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Purification of Biodiesel via Nanofluid using Liquid-Liquid Extraction in a Membrane Contactor

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Abstract: Recently, attention has been paid to nanofluids due to their contribution to enhancing heat and mass transfer in different industrial applications. Consequently, a nanofluid composed of SiO2 nanoparticles (NPs) and distilled water as base fluid was adopted as a solvent to promote the removal of impurities, methanol, and glycerol, from crude biodiesel using liquid-liquid extraction in the membrane contactor. The presence of NPs significantly enhanced the methanol and glycerol removal efficiency. The optimum concentration of NPs in nanofluid was 0.01 wt%. It was found that adding 0.01 wt% of NPs to the distilled water increased the methanol removal efficiency from 76.4% to 93.1% upon using crude biodiesel with methanol and glycerol content of 2000 ppm and 1 wt%, respectively, at a constant flow rate of solvent and biodiesel of 200 mL min–1. Meanwhile, the glycerol removal efficiency increased from 76.2% to 94.5%. The results revealed that the solvent flow rate was the controlling mass transfer step.

تنقية الديزل الحيوي بواسطة المائع النانوي باستخدام طريقة استخلاص سائل-سائل في الملامسات الغشائية

سعاد حسين احمد، قسم الهندسة الكيمياوية / كلية الهندسة / جامعة تكريت / تكريت - العراق.
حارث نوري محمد قسم الهندسة الكيمياوية / كلية الهندسة / جامعة تكريت / تكريت - العراق. مدرسة الهندسة الكيمياوية/ جامعة سانس ماليزيا/ بولايو بينانغ / ماليزيا.
عبدالله عدنان عبدالكريم المركز العراقي للتآكل / هيأة البحث والتطوير الصناعي / وزارة الصناعة والمعادن العراقية/ بغداد/ العراق.

الخلاصة

زاد الاهتمام مؤخراً بالمحاليل النانوية لمساهمتها في تحسين انتقال الحرارة والمادة في التبيقات الصناعية. لذالك، سائل نانوي يتكون من جزيات نانوية من SiO_2 (NPs) وماء مقطر كسائل اساس قد اعتمد كمذيب لأزالة الشوائب، الميثالنول والكليسيرول، من الديزل الحيوي الخام باستخدام الاستخلاص سائل-سائل في الملامسات الغشائية. وجود NPs زاد بشكل مؤثر على كفاءة الازالة لكل من الميثانول والكليسيرول. أفضل تركيز لل NPsفي المحلول النانوي كان 0.01 wt%. لوحظ عند اضافة 0.01 wt% من NPs الى الماء المقطر ازدات كفاءة ازالة الميثانول من 76.4% الى 93.1% عند استخدام ديزل حيوي خام يحنوي على ميثانول وكليسيرول 2000 ppm و 1 wt%، على التوالي، عند معدل جريان ثابت لكل من المذيب والديزل الحيوي قيمته 200 mL min^{-1}. في تلك الاثناء كفاءة الزالة الكليسيرول ازدات من 76.2% الى 94.5%. بينت النتائج ان جريان المذيب هو الخطوة المحددة لانتقال المادة.

الكلمات الدالة: ديزل حيوي، استخلاص، بولي بروبلين، SiO_2، جزيئات نانوية.

1.INTRODUCTION

Emissions from burning fossil fuels, which are responsible for climate change, are dramatically increased. Therefore, renewable energy as an alternative to fossil fuels has become a critical issue [1]. Biodiesel has been considered a renewable and cleaner energy source than fossil fuel [2]. Biodiesel is a mixture of fatty esters produced from different biomass sources, such as vegetable oils, animal fats, or recycled greases. Typically, Biodiesel is produced by the transesterification reaction in which triglyceride reacts with alcohol in the presence of a catalyst to produce a mixture of fatty esters, glycerol, soap, trace amounts of residual catalyst, triglyceride, and excess alcohol [3]. The purification of crude biodiesel is a crucial issue in producing biodiesel that meets technical requirements. Biodiesel is purified by conventional methods, i.e., wet and dry methods [4]. In the wet method, huge amounts of water are required to remove excess contaminants and by products, which increases the process cost and production time. Furthermore, the wastewater treatment process is required; however, it represents an additional weakness to the wet method. On the other hand, the dry process uses an ion exchange resin or magnesium silicate powder to neutralize the impurities [4]. Recently, the liquid-liquid extraction method has been employed for crude biodiesel purification [3]. To overcome the conventional liquid-liquid extraction columns' disadvantages, membrane contactors are proposed. This method has several advantages, such as large surface area, lack of emulsion, unrequired difference between phases densities, the surface area unaffected by changing phases flow rate values, and no agitation required [5-9]. Suspending nano-scale materials into liquids called nanofluids, have received a great attention due to their contribution to heat and mass transfer enhancement in many industrial processes. Subsequently, nanofluids have been widely used in gas absorption and desorption to improve process performance [10, 11]. Various studies have focused on implementing nanofluids in liquid-liquid extraction [12-17]. For instance, Saien and Bamdadi [12] used magnetite and alumina nanoparticles to investigate the behavior of nanofluids in liquid-liquid extraction for a toluene–acetic acid–water system. They pointed out that at 0.002 wt% nanoparticles concentration, the mass transfer rates were enhanced by 157% and 121% for magnetite and alumina, respectively. Li et al. [15] investigated the effect of Al_2O_3 and TiO_2 nanoparticles on the extraction performance of the n-butanol-succinic acid-water system. They found that the extraction efficiency upon using Al_2O_3 nanofluid reached 90% compared with less than 50 % for the free-nanoparticles system. Amelio et al. [9] adopted water as a solvent to remove the biodiesel impurities using a liquid-liquid extraction method in a flat sheet in a membrane contactor. This study is aimed to investigate the impact of nanofluid on biodiesel purification using the liquid-liquid extraction method in a hollow fiber membrane contactor. Nanofluid was adopted as a solvent to remove methanol and glycerol from crude biodiesel. Silicon dioxide (SiO_2) was considered for preparing water/SiO_2 nanofluid due to its chemical stability, hydrophilicity nature (reduce the agglomeration probability), and low cost. House-made extraction membrane contactor module was used, which involved a polypropylene (PP) hollow fiber membrane. Biodiesel is prepared from canola oil via a transesterification reaction. The effect of nanoparticles concentration, solvent flow rate,

crude biodiesel flow rate, and impurities concentration on the extraction performance was evaluated.

2. EXPERIMENTAL

2.1. Materials

PP hollow fiber membranes were obtained from Microdyn-Nadir (German). Canola oil was purchased from local market (Re-CO, Spain). Analytical grade methanol (99.5%) and Glycerol (99.5%) were purchased from Thomas Baker, India. Potassium hydroxide (99.9%) was provided from Applichem GmbH, Germany. SiO_2 nanoparticles (NPs) was purchased from US Research Nanomaterials, Inc.

