higher flux decline. The first phase flux decline was very sharp and later a steady state decline was observed. Rejection was observed to be increased with time. The maximum rejection was found to be 93% at 41 min for an initial oil concentration of 200 mg/L at 138 kPa. Due to the use of low-cost raw materials for preparing the ceramic support, the final cost of the composite membrane was much less than that of the available commercial membranes.

Madaeni et al. (2012) utilized γ-Al_2O_3 based ceramic microfiltration membrane to remove coke particles from oily wastewaters before introducing to the coalescers. Perfect elimination of coke particles from oily wastewaters was achieved. Influence of temperature and some operating conditions such as filtration time and reusability was examined. Analysis results showed that the extent of volatile organic compounds (VOC) was not noticeably changed after the process; however, suspended solids were effectively retained by the ceramic membrane. The results indicated that most of the light organic compounds (e.g. gasoline) passed through the membrane but the troubling coke particles did not. By increasing temperature, the flux was increased due to viscosity reduction as well as solvents diffusivity enhancement. Microfiltration was performed at a constant trans-membrane pressure of 1.5 MPa, cross-flow velocity of 2 m/s and varied temperatures (20–80 °C). Moreover, reusability of the membranes was examined using HCl, NaOH and SDS as eluting agents. Normal flux recovery was obtained utilizing NaOH whereas HCl did not suggest an acceptable flux recovery.

Salahi et al. (2013) employed a sheet nano-porous membrane (PAN), nominal pore size 10 nm in order to treat the oily wastewater in a desalter plant. The results show that nano-porous membrane is efficient for the treatment of petroleum refinery waste water, so that total suspended solids, total dissolved solids, oil and grease content and chemical and biochemical oxygen demands are increased to 100%, 44.4%, 99.9%, 80.3% and 76.9%, respectively. The treated water by the proposed method meets the process and industrial water quality requirements for the discharge to the environment or reuse as agricultural water. Fig. 2 is a schematic diagram of the laboratory scale cross flow filtration system.

Sarfaraz et al. (2012) employed the nano-porous membrane–powdered activated carbon (NPM–PAC) to treat the oily wastewater. Results demonstrated NPM alone was ineffective in removing TSS, COD, and TOC. In the NPM process the removal of COD and TOC are around 62.5% and 75.1%, respectively, and the steady permeation flux (SPF) is around 78.7 L/(m^2 h). Optimum PAC dosage, which leads to a less deposit layer with a high porosity on the membrane surface, could increase the permeation flux up to 133.8 L/(m^2 h), the removal of COD and TOC, 78.1% and 90.4%, respectively, and also decreased steady fouling resistance (SFR) around 46.1%. Thus, a NPM–PAC hybrid membrane system has the potential to be an effective method to improve NPM removal efficiency in high percentages as well as to improve membrane fouling and permeation flux in the desalter plant. Fig. 3 is the schematic diagram of the laboratory scale cross flow filtration system.

Tomaszewska et al. (2005) investigated the possibility of bilge water treatment in the integrated ultrafiltration/reverse osmosis (UF/RO) system. The studies on the two stage treatment of bilge water combining UF and RO have demonstrated a high effectiveness of purification. The permeate from the first stage of bilge water treatment had the oil content below 10 ppm and was free of suspended solids whereas almost all turbidity was removed. The second stage of the treatment resulted in the removal of TOC in more than 70% and in 90% of all cations examined (Na^+, K^+, Mg^{2+}, Ca^{2+}, Zn^{2+}, Mn^{2+}, Al^{3+}, Li^+), P_2O_5 and the sulfate anion. The obtained RO permeate was free of oil. The permeates obtained in the UF and RO processes comply with the regulations concerning the effluents discharged into the environment. New membrane and the continual emergence of new technology make membrane separation technology in oily wastewater treatment to be more widely acceptable. Table 4 depicts oily wastewater treatment by membrane separation technology.