2.2 Methods

2.2.1 Preparation of Biodiesel

The biodiesel used in the present study was prepared via a transesterification reaction. One gram of potassium hydroxide was dissolved in 24 ml of methanol, and the solution was added to 100 ml of canola oil. The mixture was stirred using a magnetic stirrer for 10 min, then sonicated for 1 hr at 60°C using a water bath sonicator. The obtained crude biodiesel was left in a separating funnel for 24 hours to separate biodiesel from impurities. Depending on the density difference, the liquid at the top layer was withdrawn as pure biodiesel.

2.2.2 Inspection of Biodiesel

In order to demonstrate the composition of the obtained biodiesel, a Mass Spectrometer (Thermo Scientific TSQ Quantum, USA) with a capillary column (Thermo Scientific TraceGOLD TG-5MS, USA) was adopted. The Higher heating value (HHV) of the biodiesel was determined by using CAL2K-Oxygen Bomb Calorimeter (South Africa), while the flash point was measured using automated Pensky-Martens closed cup flash point tester APM-7 from TANAKA, Japan. The density and viscosity of biodiesel were measured using density meter DA-645 and kinematic viscosity measuring system AKV-202 from TANAKA Japan.

2.2.3 Characterization of SiO_2 NPs

Scanning electron microscopy (SEM) (FEI INSPECT F50, Netherlands) was used to demonstrate the morphology of SiO_2 NPs. The sample was coated with gold using plasma sputtering (YKY, China). The particle size distribution for SiO_2 was determined via a particle size analyzer (NanoBrook 90Plus from Brookhaven Instruments, USA). SiO_2-NPs were dispersed into distilled water using an ultrasonic water bath (Unisonic, Australia) for 1 hr before analyzing it in a particle size analyzer. The elemental composition of SiO2-NPs was demonstrated using Energy-dispersive X-ray (EDX) spectroscopy from Thermoscientific (Netherlands).

2.2.4 Preparation of Nanofluid and Crude Biodiesel

The nanofluid was prepared by dispersing a predetermined amount of SiO_2-NPs in distilled water with an ultrasonic bath. Each solution was put in the ultrasonic bath for about 60 min at ambient temperature. Crude biodiesel was prepared by mixing the obtained pure biodiesel with predetermined quantities of methanol and glycerol as impurities.

2.2.5 Extraction System

The membrane contactor module was fabricated by packing five PP fibers into a stainless-steel housing and sealing it with epoxy resins (Alteco, Singapore). The dimensions of the membrane module and hollow fiber specifications are listed in Table 1.

Table 1 Specifications of the Membrane Module.

Properties	value
Module ID, mm	127
Fiber inside diameter (mm)	1.8
Wall thickness (mm)	0.5
Number of fibers	5
Effective fiber length, cm	20
Overall porosity (%)	70.6
Pore size (μm)	0.2

The crude biodiesel was pumped from the storage tank to the tube side of the membrane contactor module, and the outlet stream was recycled to the biodiesel storage tank. In contrast, nanofluid as solvent was introduced to the shell side of the membrane contactor module, and the exiting stream was sent to the solvent storage tank. The biodiesel and solvent flow through the membrane module were in parallel configuration (co-current flow). Two flowmeters with a flow rate range of 0–500 mL min^{-1} (Zyia Instrument, China) were used to adjust the biodiesel and solvent flow rates, which were calibrated prior to start the experiments. The pressure difference between the tube and shell sides was maintained at 0.4 bar to achieve a constant mass transfer film at the membrane surface. The schematic diagram of the extraction system is presented in Fig. 1. The extraction process was operated for one hr, and samples from inlet and outlet biodiesel streams were collected at 10 min intervals. The methanol concentration in the biodiesel was detected using gas chromatography (GC) (SHIMADZU, GC-2030, Japan) and a Capillary column (Rt-Q-BOND) from RESTEK (USA). The glycerol inspection in the collected solvent was performed by visible spectrophotometer (V-530 JASCO, Japan) using the FOLIN-CIOCALTEAU reagent. 5 mL of solvent was mixed with 5 mL of 2 M sodium hydroxide solution. Five drops of FOLIN-CIOCALTEAU reagent were added to the mixture and left for one h before inspection in the visible spectrophotometer. The glycerol was located at the wavelength of 560 nm.

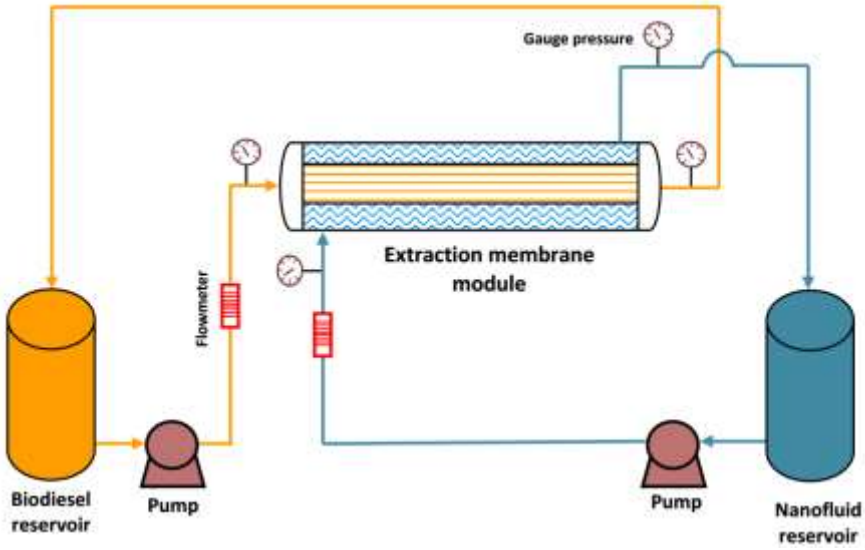


Fig. 1 Schematic Diagram for Extraction in Membrane Contactor.

2.3 The Evaluation of Extraction Performance

The performance of the extraction process was assessed through the removal efficiency and flux of methanol and glycerol, which was calculated as follows

$$\text{Removal effeciency (\%)} = \frac{(C_{initial} - C_{out})}{C_{initial}} \times 100 \quad (1)$$

$$\text{Flux (mol m}^{-2}\text{s}^{-1}) = \frac{Q_{bio}(C_{initial} - C_{out})}{A \times 6 \times 10^5} \quad (2)$$

where $C_{initial}$ (mol m^{-3}) is the initial concentration of the impurities in the crude biodiesel, C_{out} (mol m^{-3}) is the impurities concentration at the outlet stream of the tube side of the membrane module, Q_{bio} (mL min^{-1}) is the flow rate of crude biodiesel, and A (m^2) is the mass transfer area.

3. RESULTS AND DISCUSSIONS

3.1 The Analysis of Prepared Biodiesel

The biodiesel was separated by a separating funnel depending on the density difference between the phases in crude biodiesel produced by the transesterification reaction. Fig. 2 demonstrates the created layers in the separating funnel. The upper layer represented pure biodiesel, while the glycerol was accumulated at the bottom of the funnel. The result obtained from GC-MS chromatography verified that the fatty acid methyl esters (FAME) represented 99.78 % of the total compositions of the produced biodiesel. The main specifications of the prepared biodiesel, American Society for Testing and Materials (ASTM) [18] and the European Committee for Standardization (EN) [19] are listed in Table 2. It can be observed that the prepared biodiesel specifications are well agreed with ASTM and EN standards. Furthermore, the HHV for the prepared biodiesel was 42 MJ/kg. However, Fassinou [20] reported that the waste cooking oil and soybean oil produced biodiesel with slightly lower HHV values of 40.11 MJ/kg and 39.77 MJ/kg, respectively.

3.2 Characterization Results of SiO_2-NPs

The morphology of SiO_2 was investigated via SEM, as shown in Fig. 3. It was shown that SiO_2-NPs had a spherical shape and agglomerated with each other's to form clusters. The element composition of the SiO_2-NPs, which were obtained from EDX spectra, is shown in Fig. 4. It can be observed that NPs composition was mainly Si and O, which are related to SiO_2. While C and N represented the impurities in NPs. The atom percentage and weight percentage for all elements obtained from EDX analysis are presented in Table 3. Another essential characteristic is the size of SiO_2-NPs used in the present work; therefore, particle size analysis was performed, as shown in Fig. 5. As shown in this figure, a unimodal distribution is obtained and the mean particle size diameter of SiO_2 was 62.6 nm.

Table 2 Main Specifications of the Prepared Biodiesel and Standards Values.

Property	Prepared Biodiesel	ASTM	EN
Density at 15°C, kg m^{-3}	884	860-890	860-900
Viscosity at 40°C, mm^2 s^{-1}	4.6	1.9-6.0	3.5-5.0
Flash point, °C	134.5	130 (min)	101 (min)
FAME, wt%	99.78	-	96.5 (min)
Total glycerol, wt%	0.01	0.24(max)	0.25 (max)

Table 3 Element Analysis of SiO_2-NPs.

Element	Symbol	Atomic (%)	Weight (%)
Carbon	C	13.4	8.6
Oxygen	O	60.4	51.9
Sodium	Na	0.3	0.3
Silicon	Si	26.0	39.2

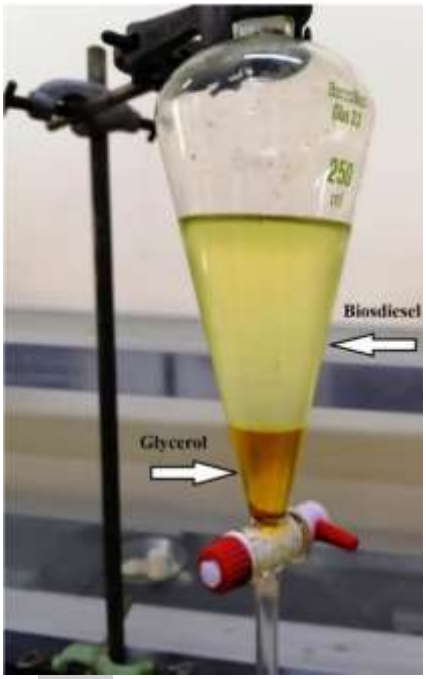


Fig. 2 Biodiesel and glycerol in the separating funnel

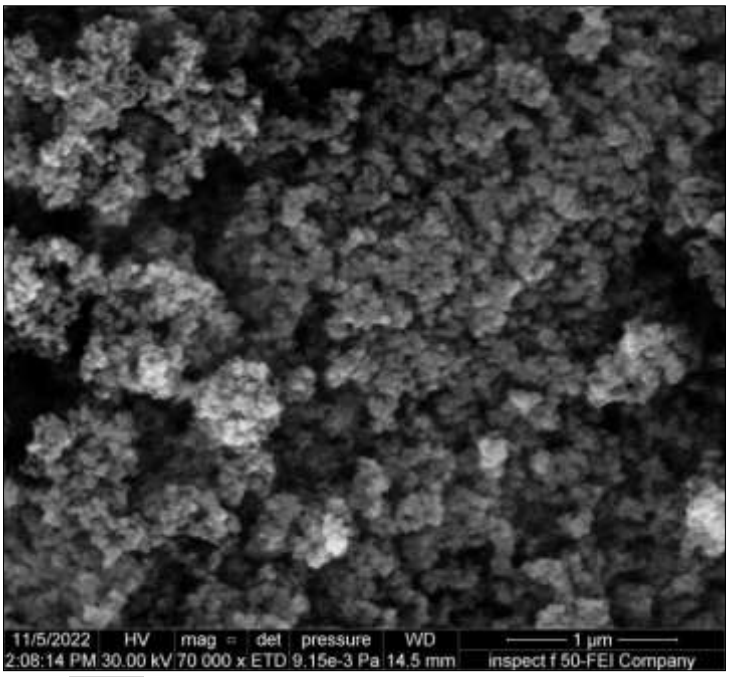


Fig. 3 SEM for SiO_2-NPs.

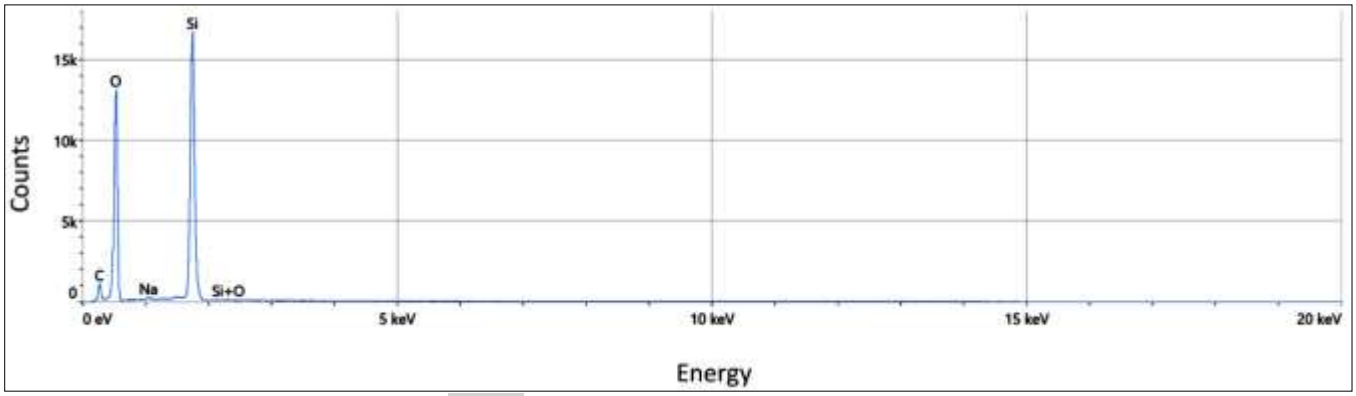


Fig. 4 EDX Spectra Result for SiO_2 NPs.