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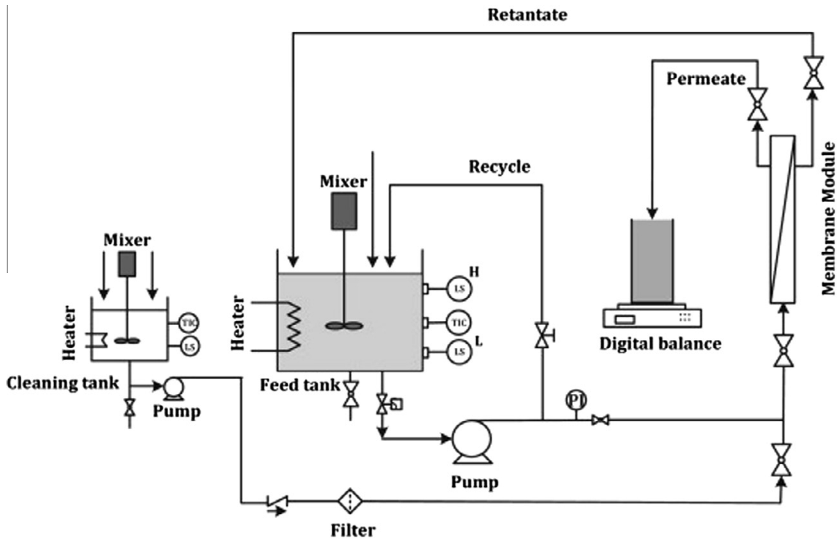

Figure 2 Schematic diagram of the laboratory scale cross flow filtration system (Salahi et al., 2013).

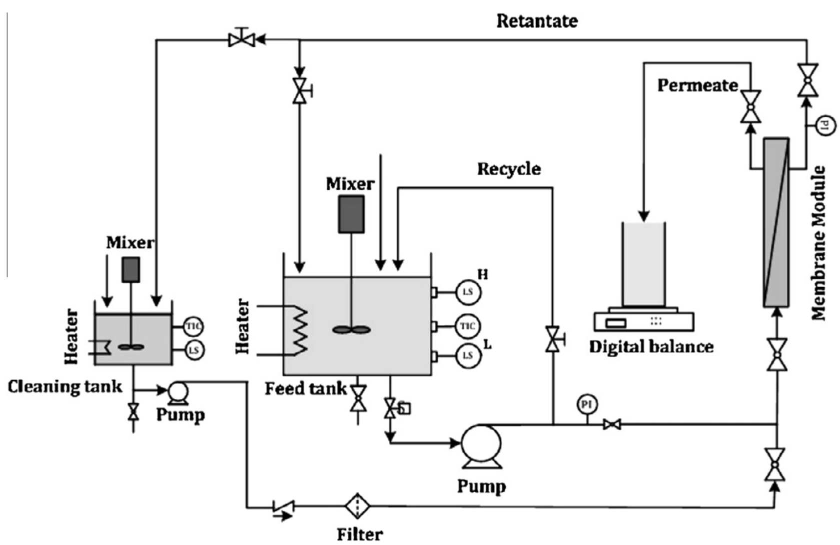

Figure 3 Schematic diagram of the laboratory scale cross flow filtration system (Sarfaraz et al., 2012).

3. Combined technologies

Of oily wastewater treatment ways, each method has its specific scope, the need for different situations studied, to determine the appropriate process. Due to the complexity of oily wastewater, using a single method is difficult to achieve national emission standards for industrial wastewater, oily wastewater deals with multi-level processing. By using a multi-stage treatment process, wastewater can be integrated into components, the presence of oil state, handling and other factors, the depth etc,, so that wastewater treatment is able to achieve satisfactory results.

Wang et al. (2007) studied the electrochemical green processing technology, the process is: petrol stations runoff → electrical

Table 4 Oily wastewater treatment by membrane separation technology.