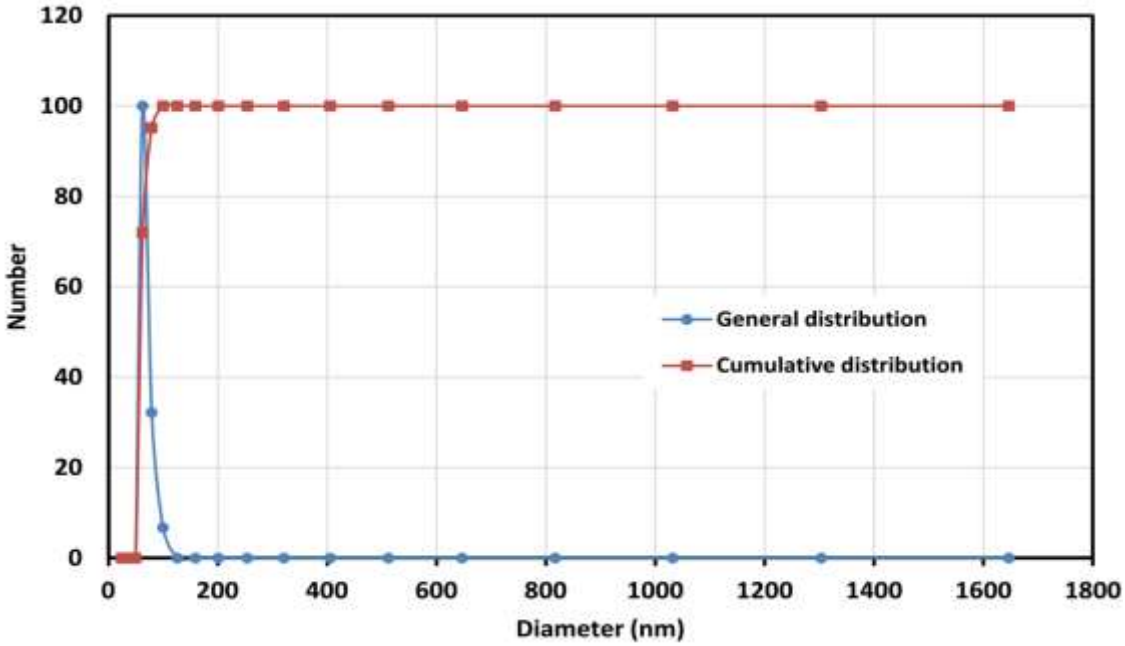


Fig. 5 Particle Size Distribution Results for SiO_2 NPs.

3.3.1 Methanol Concentration

The effect of methanol concentration in the crude biodiesel on extraction performance was investigated. Thus, the phenol concentration in the crude biodiesel varied from 2000 ppm to 5000 ppm. Meanwhile, the Q_{bio} and solvent flow rate (Q_{sol}, mL min^{-1}) were fixed at 100 mL min^{-1}, and free-NPs distilled water was used as a solvent. The methanol removal efficiency and flux are presented in Fig. 6. As shown in Fig 6a, the methanol removal efficiency increased dramatically after 40 minutes. Also, it was observed that the removal efficiency decreased with the methanol concentration increase in the crude biodiesel. It is well known that the removal efficiency of a substance in industrial equipment decreases with the substance concentration's increase at constant operating conditions. The methanol flux increased when the methanol concentration in the crude biodiesel increased, as shown in Fig. 6b. An increase in the methanol concentration in the crude biodiesel could increase the mass driving force and thereby increase the methanol flux.

3.3.2 The SiO_2-NPs Concentration

The effect of NPs concentration in nanofluid (solvent) on the methanol removal efficiency and methanol flux was investigated without glycerol. SiO_2-NPs concentration was changed from 0.005 wt% to 0.02 wt% at a methanol concentration in the crude biodiesel of 2000 ppm. Meanwhile, Q_{bio} and Q_{sol} were fixed at 100 mL min^{-1}. Fig 7 illustrates the effect of NPs concentration in the nanofluid on the removal and flux of methanol. Obviously, the methanol removal efficiency and flux were significantly enhanced in the presence of NPs. At the end of the experiment (after 60 min), it was noticed that the removal efficiency enhanced, i.e., increased from 79.3% to 87.6% upon using 0.005 wt% of NPs. This enhancement could be attributed to the enhancement in Brownian motion in the shell side of the membrane contactor. Moreover, the highest removal efficiency and flux were obtained at 0.01 wt% of NPs. However, there was a decline in the removal efficiency and flux at NPs concentrations of more than 0.01 wt%. This behavior was due to the possible NPs aggregations at high NPs concentrations which were responsible for the retreating in the extraction performance.

3.3.3 The Effect of Hydrodynamics

The effect of hydrodynamics on the extraction performance was evaluated by changing Q_{bio} and Q_{sol}. The values of Q_{bio} were varied from 100 to 250 mL min^{-1} at constant Q_{sol} of 100 mL min^{1}. The experiments were implemented with methanol alone as an impurity with a concentration of 2000, and the NPs concentration in the nanofluid was 0.01 wt%. The experimental results are presented in Fig. 8. From the obtained results, it was found that the increase in Q_{bio} led to a significant increase in the methanol removal efficiency and flux within the first 30 minutes of the experiment. The methanol concentration in the biodiesel within the first 30 min was high. Consequently, the mass driving force during this period was high therefore promoted the extraction performance. In addition, the results demonstrated that the removal efficiency and flux with the presence of NPs were higher than that obtained in the absence of the NPs. The results demonstrated that the removal efficiency and flux with the presence of NPs were higher than that obtained in the absence of the NPs. The higher removal efficiency after 60 min was 91.8%, achieved at Q_{bio} of 250 mL min^{-1}. Fig. 9 represents the effect of Q_{sol} on the methanol removal efficiency and flux at a constant Q_{bio} of 100 mL min^{-1}. The experimental results revealed that the effect of Q_{sol} on extraction performance had an almost similar trend to that obtained from changing Q_{bio}. After 60 min of extraction process, the removal efficiency was 98.4%, obtained at Q_{sol} of 250 mL min^{-1}. The removal efficiency was higher than that presented in Fig. 8a. Consequently, the solvent flow rate was considered the controlling mass transfer step. Increasing the solvent flow rate could reduce the mass transfer resistance and enhance the mass transfer rate. The maximum methanol removal efficiency achieved was 98.4% at Q_{sol} 250 mL min^{-1} and NPs of 0.01 wt%. However, the methanol removal efficiency at Q_{bio} of 250 mL min^{-1} was 91.8 %. Amelio et al. [9] performed experimental work on methanol removal from biodiesel by liquid-liquid extraction in a membrane contactor. They reported that extraction flux increased from 1.9 × 10^{-4} to 2.3 × 10^{-4} g min^{-1} cm^{-2} when the solvent flow rate increased from 0.2 to 1.8 L min^{-1} at constant Q_{bio} of 0.4 L min^{-1}. While the flux increased from 2.3 × 10^{-4} to 3.3 × 10^{-4} g min^{-1} cm^{-2} when Q_{bio} changed from 0.4 to 1.5 L min^{-1} at constant Q_{bio} of 1.8 L min^{-1}. The deviation between the behavior of Amelio et al. results and the present work could be attributed to the high concentration of methanol (5 wt%) in crude biodiesel compared to the low methanol concentration of 2000 ppm considered in this investigation.

3.3.4 The Glycerol Concentration

Glycerol and methanol were added to the crude biodiesel as impurities. The glycerol concentration varied from 1 wt% to 5 wt%, while the methanol concentration was fixed at 2000 ppm. The Q_{sol} and Q_{bio} were kept constant at 2000 ppm. The experiments were implemented using free-NPs solvent and 0.01 wt% NPs solvent. The removal efficiency and flux for methanol and glycerol are presented in Fig.10. It could be seen that the methanol

removal efficiency and methanol flux declined with increasing the glycerol concentration, as shown in Fig. 10 (a and b). Increasing the glycerol content could reduce the mass transfer area for methanol and reduce the methanol removal efficiency and flux. The presence of NPs significantly enhanced the impurities' removal efficiency. As shown in Fig. 10 (a and c), at 60 min (at methanol and glycerol content of 2000 ppm and 1 wt%, respectively), the methanol removal efficiency increased from 76.4% to 93.1% when NPs were added to the solvent (water). At these conditions, the glycerol removal efficiency increased from 76.2% to 94.5%. However, the glycerol removal efficiency was more affected by increasing the glycerol content than the methanol removal efficiency. This behavior could attribute to the limited solubility of biodiesel in water compared to methanol's complete solubility. On the other hand, due to the glycerol's high inlet concentration, the glycerol flux was higher than the methanol flux, as shown in Fig. 10 (b and d). Furthermore, the addition of NPs remarkably increased the methanol and glycerol flux.

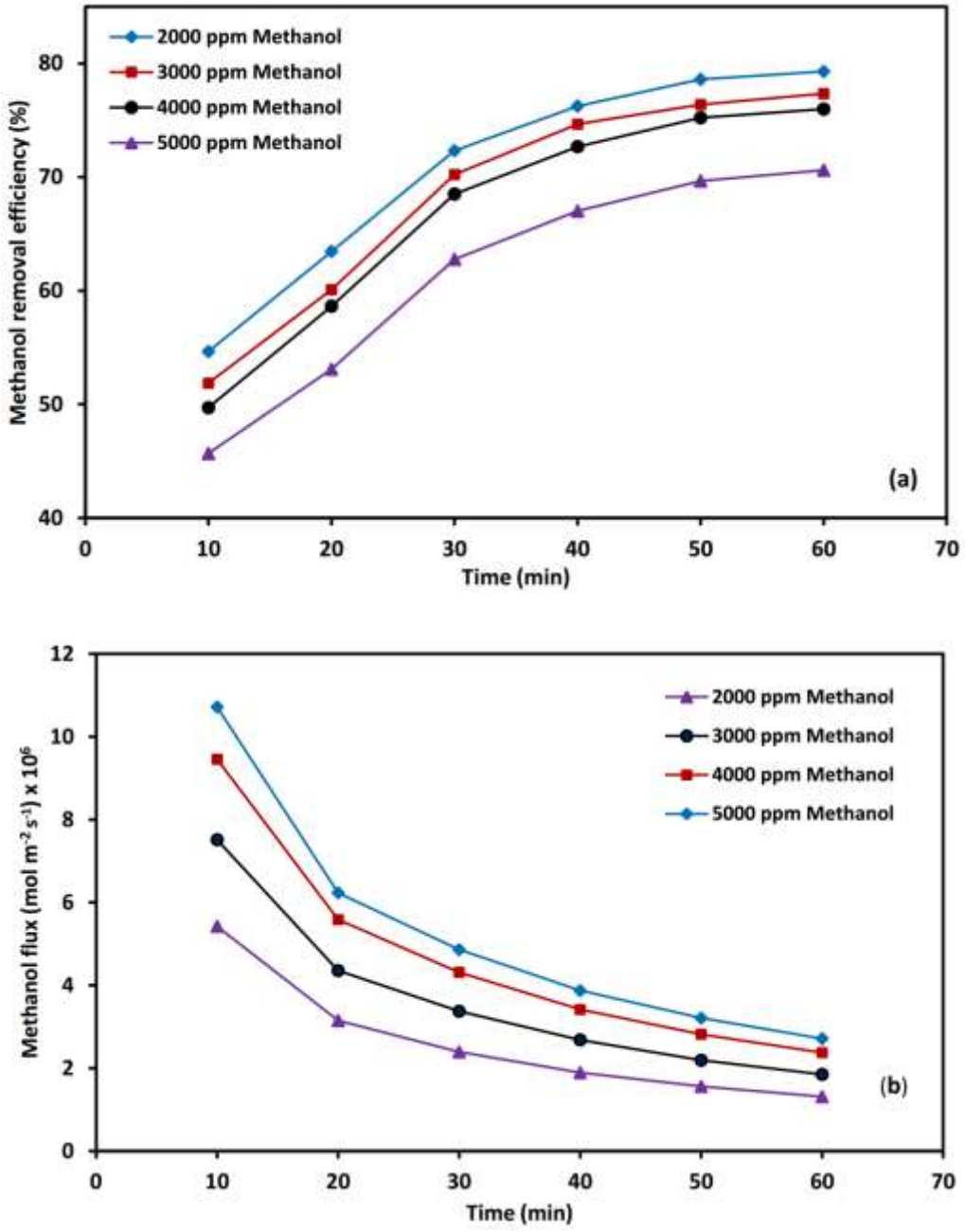


Fig. 6 Effect of Methanol Concentration on **(a)** Methanol Removal Efficiency with Time and **(b)** Methanol Flux with Time. Q_{bio} and Q_{sol} are 100 ml Min^{-1}.