Membrane separation technology type	Treatment effect	References
UF	Oil content is below 1 mg/L	Yu et al. (2006)
Microfiltration	Oil removal is 97%	Song et al. (2006)
Dynamic membrane	Oil removal is 99%	Yang et al. (2011)
Microfiltration	TOC removal is 92.4%	Hua et al. (2007)
Microfiltration	Oil removal is 99%	Cui et al. (2008)
Nano-porous membrane	COD removal is 76.9%	Salahi et al. (2013)
Nano-porous membrane-powdered activated carbon	TOC removal is 71.5%	Sarfaraz et al. (2012)

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resistance scale flocculator liquid multiphase pump flotation device → double filter canister line detection concentration of oil → Electric → water disinfection station reinjection. Innovations of this approach: the use of electrical activity generated in situ electrochemical method flocculants; electrophoresis breaking; voltage electric field generated in situ electrochemical methods of sterilization and oxygen, chlorine achieved sterilization; voltage electric field to change the physical properties of water to achieve scale; electrochemical oxidation – reduction method to achieve inhibition function; in situ electrochemical method to produce hydrogen, oxygen, chlorine, etc. so that the oil float on separation. After treatment oily wastewater can meet the national emission standards. Wang et al. (2006a,b) used a flocculation-NaClO/carbon oxidation – adsorption method, the process is: The oily wastewater flocculation after adjusting the pH value added NaClO, NaClO in water, hypochlorous acid and hypochlorite ions. Hypochlorous acid has a strong oxidation resistance, in acid solution, sodium hypochlorite can greatly accelerate the hydrolysis reaction, until the reaction is complete. When the solution in the presence of activated carbon, activated carbon containing iron, nickel and the like which are dissolved into ferrous ions, nickel ions, sodium hypochlorite catalyzed by these metal ions have a very strong activity of oxygen atoms [O], hypochlorous acid, and atomic oxygen [O] can destroy organic oily wastewater. Activated carbon for petroleum and petroleum wastewater with hydroxy, amino, carbonyl groups such as the impact of trace organic pollutants COD adsorption enrichment, iron, nickel and other catalytic oxidation, decomposition of organic matter can reduce the activation energy. NaClO/activated after oxidation of waste oil by the adsorbent, further reducing effluent COD, to reach the standard efflux. Yang et al. (2006) developed a combined process, the process is as follows: the raw water → - three ultrasonic Flocculator electrocell a flotation device → continuous automatic backwash sand filter → ultrasonic generator ozone generator ultrasonic processor → water, part of the application in the purification of ultrasonic chemistry, electrochemistry and continuous automatic backwashing sand filter combination technology, and degradation of organic compounds and COD chose electrochemistry, chemical combination of ozone and sound technology. This process was applied in Shengli Oilfield oily wastewater treatment, and good results were achieved. Wang (2008) applied Ozone-Biological Aerated Zeolite processes to treat oily wastewater. Results demonstrated that the effluent quality was improved using the process of ozonation and biologically aerated zeolite in a series at the best running condition. Condition of entered water: COD: 35 mg/L; ammonia nitrogen: 2.0 mg/L; oil: 3.0 mg/L. The content of oil in the effluent was stabilized at 0.15 mg/L, and COD at 11 mg/L around. And the removal of ammonia nitrogen was close to 100%. COD and ammonia nitrogen of effluent reached class I of surface water environmental standard water, and the content of oil to class IV. The process of ozonation-biological aerated zeolite of oily wastewater treatment is feasible in technic.

Bi (2012) applied CAF-BAF combination technique to treat oily wastewater. Results demonstrated that the removal rate of CAF to the suspended matter is as high as 90%. The removal efficiency of COD achieves the best effect and the removal rate of COD can reach 90% when COD and P ratio for 200. Engineering practice showed that in the refinery oily wastewater by CAF-BAF, the water of the water quality indicators is stable up to the provincial standard ''water pollutant emission limits'' (DB44/26-2001). The combined process in the refinery oily wastewater treatment works will have wide application prospects. Zhong et al. (2003) studied the treatment of oily wastewater produced from post-treatment unit of refinery processes using flocculation and micro-filtration with zirconia membrane. The results show that the oil content and COD value were decreased dramatically by flocculation, and the optimum flocculent is 3530S which is a derivative of polyacrylamide. The influence of flocculation conditions on flocculation results is also investigated by orthogonal experiments, and the optimum conditions are a dosage of 70 mg/l, temperature of 40 °C, stirring time of 90 min and holding time of 90 min. After flocculation, the effluents were treated with micro-filtration using zirconia membrane. The results of filtration tests show that the membrane fouling decreased and the permeate flux and permeate quality increased with flocculation as pretreatment. The permeate obtained from flocculation and micro-filtration can meet the National Discharge Standard and the recommended operation conditions for pilot and industrial application are transmembrane pressure of 0.11 MPa, and cross-flow velocity of 2.56 m/s. Benito et al. (2002) designed a modular pilot size plant involving coagulation/flocculation, centrifugation, ultrafiltration and sorption processes. The pilot plant can be used for the treatment of different water-based coolants and oily wastewaters, generated in metalworking processes and steel cold rolling operations. Different treatments are considered depending on the nature of the oily waste emulsion. The main advantage of the plant is its versatility, allowing the combination of several of the aforementioned treatments. It is a feasible waste management alternative with potential savings as a result of a better control of the elimination of oily wastes and water reuse, with the result of environmental and economic benefits.