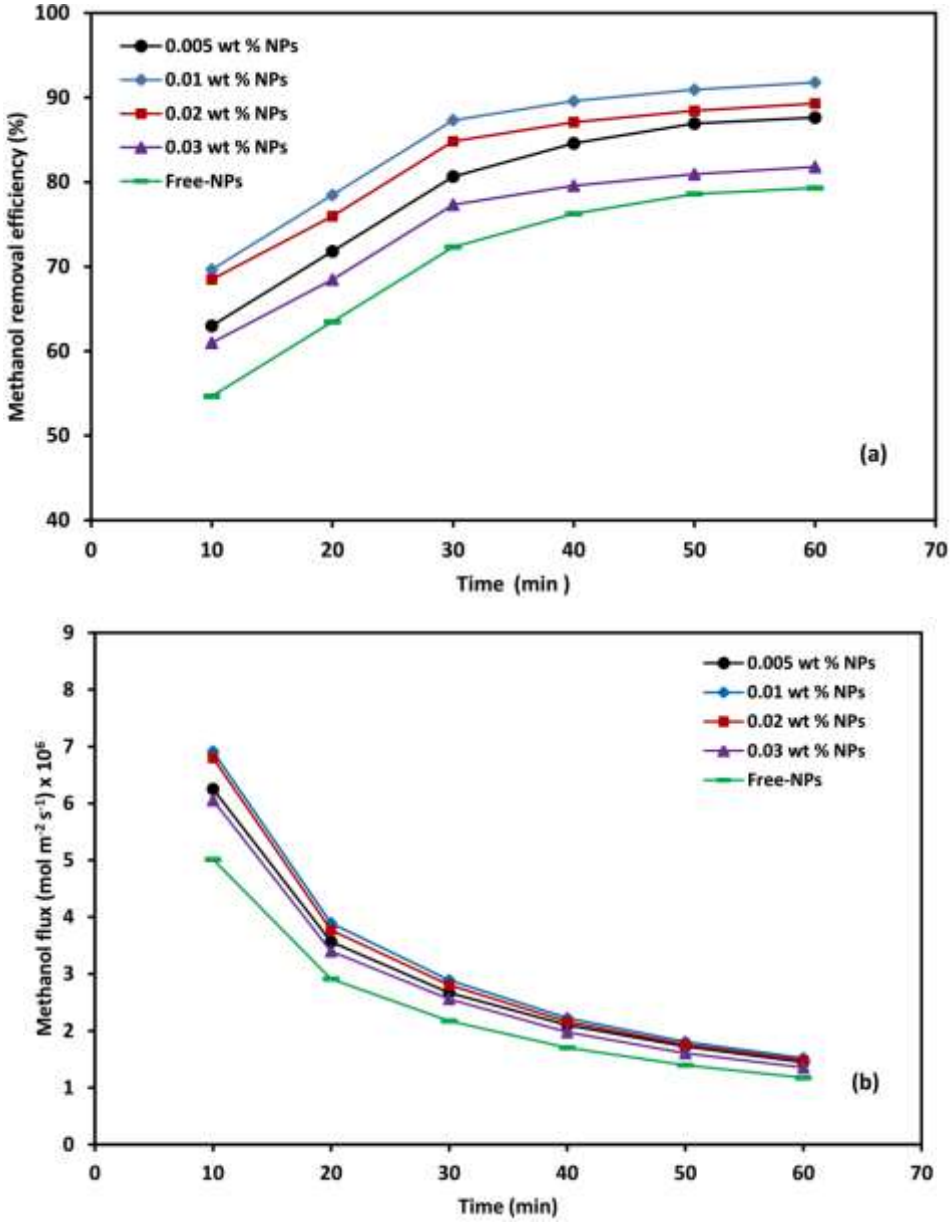
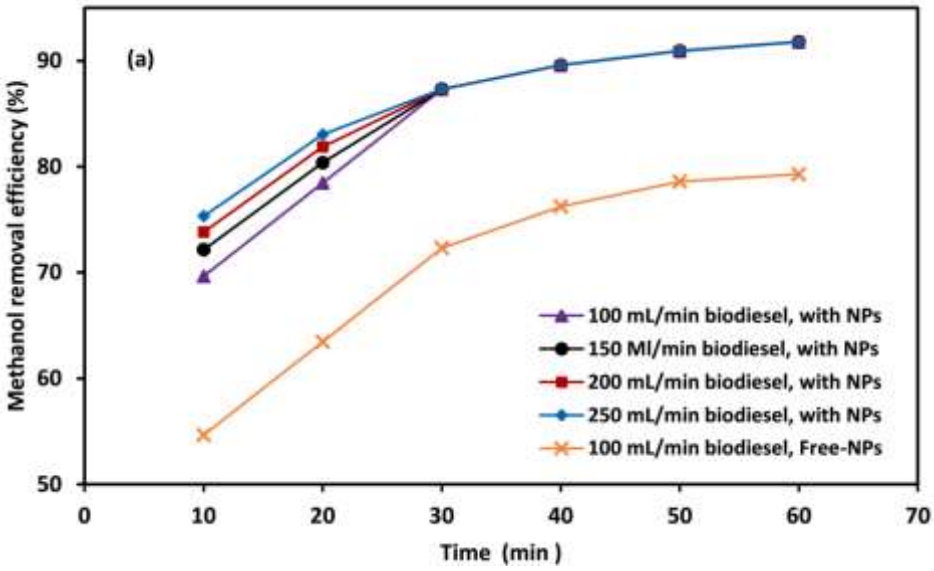


Fig. 7 Effect of NPs Concentration on **(a)** Methanol Removal Efficiency **(b)** Methanol Flux. The Q_{bio} and Q_{sol} are 100 mL min^{-1}; the Methanol Concentration in Crude Biodiesel is 2000 ppm.



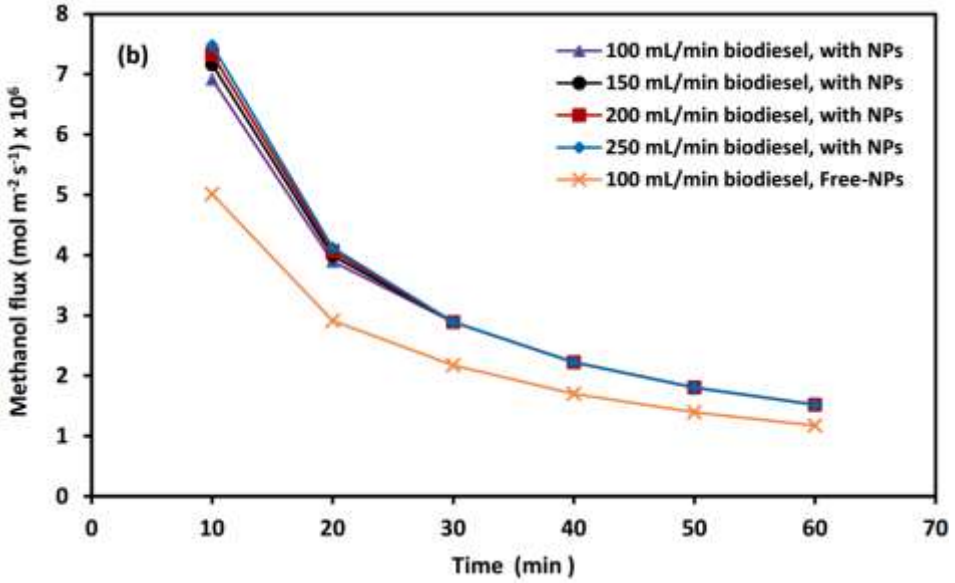


Fig. 8 Effect of Q_{bio} on **(a)** Methanol Removal Efficiency **(b)** Methanol Flux. Q_{sol} was 100 mL min¹; the Methanol Concentration in Crude Oil was 2000 ppm.

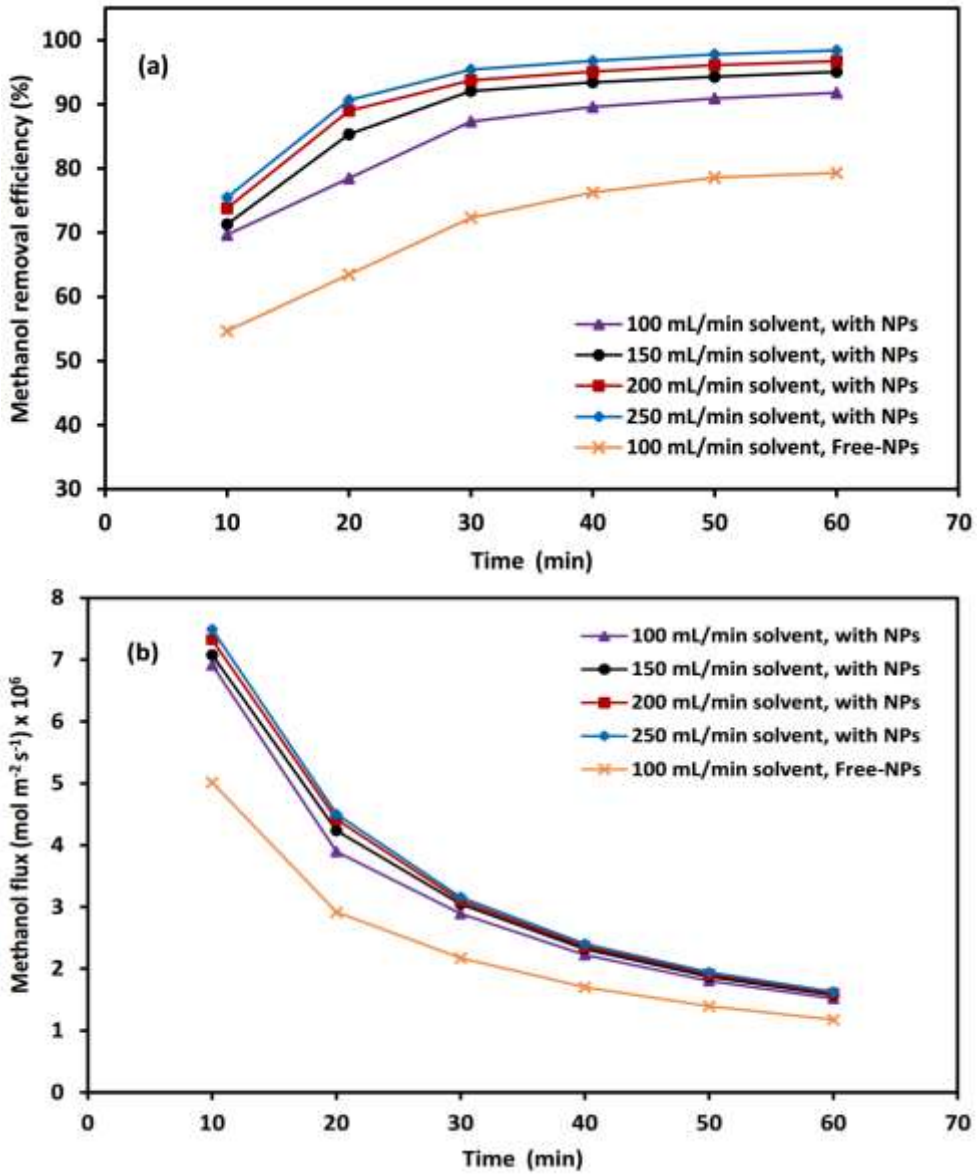
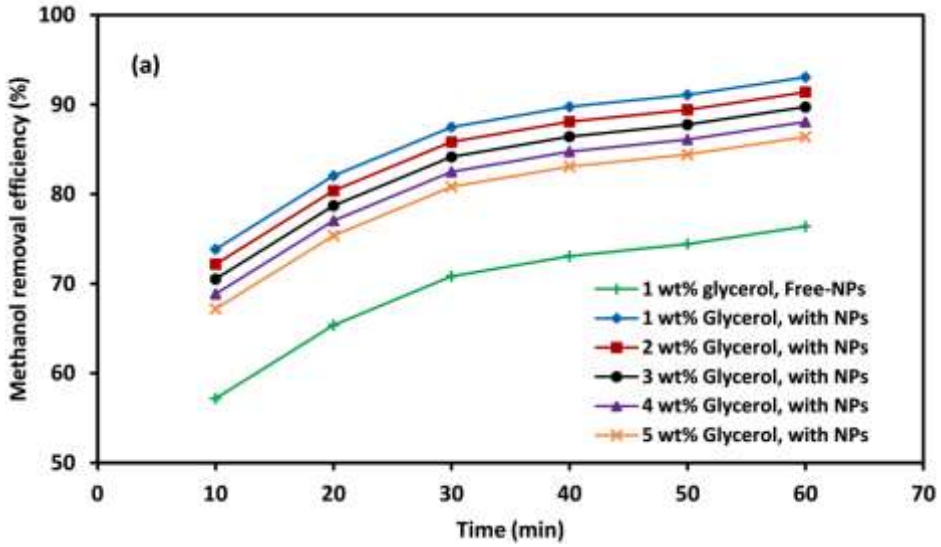
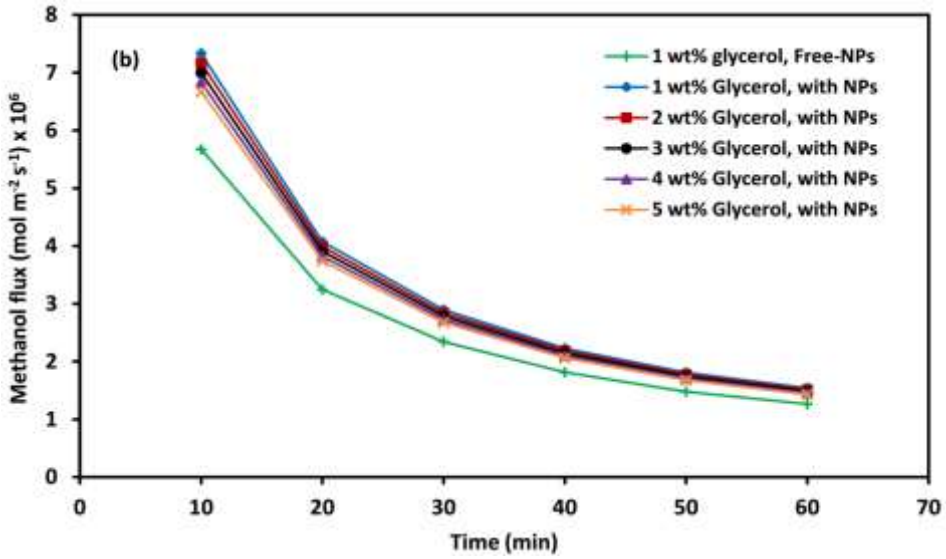
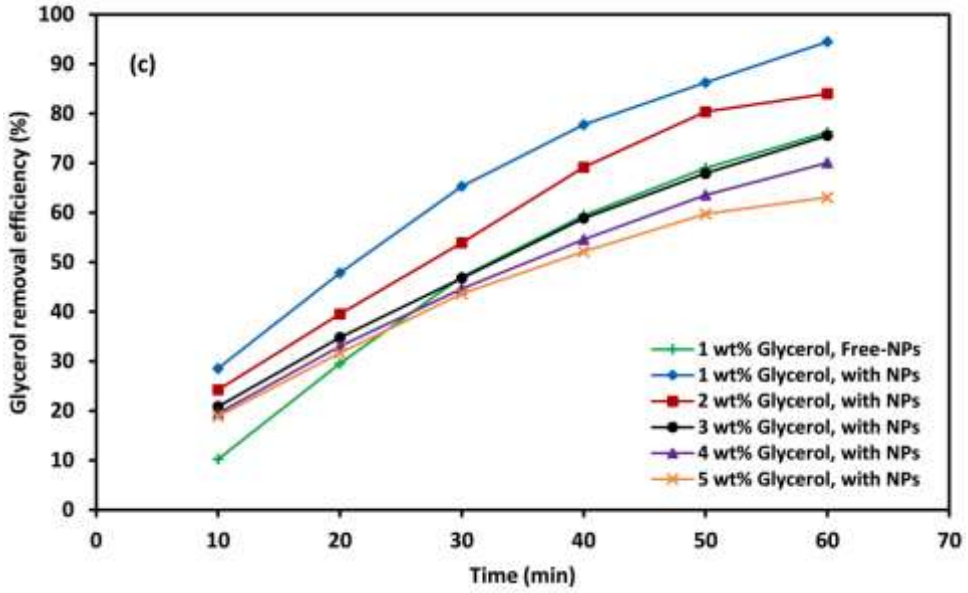