In addition, there are some oily wastewater treatments that can be effectively combined in a method. Such as flotation softening → purification → Filter → Anti-osmosis water recovery combined process, electrolysis-Fenton method, electrical float – contact oxidation process and sedimentation, flotation oil and biochemical degradation the three treatment methods, proven, are to make the water meet emission standards. In practical applications also use of a more joint approach, and the formation of multi-stage treatment process, can give full play to the advantages of various methods and to make up for their shortcomings. Researchers have been pursuing and developing to effectively deal with a large-scale application of oily wastewater and economical treatment process . Centrifugation → membrane separation → electrocoagulation three treatment processes in the practical application of oily wastewater treatment will be more potential. First the centrifugal separation method can effectively remove suspended solids and can be slick, and then the electroflocculation and France biodegradable organics and some emulsified oil, and can reduce the COD value and the ammonia content, etc., with the final membrane separation method can further achieve water separation, the waste water meets the national emission standards. The process is not only a simple equipment and the economy, but also to avoid secondary pollution.

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4. Advanced oxidation process

4.1. Electrochemical catalysis

Electrochemical oxidation catalytic system is generated by the electrochemical oxidation of the hydroxyl radical with a highly organic matter between addition, substitution and electron transfer processes such as the degradation of pollutants, mineralization, with no secondary pollution, easy to build airtight circulation, etc., in the water treatment industry acclaimed (Li et al., 2003; Koper, 2005).

Santos et al. (2006) applied electrolysis to treat the oily wastewater. Electrolysis of the oily wastewater leads to a time-dependent reduction in chemical oxygen demand (COD) in the sample that could be attributed to: (i) the direct oxidation of oil components at the electrode, by the metal oxide itself or by OH radicals available at the electrode surface, (ii) the indirect oxidation of oil components by intermediate oxidizing agents formed in parallel reactions (ex. ClO^-), and (iii) the aggregation of suspended oil droplets by electroflotation. The largest reduction (57%) in COD was obtained following the electrolysis of an oily sample for 70 h at 50 °C with a current density of 100 mA cm^{-2}. The stability of DSA electrodes for use in oily wastewater remediation has been assessed. Ma and Wang (2006) treated oily wastewater by an electrochemical process in laboratory pilot-scale plant, using double anodes with active metal (M) and graphite (C) and iron as cathode and a noble metal content catalyst with big surface. It can be concluded that the catalytic electrochemical treatment of oily wastewater is effective. Both chemical oxygen demand (COD) and biochemical oxygen demand (BOD) were reduced by over 90% in 6 min, suspense solids (SS) by 99%, Ca^{2+} content by 22%, corrosion rate by 98% and bacteria (sulfate reducing bacteria (SRB), saprophytic bacteria (TGB) and iron bacteria) by 99% in 3 min under 15V/120A. These results indicate that this catalytic electrochemical method could be used for an effective oily wastewater treatment for injection purposes. Fig. 4 is the flow diagram of electrochemical pilot-scale plant.