Fig. 9 Effect of Q_{sol} on **(a)** Methanol Removal Efficiency **(b)** Methanol Flux. Q_{bio} was 100 mL min¹, and Methanol Concentration in Crude Oil was 2000 ppm.


(a)
Methanol removal efficiency (%)
Time (min)
1 wt% glycerol, Free-NPs
1 wt% Glycerol, with NPs
2 wt% Glycerol, with NPs
3 wt% Glycerol, with NPs
4 wt% Glycerol, with NPs
5 wt% Glycerol, with NPs


(b)
Methanol flux (mol m-2 s-1) x 10^6
Time (min)
1 wt% glycerol, Free-NPs
1 wt% Glycerol, with NPs
2 wt% Glycerol, with NPs
3 wt% Glycerol, with NPs
4 wt% Glycerol, with NPs
5 wt% Glycerol, with NPs


(c)
Glycerol removal efficiency (%)
Time (min)
1 wt% Glycerol, Free-NPs
1 wt% Glycerol, with NPs
2 wt% Glycerol, with NPs
3 wt% Glycerol, with NPs
4 wt% Glycerol, with NPs
5 wt% Glycerol, with NPs

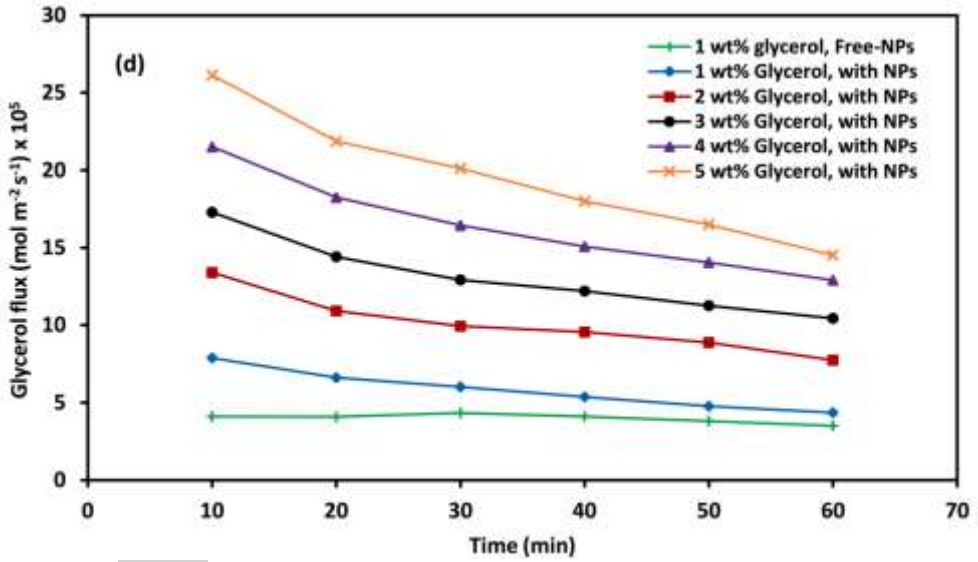


Fig. 10 Effect of Glycerol Concentration on **(a)** Methanol Removal Efficiency, **(b)** Methanol Flux, **(c)** Glycerol Removal Efficiency, and **(d)** Glycerol Flux. The Methanol Concentration was 2000 ppm, and Q_{sol} and Q_{bio} at a Constant Value of 200 mL min^{-1}.

4. CONCLUSIONS

The effect of nanofluid on the purification of biodiesel using liquid-liquid extraction in a membrane contactor was investigated. The nanofluid was composed of SiO_2-NPs and distilled water. The optimum concentration of SiO_2-NPs in nanofluid that exhibited the highest extraction performance was 0.01 wt%. The extraction time was 60 min, and the impurities removal efficiency and flux were determined at a 10-min interval. The extraction performance was significantly enhanced in the presence of NPs. This could be attributed to the enhancement in Brownian motion in the solvent. After an extraction time of 60 min, the methanol's removal efficiency increased from 76.4% to 93.1% at 200 mL min^{-1}. This increase was achieved when NPs were added to the distilled water at methanol and glycerol content of 2000 ppm and 1 wt% in the crude biodiesel, respectively, and constant Q_{sol} and Q_{bio} values of 200 mL min^{-1}. Meanwhile, the glycerol removal efficiency increased from 76.2% to 94.5% at similar operating conditions. The glycerol removal efficiency deteriorated more than the methanol removal efficiency with increased glycerol content in the crude biodiesel. The extraction performance was significantly influenced by Q_{sol}, which represented the controlling mass transfer step rather than Q_{bio}. The mathematical modeling for the liquid-liquid extraction in a membrane contactor using nanofluids as solvent is recommended for future work.

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