4.2. Supercritical water oxidation

Supercritical water oxidation (SCWO) is a process that oxidizes organic solutes in an aqueous medium using oxygen or hydrogen peroxide as oxidants, at temperatures and pressures above the critical point of water (374.3 °C and 22.12 MPa). The primary use of SCWO is to destroy organic wastes. Conversion rates higher than 99% can be achieved with residence times shorter than 1 min (Tester and Cline, 1999; Kritzer and Dinjus, 2001). And it is a clean, pollution-free, environmental friendly organic waste treatment technology. It has a unique effect on treating toxic and biodegradable organic waste. The final emission of organic matter treated by SCWO is CO_2, H_2O, N_2, etc., so it will not result in secondary pollution. The technology of treating sewage by SCWO is a deep oxidation technology proposed by Medoll (1982), it can completely and thoroughly destroy the structure of organic effluent, and the reaction completes in a very short time. At present, the United States have applied the technology to rocket fuel, nuclear waste, chemical residues, explosives, and volatile acids, industrial waste slurry, physiology garbage (Takahashi et al., 1991) and other environmentally harmless treatments. Germany, France, Sweden, Spain and Japan have gained important achievements on effective treatments such as industrial toxic waste, diesel, urban waste, the degradation of polymers (Watanabe et al., 2001) and dioxins (Meng et al., 2000) in the burning fly ash, etc. Some researchers in China (Xiang et al., 2002, 1999; Ding et al., 2000; Zhao and Zhao, 2001) have made experiments and researches on the alcohol, phenols, benzene, nitrogen and sulfur and other organic wastewater treatments by SCWO in recent years, achieving satisfactory results. However, supercritical water oxidation for the treatment of oily wastewater is reported by few.

Wang et al. (2005) studied oily wastewater treated by supercritical water oxidation technique (SCWO) in intermittent equipment at 390–430 °C, 24–28 MPa, reaction residence time 30–90 s. Experimental results showed that SCWO is a high-efficiency organic waste treatment and disposal technique, and temperature and residence time are the main influencing factors in removing COD from oil-bearing sewage and the removal rate of COD obviously increases as temperature and residence time extend. Wang et al. (2006a,b) treated oily wastewater by supercritical water oxidation (SCWO). The experimental results show that SCWO is a high-efficiency treatment and disposal technique for organic wastes. Temperature and residence time serve as the main influence factors in removing COD of oily wastewater, with which the COD removal rate obviously increases.

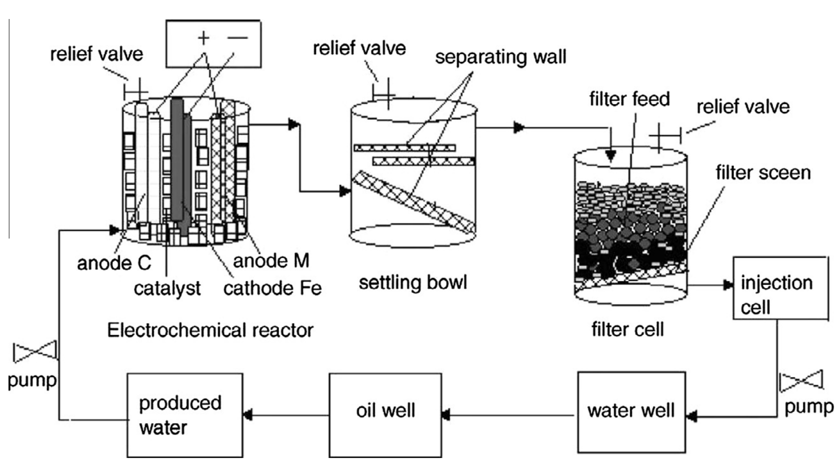

Figure 4 Flow diagram of electrochemical pilot-scale plant (Ma and Wang, 2006).

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5. Conclusions

With the continuous improvement in environmental requirements, the quality of oily wastewater treatment effluent is required to improve the existing methods that have been unable to meet the current requirements of people and for the environment, the use of new, more efficient approach is imperative. Oily wastewater treatment technology for future trends should be focused on the following areas:

(1) For the existing problems of technology and processes, research and development of a new combined process and maximizing the advantages of various methods to avoid its limitations.
(2) In-depth study of oily wastewater degradation mechanism, to improve oily wastewater treatment efficiency and reduce processing costs provides a solid theoretical foundation.
(3) To strengthen the ''environmentally friendly'' approach to research. Among them, the supercritical water oxidation technology to avoid secondary pollution, good effect, wastewater treatment rate, the device is relatively simple and easy automatic control, etc., should have a more prominent development potential.

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